Novel family of broadband nanocomposite microwave absorbers with carbon nanotubes in solid polymer films

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Abstract—**Nanocomposites absorbers with carbon nanotubes (CNTs) in solid polymer films are proposed for high EMI absorption performances. These conductive films exhibit a low permittivity at microwaves, which means a low reflection, with a high absorption capacity. Compared with usual solution based on foamed conductive composites, we indeed show that solid polymer films with two phases matrix and carbon nanotubes charges can be a great alternative to these foams. The two phases considered are polypropylene (PP) and poly[styrene-b-(ethylene-alt-propylene)-b-styrene] (SEPS) copolymer. The electrical conductivity, the permittivity and EMI absorption are correlated with the quality of the dispersion. As a result of the low and constant permittivity of the obtained composite, the absorption performances are not limited by reflection mechanisms but fully controlled by the level of conductivity, fixed by the dispersion and weight content in CNTs.**

Keywords— *microwave absorbers, nanocomposites, polymer films*

I. Introduction

Due to the generalization of electronic devices in most human technologies and the growth of wireless communications and radar detection, electromagnetic interference (EMI) shielding has become essential for keeping the external environment unpolluted from potential radiations as well as for proper operation of the electronic devices. For stealth applications related to radar technology, the absorption of EMI can be required, leading to the concept of Radar Absorbing Materials (RAMs). Thanks to the formation of a percolating network, a relatively low amount of Carbon based fillers such as carbon nanofibres and carbon nanotubes (CNT) dispersed in polymer matrices, typically smaller than 1-2%, is sufficient to raise the electrical conductivity of the insulating polymer in the range of 1 S/m. However, this effect goes hand in hand with the increase of the relative permittivity of the material promoting EM wave reflections, undesirable for RAMs. Decreasing the permittivity of materials can be achieved by foaming [1,2,3,4,5]. Electrical EMI absorption is thus an important and useful property of several carbonated composites, especially for carbon nanotubes or graphene composites. In this article, we characterize nanocomposite polypropylene (PP)/ Poly[styrene-b-(ethylene-alt-propylene)-b-styrene] (SEPS) /CNT samples over the 0.01Hz to 67 GHz large range of frequencies. The relative dielectric constant, the electrical conductivity and the absorption are determined from two different methods of measurements with different models and treatments for the measurement's results. We demonstrate over this frequency range that the electrical conductivity follows a power law associated to electrical percolation and assesses the quality of the dispersion of CNTs inside the polymer film. We also show than the EMI absorption is highly correlated to the electrical conductivity behavior, thanks to a low and constant permittivity. It induces a low reflection, as was observed previously in foamed polymer carbon nanotubes composites [2]. Indeed, the inclusion of conductive loads inside insulating matrix results in an increase of conductivity and dielectric constant as well. To decrease the latter parameter while preserving the conductivity, foams are used because the air presence in the material decrease the permittivity of the bulk. In this paper, we demonstrate that we now can obtain the same result with solid PP/SEPS polymer films loaded with low weight loadings of carbon nanotubes.

II. Experimental part

A. Sample process

The samples consist in a polymer polypropylene (PP) matrix with 2% wt. of carbon nanotubes (CNT) dispersed inside. Poly[styrene-b-(ethylene-alt-propylene)-b-styrene] (SEPS) copolymer is added to the melt and improves the dispersion of CNTs. A sample combining PP 98 % wt with CNT 2%wt, and four samples with different composition in PP/SEPS/CNT: 93/5/2, 90/8/2, 68/30/2, and 50/48/2 respectively, were prepared. The process consists in a blending, following by extrusion, with a twin-screw mini-compounder (DSM Microextruder 15cm^3). The conditions are 220°C, 250 rpm and 10 minutes compounding. The samples are molded by compression at 190°C, under 10 tons, for 1 or 10 minutes (annealing time).

B. Low frequency measurements – from 0.01 Hz to 1 MHz

At low frequencies, the Novocontrol Alpha-A High Performance Frequency Analyser with a Agilent Dielectric Test Fixture is used (Fig. 1a). The samples are placed between two electrodes and the measurement gives the both resistance and capacitance, using a parallel equivalent circuit for modeling the sample behavior (Fig. 1a).

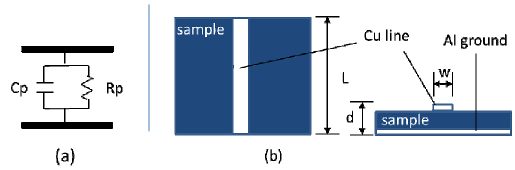

Fig. 1. Experimental setups for nanocomposite characterisation (a) Agilent Dielectric Test Fixture. and associated equivalent parallel Cp/Rp circuit (b) topology for microstrip measurements.

The extraction of the permittivity defined as

$$\varepsilon_{eff} = \varepsilon_r - j\sigma / \omega\varepsilon_o \qquad (1)$$

where ω is the angular frequency and ε_o the vacuum permittivity, is obtained according to the equations:

$$C = \varepsilon_r \,.\, \varepsilon_0 \, A/\, d \qquad (2)$$

where C is the capacitance, εr is the relative permittivity of the sample under scope, *A* is the sample's surface and *d* the sample's thickness.

$$R = 1/\sigma \,.\, d/A \qquad (3)$$

where R is the resistance and σ is the electrical conductivity of the sample.

This type of measurement gives very accurate and very reproducible results for flexible samples in the 0.01 Hz-1MHz range of frequencies.

C. High frequency measurement – from 1 GHz to 67 GHz

For higher frequencies, a Vector Network Analyzer PNA X 67 GHz Model N5247A from Agilent is used with a Anritsu Model 3680V test fixture. From the measurements of S-parameters performed on microstrip lines deposited on the polymer samples under investigation (Fig. 1b), according to the method described in [3], the electrical conductivity and the permittivity are extracted over the frequency range [1 GHz- 67 GHz] using the chain matrix formalism detailed in [2]. In order to remove the influence of the air around the line and extract the actual permittivity ε_r of the polymer film, the following inversion formula is used [7]:

$$\varepsilon_r = 2\,(\varepsilon_{line} - 1) / \left(1 + 1/\sqrt{1 + 10d/w}\right) \qquad (4)$$

where ε_{line} is the effective permittivity of the microstrip line as extracted from S-parameters measurements [7], *d* is the thickness of the sample and *w* the width of the microstrip, as shown in Fig.1b. The range of validity for formula (4) is 10*d* << *w*, which is the case for all samples considered in this paper.

By using this treatment, we can notice a difference in the result as shown in Figure 2. The magenta curves show the extracted parameter with surrounding air contribution, and the blue curves the polymer parameters free from air influence, after inversion using formula (4).

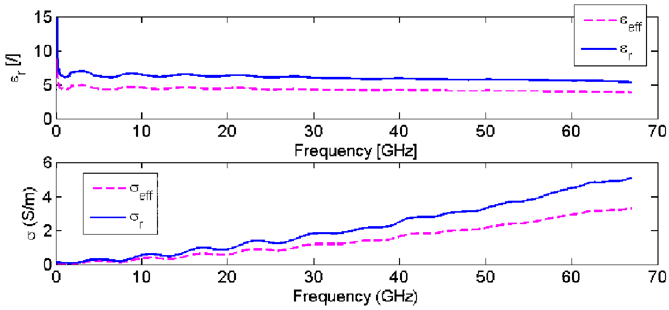

Fig. 2. Dielectric constant and electrical conductivity for PP/SEPS/CNT 93/05/2 samples versus frequency, with air correction (magenta curve) and without correction (blue curve).

D. Extraction of absorption at all frequencies

As extensively derived in [5], the absorption capability of a material slab of thickness *t* can be expressed using its (complex) permittivity (1) combining the electrical conductivity and relative dielectric constant. The reflection coefficient Γ at input interface of the slab and the transmission factor T over slab thickness *t* are defined respectively as:

$$\Gamma = \left(\sqrt{\varepsilon_{eff}} - 1\right) / \left(\sqrt{\varepsilon_{eff}} + 1\right) \qquad (5)$$

$$T = \exp(-j\omega t \sqrt{\varepsilon_{eff}} / c_o) \qquad (6)$$

while the absorption index is given by :

$$A = 1 - \left|\frac{\Gamma\left(T^2 - 1\right)}{1 - \Gamma^2 T^2}\right|^2 - \left|\frac{T\left(1 - \Gamma^2\right)}{1 - \Gamma^2 T^2}\right|^2 \qquad (7)$$

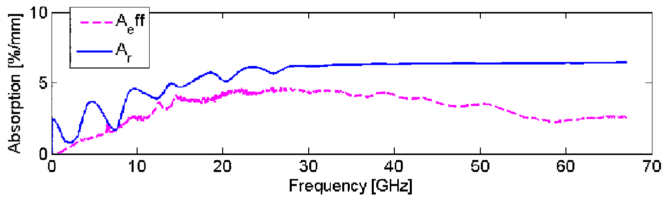

Fig. 3. Absorption in %/mm versus frequency for PP/SEPS/CNT 93/05/2 samples, with air lost correction (magenta curve) and without correction (blue curve).

The absorption index is defined as the ratio of power absorbed inside the slab to the incoming source power. It can be further expressed in percent and normalized to the thickness of the slab, as represented in Fig. 3, using effective permittivity with air contribution (magenta) or without (blue). An important preliminary observation is that despite the increase of dielectric constant observed at Fig. 2 when bulk polymer substrate is considered, the corresponding absorption index increases as well, accordingly with the conductivity, proving that dissipative losses inside nanocomposite dominate over reflection at its interfaces with air, making such polymer excellent candidates for microwave absorbers.

III. RESULTS

In this section, the measurements for the low and high frequency ranges are compared for the nanocomposite polymer samples processed in Section II.A.

A. Broadband dielectric constant

For measurements on each sample, the value of the dielectric constant stays close to its low frequency value over the whole range of frequencies. The following table gives some quasi-static values of dielectric constant for the various samples.

TABLE I. QUASI-STATIC VALUE FOR THE DIELECTRIC CONSTANT, DEPENDING OF THE ANNEALING TIME

	Permittivity	
	1 min annealing	***10 min annealing***
PP/CNT 98/2	3.5	4.5
SEPS/CNT 98/2	4.2	4
PP/SEPS/CNT 50/48/2	6	5
PP/SEPS/CNT 68/30/2	3.6	3.9

B. Correlation between the electrical RF conductivity and the EMI absorption behavior

Figure 4 shows the conductivity and the absorption index per mm for the sample PP 98 % wt with CNT 2%wt, and the 4 samples PP/SEPS/CNT. The first observation is the nice continuity for the results at low and high frequencies, which means that the combination of the two methodologies is efficient for a broadband analysis of thin polymer conductive nanocomposites. Indeed, a power law behavior describes conductivity versus frequency behavior in double logarithmic scale. The dependence is linear in the upper range of the frequency spectrum, while at very low frequencies the conductivity shows a nearly constant (or "plateau") behavior versus frequency, denoting the existence of a percolating conductive network [6], correlated to TEM micrography in Section IV. The second observation is the high correlation between the electrical conductivity and the absorption rate behavior, thanks to a constant and low dielectric constant. This means that a good control of this conductivity allows to tune the absorption performances of these samples.

IV. NANOCOMPOSITE OPTIMIZATION

From the electrical measurements and the TEM images (characterization of the sample at the microscale), we can compare the dispersion of the CNT load inside the matrix to the electrical behavior (depending of the annealing time used for the process) in order to identify the best candidates for broadband EMI absorption.

A. Dispersion of CNT in the composite

The annealing time during process influences significantly the CNT dispersion: its increase improves the dispersion. However, since a very high annealing time results in a high rate of damaged CNT inside the matrix, we restrict the study to 1 min and 10 min annealing times.

The TEM images shown in Figure 5 give us some information about the matrix composition and local dispersion of 2% wt. CNTs inside, before annealing. Fig. 5(a) shows the inclusion of 10% wt of SEPS inside the PP (90% wt) polymer.

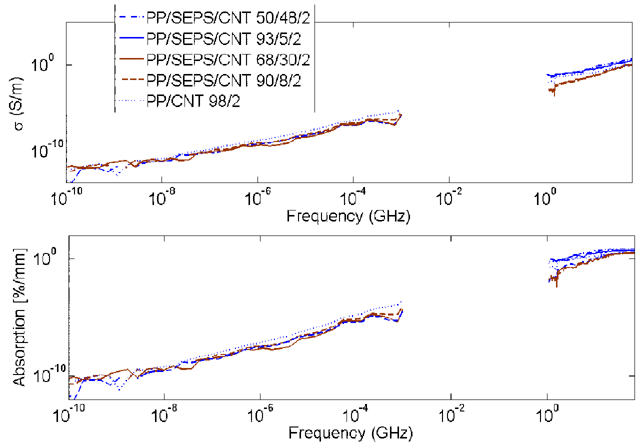

Fig. 4. Conductivity and EMI absorption index (per mm) versus frequency, for samples PP/CNT 98/2, PP/SEPS/CNT 93/5/2, PP/SEPS/CNT 90/8/2, PP/SEPS/CNT 68/30/2, PP/SEPS/CNT 50/48/2.

Figure 5(b) and 5(c) show 2 %wt of CNT dispersed inside 98% wt of PP and of SEPS respectively. We can observe a good dispersion inside SEPS and a poor dispersion in PP. For 10 minutes annealing, we increase the dispersion of the CNT load inside PP and have almost the same dispersion for SEPS sample. This is assessed by the corresponding increase in conductivity observed in Fig. 6, being much higher for the PP/CNT sample than for the SEPS/CNT sample: the relative increase is around 44% for the PP/CNT 98/2 sample and around 6% of the SEPS/CNT 98/2 sample. Finally Fig. 5(d) shows the dispersion of 2%wt CNT in PP/SEPS/CNT 50/48/2 sample: it is significantly better in this composite than in the PP/CNT composite. Accordingly, the highest conductivity level is obtained for the sample PP/SEPS/CNT 93/5/2 composite, for 10 min annealing time as well.

B. Behavior of the EMI absorption, permittivity and electrical conductivity at high frequencies

Figure 7 reveals a similar tendency for the dielectric constant, the electrical conductivity and the absorption index: better is the dispersion, higher is the extracted value for each parameter, for 1 min and 10 min annealing time. We observe absorption index per mm in the 2 to 8 %/mm range. This is superior to the absorption level observed for foamed carbon nanotubes composites with 2wt% content. Indeed a 30 mm thick sample was required to obtain 40dB shielding and -5dB reflectivity, corresponding equivalently to less than 50% of power absorbed in the sample [2]. With the new composite proposed in this paper, only a thickness of 5 mm is required to achieve the same absorption, meaning that one centimeter of polymer coating is sufficient to achieve total absorption, while foamed samples as presented in [2] would require 6 cm. In the former foamed cases, the polymer matrix contains air phase (bubbles) which lower the dielectric constant. In the present case, one of the polymers phases acts as the air phase in the foam. The great advantage for the nanocomposites presented in this paper is the perfect control and easiness of the fabrication, since no foaming process is required, and the dramatic size reduction at fixed CNT content. This novel family of broadband nanocomposite absorbers is useful for systems which need composite materials without air inside (as in some spatial applications). Additional expected advantages are better thermal properties for these materials than in foamed carbon nanotubes composite for the same EMI properties.

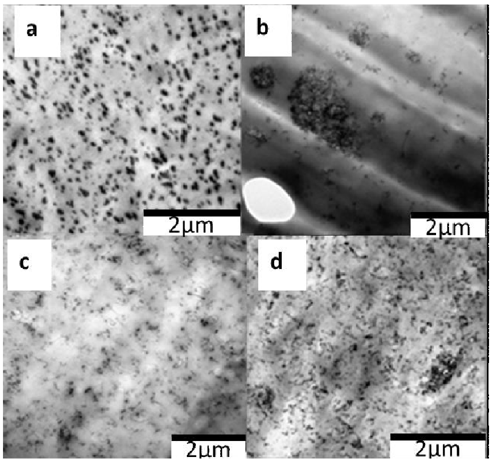

Fig. 5. TEM images of the processed samples (a) PP/SEPS 90/10 (b) PP/CNT 98/2; (c) SEPS/CNT 98/2; (d) PP/SEPS/CNT 50/48/2

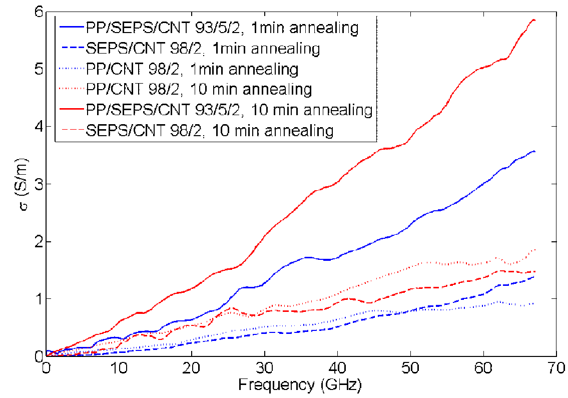

Fig. 6. Conductivity versus frequency for the PP/CNT 98/2, SEPS/CNT 98/2 and PP/SEPS/CNT 93/5/2 samples, with 1 min and 10 min annealing time.

V. Conclusion

We have discussed the dispersion of CNTs load inside polypropylene (PP)/ Poly[styrene-b-(ethylene-alt-propylene)-b-styrene] (SEPS) the matrix and the electrical parameters behaviors. The annealing time is an important process parameter which influences significantly the CNT dispersion. The particular composition of the polymer matrix reduces the dielectric constant of the samples, which, together with a efficient dispersion of CNTs, induces a high absorption index per mm, superior to that usually observed for foamed samples. We have several degrees of freedom to control the electrical parameters: the matrix composition and the CNT % wt load. Future investigation of impact of CNT load in PP/SEPS matrices will further optimize the absorption performances of the nanocomposites.

This novel family of broadband nanocomposites absorbers can be a good solution for aerospace applications, which would require the absence of air in material while preserving high EMI absorption and low reflection. The main advantages of the nanocomposites presented in this paper are the perfect control and easiness of the fabrication, since no foaming process is required, and the dramatic size reduction at fixed CNT content.

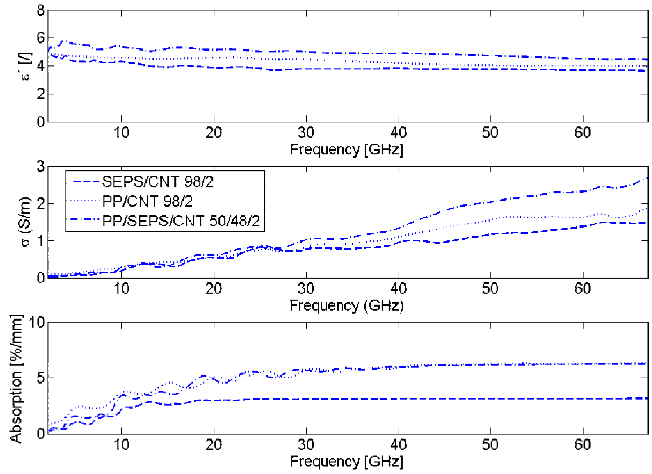

Fig. 7. Permittivity, electrical conductivity and absorption depending of the frequencies for 10 min annealing.

Acknowledgment

The support of Pascale Lipnick for obtaining TEM images of PP/SEPS polymers and of Pascal Simon for electromagnetic experiments are gratefully acknowledged. The authors are also grateful to Isabel Molenberg for fruitful discussions and to the National Fund for Scientific Research (F.R.S.-FNRS) for financial support.

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