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Bio- and Soft Matter

**DISPERSION OF CARBON
NANOFILLERS IN MONO- AND
BIPHASIC POLYMER MATRICES:
THERMODYNAMIC VS. KINETIC
CONTROL AND INFLUENCE ON
HIGH-FREQUENCY ELECTRICAL
PROPERTIES**

September 2011

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ACKNOWLEDGMENTS

J'aimerais exprimer ma sincère reconnaissance envers toutes les personnes qui ont contribué, directement ou indirectement, à la réalisation de ce travail de thèse.

Je tiens d'abord à remercier mes promoteurs Christian Bailly et Jacques Devaux, qui m'ont aidé à définir ce projet de thèse et à le réaliser. Je les remercie pour la confiance et le temps qu'ils m'ont accordés mais aussi pour m'avoir laissé beaucoup d'autonomie pour la réalisation de ce projet.

I am also grateful to Prof. Isabelle Huynen, Prof. Jean-Michel Gloaguen, Prof. Paula Moldenaers and Prof. Sophie Demoustier who accepted to be part of the jury.

J'aimerais ensuite saluer l'ensemble des personnes dont j'ai sollicité l'aide pour des techniques ou des domaines pour lesquels elles sont plus qualifiées que moi.

Ainsi je remercie Isabelle Huynen, Isabel Molenberg, Pascal Simon et David Spote pour leur accueil en EMIC puis en ICTEAM et Welcome. Votre expertise, votre disponibilité et votre enthousiasme m'ont été précieux dans la réalisation de ce travail. David j'attends toujours ton gâteau au chocolat !

Je remercie également Bernard et Laurianne pour le temps qu'ils m'ont consacré pour la caractérisation électrique locale en CS-AFM. Je n'ai toujours pas percé les mystères de cette technique, et pourtant il suffit de changer les gains ! ;-)

Je remercie toutes les personnes qui se sont essayées à la tomographie sur mes échantillons : Jean-Michel Gloaguen, Karine Masenelli-Varlot et Kangbo Lu. Certaines tentatives furent fructueuses, d'autres moins, mais aussi, quelle idée d'avoir choisi des polymères instables sous le faisceau !

Je remercie Michel ainsi que toute l'équipe qui travaille ou a travaillé en mise en œuvre, Jo (qui a failli nous tuer avec une pulvérisette !), Dim, Xavier, Nicolas, François, Naïma (qui nous force à enfiler nos masques et masques de plongée), Remi, Edwin, pour leur bonne humeur et leur aide. Ce fut un réel plaisir de travailler avec vous et les journées DSM m'ont paru nettement moins longues... Je me rappelle aussi des excursions à Geleen pour faire réparer cette foutue machine qui nous en aura fait voir !

Je remercie également Colette et Pascale pour les formations aux microscopies optiques et électroniques. Votre patience, votre disponibilité et votre gentillesse ont été pour moi sans limite. Je ne suis pas sûre que faire des coupes me manquera beaucoup !

Merci à Pascal pour sa patience et sa gentillesse pour les différents dépannages en analyse thermique et pour la GPC.

Thanks to Dietmar for his advice and help in rheology. Never trust his 99%! ;-)

Je remercie également Michel Genet et Delphine pour les analyses XPS.

Je tiens à remercier également les mémorants que j'ai eu le plaisir d'encadrer et qui ont contribué à la réalisation de ce travail, Benjamin, Rémi et Benoît, à qui je souhaite beaucoup de réussite dans la réalisation de sa thèse.

Je remercie particulièrement Aurore pour l'ensemble des services qu'elle m'a rendus dans la bonne humeur tout au long de ma thèse.

Je remercie également Cécile, Colette et Alexandra pour les activités COGF. J'ai pris beaucoup de plaisir à organiser les différentes « guindailles et festivités » avec vous. Combien d'heures à emballer des sachets de St-Nicolas et des œufs de Pâques ou à organiser des journées récréatives et autres repas... Merci aussi à l'équipe Barbecue qui a pris le relais dans l'organisation de moments de détente au sein du labo.

Je tiens à saluer l'ensemble des membres du laboratoire POLY que j'ai eu le plaisir de côtoyer pendant ces cinq années. Parmi eux je remercie tout spécialement Ali, David (courage, bientôt la fin !), Evelyne, Jun, Naïma et Nicolas, pour l'excellente ambiance qu'ils ont apportée dans le bureau (et accessoirement, pour avoir supporté mon haut débit et mon expansivité!). Vive les jeudis gâteaux et les ateliers bricolage ! Votre bonne humeur et votre soutien ont beaucoup compté pour moi. Merci aussi à Laurianne (la meilleure des cagoles), Cécile (pour tous les bons moments et sa franchise), Jessem (une petite thérapie à l'occasion...), Dimitri (chaud patate ! Vive les journées Review qui nous donnaient mal au ventre !), Colette (merci pour tout et pour la réglisse ! Je te préviens pour le prochain concert de Jean-Louis !), Delphine (Dream Team K-Fet), Houssein (Dream Team K-Fet aussi ! et le roi des jeux de mots), Elodie (et les bisounours !), Pascale (ah les journées coupes et les voyages à Eindhoven !), Karine (et ses viedemerde.fr), Loïk (en fait ce qui se passe... oui on sait la pétrochimie c'est le passé... !), Guido (ou « red pants », toujours enthousiaste... surtout pour mettre des cartons jaunes ! C'est aussi le roi des carbonades et des crevettes ! A quand une revanche au badminton ?), Remi (qui ne tape pas les filles, hein ! Mongoose te remercie), Cédric (les buissons ne me manquent pas...), Xavier (merci pour ton introduction aux labos de chimie, tiens il me reste un livre de solfège !), Xavier (mais je ne sais pas pourquoi je pleure ! Mongoose te remercie aussi !), Nasima (got some chocolate and play the Princess ?!), Julian (veux-tu bien raccrocher ton téléphone !?), Lucas (et ses points de vue contestataires...), Sadia et Jean-Michel (et les soirées Brasse-Temps – Guinch), François (« Je suis ton père ! »... ou pas !

*Toujours prêt à lancer les pires piques... (et à en recevoir!), Cédric, Sybille (et ses bons plans cuisine), Pascal, Maksim, Edwin, François (à la recherche d'exotisme et qui a enrichi mon vocabulaire de mots tels que « bou**ve » ; review is not dead !), Bertrand, Benoît, Antony et tous les autres... pour tous les moments de détente et les franches rigolades...*

Je remercie tous les sportifs du POLY pour les séances de volley, de badminton et de natation. Et David... cours !

Merci aussi à mes amis proches, Ju, Ru, Steph, Fab, Mickey (courage bientôt la fin pour toi aussi !) et tout spécialement à Val pour sa compréhension, son écoute et ses très très très nombreux encouragements !

Je termine ce difficile exercice en remerciant de tout cœur mes proches.

Je remercie mon parrain et tante Clairette pour les « guindailles » que nous avons partagées.

Je remercie Julien et Louise pour leur soutien et leurs encouragements.

Je remercie en particulier mes parents de m'avoir toujours entourée, encouragée et soutenue. Merci pour tout ce que vous avez fait pour moi!

Enfin, merci de tout cœur à Vincent pour m'avoir soutenue pendant cette thèse et particulièrement pendant les deux mois intenses de rédaction. Sa bonne humeur et son enthousiasme ont toujours su me rendre le sourire et la motivation nécessaire pour avancer. Si ce travail a abouti c'est aussi beaucoup grâce à lui...

ABSTRACT

Electronic devices are omnipresent in our daily life. There is therefore a need for electromagnetic interference shielding devices. In this context, the interest of researchers for the development of conducting polymer, based on the incorporation of conductive fillers is increasing exponentially. Among conductive fillers, carbon nanotubes (CNT) and, more recently, graphene have attracted tremendous attention due to their exceptional mechanical, electrical and thermal properties. The main key challenge remains however the dispersion of CNT in selected polymers. The objective of this thesis is to answer some fundamental questions related to the dispersion and distribution of CNT and other nanofillers in single-phase polymer matrices and immiscible polymer blends.

First the key aspects controlling the dispersion of CNT in different polymer matrices are described. They are from both thermodynamic and kinetic origins. The enthalpic contribution is dominated by van der Waals (VDW) interactions between as-produced CNT. To minimize these interactions, the difference between the dielectric constants and refractive indexes of the CNT and the matrix has to be minimized. The kinetic parameters are described by the mixing energy, which must overcome the strong attractive interactions between CNT. Increasing mixing energy, by increasing mixing rotation speed and time and decreasing compounding temperature, leads to improved dispersion. However, the electrical properties are reduced. The achievement of a very good dispersion state can thus be harmful to the formation of a conductive network.

Second, as the best electrical properties are not always obtained for the best dispersion states, the formation of percolating networks in ethylene-acrylate copolymers (EA) and the resulting Radio Frequency (RF) electrical properties are analyzed using rheological and electrical characterizations. The initially well dispersed CNT form interconnected agglomerates when annealing the sample in the melt state. The modulus, G' , and the conductivity are thus enhanced. This phenomenon is called secondary agglomeration and is time and temperature dependent. For CNT content lower than the percolation threshold (1 and 2wt.-% CNT), the formation of the interconnected network occurs faster when increasing temperature. Above the percolation threshold (5wt.-% CNT),

the formation of the network is independent of temperature. The network structure is also more quickly achieved when increasing the CNT content.

In order to elaborate conducting materials with decreased conducting filler content, immiscible polymer blends can be used to exploit the concepts of double or triple percolation. Indeed, when dispersing CNT in a blend of two immiscible polymers, they can either locate in one phase or in both or at the interface. It is therefore essential first to understand the parameters that govern the localization of CNT in immiscible polymer blends. The CNT equilibrium position is determined by thermodynamics and more precisely by the evaluation of the wetting coefficient. According to this coefficient, at the equilibrium, the CNT should locate in one phase (called preferred phase) or at the interface. The mixing strategy and the relative viscosities have also a high effect on the final morphology of the blends. When the carbon nanotubes are first dispersed in the preferred phase, whatever the relative viscosities, they stay well dispersed in this phase. On the contrary, when they are first dispersed in the less preferred phase, they migrate towards the preferred phase. However, the total transfer can be hindered if the preferred phase presents a very high viscosity compared to the less preferred phase or if the less preferred phase is adsorbed on the CNT surface. In these cases, migration in the preferred phase is partially or totally prevented and at least a fraction of the CNT is observed at the interface of the phases. As a consequence of the interfacial confinement of CNT, the morphology of blends presenting a sea-island morphology is stabilized due to the presence of a deformable barrier at the interface, preventing coalescence of the dispersed droplets. This stabilization is observed for EA / polyamide (PA) blend for long mixing time (at least 60 min) and low CNT content (0.5 wt.-% CNT).

The interfacial localization observed for the blend EA/PA6 is next exploited to elaborate triple continuous systems. The effect of CNT on co-continuous morphology and the resulting electrical properties are studied. Two different mixing strategies are used: predispersion of CNT in EA and predispersion of CNT in PA6. Both mixing strategies lead to the formation of a conductive pathway at the interface. However, for the predispersion in EA, the conductivity is dominated by agglomerates. The co-continuous domain is wider in the presence of CNT than in the absence of CNT, whatever the mixing strategy. The blends exhibiting a triple continuous structure however exhibit low RF conductivities. This can be partially explained by the presence of a high number of sub-inclusions surrounded by CNT, which are therefore lost for the elaboration of a conductive network, and possibly also by the high anisotropy of the structure. In comparison, a blend exhibiting a sea-island morphology

with large interconnected dispersed droplets present a much higher conductivity. Surprisingly, the triple continuity is therefore not ideal for the elaboration of conductive composites. Note finally that in the presence of CNT, the co-continuous blends, exhibit improved stability. The stabilization is more efficient for systems with predispersion of CNT in EA because of the better CNT interfacial confinement. For predispersion in PA6, a coarsening of the morphology is observed but the co-continuous morphology is preserved. However, the electrical properties are not significantly affected. A full knowledge of the system modification resulting from polymer degradation is however required to analyze rigorously the stability.

Next, the concepts developed for CNT are extended to graphite-based platelets. As for CNT, the dispersion of graphite nanoplatelets (GNP) in single-phase polymer matrices is correlated to the minimization of the Hamaker constant. Furthermore, the dispersion of high amounts of GNP (>15wt.-%) followed by compression highly orients the platelets. A resonant effect in the RF electrical properties is associated to this orientation. The system behaves like an electrical circuit consisting of a resistor, an inductor, and a capacitor, connected in series (RLC circuit). On another hand, when dispersing graphite-base platelets in immiscible polymer blends (EA/PA6), depending on the mixing strategy, the platelets either partly migrate towards the interface, when predispersed in the less preferred phase (EA) or remain dispersed in the preferred phase (PA6). However, the PA6 domains are not so well surrounded by platelets than by CNT.

Finally, we study the combination of CNT and silver nanoparticles (Ag-NP) in a single polymer matrix (PA6) and immiscible polymer blends (EA/PA6) and the resulting electrical properties. Both fillers are homogeneously dispersed in PA6. An affinity between the fillers is observed. However, it does not enhance the electrical properties at high frequencies. When dispersed in immiscible polymer blends (EA/PA6), both fillers migrate towards the interface. The concentration of the fillers leads to improved electrical properties at high frequencies for co-continuous polymer blends and to enhanced local DC conductivity for blends with a sea-island structure.

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Overview

Nowadays, electromagnetic (EM) waves from electronic systems (radios, televisions, computers, mobile phones...) are everywhere. These waves are confined inside the devices or transmitted to the external environment by conduction or radiation. The EM waves may cause malfunctions and perturbations, potentially leading to serious problems: machine breakdown, intermittent automats breakdown, erroneous display... To avoid interferences, there is a need first to reduce the unwanted EM waves emissions and second to decrease the sensitivity of the receptors in the presence of unwanted or unplanned electromagnetic disturbance by producing “compatible” equipments. Electromagnetic compatibility (EMC) is defined as “the correct operation, in the same electromagnetic environment, of different equipments or systems using electromagnetic phenomena, and the avoidance of any interference effects”.

Since January 1st 1996, European directives¹ require the EMC of all the devices sold in the European Community. There is therefore a need for electromagnetic interference shielding devices, such as boxes or hoods.

The quality of a shielding material is characterized using two parameters: the shielding effectiveness² (SE), which is proportional to the ratio between the incident and transmitted powers and the reflectivity (R), which is proportional to the ratio between the reflected and incident powers (Figure 1). The incident power can be either reflected on the material or go through it or be absorbed inside the material.



Figure 1 – Schematic diagrams for a conventional metallic shielding material (left) and for a microwave absorber (right) [3]

¹ 89/336/CEE, 93/68/CEE, 2004/108/EC

² $SE = 10 \log \left(\frac{P_{in}}{P_{out}} \right) \quad R = 10 \log \left(\frac{P_{ref}}{P_{in}} \right)$

³ Molenberg I, Huynen I, Baudouin A-C, Bailly C, Thomassin J-M, Detrembleur C, Chapter 23 - Foamed Nanocomposites for EMI Shielding Applications, In Advanced Microwave and Millimeter Wave Technologies: Semiconductor Devices, Circuits and Systems, Edited by M Mukherjee

The power reflected at the interface air-material depends on the difference between the dielectric constants (ϵ) on both sides of the interface. It increases when this difference increases. For a material in the air ($\epsilon_{\text{air}} = 1$), P_{ref} , and thus R , increases when the dielectric constant of the material increases. Note that the reflection at the second interface is not taken into account here. For good levels of attenuation, it can be neglected.

Different shielding solutions are conceivable: metallic boxes, metallised plastic boxes or conducting polymers. Metallic boxes, such as aluminium cast boxes, exhibit major drawbacks: they are heavy, bulky and hard to shape in complex forms. The metallisation of plastic boxes also present drawbacks: the adherence of the metallic layer must be optimized to prevent metallic layer damage during assembly or handling, they cause health risks for workers and environment pollution (painting, nickel plating...). These two solutions are also often expensive. Although they present a good SE, metals are not ideal candidate for high frequency EMI shielding because almost the whole incident power is reflected. Compared to metals, conducting polymers show many advantages: they are light, flexible, corrosion resistant and their processing is easy. However, most of the polymers are insulators. The conductivity can be obtained by different strategies. The first one is the addition of non permanent additives (ionic materials: quaternary amines, alkylamines...). They migrate to the surface and react with ambient humidity leading to the formation of a moisture film on the surface and thus decreasing the resistivity. This is nevertheless a non permanent method. The second strategy is the use of conducting polymers (polyaniline, polypyrrole...). However, their stability is limited; they are difficult to process and also very expensive. Finally, the third one is the addition of highly conducting fillers (metallic fibres, carbon black, graphite, carbon nanotubes...), which can lower the surface and bulk resistivities in a permanent way.

This last strategy is therefore the most promising and also most studied solution. Among conductive fillers, carbon nanotubes (CNT) have attracted tremendous attention since their discovery by Iijima in 1991. They exhibit a very high aspect ratio (length to diameter ratio), unique mechanical properties as well as excellent electrical and thermal conductivities. They are therefore presented as ideal candidates for the elaboration of conducting polymers with improved mechanical and thermal properties. More recently, graphene or exfoliated graphite nanosheets have also attracted a great deal of attention due to their great potential for improving mechanical, electrical, thermal, and gas barrier properties of polymers. Due to their 2D structures they are expected to be even more efficient to form a conductive structure than CNT. Unfortunately,

contrary to CNT, graphene is not available in large quantities up to now. However, exfoliated graphene nanosheets, consisting of a few stacked layers exist on the market.

The interest of researchers for these subjects is clearly highlighted by the number of publications. A simple search with *carbon nanotubes* or *graphene* as a keyword using three of the most common databases (SciFinder, ISI-Web of Science and ScienceDirect) indicates rapid growths of the publications post 1998 for CNT and post 2005 for graphene with more than 13000 and nearly 6000 publications in 2010 for CNT and graphene respectively (Figure 2). It is also worth noting that a similar trend in number of publications is observed using the terms *carbon nanotubes composites* or *graphene composites*.

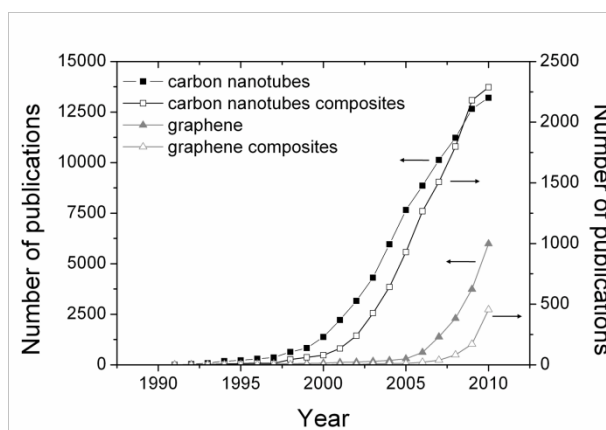


Figure 2 – Number of publications returned using carbon nanotubes, carbon nanotubes composites, graphene or graphene composites as keywords in SciFinder (duplicates are not removed)

This thesis takes place in the broad research field of polymer – carbon nanofillers (CNT or exfoliated graphene nanosheets) nanocomposites for improved electrical properties. The cost of production of CNT has, for a long time, been presented like a major obstacle for the production of polymer/CNT nanocomposites. However, with the implementation in 2010 of a 400 tons/year plant for the production of NC7000 ^[4] by Nanocyl™ and of a 200 tons/year plant for Baytubes® of Bayer MaterialScience ^[5], the CNT producers

⁴ Nanocyl to expand global production capacity of carbon nanotubes, 2009; <<http://www.nanocyl.com/News/Nanocyl-to-Expand-Global-Production-Capacity-of-Carbon-Nanotubes>> [accessed 30.03.2011]

⁵ Bayer MaterialScience open world's largest carbon nanotubes pilot facility, 2010;

are on their way towards the large-scale production of CNT. A decrease of the prices and the opening of new markets to more and more applications are thus expected. The key challenge remains, however, to de-agglomerate the CNT and to disperse them in selected polymer matrices. In that context, this work has for objective to answer some fundamental questions.

First, very different dispersion states are observed depending on the matrix and processing conditions used. Figure 3a presents a poor to good dispersion of CNT in polypropylene (PP) and Figure 3b presents an excellent dispersion of CNT in polycarbonate (PC)⁶. The first objective is thus to understand the key aspects controlling the dispersion of CNT in different polymer matrices.

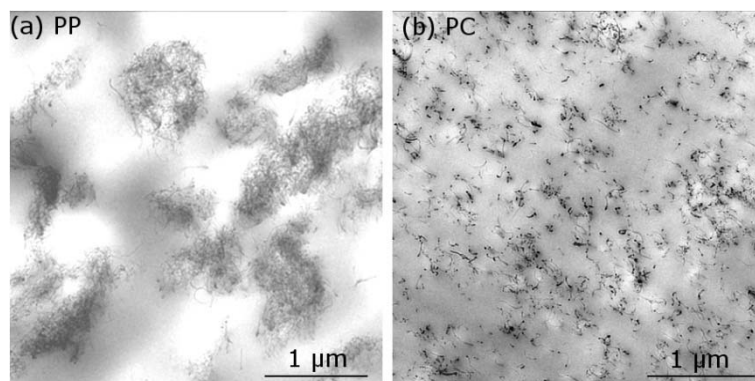


Figure 3 – TEM micrographs of the dispersion of CNT in (a) polypropylene; (b) polycarbonate

Second, as the best electrical properties are not always obtained for the best dispersion states, the formation of percolating networks and the resulting electrical properties must be analyzed using rheological and electrical characterizations.

In order to elaborate conducting materials with decreased conducting filler content, immiscible polymer blends can be used. Indeed, if the fillers form a percolating network in a phase, which percolates through the blend, higher electrical conductivities can be obtained compared to single-phase polymer composites with the same filler content, due to the concentration of the fillers in one phase. This phenomenon is known as the double percolation. Triple

http://www.baytubes.com/news_and_services/pr_100129_new_facility.html>
[accessed 30.03.2011]

⁶ See experimental section in Appendix 1 or Chapter 2 for more details. These blends are processed in similar conditions of viscosity and time.

percolation can also be achieved when the fillers are selective localized at the interface of two immiscible polymers presenting a co-continuous structure. When dispersing CNT in a blend of two immiscible polymers, they can either locate in one phase or in both or at the interface (Figure 4). However, literature remains unclear concerning the parameters governing the localization of CNT in immiscible polymer blends. Moreover some contradicting results are described. The third objective of this thesis is therefore to present a comprehensive study of the thermodynamic and kinetic parameters governing the localization of CNT in immiscible polymer blends.

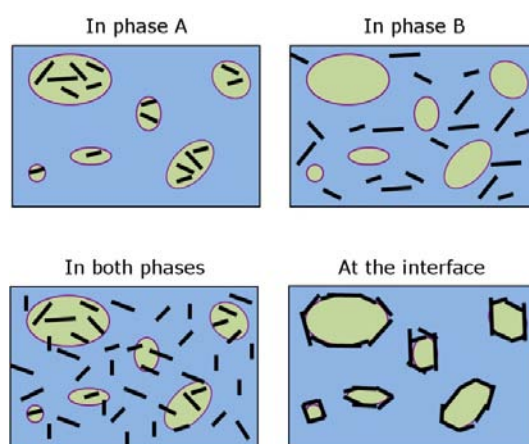


Figure 4 – Scheme of the different possible localization of CNT in immiscible polymer blend presenting a sea-island morphology

Based on these considerations, the fourth objective is to study the influence of CNT on co-continuous morphology and the resulting electrical properties (Figure 5).

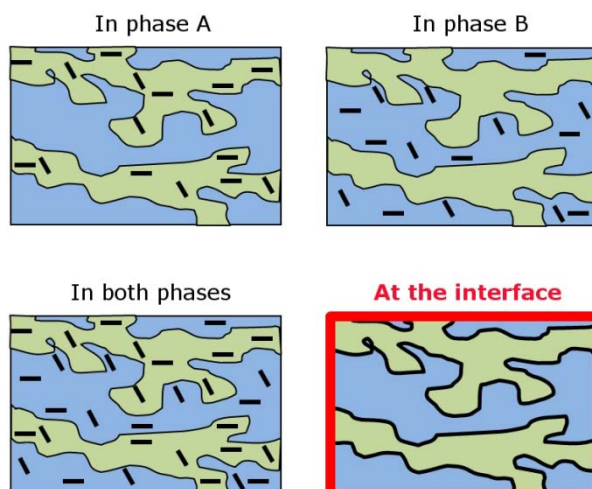


Figure 5 – Scheme of the different possible localization of CNT in immiscible polymer blend presenting a co-continuous morphology

Finally the last objective is the extension of the concepts developed with CNT to other nanofillers, as graphite-based nanoplatelets, and to combine the CNT with other nanoparticles as silver nanoparticles.

Based on these objectives, the thesis is divided into seven chapters.

The first chapter of this manuscript is a literature survey and is divided into three parts. The first one briefly describes the carbon nanotubes, their properties and their synthesis methods. The second part gives a presentation about their dispersion inside polymer matrices. The factors influencing the dispersion based on general thermodynamic considerations are first developed. Next the different dispersion methods are briefly described with a special focus on melt blending, which is the dispersion method used in this work. Finally the resulting properties of the nanocomposites are described in brief. In the third part, electrical properties of nanocomposites based on CNT are more extensively addressed. The application of percolation theory to the electrical conductivity and the parameters influencing percolation threshold are extensively described in literature reviews and are thus only quickly reviewed. A more detailed survey is done on the formation of conducting networks by secondary agglomeration of initially well-dispersed CNT.

The second chapter is divided into two parts. In the first one the different parameters governing the dispersion in different polymer matrices are studied, first based on thermodynamic considerations and second based on kinetic parameters such as mixing rotation speed, mixing time and mixing temperature. In the second part, a time-resolved study of the rheological parameters is performed in parallel with a characterization of the electrical conductivity at high frequencies to analyze the formation of CNT conductive networks at high temperature.

Chapter III presents the thermodynamic and kinetic parameters governing the migration and localization of CNT in immiscible polymer blends presenting a sea-island morphology. A large variety of immiscible polymer blends is studied. Thermodynamics based on the minimization of the interfacial energy predicts the equilibrium position of the CNT in the blends. The differences between thermodynamical predictions and the observed morphologies are discussed and explained by the mixing strategy, polymer adsorption and relative viscosities of the phases. A general mechanism for the localization of CNT in immiscible polymer blends taking into considerations all these effects is then proposed.

In Chapter IV, the effect of CNT interfacial confinement on the stabilization of the dispersed droplets phase in immiscible polymer blends is exposed and a stabilization mechanism is proposed.

In Chapter V, the selective interfacial confinement of CNT is applied to co-continuous blend. This chapter is divided into two parts. First, the development of a co-continuous morphology in the absence of CNT is studied. Second, the blends in presence of CNT are analyzed. First, the selective localization of CNT over a large range of compositions of the blends is checked and the presence of a conductive network at the interface is demonstrated. Then the development of the co-continuous morphologies in the presence of CNT is studied. Finally, the resulting Radio Frequency (RF) electrical properties of these blends are measured and compared to the properties of blends presenting a sea-island morphology.

Chapter VI proposes a broadening of the dispersion and selective localization studies to other carbon-based fillers: Graphite NanoPlatelets (GNP) and Functionalized Graphene Sheets (FGS). Their dispersion in various polymer matrices and the resulting electrical properties are first studied. Second, their localization in immiscible polymer blends is investigated.

Finally, in Chapter VII, the influence of the combination of CNT and Ag nanoparticles (Ag-NP) in polymer nanocomposites is studied. First, the dispersion of the fillers, their interactions and the resulting RF electrical conductivity are investigated in a single-phase polymer matrix. Next, the localization of these nanoparticles in immiscible blends and the electrical properties of these systems are examined.

The characterization of the materials and the description of the experimental methods are exposed in Appendix 1. A literature review of the evaluation of the surface energies of the CNT is presented in Appendix 2.

Chapter 1

STATE OF THE ART

INTRODUCTION

Composites materials have been used and produced since the dawn of time. In ancient Egypt, craftsmen already added short lengths straw to fresh clay to improve the mechanical properties of their bricks. Moreover, some natural materials such as wood (cellulose fibres in lignin matrix) or bones (complex blend of collagen and calcium phosphate) are composites materials ^[1]. After the discovery of plastics, they have been used as matrices for the production of composites. One of the most widely used classes of reinforcing materials is the fibres, such as glass fibres, carbon fibres or aromatic polyamide fibres. In addition to fibres, other fillers have been used to improve the properties of the plastic materials: wollastonite for reinforcing mechanical properties and decreasing the density of the resulting material; antimony oxide, aluminium or magnesium hydroxides to increase fire resistance; copper, aluminium, iron or carbon black to produce conductive composites... For at least twenty years, in addition to macro- or microscopic fillers with dimensions of the order of several microns or more, there has been a growing interest for nanoscale fillers, exhibiting at least one dimension in the nanometer range. Among these nanomaterials, the introduction of carbon nanotubes (CNT) exhibiting two dimensions of the order of the nanometers has opened a new field of investigations. The dispersion of nanometer-size tubes improves the properties of the nanocomposites in comparison with unfilled polymers or classic microcomposites.

In that context, a brief introduction to carbon nanotubes, their synthesis and properties is first exposed. The functionalization of CNT is extensively described in literature [2- 5,8,50]. It is not addressed here since only unfunctionalized CNT are used.

Although CNT exhibit exceptional properties, the key challenge for the development of polymer/CNT composites remains the disentanglement and the dispersion of primary agglomerates. The CNT are entangled from synthesis and van der Waals interactions and depletion forces hold the CNT together in bundles or agglomerates. The depletion forces are attractive forces attributed to the loss of conformations of the macromolecules that are close to the CNT surface. The conformational entropy is reduced when the distance between to CNT is smaller than the gyration radius of the macromolecules. If the CNT are closer than R_g , the coils will be pushed out from the gap, resulting in reduced polymer concentration between the surfaces. The dispersion of CNT in polymer matrices is thus discussed. First the van der Waals interactions

between CNT are described. The depletion forces are not described here as they are not addressed in the experimental part of this thesis. Second, the most common dispersion methods are briefly presented and much attention is paid on melt blending, which is the dispersion technique used in this work. Next, the different characterization methods used to evaluate the dispersion of CNT are discussed. Subsequently, the properties of the polymer/CNT are briefly exposed.

Finally, as this thesis takes place in the research field of polymer – carbon nanofillers nanocomposites for EMI shielding applications, the electrical properties of polymer/CNT nanocomposites are more extensively described. The application of the percolation theory to the conductivity and the factors influencing the percolation threshold are first exposed. Then, the secondary agglomeration of CNT and the resulting electrical properties are developed.

CARBON NANOTUBES

1 Introduction to carbon nanotubes

Until 1985, only two crystalline phases of carbon are known: diamond and graphite. Then in 1985, Kroto, Curl and Smalley ^[6] publish the discovery of fullerenes. These materials consist of carbon cages made of 60 carbon atoms exhibiting hexagonal and pentagonal faces, similar to a soccer ball. In 1991, Iijima has observed for the first time tubular carbon nanotubes (CNT) ^[7]. Depending on the process for CNT elaboration, two types of CNT can be produced: singlewalled CNT (SWNT) or multiwalled CNT (MWNT). SWNT consist of a single graphene layer rolled up, while MWNT consist of several cylindrical shells of concentric graphene layers with adjacent shell separation of ~0.34nm. According to the rolling angle of the graphene layer, CNT presenting different chiralities are produced: armchair, zigzag, chiral. The chirality (Figure 1) is defined by the chiral vector:

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$$

where n and m are integers defining the number of steps along the unit vectors $\vec{a}_1$ and $\vec{a}_2$ of the hexagonal lattice. If n=m, the CNT are called “armchair”, if m=0, the CNT are called “zigzag” and otherwise, they are called “chiral”. The

chirality has an important impact on the transport properties. That is how, for a given (n,m) nanotube, if $(2n+m)$ is a multiple of 3, the nanotube is metallic and otherwise, it is semiconductor. For the MWNT, each layer has its own chirality, the prediction of their physical properties is therefore more complicated [8-11].

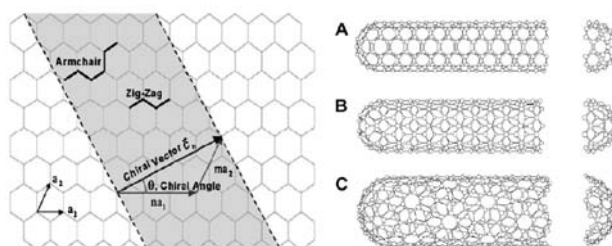


Figure 1 – Schematic diagram showing how a hexagonal sheet of graphene is rolled to form a CNT with different chiralities (A: armchair; B: zigzag; C: chiral).
After [10,11].

2 Properties

CNT are entirely composed of sp^2 carbon-carbon bonds. This bonding structure provides them very high mechanical properties, with Young's modulus as high as 1.2 TPa and tensile strength in the range of 50-200 GPa [12-14]. In addition to these outstanding mechanical properties, CNT possess excellent physical properties, summarized and compared to other carbon materials in Table 1 [8,15]. Their electrical and thermal conductivity are very high, as well as their thermal stability. These properties, combined with their very high aspect ratio (ratio length to diameter), make them a promising candidates for structural applications.

Table 1 – Physical properties of different carbon materials (reproduced from [8])

Property	Carbon materials				
	Graphite	Diamond	Fullerene	SWNT	MWNT
Specific gravity (g/cm^3)	1.9-2.3	3.5	1.7	0.8	1.8
Electrical conductivity (S/cm)	4000p, 3.3c	10^{-2} - 10^{-15}	10^{-5}	10^2 - 10^6	10^3 - 10^5
Electron mobility ($cm^2/(Vs)$)	2.0×10^4	1800	0.5-6	$\sim 10^5$	10^4 - 10^5
Thermal conductivity (W/(mK))	298p, 2.2c	900-2320	0.4	6000	2000
Coefficient of thermal expansion (K^{-1})	-1×10^{-6} p 2.9×10^{-5} c	$(1 \sim 3) \times 10^{-6}$	6.2×10^{-5}	negligible	negligible
Thermal stability in air ($^{\circ}C$)	450-650	<600	~ 600	>600	>600

p: in plane; c: c-axis

3 Synthesis

The CNT are mainly produced by three methods: arc-discharge, laser-ablation, and chemical vapour deposition [9,16-19]. After synthesis, the CNT can be purified to remove impurities such as amorphous carbon, metallic catalysts, small fullerenes... Different purification methods are usually used: oxidation, acid treatments, sonication, filtration...

The arc-discharge technique requires the passage of a direct current through two high purity graphite electrodes separated by 1-2 mm in an inert atmosphere (typically He or Ar). A deposit forms on the cathode while the anode is consumed. In the laser-ablation technique, pure graphite targets are vaporized by a high power laser inside a furnace at 1200°C in inert atmosphere. For the chemical vapour deposition (CVD), a mixture of hydrocarbon gas, acetylene, methane or ethylene and nitrogen is introduced in the reactor. During the reaction, CNT are formed on supported catalysts by decomposition of hydrocarbons at 500-1000°C. With CVD, high purity CNT can be produced on a large scale, therefore minimizing the purification process. It is therefore appropriate for scaling-up and to decrease production costs.

CNT DISPERSION IN POLYMER MATRICES

1 Introduction

In 1994, Ajayan et al. [20] have published the first introduction to polymer/CNT nanocomposites. Since then, many research teams have concentrated their efforts on the production of polymer/CNT nanocomposites. However, the results are limited due to the difficulty to disperse the entangled CNT during processing and to the poor interfacial interaction between CNT and the polymer matrix. Indeed, CNT are usually synthesized as bundles. van der Waals interactions and depletion forces hold the bundles together. van der Waals interactions between CNT are first presented. Next, the methods used to disperse CNT in polymer matrices are described. The methods used to characterize the dispersion are presented afterward. Finally, the properties enhanced owing to the incorporation and dispersion of CNT in polymers are reported.

2 van der Waals interactions between CNT

It is necessary to overcome the inter-tube van der Waals (VDW) attraction to disperse the CNT in a polymer matrix. In the case of CNT, VDW interactions are strong due to the high polarizability of the tubes. Depending on the CNT size and mutual orientation, the VDW attraction can act on distances up to a few nanometers ^[21].

VDW interaction between two mesoscopic cylinders can be derived from the pair interaction between two molecules. To derive the equations for the cylinders, it is first necessary to relate the pair interaction between two molecules to the interaction between a molecule and a flat surface ^[22,23]. The pair potential between two atoms or small molecules is assumed to be purely attractive and of the form:

$$w(r) = -C/r^n$$

where r is the interatomic distance, $n=6$ for VDW interactions and C is a fundamental constant (interaction constant).

Next, with the assumption that the interaction is non-retarded and additive, the net interaction energy between a molecule and a surface is the sum of the interactions between the molecule and all the molecules of the planar body. It is assumed that inside the body, the molecules of atoms do not interact one with each other. The net interaction at a distance D of the body is therefore:

$$w(D) = -\pi C \rho / 6D^3$$

where ρ is the number density of molecules in the solid.

Based on these considerations, it is possible to evaluate the interaction between macroscopic bodies. The interaction energy of a large sphere of radius R and a flat surface can now be derived. Therefore the interactions between the volume of a thin circular section of the sphere, at a certain distance of the surface, and the surface are integrated on the volume of the sphere (Figure 2).

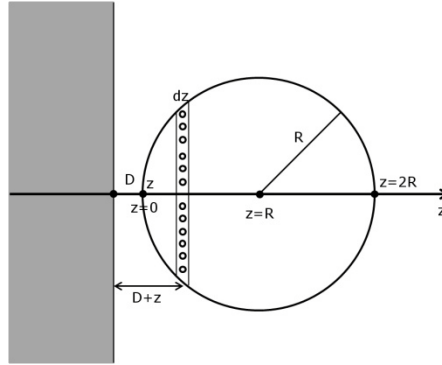


Figure 2 – Methods of summing (integrating) the interaction energies between molecules in condensed phases to obtain the interaction energies between macroscopic bodies for a spherical particle near a wall ($R \gg D$)

For $D \ll R$, only the thin sections close to the planar surface contribute to the integral and the interaction is therefore written as:

$$W(D) = -\pi^2 C \rho^2 R / 6D$$

Note that the interaction energy is proportional to the radius of the sphere and decays as $1/D$, which is much slower than the $1/r^6$ dependence of the intermolecular pair interaction.

For $D \gg R$, the expression is:

$$W(D) = -\frac{2\pi C \rho \left(\frac{4\pi R^3 \rho}{3} \right)}{(n-2)(n-3)D^{n-3}}$$

At intermediate separation ($R \approx D$), the expression for the interaction potential is more complicated and is not described here.

Now, the interaction energy for two planar surfaces can be described. For two planar infinite surfaces, the energy would be infinite. Thus the interaction described here is an interaction per unit area. For a unit area of one surface interacting with an infinite area of another surface, the interaction energy is:

$$W(D) = -\pi C \rho^2 / 12D^2 \quad \text{per unit area}$$

In a similar way, VDW interactions between two mesoscopic cylinders of length L , radii R_1 and R_2 and separated by a short distance D (Figure 3) are expressed as:

$$W = -\frac{\pi^2 C \rho_1 \rho_2}{6D} \sqrt{R_1 R_2} \quad \text{for two crossed cylinders}$$

$$W = \frac{\pi^2 C \rho_1 \rho_2 L}{12\sqrt{2}D^{3/2}} \left(\frac{R_1 R_2}{R_1 + R_2} \right)^{1/2} \quad \text{for two parallel cylinders}$$

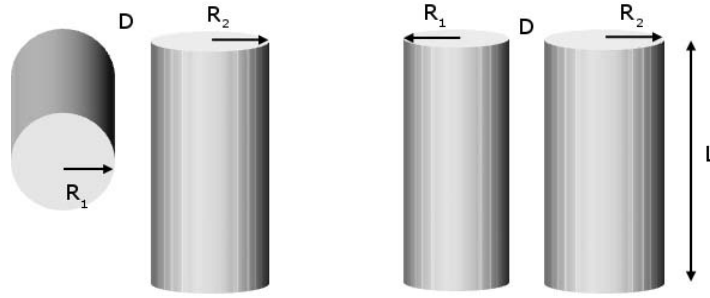


Figure 3 – Schematic drawing of cylinders configurations

It is worth noting that the interaction energy for two macroscopic bodies decays much more slowly than for two molecules. The interparticles are thus longer-range forces.

It is also important to relate the force $F(D)$ between two curved surfaces to the interaction free energy $W(D)$ between two planar surfaces:

$$F(D) = -\frac{\partial W(D)}{\partial D}$$

The Derjaguin approximation gives the force between two curved surfaces in terms of the energy per unit area of two flat surfaces at the same separation D , for $D \ll R_1$ and R_2 . For two cylinders crossed at an angle θ to each other, the Derjaguin approximation is:

$$F(D) = \frac{2\pi\sqrt{R_1 R_2} W(D)}{\sin \theta}$$

It is a useful theoretical tool, since it is often easier to derive the interaction energy for two planar surfaces than for two curved surfaces.

The interaction laws for the common geometries can be given in terms of the conventional Hamaker constant:

$$A = \pi^2 C \rho_1 \rho_2$$

Where ρ is the number of atoms per unit volume in two interacting bodies (m^{-3}); C is the coefficient in particle-particle interactions (J m^6).

For two cylinders, the interaction energy becomes:

$$W = -\frac{A}{6D} \sqrt{R_1 R_2} \quad \text{for two crossed cylinders}$$

$$W = \frac{AL}{12\sqrt{2}D^{3/2}} \left(\frac{R_1 R_2}{R_1 + R_2} \right)^{1/2} \quad \text{for two parallel cylinders}$$

The assumption of pairwise additivity works for bodies interacting in vacuum or in gases (where the interactions with the continuous phase are non-existent or minimal), but it can not be applied when a condensed phase, such as a polymer matrix, is present. When evaluating the van der Waals interaction between macroscopic particles, the influence of the neighbouring atoms has thus to be taken into account. The Lifshitz theory allows the evaluation of these forces ignoring the atomic structure of the bodies and considering the forces between large bodies treated as continuous media. The Lifshitz theory does not change the general expression of interaction energy between the particles, but only the way to calculate the Hamaker constant. According to this theory, the Hamaker constant is calculated based on bulk properties such as their dielectric constant, ϵ , and refractive index, n . The Hamaker constant evaluated according to this theory applies for all media, on the contrary to the conventional expression. Note that the original Lifshitz theory requires a thorough working knowledge of quantum field theory for its understanding. The detail of the calculations will therefore not be presented here.

Based on Lifshitz theory for a symmetric case of two identical CNT interacting across a polymer, the Hamaker constant can be expressed as:

$$A \approx \frac{3}{4} k_B T \left(\frac{\epsilon_{CNT} - \epsilon_{polymer}}{\epsilon_{CNT} + \epsilon_{polymer}} \right)^2 + \frac{3h}{4\pi} \int_{\nu_1}^{\infty} \left(\frac{\epsilon_{CNT}(i\nu) - \epsilon_{polymer}(i\nu)}{\epsilon_{CNT}(i\nu) + \epsilon_{polymer}(i\nu)} \right)^2 d\nu$$

Where k_B is the Boltzmann constant, T is the temperature, h is the Planck constant, ϵ_{CNT} and $\epsilon_{polymer}$ are the static dielectric constants of the CNT and polymer, $\epsilon_{CNT}(i\nu)$ and $\epsilon_{polymer}(i\nu)$ are the values of dielectric permittivity at imaginary frequencies ν .

However, because the whole spectrum of dielectric permittivity is not known for most materials, the Hamaker constant is often written in terms of refractive indexes:

$$A = \frac{3}{4} k_B T \left(\frac{\epsilon_{CNT} - \epsilon_{polymer}}{\epsilon_{CNT} + \epsilon_{polymer}} \right)^2 + \frac{3h\nu_e}{16\sqrt{2}} \frac{(n_{CNT}^2 - n_{polymer}^2)^2}{(n_{CNT}^2 + n_{polymer}^2)^{3/2}}$$

Where ν_e is the main electronic absorption frequency in the UV typically around $3 \cdot 10^{15} \text{ s}^{-1}$, n_{CNT} and $n_{polymer}$ are the refractive indexes of the CNT and polymer.

The van der Waals force between two identical bodies in a medium is always attractive (A positive). The interaction energy between two carbon nanotubes is therefore depending on the dielectric constant and refractive indexes differences between the CNT and the polymer. In order to disperse properly the CNT in the polymer matrix, the value of the Hamaker constant has to be minimized to decrease the interaction energy between CNT.

It is worth noting that this equation has been developed for dielectrics. Conducting materials, such as metals, exhibit a very high dielectric constant. Therefore, due to their high polarizability, the Hamaker constant of metals can be up to an order of magnitude higher than those of dielectrics. For interactions involving conducting media, another expression has to be developed.

The Lifshitz theory avoids completely the pairwise additivity by assuming that the attraction is due to a fluctuating electromagnetic field in the gap, which arises due to spontaneous electric and magnetic polarisations within the media. Moreover, as the Lifshitz theory is based on the equations of the electromagnetic fields, the retardation effect, which was the second major drawback of the Hamaker-based theory, is also avoided. Remind that the

retardation effect is observed when the time for the electric field of the first body to reach the second one and return becomes comparable to the period of the fluctuating dipole itself.

Some authors [24-28] use this classical solution to evaluate the VDW interaction for the dispersion of MWNT in polymers. They do not evaluate the Hamaker constant for CNT in a precise medium but give a rough approximation, $A \approx 2 \times 10^{-19}$ J, for a medium presenting a permittivity $\epsilon \geq 1$ [24]. For two identical tubes of radius $R = 5$ nm and contour length $L = 10 \mu\text{m}$, parallel to each other with a separation distance $D = 1$ nm, the VDW interaction is $\sim 2 \times 10^{-16}$ J and for a crossing configuration, the energy is $\sim 3 \times 10^{-19}$ J. Separation of the tubes from a bundle thus requires a shear energy exceeding the characteristic values associated to these configurations [25]. Shvartzman-Cohen et al. [24] show that VDW interaction is significant even at distances larger than the particle radius due to the additivity of the VDW interactions manifested in the Hamaker constant (Figure 4).

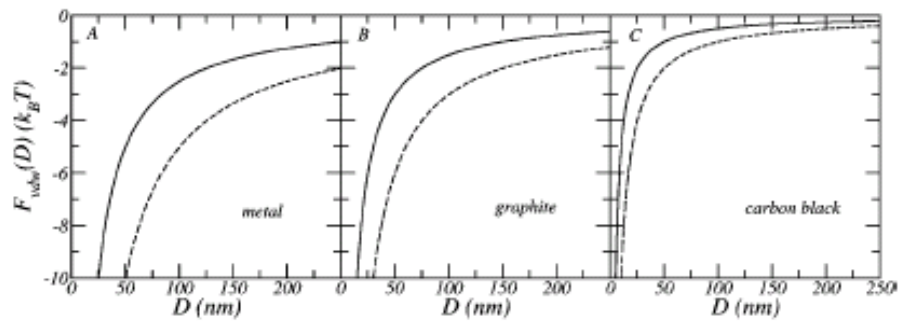


Figure 4 - VDW free energy between two spherical particles as a function of interparticle separation (D). The relation was calculated using the expression

$$W = -\frac{A}{6D} \frac{R_1 R_2}{R_1 + R_2} \text{ for particles of a diameter of 50 nm (full line) and 100 nm}$$

(dashed line) of (A) metal, characterized by $A = 5 \times 10^{-19}$ J; (B) graphite, $A = 3 \times 10^{-19}$ J; and (C) carbon black, $A = 1 \times 10^{-19}$ J. [24]

Rajter et al. [28] show that for systems with anisotropic dielectric response, such as CNT, the van der Waals–London should be described in terms of transverse and longitudinal dielectric responses (Figure 5). They start from Lifshitz interaction energy for two plane-parallel semi-infinite anisotropic media but then use the Parsegian method of composite anisotropic media for both of them. They decompose the interaction energy between the far-limit and the near-limit and propose an interpolation that covers the whole regime of separations (for more details see additional information).

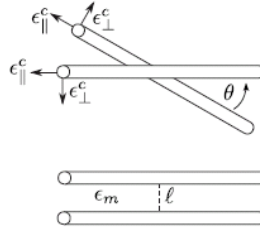


Figure 5 - Schematic showing the geometry of the anisotropic cylinder - anisotropic cylinder systems [28]

However, there is no consensus on a general way to calculate the VDW interactions between CNT in a polymer media.

Some authors [29-31] state that the application of the Lifshitz theory to the dispersion of CNT in polymers causes problems because CNT cannot be characterized by the concept of a frequency-dependent dielectric permittivity. Nevertheless, Klimchitskaya et al. [32] show that the macroscopic concept of graphite dielectric permittivity is already applicable for CNT with only two or three walls. Moreover, other authors [33-38] also evaluate the dielectric constant of CNT, using, for example, scanning force microscopy.

Two other types of methods are commonly used to describe the van der Waals cohesive properties of graphitic systems: one is based on density functional theory (DFT) and the other on empirical model potentials. These models are however in good agreement when properly applied [39]. The model potentials are based on empirical functions whose parameters are obtained from empirical fits. Albeit VDW forces between two adjacent CNT can deform the cylindrical symmetry [40], the deformations are very small for small SWNT and for MWNT with many inner shells [41-43], and therefore do not prevent the application of the model. Zhbanov and co-workers [29,44] give analytical expressions for the VDW potential energy and force between two crossed CNT. They use the Lennard-Jones (LJ) potential between pairs of carbon atoms and the model developed by Girifalco et al. [39,45]. The LJ potential for two carbon atoms in graphene-graphene structure is expressed as:

$$\varphi(r) = \frac{A}{r^6} + \frac{B}{r^{12}}$$

Where r is a distance, $A = 15.2 \text{ eV} \cdot \text{\AA}^6$ and $B = 24100 \text{ eV} \cdot \text{\AA}^{12}$ are the attractive and repulsive constants, respectively [21]. Following Girifalco [45], the potential between two crossed SWNT is approximated by integration of the LJ potential:

$$\varphi_{tt} = \nu^2 \int \varphi(r) d\Sigma_1 d\Sigma_2$$

Where the mean surface density of carbon atoms for a hexagonal structure is:

$$\nu = \frac{4}{3\sqrt{3} a_1^2}$$

where $a_1 = 1.42 \text{ \AA}$ is the observed value of the C – C bond length for periodic graphite [46]. The interaction between MWNT is obtained by summation over all pairs of layers based on the VDW interaction between two SWNT [47].

A schematic illustration of the interaction between two crossed CNT is presented on Figure 6. The potential energy and VDW force are inversely proportional to the sine of the angle, γ , between two tubes. When the tubes are perpendicular, the attractive force is minimal and when the tubes are almost parallel, the forces approach infinity.

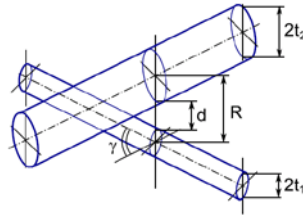


Figure 6 – Schematic drawing of interaction between two CNT [44]

The paper describes the equilibrium distance, potential energy and maximal attractive force for perpendicular CNT. The optimal distance for two crossed SWNT is $d = 2.93 \text{ \AA}$ and for two MWNT, $d = 2.87 \text{ \AA}$. The presence of multiple layers decreases the optimal distance. The potential energies for interaction and the VDW interactions between pairs of identical SWNT and of MWNT with 11 layers equivalent size are presented in Figure 7 and Figure 8.

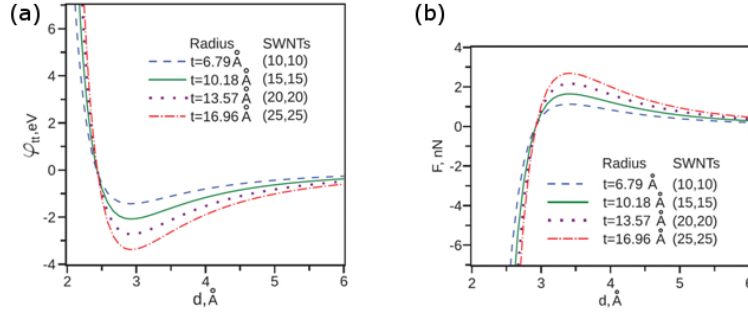


Figure 7 – (a) Potential energies for interaction; (b) VDW forces; between pairs of identical SWNT ($\gamma=\pi/2$) [29]

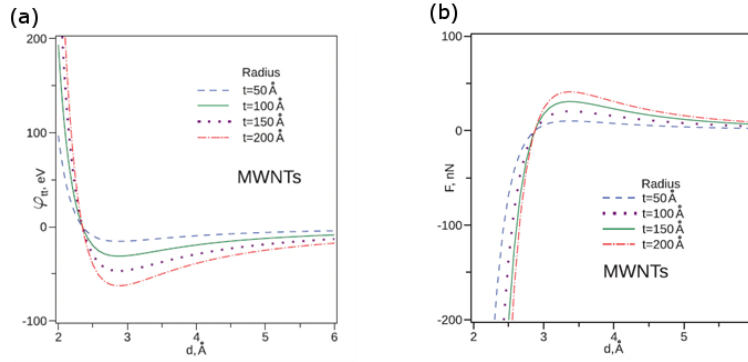


Figure 8 – Potential energies for interaction; (b) VDW forces; between pairs of MWNT of 11 layers and equivalent size ($\gamma=\pi/2$) [29]

3 Dispersion methods

To elaborate polymer/CNT nanocomposites, the dispersion methods must overcome the attractive interactions between CNT. Three methods are commonly used to disperse the CNT in polymer matrices: solution mixing, in situ polymerization and melt blending [8,48-52]. However, other methods, including the latex technology [53,54], are also described in literature [50]. As the melt blending is the dispersion methods used in this work, it is more extensively described than the other methods.

3.1 Solution mixing

The polymer is dissolved in a solvent and the same solvent is used to disperse the CNT. The dispersion of the CNT is generally performed separately from the polymer dissolution. Indeed, the conditions required to disperse the CNT are severe and would likely cause molecular weight degradation of the polymer.

This processing route is not a continuous process and multiple steps are required. Moreover, large volumes of solvent are required to disperse the CNT and dissolve the polymer, therefore preventing commercial applications. Another important issue encountered with this technique is the solvent removal. Indeed, the solvent must be removed quickly to prevent reaggregation at the nanoscale [55,56]. This is usually done by evaporation of the solvent [57-61] or by using an anti-solvent for the polymer, which does not disperse the CNT [62,63].

To solve the problems of solvents, water can be used instead. However, CNT do not disperse well in water, addition of surfactants [64] or functionalization [65,66] of CNT is thus required. In this case, either water-soluble polymers or water-dispersable polymers can be used.

Solution mixing has been used to produce polymer/CNT composites, including PS [57,61,67-71], PP [58], PMMA [59], PC [60], PA[72], PU [73], epoxy [74-76], poly(vinyl alcohol) [77], polyacrylonitrile [78] and UHMWPE/CNT [79]. It is also the dispersion method used for biological applications [80-84].

3.2 *In situ polymerization*

In situ polymerization is an efficient way to produce polymer/CNT composites. The CNT are dispersed in the monomer, either in the presence or in the absence of a solvent, and then the monomer is polymerized. Thermoplastic and thermoset composites have been produced by this way. It is however more common for the dispersion of CNT in thermosets. Here also, dispersing agents can be used to assist the dispersion. Functionalization can also be used to assist dispersion and to improve CNT/polymer adhesion. This method enables the production of composites with very-high CNT loadings.

In situ polymerization has been used to produce polymer/CNT composites, including epoxy [85-91], PS [92-96,97], PMMA [97,98], polypyrrole [99,100], PU [101] and poly(methyl methacrylate-co-n-butyl acrylate) [102].

3.3 *Melt blending*

For melt blending, the polymer is melted and mixed with CNT in a high-shear process. It is a common method for the elaboration of thermoplastics-based nanocomposites. Melt processing presents two main advantages. First, it uses the conventional polymer processing technologies; it can thus be adapted to most industrial set-ups already in place. Second, it does not use solvents and is therefore environmentally friendlier than the two previous methods.

Two ways can be used to introduce CNT inside the polymer matrix: the direct incorporation into the polymer matrix or the dilution by pure polymer of commercially available masterbatches of polymer/CNT composites [103,104]. The masterbatch can be produced by melt blending or in situ polymerization and is a highly concentrated material, in which the CNT are already percolated. Albeit the direct incorporation method offers more flexibility, masterbatch technology can be more convenient for small and medium size enterprises since existing equipment can be used without big changes.

Generally, twin-screw extruders operating in co-rotating mode are used to mix CNT and polymer. The co-rotating mode is preferred to the counter-rotating mode because of the higher dispersive mixing. Small conical twin-screws are very popular due to the small amount of material that is required and to the possibility to adjust the compounding time independent of shear rate, using a bypass allowing the material to circulate for defined periods.

The mechanisms controlling the dispersion of CNT in polymer matrices by melt blending are described by Kasaliwal et al. [27,105,106] for the dispersion in small laboratory compoundingers. The transformation of primary agglomerates into well-dispersed nanotubes is a combination of different processes running in parallel. During melt mixing, several stages occur: filler incorporation, wetting and infiltration by polymer melt, followed by dispersion, distribution, and flocculation (of filler in the polymer melt). During filler dispersion, the large initial filler agglomerates are reduced in size up to the smallest dispersible unit. Two mechanisms are responsible of the size reduction of agglomerates: rupture and erosion (Figure 9 and Figure 10). The rupture is a bulk mechanism occurring under the action of the shear forces present in the compounder. The large agglomerates are reduced in smaller ones in short times (Figure 9a). However, this mechanism may cause breakage of the dry agglomerates and therefore of the CNT (mainly on defect locations), thus reducing their aspect ratio. The erosion is a surface phenomenon (Figure 9a,b). The agglomerates are eroded into smaller ones by removing single or bundles of nanotubes from agglomerates surface. The erosion mechanism is slow but leads to infiltrated agglomerates and therefore may not lead to CNT breakage. For low mixing speed, the rupture and erosion have about the same extent. When increasing mixing speed, the impact of erosion decreases while the one of rupture increases. Rupture is therefore the dominant mechanism at high mixing speeds. Note that the same kinds of mechanisms have also been reported for other fillers such as carbon black, silica, calcium carbonate... [107-122]. It is also worth noting that the melt infiltration step must not be neglected since it plays an important role in lowering the size of the agglomerate both by erosion and

rupture mechanisms. The infiltration is faster at low melt viscosities and low molecular weights of the matrix.

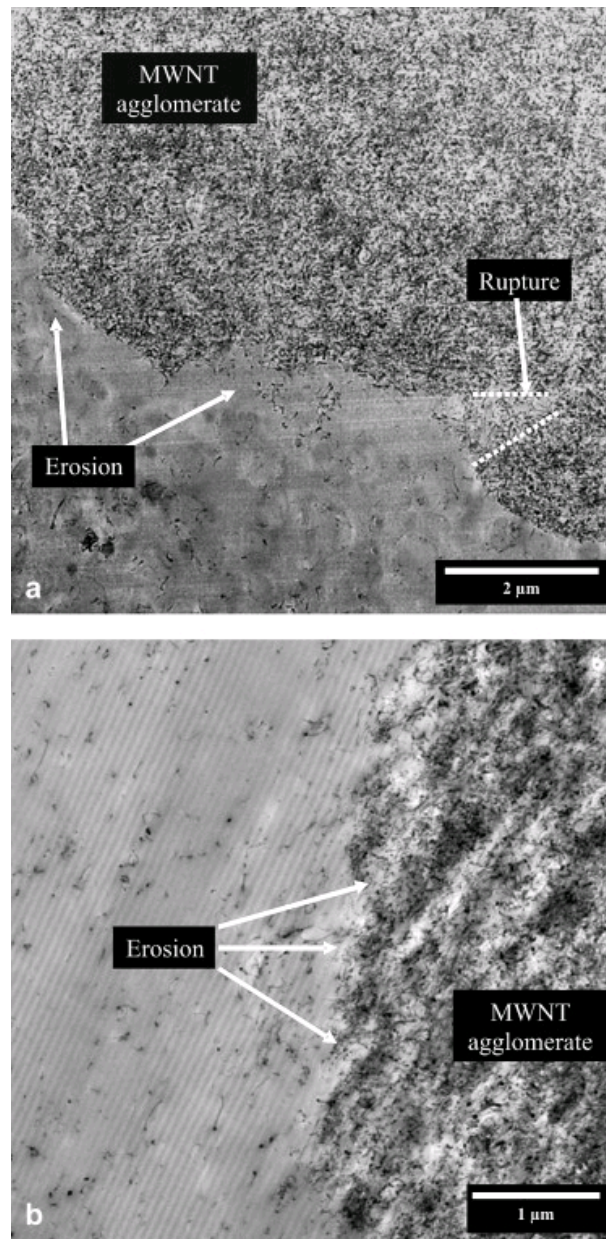


Figure 9 – Illustration of (a) rupture and erosion and (b) erosion of agglomerates (dotted lines in indicates region of crack propagation) [27].

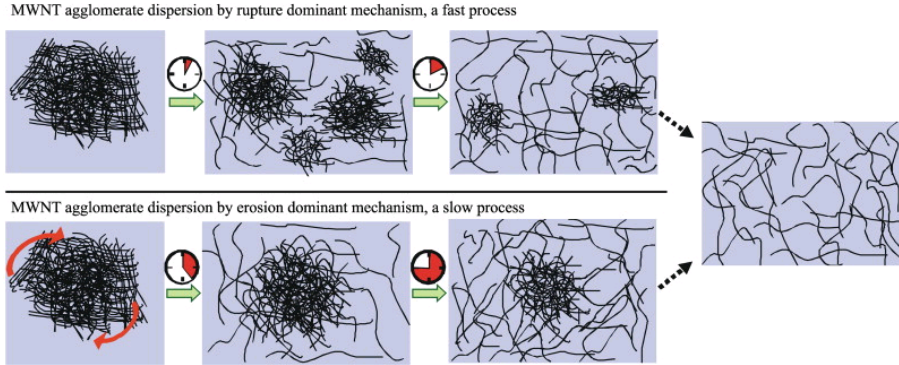


Figure 10 – Schematic descriptions of MWNT agglomerate dispersion mechanisms [27],

According to these dispersion mechanisms, the processing conditions must be optimized for the whole range of polymer/CNT combinations [123-126]. Pötschke and coworkers [105,106,127-129] have given a detailed study on the parameters influencing the dispersion of CNT in polymer matrix. They first showed that CNT are well dispersed in PC using a microcompounder. No segregation to the surface of the extruded strand and no preferred alignment are observed. Generally, the dispersion is improved by increasing the mixing energy, which is expressed as:

$$E = \int_0^t P dt = \int_0^t 2\pi \cdot N \cdot \tau dt$$

Where P is the engine output dependent of the time, N is the rotation speed in revolution per minutes (rpm), τ is the torque measured during mixing and t is the mixing time. A relation between the dispersion index or the circle equivalent diameter and the mixing energy is presented on Figure 11. The dispersion index, D , of CNT agglomerates in a polymer matrix is evaluated on light microscopy images. It is evaluated using the relation:

$$D = \left(1 - f \frac{A/A_0}{V} \right) \cdot 100\%$$

Where D is the dispersion index classified under macro dispersion, f is the factor describing the effective volume of the filler in agglomerate and was set to 0.25 for CNT [130], A/A_0 is the ratio of area of agglomerates (with size $>5 \mu\text{m}$) to the total area in %, and V is the filler volume in vol.-% (density of CNT assumed to be 1.75 g/cm^3). A complete dispersion without any agglomerates is characterized by a D value of 100%.

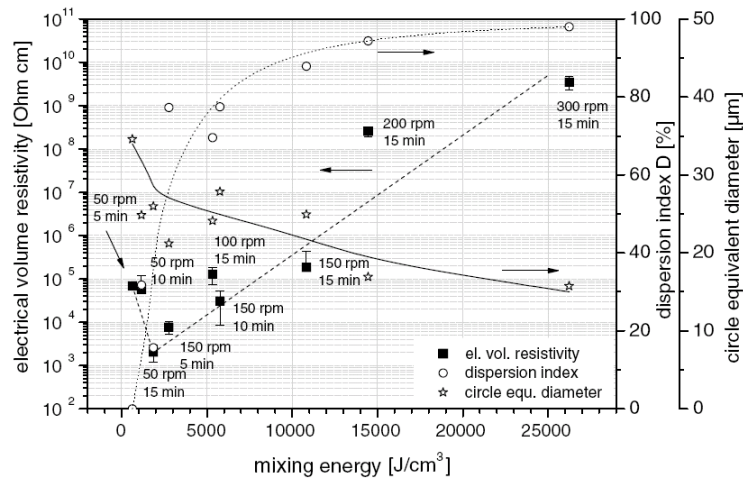


Figure 11 – Electrical volume resistivity, dispersion index D and mean agglomerate size (circle equivalent diameter) in dependence on mixing energy input for PA6 with 5wt.-% CNT at different mixing conditions (lines are guides for the eyes) [129]

Increasing mixing temperature leads to reduced polymer viscosity. The mobility of the polymer chains is therefore increased, leading to a better and faster wetting of the CNT within or at the surface of the CNT agglomerates. On the other hand it also leads to reduced shear stresses and thus to lowered rupture mechanism.

Increasing mixing time improves the quality of the dispersion. Indeed, a certain time is necessary for the diffusion of polymer chains between the CNT aggregates.

Increasing screw rotation speed leads to higher shear forces acting from the melt on the primary CNT aggregates. It therefore promotes the rupture of agglomerates. At low rotation speeds, the erosion process is favoured. Note also that increasing rotation speed lead to higher breakage of the CNT [131,132].

Finally, matrixes presenting lower molecular weight lead to better dispersion due to favoured infiltration in primary agglomerates.

Note that different miniature mixers are compared by Lin et al. [133] for the dispersion of CNT in PC using the masterbatch dilution method.

Some authors addressed the effect of processing conditions in industrial process such as twin-screw extrusion or injection molding [134- 138].

For extrusion, the influence of rotation speed, residence time, design of the screws and CNT loading on the dispersion of CNT in masterbatches is investigated. The most important parameter is found to be the screws rotation speed. Increasing the speed leads to improved dispersion up to a certain point, although it decreases the residence time. Indeed, above a certain speed, increasing the speed is not further efficient at disentangling primary CNT agglomerates and sometimes even deficient due to shorter residence times. Mixing sections, as opposed to kneading sections, improve dispersion. Finally, highly filled masterbatches present a lower number of big agglomerates while less filled masterbatches present a larger number of smaller aggregates.

For injection molding, the following parameters have been investigated: holding pressure, injection velocity, mold temperature and melt temperature. The highest impact is attributed to the injection velocity followed by the melt temperature and the interaction of both. A high injection velocity leads to a highly oriented skin layer, which is therefore electrically insulating. There is a decreasing orientation from skin to core region. At a certain distance from the walls of the mold, a percolated network is observed. High melt temperatures lead to low melt viscosity and high mobility of the CNT, therefore supporting the formation of the network.

Melt mixing has been used for the production of polymer/CNT composites, including polyethylene (PE) [139-141], poly(propylene) (PP) [142,143], poly(methyl methacrylate) (PMMA) [144], polyamide (PA) [145-148], polystyrene (PS) [69,143], acrylonitrile/butadiene/styrene (ABS) [143] and polycarbonate [149]. Note that melt blending is generally limited to MWNT, since in the case of SWNT, it seems to not be able to exfoliate completely the single tubes [150].

3.4 Other methods

Less classical methods for the preparation of polymer/CNT nanocomposites are described here.

3.4.1 Latex technology

A latex is a colloidal dispersion of discrete polymer particles, usually in an aqueous medium. Koning and coworkers [151-155] prepare composites by mixing an aqueous solution of CNT and sodium dodecylsulfate (SDS) with a polystyrene latex. The whole mixture is then freeze dried and then compression molded to produce nanocomposite films. The nanocomposites prepared by this way present well-dispersed CNT and good electrical conductivities.

Note that this technology is applicable to most of the polymers that can be produced by emulsion polymerization or be brought into the form of an emulsion. Moreover, it presents many advantages: it is an easy, reproducible, and reliable process allowing the dispersion of CNT in highly viscous matrices. Since the solvent used for the dispersion is water, the process is environmentally-friendly, safe and cheap. And finally, the polymer latex is now produced on an industrial scale. This method could therefore be applied to industrial production of polymer/CNT composites.

3.4.2 Other methods

Other methods are also used for the preparation of polymers/CNT nanocomposites. Among them, incorporation of CNT fibres, densification, coagulation spinning, electrospinning and layer-by-layer deposition are very briefly described here.

Windle and co-workers [156-159] have developed an alternative method to produce CNT-based materials with improved properties using CNT fibres. The CNT fibres are made by direct spinning from a CNT aerogel formed during synthesis by CVD. The fibres can be continuously withdrawn from the gas phase and wound on a reel. They are condensed by the stretching action of the draw, and by spraying with acetone, which immediately evaporates. They can then be wound up like cotton yarns. These fibres are next incorporated in polymer matrices in the same way that most fibrous materials.

During densification, the as-grown CNT forest can be directly transferred to a pool of uncured epoxy. The matrix penetrates inside the forest and is then cured. Epoxy/aligned CNT composites are thus produced [160].

Coagulation spinning can be used for the elaboration of polymer/CNT fibres. First, CNT are predispersed in water using a surfactant. This dispersion is then injected in a rotating bath of polymer dissolved in water, such that CNT and polymer dispersions flow in the same direction at the injection point. Polymer molecules replace the surfactants molecules on the CNT surface, causing the collapse of the dispersion into a fibre [161-163].

The electrospinning technique requires a dispersion of polymer and CNT. The dispersion is ejected out of a nozzle onto a metallic counter electrode when the solution becomes charged. Note that charging the solution causes rapid evaporation. This method is therefore used for the elaboration of fibres [164].

The layer-by-layer deposition allows the fabrication of nanocomposites by dipping alternatively a substrate into CNT dispersions and polyelectrolyte solutions, possibly followed by crosslinking to improve the structural integrity of the film [165-168]. The main advantages of this method are that the thickness, as well as the ratio of polymer and CNT can be controlled. Moreover, very high CNT contents can be achieved.

Other methods including pulverisation, swelling technique and buckypaper-based approach are described in literature [8,48,53,169].

4 Characterization of the dispersion state

The characterization of the dispersion state of CNT [170] in polymer matrices is perilous. Direct microscopic observations and indirect methods are used in literature.

Direct microscopic observation of the dispersion is difficult due to the high differences in the radial and axial dimensions of the nanotubes. Optical microscopy (OM) gives information about the presence of very big agglomerates but can not assess the submicron scale [68,143,171,172]. Scanning Electronic Microscopy (SEM) and Atomic Force Microscopy (AFM) show a cross section of the three-dimensional arrangement of the nanotubes. It is therefore difficult to observe an entire CNT or to distinguish several CNT [68,173,174]. Moreover, it is usually difficult to distinguish bundles from individualized CNT using SEM [175,176]. Transmission Electron Microscopy (TEM) on thin section allows the visualization of all CNT segments located within the thickness of the section. It remains however difficult to visualize the three-dimensional arrangement and the state of dispersion of the CNT. Visual observation of dispersions of CNT composites in a polymer solvent can help to distinguish the dispersion state [172]. Recently, a new tool has been developed to obtain volume information of multiphase objects with nanometer resolution: the tomography. While TEM tomography methods are only applicable to specimens with a maximum thickness of a few hundred nanometers, Scanning TEM (STEM) tomography allows a resolution down to a few nanometers for up to several micrometer ultrathick samples [177]. The 3D structure is reconstructed from tilt series acquired by tilting the sample and simultaneously correcting the image shift and focus changes. Moreover, the 3D electrical properties of polymer/CNT nanocomposites with nanometer resolution can be addressed using conductive atomic force microscopy (C-AFM) on bulk samples [178]. The principle is to combine a microtome with an atomic force microscope.

The bulk sample is sectioned by the diamond knife of the microtome and the remaining sample, which is electrically grounded, is subsequently investigated by C-AFM. The procedure of cutting and subsequent imaging is repeated several times and the data are reconstructed to achieve 3D information.

The CNT bundle fraction can be evaluated by UV absorbance band. This method has been firstly developed for solutions but it has been extended to polymers [179]. However, many polymers have significant absorption in the UV region and this method is thus generally not applicable.

Besides these direct characterization methods of the CNT dispersion state, indirect methods have also been developed. Electrical conductivity and melt rheology have been found to be powerful tools for the dispersion characterization [127,180-182]. Moreover, the characterization of the rheological properties offers a cost-effective alternative to microscopy to assess the dispersion of nanofillers in polymer matrices. The percolation threshold is the filler concentration, where the fillers exhibit a long-range connectivity. Lower rheological and electrical percolation thresholds are often associated to improved dispersion. However, for non-uniform microscale distribution, the percolation threshold is not related to the nanoscale distribution. In addition, the rheological percolation threshold involves both polymer chains and CNT [183,184]. Finally, low rheological or electrical percolation can indicate attractive interactions rather than excellent dispersion. The measurement of the modulus to evaluate the nanoscale dispersion has also been reported [185]. However, other parameters, such as CNT alignment, changes in crystallization or glass transition temperature, also affect the modulus.

Finally, the alignment and preferred orientation of the nanotubes can be examined using either Raman spectroscopy [171,186,187] or X-Ray diffraction [188].

5 Properties of nanocomposites

Due to their outstanding properties, CNT are expected to highly improve the properties of the material in which they are dispersed. Some of these properties are briefly exposed hereafter. The electrical properties of the polymer/CNT nanocomposites are not presented here. They are discussed in details in the last section of this chapter.

5.1 Mechanical properties

CNT present low density, high aspect ratio, high surface area and exceptional mechanical properties. They are therefore very attractive for the reinforcement of composite materials. Both SWNT and MWNT have been used to reinforce thermosets, such as epoxy, PU, phenol-formaldehyde resins and thermoplastics, such as PE, PP, PS, nylon... Several factors are important for a good reinforcement: the dispersion state, the aspect ratio, the alignment of CNT, the interfacial interactions between CNT and the matrix.

First, the CNT must be well dispersed to increase the surface area available for bonding with the matrix and to prevent agglomerates to act as stress concentrators [189]. The effect of the filler loading must also be taken into account. Up to a certain loading, the addition of CNT improves the mechanical properties. Above this threshold, due to hindered dispersion or to the lack of polymerization reactions, the mechanical properties decrease [190-193].

Second, the aspect ratio must be maximum to maximize the load transfer between the polymer matrix and the CNT [185,194-196].

Third, the alignment of CNT improves the mechanical properties (strength and modulus) in the alignment direction but it is detrimental to the properties in the perpendicular direction [197].

Finally, the functionalization of the CNT enhances both dispersion and interfacial adhesion between the matrix and the CNT [198-200] and therefore contributes to a better load transfer from matrix to CNT.

Spitalsky et al. [5] have presented a comprehensive collection of published data on the mechanical properties of polymer/CNT composites. For each polymer matrix, CNT type (SWNT, MWNT, pristine/oxidized/chemically modified), weight fraction, processing method and mechanical characteristics (tensile strength at break, elastic modulus and toughness) are specified. The authors put forward the positive effect of functionalization. They have noticed that the best reinforcement is observed for in situ polymerization method while low reinforcement is observed for the melt processed bulk composites. They have also observed that the reinforcement is much more effective for ductile matrices. For brittle polymers the CNT filler does not seem to improve considerably the mechanical properties of the matrix.

5.2 Rheological properties

The study of the rheological properties is important both from a processing point of view and for the determination of the nanocomposites microstructure.

Several factors influence the rheological properties: filler loading, aspect ratio, dispersion, polymer matrix molecular weight, interfacial interaction between polymer and filler [201- 204].

The evolution of the dynamic modulus and viscosity are often used to characterize the rheological properties of the nanocomposites [104,183]. At low frequencies, pure polymer exhibits a typical Newtonian viscosity plateau and then the viscosity decreases with increasing frequency. When CNT are added, there is a significant increase of the viscosity at low frequency (Figure 12). This indicates that the relaxation of the polymer chains is hindered by the presence of CNT. The modulus is also changing with the addition of CNT. When increasing CNT content, the modulus gradually increases. This effect is more marked for the storage modulus than for the loss modulus (Figure 13). The increase indicates the transition from a viscous liquid to a solid-like behavior at a concentration known as the rheological percolation threshold.

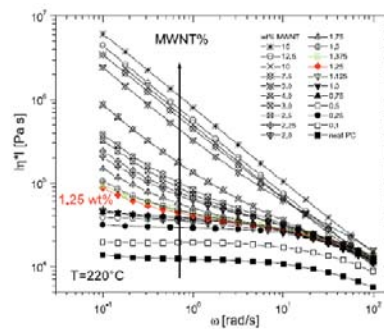


Figure 12 – Complex viscosity versus frequency for different CNT loading [183]

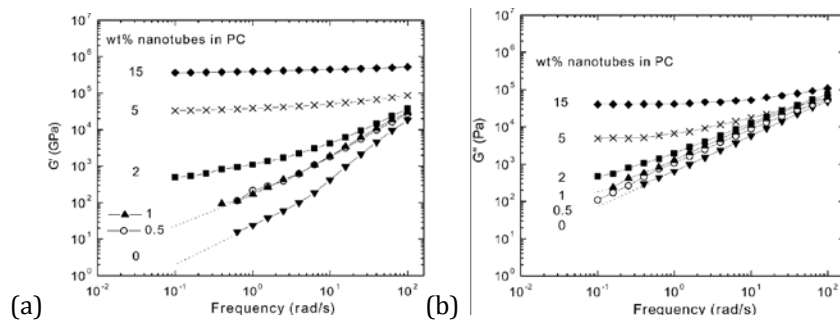


Figure 13 – (a) Storage and (b) Loss moduli versus frequency for different CNT loading [104]

Gelation theory developed by Winter and Chambon [205-208] has been extensively used to determine the percolation threshold of polymer/CNT nanocomposites [209]. According to this theory, critical gels exhibit a simple relaxation behaviour. The shear modulus is thus described by a power-law equation:

$$G(t) = S_g t^{-n}$$

where S_g is the gel strength and n is the relaxation exponent, both characterizing the critical gel. The storage and loss moduli, G' and G'' , of a critical gel also obey a scaling law with the same relaxation exponent, n . In the vicinity of the gel point, the loss tangent is thus independent of the frequency:

$$\tan \delta = \frac{G''(\omega)}{G'(\omega)} = \tan\left(\frac{n\pi}{2}\right)$$

Figure 14 displays $\tan \delta$ versus nanotube concentration for a multifrequency experiment. The cross point in this plot results of the gelation concentration, also defined as gel point, at which, $\tan \delta$ is frequency independent. This point corresponds to the rheological percolation threshold.

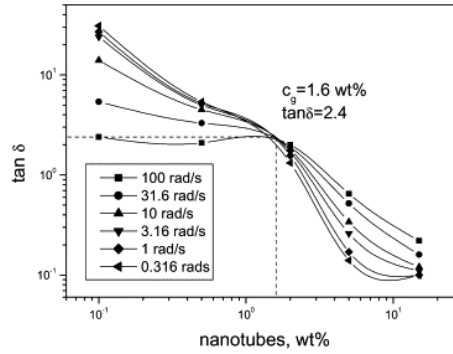


Figure 14 – The loss tangent ($\tan \delta$) as a function of nanotubes concentration for the CNT/PC composites [209]

Two factors can be responsible for the gelation behaviour: the presence of a CNT network and the interactions between polymer chains and CNT. The rheological percolation threshold of CNT/polymer nanocomposites is strongly dependent on temperature (Figure 15). Indeed, the mobility of the networks formed by polymer chains and CNT-polymer interactions can be significantly enhanced at elevated temperature [183]. Since the polymer chains contribute much to the rheological response of nanocomposites, it is easy to understand that the content of CNT required to form a rheological percolation threshold

should be much lower than that for electrical percolation. The rheological percolation threshold is thus not representative of the formation of a CNT network.

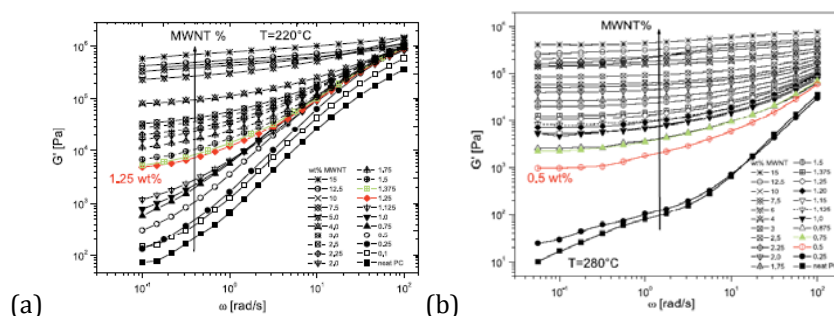


Figure 15 – Storage modulus, G' , versus frequency for different CNT loadings (a) at 220°C; (b) at 270°C [183]

5.3 Thermal properties

Most of the studies show that the thermal conductivity owing to the addition of CNT in polymer matrix is almost not increased [125,210].

The addition of CNT can modify the thermal stability of the composites. The main parameters influencing the changes of glass transition temperature, melting and thermal decomposition temperatures are CNT type, aspect ratio, dispersion, interfacial interactions with the polymer matrix...

Moreover, CNT have been shown to be very effective flame-retardants additives if they form a jammed network structure in the matrix. Indeed, the CNT network shields the neat polymer from the heat and the enhanced thermal stability inhibits the formation of cracks or openings during burning [211-213]. Functionalized CNT are expected to further improve the flammability of the composites, owing to enhanced dispersion and improved thermal stability of the nanocomposites.

5.4 Optical properties

The optical properties of polymer/CNT composites are optical non-linearity, photoluminescence, light emission and photonic devices. These properties are described in a few literature reviews [4,8] and are not developed here.

5.5 Damping properties

The damping properties of a material describe its ability of attenuate the amplitude of oscillation in an oscillatory system. For polymer/CNT nanocomposites, high damping properties can be achieved when the interfacial friction between matrix and CNT is high. The dissipation of the energy is favored when frictional sliding occurs at the nanoscale and thus for good CNT dispersion and weak interfacial adhesion [214,215].

ELECTRICAL PROPERTIES OF NANOCOMPOSITES BASED ON CNT

1 Introduction

The addition of conductive fillers in polymers leads to a high number of typical applications of conducting composites (Figure 16A) [8]. The incorporation of CNT in polymer matrices allows the production of relatively inexpensive materials, which can thus lead to many applications [53,216], such as antistatic coatings, conductive films and adhesive, electromagnetic interference shielding materials... Percolation theory explains the conducting behaviour observed when dispersing conductive fillers in insulating matrices. It defines a critical filler content, the percolation threshold, where the electrical conductivity jumps over several order of magnitudes due to the formation of a conducting network (Figure 16B) [217-219].

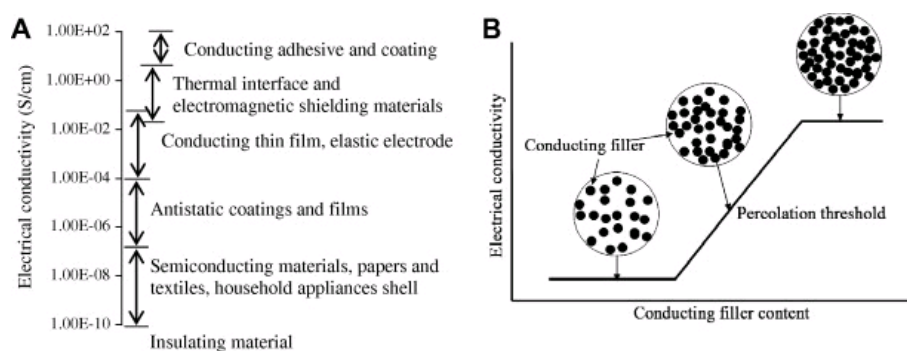


Figure 16 – Typical applications of conductive composites (A) and a schematic of percolation phenomenon and conducting network in conducting composites (B) reproduced from [8]

The critical factors determining the percolation threshold are: the intrinsic conductivity and the aspect ratio of the CNT; the disentanglement of the CNT agglomerates; and the uniform distribution of CNT and agglomerates.

In this section, the conducting behaviour of composites with fibrous conductive fillers is first explained based on the filler content, through the electrical percolation model. The different parameters influencing conductivity are next exposed. Finally, annealing in the absence or in the presence of shear significantly modifies conductivity. The influence of secondary agglomeration on the electrical conductivity and a model for the conductivity recovery are thus exposed.

2 Application of the percolation theory to the electrical conductivity

The conductivity is a direct application of the percolation theory [220-222]. Figure 17 presents different contents of CNT in PS [223]. When no CNT is present in the composite (Figure 17a), the measured conductivity is the conductivity of the polymer matrix. When a low quantity of CNT is added to the composite, the fillers are isolated. Thus only a very low increase of the conductivity is observed. The total conductivity is dominated by the one of pure polymer (Figure 17b). When increasing the amount of conductive fillers, the particles are closer and closer and for a certain amount, a three-dimensional conductive network of the filler inside the matrix is formed and the conductivity increases drastically (Figure 17c). This critical filler amount is known as the percolation threshold (ϕ_c or p_c). Above this critical content, the conductivity still increases slightly.

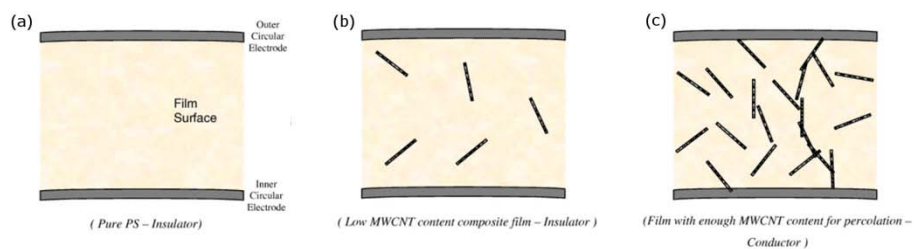


Figure 17 – Cartoon representation of the electrical percolation for: (a) pure PS film, (b) low CNT content composite film, and (c) composite film with high enough CNT content to pass the electrical percolation threshold; adapted from [223]

The percolation threshold can be determined using a power law of the form:

$$\sigma_{DC} = \sigma_0 (\phi - \phi_c)^t \quad \text{for } \phi > \phi_c$$

This law gives the DC conductivity (σ_{DC}) near the percolation threshold for a volume fraction of fillers (ϕ) higher than volume fraction of fillers corresponding to the percolation threshold (ϕ_c). σ_0 is a fitted constant that should correspond to the DC conductivity of the CNT. The critical exponent (t) depends on the system dimensionality and, according to theoretical predictions, is expected to vary between 1.6 and 2 for a 3D percolation of conducting spherical particles in an insulating matrix [224]. However, experimentally, values of t ranging from 1.2 to 7.6 are reported [225- 229]. However, the values are mainly in the range 1.3 to 4 with a peak around 2. Note that the geometrical information can usually not be extracted from the values of t because scaling is generally limited to a concentration range very close to ϕ_c and the model is based on the assumptions that the fillers are identical and homogeneously dispersed in the polymer matrix.

Note that the power law can also be expressed in function of the mass fractions:

$$\sigma \propto (m - m_c)^\beta \quad \text{for } m > m_c$$

Where m is the mass fraction of conducting particles, m_c is the electrical percolation threshold and β is the critical exponent.

Many research groups show that this relation is in agreement with the experimental data. For example, Du et al. [230] use it for PMMA/SWNT nanocomposites (Figure 18). The straight line observed is in agreement with the experimental results, giving a percolation threshold of 0.39wt.-%. By applying non linear curve fitting of the experimental results, the fitting parameters (σ_0 , m_c , t) are obtained.

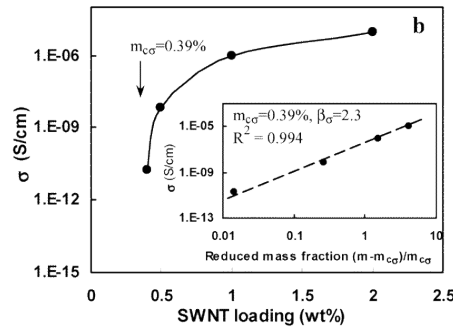


Figure 18 – Electrical conductivity of the SWNT/PMMA nanocomposites as a function of the nanotube loading. Inset: a log–log plot of electrical conductivity vs reduced mass fraction. Note that β_σ is significantly larger than β_C due to the larger magnitude of the change in σ at the threshold. Reproduced from [230]

On the other hand, Pötschke et al. [183] show that for compositions markedly above the percolation threshold, the conductivity of the composite is lower than the intrinsic conductivity of CNT. CNT are not exactly in contact with each other but the distance between them is so small that charge transfer by hopping or tunneling occurs [227,231].

Bauhofer and Kovacs [232] have published a comprehensive collection of published data concerning the percolation thresholds of different polymer matrices. Spitalsky et al. [5] present a comparison of the different polymeric matrices in terms of electrical properties. For each matrix, the CNT type and additional treatment (purification/functionalization), processing method and electrical characteristics such as room temperature maximum conductivity, percolation threshold and critical exponent are presented. However, the authors state that correlations between these parameters are difficult to establish.

Note finally that immiscible polymer blends can be used to decrease the electrical percolation threshold by selectively dispersing the CNT in the continuous phase of the blend or at the interface of a co-continuous blend [149,233–236]. This phenomenon is known as “double percolation”. The conducting fillers form a percolating conductive network in a polymer phase, which itself percolates through the blend. This continuous phase can either be the matrix of a sea-island blend or one the phases of a co-continuous blend. The confinement of the conductive fillers increases their concentration and thus decreases the electrical percolation threshold. A special case is observed when the particles are localized at the interface of the co-continuous blend. This is called triple percolation. This concept is developed in Chapter 5.

3 Factors influencing the percolation threshold and the electrical conductivity

Depending on the polymer matrix used, different percolation thresholds at different volume fractions of fillers are observed. The physical-chemistry of the system has an effect on the CNT dispersion. Different results are also observed for the same matrix, indicating that the processes involved in the synthesis of CNT/polymer nanocomposites are crucial. These processes can act on the aspect ratio of the fillers, their dispersion and their alignment. The influence of these parameters on the electrical conductivity is briefly described here after.

3.1 Geometry of the filler

The geometry of the filler or its aspect ratio (ratio between the length and the diameter of the CNT) strongly influences the percolation threshold. The percolation threshold decreases strongly when increasing filler anisotropy [237,238]. Balberg et al. [239] propose a relation to link the percolation threshold with the aspect ratio of isotropic particles. Considering CNT as randomly dispersed long rigid sticks of length L and radius r , the authors propose the following relation:

$$\left(\frac{L}{r}\right)\phi_c = 3$$

According to this relation, the percolation threshold is inversely proportional to the aspect ratio ($L/2r$) of the CNT.

Because of the very large aspect ratio of CNT, electrical percolation as low as 0.005 vol.-% or 0.002 vol.-% CNT have been achieved with respectively SWNT [237] or MWNT [225]. These thresholds are far lower than the thresholds obtained for carbon black, graphite or carbon fibers. Yang et al. [240] compare the conductivities of PS filled with 5 wt.-% of different nanofillers: Ag-nanoparticles (Ag-NP), graphite, carbon nanofiber (CNF) and CNT. The highest electrical conductivity is obtained for PS+CNT, followed by PS+CNF, then PS+Ag-NP and finally PS+graphite. The aspect ratios of the different particles are exposed in

Table 2.

Table 2 – Geometrical characteristics of the different conductive fillers

Filler	L (μm)	D (nm)	Aspect ratio (-)
Ag-NP	0.03 – 0.05	30 – 50	1
Graphite	0.45	450	1
CNF	30 – 100	100 – 200	150 – 1000
CNT	5 – 20	10 – 20	250 – 2000

Note finally that the CNT waviness also influences the percolation threshold. Monte Carlo simulations indicate that the electrical conductivity of composites with wavy CNT is much lower than that of composites with straight CNT ^[241]. The advantages of wavy CNT is that they break less easily. Their mobility is also higher. It is also better for the formation of secondary agglomerates. The disadvantage however is that the electrical conductivity is lower. Moreover, they are less able to bridge polymer droplets in immiscible blends because they tend to wrap the droplets.

3.2 Dispersion state

CNT are usually synthesized in the form of bundles. When dispersing CNT in polymer matrices, agglomerates remain. The effect of the bundles on the percolation is calculated by Grujicic et al. ^[242], who show that increasing bundles radius leads to increased electrical percolation thresholds. Indeed, well dispersed CNT present higher aspect ratios than agglomerates and thus lower percolation thresholds. This is coherent with the traditional thoughts that electrical conductivity increases when improving the CNT dispersion ^[53,229].

However, it is important to note that, on the contrary to common expectations, a good dispersion is not always correlated with good electrical properties. Figure 11 shows an increased electrical volume resistivity when the dispersion index increases for PA based nanocomposites ^[129]. Other authors ^[229,237,243] also show improved electrical properties for slight CNT aggregation due to the increased local interactions between the CNT. Moreover, Zang et al. ^[244,245] show that the interfacial energy influences the formation of a conductive path inside the polymer matrix. A low interfacial energy favours wetting of the CNT by the polymers and the CNT dispersion. Gojny et al. ^[246] show that stable dispersion of CNT in epoxy is detrimental to the conductivity because the epoxy forms an insulating layer around the CNT.

Functionalization can be used to facilitate dispersion and formation of conductive networks. However, covalent functionalization introduces a high

amount of defects in the structure and therefore perturbations of the π electrons and thus of the electrical properties of the CNT. The use of concentrated acids leads to breakage of CNT and reduces the aspect ratio. Non-covalent functionalization therefore represents an interesting alternative. Bose et al. [247] have developed a Na salt of 6-amino hexanoic acid (Na-AHA), which presents Na^+ functions that interact with the π electrons of the CNT and amine groups, which react with the carboxylic groups of the PA end chains. This functionalization leads to a significant decrease of the electrical threshold.

3.3 Alignment

The alignment of CNT in the polymer matrix significantly modifies the percolation threshold (Figure 19). When CNT are highly aligned in the polymer, there are fewer contacts between them and there is therefore an increase of the percolation threshold and a decrease of the electrical conductivity, compared to an identical composite with isotropically dispersed CNT. This subject has been widely studied by Du et al. [248] for CNT dispersed in PMMA. For highly oriented CNT, the conductivity of the composite filled with 2wt.-% CNT is low. When the degree of orientation decreases slightly, there is a sharp increase of the conductivity. The authors also highlight that, for an intermediate level of CNT alignment, the electrical properties are higher than for isotropic conditions.

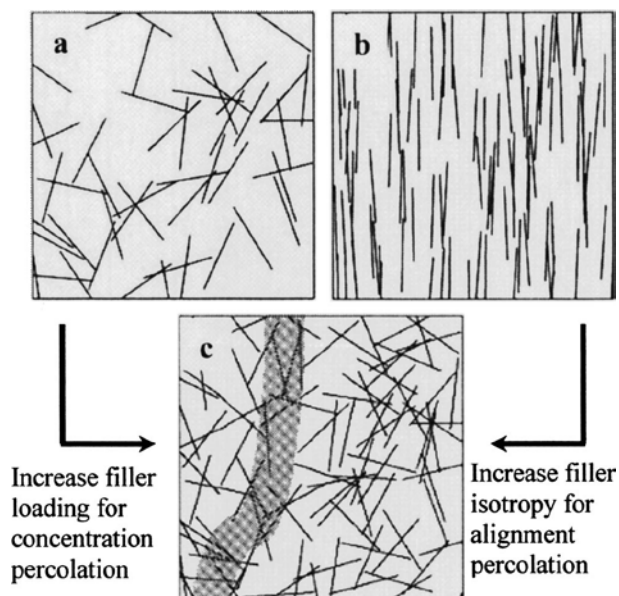


Figure 19 - 2D stick-in-unit-square simulations with stick alignment (a) 50 sticks randomly distributed; (b) 100 sticks highly aligned; (d) 100 sticks randomly distributed. Reproduced from [248]

4 Secondary agglomeration

4.1 Principle

Kasaliwal et al. [105] and Pegel et al. [249] have observed changes in resistivity measurements during compression molding at different conditions (Figure 20). According to the corresponding morphology, the increase of the conductivity can be assigned to a rearrangement in the CNT network at the nanoscale. The formation of these secondary agglomerates of initially well-dispersed CNT during processing enhances the electrical conductivity. This observation confirms that the best dispersion states do not lead automatically to the best electrical conductivity.

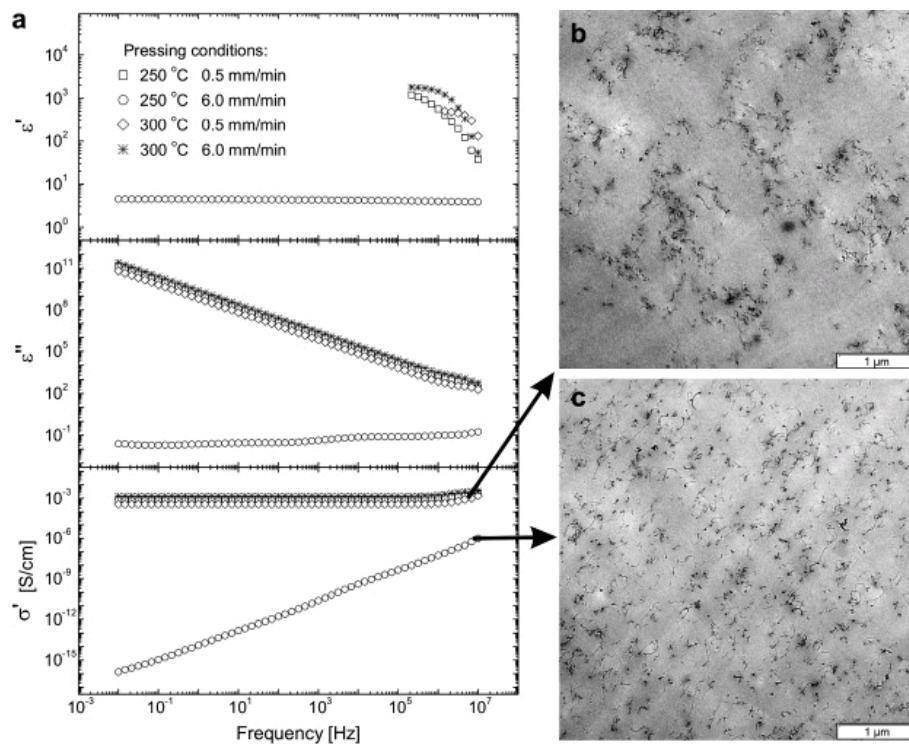


Figure 20 – (a) Frequency dependence of the real (ϵ') and imaginary part (ϵ'') of the complex permittivity and the related AC conductivity (σ') for plates pressed at different temperatures and speeds (PC + 0.875 wt%, obtained by masterbatch dilution); (b,c) TEM micrographs of the samples pressed at 300 °C, 6.0 mm/min, illustrating loosely packed agglomerates (b) and 250 °C, 6.0 mm/min, illustrating individualized nanotubes (c). Reproduced from [249]

This reorganization is known as the secondary agglomeration. Indeed, the initial or primary CNT agglomerates are first dispersed in the polymer matrix and these well-dispersed CNT agglomerate at high temperature to form secondary agglomerates. Alig and coworkers [249-253] have studied the destruction and reformation of these conductive CNT networks during thermal annealing and after well defined shear deformation. The authors observe a tremendous increase of conductivity of the composites during isothermal quiescent annealing in the absence of shear. This increase is attributed to the agglomeration of CNT and to the formation of a conductive network of interconnected agglomerates. This is highlighted in Figure 21, which presents TEM micrographs of PC+0.6 vol.-% CNT. Figure 21a presents the morphology obtained after compression moulding of the composite at 265°C: the CNT are homogeneously distributed into the polymer. When increasing the compression moulding temperature, agglomeration of the CNT occurs (Figure 21b,c). When shear is applied on the re-agglomerated samples, the conductivity decreases sharply. Then during a second annealing, the conductivity recovers due to the re-agglomeration of the broken network parts (Figure 22). As the migration is observed in the absence of shear, it is only caused by Brownian motion and the driving force for the migration is the Van der Waals interactions.

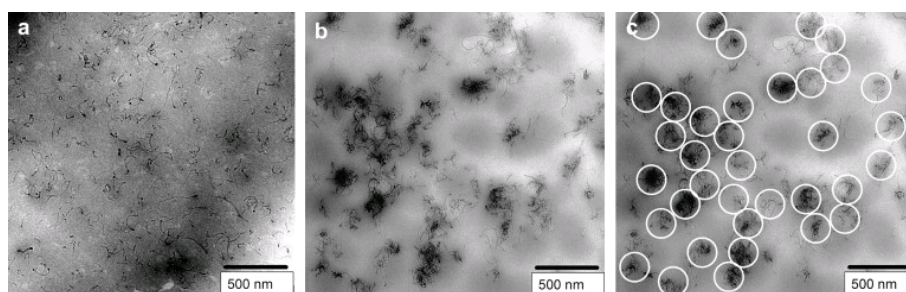


Figure 21 - Transmission electron micrographs from PC-MWNT plates with 0.6 vol% MWNT: (a) non-conductive state ($\sigma_{DC} < 10^{-16}$ S/cm) with well-dispersed nanotubes, pressed at 265 °C and (b,c) conductive state ($\sigma_{DC} = 5 \times 10^{-4}$ S/cm) with nanotube agglomerates pressed at 300 °C [251]

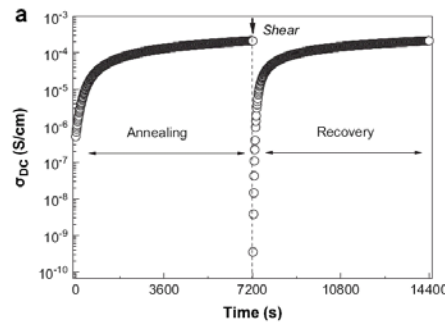


Figure 22 – DC conductivity σ_{DC} during annealing ($T=230^{\circ}\text{C}$), transient shear deformation and isothermal conductivity recovery after shear at 230°C . Adapted from [251].

The authors show that the secondary agglomeration process is a time-temperature-dependant process. It is faster for increasing melt temperature due to lowered viscosity of the melt and thus increased mobility of the CNT. It is also faster for samples with higher CNT concentration due to the lower particle-to-particle distance.

Skipa et al. [252,253] extend the study of secondary agglomeration to systems in the presence of shear. They bring to light the competition between build-up and destruction of the percolating network under steady shear. They show that the conductivity increase after steady shear pulse is much faster than for quiescent melt. This indicates that CNT agglomeration is a shear-induced phenomenon. They also show that a short duration of shear is sufficient to initiate the growth of CNT agglomerates. Moreover, the conductivity levels obtained by shear-induced agglomeration are much higher than the levels obtained for quiescent agglomeration of CNT, even for very long measuring times (>10h). However, for samples presenting a “well agglomerated” state, which means that there is a percolating network of agglomerates inside the sample, applying a shear leads to a decrease of the conductivity. Indeed, in this latter case, no further improvement of the network can be expected from applying shear, the destructive effect of the shear is therefore dominant. The authors also study simultaneously the DC electrical and rheological properties. The formation of the CNT network leads to an increase of the electrical properties but to a decrease of the mechanical reinforcement. This is linked to the different mechanisms involved in the obtention of these properties. High DC electrical properties requires charge transport via electron tunnelling at CNT contacts. Very small interparticle distances can only be achieved for densely packed CNT in agglomerates. On the other hand, an efficient mechanical

reinforcement requires well dispersed CNT and strong interfacial interactions of CNT with the matrix.

Finally, it is worth noting that the time needed for the reformation of the filler network and recovery of the conductivity is from about 10 min to several hours and considerably exceeds the usual processing times for injection moulding (below 60s) or extrusion (below 10min).

4.2 Modelling of conductivity recovery

The electrical recovery is first examined in the absence of steady-shear (quiescent agglomeration). Then the kinetic equation is extended to the presence of a steady shear flow.

4.2.1 Quiescent agglomeration

Based on the electrical conductivity recovery observed when annealing the sample, a model is introduced based on the following experimental findings:

- The systems with well dispersed CNT exhibit low conductivity
- The electrical conductivity increases during the annealing process
- Annealing leads to the formation of agglomerates
- Samples containing many agglomerates are more conductive than similar samples with good CNT dispersion

The classical percolation theory can not be directly applied to explain the evolution of the conductivity because the content of CNT is not changing with time. The time dependence of the conductivity is a “dynamic percolation”. For modelling the recovery behaviour in the melt, Alig and coworkers [250-253] therefore propose a model combining classical percolation theory with cluster aggregation. The percolation theory applies for individual homogeneously distributed filler particles. Moreover, the agglomeration is observed to be a time-dependent phenomenon. A time dependant agglomerate concentration is therefore introduced. The agglomerates are assumed to be conductive, which means that the CNT constituting the agglomerates are in close contact to allow electron tunnelling.

The classical theory of the electrical percolation gives the following expressions above or below the percolation threshold, p_c :

$$\sigma_{DC} = \sigma_{0A} \left(\frac{p_A - p_c}{1 - p_c} \right)^t \quad \text{for } p > p_c$$

$$\sigma_{DC} = \sigma_{0M} \left(\frac{p_c - p_A}{p_c} \right)^{-s} \quad \text{for } p < p_c$$

Where p_A is the volume concentration of the conductive agglomerates A contributing to the percolation network (time dependent), σ_{0A} is the conductivity of the CNT agglomerates, σ_{0M} is the conductivity of the polymer matrix, $t = 2$ is usually taken for 3-D systems [220-222,254- 258] and $s = 0.73$ is taken from literature [222,259- 261] to fit the datas.

Other percolation models have been tested to model the experimental results: the general effective medium theory (GEM) and a modified Fournier equation. The GEM is expressed as:

$$(1 - p_A) \frac{\sigma_{0M}^{1/s} - \sigma_{DC}^{1/s}}{\sigma_{0M}^{1/s} + Z \sigma_{DC}^{1/s}} + p_A \frac{\sigma_{0A}^{1/t} - \sigma_{DC}^{1/t}}{\sigma_{0A}^{1/t} + Z \sigma_{DC}^{1/t}} = 0$$

Where $Z = \frac{(1 - p_c)}{p_c}$

The modified Fournier equation [262] is based on Fermi-Dirac distribution, which describes the critical insulator to conductor transition and is expressed as:

$$\log(\sigma) = \log(\sigma_M) + (\log(\sigma_A) - \log(\sigma_M)) \frac{f(p_A(t)) - f(p_{A0})}{f(p_{A\infty}) - f(p_{A0})}$$

where $f(p_A(t)) = \frac{1}{1 + \exp(b(p_A(t) - p_c))}$, where b is an empirical

parameter, directing the change in conductance across the percolation threshold.

The elaboration of the conductive network is considered as an agglomeration process. At a certain time, two particles T, which were not contributing to the total conductivity, interact and create a sphere-like agglomerate A contributing to the percolation network. The particles T can be either single CNT or small CNT bundles or small CNT aggregates. The time-dependences of the cluster size and distribution are usually given by solving the Smoluchowski equation [263]. A second order kinetic equation (collision of two particles) is used to

describe the agglomeration ^[264] as proposed by Heinrich et al. ^[265] for the formation of an infinite filler network in elastomers:

$$\frac{dN_A}{dt} = kN_T^2$$

Where N_T and N_A are the numbers of particles T and A, respectively, per unit volume (number density), and k is the reaction rate constant. Note that the second order kinetics is a vastly oversimplified assumption. Indeed, the agglomeration of CNT and CNT aggregates is a hierarchical process on several length scales since CNT, aggregates and agglomerates of different sizes interact.

Considering the agglomeration of two particles T, the following boundary condition has to be fulfilled:

$$N_T(t) = N_{T0} - 2(N_A(t) - N_{A0})$$

Where N_{A0} and N_{T0} are the initial number densities of A and T respectively.

Solving the kinetic equation with this conditions gives the number density of agglomerates as a function of time:

$$N_A(t) = N_{A0} + \frac{N_{T0}}{2} \left(1 - \frac{1}{2ktN_{T0}} \right)$$

A similar equation in terms of volume concentrations of agglomerates A can be written assuming that V_T and V_A are the effective volumes occupied by a particle T or a spherical agglomerate A respectively. The volume concentrations are therefore $p_A(t) = V_A N_A(t)$ and $p_T(t) = V_T N_T(t)$. The volume concentration of the conductive agglomerates is then written as:

$$p_A(t) = p_{A0} + (p_{A\infty} - p_{A0}) \left(1 - \frac{1}{1 + 4k't(p_{A\infty} - p_{A0})} \right)$$

Where, p_{A0} and $p_{A\infty}$ are the starting ($t = 0$) and final ($t \rightarrow \infty$) volume concentration of the agglomerates, and k' is the modified reaction rate constant ($k' = k/V_A$). $p_{A\infty}$ can be evaluated as the ratio of the total volume concentration of CNT in the sample, p_{CNT} and the volume concentration of CNT inside an agglomerate $p_{CNT,Agglom}$: $p_{A\infty} = p_{CNT} / p_{CNT,Agglom}$. This expression of the

time-dependent volume concentration of agglomerate can be inserted in the percolations law here above to describe the electrical conductivity of a system formed of an increasing volume concentration of agglomerates.

The model is in good agreement with the experimental data. It is worth noting that the percolation concentrations of agglomerates calculated using this model is comparable to that of spherical particles (>10%). The volume occupied by the clusters must therefore contain a high number of polymer chains.

Note also that a first increase of the conductivity is sometimes observed in the first 5 minutes which then flattens off when the electrical characterization is performed during melt processing. This may be interpreted as a reorientation of individual CNT aligned in shear flow, leading to the formation of a weak conductive network of homogeneously dispersed CNT (first process). The CNT agglomeration starts simultaneously (second process). An empirical relaxation function can be used to fit the experimental datas of the first process:

$$\sigma = (\sigma_{1,\infty} - \sigma_{1,0}) \left[1 - \exp\left(-\left(t / \tau_1\right)^\beta\right) \right] + \sigma_{1,0}$$

Where $\sigma_{1,\infty}$, $\sigma_{1,0}$, τ_1 and β are empirical parameters.

Note finally that an alternative to the cluster agglomeration process described here would be to consider a spinodal decomposition into a CNT-rich phase and a CNT-poor phase.

4.2.2 Combined model including shear-induced networking

Skipa et al. [252,253] have extended the equations developed for quiescent agglomeration to the shear induced networking. The quiescent agglomeration process is expressed by the solution of a kinetic equation as:

$$\frac{dp_A}{dt} = k_0 (p_{A\infty} - p_{A0})^n$$

Where n is the order of the equation, and are the starting ($t = 0$) and final ($t \rightarrow \infty$) volume concentration of the agglomerates and k_0 is the kinetics constant for quiescent agglomeration. For the quiescent agglomeration, the data analysis shows no significant difference between an order 1 or an order 2 kinetic. For simplicity, a first order kinetic ($n = 1$) is thus considered in the following. Second order kinetics prevails when particles are homogeneously distributed in the matrix. Otherwise, the kinetics can follow the first order

governed by the diffusion of isolated small aggregates towards immobilized large aggregates [250].

In the presence of a steady-shear flow, the description of the agglomeration is extended. Two shear dependent terms representing shear build-up and shear breakdown of the agglomerates are added:

$$\frac{dp_A}{dt} = k_0 (p_{A\infty} - p_{A0}) + k_1(\dot{\gamma})(p_{A\infty} - p_{A0}) - k_2(\dot{\gamma}) p_A$$

Where $k_1(\dot{\gamma})$ and $k_2(\dot{\gamma})$ are the kinetic coefficients for shear build up and shear breakdown, respectively, of the agglomerates. The equation can be re-written as:

$$\frac{dp_A}{dt} = k(\dot{\gamma})(p_{A\infty} - p_{A0}) - k_2(\dot{\gamma}) p_A$$

Where $k(\dot{\gamma}) = k_0 + k_1(\dot{\gamma})$.

The solution of this equation can then be used in the equations for insulator-conductor transition (classical percolation, GEM or modified Fournier expressions). The solution $p_A(t)$ of the differential equation is either an exponential decay or an exponential growth function. It can thus not describe the local minimum in conductivity observed when a shear pulse is applied after an annealing period. There are two ways to describe the shape of those curves.

First a second order differential equation $\frac{d^2 p_A}{dt^2} = f(p_A, \dot{\gamma}, p_{A\infty})$ can be used for

the agglomeration kinetics. However, it is inappropriate in the present case. Second, multiple first order differential equations

$\frac{dp_A}{dt} = k(\dot{\gamma})(p_{A\infty} - p_{A0}) - k_2(\dot{\gamma}) p_A$ can be used assuming different species

participating in the agglomeration process. This case is considered here. The system involved in the network formation can be approximated by a three components system composed of:

- Large agglomerates, A
- Small agglomerates, S
- Individual CNT, T

The percolation conductive network is formed by the large and small conductive agglomerates. It is assumed that individual CNT do not contribute to the conductivity. The system can thus be described as a system of two differential equations:

$$\frac{dw_A}{dt} = -aw_A + bw_S + cw_T$$

$$\frac{dw_S}{dt} = -dw_S + fw_T + gw_A$$

Where w_A , w_S and w_T are the total weight fractions of CNT inside the large agglomerates, the small agglomerates and the individual CNT. The large agglomerates A disappear due to the shear-induced destruction (term: $-aw_A$) and appear due to shear-induced agglomeration of small agglomerates (term: $+bw_S$) and of individual CNT (term: $+cw_T$). By analogy, the small agglomerates disappear due to shear destruction (term: $-dw_S$) and appear due to shear-induced agglomeration of CNT (term: $+fw_T$) and destruction of large agglomerates (term: $+gw_A$). The coefficients a , b , c , d , e , f and g describe both quiescent and shear-induced agglomeration and destruction. They depend on the shear rate, composite history, temperature, polymer viscosity...

The following normalization condition must be applied:

$$w_A(t) + w_S(t) + w_T(t) = w_{CNT}$$

Where w_{CNT} is the total weight fraction of CNT in the composite.

For PC/CNT blends, the kinetic constant k_0 for quiescent agglomeration of well dispersed individual CNT is almost two orders of magnitude smaller than the kinetic constants for shear-induced agglomeration (k_1 and k_2). The agglomeration is thus accelerated by applying shear to well dispersed CNT (Figure 23).

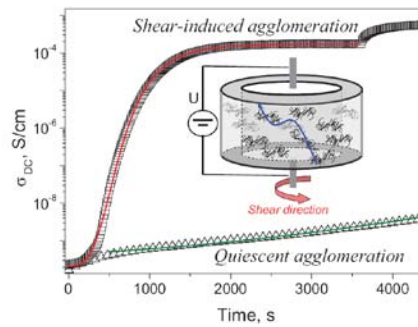


Figure 23 – DC-conductivity of PC/CNT melts measured during 3600 s of steady shear (upper curve) and 4500 s of quiescent annealing (lower curve). The solid lines represent the fits. The inset schematically shows the measuring cell with the sample; direction of the applied shear is perpendicular to the direction of measurement of electric conductivity (Reproduced from ^[252])

Note that this model is a first “additive” approach to account for the different network structures. The real network formation in shear flow is assumed to be much more complicated.

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Chapter 2

DISPERSION OF CARBON NANOTUBES IN POLYMER MATRICES AND DEVELOPMENT OF CONDUCTIVE NETWORKS

ABSTRACT

The objective of this chapter is to understand the key parameters governing the dispersion of CNT agglomerates in polymer matrices and the resulting electrical properties.

The thermodynamics is the first parameter controlling the dispersion of CNT. The ability of polymers to disperse CNT is correlated with the minimization of the attractive van der Waals interactions between CNT. According to Lifshitz theory, these interactions can be minimized by minimizing the Hamaker constant. The best dispersions are therefore achieved in polymers, which minimize the differences of both the dielectric constants and the refractive indexes between CNT and polymer.

The mixing energy is the second parameter governing the dispersion of CNT. Increasing mixing energy, by increasing mixing rotation speed and time and decreasing temperature, improves CNT dispersion. However, electrical conductivities are reduced. Improving dispersion can thus be harmful for the formation of a conductive network.

Second, the formation of a conductive network of CNT in polymer melt is studied. Annealing in the melt state increases both storage modulus (G') and conductivity owing to the formation of interconnected agglomerates. This phenomenon, called

secondary agglomeration, is reversible and time-temperature dependent. The characteristic time for reorganization decreases when increasing temperature and/or CNT content. To get electrically conductive plastic parts it is therefore necessary to first transfer the primary CNT agglomerates into individualized CNT and then to form a conductive network of secondary agglomerates.

Two publications are in preparation:

- A.-C. Baudouin, et al., *“Control of CNT dispersion in polymer matrices based on thermodynamic considerations”*, provisional title.
- A.-C. Baudouin, et al., *“Development of conductive CNT network: rheology and RF electrical characterization”*, provisional title.

We are grateful for the access to the technological platform “Welcome” and for the help of I. Huynen, I. Molenberg and P. Simon.

INTRODUCTION

Since their discovery by Iijima ^[1] in 1991, carbon nanotubes (CNT) have attracted considerable attention. Their very high aspect ratio, in the range of 100 to 1000 ^[2], in combination with their unique mechanical and electrical properties ^[3-5] make them a very attractive filler to produce nanocomposites with improved properties ^[6-10]. These new composites can be used in a wide range of industrial applications ^[11-14]: electrostatic dissipation, electromagnetic interference shielding, electrically conductive materials, etc, achieving at the same time enhanced stiffness, strength, impact properties, thermal stability ...

Different methods are widely used for preparing polymer/CNT nanocomposites: in situ polymerization, solution processing, melt mixing... Among these methods, melt mixing is the preferred method because it is environmentally friendly and it is compatible with current industrial process ^[15]. The production of nanocomposites exhibiting good electrical and mechanical properties depends on the control of the de-aggregation and dispersion of the CNT in polymer matrices ^[16,17]. Indeed, primary CNT agglomerates reduces the amount of CNT available to reach the electrical percolation and act as imperfections in mechanical tests. However, the dispersion is hindered by the existence of primary entangled agglomerates (up to diameters of several millimetres) formed during the CNT production. High van der Waals (VDW) interactions between native CNT and depletion forces also promote the presence of agglomerates ^[18]. Nowadays, there is no consensus concerning the way to evaluate the VDW interactions of CNT. For the dispersion of CNT in polymer systems, the classical Lifshitz theory using Hamaker constant is often used ^[19-23]. However, some authors ^[24-26] state that, due to the dimensionality of the CNT, this theory, initially developed for classical colloids systems, cannot be applied because the CNT cannot be described in terms of a frequency-dependent dielectric permittivity. They therefore propose other methods based on density functional theory or empirical model potentials (for more details, see Chapter 1).

To minimize the tendency of CNT to form aggregates, appropriate shear conditions must be selected ^[11,12,16,27]. The mechanisms controlling the dispersion of CNT are described by Kasaliwal et al. ^[22,28,29]. They are based on melt infiltration of the agglomerates by the polymer chains, erosion (slow process) and rupture (fast process). However, the best dispersion is not always correlated to the best electrical properties ^[17,74], especially if the processing conditions required for the dispersion cause CNT breakage.

Moreover, some authors [22,80] show that the electrical resistivity can be lowered during the compression moulding step required to shape the samples for electrical characterization by increasing temperature and time. This phenomenon is known as secondary agglomeration. Small conductive CNT clusters are formed and undergo cluster-cluster agglomeration process. In the absence of shear, the movement is caused by Brownian motion and VDW interactions (driving force). This phenomenon is reported in the literature for a wide range of systems: PC/CNT [81,82,30], PA6/CNT [80], PP/CNT [31-33], PP/CB [33], HDPE/carbon black [34], HDPE/PMMA/carbon fibres or ketjenblack [35], PS/CNT and PS/carbon nanofibres [36], PS/CB [37], PVDF/CNT [38] and epoxy/CNT [39] composites. However, some authors [36,40] state that the increase of the rheological and electrical properties occurs due to an isotropic re-arrangement of individualized CNT. They state that during the compression step required to shape the samples for further characterization, the CNT become aligned. Then, during annealing, the aligned disconnected particles form an isotropic interconnected network.

The first objective of this chapter is to understand the key parameters governing the dispersion of CNT in polymer matrices. The dispersion states of CNT in different polymer matrices are compared. The differences are explained based on thermodynamic considerations. Next, for a selected matrix, the influence of the processing parameters (mixing temperature, mixing speed and mixing time) on the dispersion is presented.

The second objective of this chapter is to study the formation of a conductive network of CNT in polymer melts. The effect of annealing above the melting or glass transition temperatures on the rheological and electrical properties at high frequencies is exposed.

EXPERIMENTAL

This is a very brief description of the materials and characterization methods used. For more details, please refer to Appendix 1.

1 Materials

The CNT used in this work are unpurified and unfunctionalized multiwalled carbon nanotubes.

The polymer used are:

Ethylene-based copolymers: EA random copolymer of ethylene and methyl acrylate; EVA: random copolymer of Ethylene and Vinyl Acetate; MAEA: random terpolymer of Ethylene, Acrylic Ester and Maleic Anhydride

Polyamides: PA4/6: copolyamide 4/6; PA6: polyamide 6; PA6/12: copolyamide 6/12; PA12: polyamide 12 ; PA*: polyamide 6/6 with a low viscosity.

Others: PP: polypropylene; PC_l: polycarbonate low viscosity; PC_m: polycarbonate medium viscosity; PES: Poly(ether sulfone) Cl terminated.

Compounding procedures are reported in Appendix 1.

2 Characterization

The composites are characterized using:

- Optical microscopy
- TEM on extruded samples and on samples annealed in the press
- Electrical characterization using a VNA from 0.04 to 40 GHz
- Rheological characterization:
 - o Multi-wave frequency sweep: the fundamental frequency was 0.1 rad/s with 5% deformation plus two additional wave forms at 1 rad/s with 1.5% and 10 rad/s with 0.5% respectively.
 - o Sequences of multi-wave frequency followed by controlled rate experiments at a shear rate of 5/s for 600s

RESULTS AND DISCUSSION

The dispersion of CNT primary agglomerates, formed during the CNT synthesis, in different polymer matrices is first analysed. Then, the formation of conductive networks by post-processing annealing at high temperature is studied by a combination of rheological, electrical and morphological characterizations.

1 Dispersion of primary agglomerates

The dispersion of unpurified and unfunctionalized CNT in different polymer matrices is first analyzed by TEM imaging and electrical properties at high frequencies. The differences observed for the different matrices are then discussed from a thermodynamic point of view. The discussion is based on the evaluation of the enthalpic contribution to the dispersion. Next, the influence of processing conditions is addressed for one polymer matrix presenting a relatively good dispersion. The morphology and electrical properties are exposed for different processing conditions.

1.1 *Influence of the polymer matrix*

1.1.1 Morphology

The dispersion of CNT is first examined by TEM for the different matrices, from an apolar one (PP) to more polar ones (PA, PC or PES), going through intermediate polarities (EA, EVA or MAEA).

The dispersion of CNT in polyolefin-based matrices is presented in Figure 1. The dispersion of CNT in polypropylene (PP) matrix is very poor (Figure 1a). There are large remaining primary aggregates and almost no individual CNT is observed. When CNT are dispersed in polyethylene-based matrices (EA, EVA, MAEA) (Figure 1b-d), smaller aggregates and individualized CNT are observed. The dispersion and distribution is more homogeneous than in PP. No significant difference in CNT dispersion state is observed between the three ethylene-based copolymers.

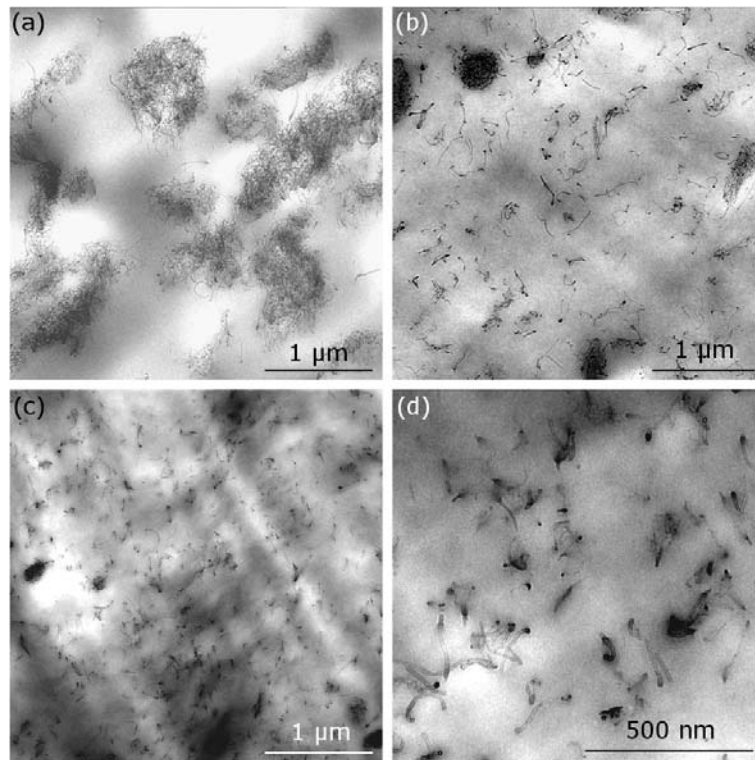


Figure 1 - TEM micrographs of polyolefin - based systems: (a) PP; (b) EA; (c) EVA; (d) MAEA

When CNT are dispersed in PA matrices (Figure 2), no microscopic aggregate is observed, except for PA*. Except for PA4/6 and PA* (Figure 2a,c), the CNT are well and homogeneously dispersed in the PA matrices.

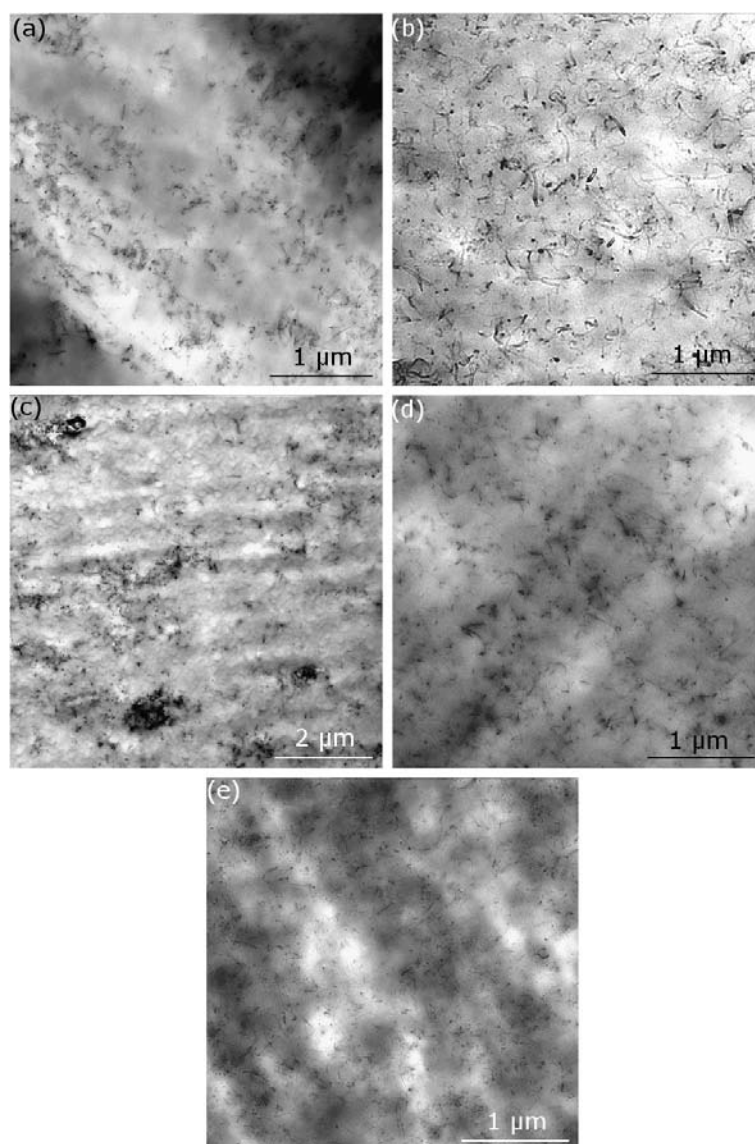


Figure 2 – TEM micrographs of polyamide – based systems: (a) PA4/6; (b) PA6; (c) PA*; (d) PA6/12; (e) PA12

When CNT are dispersed in PC or PES (Figure 3), mainly individualized CNT are observed. The dispersion is excellent.

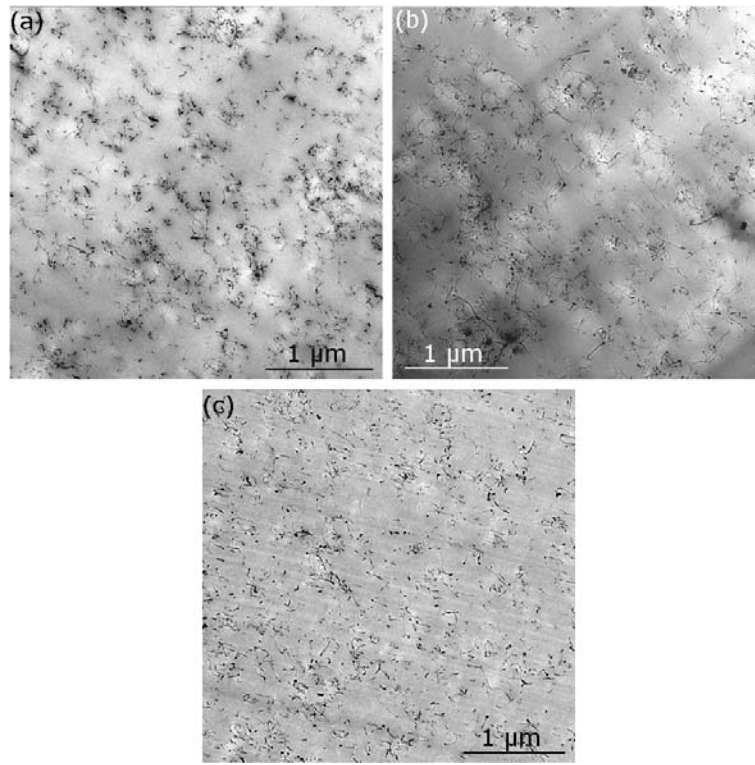


Figure 3 – TEM micrographs of 2wt.-% CNT dispersed in (a) PC_i; (b) PC_m; (c) PES

1.1.2 Electrical properties

The difference of dispersion of the primary agglomerates is correlated with the electrical properties. The Radio Frequency (RF) electrical properties of the composites containing CNT have been electromagnetically quantified in the microwave frequency range (40MHz to 40GHz) using microstrip transmission lines. Figure 4 presents the electrical conductivity versus the frequency for three different matrices filled with 2wt.-% CNT characterized by different dispersion states. For all matrices, the conductivity level tends to zero at low frequency. This can be explained by the fact that the CNT don't touch each other over the whole composite. However, at higher frequencies, the conductivity increases in presence of CNT. At these frequencies, when the distance between CNT is small compared to the wavelength, there exists a high capacitive coupling between the CNT, which becomes equivalent to an electrical short-circuit.

The conductivity of the pure matrices is very low and no significant difference of conductivity is observed between them. They are therefore not presented here. However, the conductivities obtained for the different composites are

very different. The conductivity of PC+2wt.-%CNT is higher than the conductivity of PA6+2wt.-%CNT, which is also higher than the conductivity of EA+2wt.-%CNT. These differences confirm the differences observed in the dispersion of the primary agglomerates.

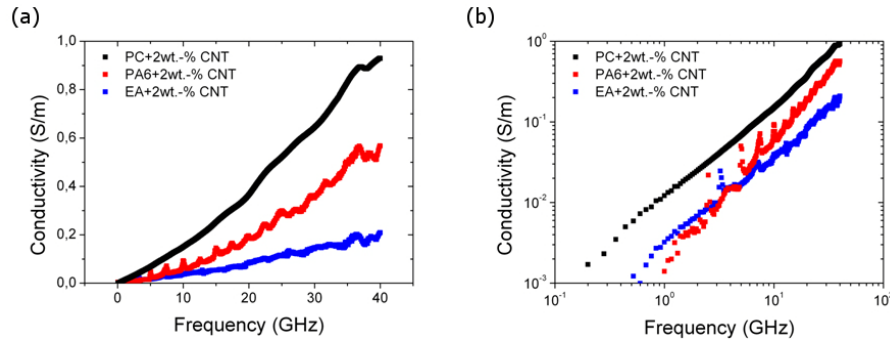


Figure 4 – RF conductivity versus frequency for PC_m, PA6 and EA filled with 2wt.-% CNT (a) linear scale; (b) log scale

1.1.3 Rheological properties

The viscosity of different polymers at their processing temperatures is presented in Figure 5. The light blue shaded area corresponds to the shear rate range of the compounder (assessed from Cox-Merz equivalence). In this shear rate range, the viscosities of EA, PC_m, PA6/12 and PA12, at their respective processing temperatures, are almost similar. The viscosities of PP and PC_i are also rather close. The viscosities of PES or PA6 are much higher. PA4/6 and PA* present much lower viscosities than the other polymers.

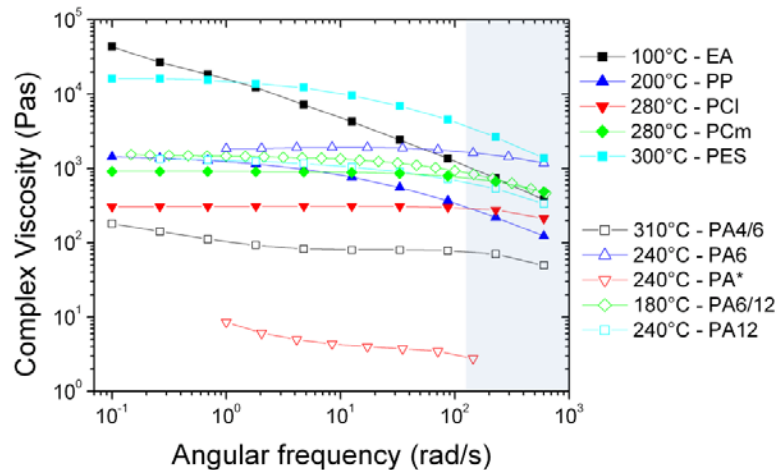


Figure 5 – Complex viscosity versus angular frequency for the different matrices

1.1.4 Thermodynamical parameters

The thermodynamic parameters influencing dispersion are dominated by the attraction between CNT, which has both enthalpic and entropic origins. Both contributions are discussed here.

a. Enthalpy contribution

CNT are usually synthesized as bundles. They present a high level of entanglements due to their synthesis. Moreover, van der Waals (VDW) forces hold the bundles together ^[41]. Because of the length of the tubes and of their high polarizability, the energy required to individualize the tubes is substantial. Effective dispersion of the CNT therefore involves overcoming the strong inter-tube VDW attraction.

Many research teams have addressed the interaction between CNT ^[19,23,24,42-56]. However, it has, to our knowledge, never been used to compare the difference in dispersion observed for different polymers. Here the classical approach based on the Lifshitz theory for the VDW interaction energies between two mesoscopic cylinders is used to assess the difference of dispersion in different polymers. The interaction energy for short range interactions is given by Israelachvili et al. ^[57] and is presented in Chapter 1.

The geometry of the system is identical for all composites since the same CNT are dispersed in the different matrices. The only changing parameter is thus the Hamaker constant, which depends on the polarizability of the particles and the surrounding matrix. It is calculated based on bulk properties such as the dielectric constant (ϵ) and the refractive index (n). Based on Lifshitz theory for a symmetric case of two identical CNT interacting across a polymer, the Hamaker constant can be expressed as:

$$A = \frac{3}{4} k_B T \left(\frac{\epsilon_{CNT} - \epsilon_{polymer}}{\epsilon_{CNT} + \epsilon_{polymer}} \right)^2 + \frac{3h\nu_e}{16\sqrt{2}} \frac{(n_{CNT}^2 - n_{polymer}^2)^2}{(n_{CNT}^2 + n_{polymer}^2)^{3/2}}$$

Where k_B is the Boltzmann constant, T is the temperature, h is the Planck constant, ϵ_{CNT} and $\epsilon_{polymer}$ are the static dielectric constants of the CNT and polymer, ν_e is the main electronic absorption frequency in the UV typically around $3 \cdot 10^{15} \text{ s}^{-1}$, n_{CNT} and $n_{polymer}$ are the refractive indexes of the CNT and polymer (for more details, see Chapter 1).

The van der Waals force between two identical bodies in a medium is always attractive (A positive). The interaction energy between two carbon nanotubes

depends on the dielectric constants and refractive indexes differences between the CNT and the polymer. In order to disperse properly the CNT in the polymer matrix, the value of the Hamaker constant has to be minimized to decrease the interaction energy between the CNT.

The evaluation of the static dielectric constant of carbon nanotubes is however not easy. Matsumoto et al. [58] have measured a static dielectric constant of 4.4 ± 0.5 or 4 ± 1 depending on the singlewalled CNT (SWNT) type. The static dielectric constant of semiconducting single SWNT in a form of thin straight bundles is estimated to be ~ 4.5 . Lu et al. [59] have reported the experimental measurement of near-DC polarization of individual SWNT by using modified scanning force microscopy. Their experimental measurements can be fitted with an isotropic dielectric constant of about 10. Variations in chirality and size influence dielectric properties. The longitudinal dielectric properties thus differentiate metallic and semiconducting SWNT. Metallic CNT exhibit an approximate longitudinal dielectric constant of 1000, while semiconducting ones exhibit one of 30. In both cases, the transverse dielectric constant can be approximated by a cylindrical media with a dielectric constant of about 10. For MWNT [60,61], the depolarization effects along the axis are negligible and the constituent tubes have very weak dielectric interactions. The total longitudinal polarizability is the sum of the polarizabilities of the constituents SWNT. The largest contributions to transverse polarizabilities come from the outer few layers. The inner layers play a negligible role due to a combination of screening and their smaller radii. MWNT show a metallic longitudinal response and an insulating transverse response. Other studies present a dielectric constant of 2.4 for semiconductive CNT by analogy with graphite [62] or a dielectric constant of 1 for quasi two-dimensional semiconductors [63]. Although Rajter et al. [23] have given an expression for the interaction free energy taking into account both longitudinal and transverse responses of the dielectric constants, we use here an isotropic value of ϵ to draw rough trends about the dispersion of CNT in polymer matrices.

It is generally assumed that the refractive index of MWNT is around 1.9-2.1, by analogy to graphite [64,65].

The dielectric constant and refractive indexes of the polymers are reported in Table 1. These properties are not reported in literature or handbooks for all polymers. This is the case for polyethylene-based copolymers (EA, EVA, MAEA) and for polyethersulfone (PES). The polyethylene-based copolymers are mainly composed of ethylene (>72wt.-%). Their constants can therefore be roughly approximated by the ones of PE. For PES, the producer gives the

dielectric permittivity at these frequencies: 3.51 at 60Hz, 3.50 at 1kHz and 3.54 at 1MHz and no indication about the refractive index ^[66]. However, dielectric constants between 2.8 and 5.2 for polyether resins ^[67] and refractive index of 1.63 for polysulfone were reported ^[68].

Table 1 – Properties of polymer and dispersability of CNT in polymer matrices ^[66-69]

Polymer type	Dielectric constant (DC)	Refractive index	Dispersability of native CNT
Polypropylene (PP)	1.5	1.5	Poor
Polyethylene-based copolymers (EA, EMA, EVA)	(n.a)	~1.5	Poor to good
Polyethylene (PE)	1.5 (pellets) – 2.2-2.4	1.51	Poor
Poly(ethyl acrylate)	(n.a)	1.464	(n.a)
Ethylene vinyl acetate (28%) (EVA)	(n.a)	1.4845	Good
Polyamide (PA)	2.5-2.6	1.53-1.56	Very good
Polycarbonate (PC)	2.9-3.0	1.59	Excellent
Polyethersulfone (PES)	~3.5	(n.a)	Excellent
Polyether resin	2.8-5.2	(n.a)	(n.a)
Polysulfone	(n.a)	1.63	(n.a)

According to the expression of the Hamaker constant and to the relatively high value of the transverse dielectric constant and refractive index of the CNT, the polymers presenting the higher dielectric constant as well as the higher refractive index will minimize the VDW interactions between CNT. Note that Gabor et al. ^[70] have found a correlation between the dispersability and the relative permittivity of different solvents. They compare the dispersability of as received CNT in different organic solvents and stable suspensions are obtained with solvents having a relative permittivity between 7.58 (THF) and 24.55 (ethanol). Out of this range, the CNT coagulate.

b. Entropic contribution

When the CNT are dispersed in polymers, there is also an attractive force due to the entropic contribution. This attraction is caused by the decrease of conformational possibilities for the macromolecules close to the CNT, causing a polymer depletion in the vicinity of the CNT. There is thus an osmotic pressure which causes attraction between the CNT. This effect is intrinsic to colloids dispersed in polymers ^[71-73]. In the absence of strong favorable enthalpic interactions between the tubes and the polymer, the preferred configuration of the nanotubes is therefore a bundle arrangement due to an increase of the total conformational entropy.

1.1.5 Discussion

The TEM morphologies and the electrical conductivities presented here above indicate significant differences of CNT dispersion depending on the polymer matrix used. The CNT are poorly dispersed in PP. Their dispersion is average in the ethylene-based copolymers (EA, EVA, MAEA) and in PA4/6 and PA*. Their dispersion is good in PA6, PA6/12 and PA12. Finally, their dispersion is excellent in PC_i, PC_m and PES.

These differences can be explained either by a difference in the processing conditions or by differences in the interactions between CNT and polymers (thermodynamic contribution).

The different PA present similar structures. However, the state of dispersion of the CNT is average for PA4/6 and PA* while it is good for other PA. This can be explained by differences in the processing conditions. Indeed, PA4/6 and PA* exhibit very low viscosities at their processing temperatures. The shear stresses encountered in the compounder are thus lower and a worst dispersion state is obtained for these polymers.

On the contrary, some polymers present similar viscosities in the shear rate range of the compounder at their processing temperature: PP and PC_i on the one hand; and EA, PA6/12, PA12 and PC_m on the other hand. The processing conditions for the incorporation of CNT in these polymers are thus similar. The influence of the matrix viscosity and thus of the shear stresses can thus be excluded. However, the CNT dispersion states are significantly different. These differences can therefore be attributed to thermodynamic parameters and more precisely to the enthalpic contribution. The attraction between CNT can be minimized by minimizing the Hamaker constant and thus the difference between the dielectric constants (ϵ) of the CNT and polymer and the difference between the refractive indexes (n) of the CNT and polymer. For example, for PP, $\epsilon \approx 1.5$ and $n \approx 1.5$, while for PC, $\epsilon \approx 3.0$ and $n \approx 1.6$. For identical shear stresses and compounding parameters, the dispersion of CNT in PC is thus better than in PP. Similarly, the dispersion of CNT is better in PC than in PA, which in turn presents a better dispersion than in ethylene-based copolymers. If the processing parameters are decoupled from the enthalpic contribution, the dispersion state is correlated with the minimization of the Hamaker constant. The higher the dielectric constant and the refractive index, the better the dispersion.

PES exhibits a $\epsilon \approx 3.5$ and $n \approx 1.6$, indicating that a better dispersion should be achieved than for the other systems. However, in this case, the viscosity of PES

is very high and the viscosity effect could not be decoupled from thermodynamic considerations.

Note finally that the effect of the chain length is not studied here. The entropic contribution to the dispersion is thus not taken into consideration.

1.2 Influence of processing parameters

The influence of processing parameters (compounding temperature, screw rotation speed and compounding time) on the morphology and electrical properties of the nanocomposites is reported for a system based on ethyl acrylate copolymer (EA) filled with CNT.

1.2.1 Variation in mixing temperature

First the influence of the mixing temperature is investigated. Two different mixing temperatures are used: 100°C and 150°C. The dispersion at 100°C and 150°C are compared respectively in Figure 6 and Figure 7 (optical micrographs) and in Figure 8 and Figure 9 (TEM micrographs). The optical micrographs show that larger aggregates are observed for compounding at 150°C. Moreover, TEM micrographs show that more individualized CNT are observed for mixing at 100°C. Increasing mixing temperature decreases melt viscosity and therefore reduces screw torque and corresponding shear stress at a given rotation speed. Figure 10 presents the measured torques for different processing conditions (100°C or 150°C and 50 rpm or 250 rpm). It is clear that whatever the mixing speed, the torque is much higher at 100°C than at 150°C.

On the other hand, increasing the processing temperature does not lead to significant changes of RF conductivity (Figure 11). For each mixing time and speed, the conductivities measured on the samples compounded at 100°C or 150°C are similar. Note that the peaks observed are parasites. Only the general trends of the curves must be taken into consideration.

1.2.2 Variation of mixing speed

Variation of mixing speed strongly influences morphology. OM micrographs (Figure 6) show that increasing mixing speed reduces the amount and size of CNT aggregates. This is particularly visible for low mixing time (5min). TEM micrographs also show an improvement of CNT individualization (Figure 8). Increasing mixing speed also affects the required screw torque at a given temperature. Figure 10 shows that the torque is higher for a rotation speed of 250rpm than for a rotation speed of 50 rpm.

However, increasing mixing speed decreases the electrical properties of the material (Figure 12).

1.2.3 Variation of mixing time

Increasing mixing time decreases the number and size of large CNT aggregates whatever the mixing speed used. Figure 6a and c show that, for short mixing time (5min), large aggregates of up to 50 μ m diameter are present. When increasing mixing time (15min) the number and size of aggregates are significantly decreased (Figure 6b and d). Increasing mixing time also leads to a more homogeneous dispersion of individualized CNT (Figure 8).

Figure 12 shows the effect on RF conductivity. For low mixing speed (50rpm), increasing mixing time leads to decreased conductivity values. For high mixing speed (250rpm), conductivity is already very low and no effect of mixing time is observed when changing compounding time.

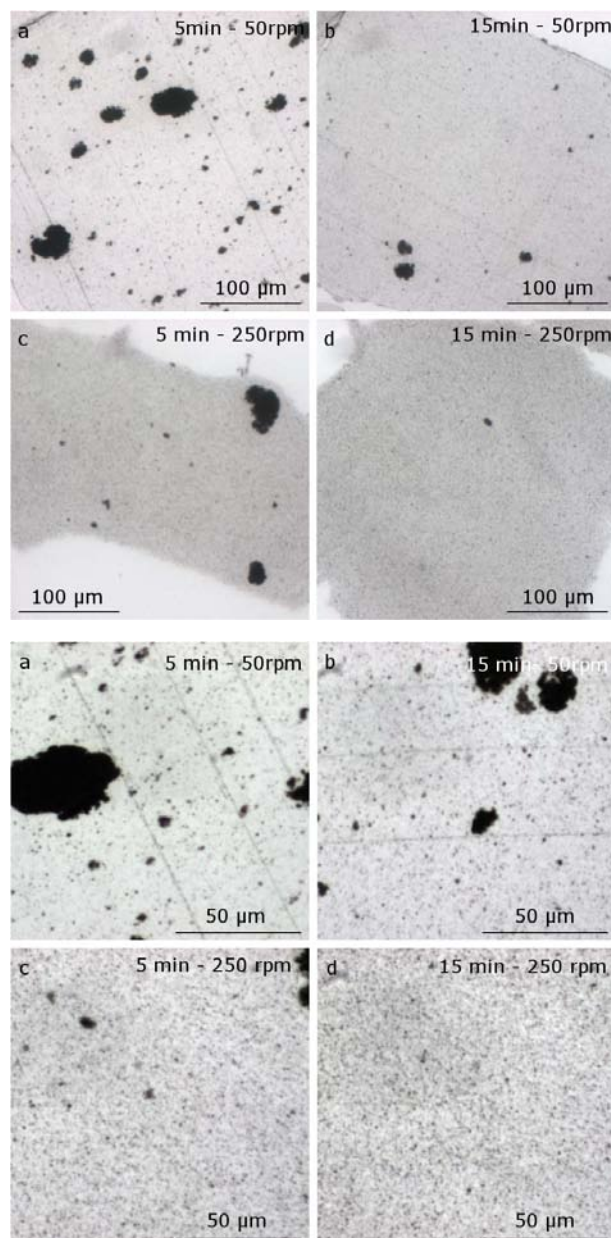


Figure 6 – Optical micrographs of EA+2wt.-% CNT mixed at 100°C (a) 5min, 50 rpm; (b) 15min, 50rpm; (c) 5 min, 250rpm; (d) 15min, 250rpm

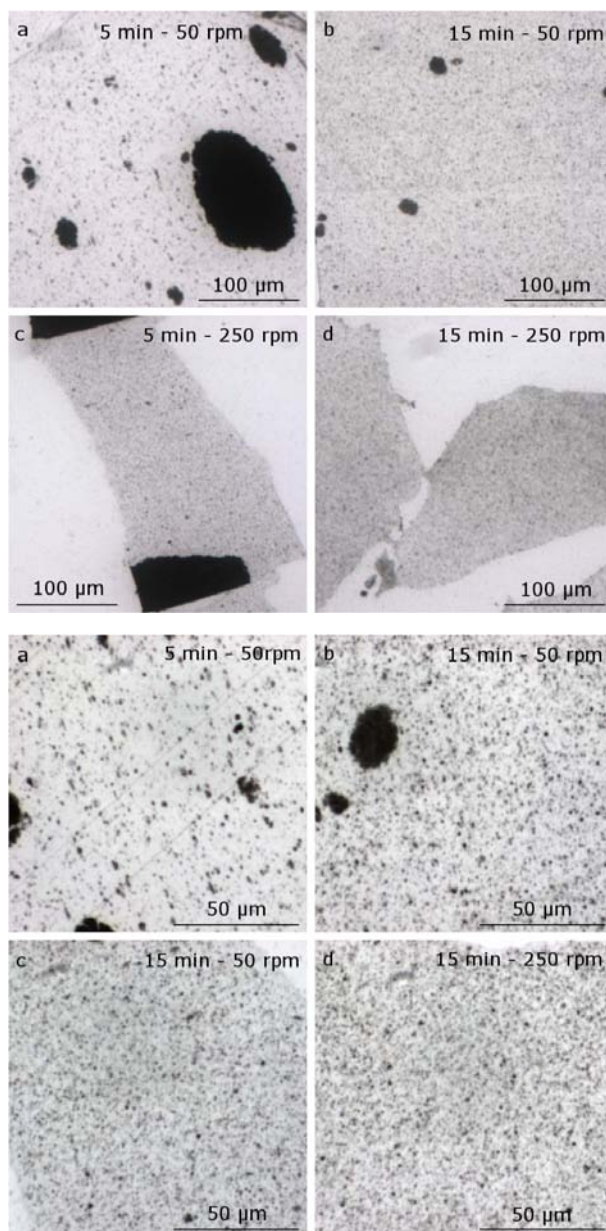


Figure 7 - Optical micrographs of EA+2wt.-% CNT mixed at 150°C (a) 5min, 50 rpm; (b) 15min, 50rpm; (c) 5 min, 250rpm; (d) 15min, 250rpm

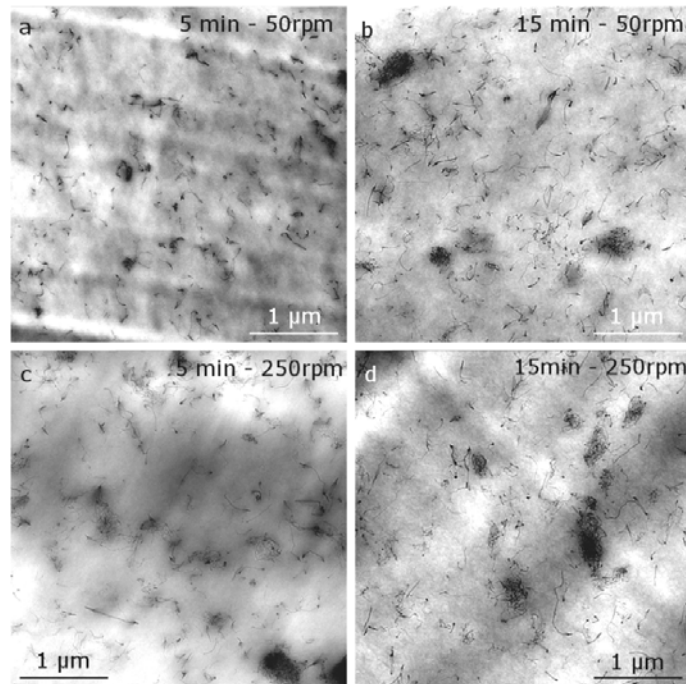


Figure 8 - TEM micrographs of EA+2wt.-% CNT mixed at 100°C: (a) 5min, 50 rpm; (b) 15min, 50rpm; (c) 5 min, 250rpm; (d) 15min, 250rpm

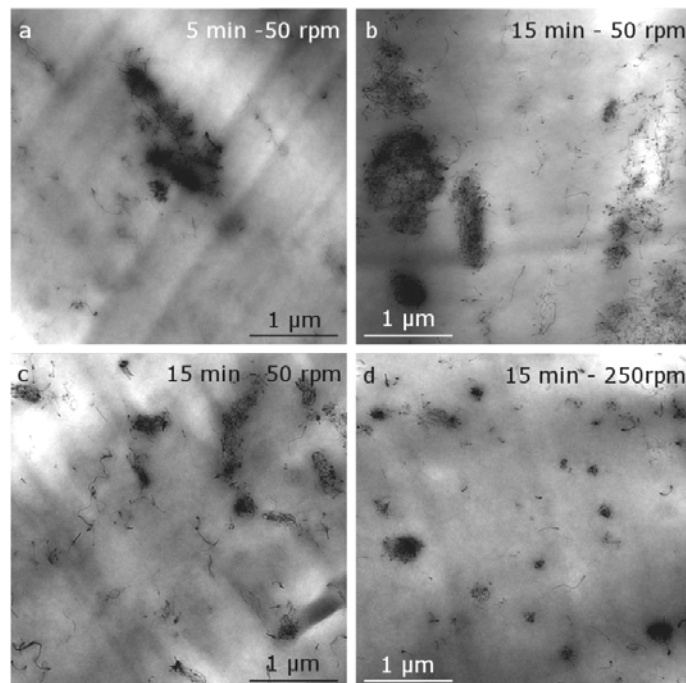


Figure 9 - TEM micrographs of EA+2wt.-% CNT mixed at 150°C: (a) 5min, 50 rpm; (b) 15min, 50rpm; (c) 5 min, 250rpm; (d) 15min, 250rpm

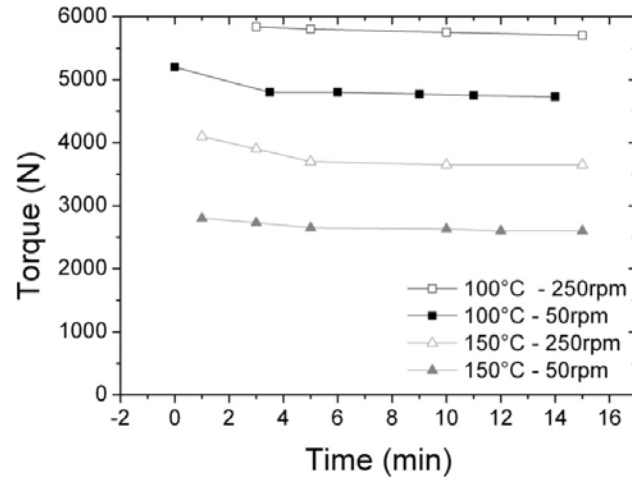


Figure 10 - Evolution of the compounding torque in the compounder with mixing time at different temperatures (100°C and 150°C) and different mixing speeds (50rpm and 250rpm)

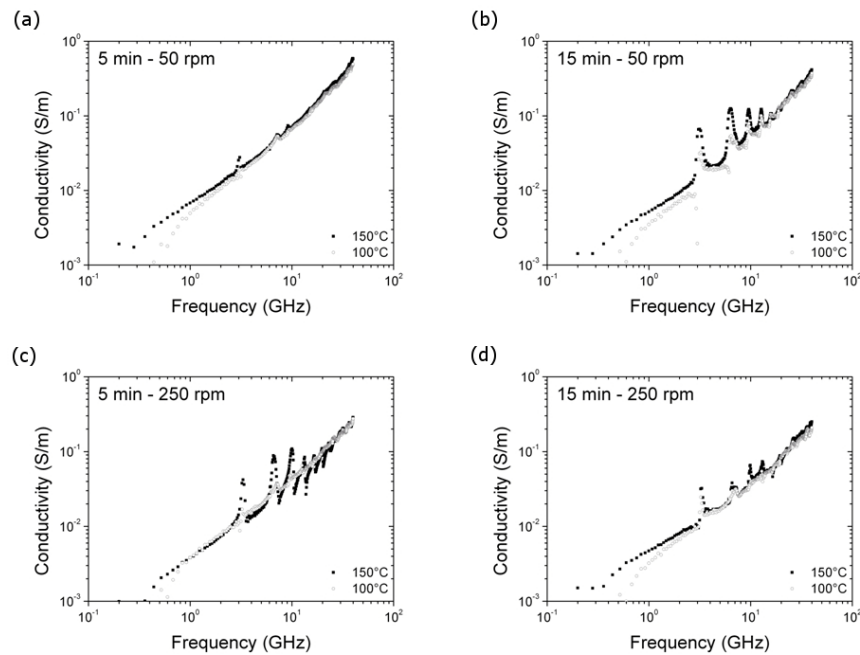


Figure 11 - RF conductivity versus frequency for EA+2wt.-% CNT, influence of the mixing temperature (a) linear scale; (b) logarithmic scale

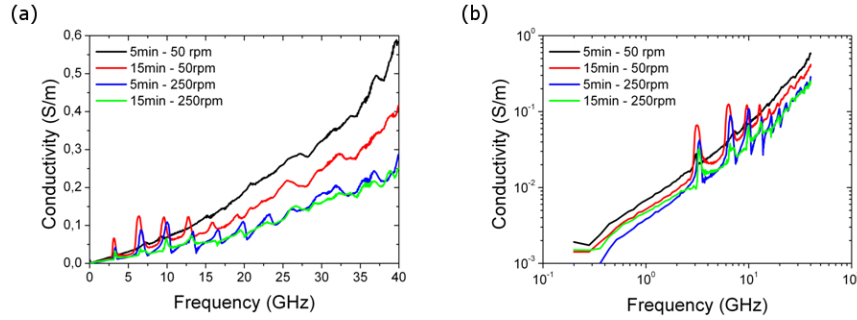


Figure 12 – RF conductivity versus frequency for EA+2wt.-% CNT (a) linear scale; (b) logarithmic scale

1.2.4 Discussion

The relation between mixing conditions and dispersion of the CNT primary agglomerates follows the common expectation. The dispersion is improved by increasing mixing energy, which is expressed as:

$$E = \int_0^t P dt = \int_0^t 2\pi \cdot N \cdot \tau dt$$

Where P is the engine output dependent of the time, N is the rotation speed in revolution per minutes (rpm), τ is the torque measured during mixing and t is the mixing time [74]. The best dispersion is therefore obtained by increasing both mixing time and rotation speed and by decreasing temperature. Therefore, the composite with the best dispersion is obtained at low temperature (100°C), high rotation speed (250rpm) and for long mixing time (15min). However, this composite shows the worst electrical conductivity. On the contrary, the sample presenting the larger amount of aggregates (150°C, 5min, 50rpm) presents the best conductivity. This indicates that the conductive network is formed by clusters connected by individual CNT rather than by well dispersed individualized CNT.

Increasing **mixing temperature** leads to a lower viscosity of the matrix. The mobility of the polymer chains is increased. There is therefore a better infiltration of polymer chains due to easier chain diffusion into primary agglomerates. The erosion of CNT from the surface of agglomerates is therefore easier. However, the viscosity decrease also results in lower shear stresses and thus in a decrease of the mixing energy (τ decreases). The agglomerates rupture mechanism is therefore less efficient. Two counteracting effects of the matrix viscosity are thus observed: the agglomerate infiltration and the agglomerate dispersion. Krause et al. [74] have found a better dispersion

of the CNT at high temperature for PA-CNT composites, indicating that the wetting and infiltration by polymer chains is the dominant mechanism. On the other hand, Socher et al. [75] have observed a better dispersion for the composites based on high viscous PA12 rather than low viscous PA12, indicating that the enhanced rupture mechanism is dominant. Kasaliwal et al. [29] have shown that up to a certain mixing speed, a better dispersion is achieved in the matrix with the higher viscosity. Above a certain mixing speed, similar dispersion states are observed, whatever the viscosity. Here the dispersion is slightly improved by mixing at lower temperature. However, these changes are not high enough to have an impact on the electrical properties. We can therefore not assume that a single dispersion mechanism is dominant.

Increasing **mixing speed** leads to a decrease of the number and size of CNT agglomerates. However, a decrease of the conductivity is observed. When increasing mixing speed, the mixing energy is increased (N and τ increase). The shear forces acting on the agglomerates are increased. There is therefore a stronger disruption and distribution of the agglomerates and a better dispersion of single CNT. Increasing mixing speed also leads to CNT breakage [17,27,76]. Li et al. [76] have shown that, in epoxy composites, large CNT agglomerates are obtained when using long CNT while almost no CNT agglomerates are observed in the composites prepared with short CNT. CNT breakage therefore leads to better dispersion but also to an increase of the percolation threshold and a reduction of the electrical properties.

Increasing **mixing time** leads to increased mixing energy (t increases) and to improved dispersion. Indeed, the polymer chains have a longer diffusion time to flow inside the CNT mesh during processing. Similar results are observed by Pötschke et al [77]. However, for low mixing speed (50rpm) a decrease of the conductivity is observed. For higher rotation speed (250rpm), increasing mixing time does not change the electrical conductivity. Actually, for high mixing speeds, the mixing energy is already high and CNT have already encountered breakage. The mixing time is thus less important. On the other hand, for low mixing speed, the processing conditions are softer and increasing mixing time leads to more CNT breakage. Andrews et al. [27] have shown that increasing mixing energy by increasing mixing time, for a constant mixing speed, improves the dispersion but leads to CNT breakage up to 25%.

Although increasing mixing energy, by increasing compounding speed and time and decreasing temperature, leads to better dispersion of the CNT, high shear forces and long residence times increases the probability of reducing the aspect

ratio of CNT. Moreover, the best dispersion state is not systematically correlated with the best electrical properties. This observation is in good agreement with results already reported in literature [17,74,78]. To produce polymer composites exhibiting high electrical conductivity at low concentration, an uniform dispersion of the CNT can thus be a disadvantage.

2 Development of conductive networks – secondary agglomeration

In the previous section, it is shown that the achievement of a good dispersion state is not always required and is sometimes harmful to the formation of a conductive network. In this section, the influence of annealing at a temperature above the glass transition or melting temperature of the matrix is exposed. The rheological and electrical responses and the modification of the morphology are presented.

2.1 Rheological properties

The rheological properties of the EA/CNT composites, processed for 15min at 250 rpm and 100°C, are measured in the melt state at different temperatures: 100°C, 125°C, 150°C and 170°C. Data are collected in linear oscillatory shear using the multiwave approach. The fundamental frequency is 0.1 rad/s with 5% deformation plus two additional wave forms at 1 rad/s with 1.5% and 10 rad/s with 0.5% respectively.

Figure 13 shows the time sweep of the storage modulus, G' , at 125°C, for a sample filled with 2 wt.-% CNT. Low frequencies measurements are the most sensitive to the structure of the composites and thus give useful information on the dispersion state of the CNT. Only the storage modulus, G' , at 0.1 rad/s is thus presented hereafter.

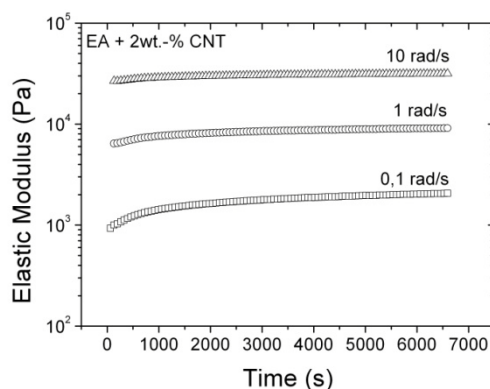


Figure 13 – Evolution of the elastic modulus G' at 125°C for EA+2wt.-% CNT

Figure 14a shows the time sweep of the storage modulus, G' , at 0.1rad/s at 170°C, for different CNT loadings (1, 2, 5wt.-%). For pure EA, G' increases very slightly with residence time in the rheometer. The polymer is thus relatively stable under the applied conditions and for the duration of the test. Note that for longer times, a sharp increase is observed due to crosslinking occurring at the rim of the polymer disk. When CNT are added, the values of G' increase sharply for short residence times and then increase slightly, like for the pure polymer matrix (“plateau”). This increase at long times is not caused by the presence of CNT. As expected the value of G' at the “plateau” is increasing with increasing CNT loading. The “plateau” is also reached faster with increasing CNT content. The same observations are found at 125°C (Figure 14b). However, at this temperature, the increase of the storage modulus looks slower than at 170°C, especially for 1 and 2 wt.-% CNT. Figure 15 presents, for different CNT contents, the influence of the annealing temperature on the time evolution of the elastic modulus. For 1 and 2 wt.-%CNT, the final value of the storage modulus decreases when increasing temperature due to the lower viscosity of the matrix at higher temperature. When 5wt.-% CNT are added to the polymer, the final value of G' is similar at 150°C and 170°C and, surprisingly, is slightly higher than the values observed at lower temperature.

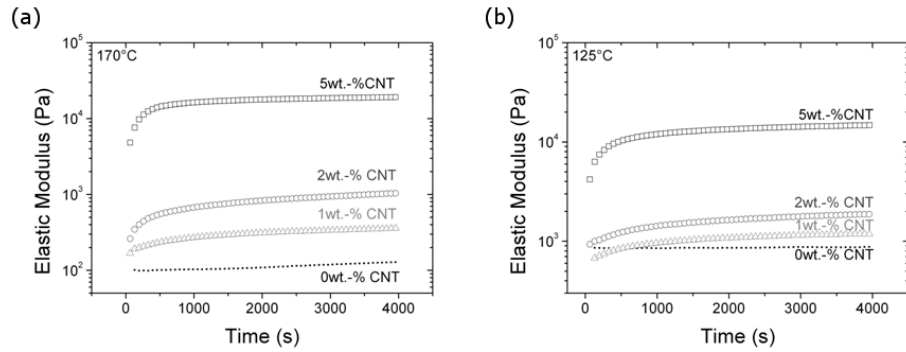


Figure 14 – Evolution of the elastic modulus G' (0.1rad/s) at 170°C for different CNT loading (a) 170°C; (b) 125°C

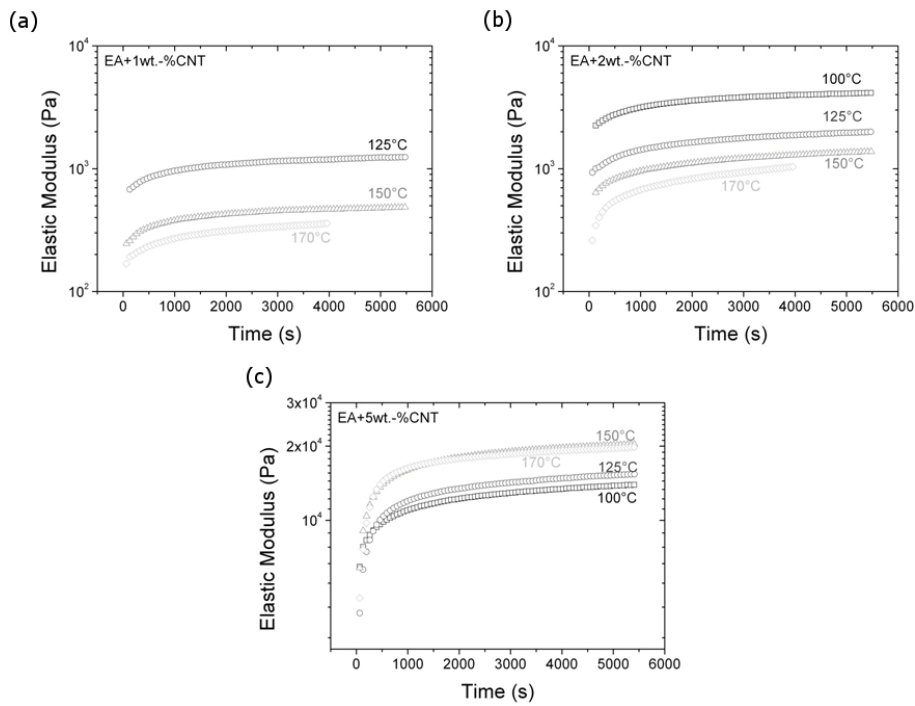


Figure 15 – Evolution of G' versus time as a function of the annealing temperature for different CNT content (a) EA+1wt.-%CNT; (b) EA+2wt.-%CNT; (c) EA+5wt.-%CNT

The effect of increasing temperature on the time to reach the “ G' plateau” can be assessed in terms of characteristic time. Ideally, if a completely flat plateau was reached at long residence times, an exponential law would fit the data as presented in Figure 16.

The characteristic time, τ , would therefore be extracted from the following relation:

$$G'(t) = G_0' + (G_\infty' - G_0') \left(1 - \exp\left(-t/\tau\right)\right)$$

or

$$G'(t) = G_\infty' - (G_\infty' - G_0') \exp\left(-t/\tau\right)$$

Where t is the residence time, G_∞' is the asymptotic value for very long residence time and G_0' is the initial value of $G'(t)$.

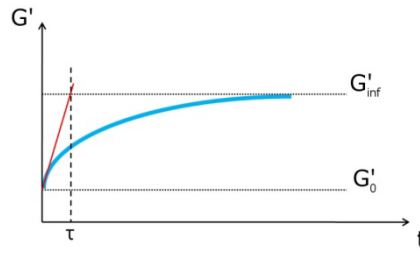


Figure 16 - Scheme of the evolution of the storage modulus (G') with time (t) for polymers filled with CNT

However, the storage modulus of the pure polymer matrix is not constant with residence time. It can be well fitted by an exponential curve with a longer characteristic time. $G'(t)$ for the composite is therefore fitted by a sum of two exponentials in the form:

$$y = y_0 + A_1 \exp(-x/\tau_1) + A_2 \exp(-x/\tau_2)$$

The first exponential gives a characteristic time τ_1 representing the evolution of $G'(t)$ for short residence times, associated to the presence of CNT, while τ_2 gives an indication of the evolution for long residence times, related to the polymer. The characteristic time of interest here is τ_1 and its values for different CNT content and temperatures are presented in Table 2. It is worth noting that these values must be handled with caution. Indeed, to prepare the samples for rheological characterization, the extruded strands are first compression moulded at 100°C for a few minutes. Then, after sample loading in the rheometer, stabilization of the temperature takes some time. The evolution of

the rheological properties is not recorded during these two steps. The first points of the reorganization are therefore “lost”. However, rough trends, confirming the observation made in Figure 14 and Figure 15, can be extracted. First, the composites filled with 1wt.-% or 2wt.-% CNT present roughly identical characteristic times. Second, for these contents, increasing temperature leads to shorter characteristic times. Then, for 5wt.-%CNT, no change in the characteristic time is observed when increasing temperature. Above a certain filler content, it appears thus that the reorganisation kinetics is independent of the annealing temperature. Finally, the characteristic times for 5wt.-%CNT are lower than for 2wt.-%CNT and for 1wt.-%CNT. Increasing CNT content leads thus to faster reorganisation kinetics.

Table 2 – Characteristic times (s) as a function of the CNT loading and annealing temperature

Temperature	CNT content		
	1wt.-%CNT	2wt.-%CNT	5wt.-%CNT
100°C	n.a.	623	217
125°C	509	569	222
150°C	347	376	204
170°C	(459)	220	211

The observed increase of rheological properties is a reversible phenomenon. Figure 17 presents the elastic modulus versus residence time for different consecutives runs. The network formed after a first annealing at 125°C in the rheometer is destroyed by a controlled rate step at a shear rate of 5/s for 600s. Then the sample is annealed and G' increases again. The apparent values of G' after the first run (run1) are lower because the gap has not been adjusted between the first experiment and the following. However, the shape of the curves remains similar. After the second time sweep experiment, the gap has been adjusted before each run. Thus the different curves are well superimposed. A similar behaviour is observed at 170°C and for samples with 1 or 2wt.-%CNT.

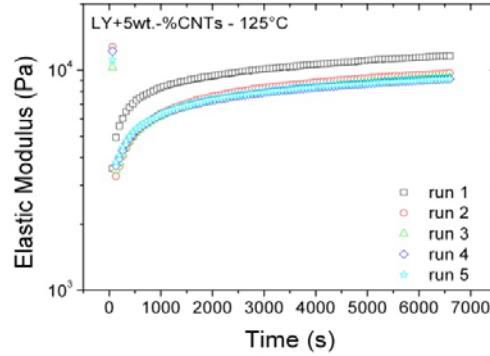


Figure 17 – Consecutive sweeps at 0.1rad/s and 125°C for EA+5wt.-%CNT

2.2 Electrical properties

The RF electrical properties of the composites after annealing are also investigated. No significant change is observed for the pure polymer after annealing. However, for EA filled with CNT, a strong effect is observed.

The influence of annealing for 2h at 170°C on composites with 2wt.-% CNT processed under different conditions is presented in Figure 18. For all samples, a high conductivity increase is observed. The highest conductivity is observed for the sample processed during 15min at 50rpm. The worse conductivity level is observed for the sample processed during 15min at 250rpm.

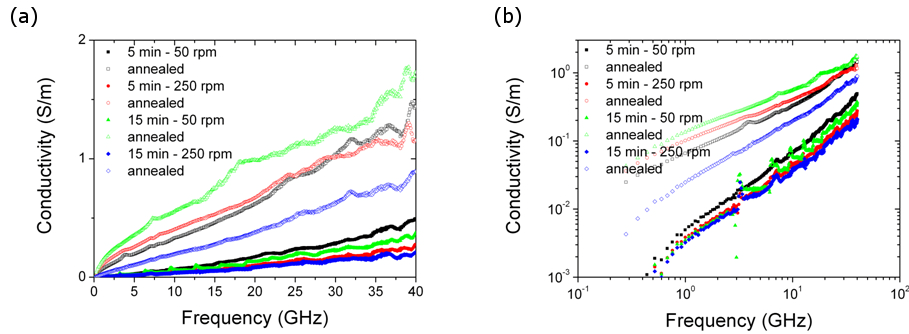


Figure 18 – Effect of annealing 2h at 170°C on RF conductivity of EA+2wt.-%CNT composites for different processing conditions (100°C, mixing time =5 or 15min, $v = 50$ or 250rpm) (a) linear scale; (b) log scale

The influence of the annealing temperature and time is examined in Figure 19. Whatever the annealing conditions, an increase of the conductivity is observed. Upon annealing the sample at 125°C for 2 hours, the conductivity slightly

increases (about a factor 2). Increasing the annealing time from 2h to 4h increases the conductivity. When annealing the sample for 2h at 170°C, the conductivity is much higher than when the annealing temperature is 125°C. Increasing annealing time and temperature thus leads to improved electrical properties.

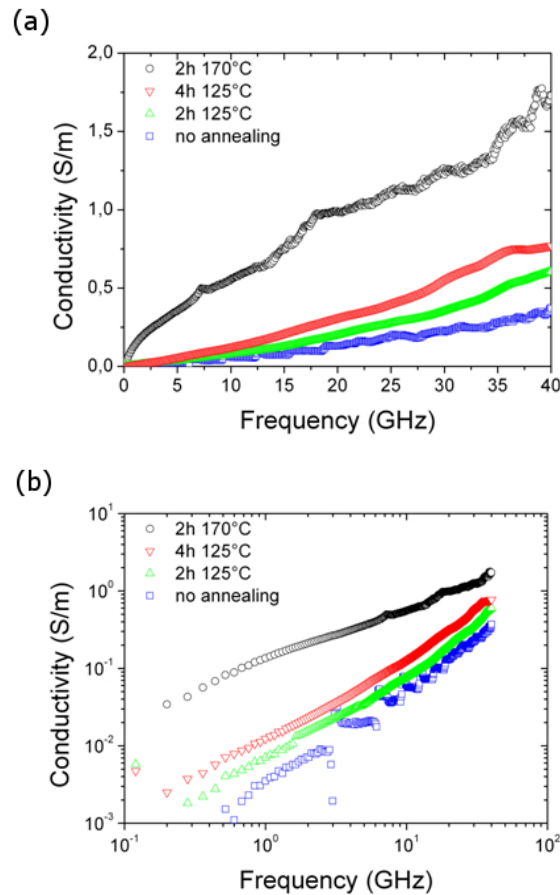


Figure 19 – Influence of annealing conditions on RF conductivity of EA+2wt.-%CNT processed at 100°C, 15min, 50rpm (a) linear scale; (b) log scale

The effect of annealing on samples with different filler loadings is exposed in Figure 20. The conductivities are compared in linear scale in Figure 20a. The same comparison is made in logarithmic scale in Figure 20b-d. A conductivity increase is observed for all samples. For the three CNT loadings, the slope of the frequency dependence is decreasing after annealing. To better highlight the conductivity changes, the conductivity at three different frequencies (1GHz, 10GHz and 40GHz) before and after annealing is reported in Figure 21. The results confirm the slope change. The changes are higher at lower frequency.

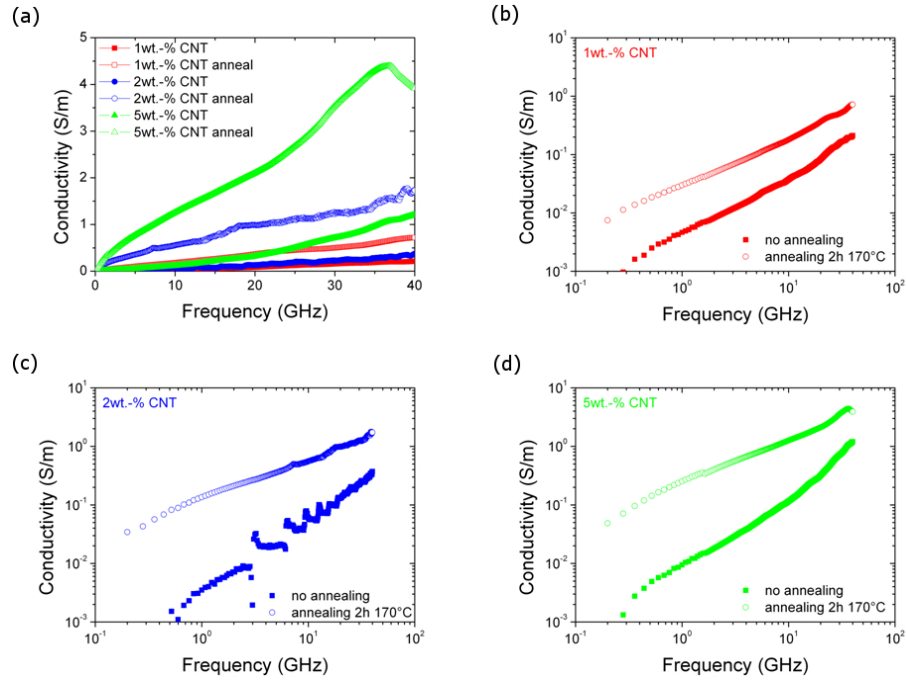
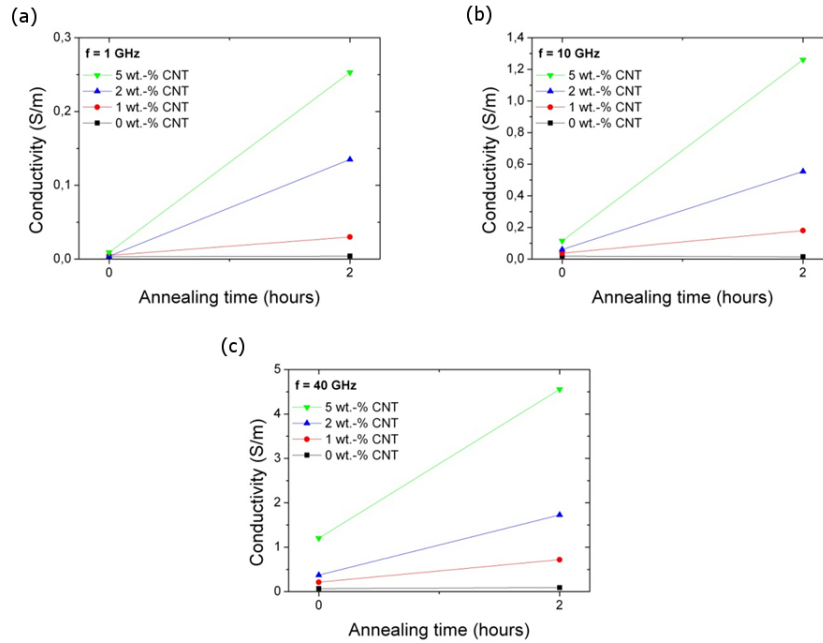


Figure 20 – Effect of annealing 2h at 170°C on the conductivity of EA/CNT composites for different CNT loading (1wt.-%, 2wt.-%, 5wt.-% CNT) (processing conditions : 15min and 50rpm): (a) linear scale; (b-d) log scale



(d) Conductivity (S/m)

Frequency	1wt.-% CNT		2wt.-% CNT		5wt.-% CNT	
	Before annealing	After annealing	Before annealing	After annealing	Before annealing	After annealing
1GHz	0.005	0.030	0.004	0.135	0.009	0.253
10GHz	0.037	0.180	0.060	0.555	0.115	1.261
40GHz	0.211	0.718	0.371	1.728	1.203	4.557

Figure 21 – Evolution of RF conductivity before and after annealing 2h at 170°C for different CNT loading and at three frequencies (a) 1GHz; (b) 10GHz; (c) 40GHz; (d) conductivity values

The effect of annealing is also examined on the RF electrical properties of PC/CNT composites (Figure 22). The samples are annealed for 1hour at 200°C and, except for pure PC, the electrical properties are highly improved. The curves also show that the improvement is more significant at low frequency. Moreover, the improvement is higher for PC+1wt.-%CNT than for PC+2wt.-%CNT.

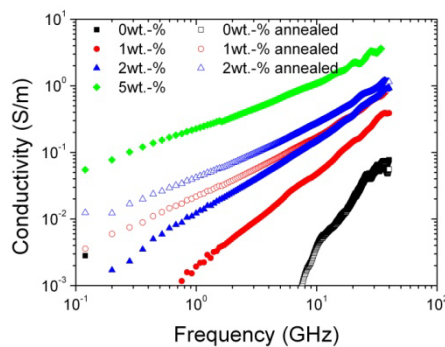


Figure 22 – RF conductivity versus frequency of PC_m without or with different CNT loadings without annealing or with annealing 1h at 200°C

2.3 Morphology

To investigate the effect of annealing on the dispersion state of CNT in EA+2wt.-%CNT composites, processed in different conditions, TEM is performed on annealed samples (Figure 23ii) and compared to the unannealed ones (Figure 23i). TEM micrographs reveal the formation of a network of agglomerates and individual CNT after annealing 2 hours at 170°C, evidenced by grey lines in Figure 23ii. Less individualized CNT are visible. The CNT are grouped together in small agglomerates and there are zones totally free of CNT. Such an agglomeration process after annealing has already been reported in literature [79-82] and is coherent with the increase of RF electrical conductivity observed on Figure 20.

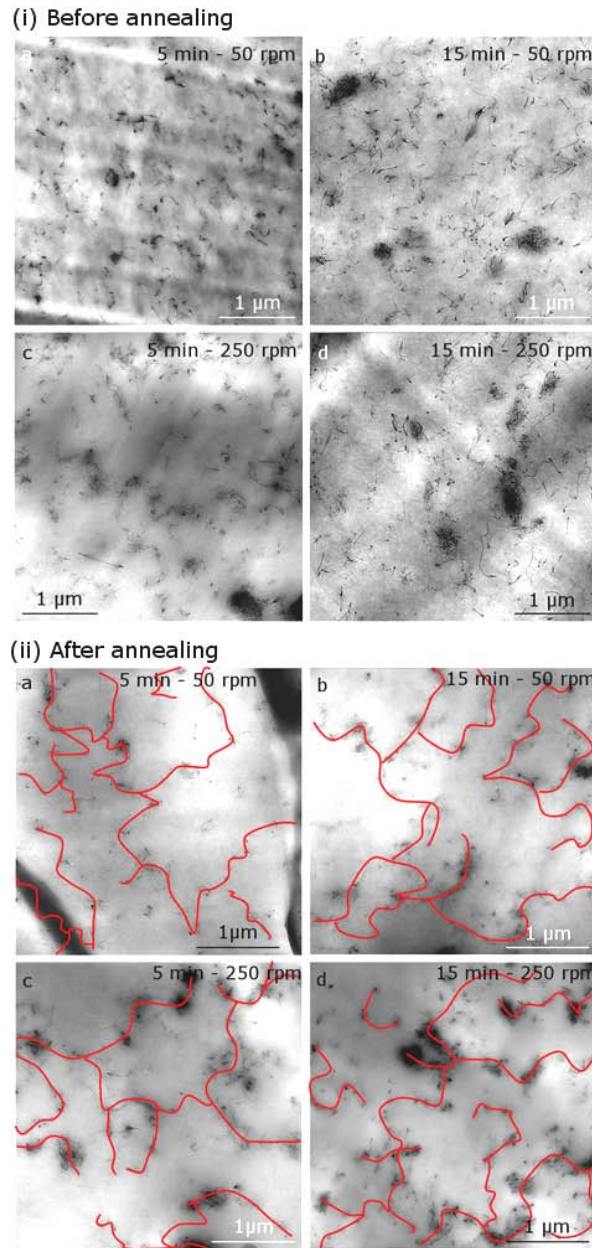


Figure 23– TEM micrograph of EA+2wt.-% CNT mixed at 100°C (i); and then annealed for 2h at 170°C (ii). Compounding parameters: (a) 5min, 50 rpm; (b) 15min, 50rpm; (c) 5 min, 250rpm; (d) 15min, 250rpm.

2.4 Discussion

The rheological and electrical properties of EA/CNT composites highlight the development of a network structure when annealed in the melt state. Moreover, the redistribution process of the CNT is confirmed by TEM. The analysis of the morphology shows that the improvement of both rheological and electrical properties can be attributed to the agglomeration of CNT and to the formation of a conductive network of interconnected agglomerates. This corroborates Sumita and Wessling^[83-85] observations, which shows that the dispersion process of filler nanoparticles in a polymer matrix never leads to thermodynamic equilibrium. Moreover, agglomeration appears as a general phenomenon occurring in polymer/CNT nanocomposites. Indeed, it is observed for different types of matrices (EA and PC) and has already been reported in literature^[31,80-82].

Rheological measurements at low frequency (1 rad/s) are performed at different temperatures and for different CNT contents. A dynamic percolation behavior is detected. The network formation through chemical reaction can be excluded since the observed behavior is reversible. The kinetics of the network formation is faster at higher temperatures and CNT content. However, above a certain CNT content (between 2 and 5 wt.-% CNT in EA), it becomes independent of temperature. The attractive interactions between particles (weak attractive forces between nanoparticles and depletion interactions with the polymer chains) are the driving force for the formation of the network. In literature, secondary agglomeration is usually explained by the diffusion of CNT due to Brownian motion^[31,80-82]. According to Einstein-Stokes law for the diffusion in solutions, in the absence of shear, the agglomeration rate of the particles is controlled by the viscosity of the polymer matrix, η , and by size of the filler or aggregates particles:

$$D = \frac{k_B T}{6\pi\eta R}$$

Where D is the diffusion coefficient, k_B is the Boltzmann constant, R is the radius for spherical particles and T is the temperature. The higher the melt viscosity of the polymer or the bigger the size of the particles, the longer is the time for reorganization. For isotropic particles of size a , the time for a particle to migrate on a distance equal to its radius is expressed as t_D :

$$t_D = \frac{6\pi\eta a^3}{k_B T}$$

In polymer melts ($\eta_{EA} \approx 3.10^3 \text{ Pa.s}$), the time scale for the migration of particles of radius 10 nm over 10 nm is around 9.25s; for a particle of radius 100nm, the time goes up to 2.6h. This time is very long and does not correspond to the characteristic times observed on time sweeps of the storage modulus.

The formation of the conductive network can thus more probably be attributed to the diffusion of the polymer chains. CNT can be considered as passive objects in a mobile medium constituted of polymer chains. CNT approach each other first by local bending under attractive forces. Then, because of this driving force, more contacts between the CNT are made and they progressively agglomerate. The speed of reorganization is controlled by polymer chains diffusion.

At higher temperature, the mobility of the polymer chains increases and the reorganization of CNT is thus quicker. In addition, the network formation occurs even more rapidly when the CNT content increases. Indeed, if the content of CNT is higher, the network will be more easily formed due to the increased probability of CNT or agglomerates contacts because of the lower particle-to-particle distance.

The RF electrical properties are also found to be highly improved by annealing at high temperature. The agglomeration decreases the distance between CNT and thus facilitates the formation of conducting paths. The network formation is highly improved when increasing annealing temperature and/or time and electrical conductivities higher than 1S/m (target value for good EMI shielding) can be obtained. However, the time scale is different from the time scale observed for the formation of the rheological network. For the sample filled with 2wt.-%CNT, after 2h annealing at 125°C, the conductivity still increases. Indeed for 4h annealing, even higher electrical conductivity values are observed. On the other hand, for the same sample, G' increases only very slightly after 2000s. This can, first, be attributed to the different networks involved for rheological and electrical percolations. On the one hand, the rheological percolation is attributed to the formation of a combined network of CNT and polymer chains. On the other hand, the electrical percolation threshold is attributed to the formation of a CNT network. For the development of a conductive network, CNT must thus be close. However, the conductivity is here characterized at high frequencies (40MHz to 40 GHz). Therefore, CNT do not need to be very close. Another suggestion is that annealing before electrical characterization is performed in total absence of shear, while small oscillations are performed in the rheometer. Indeed, CNT

agglomeration is a shear-induced phenomenon [86,87]. Combined rheo-dielectrics measurements are thus required to elucidate this difference.

Note also that the conductivity increase is higher at low frequencies than at high frequencies. This can be simply explained: at low frequencies, contact or very small intertube distances are required for electrical conductivity. Clustering thus highly promotes the conductivity at low frequency. On the other hand, at higher frequencies, even in the absence of physical or “electrical” contacts, there is a capacitive coupling between CNT. The clustering has therefore a lower impact.

Finally, below a critical CNT content participating in the formation of the network, secondary agglomeration does not allow the formation of a well-conducting network. On the other hand, at high CNT content, secondary agglomeration has only small effect on the electrical conductivity, since the morphology is already closed to a percolating network. An optimum CNT loading, where the effect of annealing on the conductivity is maximized, therefore probably exists and depends on each matrix and on each initial dispersion state.

CONCLUSION

The CNT dispersion in polymer matrices is controlled by thermodynamics and kinetics.

First, according to Lifshitz theory, van der Waals interactions between CNT can be minimized by minimizing the Hamaker constant. The best CNT dispersions are observed in polymer matrices, which minimize the difference of both the dielectric constants ($\epsilon_{CNT} - \epsilon_{polymer}$) and the refractive indexes ($n_{CNT}^2 - n_{polymer}^2$) between CNT and polymer. This prediction is in good agreement with experimental results.

Second, the processing parameters governing dispersion are studied in terms of mixing energy. Increasing mixing energy by increasing mixing time, speed and/or decreasing temperature, improves the quality of the dispersion. Indeed, at low temperature and/or high screw rotation speed, the mixing torque is high and the agglomerates are disrupted and dispersed by a rupture mechanism. The extent of this phenomenon is time dependent. Therefore, at long mixing times, better dispersion is observed. However, improving the dispersion by varying processing parameters does not lead to improved RF electrical

conductivities. Indeed, increasing mixing energy results in more CNT breakage. Their aspect ratio is thus reduced, preventing the formation of a conductive network. Moreover, even for equivalent CNT lengths, the best electrical properties are not always observed for the best dispersion states.

Second, the formation of a conductive network is enhanced by annealing in the melt state. The network formation is first highlighted on rheological properties. For pure polymer, the storage modulus (G') at low frequencies increases slightly when increasing residence time in the rheometer. On the contrary, for polymer/CNT composites, G' increases sharply at the beginning of the annealing and then slightly, as the pure polymer, for longer residence times. This behaviour is reversible. After applying shear, the structure is destroyed and after annealing again, G' recovers. The characteristic time for recovery is shorter at higher temperature and higher CNT content. Annealing also improves RF conductivity. The formation of a conductive network is favoured at high temperature and for long residence time. The increase of the storage modulus and the electrical conductivity are attributed to the formation of a cluster-to-cluster network formed by the secondary agglomeration of CNT during annealing.

To get electrically conductive plastic parts it is therefore necessary to first transfer the primary CNT agglomerates in individualized CNT and then to form a conductive network of secondary agglomerates.

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Chapter 3

THERMODYNAMIC AND KINETIC PARAMETERS INFLUENCING THE LOCALIZATION OF CARBON NANOTUBES IN IMMISCIBLE POLYMER BLENDS

ABSTRACT

In the present chapter, the thermodynamic and kinetic parameters influencing the localization of carbon nanotubes (CNT) in immiscible polymer blends are studied. The CNT equilibrium position is determined by the thermodynamics and more precisely by the evaluation of the wetting coefficient. According to this coefficient, at the equilibrium, the CNT should locate in one phase (called preferred phase) or at the interface. The mixing strategy and the relative viscosities were found to have a high effect on the final morphology of the blends. When CNT are first dispersed in the preferred phase, whatever the relative viscosities, they stay well dispersed in this phase. On the contrary, when they are first dispersed in the less preferred phase, they migrate towards the preferred phase. However, total transfer can be hindered if the preferred phase presents a very high viscosity or if the less preferred phase is adsorbed in an at least partially irreversible way on the CNT surface. In these cases, a partial and even total interfacial localization CNT is observed.

Two publications have been extracted from this chapter:

- Anne-Christine Baudouin, Christian Bailly, Jacques Devaux, *Interface localization of carbon nanotubes in blends of two copolymers*, Polym. Deg. Stab. 2010; 95: 389-398
- Anne-Christine Baudouin, Jacques Devaux, Christian Bailly, *Localization of carbon nanotubes at the interface in blends of polyamide and ethylene-acrylate copolymer*, Polymer 2010; 51: 1341-1354

A publication is in preparation:

Anne-Christine Baudouin, et al. *Dispersion of CNT in immiscible polymer blends: thermodynamic vs. kinetic control*, provisional title.

INTRODUCTION

Carbon nanotubes (CNT) exhibit unique atomic structure and properties such as very high aspect ratio (1000 to 10000), high strength to weight ratio, high mechanical properties, and high thermal and electrical conductivities [1- 7]. They are thus ideal candidates for the elaboration of conductive materials. However, the elaboration of such materials still requires a significant amount of CNT. To reduce the filler content required for the production of conductive composites, CNT can be introduced into immiscible polymer blends. When dispersing CNT into blends of two or more immiscible polymers, the filler can be located either in one or both phases or at the interface. The achievement of improved electrical properties requires a co-continuous morphology and the selective localization of the CNT either at the interface or in only one phase of the blend. Therefore, many authors have studied the selective localization of CNT in a wide variety of blends. The localization of nanofillers in polymer blends is given by a competition between thermodynamic and kinetic factors [8]. The evaluation of the interactions between the surface of the particles and the polymers, through the evaluation of the wetting coefficient, predicts the equilibrium position of the nanofillers.

Selective localization of CNT

In literature, most of the authors have found a localization of unmodified CNT in agreement with these thermodynamical predictions. Pötschke et al. [9,10] have worked with composites of polycarbonate (PC), polyethylene (PE) and multiwall carbon nanotubes (MWNT). The CNT stay in the PC phase. The authors have also studied blends of PC containing CNT with PP containing nanoclay [11]. The CNT stay well-dispersed in the PC while the nanoclay migrate from PP towards the interface. Wu and Shaw [12,13] have studied composites of poly(ethylene terephthalate) (PET) filled with CNT. These formulations were then mixed with poly(vinylidene fluoride) (PVDF) or polyamide 6,6 (PA6,6). The wetting coefficients predicts that CNT should stay in PET and the experimental results confirm this prediction. Li and Shimizu [14] have studied conductive co-continuous blends of PVDF/polyamide 6 (PA6) filled with carbon nanotubes. The CNT are exclusively located in PA6. Meincke et al. [15] have studied the properties of CNT filled PA6 and its blends with acrylonitrile/butadiene/styrene (ABS). The CNT stay in the PA6 phase also creating a continuous structure. As the filler is first added in the more favourable phase, in the blends presented here above, it is not possible to determine if high aspect ratio nanoparticles are able to transport from one

phase to the other one or to the interface. More recently, Pötschke et al. [16] have presented migration of CNT from HDPE concentrates to PC and PA. The CNT are well dispersed in the PC and PA matrix and electrical percolation is achieved at lower CNT contents as compared to direct incorporation. In another paper [17], Pötschke and coworkers have introduced CNT into blends of PC and poly(styrene acrylonitrile) (SAN) by melt mixing. In all blends, even when the CNT are first dispersed in SAN, the CNT are exclusively located in the PC phase despite the minor differences in the wetting behaviour between the two phases. The electrical resistivities are lower as compared to PC and SAN with the same CNT content. The authors explain the CNT transfer based on a theoretical work given by Krasovitsky and Marmur [18] concerning the penetration of particles with different aspect ratios into a liquid drop surrounded by another liquid. They have shown that particles with very high aspect ratio exhibit complete penetration into the better wetting liquid even for very small differences in the wetting behaviour. From those theoretical calculations, Pötschke and coworkers [17] have concluded that the localization of very long particles at the interface is an instable transition state and thus highly improbable in the final blend morphology. Only particles oriented completely parallel to the interface might be jammed there. Hom et al. [19] have studied immiscible blends of PP and ethylene octene comonomer (EOC) filled with purified CNT or carbon black (CB). CNT or CB are initially melt mixed for 10 minutes with the PP and the EOC is then added and mixing is performed for 5 min more. Both CB and CNT migrate towards the EOC phase during melt-mixing, despite the higher melt viscosity of EOC than PP. The thermodynamics aspects are thus dominating the melt viscosity factor in governing the CB or CNT state of dispersion. Zhang et al. [20,21] have studied PP/PA6 blends with unpurified CNT. When the CNT are predispersed in PP, most of them are located in PA6 phase and a small amount of them are dispersed both in PP and at the interface, indicating that the CNT can migrate from PP to PA6. When the CNT are predispersed in the PA6 phase or for simultaneous blending, they preferentially locate in PA6 phase also. The selective localization of the CNT in PA6 is attributed to the high polarity and the low viscosity of the PA6 phase.

In other studies, the thermodynamic predictions are not correlated with the experimental results. Wu and Shaw [12] have studied composites of poly(ethylene terephthalate) (PET) filled with CNT. These formulations were then mixed with polypropylene (PP) or high density polyethylene (HDPE). The wetting coefficient evaluation predicts that the CNT should locate at the interface but the fraction of CNT which migrates from PET is only 7%. However, no explanation is given. More recently, Gao et al. [22] have studied

anisotropically conductive polymer composite based on carbon nanotubes as well as polycarbonate (PC) and polyethylene (PE). The composite is prepared by first coating HDPE fine particles with CNT. Then these particles are melt mixed in an extruder with PC and extruded through a slit die. Next, the extrudate is hot stretched. The PC forms aligned fibrils in a continuous PE matrix and the CNT migrate to the surface of the fibrils. The authors have found that the CNT are preferably located on the surface of the PC fibrils, although a small quantity of CNT remains in the HDPE matrix. Almost no CNT are observed in the PC phase. According to the theoretical predictions, the CNT should locate in PC. The authors claim that the difference between the observed morphology and the prediction is due to the difference of viscosity of the phases. PE presents a lower viscosity than PC. The migration of CNT from PE to PC is thus facilitated. However, the high melt viscosity of PC can prevent the CNT to penetrate inside PC. The CNT should thus be jammed at the interface.

Other authors do not examine the thermodynamical predictions to explain the localization of the CNT. Khare et al. [23] have shown that in PP/ABS blends, purified CNT are localized in the PP phase. The authors states that the lower melt viscosity of PP than ABS can probably explain the localization of the CNT in the PP phase. Ko et al. [24,25] have studied immiscible blends of poly(lactic acid) (PLA) and poly(butylene adipate-co-butyleneterephthalate) (PBAT) with pristine CNT. After compounding, CNT are selectively localized in the PBAT phase, which presents the lowest viscosity at the compounding temperature. The authors have not studied the interfacial tension between the components and no theoretical prediction has therefore been done. According to the authors, the selective dispersion of CNT is related to the affinity of the CNT with the PBAT, which presents a chemical structure with aromatic molecules.

Finally many research teams have focalized on the localization of functionalized CNT in polymer blends.

Zou et al. [26] have studied the morphology of poly(phenylene sulfide)/polyamide 6,6 blends with various amounts of acid treated CNT. CNT are preferentially located in the PA6,6 phase. Shen et al. [27] have studied the influence of different functionalized CNT on the morphology of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) / PA6 blends. Functionalized (CNT-OH, CNT-NH₂, CNT-COOH) and unfunctionalized CNT are exclusively located in the PA6 phase. Li et al. [28] have made hybrid nanocomposites of PP and ultra high molecular weight polyethylene (UHMWPE) with CB and carboxylated CNT.

They show that CB particles are selectively localized at the interface of the blend. A synergy between CB and CNT is moreover observed. The CNT are well dispersed in PP and a network is formed between the CNT and CB particles.

Functionalized CNT are also used to achieve an interfacial localization of the CNT. In that context, Bose et al. [29,30] have elaborated blends of PA6 and ABS in the presence of styrene-maleic anhydride copolymer (SMA) and CNT. The CNT are chemically coupled to the SMA, which tends to locate at the interface. Therefore, the CNT are localized at the interface. In another paper, Bose et al. [31] have studied the dispersion of CNT in co-continuous PA6/ionomers blends. Depending on the mixing sequence, Na salt of 6-amino hexanoic acid (Na-AHA) modified CNT are locked at the interface of the PA6/ionomers blends due to specific interactions between the CNT and both polymers. The same modified CNT have also been dispersed in co-continuous blends of PA6 and ABS [32]. The CNT are uniformly and selectively dispersed in the PA6 phase and led to significant refinement of the co-continuous structure. Liu et al. [33-36] have elaborated polypropylene (PP) / ethylene-co-vinyl acetate (EVA) blends with maleic anhydride functionalized carbon nanotubes (CNT-g-MA). The CNT-g-MA distribute at the interface in blends exhibiting a sea-island morphology while most of them distribute in the EVA phase and some of them span the two phases for co-continuous morphology. The blending sequence is shown to strongly influence the CNT-g-MA localization. When the ternary blends are made by dilution of a PP/CNT-g-MA, the CNT-g-MA are mainly localized in the PP matrix, where their distribution is poor. A few CNT-g-MA are also observed in the EVA phase. When the ternary blends are made by using EVA/CNT-g-MA, the CNT-g-MA are mainly localized in the EVA phase. Wu et al. [37] have studied immiscible poly(ϵ -caprolactone) (PCL) / polylactide (PLA) blend with functionalized CNT. Although a large part of the CNT is selectively localized in the PCL phase, part of them is confined at the interface due to good affinity of the carboxylic groups present on the CNT surface with both PCL and PLA. In the same conditions, no interfacial confinement is observed for unfunctionalized CNT. Lim et al. [38] have prepared ternary systems of poly(styrene-co-acrylonitrile) (SAN), poly(vinyl chloride) (PVC) and CNT using solution mixing and the SOAM (solution mixing and melt blending) method. The CNT are functionalized using an acid treatment. In agreement with the thermodynamical predictions and although it is not clear from the SEM and TEM micrographs presented, the authors state that CNT are located at the interface between both phases and lead to improved mechanical properties. Finally, Bose et al. [39] have used the phase separation of poly[(α -methyl styrene)-co-acrylonitrile]/poly(methyl methacrylate) (P α MSAN/PMMA) to

control the dispersion of amine functionalized CNT (NH₂-CNT) in the composite. The NH₂-CNT are distributed randomly in the homogeneous blend. After complete phase separation, the NH₂-CNT are relatively well dispersed and mainly present in the PαMSAN phase. This is in good agreement with thermodynamic predictions. Some NH₂-CNT are however present at the interface of the blend. This interfacial confinement is attributed to the reaction between the NH₂-groups on the CNT surface and the –O-C=O groups of PMMA.

Migration mechanisms

Although the localization of particles in polymer blends is extensively described in literature, the mechanisms allowing particles to migrate from one phase to another are not widely discussed. Elias et al. [40] and Fenouillot et al. [8] have given a qualitative discussion on these mechanisms. The migration of particles first implies that the particles approach the interface. According to these authors, at least three mechanisms can be involved: the Brownian motion, the particles movement induced by shear and the trapping of particles in the inter-droplet zone during collisions between dispersed drops. The Brownian motion is a self diffusion mechanism of the particles, since it does not require shear. However, the time required for migration is usually not compatible with the standard mixing times of a few minutes. The high viscosity of the molten polymers is thus believed to hinder the particle motion by Brownian motion. The second possible mechanism is the particle motion induced by shear. The inorganic particles and dispersed phase droplets are moving into the matrix and collisions occur between them. The particles are subjected to a high number of collisions with the drops. Moreover, the solid particles are very small and rigid. The drainage of the polymer matrix film trapped between the droplet and the particle is therefore easier than for the collision between two polymer droplets [41] or for the collision between a large particle and a droplet [42]. Considering this latter remark and the high collision frequency, we can assume that the particle movement induced by the shear is one of the dominant mechanisms in particle migration. The situation where the particles are initially dispersed in the polymer droplets and move towards the matrix is almost not described in the literature. However, some authors [40,43] show that there is a velocity field inside the dispersed phase droplets allowing the particles to migrate. Finally a third mechanism, proposed by Fenouillot et al. [8], is the trapping of particles in the inter-droplets region during droplets collisions. In this mechanism, the particles are transferred inside one phase during coalescence. The efficiency of this mechanism is linked to the size and

the deformability of the droplets. Highly deformable droplets should trap more easily the particles.

Objective and strategy

The above mentioned literature survey illustrates the abundant research done on the dispersion of CNT in immiscible polymer blends. Despite this abundance, there is no clear consensus concerning the parameters governing the localization of CNT in immiscible polymer blends. Moreover the interfacial confinement of unfunctionalized CNT is described as almost impossible [17]. The objective of this chapter is therefore to present a comprehensive study of the parameters governing the localization of CNT in immiscible polymer blends. A special attention is also dedicated to the selective localization of CNT at the interface of two immiscible blends.

For this purpose, the morphology of various immiscible polymer blends filled with CNT is first studied.

The first system has been selected based on the thermodynamic prediction of CNT localization. It is a system based on a matrix of ethylene-acrylate copolymer (EA) and a dispersed phase of polyamide (PA). As the morphology is promising, different dispersed phases are used while keeping the same matrix. First, different PA are used to assess the influence of small modifications of the dispersed phase on the morphology. A PA presenting a very low viscosity is also used to determine the influence of the viscosity on the morphology. Next, as the dispersion of CNT in polycarbonate (PC) is excellent, PC is used as minor phase. Finally, polymers presenting an aromatic ring in their backbone (poly(ethylene terephthalate) and poly(butylene terephthalate)) are used as dispersed phases.

In a second step, the matrix is slightly modified: ethylene vinyl acetate copolymer (EVA) and a random terpolymer of ethylene, acrylic ester and maleic anhydride (MAEA) are used. Besides the slight difference of structure compared to EA, this latter polymer introduces a new parameter since it can react with PA to form copolymer at the interface.

In these two first steps, very similar systems, with an ethylene-based matrix, are used. The third step therefore implies the use of totally different systems, exhibiting different affinities for the CNT. First, blends of PC and poly(ether sulfone) are used because, due to the presence of aromatic rings, both polymers present a high affinity for CNT. Next, a blend of PP and PA is used to extend the results to a commodity polymer, in which the dispersion of the CNT is bad.

Third, a blend of PC and PA6, in which reactions occur between both polymers is used. Finally a blend of PA and EA is studied, in which PA forms the matrix and EA the dispersed phase to check if the CNT are also able to migrate easily from the dispersed phase.

The thermodynamic predictions associated with all these systems are exposed. The differences between the experimental results and the thermodynamic predictions are discussed. The observed differences are explained by kinetic factors: mixing strategy and polymer adsorption, as well as relative viscosities of the phases. A general mechanism for the localization of CNT in immiscible polymer blends is finally proposed, which takes into account the competition between thermodynamic and kinetic effects.

EXPERIMENTAL PART

This is a very brief description of the materials and characterization methods used. For more details, please refer to Appendix 1.

1 Materials

The blends under study are composed of polymers that are fully immiscible at the start. The different polymers used are listed here below:

- *Ethylene-based copolymers*: EA: ethylene-acrylate copolymer; EVA: is a random copolymer of Ethylene and Vinyl Acetate; MAEA: random terpolymer of Ethylene, Acrylic Ester and Maleic Anhydride
- *Polyamides*: PA4/6, PA6, PA6/12, PA12, PA* (very low viscosity PA)
- *Others*: PP: polypropylene; PC_m: polycarbonate medium viscosity; PC_l: polycarbonate low viscosity; PES: Poly(ether sulfone) Cl terminated; PET: poly(ethylene terephthalate); PBT: poly(butylene terephthalate)

The CNT are unpurified and unfunctionalized with a minimum purity of 90%.

2 Blends preparation

2.1 *Kinetic study*

A kinetic study of the morphology has been realized on some systems: EA/PA6 and EVA/PA6. The introduction of the polymers and CNT into the mixing device takes around 1 minute. When it is fully introduced, a first sample is removed (labeled 0min). Then after 30s, 1min30s, 3min30s and 5 min, other samples are removed from the compounder. The other preparation parameters are a mixing temperature of 240°C and a mixing speed of 50 rpm.

2.2 *Multilayer experiment*

EA+1wt.-%CNT is hot pressed at 100°C and PA6 at 240°C to form two films of about 1 mm thickness. These films are then annealed in the press for 1h at 240°C on top of each other to form a multilayer.

3 Characterization

3.1 *Microscopy*

The samples are characterized by microscopy techniques: TEM on ultrathin sections of 95 nm in thickness and SEM on cryofractured surfaces. Optical microscopy on 1µm thick slices is also performed.

3.2 *Rheology*

The viscosity of the polymer at the compounding temperature is assessed using plate-plate rheology. The polymers are analyzed under nitrogen in the linear viscoelasticity range. Frequency sweep experiments are conducted in the frequency range of 0.1-600 rad/s with either 1 or 5% deformation. The thermal stability of the EVA is analyzed using the multiwave-frequency option. The fundamental frequency is 0.1 rad/s with 5% deformation plus two additional wave forms at 1 rad/s with 1.5% and 10 rad/s with 0.5% respectively.

3.3 Extraction of the CNT

CNT have been extracted from the composites using a Soxhlet device or by filtration and then analyzed by Thermogravimetry Analysis (TGA).

3.3.1 Soxhlet

A Soxhlet device has been used to extract the CNT from the composite EA+2wt-%CNT. The extraction has been performed using chloroform at 65°C. Two different extraction durations have been used: 24hours and 5 days. A control Soxhlet has also been performed with pure polymers for 5 days.

3.3.2 Filtration under pressure

The PA6+2wt-%CNT composite is first dissolved in 1 volume of formic acid at room temperature. Next, the solution is sonicated for 2hours. The solution is next filtrated at room temperature. . The suspension is next rinsed with either 2 volumes of solvent (PA6+2wt-%CNT (2rinses)) or 10 volumes of solvent (PA6+2wt-%CNT (10rinses)). In both cases, 2 volumes formic acid is poured in the under pressure filtration device and no pression is applied for 15min. Next, a pressure of 1 bar is applied to ensure a slow filtration. For PA6+2wt-%CNT (10rinses), these operations are repeated 5 times. After rinsing, the aluminium oxide membrane is rinsed with demineralised water and dried. A solution of pure PA6 in formic acid is also filtrated in similar conditions (10 rinses).

The PA12+2wt-%CNT composite is dissolved in m-cresol at room temperature and the same strategy is applied. A reference of pure PA12 with 10 rinses is also made.

3.4 Decantation tests

The nanocomposites PA6+2wt-%CNT and PA12+2wt-%CNT are dissolved in m-cresol (20mg in 40ml) at room temperature. For comparison, as produced CNT are milled during 30 minutes with the help of a vibrating mill. Next, these CNT are next also dispersed in m-cresol at room temperature. All the suspensions are next sonicated during 2h in m-cresol, followed by centrifugation at 13400 rpm during different times.

RESULTS AND DISCUSSION

The CNT are first dispersed in one polymer. This composite is then blended with another polymer to form an immiscible blend. The dispersion of the CNT in the different matrices used here is presented in Chapter 2. The CNT form large aggregates in PP. They are quite well dispersed in the ethylene – based matrices (EA, EVA, MAEA). The dispersion in PA matrices is, on the whole, rather good, although some differences are observed. The CNT are well and homogeneously dispersed in PA6, PA6/12 and PA12. The dispersion in PA4/6 and PA* is less homogeneous. This is linked to the very low torques encountered during processing these PA because of their very low viscosities at the compounding temperature. Finally, the CNT are very well dispersed in PC_m, PC_i and PES.

The single-phase composites presented in Chapter 2 are mixed with another polymer to form immiscible polymer blends. The different parameters influencing the localization are presented. First the equilibrium position is predicted based on thermodynamic considerations for the minimization of interfacial energy. Second, the influence of mixing strategy is exposed. However, this parameter is present in all parts of this work since it cannot be decoupled from the other effects. Next, the effect of the relative viscosities of the phases is analyzed. Finally a general mechanism explaining the observed morphologies is proposed.

1 Morphology of immiscible blends containing CNT

The morphology of different blends is first presented. First an ethylene methyl acrylate copolymer (EA) matrix is chosen and different dispersed phases are used. Second, different matrices based on ethylene copolymers (EVA, MAEA) are used. Finally blends based on other matrices (PP or PC) are studied.

For each system, two compounding methods are used: the predispersion of the CNT in the main phase of the blends, which forms the matrix, and their predispersion in the minor phase, which forms the droplets in the blend.

1.1 EA as matrix: influence of changing droplets phase

First an ethylene – methyl acrylate copolymer (EA) is used as the matrix and different droplets phases are used: PA, PC, PET, PBT.

1.1.1 EA/PA blends

First the morphology in the absence of a shear field is presented. Then the morphology obtained during mixing in the melt is described.

a. In the absence of a shear field

A multilayer experiment in the absence of shear was first performed. Figure 1 presents the morphology obtained after annealing 1h at 240°C EA+1wt.-% CNT in contact with PA6. There was no adhesion between the two polymers. Therefore, when cutting the sample, both phases were separated. The left part of the figure presents the PA6 phase where no CNT is present. On the right part, CNT are exclusively agglomerated in the EA phase. No CNT accumulation at the interface is observed. In the absence of shear, no migration of the CNT towards the interface is observed even for long times at high temperature.

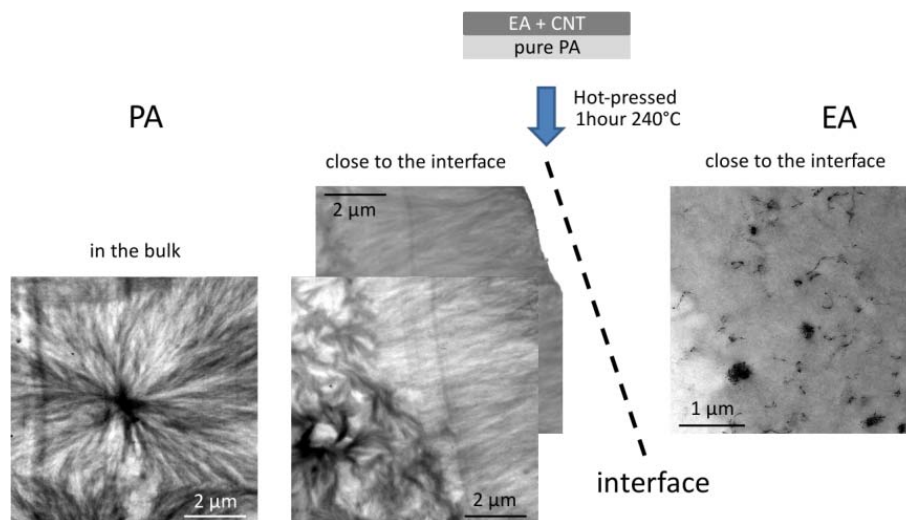


Figure 1 – Morphology of EA+1wt.-% CNT hot pressed for 1hour at 240°C on pure PA6 (without shear): on the left: PA side, on the right, EA+1wt.-% CNT side

In the absence of shear, the only mechanism that can be involved in the CNT migration is the Brownian motion. For isotropic particles of size a , the time for a particle to migrate on a distance equal to its radius in a polymer matrix of viscosity η and at a temperature T is expressed as t_D :

$$t_D = \frac{6\pi\eta a^3}{k_B T}$$

Thus in our case, a rough estimate ($\eta=2.10^3$ Pa s, $T=513$ K) gives a diffusion time of the order of 5 s for $a \approx 10$ nm and of 5300 s for $a \approx 100$ nm. The time for a CNT to move towards the interface is therefore very long. The migration of the CNT can thus not occur under static conditions. This conclusion is in agreement with the results reported for nanosilica particles [44].

The localization of CNT in immiscible polymer blends is thus not attributed to the migration of CNT, but is mainly a consequence of the convection of molten polymer chains during melt blending, which can induce contacts between CNT and their preferred localization. However, for simplicity, we refer to “CNT (apparent) migration” in this manuscript.

b. In the presence of a shear field

Figure 2 and Figure 3 present the TEM micrographs of blends of EA, various PA and CNT (90wt.-%EA-10wt.-%PA). A morphology of PA droplets dispersed in the EA matrix is observed.

Figure 2 presents the morphology observed when the CNT are dispersed in the EA phase before mixing with the different PA ((EA+CNT)-PA). In all blends, CNT are mainly localized at the interface while some of them remain in the matrix. However, for PA6/12 and PA12 as dispersed phase, a part of the CNT partially penetrates inside the PA droplets as presented in Figure 2 c and d. Moreover, when a polyamide with a very low viscosity is used (PA*) as the dispersed phase, some CNT penetrate inside the PA phase (Figure 2e). The interfacial localization is also presented on SEM micrographs in Figure 4a,c,e for PA6, PA6/12 and PA12 respectively. These micrographs present cryofractures of the blends and CNT are clearly present on the droplets surfaces.

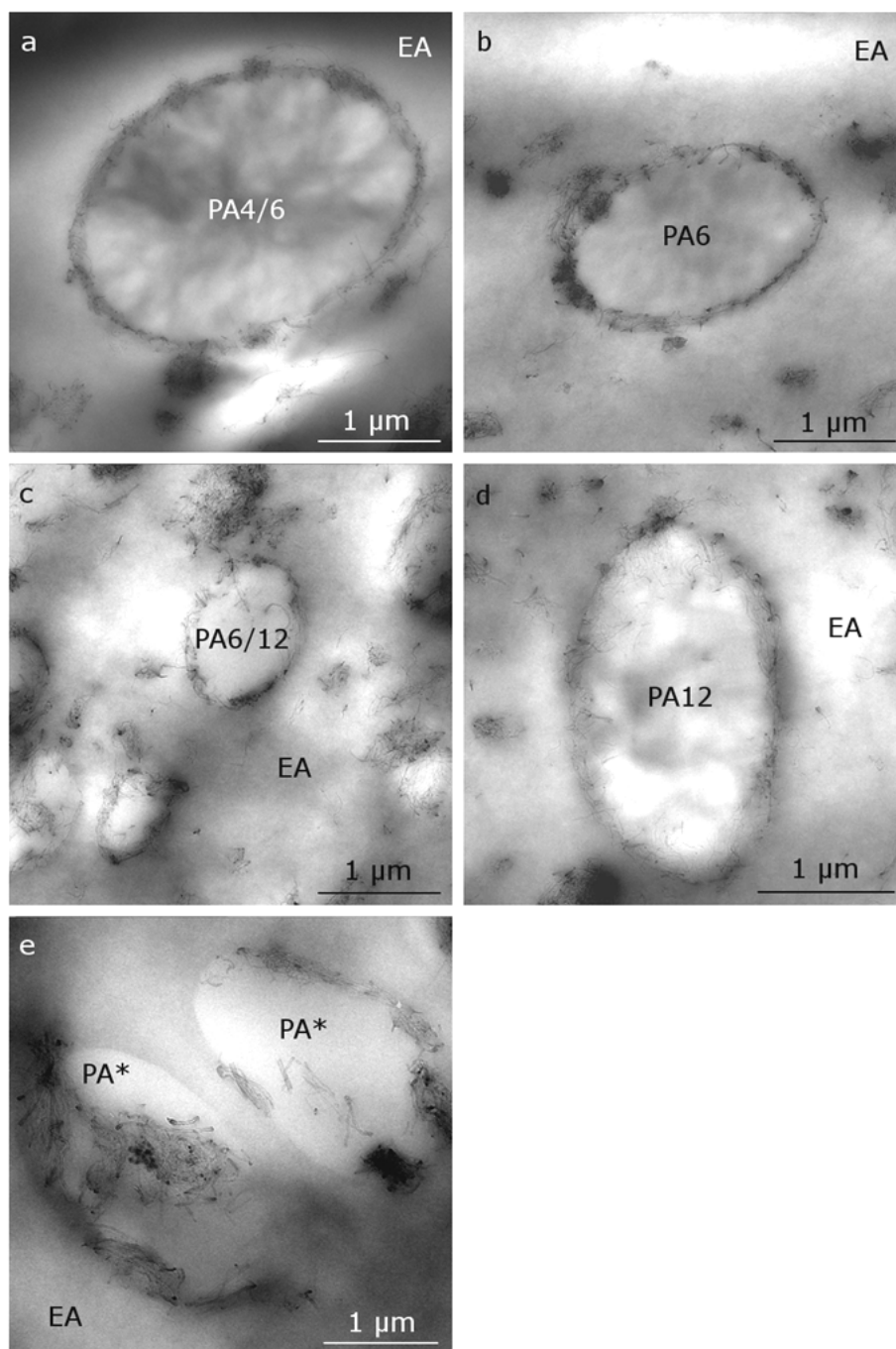


Figure 2 – TEM micrographs of the predisposition of CNT in the EA phase before mixing with different PA ((EA+CNT)-PA): (a) PA4/6; (b) PA6; (c) PA6/12; (d) PA12; (e) PA*

Figure 3 presents TEM micrographs of blends, in which the CNT are predispersed in the PA dispersed phase ($EA-(PA+CNT)$). When the CNT are predispersed in the PA droplets, different behaviors are observed depending on the PA used. When the CNT are predispersed in PA4/6 or PA6, they migrate towards the interface but remain inside the PA droplets. SEM micrograph of cryofractured samples highlights this behaviour for PA6 (Figure 4b). White spots corresponding to CNT are visible on the surface of the nodule. However, there is no CNT in the cavity remaining in the EA matrix after the cryofracture. Thus, although the CNT are at the interface of the blend, they are more embedded in the PA6 phase and no CNT is present in the EA matrix. When CNT are predispersed in PA6/12, PA12 or PA*, they remain dispersed in this phase and their dispersion state is similar to the dispersion state observed in the homogeneous matrix of these polymers. This is also clear on the SEM micrographs presented in Figure 4d,f. No CNT is pulled out of the interface or in EA, indicating that the CNT are localized in the PA droplets. Note that PA4/6 presents two different droplets population: there are very big droplets, where CNT are present at the interface and in the dispersed phase and smaller droplets, where the CNT are mainly located at the interface (Figure 5).

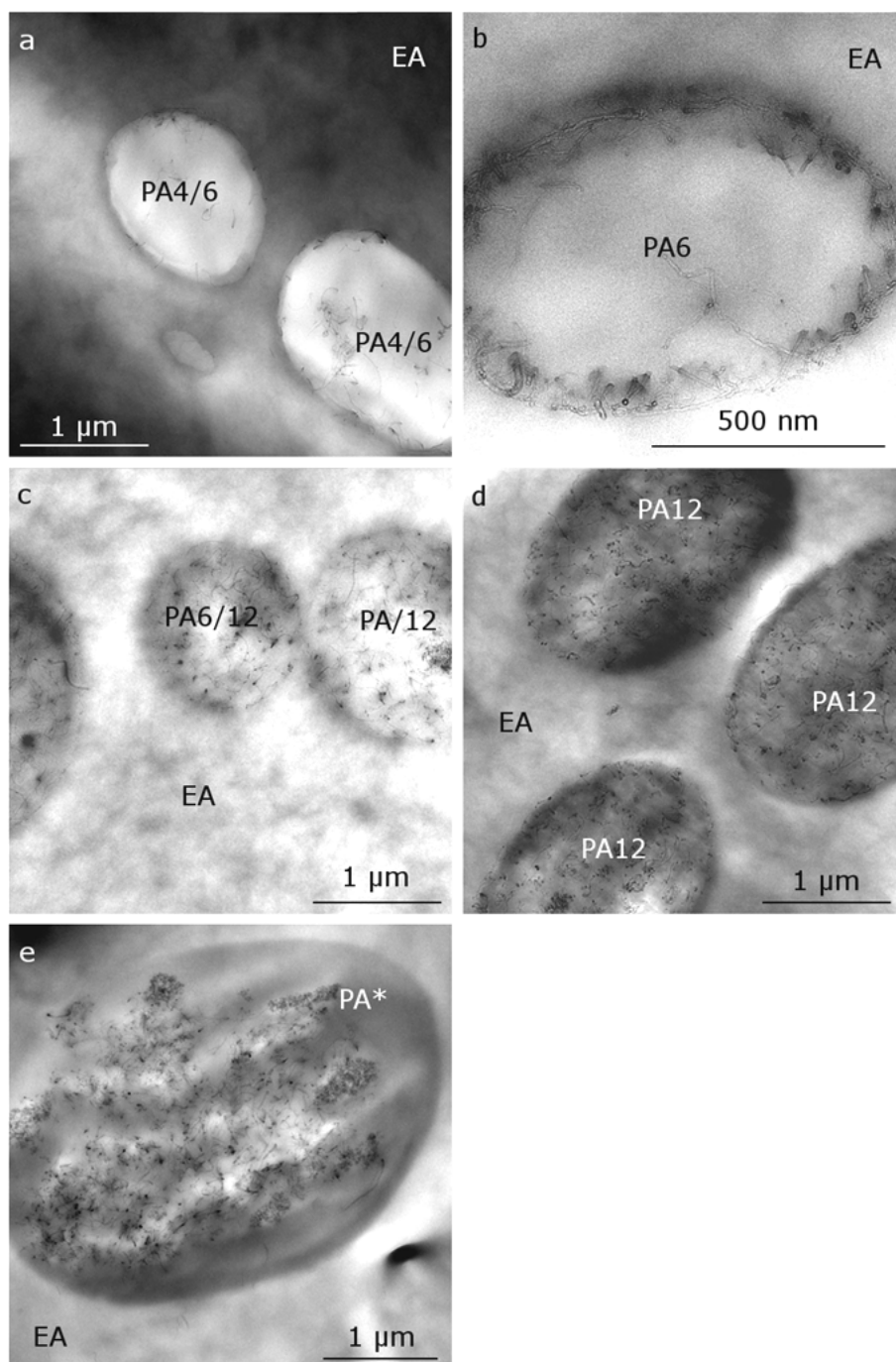


Figure 3 – TEM micrographs of the predispersion of CNT in PA phase (a) PA4/6; (b) PA6; (c) PA6/12; (d) PA12; (e) PA*; before mixing with the EA matrix

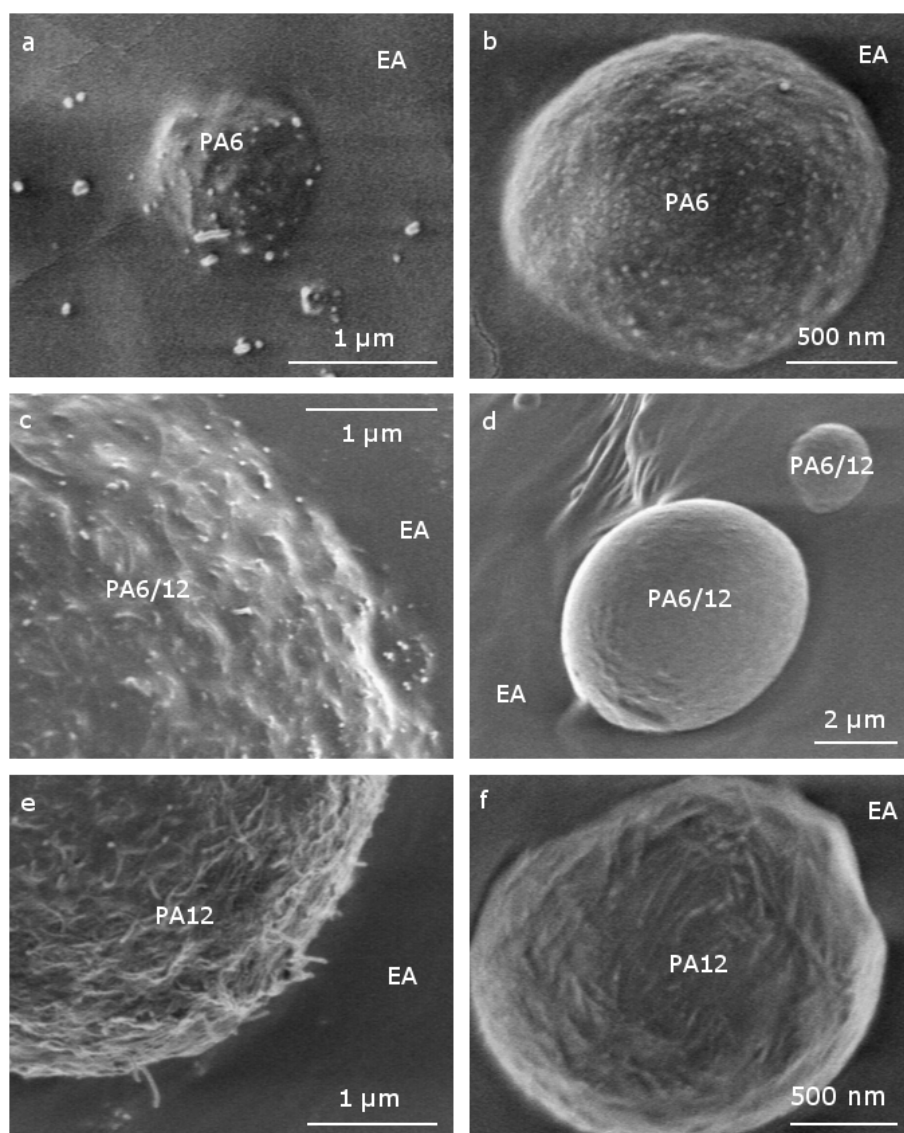


Figure 4 – SEM micrographs of blends of EA with various PA : (a, c, e) Predispersion in EA; (b, d, f) Predispersion in PA6, PA6/12, PA12

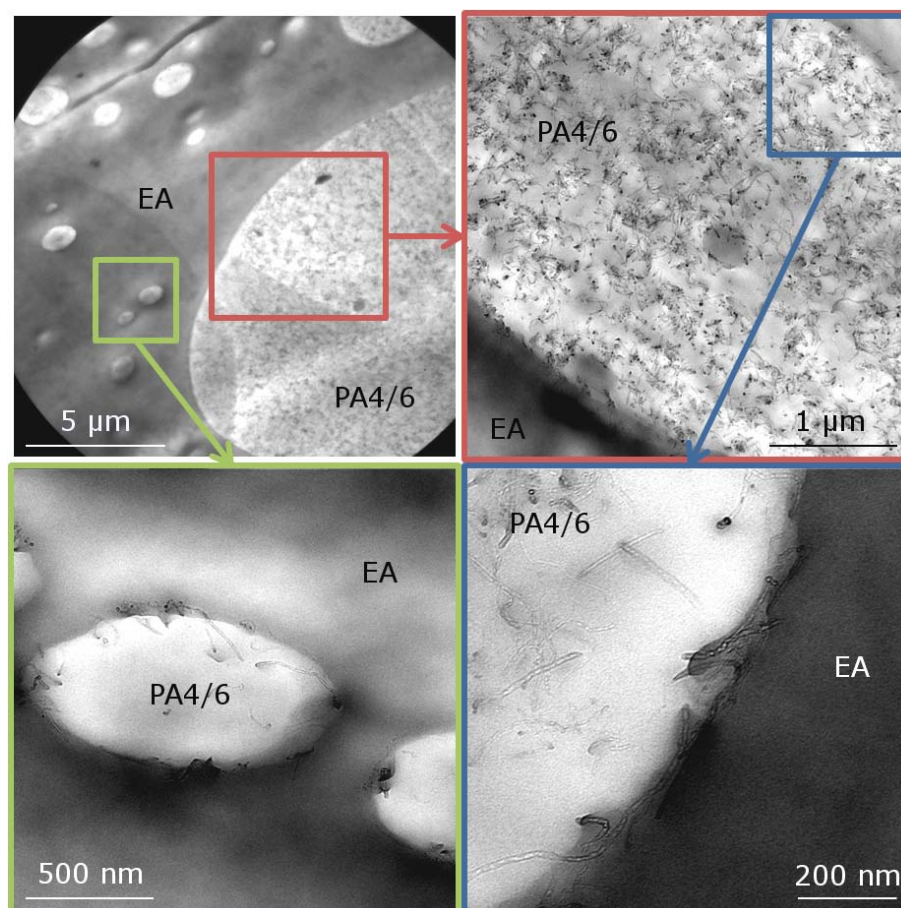


Figure 5 – TEM micrographs of the blend EA-(PA4/6+CNT)

It is also worth noting that the migration occurs very fast and is stable for long mixing times (at least 60 min). A kinetic study is presented in Figure 6 for EA/PA6 blends. The TEM micrographs show that the interfacial confinement of the CNT occurs very fast. The time to fill the compounder is about 1 minute. If the blend is immediately removed from the compounder after total filling, the CNT are already localized at the interface (Figure 6a). Moreover, the localization appears to be stable for long mixing time (at least 60 min), indicating that the localization of CNT at the interface is not a transitory state. Note finally that the interfacial confinement of the CNT is also stable when the CNT are predispersed in the PA6 phase. Figure 7 presents the morphology of a blend EA/PA6, in which the CNT were predispersed in the PA6 phase. After 60 min compounding, the CNT are still jammed at the interface of the blend, indicating that this position is very stable. For PA4/6, PA6, PA6/12 and PA12 and whatever the blending strategy used, the morphology obtained after 60

min is the same as the one presented here for 10 min. The interfacial confinement of the CNT is thus not a temporary state before migration towards the other phase. Further processing will not change the CNT selective localization.

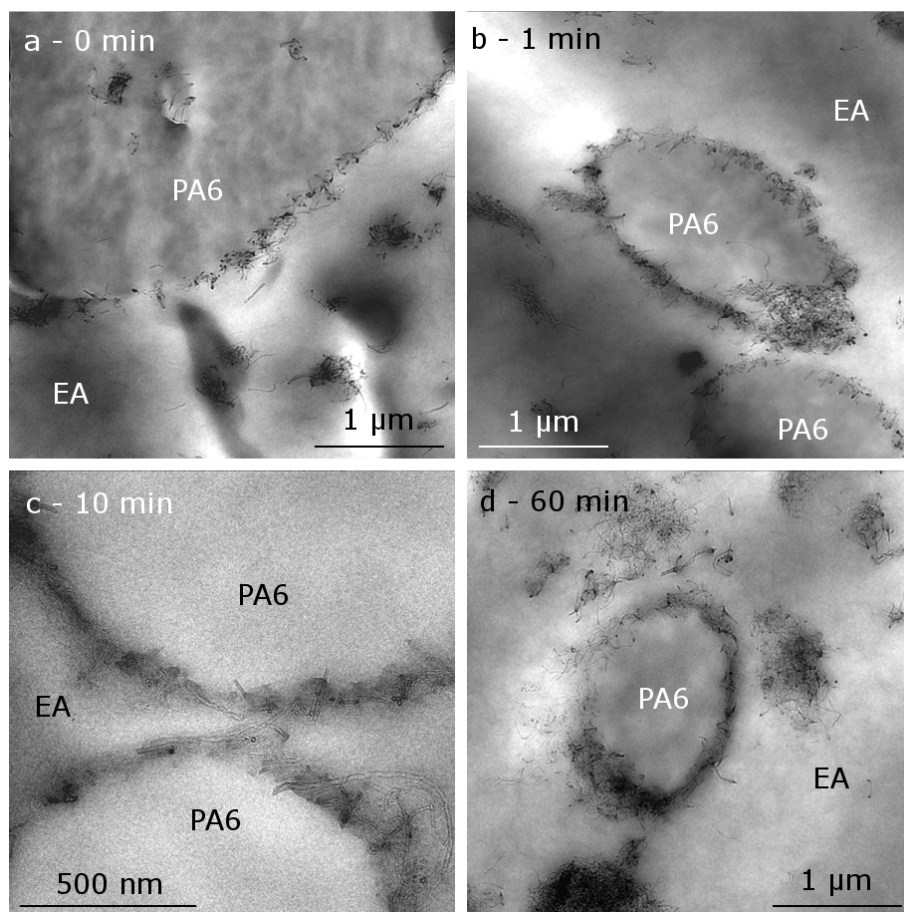


Figure 6 -Evolution of the CNT localization in EA/PA6 immiscible blends for different mixing times: (a) 0 min, (b) 1 min, (c) 10 min, (d) 60 min

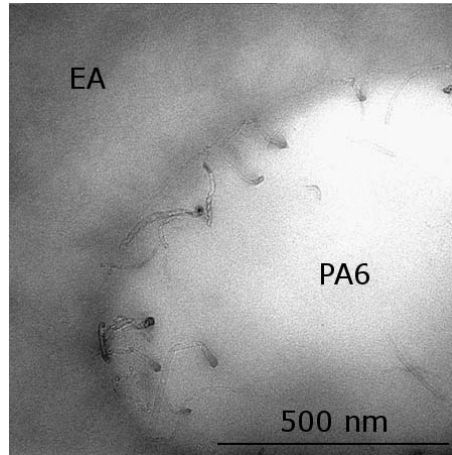


Figure 7 – TEM micrograph of of the predisposition of CNT in PA6 phase before mixing with the EA matrix for 60 min

1.1.2 EA/PC blends

Two different PC are used: PC_m presenting a medium viscosity and PC_l presenting a low viscosity. When the CNT are first dispersed in EA, they mainly migrate towards the interface of the blend (Figure 8 and Figure 10a), whatever the PC used. On the contrary, when the CNT are predisposed in the PC, they remain well-dispersed in the droplets (Figure 9 and Figure 10b).

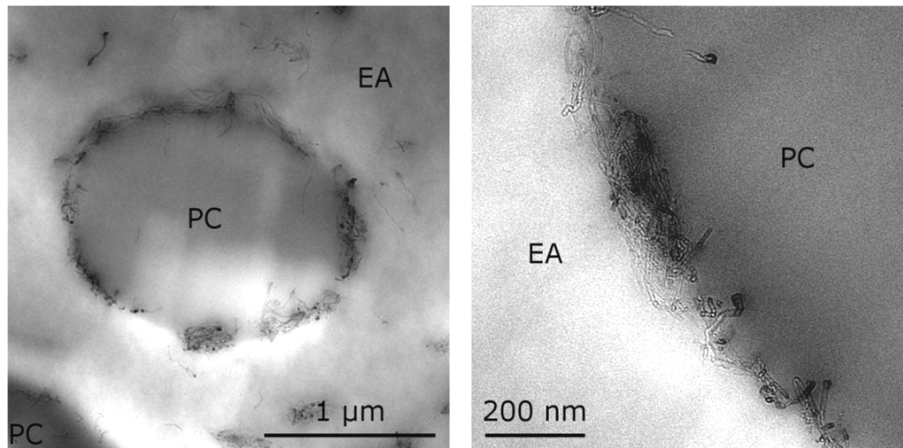


Figure 8 – TEM micrograph of the predisposition of the CNT in EA phase before mixing with PC_m : (EA+CNT)- PC_m

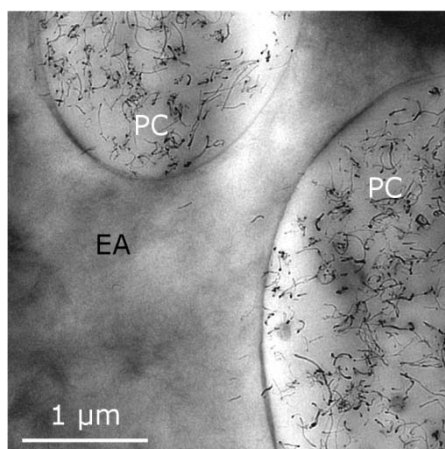


Figure 9 – TEM micrograph of the predispersion of the CNT in PC_m phase before mixing with EA matrix: EA-(PC_m+CNT)

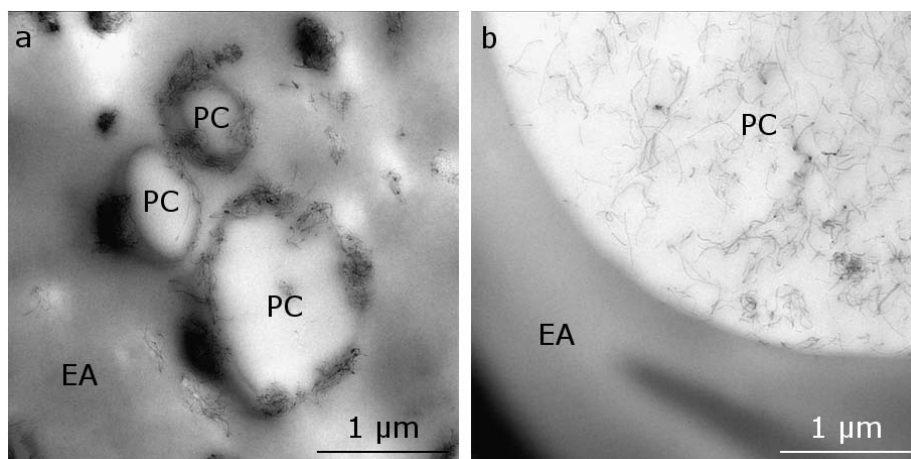


Figure 10 – Blends of EA, PC_i and CNT (a) Pre-dispersion of CNT in EA ((EA+CNT) - PC_i), (b) Pre-dispersion of CNT in PC_i (EA - (PC_i+CNT))

1.1.3 EA/PET and EA/PBT blends

Finally, the behaviour of the CNT for EA/PET and EA/PBT is presented in Figure 11. For both dispersed phases, when the CNT are premixed with EA, some of them migrate towards the interface of the blend while many of them remain in the EA phase. For these blends, the droplets are not as well covered by CNT as for PA or PC dispersed phases. Moreover, when PET is used as the dispersed phase, CNT partly penetrate inside the PET. It is also worth noting that thermal degradation can happen during processing at 280°C and therefore modifying the system. Thermal degradation of PBT was recorded between 240° and 280°C. A mechanism of chain scission occurs, followed by elimination of butadiene [45]. PET is also subject to various types of degradation during

processing. The main degradation mechanisms that can occur are hydrolytic, thermal and, probably most important, thermal oxidation.

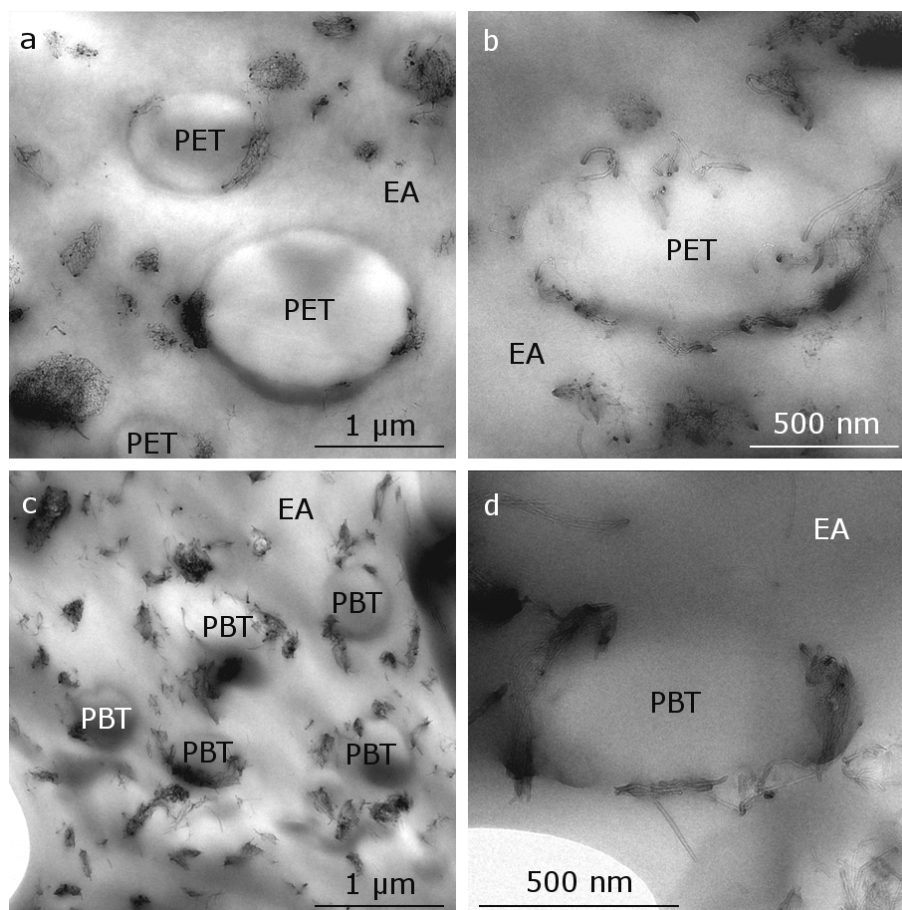


Figure 11 – TEM micrographs of CNT predispersed in EA before mixing with (a,b) PET and (c,d) PBT

1.2 Ethylene – based copolymers as matrices: influence of different matrices

In the previous section, it is shown that the interfacial confinement of CNT can be obtained when using ethylene – methyl acrylate copolymer (EA) as matrix for the blends and different polymers as dispersed phase. It is important to see how slight changes in the matrix composition affect the morphology. Other ethylene – based copolymers are thus used as matrix. The first studied system is based on ethylene-co-vinyl acetate (EVA). The second system is based on a random terpolymer of ethylene, ethyl acrylate and maleic anhydride (MAEA).

1.2.1 EVA – based systems

Figure 12 presents the morphology observed for blends of EVA/PA6/CNT (Figure 12 a,b) and for blends of EVA/PC/CNT (Figure 12c,d). When CNT are predispersed in EVA, they mainly migrate towards the interface for both PA6 and PC (Figure 12a,c). However, at the interface they are mainly present in the form of large agglomerates and the droplets are not well covered. When CNT are mainly predispersed in the droplet phase, either PA6 or PC, they remain in the dispersed phase and tend to agglomerate inside the droplets (Figure 12b,d). When PA6 is the dispersed phase, some CNT are observed at the interface of big droplets. Moreover, very small PA6 droplets are observed in the blend and for these droplets, CNT are essentially located at the interface (Figure 12b).

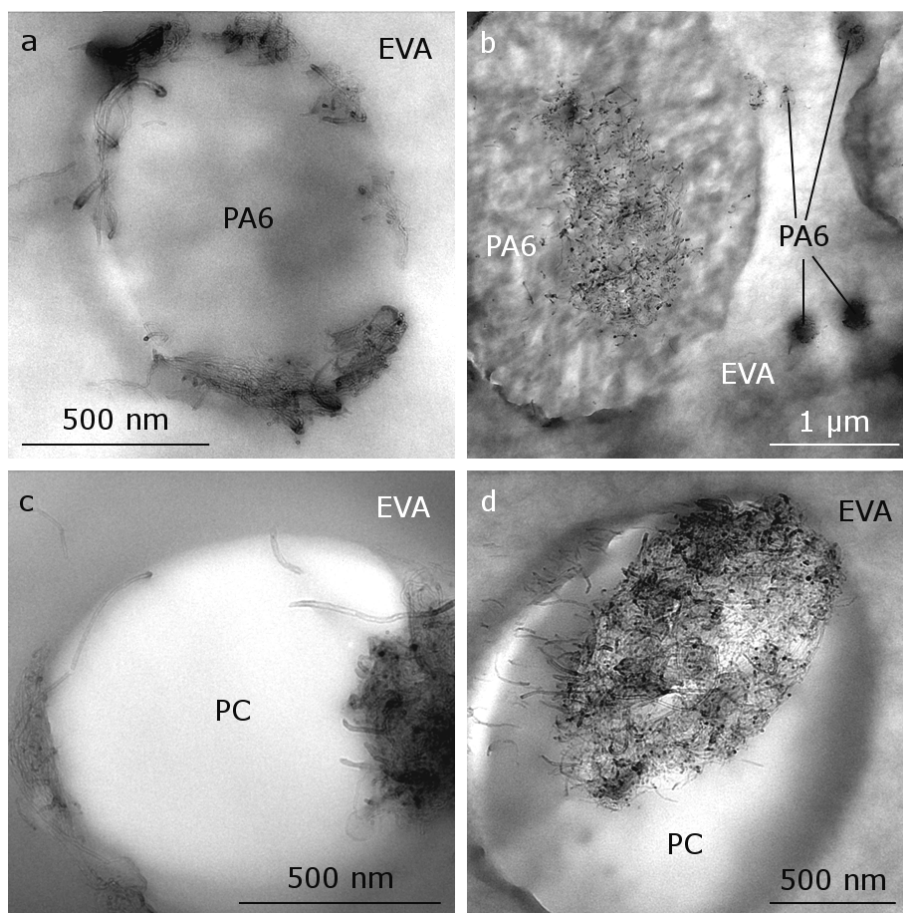


Figure 12 – TEM micrographs of EVA/PA6/CNT and EVA/PC/CNT blends (a) (EVA+CNT)-PA6; (b) EVA-(PA6+CNT); (c) (EVA+CNT)-PC; (d) EVA-(PC+CNT)

The behaviour observed in Figure 12 is unusual and can only be explained by chemical modification of the blend occurring during mixing. The degradation of EVA at high temperature is a well-known phenomenon. The thermal degradation is a two step process with the first step starting at ca. 150°C but speeding up significantly at ca. 190°C. The first step is due to the loss of acetic acid and the second step is assigned to main chain cleavage. The deacetylation of EVA is catalyzed by acetic acid [46]. Polymer chain extension and crosslinking can also occur (Figure 13) [46]. The thermal degradation of EVA is brought to light in Figure 14. When compounded at low temperature, EVA is not degrading but when compounded at higher temperature, some unwanted crosslinking occurs during the extrusion time, which is highlighted by rheological measurements (Figure 14). A multiwave frequency time sweep was performed at the different compounding temperatures: 100°C, 240°C and 280°C. The changes in molecular structure are known to be particularly visible at low frequencies. From Figure 14, presenting the evolution of the storage modulus, we can conclude that there are no or very little chemical changes linked to thermal degradation during the experimental time at 100°C. On the contrary, at 240°C and even more clearly at 280°C, the elastic modulus is increasing when increasing compounding time. This effect is particularly visible at low frequency, confirming the unwanted crosslinking.

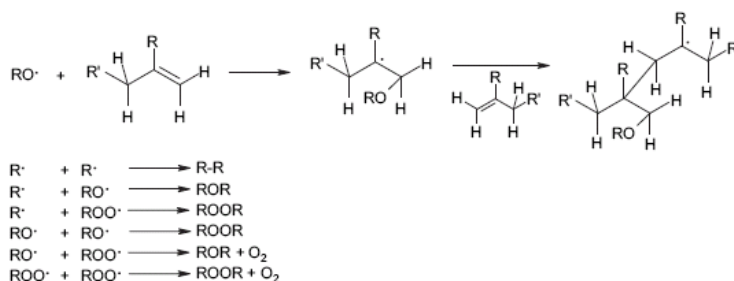


Figure 13- Chain extension, crosslinking and combination mechanisms [46].

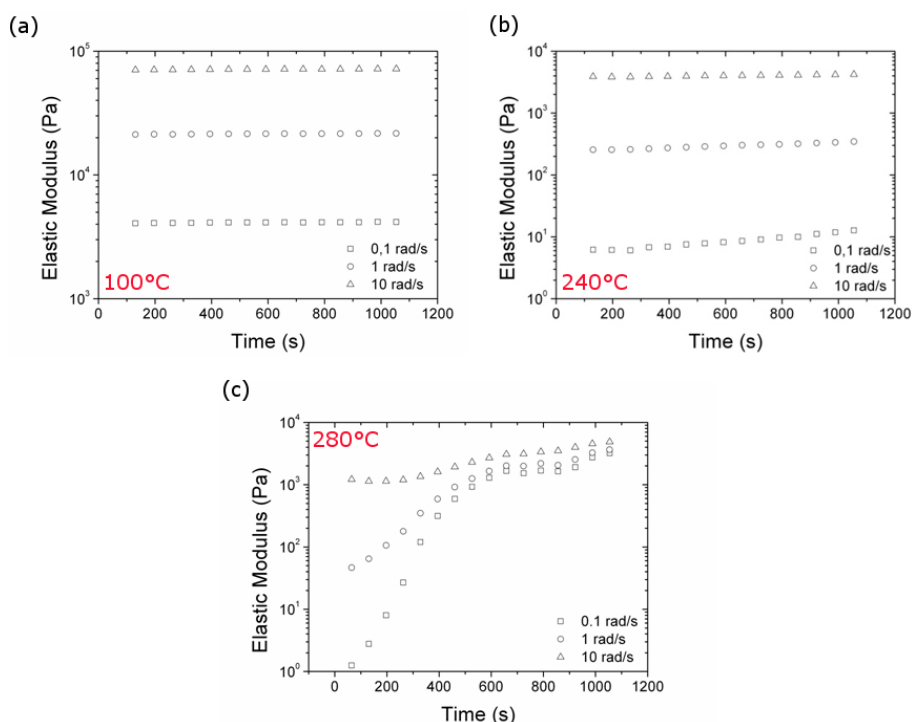


Figure 14 – Time evolution of G' for different frequencies (0.1 rad/s, 1 rad/s and 10 rad/s) at (a) 100°C ; (b) 240°C ; (c) 280°C

Moreover, in the melt, the acetic acid produced by the deacetylation of the EVA cannot escape. It therefore promotes the degradation of PA and PC by chain scission. These reactions could explain the agglomeration of CNT in the dispersed PA6 and PC phase when mixing 10 minutes at high temperatures (240°C and 280°C).

Moreover, when processing at high temperature, the good dispersion of the CNT in ethylene – based matrices can be altered as it is observed for EVA in Figure 15. After mixing 15 minutes at 100°C, the CNT are initially well dispersed but after compounding 10 minutes more at high temperature (240°C or 280°C), they spontaneously form aggregates. The agglomeration at high temperature can occur because of the matrix degradation or due to secondary agglomeration. Indeed, Pegel et al. [47] showed that CNT initially well dispersed in PC form agglomerates when a subsequent mixing step at higher temperature is performed. Whatever its origin, the agglomeration at high temperature explains the presence of CNT in the form of large aggregates at the interface of the blends when they are premixed with EVA.

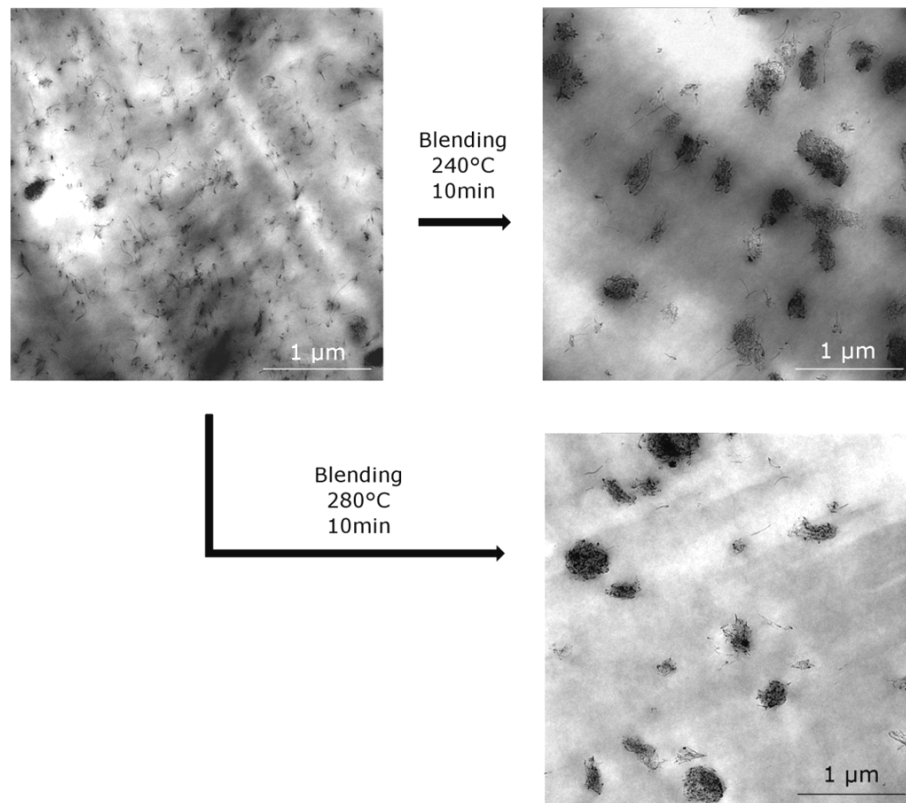


Figure 15 – Dispersion of CNT in EVA (100°C, 15min) followed by mixing at 240°C for 10 minutes or 280°C for 10 minutes

To check the influence of the EVA degradation on the morphology, the evolution of the morphology with mixing time for the EVA/PA6 blend is presented in Figure 16 and Figure 17.

Figure 16 presents the evolution of the morphology with mixing times from 0min to 3min30s for systems where the CNT are premixed with the EVA. The CNT are localized at the interface even for very short mixing times, confirming the fastness of the interfacial localization already observed for EA/PA6 systems (Figure 6), and they stay there even after slight degradation of the matrix for 10 minutes blending at high temperature (Figure 12 a and b). The same behavior is observed when the EVA+CNT is blended with PC (Figure 12 c and d). However, for these long mixing times, the matrix degradation is higher and the CNT have formed larger aggregates (see Figure 15). Nevertheless, these aggregates are present at the interface of the immiscible polymers.

When the CNT are predispersed in the minor PA6 or PC phase, the evolution of the blend morphology with the extrusion time is shown in Figure 17 for compounding times from 0 to 3min30s. For short times, the CNT are localized in the PA phase. However, with increasing mixing time, the CNT tend to aggregate inside the dispersed phase (PA or PC) for large nodules or tend to accumulate at the interface for large and small droplets. Although it is observed for PA (Figure 12b), the formation of aggregates inside the droplets is even more spectacular inside the PC droplets (Figure 12d), where the initial dispersion is excellent. Although the migration of the CNT from dispersed droplets is known ^[8,44] to be slower than the migration from the matrix towards the dispersed phase, the CNT accumulation in the centre of the droplets results probably more from the EVA degradation inducing PA or PC degradation by acetic acid rather than from an equilibrium state due to the minimization of the interfacial energies.

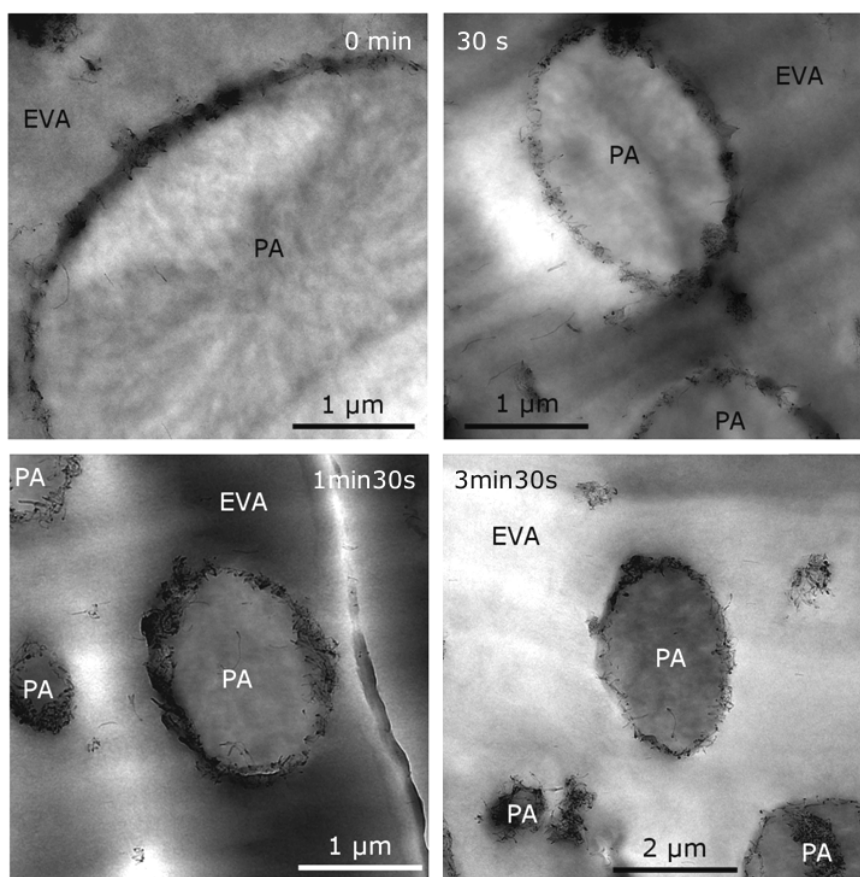


Figure 16 – TEM micrographs of the evolution of the morphology for the predisposition of CNT in EVA prior to blending with PA ((EVA+CNT)-PA6) for increasing mixing times (0min, 30 s, 1min30s, 3min30s)

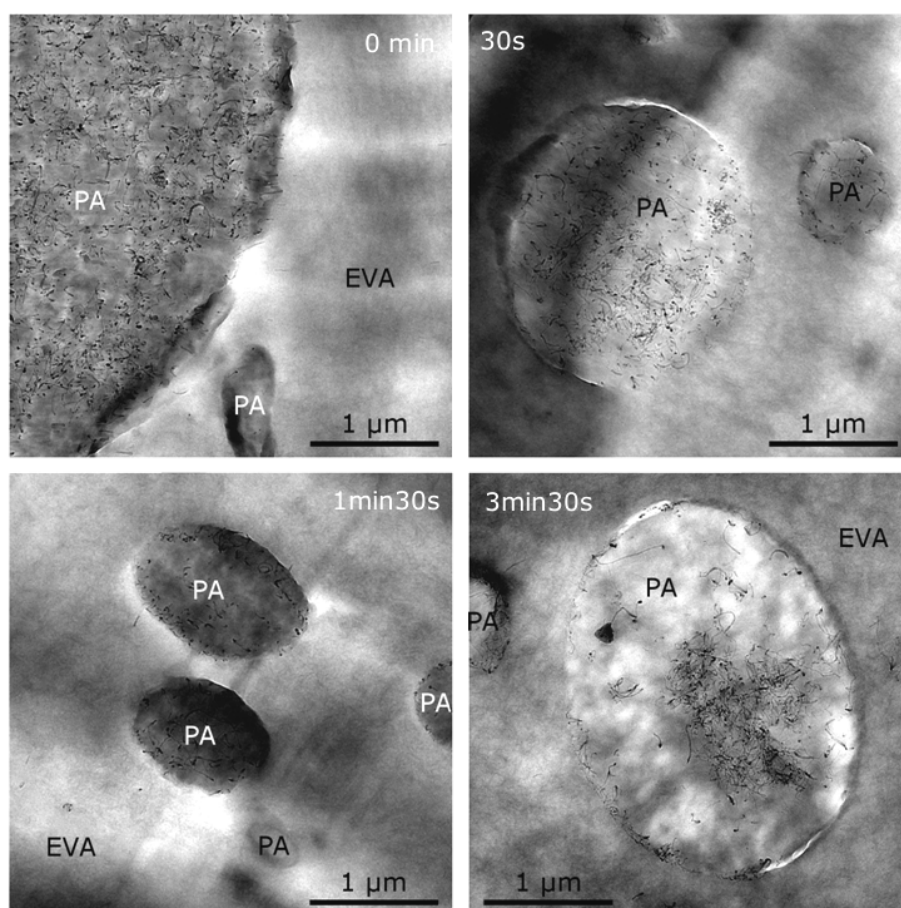
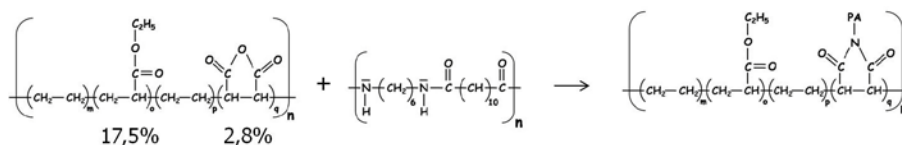


Figure 17 – TEM micrographs of the evolution of the morphology for the predispersion of CNT in PA6 prior to blending with EVA ($EVA-(PA6+CNT)$) for increasing mixing times (0min, 30 s, 1min30s, 3min30s)

In MAEA/PA blends, the maleic anhydride functions of MAEA can react with the amine endgroups of the PA to form imide groups (Figure 18). The reaction was evidenced by annealing a sheet of MAEA on a sheet of PA6/12 for 1h at 180°C in the absence shear (Figure 19). The reaction at the interface between both polymers is evidenced by the presence of dark particles in the MAEA phase (bright phase).



MAEA

PA6/12

1 μ m

The blends of MAEA with PA present a sea-island morphology where the PA forms the dispersed phase and MAEA forms the matrix. When the CNT are first dispersed in the MAEA phase, they mainly migrate towards the interface of the MAEA/PA blend for the three PA under study (Figure 20a,c,e), although some of them remain in the MAEA phase. When they are first dispersed in the PA phase, they remain well dispersed in the PA for the three PA studied (Figure 20b,d,f).

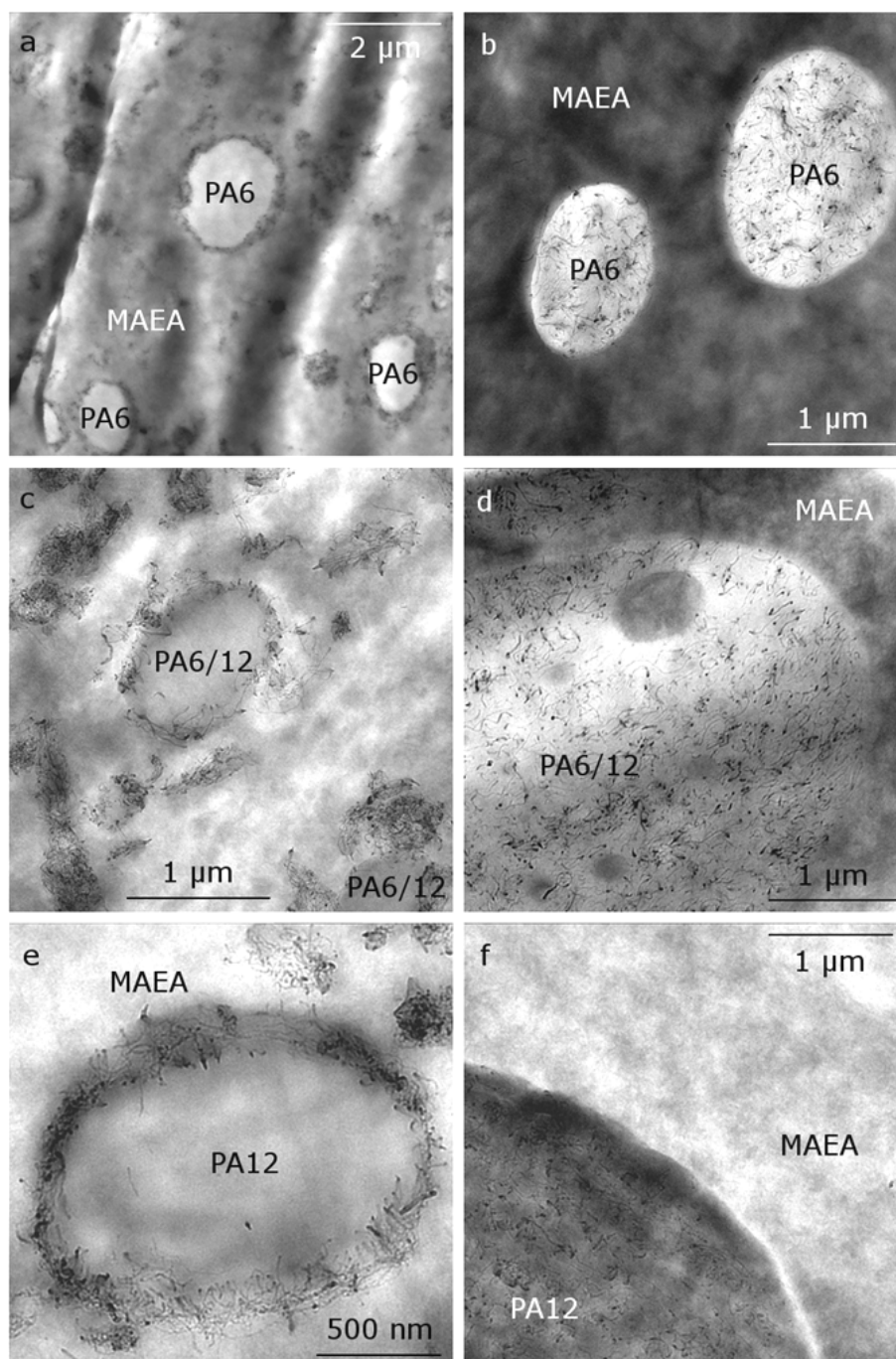


Figure 20 – TEM micrographs of MAEA – based systems (a, b) PA6 as dispersed phase (a) predispersion in MAEA (b) predispersion in PA6 ; (c, d) PA6/12 as dispersed phase (c) predispersion in MAEA (d) predispersion in PA6/12; (e, f) PA12 as dispersed phase (e) predispersion in MAEA (f) predispersion in PA12

1.3 *Other matrices*

1.3.1 PC-based systems

a. PC/PES blends

The blends exhibit a sea-island morphology with PES droplets dispersed in a PC matrix. When the CNT are predispersed in the PC phase, the CNT remain mainly well dispersed in the PC phase but a migration towards the interface is also systematically observed (Figure 21). On the other hand, when the CNT are predispersed in the PES phase (Figure 22), they stay well dispersed in the PES droplets although some of them are localized at the interface. Note that, for the predispersion of CNT in PC the interfacial confinement of the CNT seems to prevent the coalescence of the droplets, while for the predispersion in PES, coalescence is widely observed throughout the sample. Note also that at 300°C, a slight thermal degradation of the PC can occur. Although TGA analysis shows no noticeable weight loss below 450°C, Abbas ^[48] has shown that Bisphenol A PC is thermally degraded in a rheometer barrel at temperatures from 300 to 330°C.

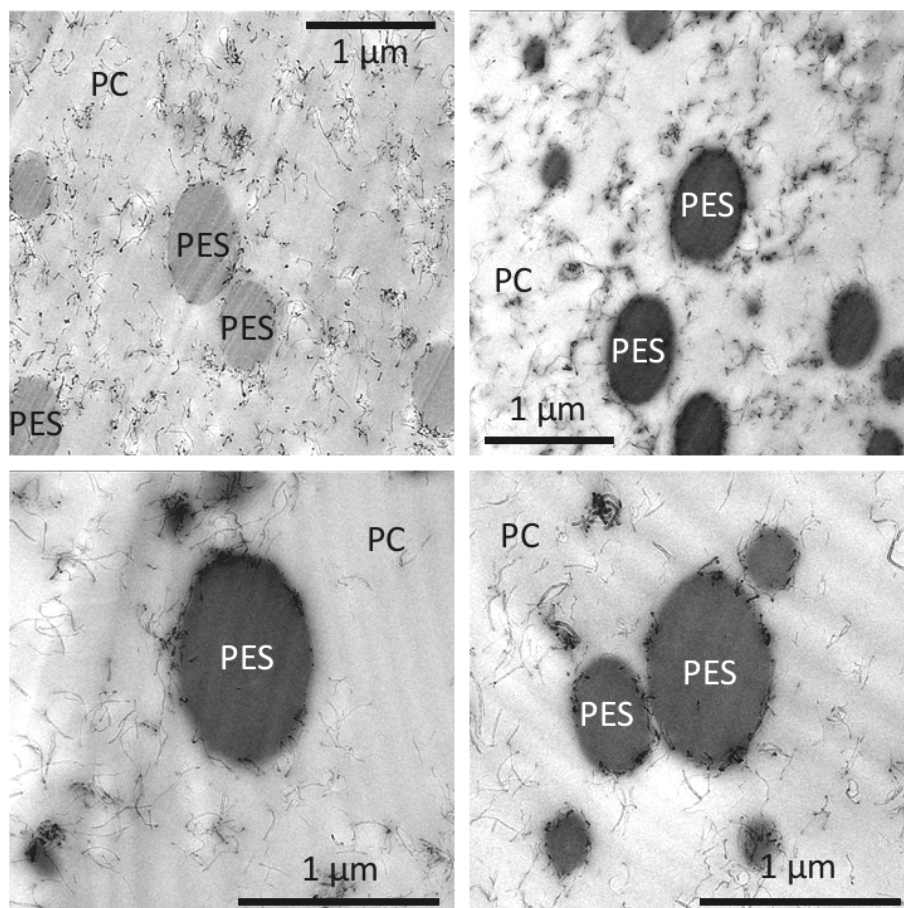


Figure 21 – Predispersion of the CNT in PC phase followed by mixing with PES

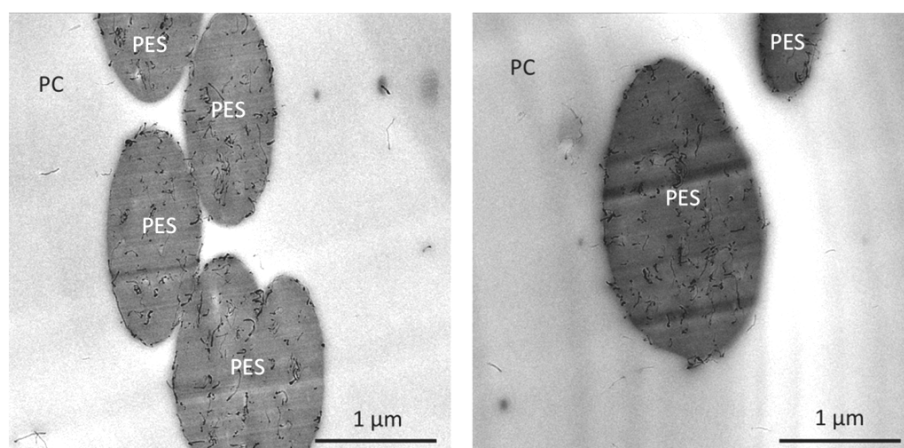


Figure 22 – Predispersion of the CNT in PES phase followed by mixing with PC

b. PC/PA6 blends

When CNT are predispersed in PC_m or PC_i before mixing with PA6, they totally migrate inside the dispersed phase (Figure 23a,b; Figure 25a). When the CNT are predispersed in the PA6 phase, they remain dispersed in the droplets (Figure 23c,d; Figure 25b). However, their dispersion is not as homogeneous as the initial dispersion observed for PA6/CNT composites. This behaviour is explained by a modification of the polymers structure. Indeed, exchange reaction can occur in polyamide-polycarbonate blends. Gattiglia et al. [49] showed that PA6 and PC are incompatible over the whole range of compositions. For high PA6 content and long mixing times at 235°C, however, no more phase separation was observed. This is confirmed in Figure 24, where a premix of (PA6+2wt.-%CNT) is blended with PC in the weight ratio 90-10. No phase separation is observed, the blend is fully homogeneized. The possible exchange reactions include acidolysis, aminolysis and amidolysis (Table 1). Nevertheless, it was found that amidolysis is less probable and kinetically slower than acidolysis and aminolysis [50]. Aminolysis of PC can lead to crosslinking and thus to an increase of the viscosity of the droplets. Note finally that the white disks observed in Figure 25b are holes in the sliced sample, which can be attributed to the production of CO₂ resulting from the degradation of PC.

Table 1 – Possible exchange reactions between PC and PA6 [50]

Acidolysis	$\text{PA6-CO-OH} + \text{PC-O-CO-O-PC} \rightarrow \text{PA6-COO-PC} + \text{PC-O-COOH}$ $\text{PC-O-CO-OH} \rightarrow \text{PC-OH} + \text{CO}_2$
Aminolysis	$\text{PA6-NH}_2 + \text{PC-O-CO-O-PC} \rightarrow \text{PA6-NHCOO-PC} + \text{PC-OH}$
Amidolysis	$\text{PA6-CONH-PA6} + \text{PC-OCOO-PC} \rightarrow \text{PA6-CON(PA6)-PC} + \text{PC-O-COOH}$

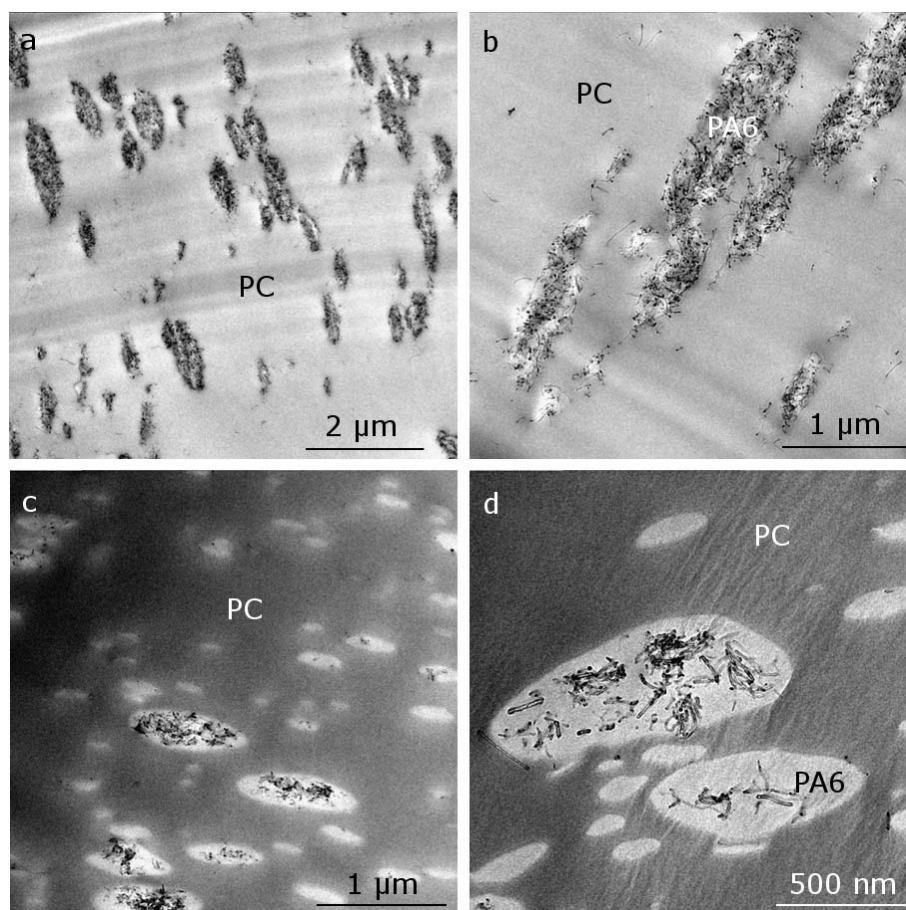


Figure 23 – TEM micrographs of the blends of PC_m and PA6; (a, b) predispersion in PC_m: (PC+CNT)-PA6 ; (c, d) predispersion in PA6: PC-(PA6+CNT)

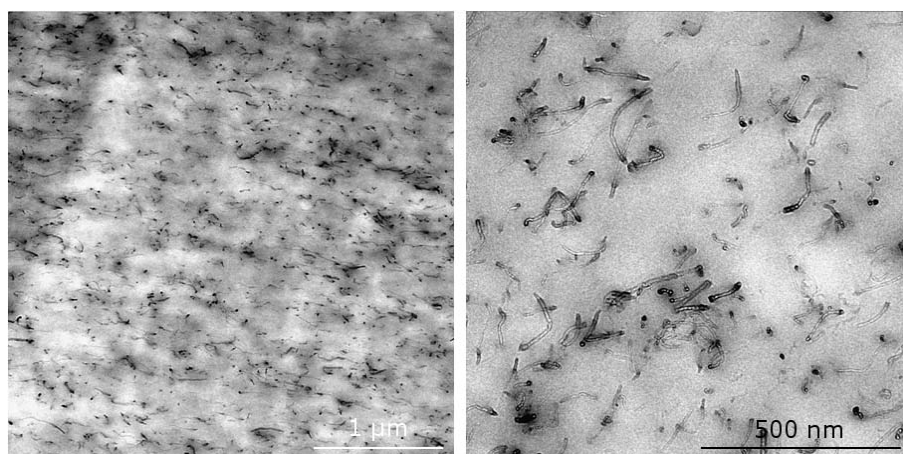


Figure 24 – TEM micrographs of a predisposition of CNT in PA6 (90wt.-%) before mixing with PC_m (10wt.-%): (PA6+CNT)-PC_m

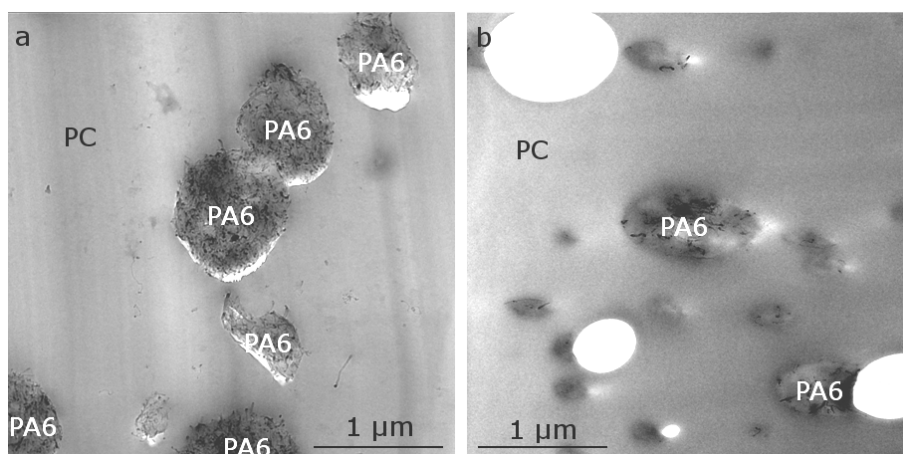


Figure 25 – TEM micrographs of the blends of PC_i and PA6 ; (a) predisposition in PC_i: (PC+CNT)-PA6 ; (b) predisposition in PA6: PC-(PA6+CNT)

1.3.2 PP – based systems

When the CNT are first mixed with PP, they are in the form of big agglomerates. When mixing (PP+CNT) with PA6/12, these agglomerates migrate towards the PA6/12 droplets. Some of the agglomerates are at the interface between both phases and some others seem to penetrate inside the PA6/12 droplets. It is however not clear if the agglomerates are inside the PA6/12 or in sub-inclusions of PP. Moreover, the droplets do not present spherical shapes; possibly indicating that coalescence has just occurred, which would also lead to the presence of CNT agglomerates inside the droplets. When the CNT are predispersed in the PA6/12, they remain well dispersed in the PA phase. No migration towards the interface or towards the PP is observed.

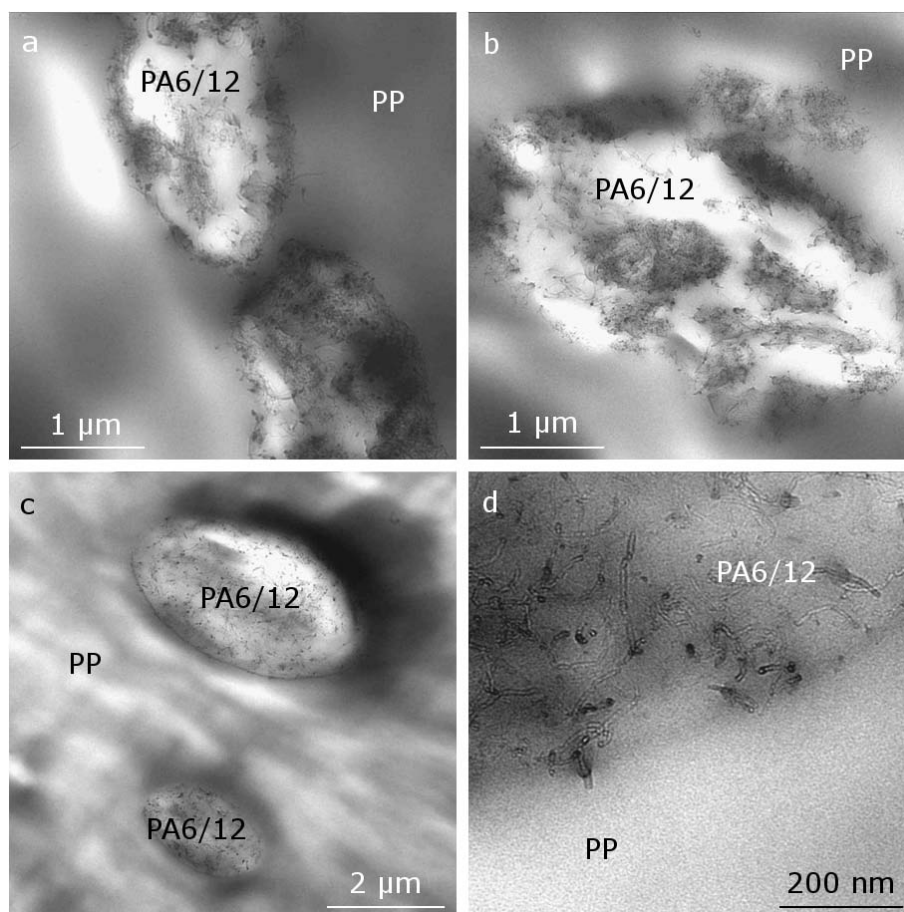


Figure 26 – Immiscible blends of PP, PA6/12 and CNT; (a, b) predispersion in PP; (c, d) predispersion in PA6/12

1.3.3 PA6 – based systems

Finally, the last system studied is made of PA6 and EA. However, here, the PA6 forms the matrix and the EA is the dispersed phase as presented in Figure 27 and in Figure 28. This is thus composition inverse of the previous blends presented in Figure 2b and Figure 3b. When the CNT are premixed with EA, they migrate towards the interface of the blend. They are jammed in the interface and no CNT is found in the PA matrix (Figure 27). When the CNT are predispersed in the PA6 phase, a few of them remain in the PA phase and the interface between the phases is well covered by CNT (Figure 28). The behaviour of the CNT observed here is identical to the behaviour observed when the PA is the dispersed phase (see 1.1.1 EA/PA blends on page 13). The

weight ratio between the phases has thus no influence on the final localization of the CNT in the blend.

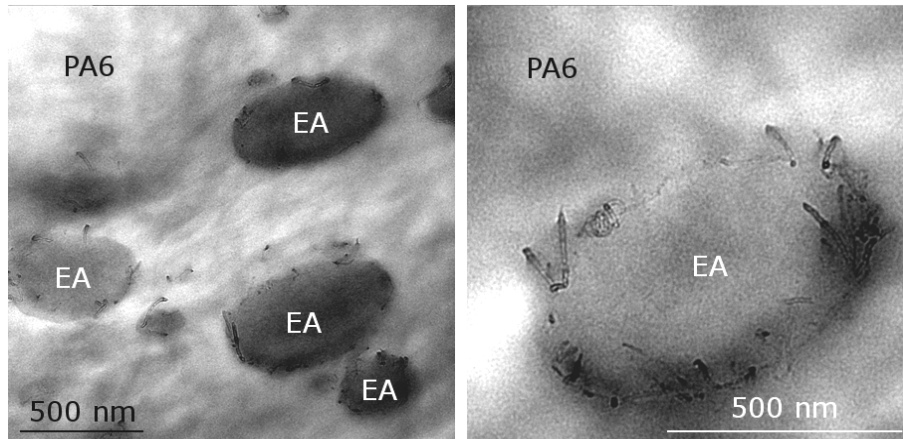


Figure 27 – TEM micrographs of the predispersion of CNT in EA phase before mixing with the PA6 matrix (10wt.-(EA+2wt.-%CNT)-90wt.-PA6)

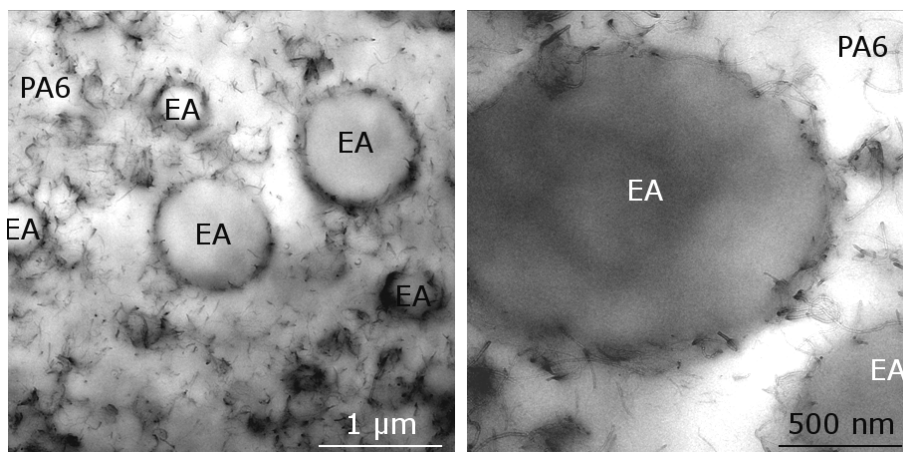


Figure 28 – TEM micrographs of the predispersion of CNT in PA6 before mixing with EA (25wt.-%EA-75wt.-%(PA6+2wt.-%CNT))

2 Thermodynamical predictions

Classical thermodynamics can be used to predict the position of fillers in blends of immiscible polymers. In the equilibrium state, the location of a filler in a polymer blend can be predicted by the minimization of the interfacial energy. According to Young's equation, it is possible to find the equilibrium position of the filler by evaluating the wetting coefficient ω_a [51]:

$$\omega_a = \frac{\gamma_{C-Pol B} - \gamma_{C-Pol A}}{\gamma_{Pol A-Pol B}}$$

where $\gamma_{C-Pol A}$, $\gamma_{C-Pol B}$, $\gamma_{Pol A-Pol B}$ are the interfacial energies respectively between CNT and polymer A, between CNT and polymer B and between polymer A and polymer B. If the wetting coefficient is higher than 1, the filler will preferentially be located in polymer A; if the wetting coefficient is lower than -1, the filler will preferentially be located in polymer B, and if the wetting coefficient is between -1 and 1, the filler will be located at the interface between the two polymers.

The interfacial energy can be evaluated from the surface energies of the components. Two main approaches can be used depending on the type of surfaces: the harmonic-mean equation and the geometric mean-equation. The harmonic-mean equation is valid between low-energy materials and the geometric-mean equation is valid between a low-energy material and a high energy material:

$$\text{Harmonic-mean equation: } \gamma_{12} = \gamma_1 + \gamma_2 - 4 \left(\frac{\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \right)$$

$$\text{Geometric-mean equation: } \gamma_{12} = \gamma_1 + \gamma_2 - 2 \left(\sqrt{\gamma_1^d \gamma_2^d} + \sqrt{\gamma_1^p \gamma_2^p} \right)$$

where γ_1 , γ_2 are the surface tensions of components 1,2; γ_1^d , γ_2^d are the dispersive parts of the surface tensions of components 1,2; and γ_1^p , γ_2^p are the polar parts of the surface tension of components 1,2.

2.1 Surface energy of polymers

The values of the surface energy of polymers in the melt state have been extrapolated from literature values at 20°C and are summarized for the different compounding temperatures in Table 3 to Table 8 with the simplifying hypothesis that the polarity is independent of temperature.

Due to the lack of data concerning the polymers in the literature, some approximations have to be made.

The surface tensions for EA and MAEA have been found by using an arithmetic mean value adapted to random copolymers:

$$\gamma = x_1\gamma_1 + x_2\gamma_2$$

Where γ is the surface tension and x is the mole fraction. The subscripts 1 and 2 refer to the components 1 and 2 respectively. Note that for MAEA, the content of maleic anhydride is very low and is therefore not taken into consideration here.

Table 2 – Surface tension, temperature coefficient and polar fraction of the constituents of EA and MAEA

	Surface free energy, γ (mN/m)	Temperature coefficient, $-d\gamma/dT$ (mN m ⁻¹ °C ⁻¹)	Polar fraction (-)
PMA	41	-0,077	0,25122
PEA	37	-0,077	0,17027027
PE	35,7	-0,057	0

The surface tension and polarity of EVA with 28wt.-%VA at 25°C are 35.9 mN/m and 0.07. The temperature coefficient is -0.064 [8,52].

The surface tension of PA4/6 was not found in literature, it was therefore approximated by the values of PA4 [53]. At 20°C, the total surface energy is 48.5 and the polarity is 0.43). The surface tension of PA6 is given by Wu et al. [51] at 265°C, $\gamma = 36.1$ mN/m. The polarity of PA6 has been evaluated by Son [54] to be 0.28. The surface tension and polarity of PA* are the one of PA6/6 ($\gamma = 46.5$ mN/m, $x^p = 0.3$) [51, 55]. The surface tension of PA6/12 was approximated by the values of PA6/10 at 22°C [56] ($\gamma = 40.5$ mN/m) and its polarity is chosen to be intermediate between the polarity of PA6 and PA12, by an arithmetic mean: $x^p = 0.2$ [54, 55]. The surface tension of PA12 at 20°C is 40.7 mN/m and its polarity is 0.12 [55]. The temperature dependence of all polyamides has been approximated by the one of PA66 ($-d\gamma/dT = 0.065$ mN m⁻¹ °C⁻¹) [51,55] due to the similar chemical structure.

The surface tension of PC at 20°C is 34.2 mN/m, its polarity is 0.19 and its temperature dependence is $-d\gamma/dT = 0.04$ mN m⁻¹ °C⁻¹ [51,55].

The surface tension of PET at 20°C is 44.6 mN/m, its polarity is 0.221 and its temperature dependence is -0.0065 [51,55]. Due to their very similar structures,

the values of PBT are considered as similar, although the PBT should be more apolar due to the higher number of $-(CH_2)-$ functions.

The surface tension and polarity of PES are $\gamma = 47 \text{ mN/m}$, $x^p = 0.149$ [57]. However, no temperature dependence was found in literature, it was therefore approximated by the one of PC: $d\gamma/dT = 0.04 \text{ mN m}^{-1} \text{ } ^\circ\text{C}^{-1}$.

Table 3 – Surface energies of the polymers at 180°C

Material	Total surface energy, γ mJ m^{-2}	Dispersive surface energy, γ^d mJ m^{-2}	Polar surface energy, γ^p mJ m^{-2}
EA	26.9	25	1.9
MAEA	26.4	26.1	0.3
PA6/12	30.1	24.1	6

Table 4 – Surface energies of the polymers at 200°C

Material	Total surface energy, γ mJ m^{-2}	Dispersive surface energy, γ^d mJ m^{-2}	Polar surface energy, γ^p mJ m^{-2}
PP	22.9	22.9	0
PA6/12	28.8	23.0	5.8

Table 5 – Surface energies of the polymers at 240°C

Material	Total surface energy, γ mJ m^{-2}	Dispersive surface energy, γ^d mJ m^{-2}	Polar surface energy, γ^p mJ m^{-2}
EA	23.3	22.5	0.8
EVA	22.1	20.6	1.5
MAEA	22.9	22.6	0.3
PA6	37.7	27.2	10.6
PA12	26.4	23.2	3.2
PA*	32.2	22.5	9.7

Table 6 – Surface energies of the polymers at 280°C

Material	Total surface energy mJ m^{-2}	Dispersive surface energy, γ^d mJ m^{-2}	Polar surface energy, γ^p mJ m^{-2}
EA	20.9	20.2	0.7
EVA	19.6	18.2	1.4
PA6	35.1	25.3	9.8
PC	23.8	19.3	4.5
PET	27.7	22.2	5.5

Table 7 – Surface energies of the polymers at 300°C

Material	Total surface energy mJ m^{-2}	Dispersive surface energy, γ^d mJ m^{-2}	Polar surface energy, γ^p mJ m^{-2}
PC	23.0	18.6	4.4
PES	35.8	30.5	5.3

Table 8 – Surface energies of the polymers and CNT at 310°C

Material	Total surface energy mJ m^{-2}	Dispersive surface energy, γ^d mJ m^{-2}	Polar surface energy, γ^p mJ m^{-2}
EA	19.1	18.4	0.7
PA4/6	29.7	17.0	12.7

2.2 Surface energy of CNT

Only very few data concerning the surface tension and polarity of CNT can be found in literature. Accurate measurement of the surface tension of nanoparticles is indeed extremely complicated. This value depends on many factors such as sample size, microstructure, surface functionalization, and even measuring methods [58-60]. In the present study, the polarity of the CNT is expected to be very low owing to the absence of functional groups on the CNT surface. However, in literature, the CNT are generally found to locate in the most polar phase even if they are unfunctionalized. The surface free energy values generally used in literature and which are leading to the most consisting results are given by Barber et al. [61]. They measured a total surface tension of 27.8 mJ m^{-2} with dispersive and polar components respectively equal to 17.6 mJ m^{-2} and 10.2 mJ m^{-2} . More details about the surface energy of CNT are given in Appendix 2.

2.2.1 Wetting coefficient evaluation

Based on the surface tensions of polymers and CNT, the wetting coefficient according to the harmonic-mean equation and according to the geometric-mean equation can be evaluated and the CNT location according to these predictions can be written. Table 9 presents the wetting coefficients and predictions for the EA-based systems. Table 10 presents the wetting coefficients and predictions for the other ethylene-based systems. Finally, Table 11 presents the wetting coefficients and predictions for the other systems.

Table 9 – Wetting coefficient evaluated according to harmonic mean equation and geometric mean equation and corresponding prediction for EA – based systems

Materials Polymer 1/Polymer 2	Wetting coefficient according to harmonic mean equation	Wetting coefficient according to geometric mean equation	Prediction
EA/PA4/6	-0.74	-0.73	interface
EA/PA6	-0.75	-0.79	interface
EA/PA6/12	-1.90	-2.09	PA
EA/PA12	-2.90	-4.01	PA
EA/PA*	-1.06	-1.07	PA
EA/PC	-2.21	-2.68	PC
EA/PET or EA/PBT	-1.71	-2.01	PET or PBT

Table 10 – Wetting coefficient evaluated according to harmonic mean equation and geometric mean equation and corresponding prediction for other ethylene – based systems

Materials Polymer 1/Polymer 2	Wetting coefficient according to harmonic mean equation	Wetting coefficient according to geometric mean equation	Prediction
EVA/PA6	-0.61	-0.65	interface
EVA/PC	-2.65	-3.19	PC
MAEA/PA6	-0.78	-0.83	interface
MAEA/PA6/12	-1.70	-1.85	PA
MAEA/PA12	-2.30	-3.20	PA

Table 11 – Wetting coefficient evaluated according to harmonic mean equation and geometric mean equation and corresponding prediction for other systems

Materials Polymer 1/Polymer 2	Wetting coefficient according to harmonic mean equation	Wetting coefficient according to geometric mean equation	Prediction
PC/PES	0.90	0.89	interface
PC/PA6	-0.32	-0.34	interface
PP/PA6/12	-1.55	-1.65	PA
PA6/EA	0.75	0.79	interface

3 Discussion

First, it is worth noting that the migration from one phase to the interface or to the other phase can only occur in the presence of shear, when CNT have the opportunity to meet the interface. Indeed, for the EA/PA6 system in the absence of shear, no filler transfer is observed.

Then, in the presence of a shear field, the thermodynamical predictions based on the evaluation of the wetting coefficient can be compared to the observed morphologies.

For the EA – based systems, the thermodynamic predictions are in good agreement with the observed morphology, when CNT are predispersed in the dispersed phase, which is the more polar phase. When CNT are predispersed in PA4/6 or PA6, the thermodynamics predicts that there is no preferred phase and CNT migrate towards the interface. When they are predispersed in PA6/12, PA12, PA* or PC, they remain well dispersed in this phase, which is the thermodynamically preferred phase. The predispersion in PET and PBT has not been studied. However, when CNT are predispersed in EA, the behaviour is quite different. CNT are mainly localized at the interface, whatever the dispersed phase used. Some CNT also remain in the EA phase. In PET and even more in PA*, some CNT are regularly present inside the droplets.

For EVA – based systems, thermodynamics predicts the localization at the interface when PA6 is used as the dispersed phase and inside the droplets when PC is used. Owing to the degradation of the EVA during processing at high temperature, it is however delicate to discuss the observed morphology. Indeed, at high temperature, the degradation of EVA produces acetic acid,

which turns out to modify the PA or PC dispersed phase. However, this chemical change is not instantaneous. It can be kinetically followed and at least partially decoupled from the thermodynamic equilibrium morphology. The morphology is quickly established when premixing CNT in the matrix due to high velocity fields and the morphology after short mixing time can thus be discussed. When CNT are predispersed in the EVA matrix, for short blending times, the interface between both polymers is “covered” with a homogeneous layer of CNT. Nevertheless, for long mixing times, only large CNT aggregates are observed at the interface. However, when CNT are premixed in the dispersed phase, the time scale for the establishment of the morphology is assumed to be longer. When CNT are predispersed in the PA or PC dispersed phase, for very short mixing times, CNT remain well dispersed and when PA is used, some of them migrate towards the interface. Nevertheless, for 10 minutes mixing, for PA and PC, an accumulation at the centre of the droplets of the dispersed phase is observed. We can thus conclude that in this case also, when CNT are predispersed in the most polar phase (PA or PC), they follow the rough trends predicted by the thermodynamics. On the contrary, when predispersed in the less polar phase (EVA), the CNT are jammed at the interface.

For MAEA – based systems, for the three different PA used (PA6, PA6/12 and PA12), the same behavior is observed. When CNT are predispersed in the more polar phase, CNT remain dispersed in this phase. On the contrary, when CNT are predispersed in MAEA, they are mainly jammed at the interface between the phases. Note that the formation of copolymer at the interface due to reaction between the maleic anhydride functions and the amine groups has no influence on CNT interfacial localization. This is probably due to the very low amount of maleic anhydride groups in the MAEA (2.8wt.-%). Thermodynamics predicts the localization at the interface in the presence of PA6 and, in the PA droplets in the presence of PA6/12 or PA12. The observed behavior is thus in agreement with the thermodynamics for predispersion in the most polar phase for PA6/12 and PA12, but not for PA6 and not for predispersion in MAEA.

For PC/PES system, the expected morphology is a localization of the CNT at the interface. Although we observe the localization of part of the CNT at the interface, whatever the mixing sequence, it is clear that CNT mainly remain dispersed in the first phase in which they are dispersed.

For PC/PA6 systems, the wetting coefficient predicts that CNT should be localized at the interface. However, owing to reactions occurring in the blend

between PC and PA6, there is no interface anymore. The prediction can thus not be used to explain the morphology of this blend.

For the PP/PA6/12 system, according to the thermodynamic predictions, CNT should be localized inside PA. When CNT are predispersed inside PA, the morphology totally agrees with this prediction. However, when CNT are predispersed in PP, they mainly migrate to the interface and some aggregates are present inside the PA droplets. However, it is difficult to exclude the possibility of the presence of PP sub-inclusions inside PA. Moreover, PA6/12 droplets exhibit an atypical shape. CNT could thus be present inside PA6/12 due to droplet coalescence.

Finally, the PA6/EA blend agrees with the interfacial localization prediction for CNT, whatever the mixing sequence used.

Although the predictions are generally well followed when CNT are predispersed in the preferred phase, they must be handled with care due to uncertainties on the surface tensions values concerning both CNT and polymers. Indeed, although CNT are apolar objects, the surface energy used here presents a non negligible polar contribution. Accurate measurement of the surface tension of nanoparticles is extremely complicated and very different values are found in the literature (see Appendix 2 for more details). Moreover, the polymers used here are commercial resins. They contain low molecular weight additives, which are able to migrate to the interface. This effect is not taken into account. Moreover, the extrapolation of values measured in the solid state at room temperature to high temperature, where the thermoplastics are molten, is delicate.

If the CNT have the possibility to migrate, i.e. in a shear field, thermodynamics predicts their equilibrium position. However, this prediction could turn out to be wrong if the polymers are modified during blending. It occurs, for example, when the polymers react or degrade at high temperature. Their chemical nature changes and side products, able to react with or to modify the other polymer present in the blend, are possibly produced. The predictions based on the evaluation of the wetting coefficient can also turn out to be wrong if the filler surface is modified during blending. The final localization in the blend is indeed highly depending on the mixing strategy. Thermodynamics based on surface tensions of the neat polymers and as produced CNT are thus not sufficient to predict the localization of the CNT in the polymer blends under study here.

4 Influence of mixing strategy

The mixing strategy can influence the final localization of CNT in polymer blends. Dasari et al. [62] have shown that the blending sequence has an influence on the microstructure of ternary nanocomposites prepared from PA66 / styrene-ethylene/butylene-styrene triblock copolymer grafted maleic anhydride (SEBS-g-MA) / organoclay. The localization of the organoclay and the size of the dispersed SEBS-g-MA in the blend depend on the blending sequence owing to reactions that can occur between the organoclay and the different components of the blend.

Three mixing strategies can be used to mix CNT with two immiscible polymers. CNT can be premixed with one polymer or the three components can be simultaneously blended. Different final morphologies are observed depending on the mixing strategy used. The morphologies observed by simultaneous blending are first briefly described. Then the influence of premixing with one polymer is studied.

4.1 Simultaneous blending

Two categories of blends have to be considered; first, the blends in which the preferred phase is the first to be molten and, second, the blends in which the “less preferred phase” is the first to be molten.

4.1.1 Preferred phase molten first

When CNT are directly mixed with PP ($T_{m,PP} \approx 170^\circ\text{C}$) and PA6/12 ($T_{m,PA6/12} \approx 130^\circ\text{C}$), they are selectively localized in PA6/12 phase (Figure 29). PP does not contain CNT. This localization occurs very fast. Indeed, after 2 min compounding (Figure 29a), CNT are already located in the PA6/12 droplets. As expected, this localization is stable even for longer mixing times (at least up to 20min).

When the preferred phase is the first to be molten, CNT thus directly locate in this phase, even if it is the minor phase.

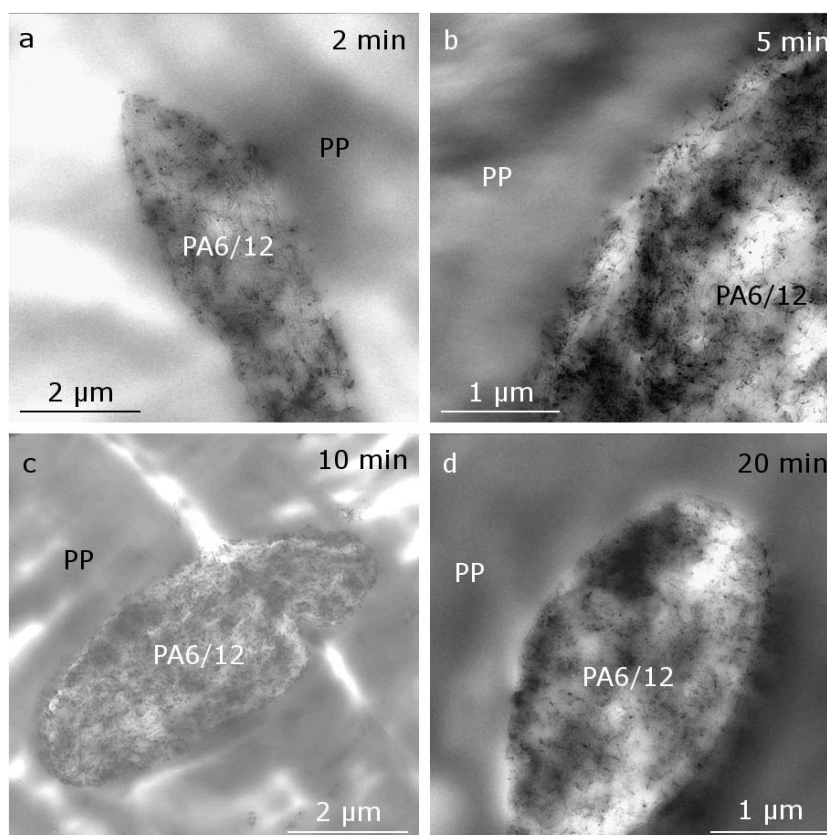


Figure 29 – TEM micrographs simultaneous blending of PP, PA6/12 and 2wt.-% CNT (a) 2min blending; (b) 5min blending; (c) 10 min blending; (d) 20 min blending

4.1.2 Less preferred phase molten first

Figure 30 presents TEM micrographs of EA or MAEA blended with 3 different polyamides (PA6, PA6/12 and PA12). The blends exhibit a sea-island morphology where the PA forms the dispersed phase in ethylene – based matrices. When the three components are simultaneously mixed, CNT are preferentially located at the interface between both. The behaviour observed using this dispersion method is the same as when CNT are premixed with EA or MAEA. This result is firstly explained by the large amount of EA present in the system as compared to PA. The probability for the CNT to first meet EA is thus higher than the probability to first meet PA. Secondly and more important, PA and EA or MAEA exhibit very different melting points. The melting temperature of PA6 is around 220°C, of PA6/12 around 130°C, of PA12 around 180°C, of EA around 65°C and of MAEA around 75°C. The ethylene-acrylate copolymer is therefore molten before PA and is thus the first polymer to “wet”

the CNT. The morphology is thus mainly similar to the morphology observed when premixing with EA or MAEA.

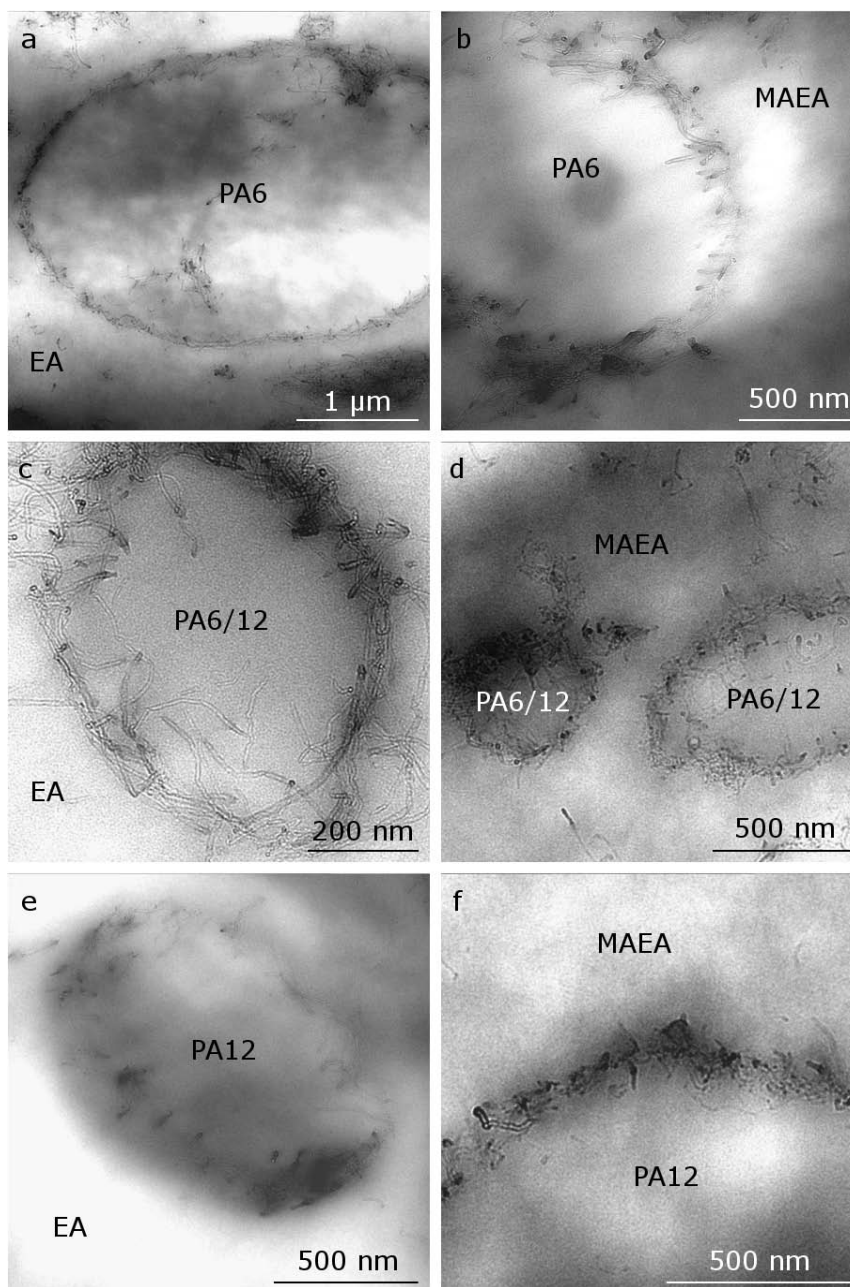


Figure 30 – TEM micrographs of a simultaneous blending of EA or MAEA and different PA ; (a) EA/PA6 ; (b) MAEA/PA6 ; (c) EA/PA6/12 ; (d) MAEA/PA6/12 ; (e) EA/PA12 ; (f) MAEA/PA12

4.1.3 Discussion

The melting point of the phases is an important parameter in the elaboration of the blends. When the preferred phase has a lower melting point than the other one, CNT are directly localized in this phase. When the preferred phase has the highest melting point, CNT are localized at the interface. The final morphology during simultaneous blending is the same morphology as the one obtained by predispersing the CNT in the polymer with the lowest melting point. The proportion of the phases seems to have less importance. The first polymer in contact with the CNT seems thus to highly influence the morphology. It is discussed in the following section.

4.2 *Influence of first polymer in contact with the CNT*

The observed morphology of the nanocomposite is not only depending on the polymers used but also on the mixing sequence. This dependence can be explained either by kinetic effects if the system has not reached its equilibrium state or by a modification of interfacial thermodynamics during early stages of mixing. The observed morphologies are stable even after 60 minutes mixing, indicating that longer mixing times will not lead to a different confinement. There should thus be a modification of the surface properties of the CNT and hence of interfacial thermodynamics during the premixing step or during the early stages of simultaneous compounding.

Baskaran et al. [63] have prepared polymer nanocomposites containing variable amounts of CNT using solution dispersion and melt-shear mixing. They have brought to light the non specific adsorption through interactions of the polymer CH groups with CNT. Moreover, they have stated that the coating or wrapping of the CNT by polymer chains is a “general phenomenon occurring between polymers and carbon nanotubes”. Beigbeder et al. [64] have also evidenced the CH- π interactions between the methyl groups of the polymer and the nanotube surface using simulations. According to their model, “CH-rich” polymers should strongly interact with the pure CNT surface. However, the chain flexibility and ability to crystallize of certain polymers, such as PE or PP, can reduce the density of CH- π interactions. The authors have also stated that the presence of polar groups or chemical defects on CNT decreases the strength of the CH- π interactions. Srebnik and coworkers [65,66] have used Monte Carlo simulations to suggest that weakly attractive van der Waals forces are sufficient to induce polymer helical wrapping around CNT. Semiflexible polymer chains adsorb in the form of single or multiple helices while flexible chains adopt a random coil ‘cloud’ conformation around the tubes.

Wrapping of polymer chains is also found to occur in the presence of polymers containing aromatic rings due to an especially strong interaction due to π - π stacking formed with the graphitic sidewalls of the CNT [67-70].

In the present blends, EA, EVA and MAEA can be considered as “CH-rich” polymers. The CNT are unfunctionalized and unpurified. We can therefore expect strong interactions between these polymers and the CNT. If they are the first to come in contact with the CNT, one can thus expect that they adsorb in a partially irreversible way on the CNT. This partial coating of CNT could thus prevent the total transfer of the nanotubes from one phase to the other. On the other hand, PP is also a “CH-rich” polymer. However, due to the presence of methyl groups, the chain is not much flexible and adsorption on CNT is less efficient. PC and PES are expected to adsorb on the CNT during melt blending due to π - π stacking.

The adsorption of EA or PA (PA6 or PA12) on CNT surface has been checked by different methods. First, the presence of adsorbed EA is evidenced using TGA. Next the adsorption of PA is demonstrated using TGA and decantation tests.

4.2.1 EA adsorption

The CNT are extracted from an EA nanocomposite containing 2wt% CNT with the help of a Soxhlet with boiling chloroform. Due to their short size after compounding, CNT are retained between the fibres in the glass fibres thimble and it was not possible to extract them from the glass fibres. To check the polymer extraction kinetics, Soxhlet have been performed for one day and 5 days. A Soxhlet with virgin EA is performed under the same conditions for comparison.

a. Thermogravimetric analysis (TGA)

Figure 31 presents the TGA analysis under dry air for the glass fibres retaining the CNT from the composite EA+2wt.%CNT (Soxhlet 24h, Soxhlet 5 days), the glass fibres thimble after extraction of pure EA for 5 days (EA on glass fibre thimble), the pure glass fibres thimble (glass fibres thimble), the pure EA (EA) and the as-produced CNT (MWNTs). The overall relative mass and derivative weight are presented on Figure 31a and Figure 31b to assess the degradation steps of the polymer and the CNT. Figure 31c clearly shows two weight loss transitions for the CNT extracted from the composite (Soxhlet 24h and Soxhlet 5 days). The first one, around 600K, is attributed to the presence of adsorbed polymer while the second one, over 800K, is attributed to the CNT oxidation under air atmosphere. These two weight losses are highlighted in Figure 31d,

which represents the derivative of weight versus temperature. The peaks linked to the polymer degradation are surrounded with a dashed oval and the peaks linked to the CNT degradation are surrounded with a dotted oval. It is worth noting that no significant weight loss is observed for the glass fibres after EA extraction for 5 days. The polymer degradation peaks observed for both Soxhlet 24 and Soxhlet 5 days are thus not due to polymer chains sticking to the glass fibres but to adsorption on the CNT. Although it is impossible to get fully quantitative analysis of the amount of adsorbed polymer due to the presence of a large amount of glass fibres, we can conclude that the weight of the adsorbed polymer is nearly equivalent to the weight of CNT. This evaluation is consistent for both extraction times, 24 hours and 5 days, indicating that this polymer is adsorbed and further washing will not remove it. It is clear that such an amount of polymer represents the adsorption of more than one monolayer. This is likely due to tight entanglements between adsorbed chains and non-adsorbed chains.

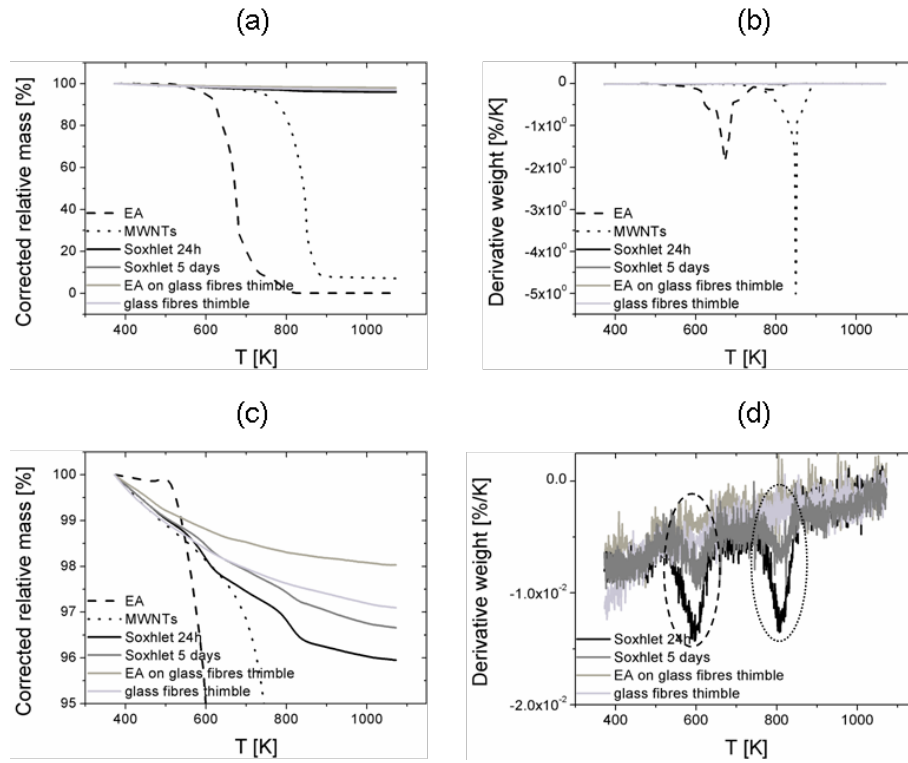


Figure 31: (a) Weight loss curves presenting the relative mass, (b) the derivative weight and (c) relative mass for high mass fractions, versus the temperature for pure EA, pure CNT, the glass fibres containing the CNT extracted from the composite EA+2%CNT using a Soxhlet during 24 hours or 5 days, the glass fibre

thimble after EA extraction for 5 days and the pure glass fibre thimble; (d) derivative weight versus sample temperature for the glass fibres containing the CNT extracted from the composite EA+2%CNT using a Soxhlet during 24 hours or 5 days, the glass fibre thimble after EA extraction for 5 days and the pure glass fibre thimble (dashed oval: polymer degradation, dotted oval: carbon nanotubes degradation)

b. Modification of the CNT

In order to prove that the adsorption of EA on CNT has an influence on the morphology, the CNT were modified by a forced adsorption of EA. The EA was dissolved in boiling chloroform and CNT are added to this solution. The ratio of EA added to the CNT was 10 wt% of the weight of CNT. After evaporation of the chloroform, the CNT with 10 wt% EA (CNT_{modifEA}) were recuperated and dispersed in PA6/12. Some aggregates are present in the blends but those modified CNT are quite well dispersed in the PA6/12 (Figure 32). The premix of PA and modified CNT was then mixed with the EA. The obtained morphology was really different from the one observed when as-produced CNT were premixed in PA. Due to the “forced adsorption” of EA in solution, the CNT migrated from the PA nodules towards the interface of the blend (Figure 33). This is also observable on the SEM micrographs after cryo-fracture of the blend (Figure 34). CNT are clearly visible on the surface of the PA nodules while no CNT are present in the EA matrix. This morphology is clearly different from the one observed in Figure 4d for unmodified CNT, where no CNT was present on the surface of the PA droplets.

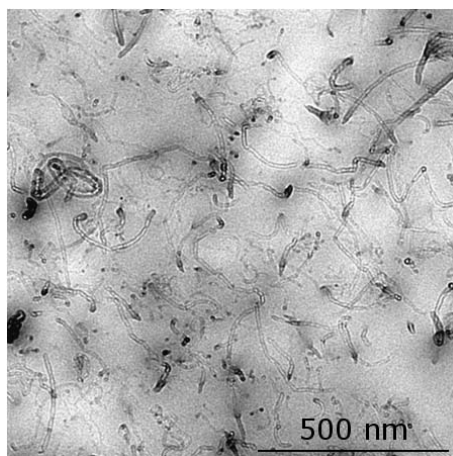


Figure 32 – TEM micrograph of PA6/12+2wt.-%CNT_{modifEA}

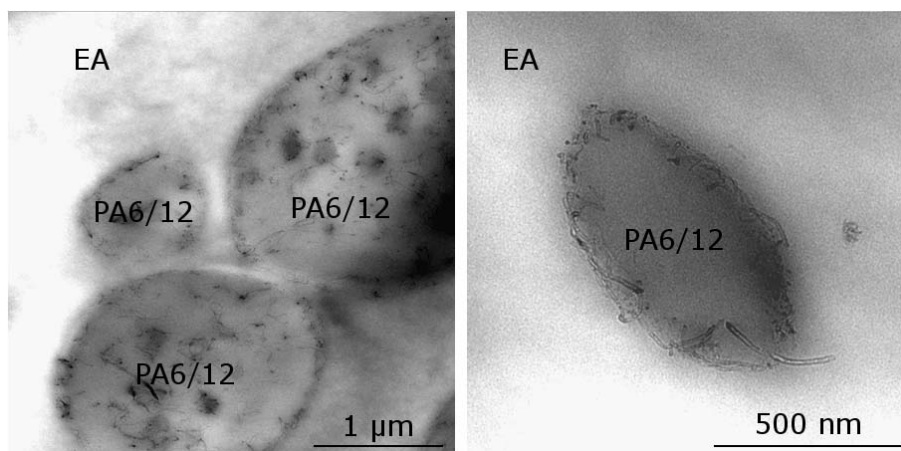


Figure 33 – TEM micrographs of a blend of 90wt% EA mixed with 10wt%PA6/12 containing modified CNT

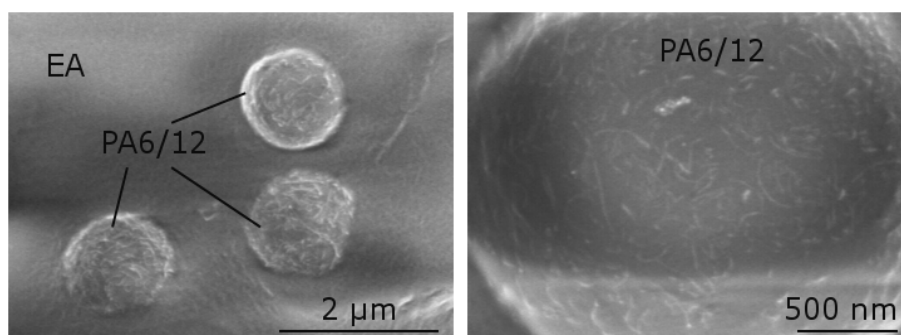


Figure 34 – SEM micrographs of nodules of PA6/12 of a blend of 90wt% EA mixed with 10wt%PA containing modified CNT, after cryofracture

4.2.2 PA adsorption

The adsorption of both PA6 and PA12 is proved by thermogravimetric analysis on CNT extracted from PA and by decantation tests.

a. Thermogravimetric analysis (TGA)

Polyamide adsorption is first proved by experiments of filtration under pressure combined with TGA. The details of the separation procedure are given in the Experimental section. Besides aluminium oxide membrane containing CNT extracted from PA6 and PA12, also the pure polymers, the neat CNT, a clean aluminium oxide membrane and an aluminium oxide membrane after filtration of a solution of pure PA are also analyzed by TGA as controls. Figure 35 and Figure 36 present the relative mass loss and the derivative weight vs. temperature for the PA – based systems. Figure 35c and Figure 36c present the

relative mass for high mass fractions. Both figures show a first mass loss around 600K which is attributed to the presence of polymer adsorbed on the CNT and a second mass around 850K which is attributed to the oxidation of the CNT. As highlighted in Figure 35d and Figure 36d, the mass loss due to the adsorbed polymer is present after 2 rinses as well as 10 rinses in approximately the same ratios, indicating that polymer is adsorbed in a partially irreversible way. However, for the PA6 based systems, due to the high background noise and the low mass losses observed, it is difficult to claim that no polymer adsorbs on the aluminium oxide membrane. Decantation tests have therefore been performed as a complementary indirect proof of PA adsorption.

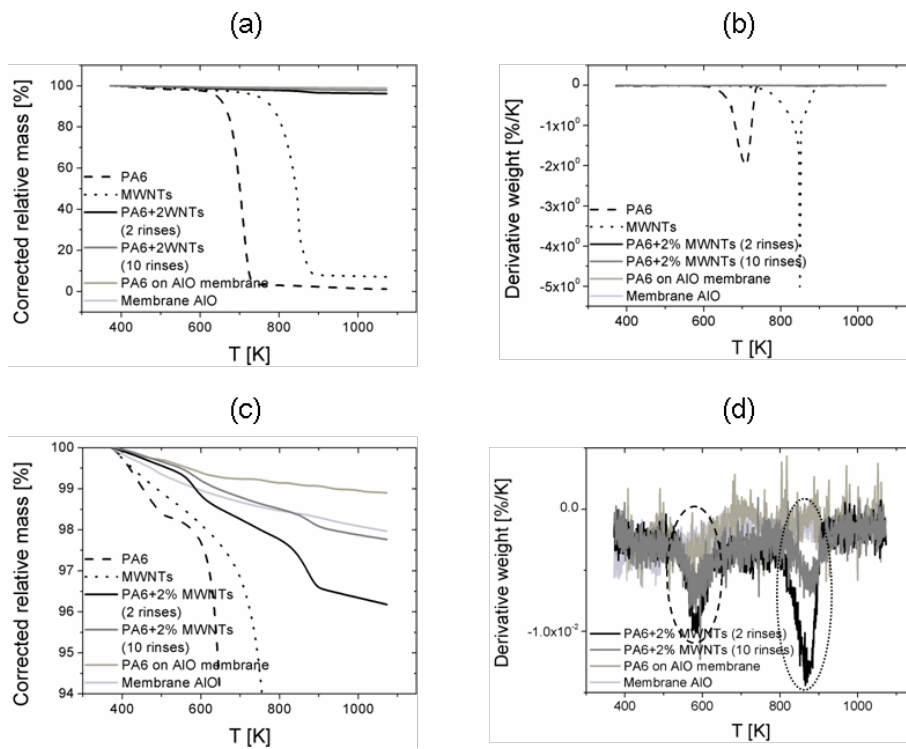


Figure 35 – (a) Weight loss curves presenting the relative mass, (b) the derivative weight and (c) relative mass for high mass fractions, versus the temperature for pure PA6, pure CNT, the aluminium oxide membrane containing the CNT extracted from the composite PA6+2%CNT using an under filtration device (see experimental section for more information) (PA6+2% CNT (2rinses); PA6+2% CNT (10rinses)), the aluminium oxide membrane after PA6 filtration and the pure aluminium oxide membrane; (d) derivative weight versus sample temperature for the glass fibres aluminium oxide membrane containing the CNT extracted from the composite PA6+2%CNT using an under filtration device (see experimental section for more information) (PA6+2% CNT (2rinses); PA6+2% CNT (10rinses)), the aluminium oxide membrane after PA6 filtration and the pure aluminium oxide

membrane (dashed oval: polymer degradation, dotted oval: carbon nanotubes degradation)

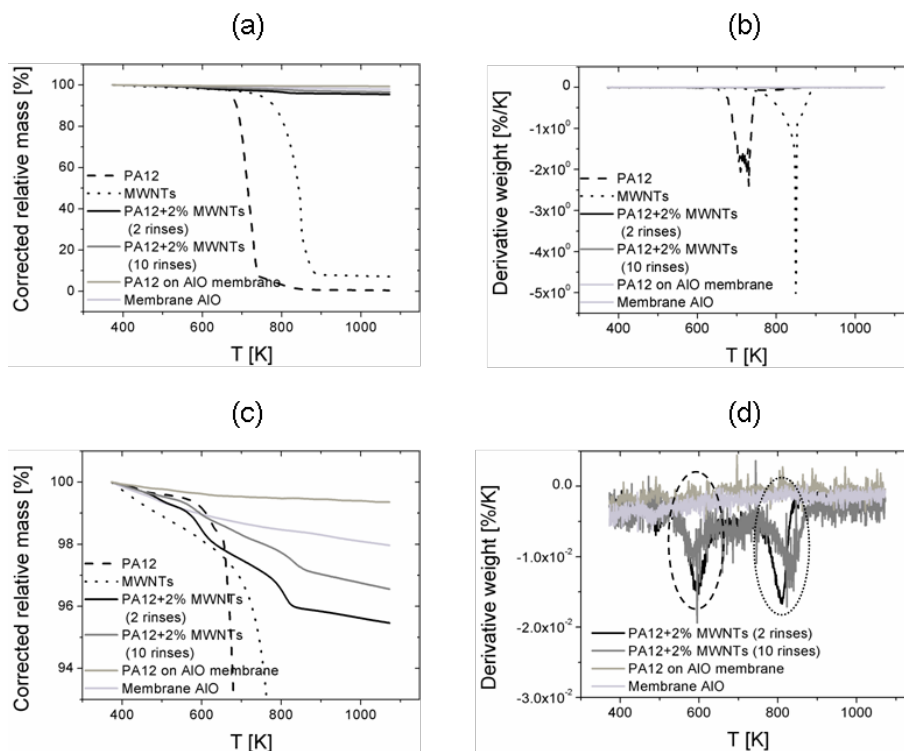


Figure 36 - (a) Weight loss curves presenting the relative mass, (b) the derivative weight and (c) relative mass for high mass fractions, versus the temperature for pure PA12, pure CNT, the aluminium oxide membrane containing the CNT extracted from the composite PA12+2%CNT using an under filtration device (see experimental section for more information) (PA12+2% CNT (2rinses); PA12+2% CNT (10rinses)), the aluminium oxide membrane after PA12 filtration and the pure aluminium oxide membrane; (d) derivative weight versus sample temperature for the glass fibres aluminium oxide membrane containing the CNT extracted from the composite PA12+2%CNT using an under filtration device (see experimental section for more information) (PA12+2% CNT (2rinses); PA12+2% CNT (10rinses)), the aluminium oxide membrane after PA12 filtration and the pure aluminium oxide membrane (dashed oval: polymer degradation, dotted oval: carbon nanotubes degradation)

b. Decantation tests

As it is not possible to fully exclude that part of the observed PA adsorption occurs on the aluminium oxide membrane, the presence of adsorbed PA is also demonstrated by decantation tests. After sonication, the solutions containing CNT were centrifugated during different times. After less than 1 minute, the milled CNT migrate towards the bottom of the flask (Figure

14a). The CNT from the composite PA6+2wt.-%CNT (Figure 14b) and the composite PA12+2wt.-%CNT (Figure 14c) partially migrate after 150 minutes but most of them are still in suspension even after at least 450 minutes centrifugation. Note also that after 6 months, no further sedimentation of the CNT in the flask is observed.

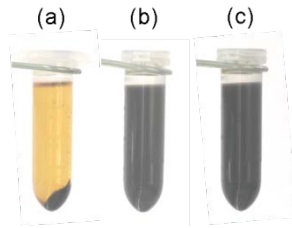


Figure 37 – Decantation tests after centrifugation; (a) milled CNT dispersed in m-cresol; (b) composite of PA6 containing CNT dissolved in m-cresol; (c) composite of PA12 containing CNT dissolved in m-cresol

The sedimentation speed v for particles can be evaluated using:

$$v = \frac{\omega^2 R (\gamma_{particles} - \gamma_{solvent}) d_p^2}{18\mu}$$

with ω the angular speed, R the centrifuge radius, γ the surface tension, d_p the equivalent particle diameter and μ the solvent viscosity. It is directly proportional to the square of the equivalent diameter of the particles. The size of the CNT, either extracted from polymer after extrusion in PA6 (Figure 37a) or PA12 (Figure 37b) or after 30 minutes milling in a vibrating mill (Figure 37c), has been measured by TEM (Figure 39). The CNT extracted from PA6 and PA12 are nearly individualized. As presented in Figure 18, the milled CNT are shorter than the extracted CNT but they are not so well individualized; aggregates are present (Figure 38).

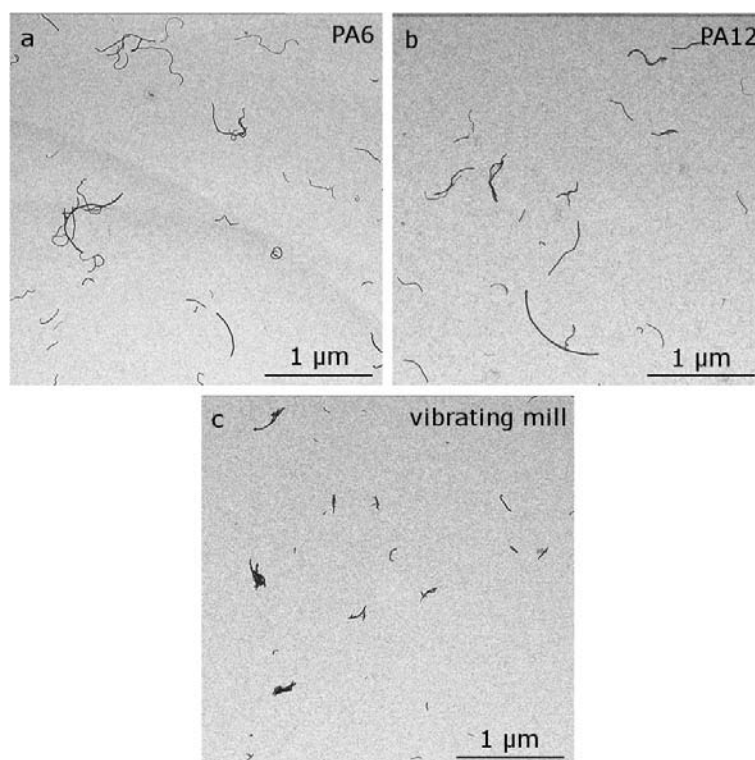


Figure 38 – TEM micrograph of the CNT (a) extracted from PA6 using m-cresol; (b) extracted from PA12 using m-cresol; (c) milled 30 minutes in a vibrating mill

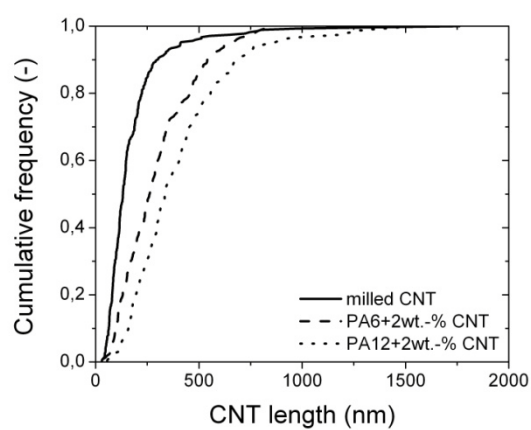


Figure 39 – Cumulative frequency of CNT from vibrating mill 30 min and extracted from PA versus the CNT length

Because the aspect ratio and aggregation is different for the different samples, the equivalent diameter of the nanoparticles is evaluated depending on their morphology. The nanotubes extracted from PA6 and PA12 are considered as cylinders presenting a diameter of 10 nm. The equivalent spherical diameter is evaluated to keep the same ratio surface-volume. The equivalent diameter for CNT extracted from PA6 and PA12 is close to 14.8 nm.

$$d_p = \frac{3d_c l_c}{2l_c + d_c}$$

For the milled CNT, two extreme cases are considered: isotropic aggregates and anisotropic aggregates or cylinders. When isotropic aggregates are considered, the average diameter of the particles is 176.7 nm. When anisotropic aggregates are considered, an equivalent diameter of 65.7 nm is found. The sedimentation speed for CNT extracted from the composites is thus predicted to be 20 to 143 times lower than the sedimentation speed of the milled CNT, depending on the morphology assumption. Theoretically, the centrifugation time of CNT from composites should therefore vary from 20 to about 140 minutes. The actual decantation results show that while a small fraction of the CNT have indeed decanted during this time range, most of them are still in suspension even for much longer centrifugation times. It is expected that the CNT remain in suspension due to the adsorption of PA on their surface and not to their very small size.

4.2.3 Adsorption mechanism

The mechanisms of adsorption of polymers on CNT have been widely studied for the non-covalent functionalization of CNT [67-71] and to improve their dispersion in organic solvents [72,73]. Some specific polymers with either ionic groups or an electron-rich backbone have already been shown to wrap around SWNT. In the absence of chemical bonding between carbon particles and polymers, the origin of the interactions is electrostatic and/or van der Waals. Xie and Soh [74] have attributed the association of CNT and amylose to non specific van der Waals forces. Baskaran et al. [63] have demonstrated that the coating or wrapping of CNT is a general phenomenon occurring between polymers and CNT. They show that coating occurs irrespective of the nature of the polymers used. This phenomenon is attributed to noncovalent and non specific molecular interactions between CH groups on polymers and CNT, leading to polymer adsorption. A few percent of polymeric adsorbents could not be removed by washing, indicating the presence of partial irreversible

coating. The authors also explain that adsorption is better in the case of melt blending or shear mixing than in the case of mixing in solution. Indeed, under these conditions, the initial contact of a chain with the CNT surface forms a CH- π interaction and successive CH groups gradually attach, leading to complete or partial adsorption of the polymer chain.

Due to this adsorption, the systems do not behave exactly as predicted by interfacial thermodynamics based on the surface properties of the neat components. This can be explained as follows: to transfer a CNT from one polymer to the other, all the macromolecules of the first polymer should be desorbed from the surface to be replaced by macromolecules of the second polymer. However, the adsorption of macromolecules is partially irreversible due to the large number of contacts between the macromolecule and the surface, leading to very high desorption activation energy. This adsorption-desorption process has already been observed and explained by Zaikin et al. [75] for the redistribution of carbon black particles in immiscible polymer blends.

5 Influence of viscosity

Although the adsorption of the first polymer in contact on the CNT can explain some deviations between the expected morphology, based on the trends provided by the wetting coefficient evaluation, and the observed morphology, it cannot explain all the differences between similar systems. For example, for a predispersion in the EA phase, when PA* or PET are used as preferred phase, some CNT are present inside the droplets of PA* or PET. On the contrary, for the same predispersion in EA, when other PA or when PC are used, no CNT is observed inside these PA or PC droplets. Moreover, in other systems where adsorption could also occur the migration from the less preferred phase to the preferred one has been observed [16]. Another parameter is thus influencing the morphology. The crystallization of some polymers is sometimes found to eject the fillers outside the crystals and concentrate them in the amorphous regions [76,77]. However, here no CNT is found between crystals in PA phase and PC is well known to be an amorphous polymer. The difference of the relative viscosities of the phases is thus studied. Indeed, it is known from literature that the relative viscosities of both phases can also play an important role in the final particles localization in the blend [8]. Some authors [78-80] have shown that the thermodynamical predictions were only achieved when the viscosity ratio is close to 1. However, it is difficult to separate the effects of viscosity from the other influent parameters. Its effect thus remains unclear. Some other authors [81] claim that the fillers locate in the more viscous phase to minimize the

dissipative energy during mixing. However, other authors state that CB particles locate preferentially in the polymer presenting the lowest viscosity [79,80]. The migration is also found to be easier in low viscosity phases [44]. Note finally that the state of dispersion of the filler in the phases significantly modifies the viscosity.

5.1 *Relative viscosities of the components*

The viscosity is a critical variable for the control of the blends morphology. Therefore, frequency sweeps at compounding temperatures have been performed for all polymers (Figure 40). The approximate shear rate range in the microcompounder, assessed by Cox-Merz equivalence, is indicated by the grey tint area.

At 180°C, PA6/12 exhibits a much higher viscosity than EA and MAEA copolymers.

At 200°C, PA6/12 exhibits a slightly higher viscosity than PP.

At 240°C, the PA* exhibits a very low viscosity compared to the ethylene based polymers (EA, EVA and MAEA). On the contrary, the PA6 and PA12 exhibit a higher viscosity.

At 280°C, EA and EVA present lower viscosities than both low and medium viscosities PC (PC_l and PC_m). PA6 presents a lower viscosity than the PC_m with medium viscosity and a similar viscosity to PC_l, with the lower viscosity. The viscosity of EA is slightly lower than the one of PBT and largely higher than the one of PET.

At 300°C, the complex viscosity of the PES is higher than the one of PC. Note also that at this temperature, PC is degrading progressively inducing a viscosity decrease at low frequency.

Finally, at 310°C, the viscosity of EA is lower than the one of PA4/6. At this temperature, EA degrades rapidly. Therefore, for low frequencies, its viscosity increases sharply. This effect is also observed, on a lower extent for PA4/6.

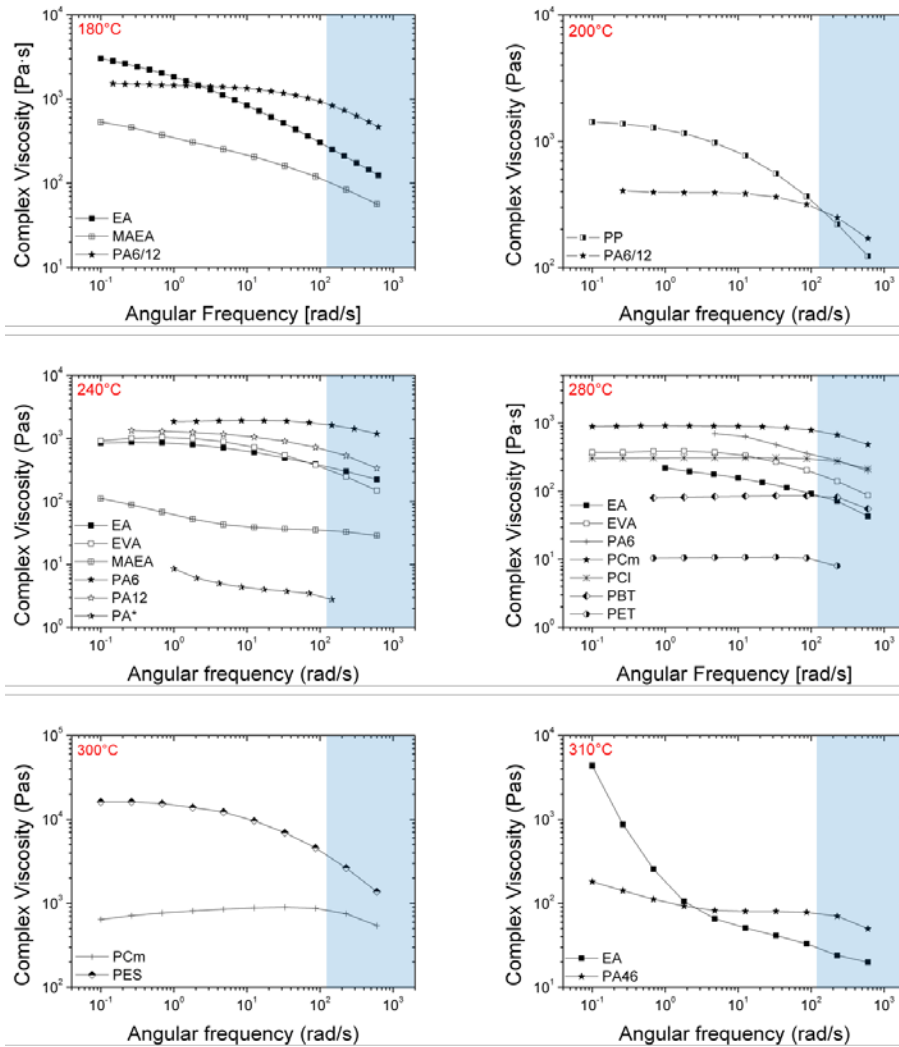


Figure 40 – Complex viscosity versus angular frequency (a) at 180°C for EA, MAEA and PA6/12; (b) at 200°C for PP and PA6/12 (c) at 240°C for EA, EVA, MAEA, PA6, PA12PA* ; (c) at 280°C for EA, EVA, PA6, PC_m, PC_i, PET and PBT ; (e) at 300°C for PC_m and PES; (f) at 310°C for EA and PA4/6

5.2 Discussion

In the following discussion, we will only discuss the blends in which no reaction between the components is observed.

In the large majority of the blends presented here, the viscosity of the most polar phase, which is often the preferred phase according to the wetting coefficient evaluation, is much higher than the one of the matrix. In the

working zone of the compounder, the viscosity of PA and PC, forming the dispersed phase, is much higher than the viscosity of the ethylene – based copolymers, forming the matrix. The preferred phase is thus the most rigid. When CNT are predispersed in the less preferred phase, they mainly migrate towards the interface and stay jammed there and a part of them remains dispersed in the matrix. Note that the interfacial confinement occurs very fast and is stable for long mixing times (at least up to 60 min).

Only the systems EA/PA* and EA/PET present a substantially lower viscosity of the preferred phase in the working zone of the compounder. In these systems, when the CNT are predispersed in EA, they are also mainly localized at the interface of the blends and some CNT remain in the EA matrix, but some of them are also present in the dispersed phase.

The high viscosity of the preferred phase could therefore prevent the migration of the filler from the less thermodynamically favoured phase towards the preferred one. If the preferred phase presents a much higher viscosity than the other phase, the filler can be blocked at the interface on a large time scale. Feng et al. [78] have observed similar results in PP/PMMA/CB blends. The thermodynamics predicts the localization of the CB in PMMA phase. The three components were mixed simultaneously and the PMMA is the minor phase. CB are found in the PMMA phase only when the phases present similar viscosities. When the viscosity of PMMA is higher than the one of PP, the particles remain at the interface and for even more rigid PMMA, CB remain in PP. Clarke et al [79] have presented similar results for blends of natural rubber (NR) and a nitrile rubber (NBR) with an acrylonitrile content of 45%.

As it is very difficult to decouple the effect of the viscosity from other parameters, the influence of the viscosity remains far from trivial.

6 General mechanism

The final localization of CNT in immiscible polymer blends is controlled by different factors. The driving force for the migration is the minimization of the interfacial energy of the blend. If the surface tensions of both polymers and CNT are precisely known, the evaluation of the wetting coefficient gives a theoretical prediction of the equilibrium position of the filler. However, adsorption phenomena must also be taken into account as it modifies the surface and thus the surface energy of the CNT. The relative viscosity of the phases also seems to influence the final CNT localization.

Based on the observations of different systems, a general mechanism for the CNT localization in immiscible polymer blends can be proposed. Thermodynamics defines the preferred localization of the CNT: either in one phase or at the interface. In the following discussion, the dispersed phase is the most polar phase, which, according to thermodynamic predictions, is also generally the preferred phase. This arbitrary choice is made because the apparent migration is known to be easier from the matrix to the dispersed phase [8], due to the presence of a more important shear field. However, the discussion can also apply to systems in which the dispersed phase is the less polar phase or to co-continuous structures.

When the interface is the preferred localization, the CNT will migrate towards the interface of the blends independently of the phase in which they are predispersed (Figure 41), as it is observed, for example, for EA/PA6 blends.

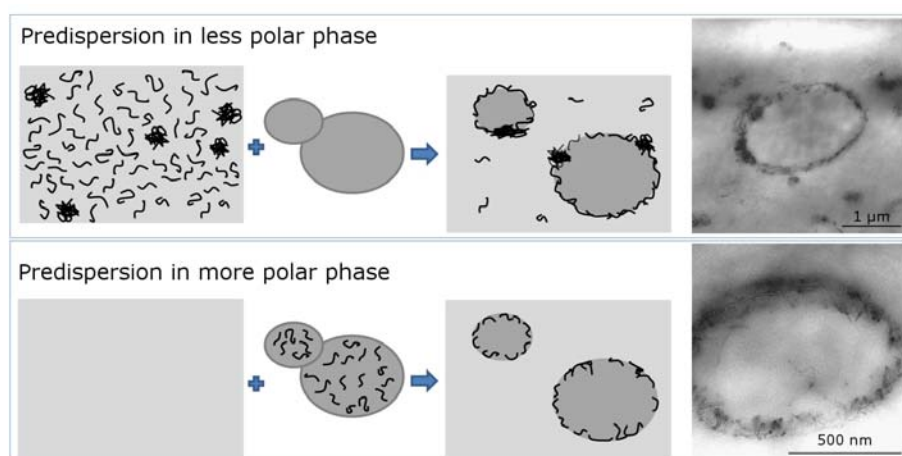


Figure 41 – Scheme of the migration for blends in which the thermodynamics predicts an interfacial localization

Figure 42 presents the behaviour of CNT in more details. When CNT are first dispersed in the more polar phase (MP) (Figure 42a), e.g. PA6, adsorption of MP macromolecules occurs on CNT. They migrate towards the interface, the predicted equilibrium position, but stay pinned on the MP side. When CNT are first dispersed in the less polar phase (LP) (Figure 42b), e.g. EA, corresponding macromolecules adsorb, at least partially, on CNT surface. CNT migrate towards the interface and stay jammed there. As there is a slight preference of the CNT for the most polar phase, it is possible that part of the less polar macromolecules desorbs in favour of the most polar macromolecules.

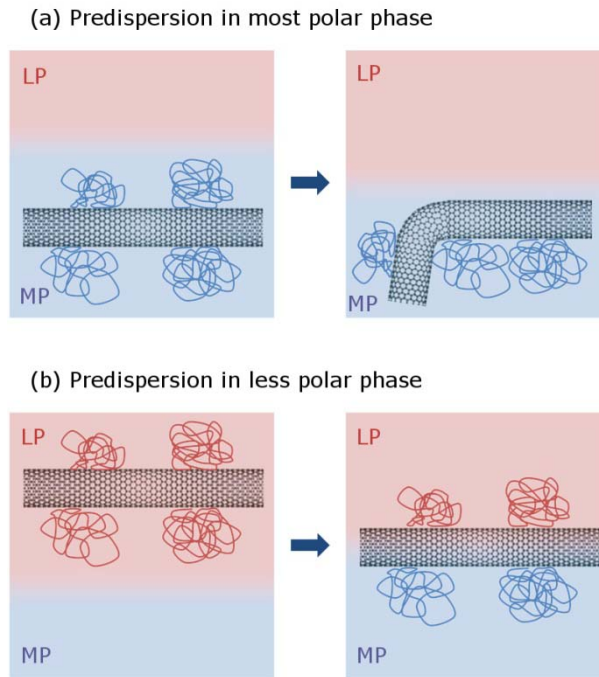


Figure 42 – Scheme presenting the influence of polymer chain adsorption on the localization of the CNT when the thermodynamics predicts an interfacial localization (a) predispersion in the most polar phase of the blend, MP; (b) predispersion in the less polar phase of the blend, LP

When the wetting coefficient predicts the CNT localization in the most polar phase, different cases can occur (Figure 43). First, if CNT are predispersed in the less polar phase (LP), CNT migrate towards the preferred phase (MP). When the dispersed phase presents a much higher viscosity than the matrix, CNT are jammed at the interface. When the dispersed phase presents a lower viscosity than the matrix, part of the CNT is jammed at the interface and part of them penetrates inside the dispersed phase. When CNT are predispersed in the dispersed phase, which is the thermodynamically favoured phase, CNT remain in this phase.

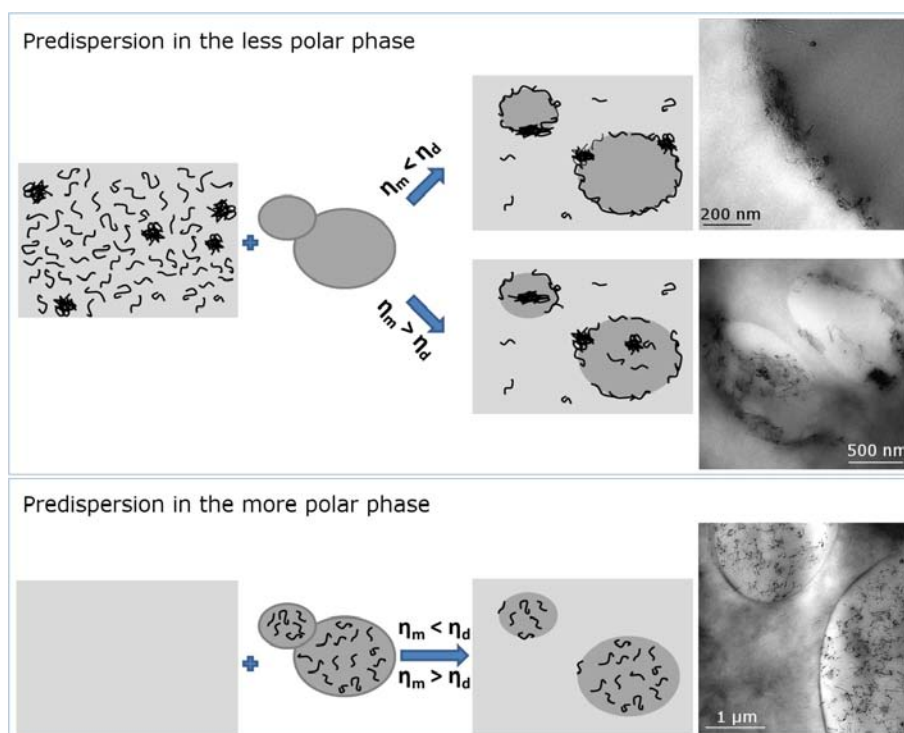


Figure 43 – Migration of the CNT for a thermodynamically “more polar phase” preferred phase

Figure 44 presents this behaviour in terms of adsorption phenomenon. If CNT are predispersed in the preferred phase (Figure 44a), macromolecules of this phase adsorb on the CNT. There is no driving force for the migration of the fillers and thus they remain in this phase. When CNT are predispersed in the less preferred phase (Figure 44b), there is a thermodynamic driving force for their migration towards the preferred phase. If the viscosity of the preferred phase is much higher than the viscosity of the less polar phase ($\eta_{MP} > \eta_{LP}$), CNT are jammed at the interface (Figure 44b1). Indeed, CNT migrate towards the interface but LP adsorbed chains prevent further migration due to the high energy required to fully desorb LP chains. Assuming that CNT are not fully covered with LP phase chains and/or that a part of the adsorbed chains can desorb, part of the CNT migrate inside the MP droplets. If the viscosity of the preferred phase is lower than the viscosity of the LP phase ($\eta_{MP} < \eta_{LP}$), part of the CNT will be jammed at the interface due to partially irreversible adsorption of LP. However, if some LP chains desorb, leading to free CNT, or if the polymer coating less efficient, then, some CNT free of LP chains will be able to penetrate inside the preferred phase (Figure 44b2).

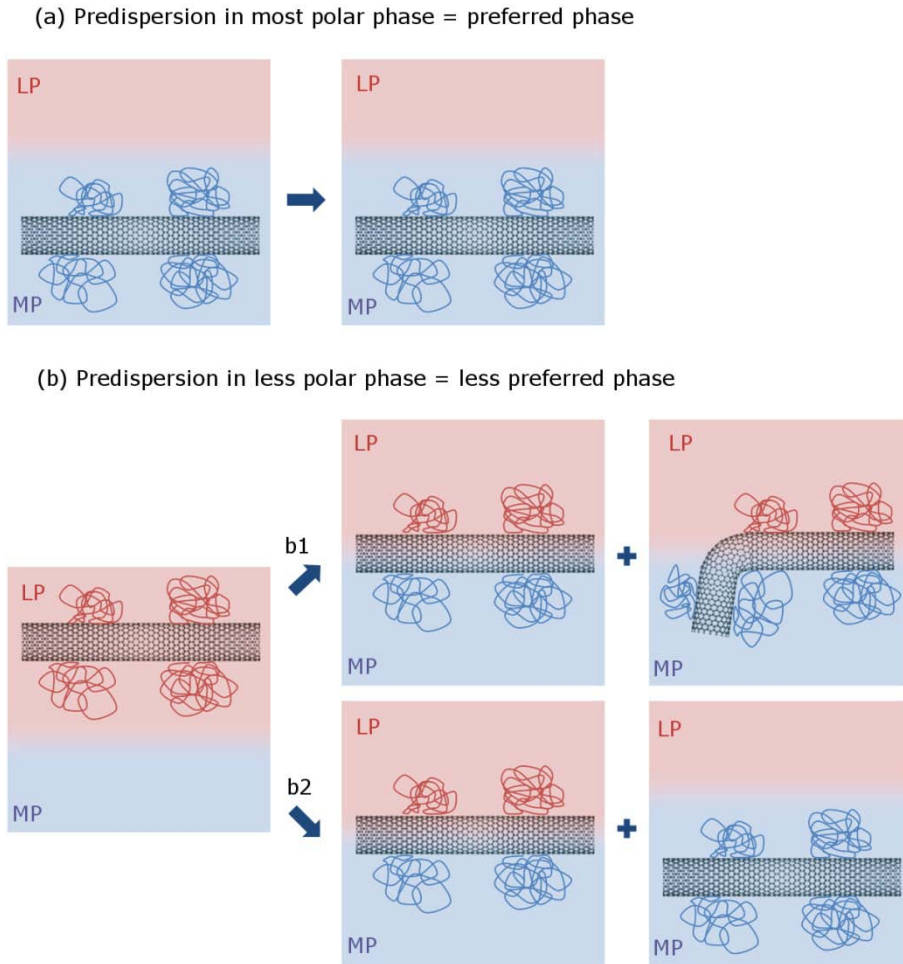


Figure 44 – Scheme presenting the influence of polymer chain adsorption on the localization of the CNT when the thermodynamics predicts that the preferred phase is the most polar one (a) predispersion in the most polar phase of the blend, MP; (b) predispersion in the less polar phase of the blend, LP with (b1) $\eta_{MP} > \eta_{LP}$ and (b2) $\eta_{MP} < \eta_{LP}$

Nevertheless, this mechanism can not describe the behaviour observed for PC/PES systems. In this case, thermodynamics predicts an interfacial localization of the CNT. It is assumed that both polymers have very good affinity with CNT due to the presence of aromatic rings in their structure. The adsorption of PC chains on CNT has been widely demonstrated in literature [82-86]. Ding et al. [86] have shown that CNT are covered with an adhered layer of polycarbonate. The layer thickness of the polymer coating observed is quite

large and comparable in size to the diameter of the as-received CNT. PES chains are expected to also adsorb on CNT surface. Although a few CNT can be trapped at the interface, the surface of the CNT can be so modified by polymer wrapping that no migration occurs anymore because the CNT do not “see” the interface anymore.

CONCLUSION

The parameters influencing the localization of carbon nanotubes (CNT) in immiscible polymer blends are studied. They are discussed in terms of thermodynamic predictions based on the evaluation of the wetting coefficient, and kinetic parameters (mixing strategy and relative viscosities of the phases). The possibility to confine unfunctionalized carbon nanotubes at the interface of a variety of blends, even for long mixing times, is demonstrated. Moreover a general mechanism for CNT localization is drawn and is presented in Figure 45. The localization of CNT is determined, on the one hand, by the interactions between the filler and the polymers and, on the other hand, by at least partially irreversible adsorption of one polymer at the surface of the nanotubes controlled by the mixing sequence. The viscosity also plays an important role.

Note that thermodynamic predictions must be handled carefully because the evaluation of the surface energy of polymers at high temperature and of CNT is not trivial. However, assuming that the surface energies of polymers and CNT are precisely known, the evaluation of the wetting coefficient predicts the equilibrium position of the fillers.

First, if thermodynamics predictions define the interface as the CNT preferred phase, the CNT migrate towards the interface independently of the mixing sequence.

Second if one phase is designed as the preferred phase, the morphology depends on the mixing strategy. First, if CNT are predispersed in the preferred phase, in the absence of chemical modification, they remain in this phase. Second, if CNT are predispersed in the less preferred phase, they migrate towards the preferred phase. Nonetheless, adsorption of the first polymer in contact with the CNT as well as relative viscosities of both phases influence CNT localization. If the first polymer in contact with the CNT adsorb, in an at least partially irreversible way, on the CNT surface, the transfer of the CNT towards the preferred phase is hindered. It is believed that if macromolecules of the first polymer in contact can desorb or if there are CNT free of polymer chains,

CNT will be able to migrate inside the preferred phase, if the viscosity of this latter is not too high. If the preferred phase presents a very high viscosity compared to the one of the matrix, it will prevent the transfer of the CNT from the less preferred phase to the preferred one.

It is worth noting that the mechanism described here above, however, does not apply to blends where important polymer wrapping occurs. Indeed if the surface of the CNT is fully coated by polymer chains, from the point of view of the surface of the object, it can not be considered as a pure CNT anymore.

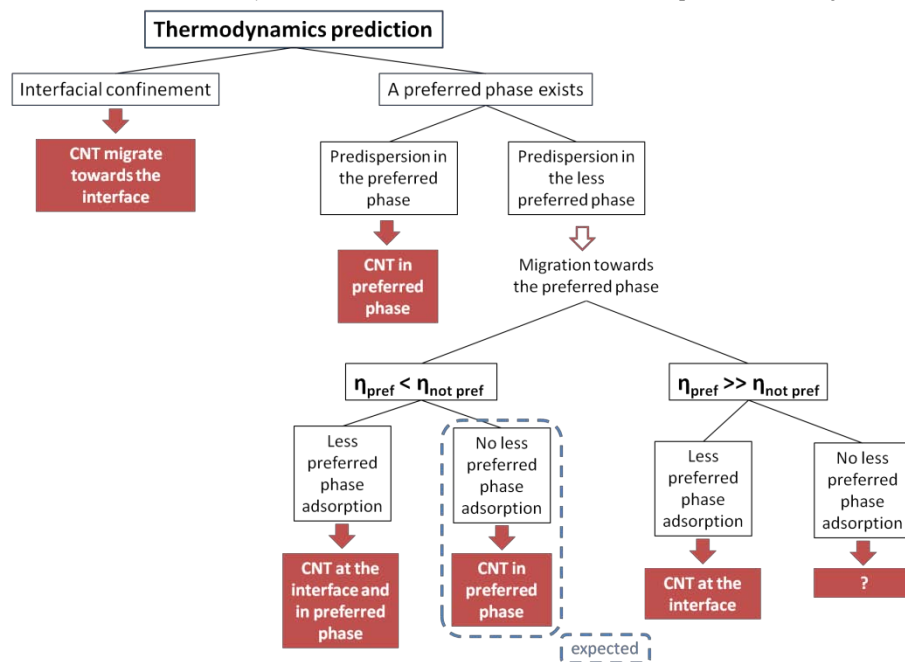


Figure 45 – General mechanism for CNT localization in polymer blends assuming that no important polymer coating occurs

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Chapter 4

MORPHOLOGY STABILIZATION BY CARBON NANOTUBES INTERFACIAL CONFINEMENT

ABSTRACT

This chapter demonstrates the effect of the interfacial confinement of unfunctionalized multiwalled carbon nanotubes (CNT) on coalescence suppression in an immiscible polymer blend exhibiting a sea-island morphology. The effect of carbon nanotubes on morphological stabilization in polyamide (PA)/ethylene-methyl acrylate random copolymer (EA) blends is studied using electronic microscopy techniques. Owing to their interfacial localization, CNT are shown to enhance both phase dispersion and stability of the dispersed phase for long mixing time (at least 60 minutes) and very low filler content (0.5 wt.-% CNT) compared to what was previously observed in literature. CNT also produce a more uniform distribution of droplets size. The main stabilization mechanism proposed is the formation of a deformable barrier network providing a mechanical barrier against coalescence. Blends stabilized by solid anisotropic nanoparticles, like CNT, could therefore offer an interesting alternative to blends compatibilized by block-copolymers.

A publication has been extracted from this chapter:

A.-C. Baudouin, D. Auhl, F. Tao, J. Devaux, C. Bailly, *Polymer Blend Emulsion Stabilization using Carbon Nanotubes Interfacial Confinement*, Polymer 2010; 52: 149-156

INTRODUCTION

Multiphase polymer blends have attracted tremendous attention to achieve valuable properties materials by taking advantage of the attractive features of each component. However, binary blends of immiscible polymers generally exhibit poor properties due to their coarse and unstable morphology ^[1]. To generate a material exhibiting the desired properties, it is therefore essential to produce a blend with fine and stable dispersed droplets.

Coalescence can be reduced by the use of interfacial block copolymers, which act as surfactants stabilizing emulsions ^[2]. Compatibilization can also be achieved with the help of nanoparticles (carbon black, clay, silica, metal oxides, polymer latex etc.), as it has been reported for a few decades ^[3- 15]. The particles can be trapped at the interface between polymers to minimize the total interfacial energy of the system. These stabilized emulsions are called Ramdsen-Pickering emulsions, as a reference to Ramsden ^[16] and Pickering ^[17] studies on the stabilization of low viscosity fluids emulsions by a small proportion of insoluble particles. The effectiveness of emulsion stabilization depends on various parameters such as the concentration, the size, the shape, the wettability and the level of interparticle interactions of the particles.^[18] Recently, Madivala et al. ^[19] and Vandebril et al. ^[20] demonstrated that sufficiently elongated particles can be effective coalescence suppressors of immiscible fluid phases, even when spherical or lower aspect ratio particles exhibiting the same wetting properties are inefficient. Thus anisotropic particles at low volume fraction lead to improved stabilization compared to spherical particles. Moreover, morphology stabilization by nanoparticles presents further advantages, compared to other methods, by adding interesting properties such as improved thermal or electrical conductivity.

Among nanofillers, carbon nanotubes (CNT) have attracted tremendous attention since their discovery in 1991^[21]. They combine a high aspect ratio with exceptional electrical, mechanical and thermal properties ^[22].

Carbon nanotubes have already shown their ability to refine the morphology of immiscible polymer blends ^[23- 26]. However, only few authors have focused on the stabilization of polymer blends by carbon nanotubes. Recently, Bose et al. ^[27] used amine functionalized multiwall carbon nanotubes (NH₂-CNT) to stabilize poly(methyl methacrylate) (PMMA) phase in poly[(α -methyl styrene)-co-acrylonitrile] (P α MSAN) / PMMA blends. NH₂-CNT were randomly dispersed in the homogeneous blends. Due to thermodynamic considerations, the NH₂-

CNT were localized only in the P α MSAN after phase separation. It was observed that a typical loading of 1.25wt.-% NH₂-CNT totally suppresses the coalescence on a practical time scale (at least 2500 seconds).

In the previous chapter and in published contributions [28,29], we have demonstrated the interfacial localization of unfunctionalized CNT in immiscible polymer blends. In this context, we explore the morphology of blends of polyamide (PA), ethylene methyl acrylate copolymer (EA) and CNT. Here we study the stabilization of a simple sea-island morphology by unfunctionalized CNT localized at the interface, with the aim to extrapolate these results to co-continuous structures in the future. The implication of CNT interfacial confinement on the stabilization of blend morphology is investigated in the present paper by a combination of TEM and SEM techniques. The overall objective is to demonstrate that unfunctionalized CNT, if localized at the interface, produce stabilized morphologies at lower filler content than was previously reported in literature.

EXPERIMENTAL

1 Materials

The blends under study are composed of two immiscible polymers: a polyamide 6/12 (PA) and a random copolymer of ethylene and methyl acrylate (EA). This particular blend has been selected due to the very good stability of both polymers at 180°C. The CNT are unpurified and unfunctionalized.

2 Compounding Procedure

Blends of 90wt.-% EA and 10wt.-% PA with and without CNT have been prepared in a co-rotating twin-screw minicompounder at 180°C and 250 rpm. The mixing time is either 10 or 60 minutes. Two kinds of blends have been prepared by simultaneous mixing: binary blends of EA and PA without CNT and ternary blends of EA and PA with various amounts of CNT. The torque has been measured during the compounding of neat polymers and composites to follow their evolution with extrusion time.

3 Characterization

3.1 Microscopy

Scanning electron microscopy (SEM) has been performed on cryo-fractured samples.

Transmission electron microscopy (TEM) has been performed on ultrathin sections of approximately 95 nm in thickness. The droplets diameter has been evaluated on TEM micrographs. Although the measured diameter is not the actual diameter of the droplets, this measurement allows following the morphology evolution with time. A LogNormal law is used to fit the datas of relative frequency (Figure 11, Figure 12) and is also integrated for cumulative frequency curves.

3.2 Rheology

The measurements have been performed under nitrogen, to avoid thermo-oxidative degradation, at the compounding temperature, i.e. 180°C. The thermal stability of both polymers is analyzed using the multiwave-frequency option. For the EA copolymer, the fundamental frequency is 0.1 rad/s with 5% deformation plus two additional wave forms at 1 rad/s with 1.5% and 10 rad/s with 0.5% respectively. For PA, a higher deformation has been applied to minimize noise at low frequency. The fundamental frequency is therefore 0.1 rad/s with 10% deformation and two other frequencies of 1 rad/s with 3% and 10 rad/s with 1%. The frequency sweep experiments were conducted in the frequency range of 0.1-600 rad/s.

RESULTS AND DISCUSSION

1 Rheological behaviour of EA and PA

The viscosity ratio is one of the most critical variables controlling blend morphology. Torque was monitored during compounding and rheological experiments performed in order to assess the possible influence of chemical changes during processing on this parameter.

The evolution of the torque in the extruder was followed during compounding (Figure 1). The initial values are around 2500N and 4800N for EA and PA

respectively. This is a good hint that PA is more viscous than EA under these flow conditions.

The torque of EA is slightly decreasing with compounding time, indicating the polymer is slowly degrading over long processing times.

For PA, a torque increase of about 15% is observed during the first 20 minutes. This increase is probably related to condensation reactions occurring in the compounder. At later times, the PA torque is decreasing, reflecting a slow degradation.

The torque behaviour of the blend (circle symbol) is very similar to the data obtained by averaging the EA and PA values (cross symbol). Most probably, the two polymers behave in the blend approximately the same way as when compounded alone.

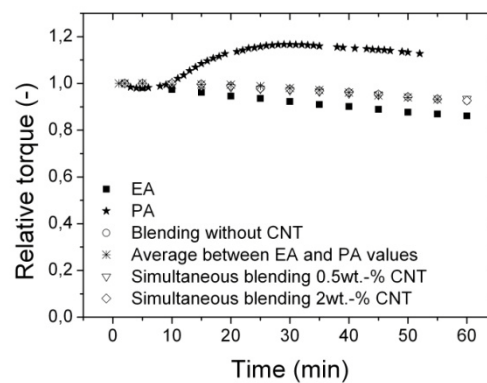


Figure 1 – Relative torque versus compounding time for pure polymers as well as unfilled and filled blends at 180°C and 250rpm.

A frequency sweep at compounding temperature (Figure 2) confirms the higher viscosity of the minor phase by comparison with the continuous one. In the shear rate range of the compounder, the PA viscosity is 2-3 times higher than the viscosity of EA (assessed from Cox-Merz equivalence). This is consistent with the torque ratio observed in the compounder.

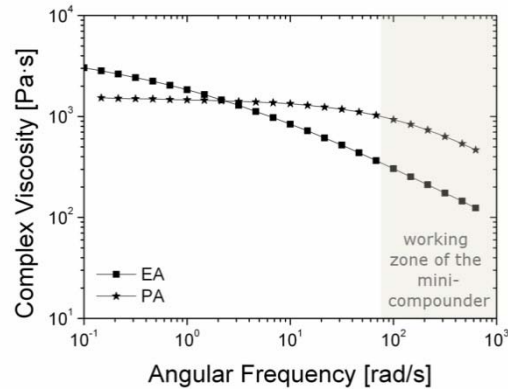


Figure 2 – Complex viscosity of EA and PA versus angular frequency. The approximate shear rate range in the minicompounder is indicated by the grey tint area

In order to assess the thermal stability of both polymers at high temperature, we have also performed a multiwave-frequency time sweep of the pure polymers at compounding temperature. From this test (Figure 3), we observe essentially no evolution of the dynamic moduli up to 4000 s. at the tested frequencies and we can conclude that there is very little thermal degradation during the experimental time. The torque data in the extruder and the dynamic moduli in the rheometer show different trends but those differences can be understood. The torque decrease in the extruder highlights a shear-induced degradation, while in the rheometer, the pure thermal degradation appears very limited in the same time and temperature window. The torque increase observed for PA at short times in the extruder is not paralleled by a viscosity increase in the rheometer and must be due to a condensation reaction that is enhanced by mixing.

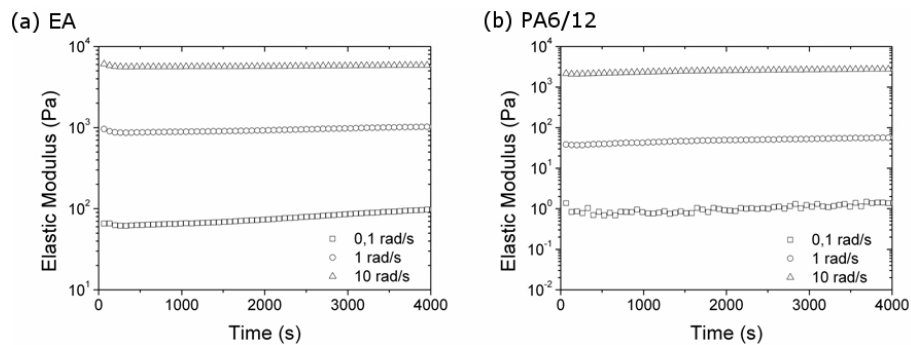


Figure 3 – Time evolution of the elastic modulus with time at 180°C for different frequencies ($\omega = 0.1, 1, 10$ rad/s) for (a) EA and (b) PA

2 Blend morphology of EA/PA/CNT nanocomposites

The morphology of the blend without CNT is shown on Figure 4. TEM micrographs show that in absence of CNT, many EA sub-inclusions are present in the PA dispersed phase. Figure 4a shows a droplet of PA dispersed in the EA matrix after 10 minutes of mixing. Figure 4b presents a droplet after 60 minutes of mixing with a very high number of EA sub-inclusions.

The morphology of the blend in the presence of CNT is shown on Figure 5. In the presence of CNT, there are nearly no EA sub-inclusions, even after 60 minutes of mixing (Figure 5a - c). The CNT are mainly localized at the interface, whatever the CNT amount used, after 10 minutes or 60 minutes mixing. The interfacial localization is also clear from the SEM micrograph after cryofracture (Figure 5d), which presents a PA droplet covered with CNT. The observed confinement can be rationalized by thermodynamics and irreversible polymer adsorption on CNT^[28,29].

Sub-inclusions of the matrix phase are spontaneously formed by coalescence of poorly stabilized dispersed phase during the later stage of mixing, i.e., when coalescence dominates over the melting or softening process^[30,31]. The high amount of sub-inclusions observed after 60 minutes mixing hence witnesses the dispersed phase coalescence during mixing. On the contrary, the very low amount of sub-inclusions in presence of CNT highlights a strong reduction and/or slowing down of coalescence mechanisms.

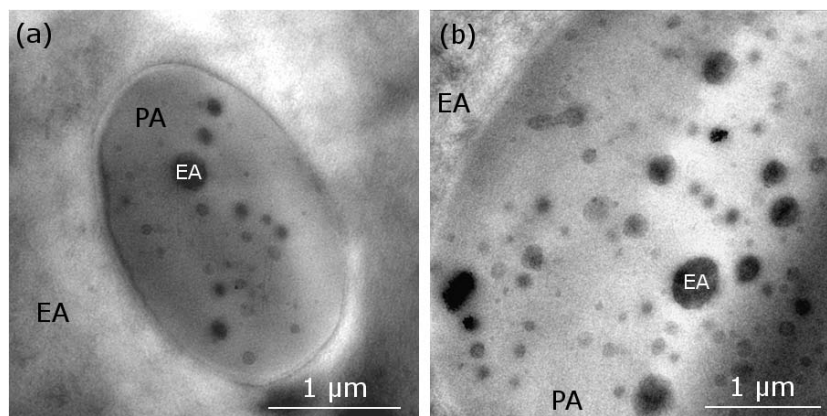


Figure 4 - (a, b) TEM micrographs of a blend of EA and PA without CNT, (a) 10 minutes mixing, (b) 60 minutes mixing

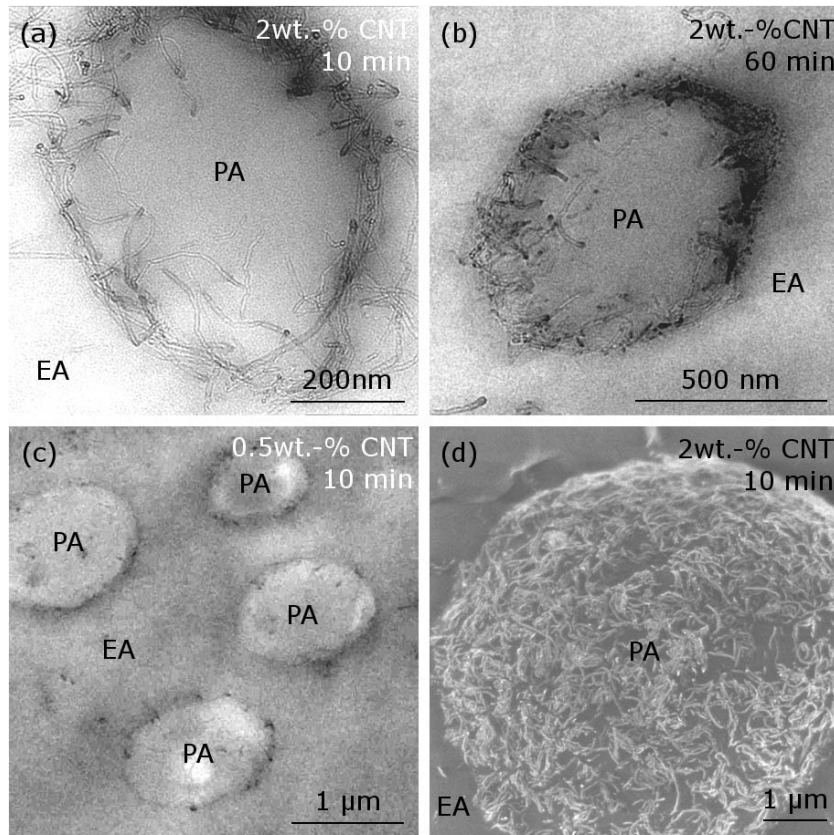


Figure 5 – (a – c) TEM micrographs of a blend of EA, PA and CNT: (a) 2wt.-%CNT, 10 minutes mixing; (b) 2wt.-% CNT, 60 minutes mixing; (c) 0.5wt.-% CNT, 10 minutes mixing ; and (d) SEM micrograph of a cryofractured blend of EA, PA and 2wt.-%CNT, 10 minutes mixing

3 Morphology Evolution with Time

The evolution of the morphology with increasing compounding time is shown in Figure 7 and Figure 8. In the absence of CNT, the morphology coarsens with increasing mixing time (Figure 7 a – d). This increase can be explained by the rheological behavior of both polymers. In the approximate deformation rate range of the minicompounder (assuming Cox-Merz equivalence and predominant shear deformation), the viscosity ratio is high, of the order of 3, with the dispersed phase being the more viscous (see Figure 2).

The critical capillary number is the minimal value of the capillary number for dispersed particle break up. The capillary number is expressed as:

$$C_a = \frac{\eta_c r_d \dot{\gamma}}{\gamma}$$

where η_c is the continuous phase viscosity, r_d is the radius of the dispersed phase, $\dot{\gamma}$ is the shear rate, and γ is the interfacial tension.

If the critical C_a is reached, a droplet will extend and break into two or more droplets. It is a function of the viscosity ratio, p :

$$p = \frac{\eta_d}{\eta_c}$$

where η_c is the continuous phase viscosity and η_d is the dispersed phase viscosity

The relationship between the critical C_a and the viscosity ratio, p , was mapped by Grace [32], for simple shear and extensional flow (Figure 6).

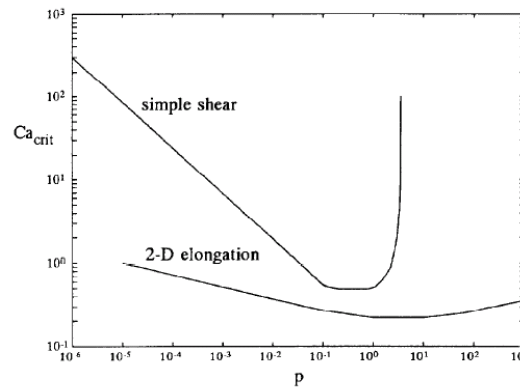


Figure 6 – Critical Capillary number vs the viscosity ratio p in simple shear and plane hyperbolic flow [33]

In the present situation, the Grace plot (critical capillary number C_a vs. viscosity ratio p) predicts a less than optimal dispersion, moreover strongly negatively affected by the viscosity ratio. It has of course to be kept in mind that the Grace plot can only be applied very qualitatively as the deformation field in the extruder is complex rather than pure shear and the phases are viscoelastic rather than purely viscous. However, rough trends should be respected. The average particle size of the unmodified EA/PA blend (Figure 7) increases approximately by a factor 3 between 10 and 60 minutes. This result is

compatible with a slight increase of the viscosity ratio, which should strongly negatively affect dispersion, as confirmed by the simultaneous torque increase of 15% observed for PA and slow decrease observed for EA (see Figure 1).

On the contrary, in the presence of CNT, the morphology is stabilized against coalescence. TEM and SEM micrographs (Figure 8 a – d) show that when EA and PA are simultaneously mixed with 2wt.-% CNT, the droplet size remains stable during mixing. No increase of the diameter is observed and small PA droplets with CNT at the interface are still present after 60 minutes compounding (inserts Figure 8b,d). This suggests that the distribution generated during the first moments of mixing is “frozen” and not further affected by the change in viscosity of the phases.

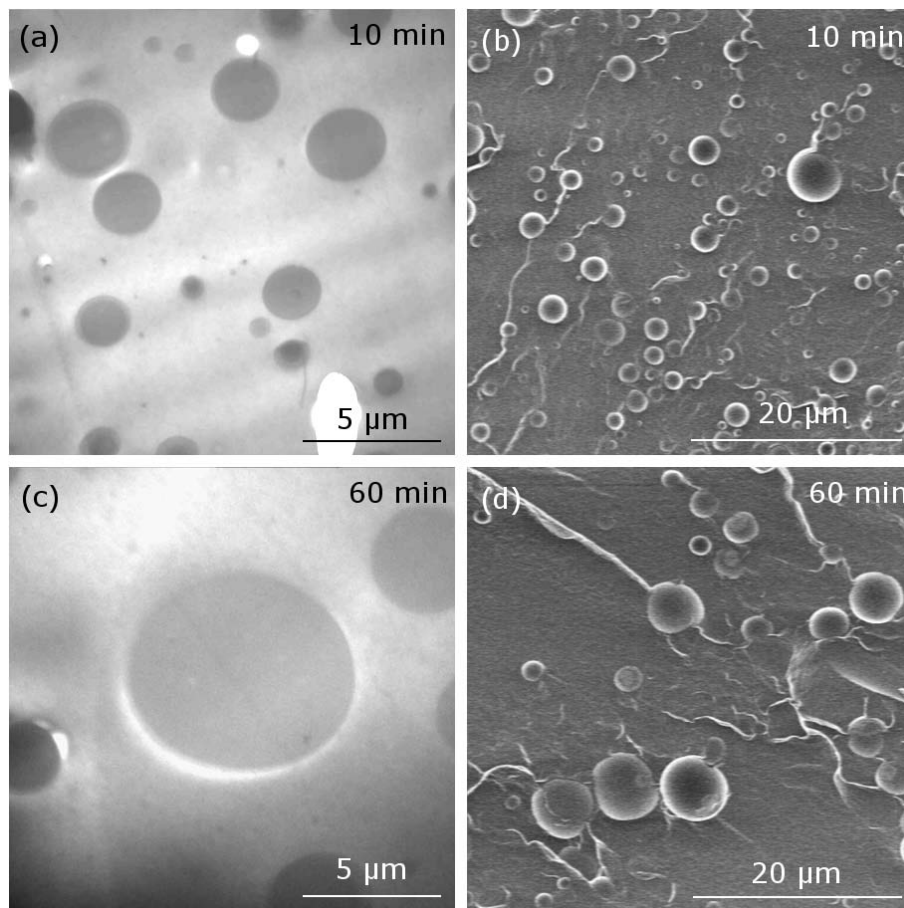


Figure 7 – TEM (a, c) and SEM (b, d) micrographs presenting the evolution of the morphology with compounding time in the absence of CNT (a, b) 10 minutes compounding and (c, d) 60 minutes compounding

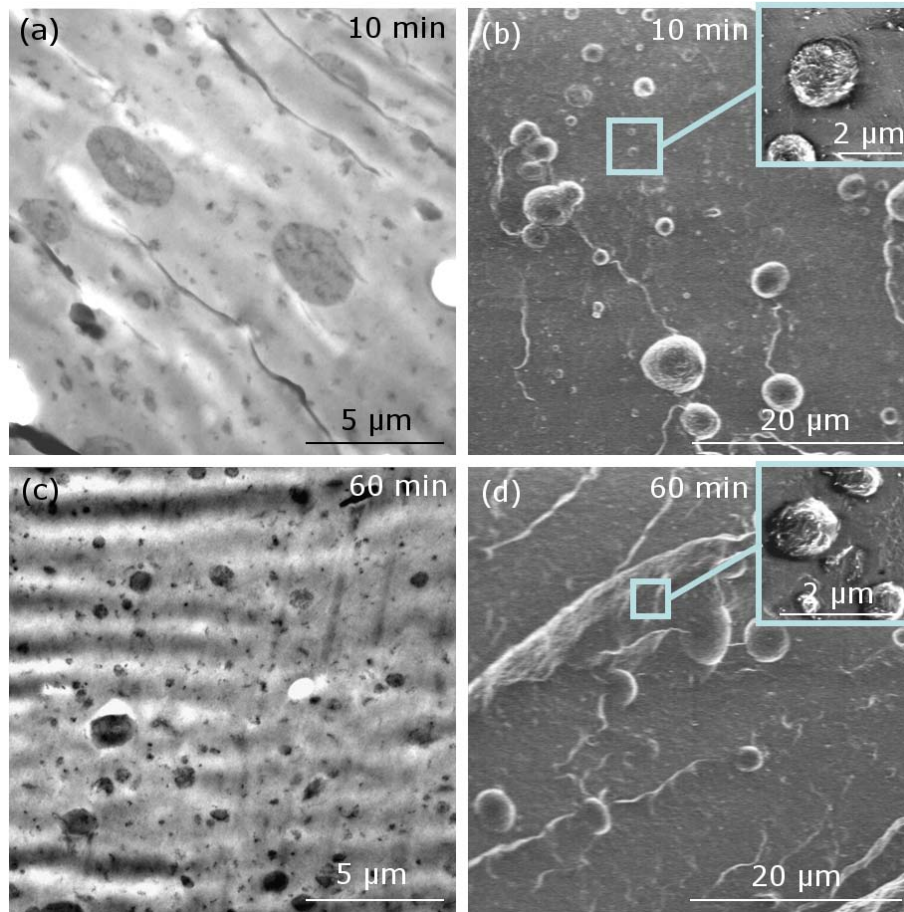


Figure 8 – TEM (a, c) and SEM (b, d) micrographs presenting the evolution of the morphology with compounding time in the presence of 2wt.-% CNT (a, b) 10 minutes compounding and (c, d) 60 minutes compounding

4 Quantitative Image Analysis

The size of the PA droplets has been measured on TEM micrographs. The cumulative frequency versus the measured droplet diameter is shown in Figure 9 and Figure 10. The data have been further processed and fitted with LogNormal law. The relative frequency is thus expressed by a LogNormal law while the cumulative frequency is expressed by an integration of the LogNormal law (Figure 11, Figure 12).

Two effects are clearly highlighted on these graphs. First, at equivalent compounding time, the droplets are smaller when CNT are simultaneously

mixed with the polymers even at only 0.5wt.-% CNT (Figure 9, Figure 11). Thus, unpurified and unfunctionalized CNT enhance phase dispersion. Indeed, the as-produced CNT exhibit a length comparable or higher than the diameter of the dispersed phase (average length $1.5\mu\text{m}$). They are therefore able to enhance phase dispersion during processing by splitting the polymer droplets into smaller particles, leading to finer dispersion as already been observed by Li et al. [34].

Second, due to the interfacial localization of the CNT, the blends behave like Pickering emulsions. The droplets of the dispersed phase are stabilized against coalescence by the CNT adsorbed at the interface. Moreover, this stabilization is effective even at very long mixing times (at least 60 minutes) and low CNT contents (0.5wt% CNT) (Figure 10). Low amounts of particles, leading to only sparsely coated droplets are thus sufficient to reduce coalescence rates, as observed for CB in EA/PA12 by Vermant et al. [3] or for hydrophobic silica in PP/PS blends by Elias et al. [35].

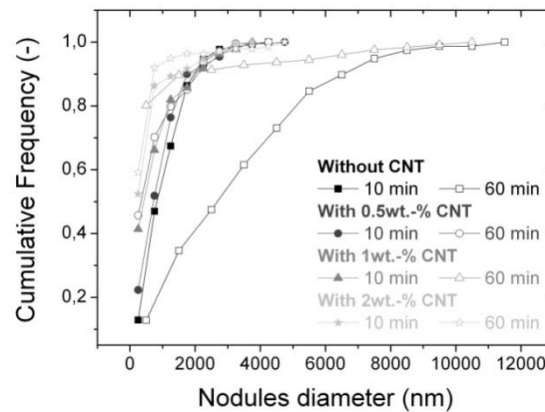


Figure 9 – Cumulative frequency versus droplet diameter for unfilled and filled blends (0.5wt.-% - 2wt.-%CNT) for 10 and 60 minutes blending (measured on TEM micrographs)

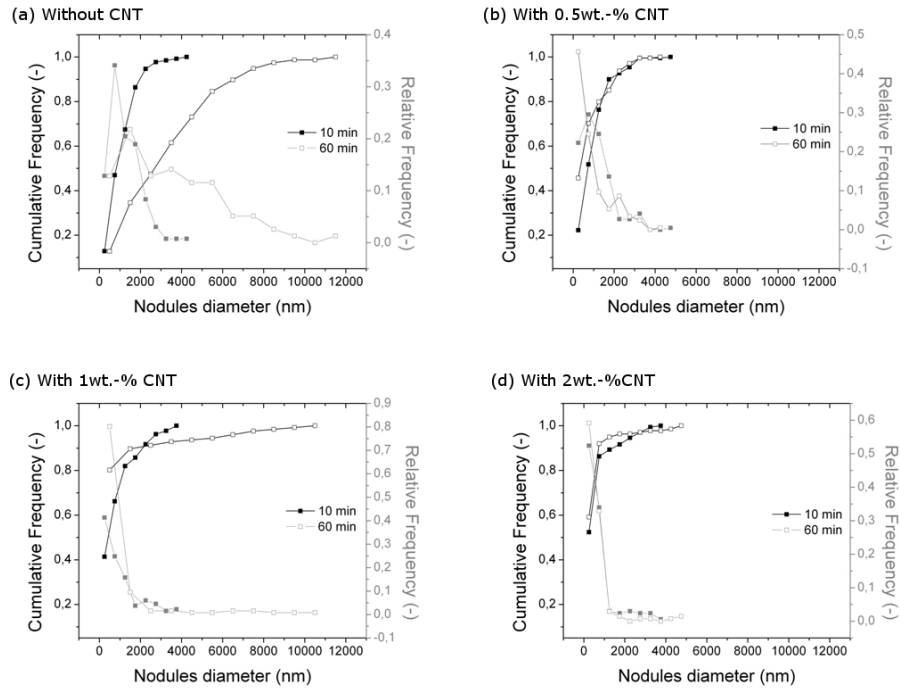


Figure 10 – (a-d) Cumulative and relative frequencies versus the droplet diameter (a) without CNT; (b) with 0.5wt.-%CNT; (c) with 1wt.-%CNT; (d) with 2wt.-%CNT (measured on TEM micrographs)

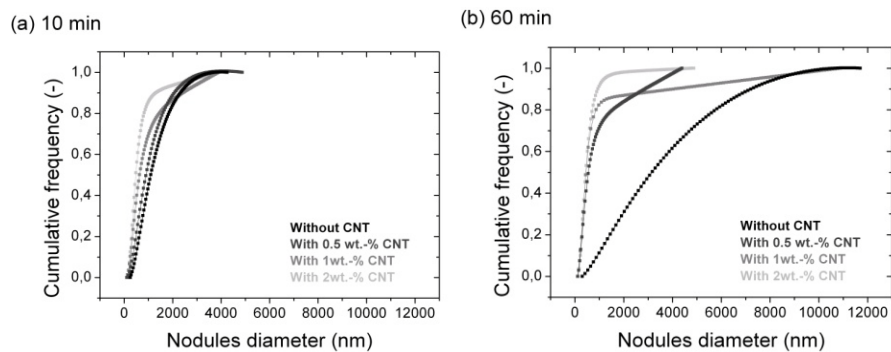


Figure 11 – Cumulative frequency versus droplet diameter for unfilled and filled blends (0.5wt.-% - 2wt.-%CNT) for 10 and 60 minutes blending (measured on TEM micrographs and after integration of a LogNormal law fitting the datas)

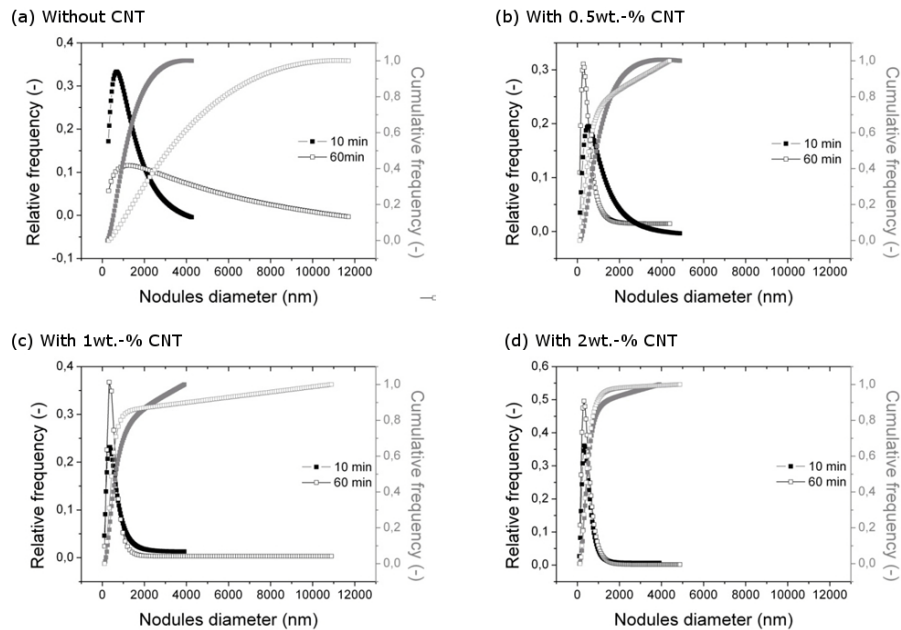


Figure 12 – (a-d) Cumulative and relative frequencies versus the droplet diameter fitted with a LogNormal law in linear scale (a) without CNT; (b) with 0.5wt.-%CNT; (c) with 1wt.-%CNT; (d) with 2wt.-%CNT

5 Mechanisms of blend stabilization

The mechanisms of stabilization by nanoparticles are not fully understood yet. Different mechanisms probably involved in the emulsion stabilization are described in literature. A first mechanism is the reduction of the interfacial energy per unit area. Many authors [7,36-41] have measured a decrease of the interfacial tension when organomodified clay is located at the interface between immiscible polymers. However, as the clay is modified by surfactants, it is not clear if the interfacial energy reduction is due to the nanoparticles themselves or to contamination by surfactant. It is thus not clear yet if unmodified particles would significantly modify the interfacial energy per unit area. A second mechanism is an increase of the major phase viscosity due to particle localization in the matrix. This viscosity increase is responsible for a slowing down of the matrix phase drainage, thus reducing coalescence.^[42] This mechanism cannot be active here since the CNT are mainly located at the interface and the overall CNT concentration is too low (well below the percolation threshold) to significantly affect viscosity. Moreover, the torque measured for both polymers does not change dramatically with increasing mixing time. A third mechanism is the formation of a dense layer at the

interface between phases due to the selective localization of particles at the interface (steric hindrance). This dense layer can form a mechanical barrier preventing the coalescence of the dispersed phase.^[11,18,43] The presence of particle-bridged domains can also produce morphology stabilization.^[44] However, this last mechanism is considered as less important and was not observed here. Finally, interfacial dynamics can also play a role on the stabilization of the morphology. This implies that the particles act as interfacial mobility modifiers. This effect was recently demonstrated for polydimethylsiloxane (PDMS)/polyisobutylene (PIB) blends ^[20]. The rigidification of the interface explains the coalescence suppression.

We do not expect a change of the interfacial energy. The effect of Marangoni stresses can thus be eliminated. Thus, overall, the formation of a dense interfacial layer is the most likely explanation for the observed morphology stabilization. The formation of a rigid interface is also a likely explanation. However, the size of the dispersed phase decreases during mixing. If the layer is considered as rigid, it is equivalent to an eggshell around the PA droplet thus it may also prevent the dispersed phase from break-up. Thus either the eggshell cracks during mixing or it is partly flexible. Some attempts were made to investigate the relaxation of the dispersed phase on the complex shear modulus in the low frequency domain. However, the system is not stable enough.

In the absence of CNT, when a collision occurs between two droplets of the dispersed phase, they coalesce and sometimes, a part of the matrix material is not drained and forms a sub-inclusion (Figure 13a). In the presence of CNT, when two dispersed polymer droplets collide, the deformable network formed by the CNT at the interface prevents them from coalescing (Figure 13b).

It is also worth noting that CNT are efficient at producing a relatively narrow distribution of droplet sizes. Indeed, the cumulative frequency curve is sharper in presence of CNT, indicating a narrower distribution of sizes. Silica particles localized at the interface have already shown this kind of uniform morphology^[35,45].

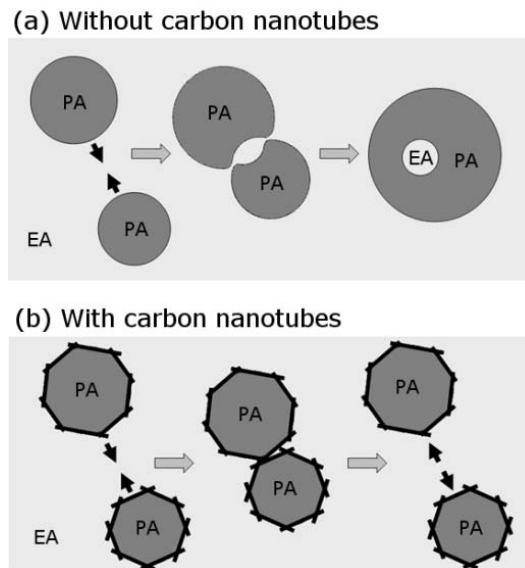


Figure 13 – Morphology development due to dispersed phase polymer droplets collision (a) in the absence and (b) in the presence of CNT

CONCLUSIONS

The influence of unfunctionalized CNT interfacial confinement on the stability of a polymer blend morphology has been demonstrated. The effect of particle concentration on the morphology and its evolution with increasing compounding time has been studied.

CNT enhance both phase dispersion and stability of the dispersed phase, even at long mixing time (60min) and low nanofiller content (0.5wt.%CNT). They also produce a more uniform distribution of droplet sizes.

Taking advantage of the CNT interfacial localization should enable the development of stable binary blends at lower filler content than previously published in literature. In the present study, the minimum CNT content was 0.5wt.% but this concentration can probably still be reduced.

The main mechanism involved most probably is the formation of a deformable barrier network at the interface, due to CNT selective interfacial confinement, providing a mechanical barrier against coalescence of the droplets. Blends stabilized by solid particles, like CNT, could therefore offer an interesting alternative to blends compatibilized by block-copolymers.

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Chapter 5

ELABORATION OF CONDUCTIVE COMPOSITES BASED ON THE INTERFACIAL CONFINEMENT OF CNT

ABSTRACT

The objectives of this chapter are first the control of the co-continuous morphology of immiscible blends in the presence of CNT and, second, to use the morphology control to control the electrical properties of the blend. In that context, a system presenting interfacial localization of CNT for the different mixing strategy (EA/PA6) is used to develop blends presenting a triple continuous structure.

First, the co-continuous domain of EA/PA6 blends in the absence of CNT is observed for compositions between 34 and 36 wt.-% EA. This domain is not stable and annealing leads to morphology coarsening and loss of the co-continuity.

Second, similar blends containing CNT are studied. Two different mixing strategies are used: predispersion of CNT in EA and predispersion of CNT in PA6. For both strategies, the presence of a conductive path at the interface of the phases is checked over a wide range of compositions using microscopy and CS-AFM. Next, the co-continuity domains are determined. They are wider than for polymer blends without CNT and range from 34 to 42 wt.-% (EA+CNT) and from 38 to 50 wt.-% EA for predispersion of CNT respectively in EA and PA6. The size of the phases is also reduced compared to pure polymer blends. Although the CNT are, at least partially, localized at the interface, the conductivity of these blends is very low. It is however, higher for blends in which CNT are predispersed in PA6 phase because of the best initial dispersion state. The low conductivity can be partly attributed to the presence of a large number of EA sub-inclusions in PA6

phase or to the strong orientation of the structure in the sample for electrical characterization. However, surprisingly, the highest conductivity is observed for a blend presenting a sea-island morphology with a high number of large dispersed domains. This is attributed to the formation of conducting networks at the interface of the PA6 domains and to the presence of CNT, bridging the different dispersed domains. The presence of CNT in the EA matrix also favours the formation of the conducting path.

Finally, in the presence of CNT, the blends exhibit improved stability upon annealing, compared to blends without CNT. The stabilization is more efficient for systems with predispersion of CNT in EA because of the better interfacial confinement. For predispersion in PA6, a coarsening of the morphology is observed but the co-continuous morphology is preserved. However, the electrical properties are not significantly affected. A systematic study of the stability would however require a full knowledge of the system chemical modification resulting from polymer degradation.

We are grateful for the access to the technological platform “Welcome” and for the help of I. Huynen, I. Molenberg and P. Simon.

We thank Pr. B. Nysten (UCL-IMCN-BSMA) for the CS-AFM characterization.

We thank Pr. K. Varlot-Masenelli (INSA Lyon-MATEIS) for STEM tomography.

INTRODUCTION

The use of polymer blends as composites matrices to produce conductive materials at low conductive filler content has been studied for more than two decades. In 1987, Geuskens et al. ^[1] have studied the electrical conductivity of polymer blends containing carbon blacks (CB). They show that the conductivity of rubber/polyethylene blends filled with CB is much higher than the conductivity of the polymer filled with CB at the same loading level. Such a result is explained by the selective localization of the CB particles in the multiphase polymeric system. This concept is known as double percolation. The carbon black-filled blend phase percolates (first percolation) and the CB forms a network within the percolated blend phase (second percolation). More recent studies ^[2-5] also have exploited the concept of double percolation for different blend systems and different conductive fillers. Among them, carbon nanotubes (CNT) attract tremendous attention since their discovery in 1991 by Sumio Iijima ^[6]. They present unique atomic structure and properties such as very high aspect ratio (1000 to 10000), high strength to weight ratio, high mechanical properties, and high thermal and electrical conductivities ^[7-13].

To develop conductive composites at low CNT concentrations, two strategies can be used: on the one hand, the CNT can be directly localized at the interface; on the other hand, the CNT can fill only one phase of the blend (double percolation).

The concept of double percolation using carbon nanotubes has been studied to improve the electrical conductivity of polymer blends. Pötschke et al. ^[14,15] have worked with composites of polycarbonate (PC) filled with multiwall carbon nanotubes. These composites are then mixed with polyethylene (PE) in order to get co-continuous structures exhibiting double percolation. The CNT are found to stay in the PC phase. The authors have also studied blends of PC containing CNT with PP containing nanoclay ^[16]. The CNT stay well-dispersed in PC while the nanoclay migrate from PP towards the interface. Gödel et al. ^[17] have introduced CNT in PC/SAN blends. The CNT are pre-compounded into PC or SAN or the three components are simultaneously mixed and co-continuous blends are prepared. The CNT are found to be only selectively dispersed in the PC phase, independently of the mixing sequence. The authors have found electrical resistivities lower than the one observed in PC or SAN composites with the same CNT content. Bose et al. ^[18-21] have studied blends of PA6 and ABS with purified and functionalized CNT. The CNT are found to locate selectively in the PA6 phase. This localization results in a decreased

electrical percolation threshold and a refinement of the co-continuous structure indicating that CNT act as compatibilizers. The mechanical properties of the blend with functionalized CNT are also improved, up to 2wt.-% CNT, as compared to the same blend with purified CNT. Khare et al. [22] study blends of PP and ABS with purified CNT. In the absence of CNT, the blends exhibit a coarse co-continuous morphology. The CNT are found to be exclusively located in the PP phase. The addition of CNT leads to a refinement of the ligament thickness in the co-continuous blends as well as a refinement of the structure in the matrix/droplets blends. The authors state that above a critical CNT content, they form a network-like structure, which acts as a physical barrier reducing coalescence. Lower electrical percolation threshold is recorded in co-continuous blends due to the double percolation. Li and Shimizu [23] have elaborated conductive poly(vinylidene fluoride) (PVDF)/PA6/CNT composite using the double percolation concept. CNT are exclusively located in the PA6 phase. Reduced percolation threshold and significantly improved electrical and mechanical properties are observed. Gao et al. [24] report the preparation of CNT filled oriented polymer fibres of PE/PP blends. The CNT are exclusively located in the PE phase and a double percolated structure is built with improved electrical and mechanical properties. Shen et al. [25] have studied the influence of different functionalized CNT on the morphology of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) / PA6 blends. Initially, the blends present a sea-island morphology in which the PPO, presenting the higher viscosity, forms the dispersed phase and the PA6, presenting the lowest viscosity, forms the matrix. Functionalized (CNT-OH, CNT-NH₂, CNT-COOH) and unfunctionalized CNT are exclusively dispersed in the PA6 phase. The addition of CNT to the blend influences the viscosity of the PA6 phase. This leads to an evolution of the phase structure of the blend from sea-island to co-continuous, except for the incorporation of CNT-COOH due to aggregation of these specific CNT. The effect of CNT addition on the mechanical properties, on the glass transition temperatures and on the rheological properties of the blends is studied. The transition from a sea-island to a co-continuous morphology has also been reported by Zou et al. [26] for poly(p-phenylene sulphide)/PA66 blends. CNT are found to localize in the PA66 phase exclusively. When adding small amounts of CNT, the morphology first evolves to a co-continuous morphology. However, when increasing further the CNT content, they form aggregates and the morphology comes back to a sea-island morphology.

All the works presented here above deal with double percolation. However, among the two strategies presented, the incorporation of the conductive filler

at the interface is the most promising to reduce to the lowest the amount of filler. Nevertheless, the interfacial localization of carbon nanotubes has so far only been shown in very few papers and mainly for functionalized carbon nanotubes. Bose et al. [27,28] have elaborated blends of PA6 and ABS in the presence of styrene-maleic anhydride copolymer (SMA) and CNT. The CNT are chemically coupled to the SMA, which tends to locate at the interface. Therefore, the CNT are localized at the interface. In another paper, Bose et al. [29] have studied the dispersion of CNT in co-continuous PA6/ionomers blends. Depending on the mixing sequence, Na salt of 6-amino hexanoic acid (Na-AHA) modified CNT are locked at the interface of the PA6/ionomers blends due to specific interactions between the CNT and both polymers. Liu et al. [30] have elaborated polypropylene/ethylene-co-vinyl acetate (EVA) blends with maleic anhydride functionalized carbon nanotubes. The CNT distribute at the interface in blends exhibiting a sea-island morphology while most of them distribute in the EVA phase and some of them span the two phases for cocontinuous morphology. Wu et al. [31] have studied immiscible poly(ϵ -caprolactone) (PCL) polylactide (PLA) blend with functionalized CNT. Although a large part of the CNT is selectively localized in the PCL phase, part of them is confined at the interface due to good affinity of the carboxylic groups present on the CNT surface with both PCL and PLA. In the same conditions, no interfacial confinement is observed for unfunctionalized CNT.

However, the covalent functionalization of CNT produces structural defaults in the graphene structure, which can lead to mechanical weakening of the nanotubes and thus of the nanocomposite and to a loss of the exceptional electrical properties of the CNT [32]. Recently, Gao et al. [33] have studied anisotropically conductive polymer composite based on CNT, PC and PE. They have found that the CNT are preferably located on the surface of the PC fibrils, although CNT are also present inside the PE and PC phases.

To reach high conductivity levels with very low levels of CNT in the polymer matrix, it is important to adjust the polymer structure and the distribution of the filler inside the polymer matrix. We show in Chapter 3 that it is possible to confine CNT at the interface between two immiscible polymers for a sea-island morphology (Figure 1). The blend presenting CNT interfacial localization for all the different mixing strategies (EA/PA6) is thus used here to create triple continuous structures.

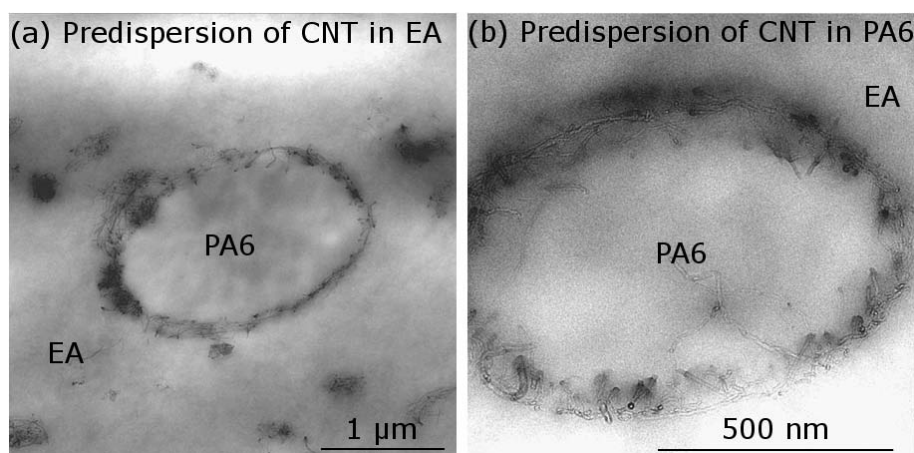


Figure 1 – TEM micrographs of the EA/PA6 blend (a) predisposition of the CNT in EA; (b) predisposition of the CNT in PA6

The first part of this chapter is dedicated to the formation of a co-continuous structure in the absence of CNT. The co-continuous domain and its stability are determined using selective extractions and microscopy techniques.

Second, the development of co-continuous structures in the presence of CNT is addressed. Two different mixing strategies are explored: the predisposition of the CNT in EA and their predisposition in PA6. For each blend, a total content of 2wt.-% CNT is used. The localization of the CNT in co-continuous blends is first analyzed to check if the interfacial localization is observed on the whole compositions domain. A local characterization of the conductivity is also performed on blends presenting a sea-island morphology to highlight the presence of an interfacial CNT conductive network. The co-continuous domains are determined for both mixing strategies using selective extractions, microscopic characterizations and Radio Frequency (RF) electrical characterizations. Finally the stability of the co-continuous domains is analysed under static dynamic conditions, i.e. upon annealing.

EXPERIMENTAL

This is a very brief description of the materials and characterization methods used. For more details, please refer to Appendix 1.

1 Materials and blend preparation

The CNT used are unfunctionalized and unpurified CNT.

The polymers used are ethylene-acrylate copolymer (EA), polyamide 6 (PA6).

Different blends are prepared:

- Pure blends of EA and PA6 with x wt.-% of EA and y wt.-% of PA6:
EA/PA6 x/y wt.-%
- Blends in which the CNT are predispersed in the EA phase before mixing with PA6 with x wt.-% of EA, in which the CNT are predispersed, and y wt.-% of PA6:
(EA+CNT)/PA6 x/y wt.-%
- Blends in which the CNT are predispersed in the PA6 phase before mixing with EA with x wt.-% of EA and y wt.-% of PA6, in which the CNT are predispersed:
(EA+CNT)/PA6 x/y wt.-%

2 Characterization

The morphology of the blends is analyzed by:

- SEM on cryofractures followed by selective extraction of EA phase using CHCl_3 or selective extraction of the PA6 using formic acid.
- OM, TEM and SEM tomography on sliced samples presenting a thickness of 1 μm , 95 nm and 500 nm respectively.

The electrical properties are evaluated locally using CS-AFM and on large frequencies range from 0.04 to 40 GHz using microstrip.

RESULTS AND DISCUSSION

1 Development of co-continuous structures without CNT

First the co-continuous domain for unfilled blends is established. Selective extraction tests and microscopy are performed on the blends to determine the co-continuous range. The stability of the structure is next studied.

1.1 Co-continuous domain determination

1.1.1 Selective extraction

To perform selective extractions, each phase is dissolved in a solvent, which is a non solvent for the other phase. The EA phase is dissolved in boiling chloroform, while the PA6 phase is dissolved in formic acid.

A co-continuous structure is generally described by the coexistence, in a same volume, of two phases that are continuous in the three dimensions of the space [34]. It therefore requires that after dissolution of one phase, the other phase remains self-supported and its mass is approximately that in the original blend.

A first screening is performed on a composition range from 20 to 80wt.-% of each phase. Below 30wt.-% EA, the PA6 is the continuous phase. Above 40 wt.-% EA, the EA is the continuous phase. Intermediate compositions between 30 and 40 wt.-% EA have thus been analyzed and the co-continuous domain is found between 34 and 36wt.-% EA.

The selective extraction experiments allow the evaluation of the continuity degree, φ , of each phase (Molau test) as the ratio between the dissolved mass of the phase and the initial mass of the phase in the sample:

$$\varphi_{phase1} = \frac{m_{phase1\ dissolved}}{m_{0, phase1}}$$

Where $m_{0, phase1}$ is the initial mass of the phase 1 in the sample and $m_{phase1\ dissolved}$ is the mass of the phase 1 that is dissolved in its selective solvent, i.e. the difference between the initial mass of the sample and the final mass of

the sample after extraction. The continuity degree of the present blend is reported in Figure 2. Three regions are presented on the graph. At low content of EA or PA6 respectively, the continuity of these phases are nil or almost nil and a sea-island morphology of the minor phase dispersed in the major phase is observed. When increasing the fraction of minor phase, its continuity degree increases and droplets connect until percolating throughout the sample. When increasing further this phase is continuous and the other one becomes dispersed. At a given composition or for a range of compositions, both structures are percolating through the sample. It is the phase inversion point or the co-continuous composition range. Here, the co-continuity domain is observed on a narrow range around 35wt.-% EA. It is however worth noting that this evaluation does not take into account the presence of sub-inclusions in the phases. This explains that in some cases we observe that the dissolved mass is higher than the initial mass of the phase.

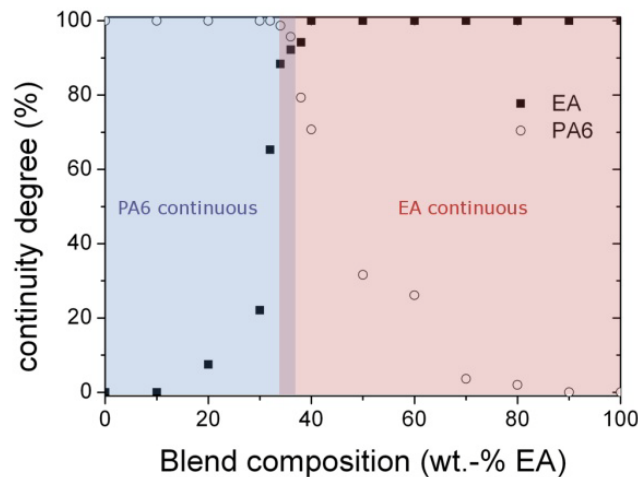


Figure 2 – Evolution of the continuity degree as a function of the blend composition (wt.-% EA)

1.1.2 Microscopy analysis

The morphology of the blends is analyzed with the help of SEM on cryofractured samples after extraction of the minor phase to visualize the sample in three dimensions. Figure 3 presents the morphology of the blends EA/PA6 30/70 wt.-% after extraction of the EA phase (Figure 3a) and of EA/PA6 40/60 wt.-% after extraction of the PA6 phase (Figure 3b). These concentrations are not in the co-continuous domain. This is also confirmed in OM micrographs taken perpendicular to the extrusion direction (Figure 4), in

which the EA and PA6 phases are respectively the light and dark phases. For the blend 30/70 wt.-% (Figure 3a, Figure 4a), elongated EA droplets co-exist with small EA droplets inside the continuous PA phase. For the 40/60 wt.-% blend (Figure 3b, Figure 4b), PA droplets and elongated filaments are observed in the EA continuous phase.

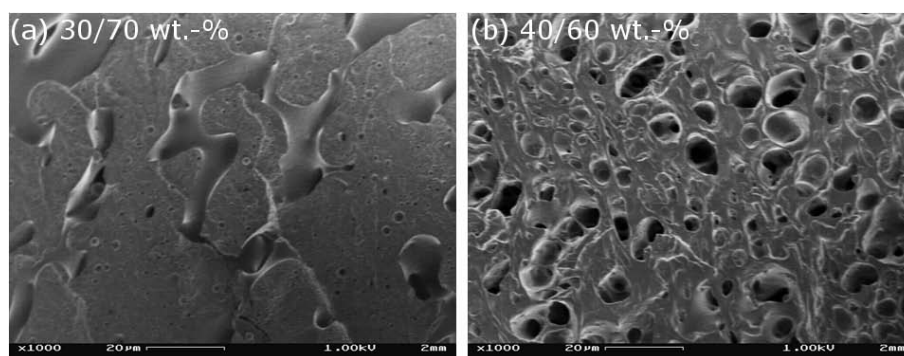


Figure 3 – SEM micrographs on cryofractured sample after extraction of one phase of the blend at different magnification (a) extraction in CHCl_3 of the EA phase of the blend EA/PA6 30/70 wt.-%; (b) extraction in formic acid of PA6 phase of the blend EA/PA6 40/60 wt.-%

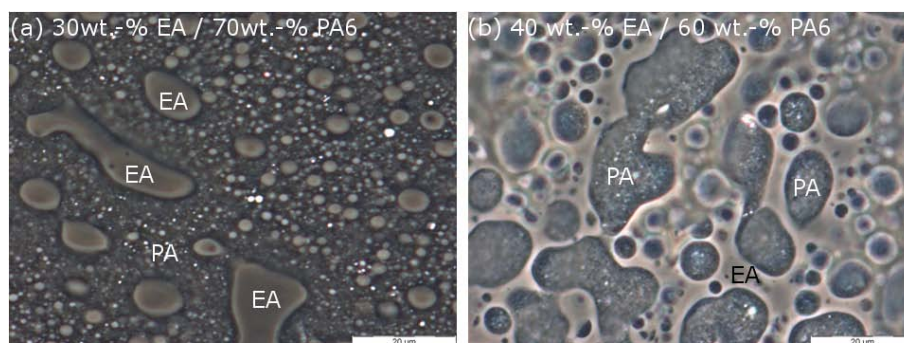


Figure 4 – Optical micrographs of EA/PA6 blends (perpendicular to the extrusion direction) (a) 30/70 wt.-%; (b) 40/60 wt.-% (scale bar 20μm)

For intermediate compositions, a more homogeneous structure is observed, especially at 34 and 36 wt.-% EA (Figure 5).

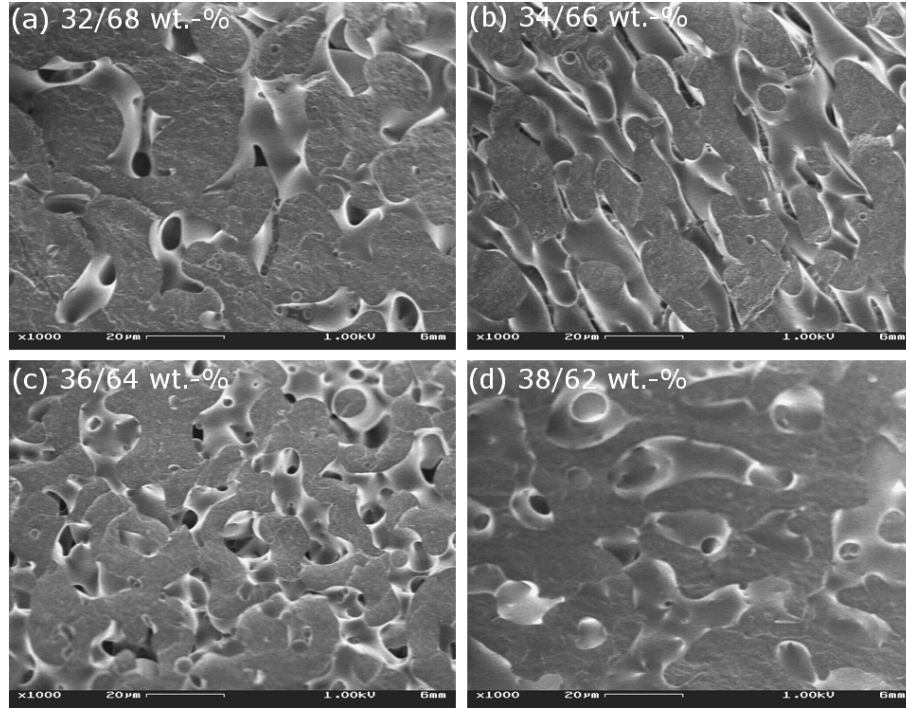
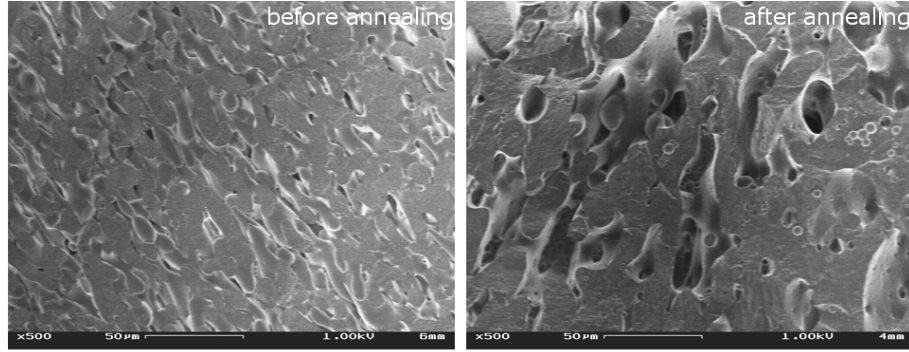


Figure 5 – SEM micrographs after extraction of the EA phase in blends of EA/PA6 containing (a) 32; (b) 34; (c) 36; (d) 38 wt.-% EA

1.2 Stability of the co-continuous domain

The stability of the co-continuous structure for annealing 1h at 240°C is studied in the co-continuous domain (34 and 36wt.-% EA). Figure 6 presents a SEM micrograph obtained after cryofracture of the blend and extraction of EA phase. The structure evolves during annealing. The co-continuous structure is not present anymore through the sample but only in some localized areas. In other areas, a sea-island morphology is observed. Moreover, the size of the phases significantly increases.

(a) 34 wt.-% EA / 66wt.-% PA6



(b) 36wt.-% EA / 64 wt.-% PA6

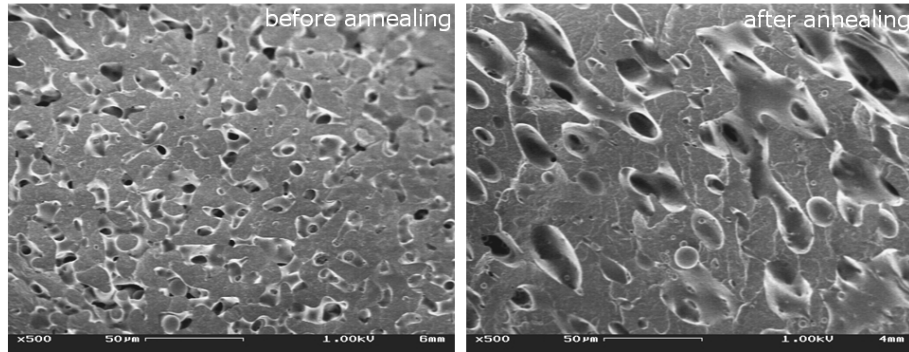


Figure 6 – SEM micrographs presenting the effect of annealing on the microstructure for EA/PA6 blends (a) 34/66 wt.-%; (b) 36/64 wt.-%

1.3 Discussion

The co-continuity domain of the blend EA/PA6 exists over a narrow range of compositions from 34/66 to 36/64 wt.-%. The results of the selective extractions are in good agreement with the microscopic characterization.

The inversion “point” occurs when EA is the minor phase. These compositions are coherent with the viscosity ratio of both components (Figure 7). Indeed, EA presents a lower viscosity than PA6. Different models determining the volume fraction of the phase inversion as a function of the viscosity ratio are presented in Figure 8. Note that these models do not include the effects of melt elasticity nor interfacial tension. One of the simplest models is given by Paul and Barlow equation [35,36], which describes the inversion phase point as:

$$\frac{\phi_{1,PI}}{\phi_{2,PI}} = \frac{\eta_1}{\eta_2}$$

Where η_i and $\phi_{i,PI}$ are respectively the viscosity and the volume fraction at the phase inversion for polymer i .

If EA is polymer 1 and PA6 is polymer 2, as the viscosity of EA is lower than the one of PA6, the co-continuous domain is observed when the volume fraction of EA is lower than the volume fraction of PA6.

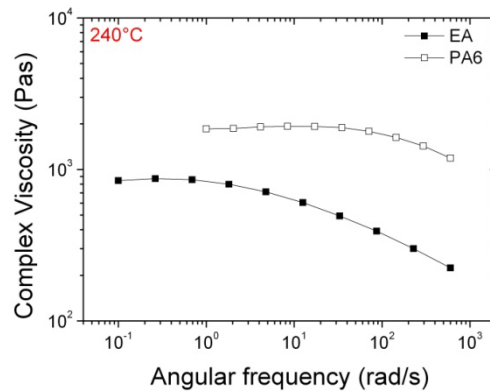


Figure 7 – Complex viscosity of EA and PA6 at 240°C

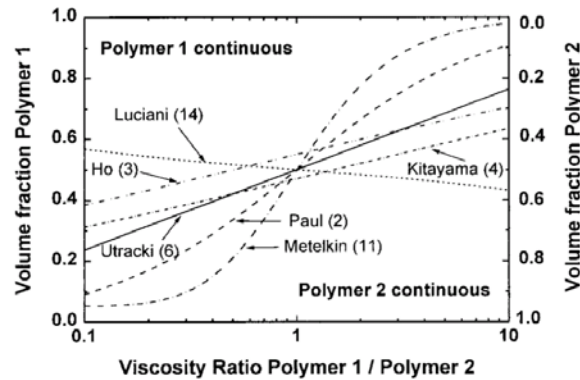


Figure 8 – Different models describing the phase inversion volume concentration as a function of the viscosity ratio ^[36]

Actually the co-continuity is not observed for one point but in a range of compositions. Willemse and co-workers ^[37,38] have developed a model giving the range of compositions for the establishment of a co-continuous structure and based on the stability criterion that the capillary number, C_a , which is the ratio between the deforming stress imposed by the flow ($\eta_m \dot{\gamma}$) and the

interfacial forces (σ/R), is 1. The minimum volume fraction at which a co-continuous morphology can exist, $\Phi_{d,cc}$, is described as:

$$\frac{1}{\phi_{d,cc}} = 1.38 + 0.0213 \left(\frac{\eta_m \dot{\gamma} R_0}{\sigma} \right)$$

Where η_m is the major phase viscosity, $\dot{\gamma}$ is the shear rate, R_0 is the radius of the strand and σ is the interfacial tension. Although the viscosity ratio does not appear directly in this model, it indirectly affects the R_0 value. This size parameter is determined by the specific conditions of the blending process and is difficult to ascertain [36]. Note that the upper limit is described by the same formula applied to the other phase.

According to this equation, the co-continuity domain is reduced for a high interfacial tension, a low major phase viscosity and a low shear rate. In the present blend, both polymers are highly immiscible, thus giving a high interfacial tension. Moreover, the viscosity of the EA phase at the compounding temperature is low, thus leading to a low upper limit of the co-continuous range.

The co-continuous structure obtained during mixing 10 min in the compounder is not stable upon further processing. The factors governing the stability are the interfacial tension, the viscosity ratio and the dimensions of the strands. The co-continuous domain is usually narrowed after annealing [36-40] owing to the break up of the strands of the minor phase. Indeed for low concentration of this phase, the strands are thin and thus break up fast. The lower limit of the co-continuous domain is thus increased after annealing. There is however a critical composition above which the structure remains co-continuous after annealing. This composition is a function of the critical aspect ratio for breakup of the strands [37,41]. The coarsening of the structure results from the restructuring of the blend occurring owing to retraction and breakup of the strands, leading to a sea-island morphology. Breakup and retraction are completed in a short time relative to coalescence [41]. Above a critical concentration, the morphology does not breakup anymore and only retraction occurs leading to a coarsening of the morphology.

2 Development of co-continuous structures in the presence of CNT

The blends filled with CNT are analyzed here. The fillers localization is first studied using SEM and TEM techniques. The formation of a conductive path at the interface is also demonstrated. The co-continuous domain and its stability in static conditions are then determined by morphological and electrical analysis.

2.1 Localization of the CNT in co-continuous structures

The dispersion of the CNT in single polymer matrices has been discussed in Chapter 2. The dispersion of the CNT in the EA matrix is good but a large number of aggregates is present (Figure 9a). The dispersion in the PA6 matrix is very good (Figure 9b).

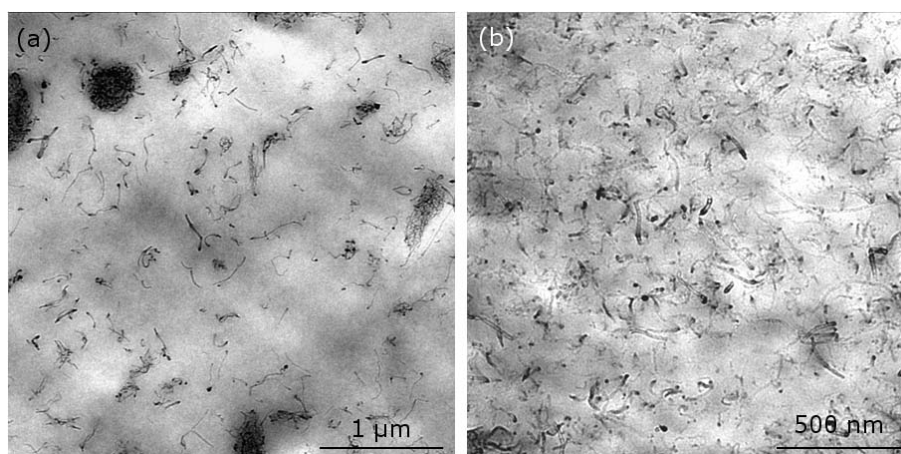


Figure 9 – TEM micrographs of the dispersion of CNT in (a) EA matrix; (b) PA6 matrix

The localization of CNT in the EA/PA6 blend has been studied for sea-island morphologies in Chapter 3. When CNT are predispersed in EA (Figure 10), they mainly migrate towards the interface of the blend when EA is the matrix (Figure 10a) and when EA is the dispersed phase (Figure 10b). When CNT are predispersed in PA6 (Figure 11), they also migrate towards the interface but some of them remain dispersed in PA6. In order to minimize CNT loading for the achievement of a percolated CNT network, it is important to check that interfacial localization of CNT is observed for all compositions in the co-continuous range and that this localization leads to the formation of a conductive path.

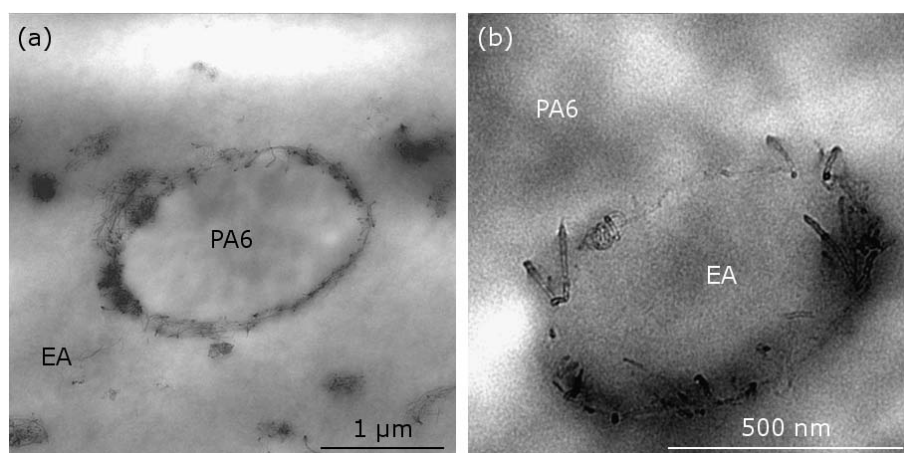


Figure 10 – TEM micrographs of EA/PA6 blends for a predispersion in the EA phase (a) EA/PA6 90/10 wt.-%; (b) EA/PA6 10/90 wt.-%

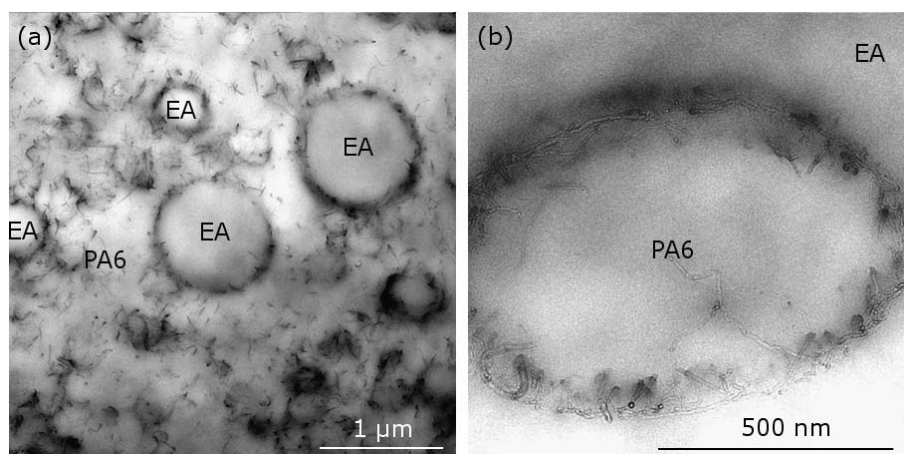


Figure 11 – TEM micrographs of EA/PA6 blends for a predispersion in the PA6 phase (a) EA/PA6 25/75 wt.-%; (b) EA/PA6 90/10 wt.-%

2.1.1 Predispersion in EA: (EA+CNT)/PA6

Figure 12 presents SEM micrographs of different (EA+CNT)/PA6 blends after cryofracture and extraction of the EA phase. CNT are observed as white filaments on the surface of the PA6 strands for all compositions. However, SEM can not assess the distribution of CNT inside the phases. TEM micrographs of a blend at different magnifications are therefore presented in Figure 13. At low magnification, the global structure is observed (Figure 13a). When increasing magnification, the presence of droplets of EA in PA6 is visible (Figure 13b,c). At higher magnification, the presence of CNT at the interface between both polymers is clear (Figure 13c,d). Unfortunately, CNT are also present on the surface of EA sub-inclusions inside PA6. Finally CNT aggregate are also present

in EA. The CNT aggregates (red circles), PA6 droplets in EA phase (green circles) and EA droplets in PA6 phase (blue circles) surrounded by CNT are highlighted in Figure 14.

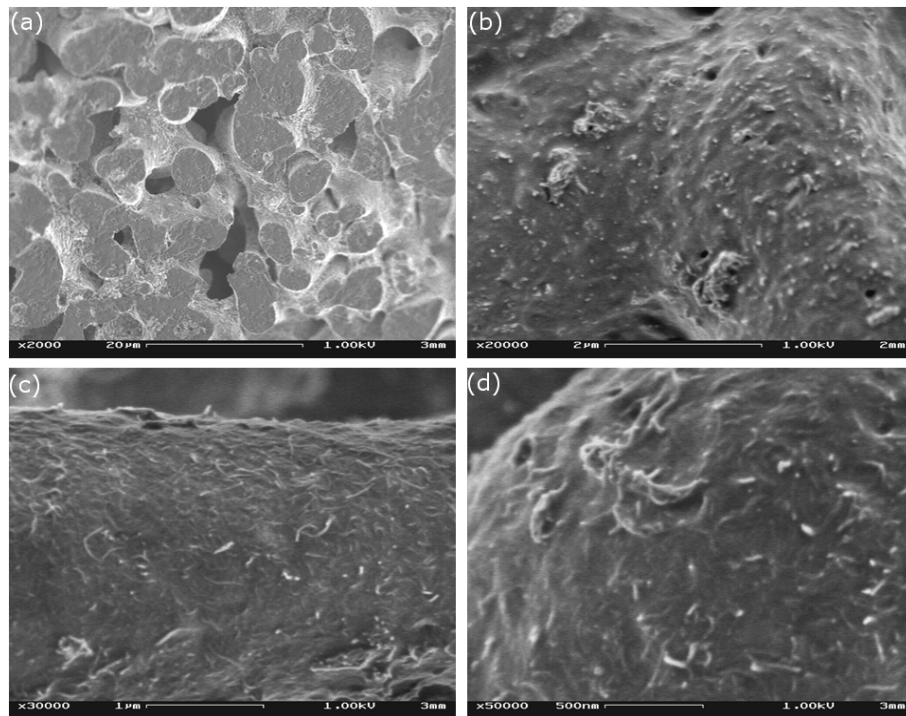


Figure 12 - SEM micrographs (EA+CNT)-PA6 after extraction of the EA phase (a,b) 40/60 wt.-%; (c) 34/66 wt.-%; (d) 36/64 wt.-%

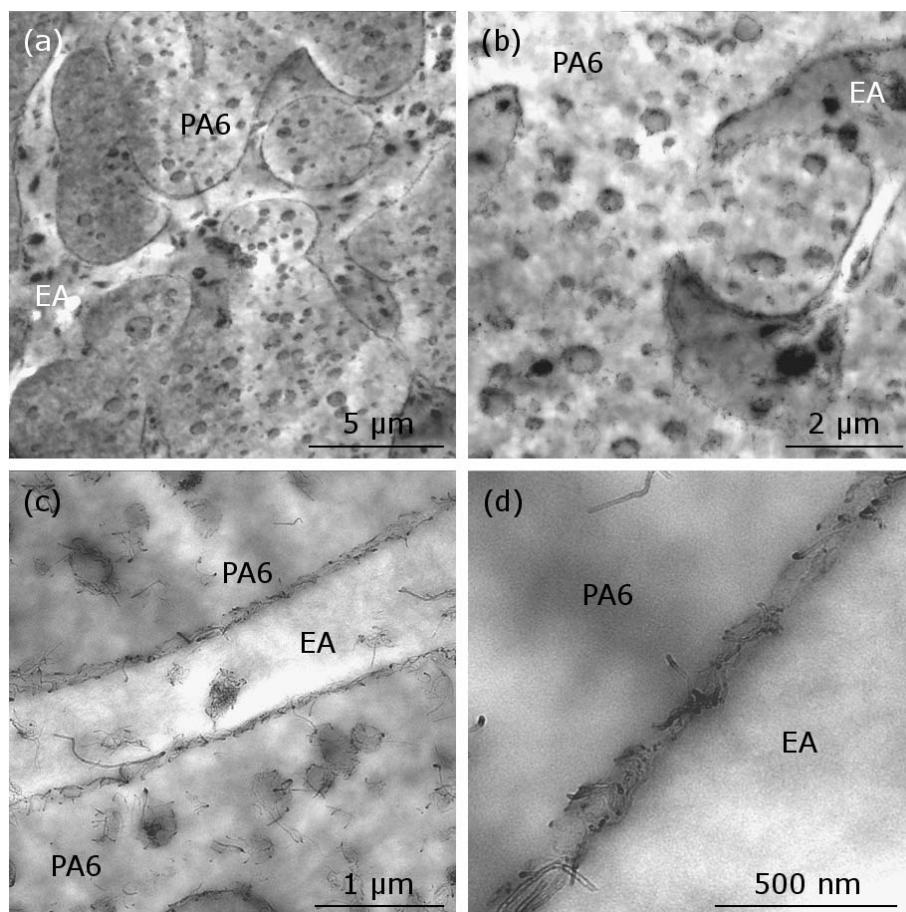


Figure 13 – TEM micrographs of the blend (EA+CNT)/PA6 36/64 wt.-% at different magnifications

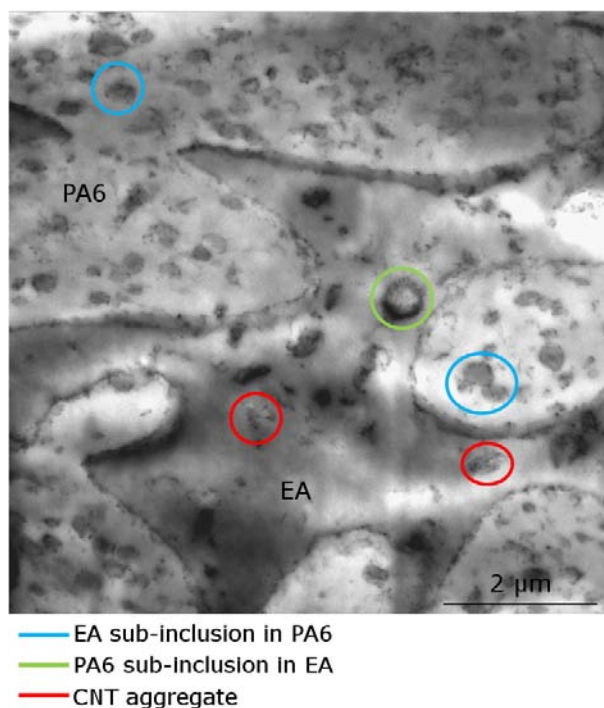


Figure 14 – TEM micrographs of the blend (EA+CNT)/PA6 40/60 wt.-%

Finally, it is worth noting that the interfacial confinement of CNT is stable, as already observed for sea-island morphologies. Indeed, after 60min compounding CNT are still localized at the interface.

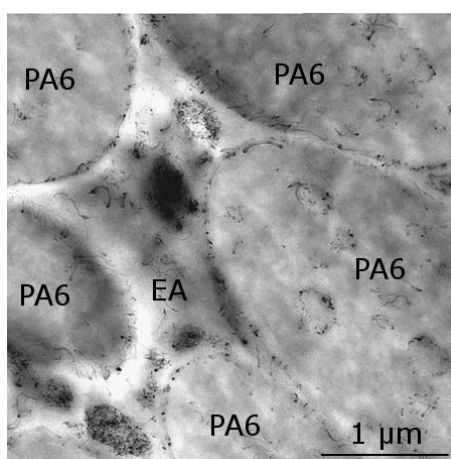


Figure 15 – TEM micrograph of (EA+CNT)/PA6 36/64 wt.-% for 60min compounding

2.1.2 Predispersion in PA6

Figure 16 presents SEM micrographs of different EA/(PA6+CNT) blends after cryofracture and extraction of the EA phase. CNT are present at the interface between the phases but they are not as evident to observe as in (EA+CNT)/PA6 blends because CNT are more embedded in PA6. TEM micrographs of a blend at different magnifications are therefore presented in Figure 17. EA droplets are present inside PA6 while no PA6 droplet is observed in EA. CNT are present at the interface of the blend, at the interface of EA sub-inclusions in PA6 but part of them also remains in PA6.

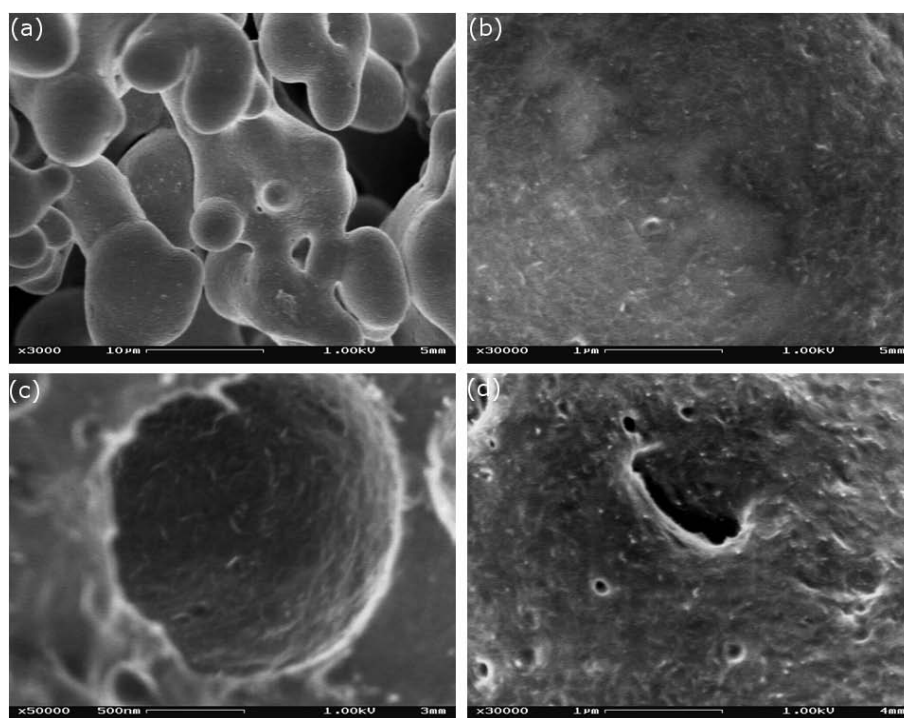


Figure 16 – SEM micrographs EA/(PA6+CNT) after extraction of the EA phase (a,b) 50/50 wt.-%; (c) 25/75 wt.-%; (d) 44/56 wt.-%

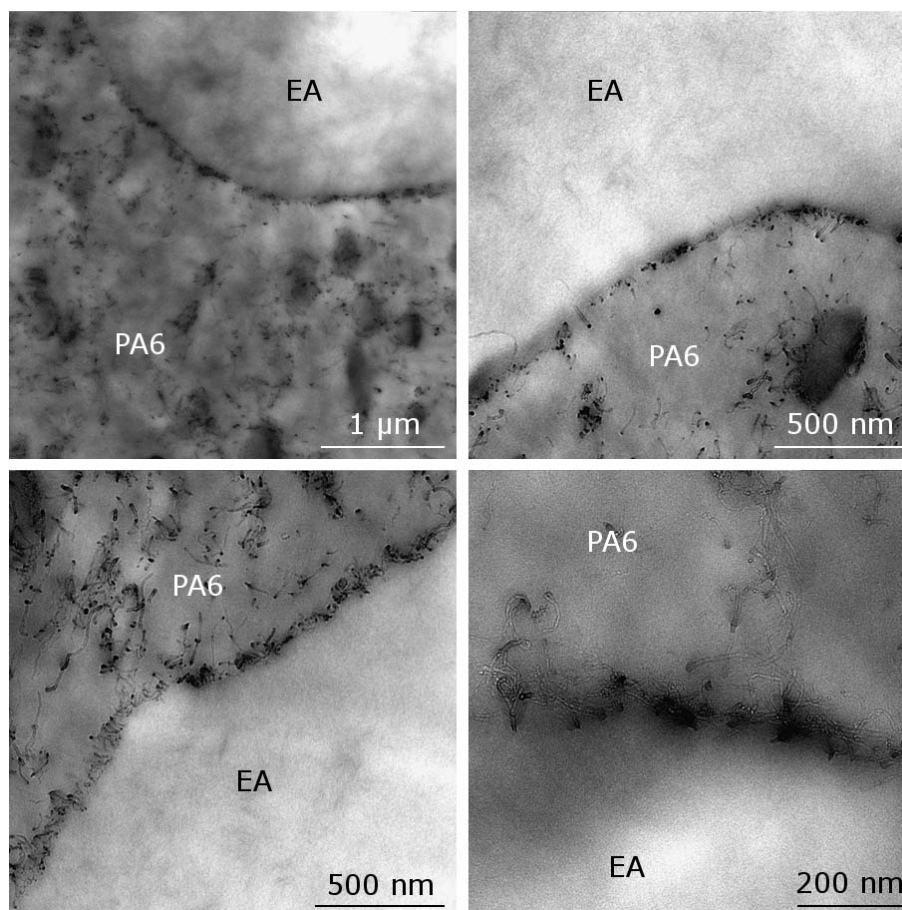


Figure 17 – TEM micrographs of the blend EA/(PA6+CNT) 38/62 wt.-% at different magnifications

2.1.3 Local characterization of the electrical conductivity

SEM and TEM micrographs show that, whatever the mixing strategy, a CNT network exists at the interface between EA and PA6. The local electrical properties of the blends are characterized using CS-AFM to highlight the presence of an interfacial conductive network. Figure 19 and Figure 21 present a mapping of the topography and the conductivity of the composites for respectively the predispersion of the CNT in EA and in PA6 in blends presenting a sea-island morphology. It is first important to note that a current can only be measured at the surface of the droplets exhibiting a diameter higher than 1 μm, which is the thickness of the slice of sample deposited on conductive support

(Figure 18). Indeed, to measure a current, a conductive path must exist between the AFM cantilever and the Au conductive layer. In Figure 18, a current will only be detected around the PA6 droplets (1) and (2). The CNT confined at the interface around droplets (3) and (4) are never part of a conductive network between the cantilever and the Au layer. For this reason, a conductive path is not present at the interface of all the droplets visible in Figure 19 and Figure 21.

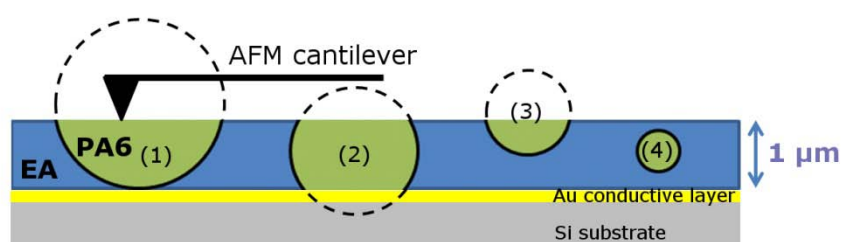
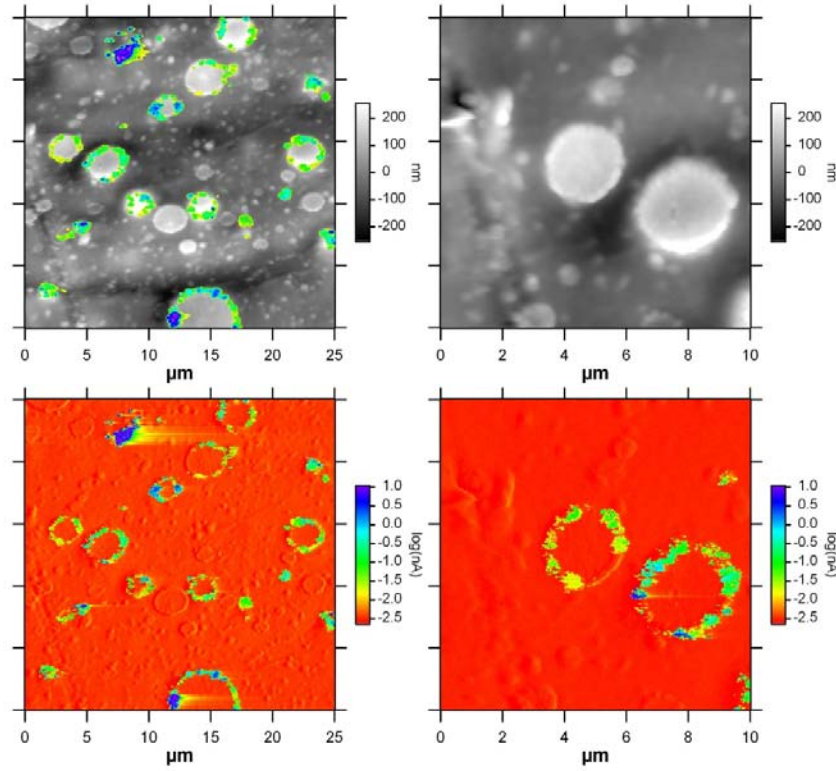


Figure 18 – Principle of the CS-AFM measurements on slices of polymer nanocomposites

Figure 19 shows that when 2wt.-% CNT are predispersed in EA, the interface of the blends is mainly conductive. However, with 1.8wt.-% CNT in total, there is not a uniform conductive shell around the PA droplets. The conductivity seems to be dominated by CNT agglomerates. To visualize the 3D structure, the morphology of the blend is studied using STEM tomography (Figure 20). On the initial STEM micrograph (Figure 20a), the CNT appear in white because their density is higher than the matrix. The analyzed volume of the same area after segmentation is presented in Figure 20b,c. Figure 20b presents the volume for a tilt angle of 0° and Figure 20c presents it for a tilt angle of 60°. CNT agglomerates are mainly at the interface of the blends but some agglomerates are also present in the EA phase and a few in the PA6 domains. These pictures after reconstruction of the volume confirm the presence of agglomerates at the interface, which are responsible of the conductivity measured using CS-AFM.



**Figure 19 – CS-AFM topography and current for the predispersion of the CNT in
EA: (EA+CNT)/PA6 90/10 wt.-%, with 1.8 wt.-% CNT in total ($V_{\text{bias}} = 3\text{V}$)**

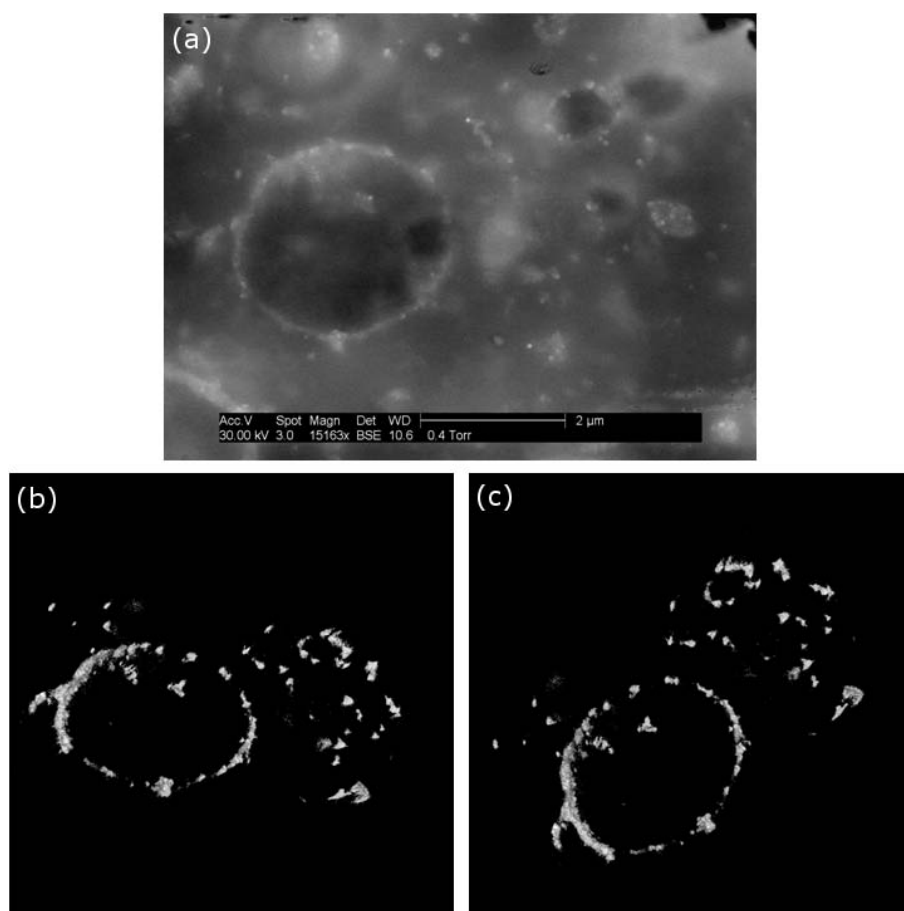


Figure 20 – (a) Initial STEM micrograph (dark field) of the blend (EA+CNT)/PA6 90/10 wt.-%; (b,c) reconstruction of the 3D micrograph of the blend based on STEM acquisition tilting the sample from +60° to -60°

Figure 21 presents the topography and current measurements when 2 wt.-% CNT are predispersed in PA6 before mixing with EA. Note that here, the total amount of CNT is only 0.2 wt.-% in the sample. The current measurements confirm the presence of the CNT at the interface of the phases. Indeed conductive path are highlighted in the figures at the interface of the PA6 droplets and of the EA sub-inclusions. Here, the conductive path is more homogeneous, demonstrating that there are less agglomerates when predispersing the CNT in PA6.

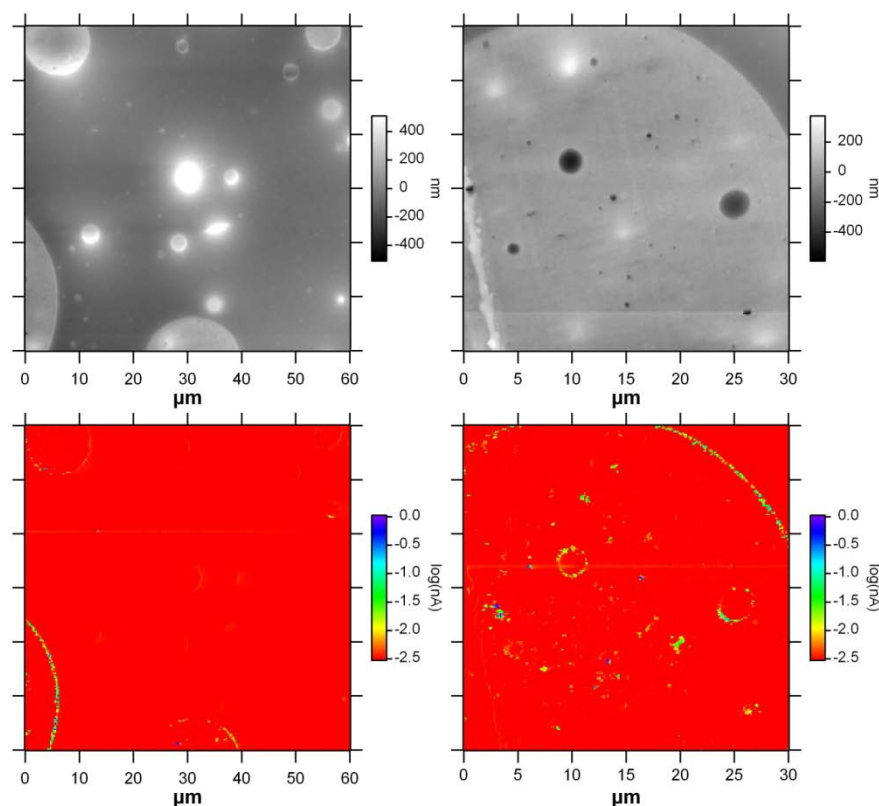


Figure 21 – CS-AFM topography and current for the predispersion of the CNT in PA6: EA/(PA6+CNT) 90/10 wt.-%, with 0.2 wt.-% in total ($V_{\text{bias}} = 10\text{V}$)

2.1.4 Discussion

SEM and TEM micrographs confirm the interfacial confinement of CNT over the whole range of blend compositions. Moreover the interfacial confinement is stable for long mixing times. When CNT are predispersed in EA, some CNT aggregates are present in EA and some CNT are localized around EA sub-inclusions in PA6. These CNT do not contribute to the formation of the percolating network. When CNT are predispersed in PA6, although an interfacial confinement is observed, some CNT are present at the surface of EA sub-inclusions and some other CNT are remaining inside PA. For this blending sequence also, part of the CNT do not contribute to the formation of the percolating conductive network.

The presence of CNT at the interface of the blend after 60 min compounding confirms that the interfacial localization is stable for long mixing times, as already observed in Chapter 3.

The local characterization of the electrical properties first confirms that the conductive particles are localized at the interface. Second, it shows that when CNT are predispersed in EA, the conductivity is mainly attributed to large agglomerates. On the contrary, when CNT are predispersed in PA6, a fine and homogeneous conducting area is present at the interface, indicating that the amount of CNT agglomerates is lower in this case.

2.2 *Determination of the co-continuous domain in the presence of CNT*

The co-continuous domain in the absence of CNT has been identified previously and ranges from 34 to 36 wt.-% EA. Here, the morphology is characterized in the presence of 2wt.-% CNT and for both mixing strategies. The co-continuous domain is defined based on selective extractions and on microscopic characterizations.

2.2.1 Predisposition in EA phase

Assuming that the CNT are mainly localized at the interface, they should not dramatically change the rheological properties of the phases. The co-continuous domain should therefore be similar to the one of EA/PA6 blends.

a. Selective extractions

Selective extractions have been performed on the blends from 30 to 50 wt.-% (EA+CNT). The results are reported in Table 1. The symbol ✓ corresponds to effective dissolution of the sample, while the symbol × indicates that the sample remains self-supported after dissolution. The symbol ✓/× corresponds to blends that are not totally self-supported in the solvent but large pieces of the phase remain self-supported. For 30 wt.-% (EA+CNT), the extraction of PA6 in formic acid leads to a complete disappearance of the sample, indicating that (EA+CNT) forms a dispersed phase. For 45wt.-% (EA+CNT), the extraction of EA in boiling chloroform leads to a complete disappearance of the sample too, indicating that (EA+CNT) forms the matrix. For 32 or 44 wt.-% (EA+CNT), extraction of respectively PA6 or EA leads to a partial dissolution of the sample, indicating that the samples present some co-continuous areas but also sea-island areas. The results show that the co-continuity domain ranges from 34 to 42 wt.-% (EA+CNT). It is thus broader in the presence of CNT than for pure EA/PA6 blends.

Table 1 – Results from the selective extraction for (EA+CNT)/PA6 samples of various compositions from 30 to 50 wt.-% (EA+CNT)

(EA+CNT) / PA6 [wt.-% EA]	Chloroform	Formic acid	Continuous phase(s)
30	×	✓	PA6
32	×	✓/×	(EA), PA6
34	×	×	EA + PA6
36	×	×	EA + PA6
38	×	×	EA + PA6
40	×	×	EA + PA6
42	×	×	EA + PA6
44	✓/×	×	EA, (PA6)
45	✓	×	EA
50	✓	×	EA

b. Microscopic characterizations

OM micrographs (Figure 22) present the evolution of the blend for compositions for 30, 35 and 40 wt.-% (EA+CNT). EA is in light grey and PA6 is in dark grey. At 30 wt.-% (EA+CNT), the (EA+CNT) phase forms small droplets and elongated droplets, which are not interconnected in the PA phase. When increasing the (EA+CNT) content (35wt.-%), the elongated structures becomes interconnected and when increasing further, the EA strands become larger and less elongated (40wt.-%).

These observations are confirmed by SEM micrographs presenting the morphology of the blend for the different compositions (Figure 23, Figure 24). Figure 23 and Figure 24a-c present the morphology after extraction of the EA phase, from 33 to 44 wt.-% (EA+CNT). Figure 24d presents the morphology after extraction of the PA6 phase, for 44 wt.-% (EA+CNT).

For 32 (results not shown) and 33 wt.-% (EA+CNT), PA6 forms a continuous phase (Figure 23a). Thin threads of EA are also present but overall the sample presents a sea-island morphology. This is coherent with the selective extraction experiments, which show that, at these compositions, the morphology is not homogeneous and some co-continuous areas co-exist with sea-island areas.

From 34 to 42 wt.-% (EA+CNT), both phases are co-continuous (Figure 23b-d). The co-continuous structure is globally homogeneous. However, a large amount of EA sub-inclusions are present in the continuous PA6 phase. They are more clearly observable in TEM micrographs (Figure 25). These sub-inclusions of EA are spontaneously formed by coalescence of poorly stabilized

PA6 phase during melt mixing [42,43]. PA6 presents a higher viscosity than EA, at the early stages of mixing, it will therefore form droplets surrounded by EA phase. Later, during mixing, the droplets will coalesce and some EA will be integrated in PA6. TEM micrographs also show the presence of CNT at the interface between EA and PA6 for the large structures and for the small sub-inclusions.

For 43 wt.-% (EA+CNT), the morphology is less homogeneous, the structure is still co-continuous in some areas (Figure 23e), but the morphology changes, PA6 begins to form elongated threads that are not interconnected anymore. The formation of droplets by breakup is more clearly visible when observing the blend in a plane parallel to the extrusion direction. The rupture of elongated threads and the formation of droplets are presented in Figure 24. This effect is even clearer for 44wt.-% (EA+CNT). A high number of elongated threads that are not interconnected is observable (Figure 24c). After extraction of PA6, EA is continuous and the holes resulting from the PA extraction show that this phase is not continuous anymore (Figure 24d).

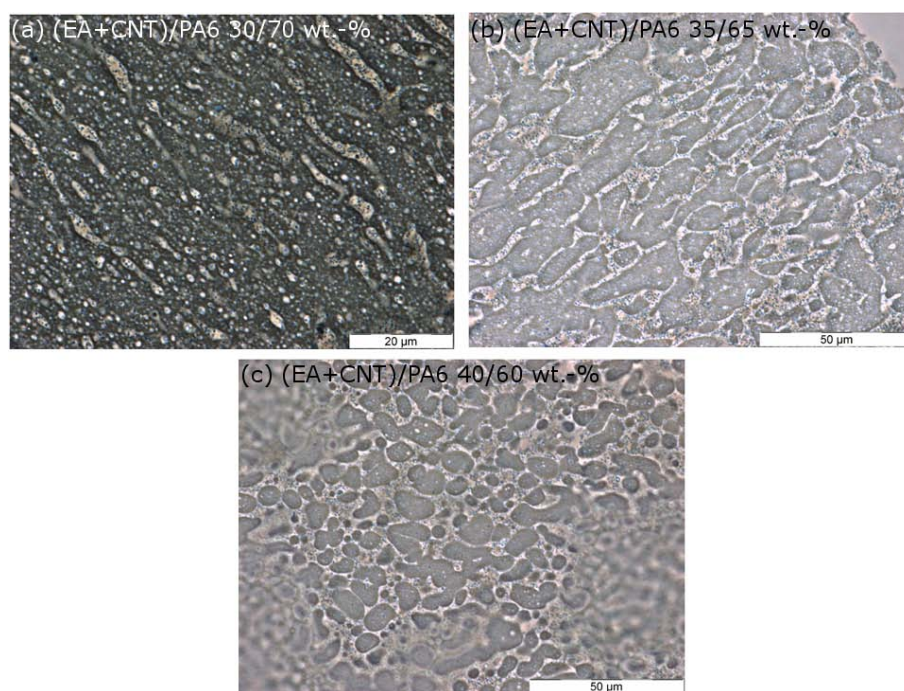


Figure 22 – OM micrographs of the blend (EA+CNT) / PA6 after extraction of the PA6 phase (a) 30/70 wt.-%; (b) 35/65 wt.-%; (c) 40/60 wt.-%. Samples are cut in the direction perpendicular to the extrusion direction.

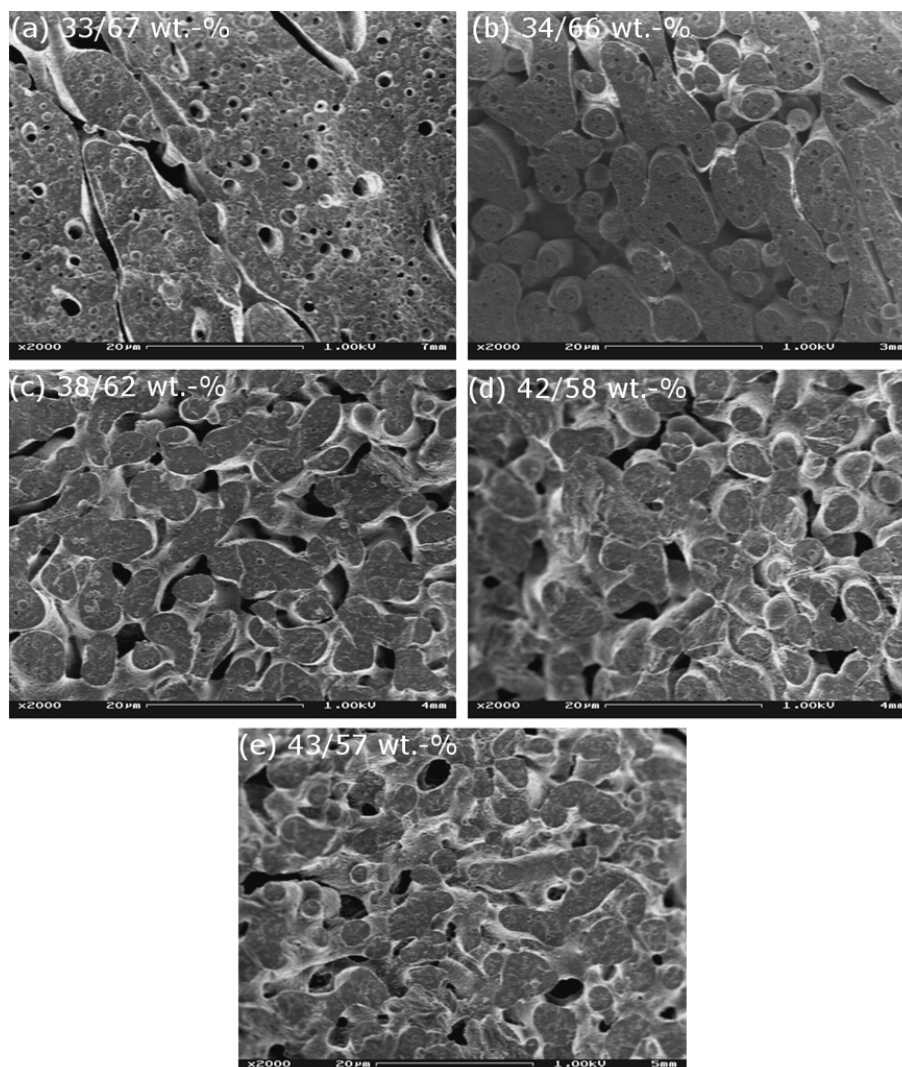


Figure 23 – SEM micrographs of the blend (EA+CNT) / PA6 after extraction of the EA phase (a) 33/67wt.-%; (b) 34/66 wt.-%; (c) 38/62 wt.-%; (d) 42/58 wt.-%; (e) 43/57 wt.-%. All micrographs are in a plane perpendicular to the extrusion direction.

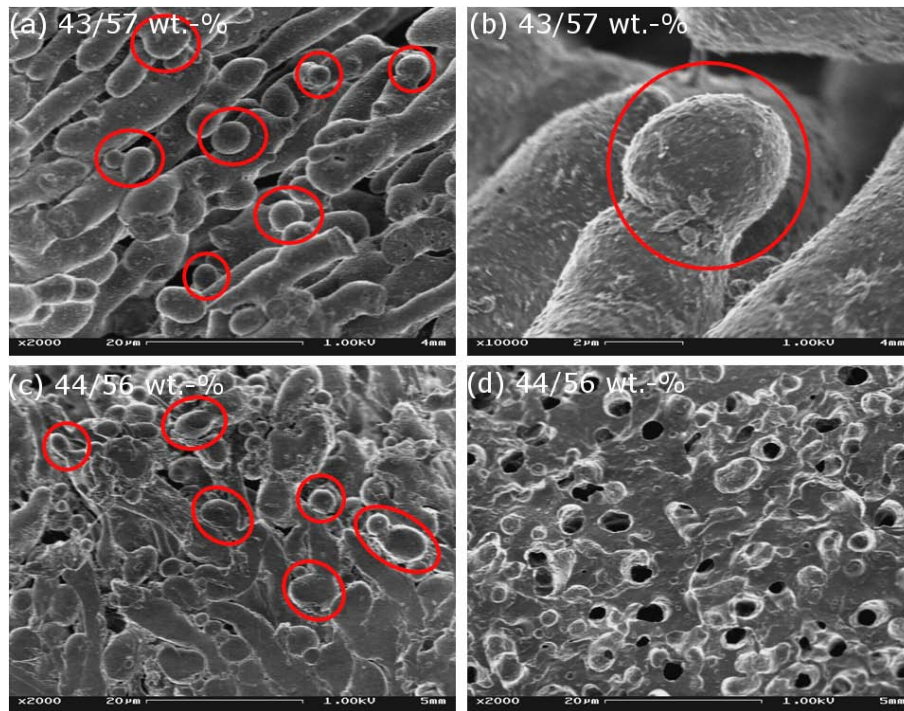


Figure 24 – SEM micrographs of the blend (EA+CNT) / PA6 after extraction of (a-c) the EA phase; (d) the PA6 phase: (a,b) 43/57 wt.-%; (c,d) 44/56 wt.-%. Micrographs a to c are in plane parallel to the extrusion direction and micrograph d is in the plane perpendicular to the extrusion direction.

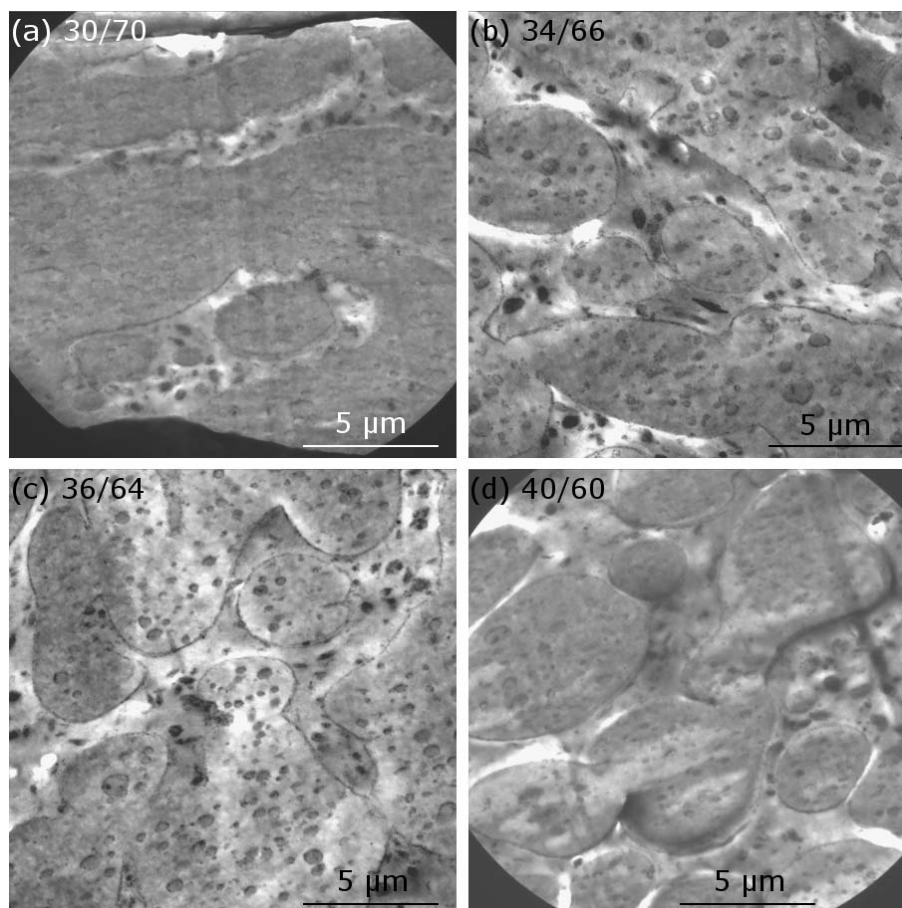


Figure 25 – TEM micrographs of the blends (EA+CNT)/PA6 (a) 30/70 wt.-%; (b) 34/66 wt.-%; (c) 36/64 wt.-%; (d) 40/60 wt.-%. The cutting plane is perpendicular to the extrusion direction.

c. Electrical characterization

The co-continuous domain is also studied in terms of RF electrical properties. For these measurements, the samples are moulded by compression in the melt state. First, the conductivity at high frequencies of pure blends in the absence of CNT is presented in Figure 26. Although PA6 presents a slightly higher conductivity, no significant difference is observed between the pure matrices and the pure blends.

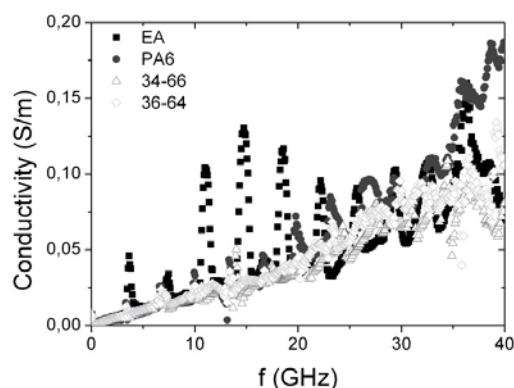


Figure 26 – RF conductivity versus frequency for pure polymers and pure EA/PA6 blends containing either 34 or 36 wt.-% EA in the direction perpendicular to the compression direction

The electrical properties of the single-phase nanocomposites containing 2wt.-% CNT are also measured to confirm the results of the dissolution tests and the microscopic observations (Figure 27). Compositions from the co-continuous domain (from 32/66 to 42/58) are presented and compared to a composition outside the co-continuous domain (50wt.-% EA) and to single-phase polymer matrices (EA+CNT, PA6+CNT). Surprisingly, for the co-continuous structures, from 34 to 42 wt.-% EA, the observed conductivities are very low. At 40 GHz, the conductivities are between 0.2 and 0.6 S/m. The conductivity is thus higher than the one obtained for pure polymers or EA filled with 2 wt.-% CNT (EA+CNT), but is lower than the conductivity of PA filled with 2wt.-% CNT (PA+CNT). The blend (EA+CNT)/PA6 32/68 wt.-%, which is at the limit of the co-continuous domain presents a conductivity similar to the one of (EA+CNT)/PA6 34/66 wt.-%. Moreover, the conductivity of the blend totally outside the co-continuous domain, (EA+CNT)/PA6 50/50 wt.-% is much higher than the conductivities of all other samples. At 40 GHz, more than 1 S/m is obtained. This blend presents a sea-island structure (Figure 28), where EA forms the continuous phase and PA6 the dispersed one. The PA6 droplets seem to be in close contact with each other. Moreover, some CNT are observed to bridge the droplets (Figure 28b). In Figure 28d, the interfaces covered with CNT are drawn with dotted red lines and the bridging CNT are drawn in red. A representative scheme of the morphology is presented in Figure 28c. CNT are present at the interface between the PA6 droplets and the EA matrix and on the surface of the sub-inclusions. CNT at the interface link up different droplets and act thus as bridges between the conducting surface of the dispersed domains.

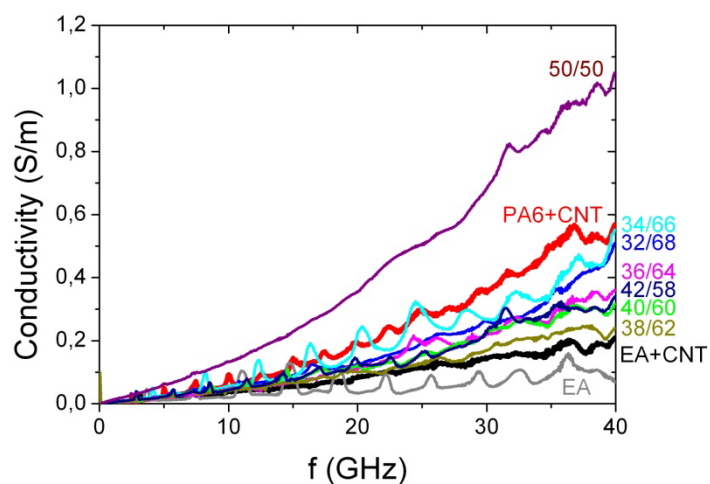


Figure 27 – RF conductivity versus frequency for (EA+CNT)/PA6 blends

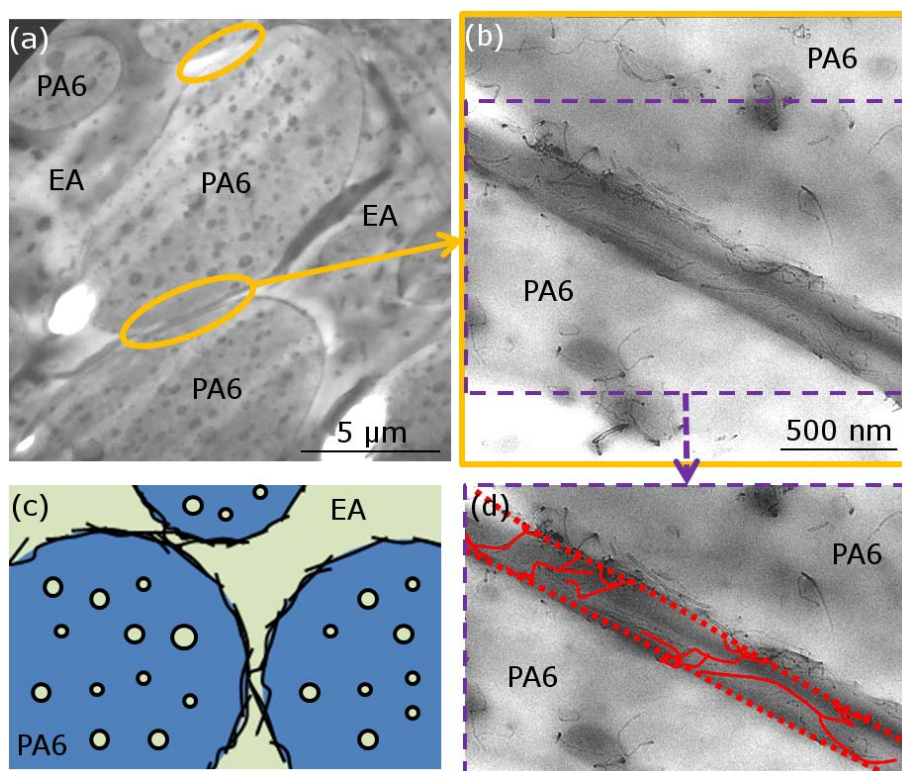


Figure 28 – TEM micrographs of the blend (EA+CNT)/PA6 50/50 wt.-%: (a) The orange ellipse indicate contacts between two PA6 phases; (b) enlargement of a contact area

2.2.2 Predispersion in PA6 phase

When CNT are initially dispersed in PA6, their dispersion is good and homogeneous. When mixing with EA, they partly migrate towards the interface and partly remain in PA6. The viscosity and elasticity of PA6 is thus assumed to be modified, compared to the pure EA/PA6 blend.

a. Selective extractions

Selective extractions have been performed on the blends from 25 to 50 wt.-% EA. The results are reported in Table 2. The symbol ✓ corresponds to effective dissolution of the sample, while the symbol × indicates that the sample remains self-supported after dissolution. The symbol ✓/× corresponds to blends that are not totally self-supported in the solvent but large pieces of the phase remain self-supported. For the predispersion of CNT in PA6, as for the predispersion in EA, the co-continuity domain is wider due to the presence of CNT. It ranges from 38 to 50 wt.-% EA, while it was only from 34 to 36 wt.-% EA in the absence of CNT.

Table 2 – Results from the selective extraction for EA/(PA6+CNT) samples of various compositions from 25 to 50 wt.-% EA

EA / (PA6+CNT) [wt.-% EA]	Chloroform	Formic acid	Continuous phase(s)
25	✓	×	PA6
30	✓	×	PA6
35	✓/×	×	(EA), PA6
38	×	×	EA + PA6
40	×	×	EA + PA6
44	×	×	EA + PA6
46	×	×	EA + PA6
50	×	×	EA + PA6
60	×	✓	EA

b. Microscopic characterizations

OM micrographs (Figure 29) present the evolution of the blend for compositions from 25 to 35 wt.-% EA in the direction perpendicular to the extrusion direction. EA is presented in light grey and PA6 is presented in dark grey. At 25 wt.-% EA, the EA forms droplets dispersed in PA6 matrix (Figure 29a). For 30 wt.-% EA, bigger EA droplets are observed as well as elongated EA structures. For 35 wt.-% EA, the EA phase is elongated and a co-continuous structure appears. Small EA sub-inclusions are present inside PA6.

These observations are confirmed by SEM micrographs presenting the morphology of the blend for the different compositions (Figure 30 to Figure 32). Figure 30 and Figure 31 present the blend morphology after the extraction of EA. Figure 32 presents the morphology after extraction of PA6.

For 25 wt.-% EA, SEM micrographs (Figure 30a) present a sea-island morphology, as confirmed by TEM observations (Figure 33a). When increasing the EA content to 30 wt.-%, the morphology is less homogeneous. The blend presents a sea-island morphology in some areas (Figure 30b) and a morphology with elongated EA threads in other regions (Figure 30c). Many EA sub-inclusions are present in the PA domains (Figure 30d). For 35 wt.-% EA, the morphology is more homogeneous, the PA domains size are reduced compared to 30wt.-% EA (Figure 30d-e). The morphology is highly oriented in the direction of the extrusion (Figure 30f).

From 38 to 50 wt.-% EA, both phases are co-continuous (Figure 31). The co-continuous structure is globally homogeneous and the structure is highly oriented in the extrusion direction. EA sub-inclusions are observable in the PA6 domains. However, for 50 wt.-% EA, the morphology is noticeably different than for the other compositions. The structure is less oriented and retraction occurs. Droplets are forming (Figure 31c,d). This is also clear after extraction of the PA6 phase (Figure 32). The size of the PA6 domain is higher for EA/(PA6+CNT) 50/50 wt.-% than for 40/60 or 46/54 wt.-%. The blend EA/(PA6+CNT) 50/50 wt.-% is the upper limit of the co-continuous domain.

TEM micrographs show that EA sub-inclusions are present in the PA6 domains for all the compositions of the co-continuous domain (Figure 33b-d).

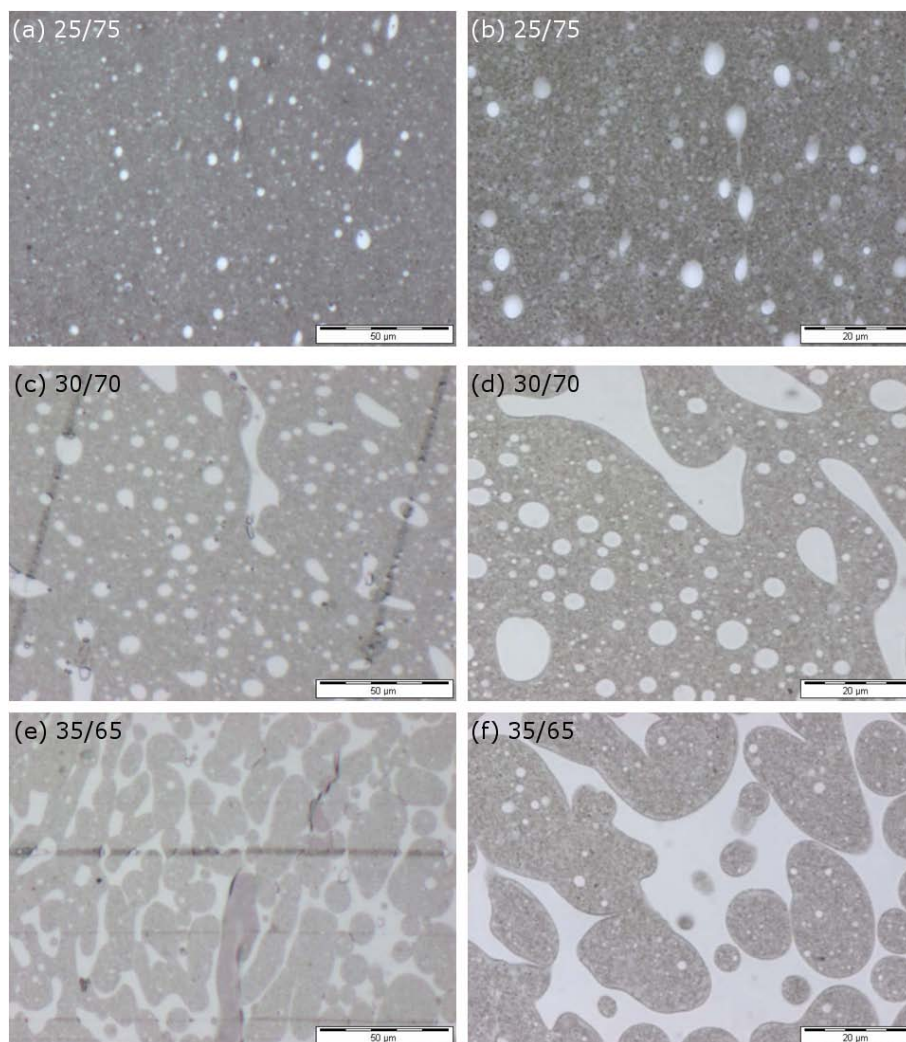


Figure 29 - OM micrographs of the EA/(PA6+CNT) blends (a,b) 25/75wt.-%; (c,d) 30/70wt.-%; (e,f) 35/65wt.-%. The samples are cut in the direction perpendicular to the extrusion direction

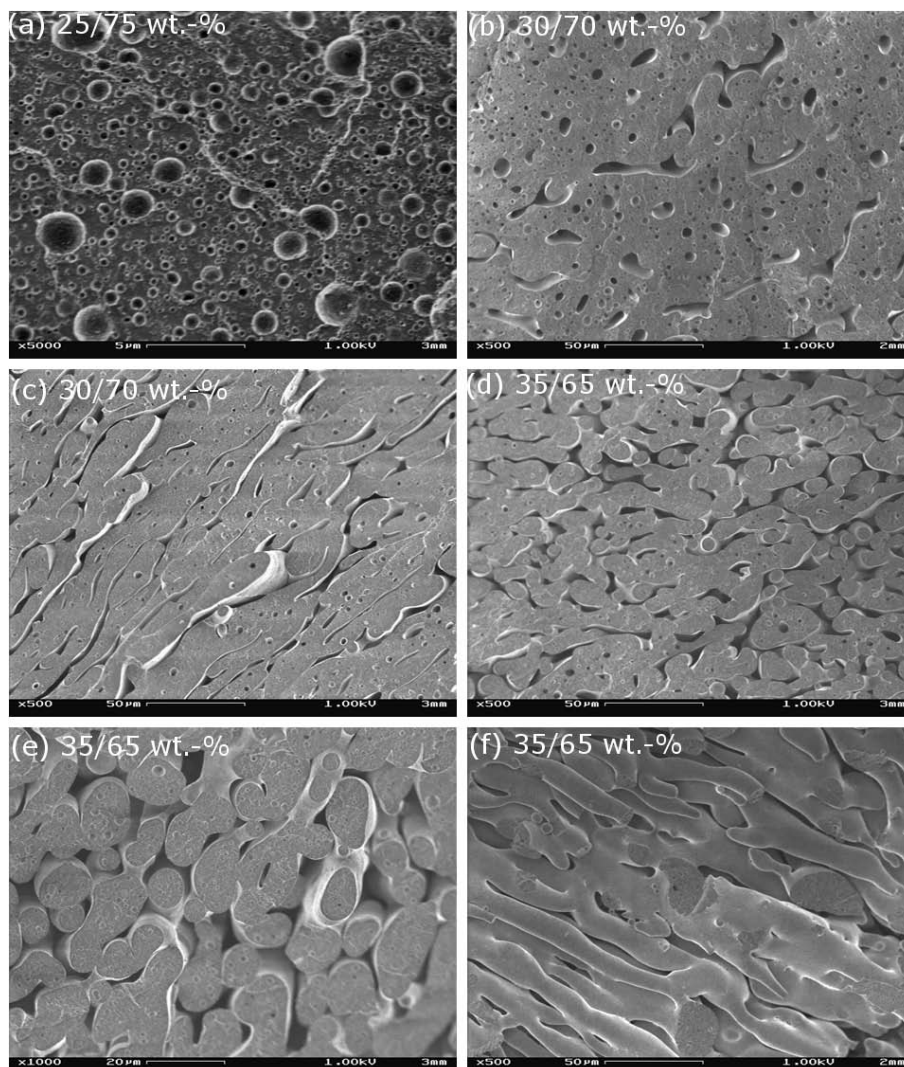


Figure 30 – SEM micrographs of the blend EA/(PA6+CNT) after extraction of the EA phase, (a-e) perpendicular to the extrusion direction; (f) parallel to the extrusion direction; (a) 25/75 wt.-%; (b,c) 30/70 wt.-%; (d-f) 35/65 wt.-%

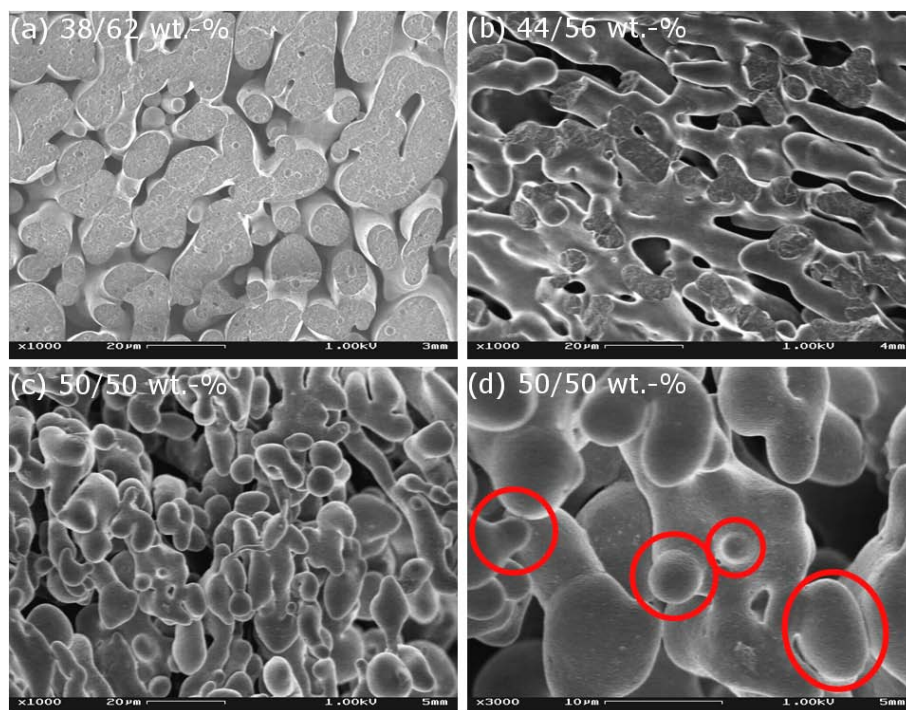


Figure 31 – SEM micrographs of the blend EA/(PA6+CNT) after extraction of the EA phase and at different magnifications (a) 38/62 wt.-%; (b) 44/56 wt.-%; (c,d) 50/50 wt.-%

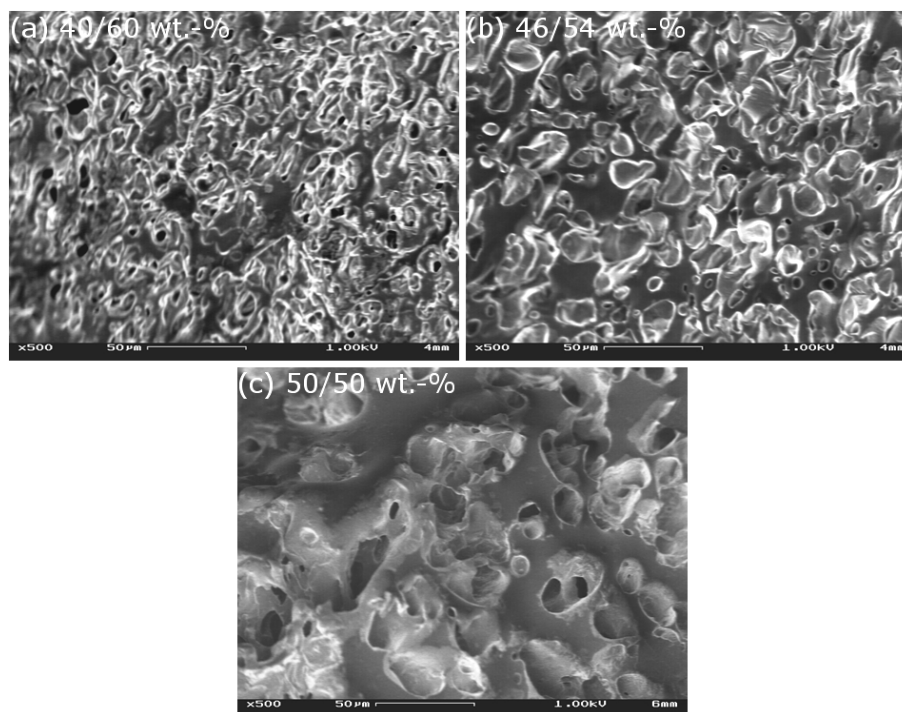


Figure 32 – SEM micrographs of a blend EA/(PA6+CNT) at different magnifications after extraction of the PA6 (a) 40/60 wt.-%; (b) 46/54 wt.-%; (c) 50/50 wt.-%

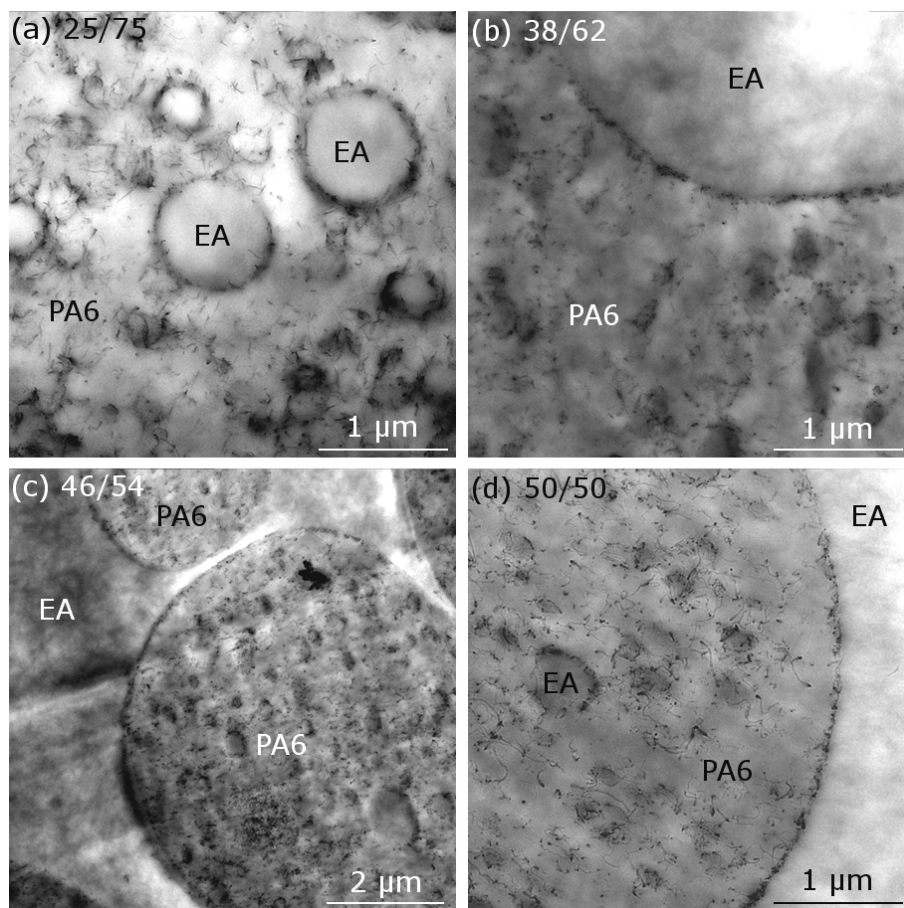


Figure 33 – TEM micrographs of the blends EA/(PA6+CNT) (a) 25/75 wt.-%; (b) 38/62 wt.-%; (c) 46/54 wt.-%; (d) 50/50 wt.-%

c. Electrical characterization

The RF electrical properties of the co-continuous blends after predispersion of CNT in PA6 are presented in Figure 34 and compared to the single-phase composites EA+CNT or PA6+CNT. The co-continuous blends show improved conductivities in comparison with the single-phase nanocomposites. However, the conductivity values achieved are not very high.

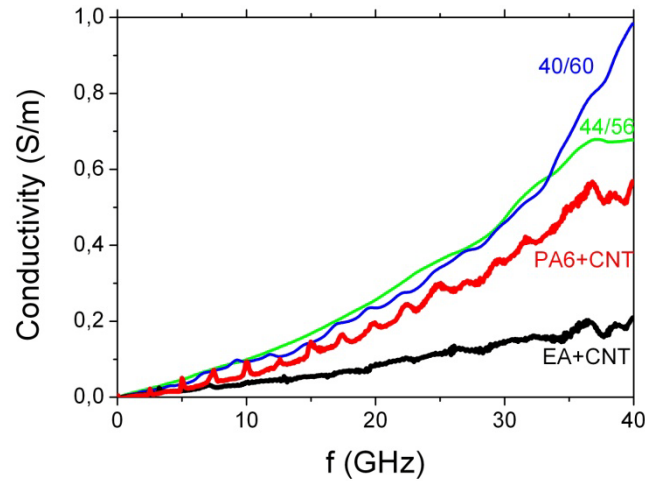


Figure 34 – Conductivity versus frequency for EA/(PA6+CNT) blends

2.2.3 Morphology anisotropy of the blends prepared for electrical characterization

For both mixing strategies, the co-continuous structure is highly oriented after compression for the preparation of the samples for the electrical characterization. The anisotropy of the structure is presented in Figure 35. The configuration of the sample after compression moulding in the z-direction for the electrical characterization is presented in Figure 35a. Figure 35b,c presents the morphology of the sample in the plane parallel to the direction of the compression (x,z-plane). Figure 35d,e presents the morphology of the sample in a plane perpendicular to the direction of the compression (x,y-plane). The structure is clearly crushed during compression and the resulting sample presents a structure highly oriented in the plane perpendicular to the direction of the compression.

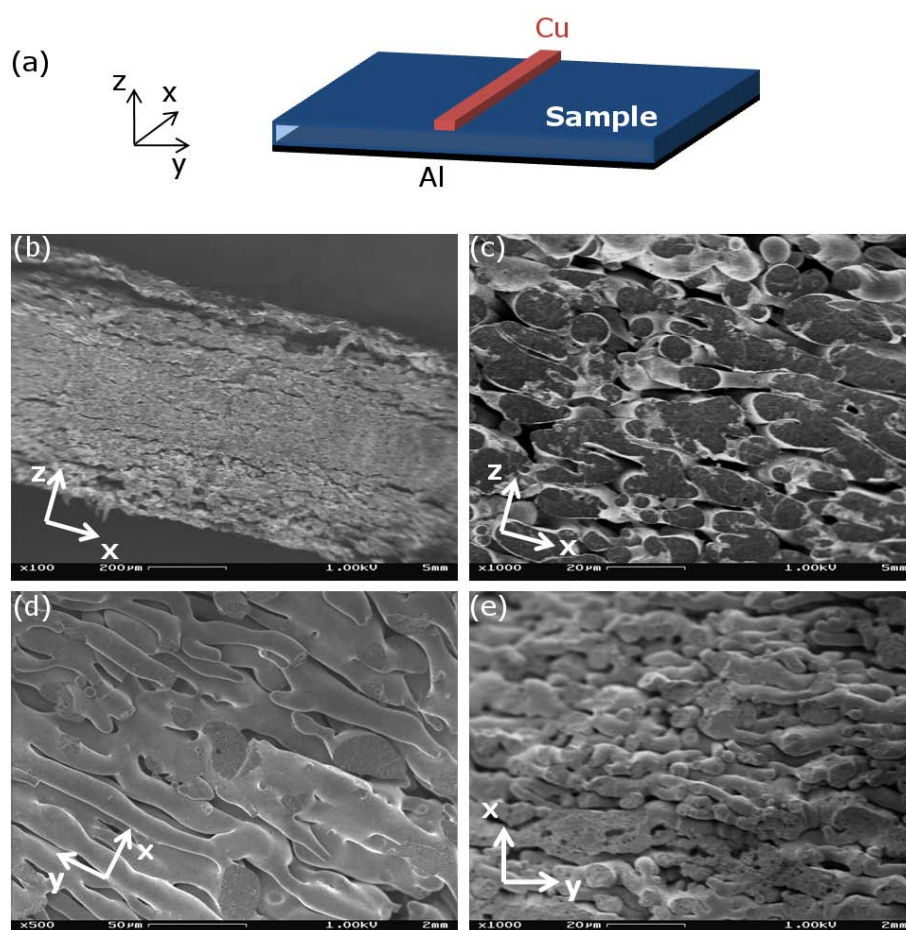


Figure 35 – (a) Scheme of the sample in the configuration for electrical characterization; (b-e) SEM micrographs of the blend (EA+CNT)/PA6 35/65 wt.-% after compression for the electrical characterization and after extraction of the EA phase: (b,c) in the compression direction (z); (d,e) in the direction perpendicular to the compression direction (x, y)

2.2.4 Discussion

First, the addition of CNT significantly extends the co-continuous domains. For unfilled blends, the co-continuous domain of the blend ranges from 34 to 36 wt.-% EA. When CNT are predispersed in EA, the co-continuous domain ranges from 34 to 42 wt.-% EA and when CNT are predispersed in PA6, it ranges from 38 to 50 wt.-% EA.

Second, the size of the domains is also very different for the different blends. Larger phases are observed in the absence of CNT (Figure 36a). In the presence of CNT, predisposition of CNT in EA leads to a drastic reduction of the size of the

phases (Figure 36b), while for predispersion of CNT in PA6, the decrease of the size of the structure is less important (Figure 36c).

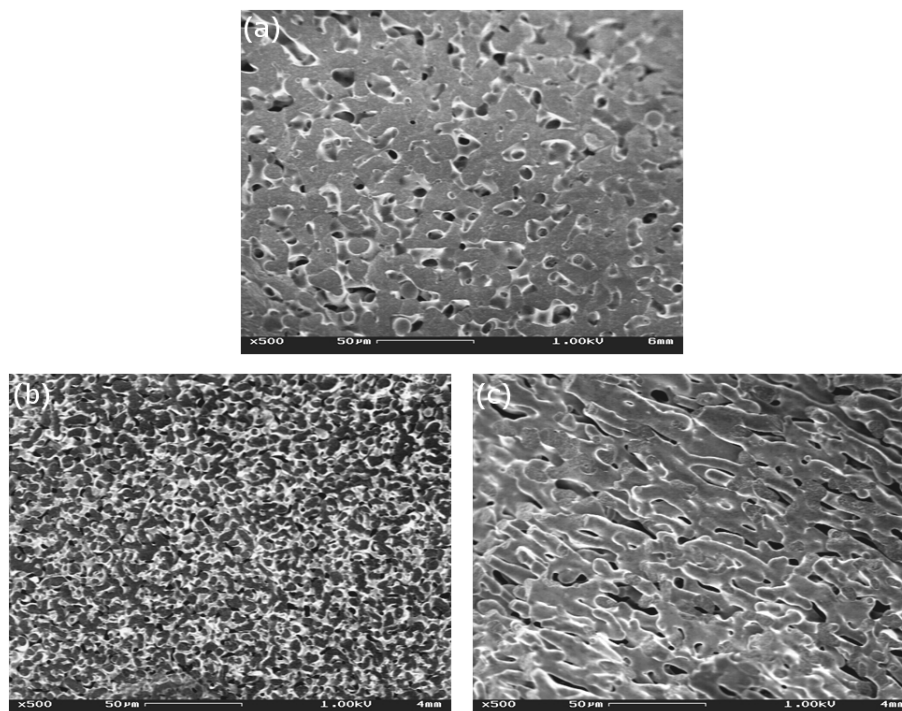


Figure 36 – SEM micrographs of the blends after cryofracture and selective extraction of the EA phase: (a) EA/PA6 36/64 wt.-% without CNT; (b) (EA+CNT)/PA6 38/62 wt.-%; (c) EA/(PA6+CNT) 44/56 wt.-%

Note that a refinement of the co-continuous morphology associated with an enlargement of the co-continuity domain has already been reported in literature for immiscible blends containing CB [2,44] or CNT [18-26]. However, in those systems, the particles are localized inside one of the phases and the inhibition of the coalescence is mainly attributed to an increase of the viscosity of the phase including the CNT. Here the CNT are mainly selectively localized at the interface of the blend, therefore stabilizing the morphology.

The compositions of the co-continuous domain is almost not shifted when CNT are predispersed in EA. However, when CNT are predispersed in PA6, the domain is slightly shifted towards higher EA contents. Although this shift is non-intuitive, it is difficult to explain without considering the degradation of PA6 and EA, which is not assessed here.

The composites presenting a co-continuous structure however do not achieve high conductivities, although CNT are confined at the interface. When CNT are

predispersed in EA, almost all of them migrate towards the interface of the blend. However, their initial dispersion state in EA is average; agglomerates and individual CNT are both present. Thus the conductivity at the interface is mainly attributed to these agglomerates (Figure 19). Moreover, TEM micrographs present some areas of the interfaces that are not covered with CNT. There are thus discontinuities in the electrically conductive pathway. CNT remaining in the EA phase do not take part to the formation of the conductive pathway neither. When CNT are predispersed in the PA6, their initial dispersion is better than in EA. The conductive pathway at the interface is therefore more homogeneous (Figure 21). However, the migration of the CNT is less efficient and some of them remain in the PA6 phase.

The co-continuous structure is highly oriented after compression for the preparation of the samples for electrical characterization. Although the structure is co-continuous, it is assumed that the orientation of the structure can be detrimental to the electrical properties, which are here measured in the direction perpendicular to the plane in which the structure is oriented.

Moreover, the presence of a high number of sub-inclusions is also detrimental to the formation of the conductive network because part of the CNT is lost at the surface of these sub-inclusions.

Finally, the highest electrical conductivity is achieved for the blend (EA+CNT)/PA6 50/50 wt.-%, which presents a sea-island morphology. In this blend there is a high number of large PA6 droplets. These droplets are in contact with each other. The CNT at the interface form conducting bridges between the PA6 dispersed droplets, which are covered with CNT. The CNT remaining in the EA phase can also help to the formation of a conductive network (Figure 37). A continuous conducting path is thus formed. Surprisingly, this structure is more efficient than a triple continuous structure to improve the electrical properties.

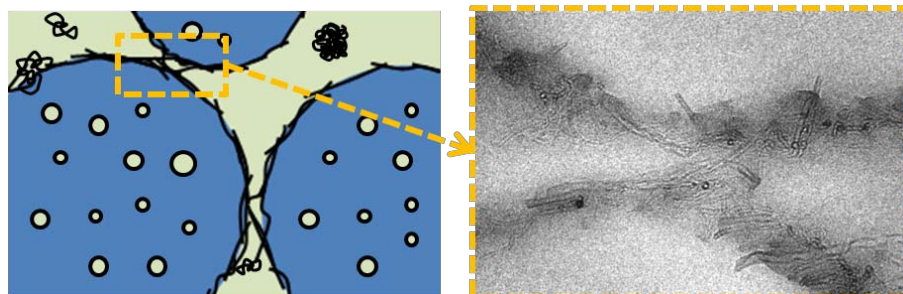


Figure 37 – Schematic representation of the blend (EA+CNT)/PA6 50/50 wt.-%

2.3 Stability

The stability of the co-continuous blends is studied in static conditions (annealing of 1 hour at 240°C). The stability of the blend in which CNT are predispersed in EA is first studied. Next, the stability for a predispersion in PA6 is analyzed.

2.3.1 Predispersion in EA

The stability of the co-continuous structure under annealing for 1h at 240°C has been studied for 2 compositions of the blends: (EA+CNT)/PA6 35/65 and 40/60 wt.-%. Figure 38 presents the SEM micrograph obtained after cryofracture of the blend and extraction of EA phase. A similar structure is obtained before and after annealing. The co-continuous structure as well as the phase size are unchanged.

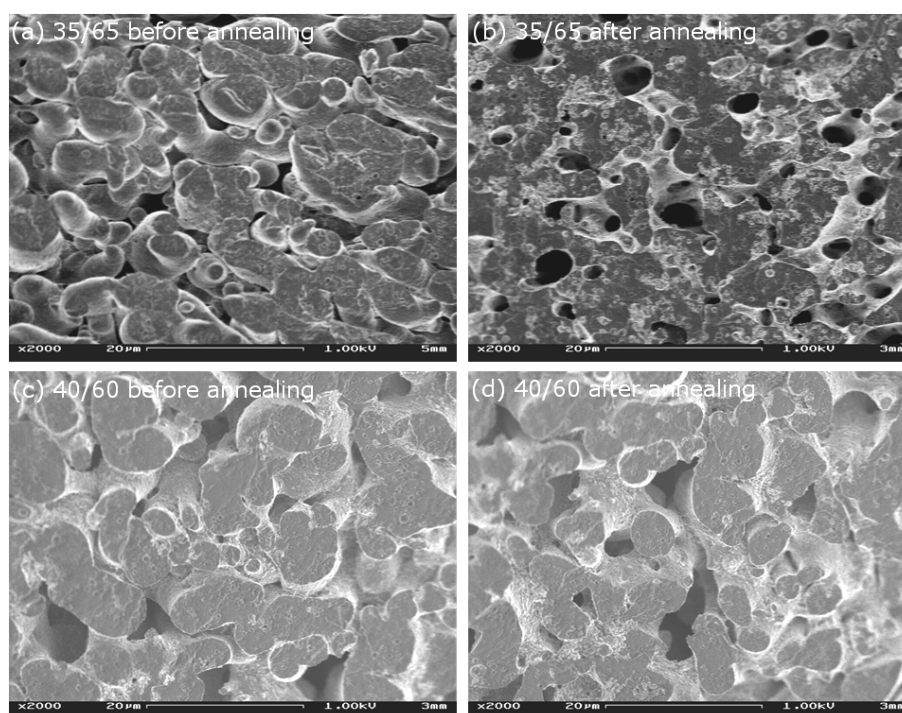


Figure 38 – SEM micrographs of the blends (EA+CNT)/PA6 (a) 35/65 wt.-% before annealing; (b) 35/65 wt.-% after annealing 1h 240°C; (c) 40/60 wt.-% before annealing; (d) 40/60 wt.-% after annealing 1h 240°C

The effect of annealing on RF electrical properties is presented in Figure 39. Annealing 1h at 240°C has almost no effect on the conductivity of the blend. This is coherent with the absence of change of the structure of the blend and it

confirms that the selective localization of CNT at the interface stabilizes the morphology.

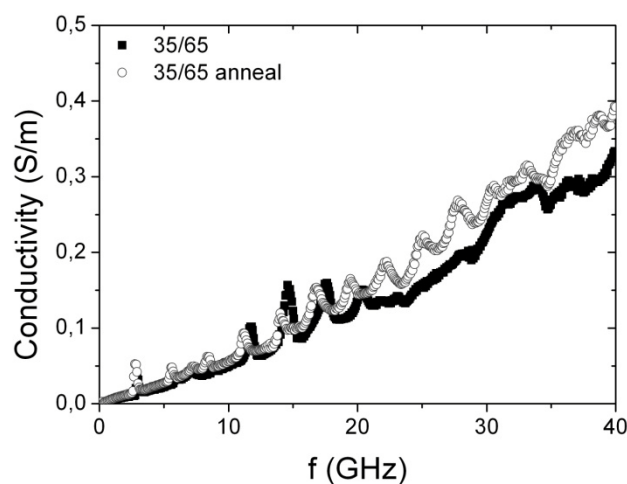


Figure 39 – RF conductivity versus frequency for (EA+CNT)/PA6 35/65 wt.-% without annealing and with annealing 1h at 240°C

2.3.2 Predispersion in PA6

The stability of the blend EA/(PA6+CNT) 44/56wt.-% after annealing 2h at 240°C is studied. The morphology is presented on SEM micrograph after extraction of EA (Figure 40). After 1h annealing at high temperature, the morphology coarsens but remains co-continuous.

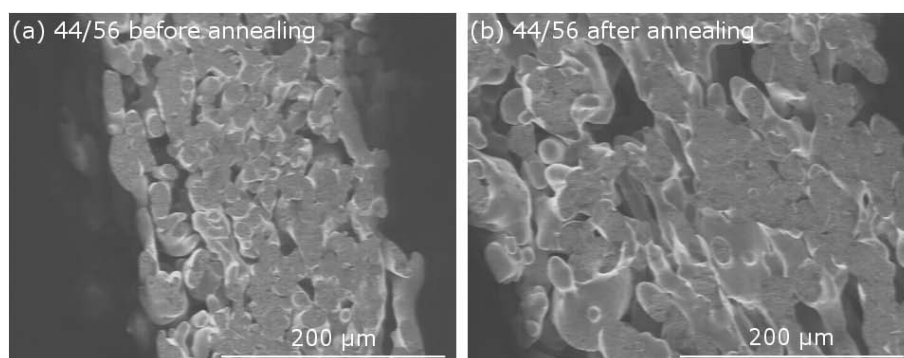


Figure 40 – SEM micrographs of the blend EA/(PA6+CNT) 44/56 wt.-% after extraction of the EA phase (a) before annealing; (b) after annealing 1h at 240°C

The effect of annealing on the electrical properties is presented in Figure 41. Annealing does not significantly affect the conductivity of the blend.

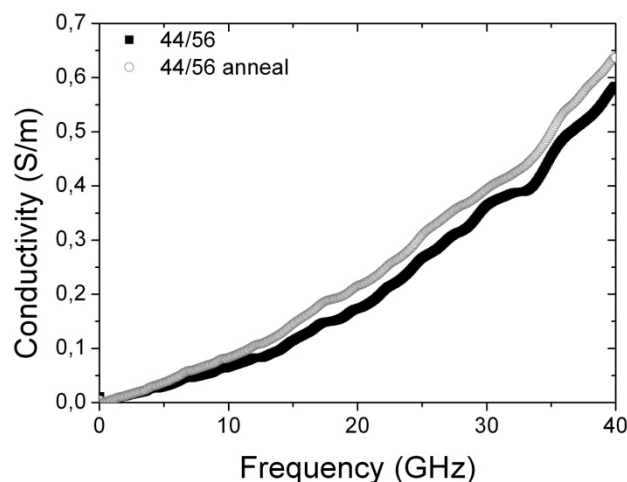


Figure 41 – RF conductivity versus frequency for EA/(PA6+CNT) 44/56 wt.-% without annealing and with annealing 1h at 240°C

2.3.3 Discussion

In the absence of CNT, annealing above the melting temperature of PA leads to significant coarsening of the morphology. Moreover, the co-continuity is lost.

In the presence of CNT predispersed in EA, the morphology is stabilized upon annealing, no change of the morphology is observed even after annealing for 1h. The conductivity is also not much affected by the annealing.

When CNT are predispersed in PA6, the morphology is less stable than for the predispersion in EA. This can be explained by the less efficient interfacial confinement of the CNT at the interface for this mixing strategy. The size of the PA6 phase is larger but the co-continuity is preserved. The coarsening of the morphology leads to less interface. A higher concentration of CNT at the interface should therefore be observed and an increase of the conductivity is expected. However, the conductivity is not drastically affected.

Steinmann et al. ^[45] have shown the stabilization of the blends by addition of particles for PS/PMMA/glass spheres. PMMA phase is filled with glass spheres and according to the authors it leads to a high increase of the viscosity and the elasticity. The relaxation processes, such as breakup or retractions, and thus the destruction of the co-continuity are thus slowed down. The authors have found that the blends are more stable upon annealing or further processing.

It is finally worth noting that to analyze unequivocally the stability of the blend, the degradation of PA6 and EA in the compounder or under static conditions should be precisely known, which is not the case here.

CONCLUSION

The development of co-continuous structures in the absence of CNT is first analyzed. Selective extractions and microscopy analysis define the co-continuous domain from 34 to 36 wt.-% EA with many EA sub-inclusions dispersed in PA6. The co-continuity is however not stable upon static annealing.

Second, the development of co-continuous domain in the presence of CNT is studied. Two mixing strategies are used: predispersion of CNT in EA ((EA+CNT)/PA6) or predispersion of CNT in PA6 (EA/(PA6+CNT)). First, the interfacial localization of CNT in the co-continuous structures is demonstrated for both mixing strategies. When predispersed in EA, CNT are found at the interface of the PA6 domains and of the EA sub-inclusions inside the PA6 domains. Agglomerates are also present in EA. When predispersed in PA6, CNT are also found at the interface of PA6 domains and of the EA sub-inclusions, but also inside PA6. Moreover, the localization of CNT is stable for long mixing times. The presence of a conductive CNT network at the interface in sea-island morphologies is also demonstrated, using CS-AFM, for (EA+CNT)/PA6 90/10 wt.-% and for EA/(PA6+CNT) 90/10 wt.-%, containing respectively 1.8 and 0.2 wt.-% CNT in total. When CNT are predispersed in EA, the conductive path is formed by CNT aggregates and it is not uniform around the PA6 droplets. When CNT are predispersed in PA6, the conductive path at the interface is more uniform. Next, the co-continuous domain is determined using selective extractions and microscopic analysis. It ranges from 34 to 42 wt.-% (EA+CNT) and from 38 to 50 wt.-% EA for the predispersion of CNT respectively in EA and PA6. The co-continuous domain is thus broadened in the presence of CNT, compared to blends without CNT. This is due to the stabilizing role of CNT, which prevent the coalescence of the phases by forming a rigid barrier at the surface of the continuous phases. Moreover, the size of the phases is reduced especially when CNT are predispersed in EA. However, surprisingly, the conductivity of these blends is low, although the CNT are localized at the interface. The structure of the blend is highly oriented when preparing the sample for RF electrical conductivity characterization. The electrical conductivity is measured in the direction parallel to the compression

direction. When CNT are predispersed in EA, the conductivity is higher than for the single-phase composites EA+CNT but lower than for single-phase composites PA6+CNT. The highest conductivity is achieved for a blend presenting a sea-island morphology with a high number of large dispersed domains. PA6 domains are covered with CNT. They are in contact with each other and CNT bridge the dispersed domains. The CNT remaining in the EA matrix phase also contribute to the creation of a conductive path through the sample (Figure 42). When CNT are predispersed in PA6, the conductivity is slightly higher than for PA6+CNT. This is probably due to the good initial dispersion of CNT in PA6, which allows the formation of a regular conductive network at the interface, contrary to predispersion in EA. It remains however lower than the conductivity observed for the sea-island blend described here above. The low measured conductivity of the co-continuous blends can probably be, at least partially, attributed to the orientation of the structure.

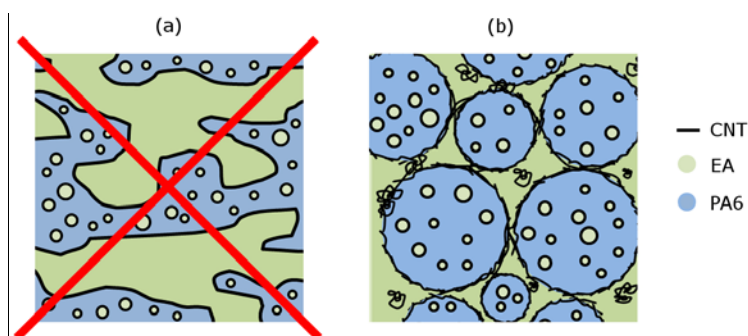


Figure 42 – (a) Triple percolation; (b) percolation of CNT at the interface of PA6 droplets

Contrary to common expectations, the best electrical properties are not observed for co-continuous structures with an interfacial localization of CNT (Figure 42a). Blends presenting a sea-island morphology with large dispersed droplets covered and interconnected by CNT leads to the formation of conducting paths (Figure 42b).

The stability of the blends is also analyzed upon static annealing. For a predispersion of CNT in EA, annealing does not change the morphology and RF electrical conductivity. The size of the phases does not coarsen. When CNT are predispersed in PA6, the morphology coarsens upon annealing but the co-continuous morphology is preserved. Despite the coarsening of the morphology and thus the reduction of the interfacial surface, no modification of the electrical properties is observed. It is finally important to note that degradation of both polymers occurs for long annealing times at high temperature and thus modifies the rheological properties.

Note finally that these conclusions can be extended to other polymer blends exhibiting an interfacial confinement of the CNT. To achieve good electrical properties, it is necessary first to disperse the primary agglomerates in the less preferred phase of the blend. Then, when mixing with the preferred phase, individualized CNT “migrate” to the interface and are pinned there, thus forming a conducting layer. Good RF electrical properties are then expected for blends presenting a sea-island morphology with large interconnected droplets.

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Chapter 6

DISPERSION OF GRAPHITE NANOPLATELETS IN HOMOGENEOUS AND IMMISCIBLE POLYMER MATRICES

ABSTRACT

In this chapter, the dispersion of graphite-based platelets in homogeneous matrices and in immiscible polymer blends is studied. Different types of platelets with decreasing number of stacked platelets are considered: graphite, graphite nanoplatelets (GNP) and functionalized graphene sheets (FGS).

As for CNT, the dispersion of the platelets in homogeneous matrices and the resulting electrical properties can be correlated to the minimization of the VDW interactions expressed by the minimization of the Hamaker constant. The electrical properties of the different platelets are compared in polycarbonate (PC).

The best electrical conductivity is obtained for FGS. They are however lower than for PC filled with CNT at the same frequency.

The effect of the orientation of GNP on the electrical properties is also demonstrated and a model is proposed.

The dispersion of platelets (GNP or FGS) in immiscible EA/PA6 polymer blends with a sea-island morphology is finally studied. When predispersing the platelets into EA, part of them migrate to the interface and part of them remain in EA. The

PA6 domains are not fully covered with platelets, contrary to what was observed with CNT. When dispersing the platelets into PA6, they remain dispersed in that phase. The final localization depends on mixing strategy and adsorption considerations.

Two publications are in preparation:

- A.-C. Baudouin et al., *RF characterization of highly-oriented graphite nanoplatelets/polymer composites*, provisional title
- A.-C. Baudouin et al., *Interfacial localization of graphite nanoplatelets in immiscible polymer blends*, provisional title

We thank R. Verdejo from CSIC, Madrid, for providing FGS samples.
We are grateful for the access to the technological platform "Welcome" and for the help of I. Huynen, I. Molenberg and P. Simon.

INTRODUCTION

Graphene is an atomically thick, two-dimensional (2-D) sheet made of sp^2 carbon atoms arranged in a hexagonal structure. The first isolation of a free-standing single-layer of graphene was achieved in 2004 by micromechanical cleavage of graphite [1]. Graphene materials exhibit outstanding properties: Young's modulus of 1 TPa, ultimate strength of 130 GPa, thermal conductivity of 5000 W/(m³ K), electrical conductivity, up to 6000 S/cm [2] and gas impermeability [3]. Moreover, they exhibit an extremely high surface area (theoretical limit: 2630 m²/g). They are therefore potential fillers for improving mechanical, electrical, thermal, and gas barrier properties of polymers [4].

Graphene can be produced by two approaches: the bottom-up approach or the top-down approach [5]. The bottom-up approach includes chemical vapour deposition, arc discharge, epitaxial growth on SiC... However, these methods do not allow the production of large amount of graphene sheets and are thus more attractive for electronic applications than for the elaboration of polymer nanocomposites. The top-down approach implies the formation of graphene or modified graphene sheets by exfoliation of graphite or graphite derivatives. Since graphite is a commodity material, large scale production of graphene is possible by this approach. A direct exfoliation of graphite can be used to produce graphene by micromechanical cleavage of graphite, by sonication, by electrochemical functionalization of graphite or through dissolution in superacids. However, apart from sonication, none of these methods is very promising for scaling-up. At the present time, the most current and most promising elaboration of graphene implies the intercalation of graphite and graphene oxide (GO). GO is composed of expanded graphene oxide sheets, obtained by oxidation of graphite [6]. Polar groups are introduced on the graphite surface and lead to the widening of the interlayer spacing between graphene layers. GO usually contains epoxide and hydroxyl groups within the graphene sheets as well as carboxyl and carbonyl groups at the sheet edges. GO is an electrically insulating material, which serves as an intermediate for the preparation of graphene nanoplatelets (GNP). Graphene can be prepared by thermally reducing GO with rapidly heating in an inert environment to produce thermally expanded graphite oxide also called functionalized graphene sheets (FGS). These compounds are electrically conducting contrary to GO. Graphite intercalated compounds (GIC) are formed by the intercalation of atomic and molecular layers of different species between the layers of graphite. GNP presenting 40 ± 15 graphene layers can be obtained from GIC. Finally,

expanded graphite (EG) is also used for the elaboration of composites. It is composed of stacks of nanosheets from 100 to 400nm. Intercalated graphite is heated over a critical temperature or exposed to microwave radiation to expand the graphite flakes. Ultrasonication can then be used to obtain thinner GNP from 30 to 80 nm. Kim et al. [5] summarized the different production techniques with their advantages and drawbacks.

As for CNT, various methods exist to elaborate polymer/graphene composites [4,5]: in situ polymerization of monomers [7], solution mixing [8,9] and finally melt mixing. Melt mixing is the most economically attractive and scalable method for the elaboration of polymer/graphene nanocomposites. Uhl et al. [10] have realized nanocomposites from PA6 and graphite or expanded graphite by melt blending. Although a good dispersion is obtained, no improvement of the mechanical properties is recorded, probably due to the lack of interaction between the polymer matrix and the fillers. Krupa et al. [11] have studied the thermal, electrical and mechanical properties of high density polyethylene (HDPE) or polystyrene (PS) / graphite composites produced by melt blending. The electrical percolation thresholds are found between 0.06 and 0.13 vol.-% for the different composites. The thermal conductivity is also improved with the addition of carbon platelets. The addition of the fillers improves the stiffness and the Young modulus of the sample. The elongation at break however decreases with the addition of the nanoparticles. Kalaitzidou et al. [12] have prepared PP/GNP composites with improved mechanical and electrical properties by melt blending. They have also combine a solution mixing with a melt blending and show that improved properties are obtained. Note that Wakabayashi et al. [13] have attempted to directly exfoliate the graphite into PP during melt mixing. However, XRD and TEM indicate that the composite contains stacks of graphite. Some authors also compare the properties of the composites obtained by melt mixing and solution mixing. Kim et al. [14] have showed that the dispersion of graphene platelets in LLDPE is more effective using solvent mixing than melt compounding. Mahmoud [15] has compared the dispersion state and resulting properties of PEO/graphene composites prepared by solvent method and melt blending. In solvent mixing, the graphene sheets are distributed parallel to the composite surface. In the melt blending method, the graphene sheets are randomly distributed in the composite. The electrical percolation threshold of the composites prepared by solvent method is lower than the one of those prepared by melt blending. The mechanical performance of the nanocomposites is also higher when using solvent mixing. The dispersion and resulting properties in different polymer matrices are exposed in several reviews [4,5,16-18].

The dispersion of graphene in immiscible polymer blends has, to our knowledge, up to now almost not been studied. Chen et al. [19] have prepared GNP/HDPE/EVA composites. GNP are exclusively distributed in the HDPE phase. The selective localization of GNP in the blend is closely related to the crystalline change of polymer blend.

In this chapter, the dispersion of GNP and FGS in various polymer matrices is studied. Next the effect of the orientation of the platelets on the electrical properties of the composites is examined. Finally, the dispersion of graphite platelets in immiscible polymer blends is evaluated.

EXPERIMENTAL

This a very brief description of the materials and characterization methods used. For more details, please refer to Appendix 1.

1 Materials

Different polymers are used for the dispersion of the graphitic-based nanomaterials: polypropylene (PP), polystyrene (PS), ethylene-acrylate copolymer (EA), polyamide 6 (PA6), polycarbonate with an antioxidant (5wt.-%) to prevent the thermal degradation during compounding (PC) and finally phenoxy resin (PKHP).

The graphitic compounds used are graphite nanoplatelets (GNP), graphite and functionalized graphene sheets (FGS). The size distribution of GNP and graphite is presented on Figure 1, according to the producer datasheets. The FGS present a few graphene layers with hydroxyl, ether and epoxy functions.

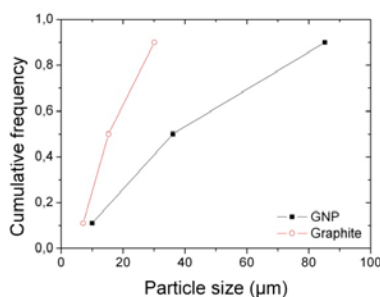


Figure 1 – Particle size distribution for GNP and graphite according to the producer datasheets

2 Characterization

The dispersion of the graphite nanoplatelets is analyzed by microscopy techniques: OM, SEM and TEM. The electrical properties are studied using a Vector Network Analyzer from 0.04 to 40 GHz.

RESULTS AND DISCUSSION

1 Dispersion in single matrices

The dispersion of graphite nanoplatelets (GNP) and functionalized graphene sheets (FGS) in various matrices is first presented. The morphology and the Radio Frequency RF electrical properties of these composites are studied.

1.1 Graphite Nanoplatelets (GNP)

The characterization of the GNP is presented in Appendix 1. They are composed of a high number of graphene sheets. XPS analysis shows that they are not functionalized. Their dispersion in different matrices is compared. Figure 2 and Figure 3 show the dispersion of 1wt.-% GNP in PP, PS, EA, PA6, PC and PKHP. When dispersed in PP and PS, the GNP are in the form of large agglomerates (Figure 2a,b) and no small particles are observed on the TEM micrograph (Figure 3a,b). When dispersed in EA, the GNP are better dispersed (Figure 2c, Figure 3c). Both OM and TEM micrographs show that the GNP present a good dispersion in PA6, PC and PKHP.

Since the best dispersion states are observed in PC and PKHP, the dispersion of 5wt.-GNP in these matrices is presented on Figure 4. Figure 4a,b present the dispersion of GNP in PC. The GNP are homogeneously dispersed in the PC matrix. Figure 4c,d present the dispersion of GNP in PKHP. The dispersion of the GNP is better in PC than in PKHP. The number of particles of intermediate size is also higher in PC.

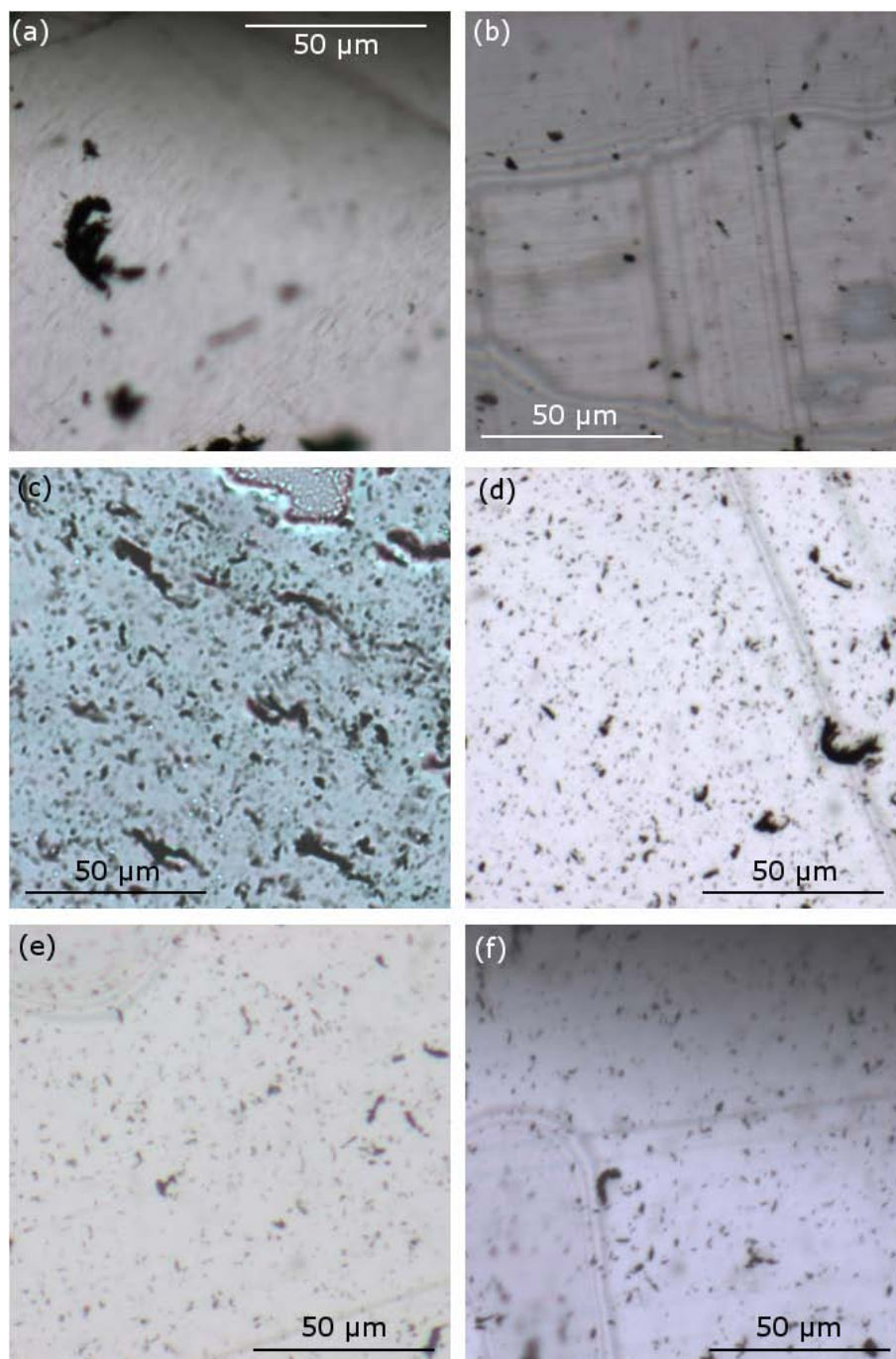


Figure 2 – OM micrographs of the dispersion of 1wt.-% GNP in various polymer matrices (a) PP; (b) PS; (c) EA; (d) PA6; (e) PC; (f) PKHP

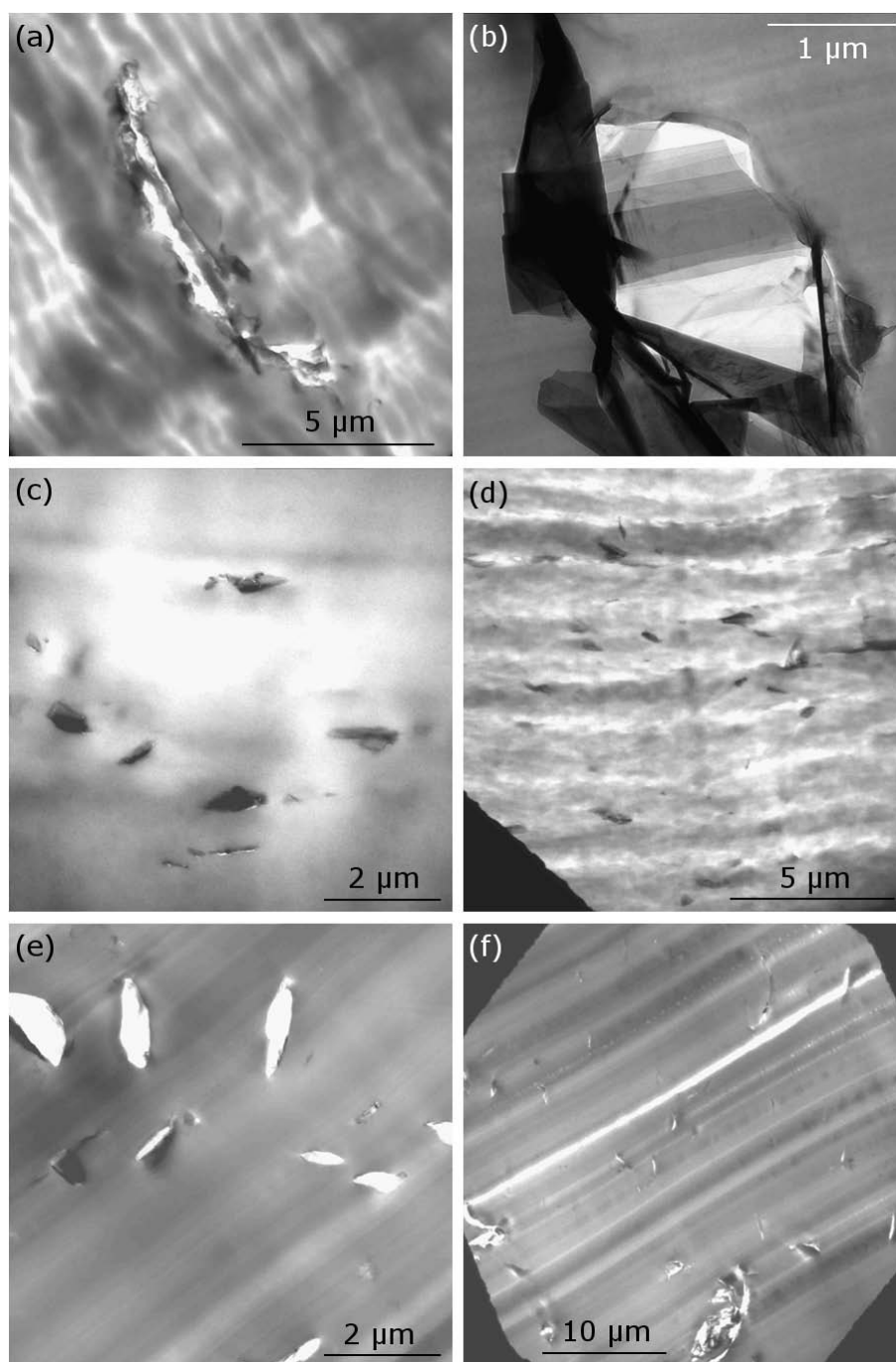


Figure 3 – TEM micrographs of the dispersion of 1wt.-% GNP in various polymer matrices (a) PP; (b) PS; (c) EA; (d) PA6; (e) PC; (f) PKHP

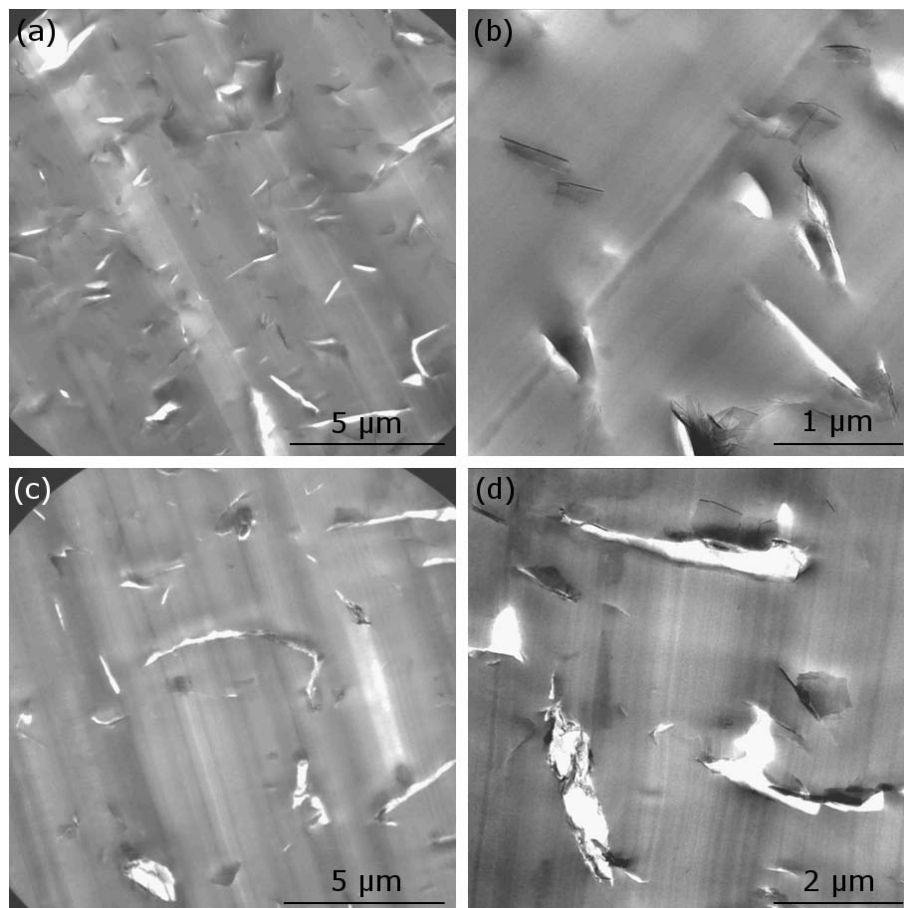


Figure 4 – TEM micrographs of the dispersion of 5wt.-% GNP in polymer matrices at different enlargements (a,b) PC; (c,d) PKHP

1.2 Functionalized graphene sheets (FGS)

The characterization of FGS is presented in Appendix 1.

As the best dispersion state of GNP is observed in PC, the dispersion of FGS is studied in that matrix (Figure 5). The FGS are not present in the state of isolated graphene sheets. The platelets are composed of a few graphene shells.

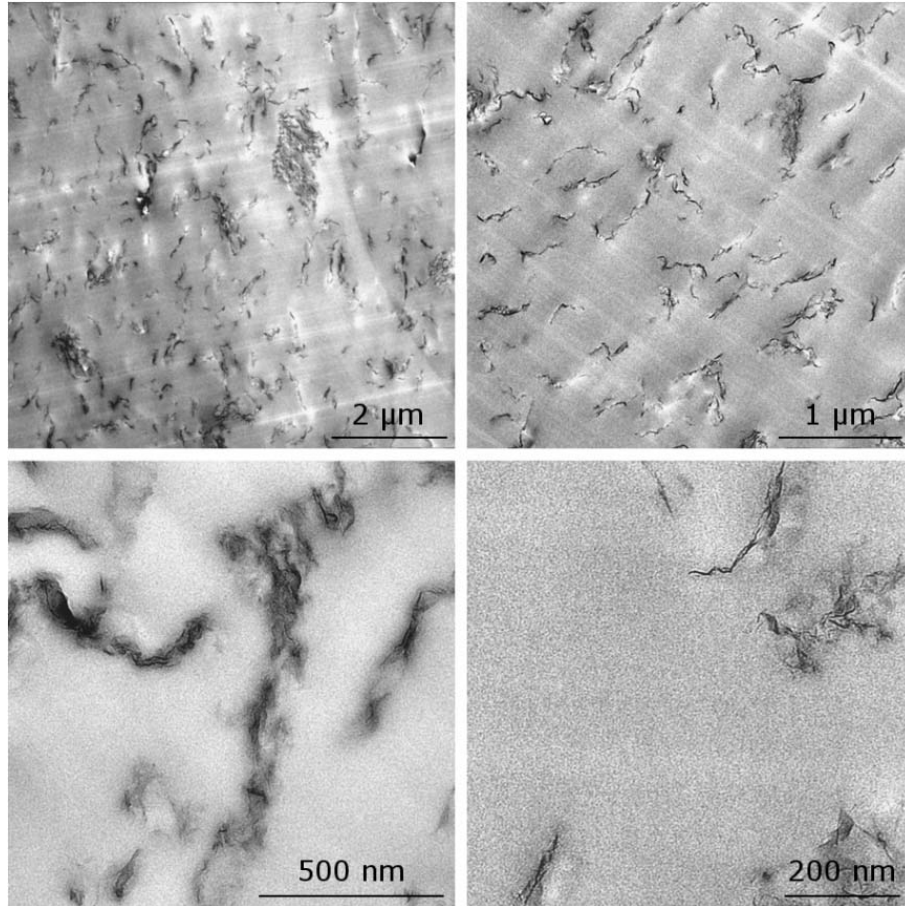


Figure 5 - TEM micrographs of the dispersion of FGS in PC at different magnifications

1.3 Electrical characterization

The RF electrical conductivity of different polymer matrices filled with 5wt.-% GNP is characterized from 0.04 to 40 GHz (Figure 6). The best conductivity is obtained for PC, followed by PKHP and then PA6. EA and PS present very bad conductivities, similar to the one observed for pure polymers. However, globally, the conductivity levels achieved are low, even for the polymer matrices in which the dispersion is homogeneous.

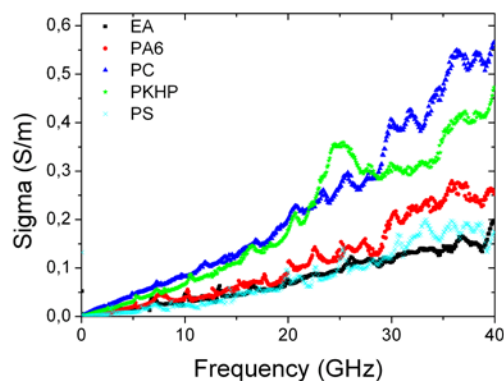


Figure 6 – RF conductivity versus frequency for 5wt.-% GNP dispersed in different polymer matrices: EA, PA6, PC, PKHP and PS

The RF conductivities of PC containing 1wt.-% of the different graphite nanofillers are compared on Figure 7. The sample containing 1wt.-% GNP (red) exhibits the same conductivity as the pure PC (green) over the frequency range. The sample containing 1wt.-% FGS (blue) presents a higher conductivity than pure PC. However, the highest conductivity over the whole frequency range is observed with CNT.

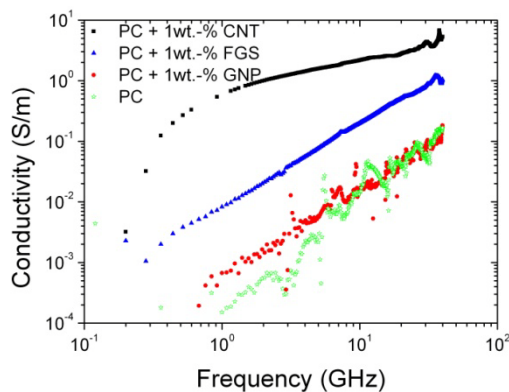


Figure 7 – Comparison of the RF conductivity versus frequency for pure PC and PC filled with 1wt.-% CNT or FGS or GNP

1.4 Discussion

TEM morphologies and electrical conductivities show that there are differences in the dispersion state of the carbon nanoplatelets in different polymer matrices. It is expected that, as for CNT, the factors influencing the dispersion are from thermodynamic and kinetic origins. Here the kinetic parameters are not studied and the different composites are compounded in similar conditions of shear stresses (for viscosity vs angular frequency data, please refer to Chapter 2). The graphene sheets are linked by van der Waals (VDW) bonds (Figure 8). The dispersion of carbon-based platelets therefore involves overcoming these VDW interactions.

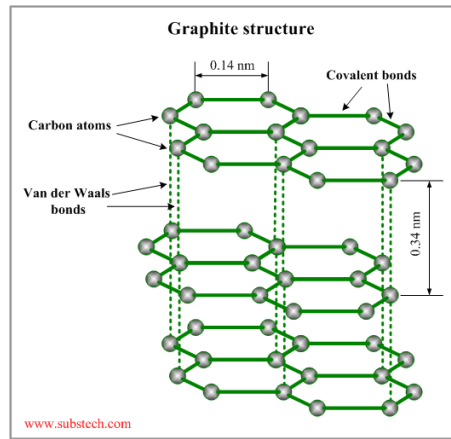
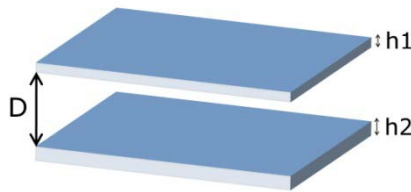


Figure 8 – Scheme of the graphite structure [20]

The classical approach based on Lifshitz theory for the VDW energy per unit area between two infinite parallel walls presenting a thickness h_1 and h_2 and separated by a distance D , is presented on Figure 9 [21].



$$W = -\frac{A}{12\pi} \left(\frac{1}{D^2} + \frac{1}{(D+h_1+h_2)^2} - \frac{1}{(D+h_1)^2} - \frac{1}{(D+h_2)^2} \right)$$

Figure 9 – Non-retarded van der Waals interaction free energies between two parallel walls (A is the Hamaker constant)

In the definition of VDW energy, A is the Hamaker constant, which is calculated based on bulk properties such as dielectric constant (ϵ) and refractive index (n). Based on Lifshitz theory for a symmetric case of two identical graphite-based platelets (GP) interacting across a polymer, the Hamaker constant can be expressed as:

$$A = \frac{3}{4} k_B T \left(\frac{\epsilon_{GP} - \epsilon_{polymer}}{\epsilon_{GP} + \epsilon_{polymer}} \right)^2 + \frac{3h\nu_e}{16\sqrt{2}} \frac{(n_{GP}^2 - n_{polymer}^2)^2}{(n_{GP}^2 + n_{polymer}^2)^{3/2}}$$

Where k_B is the Boltzmann constant, T is the temperature, h is the Planck constant, ϵ_{GP} and $\epsilon_{polymer}$ are the static dielectric constants of the graphite-based platelets and polymer, ν_e is the main electronic absorption frequency in the UV typically around $3 \times 10^{15} \text{ s}^{-1}$, n_{GP} and $n_{polymer}$ are the refractive indexes of the GP and polymer. The attractive interaction between two graphite-based platelets depends on the dielectric constants and refractive indexes differences between GP and the polymer. For the polymers, some of these values are presented in Chapter 2. The dielectric constants are typically in the range from 1.5 to 3, while the refractive indexes are between 1.5 and 1.6 (Table 1). The dielectric constant of the graphite-based platelets is evaluated to be between 12 and 15 by analogy to graphite [22]. Moreover, the refractive index of the platelets is around 1.9-2.1, by analogy to graphite [23,24]. The VDW interaction energy is thus minimized for the polymers presenting the higher dielectric constants and refractive indexes.

Table 1 – Properties of polymer and dispersability of GP in polymer matrices [25-27]

Polymer type	Dielectric constant (DC)	Refractive index	Dispersability of GP
PP	1.5	1.5	Poor
PE	1.5 (pellets) – 2.2-2.4	1.51	Poor
PS	2.4	1.59	Poor
PA6	2.5-2.6	1.53-1.56	Good
PKHP	2.8	1.5-1.6	Very good
PC	2.9-3.0	1.59	Very good

According to these values, the nanocomposites can be classified for increasing Hamaker constant: $A_{PC} < A_{PKHP} < A_{PA6} < A_{PS} < A_{EA} < A_{PP}$. The interaction energy between the carbon-based nanoplatelets is thus the lower for PC and PKHP. This is coherent with the observed morphologies, which shows that the best dispersion states of the particles are observed in PC and PKHP. It is also coherent with the measured electrical properties since the highest conductivities are observed for these two matrices.

The dispersion state and resulting electrical properties of different fillers inside PC have been compared. FGS platelets present less graphene sheets than GNP platelets and they exhibit a more uniform dispersion throughout the PC as it is clear when comparing Figure 3e and Figure 5. As the aspect ratio and dispersion state of the FGS are higher, the formation of a conductive network is favoured and the electrical conductivity of PC containing 1wt.-% FGS is therefore higher than the one of PC containing 1wt.-% GNP, which is almost similar to the one of pure PC, over the whole frequency range. However, the electrical properties of PC containing 1wt.-% FGS is lower than the one of PC containing 1wt.-% CNT. For comparison, the dispersion of CNT in the same PC matrix is presented in Figure 10. The CNT are homogeneously dispersed throughout the sample. When comparing with the dispersion state of the FGS (Figure 5), it seems that CNT form more easily a conductive network percolating through the sample. The distances between the conductive particles are indeed lower than for FGS nanocomposites. This is probably the reason of the higher conductivity observed in the case of CNT than in the case of FGS.

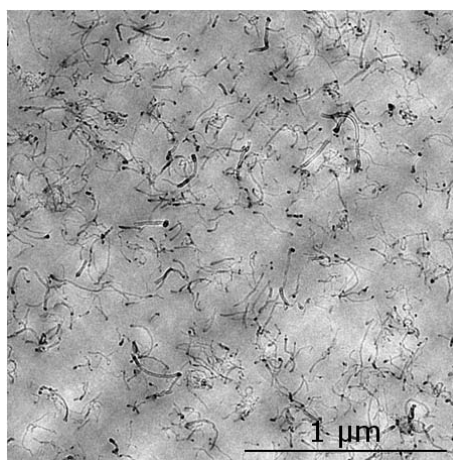


Figure 10 – TEM micrograph of the dispersion of 1wt.-%CNT in PC

2 Effect of orientation

Highly filled EA matrices have also been studied to analyze the effect of the orientation of GNP platelets on RF electrical properties. The preparation of the samples for the electrical characterization requires a compression molding step. During this step, an orientation of the platelets inside the polymer matrix is observed. The morphology of a composite containing 25wt.-% GNP after compression is presented in Figure 11 and Figure 12. OM micrographs (Figure 11) show that the large platelets are oriented in the plane perpendicular to the compression direction indicated by arrows (Figure 11 left). TEM micrographs (Figure 12) show that platelets of lower dimensions are also present in the composite. These intermediate size platelets are also oriented in the plane perpendicular to the compression direction, which is indicated by the arrows.

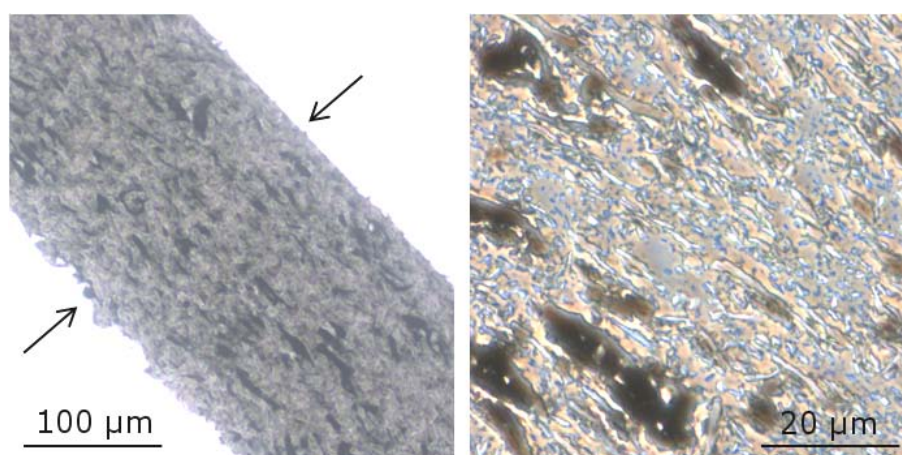


Figure 11 – OM micrographs presenting the distribution and the orientation of GNP in EA+25wt.-%GNP. The arrows indicate the direction of the compression

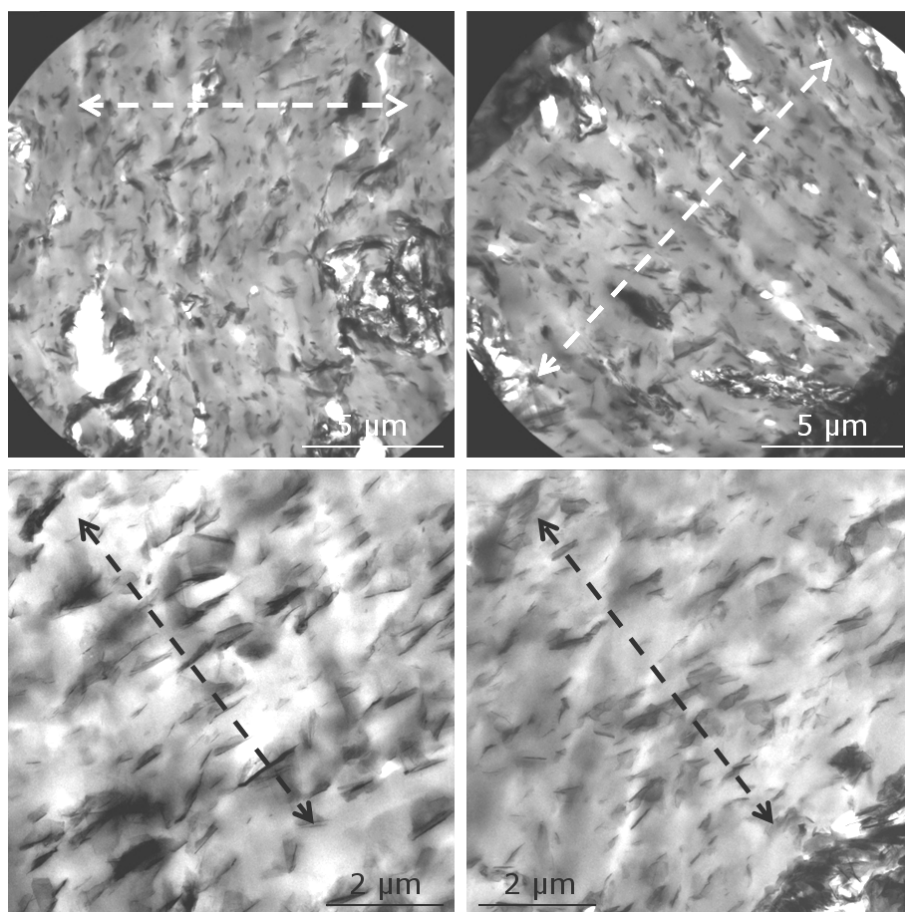


Figure 12 – TEM micrographs presenting the distribution and the orientation of GNP in EA+25wt.-%GNP at different magnifications. The arrows indicate the compression direction.

The RF permittivity and conductivity of these highly oriented materials are presented in Figure 13. Figure 13a presents the real part of the effective permittivity. Figure 13b presents the RF conductivity of the composites. Pure EA and EA+2wt.-% GNP present a similar electrical behaviour. EA+10wt.-% GNP present a typical RC circuit behaviour. The conductivity tends to zero at low frequency and increases with increasing frequencies. This behaviour is explained by an equivalent RC circuit [28]. The other composites, containing more GNP, present an atypical behaviour. The conductivity suddenly increases at a certain frequency, which depends on the amount of conductive filler in the sample. For 15 wt.-% GNP, this sharp increase is observed above around 35GHz and for 21.38 wt.-% GNP and 25 wt.-% GNP, above 20GHz. This abrupt transition is also observed on the real part of the permittivity.

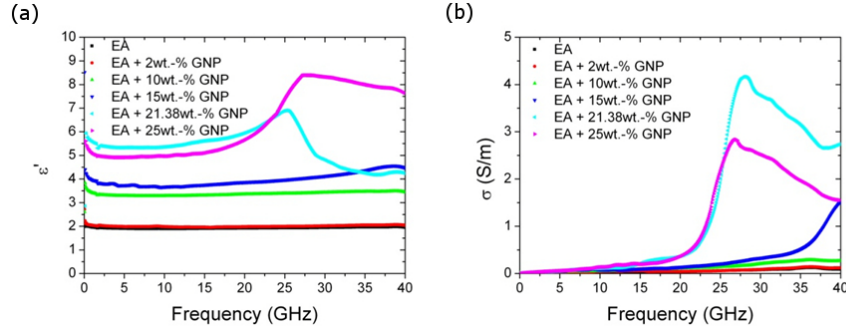


Figure 13 – Electrical properties of EA filled with various amounts of GNP: (a) real part of the effective permittivity; (b) RF conductivity

The conductivity of graphite platelets is highly anisotropic. It is around 4000 S/cm in plane and around 3.3 S/cm in the direction of the c-axis [29]. Based on this consideration and to explain the sharp increase of the conductivity, a model can be proposed (Figure 14). The random distribution of the graphite platelets (Figure 14a) can be approximated by a network of highly anisotropic particles, separated by the insulating polymer matrix (Figure 14b). Each particle is considered to be non-conductive in the direction of the electrical field and to be conductive in the perpendicular direction. The graphite platelets therefore act as microcoils for current and can be likened to an equivalent inductor. An equivalent resistor can also be attributed to the particles. Each particle is considered to be coupled to its neighbour by a capacitor. The resulting model is thus a two layered microstrip transmission line formed by the series connection of an inductor, a resistor and a capacitor (RLC circuit) (Figure 14c).

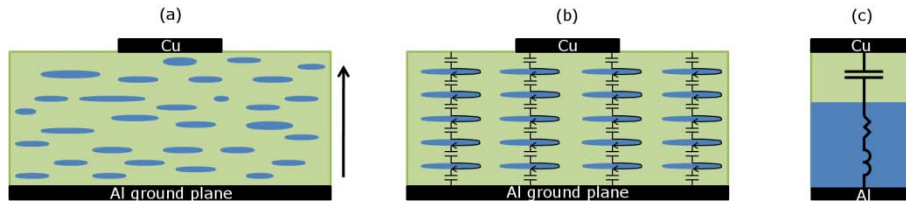


Figure 14 – Model explaining the frequency dependence of conductivity extracted from microstrip line on graphite-based composite; (a) original topology including graphite particles; (b) approximation by a network of microcoil platelets separated by an insulating polymer matrix; (c) equivalent admittance per unit length of microstrip (RLC circuit)

The impedance of a RLC series circuit is the defined as:

$$Z_s = R + j\omega L + \frac{-j}{\omega C}$$

In these systems, resonance can occur when there is total energy exchange between the capacitor and the inductor. The angular resonance frequency is expressed as:

$$\omega_0 = \sqrt{\frac{1}{LC}}$$

The RLC circuit is measured in microstrip configuration, characterized by the impedance, Z , of the inductor associated to the microstrip configuration and by the admittance of the sample, Y_s (Figure 15).

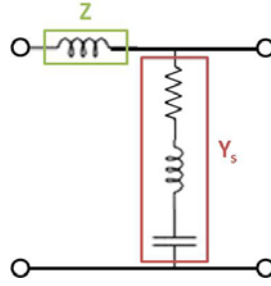


Figure 15 - Equivalent circuit corresponding to the measurement of the sample in microstrip configuration

The propagation constant, γ , is expressed as:

$$\gamma \triangleq \sqrt{Z \cdot Y_s} = \sqrt{\frac{Z}{Z_s}} = \frac{j\omega\sqrt{\varepsilon}}{c_0}$$

Where c_0 is the light velocity and ε is the complex permittivity, which is expressed as:

$$\varepsilon = \varepsilon' - j\varepsilon'' = \varepsilon' - j \frac{\sigma}{\omega\varepsilon_0}$$

Where ε' and ε'' are respectively the real and imaginary parts of the permittivity, σ is the conductivity and ε_0 is a constant representing the permittivity in vacuum ($8.85 \times 10^{-12} \text{ C}^2/\text{Nm}^2$).

The impedance Z associated to the microstrip is expressed as:

$$Z = j\omega L'$$

The real and imaginary parts of the conductivity can thus be expressed as:

$$\varepsilon' = -\frac{c_0^2 L' \left(\frac{\omega^2 LC - 1}{R} \right)}{\omega^2 R^2 - \left(\frac{\omega^2 LC - 1}{R} \right)^2}$$

$$\varepsilon'' = \frac{\omega^2 R c_0^2 L'}{\omega^2 R^2 - \left(\frac{\omega^2 LC - 1}{R} \right)^2}$$

According to these equations, the real part of the permittivity and the conductivity should present the shape presented on Figure 16a and Figure 16b respectively. This is coherent with the behaviour exposed on Figure 13 when the amount of oriented platelets is sufficient to form a RLC circuit. The position of the resonance peak depends on the characteristics of the materials, expressed in L and C.

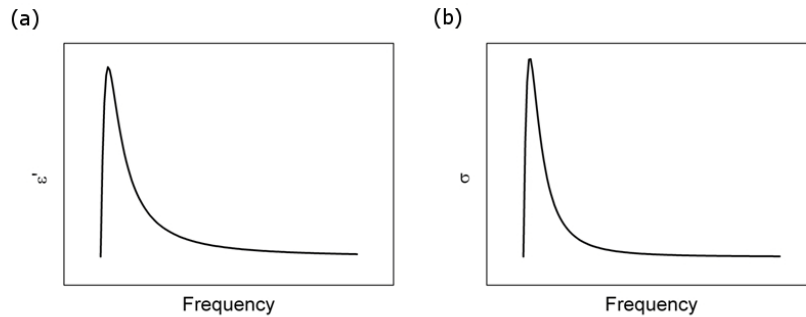


Figure 16 – Evolution of (a) the real part of the permittivity and (b) the conductivity versus the frequency, according to the RLC model

To determine if this behaviour is caused by the orientation of the large or small particles, other blends have been prepared using graphite or FGS.

The morphology of the dispersion of 25wt.-% graphite in EA followed by compression is presented in Figure 17. The compression direction is indicated by arrows. OM micrographs (Figure 17a,b) show that the large graphite platelets are highly oriented in the matrix after compression molding. TEM micrographs (Figure 17c,d) show that there are less small particles than in the GNP and the small particles are less oriented. The resulting electrical properties as a function of the frequency are presented on Figure 18. For

graphite contents up to 20wt.-%, the conductivity (σ) and the real part of the permittivity (ϵ') show a standard behaviour (equivalent RC series circuit). For 25wt.-% graphite, a sharper increase of σ is observed above 35GHz. A peak in the ϵ' curve is also observed. However, this increase is not as sharp as the increase observed for GNP-filled samples and the conductivity values reached are low. Moreover, it occurs for higher frequencies.

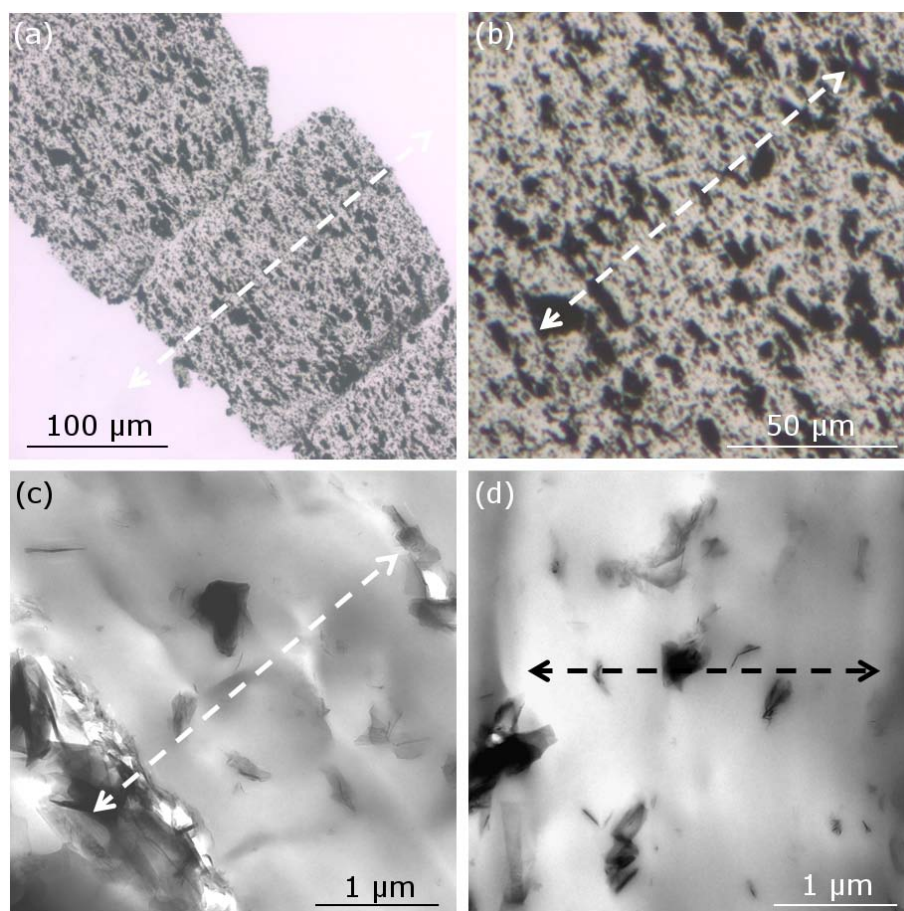


Figure 17 – (a,b) OM micrographs and (c,d) TEM micrographs of the blend EA + 25wt.-% graphite. The arrows indicated the compression direction

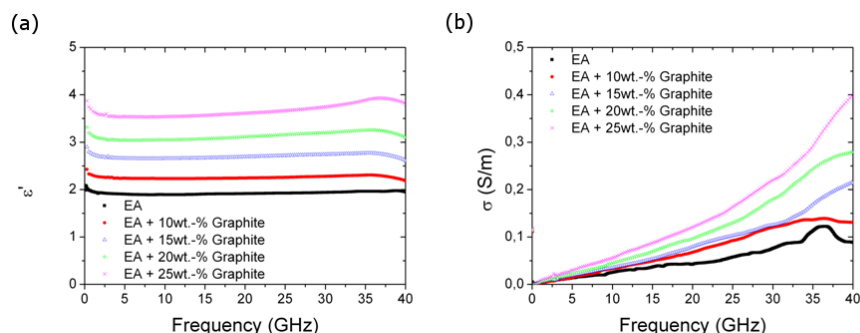


Figure 18 – Electrical properties of EA filled with various amounts of graphite: (a) real part of the effective permittivity; (b) RF conductivity

The dispersion of 1wt.-% FGS is presented in Figure 19. The compression direction is indicated by arrows. In some areas, the platelets are not oriented (Figure 19a) while in others they are oriented in the direction perpendicular to the compression direction (Figure 19b). For this sample, no sharp increase of conductivity is observed (Figure 20). However, it is worth noting that the filler fraction is very low compared to the other composites containing either GNP or graphite.

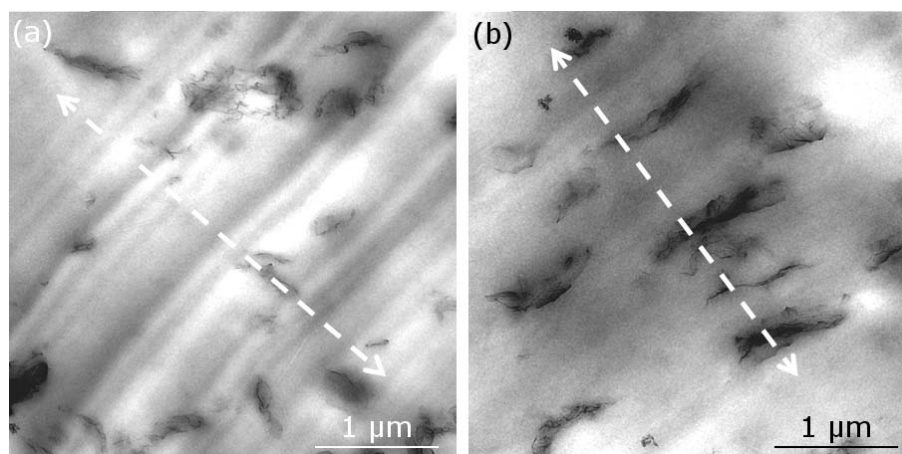


Figure 19 – TEM micrographs of the blend EA + 1wt.-% FGS. The arrows indicated the compression direction

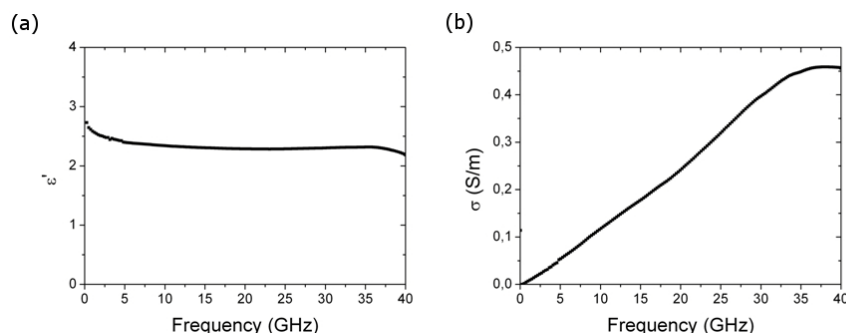


Figure 20 – Electrical properties of EA + 1wt.-% FGS: (a) real part of the effective permittivity; (b) RF conductivity

The resonance observed in Figure 13 for GNP is not observed for the other platelets, at least not with the same intensity. The composite filled with 25 wt.-% graphite shows an increase of the conductivity at high frequency. However, these composites present a low content of particles of intermediate size. Indeed, when comparing Figure 12 and Figure 17c,d, there is a high amount of smaller particles between large particles when GNP is used and not when graphite is used. When FGS is used, the filler amount is very low and the particles are less oriented than the GNP platelets. Two reasons can explain this lack of orientation: first the low content of filler and second, the absence of large particles oriented by compression. Indeed, the orientation of the large particles is expected to force the orientation of the smallest particles. The resonance is therefore attributed to the presence of intermediate size particles that are oriented perpendicular to the electric field. For GNP, they are largely present in the blend and the effect is therefore significant. For graphite, the presence of intermediate size particles is limited and the resonance could therefore be observed only for very high filler loading to ensure a sufficient quantity of intermediate particles in the blend. For FGS, the amount of particles used here is too low to observe an effect and they are not enough oriented.

3 Dispersion in immiscible polymer blends

The dispersion of GNP and FGS in immiscible EA/PA6 blends has been studied. The objective of this section is to achieve an interfacial localization of the graphitic platelets in the blend to form highly conductive composites at very low filler content. It is expected that if graphene particles can be localized at the interface of immiscible co-continuous blends they could allow the formation of conductive composites at very low conductive filler content. However, here the study will only focus on sea-island morphologies to simplify the characterization of the morphology.

3.1 Graphite Nanoplatelets (GNP)

The dispersion of GNP in immiscible blends of EA/PA6 90/10 wt.-% is presented on Figure 21 to Figure 23. The blends present a sea-island morphology in which EA forms the matrix and PA6 forms the dispersed phase.

First, the dispersion obtained after predispersion of GNP in EA is presented on Figure 21 and Figure 22. SEM micrographs on cryofractures show that some large agglomerates of GNP are present in EA (Figure 21a). However, there are also platelets present on the surface of the PA6 droplets (Figure 21b-f). This is confirmed on TEM micrographs (Figure 22), which show that GNP platelets are present in the EA and at the interface between EA and PA6. No GNP is observed inside PA6. Note also that contrary to the dispersion of CNT, the interface between the phases is not well covered by the platelets.

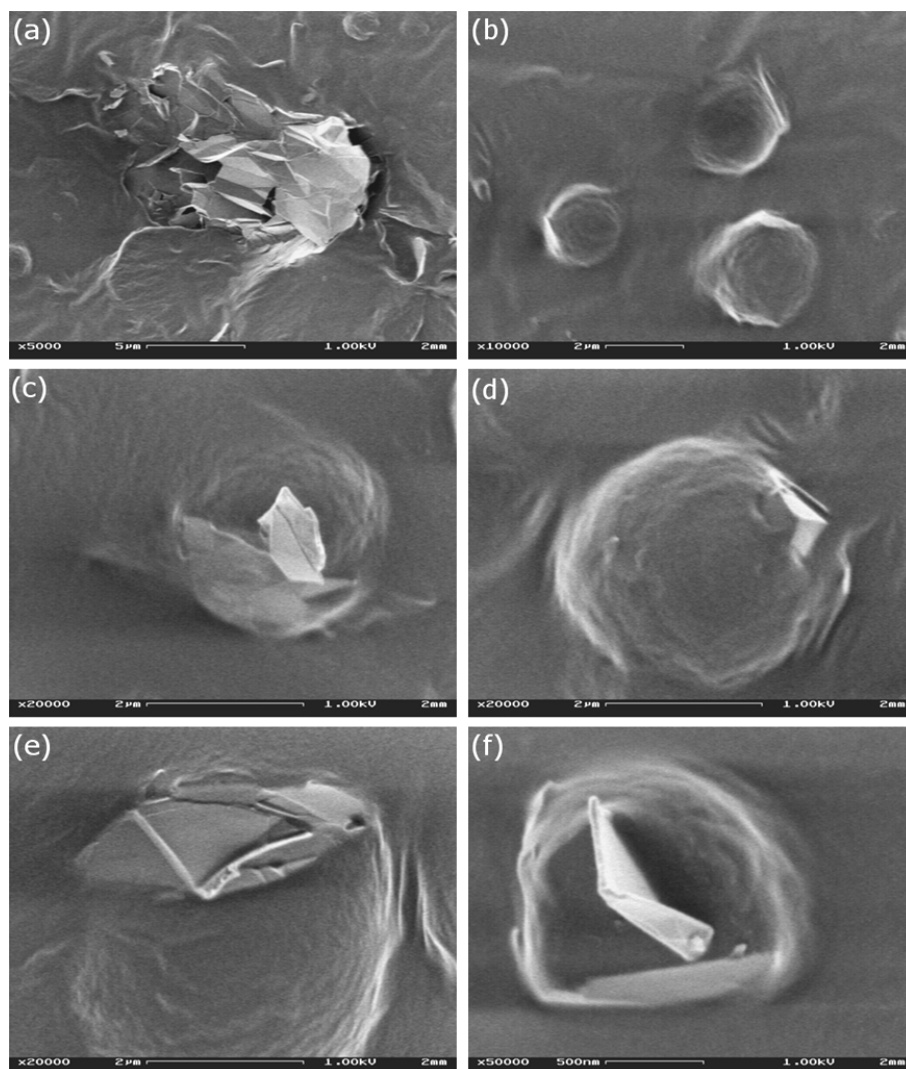


Figure 21 – SEM micrographs after cryofracture of the blend (EA+GNP)/PA6 90/10 wt.-%

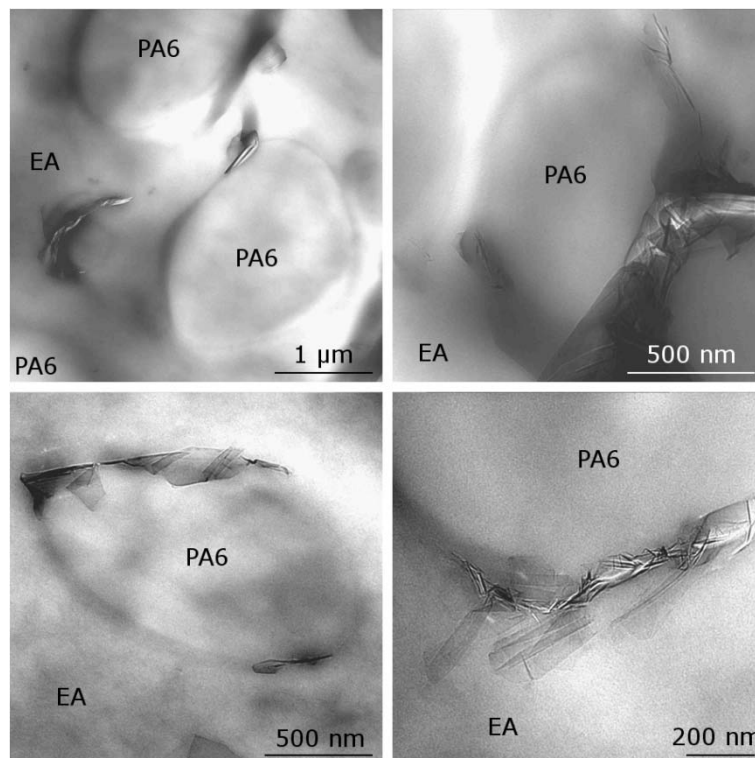


Figure 22 – TEM micrographs of the predispersion of GNP in EA before mixing with PA6 (EA+GNP)/PA6 90/10 wt.-%

When GNP are predispersed in the PA6 phase, no GNP is visible on the SEM micrographs (Figure 23). There is thus no GNP at the interface or in EA. TEM micrographs show that GNP are exclusively dispersed inside PA6 (Figure 24), where they present a dispersion state similar to the dispersion state observed in single PA6 matrix (Figure 3d).

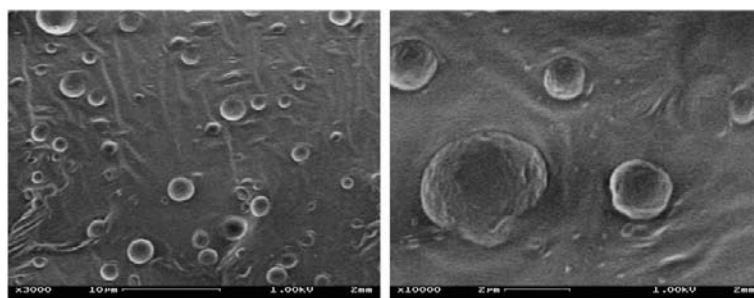


Figure 23 – SEM micrographs after cryofracture of the blend EA/(PA6/GNP) 90/10 wt.-%

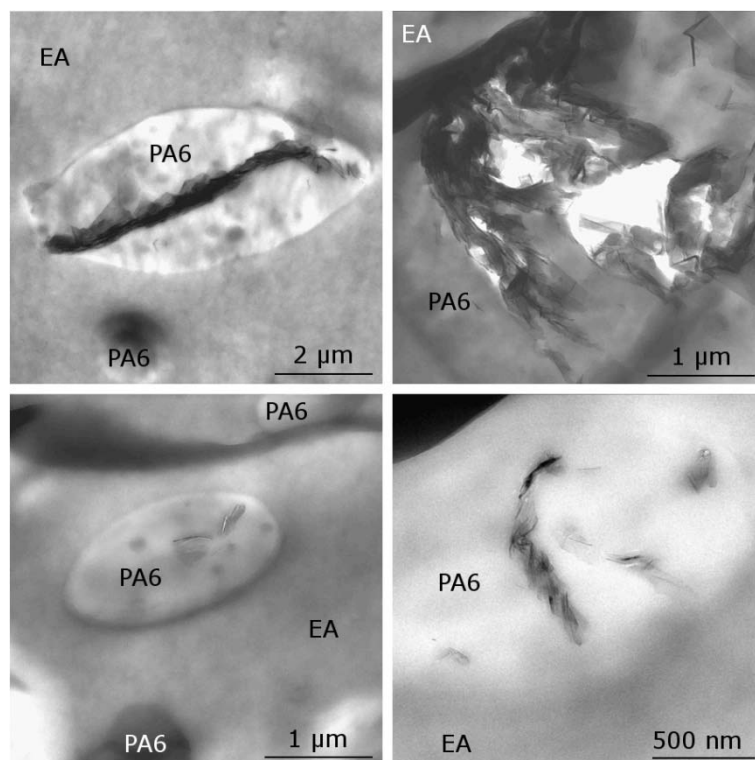


Figure 24 – TEM micrographs of the predispersion of GNP in PA6 before mixing with EA EA/(PA6/GNP) 90/10 wt.-%

3.2 Functionalized graphene sheets (FGS)

The dispersion of FGS in immiscible polymer blends has also been studied. Compared to GNP, FGS present the advantage to be composed of less graphene layers. The EA/PA6 90/10 wt.-% blends present a sea-island morphology, where PA6 forms the dispersed phase and EA forms the matrix.

The predispersion of 1wt.-% FGS in EA is first studied (Figure 25, Figure 26). Here also, the localization of FGS is not uniform. Part of them tends to migrate toward the interface between the immiscible polymers as shown on TEM micrographs, while part of them also stays inside EA. The SEM micrographs (Figure 26) show the blend after cryofracture. Here also, PA6 droplets are not homogeneously covered by FGS particles. Some droplets are covered with FGS (Figure 26c,d) while some are not at all in contact with FGS (Figure 26a). Moreover, FGS aggregate are observed in EA (Figure 26b). The morphology is therefore not uniform throughout the blend. Note finally that some PA6

droplets do not present a circular shape due to the presence of FGS at the interface.

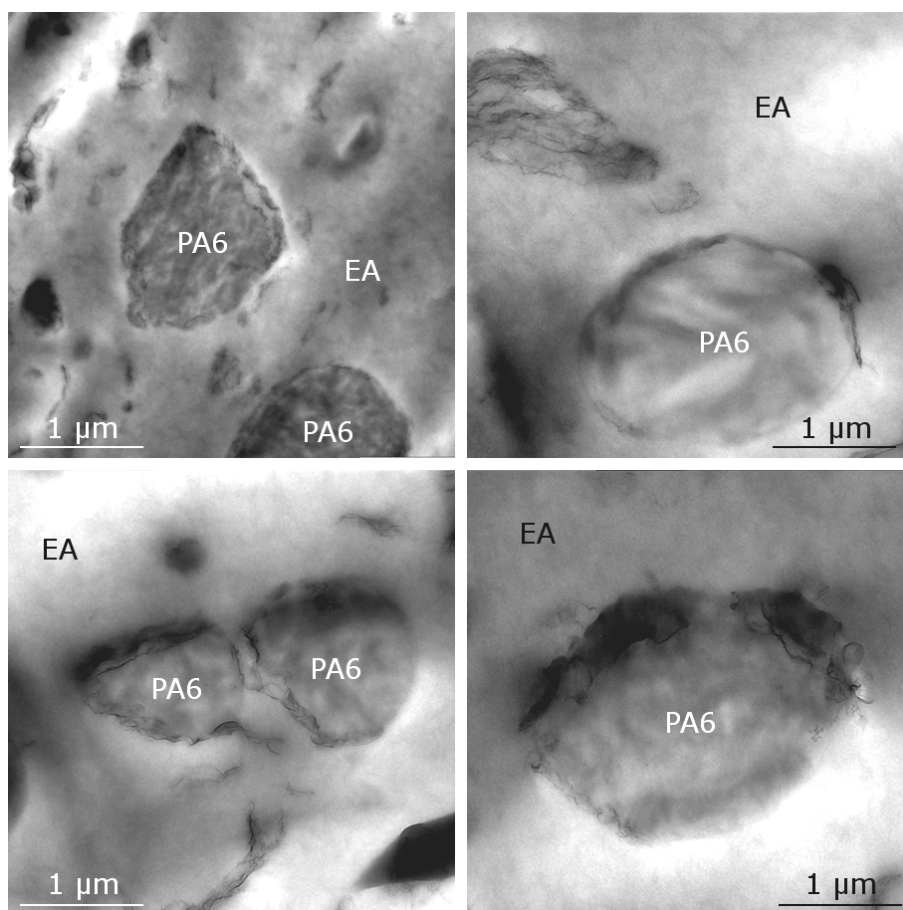


Figure 25 - TEM micrographs of the blend with predisposition of FGS in EA before mixing with PA6 (EA+FGS)/PA6 90/10 wt.-%

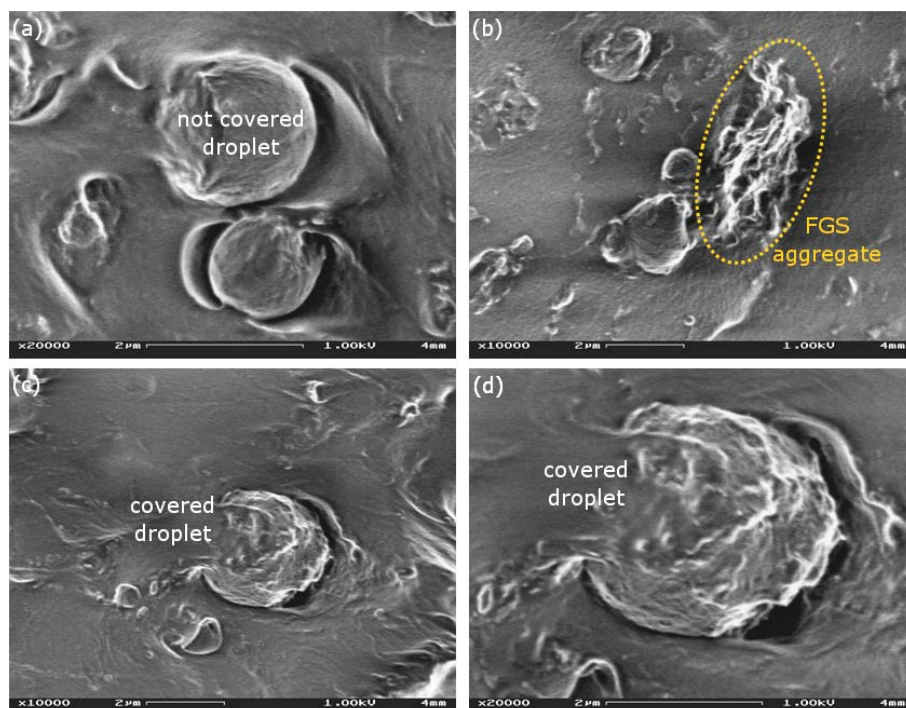


Figure 26 – SEM micrographs after cryofracture of the blend with predispersion of FGS in EA before mixing with PA6 (EA+FGS)/PA6 90/10 wt.-%

When 1wt.-% FGS are predispersed inside PA6, they exhibit a more homogeneous distribution. FGS platelets are only selectively localized inside PA6. Moreover, less FGS agglomerates are present, indicating that the initial dispersion is better in PA6 than in EA.

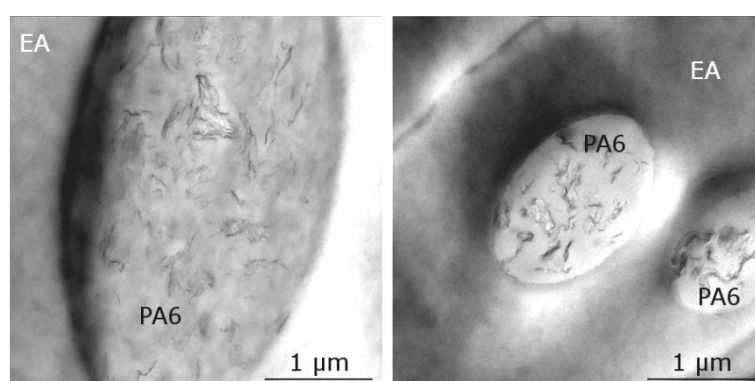


Figure 27 – TEM micrographs of the blend with predispersion of FGS in the PA6 phase before mixing with EA: EA/(PA6+FGS) 90/10 wt.-%

3.3 Thermodynamics considerations

The localization of GNP and FGS in blends of immiscible polymers can be predicted using classical thermodynamics. The equilibrium position of the filler is predicted by evaluating the wetting coefficient ω_a [30].

The values of the surface energy of polymers in the melt state, extrapolated from literature values at 20°C, are presented in Chapter 3.

The surface energy of GNP can be approximated by the one of graphite, as it is not functionalized and exhibit a similar structure. Graphite is a high energy material with a surface tension of approximately 115-120 mJ/m², which comes mainly from a dispersive contribution [31,32]. The surface energy of graphene and graphene oxide at room temperature are 46.7 and 62.1 mJ/m², respectively [33]. According to XPS analysis, the atomic fraction of oxygen compared to carbon of the FGS used here is 0.1. Contrary to graphite, the FGS are polar. They present hydroxyl, ether and epoxy groups. A polarity of 10% is thus considered for FGS.

The wetting coefficients evaluated according to harmonic or geometric mean equations are reported in Table 2. For both systems, thermodynamics predicts an interfacial localization of the fillers.

Table 2– Wetting coefficient evaluated according to harmonic mean equation and geometric mean equation and corresponding prediction for EA/PA6/GNP or EA/PA6/FGS systems

Materials	Wetting coefficient according to harmonic mean equation	Wetting coefficient according to geometric mean equation	Prediction
EA/PA6/GNP	0.21	0.76	interface
EA/PA6/ FGS	-0.83	-0.75	interface

3.4 Polymer adsorption

As for CNT, the final localization of the platelets depends also on the mixing sequence. Polymer adsorption plays an important role. Similarly to CNT, polymer adsorption is demonstrated using TGA and centrifugation. The adsorption of EA on GNP is shown after extraction using a Soxhlet device (Figure 28). PA6 adsorption is confirmed by centrifugation experiments. First GNP have been dispersed in formic acid. After centrifugation, sedimentation of the GNP has been observed. Second, GNP have been dispersed in a solution of

PA6 in formic acid. After ultrasonication followed by centrifugation, sedimentation of the GNP has also been observed. Finally, the composite PA6+GNP has been dissolved in formic acid and after centrifugation, no sedimentation has been observed, even for longer centrifugation duration. This behaviour is expected to be linked to the presence of adsorbed PA6 on the particles during melt mixing.

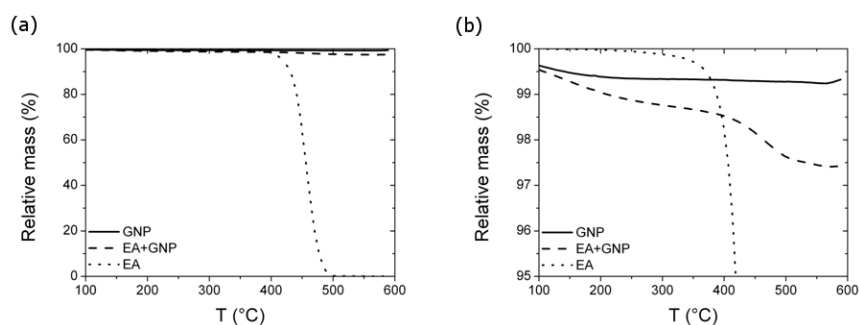


Figure 28 - (a) Weight loss curves presenting the relative mass and (b) relative mass for high mass fractions, versus the temperature for pure EA, pure GNP, the glass fibres containing the GNP extracted from the composite EA+2%GNP using a Soxhlet during 5 days

The viscosity ratio of the phases probably also plays an important role. It is however not studied here since only one system of immiscible polymers is studied, in which the dispersed PA phase exhibit a much higher viscosity than the EA matrix (for viscosity vs angular frequency curves, please refer to Chapter 3).

CONCLUSION

First the dispersion of GNP in different polymer matrices is studied. As for CNT, the ability of the different matrices to disperse GNP are correlated to the values of the dielectric constant and refractive index of the polymers and is thus linked to the minimization of the Hamaker constant. The best dispersion of GNP is achieved in PC. A very good dispersion of FGS is also achieved in PC.

The resulting electrical RF conductivity has been measured. The measured conductivities are higher for the blends exhibiting the best GNP dispersions. However, the addition of GNP does not lead to significant improvement of the conductivity. For PC, the conductivities in the presence of 1 wt.-% of the different carbon-based fillers is compared. The addition of GNP gives conductivity values similar to pure PC. FGS highly improves the electrical

properties. However, the best conductivity is achieved with CNT due to the excellent dispersion state of CNT and thus to their ability to form a conductive network.

Second, the effect of the orientation of the platelets in highly filled composites on the RF electrical properties is studied. A sharp increase of the conductivity and of the real part of the permittivity is observed in the presence of high GNP amounts. This phenomenon is linked to the orientation of the graphite platelets of intermediate dimensions, which act as microcoils for current. A model is proposed based on a resistor, an inductor, and a capacitor, connected in series (RLC circuit) and the increase of the conductivity is associated to resonance. The position of the resonance peak depends on the characteristics of the material, expressed in L and C.

Finally the dispersion of carbon platelets in immiscible polymer blends of EA/PA6 in the ratio 90/10wt.-% is studied. EA forms the matrix and PA6 forms the dispersed phase. When predispersed in EA, the platelets partly remain in EA and partly migrate towards the interface. However, the surface of the PA droplets is not well covered with carbon particles, contrary to the case of CNT. When the platelets are predispersed in PA6, they remain dispersed in PA. Thermodynamics predict an interfacial localization of the carbon platelets (GNP or FGS). As for CNT, the mixing sequence influences the final localization of the fillers because of adsorption phenomena.

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Chapter 7

HYBRID NANOCOMPOSITES FROM SILVER NANOPARTICLES AND CARBON NANOTUBES

ABSTRACT

This chapter deals with the dispersion of carbon nanotubes (CNT) and silver nanoparticles (Ag-NP) in single polymer matrices and immiscible polymer blends and the resulting electrical properties. Homogeneous dispersion of both nanofillers is observed in PA6. Although an affinity is observed between the CNT and Ag-NP, the Radio Frequency (RF) electrical properties measured for single polymer matrices are mainly additive and depend only on the volume fraction of conductive fillers used. In immiscible blends, the CNT and Ag-NP migrate towards the interface and the affinity between the CNT and the Ag-NP is confirmed. For co-continuous structures, the replacement of part of the CNT by Ag-NP results in improved RF electrical conductivity. The formation of a conductive path at the interface between EA and PA6 for sea-island structures is demonstrated using CS-AFM. In the presence of Ag-NP, the measured current and thus conductivity is increased compared to the exclusive use of CNT.

A publication is in preparation:

A-C Baudouin et al., *Interfacial localization of CNT and Ag nanoparticles in immiscible polymer blends and resulting electrical properties*, provisional title.

We thank Pr. H. Münstedt for providing PA6 samples filled with Ag-NP. We are grateful for the access to the technological platform "Welcome" and for the help of I. Huynen, I. Molenberg and P. Simon.

INTRODUCTION

The use of silver as an antibacterial agent dates back to the ancient times. The Phoenicians used silver vessels to keep water, wine and vinegar pure during their long voyages. In America, pioneers moving west put silver and copper coins in their water barrels to keep it clean. Note also that the idiom "born with a silver spoon in his mouth" is a reference to health and not to wealth. In the early 18th century, babies fed with silver spoons were healthier than those fed with spoons made from other metals. In this context, the use of silver nanoparticles as bactericidal agents is promising due to their very high surface to volume ratio. The use of metal nanoparticles for water disinfection is relatively new [1,2]. Because of their high reactivity due to the large surface to volume ratio, nanoparticles are expected to play a crucial role in water purification [1,2]. Morones et al. [3] have shown the bactericidal effect of silver nanoparticles. They show that the bactericidal properties of the nanoparticles are size dependent. The only nanoparticles exhibiting a direct interaction with the bacteria have preferentially a diameter of $\sim 1\text{--}10$ nm. Jain and Pradeep [4] have elaborated polyurethane foams coated with silver nanoparticles as antibacterial water filters. They show that the PU foams coated with Ag nanoparticles have a bactericidal effect on *E. coli*. Lukhele et al. [5] have used silver nanoparticles immobilized onto carbon nanotubes and cyclodextrin PU to remove *E. coli* and *V. cholerae* bacteria from water. Silver nanoparticles, in various chemical forms, exhibit strong toxicity towards a wide range of microorganisms [6-8]. They have been shown to be a promising antimicrobial material [9]. Elechiguerra et al. [10] have studied the interaction of silver nanoparticles with HIV-1 and show that they inhibit the virus from binding to host cells.

Silver nanoparticles can also be used as catalysts, taking advantage of their very high surface to volume ratio. Silver particles supported on silica spheres have been used to catalyze the reduction of dyes by sodium borohydride (NaBH_4) [11]. The reaction time is strongly dependent on the concentration of silver nanoparticles.

Finally, owing to their high conductivity ($6.3 \times 10^5 \text{ S/cm}$), Ag nanoparticles can be used as conductive powder. The preparation of Ag-polymer nanocomposites has been reported by a few authors [12-16]. Jiang et al. [17] have shown conductivity enhancement for polymer/Ag nanocomposites films. The Ag nanoparticles are functionalized with a diacid surfactant before their incorporation into an epoxy matrix and highly improved conductivity was

observed. Tee et al. [18] have reported an electrical percolation threshold of 5vol.-% Ag nanoparticles in epoxy composites. Mbhele et al. [19] have shown improvement of the thermal and mechanical properties of poly(vinyl alcohol) (PVA) with the addition of Ag nanoparticles (Ag-NP). However, when high metal loading is used, the stability of the nanocomposites is often observed to decrease.

Although metallic nanoparticles are highly conductive, when they are dispersed in a polymer matrix, they are separated by the insulating polymer matrix. The formation of a conductive network is thus inhibited and no improvement of the electrical properties is observed unless very high Ag-NP contents are used. An interesting solution can be achieved by combining CNT and Ag-NP in polymer matrices. Ag-NP act as bridges among the CNT and facilitate the electron transfer. From that point of view, two directions can be studied: the decoration of CNT with Ag-NP or the combined dispersion of CNT and Ag-NP. The former solution has been studied by a few research teams [20-22]. Gao et al. [20] have used functionalized CNT to entrap metal ions, such as Ag⁺ to elaborate polymer/CNT/metal hybrid nanocomposites. They show the formation of polymer covered-silver nanoclusters, with diameters between 3–10 nm, attached on the convex surface of CNT. Ma et al. [21] have dispersed Ag-decorated-CNT in epoxy. They showed that the electrical conductivity of composites containing 0.1wt.-% Ag-decorated-CNT is four orders of magnitude higher than the one of composites containing the same content of only CNT. They attribute this difference to decreased contact resistance in CNT junctions according to the presence of Ag-NP. Xin and Li [22] have shown that the addition of Ag-decorated-CNT to PP or PS improved electrical and mechanical properties. Moreover, Ag helps dispersing the CNT. However, this method requires a first step of modification of the CNT, which is not modifying the CNT structure [22] but has a cost. As an alternative, the direct dispersion of CNT and Ag-NP is therefore promising. Liang et al. [23] have dispersed Ag-NP and Ag-NP combined with CNT in PP. Ag-NP alone do not lead to improved electrical properties due to the formation of PP transcrystals, which prevent the formation of a conductive pathway, even for 50wt.-% Ag-NP. For 10 wt.-% Ag-NP, the addition of small amount of CNT (2wt.-%) highly increases the electrical properties of the composites. The CNT form bridges between the Ag-NP and therefore facilitate the formation of a conductive network. Fortunati et al. [24] have reported the elaboration of CNT/Ag-NP/poly(ϵ -caprolactone) (PCL) composites. The nanoparticles are well dispersed in the PCL and improved conductivity is reported due to the formation of Ag conductive bridges among the CNT. Moreover, the authors report that their composites are suitable as

support for primary human bone marrow-mesenchymal stem cells, thus opening the door to materials for biomaterials applications.

In this chapter, we study the influence of the combination of CNT and Ag nanoparticles (Ag-NP) in polymer nanocomposites. First the dispersion of CNT and Ag-NP in PA6 is analyzed and the Radio Frequency (RF) electrical conductivity of the composites is studied. Next, the localization of the fillers inside EA/PA6 immiscible blends is studied and the electrical properties of these systems are examined.

EXPERIMENTAL

This a very brief description of the materials and characterization methods used. For more details, please refer to Appendix 1.

1 Materials

The blends under study are composed of two types of immiscible polymers:

- unfilled polyamide 6 (PA6) or filled with 0.06wt.-% Ag nanoparticles (Ag-NP) (PA6+0.06wt.-%Ag) or with 1.5 wt.-% Ag-NP (PA6+1.5wt.-%Ag)
- ethylene acrylate copolymer (EA), which is a random copolymer of ethylene and 26–30 wt.% methyl acrylate

The carbon nanotubes (CNT) are unpurified and unfunctionalized CNT with a purity of 90%.

In the presence of Ag-NP, the torque measured in the compounder decreases sharply, indicating strong degradation of the matrix. After 10 min compounding, the torque is around 55% of its initial value. When the equivalent content of only CNT is used, after 10 min compounding, the torque reaches around 75% of its initial value. Less degradation is thus observed.

2 Characterization

The samples are characterized by SEM and TEM. The electrical properties are characterized using CS-AFM, one-line characterization in microstrip configuration technique.

RESULTS AND DISCUSSION

Blends of PA6 filled with CNT and/or Ag-NP are studied. The Ag-NP were provided dispersed in PA6. The addition of CNT to these blends and the subsequent electrical properties are studied. Then the dispersion of the nanoparticles in immiscible blends of EA and PA6 is presented.

1.1 Dispersion in single polymer matrix

The dispersion state of CNT and/or Ag-NP in PA6 is first presented. The resulting RF electrical properties of the composites are subsequently exposed.

1.1.1 Morphology

The dispersion of the nanofillers in PA6 is studied by TEM. The dispersion of 1wt.-% CNT inside PA6 is shown in Figure 1. Although CNT are generally homogeneously dispersed throughout the matrix (Figure 1 right), a few large agglomerated are also present (Figure 1 left).

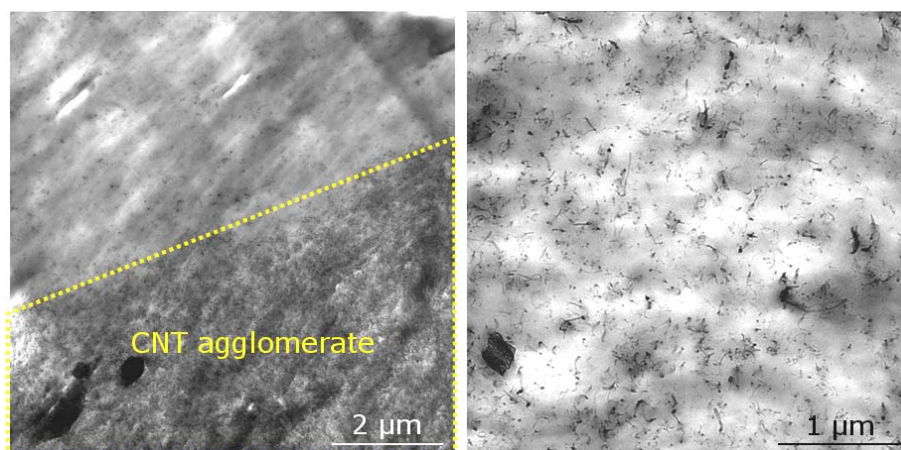


Figure 1 – TEM micrograph of the dispersion of 1wt.-% CNT in PA6 matrix (PA6+1wt.-%CNT)

The dispersion of 1.5wt.-% Ag-NP in PA6 is presented in Figure 2. The Ag-NP are well dispersed throughout the PA6.

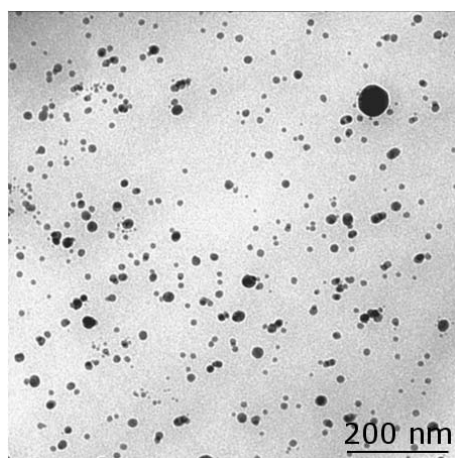


Figure 2 – TEM micrograph of the dispersion of 1.5wt.-% Ag-NP (PA6+1.5wt.-%Ag)

The addition of 1wt.-% CNT to PA6 containing 0.06 or 1.5 wt.-% Ag-NP is presented respectively in Figure 3 and Figure 4. Both fillers are well dispersed in PA6. Moreover, there seems to be an affinity between Ag-NP and CNT, as presented at high magnification for PA6+1.5wt.-%Ag+1wt.-%CNT (Figure 4). Indeed Ag-NP seem to be often in contact with CNT. However, it is important to remind that TEM micrographs present a 2D view of a 3D object. For this reason, the affinity in the melt must be considered carefully.

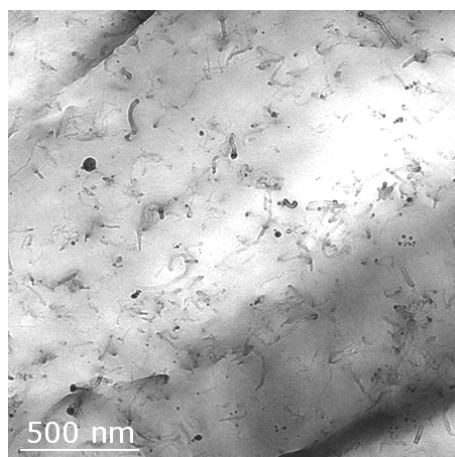


Figure 3 – TEM micrograph of the dispersion of 0.06 wt.-% Ag-NP and 1wt.-% CNT in PA6 matrix (PA6+0.06wt.-%Ag+1wt.-%CNT)

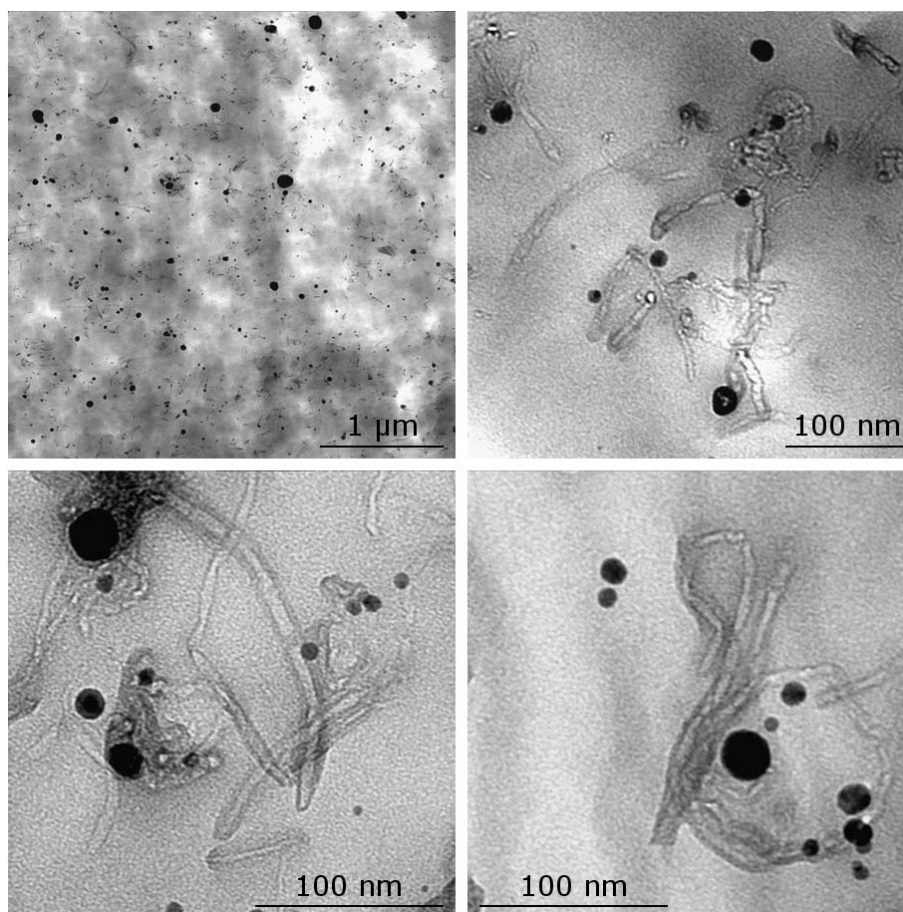


Figure 4 – TEM micrograph of the dispersion of 1.5 wt.-% Ag-NP and 1wt.-% CNT in PA6 matrix (PA6+1.5wt.-%Ag+1wt.-%CNT)

1.1.2 Electrical characterization

The conductivity versus frequency is presented in Figure 5 in linear (Figure 5a) and logarithmic (Figure 5b) scales. PA6 samples filled with only Ag-NP present conductivity values similar to pure PA6 (grey curves). Ag-NP alone do not form a conductive network. When CNT are added to the system, the conductivity is highly improved. When only CNT are dispersed in PA6, the electrical conductivity increases significantly compared to pure PA6 or PA6 filled with Ag-NP. For 1wt.-% CNT (green curve), the conductivity at 40GHz increases by more than a factor 5 (from around 0.13 S/m to around 0.73 S/m). When combining 0.06wt.-% Ag-NP with 1wt.-% CNT (red curve), conductivity values similar to only 1wt.-% CNT are obtained. No further improvement is observed. On the contrary, when 1.5wt.-% Ag particles are added, a large increase of conductivity is observed (magenta) compared to only 1wt.-% CNT. The

conductive volume fraction is however more important. For comparison, a sample containing 1.22wt.-% CNT (blue), i.e. the same volume fraction of conductive filler as 1wt.-% CNT+1.5wt.-% Ag, presents almost similar RF conductivity at high frequencies. No significant synergy between CNT and Ag-NP is thus observed on the electrical characterization at high frequencies. However, at low frequencies, the conductivity of the composite with 1wt.-% CNT+1.5 wt.-% Ag is slightly higher than the one of the composite containing 1.22 wt.-% CNT. Finally, the sample filled with 2wt.-% CNT present a much higher conductivity than all other composites over the whole frequency range.

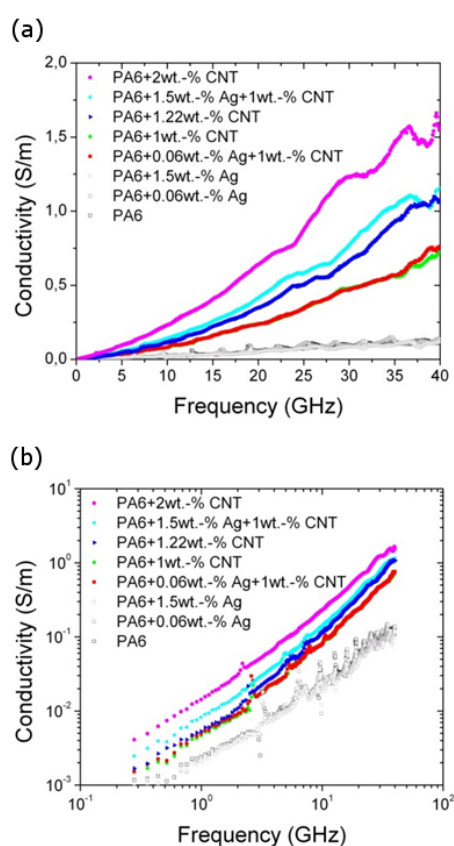


Figure 5 – Conductivity versus frequency for different PA6 samples filled with Ag-NP and/or CNT (a) linear scales; (b) log scales

1.1.3 Characterization of CNT length after compounding

The length of the CNT after compounding has been characterized using SEM. For each sample, the PA6 matrix has been dissolved in formic acid and a drop of solution has been deposited on a substrate (Figure 6). The length of individual tubes has then been measured (Figure 7).

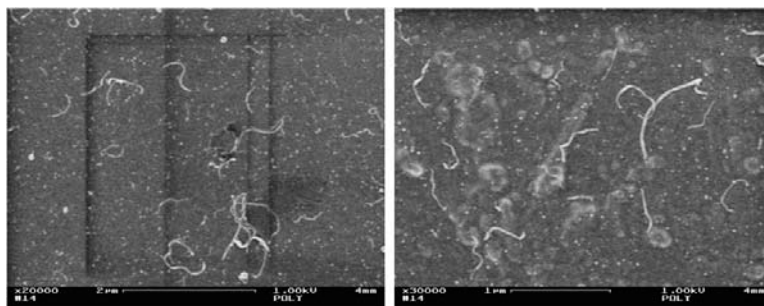


Figure 6 – SEM micrographs of the fillers after dissolution of the PA6 of the composite PA6+1.5wt.-%Ag+1wt.-%CNT

Although the polyamide matrix in PA6+1.5%Ag+1%CNT degrades more significantly than the others during processing and thus becomes less viscous, CNT are slightly shorter in this sample than in the two others, as presented in Figure 7. The relative (Figure 7a) and cumulative (Figure 7b) frequencies indicate that the size of the CNT in the composites decreases when increasing the Ag content.

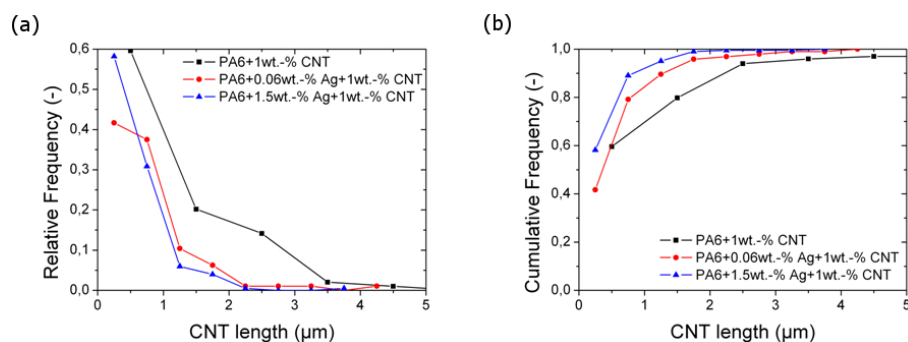


Figure 7 – Evaluation of the length of the CNT from the composites PA6+1wt.-%, PA6+0.06wt.-%Ag+1wt.-%CNT, PA6+1.5wt.-%Ag+1wt.-%CNT; (a) relative frequency; (b) cumulative frequency

The number average CNT lengths and standard deviations are reported in Table 1 for each blend. Although the standard deviations are high, it is clear that the presence of Ag-NP reduces the size of the CNT in the blend.

Table 1 – Mean value and standard deviation of the CNT length of the different blends (μm)

	PA6 + 1wt.-% CNT	PA6 + 0.06wt.-% Ag + 1wt.-% CNT	PA6 + 1.5wt.-% Ag + 1wt.-% CNT
Mean value	1.3	0.8	0.6
Standard deviation	1.6	0.7	0.4

1.1.4 Discussion

The dispersion of both CNT and Ag-NP in PA6 is good. Although a few large CNT agglomerates are present, the CNT are mainly individualized. TEM micrographs show that Ag-NP are in the neighbourhood of CNT or directly on their surface.

Ag-NP alone do not form a conductive network in PA6. This is coherent with percolation thresholds reported in literature and with the percolation theory. On the contrary, the RF conductivity of the composites is greatly enhanced in presence of both Ag-NP and CNT. Actually, the conductivity of 1.5 wt.-% Ag-NP+1wt.-% CNT is almost doubled in comparison with the one of samples containing 1wt.-% CNT or 0.06 wt.-% Ag-NP+1wt.-% CNT. However, for an equivalent volume fraction of CNT, the measured conductivity is almost similar and when using 2 wt.-% CNT the conductivity is significantly increased compared to the combination of 1wt.-% CNT and 1.5 wt.-% Ag-NP. This result indicates that the increase of conductivity seems to result only from an additive effect and no synergy between the nanoparticles is observed at high frequencies. However, as Ag-NP are expected to act as conductive bridges between CNT, the effect of their presence in the composite should be more significant at low frequencies. Nevertheless, the conductivity reported can not be extrapolated to Direct Current (DC) conductivity.

Note finally that the size of CNT after compounding is shorter when Ag-NP are present in the matrix. Although it is detrimental to the elaboration of a conductive network, at the high frequencies studied here, this effect is expected to not be a critical parameter that could mask the synergy between nanoparticles.

1.2 *Dispersion in immiscible polymer blends*

The migration of CNT inside EA/PA6 blends has been presented in Chapter 3 and TEM micrographs are reproduced in Figure 8. Whatever the mixing strategy, predispersion in EA or PA6, the CNT migrate towards the interface of the blend. The localization of Ag-NP and of a combination of Ag-NP and CNT is presented hereafter. Note that in the following sections only PA6 with 1.5wt.-% Ag is used to have a high number of Ag-NP observable.

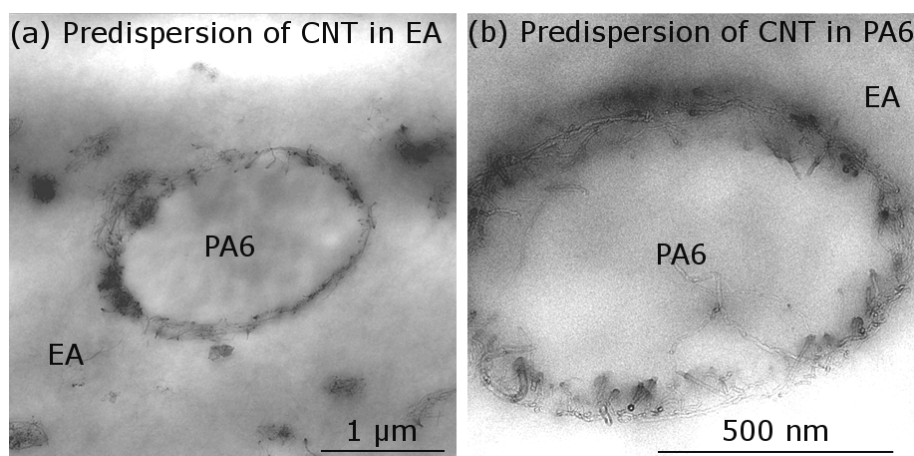


Figure 8 – TEM micrographs of (a) (EA+CNT)/PA6 90/10 wt.-%; (b) EA/(PA6+CNT) 90/10 wt.-%

1.2.1 Localization of Ag nanoparticles

Ag-NP are initially predispersed in PA6. When mixing (PA6+Ag) and EA in the ratio 10/90wt.-%, a sea-island morphology is observed. PA6 forms the dispersed phase and a large number of EA sub-inclusions is observed in PA6 (Figure 9). Ag-NP migrate from PA6, where they were initially well dispersed (Figure 2) towards the interface between the phases and towards the surface of the sub-inclusions. SEM micrograph (Figure 10) shows the surface of a PA6 droplet after cryofracture. Ag-NP are visible as white dots on the surface of the nodule.

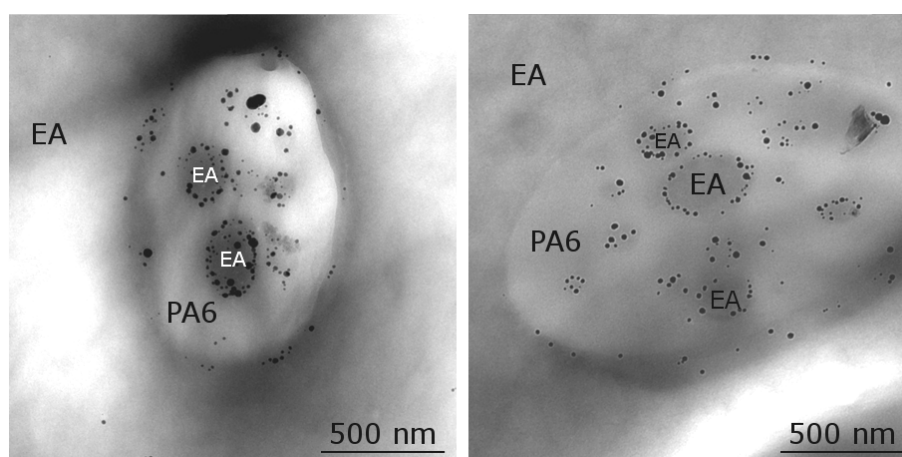


Figure 9 – TEM micrographs of the predispersion of Ag-NP in PA6 and mixing with EA: EA/(PA6+Ag) 90/10 wt.-%

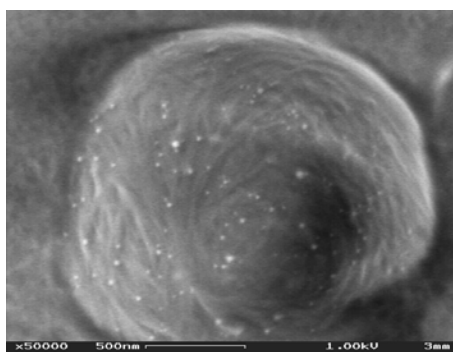


Figure 10 – SEM micrograph of the predispersion of Ag-NP in PA6 and mixing with EA: EA/(PA6+Ag) 90/10 wt.-%

1.2.2 Predispersion of both Ag-NP and CNT in PA6

When both Ag-NP and CNT are predispersed in PA6 before mixing with EA, a sea-island morphology is observed. Contrary to the EA/PA6 blend containing only Ag-NP, there is almost no EA sub-inclusion in the PA6 droplets. The fillers migrate towards the interface (Figure 11). This is coherent with the behaviour of each filler independently of the other (see Figure 8b for CNT and Figure 9 for Ag-NP). Moreover, the affinity between CNT and Ag-NP, already observed a single PA6 matrix, is confirmed. The silver nanoparticles are observed in the vicinity of CNT.

Due to the presence of CNT, Ag-NP are difficult to observe on the surface of PA droplets by SEM. SEM micrographs are therefore not presented here.

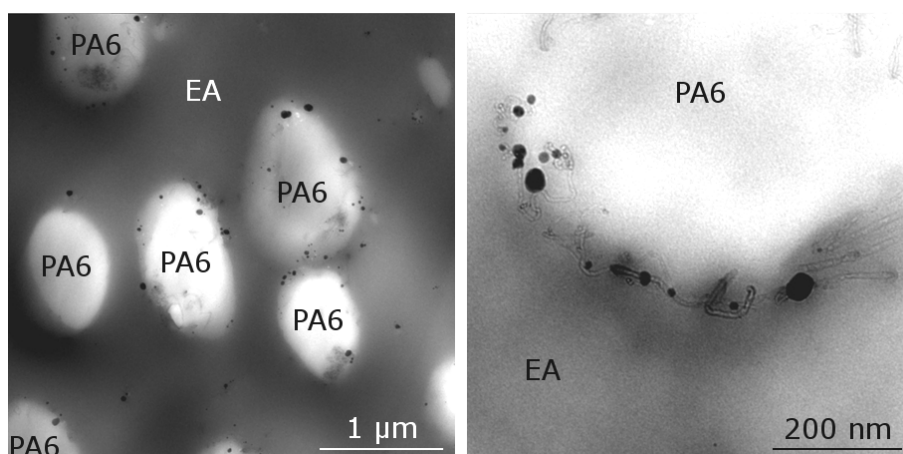


Figure 11 – TEM micrographs of the blend EA/(PA6+CNT+Ag) 90/10 wt.-%

A co-continuous blend of EA and PA6 containing both CNT and Ag-NP has also been elaborated at the composition EA/(PA6+Ag+CNT) 44/56 wt.-%. This composition has been selected based on the observation made in Chapter 4. As the content of Ag-NP in PA6 is fixed, the amount of CNT has been adapted to correspond to the same volume ratio of conductive fillers as for blends with a total of 2wt.-% CNT. In the absence of Ag-NP, the blend exhibits a co-continuous morphology (Figure 12), which is preserved in the presence of Ag-NP. TEM micrographs illustrates the localization of the nanoparticles in this blend (Figure 13). As for only CNT, the nanoparticles are localized at the interface of the blend but also in the PA6 phase.

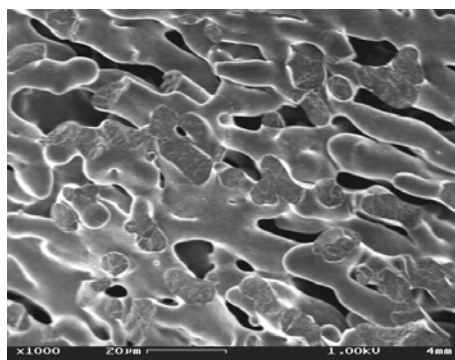


Figure 12 – SEM micrograph of the blend EA/(PA6+Ag+CNT) 44/56 wt.-%

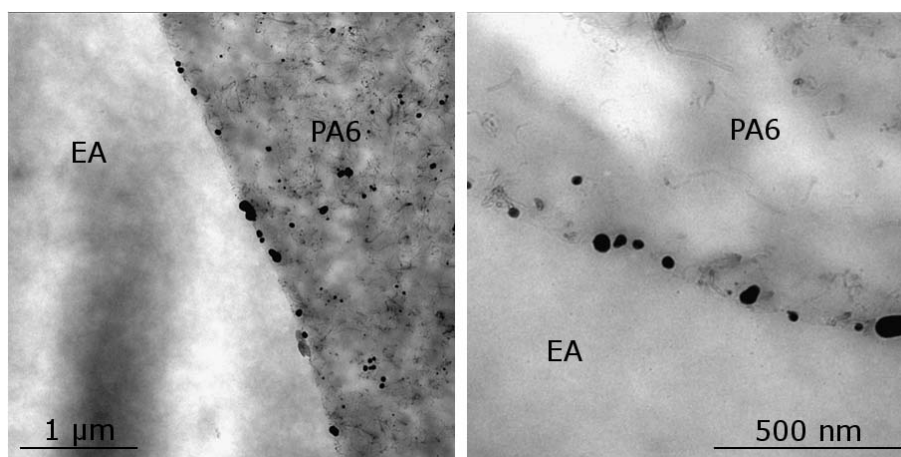


Figure 13 – TEM micrographs of the blend EA/(PA6+Ag+CNT) 44/56 wt.-%

1.2.3 Predispersion of CNT in EA and of Ag-NP in PA

When CNT are predispersed in EA and Ag-NP are predispersed in PA, a sea-island morphology is also formed and almost no EA sub-inclusion in the PA6 phase is observed. Both nanoparticles migrate towards the interface (Figure 14) as observed for CNT in the absence of Ag-NP (Figure 8) and for Ag-NP in the absence of CNT (Figure 9). Moreover, there seems to be a quite strong adhesion between CNT and Ag-NP. Indeed some Ag-NP are “attached” to CNT inside EA, while in the absence of CNT, no Ag nanoparticle is found in EA. They are presented in the yellow encircled zones in Figure 15.

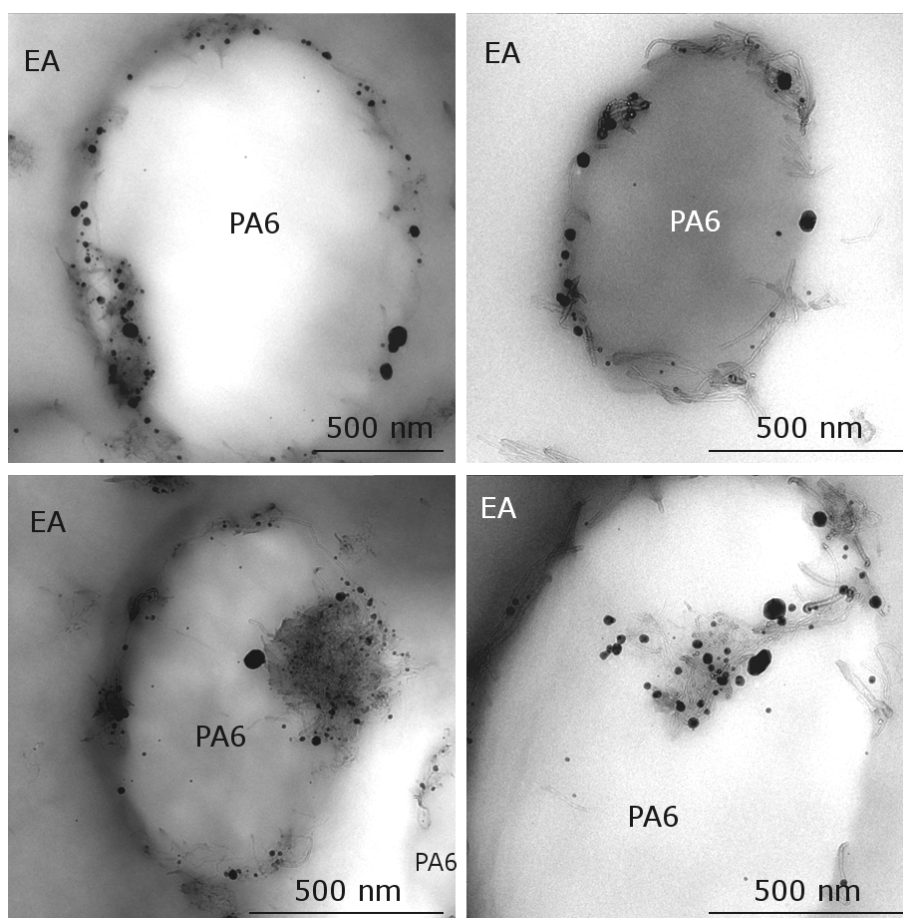


Figure 14 – TEM micrographs of the blend (EA+CNT)/(PA6+Ag) 90/10 wt.-%

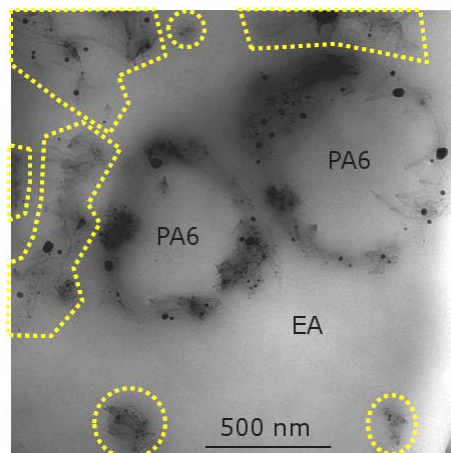


Figure 15 – TEM micrograph of the blend (EA+CNT)/(PA6+Ag) 90/10 wt.-%; the yellow encircled zone draw attention to Ag-NP driven inside the EA due to their affinity with CNT

1.2.4 Thermodynamic predictions

As was done for CNT and graphite or graphene, classical thermodynamics is used to predict the position of fillers in blends of immiscible polymers using the wetting coefficient ω_a [30]. The surface energy of Ag-NP has been reported to be sensitive to the presence of oxygen. In the air atmosphere, at 932°C, the surface energy of silver is around 450 mJ/m², while in a helium atmosphere, it is around 1140 mJ/m² [25]. Another study presents a critical surface tension of silver of 890 mJ/m² [26]. Although the surface energy of Ag-NP used here is not known, some predictions can be drawn, based on the assumption that they are apolar high energy fillers. Thermodynamics predict an interfacial localization for a large range of filler surface energies (Figure 16): from 100 to 480 mJ/m² and over the whole range of possible surface energies according to the geometric and harmonic mean equations respectively.

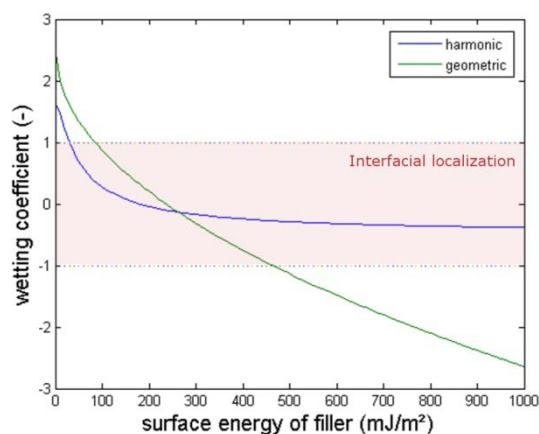


Figure 16 – Prediction of the wetting coefficient value as a function of the surface energy of the filler

However, it is worth noting, first, that the thermodynamic predictions are affected by imprecision on the values of the surface energies of neat polymers, as-produced CNT and Ag-NP. Second, the predictions are not sufficient to predict the localization of fillers in the polymer blends under study here. Viscosity as well as polymer adsorption considerations also have to be taken into consideration as presented in Chapter 3.

1.2.5 Electrical characterization

The RF electrical properties are evaluated for the co-continuous structures and for the sea-island morphology to assess the influence of the presence of Ag-NP.

a. Co-continuous structures

The co-continuous structure is highly oriented in the extrusion direction and after compression for the preparation of the samples for RF electrical characterization. Figure 17 presents the conductivity measured in the direction parallel to the compression direction and thus perpendicular to the orientation of the co-continuous structure. In the presence of Ag-NP (light grey curve), the conductivity is improved compared to the blend containing exclusively CNT (black curve).

The replacement of part of the CNT by Ag-NP thus leads to slightly improved conductivity.

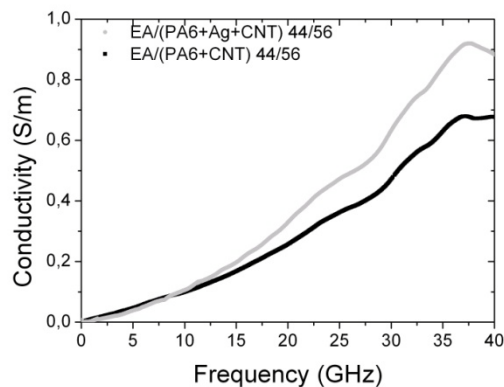


Figure 17 – Conductivity versus frequency for the blends EA/(PA6+CNT) 44/56 wt.-% and EA/(PA6+Ag+CNT) 44/56 wt.-% in the direction perpendicular to the compression direction

b. Sea-island structure

The local electrical properties of the blends (EA+CNT)/PA6 or (EA+CNT)/(PA6+Ag) 90/10 wt.-%, which present a sea-island morphology, are studied using CS-AFM. Blends of EA containing 5wt.-% CNT with PA6 containing or not 1.5 wt.-% Ag-NP have been elaborated. Therefore, the blends contain altogether either 4.5wt.-% CNT or 4.5 wt.-% CNT+0.15 wt.-% Ag. The morphology of these blends are presented respectively in Figure 18 and Figure 19. Due to the high amount of CNT initially dispersed in EA, a large number of agglomerates are observed in EA and at the interface. A few CNT agglomerates are also present inside the PA droplets.

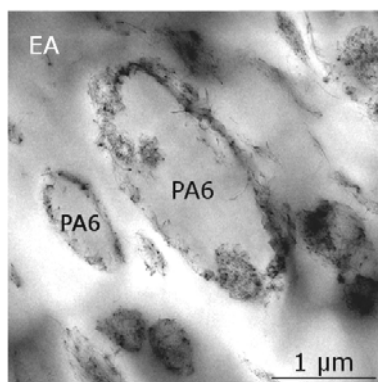


Figure 18 – TEM micrograph of the blend (EA+CNT)/PA6 90/10 wt.-% with 5wt.-%CNT predispersed in the EA

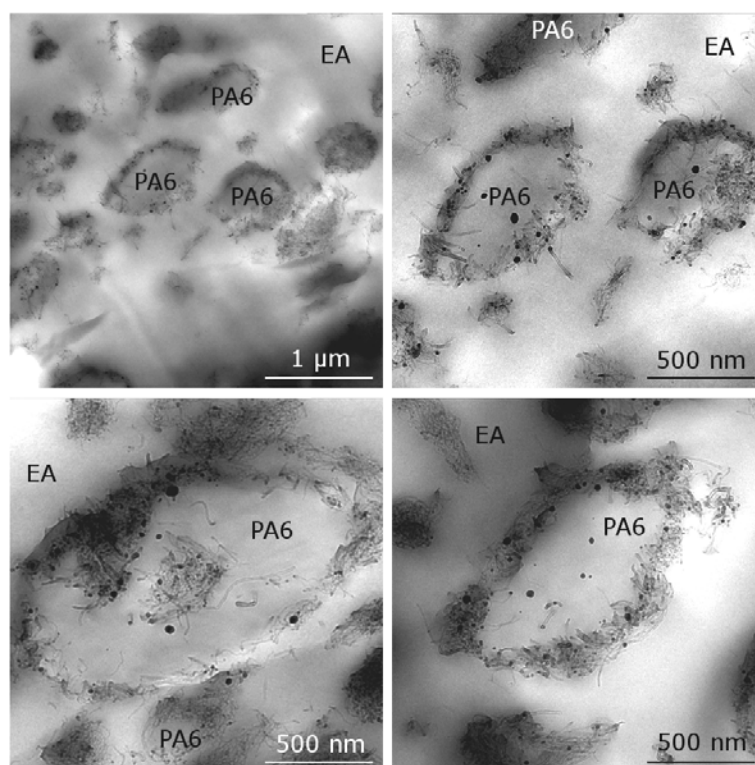


Figure 19 – TEM micrographs of the blend (EA+CNT)/(PA6+Ag) 90/10 wt.-% with 5wt.-%CNT predispersed in the EA and 1.5 wt.-% Ag-NP predispersed in PA6

The CS-AFM images of the conductivity are presented in Figure 20, Figure 22, Figure 24 and Figure 26. For each figure, (a) presents the topography, (b) presents the deflection, (c) presents the recorded current with a scale from 0 to 10nA, which is the upper limit of detection, and finally (d) presents the recorded current with a scale from 0 to 1nA. On each Figure (d), one or more lines are drawn. The conductivity profiles corresponding to these lines are drawn in Figure 21, Figure 23, Figure 25 and Figure 27.

Figure 20 and Figure 22 present the blends (EA+CNT)/PA6 90/10 wt.-% with 4.5 wt.-% CNT and no Ag-NP, when applying a voltage of 2V and 5V respectively. Figure 24 and Figure 26 present the blends (EA+CNT)/(PA6+Ag) 90/10 wt.-% with altogether 4.5 wt.-% CNT and 0.15 wt.-% Ag-NP, when applying a voltage of only 1V.

Figure 20 is obtained by applying a voltage of 2V. The figures show that the areas around the droplets are conductive. However the conductivity is

dominated by large CNT agglomerates at the interface, rather than by individualized CNT.

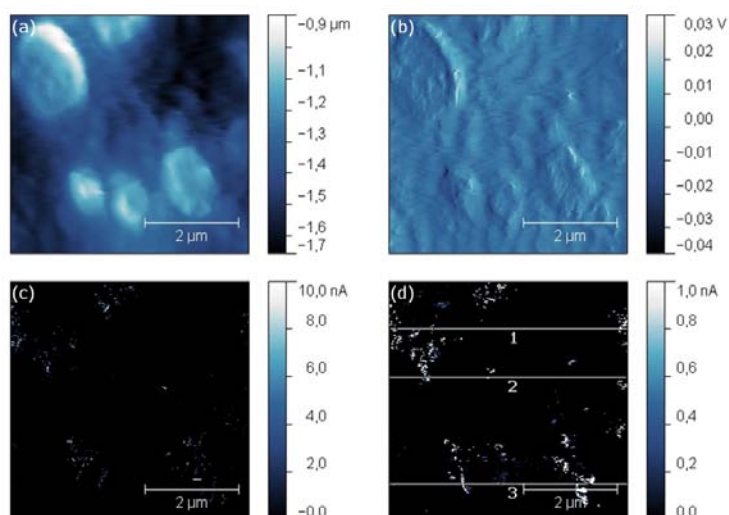


Figure 20 – CS-AFM images of (EA+CNT)/PA6 90/10 wt.-% when applying a voltage bias of 2V; (a) topography; (b) deflection; (c) current scale range 0-10nA; (d) current scale range 0-1nA with three lines to measure current profiles

Figure 21 presents three different profiles of current corresponding to the three lines drawn in Figure 20d. Although a voltage of 2V is applied, high values of current are never achieved.

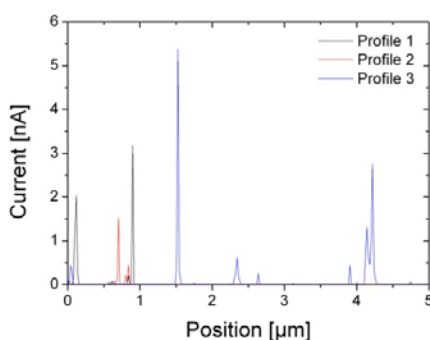


Figure 21 – CS-AFM current profiles from Figure 20d

Figure 22 is obtained in a different zone by applying a voltage of 5V. The area around the PA6 droplets is conductive but there are also some conducting areas

inside the PA6 droplets (Figure 22c,d), indicating the presence of CNT inside the PA6 droplets.

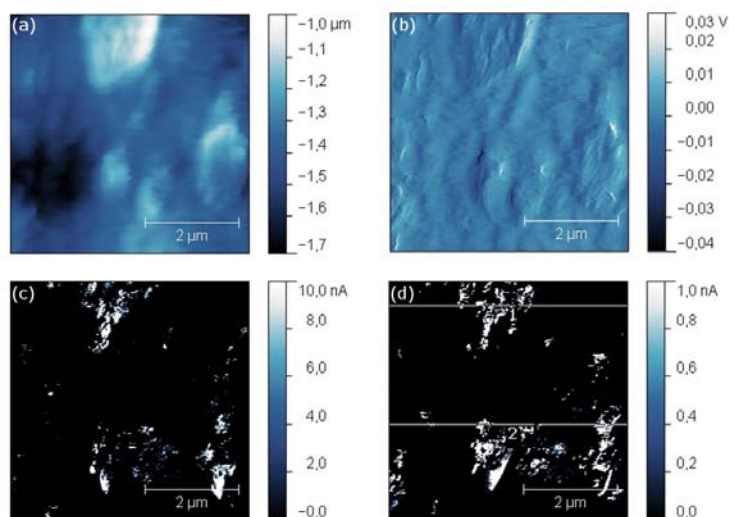


Figure 22 – CS-AFM images of (EA+CNT)/PA6 90/10 wt.-% when applying a voltage bias of 5V; (a) topography; (b) deflection; (c) current scale range 0-10nA; (d) current scale range 0-1nA with two lines to measure current profiles

Figure 23 presents two profiles of current corresponding to the lines drawn in Figure 22d. when applying 5V, higher current values are measured and saturation is achieved in some areas.

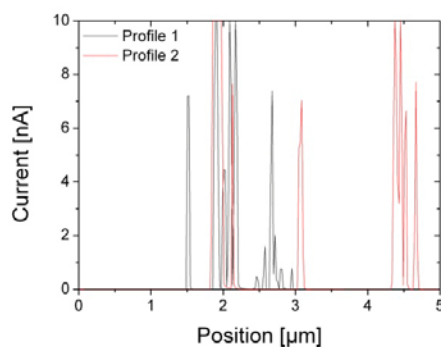


Figure 23 – CS-AFM current profiles from Figure 22d

When Ag-NP are added, Figure 24 shows that, by applying only 1V, a current of 10nA is already observed in some points (Figure 24c). The Figure 24c,d show

that the area around the PA6 droplet is conductive. Here also the conductivity is not homogeneous around the droplet but more probably linked to CNT agglomerates.

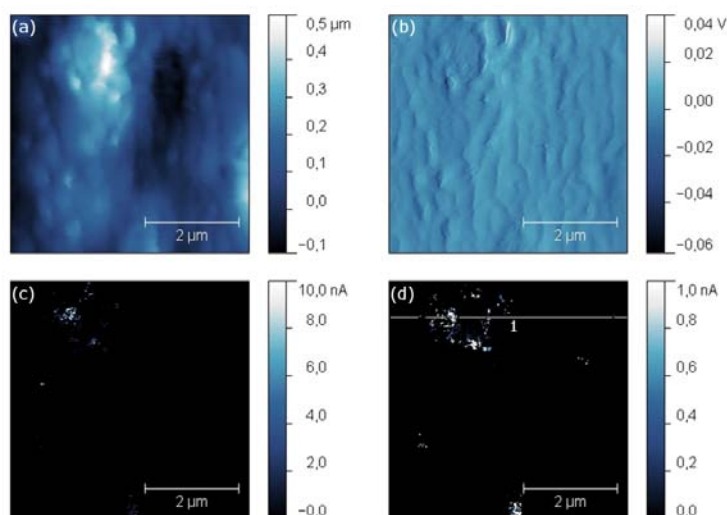


Figure 24 – CS-AFM images of (EA+CNT)/(PA6+Ag) 90/10 wt.-% when applying a voltage bias of 1V; (a) topography; (b) deflection; (c) current scale range 0-10nA; (d) current scale range 0-1nA with one line to measure current profiles

Figure 25 shows that high values of current are recorded even if the applied voltage is only 1V.

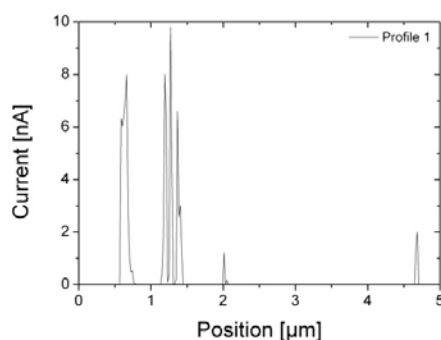


Figure 25 – CS-AFM current profile from Figure 24d

Figure 26 presents the images observed for an applied voltage of 1V for one isolated PA droplet. Here also, a conductivity of 10nA is observed in some areas (Figure 26c). The area around the PA6 droplet is conductive, while the

interior of the droplet is not conductive. The conductivity is here also dominated by CNT agglomerates.

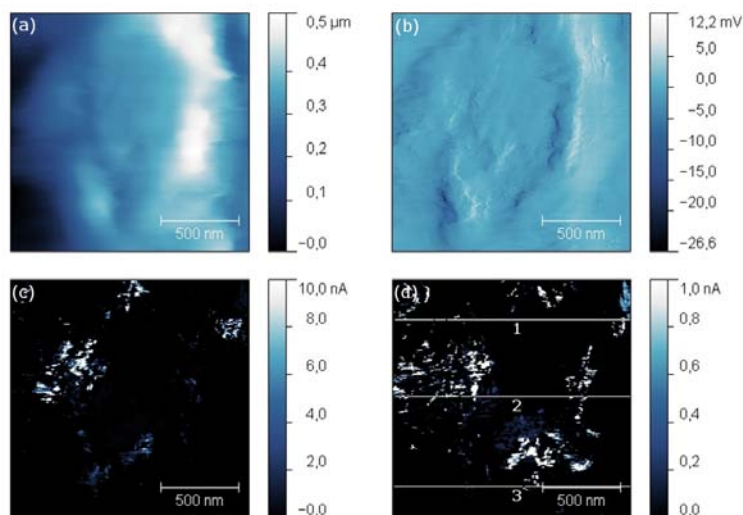


Figure 26 – CS-AFM images of (EA+CNT)/(PA6+Ag) 90/10 wt.-% when applying a voltage bias of 1V; (a) topography; (b) deflection; (c) current scale range 0-10nA; (d) current scale range 0-1nA with three lines to measure current profiles

The profile of current drawn on the lines in Figure 26d are reported in Figure 27. Here also the recorded current saturates at 10 nA in some areas.

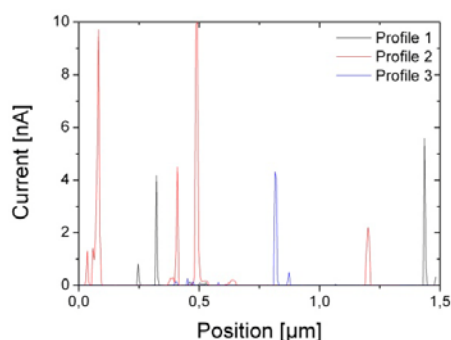


Figure 27 – CS-AFM current profiles from Figure 26d

The CS-AFM images show that higher conductivity levels are achieved in the presence of Ag-NP even for lower applied voltages. The resistivity at the interface is thus lower in the presence of Ag-NP. Although the volume fraction of conductive filler particles is higher in the presence of Ag-NP, this difference

is small in comparison with the 4.5wt.-% CNT used. Indeed, for the same volume fractions, 0.15wt.-% Ag corresponds to only 0.022wt.-%CNT. It would therefore correspond to the dispersion of 5.02 wt.-% CNT in EA. A difference of 0.02wt.-% is however too low to be precisely controlled in the compounding process used here. The observed difference is thus more probably due to the good affinity between CNT and Ag-NP confined at the interface, which decreases the contact resistance.

CONCLUSION

The dispersion of silver nanoparticles (Ag-NP) and the combination of CNT and Ag-NP has been studied in PA6 and in immiscible polymer blends of EA and PA6.

Ag-NP and CNT are well dispersed in PA6. Ag-NP alone do not form a conductive network throughout the sample and the conductivity measured for 0.06 or 1.5 wt.-% Ag is identical to the conductivity of pure PA6. A high affinity between CNT and Ag-NP has been observed. However, for identical volume fractions, the conductivity observed by a combination of CNT and Ag-NP is similar to the conductivity obtained for only CNT. No synergy between the fillers is thus observed on the electrical properties in the single polymer matrix. The electrical properties at high frequencies only depend on the volume fraction of conductive filler. Note nevertheless that the size of the CNT decreases significantly with increasing the content of Ag-NP in the matrix, which is prejudicial to the formation of a conductive network. However, the Ag-NP are expected to act as conducting bridges between the CNT, the effect of the affinity between CNT and Ag-NP would thus be more significant for DC conductivity.

When Ag-NP are used in EA/PA6 90/10 wt.-% immiscible blends, a large number of EA sub-inclusions are observed in the PA6 dispersed domain. The Ag-NP are found at the interface of the phases and at the interface of the sub-inclusions. This behaviour is coherent with the thermodynamic predictions determined based on the assumption that Ag-NP are apolar high energy fillers.

When CNT and Ag-NP are used simultaneously, the number of sub-inclusions is highly decreased. CNT and Ag-NP migrate towards the interface of the PA6 droplets, whatever the CNT mixing sequence. There is thus a kind of interfacial stiffening preventing the coalescence of droplets and thus the formation of sub-inclusions. This effect has already been shown in Chapter 4 for the interfacial

localization of CNT [27]. The high affinity between CNT and Ag-NP is confirmed in blends.

Co-continuous blends have been prepared. The replacement of part of the CNT by Ag-NP induces enhanced conductivities on a large frequencies range.

Moreover, the local DC conductivity of blends presenting a sea-island morphology has been measured using Current Sensing AFM. The conductivity is dominated by the presence of CNT agglomerates with and without Ag-NP. The measurements show a significant improvement of the conductivity at the interface of the blends in the presence of Ag-NP and that for equivalent conductive filler contents.

Ag-NP are thus improving the conductivity of EA/PA6 blends compared to CNT alone. Moreover, the combination of CNT and Ag-NP forces the migration of Ag-NP to the interface. The dissolution of the matrix followed by the recuperation of the droplets coated with a network of CNT and Ag-NP could therefore be envisaged for a use as bactericidal filters (Figure 28). However, it would require higher Ag-NP loadings.

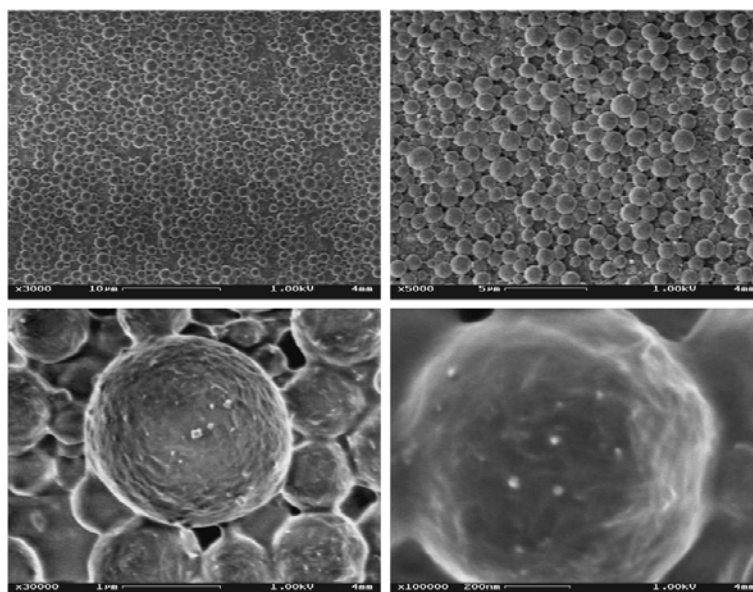


Figure 28 – SEM micrographs of the blend EA/(PA6+Ag+CNT) 90/10 wt.-% after dissolution of the EA phase and filtration on a membrane to recuperate the PA droplets

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Chapter 8

GENERAL CONCLUSIONS AND PROSPECTS

The first objective of this thesis is to understand the key aspects controlling the dispersion of carbon nanotubes (CNT) in different polymer matrices. Both thermodynamic and kinetic parameters are thus studied.

The enthalpic contribution is dominated by van der Waals (VDW) interactions between CNT. To achieve a good dispersion of the CNT it is therefore necessary to minimize these interactions. According to Lifshitz classical theory, it is possible by minimizing the Hamaker constant and thus the difference between the dielectric constants and refractive indexes of the CNT and the polymer matrix. A good correlation is observed between the theory and the experimental results: the best dispersion states are obtained for polymers presenting high dielectric constants (ϵ) and refractive indexes (n) (Figure 1).

For a selected polymer, the dispersion state also depends on the mixing energy during processing. Increasing mixing energy, by increasing mixing rotation speed and time and decreasing compounding temperature, leads to improved dispersion. However, improving the dispersion by varying the processing parameters leads to decreased electrical conductivity. The best dispersion states are thus not correlated with the best electrical properties.

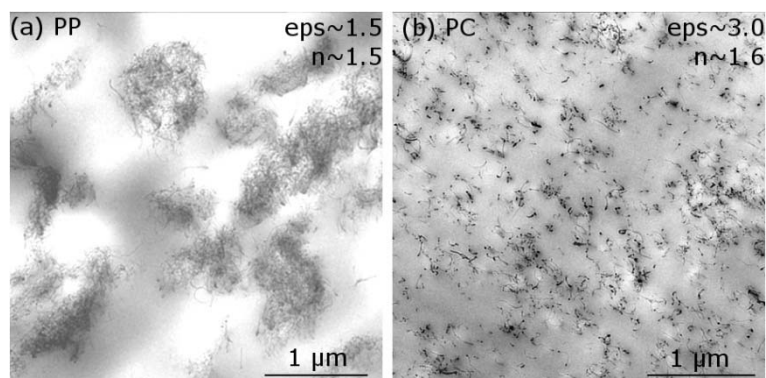


Figure 1 –The dispersion state is directly correlated to the minimization of the Hamaker constant

The second objective is to study the formation of a conductive network of CNT in the polymer melt. During annealing in the melt state, the morphology evolves towards the formation of interconnected agglomerates. This induces an increase of the conductivity and of the modulus (G') (Figure 2). This behaviour is temperature and time dependent and is reversible. Shear destroys the structure and with further annealing, recovery is observed. To get electrically conductive plastic parts it is necessary to first disperse the primary

CNT agglomerates as individualized CNT and then to form a conductive network of secondary agglomerates.

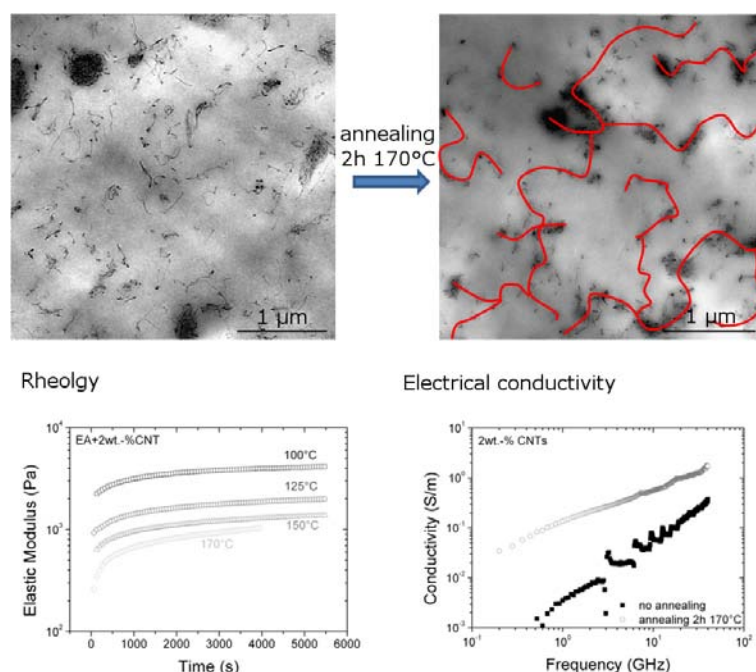


Figure 2 – A conducting network of CNT is formed by annealing the nanocomposite. This phenomenon is called secondary agglomeration.

In further studies, combined rheology and dielectric measurements should be performed on EA+CNT to follow the evolution of the structure simultaneously on the rheological and dielectrical properties. It would also help to understand the differences observed in the kinetics of electrical and rheological evolutions.

The third objective is to understand the thermodynamic and kinetic parameters governing the localization of CNT in immiscible polymer blends.

First, the possibility to jam unpurified and unfunctionalized CNT at the interface of a variety of immiscible polymer blends, even for long mixing times, is demonstrated. This selective localization leads to the formation of an interfacial percolating conductive network (Figure 3). Moreover, it suppresses the coalescence in immiscible polymer blends exhibiting a sea-island morphology (Figure 4). CNT enhance both phase dispersion and stability of the

dispersed phase for long mixing time (at least 60 minutes) and very low filler content (0.5 wt.-% CNT) and produce a more uniform distribution of droplets size. The main stabilization mechanism proposed is the formation of a deformable barrier network providing a mechanical barrier against coalescence.

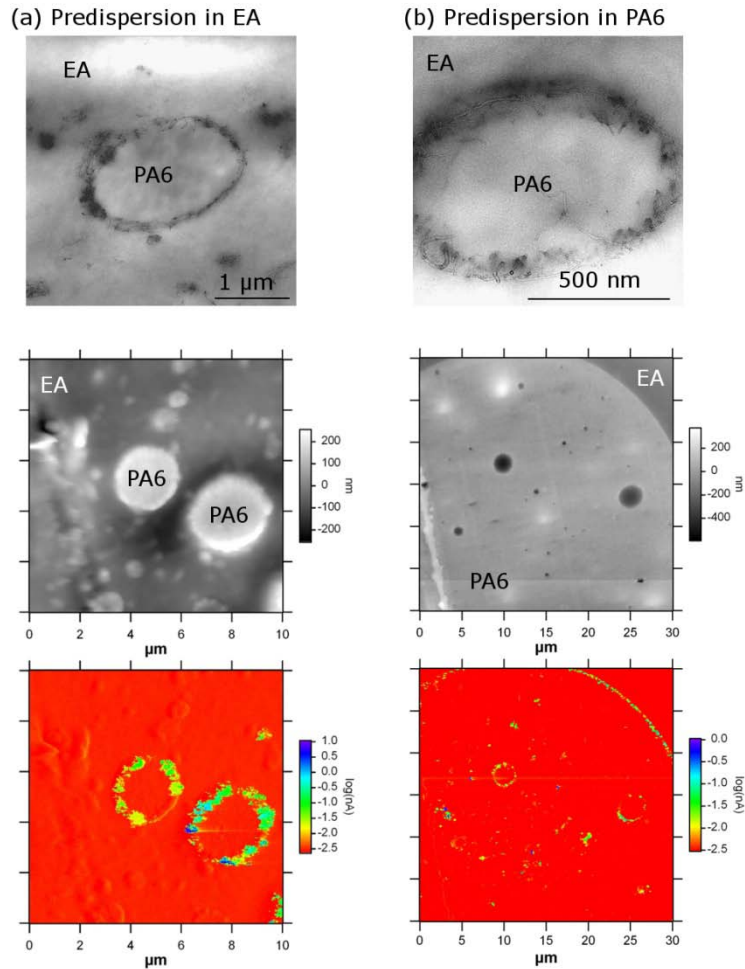


Figure 3 – CNT selectively located at the interface form a conductive network.

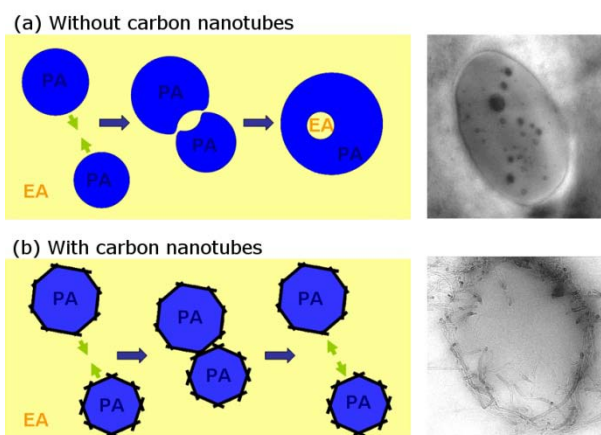


Figure 4 – Morphology development due to dispersed phase polymer droplets collision (a) in the absence and (b) in the presence of CNT

Second, a general mechanism for the localization of CNT is proposed taking into consideration thermodynamic and kinetic contributions (Figure 5). The thermodynamic contribution is governed by the interactions between CNT and polymers. The kinetic contribution is governed by the mixing sequence, polymer adsorption and the relative viscosities of the phases.

The equilibrium position, according to thermodynamics, is predicted by the minimization of the interfacial energy and thus by the evaluation of the wetting coefficient. If the thermodynamic predictions define the interface as the CNT preferred localization, the CNT migrate towards the interface independently of the mixing sequence. On the contrary, if one phase is designed as the preferred phase, the morphology depends on mixing strategy. First, if CNT are predispersed in the preferred phase, in the absence of chemical modification, they remain in this phase. Second, if CNT are predispersed in the less preferred phase, they migrate towards the preferred phase. Nonetheless, the adsorption of the first polymer in contact with the CNT as well as the relative viscosities of both phases influence their localization. If the first polymer in contact with the CNT adsorbs, in an at least partially irreversible way, on the surface of the CNT, the transfer of CNT towards the preferred phase is hindered. It is believed that if the macromolecules of the first polymer in contact can desorb or if there are CNT free of polymer chains, CNT migrate inside the preferred phase if the viscosity of this latter is not too high. If the preferred phase presents a very high viscosity compared to the one of the matrix, it will prevent the transfer of the CNT from the less preferred phase to the preferred one.

It is worth noting that the mechanism described here above, however, does not apply to blends where important polymer wrapping occurs. Indeed if the surface of the CNT is fully coated by polymer chains, from the point of view of the surface of the object, it can not be considered as a pure CNT anymore.

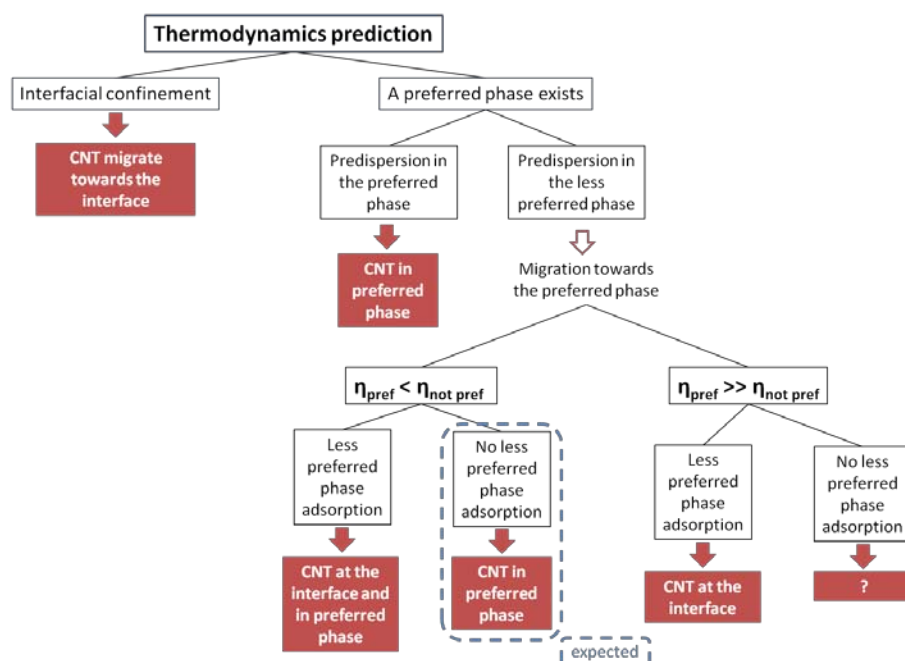


Figure 5 – General mechanism for CNT localization in polymer blends assuming that no important polymer coating occurs

Future works should be performed to complete and confirm the general mechanism proposed. Moreover, different polymer adsorption or grafting conditions on CNT should be used¹. The effect of the chain length of the adsorbed polymer and of CNT surface coverage could therefore be estimated.

In the future, interfacial rheology should be performed to determine unequivocally the origin of the stabilization mechanism. The CNT content for stabilization could also probably be reduced. Predictions on the amount of CNT required for the formation of a network at the interface and thus stabilization could also be done.

Finally, Raman could be used to assess the fraction of CNT in each phase by mapping the presence of the CNT².

The fourth objective is the control of the morphology of co-continuous immiscible blends in the presence of CNT and the improvement of the electrical properties. First, a selective localization of CNT at the interface is observed for all the compositions of a blend of immiscible polymers (EA/PA6). Second, a co-continuous morphology is achieved in the presence of CNT. A triple continuous structure is thus achieved: the blend presents a co-continuous structure with an interfacial localization of the CNT. The CNT are responsible of a broadening of the co-continuous domain compared to blends without CNT. This is attributed to the stabilizing nature of the CNT, which prevent the coalescence by forming a rigid barrier at the interface. Moreover, the size of the phases is reduced compared to blends without CNT. Next, although the triple continuous structure is achieved, the corresponding electrical conductivities are very low. Surprisingly, much higher conductivities are observed for a blend presenting a sea-island morphology in which the droplets are surrounded with CNT and are very close to each other (Figure 6). Indeed, in this case, the CNT form a conductive path at the interface of the droplets and form bridges that connect the droplets. This is also confirmed in other systems developed in the lab. However, sub-inclusions of the phase presenting the lowest viscosity (EA) in

¹ Tao F, Nysten B, Baudouin A-C, Thomassin J-M, Vuluga D, Detrembleur C, Bailly C, *Influence of nanoparticle-polymer interactions on the migration behaviour of carbon nanotubes in immiscible polymer blends*, submitted

² Mayo JD, Behal S, Adronov A. J. Polym. Sci. A Polym. Chem. 2009; 47: 450–458

the phase presenting the highest viscosity (PA6) are observed. These sub-inclusions are parasites because the CNT at their interface do not contribute to the formation of a conducting path.

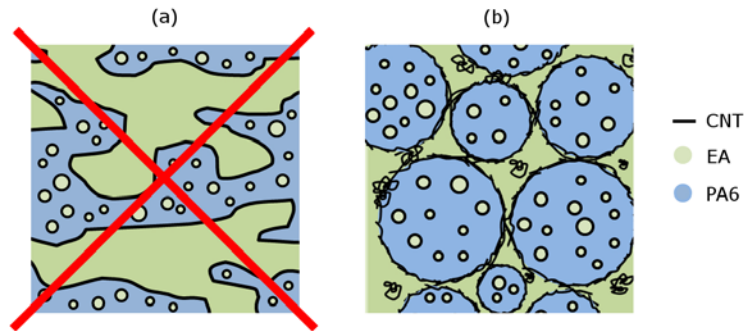


Figure 6 –(a) The triple continuous structure with the interfacial localization of the CNT does not lead to improved electrical conductivity. (b) The selective localization of CNT at the interface of large dispersed droplets and the bridging of the droplets by the CNT lead to the formation of a conducting path and to improved electrical conductivity.

In the future, the conductivity of other compositions presenting a sea-island structure should be measured to confirm the mechanism attributed to the formation of the conductive network. In that context, TEM and STEM tomography could be performed to study in three dimensions the formation of the interfacial network of CNT.

Further works should also address the problem of the sub-inclusions. Other systems presenting different rheological properties should be studied to minimize or even totally suppress the sub-inclusions.

As the structure is highly oriented, the electrical properties in the plane perpendicular to the compression direction should finally be measured.

Finally the last objective is the extension of the concepts developed with CNT to other nanofillers.

First, CNT are replaced by graphite-based nanoplatelets. The thermodynamic considerations concerning the dispersion of CNT in different polymer matrices can be extended to graphite nanoplatelets (GNP). The best dispersions of GNP are observed for matrices, which minimize the Hamaker constant. The

resulting electrical properties are in good agreement with the dispersion states observed.

Radio Frequency (RF) electrical properties of highly filled composites show an atypical behaviour attributed to the orientation of platelets, which act as microcoils for current. This conductivity can be modelled by an electrical circuit consisting of a resistor, an inductor, and a capacitor, connected in series (RLC circuit) (Figure 7).

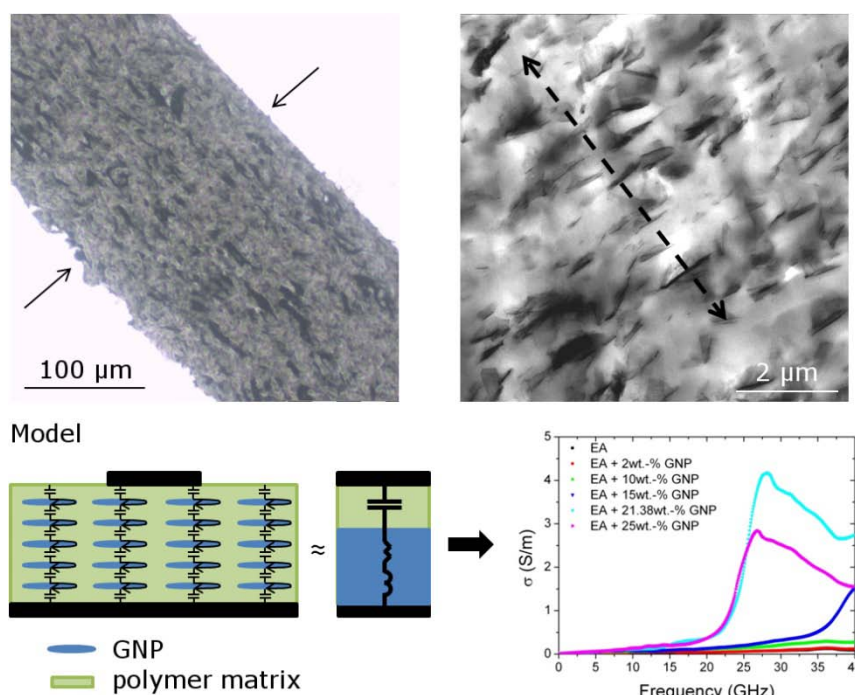


Figure 7 – Orientation of the GNP platelets and resulting behaviour. The arrows indicate the compression direction.

Next the dispersion of GNP and functionalized graphene sheets (FGS) in an immiscible blend in which the CNT present an interfacial confinement is studied. Migration of GNP and FGS is observed but the effect is not as spectacular as for CNT. A large number of platelets are observed in the polymer in which they are predispersed.

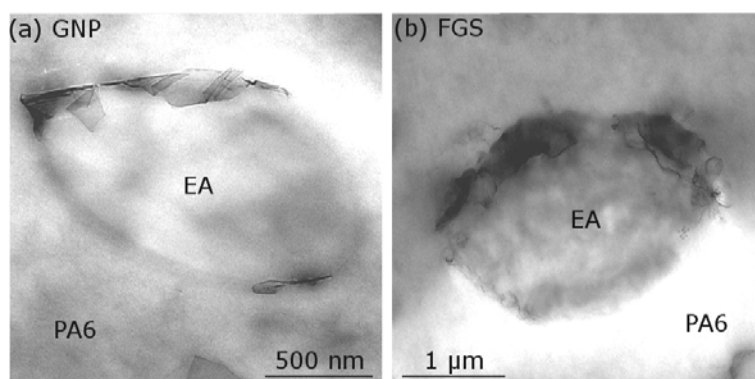


Figure 8 – Interfacial localization of (a) GNP ; (b) FGS in EA/PA6

In the future, the type of particles responsible of the resonance should be confirmed. Higher graphite contents should be used in single-phase matrices to achieve a higher content of particles presenting an intermediate size. Moreover, higher FGS content should also be used. Different particle contents and type could then be used to adjust the position of the resonance peak.

Due to their morphology, FGS could be an interesting alternative to CNT in immiscible polymer blends. However, better interfacial confinement should first be achieved. Indeed, although the results are promising, the dispersed droplets are not fully covered with FGS and not all of them present FGS at their interface. To facilitate the migration towards PA6 domains, the FGS could be modified with amine, amide or anhydride functions. If higher degree of dispersed phase covering is reached, the conductivity at the interface between the droplets and the matrix should be measured using Current Sensing-AFM to determine if FGS can offer improved properties as compared to CNT.

Second, a combination of CNT and silver nanoparticles (Ag-NP) is used. A high affinity between CNT and Ag-NP is observed (Figure 9a). However, no synergy between the fillers is observed on the electrical properties at high frequencies in a single polymer matrix. A simple additive effect is observed. A slight improvement is however observed at low frequencies.

Next, an interfacial confinement of CNT and Ag-NP is observed in immiscible polymer blends (Figure 9b-d). Ag-NP improve the conductivity of the immiscible blends compared to CNT alone for co-continuous blends and the

local conductivity for blends presenting a sea-island morphology. Ag-NP act as conducting bridges between the CNT and thus improve the electrical properties.

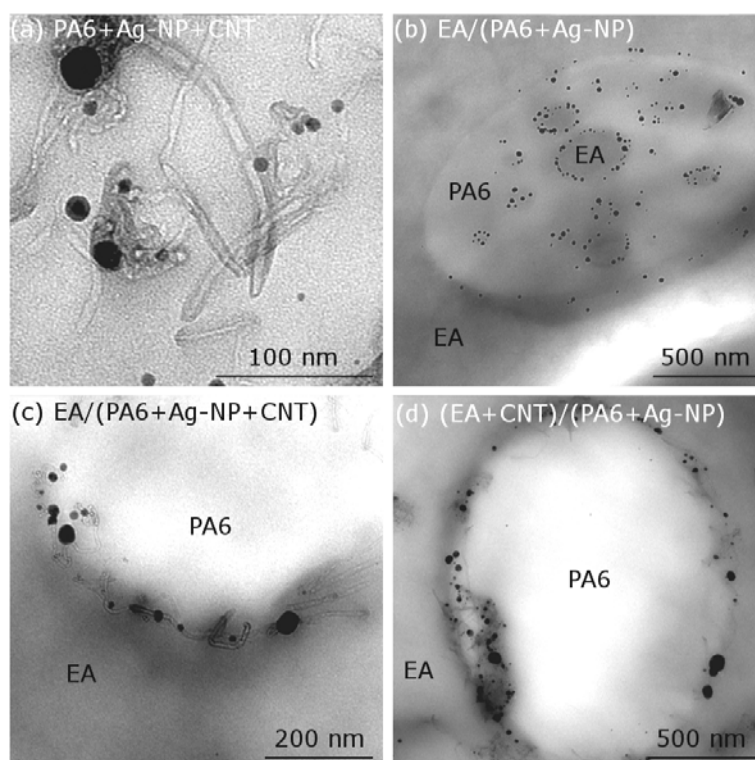


Figure 9 – (a) There is a high affinity between Ag-NP and CNT dispersed in PA6; (b) Ag-NP migrate from PA6 to the interface; (c) CNT and Ag-NP migrate from PA6 to the interface; (d) CNT and Ag-NP migrate respectively from EA and from PA6 to the interface.

The properties of the nanocomposites polymer/CNT/Ag-NP should first be studied in DC (Direct Current). Indeed, Ag-NP are expected to act as conductive bridges between CNT and facilitate the electron transfer. The effect of the addition of Ag-NP should thus be more significant in DC than in RF characterization.

Next, higher amounts of Ag-NP dispersed in PA6 should be used to analyze the influence of the Ag-NP more systematically on the electrical properties of single-phase matrix and on immiscible polymer blends.

Moreover, the interfacial localization of higher Ag-NP amount could be used to elaborate bactericidal filters. With the help of CNT, the number of sub-inclusions is reduced and the Ag-NP migrate to the surface of the PA6 domains. After dissolution of the EA matrix, the covered droplets can be recuperated and act as filter (Figure 10).

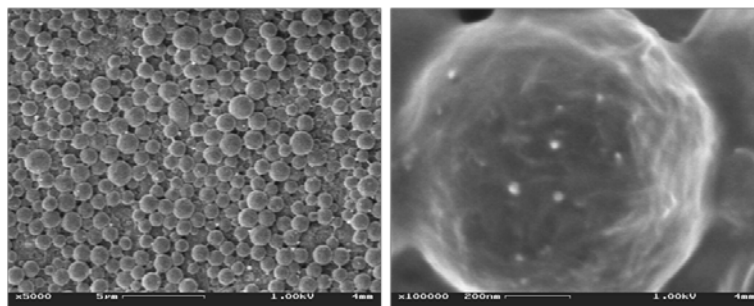


Figure 10 – Close packing of PA6 droplets with Ag-NP located on their surface could be used for the elaboration of bactericidal filters.

Finally, as the results are promising for Ag-NP, the dispersion of metallic nanowires in polymer matrices and next in immiscible polymer blends is of great potential interest for the preparation of conducting composites.

Appendixes

Appendix 1: Materials and characterization methods

Appendix 2: Surface energy of CNT

We thank:

- Pr. H. Münsterdt for providing PA6 samples filled with silver nanoparticles
- Dr. R. Verdejo from CSIC, Madrid, for providing FGS samples
- Nanocyl for providing NC7000 (CNT)
- Timcal for providing TIMREX – BNB90 (GNP) and TIMREX – KS5-25 (graphite).
- Arkema for providing LY28MA07 (EA)

APPENDIX 1:

MATERIALS AND CHARACTERIZATION METHODS

INTRODUCTION

The objective of this appendix is a presentation of the different materials and characterization methods used in this thesis. The different materials are first presented; first the nanofillers: carbon nanotubes, graphite nanoplatelets, graphite, functionalized graphene sheets; second the different polymer matrices and finally the solvent. Next the preparation conditions of the samples are described. Third the different characterization methods are exposed. The methods used for the characterization of the carbon fillers are first exposed. Second the methods used for the characterization of the different polymers are described. Third, the characterization methods used to analyze the morphology and properties of the single-phase composites and the immiscible polymer blends are exposed. Finally, the methods used to check polymer adsorption on the nanofillers are presented, including the methods used for the extraction of the nanofillers.

MATERIALS

1 Carbon fillers

The carbon fillers are subdivided in two categories: the carbon nanotubes and the graphite-based platelets.

1.1 Carbon nanotubes (CNT)

The CNT used in this work are unpurified and unfunctionalized multiwalled carbon nanotubes. They are produced in multi-tons, via the Chemical Vapor Deposition (CVD) process by Nanocyl S.A., Belgium (Nanocyl®-7000). Their specifications according to the producer ^[1] are presented in Table 1.

Table 1 – Characterization of the CNT according to the producer

Property	Unit	Value	Method of measurement
Average diameter	nm	9.5	TEM
Average Length	microns	1.5	TEM
Carbon Purity	%	90	TGA
Metal Oxide	%	10	TGA
Amorphous carbon	-	Pyrolytically deposited carbon on the surface of the CNT	HRTEM
Surface area	m ² /g	250-300	BET

However, we present hereafter a characterization of the CNT by different means: SEM, TEM, Raman, TGA and XPS.

Figure 1 presents SEM micrographs of the CNT at different magnifications ^[2]. The CNT are synthesized as bundles of highly agglomerated nanotubes.

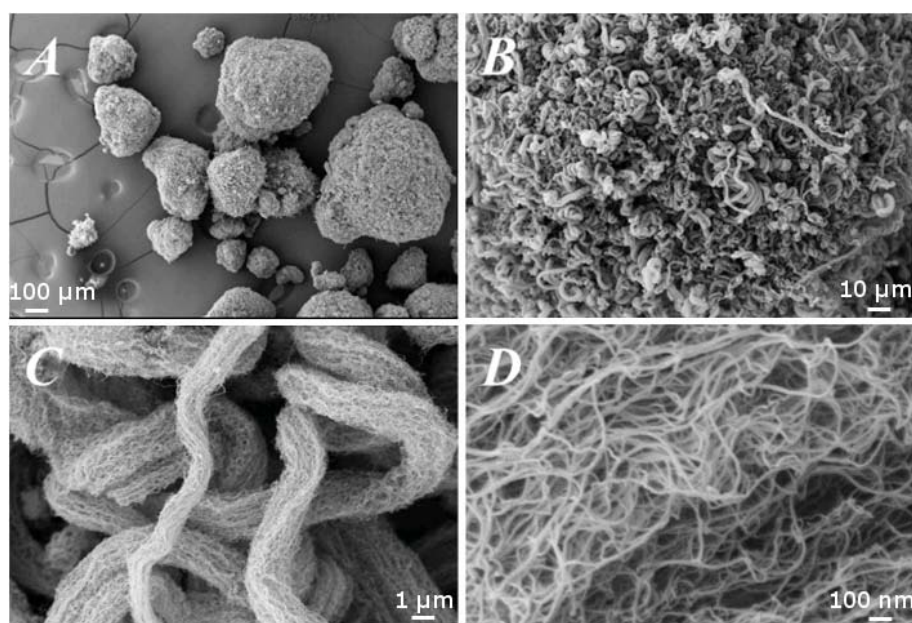


Figure 1 – SEM images of pristine CNT powder at different magnifications; adapted from Villmow et al. ^[2]

Figure 2 presents a TEM micrograph of the as-produced CNT. The length of about twenty CNT has been measured. The CNT were dispersed in toluene and then sonicated for 10 minutes. Then a few droplets of the solution are dropped

on a holey carbon grid. The arithmetic mean length is about 2 μm and the standard deviation is 1 μm . The external radius is about 12 nm and the internal radius is around 5 nm. The average number of graphene layers is 8. The CNT are covered by a thin amorphous carbon layer.

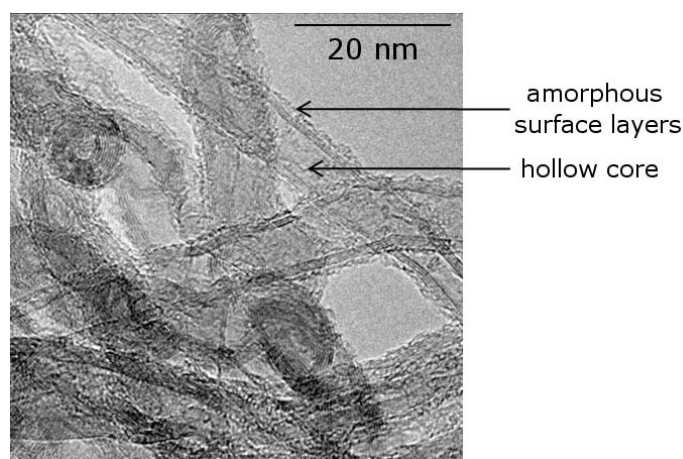


Figure 2 – TEM micrograph of CNT

Raman spectroscopy is also a very useful tool in the characterization of carbon-based nanostructures [3-6]. It has been widely used for the characterization of singlewalled carbon nanotubes (SWNT). However, the characterization of multiwalled carbon nanotubes (MWNT) remains more delicate due to multiple absorptions and emission between concentric cylindrical structures [7]. The Raman spectra of CNT have been recorded using three different wavelengths: 532 nm, 633 nm and 780 nm (Figure 3).

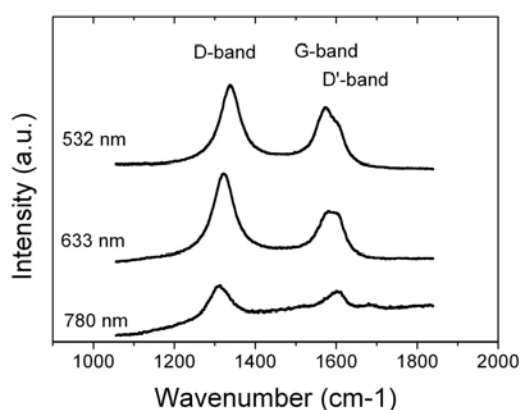


Figure 3 – Raman characterization of as-produced CNT for three different wavelengths (532, 633 and 780 nm)

Figure 4 presents the Raman spectrum of the CNT for a laser excitation at 532 nm. The spectrum consists of three characteristic bands, the D-band at ~ 1338 cm^{-1} , the G-band at ~ 1569 cm^{-1} and the D'-band at ~ 1596 cm^{-1} . The G-band, typically observed around 1600 cm^{-1} , is linked to in-plane tangential stretching of the C-C bonds of graphene sheets. It is often used to distinguish semiconducting from metallic singlewalled CNT. The D-band, typically observed at 1300-1400 cm^{-1} , is usually attributed to the presence of amorphous or disordered carbon, due to finite or nanosized graphitic planes and other forms of carbon (defects in nanotubes walls, vacancies, heptagon-pentagon pairs, hetero-atoms). Finally, the D'-band, which is usually a weak shoulder of the G-band at higher frequencies is also induced by defects and disorder. The ratio between the D-band and G-band (I_D/I_G) has been extensively used to measure the quality of the CNT: a small I_D/I_G ratio corresponds to a low amount of defects. In our case, the I_D/I_G ratio for the different laser wavelengths is presented in Table 2. This ratio is high, indicating the presence of a large number of defects. Note that the radial breathing modes (RBM), appearing between 150 and 300 cm^{-1} , are not presented here. They correspond to the vibration of the C atoms in the radial direction. The energy or wavenumber of these modes depends on the diameter of the CNT. However, for CNT presenting a diameter larger than 2nm, which is the case here, their intensity is very weak.

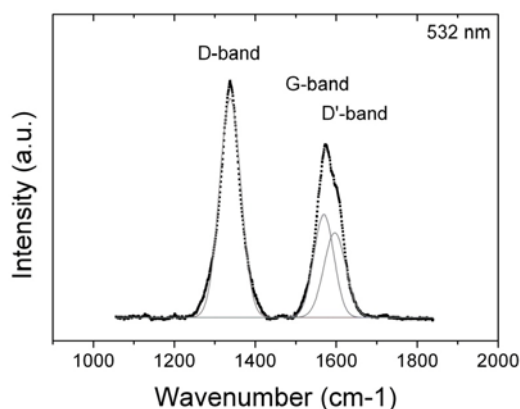


Figure 4 – Raman spectrum of CNT (excitation : 532 nm)

Table 2 - I_D/I_G ratio for the different laser wavelength

Laser wavelength (nm)	532	633	780
I_D/I_G	2.1	1.7	2.1

The thermogravimetric analysis of CNT in dry air environment shows weight change of the sample during heating. The initial burning of the CNT occurs

above 400°C. The residual fraction after burning is around 10wt.-%, confirming the producers data.

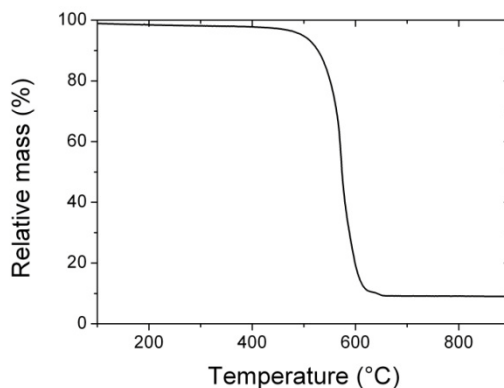


Figure 5 – Thermogravimetric analysis of CNT

X-ray photoelectron spectroscopy is used to evaluate the chemical nature of the CNT surface. In X-ray photoelectron spectroscopy (XPS) a sample, introduced in an ultra high vacuum chamber, is irradiated with an X-ray beam. The kinetic energy (in electron volt, eV) of electrons of all elements (except H and He) present at the surface is measured with a precision of about 0.2 eV. The probed depth is between 1 and 10 nm. Shape and position of recorded peaks depend on the chemical state (the so-called "chemical shift" effect). Peaks areas normalised with respect to acquisition parameters and corrected with elemental sensitivity factors allow calculating mole fractions. The detection limit depends on the element and is close to 0.1 %. A detailed analysis of well-resolved peaks allows quantifying chemical functions (Figure 6).

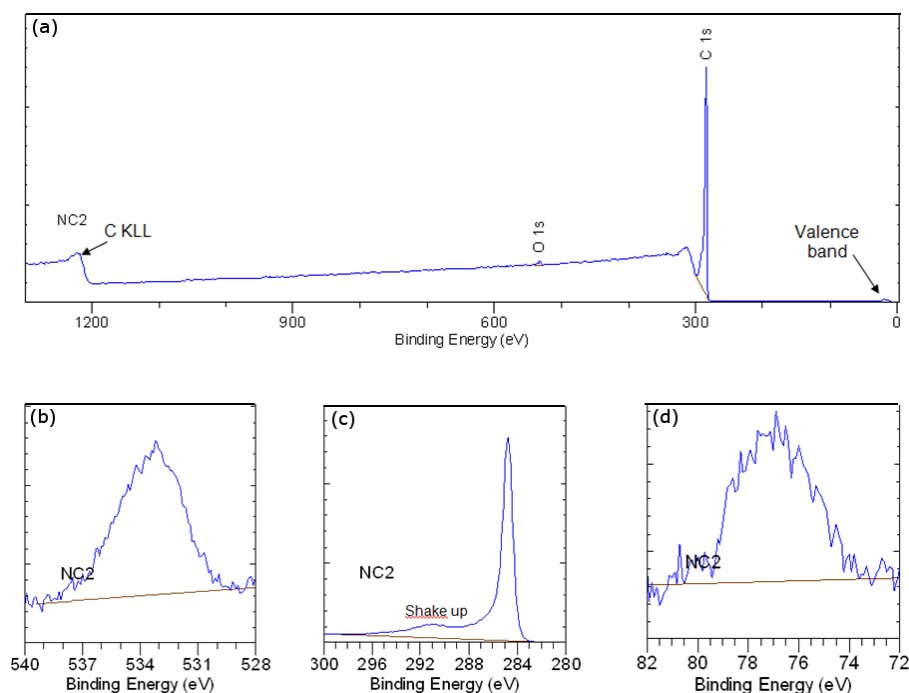


Figure 6 - (a) Overview of XPS spectrum for CNT; (b) XPS O1s spectrum; (c) XPS C1s spectrum; (d) XPS Al2p spectrum

The analysis of the XPS spectrum allows the quantification of the elements present in the sample (Table 3). The analysis shows that the CNT are mainly composed of carbon. The presence of oxygen is very weak, an analysis of the chemical functions present on the CNT is therefore not possible. Moreover, Al is present in the samples. At least part of the O functions detected therefore comes from O linked to Al, in the form Al_2O_3 or $\text{AlO}(\text{OH})$. It is thus assumed that the CNT present almost no function on their surface.

Table 3 – Recorded results from XPS analysis of CNT

Element	O	C	Al
Electronic level	O 1s	C 1s	Al 2p
Energy (eV)	533,2	284,8	76,9
Width at half height (eV)	3,8	1,0	3,4
Molar fraction (%)	0,5	99,2	0,3

1.2 Graphite-based platelets

The different graphite-based platelets are characterized using TEM, Raman and XPS.

According to literature, for these materials, the position of the Raman characteristic peaks G and G' depends on the number of graphene shells composing the sample. The G' peak is around 2726 cm^{-1} for graphite, while it is around 2683 cm^{-1} for one sheet of graphene for a laser with a wavelength of 514,5nm (2,41eV) [8]. Here the laser wavelength is 532 nm (2.32 eV). The shift corresponding to G' peak therefore needs to be adjusted (shift of 100 cm^{-1}/eV) to allow comparison of the results with literature values. Another important point is the spectral resolution, which is around 5 to 8 cm^{-1} . Note that above 5 or 6 layers of graphene, the Raman spectrum can not distinguish GNP from graphite [8,9].

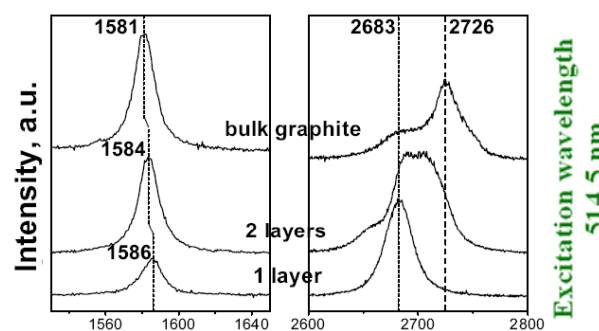


Figure 7 – G and G' peak as a function of the number of graphene layers on a SiO_2 substrate (laser 514,5nm (2,41eV)) [8]

1.2.1 Graphite nanoplatelets (GNP)

GNP is graphite intercalated with sulfuric and nitric acid. Then the sample is heated to exfoliate the graphite platelets. The obtained product is called expanded graphite (EG). To obtain the GNP, the EG is then milled.

The GNP used in this study is TIMREX®-BNB90 from TIMCAL. Its characteristics, according to the producer, are reported in Table 4 and Table 5.

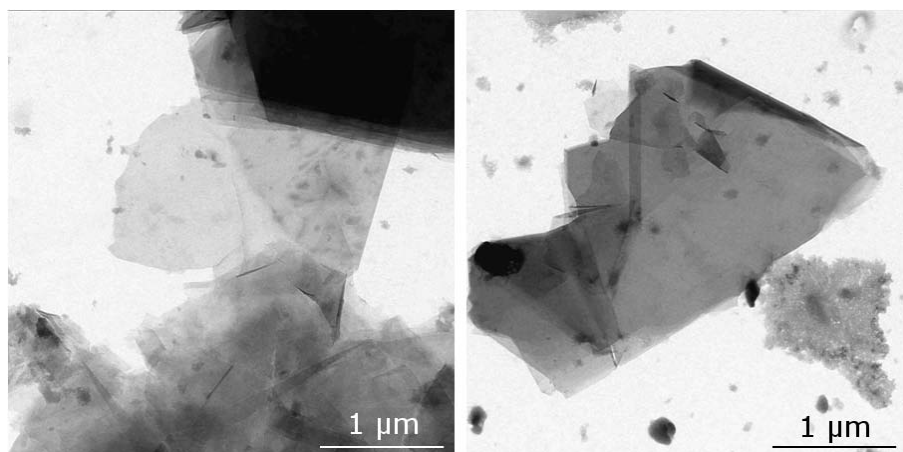
Table 4 – Guaranteed values of the GNP

Ash	0.25 % max
D90 (Laser Malvern)	100 μm max

Table 5 – Particle size distribution (Laser Malvern) of the GNP

D10	10 μm
D50	36.1 μm
D90	85.2 μm

Figure 8 presents TEM micrographs of the GNP. The size distribution of the GNP is not homogeneous. Stacks composed of a high number of graphene sheets (on the left) coexist with stacks of a few layers (on the right).

**Figure 8 – TEM micrographs of the GNP**

Raman spectroscopy is used to determine the number of graphene sheets of the GNP (Figure 9). The characteristic peaks G' and G are observed around 2707 cm^{-1} and 1573 cm^{-1} respectively. Another peak, corresponding to the D band, is observed around 1334 cm^{-1} . This peak is characteristic of the disorder of the sample, for example on the edges.

Applying the corrections, the G' peak of GNP is around $2713 \pm 8 \text{ cm}^{-1}$, which looks more like graphite than graphene. It is thus only possible to conclude that the GNP presents at least 6 graphene layers.

The graphite presents a crystalline structure very similar to graphene.

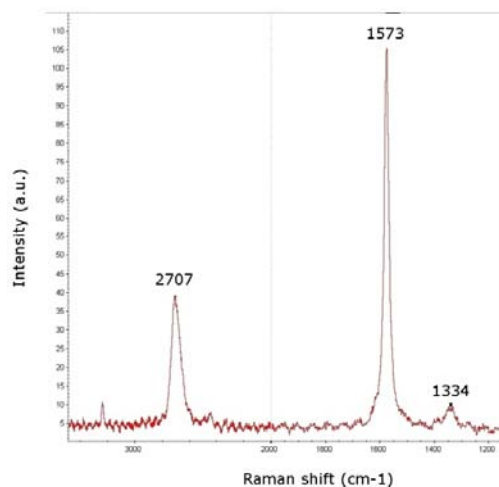


Figure 9 – Raman spectrum of the GNP (laser 532nm 1mW)

XPS characterization (results not shown) shows that less than 1mol% oxygen is present in the GNP.

1.2.2 Graphite

The graphite used is TIMREX®-KS5-25 from Timcal. Its size distribution is given by the producer (Figure 10).

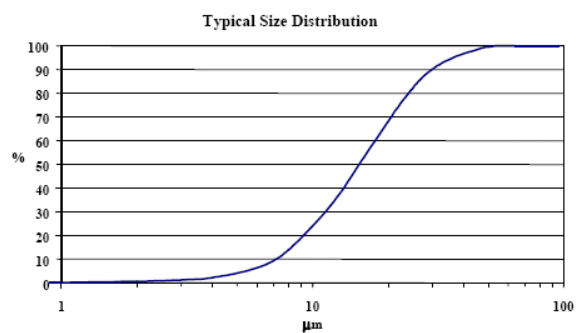


Figure 10 – Size distribution of KS5-25 according to the producer

Table 6 – Guaranteed parameters of graphite, according to the producer

Ash	0.1 % max
Moisture	0.5 % Max
Crystallite height	100 nm min
Interlayer distance	0.3354 – 0.3358 nm
D10 (Laser Malvern)	6.0 – 8.5 μm
D90 (Laser Malvern)	29.0 – 33.0 μm

As for the GNP, the graphite presents the peaks G', G and D around 2710cm^{-1} , 1572cm^{-1} and 1340cm^{-1} (Figure 11). It is a highly crystalline graphite.

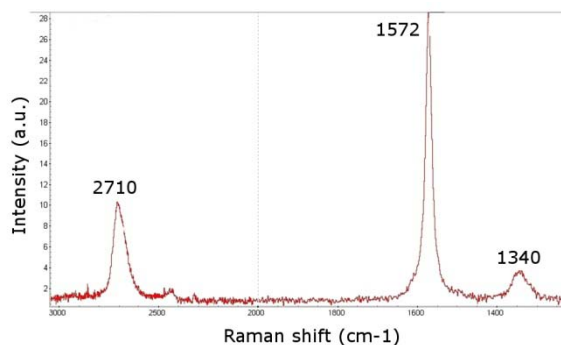


Figure 11 – Raman spectrum of the graphite (laser 532nm 3mW)

1.2.3 Functionalized graphene sheets (FGS)

Functionalized graphene sheets (FGS) are produced by R. Verdejo from CSIC, Madrid.

TEM micrographs (Figure 12) show that they are composed of only a few graphene sheets, contrary to graphite or GNP. Isolated sheets can also be observed.

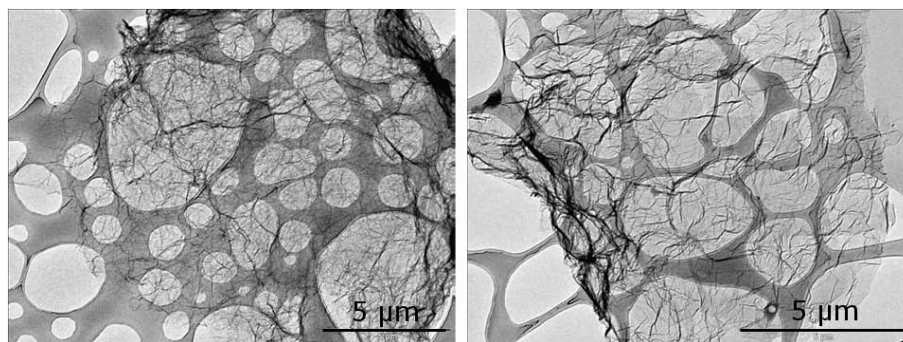


Figure 12 – TEM micrographs of the FGS

Raman spectrum shows the presence of two main peaks G and D around 1589cm^{-1} and 1334cm^{-1} . There is also a large band with a low intensity around 2700cm^{-1} .

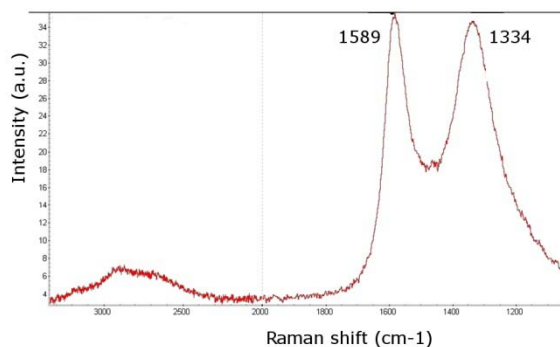


Figure 13 – Raman spectrum of FGS (laser 532 nm, 2mW)

The FGS do not present a G' peak, its microstructure seems therefore very different from the one of graphene. Only a wide band of low intensity is observed around 2700 cm⁻¹. It looks like amorphous carbon. A similar spectrum is obtained by Kudin et al. ^[10] on FGS (Figure 14). This disorder is probably linked to the presence of functional groups on the graphene sheets. It is therefore impossible to determine the number of graphene layers. However, its very low density and TEM micrographs indicate that the FGS platelets are constituted of a low number of graphene sheets.

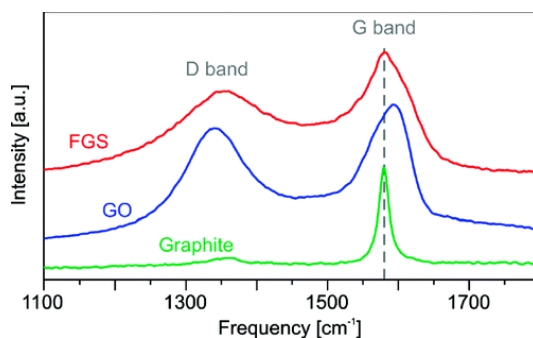


Figure 14 – Evolution of the Raman spectra during the oxidation and exfoliation processes for graphite, GO, and FGS. All of the spectra correspond to an exciting laser wavelength of 514.5 nm. The position of the G band peak in graphite is indicated by a vertical, dashed line ^[10]

The following chemical characterization of the FGS was performed by R. Verdejo from CSIC, Madrid.

The functionalized nature of the graphene sheets is determined by elemental analysis, which is carried out in the starting graphite, graphite oxide (GO) and FGS obtaining C₁₀H_{0.13}O_{1.01}, C₁₀H_{1.82}O_{3.74} and C₁₀H_{0.14}O_{1.32}, respectively. No traces of chlorine and nitrogen are found in the elemental analysis (Figure 15, Table 7).

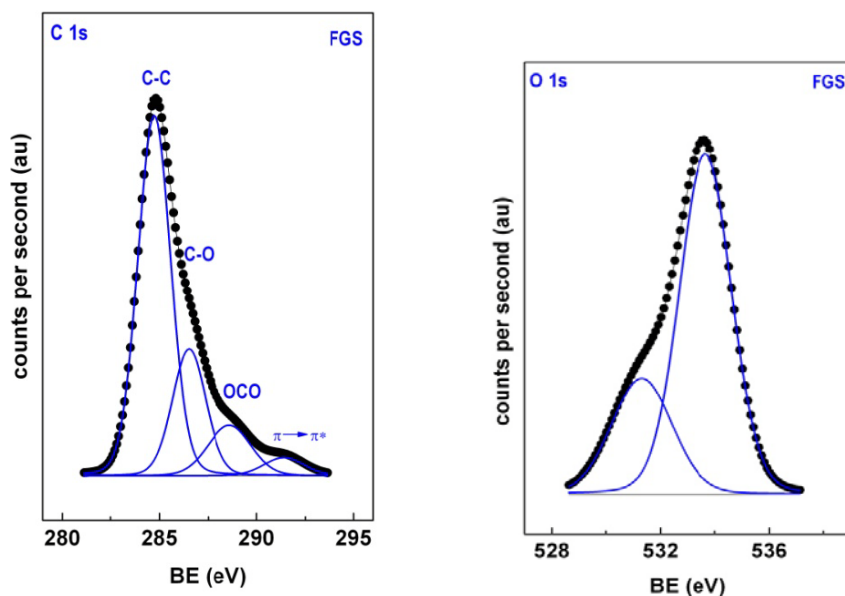


Figure 15 – XPS analysis of the FGS: on the left, XPS C1s spectrum; on the right, XPS O1s spectrum

Table 7 - Binding energies (eV) of core electrons and surface atomic ratios of FGS

C1s	O1s	at/C
284.8 (65%)	531.3 (28%)	O/C
286.5 (23%)	533.6 (72%)	0.101
288.6 (12%)		

The FTIR analysis demonstrated the presence of hydroxyl groups and water at 3400 and 1640 cm^{-1} , stretching and bending. C-O-C stretching of ether groups is observed around 1250 cm^{-1} and epoxy groups are observed with peaks around 1081, 1012 and 876 cm^{-1} .

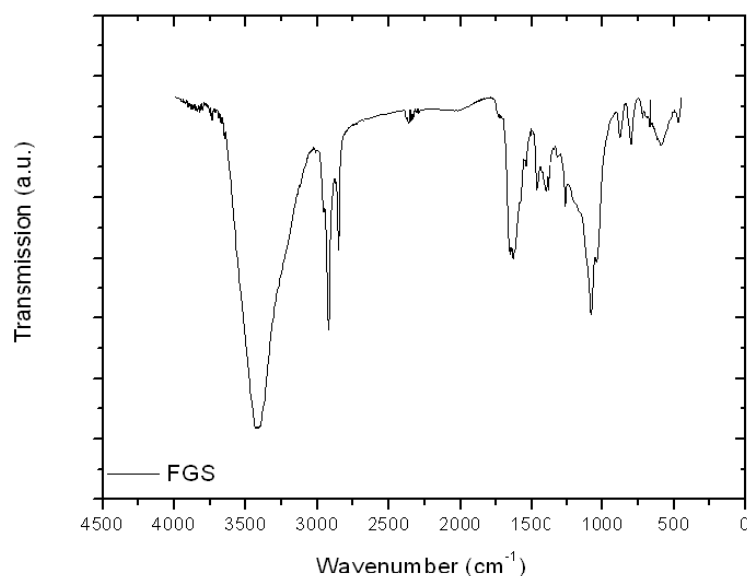


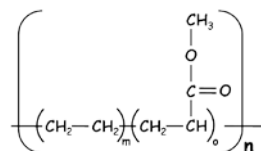
Figure 16 – FTIR spectrum of the FGS

2 Polymers

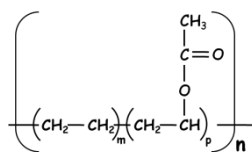
The polymers used for the elaboration of the single phase composites or immiscible blends under study are listed here below. They are classified according to their structure: first the ethylene-based copolymers, next the polyamides and finally the other polymers.

Ethylene-based copolymers:

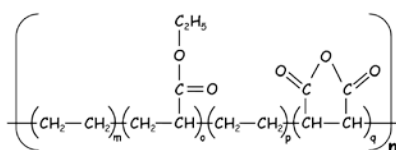
- EA : ethylene-acrylate copolymer (EA) used is a random copolymer of ethylene and 26-30 wt.-% methyl acrylate (Lotryl 28MA07, Arkema).



- EVA: is a random copolymer of Ethylene and Vinyl Acetate made by high-pressure radical polymerisation process (Evatane 2805, Arkema). The vinyl acetate content is 27 – 29 wt.-%.



- MAEA: random terpolymer of Ethylene, Acrylic Ester and Maleic Anhydride containing 17wt.-% ethyl acrylate and 2.8wt.-% maleic anhydride (Lotader 7500, Arkema)



The molecular weights of these polymers are not known. However, their melt indexes are exposed in Table 8.

Table 8 – Melt indexes of the ethylene based copolymers

Polymer	Melt index (190°C / 2,16 kg) ASTM D 1238
EA	6-8 g/10mn
EVA	5-8 g/10mn
MAEA	70 g/10mn

Polyamides:

- PA4/6 : copolyamide 4/6 (Stanyl TE300, DSM)
- PA6 : polyamide6 (Durethan B40F, Bayer); *Melt volume-flow rate 3cm³/10 min (235°C; 2.16 kg; ISO 1133)*
- PA6/12 : copolyamide 6/12 (Grilon CF6S, EMS Grivory); *Melt volume rate 180 cm³/10 min (275°C; 5 kg; ISO 1133)*
- PA12 : polyamide 12 (Vestamid L2101F, Evonik Degussa AG)
- PA*: copolyamide 6,6 with a very low mass (UNI-REZ 2722, Arizona Chemicals). According to the FTIR spectrum, this PA is a modified PA66 with a very low melting point.

Others:

- PP: isotactic polypropylene (Moplen HF500N, Lyondellbasell); *Melt flow rate: 12 g/10 min (230°C; 2.16Kg; ISO 1133); Melt volume flow rate 16 cm³/10min (230°C; 2.16Kg; ISO 1133)*

- PC_m: polycarbonate medium viscosity (Makrolon 2805, Bayer Material Science); *Melt volume-flow rate* 9.5 cm³/10 min (300 °C; 1.2 kg; ISO 1133)
- PC_l: polycarbonate low viscosity (Makrolon 2205, Bayer Material Science); *Melt mass-flow rate* 38 g/10min (300 °C; 1.2 kg ASTM D1238)
- PC*: polycarbonate with a molar mass of 29 kg/mol (PC105, General Electrics). This PC is only used in Chapter 7. It is stabilized using 5wt.-% Irganox 1010.
- PES: Poly(ether sulfone) Cl terminated (Veradel A-201, Solvay Plastics); *Melt Mass-Flow Rate* 20g/10min (380°C; 2.16 kg; ASTM D1238)
- PET: poly(ethylene terephthalate)
- PBT: poly(butylene terephthalate)
- PS: polystyrene (Edistir N2982, Polimeri Europa); *Melt volume flow rate* 26 cm³/10min (ISO 1133)
- PKHP: phenoxy resin (PKHP200, InChem)

3 Polymer-filled with silver nanoparticles

The PA6 filled with Ag-nanoparticles (Ag-NP) is provided by Pr. H. Münstedt from Friedrich-Alexander-University Erlangen-Nuremberg, Institute of Polymer Materials, Erlangen, Germany.

3.1 Preparation of polyamide 6/silver-nanocomposites

For the preparation of a PA6/Ag-nanocomposite containing 2 wt% of silver, 784 g of polyamide 6 pellets (Ultramid B3SK, Mn = 18 kg/mol, from BASF) is premixed with 25 g of silver acetate powder (Merck). The mixture is processed in a co-rotating twin-screw extruder at 230°C. The length over diameter ratio of the screw is 30, the screw has a diameter of 34 mm. During processing a thermal reduction of the silver salt into elemental silver nanoparticles occurs causing a yellow- brownish colour of the extruded strands.

3.2 Characterization of the size of Ag nanoparticles

The size of Ag-NP is determined from TEM micrographs (Figure 17a). The size distribution is presented in Figure 17b. The number average diameter of the Ag-NP measured on 300 particles is of ~14nm.

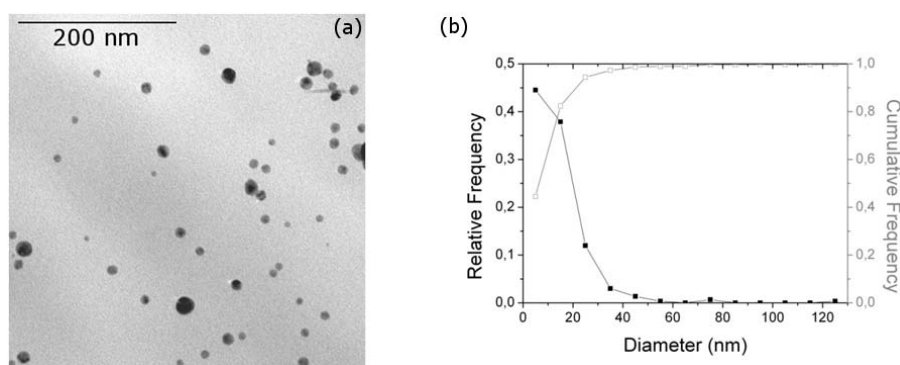


Figure 17 – (a) Example of TEM micrograph used for the determination of the size of the Ag-NP; (b) Distribution of the size of the Ag nanoparticles

4 Solvents

The solvents used in this study are formic acid (purity 98+%, Acros Organics), m-cresol (purity 97%, Acros Organics), chloroform (Chloroform for HPLC stabilized with Amylene, Biosolve) and dimethylsulfoxide (purity 99+%, Janssen Chimica).

BLENDS PREPARATION

The preparation conditions of the nanocomposites are described: first the melt compounding process, then the preparation conditions of the single-phase composites, next the multilayer experiment and next the immiscible blends.

1 Melt compounding process

Homogeneous composites as well as immiscible blends are prepared by melt mixing in a co-rotating twin-screw mini-compounder (DSM Xplore Microcompounder 15cm³) with two stainless steel screws and a bypass allowing continuous recycling of the material at the head of the mixing chamber. Rotation speed and mixing time can be independently modified.

Before melt compounding, the polymers are dried for 24hours under vacuum, at 50°C for PP, PET, PBT, EA, EVA and MAEA, at 80°C for PA and at 120°C for PC and PES.

2 Preparation conditions

2.1 Single-phase composites

The compounding parameters of the different blends are presented hereafter. The same conditions are used for the dispersion of the different carbon nanoparticles.

The following nomenclature is used:

- “Polymer + CNT” corresponds to dispersion conditions of CNT in Polymer
- “Polymer + CNT / GNP ” corresponds to dispersion conditions of CNT or GNP in Polymer
- “Polymer + CNT / GNP / FGS ” corresponds to dispersion conditions of CNT, GNP or FGS in Polymer
- “Polymer + CNT / GNP / FGS / graphite ” corresponds to dispersion conditions of CNT, GNP, FGS or graphite in Polymer

Ethylene-based copolymers based nanocomposites:

	Mixing time min	Screw rotation speed rpm	Mixing temperature °C
EA + CNT / GNP / FGS / graphite	15	250	100
EVA + CNT	15	250	100
MAEA + CNT	15	250	100

Polyamide-based nanocomposite:

	Mixing time min	Screw rotation speed rpm	Mixing temperature °C
PA4/6 + CNT	10	250	310
PA6 + CNT / GNP / FGS	10	250	240
PA6/12 + CNT	10	250	180
PA12 + CNT	10	250	240
PA* + CNT	10	250	240

Other matrices-based nanocomposites:

The PC₁ + CNT is synthesized by Nanocyl S.A., Belgium at 280°C. The other parameters are reported in the following table.

	Mixing time min	Screw rotation speed rpm	Mixing temperature °C
PP + CNT / GNP	10	250	200
PC _m + CNT	5	250	280
PC* + GNP / FGS	5	250	285
PES + CNT	5	250	300
PET + CNT	10	250	240
PBT + CNT	10	250	240
PS + GNP	5	250	170
PKHP + GNP	5	250	220

2.2 Multilayer experiment

EA + 1wt.-% CNT is hot pressed at 100°C and PA6 at 240°C in a Fontjine press to form two films of about 1 mm thickness. These films are then annealed in the press for 1h at 240°C on top of each other to form a multilayer (Figure 18).

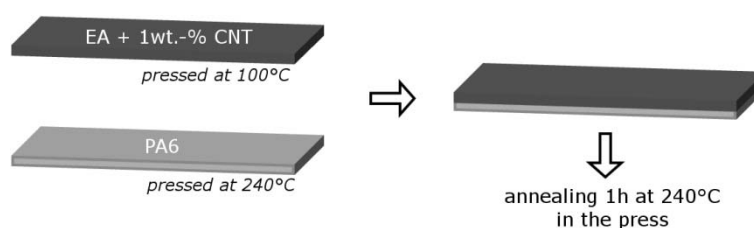


Figure 18 – Description of the procedure for the multilayer experiment.

2.3 Immiscible blends

Different mixing strategies can be used for the elaboration of immiscible polymer blends filled with nanoparticles. The elaboration methods can be a two steps methods: the nanoparticles are first dispersed in one polymer, this composite is then blended with the second polymer ((Polymer1+CNT)-Polymer2 or Polymer1-(Polymer2+CNT)); or a single step method in which all the components are simultaneously mixed.

The preparation conditions of the immiscible blends are reported in the tables hereafter.

Blends based on ethylene – based copolymers

	Mixing time min	Screw rotation speed rpm	Mixing temperature °C
EA + PA4/6 + CNT	10	250	310
EA + PA6 + CNT / GNP / FGS	10	250	240
EA + PA6/12 + CNT	10	250	180
EA + PA12 + CNT	10	250	240
EA + PA* + CNT	10	250	240
EA + PC _m + CNT	10	250	280
EA + PC _i + CNT	10	250	280
EA + PET + CNT	10	250	240
EA + PBT + CNT	10	250	240
EVA + PA6 + CNT	10	250	240
EVA + PC _m + CNT	10	250	280
EVA + PC _i + CNT	10	250	280
MAEA + PA6 + CNT	10	250	240
MAEA + PA12 + CNT	10	250	240

Blends based on polycarbonate

	Mixing time min	Screw rotation speed rpm	Mixing temperature °C
PC _m + PA6 + CNT	5	250	280
PC _i + PA6 + CNT	5	250	240
PC _m + PES + CNT	5	250	300

Blends based on polypropylene

	Mixing time min	Screw rotation speed rpm	Mixing temperature °C
PP + PA6/12 + CNT	10	250	200

Some blends are sensitive to the mixing time. A kinetic study of the morphology is therefore realized. The samples are introduced inside the compounder at 50 rpm. The introduction of the 12g of polymers and CNT takes around 1 minute. When it is fully introduced, a first sample is removed (labeled 0min). Then after 30s, 1min30s, 3min30s and 5min, other samples are removed from the compounder. The other preparation parameters are a screw rotation speed of 50 rpm and a mixing temperature of 240°C.

CHARACTERIZATION METHODS

The different characterization methods are presented here. First, the methods used for the characterization of the carbon fillers are exposed. Second, the methods applied for the characterization of the different polymers are presented. Next, the methods used to determine the dispersion state of the fillers in polymer matrices (single-phase matrices or immiscible polymer blends) and the resulting electrical properties are presented. Finally, the characterization of polymer adsorption on the CNT is exposed.

1 Characterization of the carbon nanofillers

The different carbon nanofillers (CNT, GNP, graphite and FGS) are characterized using TEM, Raman and XPS.

1.1 *Transmission Electron Microscopy (TEM)*

The different carbon nanofillers are characterized using TEM. The micrographs are imaged with a LEO 922 transmission electron microscope operating at 200 kV.

The samples are deposited on copper grids covered with a carbon film.

1.2 *Raman*

The carbon nanofillers are characterized using Raman spectroscopy with a DXR SmartRaman from Thermo Scientific operating in the microscopic mode with a 2048 pixel charge-coupled device (CDD) detector. It is coupled to a microscope Olympus TH4-200, with an objective: Olympus MPlan 10X.

The data are analyzed using Omnic 8 for dispersive Raman (Thermo scientific).

The different samples are prepared by deposition of the powder on glass slides at ambient temperature and pressure. Different lasers (wavelengths of 532, 633 or 780 nm) are used and different powers from 0.5 to 3 mW are used. These low powers are used to prevent a local heating of the sample. The pinhole aperture is set to 50 μm and a 10 times magnification objective is used. The time and number of acquisitions are respectively 60s and 5 acquisitions. The characterization of the CNT is done using the three lasers and the characterization of the graphite-based materials is performed with a 532nm laser.

1.3 X-ray photoelectron spectroscopy (XPS)

XPS analyses have been performed on a Kratos Axis Ultra spectrometer (Kratos Analytical – Manchester – UK) equipped with a monochromatized aluminium X-ray source (powered at 10 mA and 15 kV) and an eight channeltrons detector. The spectrometer is interfaced with a Sun Ultra 5 workstation. Instrument control and data acquisition were performed with the Vision2 program.

The sample powder is deposited on a double sided isolative adhesive tape stick on a small brass trough mounted on a multi specimen holder.

The pressure in the analysis chamber is about 10^{-6} Pa. The angle between the normal to the sample surface and the direction of photoelectrons collection was about 0° . Analysis are performed in the hybrid lens mode with the slot aperture and the iris drive position set at 0.5, the resulting analysed area is $700\text{ }\mu\text{m} \times 300\text{ }\mu\text{m}$. The pass energy is set at 160 eV for the survey scan and 40 eV for narrow scans. In the latter conditions, the full width at half maximum (FWHM) of the Ag 3d5/2 peak of a standard silver sample is about 0.9 eV.

Charge stabilisation is achieved by using the Kratos Axis Ultra device.

The following sequence of spectra is recorded: survey spectrum, C 1s, O 1s, Cl 2p, Al 2p and C 1s again to check for charge stability as a function of time and the absence of degradation of the sample during the analyses. The C-(C,H) component of the C1s peak of carbon has been fixed to 284.8 eV to set the binding energy scale.

Molar fractions are calculated using peak areas normalised on the basis of acquisition parameters after a linear background subtraction, experimental sensitivity factors and transmission factors provided by the manufacturer. Elemental mole fractions are provided, excluding hydrogen which is not detected by XPS.

2 Characterization of the polymers

2.1 Rheology

The viscosity of the different polymers at the blending temperature is analyzed using a stress-controlled Bohlin (now Malvern) Gemini rheometer with 25mm parallel plates. All the measurements are performed under nitrogen, to avoid thermo-oxidative degradation, at the blending temperatures (180°C, 240°C,

280°C, 300°C, 310°C). The samples are measured in the linear range of deformation.

Frequency sweep experiments are conducted in the frequency range of 0.1-600 rad/s. However, PA* presenting a very low viscosity, the upper limit of the frequency range is limited to 145 rad/s. It is also worth noting that for polymers degrading fast at high temperature, the frequency range analyzed is shortened to 1 rad/s as a lower limit.

The thermal stability of the EA, EVA and PA6/12 is analyzed using the multiwave-frequency option. The fundamental frequency is 0.1 rad/s with 5% deformation plus two additional wave forms at 1 rad/s with 1.5% and 10 rad/s with 0.5% respectively.

For rheological characterization, the polymers are pressed in the melt state and dried for at least 12h under vacuum, at 50°C for PP, PET, PBT, EA, EVA and MAEA, at 80°C for PA and at 120°C for PC and PES.

2.2 *Fourier transform infrared spectroscopy (FTIR)*

A film of PA* is characterized by Fourier-Transform Infra-Red spectroscopy (FT-IR) using a Nicolet Nexus 870 spectrometer. FT-IR spectra were taken at room temperature in the transmittance range of 600-2000 cm^{-1} . Typically, 128 scans per spectrum are recorded at 2 cm^{-1} resolution.

3 Characterization of the nanocomposites

The single-phase composites as well as the immiscible polymer blends are characterized using microscopies, electrical properties and rheology.

3.1 *Microscopy*

3.1.1 *Optical microscopy (OM)*

Optical microscopy is performed using an Olympus AX70. For the observations, samples of 1 μm are cut in the directions perpendicular the flow direction with a Reichert Microtome, using a cryodiamond knife with a cut angle of 35° (Diatome, Switzerland). Then the slices are deposited on glass slides.

For single-phase composites, depending on the matrix, the sample are either cut at ambient temperature and collected in water (PP, PA, PC, PES) or at low temperature: knife temperature -40°C, chamber temperature -70°C and sample

temperature -70°C; and collected in a blend of 60 vol% DMSO/40 vol% milliQ water (EA, EVA, MAEA).

For immiscible polymer blends, if both phases can be cut at ambient temperature (PA6/PC blends or PES/PC blends), the samples are cut at ambient temperature and collected in water. Otherwise, the samples are cut at low temperature: knife temperature -40°C, chamber temperature -70°C and sample temperature -70°C; and collected in a blend of 60 vol% DMSO/40 vol% milliQ water.

3.1.2 Transmission Electron Microscopy (TEM)

CNT dispersion in nanocomposites samples are examined by TEM. The micrographs are imaged with a LEO 922 transmission electron microscope operating at 200 kV.

Ultrathin sections of approximately 95 nm in thickness are cut with a Reichert Microtome, using a cryodiamond knife with a cut angle of 35° (Diatome, Switzerland) and collected on 300 mesh copper grids. The cut conditions of temperature are identical to the conditions described for OM imaging.

Specimens of the nanocomposites produced are cut perpendicularly to the axes of the extruded samples. The compressed samples are cut in the direction of the thinnest dimension.

The diameter of the droplets (Chapter 5) is evaluated on TEM micrographs using the iTEM software (Olympus Soft Imaging System). Although the measured diameter is not the actual diameter of the droplets, this measurement allows to follow the morphology evolution with time.

3.1.3 SEM

Scanning electron microscopy is performed on cryofractured surfaces using a LEO 982 (Zeiss).

The sea-island morphologies are observed on cryofractures fixed on support using double sided conductive tape.

The co-continuous compositions are observed after cryofracture and selective dissolution of one of the phases. EA is dissolved in boiling chloroform and PA6 is dissolved in formic acid. After dissolution, the samples are dried and glued on a support using double sided conductive tape.

STEM tomography is performed using a ESEM XL-30 FEG (FEI) with an acceleration tension of 30 kV, a partial pressure of vapour of water of 0.3 to 0.4 Torr. The detection is performed in mode STEM dark field (equivalent HAADF). This characterization is performed by Pr. Karine Varlot-Masenelli, Insa Lyon.

3.2 Electrical Properties

The AC electrical properties are characterized using a Vector Network Analyzer. The DC electrical properties are characterized using Current Sensing-Atomic Force Microscopy.

3.2.1 Vector network analyzer

The AC electrical properties were measured using a Wiltron Model 360B Vector Network Analyzer (VNA) in a wide-band frequency range from 40 MHz to 40 GHz at room temperature.

a. Sample preparation

The samples are melt pressed (Fontijne Holland Vlaandingen, SRA 106) on an aluminium sheet which acts as a zero potential sheet. The pressing temperatures are reported in Table 8 for each sample. The dimensions of the sample are of 50x30x0.8 mm ($L \times l \times h$). Finally, a microstrip line of copper (width 1.5 mm) is added on the top of the sample (Figure 18b).

Table 9 – Pressing temperatures for the preparation of samples for electrical characterization

Sample	Temperature
PP + CNT / GNP	200°C
EA + CNT / GNP	100°C
PA6 + CNT / GNP / Ag-NP	240°C
PC + CNT / GNP / FGS	200°C
Blends EA + PA6 + CNT	240°C
Blends EA + PA6 + CNT / Ag	240°C

b. One-line characterization in microstrip configuration technique ^[11]

This section is mainly a reproduction from the book chapter: "Foamed Nanocomposites for EMI Shielding Applications, Molenberg I, Huynen I, Baudouin A-C, Bailly C, Thomassin J-M, Detrembleur C, Book Chapter in "Advanced Microwave and Millimeter Wave Technologies Semiconductor Devices Circuits and Systems", InTech, Book edited by: M Mukherjee, 2010"

The One-Line method is based on the measurement of the scattering parameters (S_{ii}) of only one line, a microstrip line in this case. The sample to be characterized is used as substrate to fabricate a microstrip transmission line. A thin copper ribbon is glued to the top of the sample, serving as microstrip and a piece of aluminum tape is glued on the bottom of the solid sample, to form the ground plane (Figure 18). From the S matrix, the ABCD chain matrices can be calculated for a transmission line of length L and of characteristic impedance Z_c .

$$ABCD = \begin{pmatrix} ch(\gamma L) & Z_c sh(\gamma L) \\ \frac{1}{Z_c} sh(\gamma L) & ch(\gamma L) \end{pmatrix}$$

The propagation constant γ can then be extracted and the dielectric constant and conductivity can be determined, using the following equations:

$$\varepsilon_r = \varepsilon' - j\varepsilon'' = \left(\frac{c_0 \gamma}{j\omega} \right)^2 \quad \text{and} \quad \sigma = -\omega \varepsilon_0 \varepsilon''$$

This method is valid only if a precise LRM (Line-Reflect-Match) calibration of the VNA has been done. The reference planes must be put after the transitions, and the reference impedances in these planes must be set to $50 \, \Omega$, which is ensured using an LRM calibration. An Anritsu precision microstrip calkit and the corresponding 3680K Anritsu sample holder (including the transitions) were used for the microstrip measurements.

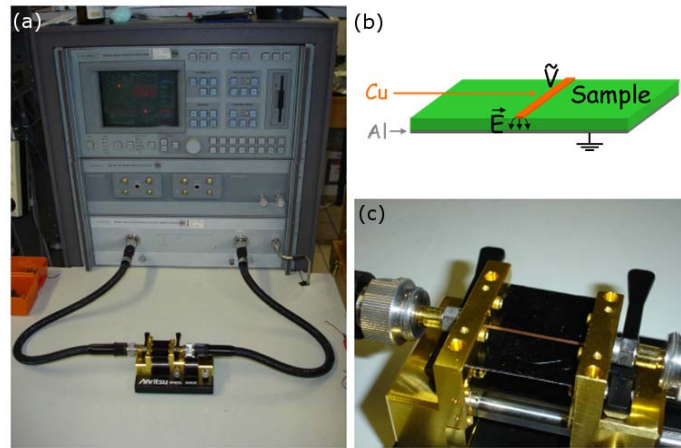


Figure 19 – Experimental set-up for the One-Line method applied to a microstrip topology (a) entire set-up; (b) scheme of the sample with Al ground plane and Cu microstrip; (c) Anritsu sample holder with the microstrip visible on top of the sample (substrate)

c. Electrical model ^[11]

It must first be noted that Carbon Black (CB) nanoparticles, i.e. relatively spherical carbon platelets, are considered here instead of CNT to simplify geometrical considerations.

The measured conductivity tends to 0 for very low frequencies. This means that the conductive nanoparticles do not form a direct conductive pathway for the electrons from one side of the sample to the other side. However, at relatively high frequency the conductivity becomes significant, indicating the presence of capacitive couplings between the nanoparticles. Said et al. ^[12] explained this behaviour by a simple model illustrated on Figure 19. The nanocomposite is placed between a ground plane and a microstrip line, to form a microstrip transmission line. The CB nanoparticles are supposed to be spherical and well dispersed inside the matrix. There is also supposed to be no direct physical contact between them, i.e. they do not touch one another (Figure 19a). This random distribution is approximated by a regular homogeneous network of purely conductive grains inside a completely insulating polymer matrix. Therefore, the electrical equivalent of each grain is a simple resistor and there are strong capacitive couplings between all the grains. Since the electric field distribution between the top and bottom conductors of the microstrip line is quasi uniform and perpendicular to those conductors, only capacitors and resistors that are parallel to that direction have to be considered (Figure 19b). This corresponds to a two-layered microstrip transmission line (Figure 19d), with an insulating top layer and a conductive bottom layer (conductivity = σ_{CL}). This line has an electrical equivalent admittance per unit length that corresponds to a simple resistor-capacitor (RT and CT) series circuit (Figure 19c).

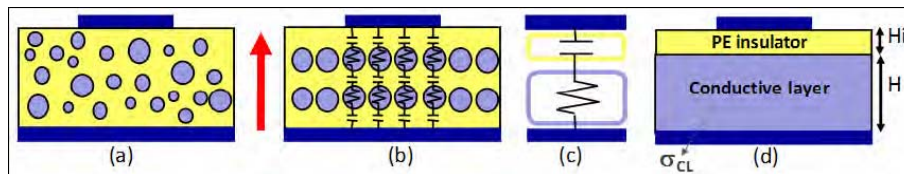


Figure 20 – Simple electrical model explaining the frequency dependence of the conductivity of the nanocomposites: (a) first approximation, the CB nanoparticles are spherical, well dispersed inside the polymer matrix and not in physical contact with one another. The arrow indicates the dominant direction of the electric field. (b) Second approximation, the CB particles form a regular network of conductive grains inside an insulating polymer matrix. (c) Equivalent admittance per unit length of microstrip line. (d) Corresponding two-layer microstrip transmission line reproduced from ^[12]

3.2.2 CS-AFM

The AFM used is a Pico+ (Agilent). Diamond coated conductive probes (NanoSensors™) are used.

a. Preparation of the samples

Samples of 1 μm (EA+PA6+CNT samples) or 500 nm (EA+PA6+CNT+Ag-NP samples) thickness are cut in the direction perpendicular to the extrusion direction.

b. Principle

CS-AFM presents the DC conductivity of thin sections of the blends deposited on silicon surfaces coated with gold. By applying a voltage between the substrate and the cantilever, a current flow is generated. This current is used to construct a spatially resolved image of the conductivity. Topography, deflection and current measurements are extracted.

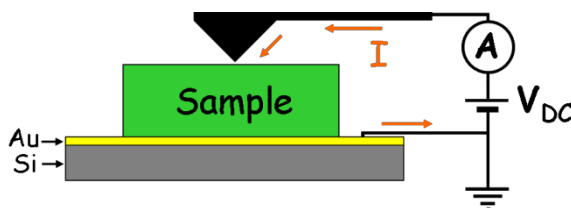


Figure 21 – Scheme of principle of the CS-AFM measurements

3.3 Rheological characterization of the secondary agglomeration

The evolution of the rheological properties with time of EA+CNT at different CNT loading (1 to 5 wt.-% CNT) is recorded using a stress-controlled Bohlin (now Malvern) Gemini rheometer with 25mm parallel plates. All the measurements are performed under nitrogen, to avoid thermo-oxidative degradation, at the different temperatures (100°C, 125°C, 150°C, 170°C). The samples are measured in the linear range of deformation. The rheological properties are analyzed using the multiwave-frequency option. The fundamental frequency is 0.1 rad/s with 5% deformation plus two additional wave forms at 1 rad/s with 1.5% and 10 rad/s with 0.5% respectively.

4 Characterization of polymer adsorption

The methods used for determining the presence of polymer adsorption on the CNT or GNP are described here. First the different methods applied for the extraction of the CNT or GNP from the polymer matrix are presented. Next TGA and decantation experiments are exposed.

4.1 *Extraction of the CNT or GNP*

Two methods are used for the extraction of the CNT or GNP from EA or PA6 matrices. For the extraction of the CNT or GNP from EA, a Soxhlet device is used and for extraction of the CNT from PA6, a device of filtration under pressure is used.

4.1.1 Soxhlet

A Soxhlet device has been used to extract the CNT from the composite EA + 2wt.% CNT. The extraction is performed using chloroform at 65°C. Two different extraction durations are used: 24hours and 5 days. 50mg EA + 2wt.% CNT are deposited in the glass fibre thimble and the extraction using 300ml chloroform is performed for the desired duration.

An identical procedure is used for the extraction of the GNP particles

A control Soxhlet has also been done, 50mg EA are deposited in the glass fibre thimble and the extraction with 300ml chloroform has been performed for 5 days.

4.1.2 Filtration under pressure

Filtration under pressure is performed with the help of a Sartorius SM 16249 pressurized filtration device supporting a maximum pressure of 10 bars and a maximum temperature of 150°C. The maximum volume is of 220ml. The solutions of PA and carbon nanotubes are filtered on Aluminium oxide membrane Anodisc 47 presenting a pore size of 0.1µm (Whatman, England).

The PA6+2wt.-%CNT composite is first dissolved in formic acid at room temperature (~20mg PA6+2wt.-%CNT in 40ml formic acid). Next, the solution is sonicated for 2hours in a Bioblock Scientific type T700 (35kHz). The solution is next filtrated using the filtration device under 4.8 bars pressure at room temperature. . The suspension is next rinsed with either 80 ml solvent (PA6+2%CNT (2rinses)) or 400ml solvent (PA6+2%CNT (10rinses)). In both cases, 80ml formic acid is poured in the device of filtration under pressure and

no pressure is applied for 15min. Next, a pressure of 1 bar is applied to ensure a slow filtration. For PA6+2%CNT (10rinses), these operations are repeated 5 times. After rinsing, the aluminium oxide membrane is rinsed with demineralised water. It is next dried on a hot plate at 80°C for 1 night and then in a vacuum oven at 50°C under vacuum.

A solution of pure PA6 in formic acid (~20mg PA6 in 40ml formic acid) is also filtrated on the aluminium membrane. The filtration is performed under 4.8 bars. The membrane is next rinsed with 400 ml solvent without pressure to ensure a quite low rinsing. The membrane is next rinsed with demineralised water and dried on a hot plate at 80°C overnight.

The PA12+2wt.-%CNT composite is dissolved in m-cresol at room temperature (~25mg in 40ml m-cresol). The solution is next sonicated for 2hours. The solution is next filtrated using the device of filtration under pressure at 4.8 bars at room temperature. The membrane is next rinsed with either 80 ml solvent (PA12+2%CNT (2rinses)) or 400ml solvent (PA12+2%CNT (10rinses)) under 4.8 bars. After rinsing, the aluminium oxide membrane is dried on a hot plate at 80°C for 1 night and then in a vacuum oven at 50°C under vacuum.

A solution of pure PA12 in m-cresol (~20mg PA12 in 40ml m-cresol) is also filtrated on the aluminium membrane under 4.8 bars. The membrane is next rinsed with 400 ml solvent under 1 bar to ensure slow filtration. The membrane is next rinsed with demineralised water and dried on a hot plate at 80°C overnight.

4.2 Thermogravimetry Analysis (TGA)

Thermogravimetry measurements are performed with the help of a Mettler Toledo TGA/SDTA 851e under dry air with a flow rate of 50 ml/min. Samples are heated at 10 K/min and the relative mass loss of the samples is recorded from 298.15 to 1273.15 K.

4.3 Decantation tests

The nanocomposites PA6+2wt.-%CNT and PA12+2wt.-%CNT are dissolved in m-cresol (20mg in 40ml) at room temperature. For the comparison, as produced CNT are milled during 30 minutes with the help of a vibrating mill (Perkin Elmer Vibrating mill (220V, 50Hz)) with a stainless steel capsule set. These CNT are next dispersed in m-cresol (0.4mg in 40ml) at room temperature. All the suspensions are next sonicated (Bioblock Scientific type T700 (35kHz)) during 2h in m-cresol, followed by centrifugation during

different times. For the sonication, solutions of polymers and carbon nanotubes are poured in 2.0 ml Eppendorf Safe Lock Tubes and then centrifuged at 13400 rpm using a Mini-Spin Eppendorf centrifuge.

The stability of PA6+2wt.-%GNP is also studied. PA6+GNP is dissolved in m-cresol at room temperature. In parallel, GNP are dispersed in m-cresol. The suspensions are then sonicated during 2h, followed by centrifugation.

APPENDIX 2:

SURFACE ENERGY OF CNT

Only very few data concerning the surface tension and polarity of CNT can be found in literature. Accurate measurement of the surface tension of nanoparticles is indeed extremely complicated. This value depends on many factors such as sample size, microstructure, surface functionalization, and even measuring methods [13-15]. For carbon materials, some general statements are however widely accepted [13,16-18]:

- graphitization treatments remove polar functions from the CNT walls and thus decrease the polar contribution of the surface tension γ_s^p
- Graphitic planes exhibit lower surface tension γ_s than other sites such as amorphous carbon, crystallite edges and cavities
- Integrated microstructures and large sizes of crystalline grains lead to low γ_s value

Barber et al. [19] have measured a total surface tension of 27.8 mJ m^{-2} with dispersive and polar components respectively equal to 17.6 mJ m^{-2} and 10.2 mJ m^{-2} .

Nuriel et al. [20] have found a total surface energy of 45.3 mJ m^{-2} with dispersive and polar components of respectively 18.4 mJ m^{-2} and 26.9 mJ m^{-2} . Their conclusion is however that the polar component should actually be lower than the measured values.

Zeng et al. [13] have assumed that the surface tension of graphitized CNT approaches the one of graphite powders due to similar graphitic microstructures. The total surface energy is thus 23.6 mJ/m^2 and the polarity is 0.1 ($\gamma_s^p = 1.8 \text{ mJ/m}^2, \gamma_s^d = 21.8 \text{ mJ/m}^2$) [21].

Zhang et al. [22] have measured a dispersive component of the surface free energy of about 120 mJ m^{-2} for purified CNT at 315.2 K by inverse gas chromatography.

Cho et al. [23] have measured a total surface free energy of untreated CNT of 72.9 mJ/m^2 ($\gamma_s^p = 57.44 \text{ mJ/m}^2$, $\gamma_s^d = 15.44 \text{ mJ/m}^2$). Here also the polar part of the surface tension is very high compared to what should be expected for untreated CNT.

Koysuren et al. [24] have measured the surface energy of the same CNT as those used here using contact angle measurements. The CNT are pressed as disks under 150 bar gauge pressure and contact angles probe liquids are determined from the pressed surfaces. The total surface energy $\gamma_s = 46.14 \text{ mJ/m}^2$, London dispersive component $\gamma_s^{LW} = 35.67 \text{ mJ/m}^2$, and acid/base component $\gamma_s^{AB} = 10.47 \text{ mJ/m}^2$ with $\gamma_s^A = 2.17 \text{ mJ/m}^2$ and $\gamma_s^B = 12.62 \text{ mJ/m}^2$ are determined.

Stöckelhuber et al. [25] have measured the surface energy of the same CNT as those used in the present study using the Wilhemy method. The CNT are fixed on a double-face adhesive tape and the advancing and receding contact angles were measured. By an arithmetic mean, a mean contact angle can also be evaluated. The surface energy values are reported in Table 9.

Table 10 – Surface energy values reported from [25]

Contact angle	Total surface energy, γ mJ m^{-2}	Dispersive surface energy, γ^d mJ m^{-2}	Polar surface energy, γ^p mJ m^{-2}	Polarity %
Advancing	23.5	23.5	0	0
Receding	31.7	29.9	1.7	5.5
Mean	30.9	30.9	0	0.1

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