Comparison of the Physical Properties of Epoxy-Based Composites Filled with Different Types of Carbon Nanotubes for Aeronautic Applications

BIAGIO DE VIVO, PATRIZIA LAMBERTI, VINCENZO TUCCI
Department of Electronic and Computer Engineering, University of Salerno, Via Ponte Don Melillo,
1-I84084 Fisciano (SA), Italy
NANO_MATES, Research Centre for NANOMAterials and nanoTEchnology at Salerno University,
Via Ponte Don Melillo, 1-I84084 Fisciano (SA), Italy

LIBERATA GUADAGNO, LUIGI VERTUCCIO, VITTORIA VITTORIA
Department of Industrial Engineering, University of Salerno, Via Ponte Don Melillo,
1-I84084 Fisciano (SA), Italy
NANO_MATES, Research Centre for NANOMAterials and nanoTEchnology at Salerno University,
Via Ponte Don Melillo, 1-I84084 Fisciano (SA), Italy

ANDREA SORRENTINO
CNR, Institute for Composite and Biomedical Materials, Piazzale Enrico Fermi 1,
I-80055 Portici (NA), Italy

Received: November 9, 2011
Accepted: April 18, 2012

ABSTRACT: The increased demand for high-quality multifunctional materials in the aeronautic industry requires the formulation and preparation of advanced nanostructured composites with superior characteristics. In particular,

Correspondence to: Vincenzo Tucci; e-mail: vtucci@unisa.it.

Advances in Polymer Technology, Vol. 31, No. 3, 205–218 (2012)

epoxy-based polymers, exhibiting excellent mechanical properties for structural stability, filled with carbon nanotubes (CNTs: single, double, and multiwalled—SW, DW, and MW), characterized by remarkable mechanical and electrical properties, allow us to manufacture a very versatile class of composites for structural applications in automotive, aeronautics, industry, electronics, etc. Many aspects concerning the optimization of such composite systems are still to be clarified. In this paper, the physical properties of samples based on the epoxy resin with the same weight percentage (0.5%) of different CNTs have been studied. The physical behavior of the nanocomposites resulted to be dependent on the type and on the chemical functionalization of the nanoinclusions. The elastic modulus and the electrical conductivity of composites based on unfunctionalized CNT are higher than those obtained for the functionalized systems. Moreover, the maximum electrical conductivity achieved for the composite based on unfunctionalized MWCNT is not far from the target required for aeronautic applications. The contrasting results obtained for the different physical properties enlighten the difficulty in choosing one of the CNT types for the realization of multifunctional materials. Adv Polym Techn 31: 205–218, 2012; View this article online at wileyonlinelibrary.com. DOI 10.1002/adv.21284

KEY WORDS: Carbon nanotubes, Composites, Dielectric properties, Mechanical properties, Nanotechnology

Introduction

In the aerospace industry the introduction so far of composite materials, driven by performance gains and weight reduction, has shown some drawbacks related to several causes such as reduced electrical conductivity, poor impact damage resistance, and low postimpact mechanical properties compared to metallic alloys.

Meanwhile, the continuously growing availability of nanometer-sized materials such as carbon nanotubes (CNTs), clay platelets, and spherical particles, coupled with a growing ability to characterize and manipulate systems at this scale, set researchers' hopes on producing nanoengineered multifunctional materials for several advanced aerospace and transport applications.[1–4] In particular, the very appealing physical and mechanical properties of CNTs, such as high elastic modulus, as well as remarkable thermal and electrical conductivity, have stimulated great interest due to the wide range of possible technological applications.

Among the current studies, a research area of particular impact is therefore currently focused on the manufacturing of CNT-reinforced thermosetting polymer matrices to further improve the composite resin physical properties.[5–7] Apart from mechanical reinforcement, one key interest is to develop conductive polymer composites for numerous applications, which include materials for electromagnetic interference (EMI) shielding and radar absorption, antistatic components, and sensor devices. Regarding aeronautic applications, notable benefits could be achieved by such systems.

Their use in large components, such as the fuselages of aircraft, may allow to significantly reduce weight. It is well known, in fact, that current composite materials are significantly less conductive than traditional metal alloys. For this reason, polymeric materials are reinforced with conductive metal fibers or metal screens to improve EMI shielding and dissipate lightning currents. In a recent paper,[8] the main advantages of adding conducting powders to carbon fiber reinforced polymer composites have been discussed as a cost-effective method of improving the shielding effectiveness. The use of nanoinclusions instead of microfillers is deemed to further increase the conductivity of the obtained systems, thus improving the overall behavior. Typical target conductivities for the nanocomposites to be used in fiber-reinforced structures are on the order of 10 S/m.

In contrast to the realization of a mechanical reinforcement by CNTs, where a homogeneous dispersion and a strong adhesion to the matrix are desired, the electrical conductivity is based on percolated pathways of conductive particles. Electrical conductivity can be explained on the basis of percolation theory, with an onset of the conductivity when a critical filler concentration, commonly called percolation threshold, is reached to form conductive pathways. The CNT dispersion inside the polymeric matrix determines the critical concentration.[9–25] However, up to now a uniform dispersion of CNT in polymer matrices is restricted due to aggregate formation, irrespective of the techniques employed for composite preparation. This is presumably due to (i) strong intertube van der Waals interaction and (ii) lack of the interfacial interaction between the polymer and the CNT.

These two issues—the ability to homogeneously disperse nanotubes throughout a matrix and formation of strong interfacial bonding—represent the two key aspects to be dealt with if CNTs are to be considered as effective reinforcement and electrical conductivity in future composites. The two effects are not strictly related, because one can have a good dispersion without achieving strong adhesion; moreover, the second effect, a determinant for mechanical properties, is less important for electrical conductivity. Both aspects, that is, dispersion and bonding to the matrix through an interface, depend on the CNT type (single, double, and multiwalled as well as on their functionalization) and on the chemical nature of the matrix.[9–16,25] An optimization of the composite may be pursued by varying the CNT type, preparation technique, and processing parameters, trying to improve all the physical properties.

In a previous paper, a variety of methods of incorporation in an epoxy matrix formed by diglycidyl ether of bisphenol A (DGEBA) cured with 4,4′-diaminodiphenyl sulfone (DDS) of several types of CNTs (single, double, multiwalled and organically modified) have been considered. The study was aimed at correlating the structural organization of the composites, depending on the nanotube type, with physical and electrical properties. The effects of different dispersion methods and cure parameters have been discussed,[16] and the best method (among those analyzed) to obtain dispersion was presented. Moreover, a comparison between multiwalled CNT (MWCNT) and MWCNT functionalized with —COOH groups, has shown that the nanotube functionalization has a strong influence on the electrical properties and results in a remarkable reduction of both the elastic modulus and the conductance of the composite. This behavior was attributed to the fact that the presence of the —COOH groups catalyzed a fraction of homopolymerization, having a lower glass transition temperature. Both dynamic mechanical analysis and transport properties of liquid water indicated the presence of two phases in the resin with functionalized CNT. The presence of this phase more adherent to the nanotubes determined a higher tunneling resistance between interacting CNTs and therefore a higher percolation threshold and lower limit of the conductivity.[25]

In this paper, samples based on the same epoxy resin with the same weight percentage (0.5%) of different CNTs have been prepared and characterized: unfunctionalized (single- and double-walled CNT, SWCNT and DWCNT, respectively) and functionalized with —NH_2 CNTs have been used, and a general comparison is done with the previously analyzed MWCNT and MWCNT-COOH.[25] The physical behavior of the resin filled with different CNTs resulted to be dependent on the type and chemical functionalization of the nanoinclusions. However, different physical properties were influenced differently by the CNT type, enlightening the difficulty to chose one of the CNT types for multifunctional materials. The electrical conductivity and permittivity of the most promising system are analyzed in detail.

Materials and Methods

The composites are manufactured by using as a base epoxy resin DiGlycidil-ether bisphenol-A (DGEBA), with DDS, as a hardener agent. The SWCNT (1100 grade), DWCNT (2100 grade), DWCNT-NH_2 (2152 grade), MWCNTs (3100 grade), and MWCNT-COOH (3101 grade) were obtained from Nanocyl S.A. (Auvelais, Belgium).

The epoxy and DDS were mixed at 120°C, and the MWCNTs were added and incorporated into the matrix by using an ultrasonication for 20 min (UP200S-24 kHz, Hielscher, Teltow, Germany; a high-power ultrasonic probe). Such an incorporation method has been chosen among other different techniques since it leads to the composites characterized by the best mechanical and electrical properties.[16] All the mixtures were cured at 150°C for 1 h and 220°C for 3 h.

In this paper, composites with CNTs and functionalized CNTs are named ENXW and EFXW, respectively, where XW represents the type of CNTs. As an example, EFDW is the epoxy resin filled with —NH_2 functionalized double-Wall CNTs. The same concentration of 0.5% w/w% of CNTs has been adopted to compare the obtained performances of the different nanocomposite systems in the same conditions.

Thermal analysis was performed with a Mettler DSC 822 differential thermal analyzer (Mettler Toledo, Greifensee, Switzerland) in a flowing nitrogen atmosphere. The curing reaction of the resins with and without CNTs was performed in a dynamic regime, by heating in the differential scanning calorimeter (DSC) at 10°C/min from room temperature to 350°C.

Dynamic-mechanical properties of the samples were performed with a dynamic mechanical thermoanalyzer (DMA 2980, TA Instruments, New Castle, DE). Solid samples in a parallelepiped shape with lateral dimensions of 4 × 10 × 35 mm were tested by applying a variable flexural deformation in a dual cantilever mode. The displacement amplitude was set to 0.1%, whereas the measurements were performed at the frequency of 1 Hz. The range of temperature was from –60 to 300°C at the scanning rate of 3°C/min.

Measurements of sorption and diffusion were performed in liquid water at 25°C for the pristine resin, the resin with different CNTs.

The measurements of the dc volume conductivity were performed by using disk-shaped specimens of about 2-mm thickness and 10–50 mm diameter. Surface leakage currents were found to be negligible with respect to volume current, whence no guard ring was used. The measurement system, remotely controlled by the software LABVIEW®, is composed of a voltage generator FUG HCN 35-6500 (FuG Elektronik GmbH Rosenheim, Germany; maximum output current 5 mA), a picoammeter Keithley 6514 (Keithley Instruments, Inc., Cleveland, OH; minimum current 10^{-13}A), and a suitable shielded cell with temperature control. For the conducting composites, the maximum of applied electric field is limited to 1.0 kV/m to avoid Joule heating of samples.

The ac measurements were performed at room temperature using the QuadTech 7600 inductance, capacitance, and resistance (LCR) meter (Quadtech, Marlborough, MA) in the range 100 Hz–100 kHz.

Results and Discussion

CURE BEHAVIOR OF THE RESIN FILLED WITH DIFFERENT CNT TYPES

This investigation of the cure behavior of different CNT-filled epoxies is very important for the design and optimization of the material fabrication. DSC investigation of the cure process in a dynamic regime was performed, with the aim to compare the pristine resin and the filled resin with 0.5% on SWCNT, DWCNT, MWCNT, DWCNT-NH_2, and MWCNT-COOH, showing the best type for improving cure kinetics.

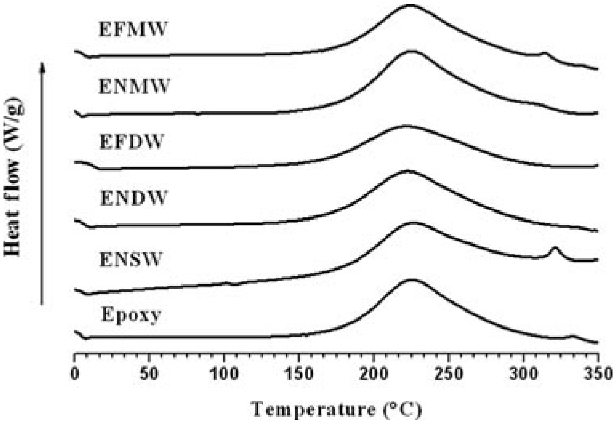

FIGURE 1. DSC heating curves for the pristine epoxy and its composites with different CNTs.

In Fig. 1, the heating curves of the pristine resin and the filled resins with all the nanotubes are shown.

A wide peak starting between 140 and 150°C with the maximum located at about 230°C and a nonsymmetric shape on the high-temperature side can be observed for all samples. Moreover, a small peak at high temperature (about 330°C) appears; this peak was previously attributed to a very small fraction of homopolymerization occurring for the unreacted resin at high temperature. The peak of the filled samples occurs at almost the same temperature, although they are more symmetric. The small peak at high temperature is particularly evident for SWCNT, indicating a higher fraction of homopolymerization with this CNT type. It is also evident in the functionalized CNT with —COOH, as already discussed in a previous paper.[24]

To better show the influence of the different CNT types on the cure kinetics, in Fig. 2 the progress of the cure reaction, as a fraction of cured resin as a function of the temperature, is shown.

It can be observed that the reaction proceeds with a similar kinetics with almost all the CNT types and is slightly accelerated only in the case of DWCNT and DWCNT-NH_2. This result agrees well with the peak temperature reported in Table I for all the samples.

The cure enthalpy, derived by the curing curve for all the samples, is 405.6 J/g for the pristine resin, whereas a lower value was found for the filled samples. A lower cure enthalpy for CNT-filled samples was interpreted as an indication of good dispersion.[25] In the present case, it could be affirmed that the best dispersion was obtained with SWCNT, showing the lowest enthalpy. These results can also be explained by considering that an efficient dispersion of the filler causes a lower cross-linking density in the immediate proximity of CNT walls. This interpretation would also explain the lower enthalpy of EFDW and EFMW with respect to ENDW and ENMW, respectively. All the numerical values are reported in Table I, where $\tau_{0.5}$(temperature of degree of curing = 50%) is reported too.

MECHANICAL PROPERTIES

The storage modulus, *E* (MPa), and the loss factor, tan δ, of the pristine epoxy and the composites with different CNTs at 0.5% concentration are shown in Figs. 3 and 4.

At low temperatures, all the samples show a very high elastic modulus, followed by two little drops due to second-order transitions between –20 and 0°C for the first and between 50 and 70°C for the second. The principal drop, due to the glass transition, is

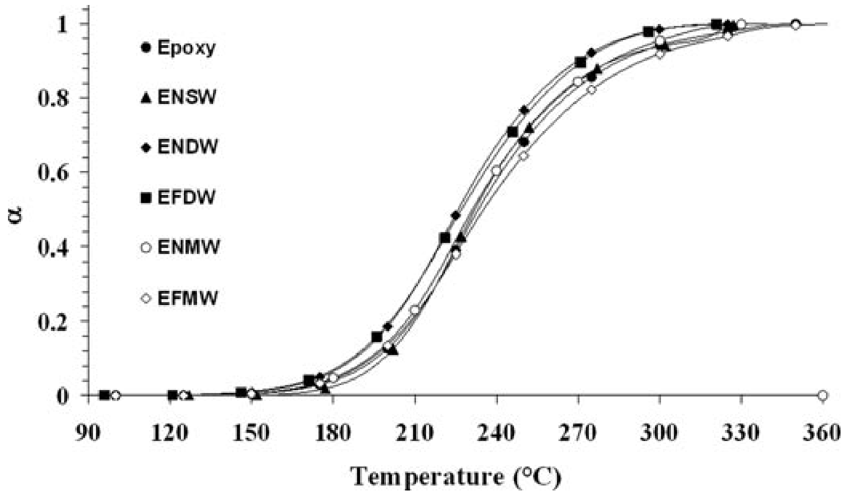

FIGURE 2. Behavior of reaction of cure of pristine epoxy and epoxy composites with different CNTs.

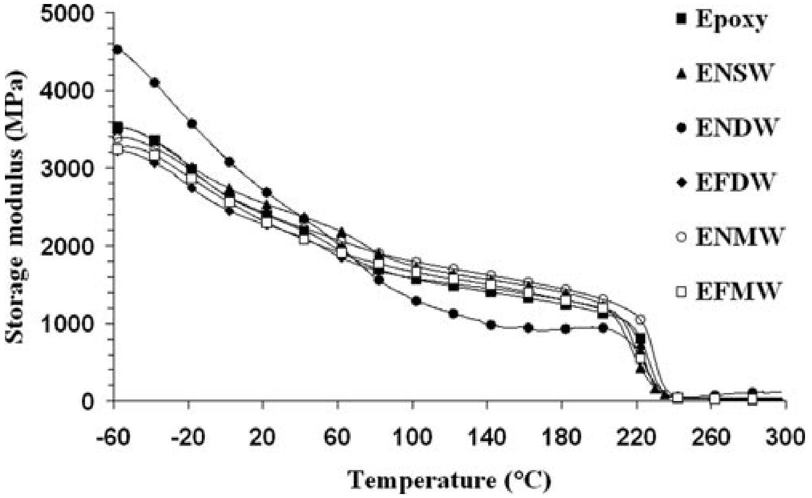

FIGURE 3. Storage modulus, *E*′ (MPa) of the pristine epoxy and its composites with different CNTs.

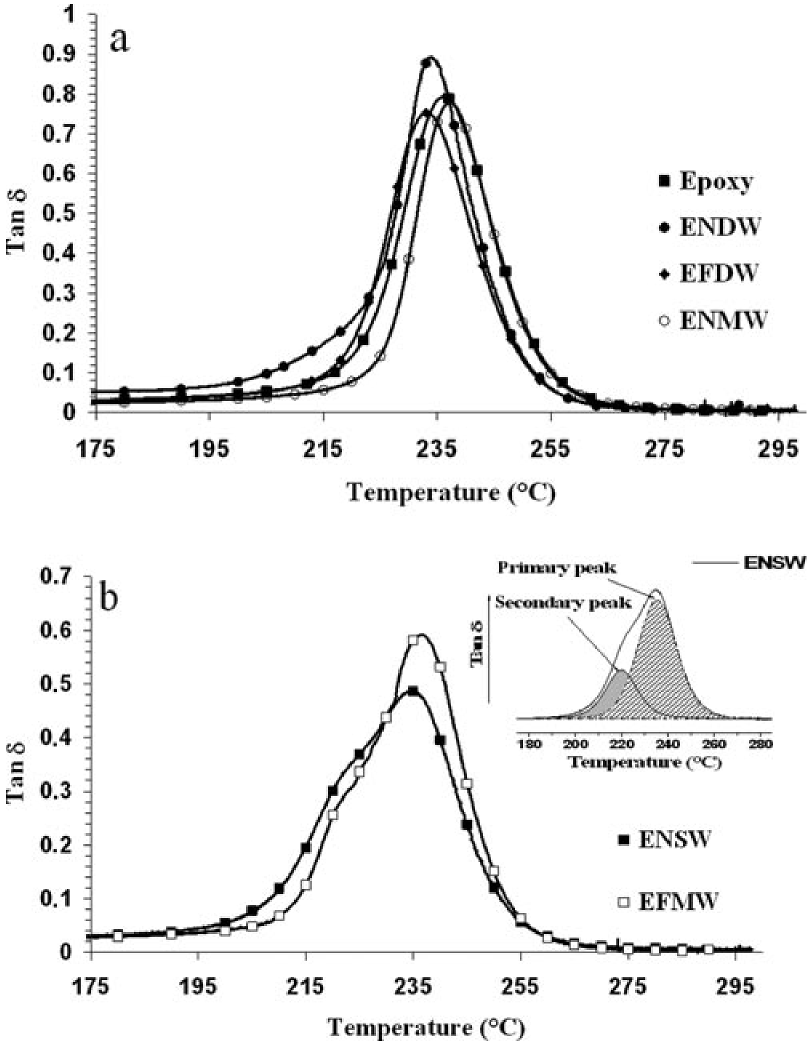

FIGURE 4. (a) Loss factor (tan δ) of the pristine epoxy and samples with DWCNT, DWCNT-NH$_2$, and MWCNT. (b) Loss factor (tan δ) of samples with SWCNT, MWCNT-COOH.

TABLE I
Peak Temperature, the Curing Enthalpy, and $\tau_{0.5}$ for Pristine Epoxy and Epoxy Composites with Different CNTs

Sample	T_{peak}(°C)	ΔH_{tot}(J/g)	$\tau_{0,5}$(°C)
Epoxy	225.53	405.55	233.18
ENSW	225.92	264.05	231.92
ENDW	222.35	312.99	225.84
EFDW	221.58	280.10	227.08
ENMW	226.29	414.61	231.11
EFMW	224.61	386.97	235.25

evident for all samples in the range 220–240°C. In this temperature range also, the tan δ curves show a peak indicating the glass transition temperature of the material. The filled samples with DWCNT, DWCNT-NH$_2$, and MWCNT present this peak very similar to the pristine resin (Fig. 4a), both as height and position, as reported in Table II. This indeed means that these CNT types, at the investigated concentration of 0.5%, have no particular effect on the relaxation phenomena leading to the glass transition of the system.

At variance single-walled and multiwalled CNTs functionalized with —COOH show a different behavior with respect to the previous ones (Fig. 4b). Both indeed show two peaks in the tan δ (inset in Fig. 4b for filled sample with SWCNT), indicating the presence of a lower glass transition temperature, besides the main transition at the same temperature

TABLE II
Storage Modulus and Glass Transition Temperature of Pristine Epoxy and Epoxy Composites with Different CNTs at Different Temperatures

	Storage Modulus				
Sample	30°C	120°C	200°C	240°C	T_g (°C)
Epoxy	2314.30	1485.65	1145.99	51.48	236.16
ENSW	2465.28	1645.75	1259.46	57.20	234.58
ENDW	2547.48	1141.81	949.27	64.82	233.92
EFDW	2205.84	1516.12	1193.96	45.67	233.08
ENMW	2329.77	1710.11	1327.61	75.24	237.20
EFMW	2207.74	1579.11	1208.73	56.04	236.52

as the pristine resin. The presence of a secondary peak in the loss factor, active at a lower temperature, was already presented by us for functionalized —COOH CNT in a previous paper.[24] The position and the height of this secondary peak were found to be dependent on the nanotube concentrations. This suggests that the presence of the —COOH groups catalyzed either a fraction of homopolymerization or an esterification reaction, giving an interphase with a lower glass transition temperature, although regarding a phase nearer to the nanotubes. Also in the present case of SWCNTs, the presence of a fraction of more mobile phase correspondent to the fraction of resin homopolymerized, as shown by the small peak in the DSC curing curves, can be envisaged. This result is in agreement with the water sorption measurements shown in the following.

As far as the storage modulus is concerned, a slight increase in all the unfunctionalized CNTs can be observed at room temperature whereas, as reported in Table II, a decrease is shown for the functionalized MW-COOH and DW-NH_2.

Indeed, the CNT-reinforcing effect is, in all the cases, less than expected. As already discussed,[5–7,27] there are many factors that influence the overall mechanical properties of CNT-reinforced composites; among these, the weak bonding between CNTs and matrix, curviness and agglomeration of CNTs, and structural parameters such as aspect ratios, diameters, and wall numbers. To deeply understand the influence of CNTs on the mechanical properties of the material, it would be necessary to factorize the contributions of all these parameters considering a large number of experiments. Undeniably, the present results, and also other ones reported in the literature, show that the CNT-reinforced composites do not reach optimum results; the improvement is always much less than expected from a simple mixing rule, or even a worsening is observed.[26] In our experience, the reinforcement role of CNTs (although below the theoretical value) can be very different and strongly dependent on the chemical nature of the epoxy matrix; this is related to the chemical nature of the epoxy precursor and hardener, their stoichiometric ratios, and curing conditions. A sound choice of the matrix components allows to modulate, within limits, the matrix stiffness. Regarding the nanofiller role, by introducing high strength, high modulus nanotubes into a low strength, low modulus matrix, an increase in the composite strength is to be expected because the load is transferred to the high-strength tubes.

The effectiveness of the load transfer depends on the difference in moduli between the nanotubes and the matrix. Indeed, it has always been found that the reinforcement role of CNTs decreases with increasing the stiffness matrix. In the present case, the high stiffness of the matrix hides the role of the nanotubes, even considering different CNT types.

WATER SORPTION AND DIFFUSION

The investigation of the water transport in epoxy resins is very interesting, both from the technological point of view, because water can damage the cross-linked structure through hydrolysis reactions, and from the structure investigation point of view, because the level of sorption and the kinetics of water passage are related to the chemical structure and the free volume in the resin. Therefore, the sorption and diffusion of liquid water in the pristine and filled with all the CNT types resins have been investigated.

In Fig. 5a, the reduced curves, C_t/C_{eq}, as a function of the square root of time, normalized for the thickness d (cm) of the pristine resin and the resin with 0.5% DWCNT, DWCNT-NH_2, and MWCNT are reported, whereas in Fig. 5b the reduced curves of SWCNT and MWCNT-COOH are shown. In the samples shown in Fig. 5a, a Fickian behavior can be observed, that is, a linear dependence of the reduced sorption on the square root of time, a curvature for $C_t/C_{\mathrm{eq}} > 0.8$ and a constant value, which represents the equilibrium of sorption. This Fickian behavior gives the possibility to derive the diffusion parameter, D (cm^2/s), by the first linear part of the curve:

$$\frac{C_t}{C_{\mathrm{eq}}} = \frac{4}{d}\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} \tag{1}$$

where $C_{\mathrm{eq}}$is the equilibrium concentration of water, C_t is the concentration at time t, d (cm) is the

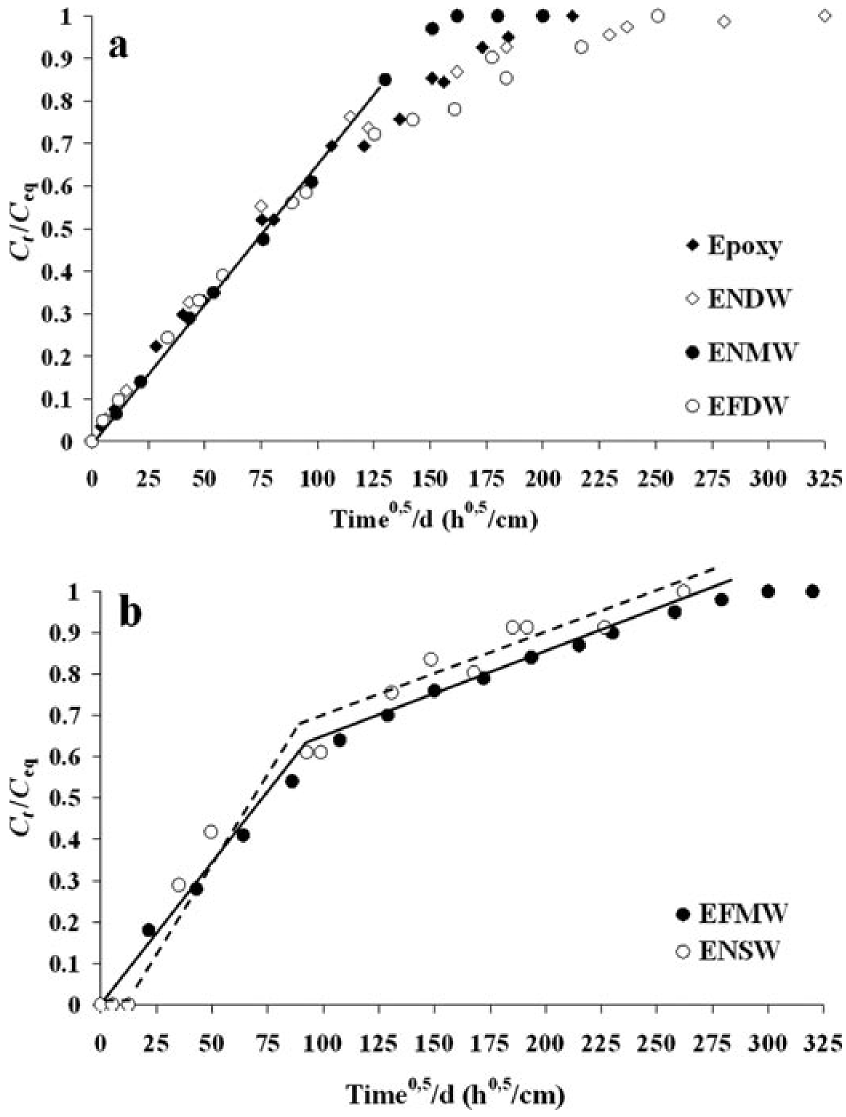

FIGURE 5. (a) C_t/C_{eq} against the square root of time of the pristine resin and resin with 0.5% DWCNT, DWCNT-NH$_2$, and MWCNT and (b) the resin with 0.5% MWCNT-COOH and SWCNT.

thickness of the sample, and D (cm^2/s) is the mean diffusion coefficient.

In Fig. 5b, the reduced curves for the composite sample with 0.5% of MWCNT-COOH and 0.5% of SWCNT show that the diffusion of water molecules into these composite samples follows two curves. In the case of the functionalized —COOH, the first part, extending up to $C_t/C_{\text{eq}} = 0.7$, is coincident with the previous curves of Fig. 5a, giving the same angular coefficient. However, a second stage appears, slowing down the diffusion process, allowing to reach the equilibrium at longer times.

In a previous paper,[24] this behavior was ascribed to the fraction of resin nearer to CNTs that contain impermeable obstacles more strictly adhering and therefore able to slow down the process in the final stage. This result can be considered as a clear indication of a second phase, reasonably correspondent to the polymer forming a layer around CNTs and therefore experiencing a different environment. In any case, the small peak in the dynamic DSC, the double peak in tan δ, and the double behavior in the reduced sorption curve, all firmly point to the presence of two phases in the resin with —COOH-functionalized CNTs. Interestingly, in the case of SWCNT an induction of sorption, a first stage and a slower second stage of sorption can be observed. Also in this case, recalling the small peak in the dynamic DSC, and the

TABLE III

Sorption Values at Equilibrium of Liquid Water and Diffusion Values of Pristine Epoxy and Epoxy Composites with Different CNTs

Sample	C_{eq}(%)	D (cm^2/s)
Epoxy	4.03	2.28E-09
ENSW	3.11	7.07E-09
ENDW	3.80	2.51E-09
EFDW	4.10	1.95E-09
ENMW	4.05	2.30E-09
EFMW	4.02	2.10E-09

double peak in tan δ behavior, the presence of two phases, as in the previous case, can be suggested. As for the diffusion, it can be observed that the first stage has the same behavior as the filled resins in Fig. 5a, and the second is slower, as in the case of —COOH functionalized CNT. In Table III, the sorption and diffusion of all the samples are reported.

Electrical Properties

In Fig. 6, the histogram of the dc electrical conductivity of the composites with the same CNT concentration (0.5%) is illustrated. Many observations can be derived from this figure. A very ample range of conductivity has been found for the different systems. First of all, it is confirmed that the best conductivity is shown by MWCNT, which has a conductivity (0.1 S/m) much higher than SWCNT (2.5×10^{-5} S/m) and DWCNT (2.8×10^{-2} S/m). In particular, the lowest conductivity is found for SWCNTs, most likely since for this last CNT-type, conductive nanotubes are only a limited fraction of the total. It is also established that the functionalization makes the conductivity worse; indeed, the DWCNT-NH_2 samples have a conductivity (3.0×10^{-4} S/m) two orders of magnitude lower than those obtained with DWCNT. The most interesting observation is that the resins that show the presence of two phases have a lower conductivity. This result considers both SWCNT and MWCNT-COOH in which the presence of a second phase was hypothesized by DSC, dynamic mechanical analysis, and water transport. As suggested in a previous paper,[24] the presence of this phase more adherent to the nanotubes determines a higher tunneling resistance between interacting CNTs and therefore a higher percolation threshold and lower limit of the conductivity.

However, a complete understanding of the relations among electrical properties, physical and chemical characteristics of the composite components (especially those pertaining to the interface between matrix and conducting inclusions), and the topological structures is still to be achieved. Therefore, additional efforts aimed at providing further information on the dependencies among electrical characteristics and the above-mentioned parameters seem valuable.

In any case, it appears that MWCNTs represent the most convenient choice among the analyzed

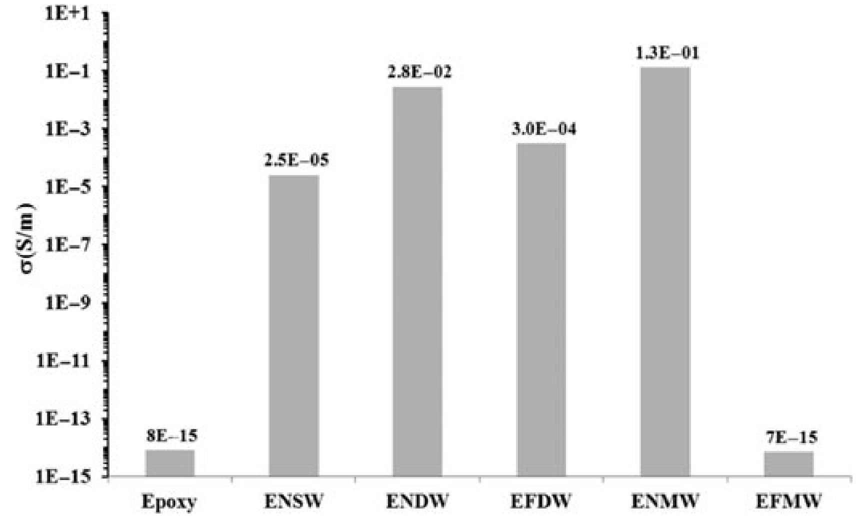

FIGURE 6. Conductivity of different composite systems with the same CNT concentration (0.5 wt%).

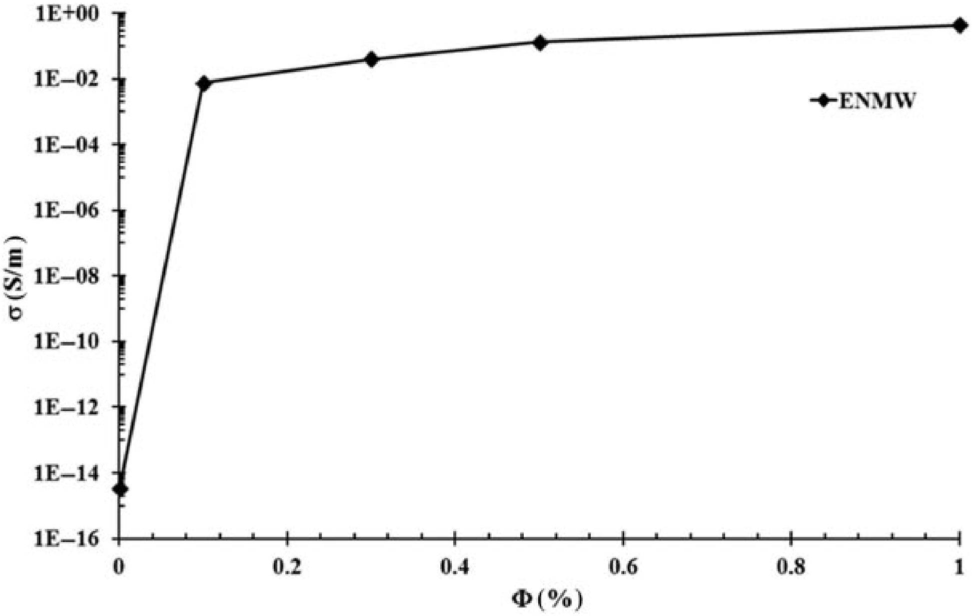

FIGURE 7. Dc conductivity vs. MWCNTs wt% concentration at room temperature.

samples to realize composites with high electrical conductivity. Therefore, the MWCNT-based system has been selected for a detailed electromagnetic characterization at different CNT loading and for different operating temperature. In particular, the dc and ac conductivity and the permittivity have been studied.

The electrical conductivity of CNT-based nanocomposites has been extensively investigated in the literature.[6,10–23] The conduction in such composites can be explained by considering the percolation theory in which the dependence of the conductivity σ on the filler concentration is described by the two-exponents phenomenological percolation equation (also known as the general effective medium equation):[28–30]

$$\frac{(1-\phi)\left(\sigma_i^{1/S}-\sigma_m^{1/S}\right)}{\sigma_i^{1/S}+A\sigma_m^{1/S}}+\frac{\phi\left(\sigma_c^{1/t}-\sigma_m^{1/t}\right)}{\sigma_c^{1/t}+A\sigma_m^{1/t}}=0 \qquad (2)$$

where $A = (1-\Phi)/\Phi_c$, Φ_c is the percolation threshold, Φ is the volume fraction of CNT, σ_m and σ_i are the conductivity of the matrix and CNT inclusions, respectively, and t is an exponent depending on the topological complexity of the obtained CNT structure. It is generally accepted that values in the range of 1.6–2.0 are representative of a three-dimensional (3D) organization of the percolating structure.

When $\sigma_m \to \infty$ or $\sigma_i \to 0$, $\Phi_c \ll 1$, and $\Phi_c < \Phi$, Equation (2) can be rewritten in the following form:

$$\sigma = \sigma_0(\Phi - \Phi_c)^t \;\forall \Phi > \Phi_c \qquad (3)$$

In Fig. 7, the dc conductivity σ vs. the CNTs concentration for the ENMW at room temperature is illustrated. As can be noted, the percolation threshold, i.e., the critical concentration of the filler at which a remarkable jump of the conductivity is obtained, is lower than 0.1 wt%. Such a low critical concentration and the high asymptotic conductivity (0.4 S/m) at a relatively small loading (1%) are, to the best of the authors' knowledge, among the most remarkable data obtained for MWCNT epoxy-based systems .[23]

The exponent, t, obtained by the interpolation is equal to 1.63; it reveals a 3D organization of the percolating structure and is in good agreement with other experimental results found for similar systems.[23] Moreover, it has been found that even at concentrations higher than 1%, the conductivity does not reach the theoretical values of pure CNTs (it has been verified that the conductivity of dense films of MWCNTs is $\geq 10^3$S/m) owing to the unavoidable barriers of resin that are interposed between clusters of CNTs, resulting in a poor electrical connection between clusters of CNTs. This leads to the suggestion that charge transport in such composite systems is controlled by thermally activated

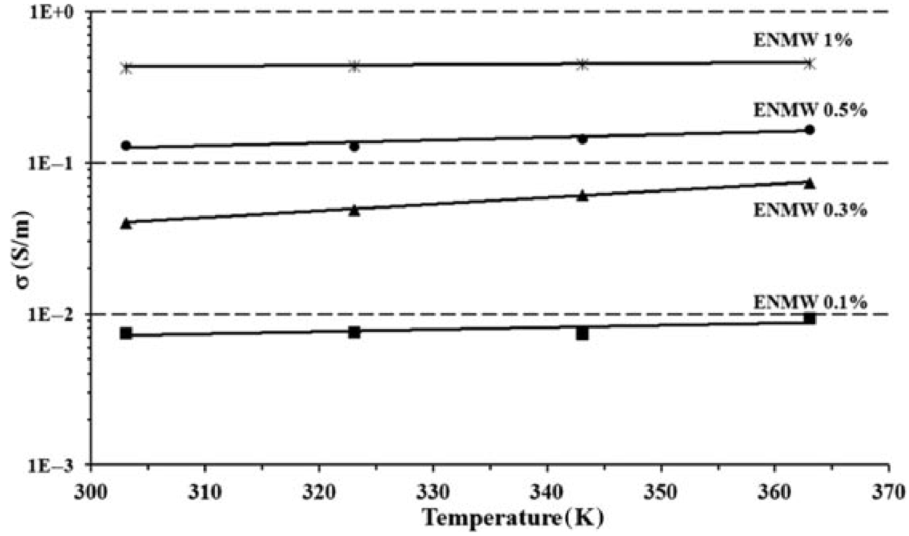

FIGURE 8. Temperature dependence of the dc conductivity for MWCNT-based composites with different concentrations.

hopping.[17,31] This conjecture is also supported by the behavior of conductivity as a function of the temperature. In Fig. 8, the plots of the conductivity vs. temperature in the range 25–90°C for different MWCNT concentrations are presented. The temperature coefficients $\Delta\sigma/\Delta T$ [S/(m K)] obtained from such plots are, respectively, equal to 0.3×10^{-5} S/(m K) for the composite with 0.1 wt% and about 0.5×10^{-4} S/(m K) for the other concentrations. The positive and increasing with temperature coefficient can in effect be attributed to thermally induced hopping transport between weakly connected parts of the network.

The ac properties of the composites as a function of the frequency are reported in Fig. 9, whereas the dependence on the filler concentration at a fixed frequency is displayed in Fig. 10. In particular, the frequency dependence of the real part of the complex electrical conductivity, $\sigma(f)$, obtained from the measured admittance $Y(f)$ of the samples for various MWCNT loadings at room temperature is shown in Fig. 9a. It can be noted that, at low CNT loadings, the conductivity is constant up to a characteristic frequency f_c, above which it increases with increasing frequency following a power law behavior typical of the so-called universal dielectric response[32]

$$\sigma(f) \propto \sigma_0 f_c^s \ \forall f > f_c \tag{4}$$

where σ_0 is the plateau value of the conductivity and s is a characteristic exponent close to unity. At higher CNT concentrations, the conductivity becomes frequency independent, evidencing that the material is characterized by a resistive behavior.

In the considered frequency range, the curves of dielectric permittivity vs. frequency, for all nanocomposites, show the typical dependence attributable to space charge polarization. In fact, space charge can accumulate at the interface between the conducting (CNTs) and the insulating (epoxy) phase. With the increasing loading of MWCNT, additional electrons supplied by CNTs may contribute to this phenomenon.

The relative dielectric permittivity ε_r at a frequency f in the region can be described by the following expression:

$$\varepsilon_r(f) = \varepsilon_0 f^{s-1} \tag{5}$$

where ε_0 is a reference value of the permittivity of composites. For the considered systems, the exponent $s - 1$ varies from 0.12 to 0.24. The complex phenomena associated with the possible formation of the capacitive–resistive networks are deemed responsible for this variability. In any case, it can be noted that the system with 1% loading is characterized by a less sensible dependence on frequency that can be useful in some applications. It has been proposed[33] that when the concentration of MWCNT increases, the interfacial potential energy decreases so that the localized charge carriers can easily hop. Therefore, the polarization is facilitated and can adapt to the higher applied frequency.

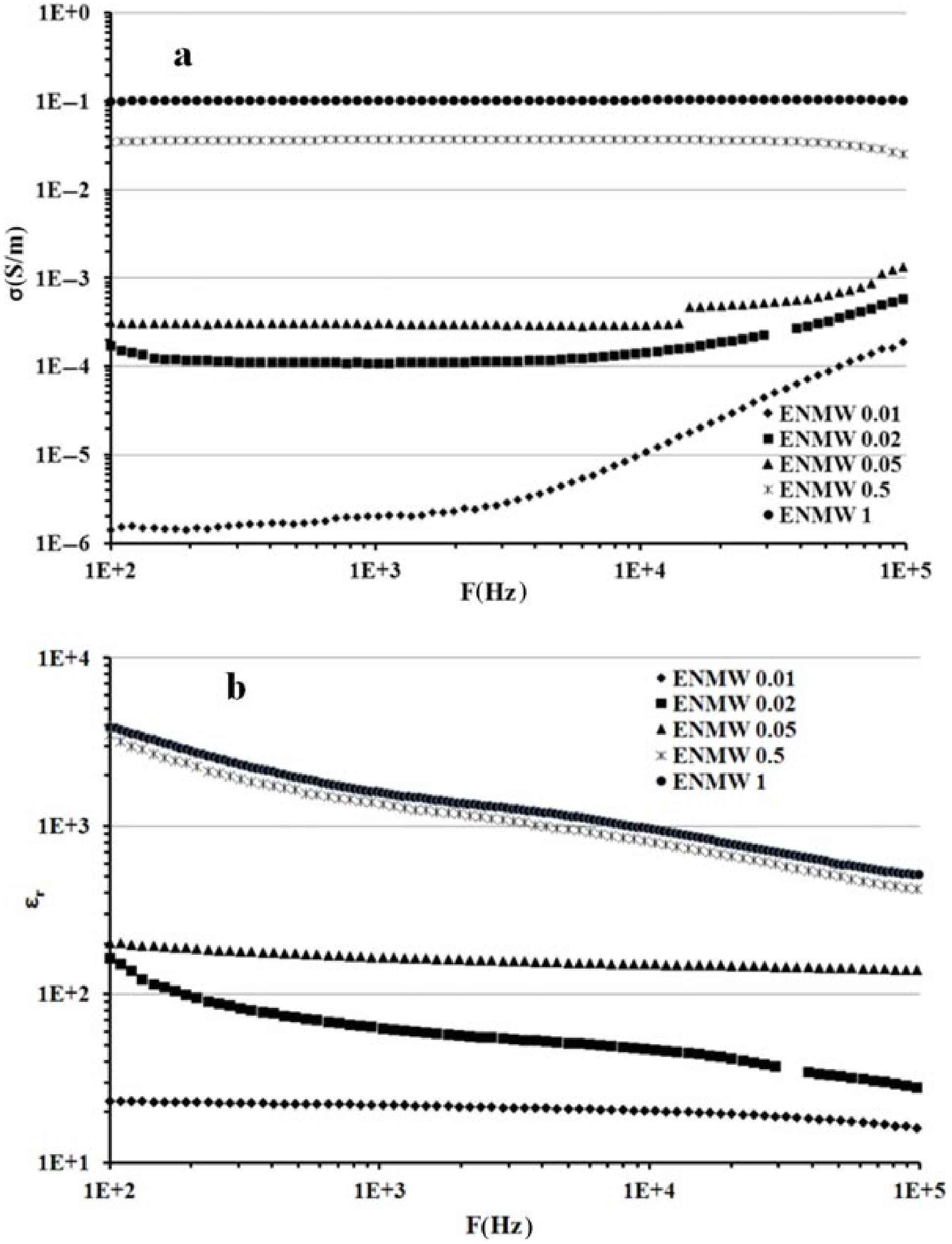

FIGURE 9. Ac conductivity (a) and relative permittivity (b) at room temperature in the low-frequency range for MWCNT-based systems.

Both the conductivity and the permittivity at 100 kHz appear to be above the percolation and are described by a power law. The exponent of the curve describing the ac conductivity is lower than that in dc conditions, indicating a system with a lower dimensionality of the system. This can be attributed to the contribution of the capacitive branches of the percolating network that are active at high frequency.

CONCLUSIONS

Different CNT types, that is SWCNT, DWCNT, DWCNT-NH_2, MWCNT, and MWCNT-COOH, have been incorporated in the same resin, at an equal concentration (0.5%), and with the same dispersion and curing methods, with the aim to find, for similar

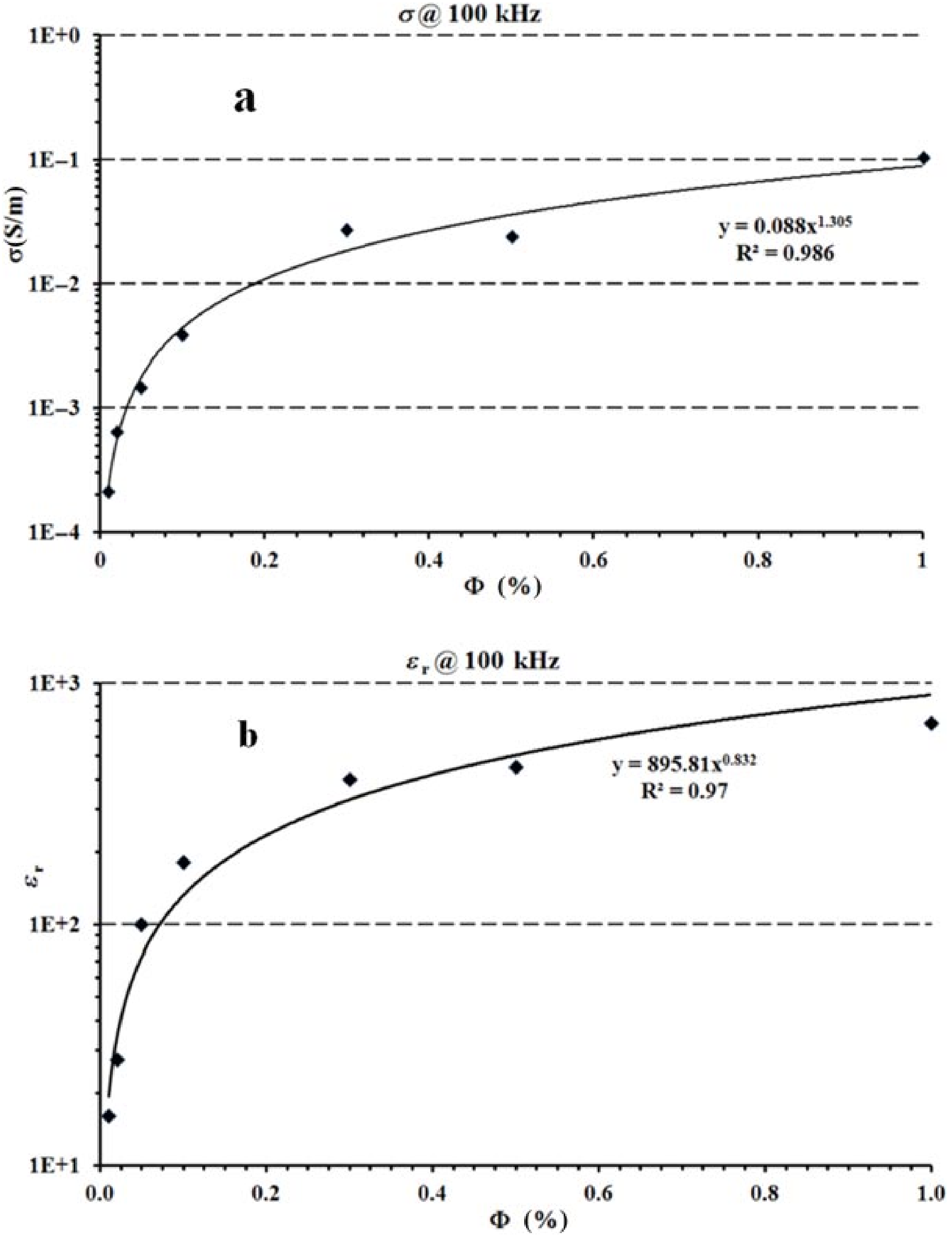

FIGURE 10. Ac conductivity (a) and relative permittivity (b) at 100 kHz as a function of the filler concentration.

experimental conditions, the best type of CNT for improving the mechanical and electrical properties. It has been found that each property is differently influenced by the different CNTs, and a choice can be done with specific reference to the application. If the physical properties of some described filled epoxy materials are compared to composite materials used in airframe and primary structures of modern aircrafts, notable benefits can be hypothesized. In particular, it has been shown for the samples ENMW and ENDW that the physical properties (electrical behavior, mechanical properties, and water sorption/diffusion properties) of these materials are promising for the future aeronautic composite structures. In particular, the maximum electrical conductivity (0.4 S/m) is not far from the target performance. Investigations are still underway aimed at further improving the electrical properties by acting on the CNT distribution inside the polymeric matrix.

To sum up, the most relevant results can be summarized as follows:

- The cure kinetics is accelerated by DWCNT and DWCNT-NH_2.
- The glass transition temperature is slightly increased for MWCNT.
- The elastic modulus is slightly increased for all the unfunctionalized CNT, whereas a decrease is observed for the functionalized.
- MWCNT-COOH and SWCNT show two phases by dynamic mechanical analysis and transport of liquid water.
- The water sorption is very similar for all the CNT types, except SWCNT that shows a slightly lower sorption, besides an induction period before diffusion of water.
- The highest electrical conductivity is achieved for MWCNT, and it is very low for MWCNT-COOH, even lower at 0.5% concentration.
- In both cases of comparison between functionalized and pristine CNT (i.e., MWCNT-COOH vs. MWCNT and DWCNT-NH_2 vs. DWCNT), the conductivity of the first is much lower than the pristine forms.
- The electrical conductivity is lower when the presence of two phases is detected by different methods. The presence of a phase more adherent to the nanotubes determines a higher tunneling resistance between interacting CNTs and therefore a lower limit of the conductivity.

References

1. Iijima, S. Nature 1991, 354, 56–58.
2. Ajayan, P. M.; Zhou, O. Z. In; Dresselhaus MS.; Dresselhaus G. Avouris Ph, (Eds.); Carbon Nanotubes: Synthesis, Structure, Properties and Applications, Vol. 80; Springer; Berlin, Germany, 2001; pp. 391–425.
3. Saito, R.; Dresselhaus, G.; Dresselhaus, M. S. Physical Properties of Carbon Nanotubes; Imperial College Press: London, 1998.
4. Thostenson, E. T.; Ren, Z.; Chou, T. W. Compos Sci Techn 2001, 61(13), 1899–1912.
5. Coleman, J. N.; Khan, U.; Blau, W. J.; Guńko, Y. K. Carbon 2006, 44(9), 1624–1652.
6. Allaoui, A.; Bai, S.; Cheng, H. M.; Bai, J. B. Compos Sci Techn 2002, 62, 1993–1998.
7. Jin, Z.; Pramoda, K. P.; Xu, G.; Goh, S. H. Chem Phys Lett 2001, 337, 43–47.
8. von Klemperer, C. J.; Maharaj, D. Compos Struct 2009, 91, 467–472
9. Martin, C. A.; Sandler, J. K. W.; Windle, A. H.; Schwarz, M. K.; Bauhofer, W.; Schulte, K.; Shaffer, M. S. P. Polymer 2005, 46(3), 877–886.
10. Sandler, J. K. W.; Kirk, J. E.; Kinloch, I. A.; Shaffer, M. S. P.; Windle, A. H. Polymer 2003, 44(19), 5893–5899.
11. Moisala, A.; Li, Q.; Kinloch, I. A.; Windle, A. H., Compos Sci Technol 2006, 66 (10), 1285–1288.
12. Kovacs, J. Z.; Velagala, B. S.; Schulte, K.; Bauhofer, W. Compos Sci Technol 2007, 67(5), 922–928.
13. Kim, Y. J.; Shin, T. S.; Choi, H. D.; Kwon, J. H.; Chung, Y. C.; Yoon, H. G. Carbon 2005, 43(1), 23–30.
14. Du, F.; Fischer, J. E.; Winey, K. I. Phys Rev B: Condens Matter Mater Phys 2005, 72(12), 121404.
15. Spitalsky, Z.; Krontiras, C. A.; Georga, S. N.; Galiotis, C. Compos, Part A: Appl Sci Manuf 2009, 40(6–7), 778–783.
16. Guadagno, L.; Naddeo, C.; Vittoria, V.; Sorrentino, A.; Vertuccio, L.; Raimondo, M.; Tucci, V.; De Vivo, B.; Lamberti, P.; Iannuzzo, G.; Calvi, E.; Russo, S. J Nanosci Nanotechnol 2010, 10(4), 2686–2693.
17. Vionnet-Menot, S.; Grimaldi, C.; Maeder, T.; Strassler, S.; Ryser, P. Phys Rev B: Condens Matter Mater Phys 2005, 71(6), 064201–64212.
18. Mdarhri, A.; Carmona, F.; Brosseau, C.; Delhaes, P. J Appl Phys 2008, 103(5), 054303–54309.
19. Barrau, S.; Demont, P.; Peigney, A.; Laurent, C.; Lacabanne, C. Macromolecules 2003, 36(4), 5187–5194.
20. Kimakis, E.; Amaratunga, G. A. J Appl Phys 2006, 99, 084302.
21. Gorrasi, G.; Sarno, M.; Di Bartolomeo, A.; Sannino, D.; Ciambelli, P.; Vittoria, V. J Polym Sci, Part B: Polym Phys 2007, 45, 597–606.
22. De Vivo, B.; Guadagno, L.; Lamberti, P.; Raimo, R.; Sarto, M. S.; Tamburrano, A.; Tucci, V.; Vertuccio, L. In: International Symposium on Electromagnetic Compatibility (EMC Europe2009), 2009, 11–12 June; pp. 1–4. doi:10.1109/ EMCEUROPE.2009.5189674.
23. Bauhofer, W.; Kovacs, J. Z. Compos Sci Technol 2009, 69, 1486–1498.
24. Guadagno, L.; De Vivo, B.; Di Bartolomeo, A.; Lamberti, P.; Sorrentino, A.; Tucci, V.; Vertuccio, L.; Vittoria, V. Carbon 2011, 49 (6), 1919–1930.
25. Tianle, Z.; Xin, W.; Xiaoheng, L.; Xiong, D. Carbon 2009, 47 (4), 1112–1118.
26. Liao, Y. H.; Marietta-Tondin, O.; Liang, Z.; Zhang, C.; Wang, B. Mater Sci Eng A 2004, 385, 175–181.
27. Gojny, F. H.; Schulte, K. Compos Sci Technol 2004, 64, 2303–2308.
28. McLachlan, D. S.; Heiss, W. D.; Chiteme, C.; Junjie, W. Phys Rev B: Condens Matter Mater Phys 1998, 58, 14880.
29. Wu, J.; McLachlan, D. S. Phys Rev B: Condens Matter Mater Phys 1997, 56, 1238.
30. Chiteme, C.; McLachlan, D. S. Phys Rev B: Condens Matter Mater Phys 2003, 67, 024206.
31. Mdarhri, A.; Carmona, F.; Brosseau, C.; Delhaes, P. J Appl Phys 2008, 103(5), 054303–54309.
32. Jonscher, A. K. Nature 1977, 267(5613), 673–679.
33. Jiang, M. J.; Dang, Z. M.; Bozlar, M.; Miomandre, F.; Bai, J. J Appl Phys 2009, 106, 084902.