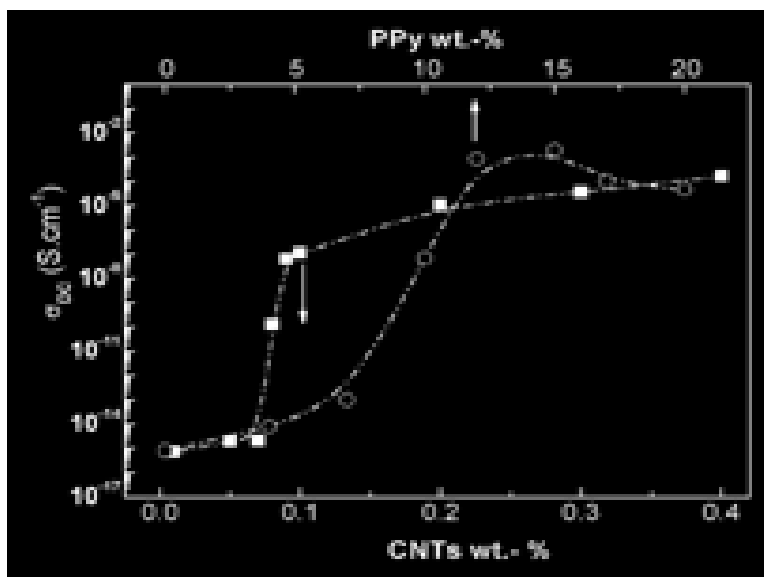


# Glass Transition Temperature Depression at the Percolation Threshold in Carbon Nanotube-Epoxy Resin and Polypyrrole-Epoxy Resin Composites

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## Abstract

**Summary:** The glass transition temperatures of conducting composites, obtained by blending carbon nanotubes (CNTs) or polypyrrole (PPy) particles with epoxy resin, were investigated by using both differential scanning calorimetry (DSC) and dynamical mechanical thermal analysis (DMTA). For both composites, dc and ac conductivity measurements revealed an electrical percolation threshold at which the glass transition temperature and mechanical modulus of the composites pass through a minimum.

## **Introduction**

Epoxy resins are widely used in coatings, adhesives, and structural components for aerospace applications[1] because of their desirable physical and mechanical properties. However, epoxy resins are electrical insulators. In order to dissipate electrostatic charges to achieve materials with antistatic properties, conducting particles, such as intrinsic conducting polymers,[2-5] or fibers,[6],[7] or carbon nanotubes,[8-15] or inorganic nanoparticles[16-19] are dispersed in the epoxy resin matrix. Conducting filler-insulating polymer composites become conductors when the filler content reaches a critical value, or threshold percolation, characterized by a sharp increase of the electrical conductivity. The percolation phenomenon defines the first active pathway of conducting fillers.[20] The percolation threshold,  $p_c$ , represents a transition from a local to an infinite conducting state. The addition of conducting particles improves the electrical properties, but what is their effect on the physical properties of the epoxy network? Some authors indicated a variation of the polymer glass transition temperature ( $T_g$ ) with particles addition.[7],[13],[19]

In this communication, epoxy resin was uniformly filled with two different types of conducting fillers: carbon nanotubes (CNTs) and polypyrrole (PPy). CNTs, discovered in 1991 by Iijima,[21] have exceptional physical properties and an electrical conductivity as high as  $1-100 \text{ S} \cdot \text{cm}^{-1}$ . [22] PPy is an intrinsic conducting polymer with electrical conductivity as high as  $3-6 \text{ S} \cdot \text{cm}^{-1}$  when it is suitably doped.[4],[5]

The nanocomposites physical properties were investigated using electrical conductivity and  $T_g$  measurements.

### **Experimental Part**

#### **Materials and Samples Preparation**

The polymer matrix used in this study, was an epoxy based on a liquid bisphenol A resin (LY5641, density of  $1.2 \text{ g} \cdot \text{cm}^{-3}$ , Hexcel Composites) and a cycloaliphatic amine hardener (HY2954, density of  $0.94 \text{ g} \cdot \text{cm}^{-3}$ , Hexcel Composites). The manufacturer recommends a 100/35 epoxy resin/hardener weight ratio.

CNTs were synthesized by catalytic chemical vapor deposition (CCVD)[23],[24] with a carbon content of 70 wt.-% (81 vol.-%). More than 85% of the CNTs are single or double-walled and almost 90% have a diameter equal to or smaller than 3 nm as characterized by high-resolution transmission electron microscopy (HRTEM). After extraction in HCl, the CNTs were washed repeatedly with distilled water and sonicated for 1 h. The CNTs were stored as a dispersion in water prior to dispersing in the epoxy resin to avoid their packing. PPy was synthesized in colloidal form by a dispersion polymerization as described in detail elsewhere.[4],[5] Finally, a fine black powder was obtained with a small average size value of the particles (100 nm).

CNT-epoxy resin composites were prepared by the dispersion of a determined amount of CNTs, ranging from 0.04 to 0.4 wt.-%. The liquid epoxy resin was added to the dilute suspension of the nanotubes and water was evaporated at  $100 \text{ }^\circ\text{C}$ . The mixture was then mechanically stirred for 1 h at 2 000 rpm. The hardener was added and the whole mixture was mechanically stirred for 15 min and then cast into a Teflon mould and degassed for 20 min under vacuum.

The liquid epoxy resin and PPy powder were mechanically stirred for 5 min at room temperature with a turax turbine at 10 000 rpm. The mixture was degassed under vacuum for 10 min. Hardener was added and the mixture was stirred under vacuum for 25 min. The whole mixture was poured into a mold and then degassed for 20 min. Following this process, PPy-epoxy resin composites with different PPy weight contents were prepared (4, 7, 10, 12, 15, 17, and 20 wt.-%).

All the CNT- or PPy-epoxy resin composites were cured at 120 °C for 20 min, and then at 145 °C for another 8 h.

### Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) experiments were carried out in a Perkin-Elmer DSC7. All the experiments were performed at a heating rate of at 10 °C · min<sup>-1</sup> from 50 to 200 °C. The glass transition temperature,  $T_g$ , was taken as the midpoint of the heat capacity change during the heating run. The cured composites were investigated to ensure a complete curing reaction. No exothermic post curing peaks were observed above the glass transition, excluding the influence of cross-linking degree on  $T_g$ .

### Conductivity Measurements

For CNT-epoxy resin composites, ac conductivity measurements were performed using a Solartron-Schlumberger gain/phase analyzer SI 1260 together with a Novocontrol interface (broad-band dielectric converter). Samples were placed between two 10-mm diameter gold-plated stainless-steel electrodes. The real part  $\sigma'(\omega)$  of the complex conductivity  $\sigma^*(\omega)$  is measured in the frequency range between  $1 \times 10^{-2}$  and  $1 \times 10^6$  Hz at ambient temperature. The dc conductivity,  $\sigma_{dc}$ , was determined as the value of  $\sigma'(\omega)$  in the region of the low-frequency plateau, i.e.,  $1 \times 10^{-2}$  Hz.

For PPy-epoxy resin composites at room temperature, the dc volume electrical conductivity was measured by a two-probe method using a Keithley 617 as the dc voltage generator and electrometer simultaneously for low conductivity samples ( $\sigma_{dc} < 10^{-5}$  S · cm<sup>-1</sup>). For higher conducting samples, conductivity was measured in a four contact configuration using a micro-ohmmeter AOIP OM21.

All the samples used in the conductivity measurements were discs with a diameter of 10 mm, and were coated with silver paste to ensure good contact of the specimen surface with the electrodes.

### Dynamical Mechanical Thermal Analysis (DMTA)

For CNT-epoxy resin composites, DMTA was performed using a Rheometrics ARES Scientific strain-controlled rheometer in the torsion rectangular mode, using a sample size of  $45 \times 10 \times 1$  mm<sup>3</sup>. The maximum strain amplitude used (0.01%) was well within the linear viscoelasticity range for the materials investigated. Dynamic storage and loss moduli ( $G'$  and  $G''$ ) were measured as a function of temperature ranging from -150 to 170 °C at 3 °C · min<sup>-1</sup> at a fixed angular frequency of 1 rad · s<sup>-1</sup>. The temperature control was accurate to within  $\pm 0.5$  °C.

For PPy-epoxy resin composites, DMTA was performed using a Polymer-Lab MKII in a tensile mode, at 1 Hz, from room temperature to 200 °C at 3 °C · min<sup>-1</sup>.

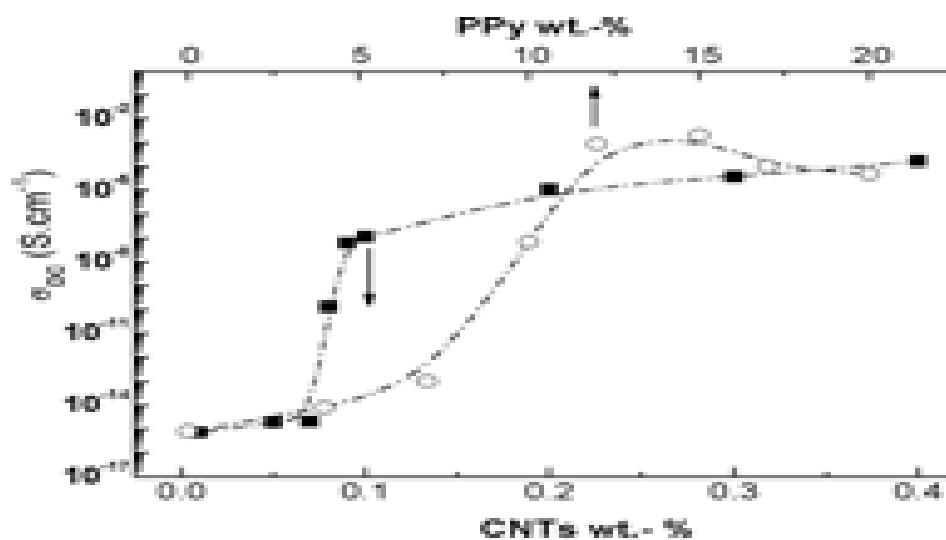
The “dynamic” glass transition temperature  $T_g$  was obtained as the maximum of the tan  $\delta$  peaks.

## Results and Discussion

### CNTs-Epoxy Resin Composites

The dc conductivity, at room temperature, of the CNT-epoxy resin composites is shown in Figure 1 as a function of the weight fraction of the CNTs. The conductivity of the parent epoxy network is about  $1 \times 10^{-15} \text{ S} \cdot \text{cm}^{-1}$ . Between 0.07 and 0.1 wt.-% CNTs, the conductivity of the composite displays a sharp increase by eight orders, and then doesn't change substantially at higher contents to finally reach  $1 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$  at 0.4 wt.-%. According to the universal percolation theory,[21] the dependence of dc conductivity on filler content,  $p$ , near the percolation threshold,  $p_c$ , is described as in Equation (1):

$$\sigma = \sigma_0(p - p_c)^t \quad (\text{for } p > p_c) \quad (1)$$

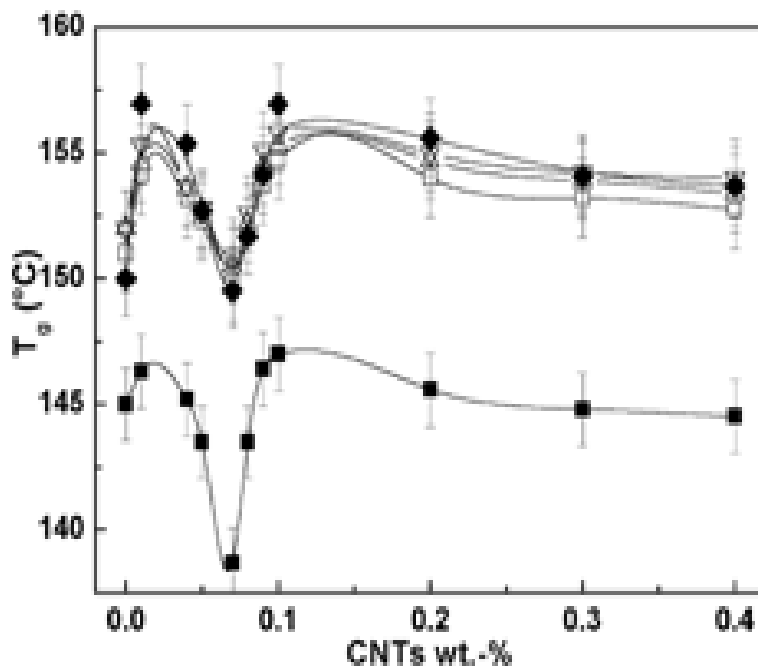


**Figure 1.** DC conductivity of the epoxy resin-based nanocomposites as a function of the conducting filler weight content: (■) CNTs wt.-%; (○) PPy wt.-%. The solid lines are visual aids.

[Normal View 6K | Magnified View 13K]

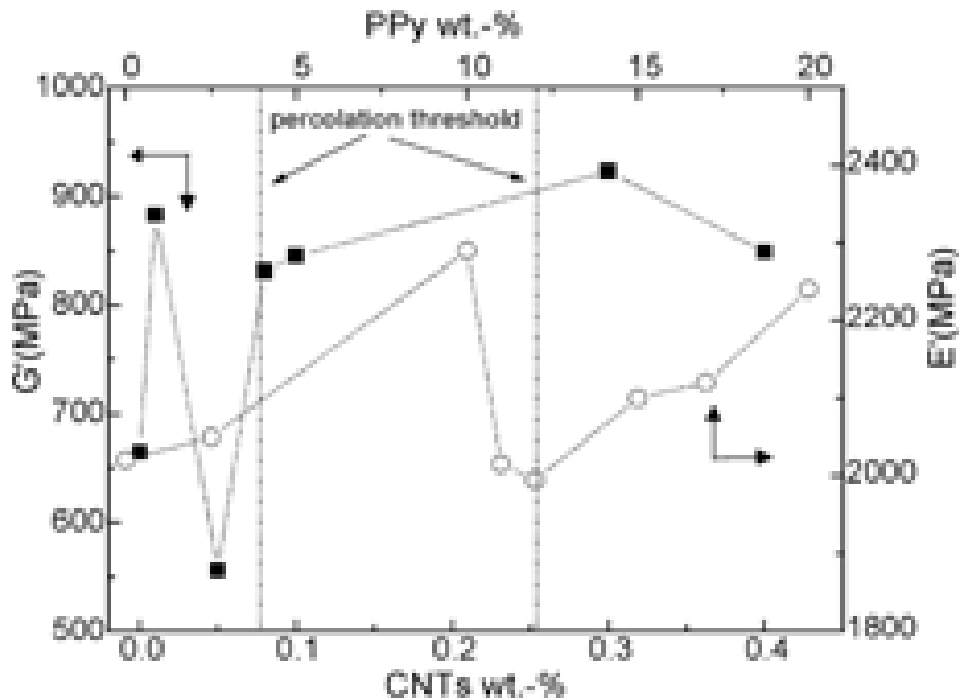
Where  $\sigma_0$  is the intrinsic conductivity, and  $t$  is a critical exponent related to the dimensionality of the system. By fitting Equation (1) to the measured  $\sigma_{dc}$  of the CNT-epoxy resin composites, one can obtain  $p_c = 0.08$  wt.-% and  $t = 2.28$ . An extreme percolation threshold is related to the very high aspect ratio (length to diameter ratio  $L/d$ ) of the CNTs in comparison with other nanoparticles.[13-15]

The CNT-content dependence of the glass transition temperature  $T_g$  is presented in Figure 2. Consecutive heating scans have been performed in order to delete the thermal history of the nanocomposites. At first,  $T_g$  increases slightly at very low CNT-content, and then decreases from 0.04 wt.-%. At lower CNT content (<0.1 wt.-%),  $T_g$  undergoes a weak depression ( $\Delta T_g$ ) of 5 °C at 0.07 wt.-%, i.e., very close to the percolation threshold  $p_c$ . This downshift is significant because the error margin in the  $T_g$  determination is less than  $\pm 1$  °C. Above  $p_c$ ,  $T_g$  increases by 4 °C up to 0.1 wt.-%, and then decreases by only 2 °C with increasing CNT content.  $T_g$  is found to be slightly higher than the value of the parent epoxy network, i.e., 151 °C.



**Figure 2.** Variation of the DSC  $T_g$  of the CNT-epoxy resin nanocomposites with CNT weight content for consecutive DSC heating scans: (■) first heating scan, (□) second heating scan, (●) third heating scan, (○) fourth heating scan. The corresponding variation of DMTA  $T_g$  is added (◆).

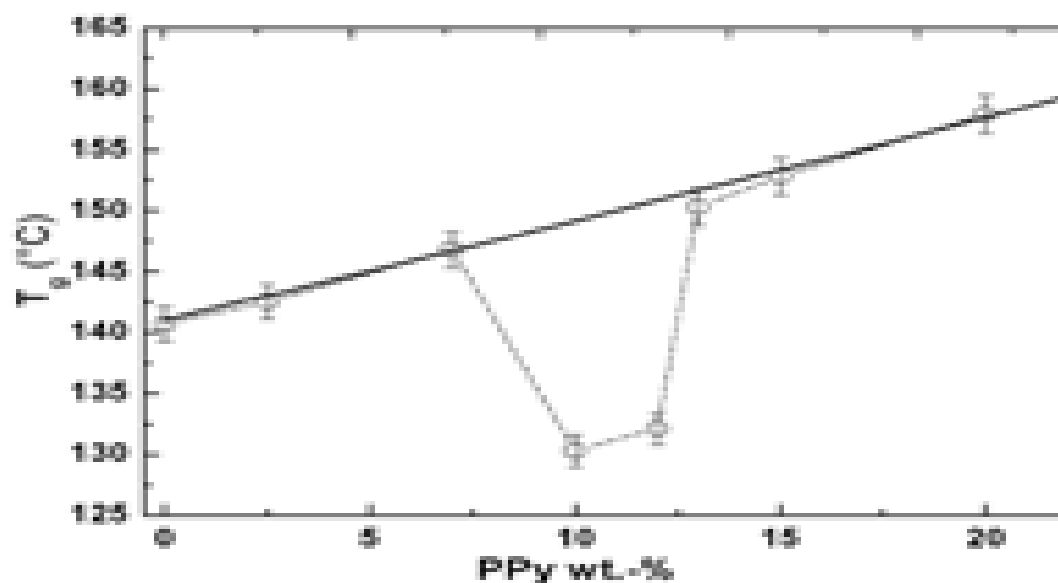
It is clear that an unexpected behavior is observed in the CNT-content dependence of the DSC results for  $T_g$ . After four consecutive heating scans, the  $T_g$  depression is always observed, as shown in Figure 2, indicating that this behavior is independent of the epoxy resin curing. To evacuate an experimental artifact, the effect of CNT-content on the DSC-determined  $T_g$  is compared to the one on the mechanical behavior of the epoxy matrix. The glassy storage modulus  $G'$ , determined at 40 °C, is plotted as a function of the CNT weight concentration and is reported in Figure 3. In the glassy state, the epoxy network modulus increases with the addition of filler. However, below the  $T_g$ , the reinforcement in terms of modulus is low because the CNT-matrix interface is probably not excellent. But this increase is not linear over the range of CNT concentrations studied:  $G'$  is at a minimum for CNT wt.-% values close to the percolation threshold ( $p_c = 0.08$  wt.-%). This trend is confirmed by the unexpected low value obtained at  $p_c$  for  $T_g$ , as opposed to the one observed at very low CNT content (0.01 wt.-%). The CNT-content dependence of DMTA  $T_{\alpha}$  is similar to the DSC  $T_g$  behavior, as shown in Figure 2, with a minimum at  $p_c$ . Beyond 0.1 wt.-%,  $T_{\alpha}$  values remain higher than the one obtained for the neat epoxy network, but the slow reduction of  $T_{\alpha}$  with increasing CNT content supports the presence of weak interactions at the filler-matrix interface and a poor reinforcement of the epoxy matrix.



**Figure 3.** Storage modulus  $G'$  of CNT-epoxy resin nanocomposites (■), at 40 °C, as a function of CNT weight content. The tensile modulus  $E'$  of PPy-epoxy resin nanocomposites (●), at 50 °C, is also shown as the function of PPy weight content (from ref.[4]). The short dotted lines are visual aids.  
 [Normal View 9K | Magnified View 21K]

### PPy-Epoxy Resin Composites

Figure 1 also shows the dc conductivity, at room temperature, of the PPy-epoxy resin composites as a function of PPy weight content. With respect to the parent epoxy network,  $\sigma_{dc}$  increases by eight orders of magnitude, up to approximately  $1 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$  at 15 wt.-% and is described well by Equation (1) with  $p_c = 11 \text{ wt.-%}$ . At higher PPy contents,  $\sigma_{dc}$  reaches a value of  $1 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$  at 20 wt.-%. Figure 4 shows the dependence of the DSC  $T_g$  on the weight fraction of PPy.  $T_g$  increases linearly with PPy wt.-% as expected in polymer blends where  $T_g$  obeys the Fox equation:



**Figure 4.** Variation in the value of  $T_g$  of the PPy-epoxy resin nanocomposites with PPy weight content. The short dashed dotted line is only a guide for the eye. The solid line corresponds to the Fox equation (Equation 2).  
 [Normal View 5K | Magnified View 11K]

Where  $m_e$  is the resin epoxy weight fraction, and  $T_{ge}$  and  $T_{gp}$  are the epoxy network and the PPy glass transition temperatures, respectively. The  $T_{gp}$  value is about 230 °C. As observed for the CNT-epoxy resin composites, the  $T_g$  undergoes a sharp depression greater than 15 °C at the percolation threshold, i.e., between 9 and 11 wt.-%. This abnormal  $T_g$  decrease at the

emergence of a percolating path via connecting PPy particles is more pronounced than in the CNT-epoxy resin composites. As for the CNT-epoxy resin composites, Cassignol[4] has shown that for the same PPy-epoxy resin composites samples, the storage modulus  $E'$ , in the glassy region ( $T < T_g$ ) (see Figure 3) or in the rubbery zone ( $T > T_g$ ), displays a minimum at the electrical percolation threshold,  $p_c$ , of the PPy particles even when  $E'$  increases with increasing PPy content. This singularity is also confirmed using the PPy-content dependence of  $T_g$  where the temperature and magnitude of the  $\tan\delta$  peak are also at a minimum at  $p_c$ .

## General Discussion

Beyond the range of the conductive filler concentration around the electrical percolation threshold, the DSC and DMTA  $T_g$  behavior is dependent on the filler shape. In epoxy resins filled with CNTs, the  $T_g$  displays a weak steady decrease with increasing CNT content above the percolation threshold but remains higher than that of the pure epoxy. In epoxy resins filled with PPy particles, the steady increase of the  $T_g$  with PPy content is a direct consequence of the higher  $T_g$  of the polypyrrole as expected for compatible polymer blends. Here, the dispersion of PPy particles using the turax method seems to be optimal. The thermomechanical behavior of both composites, presented in Figure 3, displays a reinforcement of the epoxy matrix below and above the electrical percolation threshold. This result suggests that the filler may affect the viscoelastic properties of the composites by changing the mobility of epoxy segments in the vicinity of the fillers. Because the nanotubes are nanometer sized fillers with a high aspect ratio, the reinforcement is obtained at very low CNT content, contrary to the high PPy content required to obtain a similar effect.

However, epoxy resins filled with CNTs or PPy particles display the same  $T_g$  behavior with conducting filler only at the percolation threshold: a  $T_g$  depression. It is clear that a correlation exists between the electric percolation and the glass transition phenomena in these conducting nanocomposites. The behavior at the percolation threshold is dependent on the filler shape and, more precisely, on the particle aspect ratio and the associated excluded volume because a weak depression is observed in the nanotube nanocomposites as opposed to the PPy composites where the  $T_g$  downshift is significant. In the epoxy resin-based nanocomposites, a correlation was found both with the tubular carbon particles and with the PPy spherical polymer particles. The inefficiency of the used filler as a reinforcing agent for the epoxy resins only in the vicinity of the electrical percolation threshold, is not a nanosize effect, as the PPy particles are submicrometer in size. When the dispersion of the fillers in the epoxy matrix was assisted by amphiphilic molecules, as for the epoxy resin filled with CNTs in presence of palmitic acid,[25] a depression of  $T_g$  and glassy storage modulus were observed at a percolation threshold as low as 0.04 wt.-%. These results indicate that the  $T_g$  depression origin is not the CNT dispersion state in the polymer matrix.

The conduction percolation is associated with a particular configuration of the conducting particles in the matrix. The drastic insulator-conductor transition is observed in these composites when a first conducting pathway, i.e., an infinite cluster, occurs. The percolation path is related to the conducting phase, whereas the  $T_g$  or  $T_g$  is characteristic of the segmental mobility in the epoxy matrix. The  $T_g$  downshift in the vicinity of  $p = p_c$  is interpreted as an increase of the mobility of the epoxy matrix chain segments. Just below  $p_c$ , the conducting particles form many finite size clusters. In the percolation range, the free volume accessible to the molecular motions of epoxy chain segments is maximal.

## Conclusion



A correlation between electrical percolation threshold and glass transition phenomena in epoxy resin-based nanocomposites is observed. At the filler content in the vicinity of the percolation threshold, the glass transition temperature,  $T_g$ , decreases by some degrees, and is associated with a plasticization phenomenon. The magnitude of the temperature depression is dependent on the filler shape. In composites displaying an insulator-conductor transition, DSC measurements appear as a way to estimate the percolation threshold.

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