Conducting epoxy networks modified with non-covalently functionalized multi-walled carbon nanotube with imidazolium-based ionic liquid

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ABSTRACT: Multi-walled carbon nanotube (MWCNT) was non-covalently functionalized with room-temperature ionic liquid (IL), 1-butyl-3-methyl-imidazolium tetrafluoroborate and blended with epoxy pre-polymer (ER) with the assistance of ultrasonication in the presence of acetone as a diluting medium. The ability of IL in improving the dispersion of MWCNT in epoxy pre-polymer was evidenced by transmission optical microscopy. The corresponding epoxy/MWCNT networks cured with anhydride displayed an increase of the electrical conductivity of around three orders of magnitude with the addition of IL in a proportion of MWCNT/IL = 1:5 mass ratio. The effect of IL on dynamic mechanical properties and thermal conductivity was also evaluated. The improved thermal and electrical properties was attributed to the better dispersion of MWCNT within the epoxy matrix by IL, evidenced by transmission electron microscopy of the ER/MWCNT networks cured with anhydride. Raman spectroscopy was also used to confirm the interaction between MWCNT and IL. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2016, 133, 43976.

INTRODUCTION

Carbon nanotubes (CNT) have received great interest in several fields of polymer science especially nanocomposites, because of their unique mechanical, thermal, and electrical properties and on account of their increased commercially availability thanks to efforts made by some industries to scale-up their production to reduce price. Several CNT-based polymer nanocomposites have been reported in the literature and several books and reviews have been published on this subject.[1–5] Among different polymer matrices, epoxy network is one of the most studied with the aim of improving thermal, mechanical, and electrical properties for enlarging their range of applications in the microelectronic industries, as well as, automotive, aerospace, and so forth. One of the drawbacks which limit their applications is the difficulty in achieving good dispersion of the CNTs in epoxy matrices because of their strong tendency to spontaneously agglomerate as a consequence of the Van der Waals forces and the absence of active site in their surface to promote good filler–matrix adhesion. Several strategies have been developed to attain better CNT dispersability, which are mainly based on

covalent functionalization at the CNT surface, by oxidative processes,[1] followed by the introduction of different reactive groups able to interact with the polymer matrix. Besides involving several chemical reaction steps, such procedures usually create some defects at the CNT surface, which can negatively affect the intrinsic properties of CNTs. Other approaches such as the use of volatile solvents, high shear mixing and ultrasonication, have been adopted for similar purpose.[6–13]

Recently, the so-called non covalent functionalization approach, which uses an appropriate surfactant able to interact with the CNT surface, has been appeared as a promising alternative to avoid the usual damage on the CNT structure.[14–21] In this sense, ionic liquid (IL) has been emerging as a very interesting alternative for the development of CNT-based nanocomposites. ILs are salts constituted by organic cations and organic or inorganic anions, whose hydrophobicity/hydrophilicity can be tuned by choosing appropriate cation and anion.[22–24] Their unique characteristics as low vapor pressure, low melting point (usually lower than 100 °C), thermal and chemical stabilities and good ionic conductivity justify their wide range of applications in several fields of material science. Several researchers have

studied the effectiveness of ionic liquids, especially imidazolium-based ILs, in improving the dispersion of carbon nanotubes. Indeed, by grinding imidazolium-based ionic liquids with carbon nanotubes, a bucky gel is obtained.[25,26] Such bucky gels is constituted by a permanent network as indicated by rheological measurements with exfoliated CNT bundles, which present potential applications for the development of actuators and,[27] electrochemical sensors.[28] The high ability of imidazolium-based ILs in dispersing CNT is attributed to the cation-π interactions between the IL and the CNT surface,[25] and also Van de Waals interactions.[26]

Despite the importance of this theme, very few studies have been addressed on the use of IL in epoxy resin/CNT systems, without employing any chemical approach. Palmese's group have studied the efficiency of 1-ethyl-3-methyl-imidazolium dicyandiamide (emim.DCN) as dispersing agent for the single-walled CNT (SWCNT) in epoxy resin as well as curing agent for the matrix, and observed very low percolation threshold and improved mechanical properties.[29] Maka et al.[30] have studied the curing effect of emim.DCN, trihexyltetradecyl phosphonium dicyandiamide (THTDP.N(CN)$_2$), and trihexyltetradecyl phosphonium–bis-(2,4,4-trimethylpentyl)phosphinate[31] for epoxy resin/MWCNT composite. The effectiveness of the last one phosphonium-based IL as curing agent for epoxy resin has been previously reported by our group.[32] Hameed et al.[33] have employed 3-butyl-1-methyl imidazolium tetrafluoroborate (bmim.BF$_4$) to disperse multi-walled CNT (MWCNT) in epoxy resin and used 4,4′-methylenedianiline for curing agent. The authors have employed only 0.5 wt % of the IL related to the epoxy resin and studied the dispersion effectiveness by small angle X-ray scattering analysis and high resolution scanning electron microscopy. They have also studied the mechanical and dynamic-mechanical properties but no comparative studies involving the composites without IL was described. Moreover, no electrical properties have been evaluated.

Thus, the aim of the present work is at discussing in detail the role of bmim.BF$_4$ ionic liquid as dispersing agent for MWCNT in epoxy system cured with anhydride-type curing agent. Acetone was also employed together with ultrasonication treatment to ensure better dispersion of the filler, before the addition of the hardener. The dispersion efficiency was evaluated by rheology and optical or transmission electron microscopy (TEM). Also the effect of IL on the dynamic mechanical, electric conductivity and thermal conductivity of the corresponding epoxy/MWCNT networks was investigated. For this purpose anhydride was used as the curing agent because it is able to decrease the room temperature viscosity of the system, thus making easier the processability of the dispersions. Moreover, the imidazolium-based ionic liquid (bmim.BF$_4$) was chosen to help the CNT dispersion in epoxy matrix because of the presence of the imidazolium ring, which has been reported to improve the interaction with the surface of the CNT by π-π stacking[34] and/or cation–π interactions.[25,35,36]

EXPERIMENTAL

Materials
MWCNT (NC7000) with average diameter of 9.5 nm, average length 1.5 μm, a carbon purity of 90%, and a surface area 250–300 m^2/g was kindly supplied by Nanocyl (Sambreville, Belgium). Epoxy pre-polymer based on diglycidyl ether of bisphenol A (ER) (EPON 828) (epoxide equivalent = 188–198; viscosity = 11–15 Pa s) was purchased from Shell Chemicals do Brasil. 4-Methyltetrahydrophthalic anhydride (MTHPA) (Aradure HY2123) used as the curing agent was supplied by Huntsmann (São Paulo, Brazil). The ionic liquid—1-butyl-3-methylimidazole tetrafluoroborate (bmim.BF$_4$) was supplied by Sigma-Aldrich (St. Louis, Missouri, USA).

Preparation of the Epoxy/MWCNT Nanocomposites
MWCNT was dispersed in a mixture of epoxy pre-polymer/acetone in a proportion 1:1 by weight under sonication (Branson) at 120 W for 30 min. Then, the acetone was eliminated using reduced pressure and magnetic stirring at 70 °C. After removal of the solvent and degassing the mixture, the curing agent was added to the CNT/epoxy system at an epoxy/curing agent weight ratio of 1:1, and samples were degassed under vacuum before curing at 80 °C for 3h, at 110 °C for 2h, and 130 °C for 1h. For the systems containing IL, the MWCNT was dispersed in different amount of bmim.BF$_4$ by grinding in a mortar for about 20 min. Then, the resulting paste was transferred to the epoxy/acetone solution and dispersed at the same conditions described before. For sake of clarity, the pristine MWCNT is denoted as p-MWCNT and the non-covalently functionalized MWCNT with IL is denoted as f-MWCNT.

Characterization
The rheology of the dispersions was carried out using a compact modular rheometer [MCR-302, Anton Paar (Peseux, Suisse)] with parallel plate geometry (25 mm) with a distance of 0.5 mm between the plates. The measurements were performed in an oscillatory mode at a frequency range from 1 to 103 Hz and amplitude of 10%.

Optical micrographs (OM) were obtained in an optical microscope Olympus (Tokyo, Japan) (model BX50) with polarized light. The ER/MWCNT dispersions were applied in a glass blade.

TEM was evaluated on a Tecnai G2-20, SuperTwin FEI (Hillsboro, Oregon, USA), operating at 200 kV. The samples were cut using an ultramicrotome equipped with a diamond knife, to obtain 80-nm-thick ultrathin sections.

Dynamic mechanical analysis (DMA) measurements were performed using a DMA Q800 TA Instruments (New Castle, Delaware, USA) at a fixed frequency of 1 Hz with a heating rate of 3 °C min^{-1}. The samples were tested in the temperature range between room temperature to 150 °C using single-cantilever clamp.

The alternating-current (AC) conductivity was measured with an impedance analyzer Solartron (Farnborough, United Kingdom) SI 1260 gain phase analyzer interfaced to a Solartron 1296 dielectric interface. The measurements were carried out at 25 °C from 0.1 to 106 Hz with 0.1 V oscillating voltage with electrodes of 25 mm in diameter. The samples with 1 mm thickness were previously coated with a thin layer of gold in order to improve the contact.
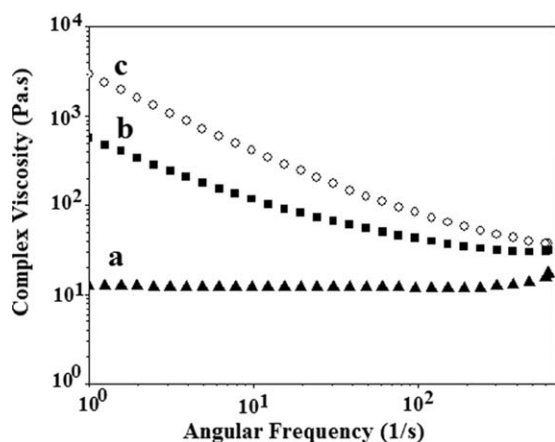
Figure 1. Complex viscosity versus frequency for (a) pure ER and the ER/p-MWCNT dispersions containing 1 phr (part per hundred part of resin) of p-MWCNT, prepared (b) in absence or (c) in the presence of acetone.

The thermal diffusivity was performed at 25 °C on a Nano Flash LFA 447 from Netzsch (Selb, Germany) equipped with xenonium lamp, according to the literature.[37] Differential scanning calorimeter Netzsch-model DSC 204-F1 was used to determine the specific heat, according to the literature.[38] The density was determined using a gas pycnometer from Micromeritics (Norcross, Georgia, USA), model AccuPyc II 1340, operating at room temperature with helium as the gas carrier.

Raman spectroscopy was performed in a laser Raman spectroscope [Renishaw (Chassier, France) inVia] with a 514 nm Argonium line as the excitation source.

RESULTS AND DISCUSSION

The Role of Acetone as Dispersing Aid for ER/p-MWCNT System

Before evaluating the effectiveness of IL on main properties of ER/p-MWCNT systems, a preliminary study involving the use of acetone during the dispersion stage of p-MWCNT into the ER matrix was performed. Figure 1 illustrates the dependence of the complex viscosity with frequency for ER/p-MWCNT dispersions. The presence of p-MWCNT causes a substantial increase of viscosity, as expected. By using acetone during the dispersion step, the corresponding ER/p-MWCNT blend, after

removal of the solvent, displays an additional increase of viscosity, which is usually related to an increase of filler-matrix interfacial area, indicating better dispersion of p-MWCNT in the ER matrix. This behavior is confirmed by OM, illustrated in Figure 2. As observed in Figure 2(b), the p-MWCNTs are homogeneously dispersed inside the matrix with smaller aggregates than those observed for the system prepared without acetone. Thus, the presence of acetone during the dispersion step by sonication contributes for a decreasing of the medium viscosity, which increases the sonication efficiency.

The DMA analyses of the ER/p-MWCNT networks are compared with that of pure ER network in Figure 3. The ER/p-MWCNT network prepared without acetone displayed a slightly decrease in the storage modulus, whereas that prepared with the assistance of acetone presented similar modulus as the pure epoxy network. Nevertheless, the presence of 1 phr of p-MWCNT resulted in an increase of the glass transition temperature (T_g), determined by the maximum of the tan delta peak. The T_g of the pure epoxy network was around 128 °C, whereas those for the systems containing p-MWCNT were 137 °C and 135 °C, for the system prepared in the absence or in presence of acetone, respectively. This result indicates that the dispersion improvement caused by the solvent assistance does not significantly affect the thermal properties.

The Effect of the IL on the Properties of ER/f-MWCNT System

Considering the better dispersion achieved with the assistance of acetone, the following studies related to the effect of the IL on the main properties of ER/f-MWCNT systems were performed by using acetone during the dispersion stage of the f-MWCNT. The viscosity of ER/f-MWCNT systems containing 1 phr of MWCNT is illustrated in Figure 4, as a function of the frequency, for different amounts of IL. The presence of IL resulted in a slight decrease of the viscosity of the system, but this behavior was not influenced by the amount of IL. This behavior highlights the ability of ILs as a processing aid for epoxy systems, as observed in other systems involving thermoplastic as polymer matrix.[39]

The effectiveness of IL in improving the MWCNT dispersion within the epoxy matrix was evaluated by optical micrograph. Figure 5 compares the micrographs obtained for ER/MWCNT
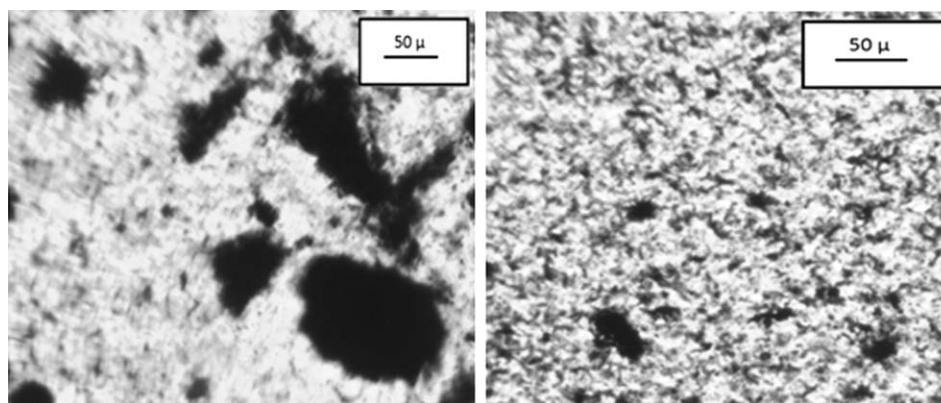

Figure 2. Optical micrographs of ER/p-MWCNT dispersions containing 1 phr of p-MWCNT, prepared (a) in absence or (b) in the presence of acetone.
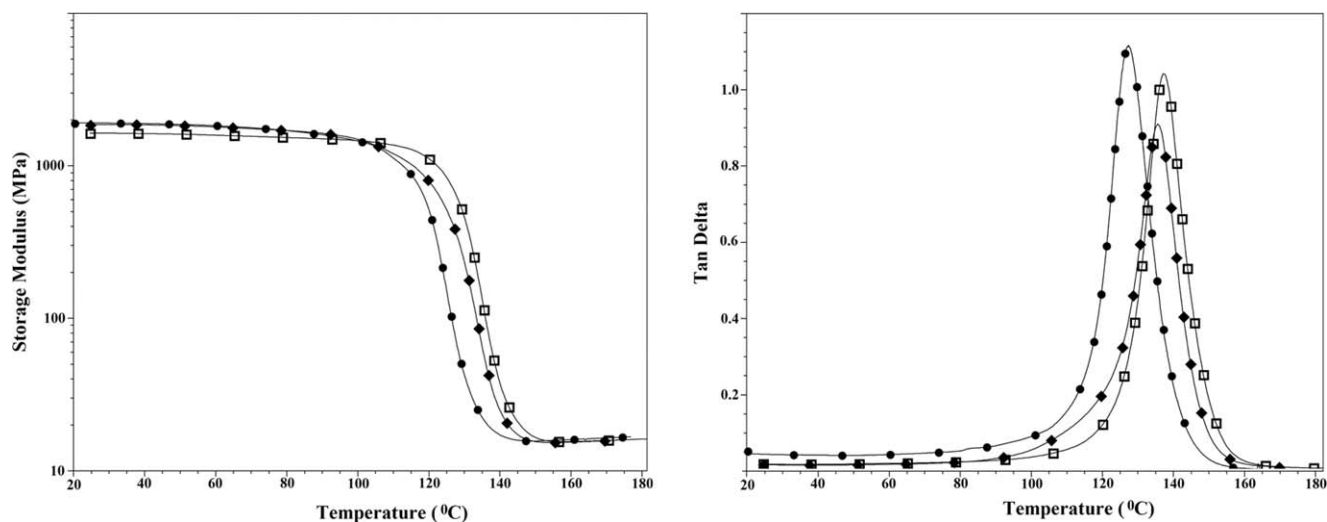
Figure 3. Dependence of the dynamic-mechanical properties with temperature for (•) pure ER network and the ER/p-MWCNT networks containing 1 phr of p-CNT, prepared (□) in absence or (◆) in the presence of acetone.

dispersions containing 1 phr of MWCNT, where it is possible to observe that the presence of IL resulted in better MWCNT dispersion and the optimum MWCNT/IL proportion for attaining better dispersion was 1:5 [Figure 5(b)]. According to these pictures, the better dispersion degree has been achieved by using the f-MWCNT/IL = 1:5. Therefore, this composition was chosen to compare the effectiveness of IL dispersion by TEM.

Figure 6 compares the TEM micrographs of ER/MWCNT networks containing 1 phr of p-MWCNT and f-MWCNT/IL (1:5). Sample prepared with p-MWCNT [Figure 6(a)] is characterized by the presence of several aggregates, whereas that prepared with f-MWCNT gives rise to nanocomposites with better dispersed MWCNT [Figure 6(b)], confirming the efficiency of the IL in dispersing the MWCNT. According to different authors, the dispersion of CNT by imidazolium-based IL may be attributed to cation-π interactions between the surface of CNT and the imidazolium ions[25,35,36] or by weak van der Waals π-cation/π-electronic interactions.[34]

The effect of the amount of IL on the dynamic mechanical properties was evaluated in terms of the dependence of storage modulus and tan delta with temperature, as illustrated in Figure 7. The presence of IL did not exert significant influence on the modulus below the glass transition temperature. These results are different to those reported by Hameed et al.[33] who have observed a significant increase in storage modulus by adding 1 wt % of MWCNT. The different features can be attributed to the different curing systems used in both works. Hammed et al. used aromatic amine to cure the epoxy/MWCNT composites and our group employed anhydride-based curing system. Regarding the rubbery region (above the T_g), it is observed a decreasing in the modulus for samples containing IL, which is an indication of a decreasing of the crosslink density.

The glass transition temperature of the ER/p-MWCNT network is higher than pure ER network but decreases as the amount of IL in the system increases. This behavior may be attributed to a decreasing on the crosslink density. The presence of IL pro-

motes a better MWCNT dispersion. The effective adsorption of the epoxy matrix at the f-MWCNT surface caused by the efficient dispersion may contribute for a non stoichiometric balance, which would result in depression of T_g. Moreover, the presence of the IL at the MWCNT surface, contributes for an increase of the ER chain mobility in this boundary region, decreasing the T_g. This behavior is contrary to that observed by Hammed et al.[33] Probably the difference is due to the different amount of IL used in both works. Hammed et al. used only 0.5 wt % of IL related to the ER matrix,[33] whereas in our system, the amount of IL varied from 5 to 15 phr, which corresponds to 4.7 to 13 wt %. This higher amount of IL may contribute for the decreasing in T_g in our system because of the plasticizing effect of the IL, which becomes important at this proportion. Additionally, Hammed et al. employed aromatic amine as the curing agent, which requires higher temperature during longer time to complete the curing process. Those conditions may also favor the additional curing process by the bmim.BF_4 IL, as stated by the authors.
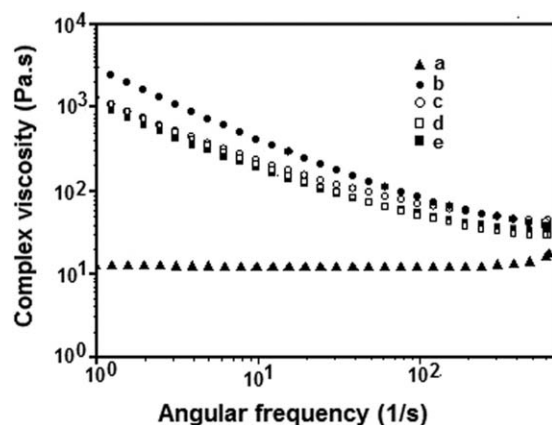

Figure 4. Complex viscosity versus frequency for (a,▲) pure ER and the ER/MWCNT dispersions containing 1 phr of MWCNT and prepared with (b,•) 0 phr (p-MWCNT), (c,○) 5 phr, (d,□) 10 phr, and (e,■) 15 phr of IL.
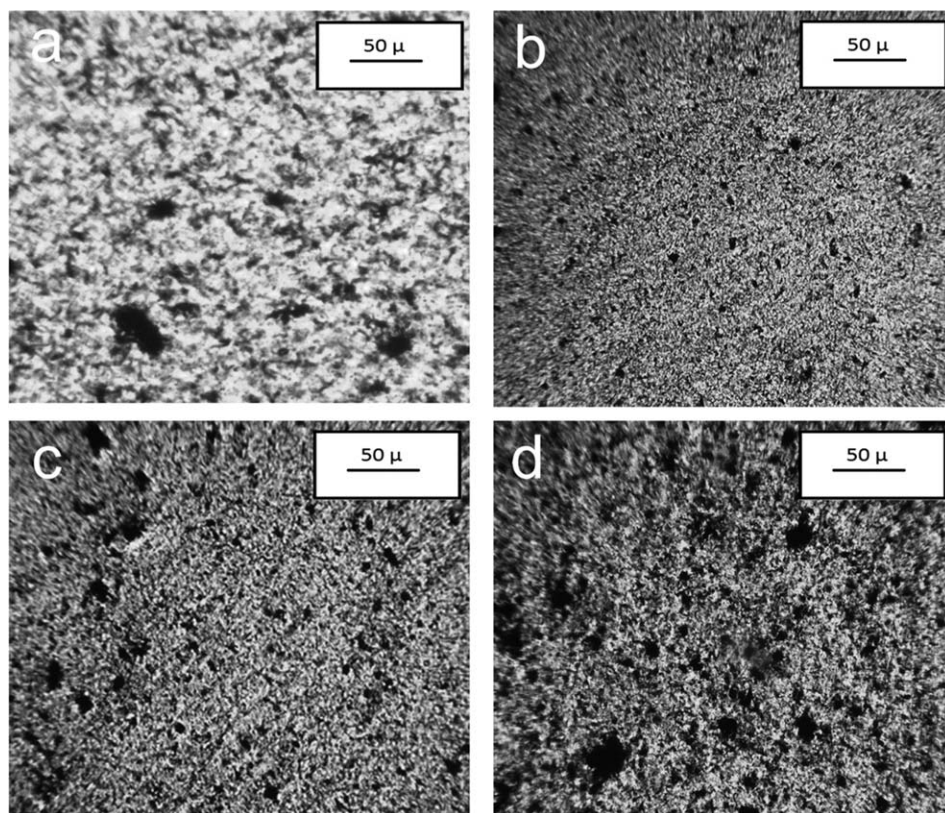
Figure 5. Optical micrographs of ER/MWCNT dispersions containing 1 phr of MWCNT and (a) 0; (b) 5; (c) 10; and (d) 15 phr of IL.

The AC electrical conductivity of ER/MWCNT networks was evaluated as a function of the IL and MWCNT contents. Figure 8 illustrates the dependence of the AC electrical conductivity with the frequency for the systems containing 1 phr of MWCNT as a function of the IL content. The pure ER network presents a linear dependence of the conductivity with frequency,
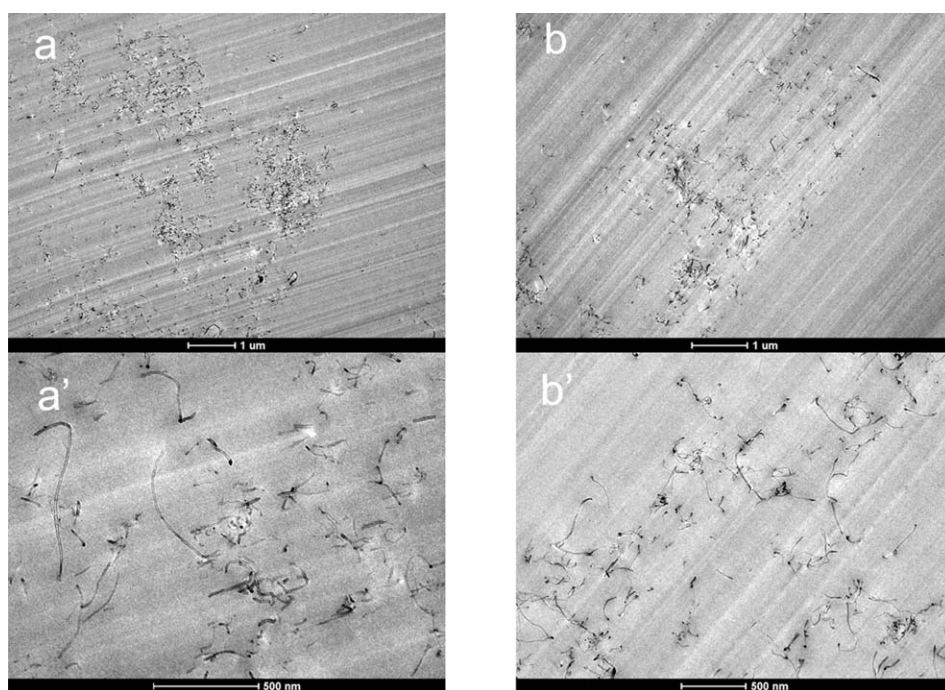

Figure 6. TEM micrographs of ER/MWCNT containing 1 phr of p-MWCNT (a,a′) or f-MWCNT (b,b′).
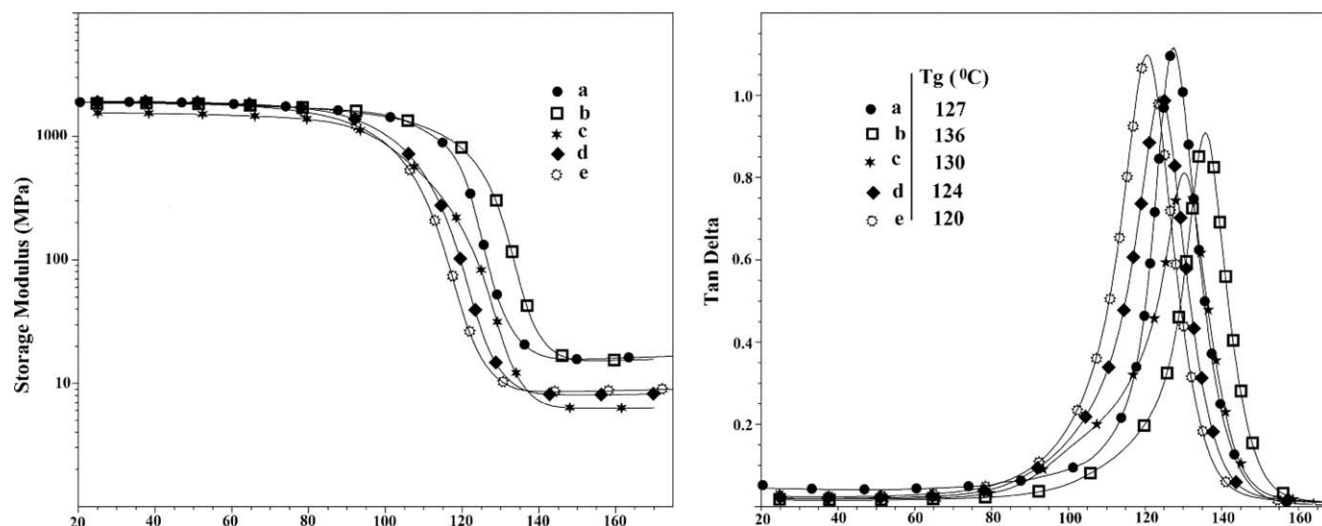
Figure 7. Dependence of the dynamic-mechanical properties with temperature for (a,•) pure ER and the ER/MWCNT dispersions containing 1 phr of MWCNT and prepared with (b,□) 0 phr, (c,★) 5 phr, (d,◆) 10 phr, and (e,○) 15 phr of IL.

which is characteristic of insulating materials. On the other hand, samples filled with 1 phr of MWCNT display significant increase in conductivity, whose values are independent on the frequency, suggesting that the conduction process starts to show an ohmic mechanism.[40] The presence of IL resulted in an additional increase in conductivity but the influence of the amount of IL on this property was not significant.

The effect of the MWCNT concentration on the AC conductivity of ER/MWCNT networks is illustrated in Figure 9 for nanocomposites without IL (p-MWCNT) and with IL (f-MWCNT). For this study a constant MWCNT/IL proportion corresponding to 1:5 mass ratio was employed because the differences in conductivity values found by using higher amount of IL is not significant. In both systems, the conductivity increases as the amount of MWCNT increases, as expected. However, for systems containing f-MWCNT the conductivity is significantly higher (almost three orders of magnitude related to the systems with p-MWCNT), confirming the effectiveness of IL in improving the dispersion of MWCNT and providing the formation of the conducting pathway. The conductivity value for the blend containing 1 phr of f-MWCNT stayed in the order of 10^{-3} S/cm. It is important to emphasize that the amount of f-MWCNT corresponds to 0.5 wt % of the whole epoxy network, considering the epoxy resin and the hardener. This value is significantly higher than those found by Maka et al.[30] for ER/MWCNT containing 1 wt % of MWCNT cured with emim.DCN (1.8×10^2 Ω m $\sim 5.5 \times 10^{-5}$ S/cm) or phosphonium-based IL (4.1×10^1 Ω m $\sim 2.4 \times 10^{-4}$ S/cm),[31] which may be explained by the previous preparation of the mixture between IL and MWCMT by grinding in the mortar adopted in our work. As stated by Fukushima et al.,[25] this process provides a better interaction between IL and MWCNT and consequently a better dispersion of the filler. The increase of the conductivity by the presence of IL has been also observed in other conducting systems involving non functionalized CNT.[39,41,42] Wang et al.[43] have observed similar behavior for the system containing CNT covalently func-

tionalized with IL and suggested that the IL reduced contact resistance between the dispersed CNT. However, the authors have not compared the electrical behavior for the systems with and without IL.

In order to provide a better insight related to the interactions between MWCNT and bmim.BF$_4$ IL, the p-MWCNT and f-MWCNT were analyzed by Raman spectroscopy. Figure 10 compares the Raman spectra in the range of 1000–2000 cm^{-1}. Both p-MWCNT and f-MWCNT present two characteristic peaks at 1345 cm^{-1} and 1575 cm^{-1} assigned as D and G bands, attributed to the defects or disorders in the nanostructure and tangential vibration of the carbon atom, respectively. There is no change in the peak position but the width of the peaks related to the f-MWCNT is broader than that observed for the p-MWCNT. The ratio of the integrated peak areas A_D/A_G can be used to estimate the degree of disorders in these samples.[44] The
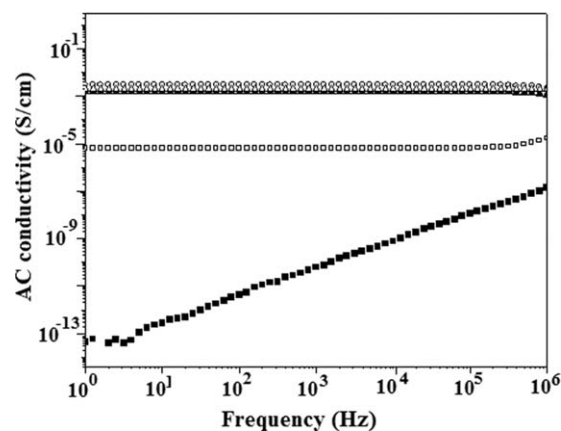

Figure 8. Dependence of the AC electrical conductivity with frequency for (■) pure ER network and the ER/MWCNT networks containing 1 phr of CNT, prepared with (□) 0 phr, (▲) 5 phr, (○) 10 phr, and (△) 15 phr of IL.
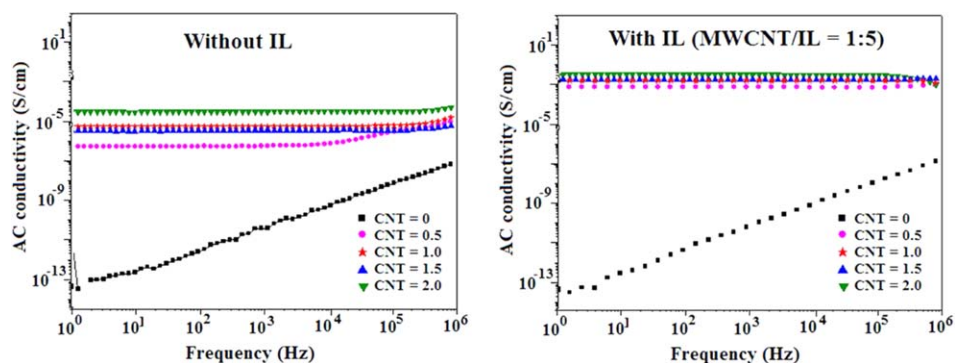
Figure 9. Dependence of the AC electrical conductivity with frequency for ER/MWCNT networks as a function of MWCNT amount. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

A_D/A_G values for the p-MWCNT and f-MWCNT were found to be 0.81 and 1.19, respectively. The higher value found for the f-MWCNT characterizes a more disordered nanostructure confirming the ability of the IL in interacting with the MWCNT thus contributing for the disaggregation of the bundles and ropes of the MWCNT. Similar features have been reported by other authors in studies related to the interaction between CNT and ionic liquids,[45,46] which was attributed to the rearrangement of the tubes in the presence of ionic liquid.[45] This behavior contributes for the outstanding electrical conductivity of the epoxy-based nanocomposites containing non-covalently functionalized MWCNT with IL (f-MWCNT).

Besides the outstanding electrical conductivity and mechanical properties, CNTs display extraordinary high thermal conductivity, which makes them promising fillers for the development of thermal interface materials.[47] Thus, the effect of the amount of IL on the thermal conductivity at room temperature of epoxy/MWCNT networks containing 1 phr of CNT has been investigated, whose results are summarized in Table I. The addition of 1 phr of MWCNT resulted in enhanced thermal conductivity of around 57%, which was somewhat higher than other data reported in the literature.[48,49] Composites prepared with f-MWCNT presented additional improvement on the thermal conductivity, whose values increased as the amount of IL increased. System containing MWCNT/IL = 1:15 displayed thermal conductivity value of 0.20 W/m.K, which corresponds to an increase of around 100% related to the pure epoxy network. Maka et al.[30] have reported thermal conductivity value of 0.28 W/m.K for ER/MWCNT containing 1 phr of MWCNT and cured with emim.DCN ionic liquid. This value corresponds to an increase of 75% related to the pure epoxy network developed in that work. It is important to emphasize that the real MWCNT content in the experiment presented in Table I corresponds to 0.45% of MWCNT, because the amount of the hardener was 100 phr related to the epoxy resin. Therefore, we observed in our system, an increase of 100% of the thermal conductivity for samples containing 0.45/7.0 wt % of MWCNT/IL. As stated by several authors, the thermal conductivity depends on the dispersion of the CNT within the polymer matrix, the intrinsic thermal conductivity of the filler, the amount of filler and the thermal resistance of the interface between filler and matrix.[50,51] Thus the increasing in thermal conductivity in ER modified with non covalently functionalized MWCNT by IL may be attributed to the enhanced interface compatibility between MWCNT and the epoxy matrix promoted by the ionic liquid, which reduces interfacial thermal resistance.
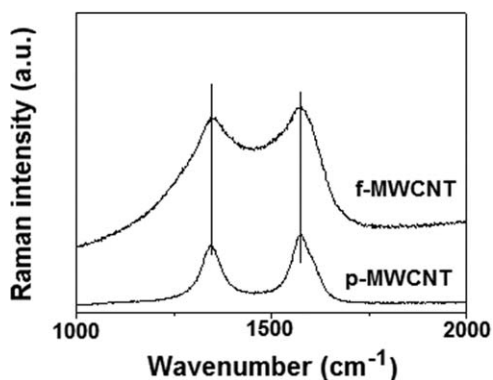

Figure 10. Raman spectra of p-MWCNT and f-MWCNT in the range of 1000–2000 cm^{-1}.

Table I. Effect of the Non-Covalent Functionalization of MWCNT by bmim.BF$_4$ on the Thermal Conductivity of the Corresponding Epoxy/MWCNT Composites Containing 1 phr of MWCNT

Composite component (phr)			Thermal conductivity	Percentage increasing related to ER
ER	CNT	IL	W/m.K	(%)
100	0.0	0.0	0.10	—
100	1.0	0.0	0.16	57
100	1.0	5.0	0.17	68
100	1.0	10.0	0.18	73
100	1.0	15.0	0.20	98

CONCLUSIONS

The present study highlights the importance of the non covalent functionalization of MWCNT by imidazolium-based room temperature ionic liquid for providing better dispersion of MWCNT in epoxy system and better electrical and thermal

properties. In fact, the addition of bmim.BF$_4$ ionic liquid in epoxy/MWCNT composites resulted in a significant increase in electrical conductivity (around three orders of magnitude related to the same system prepared with pristine MWCNT). The presence of IL does not exert significant influence on the storage modulus but strongly affects the T_g. This behavior may be attributed to the plasticizing effect of IL. Finally the thermal conductivity of the epoxy/MWCNT networks was enhanced by the previous functionalization of the MWCNT by ionic liquid. These results open new possibilities of developing epoxy-based conducting composites with improved electrical, thermal and mechanical properties.

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