

WIDEBAND ELECTRICAL CHARACTERISATION OF CARBON-BASED NANOCOMPOSITES

Isabel Molenberg

Thesis submitted in partial fulfillment
of the requirements for the degree of
Docteur en sciences de l'ingénieur

Dissertation committee:

Prof. C. Bailly (IMCN, UCLouvain, Belgium)

Dr. E. Ferain (it4ip, Belgium)

Prof. H. Happy (IEMN, France)

Prof. I. Huynen (ICTEAM, UCLouvain, Belgium)

Prof. J.-P. Raskin (ICTEAM, UCLouvain, Belgium)

Prof. M. Verleysen (ICTEAM, UCLouvain, Belgium)

June 2012

WIDEBAND ELECTRICAL CHARACTERISATION OF CARBON-BASED NANOCOMPOSITES

Isabel MOLENBERG

ICTEAM Institute

Ecole Polytechnique de Louvain

ELEN department



Université catholique de Louvain

Louvain-la-Neuve (Belgium)

*To my husband Pierre,
to my son Matthieu,
to my daughter Sophie,
you give me the strength and energy
to wake up each and every morning.*

Contents

Acknowledgments	xi
Abstract	xiii
Acronyms	xv
Author's Publication List	xvii
1 Chapter 1: Introduction	1
2 Chapter 2: State-of-the-Art on Polymer CNT Nanocomposites	7
2.1 Introduction	7
2.2 Carbon Nanotubes	9
2.2.1 Transport properties of CNTs	9
2.3 CNTs polymer nanocomposites	11
2.4 Electrical properties of CNTs polymer nanocomposites	14
2.4.1 Direct-current electrical conductivity and percolation threshold	14
2.4.2 Frequency dependence of the electrical conductivity	19
2.4.3 Dielectric constant and crossover frequency	23
2.5 Models of the frequency dependence and DC behaviour of the electrical conductivity	25
2.5.1 Universal Dynamic Response	25
2.5.2 Equivalent electrical circuit models	26
2.5.3 Percolation clusters models (charge carriers diffusion)	28
2.5.4 Thermal fluctuation induced tunnelling model	32
2.5.5 Random biased walk	36
2.5.6 Effective Medium Theory based models	38
2.6 High frequency/microwave electrical behaviour of nanocomposites	42
2.7 Conclusions	47
3 Chapter 3: Measurement Methods	55
	vii

3.1	Introduction	55
3.2	DC and low frequency characterisation techniques	58
3.2.1	DC experimental set-up	58
3.2.2	AC experimental set-up, 1kHz-1MHz	65
3.3	Microwave techniques	67
3.3.1	One line method for thin solid samples and inks (microstrip topology)	67
3.3.2	Line-Line method for bulk samples (waveguide topology)	78
3.3.3	Modified line-line method without waveguide for large samples	86
3.3.4	Comparison between the original and modified Line-Line methods	89
3.4	Free space characterisation using antennas	97
3.5	One-port characterization technique for thin film samples (with ionic conductivity)	101
3.6	Conclusions	106
4	Chapter 4: Wideband characterisation of solid nanocomposites	113
4.1	Introduction	113
4.2	Description of the samples	116
4.3	DC characterization and Scaling Laws	118
4.4	Low frequency characterisation, 1kHz-1MHz	125
4.4.1	AC electrical conductivity versus frequency: PC samples	127
4.4.2	AC dielectric constant versus frequency: PC samples	127
4.4.3	AC electrical conductivity versus frequency: PU samples	130
4.4.4	AC dielectric constant versus frequency: PU samples	132
4.4.5	AC electrical conductivity versus filler content, comparison between PC and PU samples	134
4.4.6	Note on the shape of the conductivity versus frequency plots	140
4.4.7	AC dielectric constant versus filler content, comparison between PC and PU samples	144
4.4.8	AC electrical conductivity versus frequency and power law behaviour	149
4.5	Microwave characterization (microstrip), 40MHz-40GHz	153
4.5.1	AC electrical conductivity: PC and PU samples	155
4.5.2	AC dielectric constant: PC and PU samples	164
4.5.3	Comparison between the PC and PU nanocomposites	168

4.5.4	Correlation with SEM pictures	172
4.5.5	Comparison with the DC and 1kHz-1MHz LCR characterisation	176
4.6	Comparison between rheological and electrical characterisations	186
4.7	Conclusions	191
5	Chapter 5: EMI shielding properties of nanocomposites	197
5.1	Introduction	197
5.2	EMI Shielding Considerations	199
5.3	Solid samples characterisation as a screening technique	204
5.4	Polymer CNT Foamed Composites and Characterisation	207
5.5	Simple electrical model and Comparison with measurement results	218
5.6	Optimized multilayer foams for reduced reflectivity	221
5.7	Multifunctional Hybrids for EMI Absorption	223
5.8	Conclusions	230
6	Chapter 6: Investigation on the non-ohmic behaviour of solutions of dispersed CNTs	237
6.1	Introduction	237
6.2	Brief State-of-the-Art on solutions of dispersed CNTs	239
6.3	Description of the solutions of dispersed nanocomposite	241
6.4	Experimental techniques for CNT solutions characterisation	245
6.4.1	AC characterisation using a commercial system	245
6.4.2	DC technique for the investigation of the non-linearities in the current-voltage curves	247
6.5	Influence of the constituents of the nanocomposite solutions	253
6.5.1	Influence of the CNT/graphene particles	253
6.5.2	Influence of the solvent	261
6.6	Influence of the deposition conditions and parameters	264
6.6.1	Influence of the number of deposited layers	264
6.6.2	Influence of the drying time	266
6.6.3	Application of an electric field during CNT solution drying	269
6.7	Influence of the gap geometry	275
6.7.1	Role of the gap length and gap width	275
6.7.2	Role of the shape of the gap edges	279
6.8	Influence of the junctions between interconnected CNTs	285
6.9	Conclusions	287

7	Chapter 7: Measurement of nanostructured thin-film membranes	291
7.1	Introduction	291
7.2	High frequency measurements of nanocomposite CNT/Nafion membranes	294
7.2.1	Description of the Nafion/CNT samples	294
7.2.2	Measurements results	296
7.2.3	Influence of the temperature and relative humidity	300
7.3	Microwave measurements of nanoporous track-etched polyimide membranes	301
7.3.1	Description of the track-etched nanoporous polyimide membranes	301
7.3.2	Influence of the environmental conditions on the characterisation	304
7.3.3	Influence of the characteristics of the nanoporous membranes on the bulk conductivity	309
7.4	Conclusions	315
8	Chapter 8: Conclusions	319
	Appendix A	326

ACKNOWLEDGMENTS

This thesis is actually not the first I have begun, nor the second but the third one. It is however the only one that I have completed. Somehow I had never really believed this day would finally come. It would probably never have if not for the help and support of my friends, colleagues and family. They were with me all along through several relocations, one wedding, the births of two children, nine years of great joys and happiness but also through pains and hardship.

First of all I would like to thank my advisor, Professor Isabelle Huynen for her trust and confidence in me. I will never forget her answer when I told her, during our first meeting in EMIC, about my first two unfinished theses: “the third one will be the good one”... and she was actually right. I am deeply grateful for her continued help and advice along these years, also for involving me in several interesting research projects and allowing me to focus my own research in the direction I desired. I am also thankful for her enthusiasm and optimism towards my measurement results.

I cannot write these acknowledgements without mentioning my first thesis advisor, Professor Philippe Vanderbemden who taught me so much about electrical measurements. I used to be a very theoretical physics engineer; he turned me into a passable experimentalist and contaminated me with the instrumentation virus. I also thank Professor Denis Flandre for welcoming me at UCL and DICE. My thanks to both team of researchers for their help and friendliness.

I am also very thankful to the members of my jury: Professors Christian Bailly, Henri Happy, Jean-Pierre Raskin, Michel Verleysen and Doctor Etienne Ferain. I am honoured that you accepted to be a part of my jury and I really appreciate your advice and comments, as well as for the fruitful discussions that improved the quality of my thesis.

My very special thanks to the members of our local “coffee team”: Belén Montenegro Villacieros, David Spôte, Marie-Christine Vandingenen, Ester Tooten, Stéphanie Eggermont, for your support, for having motivated me and kept me on tracks when I needed it. Thank you for creating a nice and friendly working environment. I am also especially grateful to Mar Bernal for our cooperative work during her stay in Belgium and to Judith Spiegel, who taught me so much about microwave measurements and devices, for her friendship.

I want to thank all the members of the technical staff who were always present whenever I need some technical or administrative help: Pascal Simon, David Spôte, Marie-Christine Vandingenen, Isabelle Dargent, Brigitte Dupont, Robert Platteborze, Christel Derzelle, Francois Hubin and Sylvie Baudine.

Many thanks also to all my former and present colleagues: Maryline Bawedin, Margherita Bassu, Gilles Scheen, Valeriya Kilchytska, Carlos Pereira, Vikram Passi, Renaud Vayrette, Mostafa Emam, Dina Kamel, Maribel Rocha, Julio Tinoco, Benoit Olbrechts, Yann Danlée, Aline Emplit, Pierre Bollen, Francesco Mani, Olivier Renaudin, Stanislas Sobieski, Cesar Roda Neve, Ibtissem Oueriemi, Kahina Djafri, Dragos Dancila, Samer Hourri, Philippe Laurent and Jean-Francois Fagnard but also to Professors Danielle Vanhoenacker, Benoît Vanderheyden, H.-W. Vanderschueren and Claude Oestges.

I also want to thank all the people involved in the Innopile, Picom, Harcana and Multimasec research projects that I have worked with. I am especially grateful to Nicolas Quievy and Jean-Michel Thomassin for providing me with high quality samples.

Je tiens à remercier ici tout particulièrement tous mes amis, de Bruxelles, de Liège et d'ailleurs, qui m'ont toujours soutenue, malgré la distance et le temps qui passe: Catherine Fraikin, Alexandra Mazzoli, Valérie Leroy, Pierre-Charles Lambotte, Sandra Lizin, Frédéric Joskin, Lionel Vandamme, Marie Vandamme, Laetitia Moens, Cédrine Legendre, and Didier Adams. Un merci tout particulier également à Franz Aché, Jacqueline Demeyer et Dominique Boucquey pour leurs encouragements il y a quelques années, ainsi qu'à mes camarades kangous et digiboulettes.

Finalement, last but not least, je remercie infiniment ma famille, surtout ma maman et ma soeur Laure qui m'ont toujours encouragée, elles m'ont été d'un énorme soutien et ce depuis aussi longtemps que je me souviens. J'adresse aussi mes profonds remerciements à mes grand-parents qui se sont toujours montrés fiers de moi.

Et, bien sûr, je n'ai pas de mots assez justes pour remercier mon mari, Pierre, pour son amour et son soutien de tous les jours, ainsi que mes enfants, Sophie et Matthieu, pour leur patience et leur compréhension, tout particulièrement durant les derniers mois de la rédaction où je ne pouvais pas passer autant de temps que je l'aurais voulu avec eux. Je veux qu'ils sachent quand même que c'est grâce à leur présence à mes côtés tous les jours et grâce à leur affection que cette thèse est à présent terminée.

ABSTRACT

Nanocomposite materials are composed of two or more different materials having different physical properties forming distinct ‘phases’. At least one of these constituents has dimensions of the order of the nanometre and the properties of these nanoparticles lead to the creation of a unique composite material. In particular, nanocomposites based on high aspect ratio particles like carbon nanotubes should exhibit outstanding mechanical, thermal and electrical properties at very small particle content. Carbon-based nanocomposites are a rapidly growing field of investigation. The range of available shapes, types and properties of these composites is constantly increasing and that of their possible applications is wider still.

In this thesis, the wideband electrical properties of these nanocomposite materials are investigated. First a thorough examination of the literature is presented. Different characterisation techniques are developed and their adequacy with the nanocomposite characteristics is discussed. A wideband, from DC to 40 GHz characterisation of polymer-CNT composites is presented in details and used to extract information on the material microstructure, as well as the influence of the nanoparticle content on the electrical properties. Specifically designed nanocomposites for particular applications are presented; from composite foams for EMI shielding applications to dispersed solutions of carbon particles exhibiting a non-ohmic behaviour. Finally, nanostructured membranes for fuel cell applications are also shown. The particular aim of this thesis is to find the best adequacy between characterisation method, material properties and required characteristics for a given application.

This PhD thesis is written with the hope that it may help further research on the electrical properties of nanocomposite materials and that it may facilitate the choice of a specific characterisation method.

ACRONYMS

ACTN	All connected tunnelling network
B-EMT	Bruggeman Effective Medium Theory
CB	Carbon Black
CNF	Carbon Nanofiber
CNP	Carbon Nanoparticle
CNT	Carbon Nanotube
CVD	Chemical vapour deposition
DC	Direct-current, static regime
DUT	Device Under Test
EG	Ethylene glycol
EM	Electromagnetic
EMI	Electromagnetic Interferences
EMT	Effective Medium Theory
ESD	Electro-static discharge
GO	Pure graphite oxide
LCR	Inductance (L), Capacitance (C) and Resistance (R) meter
LL	Line-Line characterisation technique
LRM	Line-Reflect-Match, calibration
MEA	Membrane-Electrode Assembly
MG	Maxwell-Garnet (EMT)
MG-S	Maxwell-Garnet (EMT) modified by Sheng
MS	Microstrip
MUT	Material/Membrane Under Test
MWCNT	Multi Wall Carbon Nanotube
NLN _r	Relative non-linearity
OL	One-Line characterisation technique
PC	Polycarbonate
PCL	Poly- ϵ -caprolactone

PEBAX	Polyether block amide
PEG	Polyethylene glycol
PEMFC	Polymer Electrolyte, or Proton-Exchange, Membrane Fuel Cell
PI	Polyimide
PmPV	Poly(m-phenylenevinylene-2,5-dioctyloxy-p-phenylenevinylene)
PP	Polypropylene
PPR	Parallel Plates Reflection characterisation method
PS	Polystyrene
PTFE	Polytetrafluoroethylene, or Teflon (commercial name)
PU	Polyurethane
PVA	Polyvinylalcohol
PVP	Poly-vinylpyrrolidone, a neutral surfactant
RGO	Reduced graphite oxide
SAN	Styrene acrylonitrile resin
SDS	Sodium dodecyl sulfate, an anionic surfactant
SEM	Scanning electron microscope
SOLT	Short-Open-Load-Through, calibration
SWCNT	Single Wall Carbon Nanotube
TE	Transverse Electric mode
TEM	Transverse Electromagnetic mode
TL	Transmission Line
TM	Transverse Magnetic mode
UCL	Université catholique de Louvain
ULg	Université de Liège
VNA	Vector Network Analyzer
WG	Waveguide

AUTHOR'S PUBLICATION LIST

Patent

1. European Patent EP10175887 "Hybrid material for electromagnetic absorption", filed: 09 September 2010.

Book Chapters

1. I. Molenberg, J.-M. Thomassin, R. Daussin, A.C. Baudouin, C. Detrembleur, C. Bailly, and I. Huynen, "Foamed Nanocomposites for EMI Shielding Applications", in "Advanced Microwave and Millimeter Wave Technologies: Semiconductor Devices Circuits and Systems", In-Tech, Austria, 2009, pp. 453-470.
2. J.-M. Thomassin, R. Jerome, I. Molenberg, I. Huynen, C. Detrembleur, "Polymer/carbon nanotube composites for electromagnetic interference reduction", in "Physical properties of polymer nanocomposites", Woodhead, UK, 2009, pp. 563-587.

Journal Papers

1. M. Bernal, I. Molenberg, S. Estravis, M. Rodriguez-Perez, I. Huynen, M. Lopez-Manchado, R. Verdejo, "Comparing the effect of carbon-based nanofillers on the properties of flexible polyurethane foams", in Journal of Material Science, available online February 2012, pp 1-7, doi.10.1007/s1085301263314.
2. J.-M. Thomassin, D. Vuluga, M. Alexandre, C. Jerome, I. Molenberg, I. Huynen, C. Detrembleur, "A convenient route for the dispersion of carbon nanotubes in polymers: application to the preparation of Electromagnetic Interference (EMI) absorbers", Polymer, vol. 53, January 2012, pp. 169-174.
3. I. Molenberg, M. Planckaert, L. Jonckheere, E. Ferain, I. Huynen, "Investigation of ionic conductivity in track-etched nanoporous polyimide membranes using a microwave technique", Microwave and Optical Technology Letters, September 2011, Vol. 53, No. 9, pp. 2060-2063.
4. I. Huynen, N. Quievy, C. Bailly, P. Bollen, C. Detrembleur, S. Eggermont, I. Molenberg, J.-M. Thomassin, L. Urbanczyk, T. Pardoen, "Multifunctional

Hybrids for Electromagnetic Absorption", *Acta Materialia.*, vol. 59, no. 8, May 2011, pp. 3255-3266.

5. D. Vuluga, J.-M. Thomassin, I. Molenberg, I. Huynen, B. Gilbert, C. Jerome, M. Alexandre, C. Detrembleur, "Straightforward synthesis of conductive graphene/polymer nanocomposites from graphite oxides", *Chemical Communications*, vol. 47, no. 9, pp ; 2544-2546, doi.10.1039/C0CC04623J.
6. J.-M. Thomassin, I. Molenberg, I. Huynen, A. Debuigne, M. Alexandre, C. Jerome, C. Detrembleur, "Locating carbon nanotubes (CNTs) at the surface of polymer microspheres using poly(vinyl alcohol) grafted CNTs as dispersion co-stabilizers", *Chemical Communications*, vol. 46, no. 19, 2010, pp. 3330-3332.
7. N. Krins, F. Hatert, K. Traina, L. Dusoulier, I. Molenberg, J.-F. Fagnard, P. Vanderbemden, R. Rulmont, R. Cloots, B. Vertruyen, "LiMn_{2-x}Ti_xO₄ spinel-type compounds ($x \leq 1$): Structural, electrical and magnetic properties", *Solid State Ionics*, vol.177, no. 11-12, 2006, pp. 1033-1040.

International Conference Proceedings

1. J.-M. Thomassin, I. Molenberg, I. Huynen, M. Alexandre, C. Jerome, C. Detrembleur, "PMMA/carbon nanotube nanocomposites foams for EMI shielding application", in *Proceedings of the International Conference on Materials for Advanced Technologies*, Singapore, July 2011, 1p.
2. M. Alexandre, J.-M. Thomassin, D. Vuluga, I. Molenberg, I. Huynen, A. Debuigne, C. Jerome, C. Detrembleur, "Locating carbon nanotubes (CNTs) at the surface of polymer microspheres using poly(vinyl alcohol) grafted CNTs as dispersion co-stabilizers", poster awarded "Best poster Award" at the *International Conference on Materials for Advanced Technologies (ICMAT2011)*, Symposium U, Singapore, June 24-July1, 2011, 1 p.
3. S. Eggermont, P. Bollen, N. Quievy, C. Bailly, C. Detrembleur, I. Molenberg, J.M. Thomassin, L. Monnereau, L. Urbanczyk, T. Pardoën, I. Huynen, "Novel Frequency Selective Electromagnetic Absorber Combining Honeycomb Waveguide and Carbon Nanotube Composites", *Proceedings of the 5th European Conference on Antennas and Propagation*, Roma, April 11-15, 2011, , pp. 2201-22044.
4. D. Vuluga, J.-M. Thomassin, I. Molenberg, I. Huynen, C. Jerome, M. Alexandre, C. Detrembleur, "An Efficient Biphasic Synthesis of Polymer-Grafted Reduced Graphite Oxide Based Nanocomposites", Poster presentation at "Advances in Polymer Science and Rubber Technology (APSRT 2011) - Challenges towards 2020 and beyond", Kharagpur, March 3-5, 2011.

5. D. Vuluga, J.-M. Thomassin, I. Molenberg, I. Huynen, A. Debuigne, M. Alexandre, C. Jerome, C. Detrembleur, "Locating carbon nanotubes (CNTs) at the surface of polymer microspheres using poly(vinyl alcohol) grafted CNTs as dispersion co-stabilizers", Belgian Polymer Group Meeting, Belgium, May 24-25, 2010.
6. I. Molenberg, J.-M. Thomassin, C. Detrembleur, C. Bailly, I. Huynen, "Les Mousses Polymeres Nanocomposites pour les Applications de Compatibilite Electromagnetiques Microondes", In: Proceedings of the Journees de Caracterisation Micro-ondes de Materiaux - JCMM 2010, Brest, France, April 2010 (invited speaker).
7. I. Molenberg, J.-M. Thomassin, E. Ferain, C. Detrembleur, I. Huynen, "RF Diagnostic Methods for Two Nanostructured Polymer Applications", in Proceedings of the 39th European Microwave Conference, Rome, Italy, September 2009, pp.1045-1048.
8. I. Molenberg, J.-M. Thomassin, C. Detrembleur, I. Huynen, "CNT polymer nanocomposites for fuel cell and EMI shielding applications", in Proceedings of the Conference "STIC et environnement", Calais, France, June 2009.
9. J.-M. Thomassin, C. Detrembleur, I. Huynen, I. Molenberg, L. Bednarz, M. Alexandre, C. Jerome, "Foams of polymer/MWNT nanocomposites for efficient electromagnetic interferences (EMI) reduction", Belgian Polymer Group Meeting, Houffalize, Belgium, May 14-15, 2009.
10. I. Molenberg, L. Bednarz, F. Hubin, I. Huynen, "High frequency characterization of polymer membranes with embedded carbon nanotubes for fuel cell applications", in Proceedings of the Journees de Caracterisation Micro-ondes de Materiaux (JCMM 2008), Limoges, Avril 2008, 2 p.
11. I. Molenberg, L. Bednarz, F. Hubin, I. Huynen, "High frequency characterization of polymer membranes with embedded carbon nanotubes for fuel cell applications", poster communication presented at the Scientific meeting of the Wallonia Network for Nanotechnologies (NANOWAL), Louvain-la-Neuve, Belgium, 18 March 2008.

*To dream the impossible dream,
To fight the unbeatable foe,
To bear with unbearable sorrow,
To run where the brave dare not go.*

from “Man of la Mancha” (1972)

*Science is facts;
just as houses are made of stones,
so is science made of facts;
but a pile of stones is not a house
and a collection of facts
is not necessarily science...*

H. Poincare

CHAPTER 1

INTRODUCTION

Nanocomposites are first defined, in the present thesis, as heterogeneous materials based on tiny bits of matter or nano-sized particles embedded inside a matrix having dimensions many orders of magnitudes larger. The combination of both materials leads to the creation of a new, composite material, combining properties from each phase, especially the unique characteristics of nanoparticles, and even sometimes exhibiting novel features.

Although nanocomposite materials are a rather recent field in engineering, they are very common in nature; bone, tooth, nacre or even some butterfly wings are actually natural nanocomposites. Today in Europe, over 2000 different kinds of nanoparticles are used in more than 800 different applications¹, from cosmetic and sunscreens to polymer car wings and golf clubs.

At the nanometre scale, the Van der Waals forces, thermal agitation and quantum tunnelling have a considerable impact on the nanoparticles, a much greater one than in the case of macroscopic objects.

This PhD thesis is written with the hope that it may help further research on the electrical properties of nanocomposite materials and that it may facilitate the choice of a specific characterisation method. This thesis should also bring information on the diversity of materials and applications and also improve our understanding of the phenomena responsible for the dispersion of the electrical properties of the carbon-based nanocomposites. This investigation is primarily focused on nanocomposites based on carbon nanotubes, in various forms and shapes (e.g. solids, foams or solutions). Though some graphene-based compos-

¹According to the report of the French Conseil National de la Consommation on the presence of nanomaterials in consumer products of June 2010.

ites were also characterised and the membranes described in the last chapter are in fact nanostructured materials rather than actual nanocomposites but the techniques and results discussed in the previous chapters can be translated to these nanostructured membranes.

Carbon nanotubes, and other carbon nanoparticles like graphene or fullerenes, have attracted a large interest since the 1980's. CNTs in particular are widely used as nanofillers because of their outstanding mechanical and electrical properties, as well as a good thermal conductivity. Besides, due to their huge aspect-ratio of about 1000, a significant effect on the material properties can already be obtained for very small CNT loadings.

Polymers are lightweight, inexpensive, flexible and versatile; their morphological, mechanical and structural properties can be tailored for virtually any application. They can be moulded in almost any conceivable shape and are durable; they are chemically stable and resistant to corrosion. They are also relatively easily recyclable.

CNT-polymer nanocomposite are bridging the gap to combine the best of both worlds.

Furthermore, over the last decades, recent advances in CNT fabrication processes were made, especially in the mass production of high quality CNTs and in the dispersion methods of these particles in polymer solutions. These developments have increased the public and industry interest in CNT/polymer nanocomposites.

Polymer/CNTs nanocomposites have various applications, from anti-static packaging or paint to electromagnetic shielding structures or microwave absorbers but also as tribological additives or even as mechanical reinforcement inside tennis rackets. Most of the current applications are rather straightforward and only scratch the surface of the full potential of CNT/polymer nanocomposite materials.

However different their applications, composite materials containing conductive nanoparticles all share some distinctive features. First, compared to more conventional composite materials, the amount of nanofillers is considerably lower and some properties of nanocomposite materials could not be obtained using classical fillers. In particular, the transport properties of nanocomposites are very interesting; a percolation threshold can be observed, i.e. for a certain fraction of nanoparticles the electrical behaviour of the composite becomes that of a conductive material (DC regime), whereas for filler contents below this threshold it is behaving as a dielectric material. The frequency dependence of the electrical conductivity and dielectric constant of the CNT/polymer nanocomposite are no less outstanding.

In the last decades, various models have been proposed in the literature to describe and explain the particular electrical behaviour of the nanocomposites; in particular that of CNT/polymer composites with different filler fractions. The most prominent of these models are discussed in a state-of-the-art in chapter 2, along with a description of the properties of CNTs and of the corresponding nanocomposites. This is presented in a ‘bottom-up’ approach, from the properties of the nanoparticles to those of the final nanocomposite. The electrical properties are particularly detailed, in static and frequency varying regimes but also at high frequency. Laws are presented to model and predict the frequency behaviour of nanocomposites with filler contents below, above and close to the percolation threshold. A special emphasis is put on the key influence of the quality of the dispersion of the CNTs in the polymer matrix. The significant influence of percolation phenomena and of quantum tunnelling are also discussed. The high frequency, even microwave, behaviour of these composites is discussed in more depth at the end of this chapter.

The backbone of the present thesis is the correlation between the physical properties of the nanocomposite samples and the available characterisation methods. These techniques differ according to the desired frequency range, direct-current, low or high (even microwave) frequency and also on the electrical and geometrical characteristics of the samples and materials. The application for which the samples are destined or foreseen also plays a role, real life or working conditions have sometimes to be emulated.

The different techniques are presented and compared in chapter 3, from classical DC resistance and low frequency current-voltage measurement and impedance characterisation to the microwave measurement of microstrip or waveguide transmission lines. The reflection based technique used to characterise the samples of the last chapter, for fuel cell applications is also shown. Some interesting results of nanocomposite characterisation are also shown for each measurement method, to illustrate the effectiveness and the usefulness of the corresponding technique but also to highlight its weaker and stronger points, and to evaluate the adequacy between the material to characterise and the technique presented.

The aim of the present thesis is to focus on the high frequency characterisation techniques but in order to compare the techniques and the results, the DC and lower frequency methods are presented in the latter chapter and they will be used in the subsequent chapters of the thesis.

Usually a measurement method has a limited frequency range in which it can be used and the results are meaningful and accurate. In chapter 4, a wideband (DC to 40 GHz) characterisation of thin plates of polymer/CNT composite is presented, involving three different experimental techniques to cover this extended frequency range. The samples are made of two different polymer matrices, polyurethane and polycarbonate, their filler mass fractions vary from 0.1 to

4 wt%. The influence of frequency and that of filler content can therefore both be investigated and compared on a very wide frequency range. The results obtained using different characterisation techniques are compared. The reproducibility of the different techniques are also discussed.

Rheological measurements can also be used to provide information on the nanocomposite properties and structures. The electrical and rheological characterisation, methods and results, are then compared in the same chapter. These results are compared to those from the literature, as presented in the state-of-the-art chapter, to confirm or invalidate hypotheses made in the latter chapter. To the best of our knowledge such a wideband characterisation of CNT/polymer composites is very rare in the literature.

The applications of nanocomposite materials are numerous but one of them in particular shows outstanding results and great potential. The CNT/polymer nanocomposites can be foamed like a simple polymer and benefit from the resulting decreased weight and dielectric constant. Such foams can be used as excellent microwave absorbers against electromagnetic interference (EMI), i.e. shielding materials that also decrease the reflectivity of the shield by absorbing the incident power instead of simply reflecting it like common metal shields.

Characterisation of the foamed nanocomposite and the corresponding results are presented in chapter 5. A simple and reliable screening technique of the solid samples, prior to the actual foaming, is described. A simple electrical model is also presented to fit and describe the nanocomposite foam measurements. Two optimized topologies are also presented to improve the EMI performances of the composite foam; the first one is obtained by playing on a gradation of the filler content inside the foam and the second one by actually fabricating a hybrid material, based on the hierarchical structure of a nanocomposite foam embedded in a metallic honeycomb.

CNT/polymer nanocomposites can be in a liquid state, either during the fabrication of the composite or as a final product. For example dispersions of CNTs inside an aqueous solvent have applications as conductive inks or paints, for anti-static applications or the fabrication of inkjet printed electronic circuits or elements. Some such dispersions are presented and characterised in chapter 6.

A non-ohmic behaviour was observed during the characterisation of those dispersions. The presence of an hysteresis and strong linearities were also present in the current-voltage curves of dried drops of the nanocomposite solutions. Finding an explanation for the latter phenomena proved to be quite complex. This non-ohmic behaviour is investigated in the latter chapter, along with the influence of different parameters. In particular the influence of the electric field, of the solvent, of the drying time, of the CNT content and that of the geometrical parameters of the experimental cell are considered. The impact of the application of an external bias during drying is also investigated. These electrical considerations are confronted to information on the microstructure provided by SEM

pictures and tentatively described by the presence of Schottky barriers at the interfaces between nanotubes.

The two types of nanocomposites presented in the last chapter of this thesis are both considered for applications in fuel cells and characterised using similar techniques. They are therefore discussed in the same chapter.

The first kind of composites are Nafion membranes with embedded CNTs. Nafion is a polymer having a Teflon backbone with associated acidic sulfonic groups and has very specific properties. In particular, it is a good ionic conductor (and thus called an ionomer), it is also very resistant to chemical wear and is permeable to water. The electronic conductivity of Nafion membranes is however very poor and to be used as membrane-electrode-assemblies in fuel cells, CNTs are added in the Nafion matrix to provide the necessary electronic conductivity.

The other family of samples, also presented in chapter 7, are not rigorously nanocomposites but they are made of a nanostructured material; nanoporous track-etched polyimide membranes. By combining heavy radiations and chemical treatments, pores nanometric dimensions are etched in thin polyimide membranes. If these membranes are immersed into water or an acidic medium, they exhibit an ionic conductivity, making them interesting for fuel cell applications (in this case the electronic conductivity would be externally provided, via an additional layer of CNT ink or gel). In particular, the influence of the density, size and shape of the pores is investigated.

Finally, the results from the different chapters are summarized and discussed in the conclusions, with a special emphasis on the adequacy between the samples, the characterisation techniques and the obtained results. Some perspectives and on-going work are also presented.

Involvement in related research projects:

During the four and a half years of my thesis (September 2007 - June 2012) I had the opportunity to collaborate to four research projects. Three of them were founded by the Walloon Region (DGTRE-RW) and a fourth one was a European Community FP7 project. Some of the results presented in my thesis were obtained in the framework of one or several of these research projects. They are listed chronologically below:

- Innopile (March 2005 - August 2008): Research on the design and improvement of new polymer membranes and electrode-membranes assemblies for fuel cell applications. They were based on persulfonated (Nafion) membranes with embedded mineral charges. EMIC was in charge of the electrical characterisation of the nanostructured membranes (and the development of a reliable and reproducible characterisation method, adequate for the membrane samples).
- PICOM (January 2008 - February 2012): Research on the design of electrode-membrane assemblies based on innovating materials, i.e. nanoporous track-etched polyimide membranes. EMIC was in charge of the characterisation of the track-etch membranes and of the determination of their ionic conductivity as well as their response to humidity, high temperature and aging.
- Multimasec (October 2008 - February 2012): Research on the design of a novel multi-material hybrid with outstanding absorption properties for impact and electromagnetic (EM) interferences absorption coupled with thermal energy dissipation capabilities. EMIC was in charge of measuring and modelling the EM performances of the hybrid (including the development of a new characterisation technique). A prototype of protective casing for signal amplifiers (distribution networks) was also fabricated and a patent was deposited for the multiscale hybrid material.
- HARCANA (July 2008 - June 2012): European Community project on the design of polymer and carbon nano-particles (CNP) based nanocomposites with improved mechanical, electrical and thermal properties at a minimum loading of nanoparticles. EMIC was involved in several workpackages, from the wideband electrical characterisation of the nanocomposites and the assessment of their EMI (electromagnetic interferences) and ESD (electro-static discharge) properties to the modelling of the electromagnetic behaviour of the solid and foamed CNT composites, as well as their correlation with their rheological behaviour.

CHAPTER 2

ELECTRICAL PROPERTIES OF POLYMER CARBON NANOTUBES COMPOSITES, A BRIEF STATE-OF-THE-ART

2.1 INTRODUCTION

Composite materials are composed of two (or more) different materials having different physical properties forming distinct ‘phases’. Such a material is said to be a ‘nanocomposite’ when at least one of its constituents has dimensions of the order of the nanometer, [1]. The properties of these smaller than microscopic elements lead to the creation of a unique composite material. For example, nanocomposites based on high aspect ratio particles should exhibit an optimal mechanical strength. Novel effects could also appear, like quantum confinement. Usually there is a main insulating phase (the polymer matrix) and one or more types of nano-fillers embedded in this matrix.

Fiber-reinforced materials have shown excellent, even superior properties in many applications. However, some combinations of these desired properties cannot be obtained with conventional polymer composites. For example, a strong mechanical reinforcement and an optical transparency or reinforced molded parts using micro-injection techniques, [2]. As stated in [1], CNT-based composites exhibit low percolation threshold¹, high quality surface finish, robust network, and good mechanical properties; a combination unheard of with other fillers.

¹The percolation threshold is the mass or volume fraction at which the behaviour of a nanocomposite becomes conductive, below this threshold its behaviour is that of a dielectric material.

Furthermore, nanocomposites have, at a lower mass or volume filler fraction than conventional composites², a larger number of nanofillers and huge interfacial³ areas. Besides, the mean distance between these nanoparticles is considerably smaller, cf. Fig. 2.1.

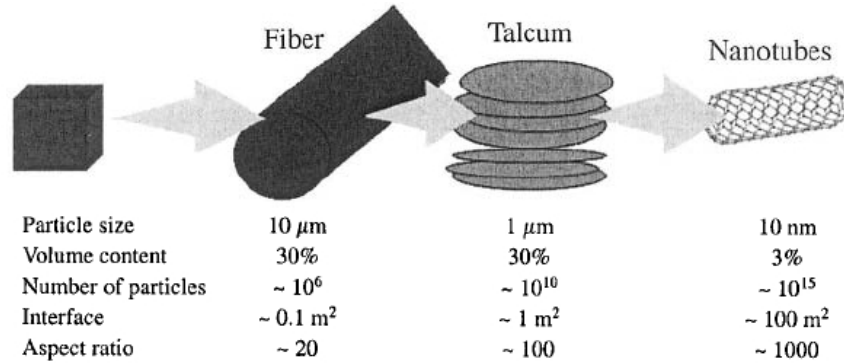


Figure 2.1.: Comparison of the particle size, volumetric filler content, number of particles, interfacial surface and aspect ratio for three different kinds of fibres, from [2].

The main challenge when fabricating nanocomposites resides in the dispersion⁴ of these very small particles inside the polymer matrix, independently of their shape and aspect ratio. They tend to form aggregates, ropes or bundles, because of Van Der Waals forces between the particles. Interactions between particles or between particles and matrix are not negligible when the particles size drops under 1 μm , [1].

Besides, should nanomaterials be regarded as very small fibres or as heavy molecules? They often have the same dimensions as the polymer molecules.

The most commonly studied carbon nanofibers nowadays are probably the carbon nanotubes depicted in the following section, but it should be noted that there are many other types of nanoparticles, such as stacks of discs or cones (herringbones) of graphene planes, [1], or metallic and/or magnetic platelets or rods.

²Conventional fiber-reinforced polymers have a typical filler content of about 70 vol.% while for nanocomposites, it is of about 1% and below, [2]

³The interfacial region is defined as the volume in which the material properties deviate from those of the bulk matrix or of the nanoparticles, [1]. In the case of nanocomposites, this interfacial region is often considered to be the entire volume of the composite.

⁴Two distinct dispersions should actually be considered. First, the dispersion of the CNTs in the solution during fabrication and second the final dispersion of the CNTs inside the solid polymer matrix.

2.2 CARBON NANOTUBES

Carbon Nanotubes (CNTs) were discovered by S. Iijima in 1991, [3], and have since attracted a lot of attention from the scientific world. They are composed of graphene planes rolled to form concentric tubes. Graphene is a flat monolayer of carbon atoms tightly arranged in a 2D honeycomb lattice [4]. CNTs have a typical diameter of about 1 – 50 nm and can be many microns long. Tubes with lengths up to one centimetre were observed, [1]. Because of their remarkable mechanical and electrical properties, they are very interesting potential fillers to be considered for the design of nanocomposite materials.

The major obstacle in the development of CNT nanocomposites is that the fabrication of high purity and quality CNTs in large quantities is not yet a simple process but synthesis techniques are currently being improved in order to overcome this difficulty.

CNTs can be of two structural types: Single Wall CNTs or Multi Wall CNTs (SWCNTs or MWCNTs). In SWCNTs, one single graphene sheet is rolled into a cylinder. MWCNTs consist of two or more coaxial cylinders, interlayer interactions being very weak⁵, [1]. SWCNTs very easily form ropes or bundles because of Van Der Waals attractions between isolated tubes. Because of their morphologies, MWCNTs are slightly less sensitive to these forces than SWCNTs.

The properties of the CNTs also differ depending on their synthesis method. High temperature evaporation using arc discharge or laser ablation produces small amounts (a few grams at most) of highly crystalline, low defect CNTs but also a lot of impurities, [1].

CNTs obtained using Chemical Vapour Deposition (CVD) or catalytic growth processes (lower temperature) are structurally less perfect and usually highly entangled. The contaminant in this case is the catalyst but it is integrated in the nanotubes. Also, larger quantities of CNTs can be produced, along with other types of Carbon Nanofibers (CNFs).

2.2.1 Transport properties of CNTs

SWCNTs exhibit a metallic or semi-conducting behaviour depending on their diameter and their helicity or chirality (how the graphene plane is rolled, e.g. zigzag or armchair nanotubes), [6]. Synthesis techniques have little control over this difference and on average, one out of three SWCNTs fabricated is metallic and two are semi-conducting. MWCNTs are reported to be generally conductive, their large external diameter leading to a small band gap semiconductor, [7]. The transport properties of isolated CNTs are very difficult, though

⁵The Van Der Waals forces between layers of graphene in a MWCNTs are modulated by the presence of defects in these layers and orbital interactions, more details in [5].

interesting, to measure and the results vary greatly depending on whether the CNTs characterized are SWCNTs or MWCNTs or bundles, [1].

SWCNTs were characterized in the literature at room temperature and their electronic conductivity was found to be of the order of 10^5 to 10^6 S/m for the metallic SWCNTs and 10 S/m for the semi-conducting ones. However, they are often found agglomerated in bundles and the conductivity of such bundles was measured between 10^4 and 10^6 S/m, in mats of SWCNTs the reported conductivity is about 200 S/m, [6]. These values are very close to the electrical conductivity of native graphite ($2.5 \cdot 10^6$ S/m). The transport properties of MWCNTs are determined mostly by the outer tube (helicity, defects). Individual MWCNTS were found to have conductivities between 20 and $2 \cdot 10^7$ S/m, [1].

Similarities between the behaviour of networks of CNTs and that of conducting polymers have been observed; their electronic conductivities can be modelled using metallic conduction and small electrical barriers (hopping or tunnelling through), [1], more details about these models will be given further in this chapter.

2.3 CNTS POLYMER NANOCOMPOSITES

Different synthesis techniques exist to fabricate CNTs polymer nanocomposites. The most attractive (and environmentally friendly) for commercial production is probably melt-blending, where the elements are mixed in liquid state. There are also solution mediated processes and in-situ polymerization techniques, [1]. The technique used has an important influence on the properties of the composite, the choice of the polymer matrix also plays a major role. Very low percolation threshold were obtained (below 0.04 wt.%) in epoxy resin, [8], or in poly-(vinyl alcohol) and conjugated polymers, [7]. Low thresholds of about 0.5 wt.% were obtained in PMMA, [6] while polycarbonate composites displayed higher values between 1 and 2 %. On the opposite it has been shown that, on the average, thermoplastic⁶ polymers exhibit a higher electrical conductivity above the threshold than thermoset⁷ polymers.

Dispersion of the particles is a key parameter in the fabrication of nanocomposites. When particles having dimensions of about 1 μm or less are dispersed in a mildly viscous medium, interactions between these particles and diffusion processes play a major role in the dispersion or reagglomeration of the CNTs inside the polymer matrix, [9].

As mentioned in the previous section, CNTs are usually entangled and tend to form bundles or aggregates. Arc-grown CNTs are less entangled than CVD ones, they are therefore more easily dispersed in a polymer matrix, [2]. In order to disperse the CNTs in the polymer matrix and break up the intermolecular bonds responsible for the aggregate formation, new dispersion techniques were developed. Melt-mixing techniques can be complemented by sonication, to help break the entanglement of the CNTs. The CNTs can also be 'functionalized' prior to their addition into the polymer solution; The CNTs are chemically treated so that defects in the tube appear and they can interact, by covalent coupling, with pieces of polymer molecules, cf. Fig. 2.2.

Functionalization is an efficient way of improving dispersion, and also the bonding to the matrix, [10]. But it can sometimes be detrimental to the properties of the CNTs. Another, more subtle, way to improve the dispersion is to obtain some alignment of the tubes using mechanical techniques or preformed substrates, and also by applying electric or magnetic fields, [9, 11]. As can be seen on Fig. 2.3, those nanocomposites can exhibit a percolation threshold⁸ orders of magnitude lower than that of non-aligned composites, [1]. The mean interpar-

⁶A thermoplastic polymer is liquid above a given temperature, it can be melted and remoulded. Polystyrene, PMMA, polycarbonate, polyurethane, polyimide, PEEK, PCL, PTFE, ionomers are example of thermoplastics.

⁷A thermoset polymer is a polymer that can be irreversibly cured, it cannot be melted and remoulded. Epoxy resins and bakelite are examples of such polymers.

⁸see section 2.4 for more details.

ticle distance decreases with the volume fraction of CNTs in the matrix, [1]. It has been calculated, [2], that for a 3% volume fraction of SWCNT this mean distance is equal to about twice the diameter of a single nanotube, leaving a very small gap for the polymer chain to penetrate. This is why a good dispersion is very difficult to obtain for high volume contents of CNTs.

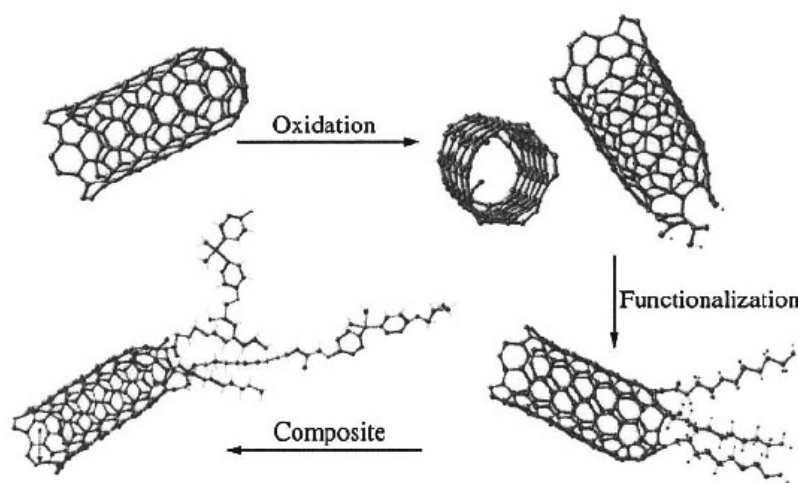


Figure 2.2.: *Schematic illustration of the functionalization process, from [2].*

The quantitative characterization of the state of dispersion of the nanofillers inside the polymer matrix is not an easy task, [8, 12]. Imaging techniques (optical, atomic force, scanning or transmission electron microscopy) can only give a very local picture of the dispersion not a global image. Furthermore, the tremendous differences in axial and radial dimensions of the CNTs, as well as their complex shapes, make it even more difficult to analyze correctly these local pictures. Indirect estimative methods such as dynamic rheological measurements and electrical characterization can give a more global image of the dispersion, [10].

The dispersion, as determined from electrical characterization, is based on resistive considerations (on the DC electrical conductivity, see further for more details) but information about the status of dispersion can also be gained from capacitive considerations especially when comparing resistive and capacitive results, cf. chapter 4 and [13].

The most important thing to keep in mind about CNT polymer composites is that there is no standard approach correlating the characteristics of the CNTs and those of the polymer with those of the nanocomposite! Besides, there is no ‘optimal’ nanocomposite, the choice of the nanoparticles, of the polymer matrix

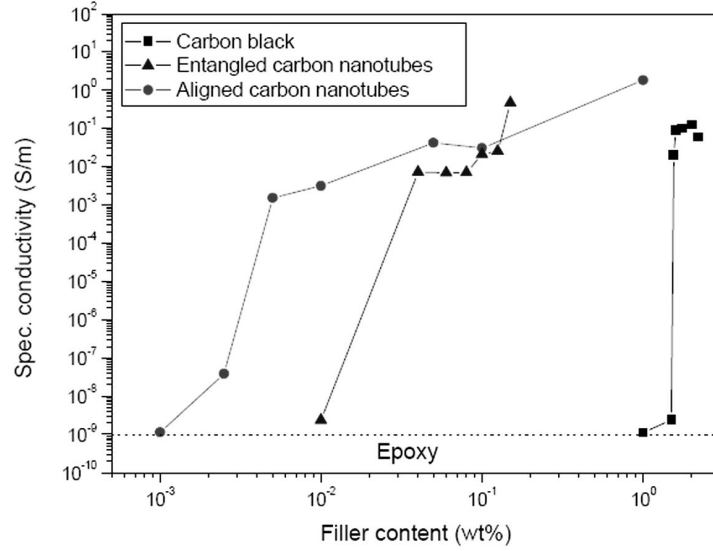


Figure 2.3.: *Electrical conductivity of an epoxy composite versus filler weight fraction for carbon black particles, for commercial entangled CNTs and for aligned CVD grown MWCNTs, from [1].*

and of the synthesis methods to use will depend on the application and the desired characteristics, [1]. The ‘ideal’ CNT composite has not yet been found and it does not seem to exist at all, so many things depending on the matrix and desired application, [9].

It is interesting to note that while this thesis is focused exclusively on the electrical properties of CNT polymer nanocomposites, they also possess remarkable thermal, optical and mechanical properties, more information on those can be found in [1].

2.4 ELECTRICAL PROPERTIES OF CNTS POLYMER NANOCOMPOSITES

The electrical conductivity of nanocomposite polymers depends on a variety of factors, the properties of the CNTs themselves (aspect-ratio, specific surface area, surface conductivity, etc.), of the type(s) of polymer(s) composing the matrix but also on their interactions (e.g. fabrication or functionalization, etc.) and, of course, on the dispersion of the nanoparticles inside the matrix, [6].

Nevertheless, polymer nanocomposites all share some similar singular transport properties.

2.4.1 Direct-current electrical conductivity and percolation threshold

Nanocomposites usually exhibit a strong non-linear increase of the DC electrical conductivity with the particle content, as can be seen on Fig. 2.4. A percolation threshold, a sharp increase of several order of magnitude, is generally present, [1], marking the change in behaviour from that of a number of isolated conductive elements to that of a network of connected particles dispersed through the matrix. For filler concentrations close to the threshold, the electrical conductivity of the nanocomposite versus filler content follows a power scaling law

$$\begin{cases} \sigma_0 \propto (\varphi - \varphi_c)^t & \varphi \gtrsim \varphi_c \\ \sigma_0 \propto (\varphi_c - \varphi)^{-s} & \varphi \lesssim \varphi_c \end{cases} \quad (2.1)$$

where φ is the filler content, φ_c is the threshold filler content, σ_0 is the DC conductivity, t and s are exponents depending on the dimensionality of the system, [7, 9]. However, the second relationship is rarely used in the literature. For three-dimensional systems, t seems to vary between 1.6 and 2 ($t \sim 1.3$ in 2D). But CNT composites sometimes exhibit a lower t , this does not seem due to a reduction in dimensionality but rather to the presence of an aggregation process during the synthesis and to other factors, [9]. Besides these values vary from author to author and depend on the kind of simulation used, [7]. More details on this scaling law will be given further in this section.

It must be noted that the symbols φ (φ_c) and p (p_c) are equally used in the literature to denote the nanoparticle filler content (percolation threshold). In the same way, σ_0 or σ_{DC} can alternatively be used to designate the DC conductivity. It is also the case in the present thesis.

Nevertheless, experimental values for percolation thresholds are not explained completely using solely the statistical, geometrical analysis. CNTs aggregation leads to the creation of a more efficient network than could occur randomly, [8, 9]. Again, particle-particle and polymer-particle interactions play a major role in network formation. Colloid theory aspects can give some further information, [14].

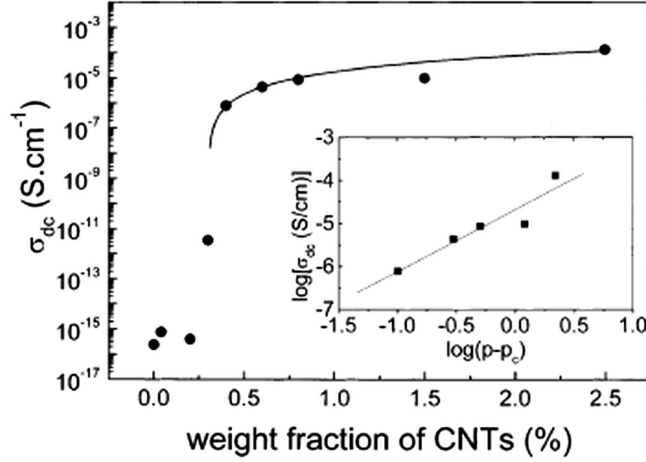


Figure 2.4.: *DC conductivity versus CNTs weight fraction for epoxy-based nanocomposites, from [6]. The solid line is a fit to the scaling law given by equation 2.1, the inset is a log-log plot of the DC conductivity versus the difference $(\varphi - \varphi_c)$ where the solid line corresponds to the best fit (from a linear fit in the loglog plot).*

The percolation threshold decreases with increasing aspect ratio of the nanoparticle, a linear decrease in the case of conducting ‘sticks’, or elongated inclusions, according to the effective medium model of Lagarkov and Sarychev, [15, 16]. It must be pointed out, however, that the CNTs inside a nanocomposite are not rigorously sticks, they have a significantly curved shape, which has been shown to be detrimental to the conductivity of the composite, [17].

Balberg et al., [18], discussed the percolation threshold of 2D and 3D systems of randomly oriented objects in correlation with their excluded volumes and aspect-ratio. The excluded volume of a particle is the volume around the particle that the center of another similar particle cannot penetrate, this concept is illustrated on Fig. 2.5. They proposed the following relation for an isotropic system of randomly long sticks (of length L and radius r)

$$(L/r)\varphi_c \approx 3 \quad (2.2)$$

where (L/r) is the aspect ratio and φ_c the critical volume fraction of the sticks. If the approximate dimensions of the CNTs in the composite are known, the determination of the percolation threshold through the electrical characterization can yield information on whether individual CNTs or bundles of nanotubes are responsible for the electrical conduction, [6].

Garboczi et al. used percolation theory to calculate the geometrical percolation threshold of randomly oriented overlapping ellipsoids, [19], based on the

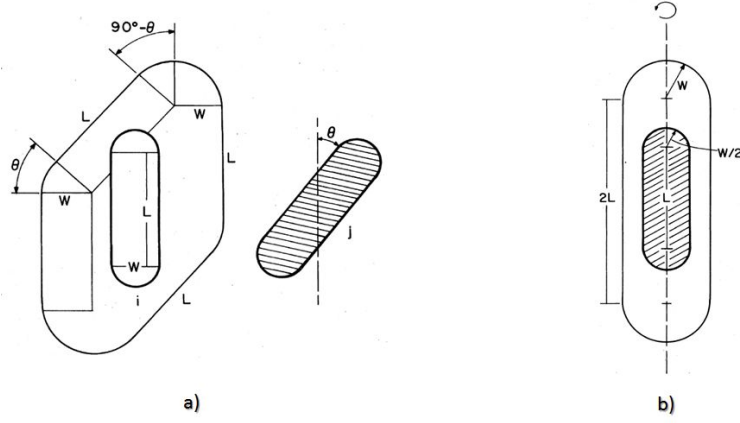


Figure 2.5.: Schematic diagrams showing the a) excluded area of the 2D stick i corresponding to stick j and b) the excluded volume of a 3D stick in a 3D all parallel stick system, from [18]. L is the length of the sticks and W their width.

excluded volumes model of Balberg, [20]. The inverse of this threshold is plotted versus aspect ratio on Fig. 2.6. It can be seen that in the extreme prolate (rods) and oblate (disks) limits the inverse of the percolation threshold scales linearly in the inverse of the aspect ratio, confirming the model of Lagarkov. The corresponding asymptotic forms are

$$\varphi_c \rightarrow \begin{cases} 0.6(\frac{b}{a}) & (\text{prolate}); \\ 1.27(\frac{a}{b}) & (\text{oblate}). \end{cases} \quad (2.3)$$

where a is the length of the symmetry axis and b the length of each perpendicular axis. From Fig. 2.6, it can also be noted that the inverse of the percolation threshold is minimized for spheres ($\varphi_c = 1$) meaning that spheric particles display the maximum percolation threshold, [19].

The above models are theoretical and based on geometrical considerations only. In the case of real CNT composites, the threshold value also depends on the type of CNTs, the polymer chosen and how the CNTs were treated and how they were inserted in the polymer matrix, [1]. Depending on the kind of CNTs, the synthesis method and polymer matrix, percolation thresholds from 0.05% to 10% were observed experimentally, [9]. It can be noted that nanocomposites having really low percolation thresholds can exhibit a strong non-ohmic behaviour indicating a dominant quantum tunnelling mechanism, [8].

The maximum conductivity is limited by the resistance between the connected particles and their intrinsic resistivity, [1, 9]. It might also be due to thermally activated transfers between neighbouring non-connected tubes. This phenomenon would also explain, partially, the low value of the exponent t . 1 S/m is a common

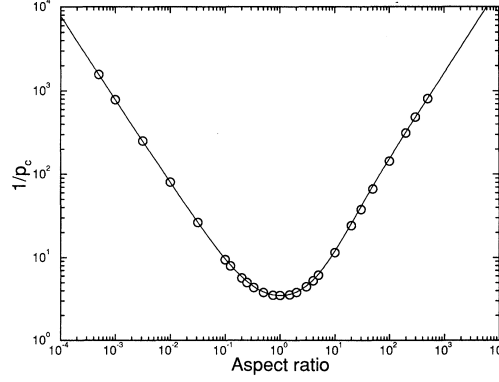


Figure 2.6.: Inverse of the percolation threshold (volume fraction, p_c) versus aspect ratio (L/r) of ellipsoids of revolution. The solid line is a Padé-type approximant, from [19].

value for this maximum conductivity, several orders of magnitude lower than the theoretical conductivity of CNTs. In [7], Kilbride et al. used such conductivity versus frequency curves (in PmPV and PVA polymer based nanocomposites⁹) and the scaling law to extrapolate the conductivity at $\varphi = 100\%$. They found an approximate value of 10^{-3} S/m, i.e. 5 or 6 order of magnitudes smaller than that expected for mat of MWCNTs, [1, 7]. An anisotropy in the dispersion of the CNTs was first considered but measurements along other axis gave similar results. Another most plausible explanation is that the CNTs are coated by an insulating polymer layer formed in the solution phase. This layer helps the solution and dispersion of the CNTs during the fabrication process but results in poor electrical contacts between neighbouring CNTs. The macroscopic effective conductivity is therefore decreased and dominated by inter-CNTs connections. Kilbride et al. also observed a low value of the critical exponent $t = 1.36$ suggesting a 2D percolation system though unlikely considering the experimental conditions (current forced to pass through the thin film sample). In another paper, [21], Reghu et al. studying transport phenomena in polyaniline networks near the percolation threshold also reported $t \sim 1.3$ at room temperature but at 10 K they found $t = 1.99$, the expected value for a 3D network, also suggesting thermally activated transfers between disconnected or weakly connected elements of the network and also confirming the presence of a thick polymer barriers between neighbouring CNTs, [7]. A decreased t value could also be explained by a decrease in the number of ‘dead’ arms in the network (because of the thin film configuration), [6, 7].

⁹PmPV stands for poly(m-phenylenevinylene-2,5-dioctyloxy-p-phenylenevinylene) and PVA for polyvinylalcohol.

It is interesting to note that, for example, the thermal conductivity of CNTs polymer nanocomposites, another transport property, does not exhibit such a percolation threshold. Instead, the thermal conductivity increases linearly with the filler content, [1], though anomalous thermal conductivity enhancement has been observed for dilute suspensions of homogeneously dispersed CNTs. Discussion about this is beyond the scope of the present thesis but more information can be found in [22, 23].

2.4.2 Frequency dependence of the electrical conductivity

The real part of the complex permittivity or dielectric constant (ϵ'), its imaginary part (ϵ'') and the corresponding electrical conductivity ($\sigma' = -\omega\epsilon_0\epsilon''$) versus frequency curves that are plotted for different MWCNT loadings (PC nanocomposites) on Fig. 2.7 are a very good illustration of the influence of the filler concentration on the electrical properties of nanocomposites, as can be found in the literature, [12]. And, the discussion below can be applied to any given nanocomposite.

It is worth noting that throughout the present thesis, the term *dielectric constant* will only be used to designate the real part of the complex permittivity.

Two different behaviours can be observed: the one of nanocomposites with CNT contents lower than 1.5 wt% and that of composites with content of 1.5 wt% and higher. The first ones exhibit a nearly constant ϵ' value with only small variations in ϵ'' and an increasing σ' with a negligible $\sigma_{DC} = \sigma'(\omega \rightarrow 0)$. This conductivity versus frequency is a straight line in the double logarithmic plot, characteristic of a power law of the form ω^s . The samples with a filler content above the threshold, on the opposite, show a sharp decrease in ϵ' and ϵ'' with increasing frequency and a constant σ' with a non-negligible σ_{DC} (characteristic of long range movement of the charge carriers). The percolation threshold should be somewhere between 1 wt% and 1.5 wt%. If frequency was further increased, the conductivity versus frequency curves would also exhibit a ω^s power law dependence, as can be seen on Fig. 2.8.

It should be noted that the composites having a filler content higher than 1 wt% were not characterized under 0.1 Hz because, as can be seen on Fig. 2.7, the DC plateau in conductivity is already achieved. Besides samples with content above 2 wt% have a high conductivity that making any accurate measurement of their dielectric constants all but impossible, [24].

The extrapolated values of the DC conductivity ($\sigma'(\omega \rightarrow 0)$) are plotted versus CNT content on Fig. 2.9. From this graph, the percolation threshold, φ_c , is around 1.5 wt%, near this concentration the conductivity increases sharply (about 10 decades). To determine the value of φ_c more precisely as well as that of the exponent t , the values of σ_{DC} above φ_c were fitted and those corresponding to the smallest root mean square error were: $\varphi_c = 1.44 \pm 0.005$ and $t = 2.1 \pm 0.1$, in good agreement with the literature.

However, a percolation threshold of 1.44 wt% is significantly higher than expected given the very high aspect ratio of CNTs. It means that only a fraction of the CNTs inside the nanocomposites composes the conducting network at percolation and the rest forms useless aggregates in the material.

The frequency dependence of the conductivity exhibits a strong dispersion, a characteristic property of conduction in disordered solids (a phenomenon also

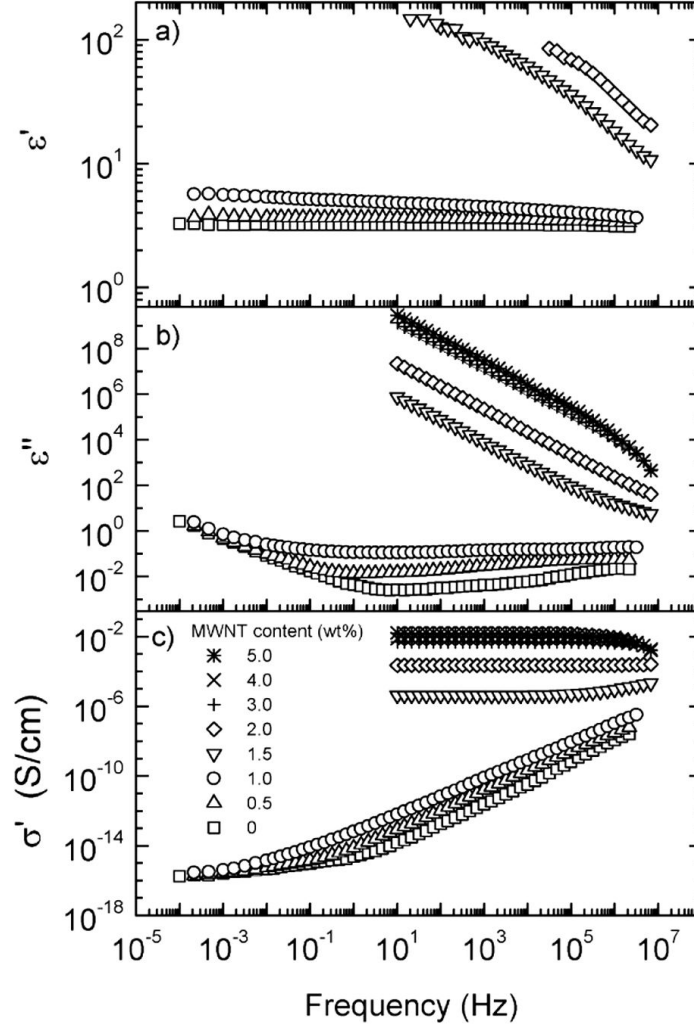


Figure 2.7.: Frequency dependence of the dielectric constant ϵ' (top), imaginary part of the permittivity ϵ'' (center) and conductivity σ' (bottom) of CNT/polycarbonate composites with filler concentrations from 0 to 5 wt%, from [12].

called “universality of AC conduction”, cf. section 2.5.4, [7, 25]. At low frequencies, well below the characteristic frequency¹⁰ ω_0 , the conductivity is independent of the frequency (plateau) while above ω_0 , the conductivity behavior can

¹⁰This characteristic frequency is usually defined by $\sigma(\omega_0) = 1.1\sigma_0$, [7]

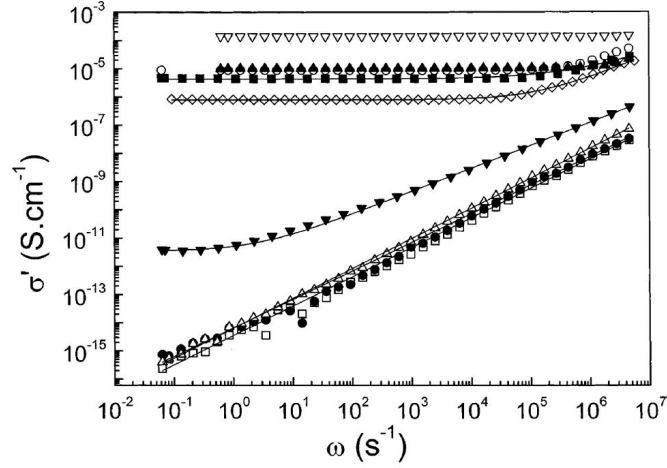


Figure 2.8.: Frequency dependence of the electrical conductivity σ' of CNT/epoxy resin composites with filler contents of 0 ($\square$), 0.04 ($\bullet$), 0.2 ($\triangle$), 0.3 ($\blacktriangledown$), 0.4 ($\diamond$), 0.6 ($\blacksquare$), 0.8 ($\circ$), 1.5 ($\blacktriangle$) and 2.5 wt% (∇), from [6]. The solid lines are fits to equation 2.5.

be approximated by a simple power law, as can be seen on Fig. 2.8

$$\sigma(\omega) \sim \omega^s \quad (2.4)$$

where s is measured as the slope of the curves from Fig 2.7 in the high frequency region. In disordered solids, such a power law associated with a s value between 0.8 and 1 is due to the hopping of charge carriers randomly arranged energy barriers (of random heights). This would support the model of fluctuations induced tunnelling conduction where the heights of the barriers between neighbouring nanotubes vary because of random temperature changes, [7, 25].

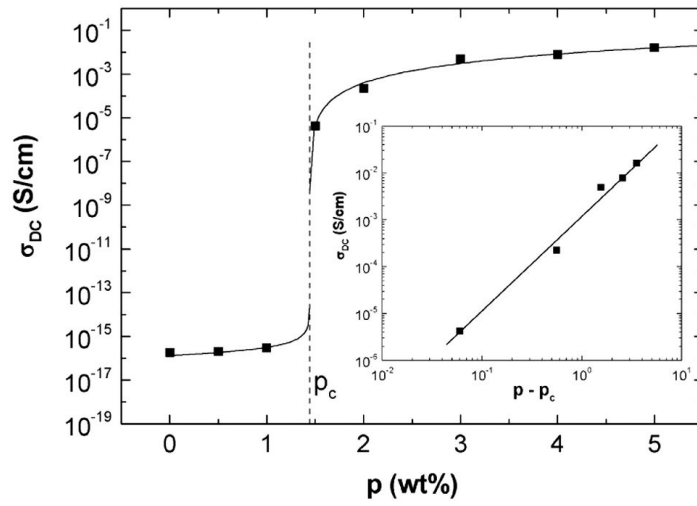


Figure 2.9.: DC conductivity, σ_{DC} , versus CNT loading for the polycarbonate composites of Fig. 2.7. In the insert: DC conductivity of the sample versus $(p - p_c)$ and fitted using the scaling law 2.1, from [12].

2.4.3 Dielectric constant and crossover frequency

The DC dielectric constant can also be extracted from the data shown on Fig. 2.7, $\epsilon_S = \epsilon'(\omega \rightarrow 0)$. These values are plotted versus CNT concentration on Fig. 2.10, ϵ_S increases with CNT content below φ_c as expected but does not decrease above the threshold, as predicted by the model described in section 2.5.2. However, even if ϵ_s could not be reliably measured above 2 wt%, it does not seem to decrease at all beyond φ_c . These experimental results are confirmed by other results from the literature, [26–28] where a $(\varphi - \varphi_c)^s$ dependence is assumed, contrary to the $|\varphi - \varphi_c|^s$ of section 2.5.2 plotted on Fig. 2.10.

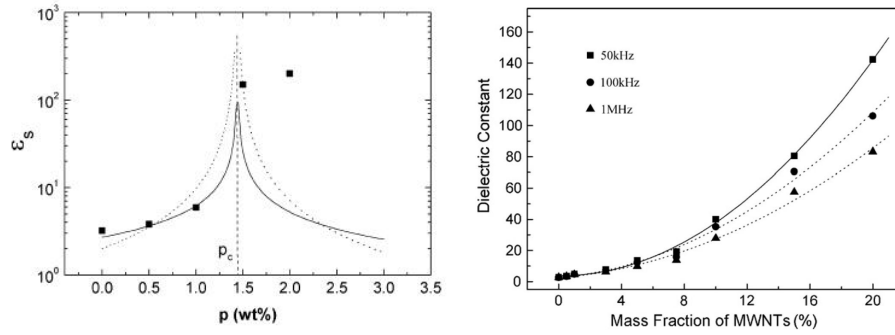


Figure 2.10.: *Left: DC dielectric constant, ϵ_s , versus CNT loading for the polycarbonate samples of Fig. 2.7, [12], the solid line a fit using equation 2.11. Right: DC dielectric constant versus filler content of the polyimide nanocomposites of [27], approximated from the value of the dielectric constant at 50 kHz (■), 100 kHz (●) and 1 MHz (▲).*

The difference between the theoretical $|\varphi - \varphi_c|^s$ dependence and experimental results, has also been observed for polymer composites containing carbon black (CB). In [12], this is attributed to the presence of ‘micro capacitors’ in the sample above the threshold or to the existence of ‘free arms’ in the material. These micro-capacitors are mainly assumed to be sort of gaps between the CNTs (‘bound rubber’ in CB networks). On Fig. 2.10, the values of ϵ_s are of the order of 10^2 , much smaller than the values usually reported for CB composites ($10^3 - 10^4$). This could be explained by the much lower number of particles per unit volume in CNT composites than in CB ones, [12]. CNTs also have a much higher aspect-ratio than CB spherical particles resulting in a smaller number of ‘micro-capacitors’ and therefore a smaller dielectric constant. In [15], the existence of a resonance phenomenon in the dispersion relations for the effective dielectric constant of composites containing elongated conducting inclusions is also investigated and a $|\varphi - \varphi_c|^s$ dependence is also considered for metal-insulator transitions in [29].

Besides σ_{DC} and ϵ_s , the crossover or critical frequency, at which the AC behaviour of the conductivity deviates significantly from the DC plateau, $f_c =$

$\omega_c/2\pi$, can be extracted from the data of Fig. 2.7. In the percolation model, this frequency corresponds to the transition from a normal diffusion process ($\sigma'(f < f_c) = \sigma_{DC} = \text{constant}$) to an anomalous one ($\sigma'(f > f_c) \propto \omega^s$). By convention, it is often chosen so that $\sigma(\omega_c) = 1.1\sigma_{DC}$, [7].

2.5 MODELS OF THE FREQUENCY DEPENDENCE AND DC BEHAVIOUR OF THE ELECTRICAL CONDUCTIVITY

The frequency dependence of the complex permittivity $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ and of the complex conductivity $\sigma^*(\omega) = \sigma'(\omega) - i\sigma''(\omega)$, as well as the DC electrical behaviour can be modelled using one or several of the following models:

1. Universal Dynamic Response
2. Equivalent electrical circuit models
3. Percolation clusters models (charge carriers diffusion)
4. Thermodynamic percolation models
5. Thermal fluctuation induced tunnelling model
6. Random biased walk
7. Effective Medium Theory based models

2.5.1 Universal Dynamic Response

It might be tempting, [6], to use the so-called “universal dynamic response” (UDR)¹¹ first introduced by Jonscher: [31].

$$\sigma'(\omega) = \sigma_0 + A\omega^n \quad (2.5)$$

with σ_0 and A thermally activated.

But this power-law dependence used a priori is non-physical even though it has been widely used for many different systems, [30]. It should not be used without further considerations except as a preliminary fitting. Models with more physical meaning should be used instead. A good fitting model not only allows interpolation (and sometimes extrapolation) but, most of all, should lead to a better understanding of the phenomena under consideration.

¹¹Actually, the Jonscher model was developed for dielectric systems (where the DC and AC responses are not related, unlike in conductive systems) and was called the “universal dielectric response”, [30].

2.5.2 Equivalent electrical circuit models

It has been shown, in section 2.4.2 and [32], that the complex effective permittivity and conductivity of the mixture of a pure conductor and a pure dielectric exhibits a singular frequency behaviour. The DC conductivity is negligible below the percolation threshold and increases as a power of $\varphi - \varphi_c$ above it (φ_c being the critical fraction of conductive material at the threshold). The AC conductivity increases with frequency below the threshold but is constant above it, the values also increase with the fraction of conductive material (φ). The DC dielectric constant diverges as φ reaches φ_c from higher or lower values. Besides, even if the conductivity and dielectric constant of the pure phases did not depend on frequency, both effective conductivity and dielectric constant of the mixture show a frequency dependence.

An explanation for this singular behaviour may be the presence of conducting channels that are spread throughout the material, corresponding to very large parallel capacitances. This would also explain strong non-linearities in the dielectric response for large values of the dielectric constant, because of the high electric fields at the thin barriers between the conductive channels. Near the percolation threshold, quantum-tunnelling through those barriers may become non negligible, [32]. More details about these tunnelling phenomena can be found further in this section.

The nanocomposite material can be modelled using series or parallel associations of resistors, capacitors or inductors.

If we consider highly conductive clusters (σ_1) embedded in an insulating matrix ($\sigma_2, \sigma_2 \ll \sigma_1$), the effective conductivity can be modelled near the percolation threshold by the scaling law¹², [12]

$$\sigma(\varphi, \omega) \propto \sigma_1 |\varphi - \varphi_c|^t \Phi_{\pm} \left(\frac{\sigma_2}{\sigma_1} |\varphi - \varphi_c|^{-(t+s)} \right) \quad (2.6)$$

where φ is the filler concentration, Φ_+ and Φ_- are scaling functions for $\varphi > \varphi_c$ and $\varphi < \varphi_c$, respectively, s and t are critical exponents. The scaling functions have to be determined by fitting of experimental data, [32]. Many different approaches (theoretical models or simulations) have been used in the literature to determine the values of the critical exponents with different results. Values of s and t for 2-D systems were found to be equal and between 1.1 and 1.4, and for 3-D models, s is equal to 0.7 – 0.75 while t varies between 1.7 and 2.0, [12]. But several authors agree on $s = t = 1.30$ for 2-D and $s = 0.75, t = 1.9$ for 3-D.

If the DC conductivity ($\sigma'(\omega \rightarrow 0)$) curve versus CNT content of Fig. 2.9 is considered, the following values were found by simple fitting: $\varphi_c = 1.44 \pm 0.005$ and $t = 2.1 \pm 0.1$. From that value of φ_c and using $s = 0.73$, arbitrary chosen, the curve fitting σ_{DC} below the threshold could be extrapolated.

¹²More detailed form of the scaling law than Eq. 2.1

The nanocomposite material can be modelled as an equivalent electrical circuit randomly composed of resistors and capacitors (total equivalent resistance: R and capacitance C), as illustrated on Fig. 2.11. Equation 2.6 then becomes, near the percolation threshold, [12]

$$\sigma(\varphi, \omega) \propto \frac{1}{R} |\varphi - \varphi_c|^t \Phi_{\pm} \left(\frac{i\omega}{\omega_0} |\varphi - \varphi_c|^{-(t+s)} \right) \quad (2.7)$$

where $\tau = 1/\omega_0 = RC$ is the relaxation time of the equivalent circuit.

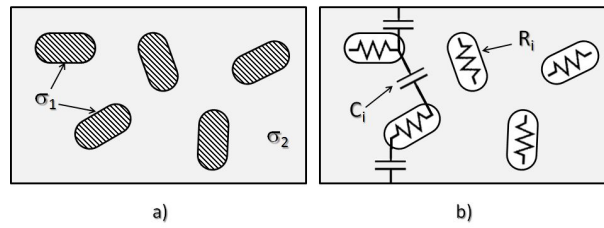


Figure 2.11.: Schematic diagram of a) a nanocomposite material composed of nanoparticles of conductivity σ_1 in an insulating matrix of conductivity σ_2 and b) electrical equivalents, if the matrix is considered to be a perfect dielectric and the particles are assumed to be purely resistive: total equivalent resistance: $R = 1/\sigma_1$ and capacitance: $C = -i\sigma_2/\omega$ (only some of the parasitic couplings are shown for clarity).

A critical time scale $\tau_c(\varphi)$ can be derived from the above equation

$$\tau_c(\varphi) \propto \frac{1}{\omega_c(\varphi)} \propto \frac{1}{\omega_0} |\varphi - \varphi_c|^t \Phi_{\pm} \left(\frac{i\omega}{\omega_0} |\varphi - \varphi_c|^{-(t+s)} \right) \quad (2.8)$$

If we consider a DC situation, the RC model corresponds to a simple conductor-insulator model, [12] and Eq. 2.7 becomes

$$\sigma_{DC}(\varphi) \propto \begin{cases} (\varphi_c - \varphi)^{-s} & \text{if } \varphi < \varphi_c; \\ (\varphi - \varphi_c)^t & \text{if } \varphi > \varphi_c. \end{cases} \quad (2.9)$$

In the AC regime, the real part of the conductivity and that of the permittivity at the percolation threshold are dependent on the frequency and the following set of laws were derived by Bergman and Imry, [32]

$$\begin{aligned} \sigma'(\omega) &\propto \omega^{\frac{t}{t+s}} \\ \epsilon'(\omega) &\propto \omega^{\frac{-s}{t+s}} \end{aligned} \quad (2.10)$$

From Eq. 2.10 with $\omega \rightarrow 0$, the DC dielectric constant dependence on filler content diverges at the threshold and is given by

$$\epsilon_s(\varphi) \propto |\varphi - \varphi_c|^{-s} \quad (2.11)$$

2.5.3 Percolation clusters models (charge carriers diffusion)

CNT nanocomposites can also be described using models based on the diffusion of charge carriers in a percolation structure (percolation/diffusion theory), [12]. Percolation is a standard model for structurally disordered systems, [33]. In a square lattice, such as the one shown in Fig. 2.12(left), sites are either occupied or empty randomly, with a p or $(1 - p)$ probability, respectively. If we consider occupied sites to be electrical conductors and empty ones to be insulators, electrical current can only pass through connected nearest neighbour conductor sites and p is the conducting particles concentrations.

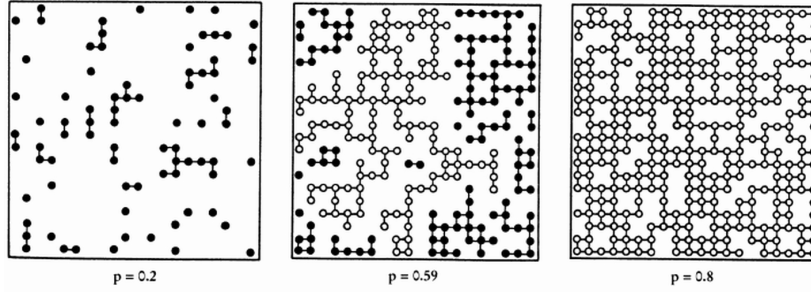


Figure 2.12.: *Percolation on a square lattice for three different concentrations: $p = 0.2$ (left), $p = 0.59$ (center) and $p = 0.8$ (right). The lines between nearest neighbour cluster sites represent the bonds between them. Solid black circles belong to finite clusters while white ones form the infinite cluster, from [33].*

At low concentration, the conducting sites are either alone or connected to small, isolated clusters and the material is essentially an insulator, no path connecting two opposite edges of the lattice, cf. Fig. 2.12(left). On the other hand, at high concentration, many paths connect opposite edges and the material is a conductor, cf. Fig. 2.12(right). There is a threshold concentration p_c , called the *percolation threshold*, corresponding to the first current percolation, the first path from one edge to the opposite one. This first cluster extending from one edge to the other is called the *infinite cluster*¹³, cf. Fig. 2.12(center), [15]. As the concentration increases above the threshold, the size of the infinite cluster increases while the average size of the finite clusters decreases, until all sites belong to the infinite cluster. This geometrical percolation threshold depends on the details of the lattice, its dimensionality and coordination number. For example, $p_c \cong 0.696$ for a 2D honeycomb lattice but $p_c \cong 0.312$ for a cubic one, [33].

Another important percolation parameter is P_∞ , the probability of a site belonging to the infinite cluster, P_∞ is plotted versus the concentration p on Fig. 2.13.

¹³The term ‘infinite’ comes from thermodynamic considerations on the cluster size.

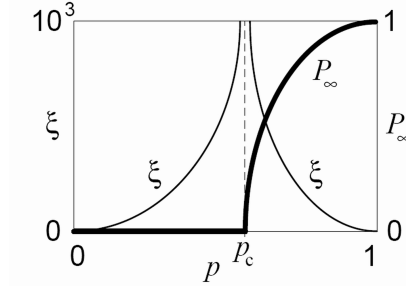


Figure 2.13.: Probability of belonging to the infinite cluster P_∞ (bold) and correlation length ξ (solid) plotted versus concentration p , from [33].

The probability P_∞ is zero below the threshold and increases above it as

$$P_\infty \sim (p - p_c)^\beta \quad (2.12)$$

The main parameter characterizing the linear size of the finite clusters is the correlation length ξ defined as the average distance between two random site belonging to the same cluster (the characteristic length scale of the percolation phenomenon). Below and above the threshold it is given by

$$\xi \sim |p - p_c|^{-\nu} \quad (2.13)$$

where β and ν are universal and do not depend on the lattice characteristics but only on its dimensionality, contrary to the percolation threshold. For a 2D lattice, $\beta \cong 5/36$ and $\nu \cong 4/3$, while for a 3D one, $\beta \cong 0.417$ and $\nu \cong 0.875$. They do not depend on the type of percolation, [33].

Capacitances are not included in such models but polarization effects are still taken into account by the existence of a finite time, characteristic of the motion of the charge carriers through the percolation clusters, [12]. This diffusion of the conductive sites leads to the dependence of the conductivity on the frequency. According to diffusion theory, the correlation time τ_ξ , during which a charge carrier cross through a cluster of correlation length ξ , can be written as follow

$$\tau_\xi \propto \xi^{d_w} \propto |p - p_c|^{-\nu d_w} \quad (2.14)$$

where d_w is the diffusion exponent and ν is the exponent in the dependence of correlation length on the filler concentration, from equation 2.13.

Therefore, the value of the correlation time increases with filler content below the threshold and decreases after it. For frequencies below $\omega_\xi = 1/\tau_\xi$, the correlation length is much larger than the average cluster dimensions and, the charge carriers can pass through several clusters during each period. This is a normal diffusion process and the conductivity is thus constant. If the frequency is higher

than ω_ξ , charge carriers cannot pass through more than a single cluster during one period and there is an anomalous diffusion at the fractal percolation clusters. And, as is measured experimentally, the conductivity value at low frequency is close to the DC value while it is much higher at high frequency. Therefore ω_ξ can be associated with ω_0 defined in section 2.4.2.

According to diffusion theory and to percolation theory through fractal a fractal structure, without any external electric field, the charge carriers follow trajectories described as *random walks* and scan an average characteristic length $L \sim \tau^{1/2}$ or $L \sim \omega^{-1/2}$ along the network, [7]. This model of a random walk has been used by Connor et al. to describe the AC conductivity and temperature dependence of polymer composites containing carbon black nanoparticles and also, the dependence of ω_0 on filler content [34].

Using results from diffusion theory on the dependence of the DC dielectric constant on filler content leads to the following relation

$$\epsilon_s(\varphi) \propto |p - p_c|^{-2\nu + \beta} \quad (2.15)$$

with β called the percolation exponent. Equation 2.11 and equation 2.15 are similar, if $s' = 2\nu + \beta$.

The solid line in Fig. 2.10 is calculated using the model of a random distribution of resistors and capacitors described in section 2.5.2, with $\varphi_c = 1.44$ from the estimation above and $s = 0.73$ (from literature). The dotted line is drawn using the percolation model described in this section and $s' = 1.33$ (from literature). The solid line seems a better fit to the experimental data than the dotted one but there are not enough data points to conclude with certainty, [12]. However both fits are in opposition with most experimental results, as discussed in section 2.4.3.

It must be pointed out that the equations given previously in this section represent the general model of percolation of charge clusters in a conductive composite material. Other statistical, thermodynamic, geometrical or structure oriented percolation models also attempt to describe the percolation threshold in terms of conductive particles distribution, content, size or shape, filler/matrix interactions and processing techniques. Several of these models are presented and discussed extensively in [35].

This percolation clusters model and its equations allow for a good fitting of experimental dielectric curves. However in several experimental studies, percolation thresholds were observed for filler contents much smaller than those predicted by the statistical percolation theory, even in CB composites. For examples, epoxy composites exhibited percolation thresholds of 1 vol.% of CB particles, more recently some experiments found percolation thresholds in CB and MWCNT composites about two orders of magnitude lower than predicted, [14].

Percolation theory suffer from two major deficiencies, [36]. First it is only valid, in a strict sense, when the components do not exhibit similar or close to similar properties. Second the percolation equations, by themselves, have no clear correlation to the microscopic properties of the composite material. Other issues with percolation models are discussed in term of correlation with quantum tunnelling phenomenon in section 2.5.4.

To improve the model, aspects from the colloid theory¹⁴ should be incorporated. Molecular-scale forces and interactions should also be considered, e.g. Van Der Waals forces that lead to the formation of aggregates while electrostatic charges or steric effects that help stabilise the dispersion. Understanding these factors and then how to optimize the formation of a network at a lower filler content could lead to the design of nanocomposites with even lower percolation thresholds.

¹⁴The colloid theory describes the behaviour of solutions containing a dispersion of fine particles.

2.5.4 Thermal fluctuation induced tunnelling model

As explained before, the CNTs inside the matrix are individually coated by a layer of polymer acting as a potential barrier for the ‘hopping’ of charge carriers between neighbouring CNTs (or conductive clusters). The conductivity is therefore probably limited by tunnelling between conductive regions, [7]. In the *fluctuation induced tunnelling model*, the conductivity behaviour is modelled using tunnelling through potential barriers of varying heights due to temperature fluctuations, [34]. The predicted electrical conductivity can be written as follows

$$\sigma_{DC} \propto \exp\left(\frac{-T_1}{T + T_0}\right) \quad (2.16)$$

where T is the temperature, k is the Boltzmann constant, $T_1 = wA\varepsilon^2/8\pi k$ and $T_0 = 2T_1/\pi w\chi$, with $\chi = (2mV_0/h^2)^{1/2}$, $\varepsilon = 4V_0/ew$, e and m the electron charge and mass, V_0 the potential barrier height, w and A are the distance and the area of the equivalent capacitance between two neighbouring CNTs, respectively. The most important thing is that, as detailed in [34]

$$\ln \sigma_{DC} \propto -w \quad (2.17)$$

If the CNTs are well dispersed inside the matrix, the filler content can be considered homogeneous throughout the material and the composite conductivity, at a given temperature, depends only on the behaviour of a single junction having a gap width $w \propto -p^{-1/3}$. As a consequence,

$$\ln \sigma_{DC} \propto -p^{-1/3} \quad (2.18)$$

This relation is a good indication of the presence of tunnelling conduction, [6], though equation 2.16 must be verified to confirm it.

On Fig. 2.14, DC and frequency independent AC conductivity data from [7] are plotted versus mass fraction (top), versus reduced mass fraction relative to the percolation threshold (center) and versus $p^{-1/3}$ (bottom), on a semi-logarithmic scale. The linear relationship between $\ln \sigma_{DC}$ and $p^{-1/3}$ is observed on Fig. 2.14(c), the solid line being a fit to the DC data to equation 2.18, in good agreement with the current limitation due to potential barriers between neighbouring CNTs.

As explained in section 2.4.2, many disordered materials exhibit the same AC conduction properties (or “universality of AC conduction”, [25]). AC conductivity data from different experiments can be plotted on the same graph using a proper scaling in conductivity and frequency, [7]. The selected scaling factors are often the σ_0 and ω_0 values. The AC data from the PVA samples of [7] has been plotted on Fig. 2.15, using these scaling factors. All the resulting curves fall on the same *master curve*, characteristic of the ‘universal’ behaviour. The following

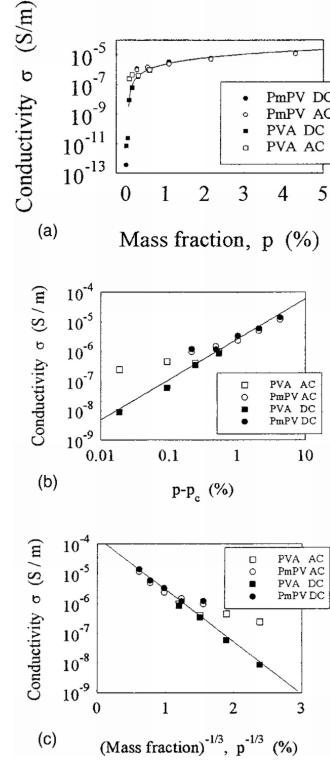


Figure 2.14.: (a) DC and frequency independent AC conductivity for PVA and PmPV nanocomposite samples. (b) Logarithmic plot of the conductivity versus reduced mass fraction ($p - p_c$), the solid line being a fit of the DC data to the scaling law. (c) Logarithmic plot of the conductivity versus $p^{-1/3}$, the solid line being a fit of the DC data to equation 2.18, from [7].

equation has been proposed for the master curve, [7]

$$\frac{\sigma(\omega)}{\sigma_0} = 1 + k \left(\frac{\omega}{\omega_0} \right)^s \quad (2.19)$$

where the parameter k allows for the arbitrary selection of ω_0 . The solid line in Fig. 2.15 is obtained by fitting the AC experimental data for PVA samples to equation 2.19. The value for the exponent s must be in agreement with the one from section 2.4.2. Good agreement can be observed between fit and experimental data at low and mid frequencies but at high frequencies, the data diverges from the power law fitting equation 2.19. This could be due to some antenna effect but a more plausible explanation is that the master curve approximation is too simple and it confirms that a more complicated model of hopping should be used, one that would be compatible with fluctuations induced tunnelling, [37].

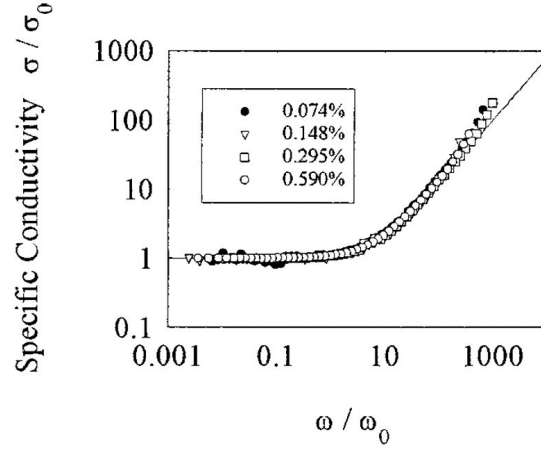


Figure 2.15.: AC conductivity for PVA nanocomposites (master curve), and the solid line being a fit to equation 2.19, from [7].

The correlated barrier hopping (CBH) model of Pike and Elliott is an interesting possibility, [6]. More information on the CBH model and its complicated temperature dependence can be found in [38] and [39].

Tunnelling conduction and percolation-based models (where there is a direct electrical contact between particles) seem a priori incompatible but values of the exponent t predicted by both theories are often very similar and close to the experimental value. Moreover the non-zero value of the electrical conductivity below the percolation threshold is commonly attributed to interparticle tunnelling, [40]. And, the application of the percolation approach is not always simple to justify. Why do percolation equations work well even for composites where there is a ‘homogeneous network of tunnelling conductors’, or *all-connected tunnelling network* (ACTN)? It is shown, in [40], that both theories are in good agreement when the conduction channels involve only tunnelling between nearest neighbours, like in carbon black (CB) composites, but diverge when next-nearest or higher order neighbours are involved (supplementary conduction channels), for example if the bias is increased.

In CB composites, as in other composites where there is conduction only between nearest-neighbours, the effective radius of the particles (~ 100 nm for CB particles) is very large compared to the characteristic tunnelling distance (d of the order of magnitude of about 1 nm), cf. Fig. 2.16(b). Therefore the distance between next-nearest neighbours is much longer than that between nearest neighbours (about equivalent to d) and conduction between non-nearest neighbours is virtually negligible. On the other hand, if the effective radius of the particles is similar to d , there may be tunnelling between higher order neighbours and results from percolation theories and tunnelling models will not agree

well, cf. Fig. 2.16(a). The diameter of CNTs vary from a couple of nanometres to several hundred nanometres, they could therefore be tunnelling between higher order neighbours and percolations models would not be adequate. Besides their twisted shapes and entanglement in bundles complicate the modelling even further. The ‘spaghetti’ shape and aggregation tendency are a very different structure than that of isolated ellipsoids.

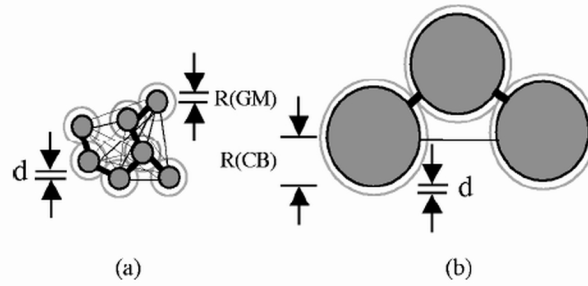


Figure 2.16.: Close up view on clusters of particles inside a composite material. The gray-filled circles are the conducting particles, their white shells represent the effective tunnelling range d , with R the particle radius. The thick black segments represent tunnelling connections between nearest neighbours while the thin lines are connections between higher order neighbours. The view illustrates the tunnelling range compared with the particle size for granular metals (a) and for CB composites (b), from [40].

2.5.5 Random biased walk

As explained at the end of section 2.5.3, the model of a random walk of the charge carriers along the CNT network can be used to describe transport phenomena in nanocomposites. But there are several issues with this approach, [7]. First, Connor et al. used the equation $L \sim \tau^{1/\delta}$ where δ is the fractal dimension of the fractal structure, [34]. In this equation, L is the average length of the straight line from the starting point of the walk to the finishing point of the random walk, which is different from the L defined previously as the distance travelled on the trail of the random walk (or the distance scanned by a charge carrier) and is given by $L \sim \tau^{1/2}$, [33]. Second, if even a very small electric field is applied, the walk is not completely random, it becomes biased. As the voltage increases, the walk becomes more strongly biased. At high voltage, the trajectory is non-random and the regime is that of charge scattering, with $L \sim \tau$ or $L \sim \omega^{-1}$.

In [7], Kilbride et al. proposed *biased random walk* along the conducting network where L is the length of the travel through this network. The two extreme cases detailed above (completely random walk and the case of carriers scattering) are also taken into account in this model

$$L \sim \omega^{-a} \quad (2.20)$$

with $0.5 < a < 1$. The frequency corresponding to a charge carrier travelling (on average) the distance L in half the period is given by the equation $\omega \sim L^{-1/a}$. This confirms that a is the level of bias (from an external electric field) imposed on the otherwise random walk. In the high frequency limit, the charge carrier scans the correlation¹⁵ length at a frequency $\omega_\xi = \xi^{-1/a}$.

If we consider equation 2.13, $\xi \sim (p - p_c)^{-\nu}$ and we combine it with the previous equation, assuming $\omega_0 = \omega_\xi$, the critical frequency can be written

$$\omega_0 \sim (p - p_c)^{\nu/a} \quad (2.21)$$

This critical frequency depends on the microscopic structure of the nanocomposite and, samples from different polymer matrices can exhibit very different behaviours, indicating differences in the quality of the CNT dispersion inside the polymer. This frequency is related to the correlation length and thus to the distance between CNT interconnections, [7]. A higher critical frequency would indicate shorter distances between connections that could be caused by a higher level of CNT aggregation, even if the DC results show little difference as AC characteristics are supposed to be more sensitive to aggregation effects. Therefore AC measurements are more sensitive to microscopic structural properties than DC ones. Kilbride et al., [7], extracted (for PmPV based nanocomposites), an exponent $\nu/a = 1.18$ (by fitting the critical frequency extracted from their measurement with equation 2.21). In a 3D systems $\nu = 0.9$, as shown previously,

¹⁵Kilbride et al. pointed out that in many material this relationship would not be valid but that it should be correct in a system of rigid conducting cylinders.

and a is then equal to 0.76, i.e. well within the defined range $0.5 < a < 1$. However for 2D systems, $\nu = 4/3$ and then a would be equal to 1.13, out of the acceptable range. Therefore transport in such a nanocomposite occurs through a 3D system, even if the value of the exponent t of the DC scaling law is lower than that expected for a 3D system ($t \simeq 2.00$), as commonly found in the literature. This could be due, at least partially, to tunnelling phenomena between neighbouring CNTs. Besides, the value of $a = 0.76$ confirms a partially biased system.

2.5.6 Effective Medium Theory based models

In Effective Medium Theories (EMT), or mean-field approximations, the real heterogeneous medium is approximated by a self-consistent homogeneous effective medium, [41]. The macroscopic properties of the effective medium are described using the properties and relative fractions of its constituting elements.

Such theories are extensively detailed in the literature. The three major mean-field approximations are the Lorentz-Lorentz expression, the Bruggeman EMT (B-EMT) and the Maxwell-Garnet approximation (MG), [42] and [15], on which almost all of the EMT theories from literature are based.

If we represent the heterogeneous material by a simple cubic lattice of points having different polarizabilities, randomly distributed, the dielectric distribution can be described by the Lorentz-Lorentz effective medium expression

$$\frac{\varepsilon - 1}{\varepsilon + 2} = f_a \frac{\varepsilon_a - 1}{\varepsilon_a + 2} + f_b \frac{\varepsilon_b - 1}{\varepsilon_b + 2} \quad (2.22)$$

where f_i and ε_i are the volume fraction and dielectric functions of the i th phase, respectively, [43]. This equation does not include molecular interactions but generalizations based on this expression (that do take into account these interactions) can be found in the literature, with varying degrees of success.

In the Maxwell-Garnet theory, heterogeneous materials are considered to be microscopically composed of regions having dimensions considerably smaller than the wavelength of light but large enough so that they have a meaningful dielectric constant, as illustrated on Fig. 2.17(b), and the effective dielectric constant is given by

$$\frac{\varepsilon - \varepsilon_h}{\varepsilon + 2\varepsilon_h} = f_a \frac{\varepsilon_a - \varepsilon_b}{\varepsilon_a + 2\varepsilon_b} \quad (2.23)$$

where f_a, f_b are the volume fractions occupied by the phases a and b , respectively. ε_h is the effective dielectric constant of the heterogeneous material. It can be demonstrated that the Lorentz-Lorentz and Maxwell-Garnet equations can be derived from the same generalized parametric equation, details in [43]. But small differences in the parameters values can lead to significant differences in the resulting values of the dielectric constant, the models being too sensitive to these parameters. Bruggeman proposed a model to solve this issue, a model in which neither phase is given preference and where the inclusions are considered as embedded in the effective medium itself, as illustrated on Fig. 2.17(a). This is the Bruggeman effective medium theory (B-EMT) given by the equation

$$0 = f_a \frac{\varepsilon_a - \varepsilon}{\varepsilon_a + 2\varepsilon} + f_b \frac{\varepsilon_b - \varepsilon}{\varepsilon_b + 2\varepsilon} \quad (2.24)$$

For low volume fractions, the effective conductivity can be calculated from the general MG equation in the case of a lossless matrix with lossy embedded

inclusions (of spherical shape), i.e. filler particles having a complex effective permittivity, [42].

$$\sigma_{eff} = \frac{9\varepsilon_e f \sigma_i}{(\varepsilon'_i + 2\varepsilon_e)^2 + \sigma_i^2/\omega^2} \quad (2.25)$$

where ε_e is the dielectric constant of the lossless matrix, ε'_i and σ_i the real part of the permittivity and conductivity of the inclusions, respectively. This expression tends to a zero value when approaching DC regime, this is acceptable only below the percolation threshold, which is valid given the assumption of a small volume fraction of conductive inclusions.

In the general case, the MG expression is used straightforwardly, [42] to obtain an expression for the effective complex permittivity of composite materials containing lossy elements.

$$\varepsilon_{eff} = \varepsilon_e' - j\varepsilon_e'' + 3f(\varepsilon_e' - j\varepsilon_e'') \frac{\varepsilon_i' - \varepsilon_e' - j(\varepsilon_i'' - \varepsilon_e'')}{(1-f)\varepsilon_i' + (2+f)\varepsilon_e' - j[(1-f)\varepsilon_i'' + (2+f)\varepsilon_e'']} \quad (2.26)$$

It is shown that in the case of an insulating matrix with lossy inclusions, [42], a small ε_i'' does not influence the results significantly. However, for very lossy embedded particles, the effective permittivity is dramatically changed, its real part displaying a peak and having a value possibly higher than that of the elements individually!

Both B-EMT and MG models consider the material of similar average microstructure and that are composed of grains smaller than the applied wavelength but the detailed microstructure considered in B-EMT or in MG theory are different. In the latter, inclusions of phase *a* are completely surrounded by phase *b* material in a coated-spheres configuration. While in the B-EMT an aggregate model is assumed where particles of phase *a* and *b* are randomly mixed, [43], cf. Fig. 2.17. Furthermore, in the calculations the grains or inclusions are assumed to be of spherical shape and non-interacting. Both are not usually satisfied in actual heterogeneous materials (where particles usually have random and complex shapes). Moreover in the specific case of CNTs, these two assumptions are especially erroneous. For example the shape of the particles has a strong influence on their screen-effect. This has a major effect on local microscopic polarizations and fields and then on the relationship between the effective dielectric constant and that of the different elements.

These two models predict different optical dielectric constants, particularly in the case of granular metals, [44]. B-EMT does not reproduce the anomalous dielectric function observed at optical frequencies while the MG model predicts its existence. It is shown in [44] that this deficiency of the EMT is due to the neglect of the interactions between neighbouring particles. Sheng generalized the MG theory to include the dielectric anomaly at optical frequencies and percola-

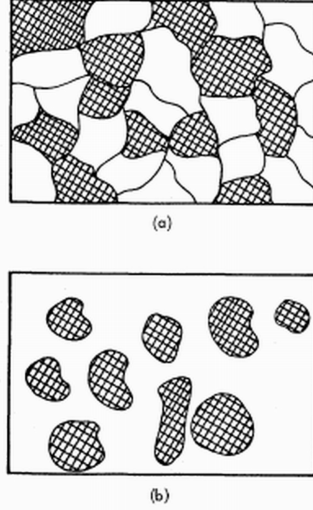


Figure 2.17.: *Schematic view of the microstructure as considered in the Bruggeman effective medium theory (a) and the one as treated in the Maxwell-Garnet approach, from [44].*

tion threshold, [45], obtaining a complicated final set of equations that implicitly contains the complex permittivity (MG-S model).

The B-EMT and MG-S are compared to each other in [15] and discussed in the case of composite containing elongated conducting particles. Both theories describe qualitatively the effective properties of the composites over the entire filler content range though MG-S was found in better agreement with experimental data on the optical properties of such composites. However only the cases of small filler contents or when the properties of the constituents are rather similar are adequately predicted by these models. Various approximations are presented in the literature to try to describe these two limiting cases but often they give threshold values that are not consistent or that depend on the conductivity of the inclusions (in contradiction with most experimental data), [42].

It must be kept in mind that both B-EMT and MG-S were originally developed in the case of material containing spherical conducting grains. They do not take into account long-range correlations in the large clusters of particles interactions, which is a distinct features of stick-like particles though, [41]. Different generalizations of B-EMT to prolate particles have been proposed, [46] and [47], but all of them give a percolation threshold proportional to the square of the aspect-ratio instead of a proportionality to the aspect-ratio. On the other hand, MG-S approximations lead to a percolation threshold value of $p_c = 0.46$ or to

a threshold depending on the square root of the particle aspect ratio, both inconsistent with experiments. These discrepancies are important, the percolation threshold corresponds to a dramatic change in the dielectric properties of the composites. In the particular case of large aspect ratio, over 100, experimental values are orders of magnitude larger than those predicted by B-EMT based models and many times smaller than either values from MG-S based theories. Both types of approximations are therefore especially ill-advised in the case of CNT composites, [15]. Furthermore, most articles in the literature agree that EMTs and mixture laws are generally not in a very good agreement with experimental results, especially at high frequency, [48].

McLachlan and co-workers, [49], developed the general effective medium (GEM) theory, combining aspects of percolation theory with EMT. It is applicable on the entire range of filler content and when the elements have similar properties. However, even though the meaning of p_c is reasonably well understood, the physical mechanisms behind the values of the exponents t and s are still somewhat of a controversy, [36].

2.6 HIGH FREQUENCY/MICROWAVE ELECTRICAL BEHAVIOUR OF NANOCOMPOSITES

As detailed in the previous section, many models for composite materials containing conductive inclusions are based on a quasi-static approach and the effects due to the coupling in time and space variations of the electric and magnetic fields are neglected. As explained previously the limit where this quasi-static approximation is not valid any more depends on the size of the conductive inclusions. But a “rule of thumb” is given in [42] where the quasi-static limit is formulated as

$$\frac{\lambda}{2\pi} > \delta \quad (2.27)$$

where δ is a measure of the size of the inclusions and λ is the wavelength of the propagating wave in the material. There are several issues raising from that approximate expression. First is the size of the particles, they are not necessary all of the same shape and size. Besides it has been shown that in the case of carbon black nanocomposites the relevant conductive elements were not the CB particles themselves but the so-called “SEM-spheres” composed of agglomerated CB particles with a polymer coating, [50]. This means that even if the particles embedded in the matrix seem much smaller than the wavelength, the size of the actual meaningful conductive ‘particles’ in the composite may be much larger. The characteristic size of the inclusions is therefore not an easy thing to determine a priori. Second, the actual wavelength of the propagating wave inside a material is not known a priori either. It depends on the properties of the material (via the wave velocity) but those of the effective medium or those of the insulating matrix or those of the particles (if large enough for the field to be considered homogeneous inside a single particle)? The correlation length is sometimes used instead, [42]. Another issue at high frequency, when particles can no longer be considered as ‘small’, are the scattering phenomena and models have to be modified to take them into account, see [42] for more details. Other models include some frequency-dependence.

In a DC field, as explained previously in this chapter, the conductivity of nanocomposite materials is related to a backbone of percolating clusters that act as transmission lines for the movements of electrons. This movement is allowed either by direct electrical contact between fillers or due to a strong electric local field between neighbouring particles, [17].

In the AC regime, as was detailed previously, dielectric constant and conductivity are related to anomalous diffusion phenomena within clusters and polarization effects between isolated clusters or branches of clusters inside the material. At higher frequency, the velocity of the electron movement is limited inside a cluster (this velocity is related to the electrical resistance within the cluster), the length of this movement is also limited and the scale of electronic displacement is dependent on the frequency of the incident field. The elements having

a scale smaller than that of the electron movement can be considered as isolated and contribute to the effective dielectric constant of the composite but not to the conductivity. While the larger parts contribute instead to the effective conductivity.

While the DC and AC conductivities are due to different phenomena inside the material, they are however closely related and complementary, [17].

At microwave frequencies, it is usually reported that the real and imaginary parts of the complex effective permittivity are proportional to the filler volume fraction, [16, 17], the imaginary part increasing more rapidly than the real part. But the rates with which they increase can be very different, depending on the type of nanoparticle and frequency band. In particular, it has been shown that this rate is slightly higher for carbon nanofibres (CNFs) than CNTs but much smaller in the case of carbon black (CBs). This is probably due to the straightness and length of the CNFs (while the shape of the CNTs is more curved). And this order is in agreement with the results from DC measurement. It has also been reported that increasing frequency leads to smaller relative differences due to the filler content, as predicted from theoretical considerations, cf. Fig 2.18 and cf. Fig 2.19.

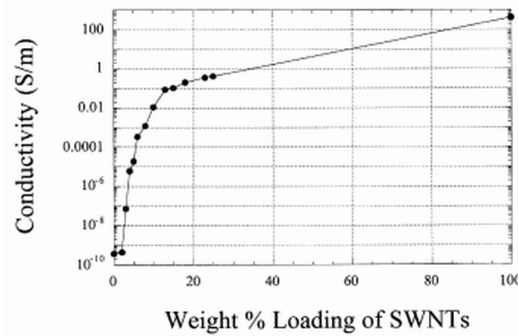


Figure 2.18.: *Measured DC conductivity of SWCNT-polymer (poly-ethylmethacrylate) composites versus mass fraction, from [16].*

Influence of the defect density of CNTs on the real permittivity has also been reported at microwave frequencies, [51]. An increase in the defect density led to an increase in the real part of the permittivity and sometimes to an increase of the conductivity. The authors also mention that defective CNTs have a semiconducting nature but allow build-up of displacement currents. More information on the influence of CNT defects on the electrical properties of nanocomposites can be found in [16, 51].

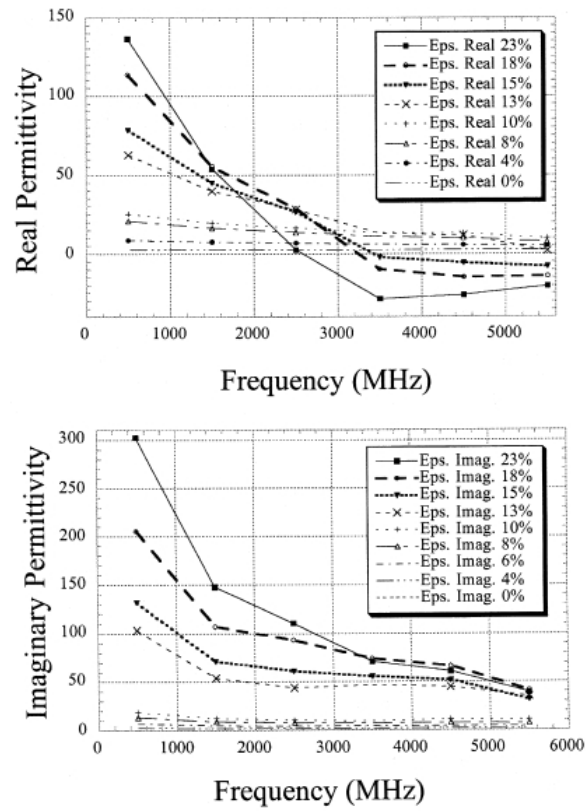


Figure 2.19.: Measured real and imaginary parts of the complex permittivity of SWCNT-polymer (poly-ethyl-methacrylate) composites versus mass fraction (0 – 23%), from [16].

Some articles can be found in the literature where the high frequency/microwave characterization of CNT-based composites is reported, but a detailed investigation or analysis is very rare, [52]. It is mostly focused on the EMI shielding properties of the nanocomposites without further considerations. Wideband investigations on the influence of the frequency are even more sparse.

In [16], Grimes et al. used the EMT for stick-like inclusions from [15] in its low frequency region and found a reasonable agreement, as shown on Fig 2.20. They considered a third of the CNT bundles to be metallic. They adjusted the real part of the permittivity of the matrix from the value $2.6 - j0.1$ obtained for a 0% CNT content to $4.6 - j3.2$ to take into account the increase in the real part of the permittivity due to the addition of SWCNTs. They assumed a complex permittivity for the CNT bundles with a conductivity of 885 S/m.

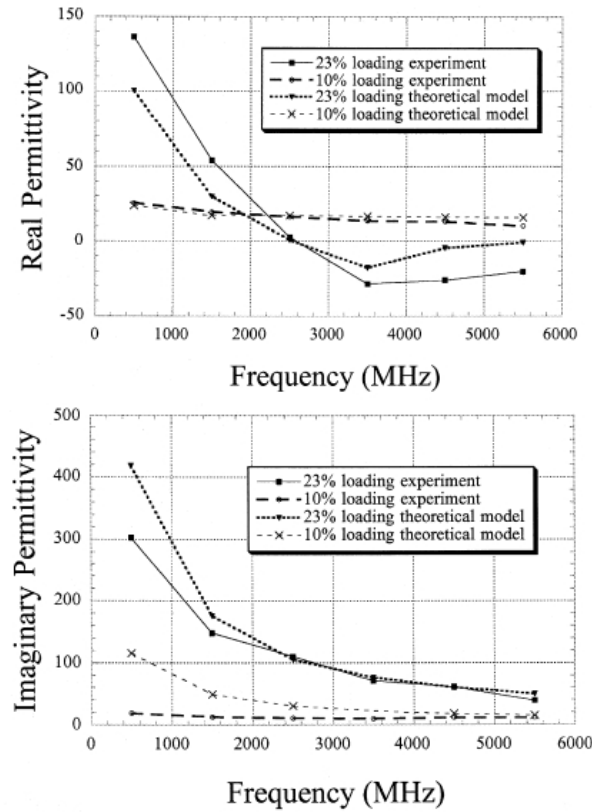


Figure 2.20.: Measured and simulated real and imaginary parts of the complex permittivity of SWCNT-polymer (poly-ethyl-methacrylate) composites versus mass fraction (0 – 23%), from [16].

In [52], Peng et al. used a simple resistance-capacitance (RC) network, similar to the one depicted on Fig. 2.11, to model the permittivity spectra of SWCNT-polymer (poly-ethyl-methacrylate) composites in the range 0.30 – 15 GHz, using the parameters and experimental results from [16]. They considered the permittivity to be constant over a selected microwave frequency range (and that there were no temperature variations either). They assumed a matrix permittivity of the form $\varepsilon_d^* = \varepsilon'_d - i\varepsilon''_d$ where ε'_d and ε''_d are constants. For the metallic SWCNT bundles, they assumed $\varepsilon_m^* = \varepsilon'_m - i\varepsilon''_m = \varepsilon'_m - i\sigma_m/(\omega\varepsilon_0)$ with ε_0 the permittivity of free space and $\varepsilon_m \approx 100$ and $\sigma_m = 885$ S/m, the DC conductivity, being constants. They also assumed the dielectric properties of the composite to be most sensitive to the influence of the metallic SWCNTs (one third of the SWCNTs) while the semi-conducting CNTs (two thirds) were viewed as effectively increasing the permittivity of the matrix.

They obtained the following equation for the complex effective conductivity of the SWCNT/polymer composite

$$\sigma^* = \left[i\omega\varepsilon_0(\varepsilon'_m - i\frac{\sigma_m}{\omega\varepsilon_0}) \right]^{f_m} [i\omega\varepsilon_0(\varepsilon'_d - i\varepsilon''_d)]^{f_d} \quad (2.28)$$

where f_m is the volume fraction of metallic SWCNTs and $f_d = 1 - f_m$ the volume fraction of the polymer matrix. The complex permittivity of the composite can be then obtained using $\varepsilon^* = \sigma^*/(i\omega\varepsilon_0)$

They found a good agreement between their numerical model and the experimental data, though little physical information could be extracted from either.

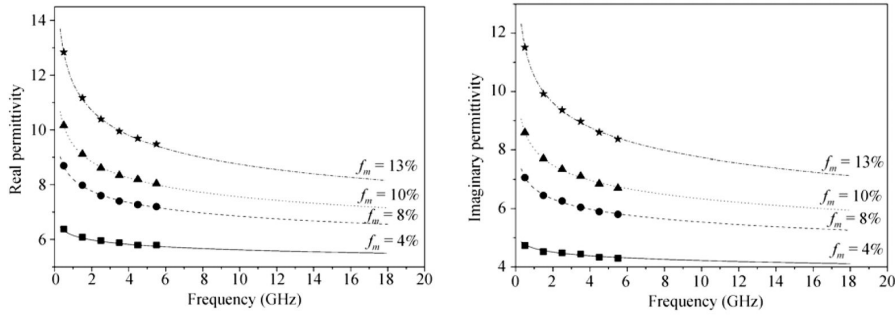


Figure 2.21.: Comparison between theoretical (lines) and experimental (symbols) values of the real (left) and imaginary (right) parts of the complex effective permittivity of SWCNT-polymer (poly-ethyl-methacrylate) composites versus frequency for various volume fractions, from [52].

2.7 CONCLUSIONS

The properties of carbon nanotubes were first introduced in this chapter, from their extraordinary aspect-ratio to their electrically conducting or semi-conducting behaviours, along with information on the different kinds of CNTs in existence and on their fabrications methods. Their outstanding transport properties in particular were also briefly presented prior to a more detailed discussion on the CNT/polymer nanocomposites. The key issue of having CNTs well dispersed, and undamaged by the dispersion process, is highlighted throughout this chapter. Besides, if there are many different types of CNTs and even more numerous polymer nanocomposites containing CNTs, they all share some distinctive features in their electrical properties.

The most widely known of these features is the existence of a percolation threshold. At low filler contents, the composites exhibit a dielectric behaviour while for high CNT loadings they behave as a conductive material. The sharp transition occurs for a filler content that is called the percolation transition. The term comes from the apparition at this filler content of a regular, well-extended network of interconnected particles. The conductivity as a function of filler content can be approximated by a power law in the threshold vicinity. It was already shown that this percolation threshold is strongly dependent on the aspect-ratio of the nanoparticles.

Second the dependence of the conductivity and dielectric constant on the frequency exhibit a strong dispersion, characteristic of the conduction in many disordered solids. Above a characteristic frequency, the conductivity as a function of frequency is another simple power law.

Both features can be reasonably well described using simple geometrical percolation theory and electrical equivalent models with diffusion aspects. Though some discrepancies remain.

From the comparison between these models and experiments it appears that CNTs are actually not in direct contact at their interconnections, they are coated by a polymer layer of varying thickness. These layers are in fact potential barriers of varying heights and the charges carriers have to tunnel through them. This is rather well described by the thermal fluctuation induced tunnelling model, but taking into account a partially biased walk instead of a totally random one. The latter model, combined with percolation aspects provides a simple and efficient understanding and prediction of the experimental results found in the literature. However, short or long-range interactions between the particles are often neglected in most models resulting in minor or major discrepancies in comparison with experimental results.

The more complicated models, the effective medium theories, presented next, do not bring much more light to the experimental results and are not perfectly adequate in the case of CNT/polymer nanocomposites. Besides they are often

very complicated to both use and interpret and do not always show a good adequacy with experimental results.

All these models present differences but rather than being in contradiction with one another, they yield complementary considerations that can lead to a better understanding of the nanocomposite materials.

The frequency models mentioned here above are only valid, in a strict sense, for DC or in the low-frequency region (quasi-static approach), neglecting the coupling effects of time-varying electric and magnetic fields. Interfacial polarisation can already occur at low frequency (depending on the size of the grains or inclusions). It is reported to be an important dispersion mechanism in many materials already at a few kHz, [42] and [53]. Furthermore, in many models the electrical field was supposed to be time-independent while losses due to alternating fields often lead to exponential attenuation if the dimensions of the lossy elements are larger than the skin depth.

Wideband investigations on several frequency decades are rather sparse, many authors considering DC measurements and percolation threshold determination to sufficiently characterise the state of the dispersion inside a nanocomposite material. As discussed in this chapter and is detailed further in chapter 4, measuring the complex permittivity on different frequency ranges can yield very interesting results.

At even higher frequencies, the distance travelled by the charge carriers is significantly decreased and may be confined to a single agglomerate of CNTs. The conductivity and dielectric constant still increase with increasing CNT content but the relative differences are smaller at high frequency than at lower frequency. But microwave characterisation are not widespread in the literature and data is rather sparse.

Bibliography

- [1] M. Shaffer and J. Sandler, "Carbon nanotube/nanofibre polymes composites," in *Processing and properties of nanocomposites*, S. Advani, Ed. World Scientific Publishing, 2006. 7, 8, 9, 10, 11, 12, 13, 14, 16, 17, 18
- [2] K. Schulte, F. Gojny, B. Fiedler, J. Sandler, and W. Bauhofer, "Carbon nanotube-reinforced polymers: a state of the art review," in *Polymer Composites from Nano- to Macro-Scale*, K. Friedrich, S. Fakinov, and Z. Zhong, Eds. Springer US, 2005. 7, 8, 11, 12
- [3] S. Ijima, "Helical microtubules of graphitic carbon," *Nature*, no. 354, pp. 56–58, November 1991. 9
- [4] R. Geim, "The rise of graphene," *Nature Materials*, vol. 6, pp. 183–191, March 2007. 9
- [5] A. Palser, "Interlayer interactions in graphite and carbon nanotubes," *Physical Chemistry Chemical Physics*, vol. 18, no. 1, pp. 4459–4464, 1999. 9
- [6] S. Barrau, P. Demont, A. Peigney, C. Laurent, and C. Lacabanne, "Dc and ac conductivity of carbon nanotubes-polyepoxy composites," *Macromolecules*, vol. 36, no. 14, pp. 5187–5194, June 2003. 9, 10, 11, 14, 15, 17, 21, 25, 32, 34
- [7] B. Kilbride, J. Coleman, J. Fraysse, P. Fournet, M. Cadek, A. Drury, S. Hutzler, S. Roth, and W. Blau, "Experimental observation of scaling laws for alternating current and direct current conductivity in polymer-carbon nanotube composite thin films," *Journal of Applied Physics*, vol. 92, no. 7, pp. 4024–4030, October 2002. 9, 11, 14, 17, 20, 21, 24, 30, 32, 33, 34, 36
- [8] J. Sandler, M. Shaffer, T. Prasse, W. Bauhofer, K. Schulte, and A. Windle, "Development of a dispersion process for carbon nanotubes in an epoxy matrix and the resulting electrical properties," *Polymer*, vol. 40, no. 21, pp. 5967–5971, October 1999. 11, 12, 14, 16
- [9] J. Sandler, J. Kirk, I. Kinloch, M. Shaffer, and A. Windle, "Ultra-low electrical percolation threshold in carbon-nanotube-epoxy composites," *Polymer*, vol. 44, no. 19, pp. 5893–5899, September 2003. 11, 13, 14, 16
- [10] Y. Song and J. Youn, "Development of dispersion states of carbon nanotubes on physical properties of epoxy nanocomposites," *Carbon*, vol. 43, no. 7, pp. 1378–1385, June 2005. 11, 12
- [11] C. Martin, J. Sandler, A. Windle, M.-K. Schwarz, W. Bauhofer, K. Schulte, and M. Shaffer, "Electric field-induced aligned multi-wall carbon nanotube networks in epoxy composites," *Polymer*, vol. 46, no. 3, pp. 877–885, January 2004. 11

- [12] P. Potschke, S. Dudkin, and I. Alig, "Dielectric spectroscopy on melt processed polycarbonate-multiwalled carbon nanotube composites," *Polymer*, vol. 44, no. 17, pp. 5023–5030, August 2003. 12, 19, 20, 22, 23, 26, 27, 28, 29, 30
- [13] W. Hsu, V. Kotseva, P. Watts, and G. Chen, "Circuit elements in carbon nanotube-polymer composites," *Carbon*, vol. 42, no. 8-9, pp. 1707–1712, April 2004. 12
- [14] C. Martin, J. Sandler, M. Shaffer, M.-K. Schwarz, W. Bauhofer, K. Schulte, and A. Windle, "Formation of percolating networks in multi-wall carbon-nanotube-epoxy composites," *Composites Science and Technology*, vol. 64, no. 15, pp. 2309–2316, November 2004. 14, 30
- [15] A. Lagarkov and A. Sarychev, "Electromagnetic properties of composites containing elongated conducting inclusions," *Physical Review B*, vol. 53, no. 10, pp. 6318–6336, March 1996. 15, 23, 28, 38, 40, 41, 45
- [16] C. Grimes, C. Mungle, D. Kouzoudis, S. Fang, and P. Eklund, "The 500 mhz to 5.50 ghz complex permittivity spectra of single-wall carbon nanotube-loaded polymer composites," *Chemical Physics Letters*, vol. 319, no. 5-6, pp. 460–464, March 2000. 15, 43, 44, 45, 46
- [17] J.-B. Kim, S.-K. Lee, and C.-G. Kim, "Comparison study on the effect of carbon nano materials for single-layer microwave absorbers in x-band," *Composites Science and Technology*, vol. 68, pp. 2909–2916, September 2008. 15, 42, 43
- [18] I. Balberg, C. Anderson, S. Alexander, and N. Wagner, "Excluded volume and its relation to the onset of percolation," *Physical Review B*, vol. 7, no. 30, pp. 3933–3943, October 1984. 15, 16
- [19] E. Garboczi, K. Snyder, J. Douglas, and M. Thorpe, "Geometrical percolation threshold of overlapping ellipsoids," *Physical Review E*, vol. 52, no. 1, pp. 819–828, July 1995. 15, 16, 17
- [20] I. Balberg, "Universal percolation-threshold limits in the continuum," *Physical Review B*, vol. 31, no. 6, pp. 4053–4055, March 1985. 16
- [21] M. Reghu, C. Yoon, C. Yang, D. Moses, P. Smith, and A. Heeger, "Transport in polyaniline networks near the percolation threshold," *Physical Review B*, vol. 50, no. 19, pp. 13 931–13 941, Novembre 1994. 17
- [22] R. Haggemueller, C. Guthy, J. Lukes, J. Fischer, and K. Winey, "Single wall carbon nanotube/polyethylene nanocomposites: Thermal and electrical conductivity," *Macromolecules*, vol. 40, no. 7, pp. 2417–2421, March 2007. 18

- [23] C.-W. Nan, Z. Shi, and Y. Lin, "A simple model for thermal conductivity of carbon nanotube-based composites," *Chemical Physics Letters*, vol. 375, no. 5-6, pp. 666–669, July 2003. 18
- [24] P. Vanderbemden, *Analyse et conception des systemes de mesures electriques*. Universite de Liege: Faculte des Sciences Appliquees, 2003. 19
- [25] T. Schroeder and J. Dyre, "Scaling and universality of ac conduction in disordered solids," *Physical Review Letters*, vol. 84, no. 2, pp. 310–313, January 2000. 20, 21, 32
- [26] H. So, J. Cho, and N. Sahoo, "Preparation and properties of the polyimide/multi-walled carbon nanotubes (mwnts) nanocomposites," *Composites Science and Technology*, vol. 66, no. 3-4, pp. 548–554, March 2006. 23
- [27] G. He, J. Zhou, K. Tan, and H. Li, "Preparation, morphology and properties of acylchloride-grafted multiwall carbon nanotubes/fluorinated polyimide composites," *Composites Science and Technology*, vol. 71, no. 16, pp. 1914–1920, November 2011. 23
- [28] K. Ahmad, W. Pan, and S.-L. Shi, "Electrical conductivity and dielectric properties of multiwalled carbon nanotube and alumina composites," *Applied Physics Letters*, vol. 89, no. 13, p. 3p, September 2006. 23
- [29] D. Stroud and D. Bergman, "Frequency dependence of the polarization catastrophe at a metal-insulator transition and related problems," *Physical Review B*, vol. 25, no. 3, pp. 2061–2064, February 1982. 23
- [30] J. Macdonald, "Comparison of the universal dynamic response power-law fitting model for conducting systems with superior alternative models," *Solid state ionics*, vol. 133, pp. 79–97, June 2000. 25
- [31] A. Jonscher, "The "universal" dielectric response," *Nature*, vol. 267, pp. 673–679, June 1977. 25
- [32] D. Bergman and Y. Imry, "Critical behavior of the complex dielectric constant near the percolation threshold of a heterogeneous material," *Physical Review Letters*, vol. 39, no. 19, pp. 1222–1225, November 1977. 26, 27
- [33] A. Bunde and J. Kantelhardt, "Introduction to percolation theory (part a)," *diffusion-fundamentals.org*, vol. 6, pp. 1–17, 2007. 28, 29, 36
- [34] M. Connor, S. Roy, T. Ezquerra, and F. B. Calleja, "Broadband ac conductivity of conductor-polymer composites," *Physical Review B*, vol. 57, no. 4, pp. 2286–2294, January 1998. 30, 32, 36
- [35] F. Lux, "Review: Models proposed to explain the electrical conductivity of mixtures made of conductive and insulating materials," *Journal of Materials Science*, vol. 28, pp. 285–301, 1993. 30

- [36] W.-Z. Cai, S.-T. Tu, and J.-M. Gong, "A physically based percolation model of the effective electrical conductivity of particle filled composites," *Journal of Composite Materials*, vol. 40, no. 23, pp. 2131–2142, 2006. 31, 41
- [37] J. Dyre, "The random free energy barrier model for ac conduction in disordered solids," *Journal of Applied Physics*, vol. 64, no. 5, pp. 2456–2468, September 1988. 33
- [38] G. Pike, "ac conductivity of scandium oxide and a new hopping model for conductivity," *Physical Review B*, vol. 6, no. 4, pp. 1572–1580, August 1972. 34
- [39] S. Elliott, "A.c. conduction in amorphous chalcogenide and pnictide semiconductors," *Advances in Physics*, vol. 36, no. 2, pp. 135–218, March 1987. 34
- [40] D. Toker, D. Azulay, N. Shimon, I. Balberg, and O. Millo, "Tunneling and percolation in metal-insulator composite materials," *Physical Review B*, vol. 68, no. 4, p. 4p, July 2003. 34, 35
- [41] A. Davidson and M. Tinkham, "Phenomenological equations for the electrical conductivity of microscopically inhomogeneous materials," *Physical Review B*, vol. 13, no. 8, pp. 3261–3267, April 1976. 38, 40
- [42] A. Sihvola, *Advanced Mixing Principles*. Padstow, England: IEE Electromagnetic Waves Series 47, 1988. 38, 39, 40, 42, 48
- [43] D. Aspnes, "Local-field effects and effective medium theory: A microscopic perspective," *American Journal of Physics*, vol. 50, no. 8, pp. 704–709, August 1982. 38, 39
- [44] P. Sheng, "Pair-cluster theory for the dielectric constant of composite media," *Physical Review B*, vol. 22, no. 12, pp. 6364–6368, December 1980. 39, 40
- [45] —, "Theory for the dielectric function of granular composite media," *Physical Review Letters*, vol. 45, no. 1, pp. 60–63, July 1980. 40
- [46] D. Stroud, "Generalised effective-medium approach to the conductivity of an inhomogeneous material," *Physical Review B*, vol. 12, no. 8, pp. 3368–3373, October 1975. 40
- [47] C. Granqvist and O. Hunderi, "Conductivity of inhomogeneous materials: Effective-medium theory with dipole-dipole interaction," *Physical Review B*, vol. 18, no. 4, pp. 1554–1561, October 1978. 40
- [48] M. Achour, M. E. Mahi, J. Miane, F. Carmora, and F. Lahjomri, "Microwave properties of carbon black-epoxy resin composites and their simulation by means of mixture laws," *Journal of Applied Polymer Science*, vol. 73, pp. 969–973, 1999. 41

- [49] D. McLachlan, M. Blaszkewitz, and R. Newnham, "Electrical resistivity of composites," *Journal of the American Ceramic Society*, vol. 73, no. 8, pp. 2187–2203, 1990. 41
- [50] J. Kaiser, "Microwave evaluation of the conductive filler particles of carbon black-rubber composites," *Applied Physics A*, vol. 56, no. 4, pp. 299–302, April 1993. 42
- [51] P. Watts, D. Ponnampalam, W. Hsu, A. Barnes, and B. Chambers, "The complex permittivity of multi-walled carbon nanotube-polystyrene composite films in x-band," *Chemical Physics Letters*, vol. 378, pp. 609–614, 1999. 43
- [52] Z.-H. Peng, J.-C. Peng, Y.-F. Peng, and J.-Y. Wang, "Complex conductivity and permittivity of single wall carbon nanotubes/polymer composite at microwave frequencies: A theoretical estimation," *Chinese Science Bulletin*, vol. 53, no. 22, pp. 3497–3504, November 2008. 45, 46
- [53] G. Banhegyi, "Numerical analysis of complex dielectric mixture formulae," *Colloid and Polymer Science*, vol. 266, no. 1, pp. 11–28, January 1988. 48

CHAPTER 3

EXPERIMENTAL CHARACTERISATION TECHNIQUES

3.1 INTRODUCTION

The electrical characterisation of materials is a very wide and varied area of expertise. Like in most engineering issues there is no straightforward solution that would be the most adequate in any case. This is even more true when dealing with nanocomposite materials. Their electrical properties can vary of several orders of magnitudes when changing slightly the composition, the filler content being the most blatant example, but also by modifying the process parameters or chemical treatments.

The initial focus of the present thesis was on the microwave techniques, their interest and advantages for the electrical characterisation of nanocomposite materials. But DC and low frequency experimental methods are also considered in this chapter as they will be compared to microwave techniques in chapter 4 and the information obtained using this techniques will be also confronted with results from higher frequency measurements. These techniques already highlight some difficulties due to the heterogeneity inherent to nanocomposites and problems of reproducibility due to measurements specificities. Besides the electrical properties of the materials to be characterised, the importance of geometric and mechanical parameters is also put forward. The major influence of the quality of the electrical contact in particular is of prime interest. In practice, low fre-

quency and high frequency techniques are very different[1]. At low frequency, the complex permittivity, containing the conductivity and dielectric constant can be determined from the impedance, the sample (and the structure holding or containing and contacting it, i.e. the measurement cell) being considered as a lumped electrical circuit. Low frequency methods are therefore essentially based on the use of impedance analysers.

At microwave frequencies, the dimensions of the measurement cell can often be comparable to that of the wavelength and extraction of the permittivity is more complicated. It is mostly done from the measurement of the complex transmission and reflection coefficients using vector network analyzers (VNA). These methods are called microwave or ‘wave’ techniques.

It can first be noted that at DC and lower frequencies, electrodes are required to provide an adequate electrical contact with the samples and these electrodes can be a non-negligible source of measurement error. At microwave frequencies materials can be characterised without the use of electrodes and these errors can then be avoided. Though other specific issues arise at high frequency. Microwave characterisation techniques are widespread both in the literature and in industrial applications in the last 20 – 30 years. Transmission and reflection based measurements can be performed using open-ended probes, closed measurement cells or free-space antenna measurements.

Coaxial and open-ended waveguide probes are used for crack detection of the characterisation of biological tissue, usually using a back conductor or dielectric half-space, [2]. Their main advantage is that they are non-destructive. But they have some limitations, especially for layered or low-level measurements. Besides, most of them are reflection based only methods, and they do not always guarantee the uniqueness of the solution (inverse problem) and, even when they do the precision of the results is not always optimum, usually much less accurate than other techniques, [1]. These methods do not work very well for thin samples, [3]. Experimental techniques combining transmission and reflection measurements are considered to be the simplest methodology and having the least constraints to determine several electromagnetic parameters simultaneously, [4]. For these reasons the coaxial probe techniques, widespread in the literature, were not used in the framework of the current thesis. Besides there were no such high frequency coaxial probes readily available in our characterisation facilities.

Guided measurement methods are considered to be among the best techniques at microwave frequencies, especially for high and medium loss materials, [1], with a theoretical uncertainty on the dielectric constant of about 1 % and they allow (depending on the specific method considered) a quite broadband characterisation. But they are also reported to suffer from two main disadvantages;

significant influence of the air gaps for solid samples and a limited resolution for the extracted electrical conductivity or loss tangent.

Several closed-measurement cell microwave techniques are presented in the current chapter:

First a microstrip One-Line method is proposed, where the sample to be characterised is used as substrate in a microstrip line and its characteristics can be determined from the propagation constant of this transmission line, cf. section 3.3.1. Second a Line-Line technique based on the measurement of the losses caused by the insertion of pieces of material inside waveguide lines, cf. section 3.3.2. Third a modified version of the previous method is presented, requiring the measurement of the scattering parameters of only one line instead of two for the standard Line-Line techniques, cf. section 3.3.3. Each method is presented and detailed. Then some results obtained using this technique are also shown and briefly discussed.

Free air measurements are also presented for information, this technique requires the dimensions of the samples to be considerable, at least as large as the width of the beam at the sample location, cf. section 3.4. Most of our samples are significantly too small for such methods. Besides, free space methods are usually less accurate than equivalent guided wave techniques, [1].

Two specific uses of a microwave reflection method to determine the value of lower frequency characteristics of Nafion-CNT composites thin films and of nanoporous polyimide membranes are also presented in section 3.5.

Of course the methods presented in this chapter do not constitute an exhaustive list of existing microwave techniques. Methods based on resonators and resonant cavities were not used despite their high precision and sensitivity, [3], because they are designed to work at a specific frequency and are well suited to low-loss dielectrics but not that well to conductive materials (and because they were not readily available in the laboratory).

The adequacy between these different techniques and the electrical, mechanical, and geometrical properties of the sample is then discussed. The results are compared and important factors in the choice of a characterisation method in function of a specific sample are finally detailed. Finally, a small comment on the selection of a characterisation method when faced to an unknown material is presented.

3.2 DC AND LOW FREQUENCY CHARACTERISATION TECHNIQUES

3.2.1 DC experimental set-up

The DC characterisation of a sample at DC is a priori the simplest form of measurement, electrodes must be put in direct contact with the material, a known voltage V is applied and the resulting current I is measured. The resistance R can then be calculated simply by using Ohm's Law: $R = V/I$. If the geometrical dimensions of the samples are known, the electrical conductivity can be calculated from Pouillet Law: $\sigma_{DC} = L/(R.S)$ where L is the length of the sample (measured between the electrodes, in the direction of the current) and S is the area of the corresponding cross-section.

While it is very simple in theory, DC measurements can be trickier in practice, especially if the samples are very conductive or on the contrary very good dielectrics. In the case of nanocomposites, even at very high filler contents they cannot be considered as very conductive (such as superconducting materials) but below the percolation threshold they are generally quite good dielectrics. Special considerations have therefore to be taken into account when designing an experimental set-up or sample holder. More information on these can be found in the master thesis I wrote for my DEA at the ULg in 2005, [5], on the electrical characterisation of insulating tapes for high critical temperature superconductors. Furthermore great care must be taken in the quality of the electrical contacts between the electrodes and the sample material. In my DEA I had investigated various possibilities and shown the superiority of solid metal electrodes pressed against the sample but with a ductile metal as buffer between sample and material, especially for samples with porous or coarse surfaces. Several tests were made again in the framework of the current thesis, yielding similar results.

Metallic coating processes (gold sputtering, vacuum metallization) or silver paint are very interesting solutions, but both of them leave a permanent imprint on the sample, preventing from possible future measurements using other methods. Besides if the material is porous (e.g. foams) metallic particles can percolate inside the material and thus increase the effective contact area and decreasing the samples effective thickness and therefore lead to a possibly significant error in the resistance measurement.

Self-adhesive copper or aluminium scotch (like the one used for microstrip measurements, cf. section 3.3.1) is often used for conductivity measurements in the industry because of its simplicity¹. However, the quality of the electrical

¹Though one must be careful, some models have a conductive glue (more expensive) but others do not.

contact is not always excellent especially if the material does not offer a smooth surface with good adhesion to the scotch and if the glue is not conductive enough, there might be ‘pockets’ of glue adding to the total resistance of the sample. Besides, the removal of the tape after use might not be easy and dried glue residues might be left on the material afterwards.

Solid metal electrodes offer a reproducible solution and do not damage the sample in any way. However the sample surfaces must be very smooth to ensure a good electrical contact between sample and electrodes. This is the reason why a layer of indium was intercalated between the sample and solid copper or brass electrodes in my DEA. But if this layer increased the accuracy of the measurements, it also added some degree of irreproducibility. Besides the samples studied in the current thesis could be fabricated with adequately smooth surfaces. DC measurements were conducted primarily on rectangular solid thin (about 1.5 mm thick) polymer/CNT composite samples².

Because the low filler content samples have a very high resistance, the first measurements were made using the prototype of the sample holder that was fabricated for my DEA master thesis, cf. Fig. 3.1. It is based on the use of a guarded electrode³ to measure the bulk resistivity of a sample (usually a dielectric) while removing the influence of the surface conductivity⁴, [6]. As can be seen on Fig. 3.2(a), the unguarded electrode (top) is connected to the high voltage output of the power source and the unguarded electrode (bottom) is connected to an ammeter, the guard ring is directly connected to the ground. This way the superficial current is shunted directly to the ground and not measured by the ammeter. As both the guard and guarded electrode are at the same potential (the voltage drop caused by a good ammeter is negligible), there is no significant current flowing between them. Besides, the guard has a supplementary advantage, if the sample is thick enough (and stretching further than the electrode outer perimeter) the electric field lines will be distorted near the edge of the sample, i.e. the edge effect, as illustrated on Fig. 3.2(b). In the zone above the guarded electrode the lines are perfectly straight and uniform. In guarded measurements they will be the only ones taken into account.

However, this plexiglas prototype was not mechanically as good as the final Teflon sample holder (still at ULg), the faces of the two electrodes⁵ not being perfectly parallel and results not very reproducible. Fabricating a completely

²Most of those thin samples were fabricated by N. Quievy at the UCL(IMCN).

³It should be noted that this guarded measurement concept is very different from the active guard principle used, for example, in triax cables and circuits.

⁴Dielectric materials usually exhibit a significant surface conductivity, compared to their very small bulk conductivity, the surface conductivity is strongly influenced by external factors such as humidity or surface wear.

⁵These new electrodes were machined in solid aluminium by D. Spote, UCL.

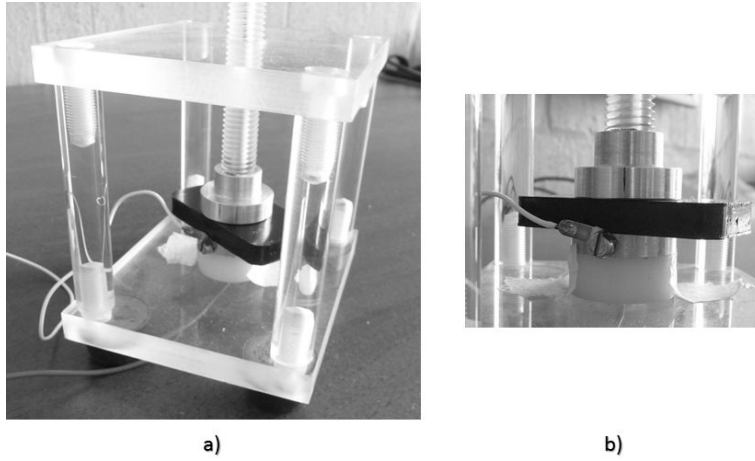


Figure 3.1.: Pictures of the prototype of the experimental set-up designed for the ULg DEA and adapted to the DC characterisation of nanocomposites.

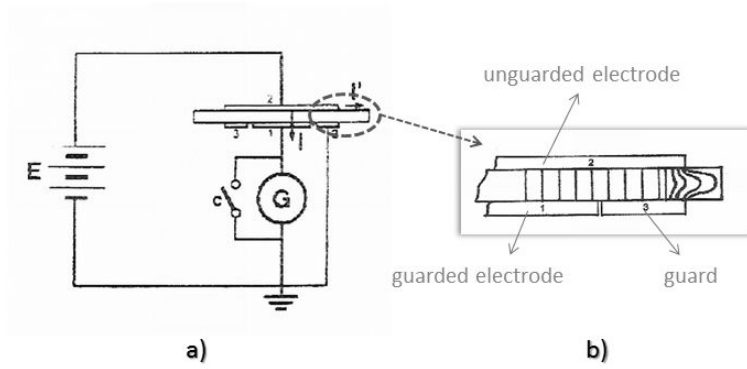


Figure 3.2.: Illustration of the principle of guarded DC measurements (a) and close-up view on the electric field lines near the edge of the sample, from [6].

new sample holder seemed to be complicated and other solutions had to be considered.

First tests were conducted using electrodes consisting in a layer of solid copper on a dielectric substrates to ensure a good but not too high rigidity, cf. Fig. 3.3. The material was placed between the copper layers and two plastic clamps were used to apply some pressure on the sample to improve the electrical contacts. The electrodes were then connected to a Keithley 2000 voltmeter in ohmmeter mode. The conductivity versus filler content of the first five samples measured using this method is shown on Fig. 3.4. The measurements were carried out inside a metallic shielding box in order to reduce the significant noise present in the measured values.

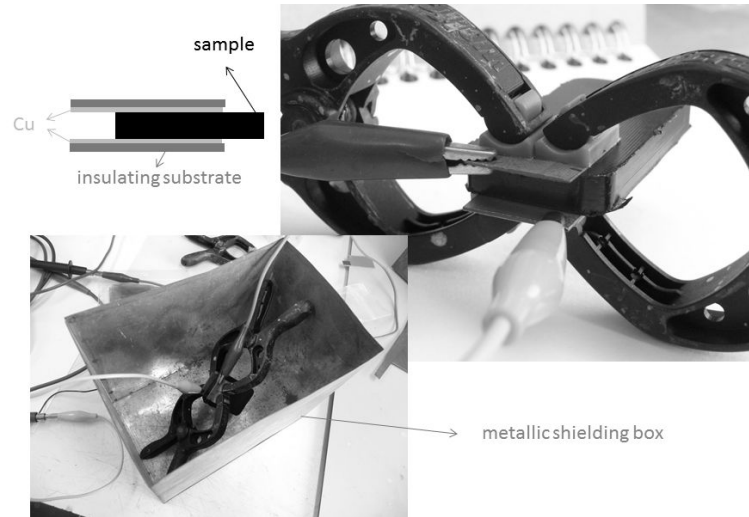


Figure 3.3.: Pictures of the DC experimental set-up with solid copper electrodes, plastic clamps and metallic shield.

This crude technique actually produced some interesting results for five samples based on a PC matrix with 0.1 %, 0.25 %, 0.5 %, 1 % and 2 wt% CNTs. The measured conductivity is plotted versus filler fraction φ on Fig. 3.4. Fitting these results⁶ using a simple power law $\sigma = A \cdot \exp(\varphi - \varphi_c)^t$ (the basic scaling law from chapter 2) yielded $A = 0.0027$, the percolation threshold $\varphi_c = 0.27$ wt% and the critical exponent $t = 1.7155$ which is well within the theoretical 3D percolation range of 1.6 – 2, cf. section 2.4.

⁶It must be pointed out that only 3 samples had a measurable conductivity value (the resistance of the first two samples was too high) and the fitting is therefore done on only those three points.

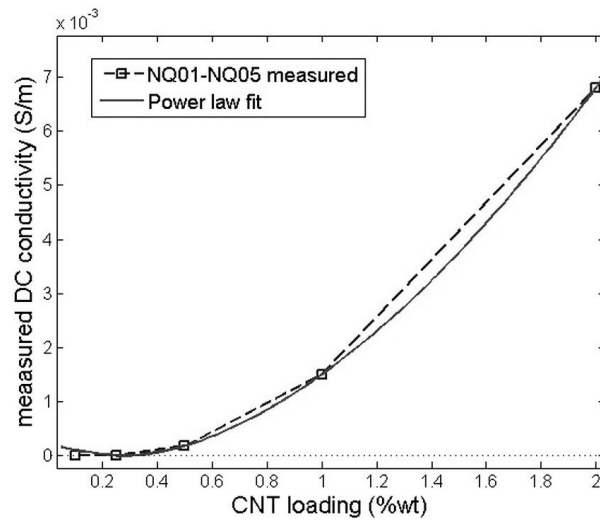


Figure 3.4.: DC conductivity as a function of CNT content for five PC samples with 0.1 %, 0.25 %, 0.5 %, 1 % and 2 wt% CNTs, measured values (dashed) and fit using power law $\sigma = A \cdot \exp(\varphi - \varphi_c)^t$ (solid). The obtained fit parameters are: $A = 0.0027$, $\varphi_c = 0.27$ wt% and $t = 1.7155$

The major issue of this method is the reproducibility, mostly due to the heterogeneity of the sample because of the CNT distribution. Percolation is a local phenomenon, if the electrodes cover the entire surface of the sample any percolation path appearing will cause a sharp decrease of the measured resistance. But if this is not the case, as illustrated on Fig. 3.5, and percolation occurs in an area not located in the zone between the electrodes (A), it will not be seen from the measurements. Because of this, measurements of the resistance made in different spots of the sample can yield very different results. In our case, the samples are 30 by 50 mm² while the guarded electrode has a diameter of 5 mm, their area is therefore much smaller than that of the entire sample. For example the measured resistance of the PC composite sample with 0.1 wt% had a measured resistance varying from 25 M Ω to 40 G Ω . Usually five measurements were done in five different locations on the sample and the smaller one was considered. There was also very often some oscillation of the displayed value and, in that case the mean value was selected. Measurements were made allowing a ten seconds stabilization of the ohmmeter value.

Another irreproducibility factor is probably caused by the significant influence of the pressure that is applied to the sample and electrical contacts. Changing the clamps or surface of the electrodes lead to significant variations in the results. A commercial sample holder, actually an accessory to the LCR used for low frequency measurements has been used to improve the pressure control (its pressure control mechanism is especially designed for that objective). This sample holder is detailed in the next section and further results and information on the DC characterisation of nanocomposites can be found in section 4.3.

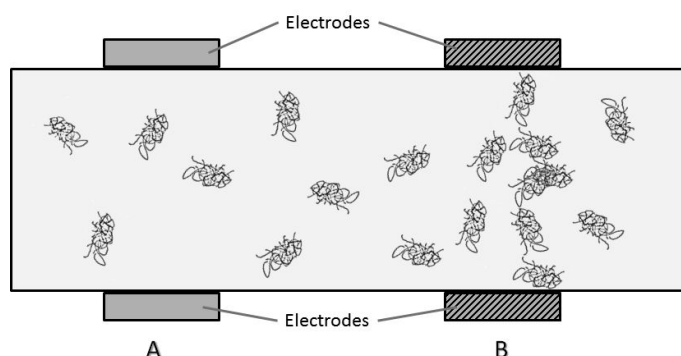


Figure 3.5.: Illustrative drawing of the role of the electrode position relative to a localised percolation path. If the dispersion of the CNTs is not adequate, percolation may occur only locally. If the electrodes are placed in (A), no percolation will be observed from resistance measurements, while is they are in (B), the resistance will be significantly lower than in A due to the percolation. The CNTs length scale is considerably enlarged for illustrative purposes.

It must be noted that the above methods measure the bulk resistivity of the material. to characterise the surface conductivity of the samples, other methods must be used. In order to investigate this, a commercial instrument was bought, the ‘SP4 Four Point Probe Head’ from Lucas Labs, to measure the sheet resistance of thin film samples using the four colinear probes method, pictures and illustrations of the operating principle on Fig. 3.6. However no interesting results could be obtained for our nanocomposite samples using this instrument. The samples surfaces were probably not smooth enough or the surface conductivity was too low. Or, as discussed further in this chapter, it may be due to the presence of insulating layers (devoid of CNTs) at the lower and upper surfaces of the samples.

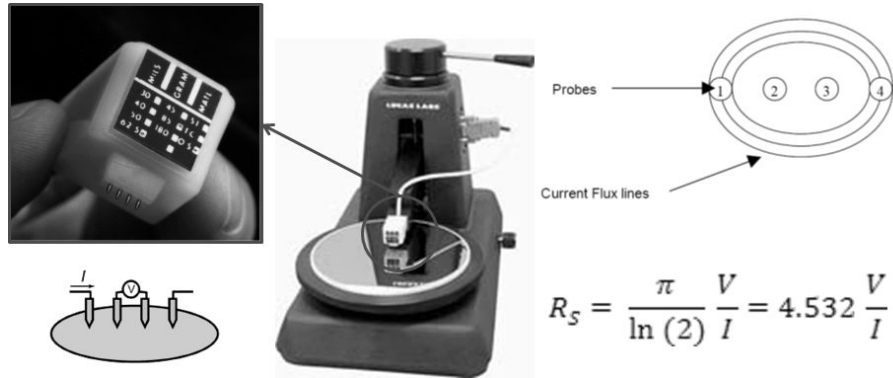


Figure 3.6.: Pictures of the commercial instrument for the measurement of the sheet resistance of thin film materials and basic information on the four colinear probes method.

3.2.2 AC experimental set-up, 1kHz-1MHz

For material characterisation in the 1 kHz – 1 MHz range, an Agilent LCR 4284A was used. First solid copper electrodes or the DEA set-up were used, with the same issues as in DC, with the added problem of capacitive couplings. To overcome these issues an accessory for this LCR was bought to provide good electrodes for guarded measurements, along with a reproducible pressure control system; the Agilent 16451B dielectric test kit, cf. Fig. 3.7. This sample-holder was also used for DC measurements, see previous section and chapter 4. The parallel capacitance C and resistance R of the samples are measured by the LCR (or e.g. the magnitude and phase of the impedance). These values are then converted into conductivity and dielectric constant using the Pouillet Law (see previous section) and $\varepsilon_r = C.L/S$ where L is the length between the electrodes and $S = \pi r^2$ is the area of the *guarded* electrode of radius r .

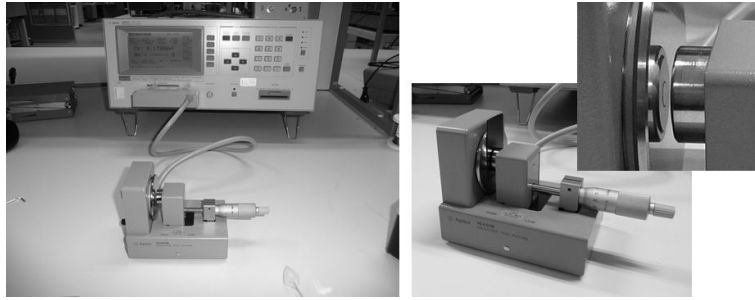


Figure 3.7.: Pictures of the Agilent LCR 4284A with the 16451B dielectric test kit and close-up view on the electrodes.

To test the precision and reproducibility of this set-up, a 500 μm -thick sheet of Teflon® (PTFE) was characterised, this material is known to exhibit a negligible conductivity and a dielectric constant of 2. As can be seen on Fig. 3.8, the maximum conductivity is of the order of magnitude of 5.10^{-8} S/m, even negative for some frequency indicating the resistance is so high it reaches the limit of the equipment. A variation of 0.5 % can be observed between dielectric constant versus frequency measurements made at a 24 hours interval, even after another calibration and the differences in the conductivity curves are negligible. It must be noted that the ‘jump’ that can be observed on Fig. 3.8 at 200 kHz is a well-known instrument artefact.

However when measuring nanocomposites the heterogeneity due to the dispersion of the CNTs must be taken into account. As detailed in the previous section the DC geometrical percolation is a local phenomenon. At the operating frequencies this dependence is less evident but the material most probably cannot yet be considered homogeneous and characterisation results of nanocom-

posite samples using this method are still irreproducible. More details on this issue can be found in chapter 4, along with a more in-depth discussion on the DC and AC results using the LCR on a wider range of samples. But it can already be seen from the results of Fig. 3.9 that even if the exact value of the conductivity and dielectric constant is not very reproducible, the behaviour of the curves can be related to the percolation threshold. The curves have different shapes depending on whether the sample has a filler content above or below the percolation thresholds.

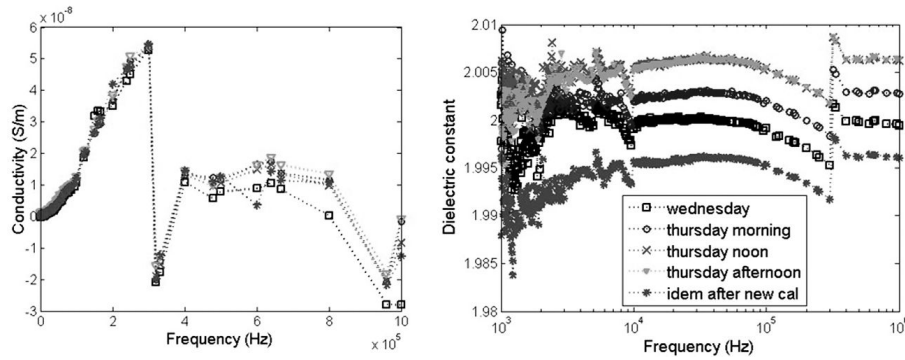


Figure 3.8.: Conductivity (left) and dielectric constant (right) of a 500 μm thick PTFE sheet, as a function of frequency, measured with the LCR and the 16451B dielectric test fixture.

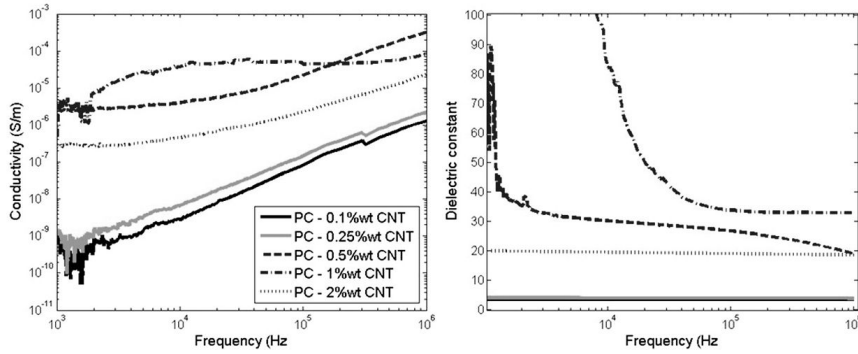


Figure 3.9.: Conductivity (left) and dielectric constant (right) of five polycarbonate-based nanocomposite samples, 650 μm thick, with 0.1 %, 0.25 %, 0.5 %, 1 % and 2 wt% CNTs, as a function of frequency, measured with the LCR and the 16451B dielectric test fixture.

3.3 MICROWAVE TECHNIQUES

3.3.1 One line method for thin solid samples and inks (microstrip topology)

Different transmission line (TL) topologies have evolved from the coaxial lines, from striplines to microstrips to more exotic topologies. The characteristics of planar transmission lines (e.g. stripline, microstrip or coplanar TLs, cf. Fig. 3.10) are controlled by selecting the dimensions of a single plane. They can therefore be easily fabricated using photolithography or chemical etching techniques and be used in microwave integrated circuits, [7].

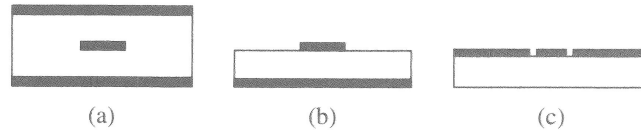


Figure 3.10.: *Cross-sectional views of three types of planar transmission lines: (a) stripline, (b) microstrip and (c) coplanar waveguide, from [7].*

A microstrip line, cf. Fig .3.11, consists in a strip conductor and a ground plane separated by a thin dielectric substrate. This TL is easy to manufacture with a very good reproducibility and its central conductor is easily accessed, facilitating integration in circuits and tuning, [8].

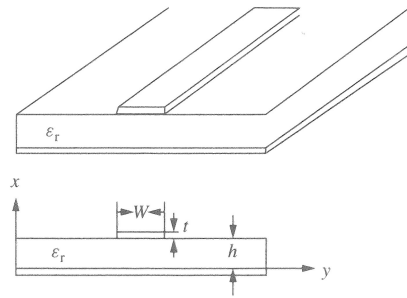


Figure 3.11.: *Geometry of a microstrip transmission line, with W the width and t the thickness of the microstrip, and h the thickness of the substrate, from [7].*

The dielectric above the strip (usually air) is different from the dielectric underneath (substrate). Because of this no true TEM mode can travel along a microstrip TL (unlike the stripline TL), neither can true TE or TM modes. The

most widely used approximation is that of the quasistatic approach. The lowest order wave is considered quasistatic and the fields distribution is nearly the same as for static fields, [9], and is called a quasi-TEM mode. This approximation is a very useful and widely used one but it has some limitations, such as w/d ratio (d is the substrate thickness and w the microstrip width) or finite strip thickness.

Microstrip TLs can also be used for material characterization, [7]. The material-under-test (MUT) must be a thin smooth membrane that will be used as substrate for the microstrip TL. A thin (thickness $< 1\text{mm}$) strip is then firmly glued on top of it and the other face is entirely covered by a metallic film. A MUT converted into a microstrip TL is shown on Fig. 3.12, where the conducting strip is made with self-adhesive copper tape and the back ground plane consists in a piece of adhesive aluminium foil, both tightly pressed against the MUT in order to minimize the insulating barrier between them.

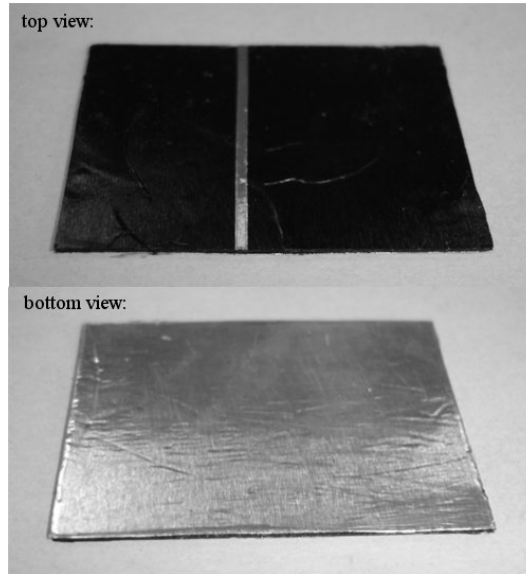


Figure 3.12.: *MUT used as substrate in a microstrip TL, the conducting strip is a thin adhesive copper tape and the ground plane at the back is made of adhesive aluminum tape. The MUT has a thickness of $650\ \mu\text{m}$ and is 30mm wide by 50 mm long.*

The MUT is fitted into an Anritsu model 3680K sample holder to connect the ends of the strip line and ground plane to two ports of a Vector Network Analyzer (VNA), cf. Fig. 3.13 and Fig. 3.14, that measures the scattering parameters ($\mathbf{S}$ matrix)⁷. In this case $\mathbf{S}$ is a 2x2 matrix (2-port network), cf. Fig. 3.15.

⁷For more information on the $\mathbf{S}$ parameters and their physical interpretation, see [10] or [8]



Figure 3.13.: *MUT used as substrate in a microstrip TL fitted in an Anritsu model 3680K sample holder, to be connected to a VNA.*

The **ABCD** chain matrix can then be extracted from the measured **S** parameters using the equations below, [10]. It relates the output current and voltage to the input current and voltage of the 2-port network.

$$\mathbf{A} = \frac{Z_{N1}^* + Z_{N1}S_{11} - Z_{N1}^*S_{22} - Z_{N1}\Delta_s}{2S_{21}\sqrt{\Re(Z_{N1})\Re(Z_{N2})}} \quad (3.1)$$

$$\mathbf{B} = \frac{Z_{N1}^*Z_{N2}^* + Z_{N1}Z_{N2}^*S_{11} + Z_{N1}^*Z_{N2}S_{22} + Z_{N1}Z_{N2}\Delta_s}{2S_{21}\sqrt{\Re(Z_{N1})\Re(Z_{N2})}} \quad (3.2)$$

$$\mathbf{C} = \frac{1 - S_{11} - S_{22} + \Delta_s}{2S_{21}\sqrt{\Re(Z_{N1})\Re(Z_{N2})}} \quad (3.3)$$

$$\mathbf{D} = \frac{Z_{N2}^* - Z_{N2}^*S_{11} + Z_{N2}S_{22} - Z_{N2}\Delta_s}{2S_{21}\sqrt{\Re(Z_{N1})\Re(Z_{N2})}} \quad (3.4)$$

where Z_{N1} and Z_{N2} are the reference impedances of the two ports and $\Delta_s = S_{11}S_{22} - S_{12}S_{21}$.

For a transmission line section of length ℓ , the **ABCD** matrix can be written as

$$\mathbf{ABCD} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & \mathbf{D} \end{pmatrix} = \begin{pmatrix} \cosh(\gamma\ell) & Z_0 \sinh(\gamma\ell) \\ \frac{1}{Z_0} \sinh(\gamma\ell) & \cosh(\gamma\ell) \end{pmatrix}. \quad (3.5)$$

where Z_0 is the characteristic impedance and $\gamma = \alpha + j\beta$ is the propagation constant of the TL, [10].

Therefore

$$\gamma\ell = \operatorname{argcosh}\left(\frac{\mathbf{A} + \mathbf{D}}{2}\right) \quad (3.6)$$

Besides, the propagation constant of a TEM wave is given by the formula

$$\gamma = \frac{j\omega}{v_p} = j\omega \frac{\sqrt{\varepsilon_{eff}^*}}{c_0} \quad (3.7)$$

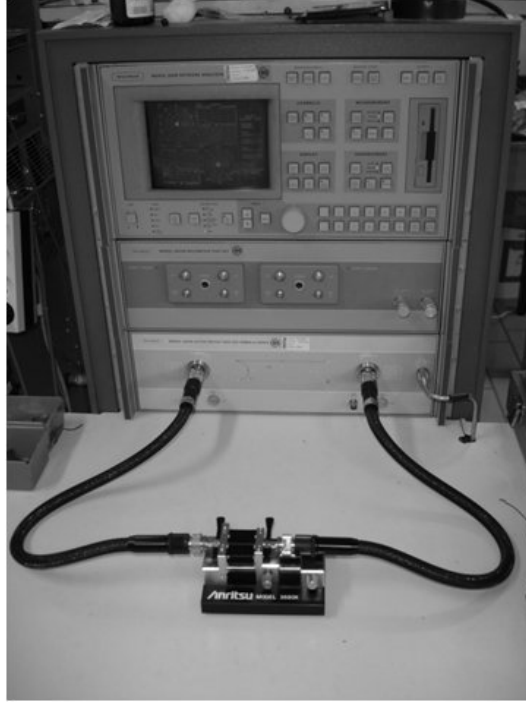


Figure 3.14.: *MUT and Anritsu model 3680K sample holder connected to an Anritsu Wiltron 360 VNA.*

where v_p is the phase velocity of the TEM wave, c_0 the speed of light in vacuum and ε_{eff}^* the effective complex permittivity of the medium in which the wave is propagating, [7].

In a microstrip TL, ε_{eff}^* is not strictly equal to the permittivity of the MUT, ε_r^* , because the dielectric above the microstrip is air, [7]. A priori, if ε_r^* is much larger than 1 and the electric field is concentrated near the substrate. In a widely used static approximation, [9, 11], ε_{eff}^* and ε_r^* are related as follows

$$\varepsilon_{eff}^* = 1 + \frac{\varepsilon_r^* - 1}{2} \left[1 + \frac{1}{\sqrt{1 + 10d/w}} \right] \quad (3.8)$$

Which means that if $10d \ll w$, $\varepsilon_{eff}^* \cong \varepsilon_r^*$. In other words, if the thickness of the MUT is much smaller than 10 times the width of the microstrip, ε_{eff}^* and ε_r^* can be considered equal.

If the above condition is fulfilled then

$$\varepsilon_r^* = \left(\frac{c_0 \gamma}{\omega} \right)^2 \quad (3.9)$$

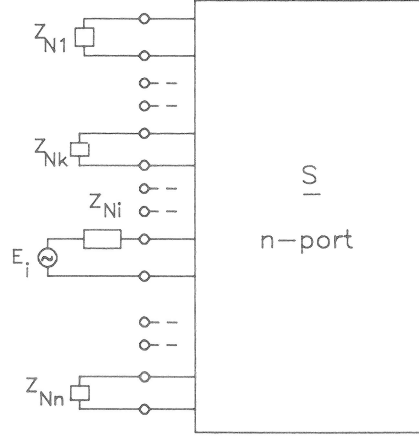


Figure 3.15.: Multiport excited at the i th port and loaded with matched terminations at the other ports, from [10].

And once the complex permittivity is extracted, the dielectric constant ε_r and electrical conductivity σ of the MUT are given by

$$\varepsilon_r = \Re(\varepsilon_r^*) \quad (3.10)$$

$$\sigma = -\varepsilon_0 \omega \Im(\varepsilon_r^*) \quad (3.11)$$

However, in most of our measurements, the actual values of the microstrip do not satisfy $10d \ll w$. Usually the width of the thin copper line, d , is about 1 to 1.5 mm-thick while the substrates have a thickness of 500 μm to 1 mm. The actual permittivity of the membrane must be extracted using the full equation 3.8 instead and the conductivity and dielectric constant of the MUT must be calculated from it. As shown on Fig. 3.16, the dielectric of a Teflon sheet ($\varepsilon_r^* = 2.1$) obtained considering $\varepsilon_{eff}^* \cong \varepsilon_r^*$ (grey) instead of equation 3.8 (dark) yields significantly different results. The mean dielectric constant from the first is 1.779 between 40 MHz and 40 GHz, instead of the expected 2.1, while using the complete equation, the average value on the entire range is 2.106, which is very good⁸.

However, as mentioned previously, equation 3.8 is a static relationship. In [9, 12], the correction that should be added to the static effective permittivity $\varepsilon_{eff}^*(0)$ used here above to obtain the correct $\varepsilon_{eff}^*(\omega)$ for any given frequency, ω is given by the equation

⁸The result is especially good since Teflon is a very low loss material and therefore the signal-to-noise ratio of the out-of-phase signals can be quite low.

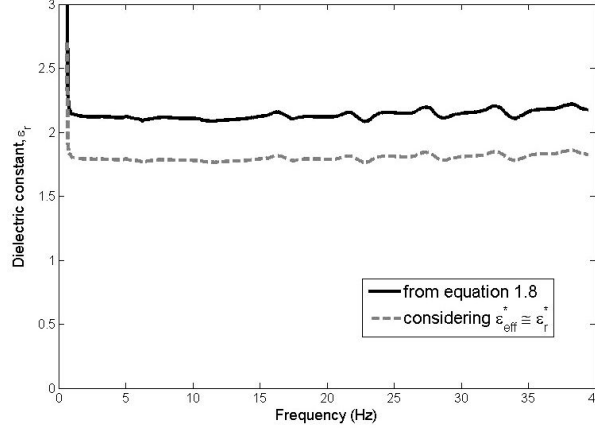


Figure 3.16.: Measured dielectric constant versus frequency of a 500 μm -thick Teflon sheet; considering $\varepsilon_{eff}^* \cong \varepsilon_r^*$ (grey) and using equation 3.8 (black).

$$\sqrt{\varepsilon_{eff}^*(f)} = \frac{\sqrt{\varepsilon_r^*} - \sqrt{\varepsilon_{eff}^*(0)}}{1 + 4F^{-1/2}} + \sqrt{\varepsilon_{eff}^*(0)} \quad (3.12)$$

But considering our typical microstrip dimensions, the relative difference between the static and high frequency value of the dielectric constant, or conductivity, was smaller than 0.6 % at 100 MHz for a teflon sheet and, of about 1.3 % at 100 GHz. Even considering a very high dielectric constant of 20, the difference at 100 MHz is of about 0.2 % (1.5 % at 100 GHz). The additional dependence of the effective permittivity on the frequency caused by the one-line technique can therefore be neglected and equation 3.8 can be used in the 40 MHz-40 GHz range without further correction.

An example of measurement results obtained using the One-Line microstrip technique is shown on Fig. 3.17 and on Fig. 3.18, for illustration purposes. The samples characterised here, using the technique that was just described, are thin plates (about 0.5 mm-thick) of CNT composites based on different polymer matrices but all with the same 1 wt% CNT content, except one PMMA sample with 2 wt% CNTs. From these results it can be seen that PEBAX, i.e. polyether block amide, exhibits the highest conductivity and also the highest dielectric constant. It can also be observed that two PMMA, i.e. poly(methyl methacrylate), samples with different CNT fractions exhibit a similar dielectric constant but the conductivity of the sample having a 2 wt% CNT content is twice as high at 40 GHz that the conductivity of the sample with a 1 wt% CNT content.

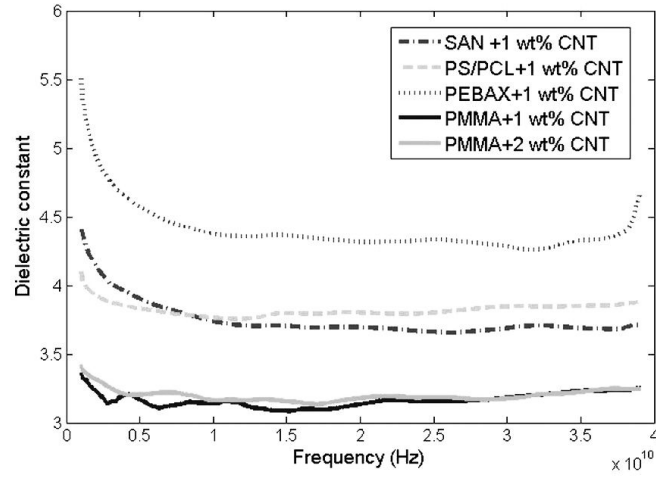


Figure 3.17.: Measured dielectric constant versus frequency for solid nanocomposite samples based on different polymer matrices, SAN (Styrene acrylonitrile), PS/PCL (polystyrene-polycaprolactone mix), PEBAX (polyether block amide) or PMMA (poly-methyl methacrylate) all containing 1 wt% CNT and a PMMA composite with 2 wt% CNT.

It must be kept in mind that the One Line method is valid only if a precise LRM (Line-Return-Match) calibration of the VNA has been done. The reference planes must be after the transitions and the reference impedances of the VNA must be set to 50Ω , which is ensured using a LRM calibration, [13]. This calibration can be performed using the special high precision microstrip standard kit suited to the Anritsu model 3680K sample holder. It is a very easy, reproducible and reliable method, especially useful to compare large quantities of samples. But the sample shapes must be thin plates (1.5 mm-thick at maximum) otherwise the Anritsu 3680K sample holder and its calibration kit cannot be used. In that case the quality of the characterisation results would be very dependent on that of the calibration method or kit used.

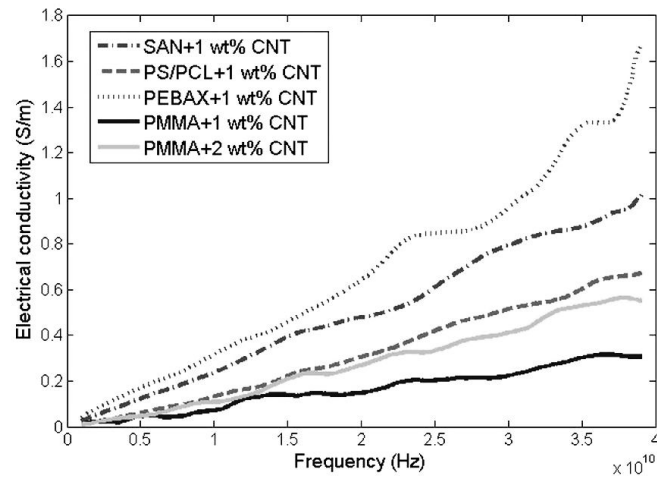


Figure 3.18.: Measured conductivity versus frequency for solid nanocomposite samples based on different polymer matrices, SAN (Styrene acrylonitrile), PS/PCL (polystyrene-polycaprolactone mix), PEBAX (polyether block amide) or PMMA (poly-methyl methacrylate) all containing 1 wt% CNT and a PMMA composite with 2 wt% CNT.

Note on coplanar waveguides. [3]

Investigations were also conducted on the frequency behaviour of the liquid dispersions of CNTs (often simply called ‘inks’) in the framework of the Innopile project. LCR characterization did not yield very interesting results, most probably because making frequency measurements using the same set-up (interrupted microstrip line) as for DC sweep measurements only amplified the irreproducibility issues, cf. chapter 6.

At high frequency, another transmission line configuration might be more effective for conductive liquids characterization. The coplanar waveguide transmission line, cf. Fig. 3.19, if the CNT dispersion is deposited on top of the coplanar line, it will flow in the grooves on both sides of the central conductor, where the electric field is strongest (as a comparison, at high frequency, the electric field in a microstrip line is essentially confined in the substrate, under the microstrip).

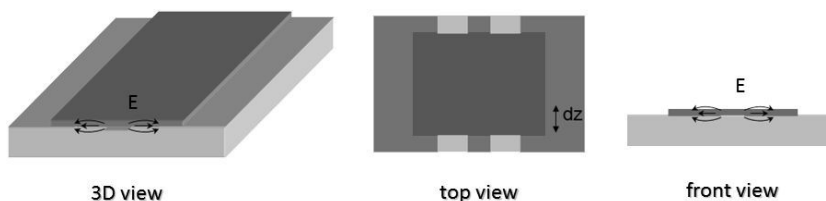


Figure 3.19.: Schematic diagrams of a coplanar waveguide with a square layer of (dried) liquid dispersion of CNTs on top, 3D view (left), top view (center) and ‘cross-section’ view (c).

A nanocomposite dispersion fabricated by the Certech (Centre of Technological Resources in Chemistry, Seneffe) was characterised using coplanar waveguides. It was a viscous, heterogeneous liquid containing 70 wt% of a CNT/platinum mix and 30 wt% of Nafion. These solutions were designed to be printed on Nafion membranes to increase their conductivity, see chapter 7. The dispersions were deposited as shown on Fig. 3.19 and they were first characterised immediately after deposition then after 15 minutes of drying (though the dispersion seemed dry already after 5 minutes). It must be noted that the adhesion of the dried residue to the substrate was poor and it quickly began ‘flaking-off’⁹. It can be seen on Fig. 3.20 that the addition of a layer of conductive residue on the coplanar waveguide decreases the transmission of power from one port to the other (S_{12}), because of the losses in the conductive layer. However this effect is decreased as the solution dries (and probably is detaching itself from the substrate).

The simple model of Fig. 3.21(a), assuming a purely resistive layer of CNT solution between the conductor strip and the ground planes, does not fit the measurement results for the equivalent resistance and capacitance of the ink

⁹Subsequently fabricated dispersions showed a slightly improved adhesion but the structure consisting in a CNT layer glued to a nafion membrane was abandoned not long afterwards.

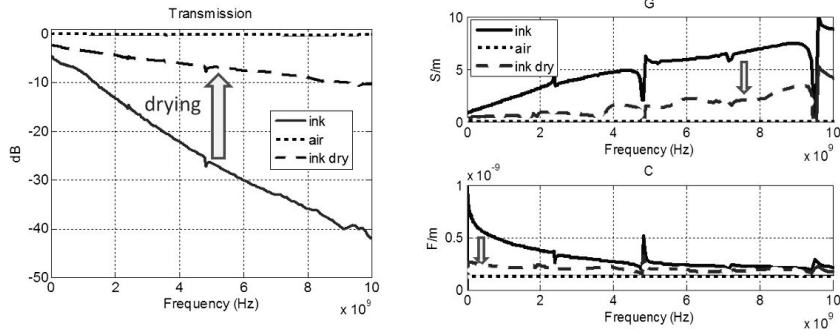


Figure 3.20.: S_{12} parameters of the coplanar waveguides, without ink, with ink and with dried ink, versus frequency (left) and dielectric constant and electrical conductivity versus frequency for the same waveguides (right).

layer, cf. Fig. 3.21(c). However, considering an insulating layer between the CNT layer and the metal electrodes leads to a quite good fitting of the model of Fig. 3.21(b) and the measurements results. The presence of this insulating layer might be due to a bad dispersion of the CNTs but the poor adhesion of the residue to the substrate and the metal electrodes probably also plays an important role.

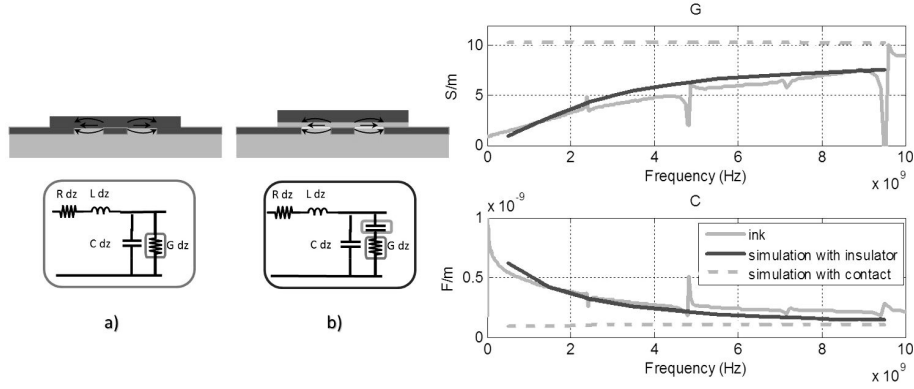


Figure 3.21.: (a) Equivalent electrical model of the coplanar waveguide with a layer of purely resistive ink deposited on top of it, (b) same model as (a) but assuming an insulating layer between the ink layer and the metal electrodes and, (c) the conductance and capacitance plots, measured values and values obtained by fitting using model 'a' (dashed) and model 'b' (solid).

Other CNT solution deposition methods have been tested by the Certech to improve the adhesion of the ink layer but none was truly successful and they often lead to damages to the metal electrodes, cf. Fig. 3.22. This coplanar waveguide

method showed itself to be not very sensitive to small variations in the samples characteristics and no definite conclusion can be made from those measurements.

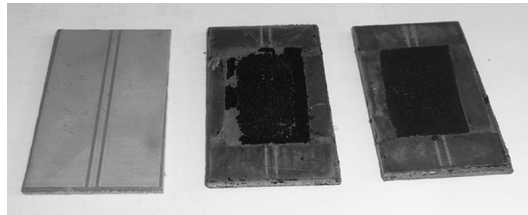


Figure 3.22.: *Picture of the coplanar waveguides, before ink deposition (left) and, after ink deposition by Certech (center and right).*

A permittivity extraction method similar to that used for microstrip transmission lines could also be developed for coplanar waveguide. This has not been necessary for the current thesis but one such technique can be found in [3] with a reasonable accuracy in the 1-5 GHz frequency range.

3.3.2 Line-Line method for bulk samples (waveguide topology)

Waveguides are basically metallic hollow-pipe guides along which EM waves can propagate, [9]. Ideally, both conductor and dielectric (usually air) are made of loss-free materials. Three main waveguide topologies can be used, as illustrated on Fig. 3.23.

The simplest one is the parallel-plate waveguide, propagation occurring at all frequencies, even direct current. It is also a TL because it is a 2-conductor line. In theory it does not radiate ($\mathbf{E} \times \mathbf{H}$ only in Z direction) but even tiny imperfections or discontinuities lead to some energy leakage and radiation loss. Besides, some kind of mechanical support is necessary.

Circular waveguides are easy to manufacture but suffer from a major disadvantage; the polarization of the electric field can rotate as the wave propagates along the waveguide, because of irregularities and the receptor at the other end might not receive all the energy that was originally sent.

The rectangular waveguide does not suffer from the same limitations and is therefore the most commonly used topology in many microwave applications. A picture of the complete range of rectangular waveguides available in the Welcome characterisation facility at UCL, covering the 1.2 to 40 GHz frequency range is shown on Fig. 3.24.

It should be noted that a TEM mode cannot propagate in waveguides (except the parallel plate), because no static field can exist in a region bounded by a single conductor (no axial component to carry the current, like in coaxial line, for example). However, they support TE or TM modes. The dominant mode of a rectangular waveguide is TE_{10} . Other modes can propagate inside the waveguide but their cut-off frequencies are higher, as shown on Fig. 3.25. This means that a particular waveguide can only be used only inside a specific frequency range, between its own cut-off frequency and that of the closest higher order mode (to avoid multi-mode propagation). Its cut-off frequency is independent on one of the cross-section dimensions which means that the geometry can be used to ‘tune’ the waveguide frequency band, [9]. The field polarization of TE_{10} is fixed, $\mathbf{E}$ passing from top to bottom of the waveguide. Attenuation due to copper losses is not excessive, for a given frequency.

Waveguides are mostly used as transmission lines at microwave frequencies, e.g. connecting receivers or transmitters to antennas. Since the presence of a material (σ , ϵ_r) sample inside a waveguide modifies its properties, it can be used to characterize electrically this sample. Part of the energy will be absorbed by the material (depending on its properties) and there will be a difference between the power emitted, P_{in} , and the sum of the one received on the other end, P_{out} , and that reflected back to the emitter, P_{ref} ; this is the power absorbed by the material, P_{abs} . Besides the reflected power will also be different in presence of

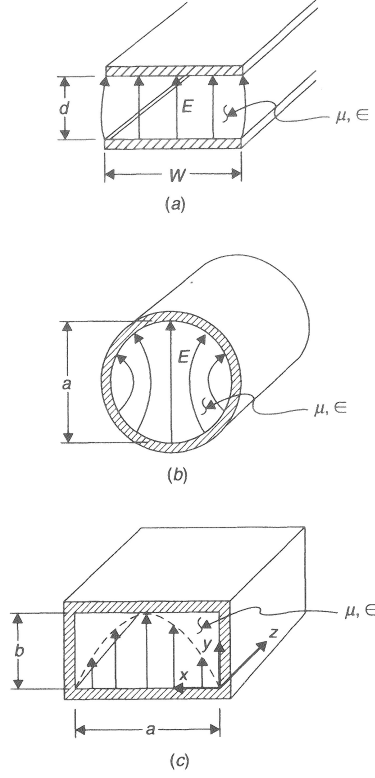


Figure 3.23.: Waveguide types and the cross-sectional $\mathbf{E}$ field pattern of the dominant mode: (a) parallel plates waveguide where d is the distance between the plates and W the plate width, (b) circular waveguide, where a is the diameter of the waveguide and (c) rectangular waveguide with a and b the lengths of the waveguide sides (the short and the longer one, respectively), from [8].

an obstacle inside the waveguide. This can be summarized as follow

$$P_{in} = P_{out} + P_{ref} + P_{abs} \quad (3.13)$$

If this waveguide is then connected to both ports of a VNA, the above equation can be written in terms of scattering parameters

$$\frac{P_{abs}}{P_{in}} = 1 - |S_{11}|^2 - |S_{21}|^2 \quad (3.14)$$

A very clean and efficient technique to characterize materials using waveguides is the Line-Line method, described in [14] and [15]. Only the measurement of the

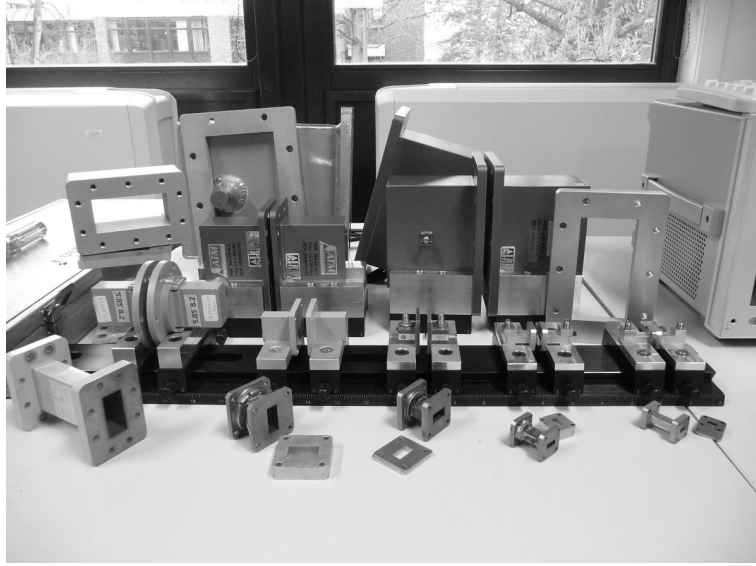


Figure 3.24.: Rectangular waveguides available in the Welcome-UCL characterisation facility, covering the entire 1.2 to 40 GHz frequency range.

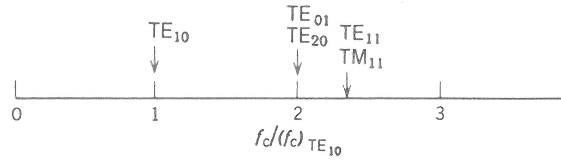


Figure 3.25.: Relative cut-off frequencies of waves in a rectangular waveguide ($b/a = 1/2$), from [9].

S parameters of two lines of different lengths is needed, S_{ii}^S for the shorter line and S_{ii}^L for the long one (after a coaxial calibration of the VNA). These lines are in this case waveguides of different lengths entirely filled with the material to characterize. This method has been shown to be quite equivalent to standard transmission-reflection and resonant cavity methods, [15]

The measurement matrices, M_S and M_L , are defined as follow

$$M_k = \left(\frac{1}{S_{21}^k} \right) \begin{pmatrix} S_{21}^k S_{12}^k & S_{11}^k \\ -S_{22}^k & 1 \end{pmatrix} \quad (3.15)$$

where $k = S$ for the short line and $k = L$ for the long one.

And from [14]

$$e^{-\gamma \Delta L} + e^{\gamma \Delta L} = \{M_L M_S^{-1}\}_{11} + \{M_L M_S^{-1}\}_{22} = A \quad (3.16)$$

where γ is the propagation constant and ΔL the length difference between the long and the short lines. The previous equation has an explicit solution

$$\gamma = \frac{1}{\Delta L} \ln X_{sym} \quad (3.17)$$

with X_{sym} one of the roots of equation 3.16

$$X_{sym} = \frac{A \pm \sqrt{A^2 - 4}}{2} \quad (3.18)$$

There are therefore two possible values for X_{sym} but only the one that verifies $|X_{sym}| < 1$ is usually significant.

The complex permittivity can be extracted from the propagation constant for a transmission line, [7, 16]

$$\gamma = j \sqrt{\frac{\omega^2 \varepsilon_e^*}{c^2} - \left(\frac{2\pi}{\lambda_c}\right)^2} \quad (3.19)$$

where $\lambda_c = 2\pi/k_c$, the cut-off wavelength, with $k_c = \pi/a$ the cut-off wave number of the TE_{10} mode and c being the speed of light in vacuum.

Finally the complex effective permittivity is given by the formula

$$\varepsilon_e^* = c^2 \frac{-\gamma^2 + \pi^2/a^2}{\omega^2} \quad (3.20)$$

And, as in the previous section, the dielectric constant and electrical permittivity are given by

$$\varepsilon_r = \Re(\varepsilon_r^*) \quad (3.21)$$

$$\sigma = -\varepsilon_0 \omega \Im(\varepsilon_r^*) \quad (3.22)$$

An example of measurement results obtained using the Line-Line waveguide technique is shown on Fig. 3.26, for illustration purposes. Two PMMA based foams were characterised using the Line-Line method, in this case an increase of the conductivity with an increase of the CNT content but no significant influence can be seen on the dielectric constant curves. Such foamed nanocomposites are discussed extensively in chapter 5.

Only a simple coaxial SOLT (short-open-load-through) calibration of the VNA is required this time and the final values of permittivity and conductivity depend only on the length difference ΔL . It is therefore especially well suited to waveguide measurements, because there is no precision waveguide calkit available in our laboratory that would be necessary for more complex and accurate calibrations. The comparison between the simple SOLT calibration method and

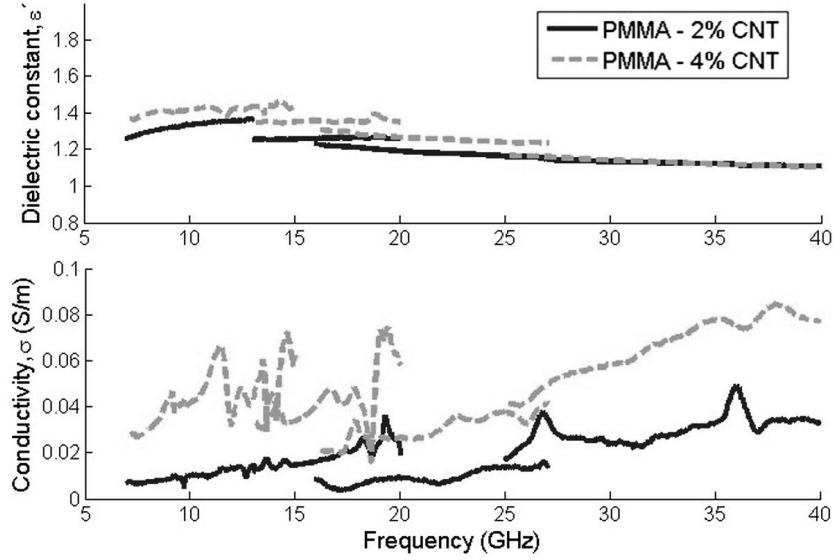


Figure 3.26.: Measured conductivity and dielectric constant of PMMA foamed nanocomposite samples, with CNT contents of 2% (solid) and 4% (dashed), versus frequency.

a LRM (Line-Reflect-Match) method, a more precise technique using a reference calkit, cf. section 3.3.1, is illustrated on Fig. 3.27. With an LRM calibration, the reference planes of the VNA are brought after the coaxial-microstrip transitions, so that the VNA measures the scattering parameters of the line under test only. With a SOLT calibration, the VNA reference planes are before these transitions and their influence on the measurements is not eliminated. Nevertheless, the SOLT calibration is sufficient to make sure the $T_{\Delta L}$ matrix being diagonal and, therefore ensuring the validity of the LL method.

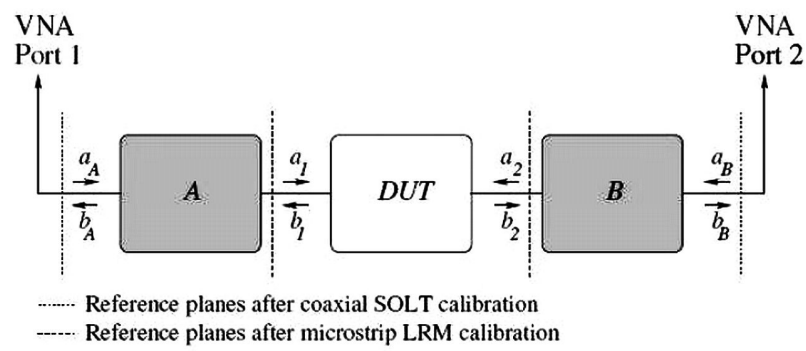


Figure 3.27.: Schematic diagram of the measurement setup where A and B correspond to the coaxial-to-microstrip transition, and DUT to the device-under-test, from [17].

Partially filled waveguides. The fore-mentioned equations are valid only if the volume of the material to characterize fills the waveguides entirely. If this is not the case numerical methods can be used to correct the measured values. There are two possibilities; either the material has the same cross-section as the waveguide but not the same length, with a length of air in the waveguide as illustrated on Fig. 3.28(a), or the cross-section of the material is smaller than that of the waveguide, cf. Fig. 3.28(b). The latter is much more complicated and numerical solutions of Maxwell equations are needed, [1], like the numerical deembeddings that can be found in [18, 19] or computations based on Nicholson-Weir-Ross algorithms, [7, 20, 21], for example. But these techniques often lead to a considerably decreased accuracy and exactness.

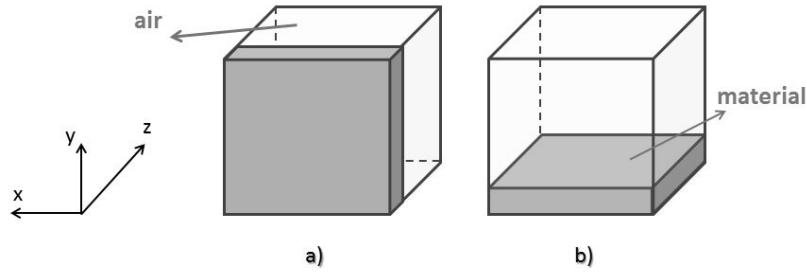


Figure 3.28.: Schematic diagram of the two configurations of the partially filled waveguides, the first one (a) where sample and waveguides have the same cross-section and the second one (b) where they have the same base.

The first configuration (a) is the simplest, the phase shift due to the length of air has to be subtracted from the measurements. This can be done easily by measuring the S parameters of the waveguide (partially) filled by the sample but also of the empty waveguide. If the S parameters are then converted into the ABCD chain matrices, cf. section 3.3.1, the ABCD matrix of the line without the length of air, $\mathbf{ABCD}_{net}$, is given

$$\mathbf{ABCD}_{net} = (\mathbf{ABCD}_{air})^{-1} \times \mathbf{ABCD}_{fill} \quad (3.23)$$

where $\mathbf{ABCD}_{air}$ is the ABCD matrix from the S parameters of the empty line and $\mathbf{ABCD}_{fill}$ is the one from the measurement of the partially filled waveguide.

Finally, the ‘net’ S parameters for both the short and the long lines can be determined from $\mathbf{ABCD}_{net}$ and the Line-Line technique can be efficiently used. The raw and corrected S parameters of a partially filled waveguide, configuration (a), are shown on Fig. 3.29. For samples having an absorption of the incident waves significant compared to air, the correction is quite negligible. In case the correction is significant, noise in the measurement often causes the corrected

values to exhibit even more noise. Therefore it is usually preferable to fill the waveguides as completely as possible. Besides even that way, the sample shape is rarely perfect, cutting or polishing the sample in the desired shape leads to some raw edges or faces that are not perfectly flat (especially if the material is fragile or brittle). Sometimes the thickness of the sample is not large enough to fill the entire length of the waveguide. Better results are often obtained by filling this gap using pieces of the sample rather than leaving a length of air. Or on the opposite, if the sample is flexible, like a foam for example, it is important that it is not larger than the waveguide, otherwise it might be compressed inside and the apparent density of the material might be higher than the actual one. It is not always easy to avoid compression when inserting a foamed sample into the waveguide, especially when the waveguide has a thin long shape.

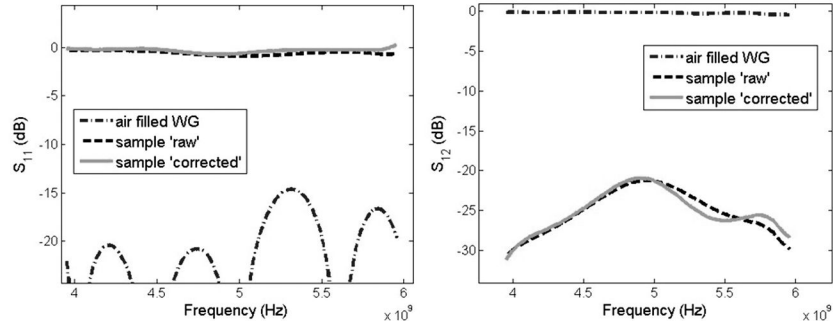


Figure 3.29.: S parameters from Line-Line measurements of an empty waveguide (dot), of the waveguide partially filled with a sample, in configuration (a), from 'raw' measurements (dashed) and after the correction for the length of air (solid).

3.3.3 Modified line-line method without waveguide for large samples

As detailed in the previous section, the Line-Line technique is very efficient but requires (for optimum results) that the samples be cut to present the same-cross section as the waveguides used. And these cross-sections are very different for each frequency band desired. Therefore this technique used for the broadband characterization of materials must be considered destructive, even though in principle it is not. Besides some samples are just too hard or too brittle or even too precious to cut even once to the adequate dimensions. Furthermore, for very high frequencies, the waveguides cross-section is very small and the results can be only a very local image of the MUT (material under test) and must then be repeated several times in several locations in order to give a more global picture of the sample. Besides, because of fabrication tolerances, small gaps in this cross-section or in the material will lead to errors that can be significant, especially at high frequency.

A modified Line-Line technique has been developed in the framework of the Multimasec project that does not require the use of a waveguide¹⁰. The MUT, which has to be a rather thin plate (less than about 1 cm thick) and to have two very flat and parallel faces, is put directly between the coaxial-to-waveguide transitions of the desired frequency band. The transitions are connected to a VNA and the S parameters measured. They must also be measured without the sample, once with the transitions pressed close to one another and a second time with the transitions separated by a length of air equal to the thickness of the sample, cf. Fig. 3.30. It must be noted that this method has the added advantage of emulating real-life conditions of use for EMI shielding materials.

The measurement with the sample between the transitions is then the *long line* of the Line-Line technique, while the measurement without sample and with the transitions pressed against one another is the substitute for the *short line*. The measurement of the length of air is used as a correction to the sample measurement to compensate the absence of a waveguide. Inside a waveguide, there is single mode propagation in a given frequency band, without a waveguide, the wave is propagating in free space or inside a sample which means higher order modes can be excited, especially if the dielectric constant of the sample is high. The energy stored into these higher order modes is not collected by the receptor on the other port (for S_{12} and S_{21}) nor on the same port (for S_{11} and S_{22}) and is then lost, leading to an extracted absorbed power higher than the one really absorbed by the sample. Besides, using the transitions without a waveguide and separated by a layer of air is similar to free-space operation of a pair of antennas and the coax-to-waveguide to transitions are not necessarily very directive antennas. It means that the emitted field has the shape of a cone, of unknown dispersion, and part of it might not reach the opposite transition or be reflected by the flanges... Because the short line here is not really a 'line'

¹⁰The reasons behind this are developed in section 5.7

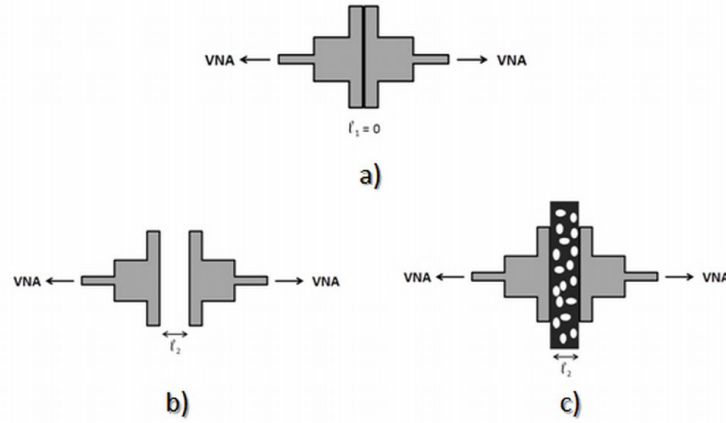


Figure 3.30.: *Diagram of experimental set-up for the modified Line-Line technique, with the transitions against one another (a), with the samples inserted between the transitions without waveguide (b) and the transitions separated by a length of air corresponding to the thickness of the sample (c).*

and because of these two limitations, the modified Line-Line technique is, a priori, less exact and sensitive than the original Line-Line technique. Besides the effective area ‘seen’ by the measurement is that of the transitions of the desired frequency range, the same as the corresponding waveguide cross-section and the small size limitation at high frequency remains.

A polypropylene (PP) foam was characterised using the fore-described method, the extracted dielectric constant and electrical conductivity are plotted as a function of frequency on Fig. 3.31. The same procedure was applied to a spacing of air between the transition equal to the thickness of the PP composite foam (7 mm) and the latter results are plotted on the same graph. The measurement of layer of air yielded, as expected, a negligible conductivity. But the extracted dielectric constant is smaller than the theoretical 1 of air, with an average deviation between 50 and 35 % due to the non-directivity of the transitions considered as antennas here. The samples exhibits a considerably higher conductivity and dielectric constant than air, losses by absorption and reflection are therefore considerably larger than the one due to the ‘leaks’ between the transitions.

However, if the dielectric constant of the material is significantly higher than 1, the electric field is concentrated in the material and the extraction is more accurate.

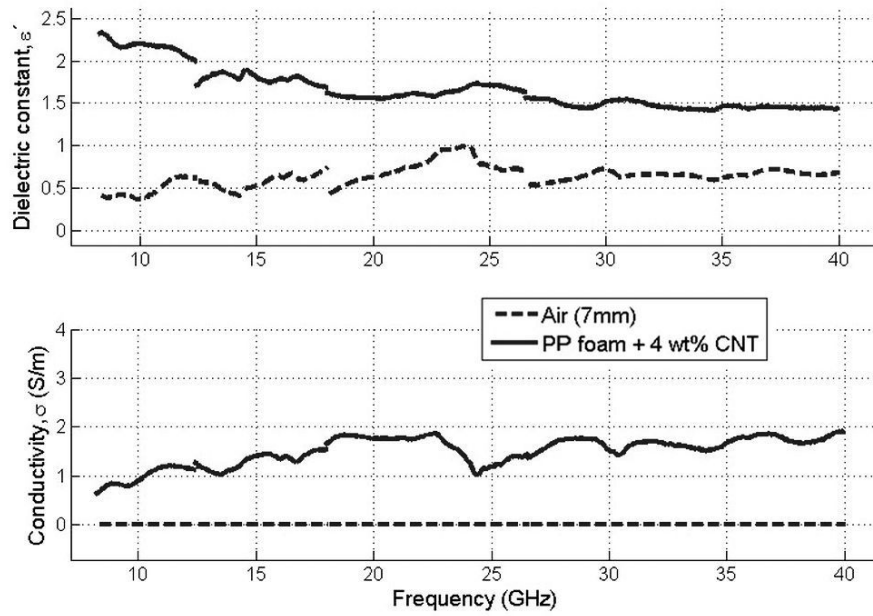


Figure 3.31.: Dielectric constant ϵ' (top) and electrical conductivity σ (bottom) as a function of frequency, for a polypropylene (PP) foam containing 4 % CNT (solid) and for an air spacing equal to the foam thickness, i.e. 7 mm (dashed).

3.3.4 Comparison between the original and modified Line-Line methods

The Line-Line technique using waveguides filled with the material to characterise, is shortened in this section as ‘original’ method, and the so-called modified Line-Line method without waveguides, is shortened here to ‘modified’ method, where the samples is inserted between the coax-to-waveguide transitions. They have been described in the previous sections and results have been presented for both methods. But the important question is whether the two methods produce the same results for the same material? Finding a material that could be adequately characterised using both methods has not been as easy as first expected. The material had to be solid enough to be cut into regular shapes (at least two rather smooth parallel faces) but not too hard otherwise cutting it clean becomes a problem. The material must be lossy but not too much. For example commercial absorber material did not yield exploitable results, neither did natural sponge (probably because of moisture) nor many commonly available materials that I tested.

If the material is not lossy enough, the scattering parameters of the sample and of a slab of air with the same thickness will be too similar and the noise fluctuations will become dominant in the results obtained using the modified method. As an example, a low-density flexible PU based foam¹¹ containing 0.35 wt% of CNTs was characterised, a picture of the foam is shown on Fig. 3.32. The extracted dielectric constant and conductivity are shown on Fig. 3.33 using the original technique and on Fig. 3.34 using the modified method. It can be observed that the results using the original method are smooth, with a very good overlap at the transition between bands and, that the difference between air and material is significant. Results for the layer of air and the PU sample are not very different when using the modified method and there is considerable noise.

Furthermore, the dielectric constant of air extracted using the original technique is very close to the theoretical value of 1, though with the modified method it is significantly smaller. The values of the dielectric constant and electrical conductivity of the foam is also significantly smaller using the latter method than with the original technique.

Measurements up to 40 GHz could be made with the modified method, cf Fig. 3.34 but not with the original technique because the foam was not dense enough to retain cohesion when cut to the dimensions of the waveguides for the upper frequency ranges. It can be noted that even at high frequency, the results for the foam are not very different from those of a slab of air of the same thickness. Besides, the minimum frequency was 8 GHz because the dimensions of the

¹¹This foam was fabricated by M. Bernal from CSIC Madrid, by chemical foaming, as detailed in [22], and measured at UCL.



Figure 3.32.: Picture of the low-density flexible PU based foam containing 0.35 wt% of CNTs fabricated at CSIC, the homogeneous grey colour of the sample is usually the sign of a good dispersion of the CNTs.

waveguide for frequencies below 8 GHz are too large compared to the volume of foam at our disposition.

If a high-loss material is characterised, the situation is very different. Two rigid polypropylene (PP) foam¹² samples containing 4 and 8 wt% CNTs have been characterized. They were a lot more rigid than the previous foam but also more difficult to cut. They were fabricated in the shape of a plate 7-mm thick (especially for characterisation using the modified technique). In order to be also measured using the original method with the electric field in the same relative position to the sample geometry, the plates were cut in little blocks to fill the waveguides entirely, cf. Fig. 3.35. The extracted values of the conductivity for both samples are plotted versus frequency on Fig. 3.36 using the original technique and on Fig. 3.37 using the modified method. This time the measured values using the modified method of the samples are well distinct from those of air and smoother than the results from the original technique. A major difference between the results obtained with these two methods resides in the significantly higher value of the dielectric constant using the original technique.

Using the original method, dielectric constant values of 1.12 (air), 2.74 (4 % CNT) and 10.02 (8 % CNT) were obtained at 12GHz and using the modified technique we obtained for ϵ_r : 0.63 (air), 2.05 (4 % CNT) and 3.83 (8 % CNT). This latter value for air is slightly smaller than 1 indicating a slight underestimation compared to the actual value, as already observed previously. Keeping this in mind, the dielectric constant values for the 4 % CNT composite using both methods are rather similar. The difference however is much more significant for the 8 % CNT foam but it may be due to the existence of a kind of ‘skin’ on

¹²These foams were fabricated by J.-M. Thomassin from ULg, using supercritical CO_2 , and characterised at UCL.

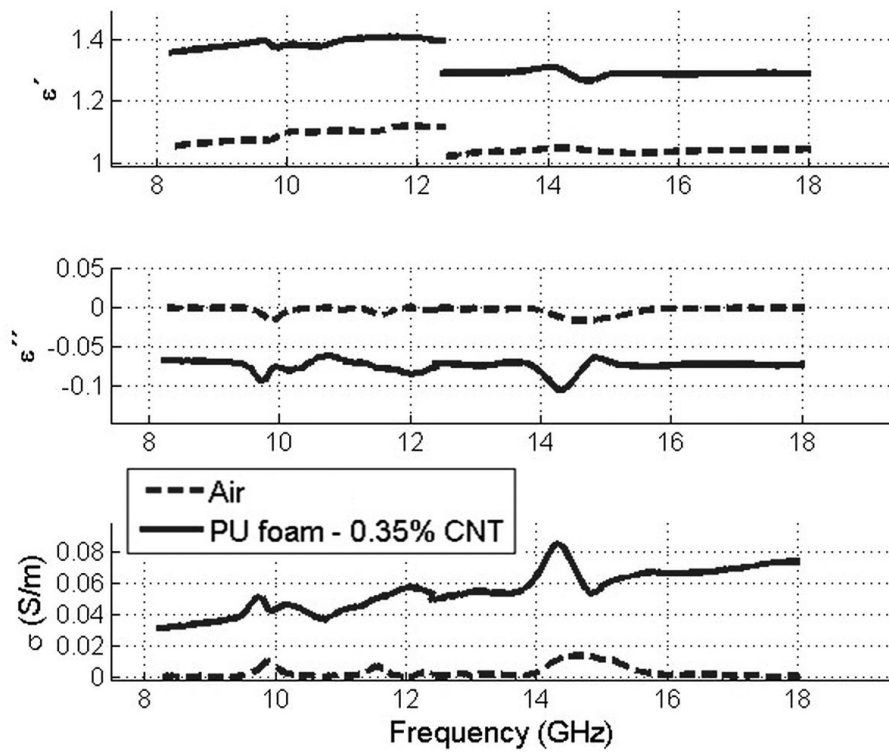


Figure 3.33.: Dielectric constant ϵ' (top), imaginary part of the complex permittivity ϵ'' (middle) and electrical conductivity σ (bottom) versus frequency for air (dashed) and for the flexible PU foam with 0.35 wt% CNTs from CSIC (solid), values measured using the original Line-Line method (waveguides).

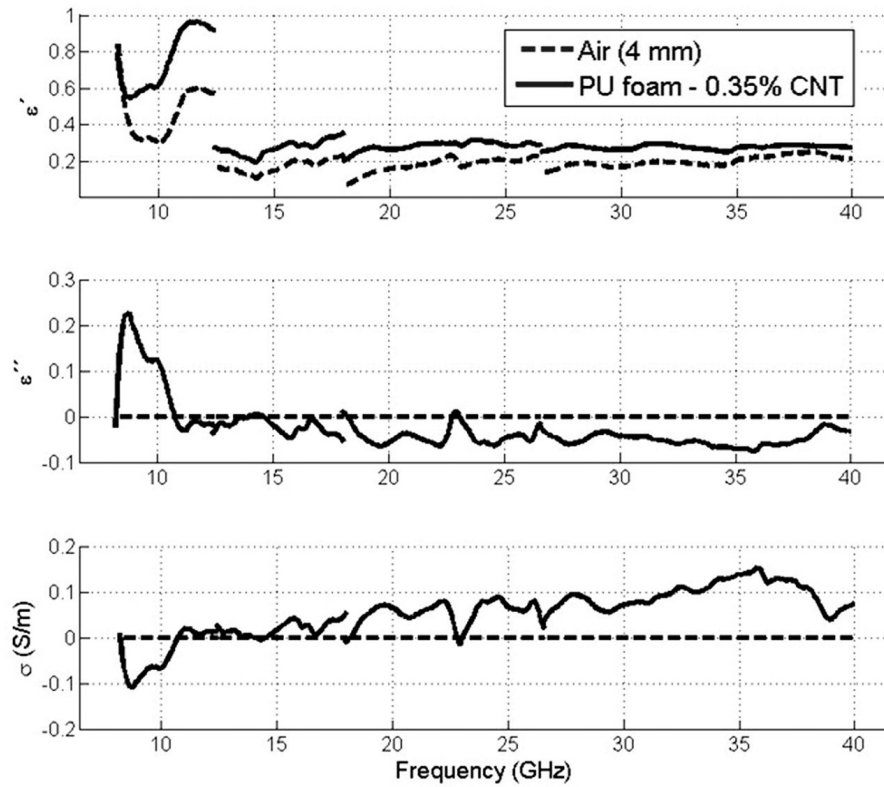


Figure 3.34.: Dielectric constant ϵ' (top), imaginary part of the complex permittivity ϵ'' (middle) and electrical conductivity σ (bottom) versus frequency for air (dashed) and for the flexible PU foam with 0.35 wt% CNTs from CSIC (solid), values extracted using the modified Line-Line technique (no waveguide).



Figure 3.35.: Picture of the rigid PP based foam containing 8 wt% of CNTs fabricated at ULg, the very dark colour of the sample hinting at a high electrical conductivity of the sample.

the foams, the sample exhibit a sort of layer having a higher density than in the interior of the foam.

When it is measured using the modified Line-Line, this ‘skin’ is present only twice while in the original technique, 4.5 pieces had to be cut to fill the waveguide entirely, i.e. 9 layers of this ‘skin’. It is discussed in chapter 5, and briefly shown in the previous section, that the denser the foam, the higher the dielectric constant. By multiplying the number of these denser layers and also the number of interfaces (losses due to multiple reflections), the extracted dielectric constant value is overestimated, especially for samples with a high filler content. From the literature, high CNT loadings often yield a poor distribution and the CNT content in the skin layer might be higher in high CNT content samples than in those with a lower filler fraction.

On the other hand, not using a waveguide means that higher order modes of propagation can be excited by the incident waves and this should be stronger if the dielectric constant is higher. The energy stored in these non-dominant modes would not be ‘seen’ by the other VNA port (only tuned to the lowest-order dominant mode, yielding to a higher measured total loss and the extraction algorithm would then give a higher dielectric constant and/or conductivity.

The conductivity curves are very similar in both cases, highlighting the probable influence of the characterisation technique chosen on the dielectric constant and not on the conductivity. At a 12 GHz frequency, the conductivity of the 4 % CNT foam is equal to 1.1 (original method) or 1.16 S/m (modified) and that of the 8 % CNT composite is 5.73 (original) or 6.25 S/m (modified). In each case the conductivity of the 8 % sample is 5 times higher than that of the 4 % CNT foam, not twice as high. This would contradict the hypothesis of a worse

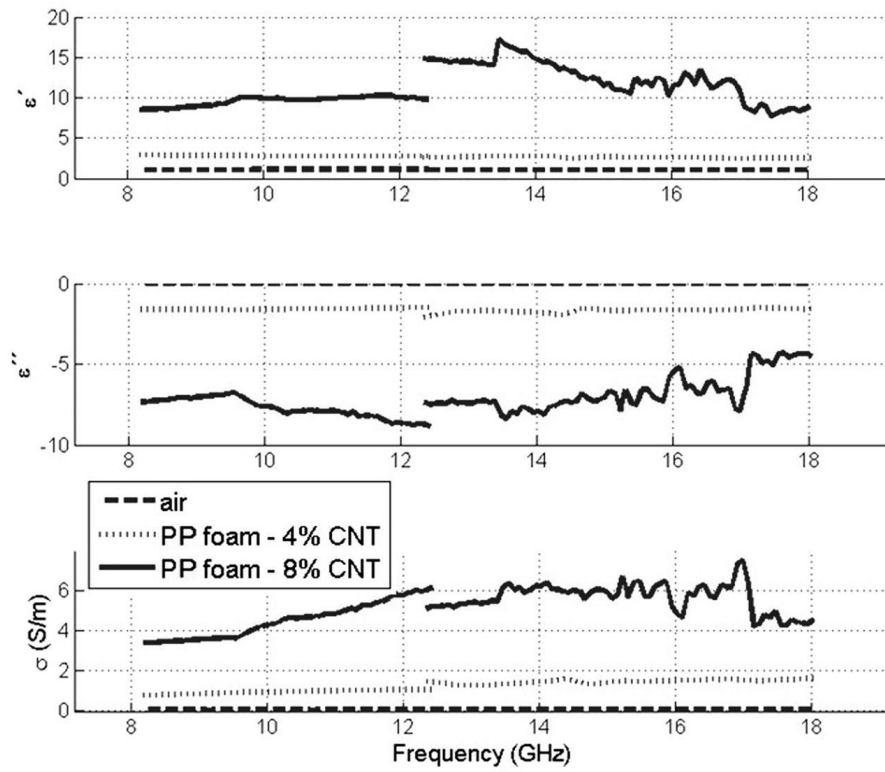


Figure 3.36.: Dielectric constant ϵ' (top), imaginary part of the complex permittivity ϵ'' (middle) and electrical conductivity σ (bottom) versus frequency for air (dashed) and for the PP foams from ULg with 4 wt% CNTs (dotted) and 8 wt% CNTs (solid), values extracted using the original Line-Line technique (waveguides).

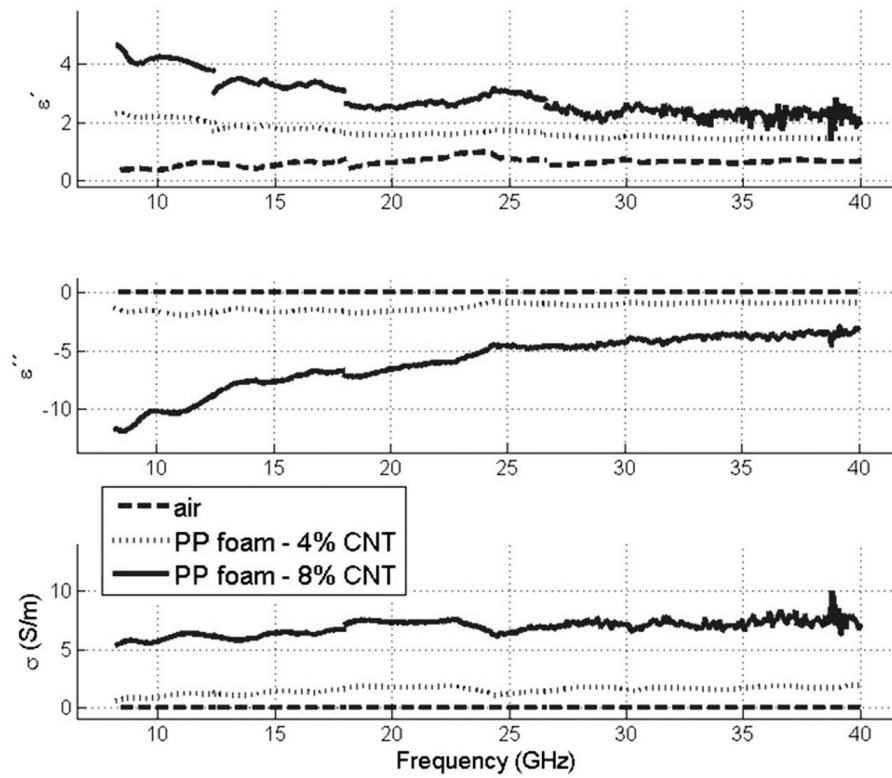


Figure 3.37.: Dielectric constant ϵ' (top), imaginary part of the complex permittivity ϵ'' (middle) and electrical conductivity σ (bottom) versus frequency for air (dashed) and for the PP foams from ULg with 4 wt% CNTs (dotted) and 8 wt% CNTs (solid), values extracted using the modified Line-Line technique (no waveguide).

distribution with higher CNT loading in our case but the ‘skin’ layers might also have an influence. SEM pictures could help to better understand those results.

These two composite foams were quite dense and difficult to cut in the exact desired shape. Therefore we did not investigate beyond 18 GHz using the original technique, because of the increasing relative importance of air voids due to shape differences between the piece or pieces of foam and the waveguide volume. This influence of the volume of air inside the waveguide is probably the cause of the significant noise already present in the 12 – 18 GHz measurements. However, a complete 8 – 40 GHz characterisation of the two foams was made using the modified method.

To conclude, the original Line-Line method is an excellent characterization technique yielding high quality, very reproducible results with various materials. Its main limitation resides in the necessity to cut the sample to the exact dimensions of the waveguide inner volume, this method will not be accurate nor simple for too hard or too brittle or fragile materials. Besides if the waveguide is entirely filled with a high-loss material there might not be much power transmitted through the material from one port of the VNA to the other and the measurements could be very noisy as a consequence. The original Line-Line method is especially well suited in the case of low-loss materials that can be easily shaped to fit the waveguide cavities, cf. Fig. 3.33 while the modified technique is better suited to high-loss materials, especially those that cannot be cut to fit the waveguides and having two flat parallel faces, cf. Fig. 3.37.

The modified Line-Line technique does not require the use of waveguides. It has therefore a major advantage over the original technique, it is *non-destructive*, materials do not have to be cut into pieces that are smaller and smaller as the frequency increases! Furthermore, because of this, a wider range of frequencies can be investigated for the sample volume of sample and samples that could not have been measured using the original method can now be characterised. However, the modified method suffers from different disadvantages; a decreased sensitivity for low-loss material, the possible excitation of higher order mode in the sample material and, the necessity of a very precise alignment and distance between the coax-to-waveguide transitions (the use of a special set-up to improve this is detailed in chapter 5). Besides a systematic underestimation of the dielectric constant has been observed with this modified technique.

The choice between one method or the other will therefore depends on the material properties, not only the electrical characteristics but also on mechanical and geometrical considerations.

3.4 FREE SPACE CHARACTERISATION USING ANTENNAS

A free space method of characterisation is briefly presented here for information purposes. It has been used in the framework of the MULTIMASEC project. The sample was placed between two horn antennas. The power reflected back from the sample and the power transmitted from one antenna to the other are measured using a VNA, cf. Fig. 3.38. The measurements were made in the 50–70 GHz frequency range, above the possibilities of the waveguides available in the laboratory at that time. Besides, the hybrid samples fabricated for the MULTIMASEC project are to be used ultimately as shielding materials (microwave absorbers), therefore free space measurements were closer to real working conditions than waveguides. The hybrid samples were composed of a metallic honeycomb inserted in a polymer-CNT composite foam, cf. section 5.7. The samples were inserted into a Rohacell® plate (material with negligible losses even at microwave frequencies and a dielectric constant similar to that of air) because of the small cross-sectional area (almost all the incident power reached the opposite antenna). But doing so significantly decreases the sensitivity of the measurements. The antennas were visually aligned then oriented so that, without any sample, the power transmitted from one antenna to the other was maximum.

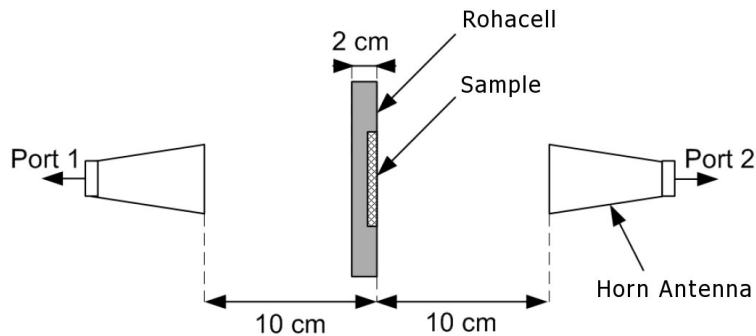


Figure 3.38.: Schematic diagram of the experimental set-up for the free space measurements.

Nanocomposite samples composed of a polyurethane-CNT composite and a similar but foamed sample were characterised and compared to a commercial foamed microwave absorber (Eccosorb®) and to a simple metallic sheet, all having the same dimensions and being inserted in the Rohacell plate. The nanocomposite samples were 2 cm wide by 5 cm long for a thickness of about 7 mm. The Eccosorb sample was cut to the same dimensions and the metallic plate had the same width and length but a thickness of about 5 mm.

The S_{12} (transmission) results are presented on Fig. 3.39 versus frequency. As expected, without any obstacle the transmission from one antenna to the other is highest for air. It is similarly decreased for the metallic sheet and for the two nanocomposite samples (foamed or solid¹³). These three samples having a comparable effect on the transmission. The commercial absorber exhibits the strongest influence on the power transmission¹⁴. The plate of metal should block almost all of the incident power but a significant fraction of it can bypass the sample if it is not large enough.

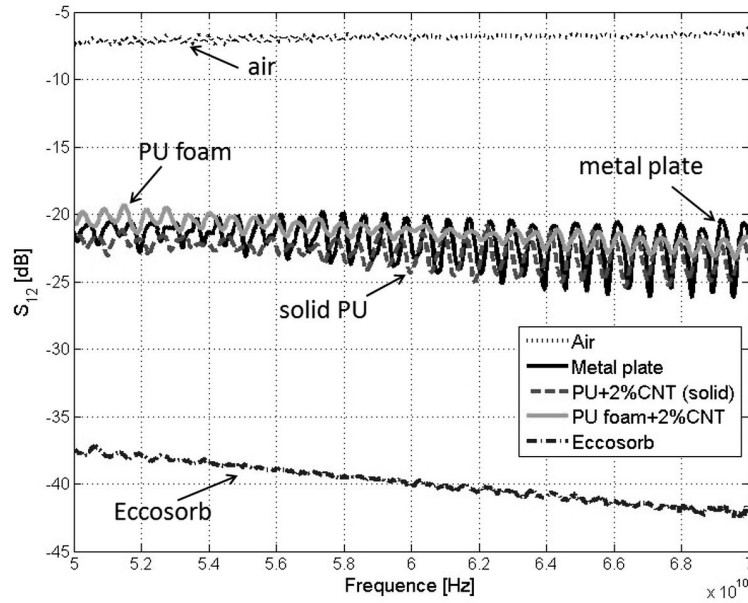


Figure 3.39.: S_{12} (transmission) parameters versus frequency for a foamed (solid, grey) and a solid (dashed) nanocomposite sample (PU with 2 wt% CNT), for a metallic sheet (solid, black), for a piece of commercial absorber (dash-dot) and, without any sample but air (dotted) between the antennas.

As can be seen on Fig. 3.40, the situation is very different for the reflection of the incident waves. The metallic sheet exhibits the highest reflectivity, because of its high electrical conductivity. The reflectivity of the solid nanocomposite is slightly lower. The commercial absorber and the foamed nanocomposite both show a reflection similar to that measured without any sample between the antennas. Though it seems the foamed nanocomposite would be slightly better at very high frequency, close to 70 GHz.

¹³The term 'solid' nanocomposite is used here in opposition to foamed material.

¹⁴The commercial foam sample was significantly larger than the other samples, it may explain the observed lower transmission with it than with a plate of metal.

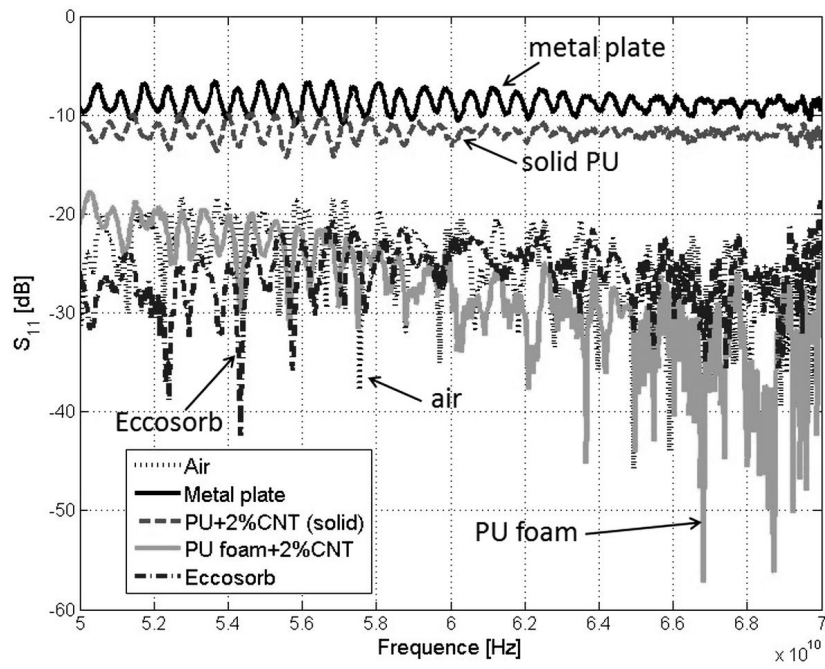


Figure 3.40.: S_{11} (reflection) parameters versus frequency for a foamed (solid, grey) and a solid (dashed) nanocomposite sample (PU with 2 wt% CNT), for a metallic sheet (solid, black), for a piece of commercial absorber (dash-dot) and, without any sample but air (dotted) between the antennas.

Therefore, the foamed nanocomposite has shown reflection performances comparable to those of the commercial absorber in the 50 – 70 GHz range, but being about half as thick and possessing other interesting properties (e.g. mechanical or thermal), cf. section 5.7 or [23] for more information on the multiscale hybrids performance). However for small samples the free space methods is not very sensitive and significantly more complicated than the waveguide based methods. Besides to obtain high quality measurements, i.e. significantly reduced noise and improved sensitivity, the characterization should be made inside an anechoic chamber using large panels of the material-under-test.

3.5 ONE-PORT CHARACTERIZATION TECHNIQUE FOR THIN FILM SAMPLES (WITH IONIC CONDUCTIVITY)

In the framework of the PICOM project (Walloon Region project) a new simple, non-destructive and reproducible technique to characterize the ionic conductivity of nanoporous track-etched membranes that avoids polarization interfacial effects has been developed for the nafion samples of the Innopile project. These membranes are very thin (12 to 200 μm thick) polyimide or nafion membranes with either a nanoporosity or embedded nanoparticles, they are mostly electronic insulators but good ionic conductors. More details on these particular membranes, their use in membrane-electrode assemblies in fuel cells and the track-etching process can be found in chapter 7.

Conventional DC methods are not well suited in this case due to interfacial polarization phenomena: AC methods are therefore used and the corresponding DC conductivity is extracted from a Cole-Cole plot (imaginary versus real part of the frequency-dependent conductivity). In many AC methods [24], the value of the DC conductivity (in our case the ionic conductivity) corresponds to the diameter of the circle in the Cole-Cole plot, cf. Fig. 3.41. A simple, non-destructive microwave characterization method, easily repeatable on large numbers of samples with a very good reproducibility was developed, [25] and [26], it was called the Parallel Plate Reflection (PPR) method.

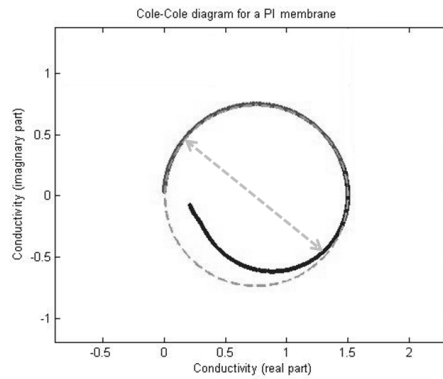


Figure 3.41.: *Cole-Cole plot for a PI membrane, the imaginary part of the conductivity is plotted versus its real part. The diameter of the circle fitting the lower frequency part of the curve is equal to the DC conductivity of the membrane.*

The membrane-under-test (MUT) is placed, after a 30 second immersion in water or acid, between two parallel metallic¹⁵ plates, cf. Fig. 3.42, and then submitted to a high frequency (from 40 kHz to 4 GHz) signal emitted by a Rhodes & Schwarz Vector Network Analyzer (VNA), [25]. The complex reflection

¹⁵Platinum to avoid corrosion in water or acid.

coefficient Γ of the membrane (metallic plates included) is then measured using the same VNA.

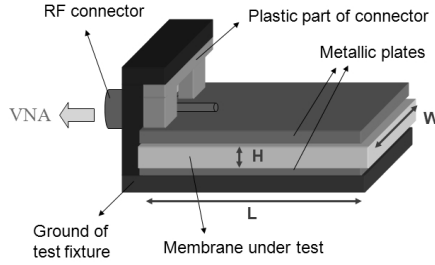


Figure 3.42.: Schematic diagram of the sample holder that is then connected to one port of a VNA, from [26].

According to equation 3.24, Γ is a function of the complex admittance Y of the membrane-plates system, [27].

$$\Gamma = \frac{Y_R - Y}{Y_R + Y} \quad (3.24)$$

with $Y_R = 1/50 \text{ S}$ the reference admittance of the VNA.

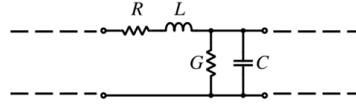


Figure 3.43.: Equivalent circuit for a transmission line (infinitesimal element per unit length in the distributed circuit represented here).

For a transmission line having the lumped-element circuit model of Fig. 3.43 (infinitesimal cell in distributed circuit), the admittance of the line can be written as follows

$$Y = \sqrt{\frac{\varepsilon_0 \varepsilon_r}{\mu_0}} \frac{W}{H} \tanh(j\omega \sqrt{\mu_0 \varepsilon_0 \varepsilon_r} L) \quad (3.25)$$

where $\varepsilon^* = \varepsilon_0 \varepsilon_r$ is the equivalent complex permittivity of the membrane, μ_0 its permeability, ω the radian frequency, W , H and L the dimensions of the electrodes, cf. Fig. 3.42 .

If the length of the electrodes, L , is much smaller than the wavelength, equation 3.25 becomes

$$Y \simeq j\omega \varepsilon_0 \varepsilon_r \frac{W L}{H} \quad (3.26)$$

which corresponds to the admittance of a simple localized RC parallel circuit; $Y = G + j\omega C$, with $R = \frac{1}{\sigma'} \frac{H}{WL}$ and $C = \varepsilon_0 \varepsilon' \frac{WL}{H}$, where the frequency dependent conductivity is given by

$$j\omega\varepsilon_0\varepsilon_r = j\omega\varepsilon_0(\varepsilon' - j\varepsilon'') = \sigma' + j\omega\varepsilon_0\varepsilon' \quad (3.27)$$

If L is not negligible compared to the wavelength, the transmission line model must be used. In our case, the length of the electrode is $L = 25\text{mm}$ (the width $W = 16\text{mm}$) and the wavelength is down to 30mm at 10 GHz , which is not negligible compared to L . We cannot use the localized elements model but the distributed one; this is confirmed by the plot shown on Fig. 3.44. It must be noted that, in order for the localized circuit model to be valid, a much smaller electrode should be used, which would not be practical. Besides it is desirable to have a measurement set-up as close as possible to operating conditions in real fuel cells. The measurement of a Nafion membrane, 0.5mm -thick, (solid black curve) is compared to simulation results using the localized model (grey, dashed) and the distributed one (grey, solid). Both simulations were made for a 0.5mm -thick membrane, with a dielectric constant of 10 and a conductivity of 3.24 S/m (and electrodes having dimensions of $16 \times 25\text{ mm}^2$). It can be seen on Fig. 3.44 that the height of the peak in the conductivity versus frequency plots corresponds to the ionic DC conductivity entered in the simulation. This is further confirmed by the results shown on Fig. 3.45 (distributed values: small circles and localized ones: dashed line); the results from simulations obtained with DC conductivities between 0.5 and 10 S/m are plotted versus frequency. The DC conductivity used in the simulation and the heights of the peaks are always identical. There is therefore no further need for circle interpolations in Cole-Cole plots.

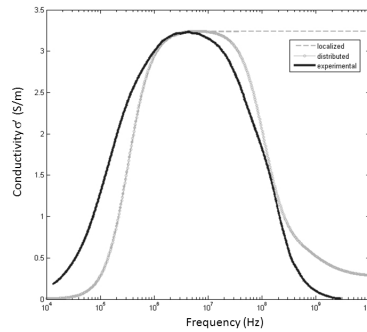


Figure 3.44.: Comparison of the conductivity versus frequency plots from experimental results (black, solid), from simulation using the localized model (grey, dashed) and using the distributed elements model (grey, circles), for a 0.5 mm -thick Nafion membrane.

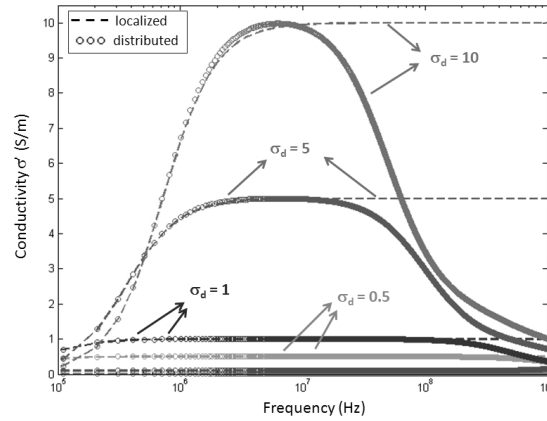


Figure 3.45.: Conductivity versus frequency plots from simulation using the localized (dashed) and distributed (circles) elements model, for initial conductivities between 0.5 and 10 S/m.

Modified set-up for temperature and relative humidity control. In the case of a fuel cell application, it is very interesting to characterize the nanocomposite membranes under various temperature and relative humidity conditions. The PPR experimental set-up was therefore modified to measure the electrical conductivity (and dielectric constant) using a climatic chamber (ESPEC-SH261, as shown on Fig. 3.46) operating between 60°C (with a 0,3°C precision) and 150°C and 30% and 95% relative humidity (with a 0,5% precision).

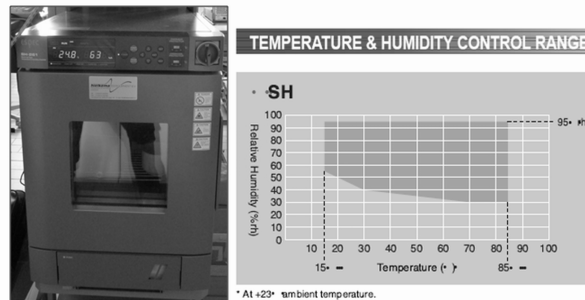


Figure 3.46.: Picture of the ESPEC climatic chamber (left) and available temperature and humidity ranges (right).

The sample holder is the same as in the PPR method used previously in this chapter and is placed inside the climatic chamber then it is connected to the VNA (as shown on Fig. 3.47). This assembly has to be cleaned thoroughly as often as possible to avoid corrosion of the metallic parts.

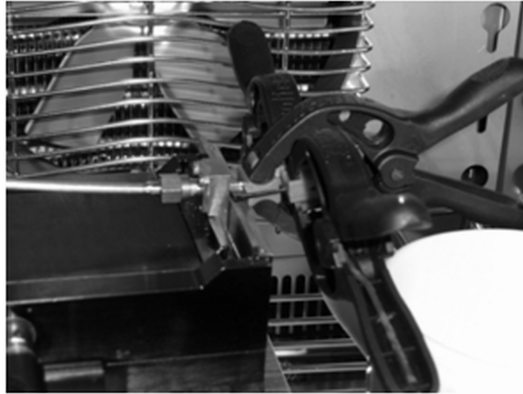


Figure 3.47.: Picture of the PPR sample holder inside the ESPEC climatic chamber.

This set-up was first tested on a standard teflon plate (0,5-mm thick) having a dielectric constant of 2.1 and a conductivity below 10^{-5} - 10^{-6} S/m at a few MHz. The DC values cannot be extracted because a pure teflon plate does not exhibit a Cole-Cole circle. Instead the value of the dielectric constant and conductivity at 1 MHz was used on the plots displayed in Fig. 3.48). The measured values are very close to the expected ones.

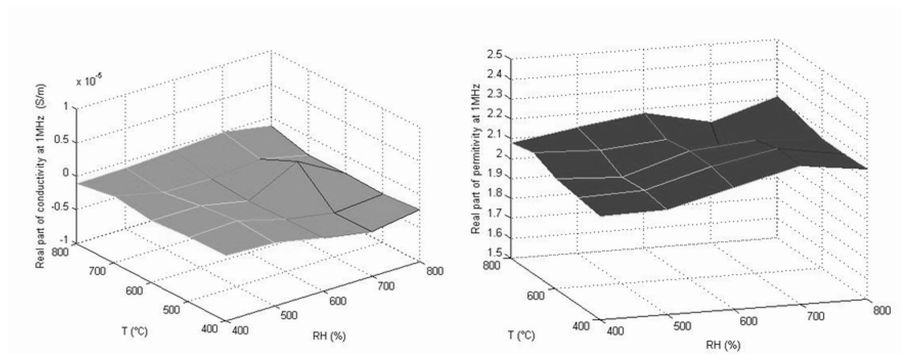


Figure 3.48.: Conductivity (left) and dielectric constant (right) of a teflon plate versus temperature and relative humidity (at 1 MHz).

3.6 CONCLUSIONS

As already stated in the introduction of this chapter there is no ‘ideal’ experimental technique that would yield the best results for all nanocomposite materials. Besides the obvious parameters such as the desired frequency range, dielectric or conductive behaviour, mechanical and geometrical considerations have to be taken into account. Instead of finding one method to suits all it appears rather that almost each particular material or considered application has its own best-suited characterisation technique.

First, DC and low frequency measurements methods were considered, the conductivity and dielectric constant can be quite easily calculated from the measured impedance, as long as the wavelength is much larger than the characteristic size of the sample or circuit under test. As it was shown at the beginning of this chapter the difficulties are in the practical details of the measurement, quality of the contacts, shielding, guarded electrodes, pressure control, etc. Our experimental low frequency AC set-up exhibited very good results for an homogeneous isotropic material, Teflon but it was more complicated for nanocomposite materials. For these materials, it was shown that the value of the conductivity depends on the position of the electrodes on the sample (even more if the dispersion of the filler particles is poor). Ideally the electrodes should have the same size as the sample but it is not always possible, nor desirable. As the frequency increase, this positioning sensitivity decreases, though it is still present. Examples of measurements results were shown: the existence of a percolation threshold and a scaling law in the DC conductivity versus filler content graph was put forward and the low frequency technique was used to obtain the corresponding conductivity versus frequency curves.

Second, guided microwave measurements do not exhibit most of the technical difficulties of the low frequency methods and have a much better reproducibility.

A One-Line technique with the nanocomposite material as substrate of a microstrip transmission line was presented. It requires only one sample measurement but a very careful calibration (high quality microstrip calkit) is required. Besides samples cannot have a thickness above 2 mm, their faces must be smooth and the sample must be solid enough to withstand the necessary manipulations. The method was illustrated by an example of comparative characterisation of nanocomposite samples having different polymer matrices. A coplanar waveguide technique for CNT dispersions was briefly presented.

A Line-Line method where the samples are inserted into waveguides of decreasing size with increasing frequency is then shown and discussed. It is a very precise and accurate method but it requires that the samples be cut into pieces to fit the inner volumes of the waveguides as best as possible. It is therefore a destructive method! Furthermore, the samples must be thick enough to avoid stacking layers and multiplying interfaces. They also have to be solid and flexible

enough to be cut and inserted without being damaged. Low-loss materials can be characterised, high loss materials also but with increasing noise in the extracted permittivity values. At low frequency considerable volumes of material might be necessary and at lower frequencies while inserting the material inside the tiny high frequency waveguides can be tricky. Two measurements, of different lengths of the same material are necessary for each sample to be characterised after a simple SOLT calibration, not requiring expensive calkit for each waveguide size, is sufficient. The characterisation of two foamed composite with different CNT contents was then presented.

A non-destructive modified version of the Line-Line method is also developed, not using waveguides and based on the measurement of only one length of material. It is not well suited to the measurement of low loss materials but yields good results of moderate and high loss materials, even better than the original technique in the latter case. As the total volume of material is a lesser issue (only a moderately thick plate of material is necessary for all frequency bands, as long as the cross-section of the sample is larger than that of the waveguide), the modified Line-Line technique is in practice more broadband than the original version. A simple SOLT calibration is also sufficient but great care must be taken in the alignment of the transitions and in measuring the distance between the transition with the sample between them or just separated by a slab of air.

A free-space characterisation technique is introduced and a few results are also briefly presented for illustration. Then a reflection based method using a basic parallel plate transmission line is shown and applications to the measurement of ionic conductivity of fuel cell membranes are given and discussed.

From all these measurement techniques and results, it appears that the geometry and the mechanical parameters play a major role in the choice of the characterisation method, sometimes even more than the electrical characteristics. The foreseen applications or uses of the sample must also be taken into account so that the characterisation is close to their actual operating conditions, for a meaningful characterisation.

I was once asked how, faced to an unknown material, I would choose a characterisation method as most suitable. Based on the discussions presented in the current chapter, this is how I would proceed: First of all I would ask information on the application and most specifically the desired frequency range. This would dictate which instruments to use. Second I would enquire about the sample itself, whether it is a bulk material or a thin film or membrane, also if it can be damaged/destroyed during characterisation (to maybe cut it to a specific size) or if it has to remain intact. Expected values of the losses and dielectric constant may also be very helpful. Depending on the circumstances, additional information may also be required: Is the sample brittle or to the contrary very hard (impossible to cut)? Is it to be used in special conditions, such as temperature, humidity, vacuum, acid environment, etc. Is a precise, absolute value desired or a comparison with other samples? With all these information in hand a characterisation technique, or several, would not be difficult to choose.

Bibliography

- [1] J. Krupka, "Frequency domain complex permittivity measurements at microwave frequencies," *Measurement Science and Technology*, vol. 17, pp. R55–R70, 2006. 56, 57, 84
- [2] M. Hyde and M. Havrilla, "Measurement of complex permittivity and permeability using two flanged rectangular waveguides," in *Proceedings of the Microwave Symposium, IEEE/MTTS International*, Honolulu, USA, June 3-8 2007, pp. 531–534. 56
- [3] A. Raj, W. Holmes, and S. Judah, "Wide bandwidth measurement of complex permittivity of liquids using coplanar lines," *IEEE Transactions on instrumentation and measurement*, vol. 50, no. 4, pp. 905–909, August 2001. 56, 57, 75, 77
- [4] M. Hyde and M. Havrilla, "Electromagnetic characterization of two-layer dielectrics using two flanged rectangular waveguides," in *Proceedings of the IEEE International Instrumentation and Measurement Technology Conference*, Victoria, Canada, May 12-15 2008, pp. 5–8. 56
- [5] I. Molenberg, "Design of an experimental set-up for measuring the electrical properties of superconducting tape insulations," Master's thesis, Universite de Liege, 2005, travail de Fin d'Etudes en vue de l'obtention du Diplome d'Etudes Approfondies en Sciences Appliquees. 58
- [6] P. Vanderbemden, *Analyse et conception des systemes de mesures electriques*. Universite de Liege: Faculte des Sciences Appliquees, 2003. 59, 60
- [7] L. Chen, C. Ong, C. Neo, V. Varadan, and V. Varadan, *Microwave Electronics, measurement and materials characterisation*. West Sussex, England: John Wiley and Sons, Ltd, 2004. 67, 68, 70, 81, 84
- [8] J. White, *High Frequency Techniques; An Introduction to RF and Microwave Engineering*. Hoboken, New Jersey: John Wiley and Sons, Ltd, 2004. 67, 68, 79
- [9] S. Ramo, J. Whinnery, and T. V. Duzer, *Fields and Waves in Communication Electronics*. New York: John Wiley and Sons, Inc., 1993. 68, 70, 71, 78, 80
- [10] J. Dobrowolski, *Introduction to Computer Methods for Microwave Circuit Analysis and Design*. Boston: Artech House, 1991. 68, 69, 71
- [11] H. Wheeler, "Transmission-line properties of a strip on a dielectric sheet on a plane," *IEEE Transactions on Microwave Theory and Techniques*, vol. 25, no. 8, pp. 631–647, August 1977. 70

- [12] R. Hoffmann, *Handbook of Microwave Integrated Circuits*. Norwood, USA: Artech House, 1987. 71
- [13] A. Saib, L. Bednarz, R. Daussin, C. Bailly, X. Lou, J.-M. Thomassin, C. Pagnoulle, C. Detrembleur, R. Jerome, and I. Huynen, "Carbon nanotubes composites for broadband microwave absorbing materials," *IEEE Transactions on Microwave Theory and Techniques*, vol. 54, no. 6, pp. 2745–2752, june 2006. 73
- [14] I. Huynen, C. Steukers, and F. Duhamel, "A wideband line-line dielectrometric method for liquids, soils, and planar substrates," *IEEE Trans. Ins. Meas.*, vol. 50, no. 5, pp. 1343–1348, 2001. 79, 80
- [15] M. Janezic and J. Jargon, "Complex permittivity determination from propagation constant measurements," *IEEE Microwave and Guided Wave Letters*, vol. 9, no. 2, pp. 76–78, February 1999. 79, 80
- [16] J. Baker-Jarvis, E. Vanzura, and W. Kissick, "Improved technique for determining complex permittivity with the transmission/reflection method," *IEEE Transactions on Microwave Theory and Techniques*, vol. 38, no. 8, pp. 1096–1103, August 1990. 81
- [17] A. Saib, "Modeling and design of microwave devices based on ferromagnetic nanowires," PhD Thesis, Université Catholique de Louvain, December 2004. 83
- [18] J. Catala-Civera, A. Canos, F. Penarada-Foix, and E. de los Reyes Davo, "Accurate determination of the complex permittivity of materials with transmission reflection measurements in partially filled rectangular waveguides," *IEEE Transactions on Microwave Theory and Techniques*, vol. 51, no. 1, pp. 16–24, January 2003. 84
- [19] A. Park and A. Dominek, "Parameter de-embedding accuracy dependency upon material sample dimensions," *IEEE Transactions on Microwave Theory and Techniques*, vol. 40, no. 8, pp. 1674–1680, August 1992. 84
- [20] A. Nicholson and G. Ross, "Measurement of the intrinsic properties of materials by time-domain techniques," *IEEE Transactions on instrumentation and measurement*, vol. 19, no. 4, pp. 377–382, November 1970. 84
- [21] B. Weir, "Automatic measurement of complex dielectric constant and permeability at microwave frequencies," *Proceedings of the IEEE*, vol. 62, no. 1, pp. 33–36, January 1974. 84
- [22] M. Bernal, I. Molenberg, S. Estravis, M. Rodriguez-Perez, I. Huynen, Lopez-Manchado, and R. Verdejo, "accepted in journal of material science," *Comparison of the effect of carbon-baed nanofillers on flexible polyurethane foams*, 2012. 89

- [23] I. Huynen, N. Quievy, C. Bailly, P. Bollen, C. Detrembleur, S. Eggermont, I. Molenberg, J.-M. Thomassin, L. Urbanczyk, and T. Pardoën, “Multi-functional hybrids for electromagnetic absorption,” *Acta Materialia*, vol. 59, no. 8, pp. 3255–3266, May 2011. 100
- [24] V. Daniel, *Dielectric Relaxation*. London: Academic Press Inc., 1967. 101
- [25] I. Molenberg, J.-M. Thomassin, E. Ferain, C. Detrembleur, and I. Huynen, “Rf diagnostic methods for two nanostructured polymer applications,” in *Proc. of the 39th European Microwave Conf.*, Roma, Italy, September 2009, pp. 1045–1048. 101
- [26] I. Molenberg, M. Planckaert, L. Jonckheere, E. Ferain, and I. Huynen, “Investigation of ionic conductivity in track-etched nanoporous polyimide membranes using a microwave technique,” *Microwave and Optical Technology Letters*, vol. 53, no. 9, pp. 2060–2063, September 2011. 101, 102
- [27] D. Pozar, *Microwave Engineering*. New York: Artech House, 2005. 102

CHAPTER 4

WIDEBAND CHARACTERIZATION OF THIN SOLID POLYMER CNT NANOCOMPOSITES

4.1 INTRODUCTION

Nanocomposite materials exhibit different electrical properties and behaviours depending whether they are characterised in the static regime (DC), at low frequency or in the microwave region. To the best of our knowledge extensive wideband electrical characterisation of nanocomposite polymer samples, from DC to microwave frequencies, is not commonly found in the literature. It is the aim of the present chapter, to investigate the electrical behaviour and properties of polymer/CNT composites, from DC to 40 GHz.

No single experimental technique can be used to characterise materials on such a large frequency range. At DC and for low frequency AC measurements, direct contact current-voltage characterisation techniques must be used. From simple DC resistance measurements to the measurement of complex impedances using a commercial set-up, the material must be placed between two parallel electrodes that are in close contact with the sample. At higher frequencies, of the order of magnitude of 1 GHz, non-contacting techniques are available. The microstrip one-line method described in chapter 3 has been selected because of its ease of use and because the same method could cover the entire 40 MHz to 40 GHz range. It was also well suited to the geometry of the samples.

Polycarbonate (PC) and polyurethane (PU) based composites with CNT contents of 0.1 to 4 *wt%* were fabricated for this study. Some of the polyurethane samples were fabricated using slightly different processing conditions to isolate the influence of these parameters. The samples are detailed in section 4.2.

As discussed in chapter 2, the conductivity of a nanocomposite submitted to a DC electric field is a function of the ‘backbone’ of percolation clusters only, i.e. on the existence or not of a conductive path through the sample. In essence the conductivity as a function of filler content is almost a on/off phenomenon.

The DC characterisation of our samples is discussed in section 4.3. In particular, the influence of the filler content is investigated and the well know scaling law presented in section 2.4 is used to fit the measurements. The percolation threshold is extracted from these results. The PC and PU samples are compared and the influence of some processing parameters is also considered.

The DC conductivity as a function of filler fraction of the nanocomposites is also confronted to the thermal fluctuation induced tunnelling model of section 2.5.4.

The PC and PU composite samples are then characterised in an alternating electromagnetic field, in the 1 kHz to 1 MHz range.

The dispersion, as determined from electrical characterization, is based on resistive considerations but information about the status of dispersion can also be gained from capacitive considerations, as discussed in section 4.4. The localized CNT-polymer-CNT structure at the interconnection between neighbouring CNTs can be compared to the metal-insulator-metal structure of an electrical capacitor, [1].

The influence of the filler fraction is investigated, as well as that of frequency. The measurements are confronted to the theoretical considerations of section 2.4.2. The results for the PC samples are confronted to those of the PU composites and the latter are compared according to their processing differences. The AC results are also confronted to some of the theoretical laws and models from the literature.

A special emphasis is put on the major importance of the reproducibility of these measurements, in relationship with the quality of dispersion of CNTs in the nanocomposites.

The nanocomposite samples are characterised at microwave frequencies in section 4.5. The conductivity and dielectric constant of the PC and PU composites are investigated as functions of filler content and frequency. These results are then compared to those obtained at lower frequency. The adequacy between these two techniques and the importance of CNT dispersion on reproducibility is discussed. The values for the PC samples and those of the PU composites are

also compared and detailed. The advantages of the microwave method are also presented. Some SEM pictures are shown and compared to the electrical results.

Furthermore, the shapes of the conductivity versus frequency curves are discussed and tentatively explained.

Another indirect¹ method of assessing the dispersion of CNTs in a matrix commonly used in the literature is the rheological characterisation. It is presented and explained in section 4.6. It is also compared to the electrical characterisation. Some information on CNT-polymer nanocomposites that can be obtained from rheological measurements is also presented even though the samples presented in this chapter were not characterised using this method.

Finally, some conclusions and perspectives are detailed at the end of the chapter.

¹The term indirect is used in opposition to other more ‘direct’ methods that can be used to examine the dispersion of nanofillers, like imaging techniques

4.2 DESCRIPTION OF THE SAMPLES

The samples characterised throughout this chapter are thin solid plates of polycarbonate (PC) or polyurethane (PU) composite with varying CNT content, as listed in tables 4.1 and 4.2.

The PC samples are fabricated by melt-blending PC Makrolon®2805 (Bayer) with a fraction of CNTs (Nanocyl 7000) inside a counter-rotating twin-screw static mixer (Brabender extruder) at 270°C for 5 min. (150 rpm). They are then pressed into thin plates (500 – 650 μm -thick) using a hot press (15 T) at 290°C for 2 min. The NQ11 sample (*) was fabricated using instead the Nanocyl Compound. Pictures of a PC sample in the LCR sample holder for low frequency characterisation and in the dielectric test fixture of the VNA for the microwave measurements are shown in Fig. 4.1.

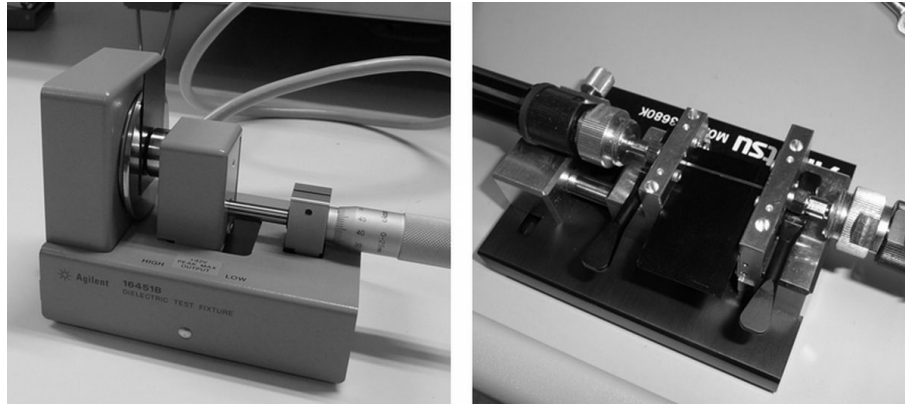


Figure 4.1.: Pictures of a PC sample in the LCR sample holder for DC and low frequency AC measurements (left) and in the Anritsu 3680K sample holder for the microwave characterisation (right).

The PU samples are fabricated using the same method, from TPU Desmopan®2590A (Bayer) and Nanocyl 7000 CNTs. The process parameters are different. The extrusion was done at 180°C, the mixing time and screws speed are listed in table 4.2. The hot pressing stage was also similar to that of the PC samples but at a temperature of 190°C, the PU plates are all about 500 μm -thick. Several PU samples were extruded with different mixing times and speed of the screws during extrusion, shaded cells in table 4.2. The latter samples are separated from the main series of PU samples (series A: NQ20-NQ23-NQ24-NQ26-NQ27-NQ29-NQ30) to form the B series (NQ21-NQ25-NQ28). One sample does not belong to either series, NQ22, due to a fabrication error.

code	CNT loading wt. %
NQ01	0,1
NQ02	0,25
NQ03	0,5
NQ04	1
NQ05	2
NQ06	0,3
NQ07	0,4
NQ08	0,75
NQ09	3
NQ10	4
NQ11	1 *

Table 4.1.: CNT mass fraction of the PC samples.

code	CNT loading wt. %	mixing time (min)	screws speed (rpm)
NQ20	0,25	5	150
NQ21	0,5	20	50
NQ22	0,75	5	100
NQ23	0,75	5	150
NQ24	1	5	150
NQ25	1	20	50
NQ26	1,25	5	150
NQ27	1,5	5	150
NQ28	2	20	50
NQ29	2	5	150
NQ30	4	5	150

Table 4.2.: CNT mass fraction and processing parameters of the PU samples.

4.3 DC CHARACTERIZATION AND SCALING LAWS

The first five samples to be characterised at DC, i.e. resistance measurement as detailed in section 3.2, were the samples NQ01 to NQ05. The electrical conductivity of these samples is plotted as a function of their CNT content on Fig. 4.2. As expected the conductivity increases with increasing filler content, φ .

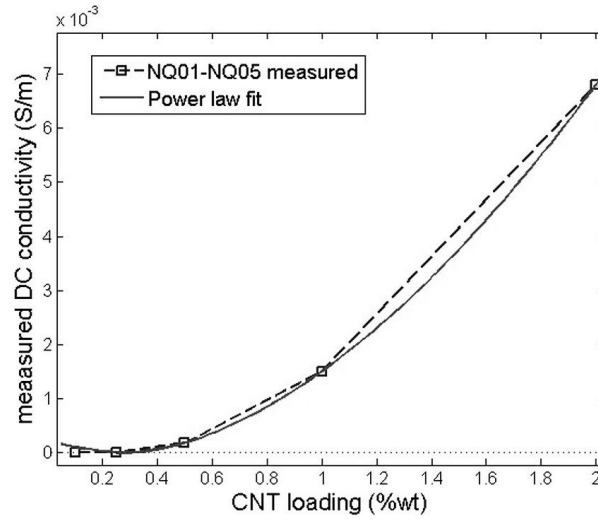


Figure 4.2.: DC conductivity as a function of CNT content for five PC samples with 0.1 %, 0.25 %, 0.5 %, 1 % and 2 wt% CNTs, measured values ($\square$) and fit using power law $\sigma = A(\varphi - \varphi_c)^t$ (solid).

The experimental points are fitted² using a power law function³ using a power law $\sigma = A(\varphi - \varphi_c)^t$, the basic scaling law from chapter 2 yielded $A = 0.0027$, the percolation threshold $\varphi_c = 0.27$ wt% and the critical exponent $t = 1.7155$ which is well within the theoretical 3D percolation range of 1.6 – 2, cf. section 2.4.

However, as explained in section 3.2, these measurement were very noisy and presented some irreproducibility (influence of the pressure for example). Commercial electrodes were then used to measure the NQ01-NQ05 samples but also all the other samples that had been fabricated in the meantime, see previous section.

The reproducibility due to the equipment and experimental set-up was indeed greatly improved but the value of the measured resistance was shown to be very

²The basis of the Matlab routine used for the power law fit can be found at <http://www.mathworks.com/matlabcentral/fileexchange/29545-power-law-exponential-and-logarithmic-fit>.

³It must be pointed out that only 3 samples had a measurable conductivity value (the resistance of the first two samples was too high) and the fitting is therefore done on only those three points.

dependent on the position of the electrodes on the sample. This is because the percolation threshold is a very localized phenomenon. It is probably caused by the existence of a conductive path through the sample. If this path is inside the region located between the electrodes, the measured resistance of the sample having a filler content equal to the percolation threshold will show the telltale sharp decrease in resistance (compared to the resistance of samples with lower filler fractions). However if the electrodes are not located near this region, there might not be a conductive path from one electrode to the other and therefore the measured resistance might not be significantly decreased. This is why several measurements were made and the lowest value of the resistance only was taken into account, cf. section 3.2.1. This consideration was again discussed here to keep in mind the unavoidable uncertainty on our measurements.

It should be noted that the humidity rate in the characterisation room is controlled and constant but not 0 and the presence of water molecules in the neighbourhood of an electric field can have a significant influence on permittivity measurements. The reproducibility of the measurements presented here could then probably be improved if they were conducted inside an environment devoid of humidity, such as a vacuum chamber or under a nitrogen flux. The presence of layers of polymer containing almost no CNTs near the top and bottom surfaces of the samples, as detailed further in this chapter, may also play a role in this reproducibility issue.

The processing conditions were in theory identical for all PC samples but the samples NQ01-NQ05 were fabricated one year earlier than the others. The conductivity of all the PC samples⁴ is plotted versus the filler content on Fig. 4.3(left). Fitting these results with a power law yields: $A = 4.51 \cdot 10^{-6}$, $\varphi_c = 0.301$ wt% and $t = 1.929$. Even if the percolation threshold is very close to the one extracted from the first five measurements⁵ of Fig. 4.2, the critical exponent value is quite higher and visually the adequacy between the experiments and the fitted curve is not excellent. But the scaling power law is valid only near the percolation threshold. If the two samples with the highest filler contents are excluded, cf. Fig. 4.3(right), the fitting is significantly improved, the residual or mean square error dropping from $1.85 \cdot 10^{-8}$ to $3.22 \cdot 10^{-13}$. and $A = 1.24 \cdot 10^{-6}$, $\varphi_c = 0.2983$ wt% and $t = 1.223$. The percolation threshold is still quite the same, the critical exponent value is slightly lower though and the results are visually improved. The critical exponent is still far from the $1.6 - 2$ values commonly found in the literature, cf. section 2.4.1, in the latter case but quite close in the first power law fit.

⁴The sample NQ11 is omitted here because its composition is different from that of the other PC samples.

⁵The so-called first five samples were measured a year before the others and there is no certitude that they are exactly the same as the one of the PC series investigated here, though in theory they should be identical.

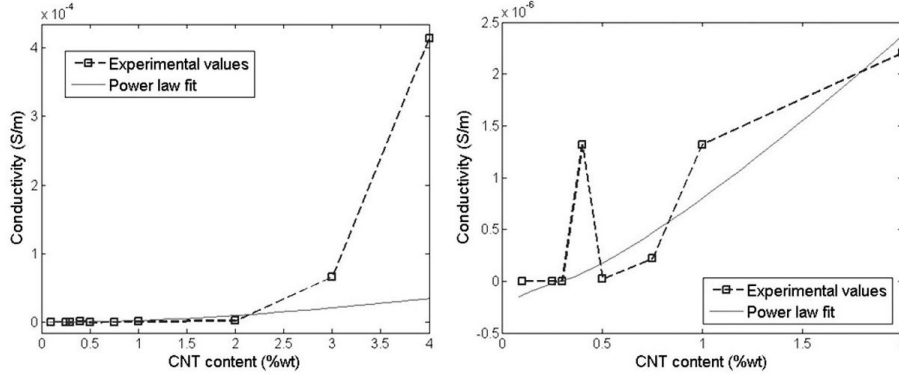


Figure 4.3.: DC conductivity as a function of CNT content for all PC samples (left) and for all PC samples excepted the samples with 3 % and 4 wt% CNTs (right), measured values ($\square$) and fit using power law $\sigma = A(\varphi - \varphi_c)^t$ (solid).

As mentioned in the previous section, there were some differences in the extrusion process for some PU samples. They are therefore separated to compare only samples with identical processing conditions. The samples with a short, high speed mixing during extrusion constitute the series A (NQ20, NQ23, NQ24, NQ26, NQ27, NQ 29 and NQ30). The composites mixed at lower screw speed during a longer time are the series B (NQ21, NQ25 and NQ26), the latter correspond to the shaded cells⁶ in table 4.2. The conductivity versus filler content curves for both series are shown on Fig. 4.4. The best fit using a power law yields, for the series A: $A = 2.25 \cdot 10^{-5}$, $\varphi_c = 0.686$ wt% and $t = 1.934$. The fitting must be considered as a very rough approximation in the case of series B, with only three experimental points available but leads to $A = 8.00 \cdot 10^{-7}$, $\varphi_c = 0.807$ wt% and $t = 2.705$. From these results, the value of the percolation threshold does not seem very sensitive to the details of the fitting algorithm or number of points while the critical exponent depends strongly on these parameters.

The conductivities of all the samples are shown on Fig. 4.5. It can be seen that the PC and PU (series A) samples have similar conductivities especially for high filler contents. PU samples, series B, are the least conductive, hinting at a best dispersion with a short high speed melt-mixing than using a lower speed for a longer time interval.

However, the percolation threshold in PC samples is significantly lower than in PU samples, series A and B having similar thresholds (despite the limited number of points on the series B curve). Furthermore, even though percolation occurs at lower filler content for PC samples, PU-based composite exhibit a

⁶Except for NQ22 that is different from both series, due to a small processing error.

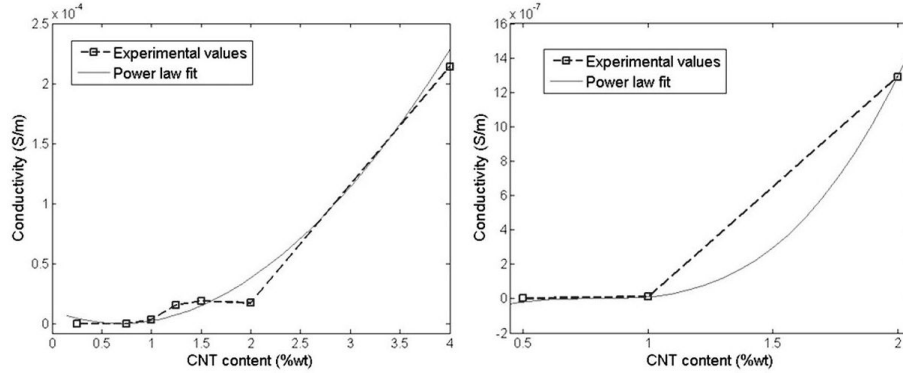


Figure 4.4.: DC conductivity as a function of CNT content for the PU samples of series A (left) and of series B (right), measured values ($\square$) and fit using power law $\sigma = A(\varphi - \varphi_c)^t$ (solid).

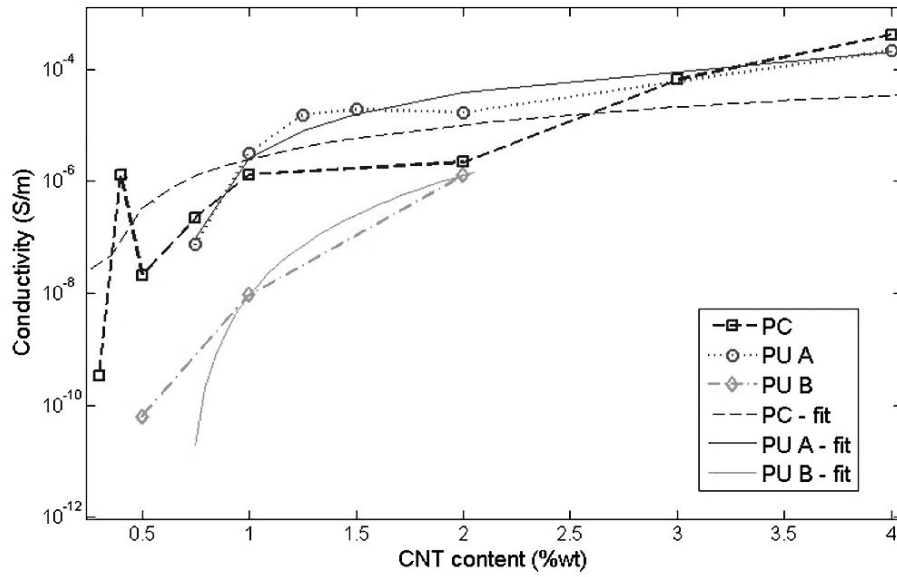


Figure 4.5.: Measured DC conductivity as a function of CNT content for all samples, PC ($\square$), PU series A ($\circ$) and PU series B ($\diamond$), and fitted power laws (solid).

similar (and even slightly higher) conductivity, at all filler fraction values, and a similar maximum conductivity (high CNT loading plateau).

As the percolation threshold is the transition from a number of isolated conductive elements to that of a network of connected particles dispersed through the matrix, cf. section 2.4.1, a lower percolation threshold would indicate a better dispersion of the CNTs inside PC matrices than in PU matrices. In [2] a lower percolation threshold is related to weaker interactions between the CNTs and polymer matrix. Strong polymer-CNT interactions are often considered to be an advantage when dispersing the CNTs in the polymer matrix because they would ‘help’ break the initial entanglements of the CNT bundles. On the other hand if these interactions are strong, the individual CNTs would tend to be coated by a thicker layer of polymer (attaching themselves to more polymer molecules) and thus the barrier height or resistance between two neighbouring CNTs would be higher. These two opposite effects could be present here, the smaller threshold indicating a better dispersion of the CNTs in the PC but the resistance between CNTs or bundles of CNTs would be higher leading to comparable overall conductivities.

On the other hand, a similar conductivity value would also hint at a similar resistance of the polymer between neighbouring CNTs or a same mean distance between them, as the DC conductivity of pure PC and PU is rather similar (below 10^{-13} S/m for PC and about $2 \cdot 10^{-13}$ S/m for PU, from Campus datasheet⁷).

The similar percolation threshold for both series of PU indicates that the differences in the mixing process had no or little effect on the length of the CNTs, but rather on the dispersion of the CNTs. Because the percolation threshold decreases with the aspect ratio of the nanoparticles, cf. section 2.4.1.

CNTs (or agglomerates of CNTs) inside a polymer nanocomposite material are coated by layer of polymer acting as a potential barrier between neighbouring CNTs and the maximum conductivity of the nanocomposite is limited by the ‘hopping’ of charge carriers through these barriers. The fluctuation induced tunnelling model was presented to describe this behaviour. As shown in section 2.5.4, the linear relationship between $\ln \sigma_{DC}$ and $p^{-1/3}$ is of tunnelling conduction, with p the filler fraction⁸. The semi-logarithmic plot of the conductivity as a function of $p^{-1/3}$ for all PC and PU samples is shown on Fig. 4.6.

Taking into account the uncertainty of our DC measurements, a linear dependence of $\ln \sigma_{DC}$ on reduced mass fraction $p^{-1/3}$ can be assumed and the thermal fluctuation induced tunnelling model may be considered as adequate for our PC and PU samples.

⁷ Available from <http://www.campusplastics.com>

⁸ As explained in chapter 2, p and φ both designate the content of CNTs in the the composite, either as a mass fraction (wt%) or as a volume fraction (vol.%). Though in this chapter it is always given as a mass fraction.

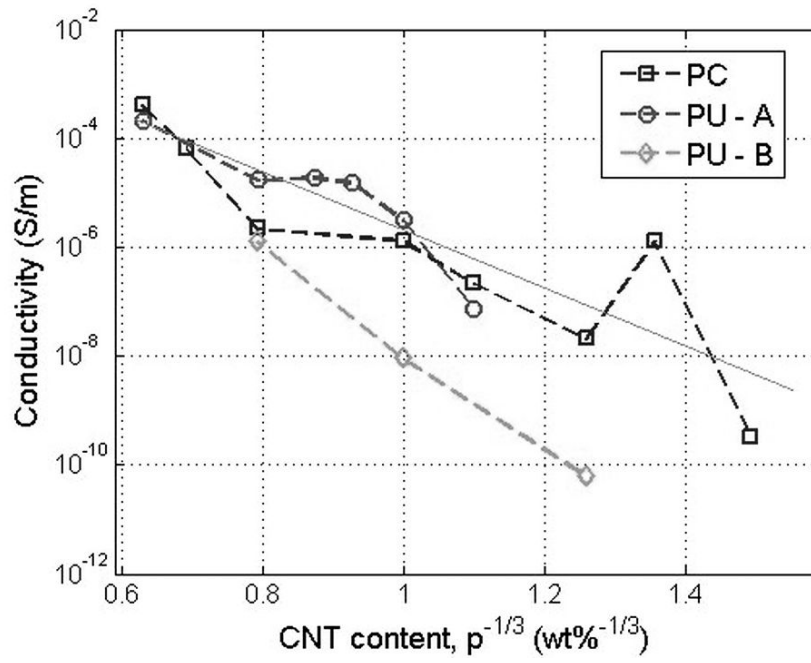


Figure 4.6.: Measured DC conductivity as a function of CNT reduced mass fraction, $p^{-1/3}$, for all samples, PC ($\square$), PU series A ($\circ$) and PU series B ($\diamond$). The solid line is just a guide to the eye.

It is also interesting to note that contrary to the nanocomposite inks presented in chapter 6, the solid samples submitted to IV curves (ramp or pulsed) did not show any non-linearity or hysteresis, even at high voltage. But this is not unexpected, from section 2.4.1, non-ohmic behaviour would mostly be expected in samples having very low percolation thresholds, [3], which is not really the case for the PU and PC samples presented here.

4.4 LOW FREQUENCY CHARACTERISATION, 1KHZ-1MHZ

Characterisation of the PU and PC thin plates were made using the method and equipment described in section 3.2.2, i.e. an Agilent LCR 4284A with dielectric test fixture for guarded measurements in the 1kHz-1MHz range.

Assuming the irreproducibility of the previous DC measurements to be due to the local character of percolation, AC characterisation even at rather low frequency should be more reproducible, as the distance travelled by the charge carriers decreases with increasing frequency. However, as can be seen on Fig. 4.7, different measurements on different locations of the NQ04 sample (PC with 1 % CNT) are different. The average conductivity and dielectric constant values from these three measurements are also plotted on the same figure (dashed). If the values from the different measurements are different, the aspect of the different curves are rather similar, except for the lower frequency noise⁹. However, as seen in section 3.2, characterisation of a Teflon® sheet showed very reproducible results, the irreproducibility observed here is thus most probably due to the nanocomposite structure, and to reliability issues of the electrical contacts, not a consequence of some set-up deficiencies. Besides as for DC measurements, conducting the measurements in a completely dry environment could help reduce this irreproducibility issue.

Furthermore the irreproducibility is decreased but still present when characterising the PU samples, as illustrated on Fig. 4.8 for the NQ30 sample (PU with 4 % CNT). If the mean values over the entire frequency range are considered and from the measurements presented here, a difference of up to 92.3 % and 82.3 % between the mean conductivity and dielectric constant values, respectively, is observed for the NQ04 sample (PC with 1 wt% CNT). In the case of NQ30 the differences are of about 43.4 % for the mean conductivity and 12.7 % for the dielectric constant. It is a considerable source of error but still less for the PU samples than in the case of PC composites.

To decrease this irreproducibility, the measurements presented in this section are averaged over at least two distinct measurements. But results on nanocomposites obtained using this technique must be analysed with caution, keeping this irreproducibility in mind.

As can be seen on Fig. 4.7, the NQ11 sample cannot be differentiated from the different NQ04 samples, the influence of the use of a commercial compound instead of the melt-mixing in the extruder cannot be investigated using this technique.

⁹The LCR measurements are less accurate in the lower frequency part of its measurement range, cf. user manual.

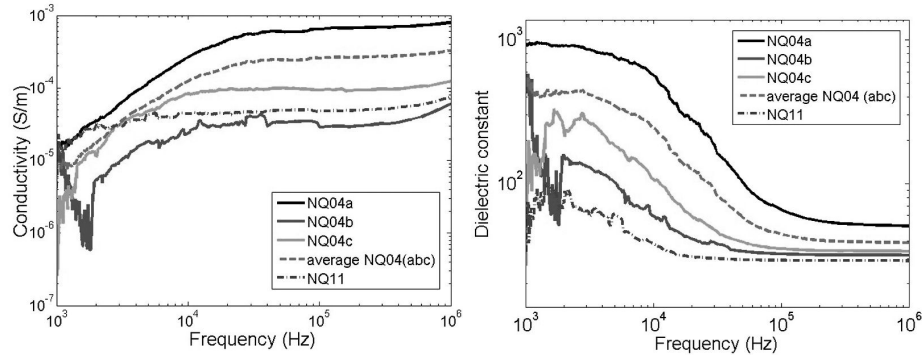


Figure 4.7.: Measured conductivity (left) and dielectric constant (right) as a function of CNT content for three measurements of the NQ04, PC with 1 wt% CNT, sample (solid lines), the average value from the three measurements (dashed) and the sample plot for the NQ11 sample, also PC with 1 wt% CNT but from a commercial compound (dash-dot).

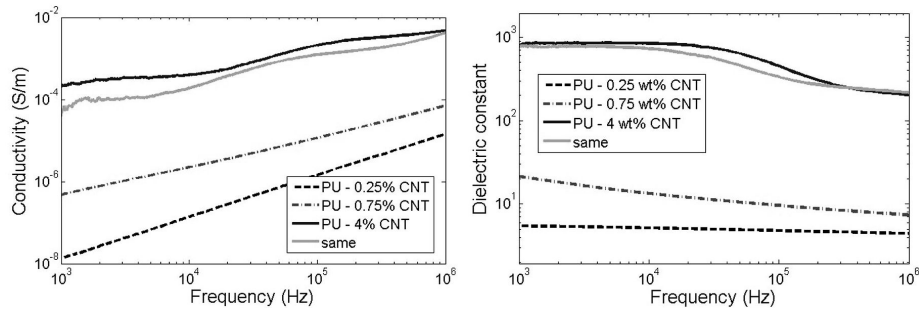


Figure 4.8.: Measured conductivity (left) and dielectric constant (right) as a function of CNT content for two measurements of the NQ30, PU with 4 % CNT, sample (solid lines), and measurements of the NQ20, PU with 0.25 % CNT (dotted) and NQ22, PU with 0.75 % CNT (dash-dot) samples, for comparison.

4.4.1 AC electrical conductivity versus frequency: PC samples

The measured conductivity, $\sigma(\omega)$, of all the PC samples is plotted versus frequency on Fig. 4.9. Except for a couple of samples, the conductivity of the nanocomposites globally increases with increasing CNT content. Though for high loadings the situation tends to be confused due to overlapping curves and because of the significant error caused by irreproducibility, as was discussed in the previous section.

However even taking these considerations into account three different conductivity behaviours can be observed. Below the threshold, the conductivity curves are straight lines in a logarithmic plot, and can be fitted using a power law of the form $A\omega^s$, as expected from section 2.4.2. At low frequency, the conductivity tends to zero, suggesting a negligible σ_{DC} , in adequacy with the DC results of the previous section.

Above the percolation threshold, the conductivity at low frequency has a significant constant value or ‘DC plateau’ indicating a non-negligible σ_{DC} . At high frequency, some of the curves tend to straight lines with a gentle slope in the log-log plot, hinting to a ω^s dependence. The transition from the DC plateau to high frequency behaviour occurs at about 50 kHz (crossover frequency)¹⁰. More details on this power law dependence of the conductivity are given further in the current section. From these curves, the percolation threshold should be somewhere between 0.25 wt% and 0.4 wt% CNT, confirming the DC results. However not all of the curves present this behaviour, some tend to a zero slope near 1 MHz, to distinguish a transient behaviour from another plateau behaviour also at high frequency, measurements have to be made at even higher frequencies. Such a characterisation is presented in section 4.5.1.

Close to the percolation threshold, an intermediary behaviour can be observed. The results of the sample containing 2 wt% CNT are abnormal, exhibiting an electrical conductivity similar to that of the sample with a filler content very close to the percolation threshold. It is probably due to some fabrication defects or a poor distribution of the CNTs inside the polymer matrix.

4.4.2 AC dielectric constant versus frequency: PC samples

Values of the dielectric constant for the PC samples were also extracted from the measurements. They are plotted as a function of frequency on Fig. 4.10. Again three different kinds of behaviours can be observed, similar to those seen on the conductivity plot, as expected from section 2.4.2.

¹⁰ Actually this transition occurs between 5 and 300 kHz for the PC samples, using the $\sigma(\omega_0) = 1.1\sigma_0$ relationship where ω_0 is the crossover frequency and σ_0 the average conductivity value of the DC plateau. The DC plateau are not visible on the PU results but some inflection point is usually present around the same frequency. It might be due to noise or fluctuations.

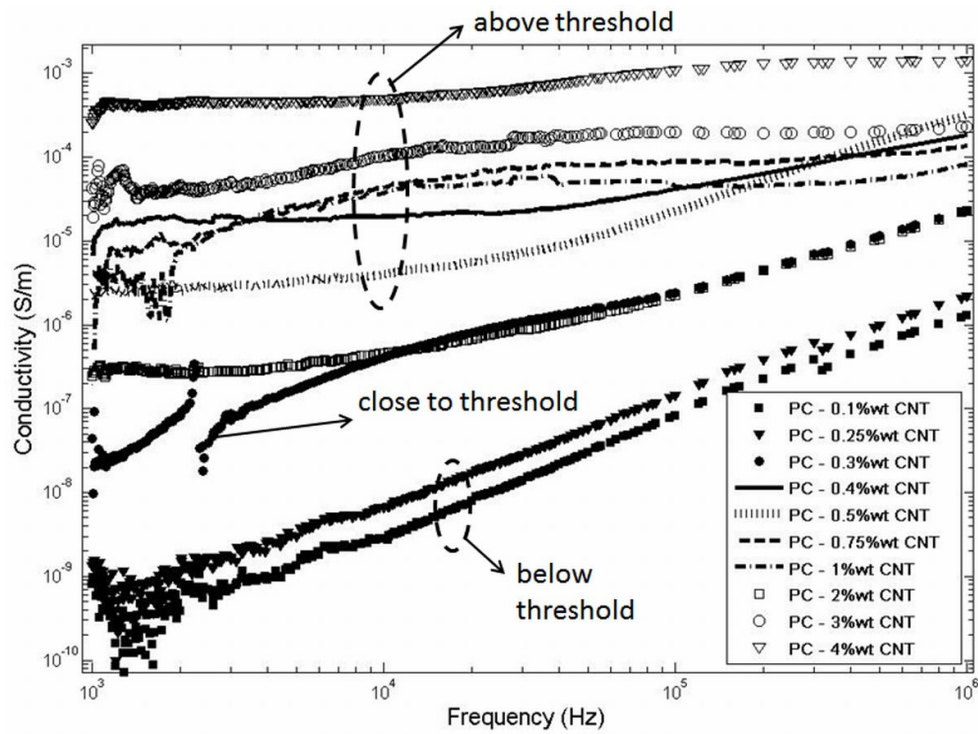


Figure 4.9.: Measured electrical conductivity as a function of frequency for the PC samples with CNT contents from 0.1 to 4 wt% CNTs.

Below the threshold, the dielectric constant has a constant value at all frequencies, typical dielectric behaviour. Beyond the threshold, the samples exhibit a sharp decrease of the dielectric constant with increasing frequency. The latter nanocomposites also exhibit a significant noise at lower frequency due to the difficulty of measuring the dielectric constant of a conductive material at low frequency, cf. chapter 3. Close to the percolation threshold, an intermediate behaviour can be observed.

Considering the dielectric constant values at the high frequency end of the curves, it is evident that they increase with increasing filler fraction, as expected from section 2.4.3. A higher CNT loading, i.e. a higher number of particles per unit volume would also mean a greater number of micro-capacitances throughout the material. Except for the sample containing 2 wt% CNT that exhibits the same behaviour as that of samples with filler fraction below the percolation threshold, though with a significantly higher value of the dielectric constant (but still below what could have been expected). It is another indication of poor dispersion of the CNTs in the material.

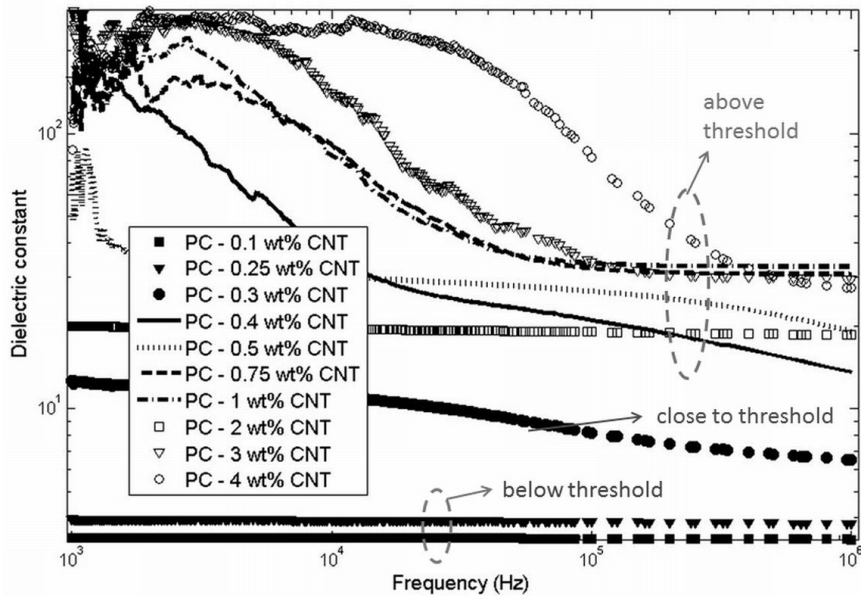


Figure 4.10.: Measured dielectric constant as a function of frequency for the PC samples with CNT contents from 0.1 to 4 wt% CNTs.

4.4.3 AC electrical conductivity versus frequency: PU samples

The PU samples were measured using the same technique. For clarity they are separated in two series, as in the previous section. Samples in each series (A or B) share the same process parameters, cf Table 4.2. The conductivity of the series A samples are plotted on Fig. 4.11 and those of series B on Fig. 4.12. The same conclusions as for the PC samples can be deduced. Below the percolation threshold (the one calculated from the DC measurements, as it is not really visible on the high frequency plots), the sample behaviour can be quite accurately modelled by a simple power law, ω^s , on the entire frequency range. Beyond the threshold, the conductivity of the sample is constant and non-negligible at low frequency then increasing as the frequency increases, to finally tend to a power law behaviour at high frequency. And close to the threshold the behaviour is intermediate. As previously the conductivity increases with increasing filler fraction though for high loadings the curves are overlapping.

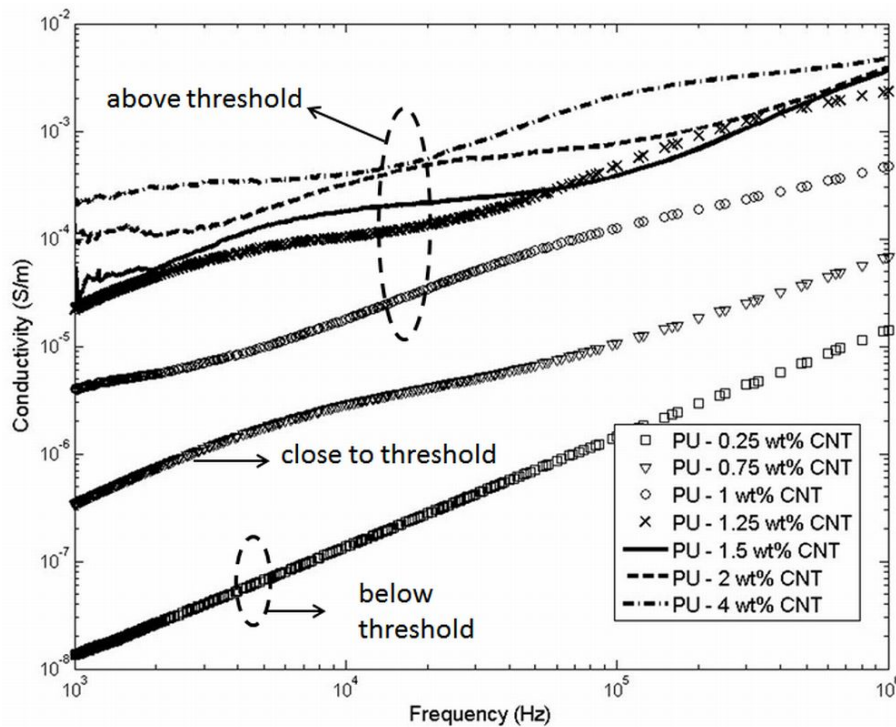


Figure 4.11.: Measured electrical conductivity as a function of frequency for the PU samples of series A (CNT contents from 0.25 to 4 wt% CNTs), with a DC percolation threshold of 0.7 wt%.

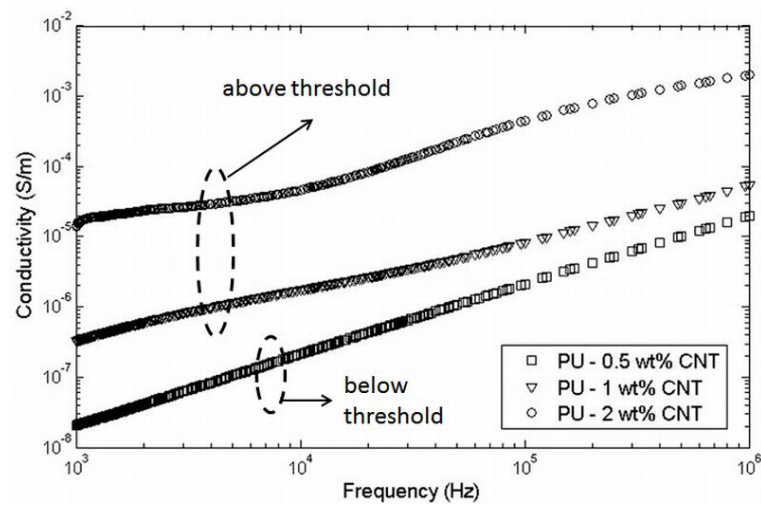


Figure 4.12.: Measured electrical conductivity as a function of frequency for the PU samples of series B (CNT contents from 0.5 to 2 wt% CNTs) with a DC percolation threshold of 0.7 wt%.

4.4.4 AC dielectric constant versus frequency: PU samples

The dielectric constant of the PU samples are plotted as a function of frequency on Fig. 4.13 for the series A and on Fig. 4.14 for the series B. The same different behaviours can be observed, as for the PC samples, depending on whether the filler content of the sample is above, below or close to the percolation threshold (p_c calculated from DC measurements). For both series the dielectric constant increases quite regularly with the CNT loading. For high filler fractions, above 1.5 wt%, this increase is less pronounced, hinting at a kind of saturation.

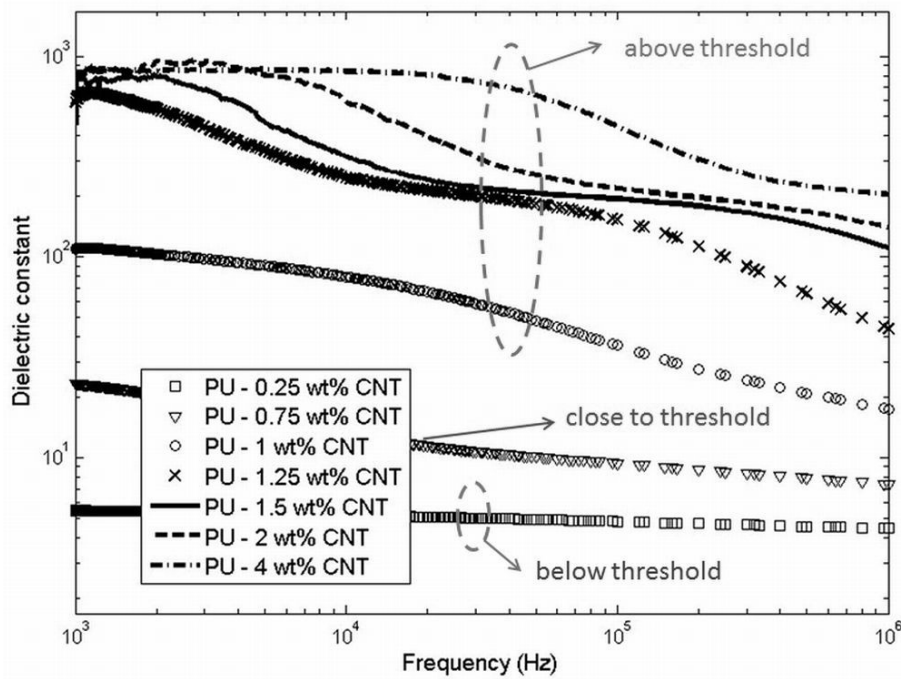


Figure 4.13.: Measured dielectric constant as a function of frequency for the PU samples of series A (CNT contents from 0.5 to 4 wt% CNTs), with a DC percolation threshold of 0.7 wt%.

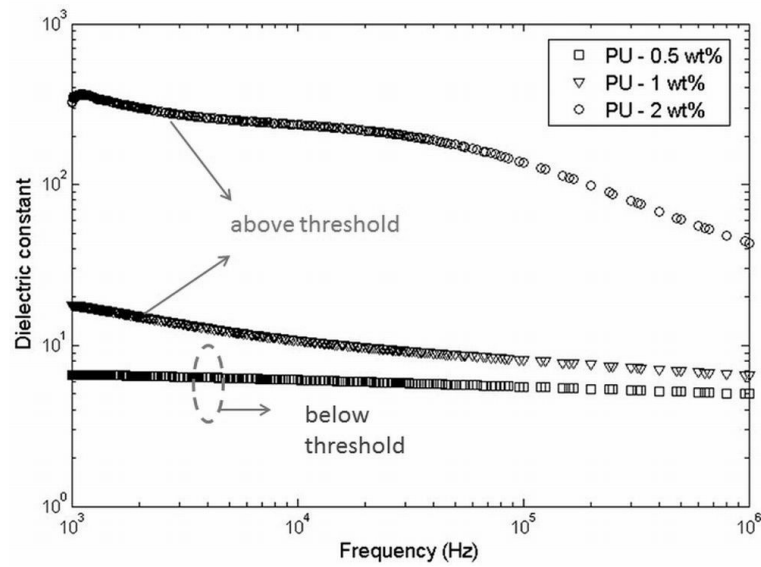


Figure 4.14.: Measured dielectric constant as a function of frequency for the PU samples of series B (CNT contents from 0.25 to 2 wt% CNTs), with a DC percolation threshold of 0.7 wt%.

4.4.5 AC electrical conductivity versus filler content, comparison between PC and PU samples

From Fig. 4.15, the conductivity of the PU samples seems to be about one order of magnitude higher than that of the PC samples, for the same loading and frequency. The comparison is not trivial because of the difference in percolation threshold. For a 0.5 wt% CNT content, a PC sample is above the percolation threshold but a PU composite is still below it. The 0.25 and 0.5 wt% CNT PU nanocomposites can be compared to the 0.1 wt% CNT PC sample as the three samples are below their respective percolation thresholds. But the amount of CNTs inside the sample, even below the threshold, is expected to have an influence on the conductivity, cf. Fig. 4.16. The same reasoning can be applied to 1 wt% CNT PU samples that might be considered too close to the threshold. But for high loadings, i.e. filler contents well beyond the percolation threshold, the comparison should be valid, cf. Fig. 4.17.

As can be seen on the same figure, the 3 wt% CNT PC sample has a conductivity about one order of magnitude smaller than that of the PU samples containing 2 wt% CNT¹¹. It is difficult to conclude whether it is due to simply a better dispersion of the CNTs inside the PU matrix, [4], or if it might be due to stronger interactions between the CNTs and the PU polymer layer coating the individual CNTs than in the case of a PC composites. A higher percolation threshold is usually related to stronger interactions between the polymer and the fillers, [2]. This would indicate stronger interactions between the CNTs and the PU molecules than with the PC chains. If we consider, as will be detailed in section 4.5.3, that the CNTs are better dispersed in PC than in PU, where they form rather large aggregates, the increased value of the conductivity of the PU composites compared to that of the PC composites is probably due to the strong PU-CNT interactions than to the state of dispersion. However the strong irreproducibility of the measurements must also be kept in mind.

¹¹The PC composite with 3 wt% CNT was plotted instead of the sample containing 2 wt% CNT because the latter exhibits a peculiar behaviour, as discussed previously.

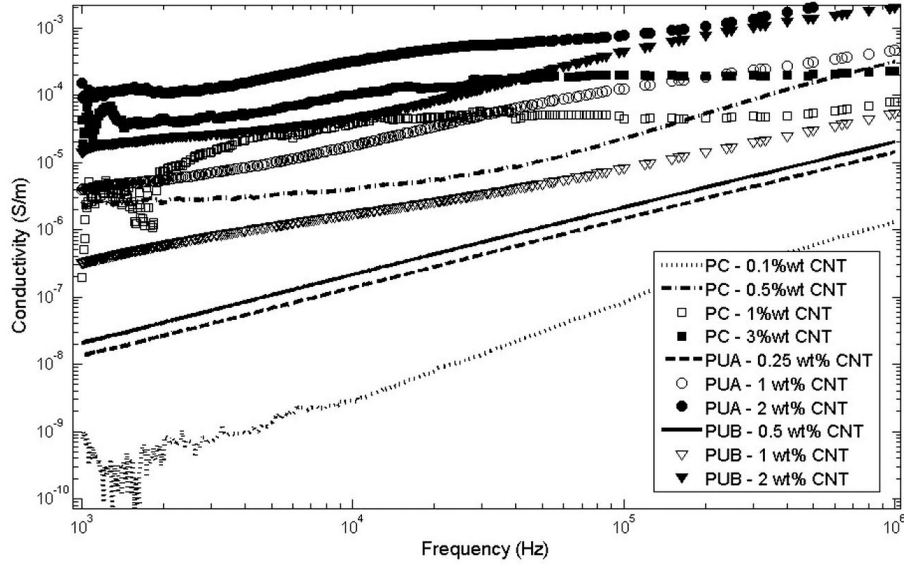


Figure 4.15.: Measured electrical conductivity as a function of frequency for PC (dotted, dash-dot and $\square$) and PU samples of series A (dashed and $\circ$) and B (solid and ∇) having similar CNT contents.

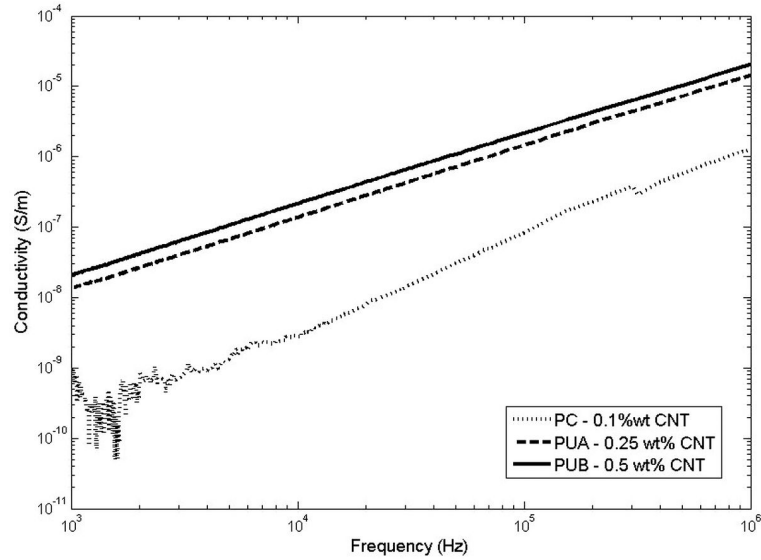


Figure 4.16.: Measured electrical conductivity as a function of frequency for PC (dotted) and PU samples of series A (dashed) and B (solid) having similar CNT contents, below their respective percolation thresholds.

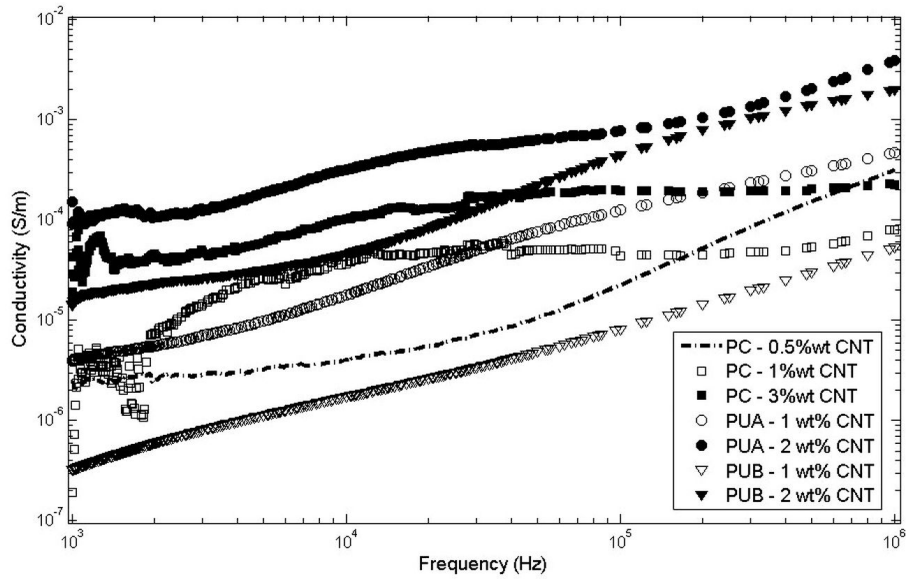


Figure 4.17.: Measured electrical conductivity as a function of frequency for PC (dash-dot and $\square$) and PU samples of series A ($\circ$) and B (∇) having similar CNT contents, above their respective percolation thresholds.

The conductivity measured for all samples at 1 kHz¹² is compared to the DC results on Fig. 4.18, the results seem very similar, with a translation upward in conductivity of about a decade in the case of the PC sample and the PU composites of series B, but an almost negligible increase for the PU samples of series A.

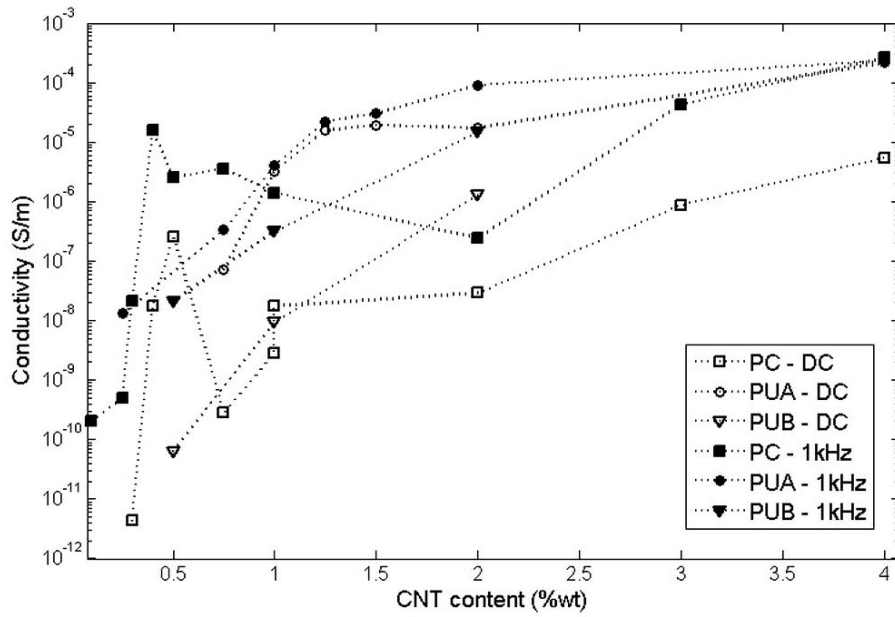


Figure 4.18.: Values of the measured electrical conductivity at DC (white) and at 1 kHz (black) as a function of filler content for PC (□-■) and PU series A (○-●) and B (▽-▼) samples.

A similar translation can be observed when the conductivity of all samples at 1 kHz is compared to the one at 1 MHz, cf. Fig. 4.19, also for the PU samples of series A.

¹²The specific frequency points are chosen to allow a clear comparison between the samples. They are spread over several decades to illustrate the behaviours as representatively as possible. They are not chosen in frequency ranges where noise is dominant or where an measurement error is suspected.

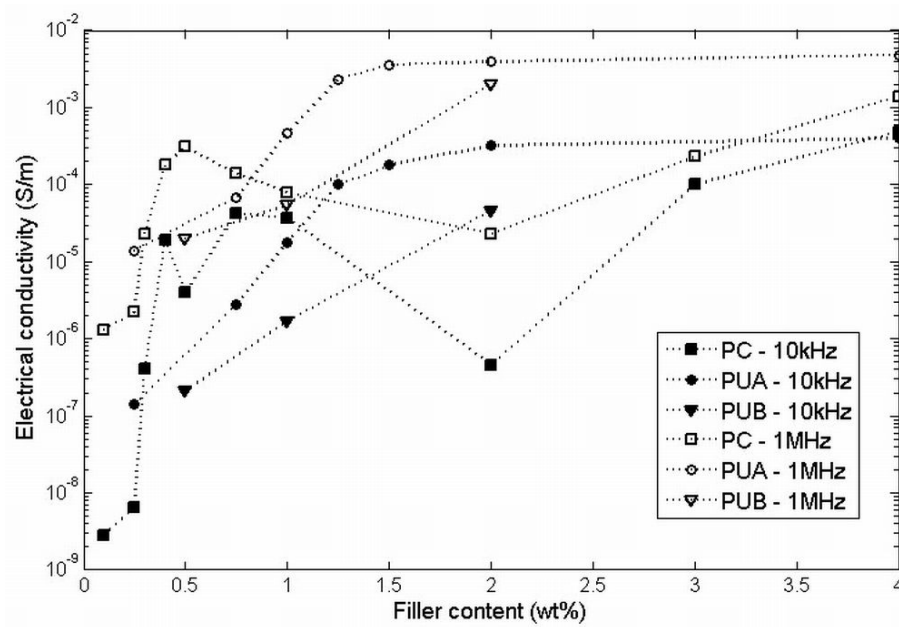


Figure 4.19.: Values of the measured electrical conductivity at 10 kHz (black) and at 1 MHz (white) as a function of filler content for PC (■-□) and PU series A (●-○) and B (▼-▽) samples.

In the particular case of the PU samples of series A¹³, the conductivity versus filler content curves can be fitted using the simple scaling law already used to fit the DC results, $A(\varphi - \varphi_c)^t$. This is shown on Fig. 4.20 at 1 kHz, 10 kHz and 1 MHz. At 1 kHz, the parameter of the scaling law were found to be: $t = 1.665$ and $A = 3.3910^{-5}$, at 10 kHz: $t = 1.489$ and $A = 1.9910^{-4}$ and, at at 10 kHz: $t = 1.437$ and $A = 4.4010^{-3}$. The steady increase of the parameter A is directly related to the increase of the conductivity with frequency, for the same filler content. However, the decrease of the exponent t is the result of a transition or threshold becoming gentler, less sharp, confirming the previous results from the conductivity versus frequency graphs.

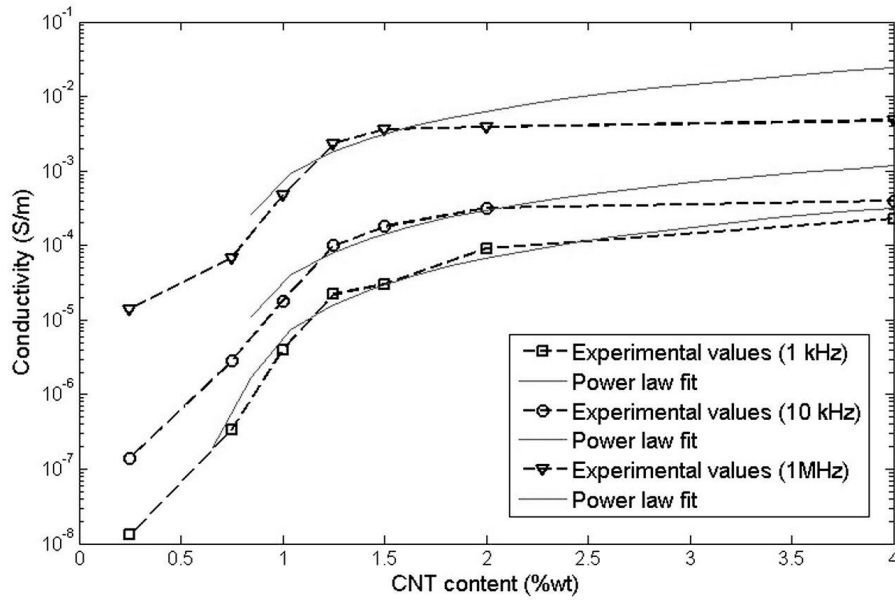


Figure 4.20.: Values of the measured electrical conductivity at 1 kHz ($\square$), 10 kHz ($\circ$) and at 1 MHz (∇) as a function of filler content PU series A samples.

¹³The results for the PC samples could not be adequately fitted using the scaling function and the PU series B consisting in 3 data points, the series A was considered a better illustration.

4.4.6 Note on the shape of the conductivity versus frequency plots

The conductivity versus frequency curves for the PC and PU samples (1kHz–1MHz) presented here differ significantly from the results of the literature as presented in chapter 2. As can be seen on Fig. 4.21 for the PU samples of series A, for samples below the percolation threshold the curves are straight lines in loglog plots, as expected. However as the nanoparticle content increases, instead of a low frequency ‘plateau’ one then several inflection points can be observed. The characteristic frequency of these points seems to increase with increasing filler content, though the behaviour at higher frequencies would be interesting to investigate (at microwave frequencies, only straight lines in loglog plots can be observed, cf. section 4.5).

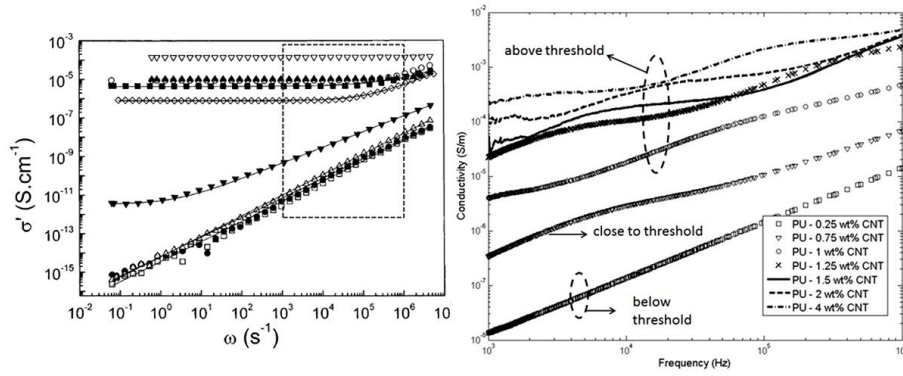


Figure 4.21.: Measured electrical conductivity as a function of frequency of the CNT/epoxy resin composites from [5] (left) and same plot for the PU samples of series A (right). The CNT/epoxy resin composites have filler contents of 0 ($\square$), 0.04 ($\bullet$), 0.2 ($\triangle$), 0.3 (∇), 0.4 ($\diamond$), 0.6 ($\blacksquare$), 0.8 ($\circ$), 1.5 ($\blacktriangle$) and 2.5 wt% (∇). The PU samples have CNT contents from 0.25 to 4 wt% CNTs).

Usually inflection points in conductivity versus frequency plots, i.e. peaks in the corresponding imaginary part of the permittivity plots, of dielectric materials are associated with relaxation phenomena.

In theory, relaxation is a delayed response to a varying stimulus (in linear systems where stimulus and response are proportional), [6]. In dielectric materials, the stimulus is an applied electric field and the response is the resulting polarization. A time delay between them means that energy is dissipated (heat losses). If the dielectric is simply modelled by a RC parallel dipole¹⁴, it has a relaxation time or time constant $\tau = RC$ characteristic of the time delay between applied voltage and capacitor charge. The corresponding real and imaginary part

¹⁴More details on the electrical modelling of CNT composites using resistances and capacitances can be found in chapter 2 and in chapter 5.

(proportional to the conductivity) of the permittivity are plotted on Fig. 4.22. The equations describing the dependence of the complex permittivity on the frequency are called the Debye equations.

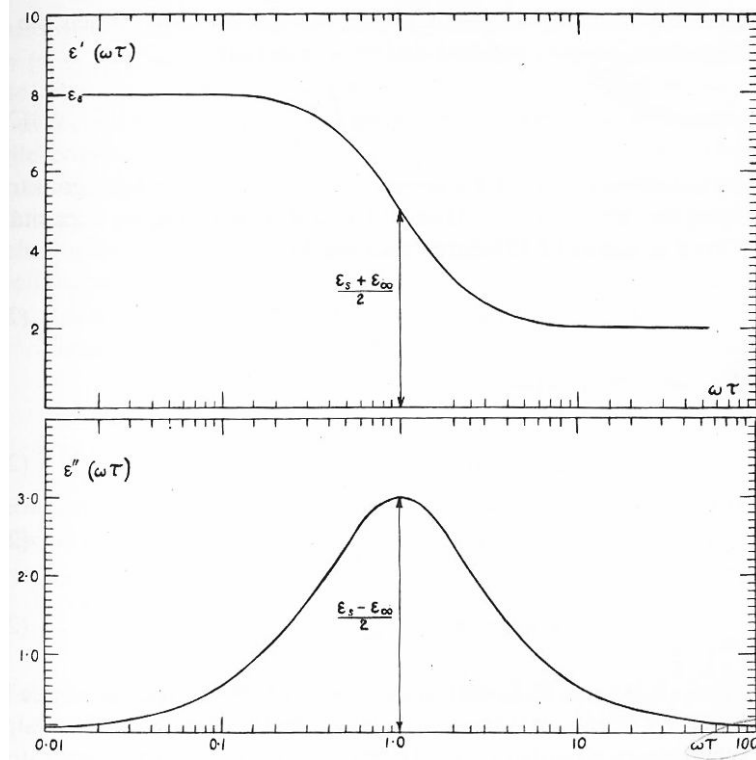


Figure 4.22.: Real (top) and Imaginary (bottom) parts of the complex permittivity as a function of frequency, for $\epsilon_s = 8$ and $\epsilon_\infty = 2$ values, from [6].

Such relaxations could explain the inflection points that are visible in the conductivity versus frequency curves of the PC and PU samples discussed in this chapter. The characteristic frequency of these points is different for curves having different filler content. This can be understood considering that the mean distance between two neighbouring CNTs decreases with increasing CNT content and that the capacitance of the corresponding RC model depends on this distance. But relaxations should also be present in the results from [5], they might be due to differences in fabrication, permanent dipoles being created, or as is detailed below to the presence of layers with different properties.

However most dielectrics cannot be accurately modelled by a single RC dipole, but rather by a number of RC dipoles, not all with the same relaxation time, and

the responses have to be superposed. The complex permittivity and conductivity Cole-Cole plots of four different circuits are shown on Fig. 4.23 illustration. The debye equations must then be replaced by the less straight-forward Kramers-Kronig relations. Besides, at microwave frequencies the models also have to take inductances into account. This adds at least one other time constant to the system and resonance absorption phenomena can occur, cf. chapter 2 and [6] for more information. Besides it can be seen from SEM measurements that there are almost no CNTs present in the region of the material near the upper and lower surfaces of the samples. This would lead to other capacitances, and other time constants, in series with the main(s) RC dipole(s). The existence of these two insulating layers in contact with the electrodes might explain why there are inflection points in the our measurements results but not in those from [5] (or others in the literature).

Nevertheless multiple relaxation times would lead to the presence of several inflection points in the conductivity versus frequency curves, as illustrated on Fig. 4.24.

It is also interesting to note that the conductivity versus frequency curves of the PU series A samples seem to exhibit more distinct inflection points than the curves for the PC samples. It might be explained by the presence of aggregates, as postulated previously in this chapter, in PU composites and a better dispersion of the CNTs in PC samples. Indeed the distance between the agglomerates could correspond to another capacitance, or relaxation time.

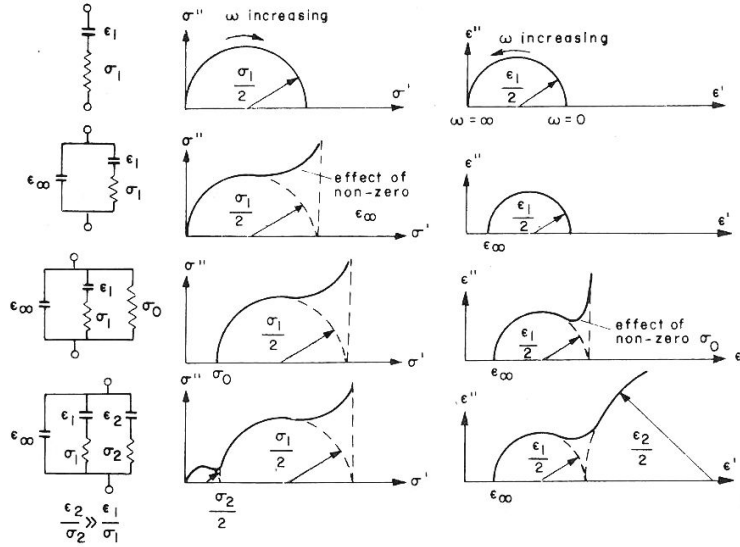


Figure 4.23.: Diagrams of the complex conductivity (σ'' against σ') and complex permittivity (ϵ'' against ϵ') for four RC circuits, from [6].

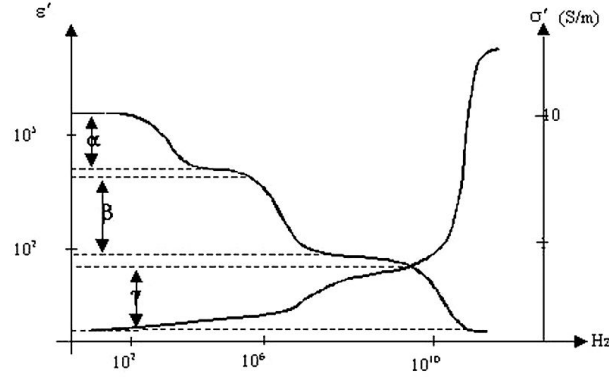


Figure 4.24.: Example of a dielectric constant (left) and conductivity (right) versus frequency plot where multiple relaxations can be observed, from [7].

In order to develop a relaxation-based model to fit these results, all these considerations should be taken into account. This is not done in the present thesis but might be part of future developments. It must also be noted that the electrode-material interface, when the material is resistive, has an associated capacitance, somewhat similar to that of a p-n junction, that should be added to the model. And the presence of conductive inclusions should also be considered as they complicated the equations but models exist to take their presence and shape into account, [6].

All these considerations can help understanding the microstructure of the composite and is a useful feedback to material engineers fabricating the composites and working to improve their properties (retrosimulation).

4.4.7 AC dielectric constant versus filler content, comparison between PC and PU samples

These dielectric constant values for the PU samples are compared to the ones of the PC composites on Fig. 4.25. The PU series A samples seem to exhibit the highest dielectric constant. It was already speculated previously in this section that there might be more interconnections between the CNTs in the PU. These interconnections are not short circuits but CNT-polymer-CNT structures or micro-capacitors. If there are significantly more of these capacitors in the PU nanocomposites, a higher dielectric constant can be expected.

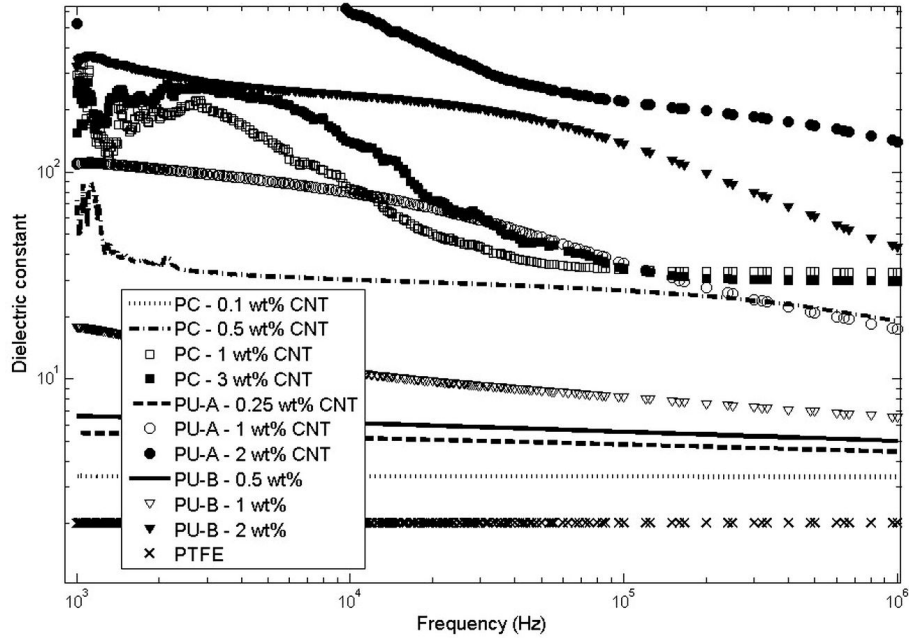


Figure 4.25.: Measured dielectric constant as a function of frequency for PC (dotted, dash-dot and $\square$) and PU samples of series A (dashed and $\circ$) and B (solid and ∇) having similar CNT contents, and for a sheet of PTFE ($\times$).

At 1 MHz, the dielectric constant values of samples below the percolation threshold are close but not identical to those of the pure polymers (from their technical datasheet), cf. Fig. 4.26. The 0.1 wt% PC sample exhibit a dielectric constant of 3.34 instead of 3.00 for pure PC at 1 MHz, i.e. a difference of about 10 %. PU samples with 0.25 (series A) and 0.5 wt% (series B) have dielectric constant of 4.43 and 5.00, respectively, instead of the 6.5 specified at 1 MHz for pure PU. The measured values are then about 32 and 23 % lower than the theoretical values of pure PU.

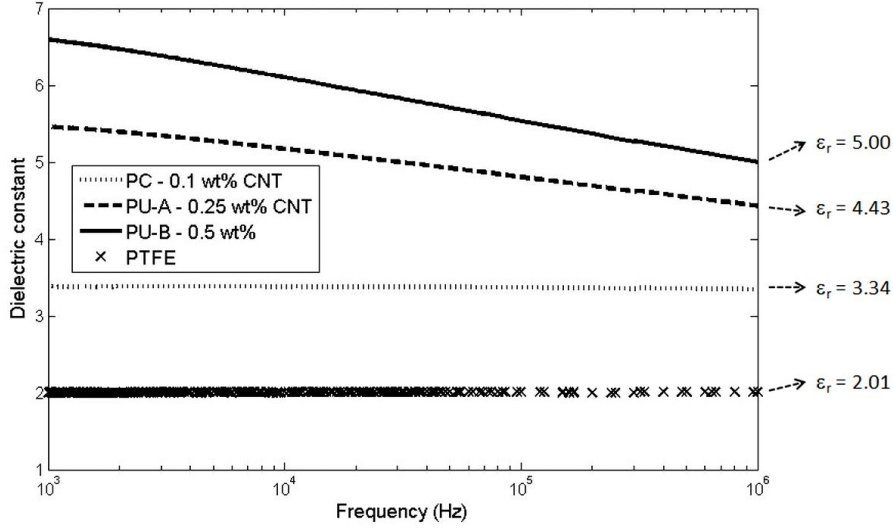


Figure 4.26.: Measured dielectric constant as a function of frequency for PC (dotted) and PU samples of series A (dashed) and B (solid) having similar CNT contents, and for a sheet of PTFE ($\times$).

The dielectric constant of Teflon at 1 MHz measured using this technique is 2.01 instead of 2.1, an error of less than 4.3 %, , cf. Fig. 4.27. This experimental error is therefore not responsible for the differences in the PU and PC dielectric constant values.

The presence of CNTs has therefore an influence on the dielectric constant of nanocomposites even below the percolation threshold, though it would be expected that the addition of CNTs would increase the dielectric content. An effect of the fabrication and mixing method when adding the CNTs can therefore not be excluded.

As discussed in section 2.4.3 of the state-of-the-art, there is some controversy on the dependence of the DC dielectric constant on filler content. Most authors agree on a $(\varphi - \varphi_c)^s$ dependence, but the model from [8] described in section 2.5.2, assumes a dependence in $|\varphi - \varphi_c|^s$ of the dielectric constant. The DC value of the dielectric constant could not be measured directly but the value at 1 kHz¹⁵ and 1 MHz are plotted for the PC and PU samples as a function of their filler content on Fig. 4.28. Our results visibly invalidate the $|\varphi - \varphi_c|^s$ model. Excluding the higher filler content results (2 and 4 wt% CNT samples) the results for the

¹⁵The measured values at the lower end of the frequency range often present significant noise for high filler fractions, especially for the PC nanocomposites, but considering instead the value obtained assuming a plateau leads yields negligible difference.

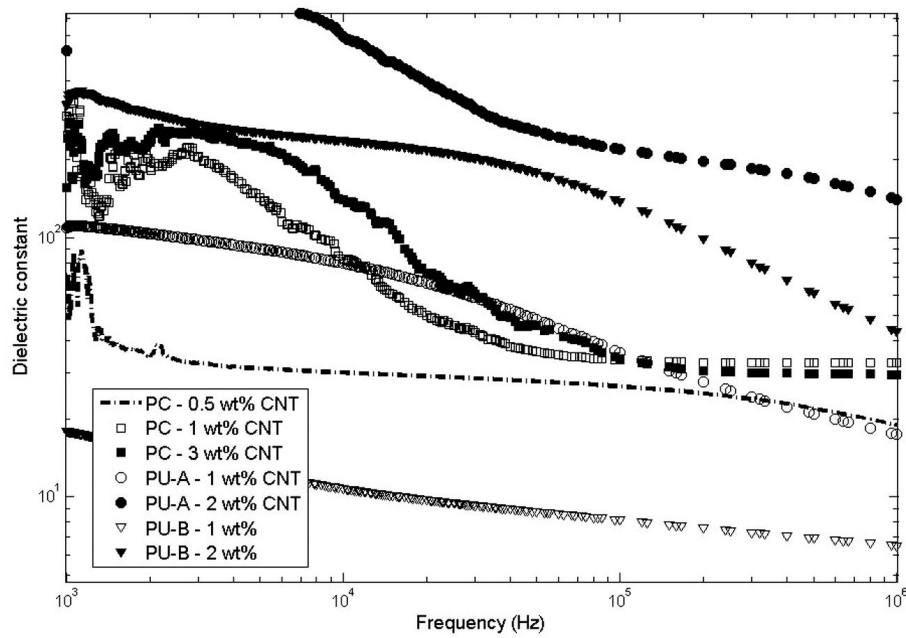


Figure 4.27.: Measured dielectric constant as a function of frequency for PC (dash-dot and $\square$) and PU samples of series A ($\circ$) and B (∇) having similar CNT contents.

PU series A samples¹⁶ at 1 MHz can be fitted using a function $A(\varphi - \varphi_c)^s$, with $A = 162.06$ and the dielectric constant critical exponent $s = 1.61$ ($\varphi_c \sim 0.76$ wt%), cf. Fig. 4.29, and at 1 kHz: $A = 1060$ and $s = 1.55$ ($\varphi_c \sim 0.67$ wt%). This s value is only slightly higher than those commonly found in the literature; 1.14 in [2], 1.41 in [9] (both: MWCNTs - polyimide). Besides, the threshold value is almost the same than for the conductivity results.

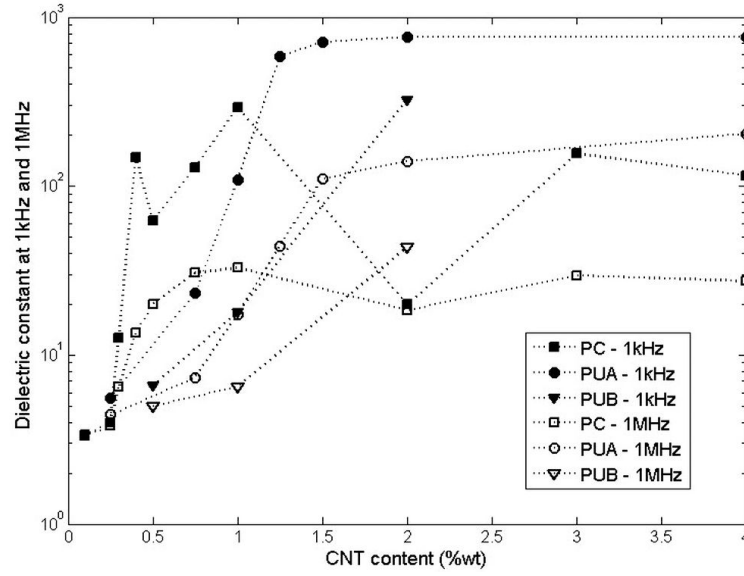


Figure 4.28.: Values of the measured dielectric constant at 1 kHz (black) and 1 MHz (white) as a function of filler content for PC (■-□) and PU series A (●-○) and B (▼-▽) samples.

¹⁶The same fitting could be done for the other samples, we limited ourselves to the PU-A results here for clarity.

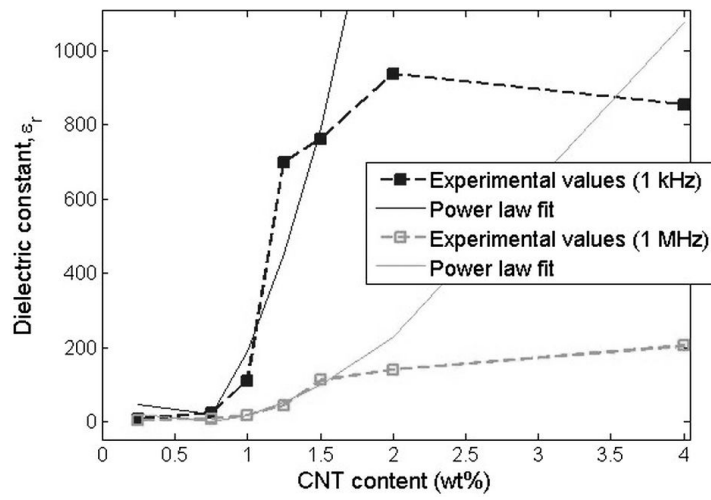


Figure 4.29.: Measured dielectric constant of the PU series A samples as a function of mass fraction, at 1 kHz (■) and 1 MHz (□), measured values (symbols) and power law fits (solid).

4.4.8 AC electrical conductivity versus frequency and power law behaviour

As mentioned previously, in the current section and in section 2.4.2, the conductivity versus frequency plots of nanocomposite samples below the percolation threshold can be fitted using a relationship $\sigma(\omega) \propto A\omega^s$. The high frequency part of the curves of samples above the percolation threshold can also be fitted using similar relationships¹⁷, as shown on Fig. 4.30 for the PC samples, on Fig. 4.31 for the PU samples of series A and on Fig. 4.32 for the PU series B. It must be noted that not all the curves could be fitted using a power law, some of them had a too flat slope near 1 MHz (the PC samples with CNT contents of 0.75, 3 and 4 wt% CNT).

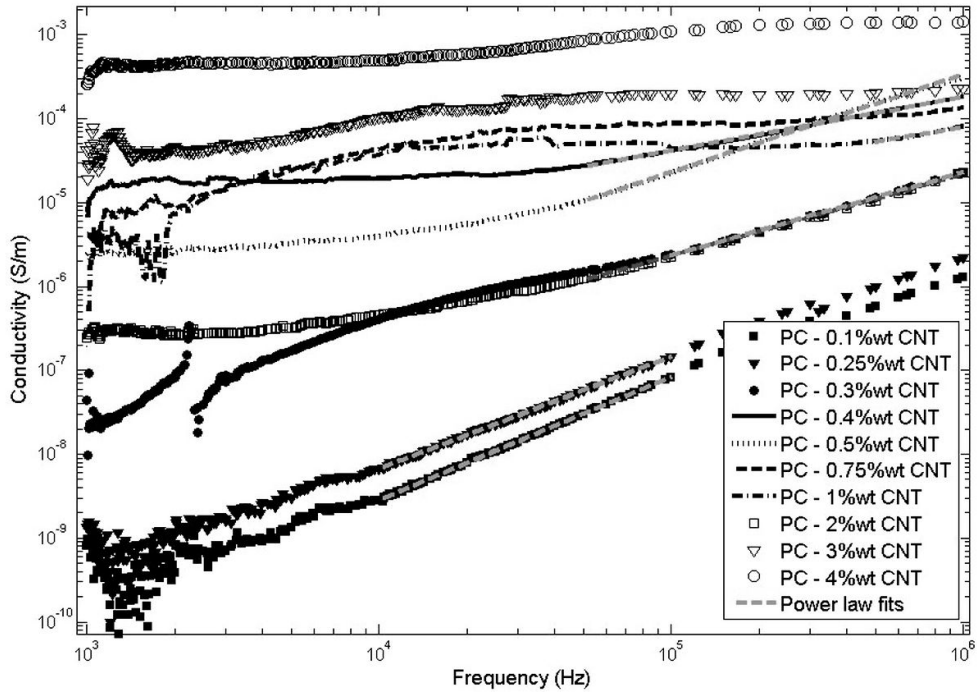


Figure 4.30.: Measured electrical conductivity as a function of frequency for the PC samples (dotted with markers) and the corresponding power law fits.

The details of the fitting power laws can be found on Table 4.3, Table 4.4 and Table 4.5, for PC samples, PU series A and PU series B composites, respectively.

¹⁷The frequency range of the power law fitting was selected to provide the best ‘visual’ fit.

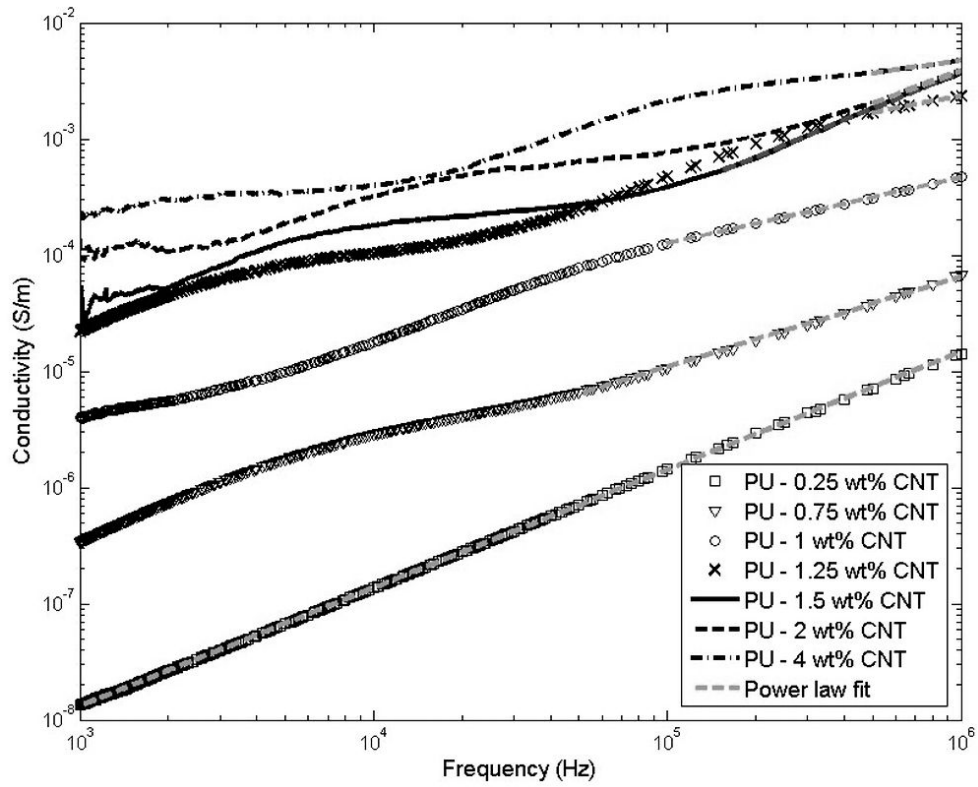


Figure 4.31.: Measured electrical conductivity as a function of frequency for the PU samples of series A (dotted with markers) and the corresponding power law fits.

CNT loading wt.%	code	s	A	Residue
0,1	NQ01	1,47	$3,7 \cdot 10^{-15}$	$1,4 \cdot 10^{-19}$
0,25	NQ02	1,34	$2,9 \cdot 10^{-14}$	$2,7 \cdot 10^{-19}$
0,3	NQ06	0,99	$2,5 \cdot 10^{-11}$	$1,7 \cdot 10^{-14}$
0,4	NQ07	0,64	$2,7 \cdot 10^{-8}$	$1,1 \cdot 10^{-12}$
0,5	NQ03	1,16	$3,6 \cdot 10^{-11}$	$2,6 \cdot 10^{-11}$
0,75	NQ08	0,25	$4,3 \cdot 10^{-6}$	$1,1 \cdot 10^{-11}$
1	NQ04	0,58	$2,8 \cdot 10^{-8}$	$1,5 \cdot 10^{-13}$
2	NQ05	0,97	$3,3 \cdot 10^{-11}$	$1,5 \cdot 10^{-13}$
3	NQ09	/	/	/
4	NQ10	/	/	/

Table 4.3.: Details of the power law $A\omega^s$ parameters used to fit the conductivity versus frequency curves (or part of these) for the PC nanocomposites.

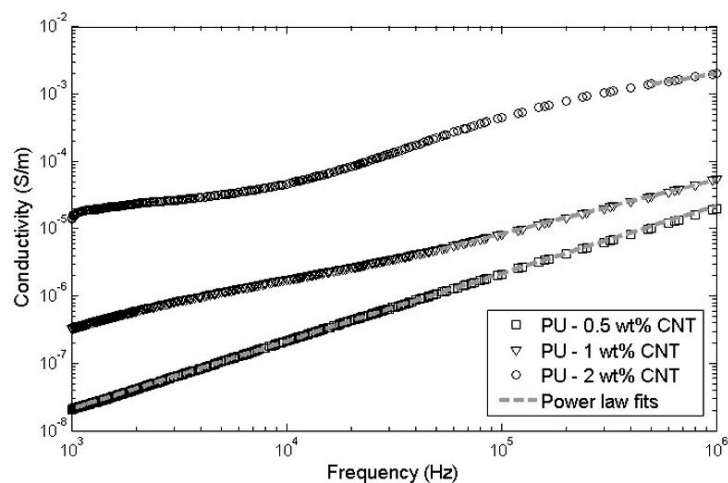


Figure 4.32.: Measured electrical conductivity as a function of frequency for the PU samples of series B (dotted with markers) and the corresponding power law fits.

CNT loading wt.%	code	s	A	Residue
0,25	NQ20	1,02	$1,2 \cdot 10^{-11}$	$3,5 \cdot 10^{-15}$
0,75	NQ23	0,78	$1,1 \cdot 10^{-9}$	$5,5 \cdot 10^{-13}$
1	NQ24	0,59	$1,4 \cdot 10^{-7}$	$6,3 \cdot 10^{-12}$
1,25	NQ26	0,48	$3,3 \cdot 10^{-6}$	$6,9 \cdot 10^{-11}$
1,5	NQ27	1,04	$2,1 \cdot 10^{-9}$	$1,4 \cdot 10^{-9}$
2	NQ29	0,92	$1,1 \cdot 10^{-8}$	$5,0 \cdot 10^{-11}$
4	NQ30	0,37	$3,1 \cdot 10^{-6}$	$7,5 \cdot 10^{-10}$

Table 4.4.: Details of the power law $A\omega^s$ parameters used to fit the conductivity versus frequency curves (or part of these) for the PU nanocomposites (series A).

CNT loading wt.%	code	s	A	Residue
0,5	NQ21	1,01	$1,9 \cdot 10^{-11}$	$3,1 \cdot 10^{-14}$
1	NQ25	0,81	$8 \cdot 10^{-10}$	$6,8 \cdot 10^{-14}$
2	NQ28	0,52	$1, \cdot 10^{-6}$	$7,5 \cdot 10^{-10}$

Table 4.5.: Details of the power law $A\omega^s$ parameters used to fit the conductivity versus frequency curves (or part of these) for the PC nanocomposites (series B).

The critical exponent s values has small meaning for nanocomposites with high CNT loading for which the DC plateau is still present at 1 MHz, it is then either impossible to extract or has a very low value. This is the case for many PC samples with significant filler content.

It is interesting to note that, except for the 4 wt% CNT samples the critical exponent s of the PU based nanocomposites lies in the range $0.6 - 1.0$ and most of them even in the $0.8 - 1.0$ range. The latter range of exponent s values is characteristic of hopping conduction in disordered solids, [10, 11], where charge carriers are hopping through randomly varying energy barriers. These values are therefore in good agreement with the thermal fluctuation induced tunnelling model presented in section 2.5.4.

As discussed in [10], the dielectric constant and conductivity below the percolation threshold should theoretically exhibit the same exponent. However this is not always observed to be the case in practice. This difference of critical exponents has also been reported in [11, 12].

4.5 MICROWAVE CHARACTERIZATION (MICROSTRIP), 40MHZ-40GHZ

The samples described in section 4.2 and discussed in the previous sections of this chapter were characterised at microwave frequencies, in the 40 MHz-40 GHz range using the One-Line microstrip technique described in section 3.3.1. As required for this method, the thin nanocomposite plates were covered on one face by adhesive aluminium tape and on the other a strip of copper scotch (1 mm wide) across the sample (3 cm long¹⁸).

It was shown that the major issue with DC and even LCR measurements (cf. previous sections) was the reproducibility of the measurements. It can be expected to improve as the frequency is increased further. Indeed, as illustrated on Fig. 4.33 and Fig. 4.34, the maximum observed difference in mean electrical conductivity is of about 24.0 % and in mean dielectric constant is of about 6.5 % for the NQ04 sample (PC with 1 wt% CNT) while in the case of NQ30 (PU with 4 wt% CNT) the errors are up to 9.7 % and 1.6 % for the conductivity and dielectric constant, respectively. It can also be seen on Fig. 4.33 that the influence of the location of the metal strip is prominent on that of imperfections in the geometry, age or adhesion of the line on the substrate (it was first thought that the adhesion would be much degraded with time).

The irreproducibility is therefore significantly decreased in comparison with the low frequency techniques. The errors in conductivity and dielectric constant were of about 92.3 % and 82.3 % for the PC sample, respectively, and of 43.4 % and 12.7 % for the PU composite. But again the reproducibility is greater for the PU samples than for the PC ones, another hint at a better dispersion, even when the charges carriers have to travel much smaller distances in the material (as the frequency is much higher).

¹⁸Except when the losses are so high that the 40 dB limit is reached in transmission. In that case, the sample is cut to shorten the length of the line to 2 or 1 cm.

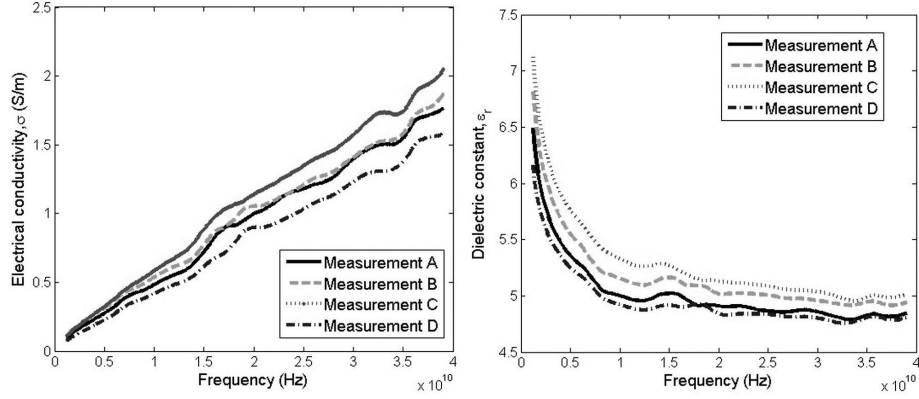


Figure 4.33.: Measured electrical conductivity (left) and dielectric constant (right) as a function of frequency for the NQ04 sample (PC with 1 wt% CNT). Four different measurements of the same sample are presented, measurement A (solid) with the tape strip placed one month prior to the other three measurements), measurement B (dashed) with a new strip glued at the same location as for measurement A, measurement C (dotted) with another line put in another location on the sample and measurement D (dash-dot) with another strip in yet another location.

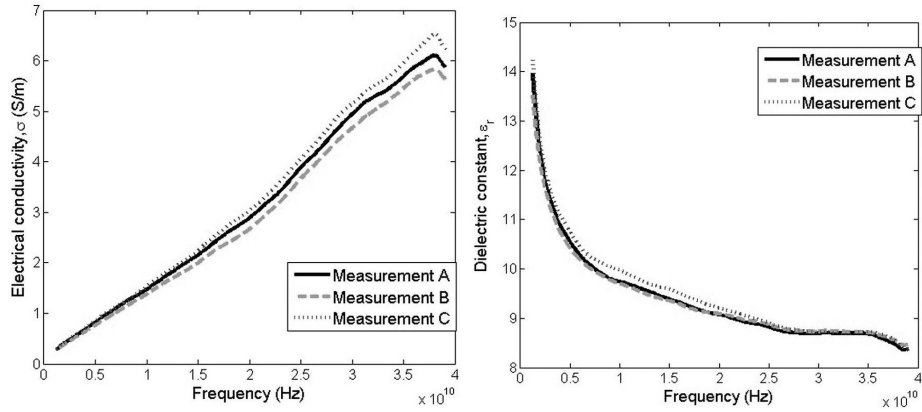


Figure 4.34.: Measured electrical conductivity (left) and dielectric constant (right) as a function of frequency for the NQ30 sample (PU with 4 wt% CNT). Three different measurements of the same sample are presented, measurement A (solid) with the tape strip placed one month prior to the other three measurements), measurement B (dashed) with a new strip glued in another location on the sample, measurement C (dotted) with another line put in yet another location on the sample.

4.5.1 AC electrical conductivity: PC and PU samples

The electrical conductivity as a function of frequency curves are shown on Fig. 4.35 for the PC samples, on Fig. 4.36 for the PU composites of series A and on Fig. 4.37 for the ones of series B. All the samples present the same kind of behaviour, detailed further in the current section, and no difference of qualitative behaviour can be observed below or above the percolation threshold. The percolation thresholds of PC and PU were found, from DC measurements, to be around 0.3 and 0.7 wt%, respectively.

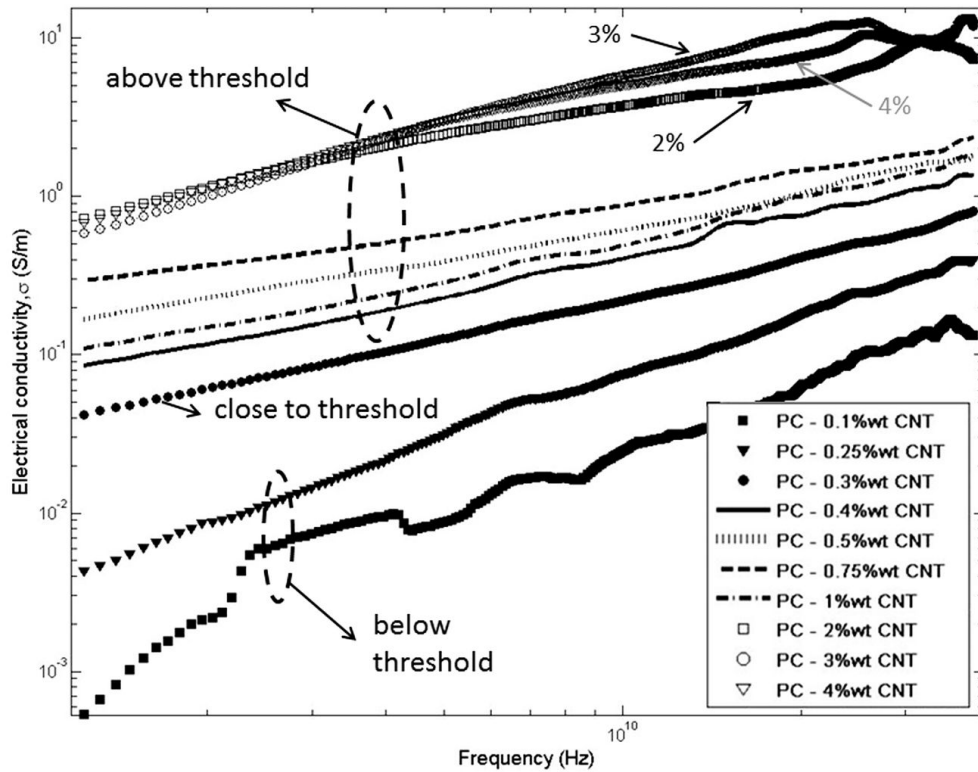


Figure 4.35.: Measured electrical conductivity as a function of frequency for the PC samples (symbols), with CNT contents from 0.1 to 4 wt%.

The conductivity of the PC samples globally increases with filler content, as expected, though the curves are too close to one another and overlapping to conclude above 1 wt% of CNTs. The measurement of the PC samples with 2 wt% CNT and of those with higher CNT loadings are not accurate beyond about 20 GHz, the conductivity being so high that the incident power is almost completely absorbed by the substrate when travelling along the line from one

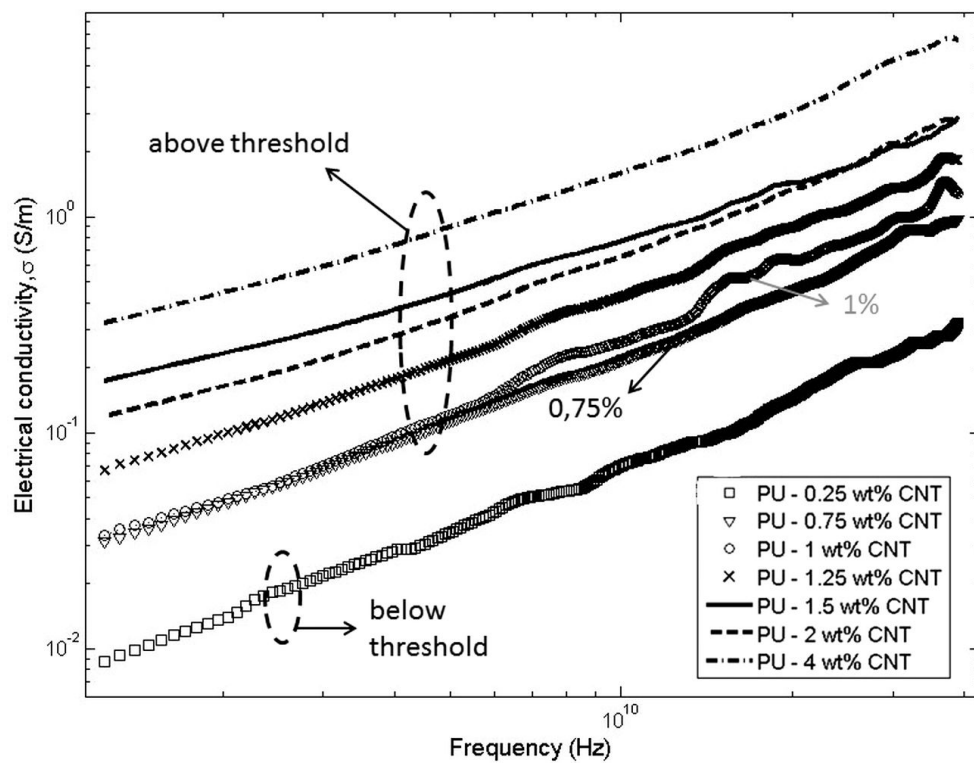


Figure 4.36.: Measured electrical conductivity as a function of frequency for the PU series A samples (symbols), with CNT contents from 0.25 to 4 wt%.

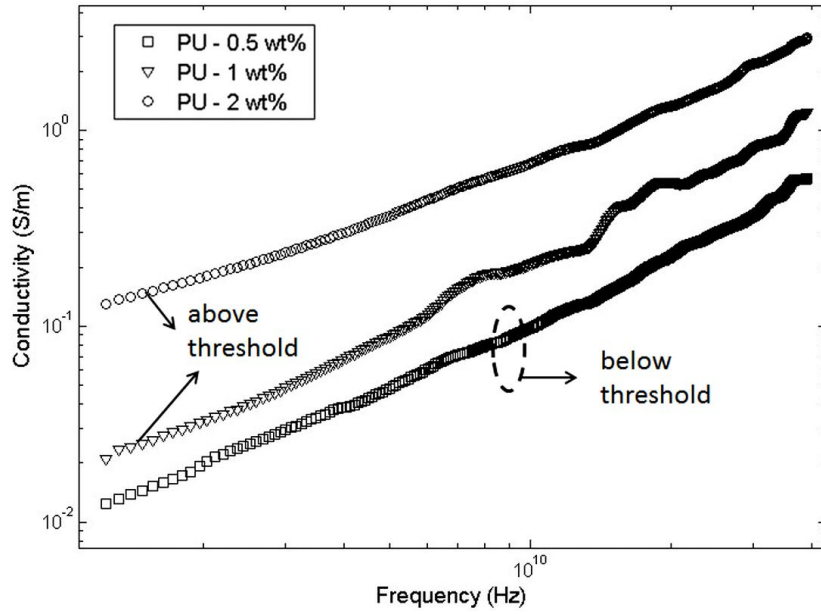


Figure 4.37.: Measured electrical conductivity as a function of frequency for the PU series B samples (symbols), with CNT contents from 0.5 to 2 wt%.

port to the other and the signal-to-noise ratio is then too poor. In the case of the PU samples of series A, the conductivity also increases with filler content except for the composites with 1.5 and 2 wt% CNT content for which the curves are intertwined. The composites of series B exhibit a similar behaviour.

The electrical conductivity at a frequency of 10 GHz are plotted for all samples, PC and PU, on Fig. 4.38 as a function of the filler mass fraction. The regular increase of the conductivity with CNT content is confirmed by the almost linear aspect of the curves. The percolation threshold is not visible from the latter plots. The conductivity of PC composites is significantly higher than that of PU, for all values of filler content and both series of PU exhibit a similar conductivity.

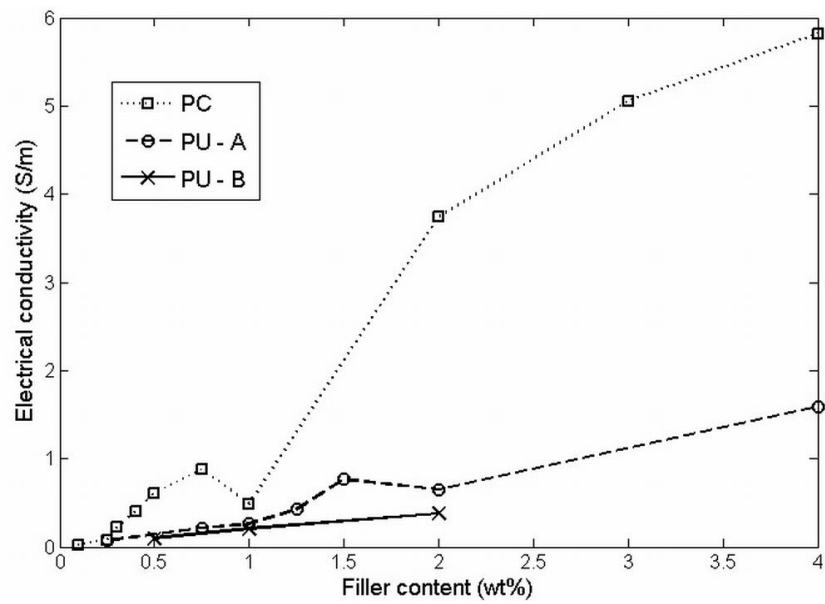


Figure 4.38.: Measured electrical conductivity at a frequency of 10 GHz for the PC (dotted), PU series A (dashed) and series B (solid) as a function of filler content.

For both PC and PU samples, the conductivity increases with frequency, linear increase in a double logarithmic environment, and can be fitted using a power law with the same form, $A\omega^s$, as for lower frequency measurements. The power law fits can be seen on Fig. 4.39, on Fig. 4.40 and on Fig. 4.41, for PC, PU series A and PU series B samples, respectively. The details of these fits, using the same method as for the low frequency measurements power law fittings, are given in Table 4.6 for the PC samples, in Table 4.7 and Table 4.8 for the PU composites of series A and B, respectively. The high loading samples (above 2 wt% CNT) were fitted only below 20 GHz, as the noise is prominent in the conductivity measurements of these samples beyond the latter frequency.

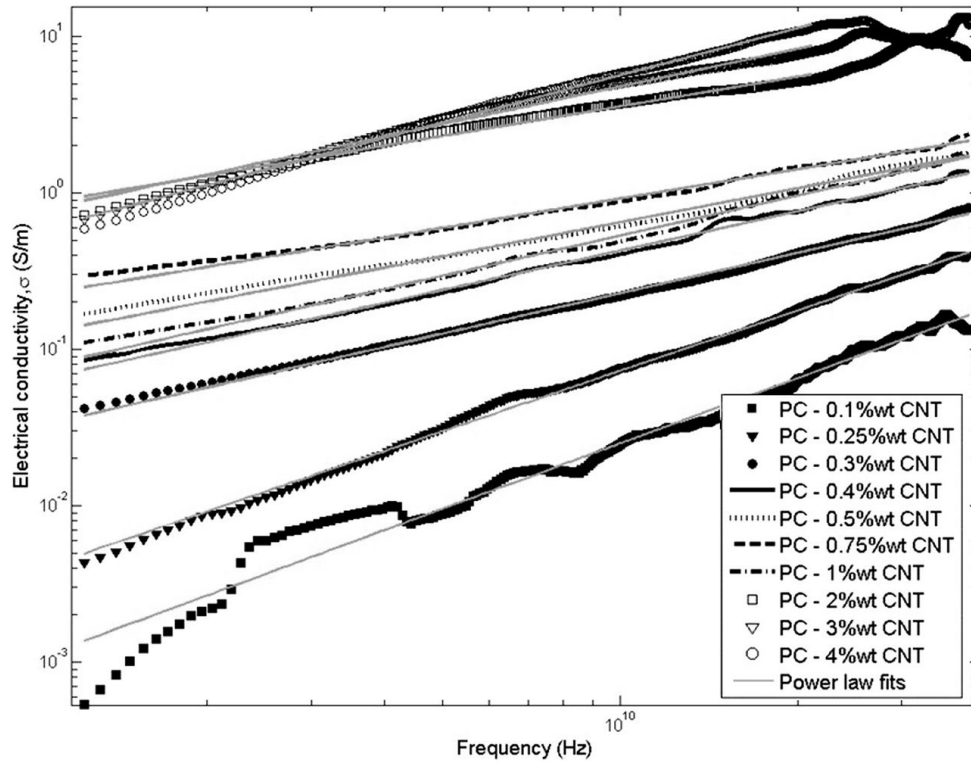


Figure 4.39.: Measured electrical conductivity as a function of frequency for the PC samples (symbols), with CNT contents from 0.1 to 4 wt%, and the corresponding power law fits.

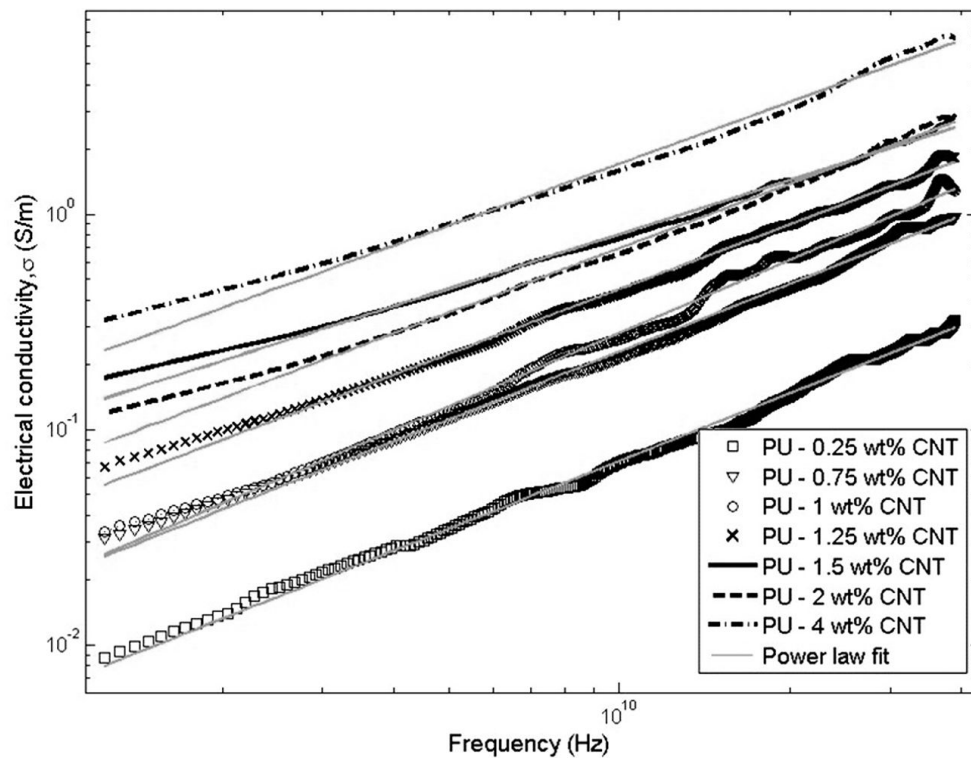


Figure 4.40.: Measured electrical conductivity as a function of frequency for the PU samples of series A (symbols), with CNT contents from 0.25 to 4 wt%, and the corresponding power law fits.

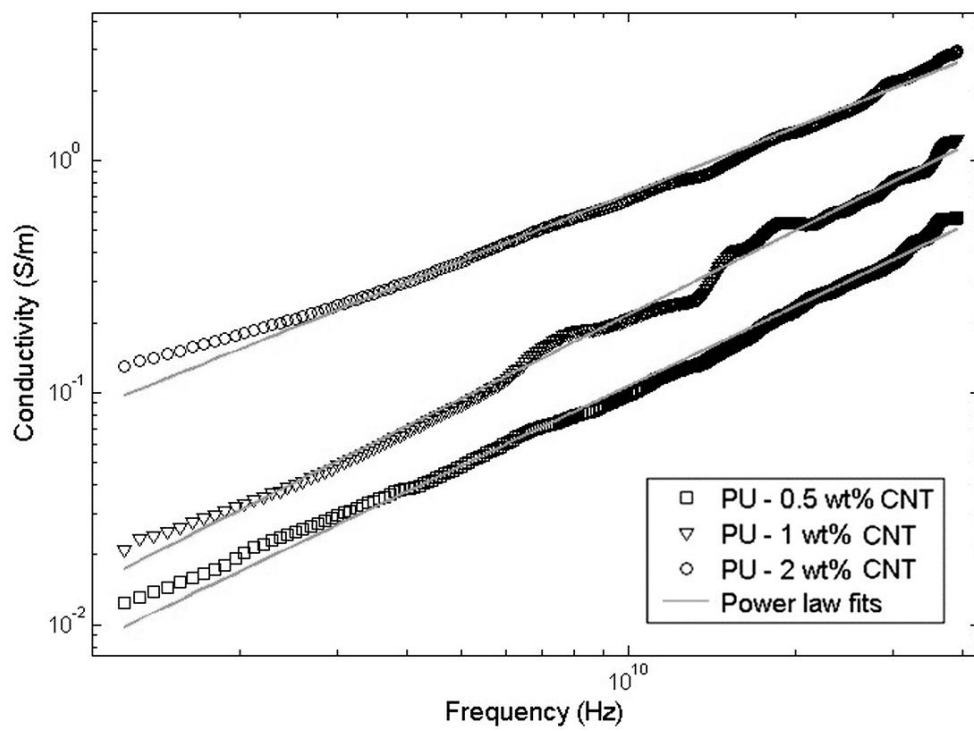


Figure 4.41.: Measured electrical conductivity as a function of frequency for the PU samples of series B (symbols), with CNT contents from 0.5 to 2 wt%, and the corresponding power law fits.

CNT loading wt.%	code	s	A	Residue	
0,1	NQ01	1,39	$3,2 \cdot 10^{-16}$	$6,2 \cdot 10^{-5}$	
0,25	NQ02	1,29	$1,1 \cdot 10^{-14}$	$4,8 \cdot 10^{-5}$	
0,3	NQ06	0,86	$5,6 \cdot 10^{-10}$	$3,7 \cdot 10^{-4}$	
0,4	NQ07	0,84	$1,8 \cdot 10^{-9}$	$8,4 \cdot 10^{-4}$	
0,5	NQ03	0,73	$3,6 \cdot 10^{-8}$	$2,7 \cdot 10^{-3}$	
0,75	NQ08	0,62	$5,2 \cdot 10^{-7}$	$3,1 \cdot 10^{-3}$	
1	NQ04	0,85	$1,5 \cdot 10^{-9}$	$1,6 \cdot 10^{-3}$	
2	NQ05	0,63	$1,7 \cdot 10^{-6}$	$4,0 \cdot 10^{-2}$	<20 GHz
3	NQ09	0,80	$4,5 \cdot 10^{-8}$	$1,1 \cdot 10^{-1}$	<20 GHz
4	NQ10	1,01	$5,0 \cdot 10^{-10}$	$6,3 \cdot 10^{-2}$	<20 GHz

Table 4.6.: Details of the power law $A\omega^s$ parameters used to fit the conductivity versus frequency curves (or part of these) for the PC nanocomposites, limited to below 20 GHz for the three samples with highest CNT content.

CNT loading wt.%	code	s	A	Residue
0,25	NQ20	1,05	$2,4 \cdot 10^{-12}$	$5,6 \cdot 10^{-5}$
0,75	NQ23	1,05	$7,6 \cdot 10^{-12}$	$9,7 \cdot 10^{-4}$
1	NQ24	1,13	$1,4 \cdot 10^{-12}$	$3,1 \cdot 10^{-3}$
1,25	NQ26	1,00	$4,4 \cdot 10^{-11}$	$3,2 \cdot 10^{-3}$
1,5	NQ27	0,84	$3,3 \cdot 10^{-9}$	$5,5 \cdot 10^{-3}$
2	NQ29	0,99	$7,9 \cdot 10^{-11}$	$9,7 \cdot 10^{-3}$
4	NQ30	0,96	$4,8 \cdot 10^{-10}$	$8,4 \cdot 10^{-2}$

Table 4.7.: Details of the power law $A\omega^s$ parameters used to fit the conductivity versus frequency curves (or part of these) for the PU nanocomposites (series A).

CNT loading wt.%	code	s	A	Residue
0,5	NQ21	1,14	$3,9 \cdot 10^{-13}$	$6,7 \cdot 10^{-4}$
1	NQ25	1,21	$1,9 \cdot 10^{-13}$	$1,8 \cdot 10^{-3}$
2	NQ28	0,96	$2,0 \cdot 10^{-10}$	$1,3 \cdot 10^{-2}$

Table 4.8.: Details of the power law $A\omega^s$ parameters used to fit the conductivity versus frequency curves (or part of these) for the PC nanocomposites (series B).

Compared with the results of the previous section, for frequencies lower than 1 MHz, all the samples could be quite adequately fitted by a power law over the entire frequency range (except for the three samples just mentioned but due to measurement limitations). Besides the s exponent values are all in the 0.6 – 1.4 range mentioned in the previous section. No exception even in the PC samples is present using microwave characterisations. It indicates that the low slope of the straight lines sometimes observed close to 1 MHz in the LCR measurements were not characteristic of the high frequency behaviour of the nanocomposites but rather a transient phenomenon, as described in the literature and chapter 2. It was already shown that the results for the PC samples exhibit more fluctuations than the PU composites. This is further confirmed here, the exponent s values for PU series A samples are all within the range 0.8 – 1.1 (0.9 – 1.2 for the series B), very close to the theoretical range previously mentioned as a characteristic of the thermal fluctuation induced tunnelling conduction model of section 2.5.4.

4.5.2 AC dielectric constant: PC and PU samples

The dielectric constant is also extracted from the microwave measurement, it is plotted as a function of frequency on Fig. 4.42 for the PC samples, on Fig. 4.43 for the PU composites of series A and on Fig. 4.44 for the ones of series B.

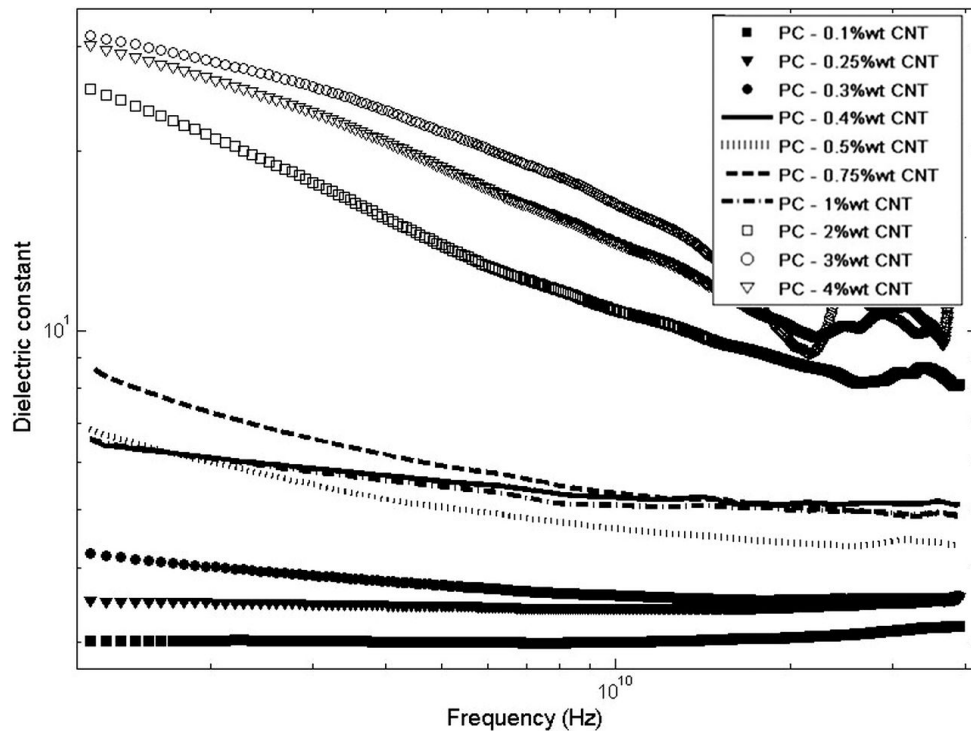


Figure 4.42.: Measured dielectric constant as a function of frequency for the PC samples, with CNT contents from 0.1 to 4 wt%.

On Fig. 4.42, it can be seen that the PC samples exhibit different behaviours depending whether their filler contents are above or below the percolation threshold. In the latter case, the dielectric constant value is constant on the entire frequency range, e.g. of about 3.0 for the sample with the lowest, 0.1 wt%, CNT fraction. The dielectric constant of samples with CNT contents between 0.4 and 0.75 wt% first decrease with increasing frequency then reach a kind of plateau at higher frequency around 10 GHz. The PC samples with filler loadings above 1 wt% decrease monotonously up to 20 GHz, beyond this frequency the measurements are very noisy not reliable any more. They probably also reach a plateau

but at a frequency higher than 40 GHz. As discussed in the previous section, this plateau is characteristic of the CNT-polymer-CNT interconnections.

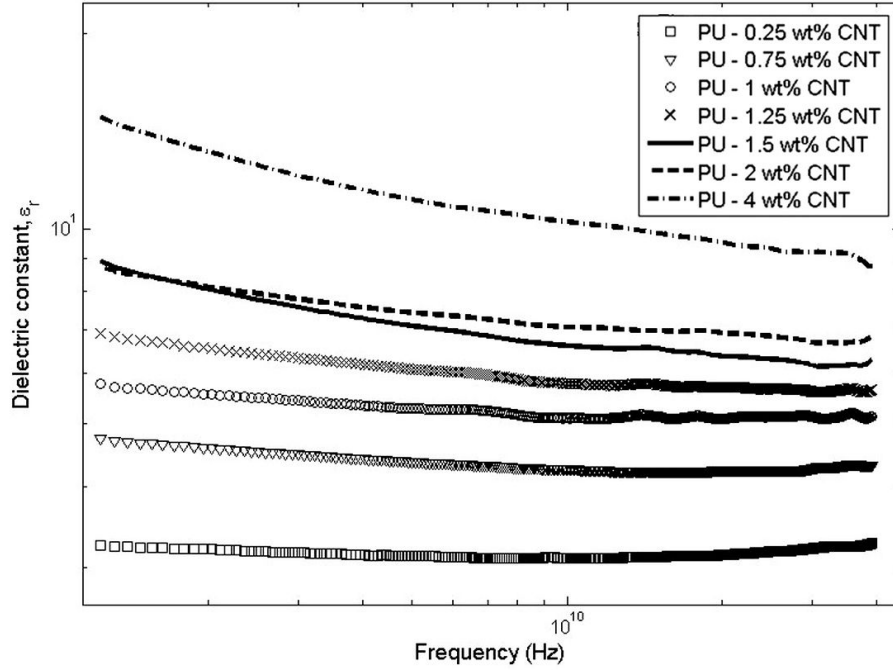


Figure 4.43.: Measured dielectric constant as a function of frequency for the PU samples of series A, with CNT contents from 0.25 to 4 wt%.

The dielectric constant values of the PU series A samples all exhibit this plateau beyond 10 GHz, except the sample containing 0.5 wt% CNT, i.e. with a filler fraction below the percolation threshold. The latter sample has a constant dielectric constant of about 3.2 over the entire 40 MHz - 40 kHz range. Compared to the results of the PC samples, the increase of the dielectric constant with increasing filler content is more evident on Fig. 4.43, even more so above 10 GHz. This is another confirmation of the improved dispersion (qualitatively similar in all the samples with varying filler fractions) of the CNTs in PU samples.

The dielectric constant results of the PU composites of series B are similar to those of the series A though the sample with 1 wt% CNT exhibits the behaviour of a sample still below the percolation threshold. But the DC percolation threshold was calculated using very few data points, the actual value might thus be slightly higher than the calculated one. The 0.5 wt% CNT sample has a constant dielectric constant value of about 3.5

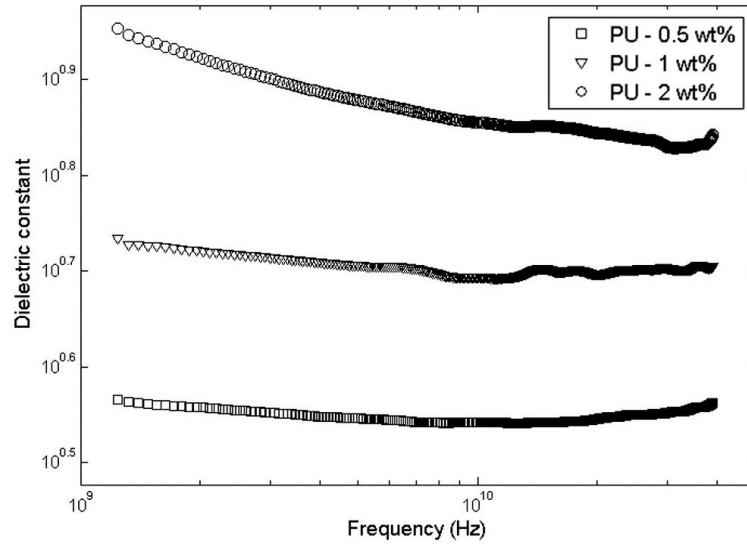


Figure 4.44.: Measured dielectric constant as a function of frequency for the PU samples of series B, with CNT contents from 0.5 to 2 wt%.

The dielectric constant at a frequency of 10 GHz are plotted for all samples, PC and PU, on Fig. 4.45 as a function of the filler mass fraction. Again the regular increase of the dielectric constant with CNT content is confirmed by the almost linear aspect of the curves and there is no evident percolation threshold. Except for the fluctuations of the dielectric constant values of the PC samples close to the percolation threshold, all samples have a rather similar dielectric constant for low CNT loadings. For higher mass fractions, the dielectric constant of the PC samples is significantly higher than that of the PU composites. Both series of PU samples have almost identical dielectric constants.

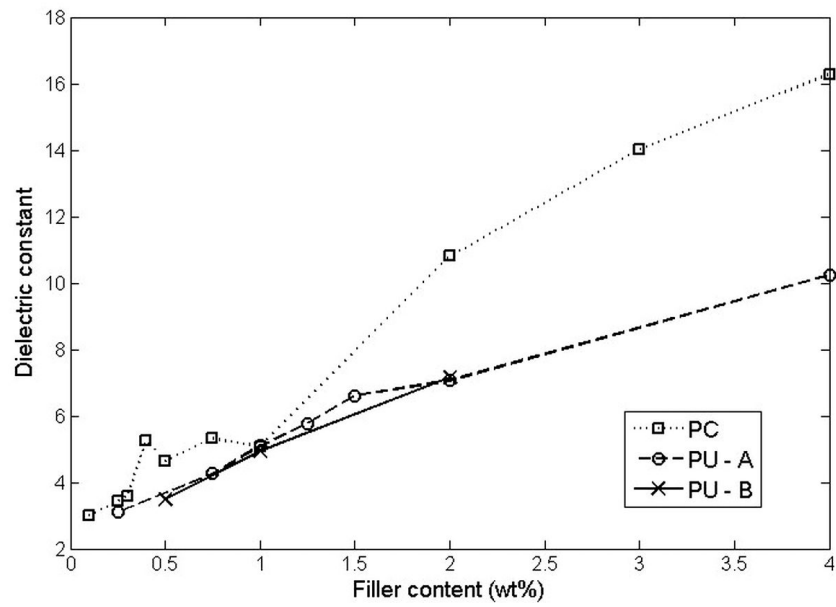


Figure 4.45.: Measured dielectric constant at a frequency of 10 GHz for the PC (dotted), PU series A (dashed) and series B (solid) as a function of filler content.

4.5.3 Comparison between the PC and PU nanocomposites

At low frequency, cf. previous section, the conductivity of the PU samples is greater than that of the PC composites. On the opposite, at microwave frequency, it can be seen from Fig. 4.47 that for the same CNT loading, the conductivity of the PC composite is about one order of magnitude greater than that of the corresponding PU samples. PU samples of series A and B having the same filler fraction exhibit almost perfectly identical conductivities. The PU samples of series A and B with filler content below the percolation threshold do not have exactly the same filler content. The conductivity of the PUB composite with a 0.5 wt% CNT content is twice as high as that the PUA sample with only 0.25 wt% CNTs. This higher conductivity of the PC samples is even more visible on Fig. 4.38.

This apparent contradiction between the low and high frequency behaviours might be related to the difference in dispersion if we assume the CNTs forming rather large agglomerate in the PU and being better dispersed, in tiny clusters inside the PC matrix, as illustrated on Fig. 4.46.

When a material is submitted to an alternating field, the charge carriers ‘scan’ a length that is directly related to period of the EM wave, [13], as discussed in chapter 2. Therefore, if the frequency increases, the mean distance travelled by the charge carriers decrease. At low frequency, this distance is longer than the average length of the CNTs bundles or agglomerates. The charge carriers have to tunnel through one or several junctions between CNTs. At high frequency, the distance travelled by the charge carriers becomes smaller than the size of the CNT agglomerates and the effective conductivity of the composite is then significantly higher.

If we assume larger CNT agglomerates in PU and smaller clusters in PC, there is an alternate frequency range where the mean distance travelled by the charge carrier is larger than the size of the PC clusters but smaller than that of the PU agglomerates. In that case the effective conductivity of the PC composite would be higher than that of the PU samples.

However, for identical filler fractions, larger agglomerates of particle mean a lesser number of agglomerates and a higher mean distance between the agglomerates, as illustrated on Fig. 4.46. The height of the potential barrier between neighbouring CNTs is expected to decrease with decreasing mean interparticle distance. The tunnelling between CNTs or clusters of CNTs would then be facilitated in the case of dispersed smaller clusters of CNTs, contributing to a higher conductivity. But from the results of section 4.3, a similar interparticle distance was assumed.

If we assume that the CNTs are better dispersed in PC than in PU, that they form tiny well dispersed clusters in PC but larger bundles or agglomerates

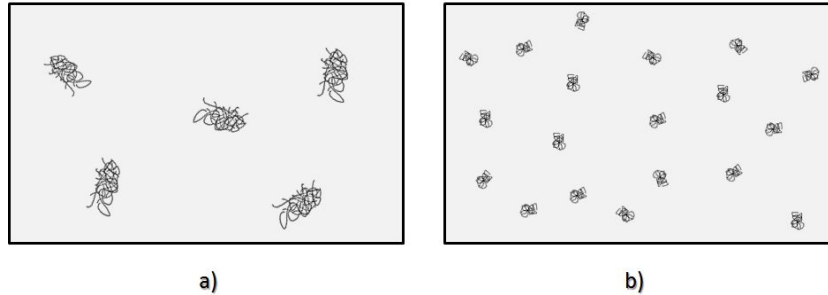


Figure 4.46.: *Illustrative (simplified) drawing of a system containing large agglomerates of CNTs (a) and a system with tiny CNT clusters (b), both having the same total CNT loading, the CNT length scale is exaggerated for illustrative purposes.*

in PU, the dimensions of the tiny clusters in PU several orders of magnitude smaller than the size of the bundles in PC. The percolation would be expected to be lower in PC than in PU. But from the DC measurements, percolation depended on the position of the electrodes in the sample. This low percolation threshold would not then be the sign of an improved dispersion. However, if a lower threshold is considered to be related to weaker polymer-CNT interactions, as in [2], then the lower percolation threshold observed in PC samples could indicate weaker CNT-polymer interconnections.

The dielectric constant as a function of frequency from samples having similar CNT contents but different polymer matrices is shown on Fig. 4.48. Again the values for both series of PU composites are nearly identical, taking into account the difference in CNT loading of the two samples below the percolation threshold. The three samples with 1 wt% CNT content have a very similar dielectric constant, and if the decrease of the 2 wt% PC is extrapolated, at high frequency the three 2 wt% samples could also exhibit a similar dielectric constant. However this is in contradiction with the hypothesis of the large CNT bundles in PC and the tiny clusters in PU, even though it was in good agreement with the LCR measurements. The cause of the significant difference in dielectric constant at high CNT loading observed on Fig. 4.45 cannot be explained by the latter hypothesis either.

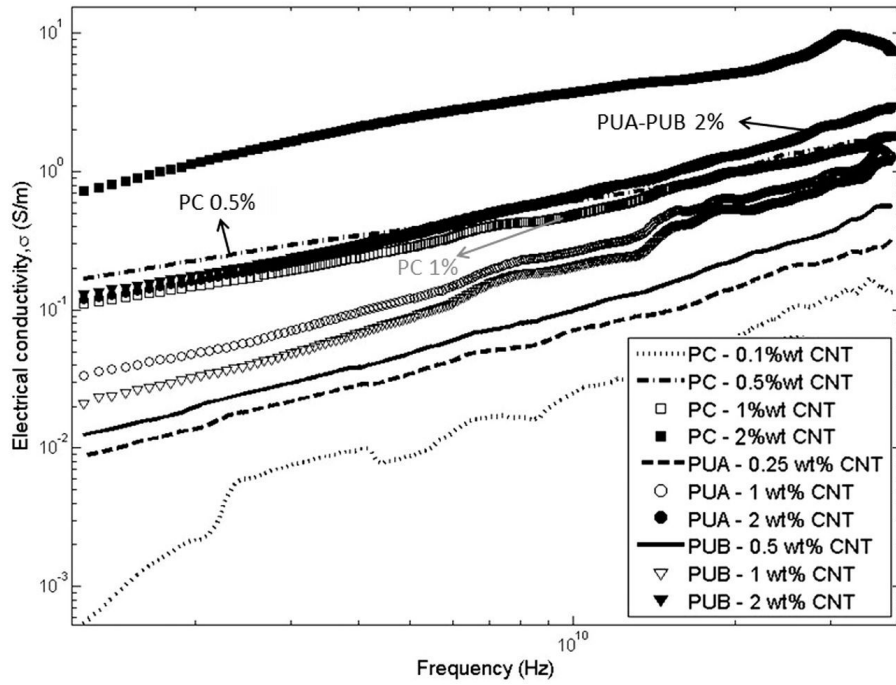


Figure 4.47.: Measured electrical conductivity as a function of frequency for PC and PU samples having similar CNT contents.

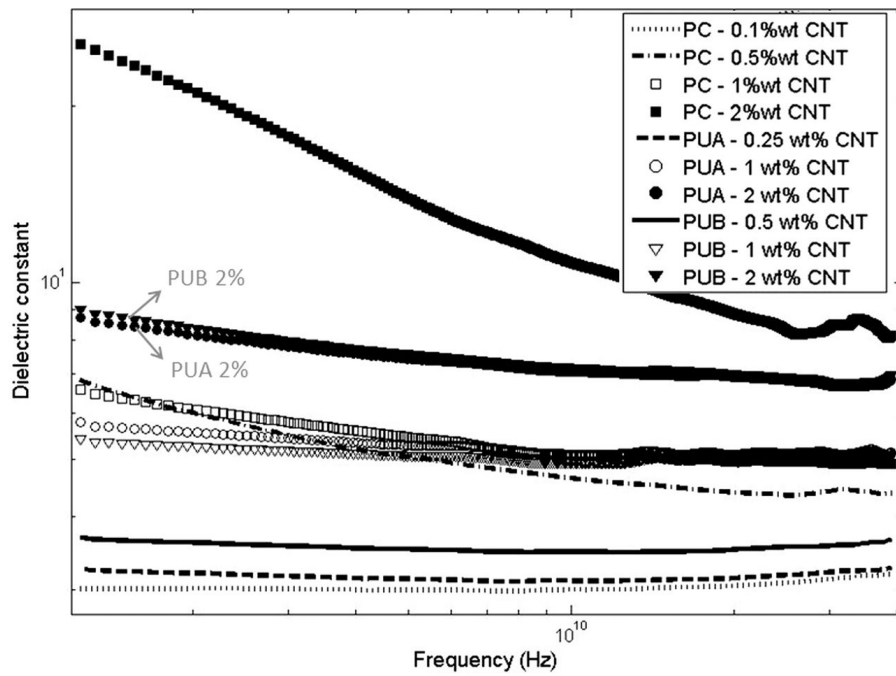


Figure 4.48.: Measured dielectric constant as a function of frequency for PC and PU samples having similar CNT contents.

4.5.4 Correlation with SEM pictures

In the previous section, the electrical characterisation results were discussed assuming a better dispersion of CNTs in the PC samples and larger bundles or agglomerates of CNTs in PU samples. This hypothesis can be confronted to pictures obtained using scanning electron microscopy (SEM). These images are difficult to obtain because the polymer material is insulating and leads to a very fast charging of the sample under the applied electric field of the SEM probe. Also, the outer surfaces of the samples were smooth and no CNT could be seen near the surface. The samples had to be cut (room temperature) and observed in their cross-section in order to find the CNTs. The exposed surface is then rather rough and deformed and the images are difficult to compare. Besides, the PC samples were best seen under a 1kV bias and stronger fields often lead to an immediate charging of the sample whereas a 3kV field was necessary to obtain clear, focused pictures of the PU samples. The charging effect and the deformations of the cross-section surface are visible on Fig. 4.49.

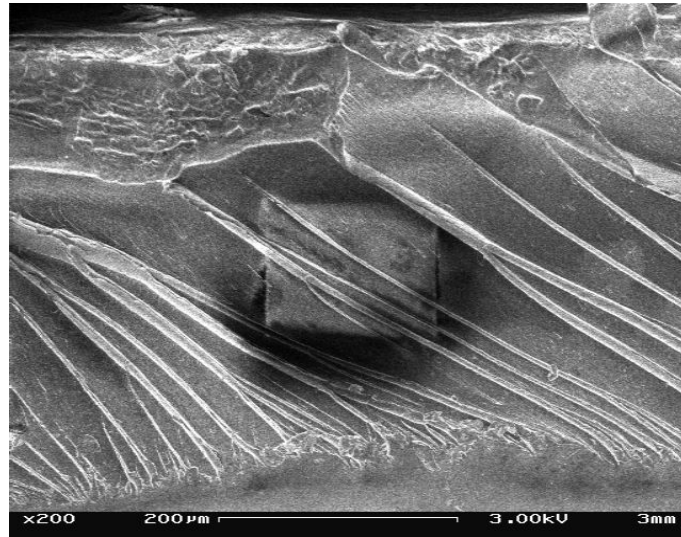


Figure 4.49.: SEM picture of the sample NQ03 cross-section (PC with 0.5wt% CNT), under a 3kV electric field. The roughness of the surface and the charging of the sample are visible.

Despite these difficulties, SEM pictures of the PC samples above the percolation threshold, cf. Fig. 4.50 and Fig. 4.51, showed reasonably well dispersed CNTs¹⁹. While those of the PU samples, even harder to obtain, showed what could be large aggregates of CNTs, as can be seen on Fig. 4.52. The darks areas on Fig. 4.53 are probably volumes devoid of CNTs in the PU, further confirming the better dispersion of the CNTs in the PC samples than in the PU ones.

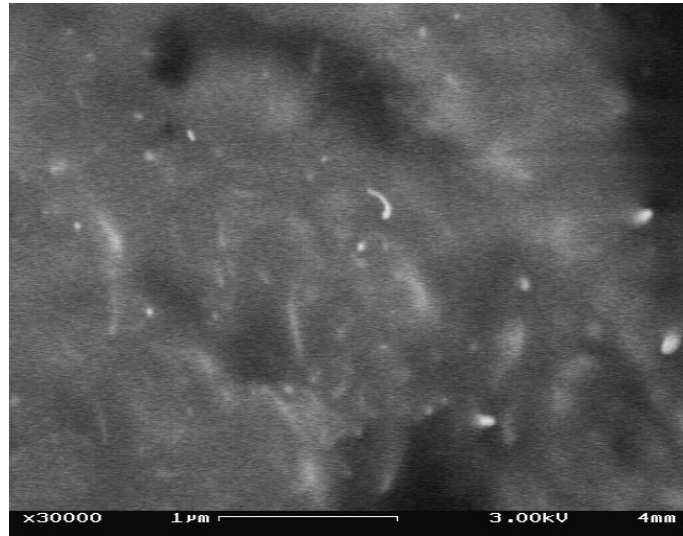


Figure 4.50.: SEM picture of the sample NQ05 cross-section (PC with 2wt% CNT), under a 3kV electric field. Individual CNTs are visible.

It must also be kept in mind that these pictures are a very local image of the dispersion, the dimensions of the sample being considerably larger than the scale of the picture. On the opposite, the electrical characterisation results yield a more global ‘image’ of the dispersion of the CNTs throughout the entire material²⁰.

¹⁹Though the two pictures showed surfaces with a very different aspect that may be due to difference in the mechanical method used to cut them.

²⁰Actually they yield a global picture of the *active* area or volume between the electrodes.

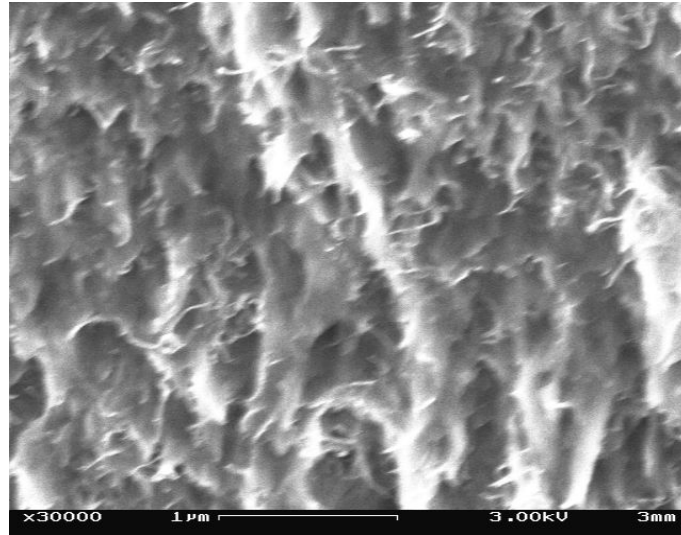


Figure 4.51.: SEM picture of the sample NQ10 cross-section (PC with 4wt% CNT), under a 3kV electric field. The tiny threads that are visible are CNTs.



Figure 4.52.: SEM picture of the sample NQ24 cross-section (PU series A with 1wt% CNT), under a 3kV electric field. The little white dots are most probably CNTs or pieces of CNTs, they are regrouped in agglomerates and there are volumes of material devoid of CNTs (dark areas).



Figure 4.53.: SEM picture of the sample NQ29 cross-section (PU series A with 2wt% CNT), under a 3kV electric field. The little white dots are most probably CNTs or pieces of CNTs, there are volumes of material devoid of CNTs (dark areas).

4.5.5 Comparison with the DC and 1kHz-1MHz LCR characterisation

The DC results, cf. section 4.3, those obtained using the low frequency LCR technique, cf. previous section, and the microwave characterisation must be compared in order to assess the adequacy between the measurement techniques. Furthermore the results in different frequency ranges can further validate one another or also yield information on different properties or behaviours of the material characterised.

The DC values of the electrical conductivity of the PC nanocomposites and those obtained with the LCR technique (between 1kHz and 1MHz), in the lower frequency region, are plotted on Fig. 4.54. The DC and low frequency values are in good agreement, especially for very low and very high CNT loadings. The adequacy between the DC and low frequency values of the conductivity is even better for the PU composites, as can be seen on Fig. 4.55 and Fig. 4.56. Though the dotted lines are only a guide to the eye, the DC values seem in good agreement with the behaviour of the low frequency curves if they could be extrapolated to $\omega = 0$.

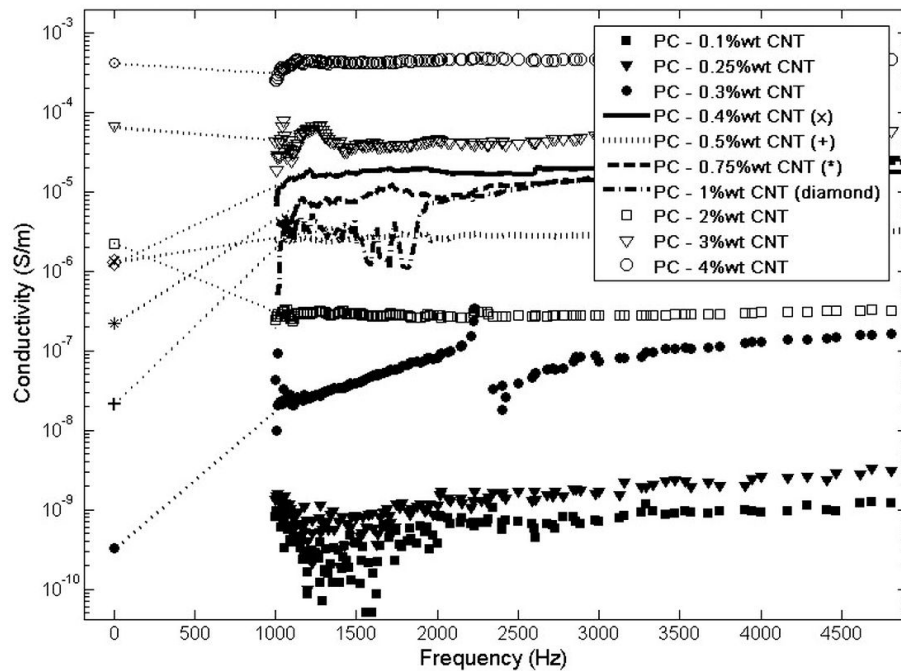


Figure 4.54.: Electrical conductivity as a function of frequency for the PC samples with increasing CNT contents (dotted with markers), measured using the DC and the low frequency LCR technique, the dotted lines are a guide to the eye.

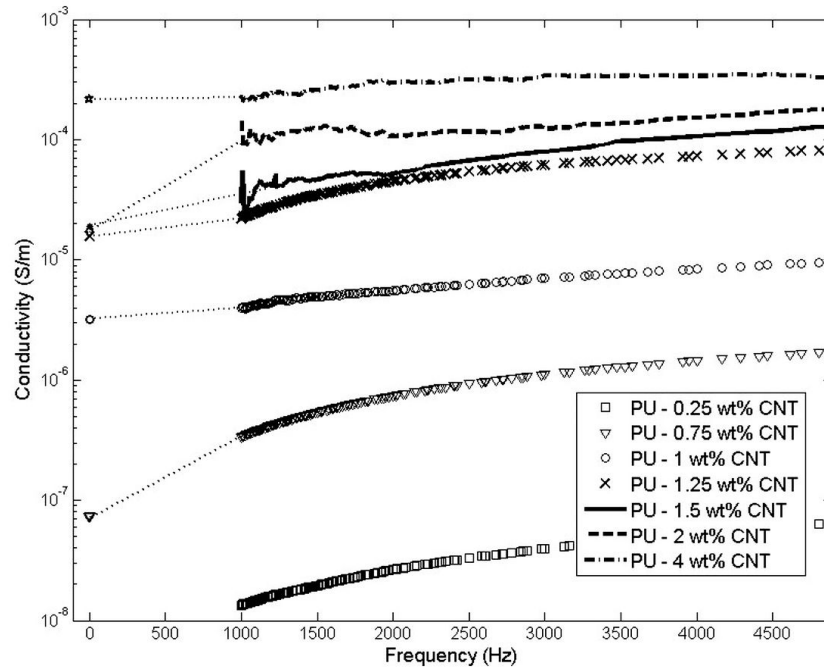


Figure 4.55.: Electrical conductivity as a function of frequency for the PU samples of series A with increasing CNT contents (dotted with markers), measured using the DC and the low frequency LCR technique, the dotted lines are a guide to the eye.

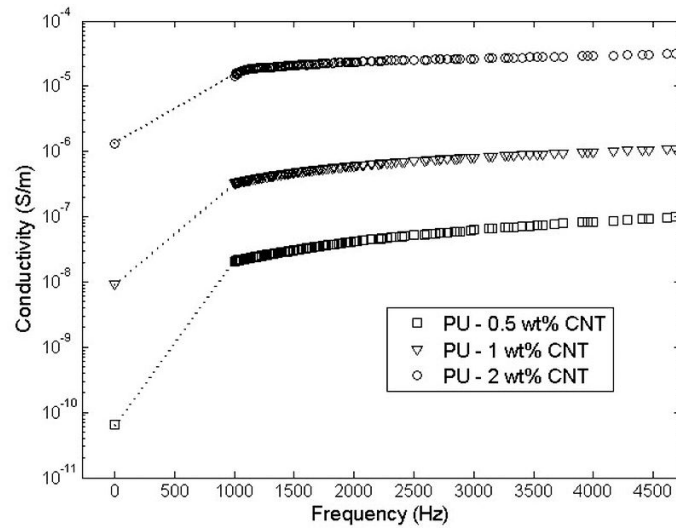


Figure 4.56.: *Electrical conductivity as a function of frequency for the PU samples of series B with increasing CNT contents (dotted with markers), measured using the DC and the low frequency LCR technique, the dotted lines are a guide to the eye.*

The conductivities of the PC samples obtained using both LCR and microwave techniques are plotted versus frequency on the same graph on Fig. 4.57. The orders of magnitude of the results from the two techniques are in very good adequacy and the general shape of the curves is coherent²¹. However the relative positions of the curves of samples with different filler contents are not in agreement, e.g. the 2 wt% CNT. The conductivity of the latter sample at high frequency is one of the highest while at low frequency it is almost similar to that of samples still close to the percolation threshold. This can be explained keeping in mind the reproducibility issue, especially important in the case of the PC composites discussed in section 4.3 and section 4.5.

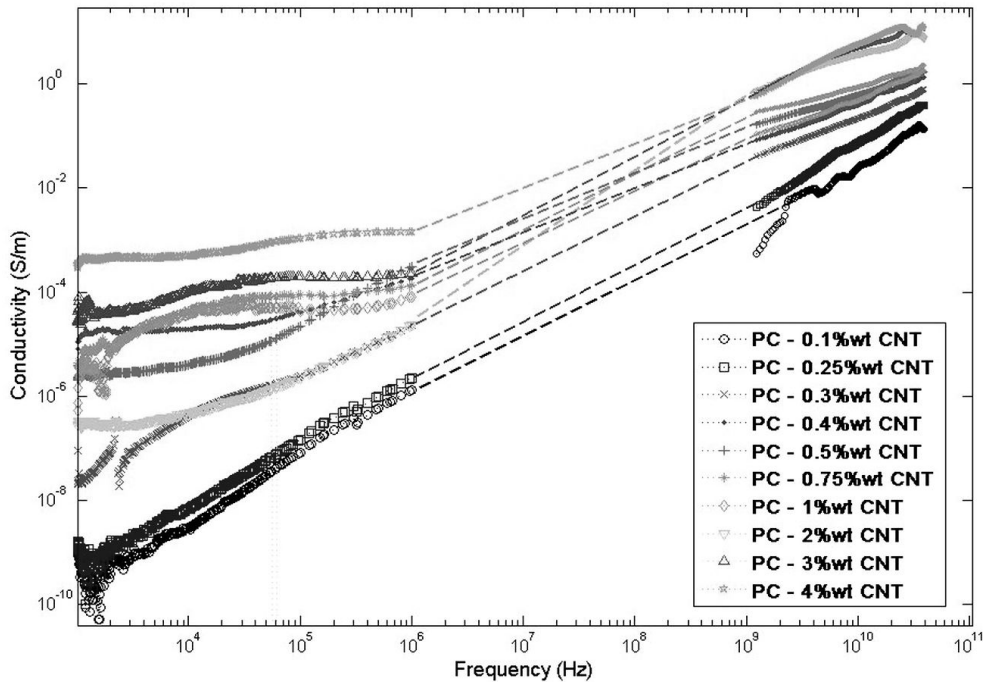


Figure 4.57.: Electrical conductivity as a function of frequency for the PC samples (dotted with markers), measured using the low frequency LCR technique and with the one-line microstrip high frequency method, the dotted lines are a guide to the eye.

²¹Given the different frequency and conductivity scales of the different measurements, it is not easy to differentiate them all from a single plot but the most important is the behaviour of the dashed line joining the two sets of measurement, whether they are parallel or they intersect. In the former case, the two sets can be considered as coherent, in the latter they cannot.

The dielectric constant values of the PC samples measured using both techniques are plotted as a function of frequency on Fig. 4.58. The order of magnitude of both type of results is in very good agreement, with the exception of the position of the curves relative to one another, as for the conductivity results of the PC samples.

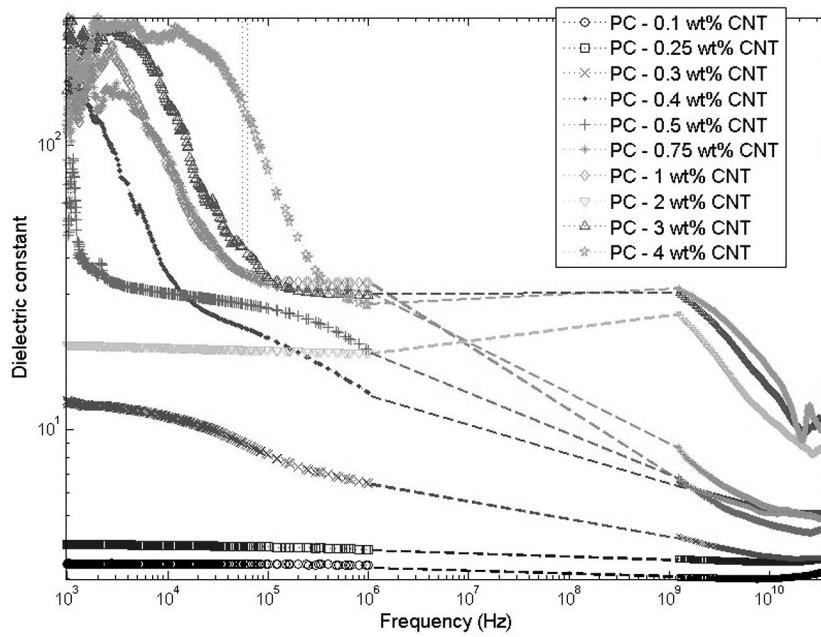


Figure 4.58.: Dielectric constant as a function of frequency for the PC samples (dotted with markers), measured using the low frequency LCR technique and with the one-line microstrip high frequency method, the dotted lines are a guide to the eye.

The electrical conductivity and dielectric versus frequency plots of the PU samples (series A), obtained using the low frequency and the microwave measurements method, are shown on Fig. 4.59 and Fig. 4.60, respectively. The agreement between results using both techniques is even better than in the case of the PC samples, qualitatively and quantitatively.

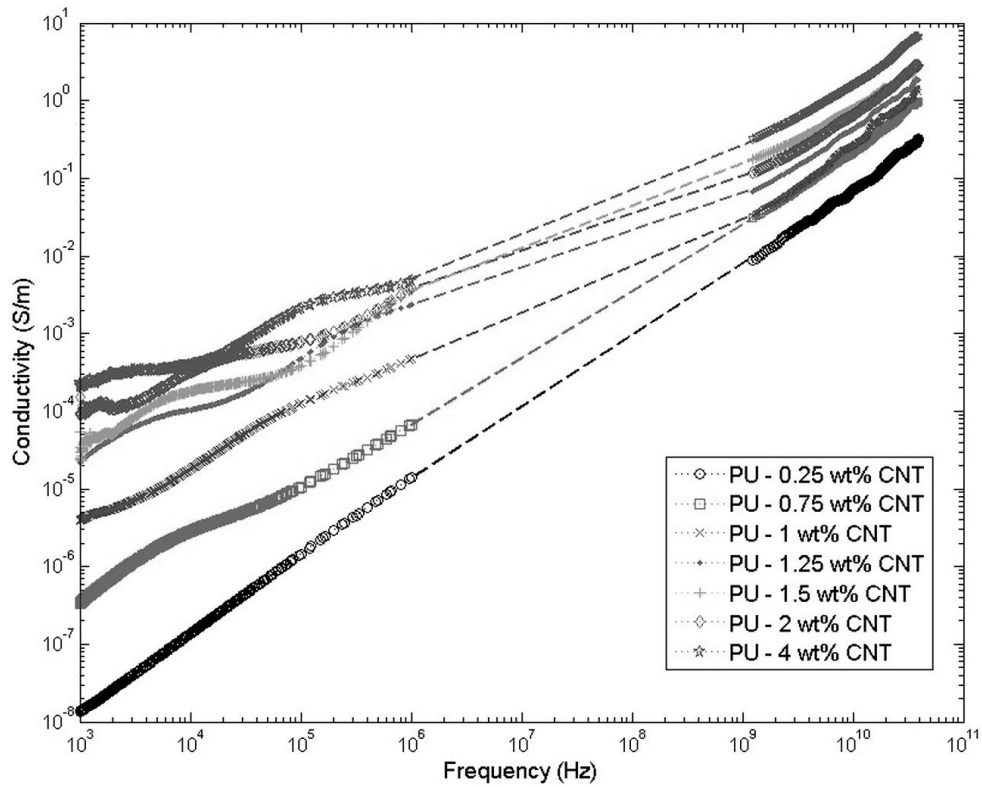


Figure 4.59.: Electrical conductivity as a function of frequency for the PU series A samples (dotted with markers), measured using the low frequency LCR technique and with the one-line microstrip high frequency method, the dotted lines are a guide to the eye.

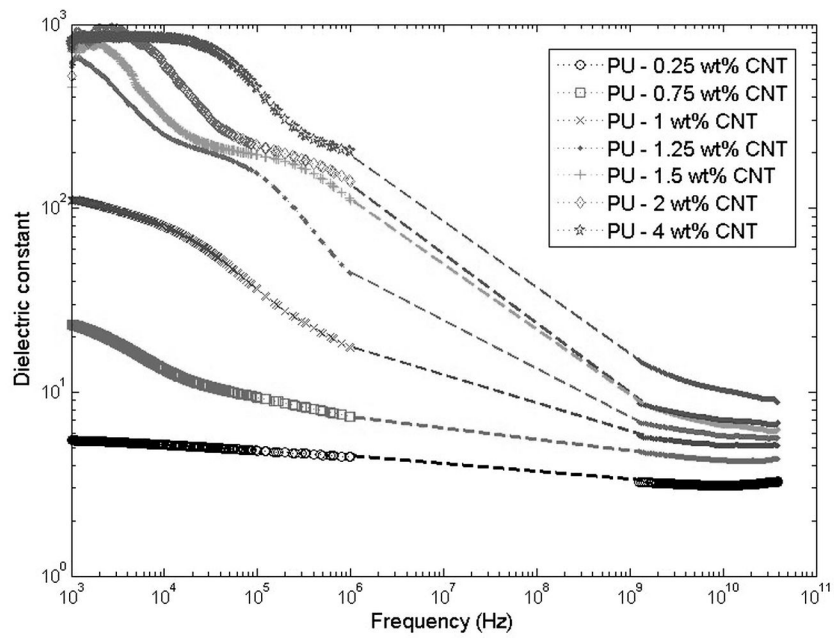


Figure 4.60.: Dielectric constant as a function of frequency for the PU series A samples (dotted with markers), measured using the low frequency LCR technique and with the one-line microstrip high frequency method, the dotted lines are a guide to the eye.

As for the series A samples, the PU series B nanocomposites results using the microwave technique are in very good qualitative and quantitative agreement with those obtained using the lower frequency LCR method.

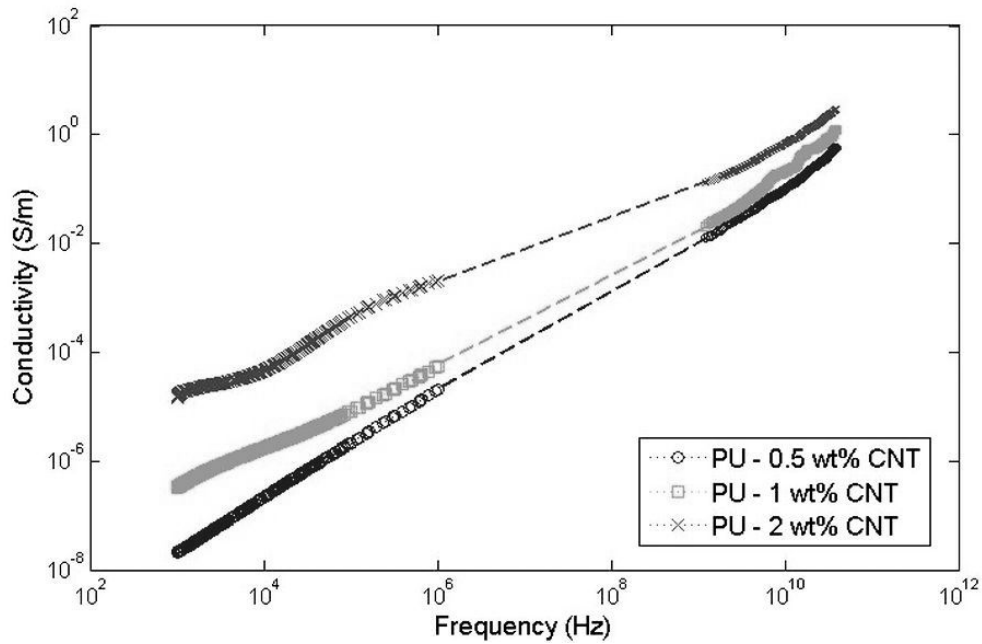


Figure 4.61.: Electrical conductivity as a function of frequency for the PU series B samples (dotted with markers), measured using the low frequency LCR technique and with the one-line microstrip high frequency method, the dotted lines are a guide to the eye.

As mentioned when examining the dielectric constant microwave measurements, nanocomposite samples with filler content below the percolation threshold exhibit a constant value throughout the 40 MHz - 40 GHz range. The dielectric constant of the PC sample with the lowest filler fraction (0.1 wt%) is of about 3.0 while the corresponding PU series A and series B samples had values of 3.2 and 3.5, respectively. From LCR measurements, cf. Fig. 4.25, the corresponding dielectric constant values were: 3.3, 4.4 and 5.0, respectively. The same PTFE sheet was characterised using the two techniques and both yielded accurate results. The experimental technique is therefore not responsible for this significant decrease. A partial explanation might reside in the known decrease of the dielectric constant of dielectric materials at very high frequency, above 1 GHz, [14].

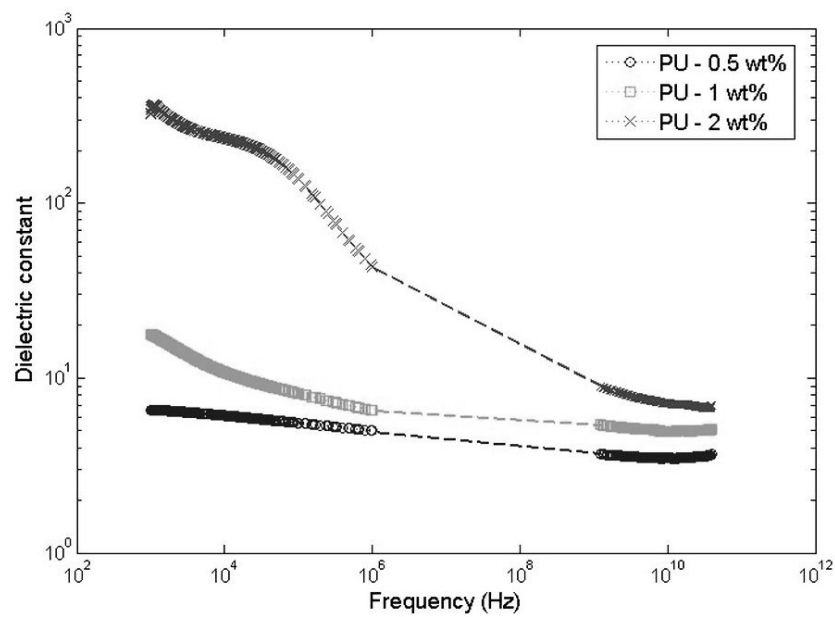


Figure 4.62.: Dielectric constant as a function of frequency for the PU series B samples (dotted with markers), measured using the low frequency LCR technique and with the one-line microstrip high frequency method, the dotted lines are a guide to the eye.

The main advantage of the microwave technique over the LCR low frequency method is its much improved reproducibility. Besides, the shape of the curves in the microwave region leads to an easier interpretation and comparison between the samples, both on their conductivity or dielectric constant. When confronted with large sets of samples to characterise, the microstrip method is much faster than the LCR technique. Only one measurement is enough for each samples (instead of having to average over several results for the low frequency method) and a single measurement with the VNA (microwave) is already faster than using the LCR.

Besides as the distance travelled by charge carriers is inversely proportional to the frequency, the conductivity obtained using high frequency measurements is an image of the dispersion of small conductive clusters in the material, whereas the conductivity extracted from lower frequency characterisation relates to larger aggregates allowing greater travel paths for the charge carriers. If both methods yield different results and little adequacy it is a good hint at a poor dispersion of the CNTs as the small clusters do not interconnect to form an extended network. In this aspect the methods are complementary.

4.6 COMPARISON BETWEEN RHEOLOGICAL AND ELECTRICAL CHARACTERISATIONS

As detailed in chapters 2 and 5, a good dispersion of the CNTs inside the polymer matrix is the key parameter for the conductivity of the nanocomposites, even for their mechanical properties. The mean distance between two CNTs should also be as small as possible. But raw CNTs, before they are incorporated in the polymer matrix, are entangled and tend to stick to one another, as confirmed by the Transmission Electron Microscope (TEM) picture shown on Fig. 4.63.

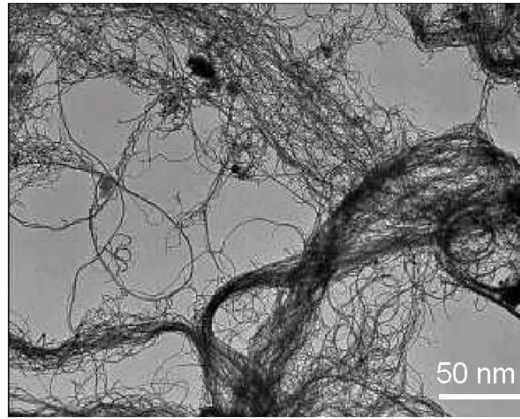


Figure 4.63.: TEM picture of raw MWNT before they are incorporated into the polymer matrix, from [15].

Rheological measurements can also be used to assess the dispersion of the CNTs, in particular the (oscillatory) frequency dependence of the dynamical complex modulus G^* , which is the ratio of stress to strain when a sinusoidal stress or strain is applied to the sample (Dynamical Mechanical Analysis or DMA), [15], the actual value of G^* depends on the microstructure of the material, [16]. For elastic materials, G^* is real; the response to the sinusoidal strain is also sinusoidal and in-phase with the stimulus. For visco-elastic materials like the polymers presented in this thesis, G^* is complex; the response is also sinusoidal but with a phase shift. The real part (G') of the dynamical modulus is the in-phase, elastic, response of the material, while the imaginary part (G'') is the out-of-phase, viscous response. G' is also called the storage modulus and G'' the loss modulus. In polymers such as PCL or PS, an increase of G' with CNT content at low frequency confirms the presence of mobile and flexible chains that are partially bound together by bridging structures, in this case the CNTs.

The storage modulus G' is plotted versus oscillatory frequency (ω) on Fig. 4.64 for poly(ether ether ketone), or PEEK, MWCNT composites, [16]. Two different behaviours can be observed; pure PEEK exhibit a linear dependence to ω^2 , also

called ‘terminal behaviour’ (or liquid-like behaviour), on the other hand the curves for high content composites are very different, the G' values are higher at low frequency and a ‘plateau’ can be observed (solid-like behaviour), [17]. This latter behaviour indicates that a network of CNTs exist in the material and that it limits the mobility of the matrix molecules. The transition from one type of behaviour to the other is defined as the *rheological percolation*. It must be noted that even if there is no low-frequency plateau yet, even the lowest filler content nanocomposites deviate from the terminal behaviour of the pure polymer. Meaning that already at those low filler contents, the CNTs restrict the mobility of the matrix but only locally that of individual chains. At the percolation threshold, these restrictions interact and the phenomenon is no longer local but global.

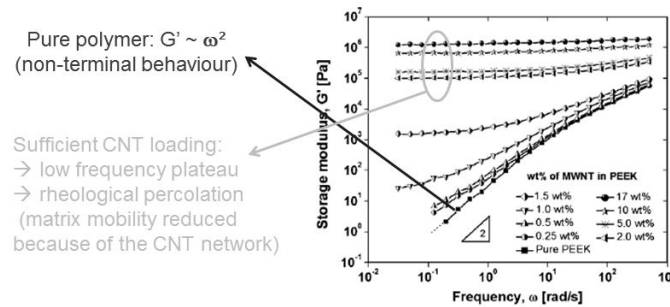


Figure 4.64.: Storage modulus versus oscillatory frequency for pure PEEK and PEEK-based CNT composites (with filler contents from 0.25 % to 17 %) , from [16].

The question arises as whether this rheological percolation threshold and the electrical are the same. They are due to the same phenomenon, the apparition of a regular, well-connected CNT network but rheological and electrical mechanisms are not identical and even if these percolations are quite logically related they might not be strictly equal. It is therefore interesting to compare experimental results.

The real part of G^* is plotted versus frequency for two sets of PS (polystyrene) and PCL (poly- ϵ caprolactone) based nanocomposites, with and without CNTs, on Fig. 4.65. The presence of a plateau at low frequency for the PCL samples containing CNTs is characteristic of the existence of a rheological percolation threshold, beyond which the CNTs form a network throughout the polymer matrix, cf. Fig. 4.65(left).

On the contrary, there is little difference between the G' versus frequency curve for the PS sample with 1 % CNTs and the one for pure PS, cf. Fig. 4.65(right). It means that the nanoparticles do not form a regular extended network inside the PS matrix.

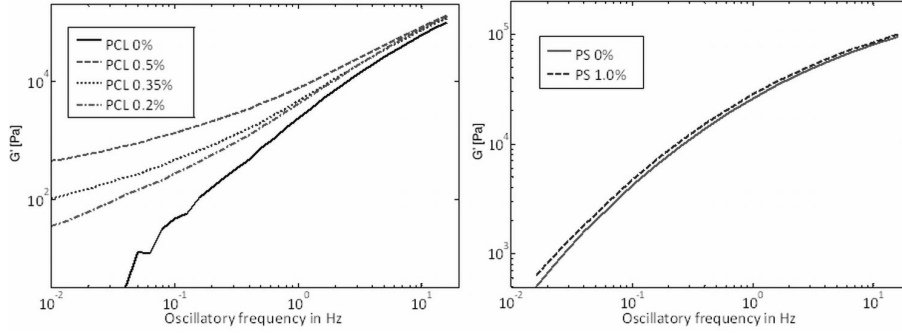


Figure 4.65.: Dynamical storage modulus (G') versus oscillatory frequency for PCL and PS based nanocomposites, with and without CNTs, from [15].

These conclusions based upon rheological considerations are confirmed by measurement of the electrical conductivity. The conductivity of the PCL nanocomposite with a 0.35 % CNT content and of the PS one with a concentration of 1 % are plotted versus frequency on Fig. 4.66. These measurements were made in the 40 MHz - 40 GHz range, using the One-Line microstrip technique, cf. section 3.3.1. The PCL composite has a much higher conductivity than the PS one, confirming the presence of a conductive network in the former and not in the latter. This is further confirmed by TEM pictures, cf. Fig. 4.67. The CNTs in the PCL sample seem well dispersed forming an extensive network while those in the PS composite are regrouped in distinct aggregates over 1 μm apart.

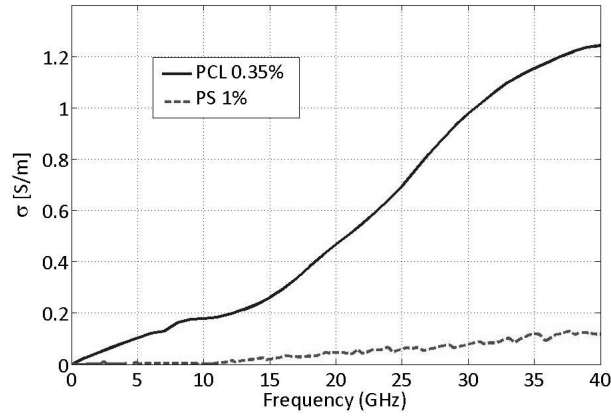


Figure 4.66.: Measured electrical conductivity versus frequency of the PCL composite containing a 0.35 % CNT content and of the PS sample with a 1 % CNT content, from [15].

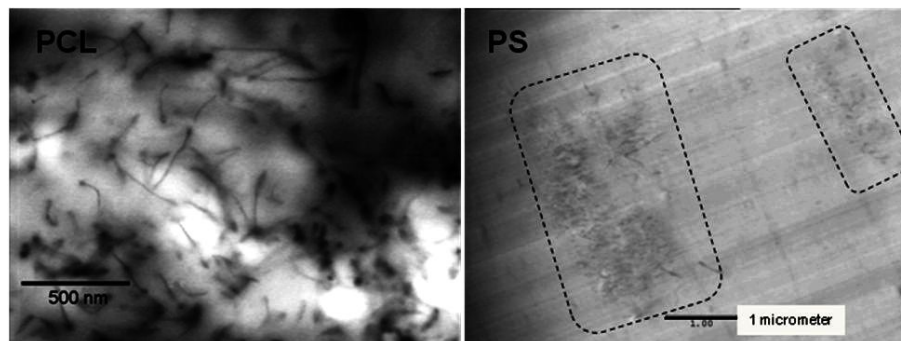


Figure 4.67.: TEM pictures of the PCL (left) and PS (right) nanocomposites, from [15].

The previous results show a good qualitative agreement between rheological and electrical characterisation but not on the actual values of the corresponding percolation thresholds. In the literature, nanocomposites usually exhibit a higher electrical percolation (p_{cE}) compared to the rheological one (p_{cR}), e.g. $p_{cE} = 0.9$ wt% and $p_{cR} = 1.3$ wt% for the PEEK composites in [16]. This difference might be explained considering the mean distance between CNTs and that the percolation threshold is inversely proportional to this distance (and the mean distance between CNTs decrease as the CNT loading is increased). Rheological percolation occurs when the regions where the motion of the polymer molecules is restricted begin interacting, i.e. when the mean distance between CNTs becomes smaller than the radius of gyration²² of these molecules. As for the electrical percolation the required mean distance is most probably the one required for the tunnelling or hopping through the barrier between neighbouring CNTs. The latter has been evaluated at about 5 nm in the case of the PEEK composites while the radius of gyration of the PEEK chains in the composites has been measured to around 20 nm. The mean distance for electrical percolation is thus smaller than that for rheological percolation, in good agreement with the observed values of percolation thresholds, [16]. However, the radius of gyration is four times as long as the tunnelling length but the electrical percolation threshold is not four times as high as the rheological threshold.

In [17], the authors observed a strong dependence of the rheological percolation threshold that is not strictly coherent with the a rheological behaviour dependent only on the formation of a CNT network. They consider the CNT composites to be composed of, in fact, three distinct networks; (i) the temporary polymer network (from entanglements), (ii) the CNTs network and (iii) a combined polymer-nanotube network, as illustrated on Fig. 4.68.

²²The radius of gyration is the characteristic length of a polymer molecule, it is proportional to the root mean square distance between the monomers.

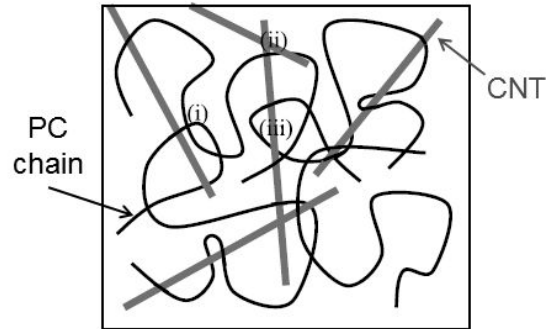


Figure 4.68.: Illustration of the different network inside the PC composites: (i) temporary polymer-polymer network, (ii) nanotube-nanotube network, (iii) combined polymer-nanotube network, from [17].

The electrical percolation is basically a geometrical percolation (for a more detailed discussion on the nature of the electrical percolation and the phenomenon that have to be taken into account like tunnelling, hopping processes, etc. see chapter 2) and therefore dominated by the all CNTs network. On the other hand, if there are polymer chains in the gaps between CNTs then it can be assumed that the rheological percolation threshold is not dominated by the nanotube network but rather by the temporary polymer network and the combined polymer-CNT one. Considering polymer-CNT connections to be more stable than polymer-polymer connections (larger disentanglement time) explains the presence of the plateau in the low frequency region of the storage modulus curves, [17]. This leads to the same conclusion as [16], that a lower CNT content is needed to form a ‘rubber-elastic’ network composed of CNT-polymer-CNT connections that it would be required for a purely geometrical network. This three networks model also explains why the storage modulus curves deviate from the pure polymer one even at very low content. Some continuous network of CNTs and polymer chains could already appear but it would be very weak bindings and the plateau value would be small. It also explains the temperature dependence observed in [17].

From the latter considerations, the rheological percolation would be more related to that of the behaviour of the nanocomposite dielectric constant as a function of frequency rather than to the DC geometrical percolation.

4.7 CONCLUSIONS

A wideband electrical characterisation of solid nanocomposite samples has been made, from DC to 40 MHz. Different measurement methods had to be used but the results from these different techniques and frequency ranges are in quite good adequacy. The nanocomposite samples were based on two different polymer matrices, polyurethane and polycarbonate, and had CNT loadings from 0.1 to 4 wt% CNT. The PU samples were separated in two series based on differences in processing conditions.

The composites were first characterised in DC regime, the conductivity versus filler content curves were fitted using the well known scaling law $\sigma = A \cdot \exp(\varphi - \varphi_c)^t$ from the literature and their percolation thresholds were extracted from these fitting laws. The percolation thresholds in PC and PU (both series) were of about 0.3 and 0.7 wt% CNT, respectively. The critical exponent t is close was found to be in most cases close to the theoretical value for 3D percolation systems.

It was speculated that the lower percolation threshold in PC than in PU with comparable maximum conductivity values for high CNT loadings would mean the CNTs are better dispersed in PC but that for high loadings the mean distance between CNTs would be comparable. But the results are not all leading to the same conclusion and the significant error margin of our measurement must be taken into account.

A linear relationship between $\ln \sigma_{DC}$ and $\varphi_c^{-1/3}$, characteristic of the thermal fluctuation induced tunnelling model, was observed. Confirming the hopping of charge carriers through potential barriers of varying heights between the CNTs.

A low frequency (1 kHz - 1 MHz) characterisation technique was then used to investigate the frequency behaviour of the nanocomposites. The main issue with those measurements, as with the DC ones, lies in their significant lack of reproducibility, significantly worse in the case of the PC samples than for the PU ones. This could be improved by conducting the measurement in a 'dry' environment, such as a vacuum or nitrogen-filled chamber.

However, different behaviours were observed for all samples, depending whether their filler content was above or below the percolation threshold (same value as the one calculated from the DC measurements). Below the threshold the conductivity of the samples exhibit a power law dependence of the form $A\omega^s$ and a constant dielectric constant on the entire frequency range. Above the threshold, a constant value (DC plateau) is observed for the conductivity at low frequency and at higher frequency a power law dependence, $A\omega^s$, is also observed.

On the other hand, the dielectric constant exhibits first a sharp decrease then reaches a plateau at higher frequency. The values of the s exponent were

extracted and most of them were closed to the theoretical expected range of $0.8 - 1$. For high filler loadings, the conductivity of the PU samples is higher than that of the PC composites, in contrast with the lower threshold of PC nanocomposites.

No definite answer could be provided, yet it lead to some very interesting speculations.

The samples were also characterised at microwave frequencies, in the 40 MHz-40 GHz range. The reproducibility was significantly improved compared to the DC and low frequency techniques. Probably because the DC and low frequency percolation threshold is a very local phenomenon, depending on the macroscopic distribution of the CNTs while at higher frequency the distance travelled by the charge carriers is much reduced and a better image of the microscopic structure.

It also allowed us to make interesting hypotheses on the dispersion and agglomeration of the CNTs in the different polymer matrices. It was speculated that the CNTs formed larger aggregates in the PU samples than in the PC ones, though it would need confirmation using other characterisation techniques. These hypotheses were confronted to some SEM pictures and the shape of the low frequency curves was tentatively explained using multiple relaxation times.

The conductivity of all the samples, PC and PU with different CNT loadings, had the same power law dependence $A\omega^s$, but this time the s values were almost all in the $0.8 - 1$ range characteristic of the hopping of charge carriers through a disordered system. The dielectric constant of all of the nanocomposites, except for the most conductive samples, had a constant value on the entire frequency range. The highly conductive samples exhibited first a rather sharp decrease with increasing frequency.

The adequacy between the microwave results and those from lower frequency characterisation was very good, especially in the case of the PU samples. However contrary to lower frequency measurements the PC samples have a significantly higher conductivity at microwave frequencies than the PU composites.

Another characterisation method used for nanocomposite materials is the rheological characterisation, more exactly to assess the dispersion of the material by considering the CNTs or CNT bundles are rather rigid 'bridges' between the polymer molecules. Below percolation the composite has an elastic or liquid-like behaviour while above the threshold the behaviour is close to that of a rigid solid sample. The characteristic feature of the latter behaviour is the low oscillatory frequency plateau that can be observed in the storage modulus versus oscillatory frequency plots.

The rheological percolation threshold and the electrical are due to the same phenomenon but rheological and electrical mechanisms are not identical and even if these percolations are strongly logically related they might not be strictly equal. These considerations led to the assumption of a third network, besides the

CNT/CNT and polymer networks, inside polymer nanocomposites, a combined polymer-CNT networks. This is analogous to the capacitive behaviour of the samples, related to the CNT-polymer-CNT interfaces.

Even though the different characterisation techniques and different frequency bands yielded significant differences in the results. They also presented a very good adequacy and they were even shown to be complementary, to validate or infirm hypothesis left open by another technique. In particular the specific advantages provided by the microwave measurement are highlighted. Besides this wideband characterisation is part of an on-going cooperation with the material engineers who fabricate the nanocomposite to help create a material with tailored characteristics and especially well suited to a particular application²³. Many possible explanations were presented but many questions are still not completely answered and more thorough investigations would be required to attempt to answer them with more certainty.

²³In a kind of ‘retro-simulation’ procedure.

Bibliography

- [1] W. Hsu, V. Kotseva, P. Watts, and G. Chen, "Circuit elements in carbon nanotube-polymer composites," *Carbon*, vol. 42, no. 8-9, pp. 1707–1712, April 2004. 114
- [2] H. So, J. Cho, and N. Sahoo, "Preparation and properties of the polyimide/multi-walled carbon nanotubes (mwnts) nanocomposites," *Composites Science and Technology*, vol. 66, no. 3-4, pp. 548–554, March 2006. 122, 134, 147, 169
- [3] J. Sandler, M. Shaffer, T. Prasse, W. Bauhofer, K. Schulte, and A. Windle, "Development of a dispersion process for carbon nanotubes in an epoxy matrix and the resulting electrical properties," *Polymer*, vol. 40, no. 21, pp. 5967–5971, October 1999. 124
- [4] H. So, J. Cho, and N. Sahoo, "Effect of carbon nanotubes on mechanical and electrical properties of polyimide/carbon nanotubes nanocomposites," *European Polymer Journal: Macromolecular Nanotechnology*, vol. 43, no. 9, pp. 3750–3756, June 2007. 134
- [5] S. Barrau, P. Demont, A. Peigney, C. Laurent, and C. Lacabanne, "Dc and ac conductivity of carbon nanotubes-polyepoxy composites," *Macromolecules*, vol. 36, no. 14, pp. 5187–5194, June 2003. 140, 141, 142
- [6] V. Daniel, *Dielectric Relaxation*. London: Academic Press Inc., 1967. 140, 141, 142, 143
- [7] B. Rigaud, J.-P. Morucci, and N. Chauveau, "Bioelectrical impedance techniques in medicine," *Critical Reviews in Biomedical Engineering*, vol. 24, no. 4-6, pp. 257–351, 1996. 143
- [8] P. Potschke, S. Dudkin, and I. Alig, "Dielectric spectroscopy on melt processed polycarbonate-multiwalled carbon nanotube composites," *Polymer*, vol. 44, no. 17, pp. 5023–5030, August 2003. 145
- [9] G. He, J. Zhou, K. Tan, and H. Li, "Preparation, morphology and properties of acylchloride-grafted multiwall carbon nanotubes/fluorinated polyimide composites," *Composites Science and Technology*, vol. 71, no. 16, pp. 1914–1920, November 2011. 147
- [10] K. Ahmad, W. Pan, and S.-L. Shi, "Electrical conductivity and dielectric properties of multiwalled carbon nanotube and alumina composites," *Applied Physics Letters*, vol. 89, no. 13, p. 3p, September 2006. 152
- [11] J. Wu and D. McLachlan, "Scaling behavior of the complex conductivity of graphite-boron nitride percolation systems," *Physical Review B*, vol. 58, no. 22, pp. 14 880–14 887, December 1998. 152

- [12] L. Wang and Z.-M. Dang, "Carbon nanotube composites with high dielectric constant at low percolation threshold," *Applied Physics Letters*, vol. 87, no. 4, p. 3p, July 2005. 152
- [13] B. Kilbride, J. Coleman, J. Fraysse, P. Fournet, M. Cadek, A. Drury, S. Hutzler, S. Roth, and W. Blau, "Experimental observation of scaling laws for alternating current and direct current conductivity in polymer-carbon nanotube composite thin films," *Journal of Applied Physics*, vol. 92, no. 7, pp. 4024–4030, October 2002. 168
- [14] S. Ramo, J. Whinnery, and T. V. Duzer, *Fields and Waves in Communication Electronics*. New York: John Wiley and Sons, Inc., 1993. 183
- [15] A. Saib, L. Bednarz, R. Daussin, C. Bailly, X. Lou, J.-M. Thomassin, C. Pagnouille, C. Detrembleur, R. Jerome, and I. Huynen, "Carbon nanotubes composites for broadband microwave absorbing materials," *IEEE Transactions on Microwave Theory and Techniques*, vol. 54, no. 6, pp. 2745–2752, june 2006. 186, 188, 189
- [16] D. Bangarusampath, H. Ruckdaschel, V. Altstadt, J. Sandler, D. Garraay, and M. Shaffer, "Rheological and electrical percolation in melt-processed poly(ether ether ketone)/multi-wall carbon nanotube composites," *Chemical Physics Letters*, vol. 482, no. 1-3, pp. 105–109, November 2009. 186, 187, 189, 190
- [17] P. Potschke, M. Abdel-Goad, I. Alig, S. Dudkin, and D. Lellinger, "Rheological and dielectrical characterization of melt mixed polycarbonate-multiwalled carbon nanotube composites," *Polymer*, vol. 45, no. 26, pp. 8863–8870, December 2004. 187, 189, 190

CHAPTER 5

EMI SHIELDING PROPERTIES OF POLYMER CARBON NANOTUBES COMPOSITES AT MICROWAVE FREQUENCIES

5.1 INTRODUCTION

The addition of nanoparticles having specific properties inside a matrix with different properties creates a novel material that exhibits mixed and even new properties, as detailed in chapter 2. The nanocomposites presented in this chapter combine the properties of *foamed* polymers (inexpensive, lightweight, easy to mould into any desired shape, etc.) with those of carbon nanotubes (CNTs). The addition of any conductive nanoparticles to an otherwise insulating matrix leads to a significant increase of the electrical conductivity. But CNTs having a very high aspect ratio, a much lower content of CNTs is therefore required to get the same conductivity increase as the one obtained with more compact nanoparticles.

This is especially interesting for *EMI (electromagnetic interferences) shielding materials* since, as will be explained in further details in this chapter, it is desirable for such materials to have a high conductivity but a low dielectric constant, in order to minimize the electromagnetic power outside the shield casing but also to minimize the power reflected back inside the casing, as is explained in section 5.2. In particular, two parameters of interest when comparing shielding materials are detailed and discussed.

The polymer/CNTs nanocomposites were fabricated and characterized using a two-step diagnostic method. They were first characterized in their solid form, i.e. before the foaming process, and the most interesting polymer matrices (with embedded CNTs) could be selected. This way, only the promising blends were foamed, therefore avoiding the unnecessary fabrication of a number of foams. These selected blends were foamed and then characterized. The samples, both solid and foamed, are described and their fabrication processes are briefly explained in sections 5.3 and 5.4. The solid (non-foamed) samples were characterized using the One-Line microstrip technique described in section 3.3.1 and the foams using the Line-Line methods, cf. sections 3.3.2 and 3.3.3.

Nanocomposite foams are not discussed extensively in the literature and, to the best of our knowledge, no simple or analytical model was designed especially for these foams. Numerical simulation tools must be used but given the different scales of the components, such simulations are rather complex and time-consuming¹. A simple electrical model modelling the measurement of the foamed samples is presented and explained in section 5.5. Measurement results are then compared to those obtained using this electrical model.

An optimized multi-layer foam topology, with an adequate electrical conductivity and a decreased dielectric constant (compared to monolayer foams) is proposed and discussed in section 5.6. A multiscale hybrid, a metallic honeycomb filled with a nanocomposite foam, with an even more improved reflectivity, that was patented, is then detailed in section 5.7.

These nanocomposite foams and their application as EMI shielding materials were actually the topic of a book chapter that I wrote in 2009, [2]. I have presented some of the results discussed in the current chapters in several conferences: [3–5]. I have collaborated and made measurements for several papers on this subject: [6–10] and, also some conference proceedings: [11–16]. The hybrid composite described in section 5.7 has been patented in 2010².

¹A case-study of numerical models of metal foams for EMI shielding applications can be found in [1].

²European Patent EP10175887 "Hybrid material for electromagnetic absorption", filed: 09 September 2010.

5.2 EMI SHIELDING CONSIDERATIONS

Electromagnetic interference (EMI) shielding refers to the protection of an object against electromagnetic radiation by using a material as ‘shield’ against those, by reflection or absorption of the waves³. For reflection or absorption of the EM radiations, the shielding material must contain mobile charge carriers, [17], it is therefore usually a rather conductive material. However, the electrical conductivity cannot be used as a scientific criterion for shielding. Indeed, it requires the existence of a conductive path through the material (percolation) but this is not necessary as the frequency increases, as detailed in chapter 4.

There are two main parameters that are used to characterize the quality of a shielding material in terms of electromagnetic power; the Shielding Effectiveness (SE) and the Reflectivity (R). The former relates the power that is transmitted through the material (P_{out}), cf. Fig. 5.1(left), to the incident power (P_{in}): $SE = 10\log(P_{in}/P_{out})$. The latter⁴ relates the power reflected back from the material (P_{ref}) to the incident power (P_{in}): $R = 10\log(P_{ref}/P_{in})$.

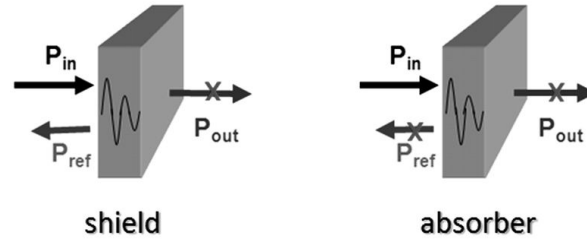


Figure 5.1.: Schematic diagrams for a conventional metallic shielding material (left) and for a microwave absorber (right), from [18].

The incident power is either reflected back, or transmitted through the material to the outer world, or absorbed inside the material, $P_{in} = P_{ref} + P_{out} + P_{abs}$, where P_{abs} is the power absorbed inside the material. $\sqrt{P_{abs}}$ is also called the attenuation and increases as the conductivity of the material increases. It also depends on the thickness of the material, [19].

The power absorbed by the material, P_{abs} can also be written as follows

$$P_{abs} = P_{in} - P_{ref} - P_{out} \quad (5.1)$$

³EMI shielding should not be confused with magnetic shielding, i.e. shielding of magnetic fields at low frequencies (~ 50 Hz and below), as the materials used and physical principles involved are very different.

⁴Rigorously, the reflectivity is measured from the reflected power but the opposite face of the sample must be backed by a metal sheet, as shown on Fig. 5.18.

where P_{in} is the incident power, P_{ref} is the reflected power and P_{out} is the total power transmitted through the sample. It can be directly obtained from S-parameters measurements as

$$P_{abs} = 1 - |S_{11}|^2 - |S_{21}|^2 \quad (5.2)$$

The parameter $A = P_{abs}/P_{in}$ quantifies the *absorption* of the material, [10]. The reflection (Γ) and transmission (T) coefficients are defined in chapter 3 as

$$\Gamma = \frac{\sqrt{\varepsilon_e} - 1}{\sqrt{\varepsilon_e} + 1} \quad (5.3)$$

$$T = \exp(-j\omega t\sqrt{\varepsilon_e}/c_0) \quad (5.4)$$

where $\varepsilon_e = \varepsilon_r - j\frac{\sigma}{\omega\varepsilon_0}$ is the complex effective permittivity, with ε_r the dielectric constant and σ the electrical conductivity, $\omega = 2\pi f$ the frequency and c_0 the velocity of light in vacuum.

The absorption parameter A can then be written as a function of those coefficients

$$A = 1 - \left| \frac{\Gamma(T^2 - 1)}{1 - \Gamma^2 T^2} \right|^2 - \left| \frac{T(1 - \Gamma^2)}{1 - \Gamma^2 T^2} \right|^2 \quad (5.5)$$

The details on the calculation of the former equation can be found in [10].

It is not always enough for a shielding material to exhibit a good SE, i.e. stopping power transmission to the outside world. For example, metallic materials have a high SE at high frequency but almost all the incident power is reflected back inside the shield casing (high R), possibly interfering with other inner elements (or even with the emitter itself). Materials that combine a high SE with a low R at microwave frequencies are called microwave absorbers, because the power is absorbed inside the material, as illustrated on Fig. 5.1(right). A material having a high SE must exhibit a high conductivity and, for a low R, it must also have a low dielectric constant (close to the 1 of air). Another advantage of foamed composites compared to ‘conventional’ EMI shielding materials resides in their mechanical properties. Metallic sheets or plates are often used but they are heavy and bulky, especially for large-scale applications, for those applications a conductive paint or coating is often used instead but with problems related to abrasion and flaking. On the other hand, polymer foams are lightweight, flexible and easy to mould into complicated shapes.

Finding a material that combines a high electrical conductivity and a low dielectric constant is not trivial. This is in fact the driving idea behind the use of foamed nanocomposites. In theory, foaming a material would decrease its dielectric constant (because of the porosity and because air has dielectric

constant of 1, [20]). On the other hand, the addition of conductive nanoparticles to a material should theoretically increase its conductivity, [2], [18], [21], etc.

Besides having a potentially low dielectric constant, polymer foams are inexpensive, lightweight and easy to mould into any desirable shape. And, the addition of conductive nanoparticles could also reinforce the polymer matrix, improving its electrical conductivity but also its mechanical properties and its thermal conductivity, [22]. Carbon nanotubes have a very high aspect-ratio (≥ 1000). They can therefore form extensive regular conductive networks with a much lower content than other nanoparticles having a more spherical or compact shape, as can be seen on Fig. 5.2, more details about this can be found in chapter 2.

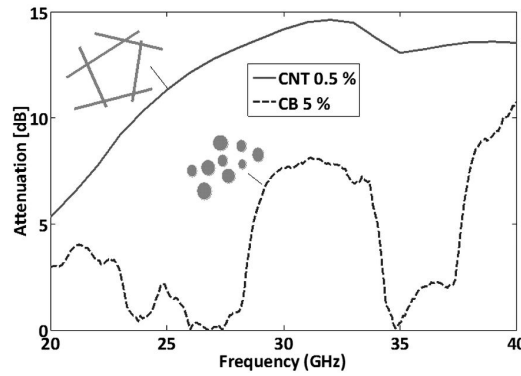


Figure 5.2.: Influence of the type of nanoparticles, CBs or CNTs, on the attenuation of a nanocomposite, from [22].

Besides reflection and absorption, there is a third shielding mechanism, [17], due to the multiple reflections at various interfaces. For classical sheet of conductive material, the multiple reflections decrease the shielding effectiveness if the shield material is thinner than the skin depth⁵ ($\delta = 1/\sqrt{\pi f \mu \sigma}$, with $\mu = \mu_0$ the magnetic permeability). They can be ignored if the material is thicker than the skin depth. Even if we assume an electrical conductivity of about 100 S/m for our CNT composites, at 10 GHz the skin depth is still about 500 microns long, usually significantly smaller than the thickness of the studied foam composites. But in the case of foams having a large surface area (multiple reflections between the pores or the external surfaces of MWCNTs), the problem is more complex. Theoretical considerations have led some to the conclusion that multiple reflections within the internal surfaces of MWCNTs have a negative

⁵The intensity of the EM field inside a material decreases exponentially as it penetrates deeper in the material. At a length δ from the surface, or skin depth, the intensity of the EM field has dropped to a value $(1/e)$ of the incident intensity.

impact on the shielding effectiveness because the MWCNTs diameter is much smaller than the skin depth, and that the multiple reflections between external surfaces of the MWCNTs are also detrimental to the SE but to a much smaller extent, [19]. But most authors agree that absorption and reflection losses dominate significantly those from multiple reflections and the multiple reflections are generally neglected. It is a bit different for multi-layered materials as the energy is partially lost at each internal interface, [23], and then absorbed by the interconnected CNTs of each layer. And, this is repeated at each subsequent layer. In this case, multiple reflections have a positive effect on the SE.

The applications of such foamed nanocomposites are numerous and varied, from electronics packaging to bionatural matrices, in aeronautics, automotive, environmental applications, and many more...

But the most promising application at the moment is certainly as shielding material, more precisely as microwave absorber. They could be made into thin, large, flexible, lightweight panels to be used as EMI shielding materials anywhere, and for little cost. Those panels could also have interesting fire retardancy or protection against electrostatic discharges properties.

It is worth noting that, according to [24], a SE of 30 dB would be sufficient for about half the industrial automotive and computer applications, and a 40 dB SE would cover over 95 % of them. The issue therefore is not so much to increase the SE compared to available EMI solutions but to offer more versatile ones, materials that combine several improved properties.

Data from the literature are very sparse on composite foams for EMI shielding and those that can be found focus on the shielding effectiveness alone and do not distinguish the part due to the absorption from that of the reflection. Nevertheless, the first reports of a nanocomposite foam were two articles from 2005 written by Yang and Gupta, [25] and [26]. In the former, a carbon nanofiber(CNF)-polymer foam was fabricated and its potential application for EMI shielding was experimentally tested (in the 8 – 12 GHz band, the X band). In the latter, a CNT-PS (polystyrene) foam was fabricated and the influence of the CNT content on the SE was studied. The maximum obtained value was a SE of about 19 dB for a 7 wt% filler content (the measured SE of the CNF foams of the previous article was of about 9 dB for the same filler content and of about 20 dB for a 20 % filler content⁶). In this latter article $R = 0.81 = -0.91dB$ which means the SE is dominated by the reflectivity. In [7] a shielding effectiveness of over 15 dB is reported for PU foams containing functionalized graphene sheet, the reflectivity is not given but given the very low density of these foams it is expected to be low.

⁶It must be noted that high filler contents have another disadvantage (besides the cost), they usually lead to poor filler-matrix bonding and the composite often exhibits poor mechanical properties.

More articles can be found on the application of solid polymer nanocomposites but results are often confusing because of the differences in the characterisation techniques used, differences in definition sometimes, also because most articles do not differentiate between reflection and absorption or do not give the thickness of their samples. The most widely studied frequency band is the X band⁷ (i.e. 8 – 12 GHz) and the solid CNT-polymer composites have shielding efficiency values between 20 and 30 dB for filler contents between 7 and 20 %.

⁷Most military and commercial applications are located in this X band also the case of weather radars, TV picture transmissions, telephone microwave relay systems, etc. [23])

5.3 SOLID SAMPLES CHARACTERISATION AS A SCREENING TECHNIQUE

The chemical processes involved in the fabrication of foamed samples are rather complex, see section 5.4 for more details. It is therefore interesting to have the possibility of a first selection on the nanocomposite blends before they are actually foamed. A two-step diagnostic method, to obtain the desired composite foam was developed; solid samples of polymer-CNTs blends were first characterized (the so-called screening tests), the best candidate blends were then used to fabricate foams and finally the foamed samples were also characterized.

Most of the CNTs used for the fabrication of the nanocomposites in this chapter are commercially available thin MultiWalled NanoTubes (MWNTs), with an average outer diameter of 10 nm and a purity over 95%. They were produced using Catalytic Carbon Vapour Deposition (CCVD) by Nanocyl SA (Belgium). The polymer/CNTs composites were fabricated using two different techniques, [21]. The first one consists in melt-blending the polymer matrix, poly(ϵ -caprolactone) (PCL), with CNTs using a DSM microextruder. The second one, called the 'coprecipitation' technique, is the solubilization of PCL in an organic solvent (tetrahydrofurane, THF, especially well suited to PCL) in the presence of the required amount of CNTs. After 30 seconds of ultrasonic treatment in order to break the CNTs bundles, the mixture is poured into heptane, which is a poor solvent for PCL. The polymer then instantly precipitates and the CNTs are trapped in it. Most of the samples studied in this chapter were fabricated by J.-M. Thomassin of the Universite de Liege. At this stage the samples are in solid form, cf. Fig. 5.3, they have not yet been foamed, they are simply referred to as 'solid samples' throughout the current chapter. They typically have a rectangular shape, of dimensions of 30 by 50 mm.

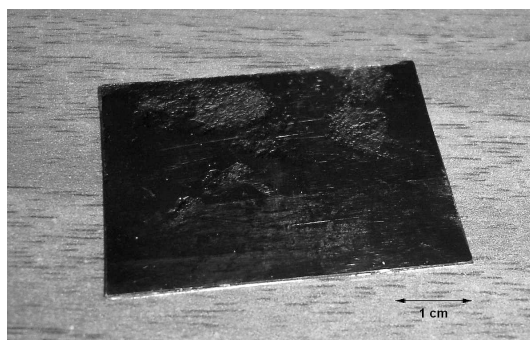


Figure 5.3.: Picture of a solid sample of PCL polymer containing 2 wt% CNTs.

Microstrip transmission lines were fabricated, using the nanocomposites thin films as substrates. By connecting these lines to a 2-port vector network analyzer (VNA), their scattering parameters were measured and the dielectric constant and conductivity of the samples were then extracted, using the One-Line method described in section 3.3.1. The results presented in this section were obtained for composites based on different polymer materials: PS (polystyrene), PCL (poly(ϵ -caprolactone)), PVC (polyvinyl chloride) and PMMA (polymethyl methacrylate), they all had a 2% CNT content. As can be seen on Fig. 5.4, the PMMA-based sample exhibited the lowest dielectric constant but not highest conductivity, while the PCL-based composite had the highest conductivity but also the highest dielectric constant.

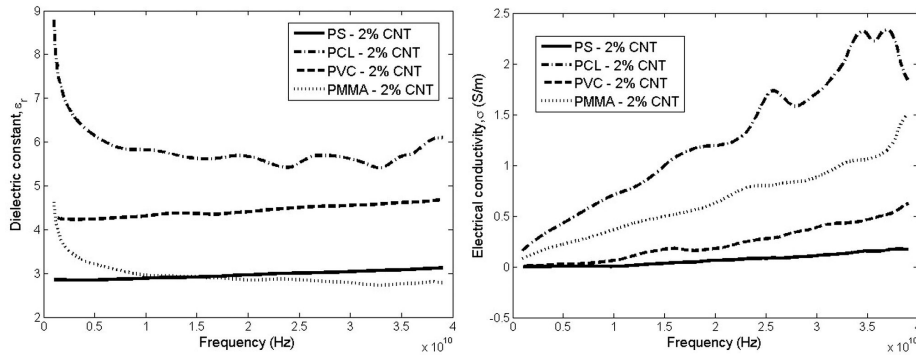


Figure 5.4.: Measured dielectric constant (left) and electrical conductivity (right) versus frequency of four nanocomposites with 2 wt% CNT content but based on different polymer matrices; PS (solid), PCL (dash-dot), PVC (dashed) and PMMA (dotted).

Once a polymer matrix is selected, an optimal content of CNTs to add into the matrix must be determined. The addition of CNTs increases the conductivity of the nanocomposite but also increases its dielectric constant, cf. Fig. 5.5 which is not desired. Since foamed samples have lower dielectric constants than solid ones with the same composition, the exact content of CNTs should be chosen after measurement of foamed samples rather than solid ones, see section 5.4 for further details on CNT content selection.

It should also be noted that, as mentioned in chapter 2, other chemical and/or physical process parameters have a non-negligible influence. Those are beyond the scope of the present chapter, but can be found in [27] or [28], for example.

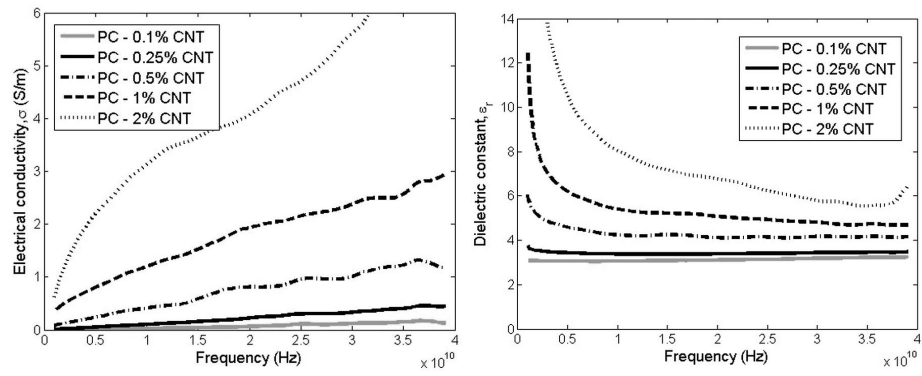


Figure 5.5.: Measured electrical conductivity (left) and dielectric constant (right) of five solid PC nanocomposite samples versus frequency (CNT contents from 0.1 to 2 wt%).

5.4 POLYMER CNT FOAMED COMPOSITES AND CHARACTERISATION

The samples were prepared by the same methods as those described in the previous section and were then foamed using supercritical CO_2 , [21]. They were first pressurized at about 200 bars at 60°C for 3 hours in order to saturate the sample with CO_2 . The pressure was then rapidly released in a few seconds leading to the foaming of the sample, more information on the supercritical CO_2 foaming method can be found in [29] and is summarized on Fig. 5.6.

A picture of a foamed nanocomposite fabricated this way is shown on Fig. 5.7, already cut into pieces in preparation prior to its characterization. The size of the foam pores depend on the filler content and also on the dispersion techniques used, as confirmed by the SEM pictures on Fig. 5.9, but are on the micrometre scale. It is also interesting to note that the addition of nanoparticles during the foaming process usually improves the nucleation⁸ efficiency and has thus an influence of the cells morphology inside the foam, [17] [30], as can be seen clearly on Fig. 5.8.

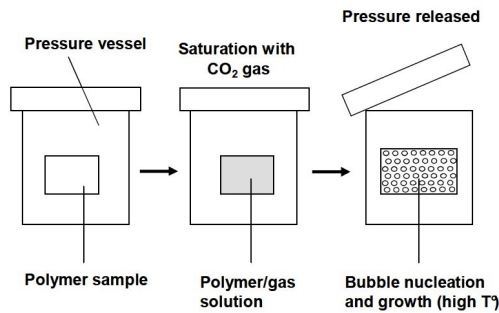


Figure 5.6.: *Illustration summarizing the supercritical CO_2 foaming method.*

Let us consider that PCL was selected as polymer matrix because it exhibited the highest conductivity in its solid form, cf. Fig. 5.4(right). Its dielectric constant was also the highest one, cf. Fig. 5.4(left), but foaming the nanocomposite should significantly decrease it. The foamed samples were inserted in four waveguides of different dimensions, covering the 8 to 40 GHz band and their scattering parameters were measured using the Line-Line method described in section 3.3.2. Of course if only the SE and R are needed, only one measurement (i.e. one waveguide) is needed instead of two for the LL method (to extract the complex permittivity).

⁸ The nucleation is the formation of the air bubbles, the future pores, inside the material.



Figure 5.7.: Picture of a nanocomposite foamed sample, PCL matrix with 2 wt% CNT content (already cut into pieces in preparation prior to its characterization).

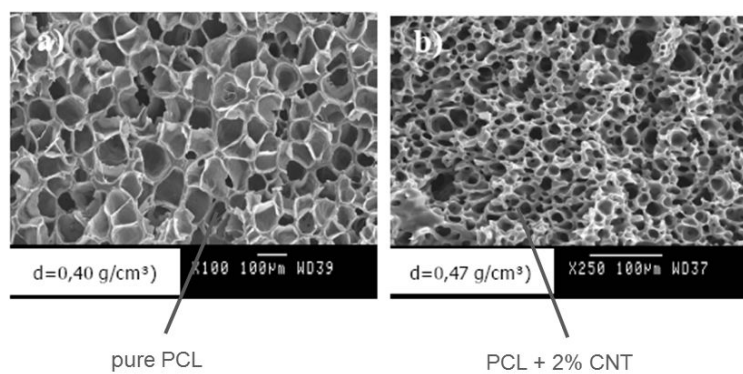


Figure 5.8.: SEM micrographs of PCL foams without CNTs (left) and with 2 wt% CNTs (right) fabricated using supercritical CO_2 .

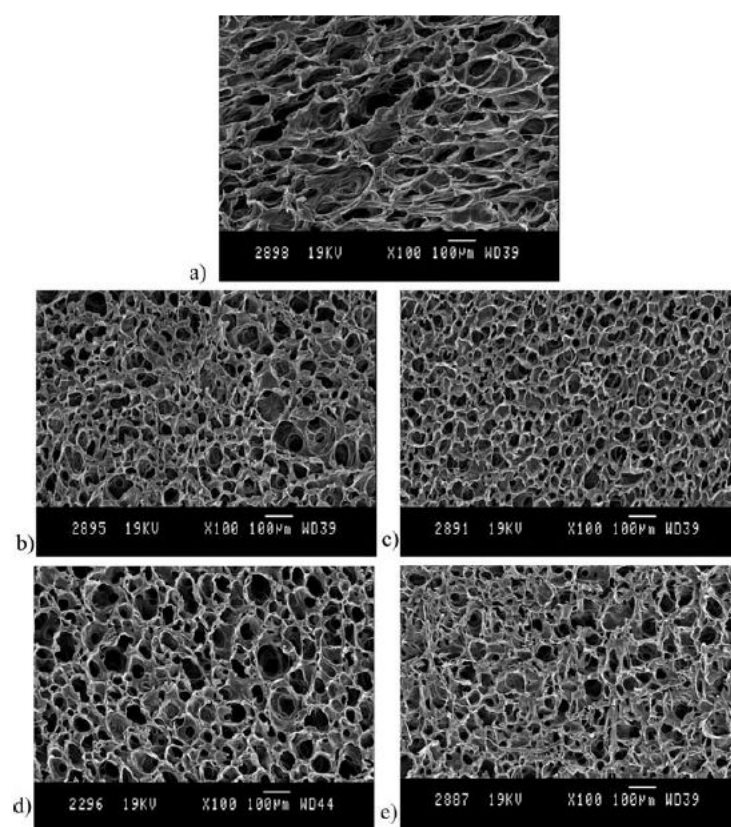


Figure 5.9.: SEM micrographs of PCL foams with a) 0 vol% of thin MWNTs, b) 0.1 vol% thin MWNTs (melt-blending), c) 0.222 vol% thin MWNTs (melt-blending), d) 0.107 vol% thin MWNTs (co-precipitation) and e) 0.249 vol% thin MWNTs (co-precipitation).

As mentioned in the previous section, a foamed material has a lower dielectric constant than a solid one of the same chemical composition. This is shown on Fig. 5.10, the black and red curves correspond to PCL samples with no CNT content, and the dielectric constant of the solid sample is twice that of the foam. It can be explained by the porosity of the foams and the subsequent presence of air inside the sample, the air having a dielectric constant of 1.

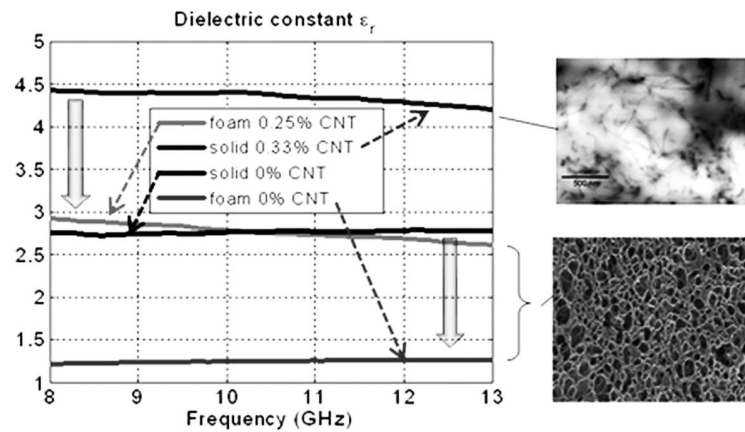


Figure 5.10.: Measured dielectric constant of solid and foamed PCL nanocomposite samples, all having a similar CNT content, from [18].

On the other hand, the conductivity of foams is usually higher than that of solid samples, mainly because the CNT are forced into the side walls of pores in the foamed material and this way can form a more regularly interconnected (dense) network. This is shown on Fig. 5.11 for a foam and a solid sample having a close (even though not strictly equal) CNT content, both PCL composites.

The latter affirmation is contradicted by results from [31]. In particular, the DC conductivity as a function of the foam density for PU nanocomposite foams with a fixed 2 wt% CNT loading is shown on Fig. 5.12. From this plot, the DC conductivity is dependent on the density of the foam but it decreases as the density decreases and even show a conductor to insulator transition is the density is low enough. The authors explain these two features using percolation theory. First they compare the thinning of the wall as the density decrease to the transition from a 3D to a 2D network which would lead to the increase of the percolation threshold and also more directly a decrease of the conductivity of the cell walls. Second, as illustrated on Fig. 5.13, a density decrease would also result in a smaller number of CNTs present at the interface between cells and therefore to a conductivity decrease. Besides, if the pores are larger because of the density decrease, the number of conductive paths is also decreased.

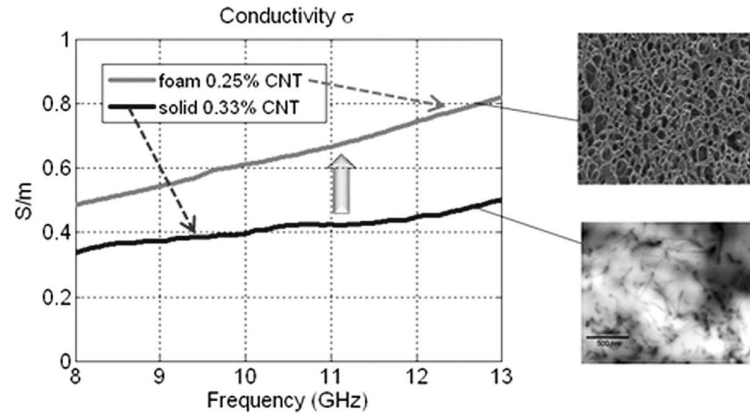


Figure 5.11.: Measured conductivity of solid and foamed PCL/CNTs nanocomposite samples with similar CNT contents, both having a similar CNT content, from [18].

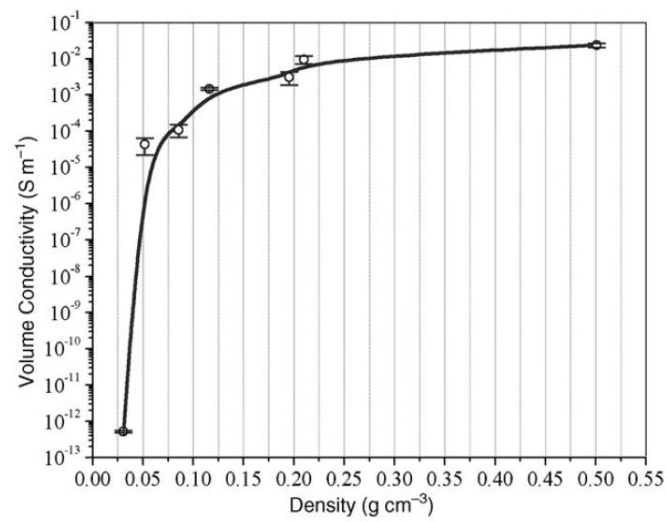


Figure 5.12.: DC conductivity of PU nanocomposite foams with a 2 wt% CNT loading as a function of the foam density, from [31].

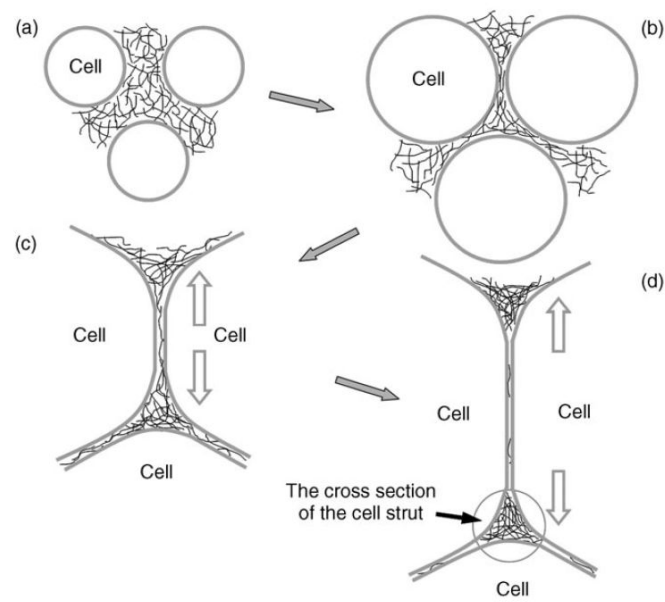


Figure 5.13.: Schematic diagram of the microstructure of the PU/CNT composite foams as the density is gradually decreased from (a) to (d), from [31]. The thin black lines represents the CNTs and the large grey ones are the cell walls of the foam. The arrows indicate the direction of growth of the air bubbles during foaming.

However, the latter discussion does not totally exclude the possibility of a conductivity increase by foaming, depending on the actual configuration of the CNTs relative to the pore walls and the existence of a regular, well-connected network of CNTs along the foam cells.

The effect of foaming a nanocomposite materials can also be considered directly on the EMI shielding properties of the material, [8]. This is shown on Fig. 5.14. Foaming the PMMA composite⁹ decreased the power reflected back from the nanocomposite from almost 50 % to only 3 %. The shielding effectiveness is also reduced but it is still of about 20-25 dB which is still very good and more than adequate for many EMI shielding applications. This is summarised in Fig. 5.14(c), the fraction of incident power absorbed by the solid composite is around 50 % only, while it is higher than 90 % for the foamed nanocomposite.

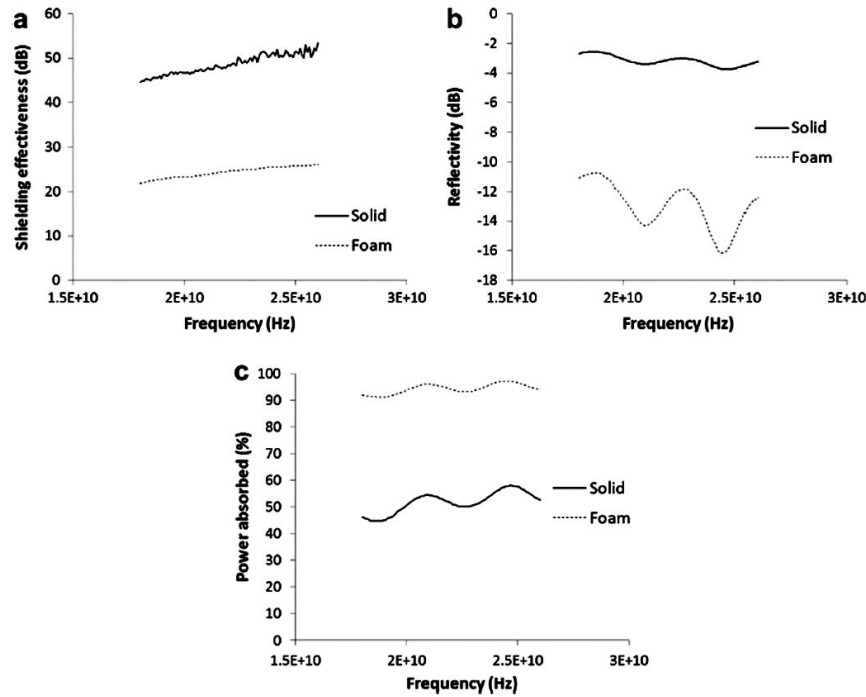


Figure 5.14.: Shielding effectiveness (a), reflectivity (b) and fraction of the incident power absorbed by the nanocomposite as a function of frequency for foamed and solid (unfoamed) PMMA composites with 2 wt% CNTs, from [8].

⁹The PMMA composite were fabricated using the coprecipitation technique detailed in [8] and foamed using the supercritical CO_2 method described previously.

In [7], the shielding effectivenesses of flexible PU foams containing different nanoparticles are compared to one another and to that of a pure PU foam. To adequately compare the different systems, the specific EMI shielding effectiveness, i.e. the SE corrected by the density of the material, is plotted versus frequency for a neat PU foam and for three PU foams containing 0.30 % pristine MWCNTs, functionalized MWCNTs (f-MWCNTs) or functionalized graphene sheets (FGS) on Fig. 5.15. It can be seen that the addition of MWCNTs leads to a significant increase of the SE but that there is little difference between the composites containing pristine and functionalized MWCNTs. On the other hand, the composite containing graphene shows and even higher SE. It might be due to the higher aspect ratio of graphene sheets forming a better-connected and widespread conductive network in flexible PU foams. Measured values of the DC conductivity are also shown in the paper, yielding the same conclusion. The fraction of the incident power reflected back are equal to 0.1, 1.5, 1.4 and 3.0 % for the neat PU foam, the one with MWCNTs, with f-MWCNTs and with FGS, respectively. The corresponding fractions of the incident power that is absorbed by the latter materials are 7.2, 10.1, 11.9 and 26.7, respectively.

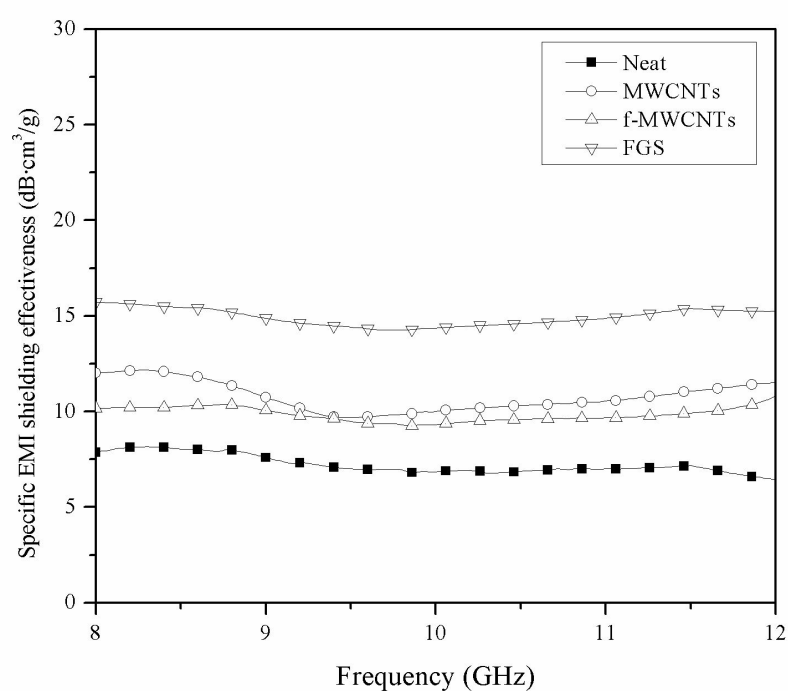


Figure 5.15.: Specific EMI shielding effectiveness as a function of frequency of flexible PU nanocomposite foams: neat PU foam (■), PU foam containing pristine MWCNTs (○), functionalized MWCNTs, f-MWCNTs, (△) or functionalized graphene sheets, FGS (▽), from [7].

In terms of shielding effectiveness and reflectivity, the conductivity of foamed nanocomposites increases significantly with the CNT content and the shielding effectiveness also increases in the same proportions, cf. Fig. 5.16. Therefore, in order to have a good SE, it appears, as could be expected, that the CNT content must be as high as possible.

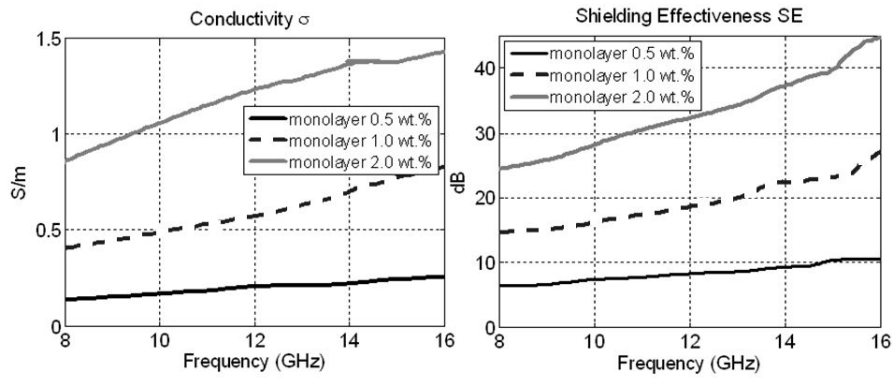


Figure 5.16.: Measured conductivity of foamed PCL nanocomposite samples with increasing CNT contents (left) and the corresponding Shielding Effectiveness (right), from [18].

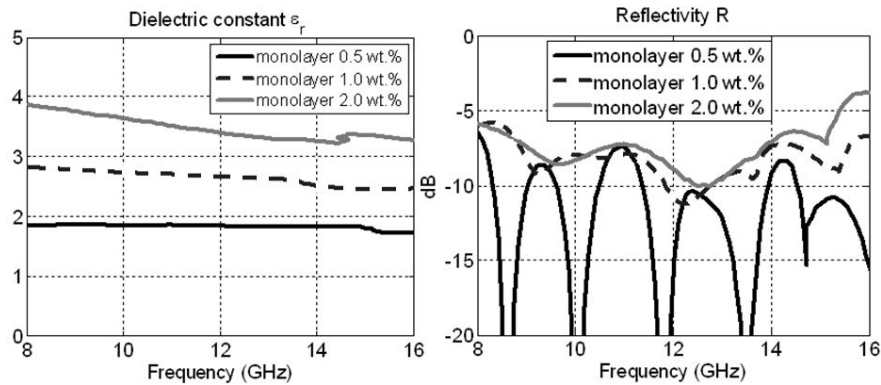


Figure 5.17.: Measured dielectric constant of foamed PCL nanocomposite samples with increasing CNT contents (left) and the corresponding Reflectivity (right), from [18].

But the addition of CNTs has an adverse effect on the reflectivity because the dielectric constant increases significantly with CNT content, cf. Fig. 5.17. To measure R correctly, a metallic sheet (or Perfect Electrical Conductor - PEC)

is added on the output interface, and the sample with the PEC sheet is then characterized (Line-line method). Part of the incident power is absorbed inside the material, the remaining power then reaches the PEC where it is totally reflected and, another part of the power is absorbed on the way back. Because of the PEC, the SE in this configuration is theoretically infinite, cf. Fig. 5.18. The power reflected back to the port 1 of the VNA (assuming PEC on port 2), is the combination of the power directly reflected back at the input interface and the power reaching the metallic plate and being reflected back (the remaining power that has not been absorbed by the material on the way back). The apparent oscillations that are visible mostly on the black reflectivity curve are due to a mismatch between the wave impedance of the sample under test and the wave impedance of air.

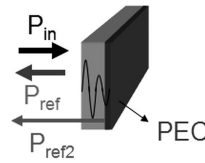


Figure 5.18.: *Illustration of the experimental set-up configuration for the reflectivity measurement, and corresponding powers, from [18].*

In conclusion, foamed nanocomposites have both a higher conductivity and a lower dielectric constant than solid samples. The first are therefore better suited for shielding applications than the latter. The optimum CNT content has to be the result of a *compromise* between shielding effectiveness and reflectivity, i.e. between conductivity and dielectric constant.

5.5 SIMPLE ELECTRICAL MODEL AND COMPARISON WITH MEASUREMENT RESULTS

As explained previously, a model especially suited to our foamed composites was not found. A very simple electrical model was used in [22] and was found in very good agreement with both electrical measurements.

This electrical model was developed for solid samples characterised using a microstrip method. This model is modified to correspond to the foam measurement using the Line-Line technique, as represented on Fig. 5.19.

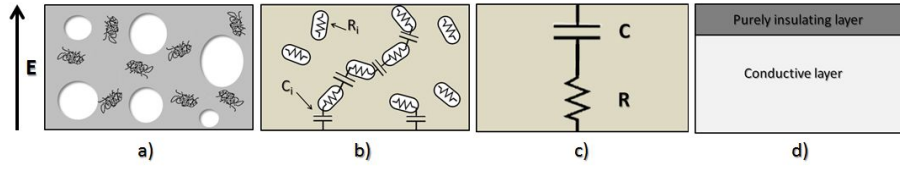


Figure 5.19.: Simple electrical model for the description of the frequency dependence of the conductivity of the nanocomposites: (a) clusters of CNTs, well dispersed inside the polymer foam matrix. The arrow indicates the direction of the electric field. (b) The CNT bundles are considered to be purely resistive and some the capacitive couplings between the CNT bundles are shown, for illustration purposes (c) Equivalent admittance per unit length of the transmission line. (d) Corresponding equivalent two-layer material.

The carbon nanotubes or CNT clusters are assumed to be well dispersed inside the foam matrix with no direct physical contact between them, i.e. they do not touch one another, cf. Fig. 5.19(a).

The CNT cluster are considered to be purely conductive grains inside a completely insulating polymer matrix. The foam is replaced by a homogeneous, solid, material having the same electrical properties as those of the foam. Therefore, the electrical equivalent of each grain is a simple resistor and there are strong capacitive couplings between all the grains, cf. Fig. 5.19(b).

Since the electric field distribution is quasi uniform and vertical, only capacitors and resistors that are parallel to that direction have to be considered, and the transmission line has an electrical equivalent admittance per unit length that corresponds to a simple resistor-capacitor (R_T and C_T) series circuit, as shown on Fig. 5.19(c).

This can also be modelled by a two-layered microstrip transmission line, of total height H , cf. Fig. 5.19(d), with an insulating top layer of height H_i and a conductive bottom layer (conductivity $= \sigma_{CL}$).

According to the above, at low frequency, since there are no physical contacts between the grains, the equivalent capacitor, cf. Fig. 5.19(c), is a virtual 'open

circuit'; and, there is therefore no current flowing through the composite. At a high enough frequency, the equivalent capacitor is a virtual 'short circuit' and the conductivity becomes constant. Its value depends then only on the conductivity, σ_{CL} , of the conductive layer of Fig. 5.19(d). In other words, at low frequency when $(\omega C_T)^{-1} \gg R_T$, the conductivity is very low. At high frequency, when $(\omega C_T)^{-1} \ll R_T$, the conductivity is constant. In between, the conductivity increases with frequency. This corresponds to a transition frequency, f_T , equal to $f_T = (2\pi R_T C_T)^{-1}$.

In Fig. 5.19(b), the matrix is considered as a homogeneous material with the same electrical properties as those of the original foam. As seen in section 5.4, more particularly on Fig. 5.10, foaming the PCL material (with or without) CNTs yields a decreased value of the dielectric constant, the value of the foam being about 2/3 of that of the solid material. As discussed in the latter section, there is still some discussion on the influence of foaming on the conductivity value.

If the simple model fore-described is used to fit the measured conductivity and dielectric constant values of the polypropylene (PP) foam with 4 wt% CNT, one of those detailed in section 3.3.4. The fit is obtained by adjusting the ratio H/H_i of the two-layer material. Solid polypropylene has a dielectric constant of about 2.2, taking into account the decrease due to foaming, a value of $\varepsilon_{foam} = 1.3$ is assumed. The height of the top insulating layer (H_i) was adjusted in order to obtain the best fit between model and measurement results. For a conductive layer having a conductivity $\sigma_{CL} = 2.5$ an adequate agreement between model and measurement is found for a H/H_i ratio of 0.71. The conductivity of the layer was also slightly adjusted, with the initial values proposed from [22], no adequate fit could be found for any value of the layer height ratio. The conductivity was thus decreased by one order of magnitude, from 25 S/m to 2.5 S/m and the agreement could be found between model and measurements, as shown on Fig. 5.20. This would favour the conductivity decrease due to foaming discussed in the previous section, though the material used in [22] and in the current study are not the same. Besides a more elaborated foam model should take into account the dimensionality of the foams, they are not really 3D networks but more similar to a 2D surface in some aspects. Their behaviour could also be modelled taking into account Maxwell (RC) models, with not only one or two but an infinity of parallel RC dipoles, modelling an infinity of characteristic relaxation times.

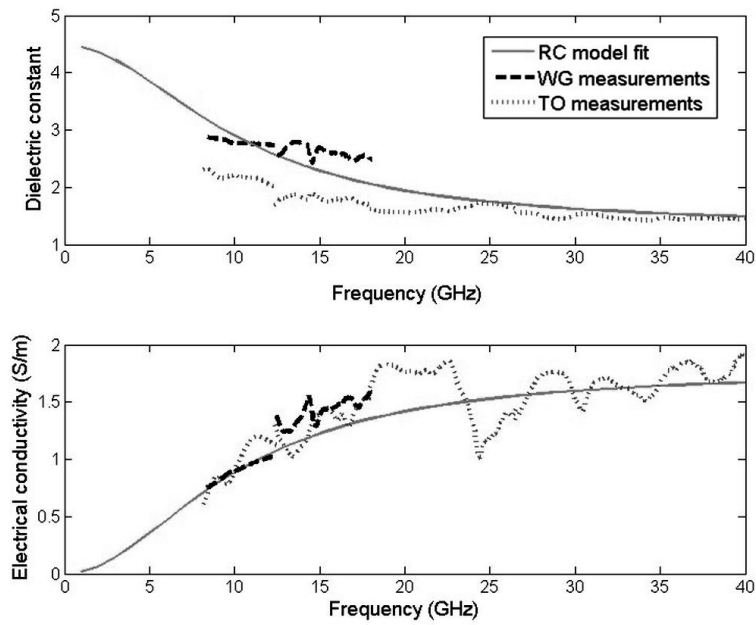


Figure 5.20.: Dielectric constant (top) and conductivity (bottom) extracted using the simple electrical model (solid) and from actual measurements (original LL method: dashed and modified method: dotted), for a polypropylene (PP) foam with CNT content of 4 wt% (model parameters: $H/H_i = 0.71$ and $\sigma_{CL} = 2.5$ S/m).

5.6 OPTIMIZED MULTILAYER FOAMS FOR REDUCED REFLECTIVITY

In order to improve the reflectivity of the shielding material, it was interesting to create a foam having a gradient of dielectric constant, ϵ , inside the material, [18], analogous to the stealth paint protecting spy aircraft from radar detection. A way to achieve this gradient is to fabricate multilayered foams, each layer having a different, increasing dielectric constant, as shown in Fig. 5.21.

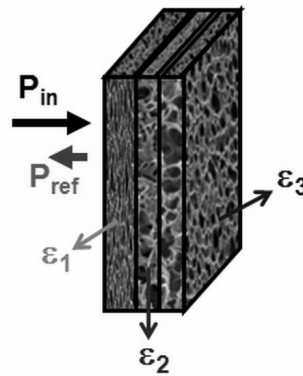


Figure 5.21.: Schematic diagram the three-layered foam, with $\epsilon_1 < \epsilon_2 < \epsilon_3$, from [18].

A multilayered foam sample with graded concentrations of CNTs, [18], should thus simultaneously exhibit a high Shielding Effectiveness and a low dielectric constant. A multi-layered foam consisting of three layers of PCL with graded CNT contents (0.5%, 1% and 2% for layers 1.2, 1.1 and 0.7cm thick, respectively) was fabricated and characterized. The total thickness of the sample is therefore equal to 3 cm and the average CNT concentration is equal to 1.03%. The conductivity and dielectric constant were measured between 8 and 16 GHz, [18]. The shielding effectiveness and reflectivity were then extracted. The results are shown on Fig. 5.22, along with the results for the mono-layered samples of section 5.4. As can be seen on these figures, the multi-layered foam has the same SE as the monolayer one with the same CNT concentration as the average CNT content of the multi-layered sample. But its reflectivity is much lower than that of all the mono-layered foams!

The graded concentration achieved by the cascade of layers with increasing CNT concentration, combined with foaming, ensures a progressive and moderate increase in dielectric constant, meaning that reflection at input interface of each layer is minimized, power entering the composite is maximized, and reflectivity is significantly reduced over a broad frequency range. The progressive increase in conductivity yielded by graded concentration contributes to the absorption of the

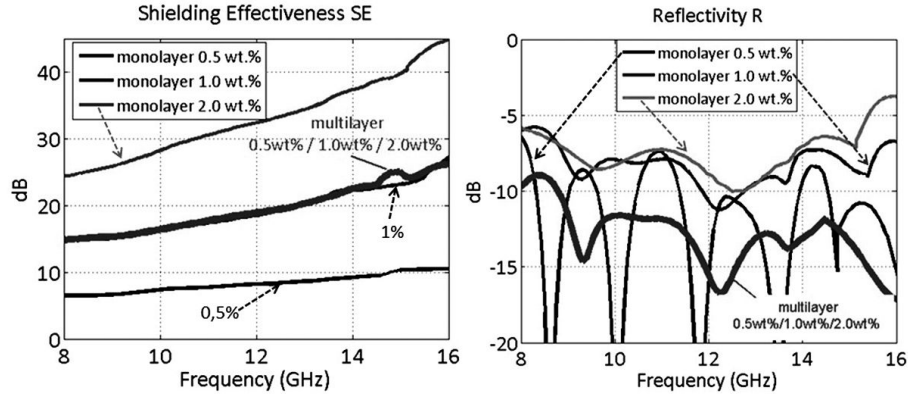


Figure 5.22.: *Shielding Effectiveness (left) and Reflectivity (right) of the multi-layered and monolayered samples, from [18].*

most part of the power over the depth of the structure by conductive dissipation. The measurements therefore confirm the high potential of multi-layered foams for EMI shielding applications.

Indeed, when compared to the values from the literature, cf. section 5.2, the foamed samples presented here have a higher or similar SE but a significantly higher reflectivity! For example, the best ones to our knowledge, the foamed samples of [26] (~ 10 wt% CNT) have $SE = 19$ dB and $R = -0.91$ dB and the solid multi-layered samples of [23] (~ 7 wt% CNT) have $SE = \sim 40$ dB and $R = \sim -7$ dB both in the X band. While the samples presented here exhibit $SE = 17$ dB and $R = \sim -8$ dB for the mono-layer foam (1 wt% CNT) and $SE = 17$ dB and $R = \sim -12$ dB for the multi-layer foam (1.03 wt% CNT, averaged).

5.7 MULTIFUNCTIONAL HYBRIDS FOR EMI ABSORPTION

In the framework of the Multimasec Walloon Region project, another solution to decrease the dielectric constant while keeping a good conductivity was proposed. A multiscale hybrid material composed of a nanocomposite foam, similar as those studied previously in this chapter, inserted in a metallic honeycomb. The hierarchical structure of this novel multiscale material is illustrated on Fig. 5.23, three different scales are present in the material structure: the CNTs at the nanometre scale, the pores of the polymer foam at micrometre scale and the cells of the honeycomb at the millimetre scale.

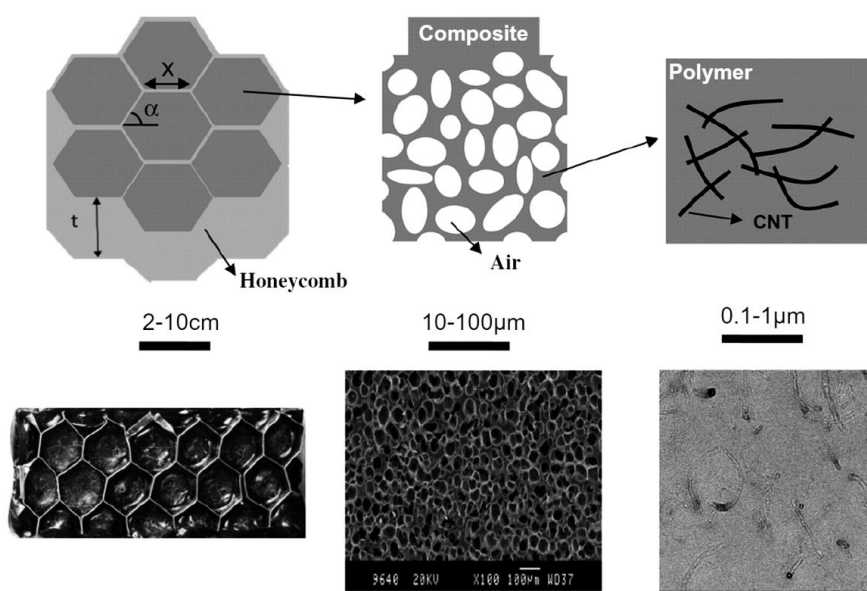


Figure 5.23.: Hierarchical structure of the hybrid material starting from the CNT-filled polymer composite at the nanometre scale, the foam level at the micrometre scale and the filled honeycomb at the millimetre scale - schematic drawings and micrographs, from [10].

The polymer used to fabricate the foams is mostly polyurethane, the CNTs are the Nanocyl 7000. Foaming was done using the supercritical CO_2 technique described previously¹⁰. The polymer CNT composites were prepared roughly as in section 5.3 though sometimes some processing parameters had to be slightly

¹⁰Though later in the project foaming has been done using chemical agents, mainly because of technical problems with the CO_2 reactor. These foams were as homogeneous and exhibited the same quality than those obtained using supercritical CO_2 .

adjusted for optimal results (heating or compression rates for example). Finally, the metallic honeycomb is heated and was slowly inserted in the nanocomposite foam by mechanically pressing them together, as illustrated on Fig. 5.24.

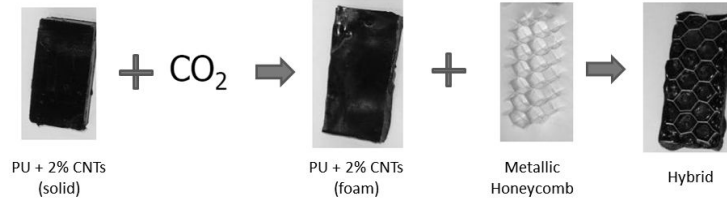


Figure 5.24.: *Illustration of the fabrication process of the multiscale hybrid samples.*

The hybrid samples were characterized using the modified Line-Line method without waveguides, cf. section 3.3.3. This technique was actually developed for these particular samples. Some of the filled honeycombs were rather large, to be measured also at lower frequency (down to 1 GHz) and also because of their potential applications, and would not fit in the waveguides. Besides this would have meant cutting them into pieces, therefore destroying them, and would also have been difficult, because of the hard metallic honeycomb. Besides, at high frequency, the sample would not have enough cohesion with only a few honeycomb cells left (given the waveguides small dimensions). But as shown in section 3.3.4, if the samples exhibit sufficient losses (due to the dielectric constant or conductivity) from those of a slab of air of similar dimensions, the modified Line-Line method can be effectively used with good results.

The hybrid samples were then measured without waveguides (between transitions), as shown on the pictures in Fig. 5.25. Initially the samples were aligned visually, with confirmation from ‘empty’ measurement (transmission, the magnitude of S_{12} , being maximum when the transitions are well aligned). But a rail was designed and fabricated (by D. Spote at UCL) to hold the transitions in good alignment and with the possibility to fix them at a given position even without a sample between them.

The measured absorption is plotted versus frequency on Fig. 5.26 (left) for a foamed sample (PU with 2 wt% CNT) inserted into a metallic honeycomb (solid) or alone (dashed). The honeycomb has a characteristic cell size $X = 6$ mm. Both foam and honeycomb have a thickness of 5 mm. The corresponding reflected power is plotted on Fig. 5.26(right). It can be seen from those graphs that absorption is higher with the honeycomb than for the foam alone and that the reflectivity is improved as well (except at lower frequencies). An absorption

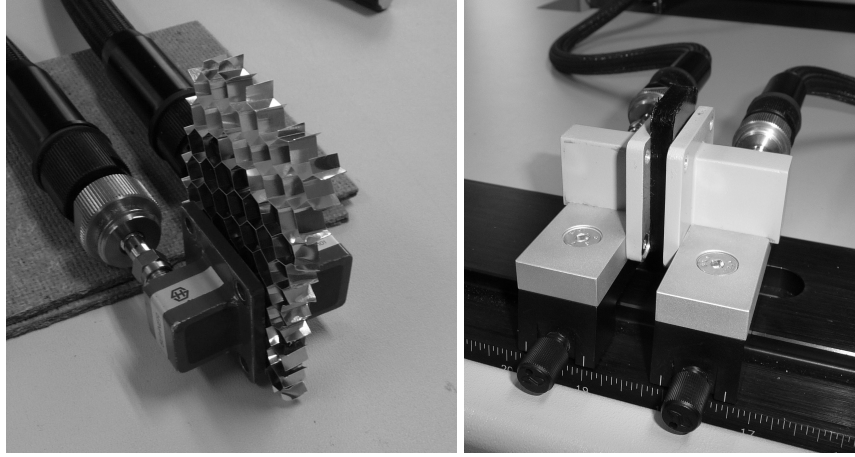


Figure 5.25.: Pictures of measurements of a hybrid sample (left) and a foam (right) using the modified LL method with manual alignment of the transitions (left) and using an especially designed rail to maintain the transitions in very good alignment and parallelism, at a given distance.

peak can also be observed around 6.6 GHz, as well as a sharp decrease of the absorption before this peak, associated with a higher reflected power.

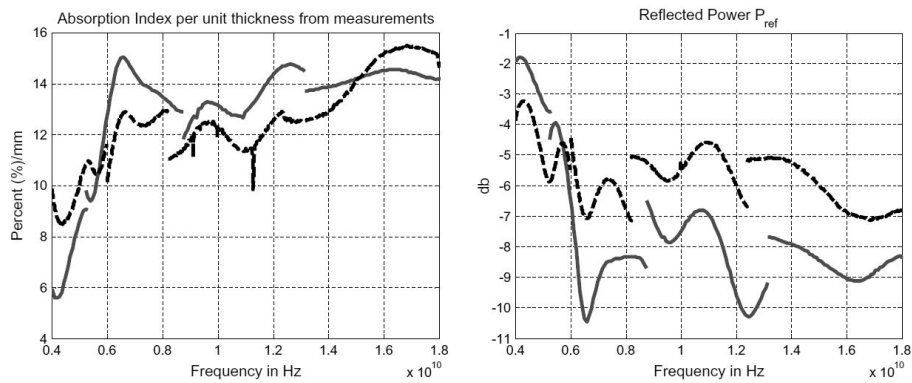


Figure 5.26.: Absorption (A) per unit thickness, in percent, versus frequency (left) for a foamed composite with honeycomb (solid) and without (dashed). Corresponding reflected power for the same samples, (right), from [10].

The metallic honeycomb can be imagined as a lattice of hexagonal waveguides, with a propagation constant and cut-off frequency. For rectangular or circular waveguides, analytical ‘canonical’ equations exist for these parameters,

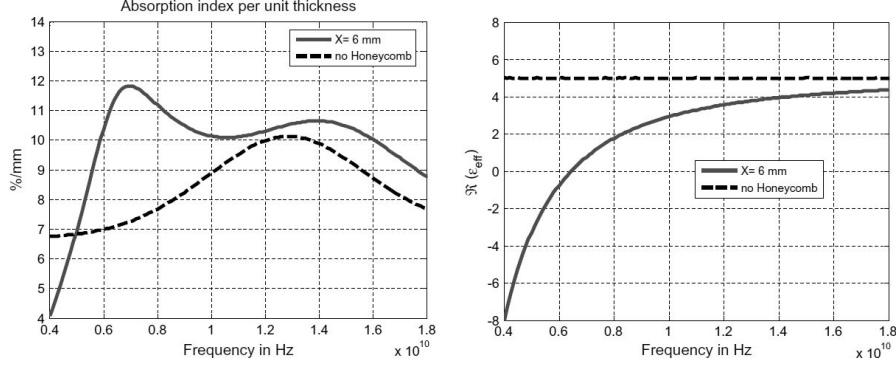


Figure 5.27.: Simulated absorption (A) per unit thickness, in percent, versus frequency (left) for a foamed composite with honeycomb (solid) and without (dashed), calculated from equation 5.5. Corresponding effective dielectric constant for the same samples, (right), calculated using equation 5.7 ($a = 60$, $\varepsilon_r = 5$, $X = 6$ mm, $m = 1$ and $n = 0$), from [10].

cf. section 3.3.2, but to the best of our knowledge, none exist that are valid for hexagonal waveguides. Nevertheless, cut-off frequency and propagation constant equations for regular hexagonal waveguides were derived from those of rectangular waveguides using perturbation theory in [10]. The propagation constant inside a regular hexagonal waveguide is then given by

$$\gamma_h = j \sqrt{\varepsilon_e \frac{\omega^2}{c_0^2} - \frac{5}{4} \left(\frac{\pi}{a} \right)^2} \quad (5.6)$$

and the corresponding complex effective permittivity

$$\varepsilon_{e_h} = \varepsilon_r - \frac{5}{4} \left(\frac{\pi}{a} \right)^2 \left(\frac{c_0}{\omega} \right)^2 - j \frac{\sigma}{\omega \varepsilon_0} \quad (5.7)$$

This expression of the permittivity is inserted in equation 5.5 and is plotted versus frequency on Fig. 5.27 (left). The simulated results are in very good adequacy with the measurements. The absorption peak at the same frequency and the decreased absorption before the peak is present as well. The real part of the effective permittivity from equation 5.7 is plotted versus frequency on Fig. 5.27(right). It is negative below the frequency corresponding to the absorption peak, the cut-off frequency, and positive beyond this frequency. It monotonously increases with frequency but is always smaller than the dielectric constant of the nanocomposite foam (without honeycomb), which means the reflectivity of the hybrid is improved, compared to the foam alone.

Numerical simulations using a commercial software COMSOL (a finite elements solver based on Maxwell equations) have confirmed the previous results (analytical and from measurements). Two geometries were investigated: a slab composed of the material (e.g. nanocomposite foam) and a regular hexagonal structure inserted in the composite slab. Both structures are drawn on Fig. 5.28. Adequate selection of the boundary conditions ensure a normal incidence (relative to the air-slab interface) of the propagating TEM wave and, also the periodicity of the honeycomb lattice, from [10].

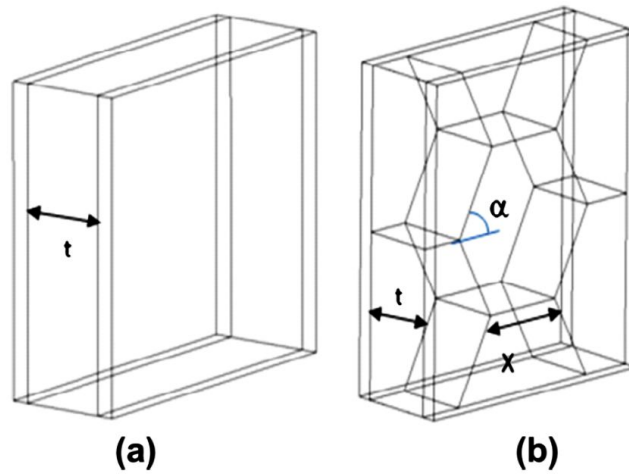


Figure 5.28.: The two geometries used in the Comsol simulations: (a) a slab of composite material of dielectric constant ϵ_r , electrical conductivity σ and thickness t , between two thin layers of air modelling the exterior environment. (b) Same slab of material with the metallic honeycomb structure of characteristic cell size X inserted, from [10].

Some Comsol simulation results are compared to those obtained with the analytical model on Fig. 5.29. For a given dielectric constant and electrical conductivity, two characteristic size cells of the metallic honeycomb are considered. It can be seen that the increase in cell size results in a significant decrease of the cut-off frequency, showing the possibility of adjusting this frequency by varying the hybrid parameters, i.e. tailoring the hybrid for the desired application. The effect of presence of the honeycomb is also shown, confirming the improved EMI properties of the hybrid compared to those of the nanocomposite foam alone. There is also a very good agreement between results from the analytical formulation and the Comsol simulations, cross-validating them as the adequacy between analytical results and experimental ones was already shown.

Furthermore, the geometrical and physical parameters of the honeycomb (X , irregular hexagons, etc.), and those of the foam (and nanoparticles) can be mod-

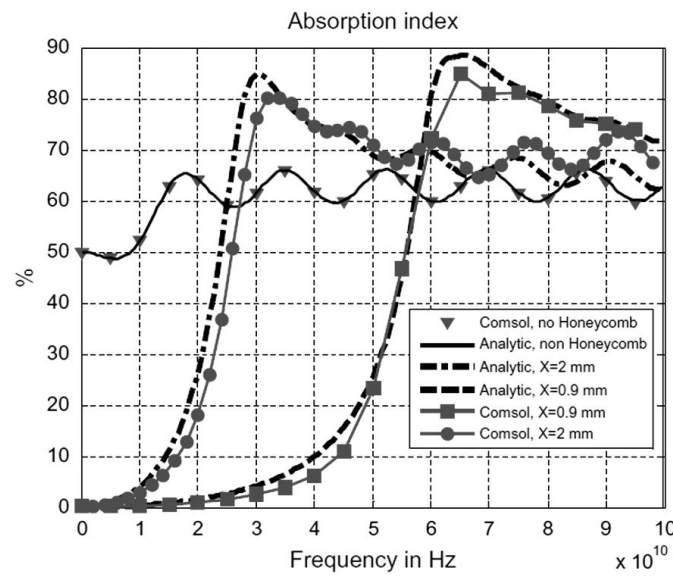


Figure 5.29.: Simulated absorption index (A), in percent, as a function of frequency, using the analytical formulation (lines) and using the Comsol solver (symbols). Two characteristic sizes of the honeycomb cell are considered: $X = 0.9$ mm (dashed or ■) and $X = 2$ mm (dash-dot or ●), the structure without honeycomb is also simulated (solid or ▼) as a comparison. Nanocomposite slab parameters: $\epsilon_r = 3$, electrical conductivity $\sigma = 1$ S/m and thickness $t = 10$ mm, from [10].

ified to ‘tailor’ the hybrid to optimize it in function of the desired application, [10]. The hybrid also exhibit interesting mechanical and thermal properties and the hybrid can be designed to optimize thermal conductivity or stiffness or total weight, etc.

In conclusion, in the framework of this Multimasec project on multiscale composite materials, a new hybrid has been developed, and patented¹¹. It is based on a nanocomposite foams, similar to the foams presented in the previous sections of this chapter, but inserted in a metallic honeycomb. It has been shown that this hybrid can exhibit an as good EMI absorption as simple nanocomposite foams but with an even improved reflectivity. These results have been analysed using perturbation theory to extend the equations on propagation inside rectangular waveguides to hexagonal ones. A cut-off frequency was highlighted, below which the effective dielectric constant of the hybrid was negative (metamaterial) and corresponding to an absorption peak. The reflectivity improvement over foams without honeycomb was also demonstrated analytically and confirmed by measurements. Furthermore the properties of the hybrid are adaptable and it can be customized for a number of applications, that are not limited to the realm of electromagnetics but also mechanical or thermal applications, ...

¹¹European Patent EP10175887 ”Hybrid material for electromagnetic absorption”, filed: 09 September 2010.

5.8 CONCLUSIONS

Throughout this chapter, it has been shown that foamed polymer/CNTs nanocomposites are very interesting materials for EMI shielding. They exhibit a high conductivity, because of the CNTs, and a relatively low dielectric constant, due to foam, leading to a high Shielding Effectiveness and a relatively low Reflectivity, although a compromise in CNT content must be found between a high SE and a low R . This has been confirmed by measurement results and discussed using a simple electrical equivalent model. This model was developed due to the difficulty of finding or creating a model especially suited to foams, a very crude model but actually quite adequate for microwave measurements modelization.

Some EMI shielding considerations were first presented. In particular, the notions of SE and R were defined and the advantage of microwave absorbers on conventional metallic shielding materials was discussed in terms of reflectivity. The samples were briefly described, both foamed and in their solid form, along with their fabrication methods. The measurement results of the solid samples and those of foams were detailed and discussed. In particular the presence of a compromise between a good shielding effectiveness and an adequate reflectivity is detailed. The influence of the filler content, of some of the processing methods are also discussed. Foams containing graphene sheets instead of CNTs were also described.

Some physical explanations were proposed. The measurement results have been compared to those obtained with a simple electrical model and were found to be in very good agreement. The results presented in this chapter all compare positively to the materials from the literature.

Two nanocomposite based materials were then proposed to decrease the reflectivity of the EMI shielding material. First an optimized multi-layered foam topology with increasing CNT contents in each subsequent layer was proposed. The three-layered foam exhibited a SE similar to that of a mono-layered sample having the same average CNT content but the R of the multi-layered foam was significantly decreased.

Second, a multiscale hybrid material was presented, based on a nanocomposite foam inserted in a metallic honeycomb. It exhibits a decreased reflectivity, compared to a single foam without honeycomb, on the entire frequency range. But, it also exhibited some exotic properties, a negative dielectric constant in a specific frequency range and a tunability of the hybrid properties by modifying some constitutive parameters (of the honeycomb, foam or particles). In particular the cut-off frequency can be adjusted. It can also be designed for other applications than EMI.

To conclude, nanocomposite foams have good EMI properties but a compromise on the CNT content must be found in order to have a high SE and also a low R. Or, more subtle, the foams can be used in a configuration that decreases the effective dielectric constant, or reflectivity. For example, they can be arranged to form a multi-layered foams with graded concentrations of CNTs, especially well suited to EMI shielding applications, having a high SE with a lower R than mono-layered samples. They can also be used in combination with other material to form hybrid, multiscale materials, like the metallic honeycomb filled with nanocomposite foam that was presented. As a future prospect, it could be interesting to develop more elaborate electrical model for these foamed materials, taking into account their not-quite 3D structure and also to investigate their electrical properties at lower frequencies.

Bibliography

- [1] O. Lusito, D. Barletta, and V. Dimiccoli, "A wide-frequency model of metal foam for shielding applications," *IEEE Transactions on Electromagnetic Compatibility*, vol. 52, no. 1, pp. 75–81, February 2010. 198
- [2] I. Molenberg, J.-M. Thomassin, R. Daussin, A.-C. Baudouin, C. Detrembleur, C. Bailly, and I. Huynen, *Advanced Microwave and Millimeter Wave Technologies: Semiconductor Devices Circuits and Systems*. In-Tech, 2010, ch. Foamed Nanocomposites for EMI Shielding Applications, pp. 453–470. 198, 201
- [3] I. Molenberg, J.-M. Thomassin, E. Ferain, C. Detrembleur, and I. Huynen, "Rf diagnostic methods for two nanostructured polymer applications," in *Proc. of the 39th European Microwave Conf.*, Roma, Italy, September 2009, pp. 1045–1048. 198
- [4] I. Molenberg, J.-M. Thomassin, C. Detrembleur, and I. Huynen, "Cnt polymer nanocomposites for fuel cell and emi shielding applications," in *Proceedings of the Conference 'STIC et environnement'*, Calais, France, June 2009.
- [5] I. Molenberg, J.-M. Thomassin, C. Detrembleur, C. Bailly, and I. Huynen, "Les mousses polymeres nanocomposites pour les applications de compatibilite electromagnetiques microondes (invited paper)," in *Proceedings of the Journees de Caracterisation Micro-ondes de Materiaux*, Brest, France, April 2010, pp. INV8.1–4. 198
- [6] J.-M. Thomassin, R. Jerome, I. Molenberg, I. Huynen, and C. Detrembleur, *Physical properties of polymer nanocomposites*. Woodhead, 2009, ch. Polymer/carbon nanotube composites for electromagnetic interference reduction, pp. 563–587. 198
- [7] M. Bernal, I. Molenberg, S. Estravis, M. Rodriguez-Perez, I. Huynen, Lopez-Manchado, and R. Verdejo, "accepted in journal of material science," *Comparison of the effect of carbon-baed nanofillers on flexible polyurethane foams*, 2012. 202, 214, 215
- [8] J.-M. Thomassin, D. Vuluga, M. Alexandre, C. Jerome, I. Molenberg, I. Huynen, and C. Detrembleur, "A convenient route for the dispersion of carbon nanotubes in polymers: application to the preparation of electromagnetic interference (emi) absorbers," *Polymer*, vol. 53, no. 1, pp. 169–174, January 2012. 213
- [9] D. Vuluga, J.-M. Thomassin, I. Molenberg, I. Huynen, B. Gilbert, C. Jerome, M. Alexandre, and C. Detrembleur, "Straightforward synthesis of conductive graphene/polymer nanocomposites from graphite oxide," *Chemical Communications*, vol. 47, no. 9, pp. 2544–2546, 2011.

- [10] I. Huynen, N. Quievy, C. Bailly, P. Bollen, C. Detrembleur, S. Eggermont, I. Molenberg, J.-M. Thomassin, L. Urbanczyk, and T. Pardoën, "Multi-functional hybrids for electromagnetic absorption," *Acta Materialia*, vol. 59, no. 8, pp. 3255–3266, May 2011. 198, 200, 223, 225, 226, 227, 228, 229
- [11] J.-M. Thomassin, I. Molenberg, I. Huynen, M. Alexandre, C. Jerome, and C. Detrembleur, "Pmma/carbon nanotube nanocomposites foams for emi shielding application," in *Proceedings of the International Conference on Materials for Advanced Technologies*, Singapore, July 2011. 198
- [12] M. Alexandre, J.-M. Thomassin, D. Vuluga, I. Molenberg, I. Huynen, A. Debuigne, C. Jerome, and C. Detrembleur, "Locating carbon nanotubes (cnts) at the surface of polymer microspheres using poly(vinyl alcohol) grafted cnts as dispersion co-stabilizers," in *Proceedings of the International Conference on Materials for Advanced Technologies*, Singapore, July 2011.
- [13] S. Eggermont, N. Q. P. Bollen, C. Bailly, C. Detrembleur, I. Molenberg, J. Thomassin, L. Monnereau, L. Urbanczyk, T. Pardoën, and I. Huynen, "Novel frequency selective electromagnetic absorber combining honeycomb waveguide and carbon nanotube composites," in *Proceedings of the 5th European Conference on Antennas and Propagation*, Rome, Italy, April 2011, pp. 2201–2204.
- [14] D. Vuluga, J.-M. Thomassin, I. Molenberg, I. Huynen, C. Jerome, M. Alexandre, and C. Detrembleur, "An efficient biphasic synthesis of polymer-grafted reduced graphite oxide based nanocomposites," in *Advances in Polymer Science and Rubber Technology*, Kharagpur, India, March 2011.
- [15] D. Vuluga, J.-M. Thomassin, I. Molenberg, I. Huynen, A. Debuigne, M. Alexandre, C. Jerome, and C. Detrembleur, "Locating carbon nanotubes (cnts) at the surface of polymer microspheres using poly(vinyl alcohol) grafted cnts as dispersion co-stabilizers," in *Belgian Polymer Group Meeting*, Houffalize, Belgium, May 2010.
- [16] J.-M. Thomassin, C. Detrembleur, I. Huynen, I. Molenberg, L. Bednarz, M. Alexandre, and C. Jerome, "Foams of polymer/mwnt nanocomposites for efficient electromagnetic interferences (emi) reduction," in *Belgian Polymer Group Meeting*, Houffalize, Belgium, May 2010. 198
- [17] D. Chung, "Electromagnetic interference shielding effectiveness of carbon materials," *Carbon*, vol. 39, no. 2, pp. 279–285, February 2001. 199, 201, 207
- [18] I. Huynen, L. Bednarz, J.-M. Thomassin, C. Pagnouille, R. Jerome, and C. Detrembleur, "Microwave absorbers based on foamed nanocomposites with graded concentration of carbon nanotubes," in *Proceedings of the 38th*

- European Microwave Conference*, Amsterdam, Netherlands, October 28-30 2008, pp. 5–8. 199, 201, 210, 211, 216, 217, 221, 222
- [19] M. Al-Saleh and U. Sundararaj, “Electromagnetic interference shielding mechanisms of cnt/polymer composites,” *Carbon*, vol. 47, no. 7, pp. 1738–1746, June 2009. 199, 202
- [20] M. Ashby, *Materials selection in mechanical design*. Oxford: Oxford, 2005. 201
- [21] J.-M. Thomassin, C. Pagnouille, L. Bednarz, I. Huynen, R. Jerome, and C. Detrembleur, “Foams of polycaprolactone/MWNT nanocomposites for efficient EMI reduction,” *Journal of Materials Chemistry*, vol. 18, no. 7, pp. 792–796, 2008. 201, 204, 207
- [22] A. Saib, L. Bednarz, R. Daussin, C. Bailly, X. Lou, J.-M. Thomassin, C. Pagnouille, C. Detrembleur, R. Jerome, and I. Huynen, “Carbon nanotubes composites for broadband microwave absorbing materials,” *IEEE Transactions on Microwave Theory and Techniques*, vol. 54, no. 6, pp. 2745–2752, june 2006. 201, 218, 219
- [23] S. Pande, B. Singh, R. Mathur, T. Dhami, P. Saini, and S. Dhawan, “Improved electromagnetic interference shielding properties of mwcnt-pmma composites using layered structures,” *Nanoscale Research Letters*, vol. 4, no. 4, pp. 327–334, January 2009. 202, 203, 222
- [24] C.-S. Zhang, Q.-Q. Ni, S.-Y. Fu, and K. Kurashiki, “Electromagnetic interference shielding effect of nanocomposites with carbon nanotube and shape memory polymer,” *Composites Science and Technology*, vol. 67, no. 14, pp. 2973–2980, November 2007. 202
- [25] Y. Yang, M. Gupta, K. Dudley, and R. Lawrence, “Conductive carbon nanofiber-polymer foam structures,” *Advanced Materials*, vol. 17, no. 16, pp. 1999–2003, August 2005. 202
- [26] —, “Novel carbon nanotube-polystyrene foam composites for electromagnetic interference shielding,” *Nano Letters*, vol. 5, no. 11, pp. 2131–2134, September 2005. 202, 222
- [27] J.-M. Thomassin, X. Lou, C. Pagnouille, A. Saib, L. Bednarz, I. Huynen, R. Jerome, and C. Detrembleur, “Multiwalled carbon nanotube/poly(ϵ -caprolactone) nanocomposites with exceptional electromagnetic interference shielding properties,” *Journal of Physical Chemistry C*, vol. 111, no. 30, pp. 11 186 – 11 192, August 2007. 205
- [28] P. Potschke, S. Dudkin, and I. Alig, “Dielectric spectroscopy on melt processed polycarbonate-multiwalled carbon nanotube composites,” *Polymer*, vol. 44, no. 17, pp. 5023–5030, August 2003. 205

- [29] L. Urbanczyk, S. Bourbigot, C. Calberg, C. Detrembleur, C. JÅ©rÅšme, F. Boschini, and M. Alexandre, "Preparation of fire-resistant poly(styrene-co-acrylonitrile) foams using supercritical co2 technology," *Journal of Material Chemistry*, vol. 20, no. 8, pp. 1567–1576, January 2010. 207
- [30] J. Lee, C. Zeng, X. Cao, X. Han, J. Shen, and G. Xu, "Polymer nanocomposite foams," *Composites Science and Technology*, vol. 65, no. 15-16, pp. 2344–2363, December 2005. 207
- [31] X.-B. Xu, Z.-M. Li, L. Shi, X.-C. Bian, and Z.-D. Xiang, "Ultralight conductive carbon-nanotube-polymer composite," *Small*, vol. 3, no. 3, pp. 408–411, March 2007. 210, 211, 212

CHAPTER 6

INVESTIGATION ON THE NON-OHMIC PROPERTIES OF SOLUTIONS OF DISPERSED CARBON NANOTUBES

6.1 INTRODUCTION

The solutions of carbon nanotubes (CNTs), or other nanoparticles, discussed in the present chapter are liquid dispersions¹ containing a solvent (often water-based), a surfactant, neutral or ionic and nanoparticles, functionalized or not. The most common use of CNT dispersions is in inks or paints for antistatic coatings but they have a very wide range of applications, from the inkjet-printing of electronic circuits on thin flexible substrates, [1] to the fabrication of textiles with a battery-like behaviour, [2], or the glazing of ceramics². Inkjet-printing can also be very useful for the fabrication of transparent conductive films (TCF), [3], but for most applications only SWCNTs are usually investigated, the electrical conductivity of MWCNTs being generally considered as insufficient to have enough interconnections along the printed lines.

In the framework of the PICOM Walloon Region project, dispersions of CNTs were investigated in order to enhance the electronic conductivity of electrode-membrane assembly in polymer fuel cells, as detailed in chapter 7. Different

¹These solutions are often called ‘inks’ for simplicity, mostly in the literature but also sometimes in this chapter as well.

²More information on available commercial CNT inks and their applications can be found on <http://www.nanocyl.com/> and <http://www.future-carbon.de>.

solutions were characterized using several measurement methods. They were first investigated at high frequency but the results were not conclusive, cf. section 6.4.1 in the current chapter and section 3.3.1 in chapter 3. Second, a DC method was developed in order to provide a better understanding of these solutions and also, clearer results.

When working on simple DC characterization of dried drops (several μl) of commercial CNT solutions, current-voltage curves exhibited unexpected hysteresis and non-linearities which led us to investigate these peculiar behaviours. Data from the literature is somewhat controversial, some authors do not observe any non-ohmic behaviour, e.g. [3], others do, e.g. [4], and others describe both behaviours, e.g. [5]. A priori if non-linearities are to be observed, small amounts of solution and thus of CNTs are required, to avoid averaging effects, as would be expected if the number of CNT interconnections is too high. But in our case the non-ohmic was observed for large drops (of about $5\ \mu\text{l}$). This is detailed in a short state-of-the-art in section 6.2.

First, the influence of the constituents is considered, i.e. of the solvent and of the particles in solution. The solutions are filtrated to extract the CNTs so that the solvent can be studied separately, including any polymer from the surfactant or other additives, to rule out any effects that could be caused by the solvent. CNTs are almost exclusively considered in the present study but some solutions containing graphene were also characterized.

Second, the different solutions that are used throughout this investigation are presented. The technique used to deposit them on various types of interrupted microstrip lines and the corresponding experimental set-up are described in section 6.4.2.

Third, the influence of the drying time of the CNT dispersions is investigated and also the number of deposited layers. The possibility of an orientation of the CNTs during drying is considered. SEM pictures are also presented to provide more insight and information on the microscopic structure. An experiment showed unexpected results while applying an external electric field during the drying of the ink.

Fourth, the influence of the electric field intensity is investigated along with the size or shape or geometry of the microstrip line and gap to achieve a better understanding of the phenomena responsible for these non-linearities. The non-linearities will be compared to the theoretical equation of the thermionic emission through a Schottky barrier between CNTs, as a function of voltage and temperature.

And finally all the results are summarized and discussed in the conclusions.

6.2 BRIEF STATE-OF-THE-ART ON SOLUTIONS OF DISPERSED CNTS

As mentioned in the introduction, the data from the literature about the non-ohmic behaviour of CNT solutions is somewhat controversial. Some authors report non linearities in the characterization of CNT dispersions, [4], or thin nanocomposite films, [6], (dried CNT solution drops are in fact very similar to very thin nanocomposite films) while some observe only ohmic behaviour, [3]. Many parameters can influence the electrical properties of the composite materials and many of them could be responsible of the observed or not non-linearities. The selection of the solvent and of its additives, the use of a surfactant and the kind of surfactant chosen, the processing and dispersion technique used, whether or not the CNTs were functionalized and how, etc.

It has been reported that the choice of solvent and dispersion methods were linked to the ohmic behaviour of inkjet printed CNT thin films, [7].

The additives in the solvent and the surfactants are in fact mostly polymers, they could play a major role in these non linearities. In [6], non-ohmic behaviour is reported for ultrathin composite films of SWCNTs with a polyurethane (PU) matrix but none was observed for polycarbonate based samples. It is there attributed to charge limited injection and transport of carriers inside the PU matrix. It is also related to the 2D structure of the CNT networks. This dependence of the polymer matrix is also reported in [5], where non-linearities exist in rubber samples but not in PMMA composites.

Non-ohmic behaviour is mostly reported for SWCNTs, but it has also been observed in bulk rubber composite with MWCNTs (containing 1 % CNT therefore well beyond the percolation threshold of 0.1 %), [5]. The authors link the non-ohmic behaviour with the tunnelling transmission between CNTs. The intersection between two metallic or two semiconducting CNTs is just a contact point but between a metallic and a semiconducting CNT, a schottky barrier is present. The non-linearities are, partly, attributed to this network of Schottky barriers. This discussion is strictly valid only for perfect SWCNTs but according to the authors, as the electronic properties of the MWCNTs depend only on those of their outer shell, cf. chapter 2, the reasoning for perfect SWCNTs can be extended to MWCNTs³. But they also point that the Schottky barriers cannot be the sole origin of the non-linearities. They characterized solution samples containing oriented CNTs, thus with less intersections between CNTS and thus much less Schottky barriers, and found little differences in terms of non-linearities. Already in 1977, Bergman and Imry, [9], hinted at large non-linearities due to 'large electric fields in thin barriers'⁴.

³Though according to other authors, e.g. [8], MWCNTs are reported to be always conductive, with a conductivity similar to that of copper.

⁴To be exact, in [9] the non-linearities were present in the dielectric response for large effective dielectric constants

The importance of the chemical additives (in the solvent, surfactant, impurities during the functionalization process, ...) is highlighted in [5] and detailed in [4]. In the latter (COOH functionalized SWCNTs in aqueous solution), it is described how the particles and molecules (even water) that are adsorbed by the CNTs during a chemical treatment can alter the local distribution of charge carriers inside the CNTs, increasing their resistance. A significant charge injection in the surrounding dielectric is also suggested.

6.3 DESCRIPTION OF THE SOLUTIONS OF DISPERSED NANOCOMPOSITE

Several CNT solutions were characterized, commercial water based dispersions containing 1%wt MWCNT from Nanocyl and Future Carbon. The ink from Future Carbon is the CarboDis ES (FC) with functionalized nanotubes (no details given on the surfactant used), this ink has undergone a multi-stage process (Future Carbon specificity, additives and chemical treatments) to ensure a high-quality and low-viscosity dispersion, [10]. The Nanocyl ink, Aquacyl (AC), contains an anionic surfactant to improve the dispersion and stability of the solution[11]. It was received later in this investigation than the other inks and is therefore not mentioned in the first results.

CNT dispersions fabricated at the Universite de Liege⁵ were also characterised. The first six solutions, JA to JF, are two series of dispersions containing 1%wt CNTs (bought from Nanocyl in powder form) having different characteristics (multi-, double-, and single-wall CNTs, M-,D- or SCNTs), as summarized in table 6.1. The first series has a neutral surfactant, poly(vinylpyrrolidone) or PVP and the second series an anionic one, sodium dodecyl sulfate or SDS.

Three older aqueous solutions were also fabricated by the ULg and studied in the current chapter, named JG to JI, they contain M-, S- and DWCNTs, respectively, and a neutral surfactant.

Aqueous based solutions containing conductive graphene instead of CNTs were also received (from ULg). The water-soluble graphene was obtained by reduced graphite oxide (RGO) methods and functionalized using poly(ethylene glycol) or PEG. The latter four solutions⁶ are given in table 6.1, D0 to D3. The first one, D0, contains pure graphite oxide (GO). The second one, D1, is based on reduced graphite oxide from one step process GO photoreduction and PEG grafting (PRGO-g-PEG). The third and fourth solutions also contain PRGO-g-PEG material but fully reduced into RGO-g-PEG, using a water-compatible reducing agent $NaBH_4$ (RGO-g-PEG ($NaBH_4$)) or under thermal conditions by using refluxing ethylene glycol (EG) as solvent (RGO-g-PEG (EG refluxing)). Except pure RGO the graphene particles are all water soluble and do not require the addition of a surfactant to keep them in aqueous solution.

A picture of the CNT dispersions from ULg can be seen on Fig. 6.1. From the colour of the solutions, it is obvious that the dispersion is not optimal for all samples, even after 30 minutes sonication (up to one hour when the dispersion of the samples seemed imperfect to the naked eyes). The graphene dispersions are shown on Fig. 6.2, the colour of the liquid is more opaque and homogeneous

⁵The CNT inks were fabricated by Dr. J.-M. Thomassin and the graphene ones by Dr. D. Vuluga.

⁶More details on these graphene solutions fabrication and characterisation can be found in [12]

Code	Nanoparticle	Surfactant
FC	MWCNT	unknown
AC	MWCNT	anionic
JA	MWCNT	PVP
JB	SWCNT	PVP
JC	DWCNT	PVP
JD	MWCNT	SDS
JE	SWCNT	SDS
JF	DWCNT	SDS
JG	MWCNT	neutral
JH	SWCNT	neutral
JI	DWCNT	neutral
D0	pure RGO	none
D1	PRGO-g-PEG	none
D2	RGO-g-PEG (NaBH_4)	none
D3	RGO-g-PEG (EG refluxing)	none

Table 6.1.: Characteristics of the different solutions of dispersed CNTs investigated in this chapter.

than that of the CNT solutions, the dispersion is therefore probably better for the graphene solutions.

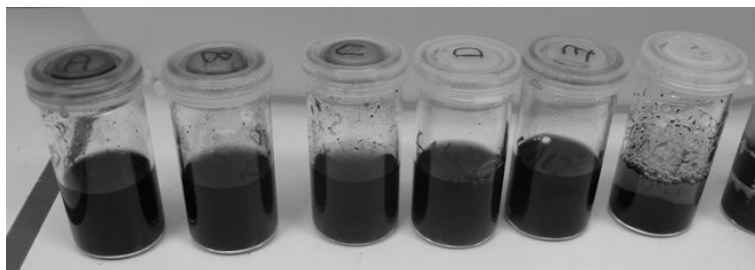


Figure 6.1.: Picture of the six solutions containing CNTs, from JA (left) to JF (right). From the colouring of the dispersions it is visible to the naked eye that for some solutions the dispersion is not very good (even after sonication).

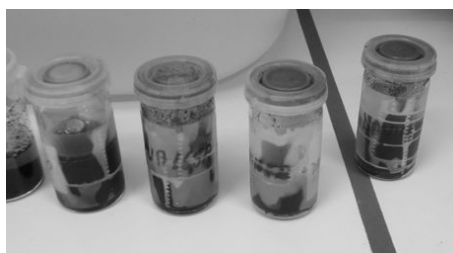


Figure 6.2.: Picture of the three inks containing graphene and the RGO reference, from D0 (left) to D3 (right). The dispersion seems better for the graphene inks than the CNT ones (same sonication and storage conditions).

This visual deduction is further confirmed by slightly shaking the bottles of the JD-JE-JF solutions, cf. Fig. 6.3. A layer of foam can then be observed on top of the liquid phase. Those foams do not have a uniform grey or black colour but are heterogeneous, this is especially remarkable for the JF solution. No such foam has been observed (after similar shaking) for the three samples containing PVP (JA-JB-JC), the foam is then most probably due to the SDS surfactant.

In comparison, the commercial dispersions (FC and AC) are totally opaque to light and their viscosity is much higher than the other inks, for the same CNT content, cf. Fig 6.4.

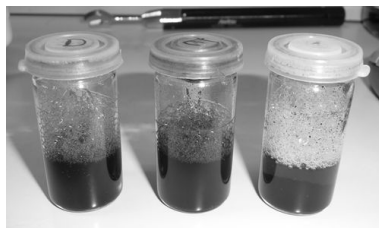


Figure 6.3.: Picture of the foaming of the JD-JE-JF solutions after being gently shaken, their color is not uniform, hinting at a poor dispersion.

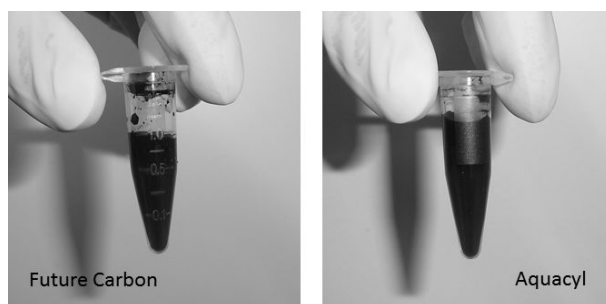


Figure 6.4.: Picture of the FC - Future Carbon (left) and AC - Aquacyl (right) solutions, they appear much darker and much more viscous than all the dispersions from the Universite de Liege (though under the same sonication and storage conditions).

6.4 EXPERIMENTAL TECHNIQUES FOR CNT SOLUTIONS CHARACTERISATION

6.4.1 AC characterisation using a commercial system

Initially the main goal of our measurements was to compare the samples and to study the differences due to the different parameters of the inks on their overall electrical conductivity and dielectric constant. A commercial equipment was first used, the Agilent E07080 dielectric probe kit that can be coupled to the PNA-X (Agilent N5242A premier-performance network analyzer), cf. Fig. 6.5. The cylindrical probe can be inserted in the liquid itself and by measuring the reflected power, the dielectric constant and conductivity of the solution-under-test can be retrieved as a function of frequency.



Figure 6.5.: Picture of the dielectric probe kit, not connected to our PNA-X but to similar equipment, from its user manual.

This experimental set-up yields very good results for alcohol or de-ionized (DI) water but does not seem well suited to the nanocomposite solutions of this study, as can be seen on Fig. 6.6. The displayed results were chosen as example. The conductivity and dielectric constant measured using this set-up for all the ULg solutions (CNT and graphene alike) are all identical to that of DI water. The FC dispersion exhibit different values but very noisy and even negative. It was speculated that for the ULg solutions there were not enough conducting particles in the vicinity of the probe aperture while the FC dispersion might be too conducting for a set-up primarily designed for the characterization of dielectric materials⁷.

⁷The Aquacyl solution was not characterized using this AC technique because it was not available to us yet and later, when the Aquacyl sample was received, this method had been abandoned.

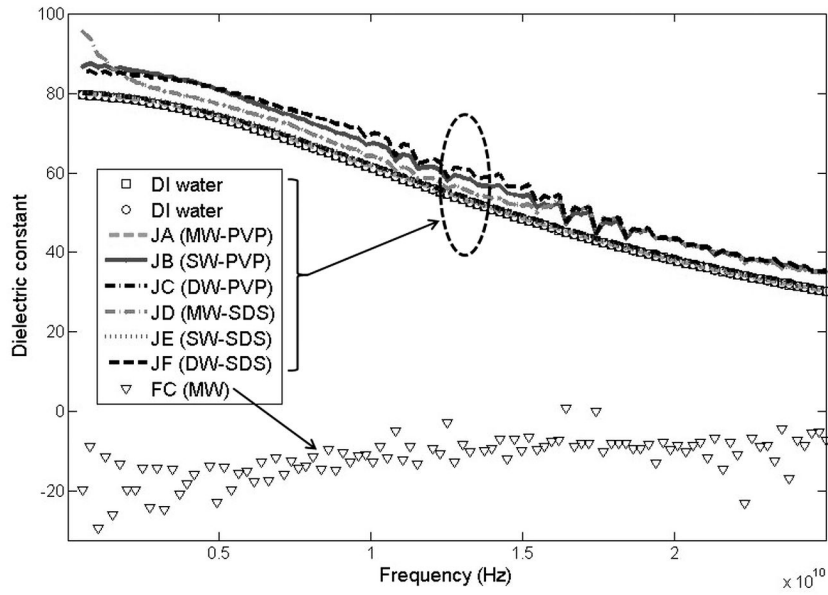


Figure 6.6.: Measured dielectric constant versus frequency of the ULg-CNT solutions and that of the FC dispersion, these results show the inadequacy of the commercial set-up in the case of the nanocomposite solutions.

6.4.2 DC technique for the investigation of the non-linearities in the current-voltage curves

The experimental set-up that was considered next is rather simple, a drop of solution (usually $5\ \mu\text{l}$, using a precision micropipette) is deposited on an interrupted microstrip line⁸, fabricated using photolithography and chemical etching, so that the interruption or gap is in fact a kind of simple 2D capacitance, cf. Fig. 6.7 and Fig. 6.8. This 2D capacitance has a width w and a length l separating the ‘electrodes’ (of width w), i.e. the ends of the metal strip.

In practical measurements, the outer ends of the microstrip line are connected to a K2636A Dual-channel System SourceMeter Instrument⁹. A voltage can then be applied on the drop of solution and the current passing through can be measured (both can be done using a single K2636). Furthermore, the K2636 can be used to generate ramps or sweeps of selected voltage, as well as measure current as low as 1 fA and as high as 10 A. It can also make pulsed measurements so that the voltage is actually applied only during a very short time and it is set to 0 between the pulses, as illustrated on Fig. 6.9. Both pulse duration and rest time between pulses can be independently chosen. The resistance of the drop can be calculated from the I-V curves obtained this way. However, the exact thickness of the drop is not precisely known and not easily measured. First it is very small. Second, it varies as the drop dries then ages. Besides the metal line has a thickness of $17\ \mu\text{m}$, much smaller than that of the drop. The electric field lines are straight lines and isotropic only in those $17\ \mu\text{m}$. An exact calculation of the electrical conductivity from the IV curve would probably require numerical simulations and the accurate measurement of the drop thickness.

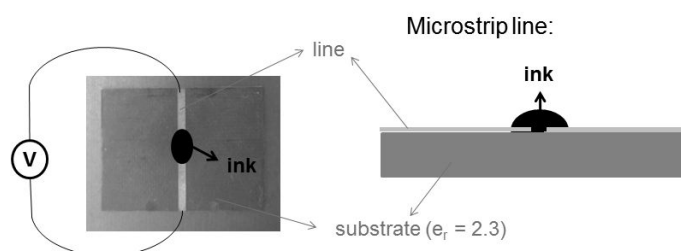


Figure 6.7.: Schematic diagram of the experimental set-up; a drop on ink deposited on an interrupted microstrip line and both ends of the line connected to outputs/inputs of a power source/voltmeter.

⁸This ‘interrupted microstrip line’ topology could also be seen as a kind of very thin slotted line.

⁹The electrical connections are made through the Anritsu model 3680K sample holder, the same that is used for the microwave microstrip measurements described in section 3.3.1.

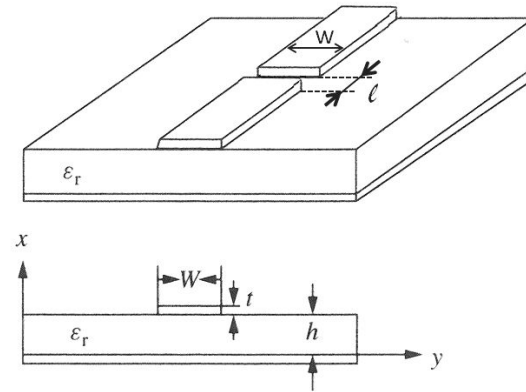


Figure 6.8.: Schematic diagram of the interrupted microstrip line with w the width of the metal line, l the length of the gap, t the thickness of the metal line and h the thickness or height of the substrate, modified from [13].

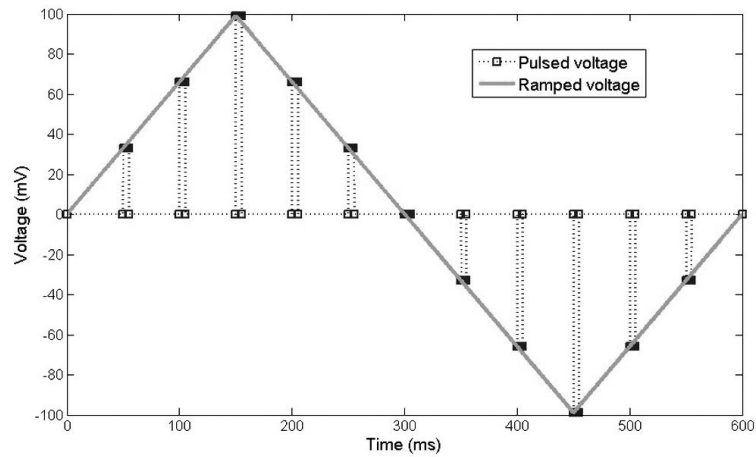


Figure 6.9.: Schematic diagram of the output voltage of the K2636 instrument as a function of time during a sweep cycle of pulsed ($\square$) and ramped measurements (solid). During pulsed measurements, the given voltage is applied only during the pulse duration and is put to zero between pulses (rest time). In ramped measurements the voltage increases or decreases linearly without pauses.

Except mentioned otherwise, all the measurements presented in this chapter used the same ‘standard’ geometry; i.e. a gap with a length of 200 μm and metal microstrip lines having a width of 1.3mm.

Because the experimental method is strictly identical, the samples characterized using it can be compared to each other from the IV curves (from its slope, yielding the conductance). But examining the first IV curves of the nanocomposite solutions, a hysteretic and non-linear behaviour was observed, cf. Fig. 6.10, and it raised several questions about the phenomena responsible of this non-ohmic characteristic.

First the hysteresis was first assumed to be of thermal origin and indeed when making pulsed measurements, cf. Fig. 6.10, (at each step of the sweep, the selected voltage is applied during 100 μs and then turned off for 50 ms before the next pulse with a step voltage) instead of a simple linear ramp, no more hysteresis can be observed (except using very high voltages but then it is due to the high electric field). This is shown on Fig. 6.10. Furthermore, if the duration of the pulse is increased, the hysteresis can be observed again, confirming the self-heating hypothesis.

On the other hand non-linearities remain even in IV curves from very short pulse measurement¹⁰. They are therefore not due to self-heating.

The major disadvantage of this method is the lack of reproducibility when the CNTs are not well-dispersed in the solution¹¹. If this is the case, one 5 μl drop of CNT ink may not contain as many CNTs or have the same microscopical structure as another 5 μl drop. Furthermore, depending on the dimensions of the aperture, or gap, of the microstrip line, the active area may be very small and not representative of a larger quantity of solution. But the length of the gap must be small (relative to the width of the metal microstrip line) in order for the electric field lines to be straight lines, parallel to one another (uniform field) inside this gap. The width of the metal line is further limited by the geometry of the sample holder (maximum possible width of about 1.5 mm).

Nevertheless, this irreproducibility can be assessed by making several measurements and sonication of the samples prior to their characterization. Two identical sets of CNT-ULg samples were characterized exactly the same way and, as shown on Fig. 6.11 and on Fig. 6.12, the results are not similar, neither quantitatively nor qualitatively. But in the case of solution having a more ho-

¹⁰The minimum duration of the pulse is limited by the time required by the SMU (Source Measure Unit) to make a measurement of the adequate precision, a low-level current is more difficult to measure and will require a longer pulse duration. A more precise measurement will also require a longer time to be completed.

¹¹In the particular case of the JF sample, even after sonication, two distinct phases were present and of course results varied depending on the phase in which the ink was taken.

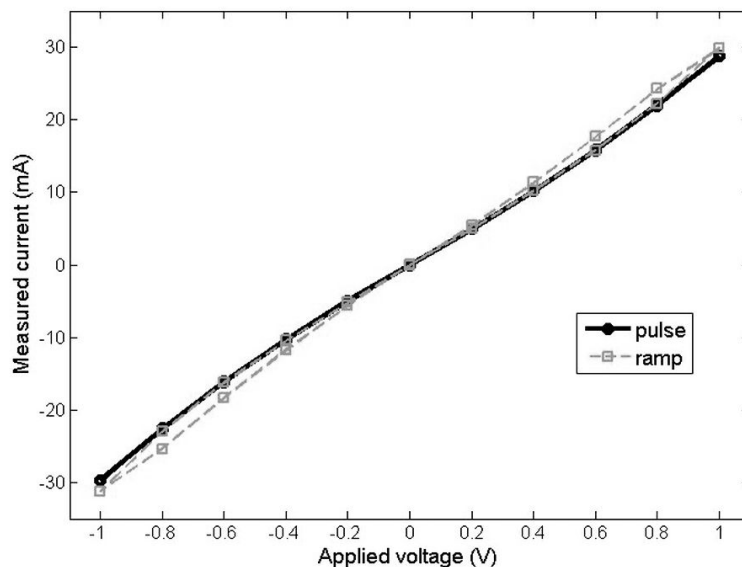


Figure 6.10.: Typical current-voltage (IV) curves of a CNT solution sample, from pulsed and ramped measurements.

homogeneous CNT dispersion, this reproducibility should increase significantly, as confirmed from the IV curves of the commercial solutions¹² shown on Fig. 6.13 and showing a much improved reproducibility.

This ‘flaw’ of the method therefore could be also an interesting method to assess the dispersion of nanocomposite solutions.

Despite the irreproducibility of these measurements, a difference can be observed between the solutions containing PVP and those with SDS surfactant. The conductivity of the former is about one order of magnitude higher than that of the SDS samples but the latter seem to exhibit stronger non-linearities.

¹²Though there were some slight differences in the microstrip lines used for some of those measurements, as will be detailed in section 6.7.

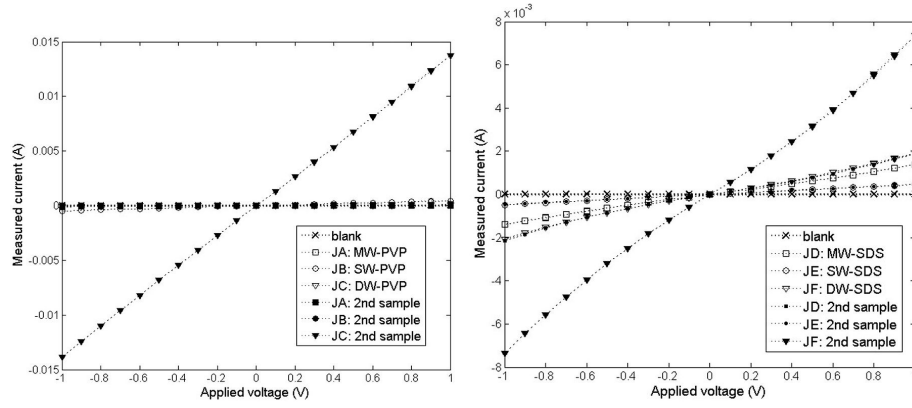


Figure 6.11.: IV curves of the CNT-ULg solutions, samples JA-JB-JC, M-,S- and DWCNTs with PVP surfactant (left) and samples JD-JE-JF, M-,S- and DWCNTs with SDS surfactant (right).

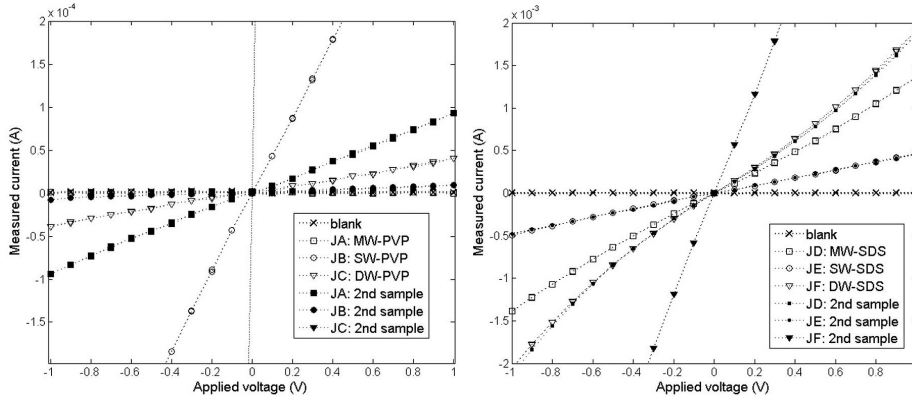


Figure 6.12.: IV curves of the CNT-ULg solutions (zoom for lower current curves), samples JA-JB-JC, M-,S- and DWCNTs with PVP surfactant (left) and samples JD-JE-JF, M-,S- and DWCNTs with SDS surfactant (right).

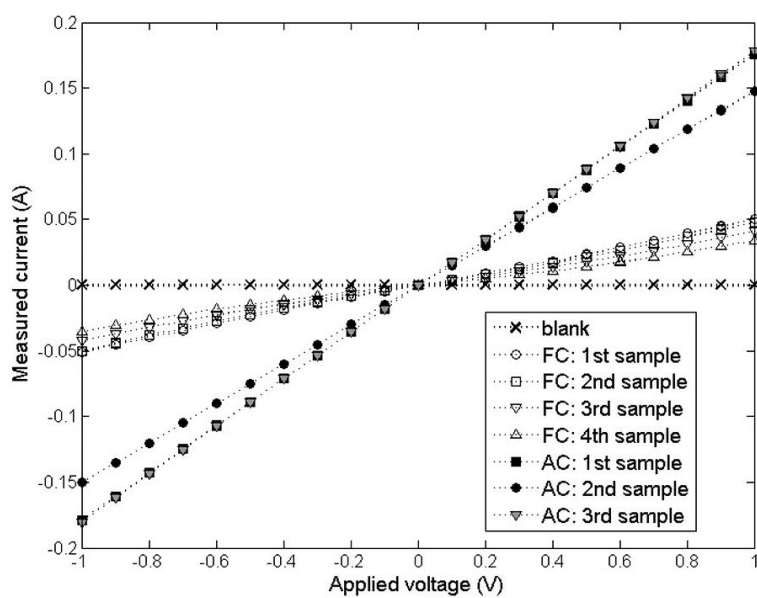


Figure 6.13.: IV curves of the FC (Future Carbon) and AC (Aquacyl) dispersions, showing a quite good reproducibility.

6.5 INFLUENCE OF THE CONSTITUENTS OF THE NANOCOMPOSITE SOLUTIONS

6.5.1 Influence of the CNT/graphene particles

As shown on Fig. 6.11, The CNT-ULg solutions results are not reproducible, not even qualitatively. It is therefore very hard to draw any conclusions from them.

Instead, the curves presented on Fig. 6.14 and Fig. 6.15 are the IV curves of older samples, also fabricated by the Universite de Liege, S-, D- and MWCNT water-based inks with a neutral surfactant, samples JG-JH-JI of table 6.1. The role of sonication on dispersion is evident on these results. Furthermore, it can easily be seen that while the FC ink has the higher conductivity, the SWCNT ink has a negligible conductivity.

It is well known, and detailed in the state-of-the-art, that obtaining a good dispersion of SWCNT in nanocomposite is always harder than for D- or MWCNTs, because the interactions between the nanotubes are much stronger than in the latter case. Furthermore there seem to be little difference in terms of conductivity between the double and multiwall CNT inks (that were sonicated).

Characterization of the CNT-ULg solutions (JA-JF) seemed to indicate that SDS solutions had higher conductivity and also a more pronounced non-linearity, on the average, than PVP ones, but given the lack of reproducibility, further study on better dispersed samples would be required before any conclusion can be made.

Attempts were also made to investigate mixes of different solutions, whether in the liquid form or as different layers atop one another, but no reproducible result could be extracted. Sometimes the mixed solution exhibited the behaviour of the bottom layer or of the most conductive solution, it could also have a conductivity of about the average of that of the original inks used or even a radically different behaviour. This would also be very interesting to investigate, probably using better dispersed solutions as well.

The relative non-linearity (NLN_r) of the curve is calculated as the deviation of the curve from the slope of the tangent at the origin (calculated as the linear interpolation of the points in the vicinity of the origin), cf. Fig. 6.16. The relative non-linearity is then the absolute difference (root mean square), for each voltage value, between the measured I value and that of the tangent, divided by the 2-norm of the current¹³. The relative non-linearity is then calculated for each

¹³The 2-norm of a vector x of length n is equal to $\|x\|_2 = \sqrt{x_1 + \dots + x_n}$

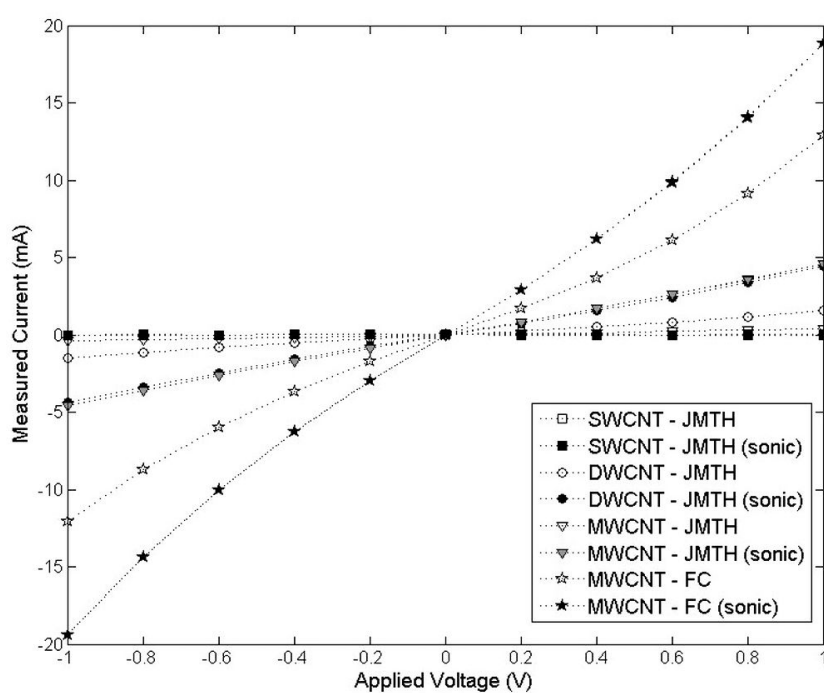


Figure 6.14.: IV curves of single- (JH:□), double- (JI:○) and multi- (JG:▽) wall carbon nanotube ink samples that were submitted to sonication prior to the characterization (black) or not (white), as well as a sample of FC dispersion (★).

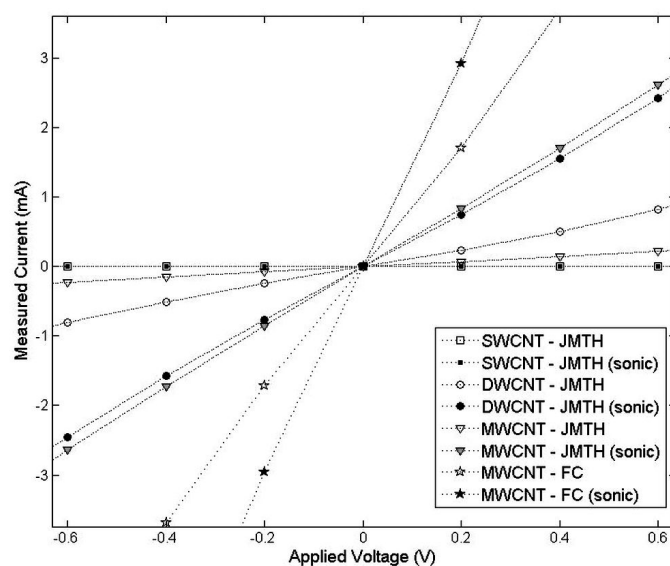


Figure 6.15.: Magnification (lower voltages) of the IV curves of single- (JH: $\square$), double- (JI: $\circ$) and multi- (JG: ∇) wall carbon nanotube ink samples that were submitted to sonication prior to the characterization (black) or not (white), as well as a sample of FC dispersion ($\star$).

applied voltage (V_i) value using the simple formula

$$NLN_r(V_i) = \frac{|I_{lin}(V_i) - I_{mes}(V_i)|}{\|I_{mes}\|_2} \quad (6.1)$$

where I_{mes} is the measured current values during a single sweep and I_{lin} is the tangent to I_{mes} at the origin (relative to the same voltage sweep).

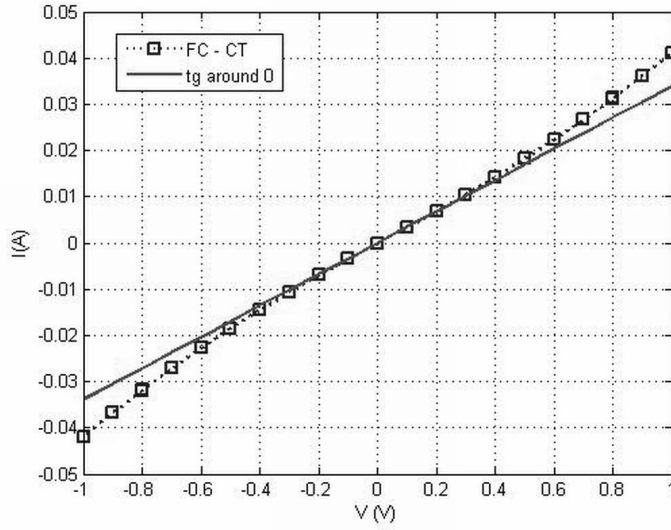


Figure 6.16.: Typical IV curve of a FC sample ($\square$) and the corresponding calculated tangent at the origin I_{lin} (solid).

The relative non-linearities calculated using equation 6.1 are shown on Fig. 6.17 for the DWCNT, the MWCNT and the FC dispersion (the SWCNT exhibiting a negligible conductivity). The Future Carbon solution (though containing MWCNTs) exhibits the highest non-linearity, followed by the ULg-DWCNT and then the ULg-MWCNT ink which is the most linear. This would indicate that the actual chemical treatments and processes, as well as the additives have more effect on the non-linearity than the type of CNTs used. But if this measurement were done on a smaller scale (smaller number of CNTs), the results would probably be very different. For example, in [14], where only one CNT is used to build a field effect transistor, the observed non-linearity in the IV curves is largely due to the contact between the metal of the electrode and the nanotube (semiconducting SWCNT).

The Aquacyl and Future Carbon solutions were compared on Fig. 6.13, it can be seen on the latter figure that the conductivity of the Nanocyl ink is

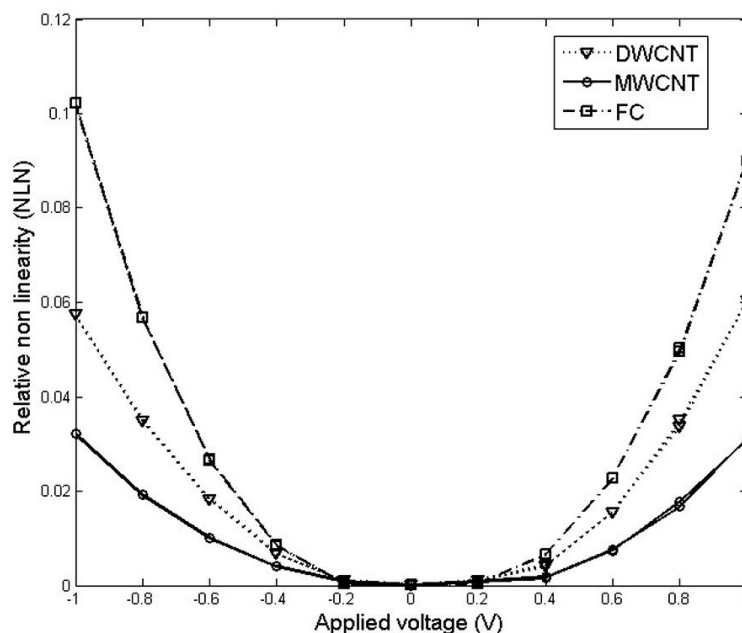


Figure 6.17.: Relative non-linearities as a function of the applied voltage for the DWCNT (JI: $\square$), the MWCNT (JG: $\circ$) and the FC (∇) solutions.

over 3 times higher than that of Future Carbon. On the other hand the relative non linearities of the FC ink are much more important than that of Aquacyl , cf. Fig. 6.18, showing that high conductivity and non-ohmic behaviour do not necessarily go hand in hand.

These differences in conductivity and relative non-linearity might be put in perspective with the SEM pictures of the FC dispersion and of Aquacyl, cf. Fig. 6.19. The size of the Aquacyl CNTs seem smaller than that of the FC nanotubes but the network of CNTs appear denser, more closely meshed, on the Aquacyl ink. Long CNTs are reported to be linked to more ohmic behaviour and weaker non-linearities, [3], due to the increased possibility of contact points between CNTs and thus of averaging, while it would lead to a decreased overall resistance. However, this is in contradiction with our measurements where FC ink exhibits stronger non linearities and lower conductivity than Aquacyl. Besides, nanotubes from the FC are most probably heavily functionalized, while the Nanocyl solutions are known to rely more on additives than on functionalization to improve the dispersion of the CNTs. A strong influence of the CNTs functionalisation on the strong non-linearities observed for FC samples must therefore to be considered as well. Furthermore, the darker shade of the Aquacyl SEM

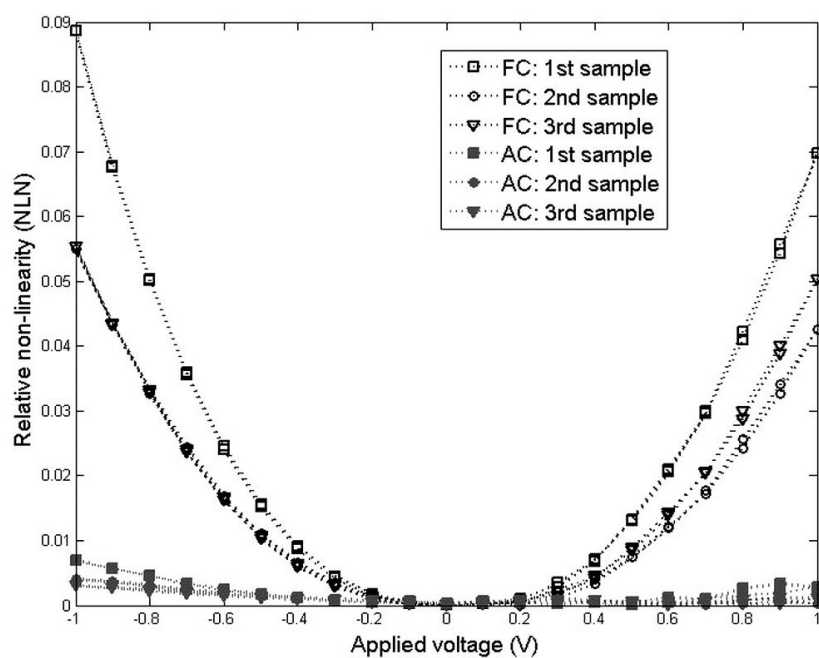


Figure 6.18.: Relative non-linearities of three Future Carbon (FC) samples (white) and three Aquacyl (AC) samples (black).

picture suggest a higher conductivity (lesser charge accumulation on the sample, though this could be a very local effect).

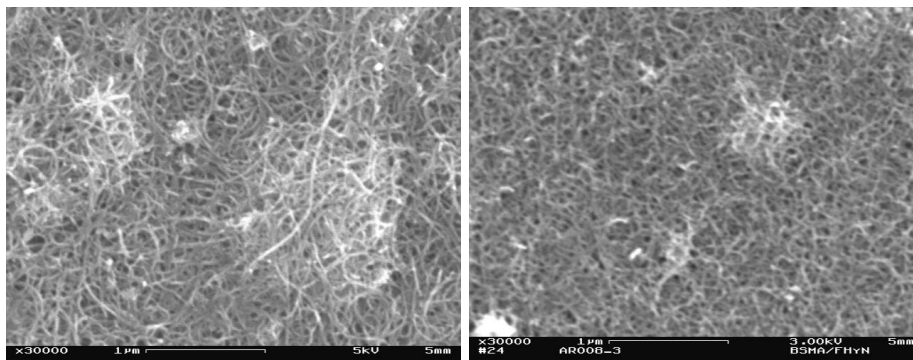


Figure 6.19.: SEM picture of the CNTs from a dried drops of Future Carbon solution (left) and SEM picture of the CNTs from a dried drop of Aquacyl (right).

Dispersed solutions of graphene. The solutions containing water soluble graphene particles presented in section 6.3 were also characterised.

But, as can be seen on Fig. 6.20, only the conductivity of the D2 solution (aqueous dispersion of RGO-g-PEG obtained with a $NaBH_4$ reduction) is non-negligible. The IV curve of this sample is also significantly non-linear. But, as the JA to JF solutions of dispersed CNTs, the reproducibility of the IV curves of the graphene sample is poor and it is then hard to take any definite conclusion. The only thing in common with all the graphene measurements made is the significantly higher conductivity of the D2 sample compared to the other solutions (all exhibiting negligible conductivity throughout the measurements). Besides, the conductivity of the D2 graphene solution is almost two order of magnitudes lower than that of the FC dispersion though in [15], the author state that given the high aspect ration of graphene sheets, graphene solutions are expected to exhibit a higher conductivity.

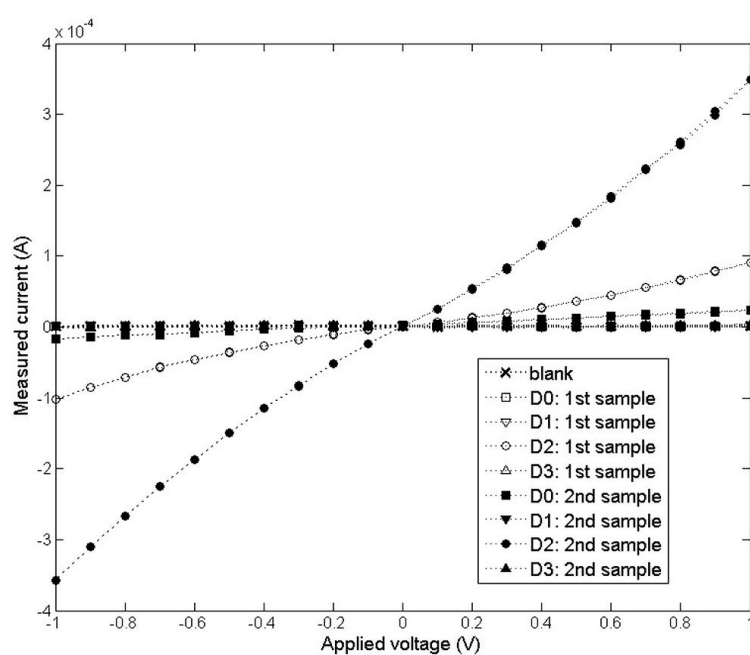


Figure 6.20.: IV curves of two series of samples of graphene solutions: the RGO reference (D0: $\square$), the PRGO-g-PEG (D1: ∇), the RGO-g-PEG via NaBH_4 (D2: $\circ$) and the RGO-g-PEG via EG refluxing (D3: $\triangle$).

6.5.2 Influence of the solvent

To isolate the response of the solvent, Aquacyl and the Future Carbon dispersions were filtrated and then characterized, using the same method as the other solutions. The pictures of the filtrated inks can be seen on Fig. 6.21. The filtrated FC dispersion is clear and transparent but the Aquacyl is also transparent though still with a pronounced grey colouring.

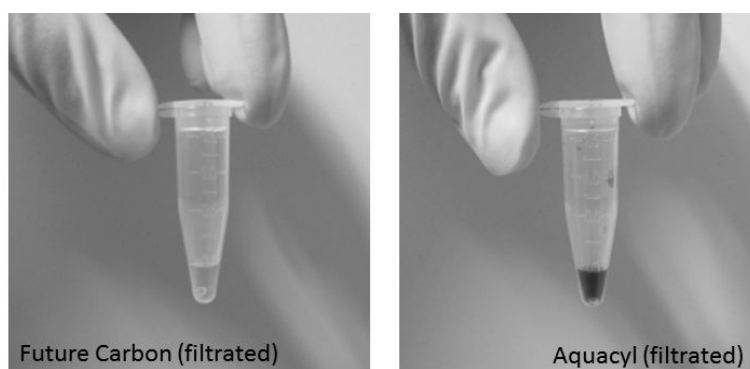


Figure 6.21.: Pictures of the FC dispersion (left) and the Aquacyl solution (right) after filtration.

The successful filtration and the subsequent effective removal of CNTs from the solutions is confirmed on the SEM pictures of the filtrated samples, cf. Fig. 6.22 and cf. Fig. 6.23. It must be noted that the filtrated solutions have a negligible conductivity and SEM picture are therefore harder to take because of the electrostatic charging of the sample. This negligible conductivity is confirmed by the IV curves of the filtrated samples of Future Carbon dispersion and of Aquacyl that are shown on Fig. 6.24. These samples have different gap geometries, as will be detailed in the beginning of section 6.7, but they all exhibit the same IV curves as that of a blank sample, containing no solutions at all.

In conclusion, the solvent has no direct effect on the conductivity nor on the non-ohmic behaviour of the solutions, whether that of Future Carbon or Aquacyl. Still, it has an indirect influence because of its role in the quality of the dispersion and stability of the ink (and probably also adhesion to the substrate material), this would require a more in depth study.

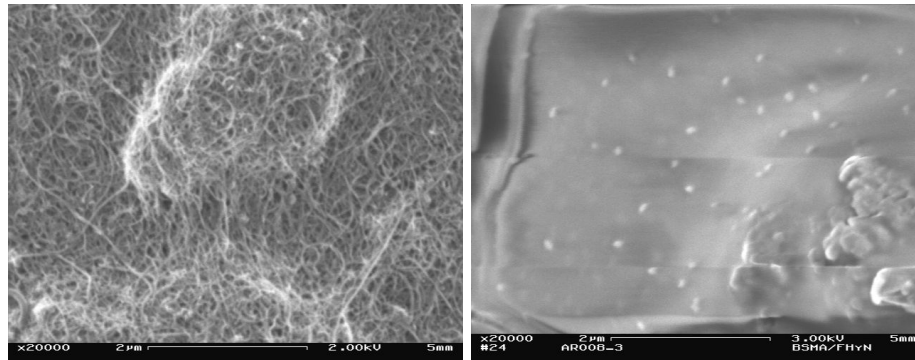


Figure 6.22.: SEM picture of the dried FC dispersion with CNTs well visible (left) and SEM picture of the filtrated FC dispersion, without apparent CNTs (right).

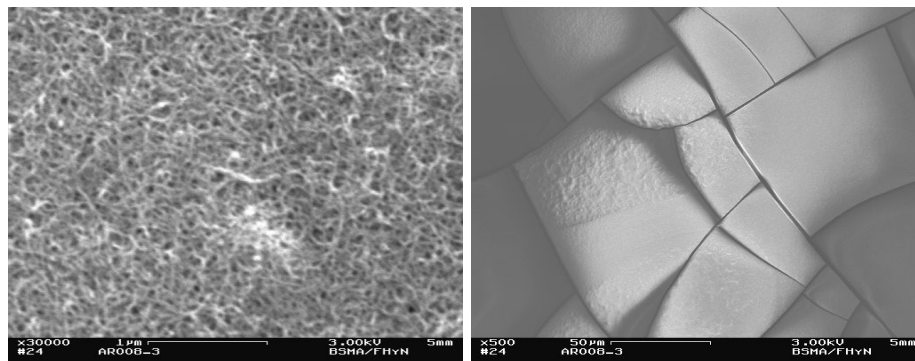


Figure 6.23.: SEM picture of the dried AC dispersion with CNTs well visible (left) and SEM picture of the filtrated AC dispersion, without apparent CNTs (right).

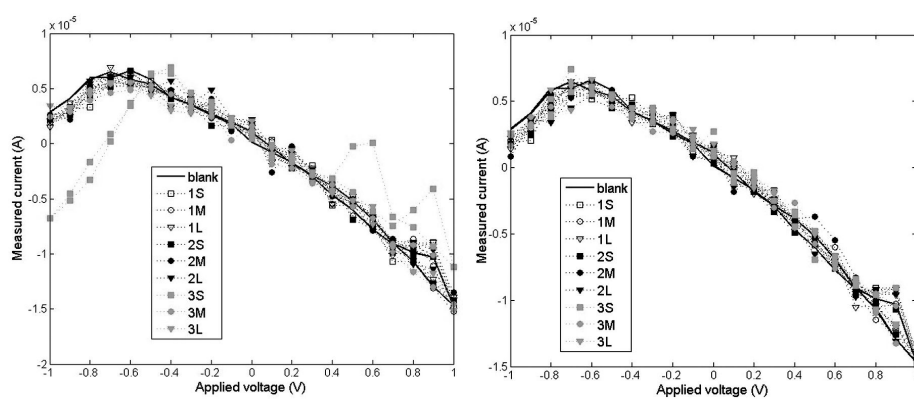


Figure 6.24.: IV curves of a series of samples of filtrated FC dispersion (left) and of a series of samples of filtrated Aquacyl (right), all showing negligible conductivity similar to that of a 'blank' sample without solution.

6.6 INFLUENCE OF THE DEPOSITION CONDITIONS AND PARAMETERS

6.6.1 Influence of the number of deposited layers

In almost all of the measurements presented in the current chapter, one single $5\ \mu\text{l}$ drop of solution was deposited. The exact shape of the drop has no or very little influence, as long as it covers the line gap well enough (stretch a little beyond the gap itself), because the electric flux lines do not spread very far from the gap. If the influence of the number of layers of dried solution¹⁴ is to be studied, some kind of ‘mask’ must be used to ensure all the solution is deposited in the active area. The mask was fabricated with a piece of scotch tape where a square window, of about $2 \times 3\ \text{mm}^2$, was carved, as illustrated on Fig. 6.25. The measurements presented here are made on Future Carbon (FC) solutions because an adequate reproducibility of these measurements was shown in the previous section. Besides Aquacyl solution was not available yet in our laboratory at the time of these tests.

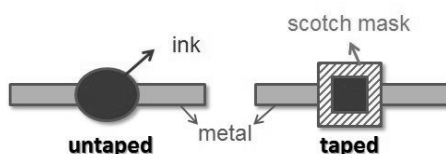


Figure 6.25.: Sketch illustrating the use of a scotch tape mask to contain the solution in the vicinity of the gap in the microstrip line (untaped line on the left, masked line on the right) with the solution deposited on the sample.

However the IV curves measured using this masking tape (peeled off before the measurement to remove the excess ink) showed little effect from the mask, cf. Fig. 6.26, compared to measurement where the drop of solution is simply deposited on the gap, as previously. The drops of solution were deposited successfully, after visible drying of the previous drop, thus forming layers of dried CNT ink. It must be noted that the result of the 3-layers taped sample was damaged during the removal of the mask and results are probably flawed as a consequence.

If the IV curves for the taped samples are compared, cf. Fig. 6.27, not taking the probably damaged 3-layers sample, the conductivity increase from 1 to 2

¹⁴Simply depositing a bigger drop of CNT may not be very pertinent because the dried residue would be larger but in an area where there is no electric field and the increase of CNT content in the ‘active area’ (in the gap and a little beyond on the sides and above it) would be hard to evaluate.

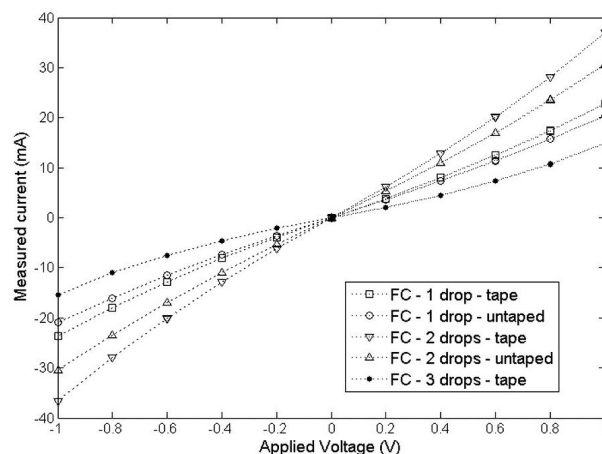


Figure 6.26.: *IV curves of the FC samples deposited on the microstrip line gap, with (tape) or without using the tape mask (untaped), with 1, 2 or 3 layers of dried solution.*

layers but by less than a factor 2, and it would probably increase by even less if the number of layers was still increased. The lines of electric fields not extending much beyond the $17\ \mu\text{m}$, the added layers contribute less and less once the gap is filled.

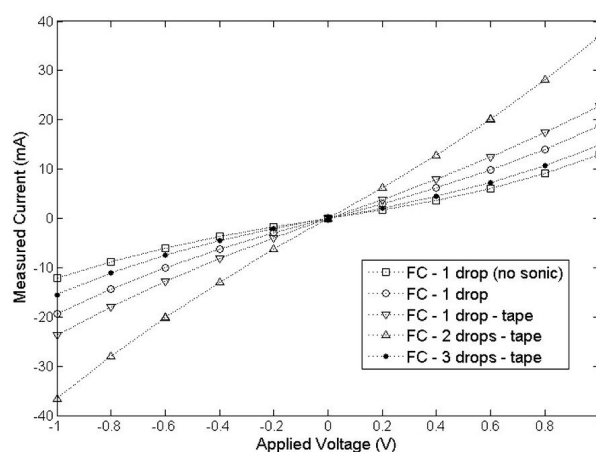


Figure 6.27.: *IV curves of the FC samples with 1, 2 or 3 layers (drops), also the curves for a 1 layer sample without masking tape and another that has not been sonicated prior its characterization (and no tape either).*

6.6.2 Influence of the drying time

Once deposited on the substrate, the solution begins to dry and from a 3D droplet it turns into a more 2D structure. Then when the solvent has completely evaporated, a thick dry residue remains and sticks rather well to the substrate, cf. Fig. 6.28. The exact thickness, colouring, opacity and adhesion to the substrate is very different from one ink to the other. Commercial dispersions are darker, thicker and more adhesive than those from Ulg, indicating not only a probably better dispersion but a formulation developed to improve the adhesion of the ink to substrate, especially interesting for coating application for example. In the literature, [16] and [3], a non uniform dispersion of the CNTs is often observed when the ink dries, the CNTs are mostly distributed along the perimeter and at the center of the drop, forming what they call a ‘coffee ring’. No such pattern was observed on our samples, the dried residue forming a uniform oval, the presence of CNTs in the gap is confirmed by the SEM pictures (except for the solutions exhibiting a poor dispersion even to the naked eye).



Figure 6.28.: Pictures of a drop of nanocomposite ink ($5\ \mu\text{l}$) a few seconds after deposition and 20 minutes later.

The discussion on the drying time that follows is based on the Future Carbon ink because of its quality and reproducibility but it is very similar with any other ink, at least qualitatively. Besides, because of the dispersion issues with the ULg-made inks, these inks had often to be sonicated for longer times than the commercial ones and there is a legitimate concern about the damage these sonications may have caused to the CNTs.

As can be seen from the curves on Fig. 6.29, the conductivity (proportional to the slope of the IV curves) is negligible immediately after the deposition of the ink and is significant only after 12 minutes of drying.

Between 12 and 40 minutes after drying, the conductivity is stable, cf. Fig. 6.30, then after a few hours its value is decreased. Two days later it is even lower. Two phenomena may explain this sharp decrease; either CNTs leave the dried drop of ink (a kind of ‘erosion’), e.g. because of air drafts, or the residue is partially detaching itself from the substrate and metallic strips which would increase the equivalent resistance of the metal-ink interface. Or both phenomena could be occurring simultaneously.

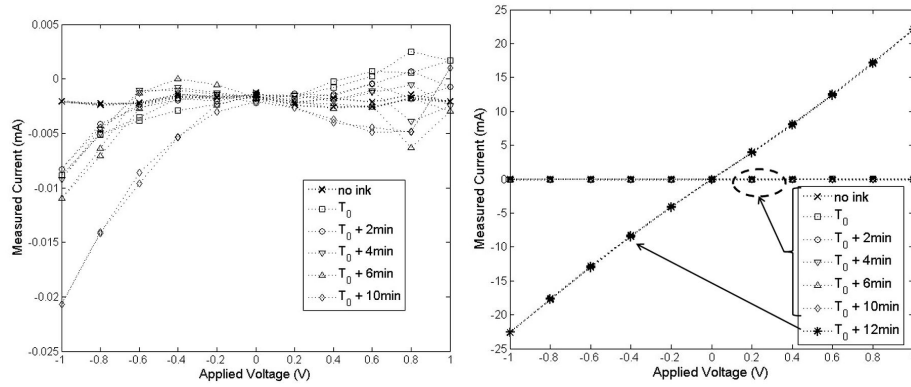


Figure 6.29.: IV curves of an FC 5 μl drop during the first 10 minutes after deposition (left) and the first 12 minutes after deposition (right). It can be seen that the conductivity is negligible during the first 12 minutes.

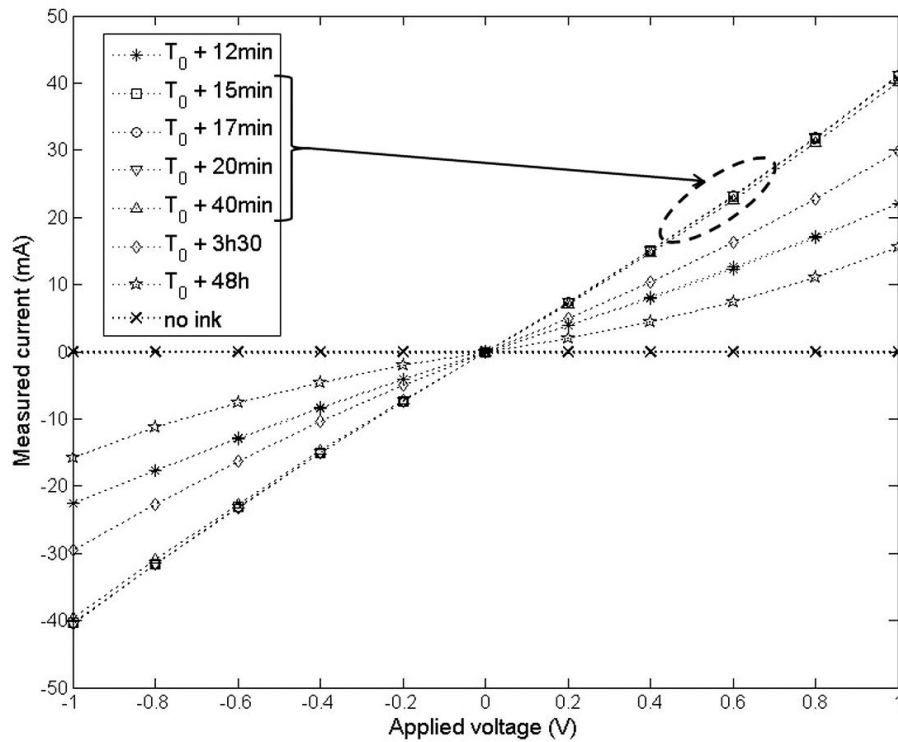


Figure 6.30.: IV curves of an FC 5 μl drop from 12 minutes (*) to 48 hours (*) after deposition. Between 15 and 40 minutes after deposition the curves are almost identical.

If the CNTs are liberated from the dried residue over time, covering the drop before the conductivity decrease would prevent that from occurring. A set of sample was thus covered using scotch tape at 45 minutes of drying. But the conductivity of the samples that were not covered by tape actually decreased less than that of the samples that were tape-protected. These results would be in favour of the second hypothesis, the dried residue detaching himself partially from the substrate, which might actually be worsened when an adhesive material is pressed on the sample. Using a protective varnish or resin instead of scotch tape might provide as good or even better protection from erosion, while applying a much smaller mechanical strain.

Unless any explicit indication to the contrary, all samples depicted in this chapter were measured between 20 and 40 minutes after deposition.

6.6.3 Application of an electric field during CNT solution drying

It is sometimes mentioned in the literature, [17] or [18], that the application of an electric or magnetic field during the fabrication of a nanocomposite (melt-blending) can lead to some form of alignment in the CNTs inside the composite. Out of curiosity, a 1 volt bias was applied during the 30-minute drying of two samples of Future Carbon dispersion. One had a pointed-edge gap and the other a straight-edge one, both with a gap length of $200\text{ }\mu\text{m}$, as shown on Fig. 6.31. Their measured IV curves and corresponding non-linearities are plotted on Fig. 6.32 and Fig. 6.33.

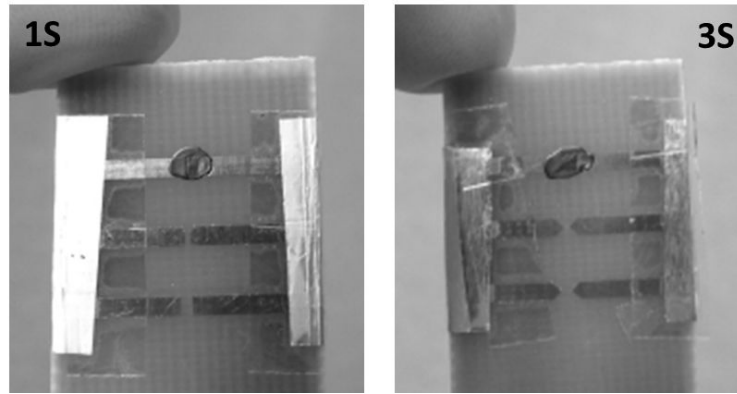


Figure 6.31.: Pictures of the straight-edge gap sample 1S (left) and of the pointed-edge gap samples 1S (right). Both samples have a gap length of $200\text{ }\mu\text{m}$.

The remarkably high conductivity of the sample with the straight-edge gap submitted to the electric field during drying (1S), compared to the three others having similar IV curves, was unexpected. On the other hand the significantly weaker relative non-linearity of the pointed-edge sample submitted to electric field while drying (3S), compared to the three others, could be explained if some degree of alignment exists in the sample. This phenomenon would be more marked in this sample than in the straight-edge one, because of the electric field would have been concentrated in the line between the tips instead of spreading along the width of the gap (possible averaging) during the drying phase. Besides there would also be less averaging during the characterisation phase.

To check whether or not there is some alignment or preferential orientation of the CNTs in the 1S, or even 3S, sample, SEM pictures were taken. No sign of CNT alignment was visible but there was something unexpected in those sample. There are little agglomerates, cf. Fig. 6.34, of unknown composition, with a diameter of about $0.5\text{--}0.7\text{ }\mu\text{m}$ well dispersed in the dried ink, among the CNTs. Those agglomerates were never observed in similar samples that dried

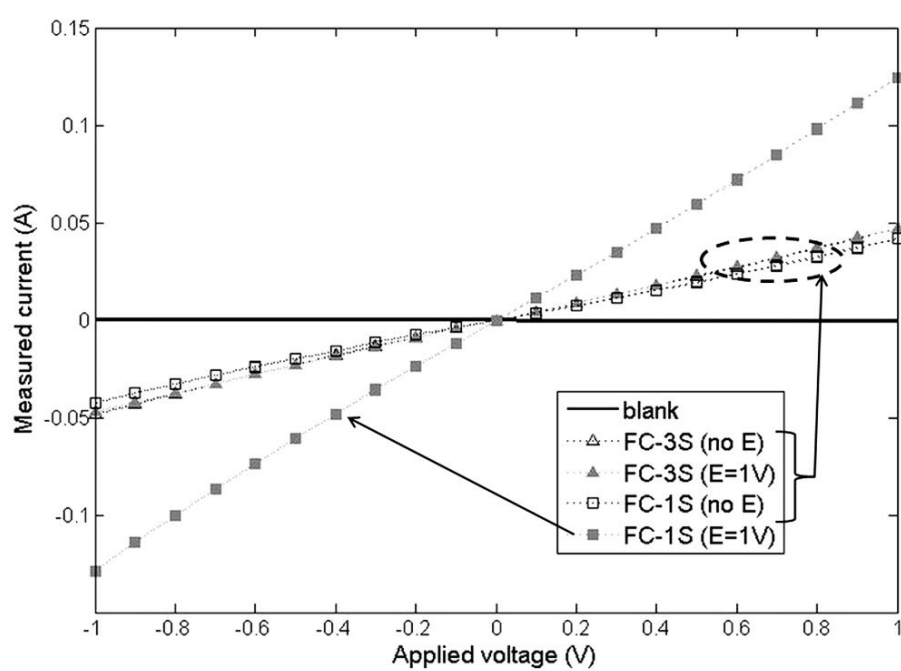


Figure 6.32.: IV curves of the FC dispersion samples with (black) and without (white) applied electric field during drying, with pointed-edge gap (3S: ∇) and with straight-edge gap (1S: $\square$).

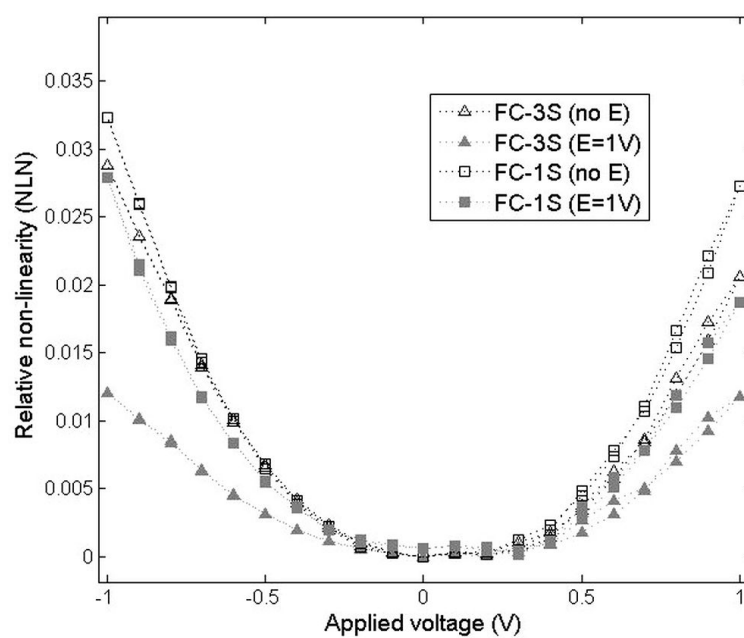


Figure 6.33.: Relative non-linearity versus applied voltage for the FC dispersion samples with (black) and without (white) applied electric field during drying, with pointed-edge gap (3S: ∇) and with straight-edge gap (1S: $\square$).

without any external electric field. The SEM pictures of the CNTs of the samples submitted to the electric field are compared to those of the samples that dried without external electric field on Fig. 6.35 for the straight-edge gap geometry and on Fig. 6.36 for the pointed-edge gap sample. Besides the presence of these aggregates, the CNTs also seem rather different.

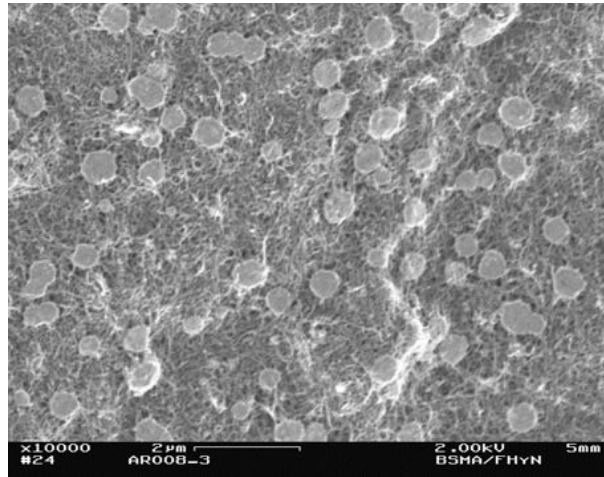


Figure 6.34.: SEM picture of the dried FC solution of the sample with straight-edge gaps that was submitted to an electric field during drying. Unexpected agglomerates of unknown composition are dispersed throughout the solution among the CNTs.

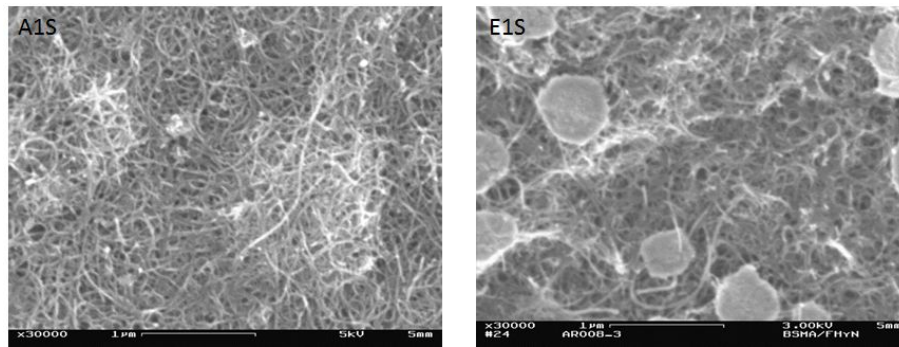


Figure 6.35.: SEM pictures of the CNTs of the samples of FC dispersion with straight-edge gap that dried under an applied electric field (right) and the one that did not (left).

Examining the SEM picture of the entire gap for those samples, differences can also be found near the edges of the gap, as can be seen on Fig. 6.37 or the pointed edge-gap samples. Areas of different shades are located near the gap edges, indicating differences in electrical conductivity. It could be due to charge accumulation at the interface metal-ink due to the electric field presence when the CNTs were still mobile. This would also explain the non-uniform spreading of the ink on both sides of the gap, on the metal edges that can be seen even macroscopically on the pictures shown on Fig. 6.31.

These unknown aggregates are present on both the samples that dried with the applied DC electric field. They cannot therefore be responsible for the increased conductance of the straight-edge gap sample, as the pointed-edge gap sample exhibited the same conductance as those that dried without any applied field. They could prove themselves to be a very interesting subject for further investigation.

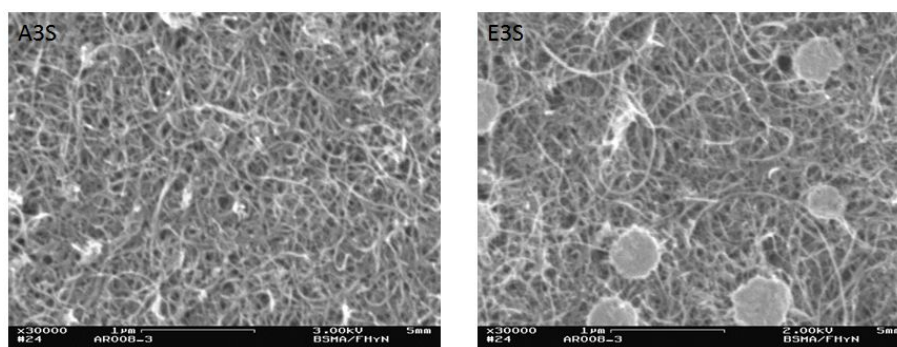


Figure 6.36.: SEM pictures of the CNTs of the samples of FC dispersion with pointed-edge gap that dried under an applied electric field (right) and the one that did not (left).

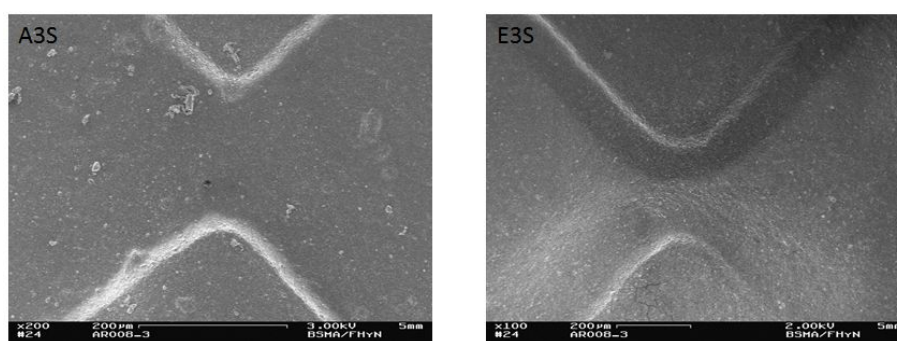


Figure 6.37.: SEM pictures of the gap of the samples of FC ink with pointed-edge gap that dried under an applied electric field (right) and the one that did not (left).

6.7 INFLUENCE OF THE GAP GEOMETRY

6.7.1 Role of the gap length and gap width

In order to study the influence of the geometry of the gap in the microstrip line on the measured non-linearities, the same solutions were first used for all samples, to increase the reproducibility and the fidelity of the comparison. The Future Carbon and Aquacyl solutions were selected, because of their very good dispersion and also because their high conductivity, compared to the other nanocomposite solutions previously characterised.

First, the width and the length of the gap were the first parameters considered, cf. Fig. 6.38. The microstrip lines were fabricated with three different gap lengths¹⁵, 200 μm (S for small), 400 μm (M for medium) and 800 μm (T for thick). There were also three different gap widths: 3 mm (A), 4 mm (B) and 5 mm (C), the various combinations are summarized on Fig. 6.39. It must be noted that previously the gap width was in fact the width of the microstrip metal line ($w = 1.3 \text{ mm}$).

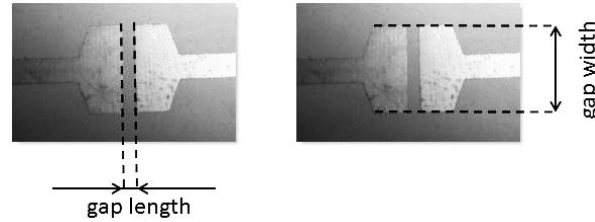


Figure 6.38.: Picture of a microstrip line gap fabricated to investigate the influence of geometrical parameters, with the parameters gap length and gap width illustrated.

The FC and Aquacyl dispersions were deposited, in 5 μl drops, on two identical series of samples each, and one series of samples was intentionally left blank. All the samples were submitted to pulsed voltage sweep as described previously (1V maximum). The resulting IV curves (each one average on the two measurements) are plotted versus applied voltage for all samples containing FC dispersion and can all be found in Appendix A.1. The discussion below is based on the values of the current and corresponding non-linearity for a bias value of -1V , representative of the sample behaviour.

¹⁵Due to fabrication tolerances, the actual gap length values were: 230 μm , 430 μm and 830 μm , respectively.

AS 	AM 	AT 	Gap width = 3 mm
BS 	BM 	BT 	Gap width = 4 mm
CS 	CM 	CT 	Gap width = 5 mm
Gap length = 200 μm Gap length = 400 μm Gap length = 800 μm			

Figure 6.39.: Schematic diagrams summarizing the different gap widths, gap lengths and corresponding code names.

For constant gap length, cf. Fig. 6.40, the conductance (proportional to the IV slope) globally increases with increasing width, as could be expected from Pouillet's law ($R = \rho \frac{l}{w \cdot t}$, where R is the resistance, inversely proportional to the conductance, and t the thickness, not known but supposed nearly identical for all samples). Though some of the curves are very close to one another, even sometimes overlapping.

On the other hand, as can be seen on Fig. 6.40, for constant gap width, the conductance does decrease with gap length for samples with gap widths equal to $w = 4$ mm and $w = 5$ mm but not for the shortest gap width, $w = 3$ mm. The IV curves, cf. Appendix A, are very close and no definite conclusion could be drawn directly from them.

The IV curves of the Aquacyl samples can be found in Appendix A.1, they are in good agreement with previous results showing them to be significantly more conductive than the FC dispersion samples, and also much more linear.

Again for constant gap length measurements, the conductance increases with increasing width. As for the FC samples, the conductance decreases with increasing gap length, for constant gap widths. Both in rather good agreement with Pouillet Law.

The relative non-linearities of all samples with FC dispersion are plotted in Appendix A.1 and the results are summarized on Fig. 6.41 for constant gap lengths as a function of gap width. The curves are very close to one another, and sometimes even overlapping, but the non-linearities corresponding to the

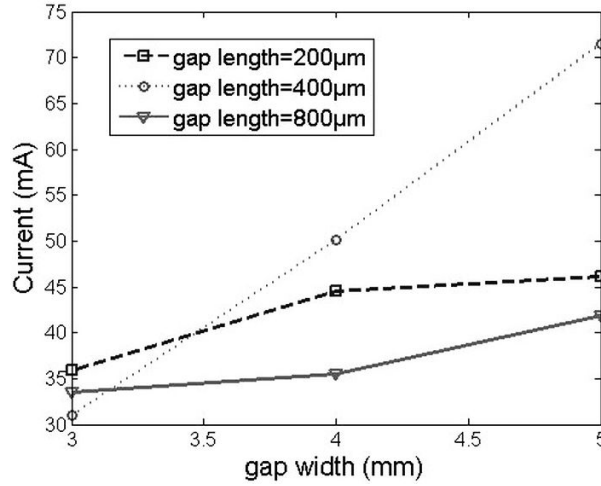


Figure 6.40.: Current value for a -1V bias as a function of gap width, for the FC dispersion samples with constant gap lengths: $l = 200 \mu\text{m}$ (dashed), $l = 400 \mu\text{m}$ (dotted) and $l = 800 \mu\text{m}$ (solid). The gap widths are equal to $w = 3 \text{ mm}$, $w = 4 \text{ mm}$ and $w = 5 \text{ mm}$.

smallest gap length (dashed) are stronger than those of samples with longer gaps. This is because the local electric field intensity is the strongest for those samples. The non-linearity decreases as the gap width increases, except for one sample. The strongest non-linearity is exhibited by the sample with the smallest gap length and smallest gap width (*AS*), though the gap width should not have any influence on the electric field intensity¹⁶.

The relative non-linearity curves of the Aquacyl samples can be found in Appendix A.1.

The non-linearity values of the Aquacyl samples are one order of magnitude below those of the FC samples. As shown for the FC results, non-linearities are stronger for samples with small gap lengths, for which the electric field intensity is stronger, confirming the link between those non-linearities and the electric field intensity.

¹⁶Except maybe for the influence of some edge effects on both edges of each gap wall.

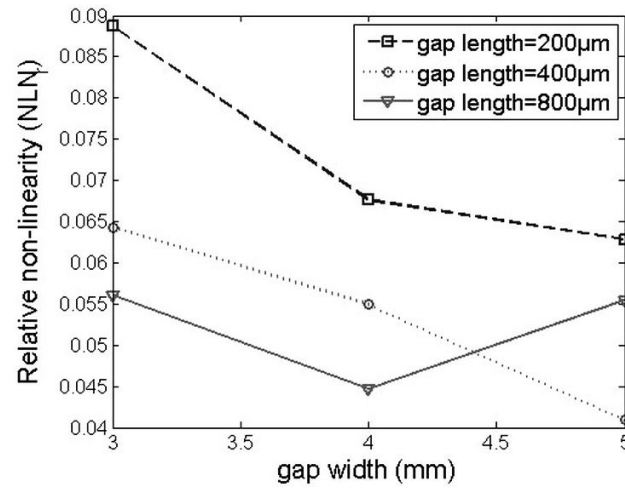


Figure 6.41.: Relative non-linearity value for a $-1V$ bias as a function of gap width, for the FC dispersion samples with constant gap lengths: $l = 200 \mu m$ (dashed), $l = 400 \mu m$ (dotted) and $l = 800 \mu m$ (solid). The gap widths are equal to $w = 3 mm$, $w = 4 mm$ and $w = 5 mm$.

6.7.2 Role of the shape of the gap edges

To investigate the role of the electric field intensity further, new interrupted microstrip lines were fabricated. The first series are identical to the ‘standard’ geometry, cf. section 6.4.2, a simple microstrip line with an interruption. The width of the microstrip line is also equal to $200\text{ }\mu\text{m}$. The second series is similar except that the corner of the gap ‘walls’ are rounded to eliminate any edge or point effect the hard angles could have previously caused. On the other hand the third series microstrip lines are shaped so that the walls of the gap are sort of tips facing one another, to maximise the electric field intensity in the region (solution-filled) located directly between these tips, cf. Fig. 6.42. However due to fabrication tolerances the tips of the pointed-edge gap samples are more like triangles than real ‘tips’. For each geometry, there were three different gap lengths, $200\text{ }\mu\text{m}$ (S for small), $400\text{ }\mu\text{m}$ (M for medium) and $800\text{ }\mu\text{m}$ (L for large). The various combinations are summarized, with the corresponding code names, on Fig. 6.43.

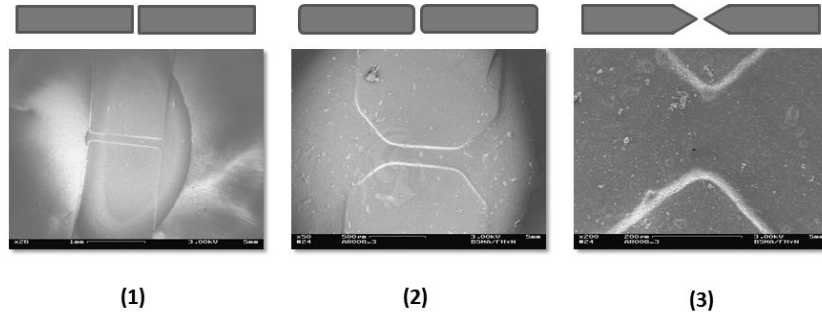


Figure 6.42.: Sketch and SEM pictures of the three kind of gap geometries, parallel walls (1), rounded parallel walls (2) and pointed tips (3).

The electric field intensity and distribution in the microstrip gap have been extracted from Comsol simulations, Comsol software is a FEM solver (based on the complete Maxwell equations). The intensity of the electric field along the x axis (along the length of the microstrip line, on the symmetry axis of the line), with its origin at the center of the gap, is plotted versus distance along the x axis on Fig. 6.44. A 1V bias is applied on one end ($x < 0$) of the microstrip line, and the other end is connected to the ground ($x > 0$). The curves are not symmetrical on both sides of $x = 0$ because of the ground plane at the bottom of the substrate.

Although the pointed edges are far from being real ‘tips’, the intensity of the electric field is significantly higher inside the gap of this configuration. Besides, comparing the curves for gap lengths of 200 and $400\text{ }\mu\text{m}$, the expected decrease of the electric field intensity with increasing gap length is confirmed. The magnitude

1L 	2L 	3L 	Gap length = 800 μm
1M 	2M 	3M 	Gap length = 400 μm
1S 	2S 	3S 	Gap length = 200 μm
Straight-edge gap	Rounded-edge gap	Pointed-edge gap	

Figure 6.43.: Schematic diagrams summarizing the different types of gap edges, the gap lengths and corresponding code names.

of the electric field, from the Comsol simulations, is mapped on Fig. 6.45 for a pointed-edge gap (200 μm long). It can be seen that the intensity of the electric field is strongest at the tip of the pointed edge, with the same bias as previously.

The measured IV curves for all samples with FC ink are plotted in Appendix A.2 and the results are summarized on Fig. 6.46 for constant gap shape plots as a function of gap length. It can be seen that, with the exception of one sample, the samples with a pointed-edge gap exhibit the highest conductivity, then the straight-edge gap ones and the rounded-edge gap samples have the lowest conductance. This is in good agreement with the simulation results of the electric field intensity inside the gap. The electric field intensity is higher, locally, for pointed-edge samples and they exhibit the highest conductance. On the other hand, the conductivity does not significantly depend on the gap length, even if the samples with a 800 μm gap exhibit the lowest conductivity, no matter the shape of the gap.

The conductivity of the Aquacyl samples is on the average about one order of magnitude higher than those of the FC samples. The plots for samples having constant gap lengths can be seen in Appendix A.2. The samples with straight-edge gap have the highest conductivity while the rounded edge ones have a slightly higher or similar conductivity as those with pointed edge (except for the longer gap samples where the straight and rounded edges gap yield a comparable conductivity). These results are in good agreement with those for FC samples having 800 μm long gaps, but not with those for samples with shorter gaps. This would mean that the most relevant shape parameter, as far

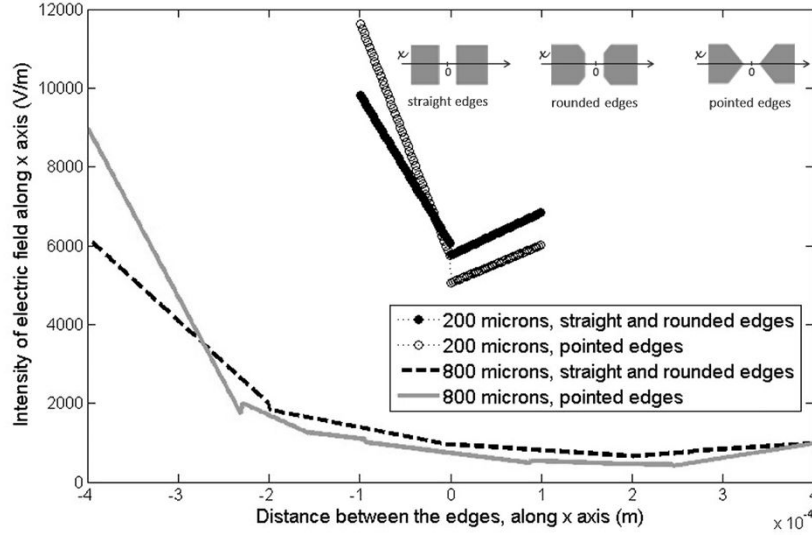


Figure 6.44.: Intensity of the electric field in the x direction as a function of distance along the same axis (x), for gap lengths of 200 (symbols) and 800 μm (lines) and in the case of a gap with straight or rounded edges ($\bullet$ or dashed) and with pointed edges ($\circ$ or solid).

as conductivity is concerned, is the width of the electrode edge perpendicular to the x axis, maximum for straight edges, slightly smaller for rounded edges and much smaller for pointed edge. There is no evidence of a point effect on the value of the conductivity from the measurements of samples with a pointed-edge gap. On average, the shorter gap samples exhibit the highest conductivity while the medium sized gap ones have a higher or similar conductivity as those with longest gaps, as could be expected.

The investigation on the relative non-linearities of these samples led to some unexpected results. The relative non-linearities of the FC samples are plotted as a function of applied voltage in Appendix A.2 and the results are summarized on Fig. 6.47 for a -1V bias.

On average, the IV curves of the samples with rounded-edge gaps exhibited the strongest relative non-linearities, while straight or pointed edge gaps yielded similar non-linearities. The latter results were surprising as pointed edge samples, though not as sharp as first imagined, were expected to yield strongest non-linearities.

On the influence of the gap shape, little can be concluded besides that the shortest gap samples had the strongest non-linearities, confirming the main influence of the electric field intensity.

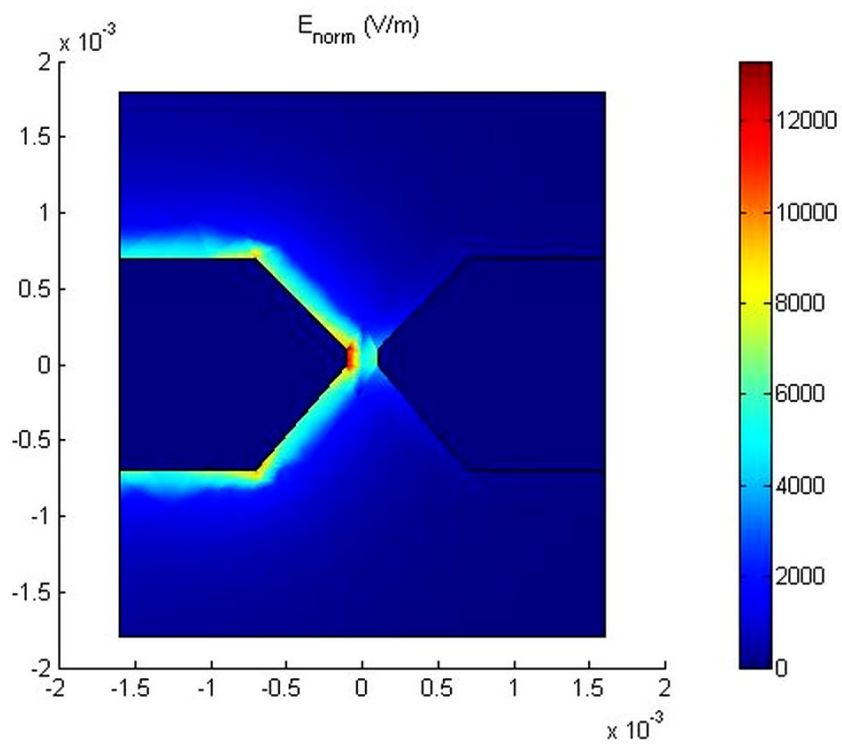


Figure 6.45.: Mapping of the intensity of the electric field magnitude of a pointed edges gap ($200 \mu\text{m}$ long).

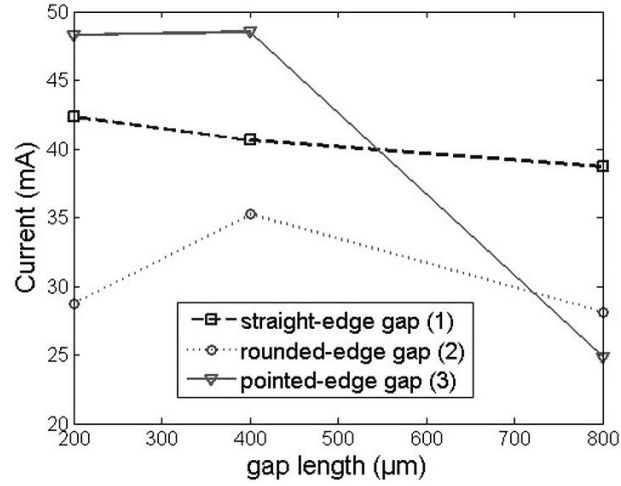


Figure 6.46.: Current value for a $-1V$ bias as a function of gap length, for the FC dispersion samples with constant gap shape: straight-edge gap (dashed), rounded-edge gap (dotted) and pointed-edge gap (solid). The gap lengths are equal to $l = 200 \mu m$, $l = 400 \mu m$ and $l = 800 \mu m$.

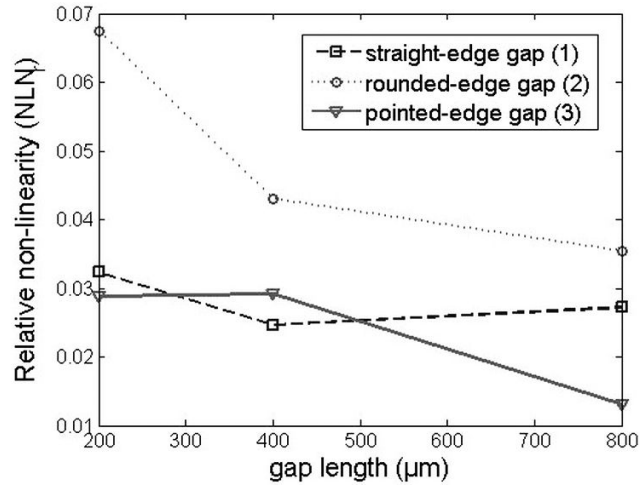


Figure 6.47.: Relative non-linearity value for a $-1V$ bias as a function of gap length, for the FC dispersion samples with constant gap shape: straight-edge gap (dashed), rounded-edge gap (dotted) and pointed-edge gap (solid). The gap lengths are equal to $l = 200 \mu m$, $l = 400 \mu m$ and $l = 800 \mu m$.

The relative non-linearity of Aquacyl samples is, on average, about one order of magnitude lower than that of the FC dispersion samples, cf. Appendix A.2. This is in good agreement with the previous non-linearity comparison between FC and Aquacyl solutions. The signal-to-noise ratio is therefore poorer for those samples, especially in the case of the measurements. However, samples with rounded-edge gaps yield higher non-linearities than the other kinds of sample and again the shortest gap samples also have strongest relative non-linearity. Both of these conclusion are in rather good agreement with the results from the FC samples.

The influence of the electric field intensity, and maybe also the distribution of the electric flux lines, has been highlighted but neither totally determined nor explained. It seems quite logical that samples with short gap lengths should exhibit strong linearities because a smaller number of CNTs is involved in the conduction process and therefore averaging phenomena should be decreased. Indeed the heights of the potential barriers between CNTs or bundles of CNTs are not identical. For a small number of junctions, the total ‘equivalent’ barrier of the composite has a single sharp value but as the number of junction increases, the height of this equivalent barrier is averaged, smoothed over the different individual heights and non-linearities become weaker. But then, the pointed-edge samples should have exhibited even stronger linearities which they did not.

6.8 INFLUENCE OF THE JUNCTIONS BETWEEN INTERCONNECTED CNTS

In [4], the authors relate the transport properties of thin films of SWCNTs (inkjet-printed from a solution of *COOH* functionalised SWCNTs) to the thermionic emission at the junctions between metallic and semi-conducting CNTs. The CNTs investigated, reliably, in the current chapter are MWCNTs, not SWCNTs but as often considered in the literature, the electrical properties of MWCNTs are those of their outer shell and are often approximated using SWCNTs. A similar assumption is made here.

At junctions between a p-type semiconducting CNT (s-CNT) and a metallic CNT (m-CNT), there are Schottky potential barriers. It can be understood as the injection of the carriers with energy higher than the barrier height into the nanotube by thermionic emission. The corresponding potential and temperature dependent current given by the equation

$$I_S(V, T) = AA^*T^2 \exp\left(-\frac{\Phi_b}{kT}\right) \left[\exp\left(\frac{q(V - RI)/m}{kT}\right) - 1 \right] \quad (6.2)$$

where $A^* = 1.2 \cdot 10^{-6} \text{ A m}^{-2} \text{ K}^{-2}$ is the Richardson constant, T is the temperature, k is Boltzmann constant and q is the elementary charge. Φ_b , the barrier height, is given the value of 253.8 meV from [4]. Initially m , the number of junctions along a percolated path, is chosen equal to 66, as in [4]. V and I are the measured values of voltage and current during a single sweep, for a $5 \mu\text{L}$ drop of FC ink¹⁷. $R = 29.73 \Omega$ was calculated from the inverse of the IV slope for large bias.

The resulting $I_S(V)$ curve was used to fit the measured non linearity. But the latter were not calculated as previously but relative the straight line joining the points corresponding to the maximum bias ($\pm 1\text{V}$ here), i.e. from $(V - RI)/R$. Therefore the measured non-linearity and $I_S(V)$ curve had the same aspect but to fit the measurements with equation 6.2, the number of junctions had to be modified from 66 to 101.54 and the obtained value for the average area of cross section of the CNTs A was found equal to $1.52 \cdot 10^{-17} \text{ m}^2$, instead of the $A = 2.3 \cdot 10^{-13} \text{ m}^2$ in [4]. But the solution used in the article was very different from that of our measurements, the deposition method and geometry of the thin films of SWCNTs is also very different from those of our dried droplets of MWCNTs. The measured values and corresponding fit are shown on Fig. 6.48.

In [4], the authors also observe a decrease of the non-ohmic behaviour as the thickness of the film increases. They explain this phenomenon by a decrease of

¹⁷The measurement of the FC solution with the AS sample geometry was used (in fact an average of two measurements), i.e. a gap length of $200 \mu\text{m}$ and a gap width of 3mm . The one that exhibited the strongest non-linearity.

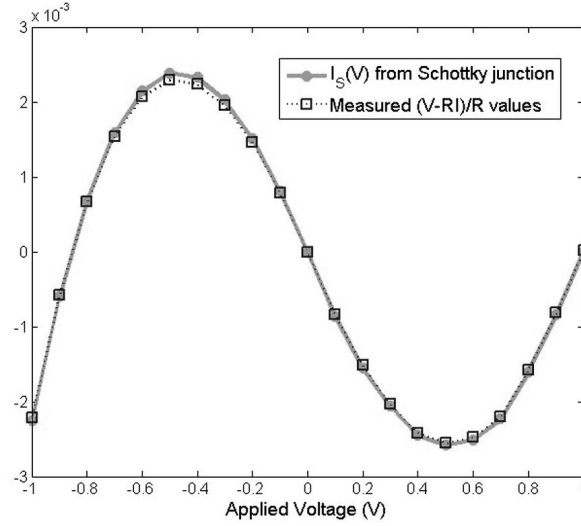


Figure 6.48.: Relative non-linearity $(V - RI)/R$ ($\square$) and fitted using equation 6.2 (solid) versus applied voltage, in the case of a FC 5 μL drop with a gap length of 200 μm and a gap width of 3mm.

the number of Schottky junctions because of increasing parallel short-circuits by metallic CNTs or bundles of CNTs as the thickness of the film increases (i.e. formation of a parallel network of metallic CNTs).

6.9 CONCLUSIONS

Nanocomposite solutions have numerous applications and a great potential still. Some examples of the applications have been given in the beginning of this chapter but it is a new technology field and a lot more are surely yet to be imagined.

During characterisation tests on solutions of dispersed CNTs for the PICOM project, the non-linearity (and possible hysteretic behaviour) of their IV curves was highlighted. The hysteresis was quickly attributed to self-heating but the non-linearities observed on the current-voltage curves were a more complex and persistent issue.

Furthermore, available data from the literature on nanocomposite solutions, and very thin films, are divergent and mostly inconclusive, especially on the possible phenomena responsible for these non-linearities.

Several parameters were then investigated, based on the IV curves measured using a simple experimental set-up especially designed for this purpose. This technique showed adequate reproducibility as long as the CNTs are well dispersed inside the ink. But this ‘flaw’ could also be used to quantify and characterise the dispersion of a nanocomposite solution, turning a negative feat into a positive one.

First, the roles played by the different constituents of the solutions were considered. Solutions containing different multi-, single- or double wall CNTs, functionalized or not, but also different surfactants, were characterized in an attempt to isolate the influence of the CNT properties and that of the additives. Commercial dispersion of CNTs from Nanocyl (Aquacyl) and Future Carbon (FC) were also measured. In particular, the length of the CNTs was shown to have an effect on both the solution conductivity and non-ohmic behaviour. Indeed, an solution containing longer nanotubes is expected to exhibit a higher electrical conductance and weaker non-linearities. An effect of the functionalisation of the CNTs was also suspected. SEM pictures were used to confirm the previous results and illustrate the microstructure of the nanocomposite inks.

The influence of the surfactant and other additives was also highlighted. And the characterisation of filtrated commercial solutions showed that the solvent was not responsible for the non-linearities observed in the IV curves of these commercial dispersions.

Second, the influence of various deposition parameters was investigated. In particular, different numbers of deposited layers of solution were considered. The role of the time allowed for the drying of the droplets was also studied. The conductance of the dried drops was constant after drying for a couple of hours but exhibited a sharp decrease afterwards. Covering the droplets to prevent CNT

‘leakage’ into the air hinted to a sort of lift off of the dried residue from the substrate.

Some samples were submitted to a bias during drying, yielding unexpected IV curves. SEM pictures of those samples were taken to investigate. They revealed the presence of aggregates of unknown composition in the midst of the entangled CNTs. One of those samples exhibited a remarkably high conductance and no fully satisfactory explanation could be provided.

Third, different topologies of the microstrip gap (containing the drop of solution) were used to investigate the suspected important role played by the electric field intensity in the non-ohmic behaviour of inks. The considerable influence of the electric field was confirmed but not explained in detail. The high conductivity with weak non-linearity behaviour of a commercial CNT dispersion and the dual behaviour, low conductivity with high relative non-linearity, of another were confirmed.

The importance of the nature of the junctions, and potential barriers, between the nanotubes was highlighted and a simple model based on the thermionic emission of a Schottky junction provided an interesting explanation for the non-linearities observed in the IV curves of the nanocomposite solutions.

Finally, the investigation presented here was more of an exploratory study, attempting to answer many questions and finally raising even more questions and many perspectives. The data collected from these experiments does not really bring a straightforward explanation to the non-linearities observed in the IV curves of dried drops of CNT ink but it certainly did show the nanocomposite inks to be a very promising and challenging topic.

Bibliography

- [1] J. Vaillancourt, H. Zhang, P. Vasinajindakaw, H. Xia, X. Lu, X. Han, D. Janzen, W.-S. Shih, C. Jones, M. Stroder, M. Chen, H. Subbaraman, R. Chen, U. Berger, and M. Renn, "All ink-jet-printed carbon nanotube thin-film transistor on a polyamide substrate with an ultrahigh operating frequency of over 5 ghz," *Applied Physics Letters*, vol. 93, no. 24, December 2008. 237
- [2] L. Hu, M. Pasta, F. LaMantia, K. Cui, S. Jeong, H. Deshazer, J. Choi, S. Han, and Y. Cui, "Stretchable, porous, and conductive energy textiles," *Nano Letters*, vol. 2, no. 10, pp. 708–714, January 2007. 237
- [3] J.-W. Song, J. Kim, Y.-H. Yoon, B.-S. Choi, J.-H. Kim, and C.-S. Han, "Inkjet printing of single-walled carbon nanotubes and electrical characterization of the line pattern," *Nanotechnology*, no. 19, pp. 1–6, February 2008. 237, 238, 239, 257, 266
- [4] T. Mustonen, J. Maklin, K. Kordas, N. Halonen, G. Toth, S. Saukko, J. Vahakangas, H. Jantunen, S. K. P. Ajayan, R. Vajtai, P. Hestio, H. Seppa, and H. Moilanen, "Controlled ohmic and nonlinear electrical transport in inkjet-printed single-wall carbon nanotube films," *Physical Review B*, vol. 77, no. 12, pp. 125 430–1–125 430–7, March 2008. 238, 239, 240, 285
- [5] C.-H. Liu and S.-S. Fan, "Nonlinear electrical conducting behavior of carbon nanotube networks in silicone elastomer," *Applied Physics Letters*, vol. 90, no. 4, January 2007. 238, 239, 240
- [6] V. Bliznyuk, S. Singamaneni, R. Kattumenu, and M. Atashbar, "Surface electrical conductivity in ultrathin single-wall carbon nanotube/polymer nanocomposite films," *Applied Physics Letters*, vol. 88, April 2006. 239
- [7] P. Beecher, P. Servati, A. Rozhin, A. Colli, V. Scardaci, S. Pisana, T. Hasan, A. Flewitt, J. Robertson, G. Hsieh, F. Li, A. Nathan, A. Ferrari, and W. Milne, "Ink-jet printing of carbon nanotube thin film transistors," *Journal of Applied Physics*, vol. 102, no. 4, August 2007. 239
- [8] P. Potschke, S. Dudkin, and I. Alig, "Dielectric spectroscopy on melt processed polycarbonate-multiwalled carbon nanotube composites," *Polymer*, vol. 44, no. 17, pp. 5023–5030, August 2003. 239
- [9] D. Bergman and Y. Imry, "Critical behavior of the complex dielectric constant near the percolation threshold of a heterogeneous material," *Physical Review Letters*, vol. 39, no. 19, pp. 1222–1225, November 1977. 239
- [10] *CarboDis Technical Data Sheet*, future Carbon GmbH <http://www.future-carbon.de>. 241
- [11] *Aquacyl Technical Data Sheet*, nanocyl s.a. <http://www.nanocyl.com/>. 241

- [12] D. Vuluga, J.-M. Thomassin, I. Molenberg, I. Huynen, B. Gilbert, P. Viville, C. Jerome, M. Alexandre, and C. Detrembleur, "Poly(ethylene glycol) functionalisation/photoreduction of graphite oxide: towards conductive water soluble graphene," *in preparation*, 2012. 241
- [13] S. Ramo, J. Whinnery, and T. V. Duzer, *Fields and Waves in Communication Electronics*. New York: John Wiley and Sons, Inc., 1993. 248
- [14] S. Tans, A. Verschueren, and C. Dekker, "Room-temperature based on a single carbon nanotube," *Nature*, no. 8-9, pp. 49–52, May 1998. 256
- [15] M. Bernal, I. Molenberg, S. Estravis, M. Rodriguez-Perez, I. Huynen, Lopez-Manchado, and R. Verdejo, "accepted in journal of material science," *Comparison of the effect of carbon-baed nanofillers on flexible polyurethane foams*, 2012. 259
- [16] K. Kordas, T. Mustonen, G. Toth, H. Jantunen, M. Lajunen, C. Soldano, S. Talapatra, S. Kar, R. Vajtaj, and P. Ajayan, "Inkjet printing of electrically conductive patterns of carbon nanotubes," *Small*, vol. 2, no. 8-9, pp. 1021–1025, 2006. 266
- [17] C. Martin, J. Sandler, A. Windle, M.-K. Schwarz, W. Bauhofer, K. Schulte, and M. Shaffer, "Electric field-induced aligned multi-wall carbon nanotube networks in epoxy composites," *Polymer*, vol. 46, no. 3, pp. 877–885, January 2004. 269
- [18] J. Sandler, J. Kirk, I. Kinloch, M. Shaffer, and A. Windle, "Ultra-low electrical percolation threshold in carbon-nanotube-epoxy composites," *Polymer*, vol. 44, no. 19, pp. 5893–5899, September 2003. 269

CHAPTER 7

HIGH FREQUENCY MEASUREMENTS OF NANOSTRUCTURED THIN-FILM MEMBRANES FOR FUEL CELL APPLICATIONS

7.1 INTRODUCTION

A Polymer Electrolyte Membrane (or Proton Exchange Membrane) Fuel Cell (PEMFC) is a special type of fuel cells where the electrolyte is a semipermeable polymer membrane, i.e. protons (H^+ ions) can pass through the membrane but electrons and gases cannot. The basic PEMFC drawn on Fig. 7.1 is fuelled by hydrogen, but other models can use methanol. Compared with other kinds of fuel cells, PEMFCs have several advantages. In particular, they are less sensitive to the presence of CO_2 gas, they can operate at relatively low temperatures (50-100°C) and they can be built very compact, e.g. for mobile applications, [1]. The protonic (H^+ ions) current is controlled by the polymer membrane placed between the cathode and the anode.

When designing PEM fuel cells, great care must be taken in the choice of the electrodes material. The electrode material must be thermodynamically stable with the electrolyte membrane but it must also satisfy the three-phase boundary condition. The electrode must allow the transport of protons of the polymer membrane, of the electrons of the current collector, and of the reactant gases, [1]. Typically an ionic conductor polymer (ionomer) like Teflon[®] is used with conductive nano-inclusions, e.g. carbon black or platinum, for the electronic conductivity.

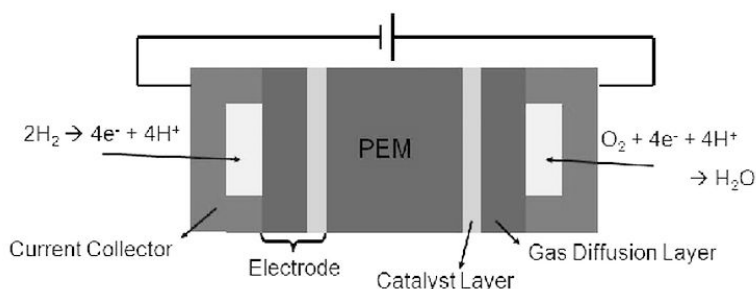


Figure 7.1.: Principle of operation of a basic PEMFC cell and different species involved in the fuel cell operation.

In the first part of this chapter, a Nafion[®] 117 with embedded carbon nanotubes alternative is studied. The addition of CNTs is expected to increase of mechanical stability and decrease the methanol permeability of the membrane, [2]. These membranes are presented and discussed in the first part of the current chapter. They were developed in the framework of the Innopile Walloon Region project.

In Nafion¹, the ionic conductivity is due to the displacement of ion clusters (protons, H^+ ions, in a hydrated environment) and to a microphase separation between hydrophilic and hydrophobic elements, [3, 4].

Some of the results on the composite Nafion membranes presented in this chapter were reported in an oral presentation, and the corresponding paper, [5], and also in a poster and corresponding paper, [6].

In the second part of this chapter, another type of nanostructured membrane is studied, a nanoporous track-etched polyimide membrane. Porous track-etched membranes are used in various applications: as filtration support for bacteria detection or cell retention in liquid based monolayer cytology (paptest), as control barrier in glucose sensors, artificial implants or drug delivery systems; but they are also intensely used to fabricate sensitive detectors and for the synthesis of nanoscale materials such as nanowires or nanotubules, [7–9]. If most applications concern polycarbonate and polyester-based membranes, track-etched membranes are also made from polyimide film with e.g. potential fuel cell applications.

¹Nafion is a fluorated polymer and fluorine is the most electronegative element in the Mendeleev table.

These nanoporous polyimide (PI) track-etched membranes are investigated in order to fabricate new membrane-electrode assemblies (MEA). Due to the high thermal and chemical resistances of polyimide, these assemblies could work at temperatures above 120°C where high performances are expected; moreover, the high aspect ratio due to the track-etched membrane morphology could also lead to a protonic conductivity enhancement.

In the framework of the Walloon Region project PICOM, nanoporous track-etched polyimide samples were studied with the objective of integrating them into novel electrode-membranes assemblies for PEM fuel cells. These membranes had previously shown unexpectedly high ionic conductivity (maybe due to local confinement effects) and should yield an improved chemical and mechanical stability than conventional sulfonated membranes, cf. PICOM project description, as well as better aging properties and internal resistance. Some of the results presented in this chapter were also reported in an article that I wrote in 2010, [10].

In PEMFCs, the parameter of prime interest for the characterization of the nanoporous membranes is their ionic conductivity, i.e. with an ionic solution filling the nanopores. However, in-situ measurement in fuel cells is not a practical characterization method, especially when dealing with numerous samples. Moreover, conventional DC methods are not well suited in this case due to interfacial polarization phenomena, a new AC technique was therefore developed, in the framework of the PICOM project. This simple, non-destructive and reproducible technique, described in section 3.5, allows for the ionic conductivity measurement of nanoporous track-etched membranes while avoiding polarization interfacial effects.

Finally, further information on those nanoporous membranes is also given and characterization results are presented for membranes with different pore densities, pore diameters and pore shapes. The influence of those parameters and in particular of the membrane porosity is shown and discussed.

7.2 HIGH FREQUENCY MEASUREMENTS OF NANOCOMPOSITE CNT/NAFION MEMBRANES

7.2.1 Description of the Nafion/CNT samples

Various Nafion membranes (about 200- μm thick) with different nanoparticle contents have been characterized. But, for conciseness purposes, only the results for a selection of two sets of membranes, both fabricated by researchers from ULg, are shown in this chapter. The first set was fabricated in October 2007 and the second set in August 2008. The fabrication details are not presented here but they are expected to be different. The pure Nafion membrane of the first set might not be rigorously the same as the pure Nafion membrane from the second set. More information on fabrication methods and parameters of these membranes can be found in the reports of the Innopile Walloon Region project.

The first series of selected samples were designed to study the influence of multilayered membranes. Bilayers are two membranes that are thermally pressed and glued together to form a single membrane. It should be noted that all the CNTs used in the current chapter were multiwall CNTs from Nanocyl s.a. (NT7000). First test of CNT composite Nafion membranes in fuel cells showed a decreased efficiency of those membranes compared to that of pure Nafion membranes². It was attributed to the possible apparition of electric short-circuits in the material because of the CNTs and the membrane loosing its insulating properties. A bilayer topology was therefore designed, one layer with CNTs and the other being a pure Nafion sheet to avoid these possible short-circuits. The other samples were fabricated for comparison purposes. The three samples characterised here are listed as follows

- Nafion + CNTs membrane (monolayer),
- Pure Nafion membrane (bilayer),
- Nafion/Nafion+CNTs bilayer membrane.

A second series samples was fabricated in order to investigate the role of the CNT functionalization and of the addition of catalyst nanoparticles in the nanocomposite membranes. Those samples are summarized below. One of them was a pure Nafion membrane that did not contain any CNT (Q172ref), the three others (Q172A, Q172C and Q172D) had the 2 wt% CNT content. The CNTs in the Q172A samples were not functionalized, cf. section 2.3), while those of samples Q172C and Q172D were chemically functionalized, i.e. grafted by carboxylic acid groups ($-\text{COOH}$), more information on this functionalization and its interest in the case of fuel cells can be found in [2]. But, as discussed

²For more details see the report and final conclusions of the Innopile project.

in chapter 2, functionalizing the CNTs should lead to a significantly improved dispersion of the CNTs in the polymer matrix. Beside CNTs, samples Q172D also contained nanoparticles of platinum (Pt). Platinum nanoparticles were added to the composite membranes in order to improve the oxidation of the methanol and improve the efficiency of the fuel cell.

- Q172ref : Pure Nafion membrane,
- Q172A : Nafion membrane + 2 wt% CNTs (NT7),
- Q172C : Nafion membrane + 2 wt% CNTs (NT7-COOH),
- Q172D : Nafion membrane + 2 wt% CNTs (NT7-COOH) + Pt.

The pure Nafion membrane was transparent while membranes containing CNTs were black and totally opaque, as can be seen on Fig. 7.2. They otherwise looked very similar to the naked eye.

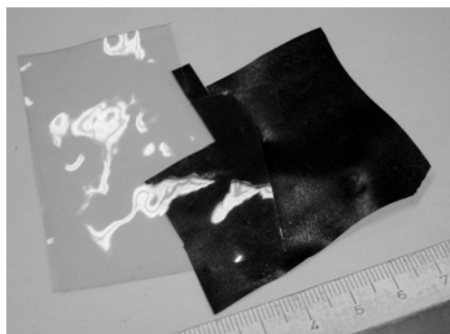


Figure 7.2.: *Picture of the pure Nafion membrane (left) and a Nafion + CNTs membrane (right).*

7.2.2 Measurements results

The samples from both series were characterized using the Parallel Plate Reflection (PPR) method described in section 3.5, after a 30-second immersion in water so that ionic conduction could take place. The waveguide techniques were not suitable because CNTs are expensive and therefore not available in large enough quantities to synthesize the volume of composite required to fill the waveguide cavities, cf. section 3.3.2. Besides, the properties of a membrane are different from that of a bulk sample. The microstrip configuration was also ruled out because of the necessity to submerge the samples into water or acid, which would not meet the requirements of the latter method, cf. section 3.3.1. Furthermore these latter techniques would have required high frequency measurements, not exactly in the range required to observe the conductivity peak, as detailed further in the present chapter and in section 3.5.

7.2.2.1 Characterisation of bilayered Nafion membranes

The real part of the conductivity of the mono-layered and the two bilayered membranes is shown on Fig. 7.3. It can be seen on that figure that peaks for the different samples occur at relatively the same frequency. The same ionic groups are therefore responsible for the ionic conductivity in all three samples, whether or not CNTs are added, [11]. It means that the chemical processes to incorporate the CNTs did not influence the nature of the ions involved in the conductivity or the size of the clusters, a priori.

As detailed in section 3.5, the maximum value of the conductivity versus frequency peak is equal to the bulk DC conductivity of the sample. It can therefore be seen on Fig. 7.3 that the peak for single layer or bilayer of nafion with nanotubes had almost the same value. In other words, the number of layers had little influence.

Furthermore, the peak intensity was much higher for the Nafion-Nafion bilayer than for the samples containing CNTs, i.e. the bulk conductivity was decreased with the addition of carbon nanotubes. It confirmed previous results of a conductivity decrease caused by the addition of CNTs to the membranes³.

In theory, well-dispersed CNTs should form conductive paths for the electrons that could then percolate through the membrane, adding an electronic conductivity to the preexisting ionic conductivity and therefore increasing the bulk conductivity of the membrane. As was just shown, this is not the case with our samples. Two hypothesis can be made at this time. Either the chemical process that was used to add the CNTs did damage the ion conduction paths and this way decreased the ionic conductivity. Or, just the presence of CNTs somewhat rigidified the ionic structures and decreased the mobility of the ions. This latter effect being stronger when the CNTs are poorly distributed, as previous results

³cf. Innopile project reports and presentations.

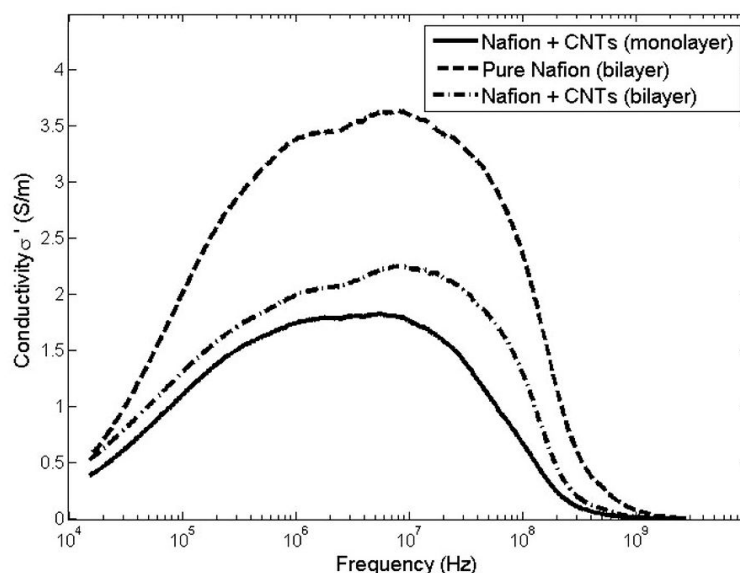


Figure 7.3.: *Real part of the conductivity as a function of frequency, for a monolayered pure Nafion membrane (solid), a bilayered pure Nafion membrane (dashed) and a mixed pure Nafion/Nafion with CNTs membrane (dash-dot).*

have shown that the distribution of nanoparticle had a very strong influence, [12]. The conductivity of the bilayer sample with CNTs is more conductive than the mono-layer with CNTs. The difference is rather small but significant. The chemical process used to fabricate the bilayers is yet to be improved and refined, a larger difference would then be expected, to avoid the negative impact on the electrical conductivity.

These conclusions, based on the electrical conductivity measurement are in good adequacy with the performance of these membranes when placed in actual fuel cells.

7.2.2.2 Influence of the properties of the nanoparticles

The samples of the second series were characterised; a pure Nafion membrane (Q172ref), one composite membrane containing 2 wt% pristine CNTs (Q172A), another one with 2 wt% *COOH* functionalised CNTs (Q172C) and a third one with the same CNTs as Q172C but with added Pt nanoparticles (Q172D). The measured conductivity is plotted as a function of frequency on Fig. 7.4.

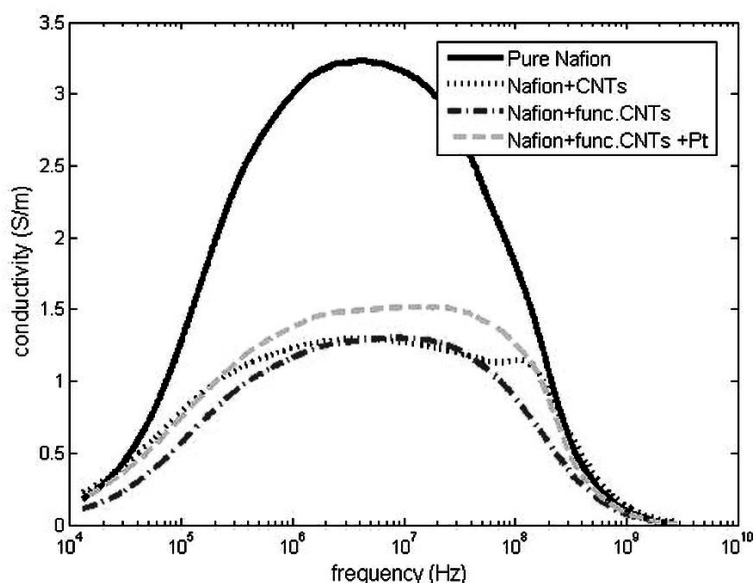


Figure 7.4.: Real part of the conductivity as a function of frequency, for samples with different nanoparticles; a Nafion membrane without CNTs, sample Q172ref (solid), a composite Nafion + 2 wt% pristine CNTs membranes, sample Q172A (dotted) and another one with 2 wt% *COOH* functionalised CNTs, sample Q172C (dash-dot) and sample Q172D identical to Q172C with the addition of platinum nanoparticles (dashed).

The bulk conductivities of the four samples were extracted from Fig. 7.4 and are given in Table 7.1. The pure Nafion membrane exhibited the highest conductivity. The samples containing pristine CNTs (Q172A) and the one with the functionalised CNTs (Q172C) had similar values of the conductivity. The addition of Pt nanoparticles seem to lead to a small increase of the conductivity, though the difference might not be large enough to be significant.

These measurements confirmed the previous results showing that the addition of CNTs in order to increase the electronic conductivity of Nafion (ionic conductor) had the adverse effect of decreasing the bulk conductivity of the

code	nanoparticles	bulk conductivity (S/m)
Q172ref	none	3.23
Q172A	pristine CNTs	1.32
Q172C	f-CNTs (COOH)	1.28
Q172D	f-CNTs (COOH) + Pt	1.52

Table 7.1.: *Characteristics of the different Nafion composite membranes characterised in the current section, and their bulk conductivities.*

nanocomposite. When platinum nanoparticles were also added, they may have partly compensated the bad dispersion of CNTs, yielding a slightly higher conductivity. The functionalization of the CNTs seemed to have little effect on the bulk conductivity. Again, those results may be mainly due to an insufficient dispersion of the nanoparticles.

7.2.3 Influence of the temperature and relative humidity

In the case of a fuel cell application, it is interesting to measure the nanocomposite membranes under different temperature and relative humidity conditions. This can be done using the PPR method and a climatic chamber (cf. section 3.5). The bulk DC value is extracted from the AC measurement as described previously.

The results for the nanocomposite membranes are shown on Fig. 7.5. Sample Q172ref was the pure Nafion membrane (dark grey), samples Q172C was a Nafion/CNT nanocomposite membrane (middle grey) and sample Q172D was a Nafion membrane containing CNTs and PT nanoparticles (light grey). The results are very different than those previously obtained. In fact, the temperature and humidity cycles, along with imperfect storage conditions, lead to an accelerated degradation of the samples; a major drawback if they are to be used in actual fuel cells.

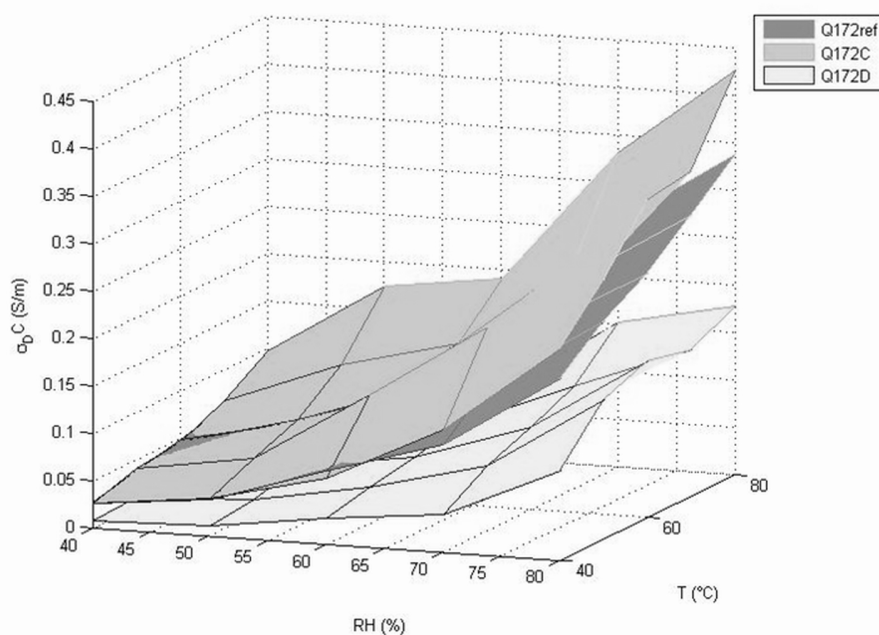


Figure 7.5.: Bulk conductivity as a function of temperature and relative humidity, for the Nafion membrane without CNTs, sample Q172ref (dark grey), the composite Nafion membrane with 2 wt% COOH functionalised CNTs, sample Q172C (middle grey) and sample Q172D identical to Q172C with the addition of platinum nanoparticles (light grey).

7.3 MICROWAVE MEASUREMENTS OF NANOPOROUS TRACK-ETCHED POLYIMIDE MEMBRANES

7.3.1 Description of the track-etched nanoporous polyimide membranes

Track-etched PI membranes are continuously produced from 7.5, 12, 25 or 50 microns thick PI films following a patented (it4ip sa, Belgium) technology⁴: the film is first beamed with energetic heavy ions leading to the creation of linear damaged tracks, and these tracks are then chemically etched to selectively reveal tracks into a random distribution of transverse pores, [9, 10]. This process is illustrated on Fig 7.6. If final pore density is defined during beaming step, final pore size (and shape) depends mainly on chemical etching conditions. Standard range for pore size (or diameter) is from 10 nm to several tenths of microns with an adapted pore density in the range 10^3 to 10^{10} cm^{-2} . A picture and a SEM image of a nanoporous track-etched membrane obtained this way are shown on Fig.7.7.

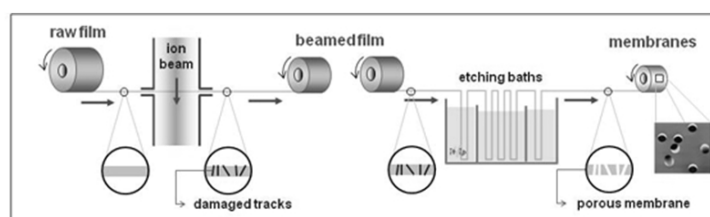


Figure 7.6.: Schematic diagram of the fabrication process of the track-etched nanoporous membranes, from www.it4ip.be.

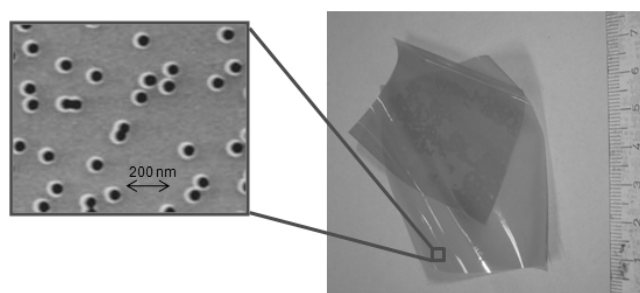


Figure 7.7.: Picture of a nanoporous track-etched PI membrane (right) and SEM picture of the pores of the membrane (left), from [5].

⁴It should be noted that it4ip can produce nanoporous membranes from either polycarbonate (PC), polyester or polyimide (PI) films that are 5 to 70 microns thick.

The characteristics (thickness, pore size and density) of the track-etched membranes studied in the current chapter are summarized in Table 7.2, Table 7.3 and Table 7.4. For these last two samples, the mean pore size given here is calculated from gas flow measurements, their pore size evaluated from microscope pictures are very different, which is characteristic of membranes with diaboloshaped pores, as detailed in section 7.3.3. For the other samples the mean pore size values given here are the rounded values from gas flow measurements⁵ as well but without any significant difference between these values and the ones from microscopy results.

Samples PI9-PI12 have been irradiated but not chemically etched. Fragilized paths in the membrane have been created during beaming but the pores were not ‘opened’ by any etching. These samples were fabricated to investigate whether there could already be some ionic conduction through the membrane even without the existence of the nanopores, i.e. to confirm that the conductivity is solely due to the presence of pores in the membrane.

Samples PI9 to PI17 are composed of three different types of polyimide membranes, from three different manufacturers (designated as type *I*, *II* or *III*), there might therefore be differences in their exact formulation, their fabrication processes, etc.

sample code	material	track density (cm^{-2})	pore size (nm)	thickness (μm)
PI9	PI type I	$4 \cdot 10^9$	irradiated	7,6
PI10	PI type II	$4 \cdot 10^9$	irradiated	25
PI11	PI type III	$4 \cdot 10^9$	irradiated	12
PI12	PI type I	$4 \cdot 10^9$	irradiated	25
PI13	PI type III	$6 \cdot 10^9$	50	12
PI14	PI type II	10^9	50	25
PI15	PI type III	10^9	50	12
PI16	PI type I	$4 \cdot 10^9$	50	25
PI17	PI type II	$6 \cdot 10^9$	50	25

Table 7.2.: *Track density, pore size and thickness of the PI9 to PI17 nanoporous track-etched polyimide membranes fabricated by it4ip.*

⁵The exact values can be found in Appendix A.3.

sample code	thickness (μm)	track density ($\times 10^9 cm^{-2}$)	mean pore size (nm)
PI21	25	1	25
PI22	25	4	25
PI23	25	6	25
PI24	25	9	25
PI25	25	10	25
PI26	25	1	50
PI27	25	4	50
PI28	25	6	50
PI29	25	1	100

Table 7.3.: Track density, pore size and thickness of the PI21 to PI29 nanoporous track-etched polyimide membranes fabricated by it4ip.

sample code	thickness (μm)	track density ($\times 10^9 cm^{-2}$)	mean pore size (nm)
PI50	50	0,5	114
PI51	50	0,5	56

Table 7.4.: Track density, pore size and thickness of the PI50 to PI51 nanoporous track-etched polyimide membranes fabricated by it4ip.

7.3.2 Influence of the environmental conditions on the characterisation

Track-etched nanoporous membranes of different thickness, pore densities, pore sizes and pore shapes were characterized, using the method described in section 3.5. First measurements were made in dry conditions, directly out of the desiccator, then after a 30-second immersion in deionized water or in sulphuric acid (1M).

7.3.2.1 Characterization in a dry environment

First attempts at characterizing membranes in dry conditions were non-conclusive. The conductivity versus frequency plots of the samples PI9 to PI17, detailed on Table 7.2 are shown on showed Fig. 7.8. No peak (other than the artefact peak around 1 GHz due to resonance in the set-up). These results confirmed that the conductivity of dry nanoporous PI membranes, at DC or high frequency, is negligible, as expected. Without water or acid no ionic conduction is expected to take place and PI being a highly resistive material, neither should there be any electronic conduction. In the presence of water or acid, hydrogen protons can move inside the material pores, acting as conducting channels through the membrane.

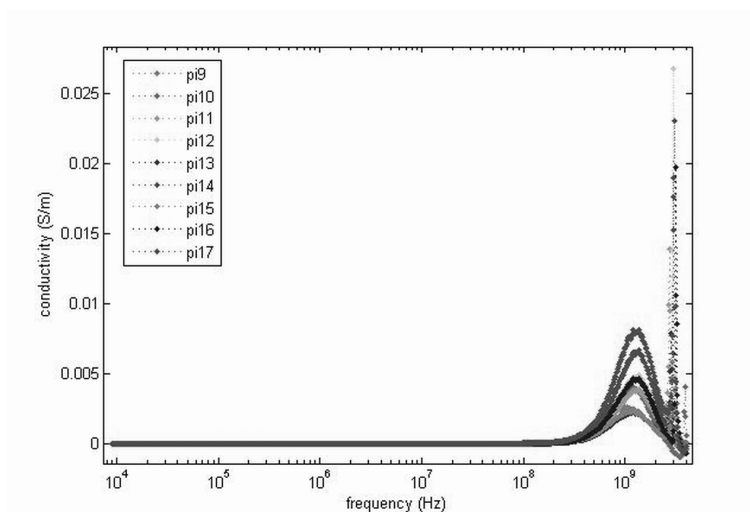


Figure 7.8.: Conductivity versus frequency for various nanoporous track-etched PI membranes (different thickness, pore size and density, cf. table 7.2) in dry conditions.

7.3.2.2 Characterization in aqueous medium

The samples in table 7.2 were characterized using the PPR method after a 30-second immersion into water⁶.

The conductivity versus frequency curves of the PI9-PI17 samples, after a 30-second immersion in water, are plotted on Fig. 7.9. It can be seen that the conductivity of the hydrated PI samples is non-negligible, instead a kind of plateau can be observed (the peaks beyond 1 GHz are actually measurement artefacts, cf. section 3.5).

These plateaus are actually flat elongated peaks and, the height of a plateau corresponded then to the conductivity of the sample. The bulk conductivities extracted from those measurements are given in Table 7.5.

sample code	material	track density (cm ⁻²)	pore size (nm)	thickness (μm)	σ in water (S/m)
PI9	PI type I	4.10 ⁹	irradiated	7,6	1,5.10 ⁻⁴
PI10	PI type II	4.10 ⁹	irradiated	25	4,8.10 ⁻⁴
PI11	PI type III	4.10 ⁹	irradiated	12	8,7.10 ⁻⁴
PI12	PI type I	4.10 ⁹	irradiated	25	0,65.10 ⁻⁴
PI13	PI type III	6.10 ⁹	50	12	16,21.10 ⁻³
PI14	PI type II	10 ⁹	50	25	4,295.10 ⁻³
PI15	PI type III	10 ⁹	50	12	3,27.10 ⁻³
PI16	PI type I	4.10 ⁹	50	25	12,3.10 ⁻³
PI17	PI type II	6.10 ⁹	50	25	16,44.10 ⁻³

Table 7.5.: *Characteristics and bulk conductivity of the PI9 to P17 nanoporous track-etched membranes (fabricated by it4ip) characterized by the PPR method after a 30-second immersion into water, data from it4ip (except last column).*

As can be seen on Fig. 7.10, the PI membrane conductivity seems to be proportional to the pore density (d). The thickness and type of PI do not seem to influence the conductivity significantly. Samples PI9-PI12 have been beamed but not chemically attacked, they have fragilized paths but no pores. Their conductivity is negligible which confirms that complete pores are necessary for the electrical conduction of the track-etched membranes, beaming is not sufficient and does not lead to a significant lowering of the insulating properties of the non-porous PI membrane. Besides confirming that the PI membrane is not conductive, these measurement show that creating damaged, fragilized path through the membrane do not lead to a significant conductivity.

It can therefore be confirmed that the conductivity is due to the membrane porosity.

⁶Tests have shown that the samples did not dry during the time needed to place them in the sample holder and make the measurements and that the measurements were stable during that time.

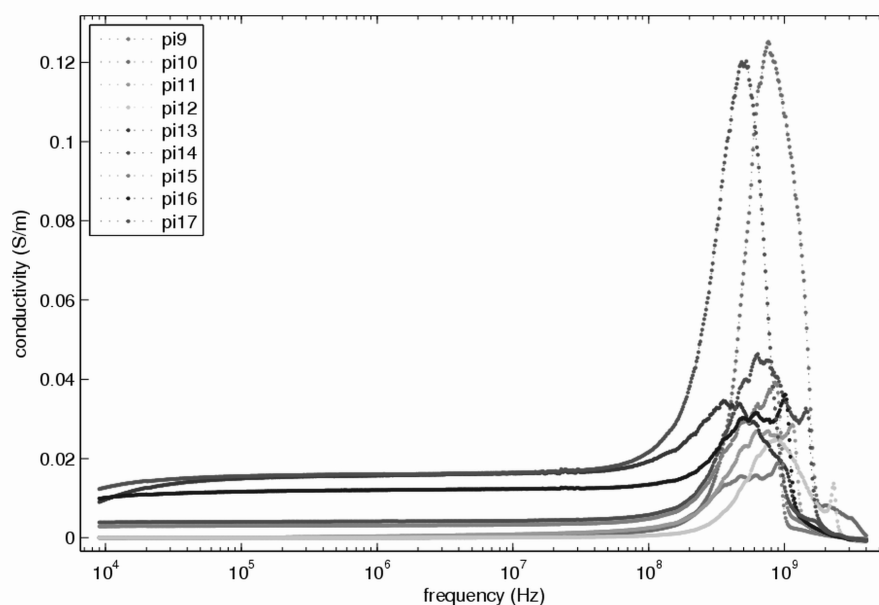


Figure 7.9.: Conductivity versus frequency for the PI9-17 samples after a 30-second immersion in water.

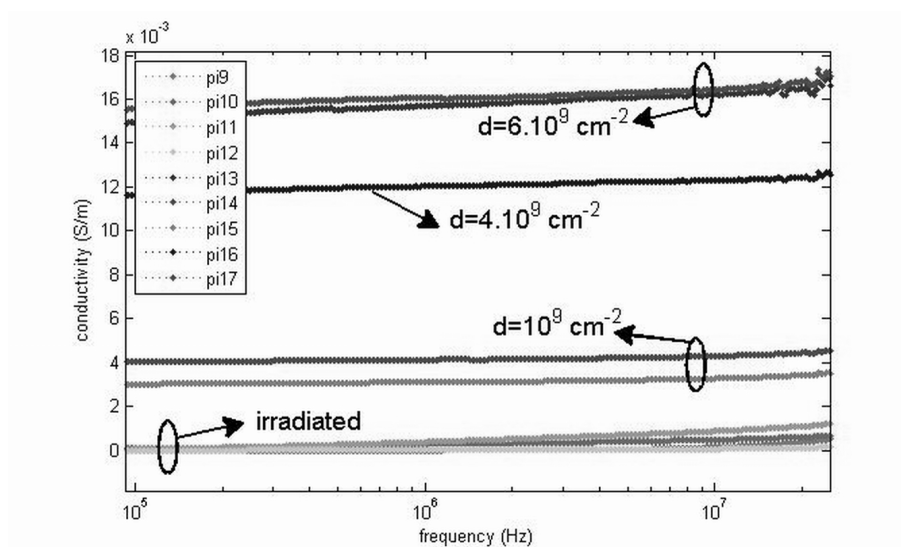


Figure 7.10.: Conductivity versus frequency for the PI9-17 samples after a 30-second immersion in water, magnification on the plateaus.

7.3.2.3 Characterization in acidic medium

The membranes were then characterized after a 30-second immersion in weak phosphoric acid (1M) so that ionic conduction occurs, more strongly than with just water, the conductivity peaks are then sharper, as can be seen on Fig.7.11.

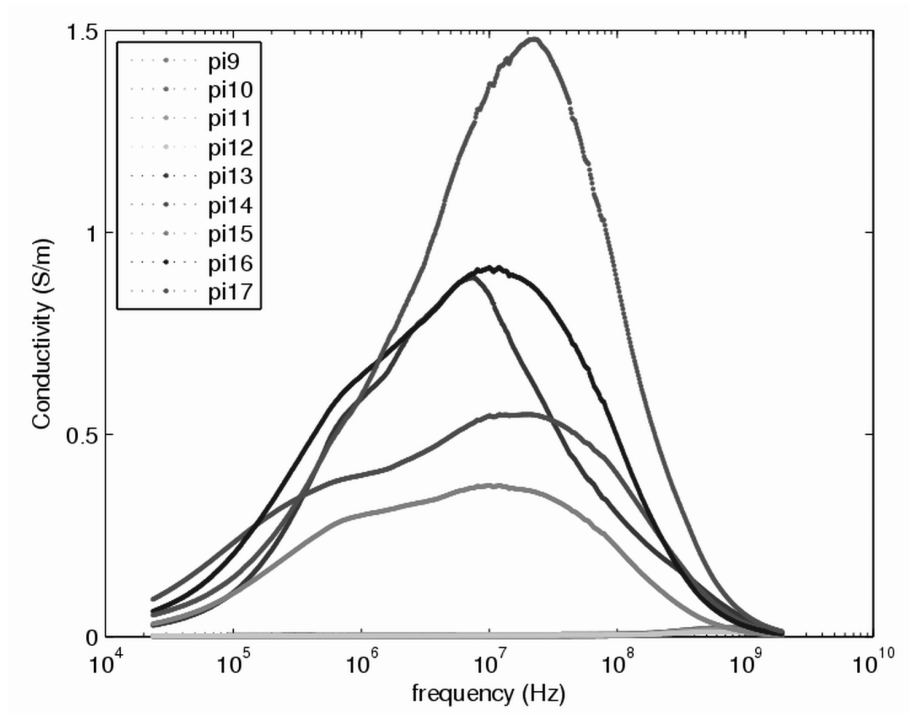


Figure 7.11.: Conductivity versus frequency for the PI9-17 samples after immersion in acid.

The pore density dependence of the conductivity of the PI9-17 (table 7.5) track-etched PI samples is further confirmed by the measurements of Fig.7.11. The figures with the conductivity versus frequency curves are shown for illustrative purposes, quantitative information can be found in Table 7.6.

As can be seen on Fig. 7.12, the conductivity seemed directly proportional to the pore density (d). Indeed both the type II ($t = 25 \mu m$) and type III ($t = 12 \mu m$) samples exhibited a conductivity about 2.5 times higher for $d = 6.10^9 cm^{-2}$ than for $d = 10^9 cm^{-2}$. The type II samples also seemed to have a higher conductivity than the type III samples, but a possible systematic error in the measurement of the exact thickness could be responsible for the difference,

sample code	material	track density (cm^{-2})	pore size (nm)	thickness (μm)	σ in water (S/m)	σ in acid (S/m)
PI9	PI type I	$4 \cdot 10^9$	irradiated	7,6	$1,5 \cdot 10^{-4}$	$2 \cdot 10^{-4}$
PI10	PI type II	$4 \cdot 10^9$	irradiated	25	$4,8 \cdot 10^{-4}$	$4,6 \cdot 10^{-3}$
PI11	PI type III	$4 \cdot 10^9$	irradiated	12	$8,7 \cdot 10^{-4}$	10^{-3}
PI12	PI type I	$4 \cdot 10^9$	irradiated	25	$0,65 \cdot 10^{-4}$	$3,5 \cdot 10^{-3}$
PI13	PI type III	$6 \cdot 10^9$	50	12	$16,21 \cdot 10^{-3}$	0,97
PI14	PI type II	10^9	50	25	$4,295 \cdot 10^{-3}$	0,56
PI15	PI type III	10^9	50	12	$3,27 \cdot 10^{-3}$	0,38
PI16	PI type I	$4 \cdot 10^9$	50	25	$12,3 \cdot 10^{-3}$	0,93
PI17	PI type II	$6 \cdot 10^9$	50	25	$16,44 \cdot 10^{-3}$	1,5

Table 7.6.: Characteristics and bulk conductivity of the PI9 to P17 nanoporous track-etched membranes (fabricated by it4ip) characterized by the PPR method after a 30-second immersion into water or sulphuric acid (1M), data from it4ip (except last two columns).

at least partly. And again, the samples that were only beamed do not exhibit any significant conductivity.

The dependence of the conductivity on the membrane thickness, pore size and density is investigated in more details in the next section.

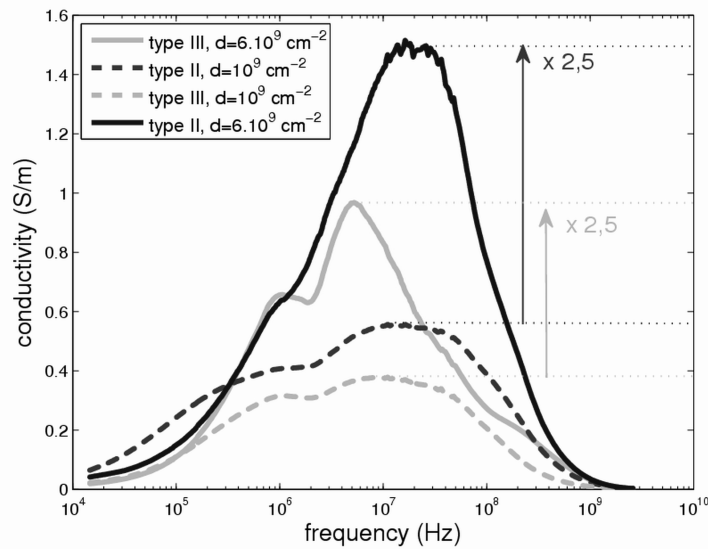


Figure 7.12.: Measured conductivity of track-etched membranes with a thickness of 12 (grey) and 25 μm (black), and a pore density of 10^9 (dashed) and $6 \cdot 10^9 \text{ cm}^{-2}$ (solid).

7.3.3 Influence of the characteristics of the nanoporous membranes on the bulk conductivity

In order to investigate first the dependence of the pore density of track-etched PI membranes on their bulk conductivity, another series of PI samples were characterized, cf. table 7.3, after a 30-second immersion in sulphuric acid (1M). The pore size in those samples varied from 25 nm to 100 nm.

sample code	track density (cm^{-2})	pore size (nm)	σ in acid (S/m)
PI21	$d = 10^9$	25	0,24
PI22	$d = 4 \cdot 10^9$	25	0,57
PI23	$d = 6 \cdot 10^9$	25	1,26
PI24	$d = 9 \cdot 10^9$	25	1,47
PI25	$d = 10 \cdot 10^9$	25	1,59
PI26	$d = 10^9$	50	0,98
PI27	$d = 4 \cdot 10^9$	50	2,08
PI28	$d = 6 \cdot 10^9$	50	3,66
PI29	$d = 10^9$	100	2,44

Table 7.7.: Characteristics and bulk conductivity of the P21 to P29 nanoporous track-etched membranes (fabricated by *it4ip*) characterized by the PPR method after a 30-second immersion into sulphuric acid (1M), data from *it4ip* (except last column).

As can be seen on Fig 7.13, the conductivity increases when the pore density increases (for a given pore size) and it also increases with the pore size (for the same pore density). The darker the curve, the higher the density (solid for the 25 nm size pore membranes, dashed for the 50nm ones and dotted for the 100 nm one).

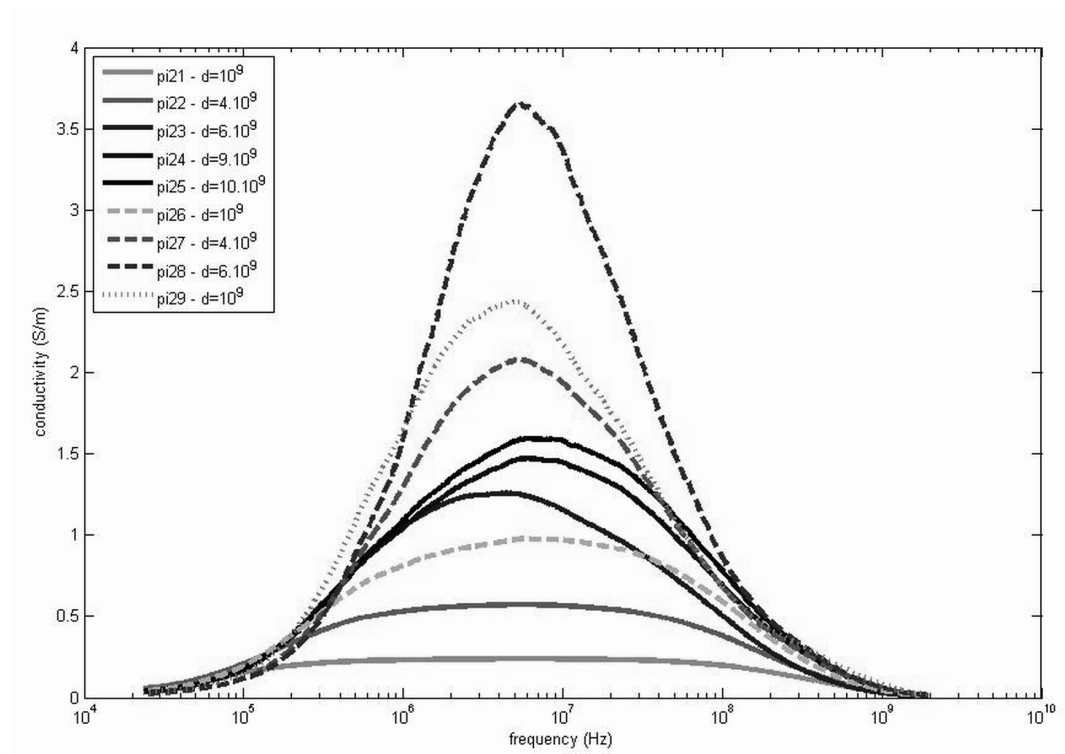


Figure 7.13.: Conductivity versus frequency for the PI21-29 samples after immersion in acid.

If the bulk conductivity is plotted versus pore density, cf. Fig. 7.14 (top), the dependence is linear, for the membranes having a pore size of 25 nm (PI21-PI25). Therefore, the bulk conductivity of a track-etched membrane is directly proportional to its pore density and to its porosity.

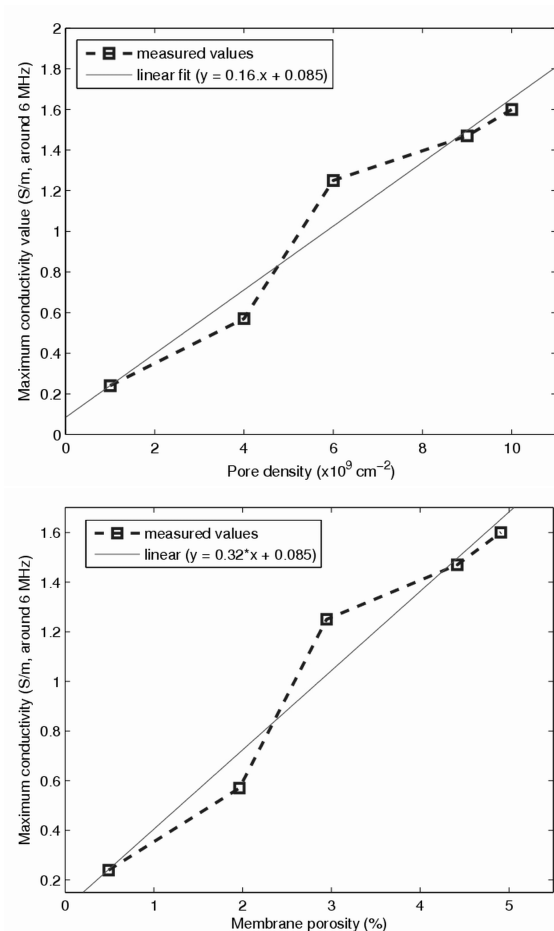


Figure 7.14.: Conductivity versus pore density (top) and versus porosity (bottom) for the PI21-29 samples after immersion in acid.

If results for the two sets of membranes (one with a pore size of 25 nm and the other with a pore size of 50 nm) are plotted on the same graph, they belong to two different lines having a different slope, cf. Fig. 7.15. The slope of the linear interpolation of these DC conductivity versus pore density plots is higher as the pore diameter increases.

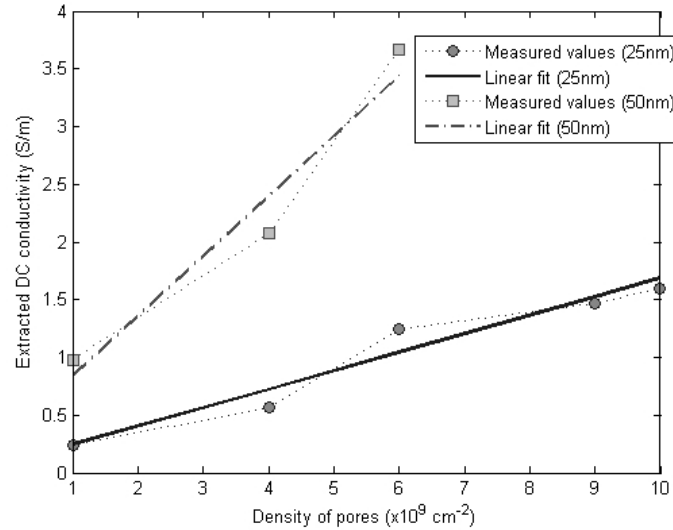


Figure 7.15.: Extracted DC ionic conductivity versus pore density for PI membranes having 25 (circles) and 50 nm (squares) pores, and their linear interpolations, from [10].

A more interesting and global parameter can be used, that combines the pore density or mean pore diameter, it is the membrane porosity. The porosity is defined as the ratio of the total volume of the membrane to the volume occupied by the pores, or more easily here by: $porosity = density \times \pi \times r^2$ with r is the pore radius. It varies from 0,5 to 12%, cf. Table 7.8.

The conductivity, cf. Table 7.7, is plotted versus pore density on Fig. 7.14 (top), showing a linear dependence. If it is now plotted versus porosity, cf. Fig. 7.14 (bottom), another linear relationship is found.

As can be seen on Fig. 7.16, the measured conductivity is linearly dependent on the porosity of the membrane, independently of the pore size or density, all measurements are aligned on a single line.

Two thicker (50 μm) PI membranes with a pore density of 5.10^8 cm^{-2} have been also fabricated; due to their high thickness, the etching conditions lead to the formation of non-cylindrical pores with a narrowing of the pores at the middle of the film. Equivalent mean pore diameter estimated from gas flow measurement is therefore different from those measured on both membrane sides using electron

sample code	thickness (μm)	track density ($\times 10^9 cm^{-2}$)	mean pore size (nm)	porosity (%)	σ in acid (S/m)
PI21	25	1	25	0,49	0,24
PI22	25	4	25	1,96	0,57
PI23	25	6	25	2,95	1,26
PI24	25	9	25	4,42	1,47
PI25	25	10	25	4,91	1,59
PI26	25	1	50	1,96	0,98
PI27	25	4	50	7,85	2,08
PI28	25	6	50	11,78	3,66
PI29	25	1	100	7,85	2,44
PI50	50	0,5	114	5,10	1,7
PI51	50	0,5	56	1,23	0,3

Table 7.8.: Characteristics and bulk conductivity (in acid) of the P21 to P29, also P50 and PI51, nanoporous track-etched membranes (fabricated by it4ip) and their calculated porosity, data from it4ip (except last column).

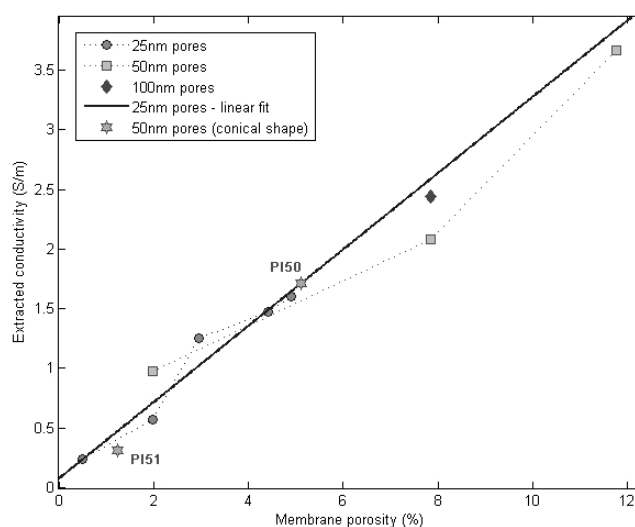


Figure 7.16.: Extracted DC ionic conductivity versus porosity for PI membranes having 25 nm (circles), 50 nm (squares), 100 nm (diamond) pores and 50 nm pores with conical shape (stars), and the linear interpolation for the 25 nm pores, from [10].

microscopy⁷; if equivalent mean pore size is equal to 56 nm and 114 nm for *PI50* and *PI51* samples, respectively, pore sizes at the membrane surface are equal to 180 nm and to 220 nm; this difference is characteristic of membranes with diabolo-shaped pores, [7].

As shown on Fig. 7.16, measured conductivities versus membrane porosity for these membranes are on the same line as the linear interpolation of membranes with cylindrical pores. This means that electrical conductivity is only proportional to free volume and that no other effect, like surface tension along the pore wall, significantly influences the membrane conductivity and that porosity is the prominent parameter when evaluating nanoporous track-etched membranes for fuel cell applications.

⁷Measurement of the pore density using these two techniques gave identical results for the other samples. They were therefore assumed to be cylindrical and having a regular shape throughout the thickness of the membrane.

7.4 CONCLUSIONS

The PPR (parallel plate reflection) method was used to characterize nafion/CNT nanocomposite and track-etched PI membranes successfully and to extract their bulk DC electrical conductivity in order to assess their interest as potential electrode material in PEMFCs. These characterisations do not yield the membranes performance in real fuel cells but allow a fast and simple selection and comparison of the potentially interesting membranes. They can also yield useful information on the nanocomposite membranes structure and on the influence of different processing or composition parameters.

In the first part of the chapter, the influence of the addition of CNTs to Nafion membranes, to improve their efficiency in fuel cell applications, was investigated. The added carbon nanotubes were a priori expected to add an electronic conductivity to the mostly ionic conductivity of pure nafion membranes. But our measurements showed that the bulk conductivity was in fact decreased with the addition of the CNTs. This is probably due to an insufficient dispersion of the CNTs and to still to be perfected chemical processes in the fabrication of the nanocomposite membranes. It could also be due to some negative impact of the CNTs on the ionic conductive pathways inside the polymer material. But the exact underlying mechanism is not yet known.

The use of multilayer composites was shown to have little or no effect on the effective bulk conductivity of the obtained membranes, even though it may still be beneficial in terms of mechanical properties.

The influence of temperature and humidity on the electrical properties of the composite Nafion membranes was tentatively studied but sample degradation invalidated any conclusion from the measurements, except that they were not resistant enough to temperature and humidity cycles. Nevertheless, these measurements lead to the optimisation of an experimental set-up that could be used for the characterisation of other materials. For example, it was used to investigate the influence of countered acids on the high temperature conductivity of impregnated fibre glass pads.

Various nanoporous track-etched PI membranes were measured using the same technique, with different pore densities, diameters and even shapes or made from other material than PI. The ones presented in the corresponding section are only a small part of them but are a very good illustration of both the technique results and the influence of porosity.

From these measurements, it was shown that the main parameter of interest is the porosity of the track-etched nanoporous membrane. No exotic pore size or density influence was observed, nor shape influence, but only two of the

available samples had a probable conical shape. More membranes with different pore shapes should be measured to confirm this last result. Given the pore sizes involved, parameters from the nanofluidics theory should probably be taken into account. They are beyond the scope of the present thesis but a detailed review on the transport phenomena in nanofluidics can be found in [13].

The PPR method used extensively in the current chapter is therefore a simple, non destructive technique to assess the quality of samples as potential future elements of MEAs in fuel cells. It was first developed as a kind of screening method. It has been demonstrated that this technique can be used to extract the DC ionic conductivity of thin-film samples exhibiting an ionic conductivity, the ionic conductivity being a parameter of prime interest in fuel cells. Besides samples were measured after a 30-second immersion into acid, quite close to environmental conditions in a fuel cell without all the complexities of in-situ measurements. The methodology developed in the present paper was shown to be simple in execution, reliable and reproducible and well suited to all kinds of thin samples, whether or not they actually contain CNTs or other nanoparticles or are pure polymer membranes.

Bibliography

- [1] S. Litster and G. McLean, "PEM fuel cell electrodes," *Journal of Power Sources*, vol. 130, pp. 61–76, May 2004. 291
- [2] J.-M. Thomassin, J. Kollar, G. Caldarella, A. Germain, R. Jerome, and C. Detrembleur, "Beneficial effect of carbon nanotubes on the performances of nafion membranes in fuel cell applications," *Journal of Membrane Science*, vol. 303, no. 1-2, pp. 252–257, October 2007. 292, 294
- [3] F. Damay and L. Klein, "Transport properties of nafion composite membranes for proton-exchange membranes fuel cells," *Solid State Ionics*, no. 162-163, pp. 261–267, January 2003. 292
- [4] R. Paul and S. Paddison, "The phenomena of dielectric saturation in the water domains of polymer electrolyte membranes," *Solid State Ionics*, no. 168, pp. 245–248, June 2004. 292
- [5] I. Molenberg, J.-M. Thomassin, E. Ferain, C. Detrembleur, and I. Huynen, "Rf diagnostic methods for two nanostructured polymer applications," in *Proc. of the 39th European Microwave Conf.*, Roma, Italy, September 2009, pp. 1045–1048. 292, 301
- [6] I. Molenberg, J.-M. Thomassin, C. Detrembleur, and I. Huynen, "High frequency characterization of polymer membranes with embedded carbon nanotubes for fuel cell applications," in *Proceedings of the Journees de Caracterisation Micro-ondes de Matériaux*, Limoges, France, April 2008. 292
- [7] E. Ferain and R. Legras, "Pore shape control in nanoporous particle track etched membrane," *Nuclear Instruments and Methods in Physics Research B: Beam Interactions with Materials and Atoms*, vol. 174, pp. 116–122, March 2001. 292, 314
- [8] J. Ackermann, D. Crawley, M. Forshaw, K. Nikolic, and C. Videtot, "Conductive polymer interconnections for three-dimensional computing structures," *Surface Science*, vol. 532-535, pp. 1182–1186, August 2003.
- [9] E. Ferain and R. Legras, "Characterisation of nanoporous particle track etched membrane," *Nuclear Instruments and Methods in Physics Research B: Beam Interactions with Materials and Atoms*, vol. 131, pp. 97–102, August 1997. 292, 301
- [10] I. Molenberg, M. Planckaert, L. Jonckheere, E. Ferain, and I. Huynen, "Investigation of ionic conductivity in track-etched nanoporous polyimide membranes using a microwave technique," *Microwave and Optical Technology Letters*, vol. 53, no. 9, pp. 2060–2063, September 2011. 293, 301, 312, 313
- [11] V. Daniel, *Dielectric Relaxation*. London: Academic Press Inc., 1967. 296

- [12] A. Saib, L. Bednarz, R. Daussin, C. Bailly, X. Lou, J.-M. Thomassin, C. Pagnouille, C. Detrembleur, R. Jerome, and I. Huynen, "Carbon nanotubes composites for broadband microwave absorbing materials," *IEEE Transactions on Microwave Theory and Techniques*, vol. 54, no. 6, pp. 2745–2752, june 2006. 297
- [13] R. Schoch, "Transport phenomena in nanofluidics," *Reviews of Modern Physics*, vol. 80, no. 3, pp. 839–883, July 2008. 316

CHAPTER 8

CONCLUSIONS

The aim of the thesis was to investigate the characterisation of electrically conductive nanocomposite materials. This generic title involved several aspects, like the multiple facets of the same stone; as we quickly discovered there is no 'ideal' nanocomposite for every situation, there is no ideal characterisation technique that would be the most adequate to any sample for any application.

Furthermore, like in most engineering topics, compromises are unavoidable and omnipresent.

A state of the art on the electrical properties of CNT/polymer nanocomposites was presented in chapter 2. The major influence of having the CNTs well dispersed, and undamaged by the dispersion process, was highlighted throughout the chapter. The outstanding electrical and mechanical properties of the CNTs were presented and detailed, from their huge aspect-ratio to their electrically conducting or semi-conducting behaviours. If there are many different types of CNTs and even more numerous kinds of polymer nanocomposites containing these nanotubes, they all share some distinctive features, especially among their electrical properties.

First of all is the existence of a percolation threshold. At low filler contents, the composite exhibits a dielectric behaviour while for high CNT loadings it behaves as a conductive material. The transition between those behaviours is sharp and occurs for a filler content that is called the percolation threshold. The

term comes from the apparition at this filler content of a regular, well-extended network of interconnected conductive particles. The conductivity as a function of filler content curve can be approximated using a scaling power law in the vicinity of the threshold.

Second, the dependence of the conductivity and dielectric constant of the nanocomposites on the frequency exhibit a strong dispersion, characteristic of the conduction in many disordered solids. Above a characteristic frequency, the conductivity versus frequency curves also follow a power law.

Both of these features can be reasonably well described using simple geometrical percolation theory and electrical equivalent models with diffusion aspects. Though some discrepancies remain and were discussed in chapter 2. From the comparison between these models and experiments it appeared that CNTs are not in direct contact at their interconnections, that they are coated by a polymer layer of varying thickness. These layers are in fact potential barriers and the charges carriers have to tunnel through them to 'hop' from on CNT to another. This is rather well described by the thermal fluctuation induced tunnelling model and taking into account a random biased walk instead of the random one. The more complicated models, e.g. effective medium theories, do not bring much more light to the experimental results and are not always perfectly adequate in the case of CNT/polymer nanocomposites.

At higher frequencies, the fore-cited models, quasistatic models, are not valid any more. Besides, the distance travelled by the charge carriers is decreased, with the wavelength, and may even be confined to a single cluster or agglomerate of CNTs. The conductivity and dielectric constant still increase with increasing CNT content but the relative differences due to filler content are smaller than at lower frequency. However, thorough microwave characterisation are not widespread in the literature and the data is rather sparse.

As was shown in chapter 3, there exists a variety of measurement methods that can be used to characterise nanocomposite materials. However, each technique is best suited to some kind of materials, having specific properties while another technique will be more adequate for samples exhibiting different properties. Besides the selection of the characterisation method will also depend on the desired frequency range and on the application considered for this composite.

The DC and low frequency characterisations are simple impedance measurements, though it was shown to actually be more complicated than was first expected. The electrical conductivity of nanocomposites cover a wide range of values, from very low to rather high conductivity values. Furthermore, these methods required a high quality and reproducible electrical contact with the sample, which was not always straightforward. In particular, the necessity of using a shielded enclosure and that of making guarded measurements were detailed and some irreproducibility issues were raised.

Guided microwave techniques, using microstrip (One-Line) or waveguide (Line-Line) transmission lines did not present these issues and exhibited a much improved reproducibility. A modified Line-Line (without the waveguides) technique was also developed; in the case the original Line-Line technique could not be used, e.g. if the samples were too large or could not be damaged.

These methods were compared to one another and discussed in details, depending on the properties of the samples, their electrical characteristics but also their mechanical and geometrical ones. Their calibration requirements as well as their advantages and drawbacks were considered as well. In particular, it was shown that the original Line-Line method was better suited in the case of low-loss flexible foams while the modified technique was found more adequate in the case of large hard plates of high-loss material.

The experimental results illustrating each characterisation technique confirmed that there is no ‘unique’ measurement method that would be the ‘best’ in most cases. Each sample and each application have to be considered thoroughly before one or several characterisation techniques can then be selected.

In chapter 4, thin plates of polyurethane and polycarbonate composites with CNT contents from 0.1 to 4 wt% were characterised from DC up to 40 GHz, using three different characterisation techniques. The obtained results were compared to those described in the state of the art. The different characterisation techniques were also compared. In particular, the local character of the percolation threshold and the major influence of the positioning of the electrodes on the sample was discussed. The latter discussion highlighted the necessity of not using solely the percolation threshold to characterise the state of dispersion in a nanocomposite.

At DC the scaling law was used to predict the percolation of all the series of samples. Despite the reproducibility issues, the critical exponent was in very good adequacy with the literature. The results were also in good agreement with the thermal fluctuations induced tunnelling model.

The low frequency results showed also a good adequacy with the literature, and the same power law behaviour. Unfortunately, as for the DC measurements, they suffer from a significant lack of reproducibility.

At microwave frequencies, the reproducibility is considerably improved. All the samples presenting the expected power law frequency with an exponent characteristic of the hopping of charge carriers in a disordered system.

The results from the different techniques showed a very good adequacy. And, they led to a tentative interpretation on the microscopic structure of the samples: It was hypothesized that the CNTs in polyurethane form large aggregates while in polycarbonate they are dispersed in tiny clusters, much smaller than the aggregates in polycarbonate. Even if questions remained, this hypothesis explained some of the results in this chapter.

The specific use of foamed polymer nanocomposites for EMI shielding applications, or more accurately as microwave absorbers, was discussed in chapter 5. Some EMI shielding considerations were first presented. Foaming the nanocomposite leads to a significantly decreased weight and dielectric constant of the composite, the latter resulting in a promising lowered reflectivity of the material. Different results for these composite foams are presented. A very simple electrical model is also developed to predict the behaviour of the electrical properties of the foamed nanocomposites, with rather good adequacy with measurement results.

It was shown that such foams can indeed be very good microwave absorbers but that a compromise had to be found between a high shielding effectiveness and a low reflectivity, i.e. between a high conductivity and a low dielectric constant. A simple RC equivalent model was developed especially suited to foams measurement and was found to fit the experimental results with a good adequacy.

Two solutions were proposed to improve the reflectivity of the absorbers: The first one was to use a graded concentration of CNTs inside a multi-layered foam. This way the shielding effectiveness could be maximized and the reflectivity minimized. These foams were characterised and their results compared positively to those of the mono-layered foams.

Another solution was the design of a hierarchical multi-scale hybrid, where the nanocomposite polymer foam is inserted inside a metallic honeycomb. The latter composite could even exhibit some exotic, metamaterial properties, among them an adjustable cut-off frequency below which the effective dielectric constant of the hybrid can be smaller than 1 or even negative.

As explained in chapter 6, during the characterisation of aqueous dispersions of CNTs (and of some solutions containing graphene sheets), a significant non-ohmic behaviour was observed in the current-voltage curves. The hysteresis was quickly attributed to self-heating but the non-linearities of the curves were more difficult to explain accurately. Furthermore, data from the literature on these non-linearities are divergent and mostly inconclusive.

Using a simple experimental DC set-up, the influence of different parameters on the non-linearities were investigated in chapter 6. The experimental method was shown to have a good reproducibility in the case of well dispersed commercial solutions, but a significant lack of reproducibility when the home-made solutions had a poor CNT distribution. The characterisation technique was also used to discriminate different solutions containing graphene particles.

The influence of the nanoparticles properties was also investigated from the results of the commercial dispersions. The influence of additives was harder to determine, little information being available on the exact composition of com-

mercial dispersions. However any direct effect of the solvent on the non-linearity was discarded, after filtration of the commercial solutions.

In particular, the influence of deposition parameters such as the number of CNT layers, the drying time or the application of an external electric field during drying were considered separately. The effect of width and spacing of the equivalent electrodes on the conductivity was also studied. The only parameter that showed significant influence on the non-linearity, defined as the relative difference from the linear behaviour, was the magnitude of the applied bias. The non-linearities could also be related to the quantum tunnelling through potential barriers between neighbouring CNTs, considering Schottky barriers.

SEM pictures were used to confirm these results and illustrate the microstructure of the nanocomposite dispersions. They also revealed the unexpected presence of aggregates of unknown composition inside sample of inks that had dried under an applied DC electric field (1V bias). One of those samples exhibited a remarkably high conductance, no completely satisfactory explanation could be provided.

A simple and non-destructive reflection based method, detailed in chapter 3, was developed to characterise and extract the DC ionic conductivity of the Nafion/CNTs nanocomposite membranes and the nanoporous track-etched thin films of chapter 7. It was proven to be an accurate and reliable technique to extract the ionic conductivity of these membranes. Besides, this method can be used to characterise all kinds of thin material membranes or films.

In the case of the Nafion membranes, the addition of CNTs was expected to yield an increase of the electronic conductivity of the membranes but instead it led to a significant decrease of the bulk conductivity of the membranes, maybe due to imperfection in the fabrication process or to an influence of the CNTs on the microstructure of the membranes. An experimental set-up was also developed to investigate the temperature and humidity influence on the membranes conductivity that showed an accelerated degradation of the samples.

The nanoporous polyimide thin films were characterised using the same technique, after been immersed in acid to emulate working conditions inside the fuel cell. It was shown that the ionic conductivity of the thin films was mostly dependent on their porosity. No major influence was found from the pore size, shape or density, nor was any exotic, nanofluidic effect observed.

Finally, this thesis does not pretend to be an extensive research and exhaustive study on all kinds of currently available CNT/polymer nanocomposites. The latter would be a daunting task. But it does show different facets of this very interesting, rapidly expanding and promising field.

Although the theory and models on the transport properties of the nanocomposite materials are not so recent, many questions remain and probably only experimental results can bring adequate solutions. We have shown that the characterisation of the nanocomposite materials is a complex topic, the characterisation techniques being as varied as the range of available nanocomposite materials and properties. Besides using different measurement methods on different frequency scales does not only bring different results but complementary information that can be helpful to understand the microstructure of the composite samples. It also highlighted the fact that the measurement of the percolation threshold alone was not sufficient to completely characterise the nanocomposite samples, or even the state of dispersion in the material, as is too often the case in the literature.

Our results are in quite good agreement with those found in the literature and could even be used to confirm or invalidate some uncertain theory points. A few particularly interesting but very different applications of these nanocomposite materials were considered. As mentioned previously, the EMI shielding properties of materials based on foamed polyurethane and polycarbonate membranes containing CNTs, the non-ohmic behaviour of dried aqueous dispersions of CNTs, the extraction of the ionic conductivity of nanocomposite Nafion membranes and that of nanoporous track-etched membranes for fuel cell applications were investigated in the framework of this thesis.

If this investigation is not completely exhaustive, it did open and close several doors and also shed light on some exciting new perspectives; the extension of the wideband characterisation to larger batches of samples with more controlled and varied properties, different polymers, different particles, different processing conditions. It would also be very interesting to compare all those results with rheological characterisations and SEM pictures. The DC measurement, especially below the percolation threshold could maybe benefit from time domain measurements, akin to those used to characterise dielectric materials. The reproducibility of these techniques could be improved. The frequency range between the low frequency LCR measurements and the microwave characterisation, 1MHz-100-MHz, is worth further investigation to confirm the current results and also to better understand the transition in behaviour between these two regions.

In particular the CNT solutions and their non-linearities are worth deeper investigation, depositing lesser amounts of CNTs, in a more controllable fashion could yield even stronger non linearities that could be exploited for electronic devices, e.g. Y-branch junctions. Experiments should be conducted on such dried dispersion at higher frequency, in different configurations. The unex-

pected agglomerates in the samples submitted to an applied bias during drying would really require further investigation. Furthermore it could be interesting to deposit the CNTs dispersions on nanoporous track-etched membranes with different properties and pore characteristics.

It would also be interesting to investigate the conductivity and dielectric constant of nanocomposite between 40 MHz and 40 GHz, to confirm the very good adequacy between the low and high frequency measurements of chapter 4. The characterisation and comparison between in-plane and out-of-plane conductivities of the thin solid and of the foamed samples could yield interesting results. New characterisation methods would have to be developed.

Furthermore, the simple electrical model of chapter 5 could be extended to include the measurement conditions. It could then be used, in comparison with the characterisation of large number of foamed samples, to find an empirical relationship between the filler content of the solid samples, that in the foam and the final electrical properties at microwave frequencies. This relationship could then be compared to the variety of mixing formulas, mostly quasistatic, found in the literature.

APPENDIX A

A.1: Influence of the gap geometry: role of the gap length and width

The FC and Aquacyl dispersions were deposited, in 5 μl drops, on two identical series of samples each, and one series of samples was intentionally left blank. All the samples were submitted to pulsed voltage sweep as described previously (1V maximum). The resulting IV curves (each one average on the two measurements) are plotted versus applied voltage for all samples containing FC dispersion on Fig. 8.1 and Fig. 8.2, for constant gap lengths and constant gap widths, respectively.

The IV curves of the Aquacyl samples are shown on Fig. 8.3 and Fig. 8.4, they are in good agreements with previous results showing them to be significantly more conductive than the FC ink, and also much more linear.

The relative non-linearities of all samples with FC dispersion are plotted versus applied voltage on Fig. 8.5 for constant gap lengths and on Fig. 8.6 for constant gap widths.

The relative non-linearity curves of the Aquacyl samples are plotted on Fig. 8.7 and Fig. 8.8. The non-linearity values of the Aquacyl samples are one order of magnitude below those of the FC samples (it also explains the lower signal-to-noise ratio), confirming previous results¹. As shown for the FC results, non-linearities are stronger for samples with small gap lengths, for which the electric field intensity is stronger, confirming the link between those non-linearities and the electric field.

¹The noise of the right part of the curves is an artefact from the measurements; for yet unknown reasons, when measuring low level currents, the SMU makes more noisy measurement on the positive-voltage part of the sweeps.

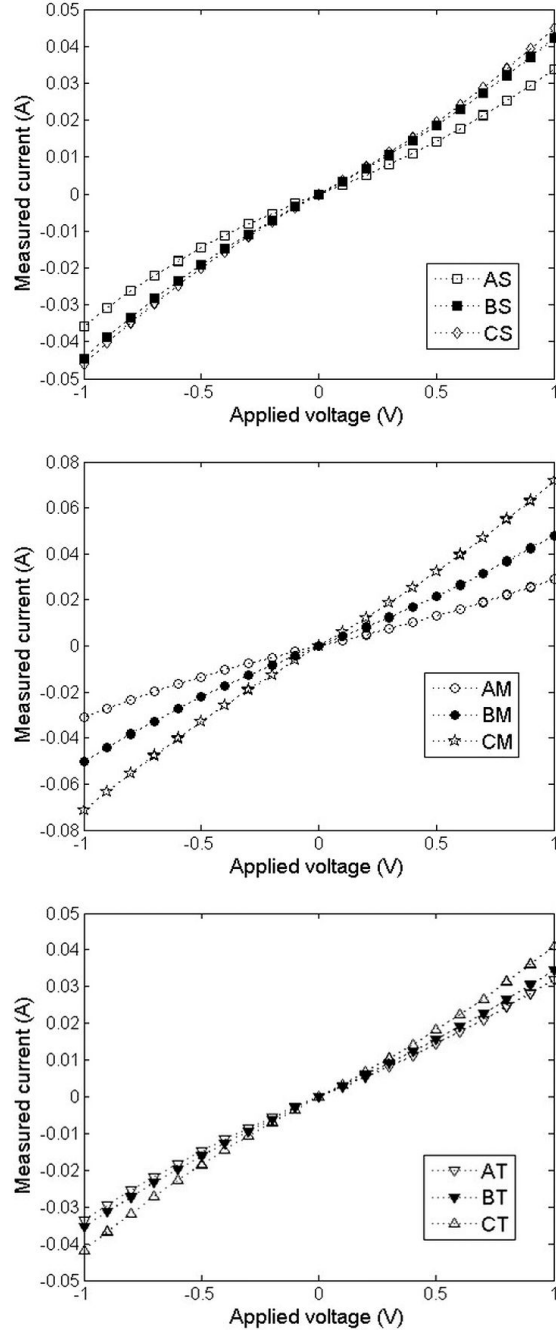


Figure 8.1.: *IV curves of the FC dispersion samples with constant gap lengths: $l = 200 \mu\text{m}$ (top), $l = 400 \mu\text{m}$ (middle) and $l = 800 \mu\text{m}$ (bottom). The gap widths are equal to $w = 3 \text{ mm}$ (A), $w = 4 \text{ mm}$ (B) and $w = 5 \text{ mm}$ (C).*

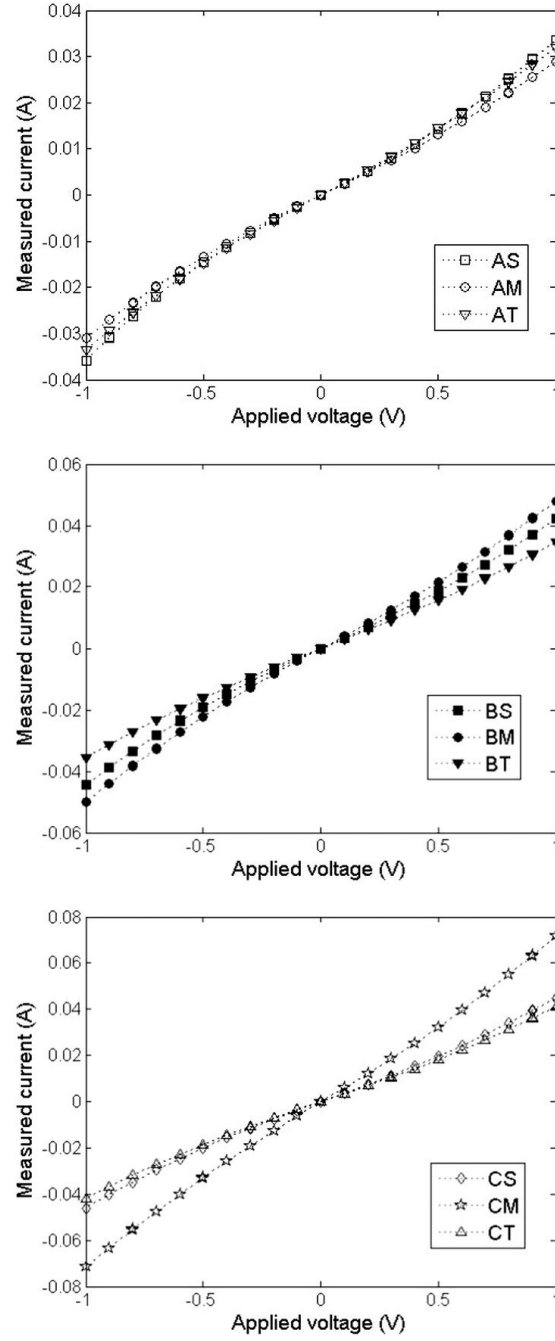


Figure 8.2.: IV curves of the FC dispersion samples with constant gap widths: $w = 3$ mm (top), $w = 4$ mm (middle) and $w = 5$ mm (bottom). The gap lengths are equal to $l = 200$ μm (S), $l = 400$ μm (M) and $l = 800$ μm (T).

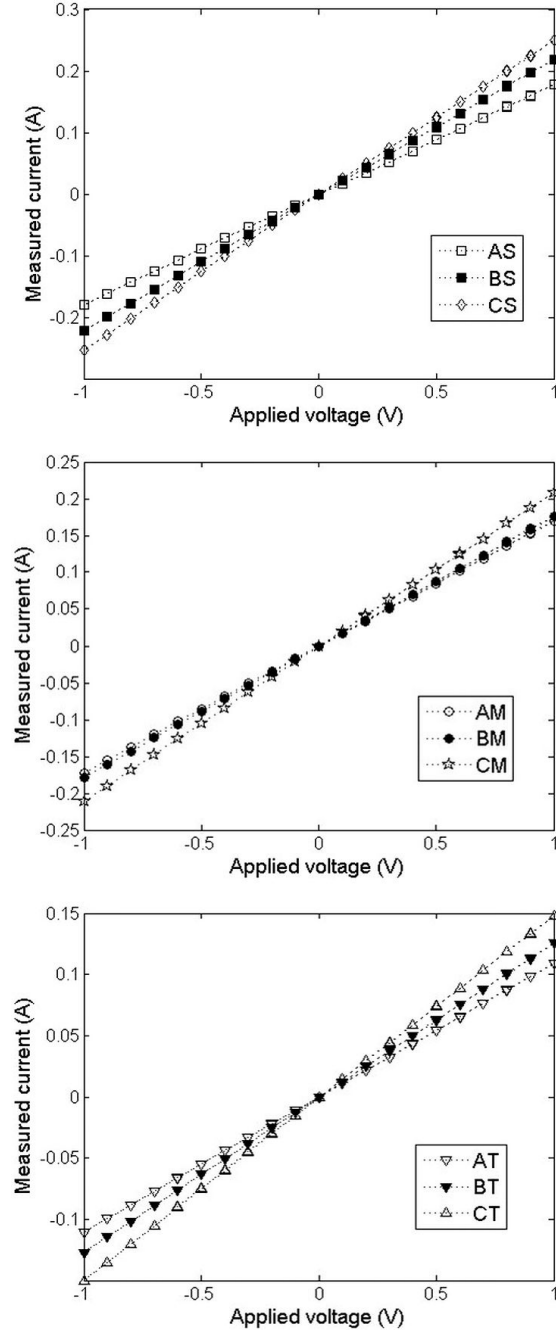


Figure 8.3.: IV curves of the Aquacyl samples with constant gap lengths: $l = 200 \mu\text{m}$ (top), $l = 400 \mu\text{m}$ (middle) and $l = 800 \mu\text{m}$ (bottom). The gap widths are equal to $w = 3 \text{ mm}$ (A), $w = 4 \text{ mm}$ (B) and $w = 5 \text{ mm}$ (C).

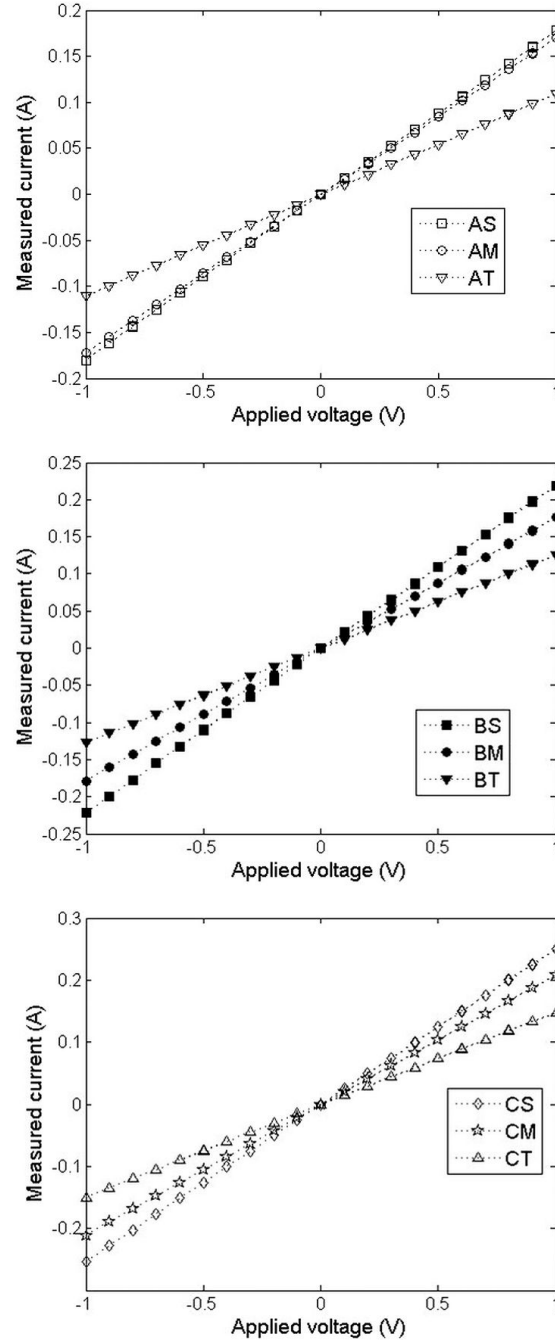


Figure 8.4.: *IV curves of the Aquacyl samples with constant gap widths: $w = 3 \text{ mm}$ (top), $w = 4 \text{ mm}$ (middle) and $w = 5 \text{ mm}$ (bottom). The gap lengths are equal to $l = 200 \mu\text{m}$ (S), $l = 400 \mu\text{m}$ (M) and $l = 800 \mu\text{m}$ (T).*

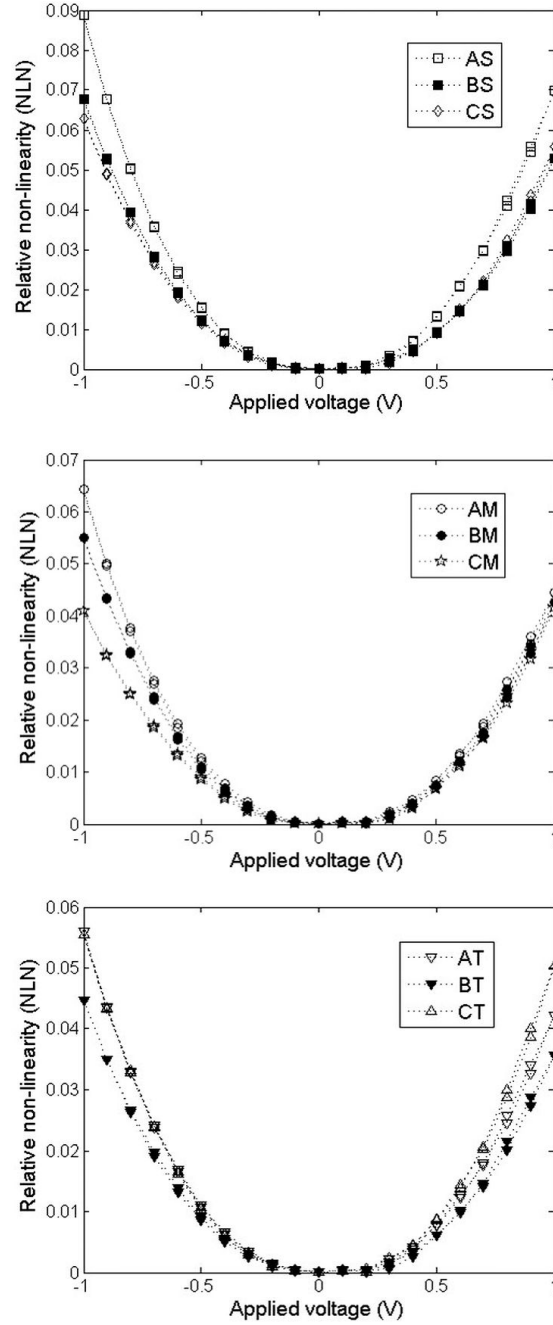


Figure 8.5.: Relative non-linearities versus applied voltage of the FC dispersion samples with constant gap lengths: $l = 200 \mu\text{m}$ (top), $l = 400 \mu\text{m}$ (middle) and $l = 800 \mu\text{m}$ (bottom). The gap widths are equal to $w = 3 \text{ mm}$ (A), $w = 4 \text{ mm}$ (B) and $w = 5 \text{ mm}$ (C).

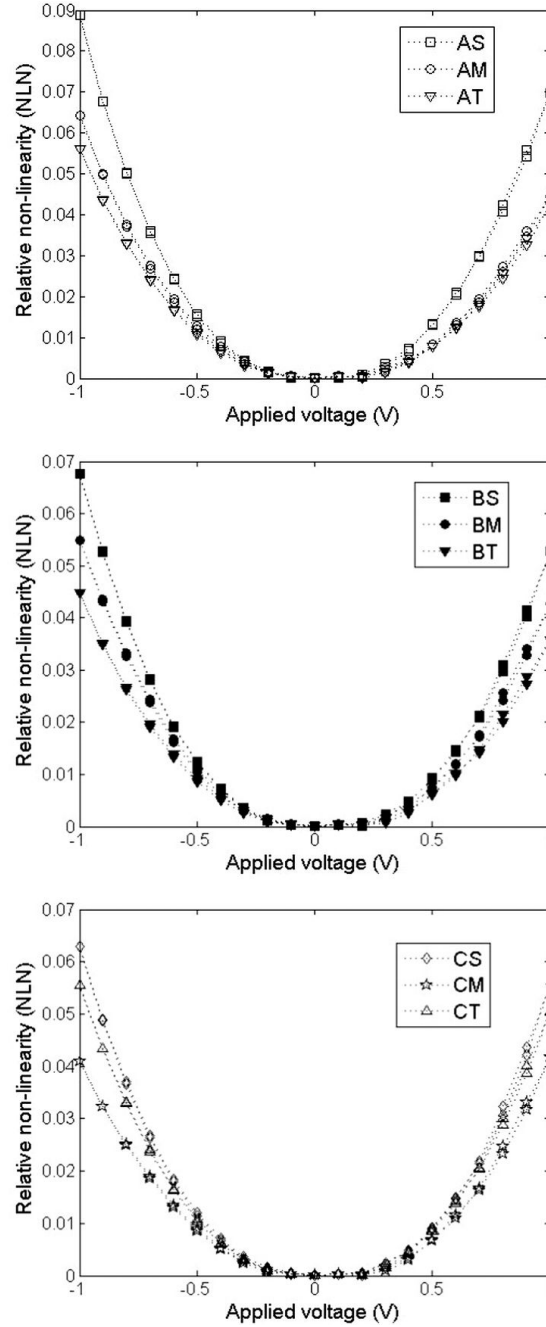


Figure 8.6.: Relative non-linearities versus applied voltage of the FC dispersion samples with constant gap widths: $w = 3$ mm (top), $w = 4$ mm (middle) and $w = 5$ mm (bottom). The gap lengths are equal to $l = 200$ μm (S), $l = 400$ μm (M) and $l = 800$ μm (T).

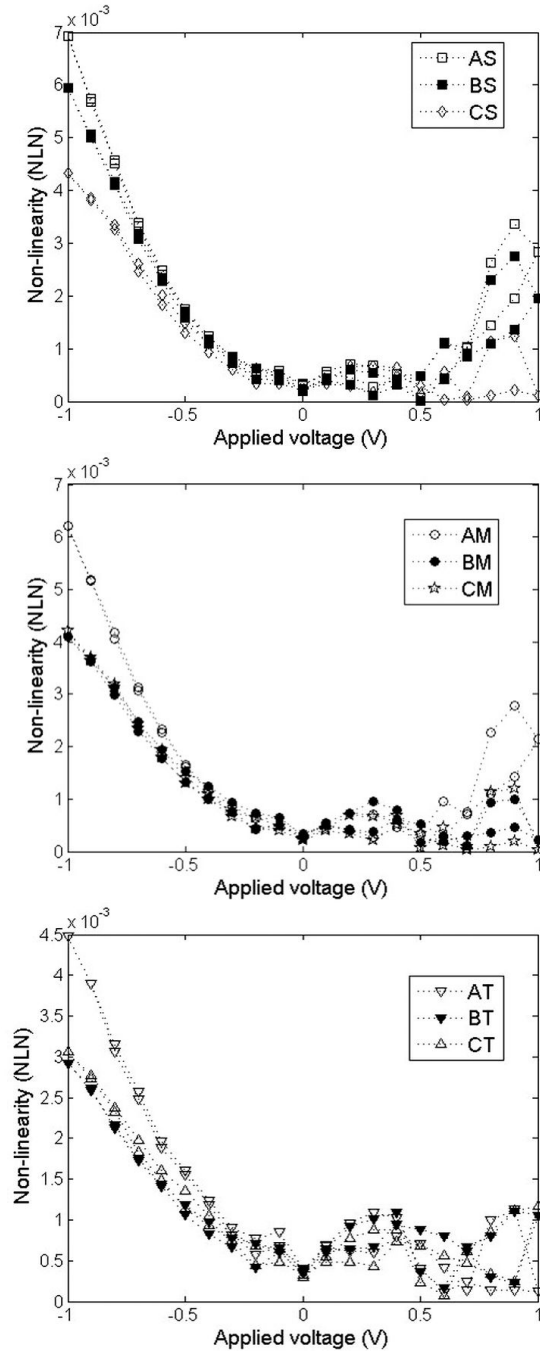


Figure 8.7.: Relative non-linearities versus applied voltage of the Aquacyl dispersion samples with constant gap lengths: $l = 200 \mu\text{m}$ (top), $l = 400 \mu\text{m}$ (middle) and $l = 800 \mu\text{m}$ (bottom). The gap widths are equal to $w = 3 \text{ mm}$ (A), $w = 4 \text{ mm}$ (B) and $w = 5 \text{ mm}$ (C).

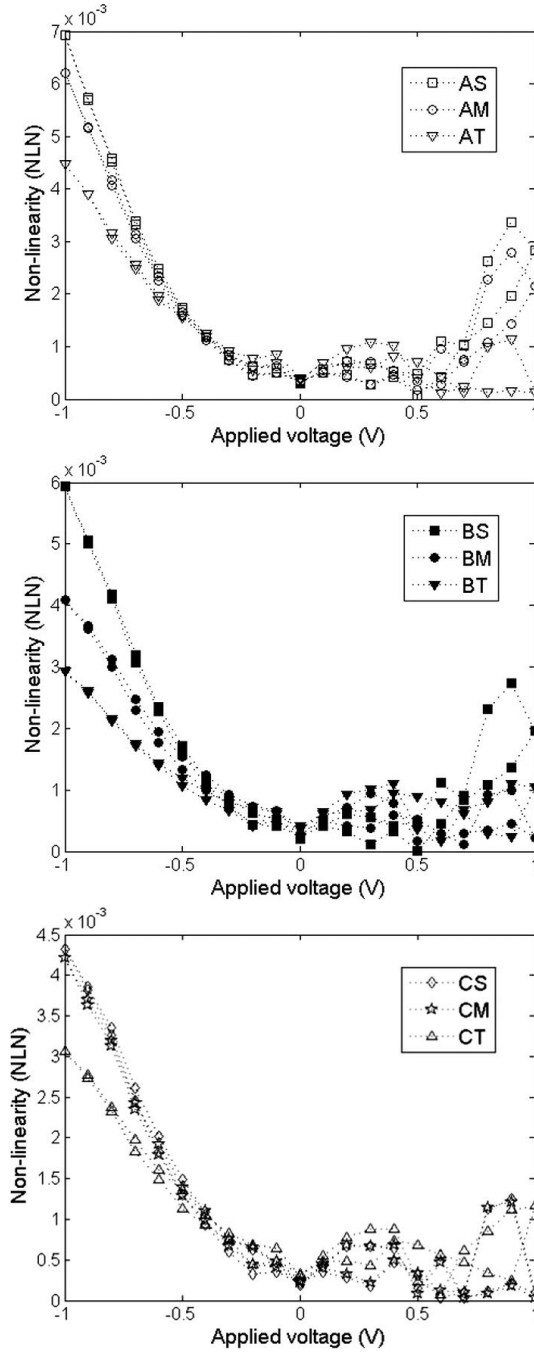


Figure 8.8.: Relative non-linearities versus applied voltage of the Aquacyl samples with constant gap widths: $w = 3$ mm (top), $w = 4$ mm (middle) and $w = 5$ mm (bottom). The gap lengths are equal to $l = 200$ μm (S), $l = 400$ μm (M) and $l = 800$ μm (T).

A.2: Influence of the gap geometry: Role of the shape of the gap edges

The measured IV curves for all samples with FC ink are plotted on Fig. 8.9 for constant gap length plots and on Fig. 8.10 for constant gap shape plots. It can be seen that for 200 and 400 μm long gaps, the conductivity of the samples with pointed-edge gaps is higher than those with straight and rounded edges, the former being more conducive than the latter. For samples with gaps of 800 μm , it is different, the straight edge sample exhibits the highest conductivity then the rounded edge one and finally the one with the pointed-edge gap.

From the constant shape plots of Fig. 8.10, little can be concluded, except that as could be expected the samples with a 800 μm gap exhibit the lowest conductivity, no matter the shape of the gap.

The conductivity of the Aquacyl samples is on the average about one order of magnitude higher than those of the FC samples. The plots for samples having constant gap lengths can be seen on Fig. 8.11.

Constant shape plots are shown on Fig. 8.12, on average, the shorter gap samples exhibit the highest conductivity while the medium sized gap ones have a higher or similar conductivity as those with longest gaps, as could be expected.

The investigation on the relative non-linearities of these samples led to some unexpected results. The relative non-linearities of the FC samples are plotted as a function of applied voltage on Fig. 8.13 for constant gap lengths, on average, the IV curves of the samples with rounded-edge gaps exhibited the strongest non-linearities, while straight or pointed edge gaps yielded similar non-linearity (sometimes higher for straight edges). The latter results were surprising as pointed edge samples, though not as sharp as first imagined, were expected to yield strongest non-linearities.

The same results are shown on Fig. 8.14 on constant shape plots but little can be concluded besides that the shortest gap samples had the strongest non-linearities, confirming the main influence of the electric field intensity.

The relative non-linearity of Aquacyl samples is, on average, about one order of magnitude lower than that of the FC dispersion samples, cf. Fig. 8.15 and cf. Fig. 8.15, for constant lengths and constant shape measurements, respectively. This is in good agreement with the previous non-linearity comparison between FC and Aquacyl solutions. The signal-to-noise ratio is therefore poorer for those samples, especially in the case of the measurements. However, samples with rounded-edge gaps yield higher non-linearities than the other kinds of sample and again the shortest gap samples also have strongest relative non-linearity. Both of these conclusion are in rather good agreement with the results from the FC samples.

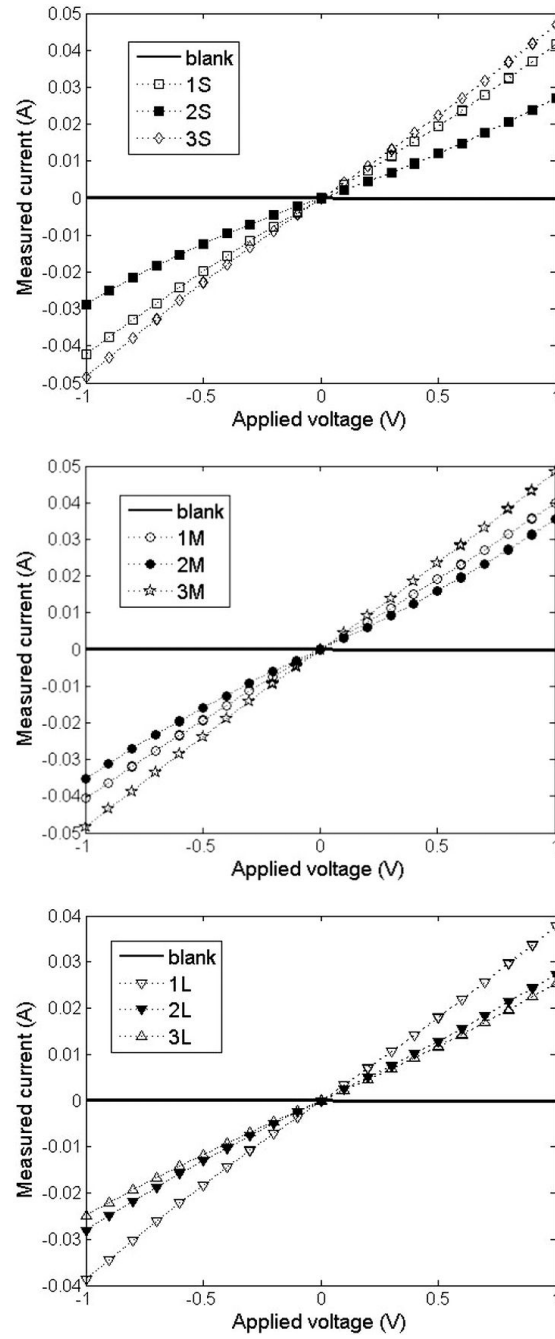


Figure 8.9.: IV curves of the FC dispersion samples with constant gap lengths: $l = 200 \mu\text{m}$ (top), $l = 400 \mu\text{m}$ (middle) and $l = 800 \mu\text{m}$ (bottom). The number 1 corresponds to straight-edge, 2 to rounded-edge and 3 to pointed-edge gap samples.

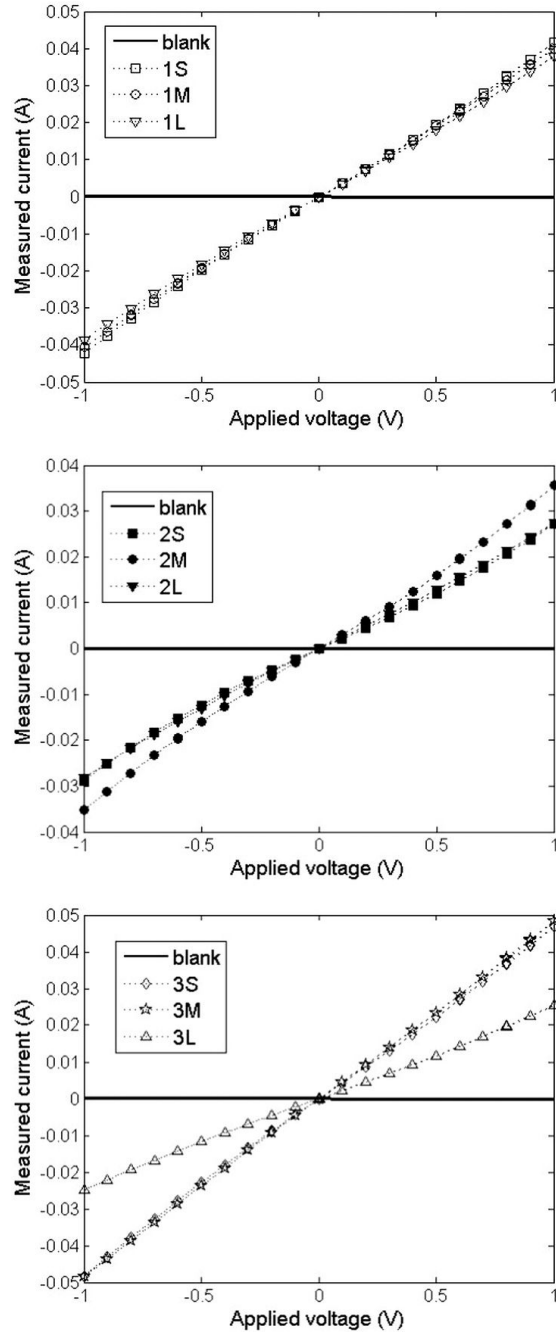


Figure 8.10.: IV curves of the FC dispersion samples with constant gap shapes: straight edges (top), rounded edges (middle) and pointed edges (bottom). The gap lengths are equal to $l = 200 \mu\text{m}$ (S), $l = 400 \mu\text{m}$ (M) and $l = 800 \mu\text{m}$ (L).

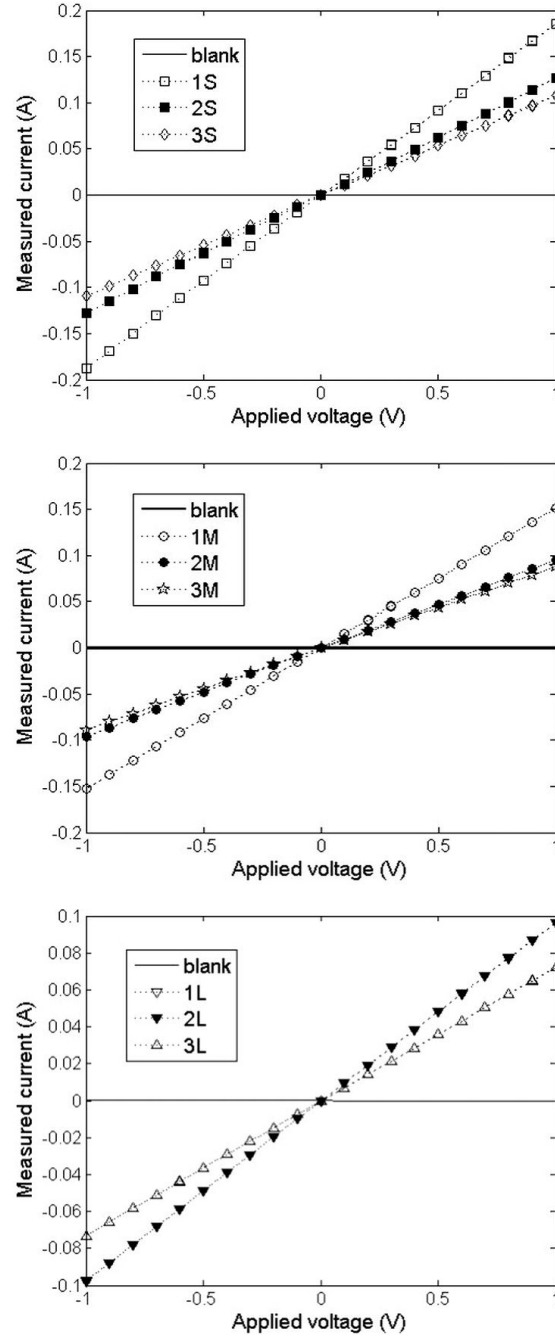


Figure 8.11.: IV curves of the Aquacyl samples with constant gap lengths: $l = 200 \mu\text{m}$ (top), $l = 400 \mu\text{m}$ (middle) and $l = 800 \mu\text{m}$ (bottom). The number 1 corresponds to straight-edge, 2 to rounded-edge and 3 to pointed-edge gap samples. It should be noted that on the lowest graph, the 1L and 2L curves are almost identical.

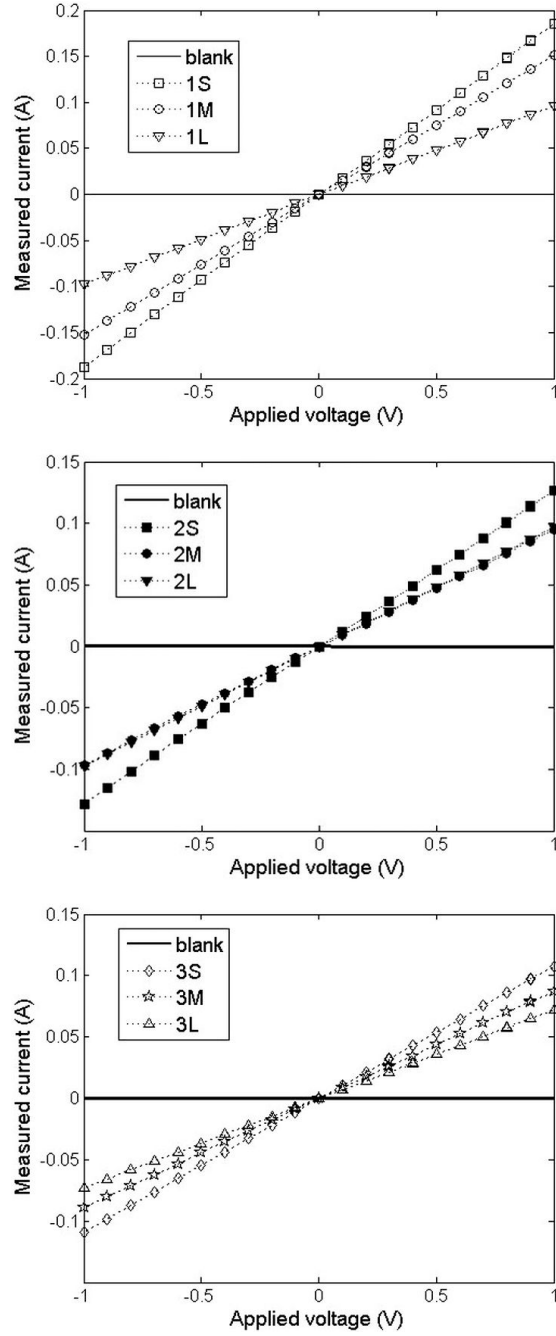


Figure 8.12.: IV curves of the Aquacyl dispersion samples with constant gap shapes: straight edges (top), rounded edges (middle) and pointed edges (bottom). The gap lengths are equal to $l = 200 \mu\text{m}$ (S), $l = 400 \mu\text{m}$ (M) and $l = 800 \mu\text{m}$ (L).

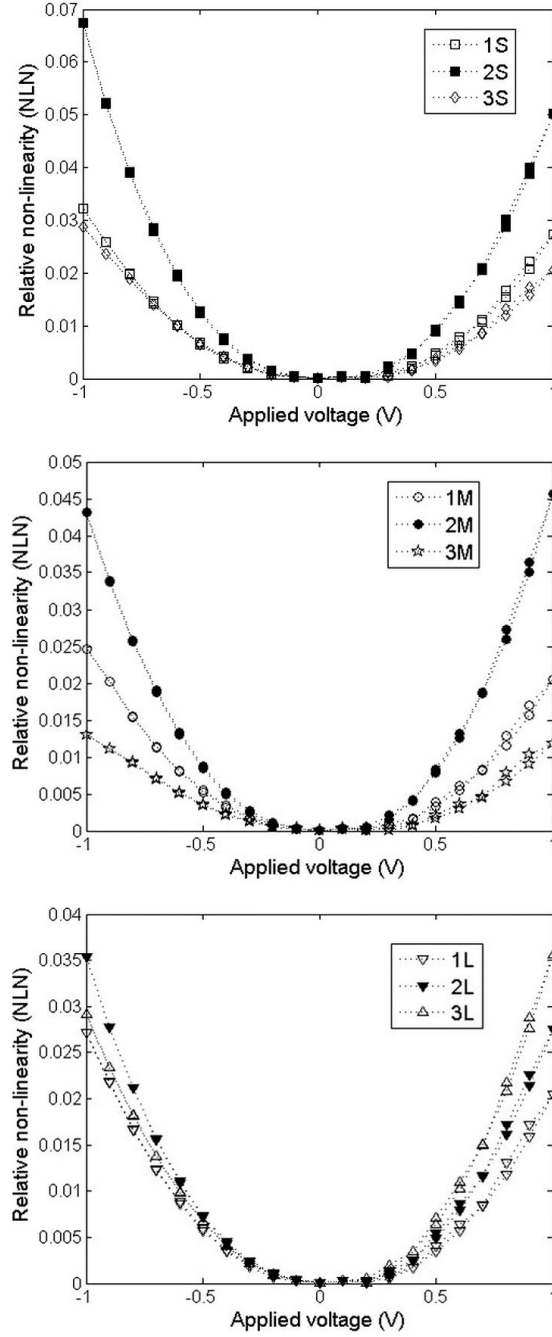


Figure 8.13.: Relative non-linearities versus applied voltage of the FC dispersion samples with constant gap lengths: $l = 200 \mu\text{m}$ (top), $l = 400 \mu\text{m}$ (middle) and $l = 800 \mu\text{m}$ (bottom). The number 1 corresponds to straight-edge, 2 to rounded-edge and 3 to pointed-edge gap samples.

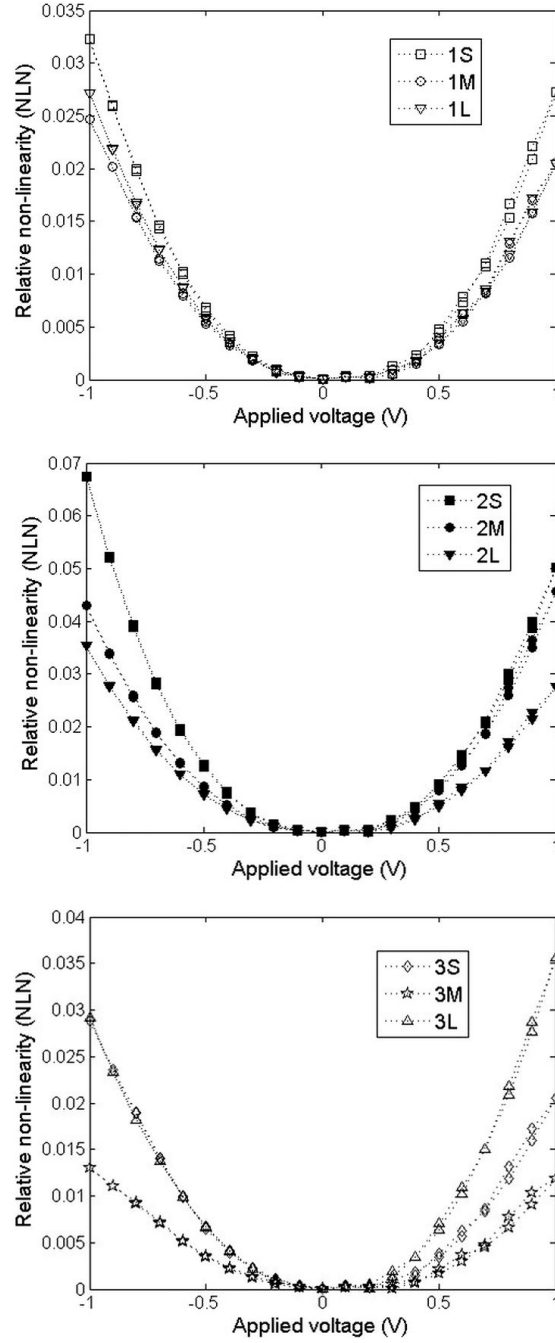


Figure 8.14.: *Relative non-linearities versus applied voltage of the FC dispersion samples with constant gap shapes: straight edges (top), rounded edges (middle) and pointed edges (bottom). The gap lengths are equal to $l = 200 \mu\text{m}$ (S), $l = 400 \mu\text{m}$ (M) and $l = 800 \mu\text{m}$ (L).*

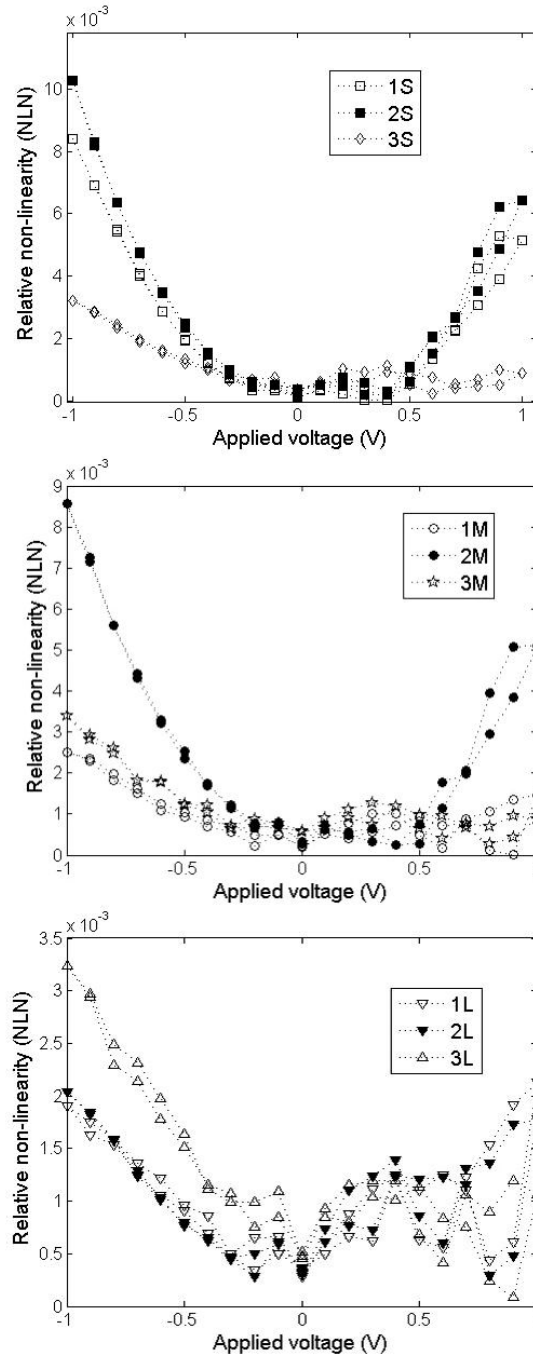


Figure 8.15.: Relative non-linearities versus applied voltage of the Aquacyl samples with constant gap lengths: $l = 200 \mu\text{m}$ (top), $l = 400 \mu\text{m}$ (middle) and $l = 800 \mu\text{m}$ (bottom). The number 1 corresponds to straight-edge, 2 to rounded-edge and 3 to pointed-edge gap samples.

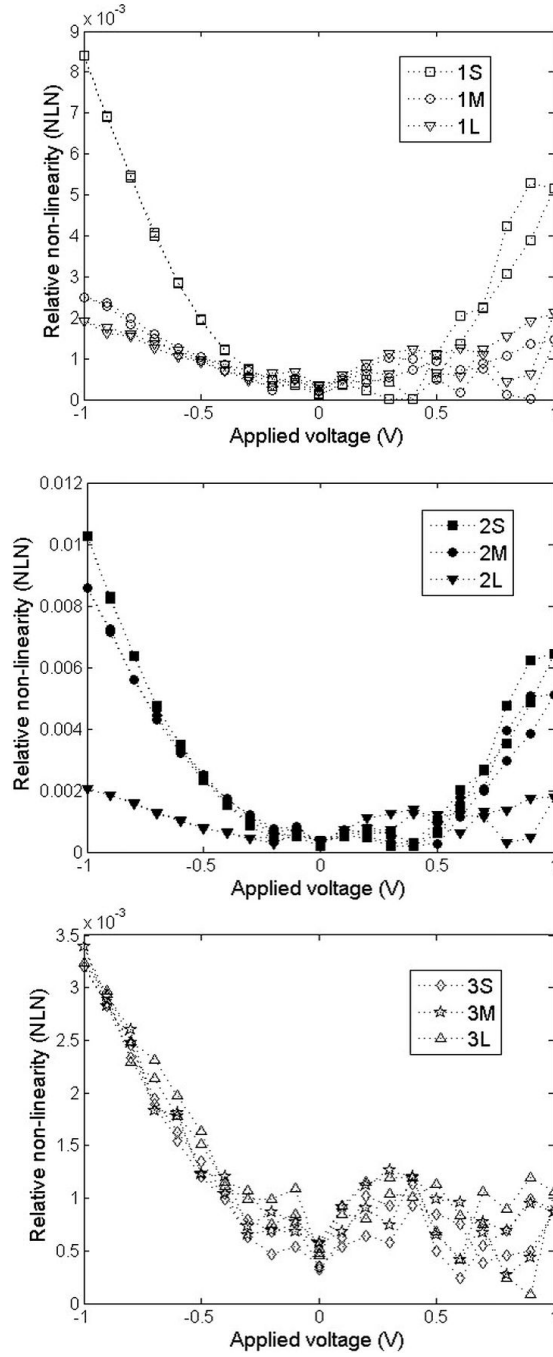


Figure 8.16.: Relative non-linearities versus applied voltage of the Aquacyl samples with constant gap shapes: straight edges (top), rounded edges (middle) and pointed edges (bottom). The gap lengths are equal to $l = 200 \mu\text{m}$ (S), $l = 400 \mu\text{m}$ (M) and $l = 800 \mu\text{m}$ (L).

A.3: Nanoporous track-etched PI membranes: Exact pore size values from gas flow measurements

The pore size values of the track-etched polyimide membranes characterised in chapter 7 are actually rounded values of the pore size calculated from gas flow measurements by it4ip. These ‘exact’ values are listed on Table. 8.1.

sample code	pore size (nm)	exact value (nm)
PI13	50	33
PI14	50	52
PI15	50	50
PI16	50	41
PI17	50	52
PI21	25	29
PI22	25	23
PI23	25	26
PI24	25	24
PI25	25	25
PI26	50	51
PI27	50	49
PI28	50	48
PI29	100	97
PI50	114	114
PI51	56	56

Table 8.1.: Code names, pore size as considered in chapter 7 and exact values of the pore size calculated from gas flow measurements (it4ip) of the PI13 to PI51 nanoporous track-etched polyimide membranes fabricated by it4ip.