

Effect of Diblock Copolymer Surfactant on the Microstructure and EM Properties of CNT Nanocomposites

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Received 28 April 2010; accepted 16 December 2010

DOI 10.1002/app.33993

Published online 18 April 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Carbon nanotubes (CNTs) were chosen due to their excellent electrical properties. As delivered, CNTs are highly agglomerated, and to exploit their high aspect ratio is then necessary to disagglomerate them as much as possible. A diblock copolymer surfactant was used to aid CNT disagglomeration. Disagglomeration in solvent was assessed by TEM, whereas composite microstructure was observed by scanning electron microscopy. X-band waveguide measurements were carried out to assess complex permittivity and absorbing performance. On a

same weight percent of filler basis, samples produced with the aid of surfactant show higher real permittivity than samples produced without. An equivalent circuit analogy is suggested to explain the results and relates composite microstructure with macroscopic permittivity. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 35–42, 2011

Key words: dielectric properties; carbon nanotube; nanocomposites; surfactants

INTRODUCTION

The possibility of combining the ease of manufacturing, flexibility of shapes, and application, low density and low cost with electric conductivity make filled polymers very attractive as a basis to produce antistatic coatings,^{1,2} smart materials,^{3,4} or microwave absorbing materials.^{5–7} Carbon nanotubes (CNT) with their high conductivity and rod-like, high aspect ratio shape are quickly replacing more traditional carbonaceous fillers, such as carbon black, leading to high efficiency and thus lower filler content,^{8–10} resulting in advantages such as ease of manufacturing and potentially thin-walled structures. Permittivity is one of the most important parameters when designing electromagnetic (EM) absorbing materials; other important properties are conductivity, permeability, material thickness, and wave frequency.^{11,12} Dielectrical properties of filled polymer composite are affected by the intrinsic features of the filler such as size, conductivity, morphology,^{13,14} affinity with the matrix,¹⁵ and dispersion.^{16,17} To our knowledge, the effect of composite microstructure on resulting macroscopic EM properties has been

reported for frequencies up to 1 MHz.^{17,18} On the other hand, the use of such materials at microwaves, and particularly in the X-band, is reflected in the variety of engineering applications from synthetic aperture radar for remote sensing,^{19,20} compact accelerators for medical applications,^{21–23} industrial nondestructive testing,²⁴ to television picture transmission, and telephone microwave relay systems.²⁵ Articles that deal with dielectric properties in X-Band (8.2–12.4 GHz) frequently do not usually relate dispersion with macroscopic dielectric properties or EM performances.²⁶ Currently, it is not still possible to take full advantage of incorporation of CNT due to their agglomeration and difficulty in their dispersion in polymer matrices. CNT produced by carbon vapor deposition reduce such problems, being produced in forests, but CNT still often result in highly tangled forms due to strong van der Waals interaction between them.²⁷ Thus, it is fundamental to take advantage of their primary particle size and anisotropy, to separate these bundles into their constituent CNT.¹⁶ To this end, many techniques have been used from ball milling²⁸ to mechanical stirring,¹⁸ sonication,^{16,29} chemical doping,^{29,30} coagulation, or precipitation.^{31,32} These methods greatly vary in complexity and results achieved, so that it is not really possible to state the most efficient one.

In this context, in this article, disagglomeration was attempted using a commercial grade of surfactant, as the best compromise between time, cost,

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complexity, and results achieved. The surfactant was used in a single-step process that can be readily integrated into the overall composite processing. Surfactants act by coating the CNT with molecules, which can induce repulsion that counterbalances strong van der Waals attraction. Their structure is composed by lyophobic (solvent-repelling) and lyophilic (solvent-attracting) blocks. The lyophobic part adsorbs onto the surfaces of CNT, whereas the lyophilic is swollen by the solution. The repulsion among the lyophilic blocks overcomes the van der Waals attractive forces between CNT, so the CNT are kept separated.^{33,34} The commercial diblock copolymer used in this work has previously been used as a surfactant in CNT application with good results by Zhao.³⁵ Surface resistivity measurements seem to indicate that percolation was not greatly influenced by its use, as reported in Sluzarenko.³⁴ In this research, EM properties were measured using the waveguide method in the X-band (8.2–12.4 GHz), whereas CNT dispersion was judged by SEM analysis on cryogenic fractured surfaces. A link between EM properties and CNT dispersion was then suggested.

EXPERIMENTAL

Materials and fabrication procedure

The multiwall CNT used in this study, Nanocyl 3150, have an average diameter of 9 nm and an average length of less than 1 μm , with a purity greater than 95 wt %, and short and thin CNTs were chosen as they are more mobile during dispersion than longer CNT.¹⁷ The resin used is DGEGBA epoxy (CTS s.r.l.), with a very low viscosity that assisted material processing; the hardener is isophoronediamine (CTS s.r.l.). A diblock copolymer DisperBYK2150 (BYK Chemie) was used as surfactant, and the ratio used is 0.6 to the weight of the filler. The solvent used in the dispersion was absolute ethanol, both because it is reported to be fully compatible with the surfactant^{33,35} and for its low boiling point, leading to quick evaporation, as described in the sample preparation methodology below. Samples with CNT content of 0.25, 0.5, 0.75, 1, and 1.5 wt % were produced (named SU-X; X = filler weight percent). As a reference, CNT samples with the same filler content were produced without the addition of surfactant (named NT-X). Neat resin (NT-0) and resin with the addition of surfactant (SU-0) samples were also produced to verify if the surfactant has any effect on the dielectric properties of the resulting composite. The manufacturing process can be summarized as follows: CNT and surfactant (if used) were weighed, solvent was added to obtain a ratio of 1 mL of ethanol to 1 mg of CNT and sonicated

1 h using a Sonics VC 750 ultrasonic probe, and ice was used to prevent heating of the suspension. Afterward resin was added, and the dispersion is stirred using a magnetic stirrer. When it was determined by weight that all the solvent had evaporated, hardener was added and thoroughly mixed. Materials were then cast into conventional X-band waveguide sample holder (spacers with a $10.11 \times 22.9 \times 4 \text{ mm}^3$ cavity), for EM measurements and cured at 60°C for 24 h.

Samples with 0 wt % of filler were produced following the method described above using the same quantity of solvent and surfactant (in the case of SU-0 sample) used in 0.75 wt % samples.

Characterization

Surfactant effectiveness in disentangling the CNT, as well as the influence of the sonication process were first evaluated by TEM (Hitachi H7500), carried out directly on CNT dispersions in ethanol. Then the stability of the dispersions was checked in time by visual inspection of precipitation times. CNT dispersion in the final cured composites was estimated by FEG-SEM analysis (LEO Supra 1530) of surfaces obtained by fracturing the samples in liquid nitrogen. Dielectric properties were measured by means of the waveguide method in the X-band using a Vector Network Analyzer (Anritsu 37247D). Such measurement offers the advantage of only requiring small samples, and the results are accurate and reproducible, whereas its main drawback is the requirement of exacting tolerances and perfect flat surfaces to avoid higher order modes reflections. All test were carried out at 25°C. Scattering parameters (namely S_{11} and S_{21})¹² were measured, moreover S_{11} measure was repeated with the configuration of metal-backed samples. These values were used as input to obtain permittivity by minimizing an error function between the measured and the numerically calculated S -complex parameters with respect to real (ϵ') and complex (ϵ'') permittivity.^{36,37} According to Knott,³⁶ real permittivity obtained using the waveguide method has a very good uncertainty of about $\pm 2\%$, whereas ϵ'' presents a wider uncertainty (about 5–7%), a more precise evaluation of ϵ'' can be performed by resonant cavity procedures that however give data at few fixed frequencies and do not allow to see the performance in a complete band as in this article. The absorption loss of the composites at different thicknesses was then simulated, using the same algorithm back to front, and in this case, ϵ' and ϵ'' from the previous step were used as input, and the absorption performances are reported for metal-backed samples.

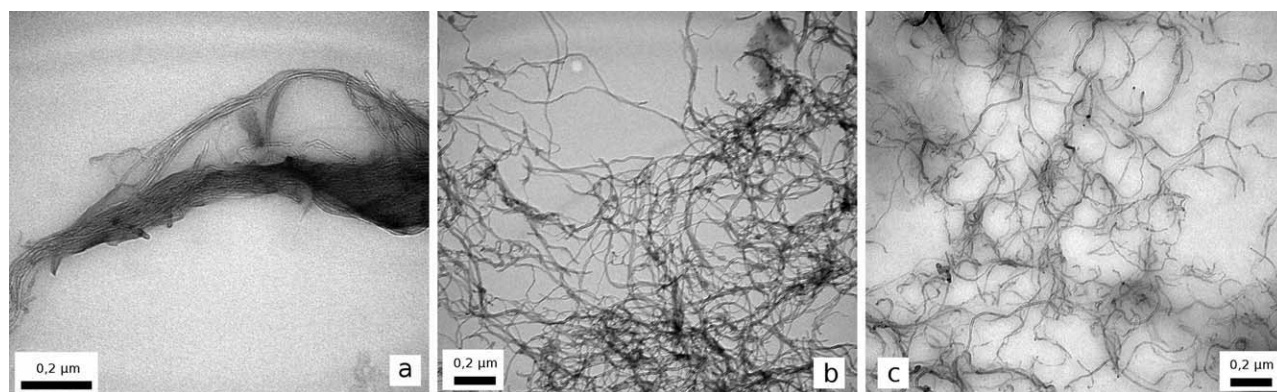


Figure 1 (a) 100-kx magnification TEM of unsonicated Nanocyl 3150 CNT and (b) 70-kx magnification TEM of CNT after 1-h sonication without surfactant and (c) with surfactant.

RESULTS AND DISCUSSION

Dispersion in solvent and in resin

The effect of surfactant and the dispersion process used in sample manufacturing has been evaluated by TEM. Before any treatment, CNTs are tightly bundled in “ropes” Figure 1(a). Figure 1(b) reports a micrograph of the CNT in ethanol, as obtained after 1 h sonication, without the aid of any surfactant (NT samples). CNT ropes are no longer present, although the CNT are still bundled together in aggregates. Figure 1(c) provides evidence of the better dispersion achieved following addition of the surfactant (SU samples), following the above reported procedure. In this latter case, a satisfying dispersion was attained: single nanotubes are visible together, with fragments of CNT, indicating the beginning of their cutting, as a consequence of sonication.

The stability of CNT dispersion in ethanol was checked over time by visual inspection. As shown in Figure 2, the stability of the dispersion without surfactant after 5 days was very poor, because of the presence of CNT bundles that precipitate in a short time. On the contrary, the surfactant-assisted dispersion led to single nanotubes or small agglomerates that enable them to be suspended for a much longer time. This ability to disperse unmodified nanotubes by the use of a commercial, physically blended surfactant makes for an easy process that is readily scalable in a commercial setting.

The quality of CNT dispersion introduced into the epoxy matrices, as cured nanocomposites, was determined by SEM analysis on cryofractured samples and shown in Figure 3 for 0.75 and 1 wt % CNT samples manufactured either without [Fig. 3(a,c)] and with [Fig. 3(b,d)] surfactant. The SEM images were taken at a magnification of 1 kX, to highlight the differences in filler distribution. In these micrographs, light gray areas represent regions with CNT in high concentration, whereas dark gray areas represent the resin alone. The quality of CNT dispersion

can be better assessed in samples with high nanofiller content, such as 0.75 and 1 wt %, where the effect of surfactant is more evident. In NT-type samples, in fact, CNTs are restricted to the well-defined light gray areas that cannot be properly called “agglomerates,” because higher magnifications [Fig. 3(e)] show them not as tightly bundled CNT but as regions with very close and tight three-dimensional net (very similar to what observed in TEM micrographs). In SU samples, instead these light gray CNT regions are more numerous, smaller, and more finely dispersed in the resin, so that at 1 wt % filler

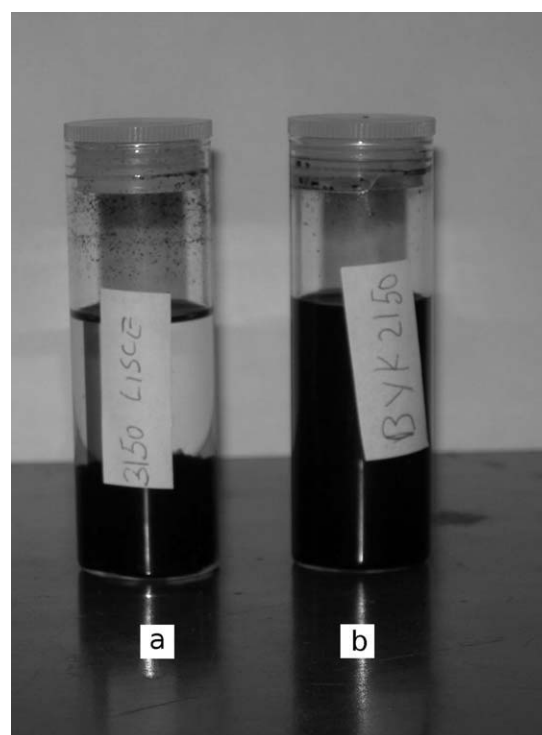


Figure 2 MWCNT precipitation after 5 days (a) without surfactant and (b) with surfactant.

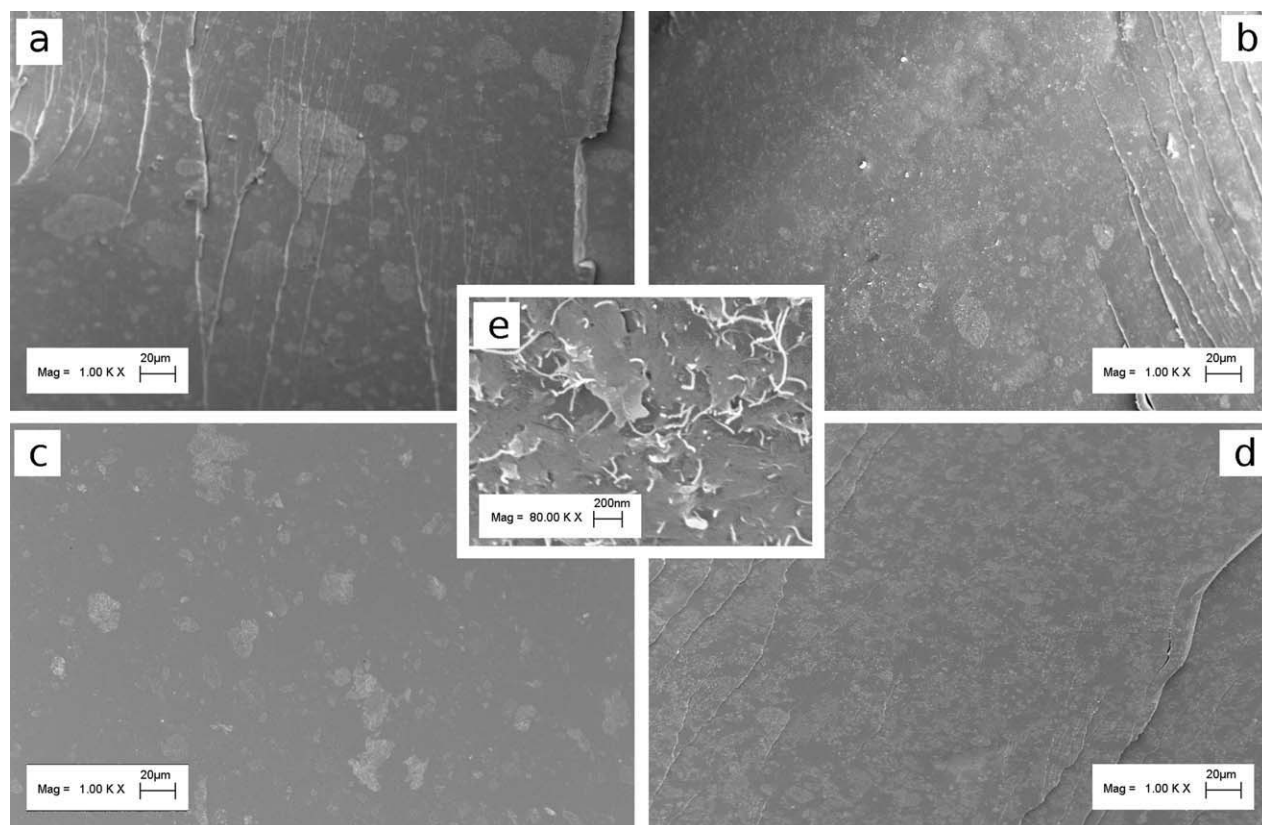


Figure 3 Cryofactured surfaces of 0.75 and 1 wt % CNT samples, with the surfactant (b,d) and without (a,c). Light gray areas are high CNT concentration regions (see inset (e) showing a 80-kx magnification of a gray zone), dark gray areas are resin. The CNT form a three-dimensional net.

concentration, they form a nearly optimal dispersion, forming more of a continuous morphology, compared with the corresponded NT ones, the fibers in the SU samples are spaced far apart.

EM measurements and dielectric properties

Figures 4 and 5, respectively, illustrate the real and imaginary part of permittivity as a function of

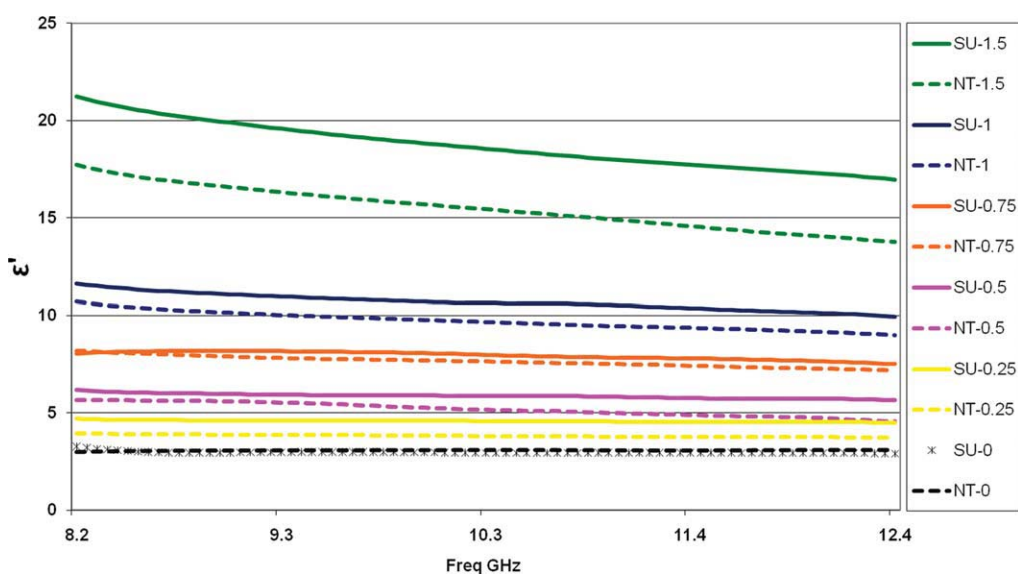


Figure 4 Real part of permittivity as a function of frequency for SU and NT samples at different wt % content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

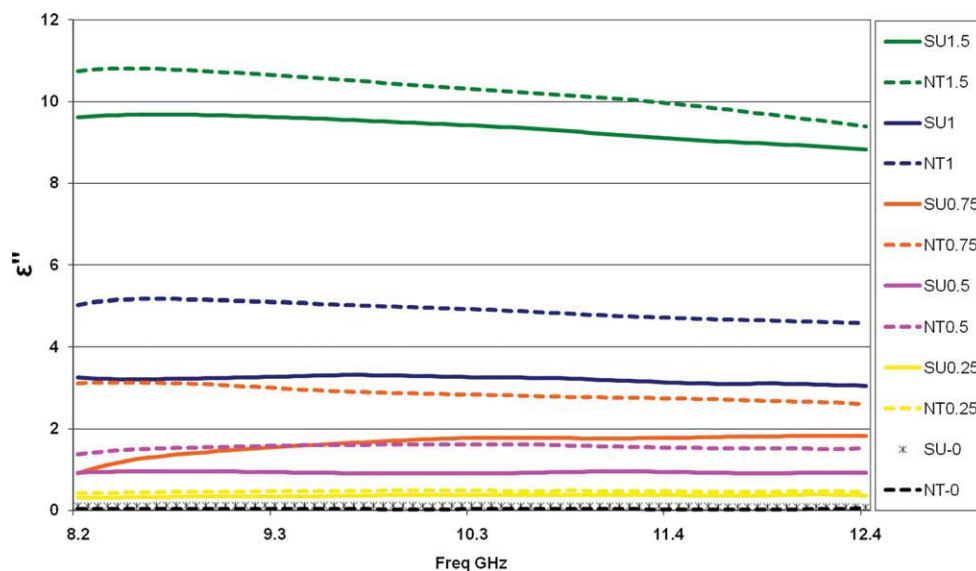


Figure 5 Imaginary part of permittivity as a function of frequency for SU and NT samples at different wt % content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

frequency, whereas Table I lists ϵ' and ϵ'' measured at 10.3 GHz.

It is possible to note that surfactant does not have a significant effect on dielectric properties, and the small effect it has is opposite to the effect of dispersion it contributes to achieve, and it is then possible to affirm that the dielectric properties of NT and SU samples filled with CNT are only affected by dispersion.

On the same weight percent filler basis, samples produced with the surfactant show a higher ϵ' and lower ϵ'' than those found in NT specimens. As a consequence, loss tangent is higher in those samples without surfactant.

These important results can be explained with reference to the different microstructures observed. In previous research using carbon nanofibers,³⁸ as well as in other works dealing with carbonaceous fillers,^{39–41} it has been suggested that the matrix-filler system can be analyzed by means of an equivalent circuit analogy, where the conductive filler is represented with a system of capacitors, separated by an

insulating matrix. The system resistance should, therefore, decrease and the capacitance increase, for increasing filler loadings. In such conditions, ϵ' , the real part of the complex permittivity (ϵ^*) related to the capacity of the material to store energy, is expected to increase, due to an increment of the number of capacitors. Moreover, this number should even increase when, on the same filler percent basis, the filler is better dispersed within the resin, and more equivalent capacitors are produced. This is the case of SU samples where, as testified by SEM micrographs, the CNTs are far better dispersed than in NT ones and, as a consequence, the system of microcapacitors formed in the resin is more efficient, and a higher dielectric constant results. This phenomenon has an increased effect and becomes more evident at increasing filler content, as in the case of 1 wt % samples, where a greater efficiency of dispersion with addition of surfactant is more evident.

In contrast, the complex part of permittivity (ϵ''), takes into account dissipation and conductivity of the medium. Referring to the reported model, ϵ'' is

TABLE I
Real and Imaginary Permittivity Measured at 10.3 GHz, it Possible to Observe that ϵ' and ϵ'' Increases as Filler Load is Increased

Weight % of filler	0 wt %	0.25 wt %	0.5 wt %	0.75 wt %	1 wt %	1.5 wt %
Sample name	NT-0	NT-0.25	NT-0.5	NT-0.75	NT-1	NT-1.5
ϵ'	3.08	3.82	5.18	7.66	9.70	15.52
ϵ''	0.03	0.48	1.62	2.85	4.95	10.34
Sample name	SU-0	SU-0.25	SU-0.5	SU-0.75	SU-1	SU-1.5
ϵ'	2.95	4.59	5.88	8.01	10.64	18.64
ϵ''	0.12	0.38	0.90	1.76	3.27	9.44

It is important to note that on the same filler wt % basis SU samples show higher real permittivity and lower imaginary permittivity than NT samples. NT-0 and SU-0 are not filled with CNT and show the effect of surfactant.

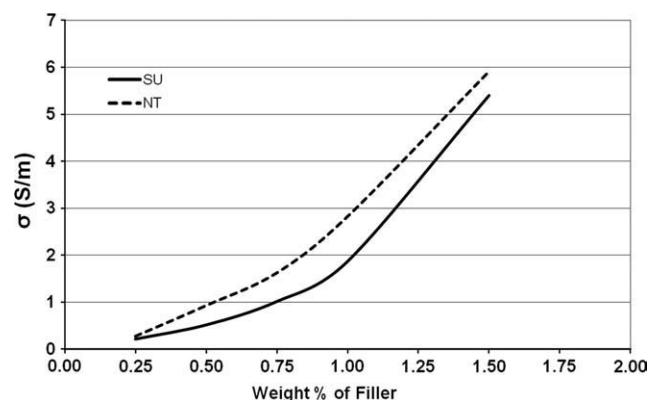


Figure 6 Samples conductivity as calculated using eq 1. It is possible to observe that the change of gradient happens around 1 wt %.

expected to increase with filler content, predominantly because of increment in the number of electrically conductive elements within the matrix. Both SU and NT samples follow this trend. The effect of filler distribution on this parameter, however, is less obvious. SU samples were found to show lower ϵ'' than the corresponding NT ones, suggesting that the use of surfactant leads to less electromagnetically dissipating media. Moreover, regarding the goal of obtaining an EM absorber, it should be recalled that the major mechanism of energy dissipation involved in such systems has been demonstrated to be related to the capacity of the sample to readily dissipate energy, largely through the Joule effect. In fact if a good, but not perfect, disagglomeration of CNT is achieved, a large amount of electrical shortcuts occurs, quickly dissipating the energy. On the other hand, better dispersed CNTs present fewer electrical shortcuts in fact, in the extreme case of an ideal perfect dispersion, and each CNT would be covered by a layer of resin hindering any possible contact between CNT. When a good dispersion is achieved, as in the case of SU samples, the energy is stored inside the CNT (as demonstrated in this work by higher values of real permittivity) and slowly dissipated.

Conductivity of both SU and NT samples (Fig. 6) was evaluated by means of the following formula^{42,43} (eq 1):

$$\sigma = 2\pi f \epsilon_0 \epsilon'' \quad (S/m) \quad (1)$$

Where f is frequency, ϵ_0 and ϵ'' are, respectively, permittivity of free space and imaginary part of permittivity of the medium. Using similar dispersion method, DC conductivity is expected to occur at around 0.5 wt %, ¹⁶ when a satisfactory disaggregation is obtained. The percolation threshold, at 10.3 GHz, as a function of filler concentration (Fig. 6) may be identified to occur between 0.75 and 1 wt %

when the gradient of both of the curves change. In any case, NT samples were again found to be more conductive, coherently with what above reported regarding the formation of branches, which facilitate the formation of conducting paths. Moreover, the results show that microwave conductivity increases almost proportionally to filler content in both NT and SU samples.

EM performance

EM performance was evaluated concurrently with the dielectric measurement, in the S_{11} step of the measurement procedure, on metal backed specimens. Although permittivity is an intrinsic property of the material, EM-absorbing qualities are influenced by external factors such as sample thickness and frequency. As this thickness is very important in terms of final component weight, and therefore practical engineering applications, it was decided to compare the results found for samples of 2.5-mm thickness. As can be seen in Figure 7, in both SU-0.25 and NT-0.25 samples, the quantity of dissipating elements is not sufficient to guarantee dissipation. The increase of lossy elements, that is, in both cases, CNT led to better absorption performance, even if a substantial difference between SU and NT samples was recorded. In fact, comparable absorbing behavior was found in the two types of samples at different filler content. In particular, the best performances were obtained in NT-0.75 and SU-1 samples. In all cases, SU samples were less dissipating than NT ones, as evidenced by the ϵ'' measurements, and therefore, good absorbing performance have to be found in higher filled samples. The better dispersion achieved in SU samples shows decreased wave absorption efficiency due to the aforesaid energy dissipation mechanism that involves the presence of electric shortcuts between the imperfectly separated CNT. Nevertheless, as often occurs in such systems,^{38,44} there is a maximum filler content, above which the system becomes too reflective and absorption ceases. It is not however possible to establish a well-established filler content threshold value to insure good microwave absorption, because it is well known that microwave absorption depends on many different parameters including both material intrinsic properties (conductivity, permittivity, etc.) and extrinsic features as frequency, shape of material, and its thickness, angle of incidence of the wave.³⁶ This means that it is important to tune time to time the correct material composition to match all other parameters so to obtain the desired absorption properties in view of the specific application.

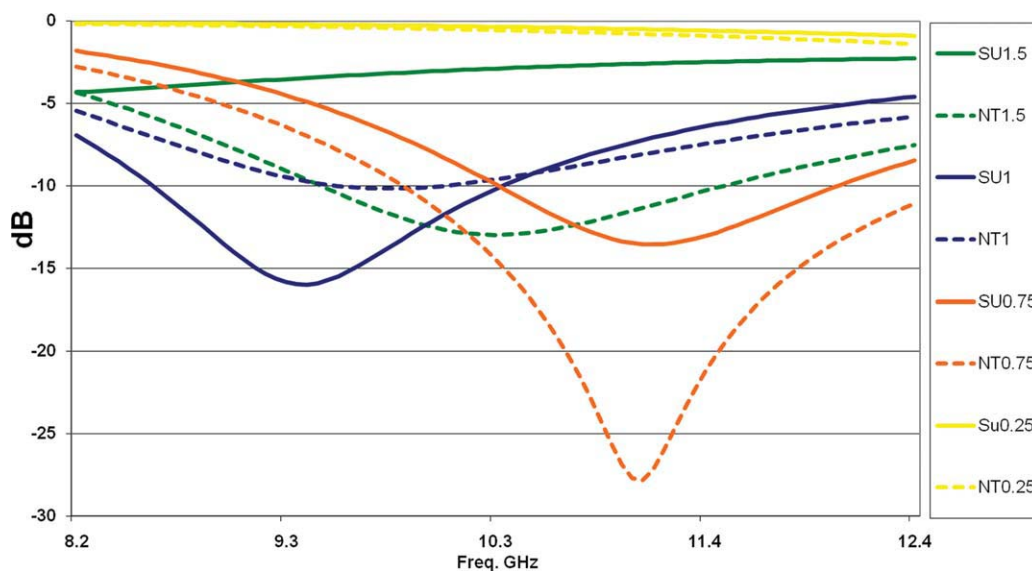


Figure 7 Absorbing performance of 2.5-mm thickness samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

The effect of diblock copolymer surfactant on the dispersion and dielectric/EM properties of CNT-filled epoxy resin has been studied. It was found that the influence of surfactant on the dispersion of CNT achieved in cured composites is significant, resulting in more finely dispersed CNT in the resin. This occurrence influences EM properties, leading to larger ϵ' and smaller ϵ'' . An explanation for this was proposed, considering an equivalent circuit analogy, in which CNT (and/or their aggregates) form a network of minicapacitors, where the presence of more numerous and closer-spaced conductive elements in the resin, as obtained using the surfactant, leads to a more capacitive material. Moreover, in such systems, the interactions among CNT are limited, resulting both in less conductivity (and hence ϵ'') and EM absorbing performance, because the energy cannot be quickly dissipated. Filler content was found to be an important factor in terms of EM absorption, because it was demonstrated that our systems showed an optimum filler quantity below which it is not particularly lossy (due to the reduced presence of conductive elements) and above which conductivity prevails, making the material mostly reflective.

The authors wish to dedicate this work to the memory of Ing. G. Gommellini special thanks are due to CEMIn s.r.l. (Componenti Elettromagnetici Innovativi, Via Della Farnesina 363, 00194 Rome, Italy) for technical support in EM measurements.

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