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Effect of carbon nanofibres dispersion on the microwave absorbing properties of CNF/epoxy composites

F. Nanni [a,b,*], P. Travaglia [a,b], M. Valentini [b]

[a] INSTM- UdR Roma "Tor Vergata" Via della Ricerca Scientifica snc 00133 Rome, Italy
[b] Dept. of Sciences and Chemical Technologies, University of Rome "Tor Vergata" Via della Ricerca Scientifica snc 00133 Rome, Italy

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ABSTRACT

Since mid-twentieth century filled polymers have been largely studied for electromagnetic (e.m.) applications, including wave absorbing materials, showing good promise. A certain knowledge was gained in the field of carbon particles filled polymers, even if there is still a lack of understanding the relationship between material microstructure and macroscopic electromagnetic performance. Moreover, the recent discover of carbon nanofibres and nanotubes, with their potentiality, introduces new field of investigation. In this work carbon nanofibers were used to increase permittivity of neat resin, in order to achieve better absorbing performance in the 8–20 GHz range. Carbon nanofibers were chosen as a way of lowering filler content, while increasing the dielectric properties of the resulting composite. Key factor is the nanofiller dispersion process: in this paper two different dispersion methods were used, both employing an organic solvent that was removed either via evaporation or filtration. The resulting microstructures, composed of well dispersed CNF as well as of microaggregates, lead to materials that, on equal filler content, present different dielectric properties and absorbing performance. Microstructures were analyzed by SEM.

1. Introduction

Electromagnetic absorbers (EMA) are currently gaining much attention especially in the field of microwave frequencies applications. These materials, historically introduced as radar absorbing materials (RAMs) [1], presently are now increasing their importance to prevent electromagnetic interference in wireless communications and electronic toll collection (ETC) systems [2]. Generally the electromagnetic absorbing performance of any material is linked to its intrinsic electromagnetic properties (i.e. conductivity, complex permittivity and permeability) as well as to extrinsic properties such as thickness and working frequencies [3]. Nevertheless, the influence of each parameter on the resulting absorbing performance is not of immediate comprehension, due to the complexity of electromagnetic waves propagation in media, that includes considerations about the impedance matching at material/wave interface as well as dissipation effects inside the medium. It is anyway clear that the mechanism of absorption is related to the possibility of the material to dissipate, as heat, the energy associated to the incident em wave. In this view, the possibilities left to material designers are confined to the ability of changing complex permittivity or permeability. Usually EMAs are made of polymer composite materials, [4,5] chosen due to their intrinsic versatility and ease of production. Adding pure dielectric or magnetic fillers to a polymer matrix is a possible way to change the material electromagnetic properties and performance [6]. Despite many successful experimental testing carried out in this direction [7–9], there is still a lack of knowledge in the comprehension of the mechanism of e.m. absorption in material. An extended study of current available literature bring to conclude that an exhaustive comprehension of these phenomena cannot be regardless of a correlation between material microstructure and em properties [10–12]. This belief is strengthened by the fact that the numerous modelizations proposed till now [13–15] fail in having a general validation, since they generally presuppose a perfect dispersion of the conductive filler in the matrix (conductive particles surrounded by insulating resin), without considering the true material mesostrucutre, which is formed by aggregates and agglomerates. As the mesostructure is closely depended on filler properties [16] and on the manufacturing process (in particular filler dispersion in the resin [17]), in this work the authors present the effect of two different filler dispersion methods on material microstructure and, hence, electromagnetic properties. To this aim microwave absorbing nanocomposite materials with different carbon nanofibres (CNFs) content were prepared and tested. Epoxy resin was chosen as polymer matrix. Moreover, samples microstructure was observed by field emission gun scanning electron

* Corresponding author. Address: Dept. of Sciences and Chemical Technologies, University of Rome "Tor Vergata", Via della Ricerca Scientifica snc 00133 Rome, Italy. Tel.: +39 06 7259 4496; fax: +39 06 7259 4328.
E-mail address: fnanni@ing.uniroma2.it (F. Nanni).

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microscope (FEG-SEM), while the em properties and absorption performance were evaluated by performing wave guide measurements in the X-band (8.2–12.4 GHz). This e.m. band, in fact, is increasing its importance in a variety of engineering applications such as polarimetric radar [18], medical accelerators [19], space radars [20], stealth purposes, etc. Carbon nanofibres (CNFs) were selected as lossy media due to their peculiar electromagnetic properties. Compared to common micrometer conductive fillers, in fact, CNFs present higher aspect ratio and electrical conductivity [21,22] that allow to obtain good em losses at low filler concentration, with a considerable reduction of thickness and weight. In fact, significant changes in composite complex permittivity can be obtained by adding small quantities of CNFs to the matrix. Differently from carbon nanotubes (CNTs) fillers, the use of which has been recently proposed by many authors [23–25], to the best of our knowledge only few data are currently available in literature on CNF-composites e.m. properties at microwave. Moreover, CNFs were chosen due since they are less expensive and more easily processed during composite manufacture than CNT, features that are very attractive when thinking mass production products.

2. Materials and methods

Samples containing different CNFs content (1, 2, 3 and 4 wt%) were prepared following two different dispersion methods. Both techniques implied CNFs dispersion in solvent, followed by its elimination either via evaporation or filtration. Such procedure is necessary to separate the supplied entangled CNFs. Among several possible dispersing techniques, successfully employed for CNT disagglomeration, such as ball milling [26], mechanical stirring [27], sonication [28], coagulation or precipitation [29,30], chemical doping [31], sonication and subsequent solvent elimination was chosen due to its simplicity, easily exploitable to industrial production. In all cases Pyrograph PR-19XT-HHT CNFs (Applied Sciences, Inc.) 30–100 μm long, with average diameter of 150 nm, were used. The first procedure implied the dispersion of CNFs in buthylglicolether (BGE, 1 ml solvent to 7 mg of fibres); the mixture was sonicated for 1 h, then epoxy resin (Araldite Ly554) was added and the mixture continuously stirred at room temperature until BGE evaporation. Finally, hardener (triethyleneammine HY956) was added and mechanically stirred for as long as all the solvent was evaporated. In the second process, CNFs were dispersed in BGE under sonication for 1 h (same solvent/filler ratio as in first procedure), then the solvent was removed via filtration before adding resin and hardener. Solvent removal was checked comparing the initial volume of solvent, with that recovered after filtration. This procedure was chosen in order to reduce processing time (from about 24 h to 1 hour) despite the fact that a less uniform CNFs distribution was expected. In both procedures cure was carried out at 60 °C for 4 h. 4 mm thick conventional X-band samples (22.8 mm large, 10.16 mm high) were prepared and inserted in wave guide flanges (Fig. 1) for e.m. measurements. A list of all manufactured samples is reported in Table 1.

Specimens microstructure was observed by field emission gun scanning electron microscope (FEG-SEM Leo Supra 35) following the suggestions reported in [32], in order to highlight filler dispersion in the resin. Moreover numerous observations were carried out in order to evaluate internal porosity, since this feature can strongly influence permittivity. The presence of porosity, in fact, introduces air, which lower complex permittivity.

Fig. 1. CNF-epoxy composite in wave guide flange.

Table 1
Prepared samples.

	Solvent removal	CNF content (wt%)	Nomenclature
Type 1	Evaporation	1-2-3-4	Type 1–wt% content
Type 2	Filtration	1-2-3-4	Type 2–wt% content

Electromagnetic testing was carried out performing wave guide measurements between 8.2 and 12.4 GHz both in transmission and reflection mode (VNA Anritsu 37247D, waveguide adapter HP X281B, cables Flexo Microwave, Inc.). In this testing procedure the material is placed in a wave guide to completely fill the wave guide transverse cross section and it is illuminated with a TE_{10} mode [33]. From the measured transmission and reflection scattering parameters (S_{11} and S_{21}) is then possible to infer the ε and μ coefficients by minimizing an error function between the measured and the numerically calculated S complex parameters with respect to ε', ε'', $\mu'$and μ''[34,35]. It is important to remark that sample preparation and placing has to be very accurate (i.e. absence of air gap between material under test and wave guide is required) in order to avoid higher order modes.

3. Results and discussion

3.1. Complex permittivity

Real and imaginary parts of ε^* for Type 1 and Type 2 samples are respectively reported in Figs. 2 and 3. In all cases it is evident that an increase of CNF content results in enhanced electromagnetic permittivity at microwaves.

Such logical result has already been found by various authors [36–38] which, moreover, evidenced that when a critical concentration of the conductive filler is reached, a drastic increase of electromagnetic characteristics is observed, which is in turn related to a change in resistivity. Some authors [39], in fact, attribute this behaviour to the onset of percolation, i.e. the formation of a network of conductive inclusion. In this conditions the system becomes semiconductive. We found the critical concentration at which a clear increase of complex permittivity is recorded to be around 4 wt% in Type 1 samples, in agreement with the value found by Fan et al in [36] with CNT in thermoplastic polymers. In Type 2 samples, instead, a visible increase was found only for ε', occurrence that will be discussed in the following. At 4 wt% content, in fact, only in samples prepared using solvent evaporation (sample Type 1-4%) the onset of percolation was achieved, as testified by the sharp increase of ε'' and, hence, conductivity (Fig. 4), since the two parameters are correlated by the [11,40]

$$\sigma = 2\pi f \varepsilon_0 \varepsilon'' \quad (1)$$

The disagreement between ε' and ε'' values found for Type 1-4% and Type 2-4% samples (Fig. 5) has most probably to be related to the different manufacturing methods which, in turn, affect the material microstructures.

In particular, it was observed that samples processed with BGE evaporation present higher complex permittivity. This result cannot be referred to a different degree of porosity of samples, that was found to be not significant (about 1%) and substantially comparable (data obtained from SEM analysis not reported here) in materials processed with the two manufacturing techniques. SEM