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Percolation threshold of carbon nanotubes filled unsaturated polyesters

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Abstract

This paper reports on the development of electrically conductive nanocomposites containing multi-walled carbon nanotubes in an unsaturated polyester matrix. The resistivity of the liquid suspension during processing is used to evaluate the quality of the filler dispersion, which is also studied using optical microscopy. The electrical properties of the cured composites are analysed by AC impedance spectroscopy and DC conductivity measurements. The conductivity of the cured nanocomposite follows a statistical percolation model, with percolation threshold at 0.026 wt. % loading of nanotubes. The results obtained show that unsaturated polyesters are a matrix suitable for the preparation of electrically conductive thermosetting nanocomposites at low nanotube concentrations. The effect of carbon nanotubes reaggregation on the electrical properties of the spatial structure generated is discussed.

Keywords: A. Carbon nanotubes, A. Nano composites, A. Polymers, B. Electrical properties, Unsaturated polyester resin

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1. Introduction

Carbon nanotubes (CNT) have been the focus of extensive research efforts in the context of multifunctional composite materials [1, 2]. The discovery of electrically conductive behaviour dominated by percolation at low filler loadings [3] has led to wide interest in the interplay between the processing and the electrical response of carbon nanotube based nanocomposites. Thermosetting epoxies have been considered as the most promising candidate matrix polymers, as early results reported conductive behaviour by the addition of less than 0.1 wt. % of multi-walled nanotubes (MWNT) [4]. Few works have investigated the addition of carbon nanotubes in unsaturated polyester resin systems [5, 6, 7, 8]; the observed percolation thresholds are about 1 wt. % for entangled CNT and about 0.1 wt. % for non-entangled CNT. Vinyl ester based nanocomposites, similarly to epoxy, follow conductive behaviour at concentrations of nanofiller below 0.1 wt. % [9]. The electrical percolation and conductivity of CNT nanocomposites is the topic of a large number of publications, which have been recently reviewed in [10]. As the authors point out, nanocomposites based on non-entangled MWNT are about 50 times more conductive than industrial MWNT.

The electrical properties of heterogeneous systems of conductive fillers in insulating matrices above the percolation threshold can be described by the statistical percolation model as follows [11]:

$$\sigma = \bar{\sigma}_0(\psi - \psi_c)^{\bar{t}}, \quad \psi > \psi_c \quad (1)$$

where σ is the conductivity of the nanocomposite, ψ denotes the volume fraction of the filler, \bar{t} is a critical exponent that depends on the geometry of the network, $\bar{\sigma}_0$ is the proportionality coefficient and ψ_c is the percolation threshold, i.e. the volume

fraction of filler necessary to form a network of contacting particles, at which the system behaviour changes from electrically insulating to conductive. The percolation threshold can be calculated analytically using the excluded volume theory [12, 13], which for a filler of cylindrical shape and high aspect ratio yields:

$$\psi_c = 1 - e \left(- \frac{1.4 [(\pi/4)W^2L + (\pi/6)W^3]}{[(4\pi/3)W^3 + 2\pi W^2L + (\pi/2)WL^2]} \right) \quad (2)$$

where W is the diameter and L is the length of the nanotubes. This result assumes straight and randomly oriented filler rods. It is expected that waviness alone, assuming ideal dispersion, leads to an increase of percolation threshold of up to a factor of two [14]. The concentrations used for the percolation model described by Eq. 1 are expressed in terms of volume fractions. Since the density of nanotubes is not known with high accuracy it is more convenient to use an expression that involves weight fractions when referring to CNT based nanocomposites. The low loading fractions allow Eq. 1 to be modified as follows:

$$\sigma = \sigma_0(\phi - \phi_c)^t, \quad \phi > \phi_c \quad (3)$$

Here ϕ is the weight fraction, ϕ_c is the weight fraction percolation threshold and σ_0 and t denote the proportionality coefficient and the exponent of the weight fractions percolation model respectively.

The quality of filler dispersion is a critical factor in the preparation of nanocomposites based on nanotubes, governing the effectiveness of electrical conductivity enhancement [15]. Materials characterised by non-homogeneous dispersion of nanofiller have improved electrical properties compared to the neat resin; however the loading required to form a percolating network is significantly higher than that predicted by Eq. 2 [10]. Commercial multi-walled nanotubes are typically wavy and mechani-

cally entangled in microscopic clusters, which must be dispersed in the resin matrix without excessively damaging their structure and without decreasing their length. Aligned multi-walled and single-walled nanotubes are easier to disperse due to the partial elimination of both waviness and entanglement. Several techniques have been used successfully to disperse nanotubes in thermosetting resins including high shear mixing, triple-roll milling and ultrasonication [16], with the route used usually being specific to the type of the matrix.

When homogeneous dispersions of filler particles are allowed to partially reaggregate during cure, the resulting electrical conductivity can be higher than that of the non reaggregated material [17]. The fractal structure of the filler network results in more contacts between nanotubes than that predicted by statistical percolation theory, leading to increased conductivity. This phenomenon has been observed initially in the preparation of carbon black reinforced epoxy composites [18] and has been confirmed in carbon nanotube reinforced epoxy nanocomposites [19, 17, 20]. During the process of dispersion the filler particles become electrostatically charged, stabilising the suspension and preventing spontaneous agglomeration. The formation and the morphology of the structure of aggregates can be influenced by the application of electric field [21] and shear [22]. However, well-dispersed suspensions of nanotubes in epoxy have been reported to reaggregate spontaneously as a consequence of hardener addition [17]. The lowest percolation thresholds reported in the literature are 0.0021 wt. % for composites based on non-entangled multi-walled nanotubes [21, 22, 19], 0.005 wt. % for single-walled nanotubes [17] and 0.011 wt. % for entangled multi-walled nanotubes [4, 20], all of which have been obtained using epoxy matrices. As Bauhofer and Kovacs point out in their review [10], with optimised dispersion a percolation threshold in the range of 0.1 wt. % might be possible for nearly any CNT/polymer system.

This work reports on the development of an unsaturated polyester/nanotube nanocomposite with low percolation threshold. The process of dispersion based on high shear mixing is monitored on-line by measuring the electrical resistivity of the liquid suspension. Microscopy is utilised to study the spatial structure of the nanotubes network formed by reaggregation during the cure of the matrix. The electrical behaviour of the cured material is investigated and its dependence on the content of nanotubes is used to evaluate the percolation threshold of the nanocomposite. This paper demonstrates that well dispersed suspensions of entangled MWNTs in unsaturated polyesters produce nanocomposites with the same levels of conductivity as these observed in epoxy/entangled-MWNTs systems.

2. Experimental

The carbon nanotubes used in this work are a commercial grade of entangled multiwalled nanotubes, prepared by carbon vapour deposition, with a carbon purity of 90%, nominal diameter and length of 9.5 *nm* and 1.5 μm respectively. The percolation threshold, calculated by equation 2 without accounting for waviness, is 0.43 vol%, which can be related to a value of gravimetric percolation threshold of approximately 0.96 wt. % [10, 23].

The matrix used for the preparation of nanocomposites is an unsaturated polyester resin (UPE, from Scott Bader), with styrene content of 30 wt. %. Neat resin and nanocomposites were cured following a standard industrial procedure, by the addition of 0.02 wt. % of cobalt octanoate and 0.3 wt. % of methyl ethyl ketone peroxide. After the addition of cobalt and peroxide the samples were placed in an oven at 40°C for 6 hours, followed by 3 hours at 120°C to obtain full cure.

2.1. Sample Preparation

A masterbatch of pre-dispersed carbon nanotubes has been prepared using the procedure described by other authors [9, 24]. Appropriate amounts of unsaturated polyester resin and masterbatch were compounded to obtain mixtures with CNT loading ranging from 0.05 to 0.3 wt. %. The dispersion in the UPE resin was carried out by high shear mixing using a lab-scale setup described in [25]. The apparatus comprises an overhang stirrer, a flow-through cell and a condenser to limit styrene evaporation. Each sample was mixed for 420 minutes at 1000 rpm, whilst the temperature was kept between 30 and 35°C. The extent of styrene evaporation has been investigated measuring the matrix-dominated high-shear viscosity of the suspensions prepared [26]. At all the filler loadings the analysis showed no measurable effect of styrene evaporation during processing.

During processing a peristaltic pump fed the material to a coaxial flow-through cell designed to measure the resistivity of the liquid [25]. The deviations of resistance due to temperature variations were corrected by assuming an Arrhenius dependence of conductivity on temperature and calculating the values of resistivity at a reference temperature of 34°C, following the procedure described in [25]. The procedure for on-line measurement of suspension conductivity is reported in [27].

2.2. Microscopic analysis

The quality of dispersion after mixing was assessed by transmission optical microscopy of the liquid suspension [28]. A sample of 20 ± 1 mg of mixed material was placed onto a microscope slide and a 16 mm cover slip was positioned on top. The liquid was uniformly spread over the whole area under the slip. The resulting thickness of liquid nanocomposite is 90 ± 10 μm . All the samples were analysed with identical sub-stage illumination.

Transmission optical microscopy and SEM charge contrast imaging were used to investigate the morphology of the nanotubes in the cured composites. The samples for optical microscopy were $100 \pm 20 \mu\text{m}$ thick slices of cured material, cut from the surface of the sample. The slices were cut using a Buehler Isomet precision sectioning saw with a diamond wafering blade. The samples for charge contrast imaging were prepared by painting a thin layer of the suspension, after the addition of cobalt and peroxide, onto an aluminium stub and oven-curing as described before. Micrographs of the surface of the samples were taken using a FEI SFEG-SEM at acceleration voltage 15 kV, working distance 5 mm and TLD detector.

2.3. Electrical measurements

AC impedance spectroscopy was carried out after cure using a Solartron SI 1260 frequency response analyser. An interdigitated copper sensor (GIA sensors, Pearson Panke) was embedded in the material by immersion in a glass tube containing the liquid resin, previously mixed with cobalt and peroxide. The glass tube was placed in a heated cell and cured using the thermal profile described previously. The measurements were performed after cure completion, at temperature of 40°C , in the frequency range between 1 Hz and 1 MHz measuring five frequencies per decade on a logarithmic scale. The AC conductivity σ of the sample was calculated from the real and imaginary parts of complex impedance (Z^*) as follows:

$$\sigma(\omega) = \frac{l}{|Z^*(\omega)|} \quad (4)$$

where ω is the angular frequency and $l = 3.93 \text{ m}^{-1}$ is the geometric constant of the sensor [29].

The DC electrical conductivity of the cured materials was determined by a two-point measurement. The two parallel faces of a cylinder of cured material (diameter 8 mm, height 4 mm) were painted with a suspension of silver in methyl isobutyl

ketone (Acheson Electrodag 1415M). After complete evaporation of the solvent, the value of resistance was measured at 20°C. High resistance samples, i.e. the neat resin, were characterised with a Keithley 6517A electrometer. Low resistance samples, i.e. nanocomposites, were characterised with a DC precision current source (Keithley 6220) and a nanovoltmeter (Keithley 2182A) using the three-point delta current reversal technique [30]. The DC conductivity of each sample has been measured four times on four different cylinders at each level of loading, calculating the corresponding standard deviations. The process of dispersion and cure has been replicated for two levels of loading, randomly chosen, namely 0.25 wt. % and 0.3 wt. %. The replicability of the process of preparation of the nanocomposite has been confirmed by the absence of statistically significant difference between the mean DC conductivity of replications.

3. Results and discussion

3.1. Dispersion of CNT

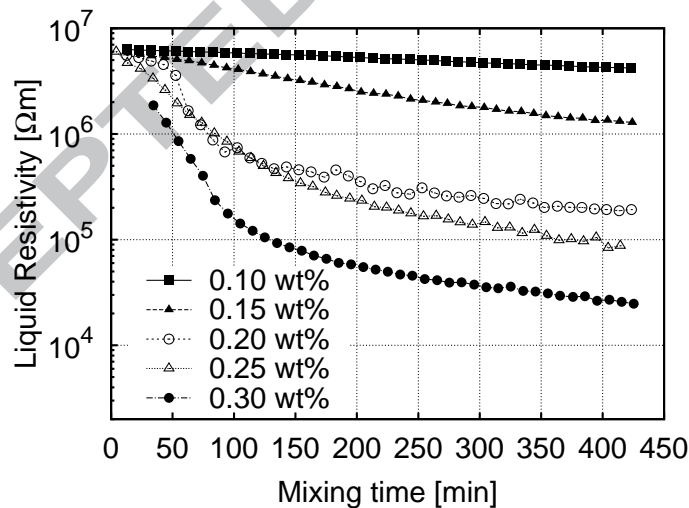


Figure 1: Evolution of liquid resistivity during the mixing of a resin suspensions.

The evolution of the liquid resistivity of a sample during processing is shown in figure 1. The evolution of resistivity for the 0.05 wt. % suspension is similar to the 0.1 wt. % loading, but the inclusion of air bubbles during mixing caused a high noise-to-signal ratio. The mixing at 0.05 wt. % has been excluded from the graph for better clarity.

At the beginning of the process the resistivity is in the order of several $M\Omega$ m, and decreases slowly with mixing. After an incubation period, whose duration varies with the filler content (e.g. about 50 minutes in the sample containing 0.2 wt. % CNT), the resistivity falls. The magnitude of the decrease is correlated with the filler loading of each mixture. This is followed by a steady decrease until the end of the process. The value of liquid resistivity at the end of processing varies between 4.2 $M\Omega$ and 24.7 $k\Omega$ at 0.1 and 0.3 wt. %, respectively.

The incubation period corresponds to the time necessary for individually dispersed CNTs to reach the onset of percolation. The amount of individually dispersed nanotubes at a certain time of processing is higher for suspensions with higher filler loading. The interpretation of the liquid suspensions in terms of percolation explains the sharp fall of resistivity observed for loadings 0.2 wt. % and above, which is typical of such systems at percolation. The downward trend in the final part of processing suggests that dispersion is not complete after 420 minutes of mixing.

Figure 2 illustrates the filler dispersion during the mixing of the 0.15 wt. % suspension. Clusters of undispersed nanotubes appear as isolated dark particles. The dimension of these particles decreases with mixing. Dark areas with size of several tens of micrometres are observed after 160 minutes. At the end of processing the suspension appears homogeneous and optically dispersed [28], with dimension of residual clusters of undispersed nanotubes below 5 micrometres. The total area covered by the residual clusters appears small compared to the samples before shear

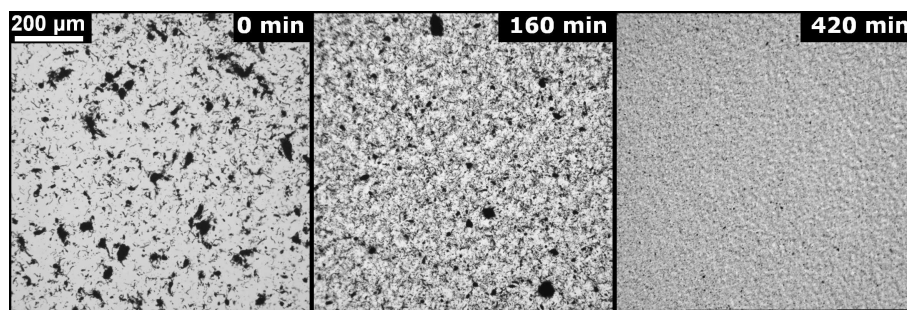


Figure 2: Optical micrographs of 0.15 wt. % suspension before, during and after mixing.

mixing (not shown here) and the residual area is similar between all loadings. The existence of undispersed nanotube clusters corroborates the suggestion of incomplete dispersion based on the continuous drop of liquid resistivity.

3.2. Morphology of CNT in cured nanocomposites

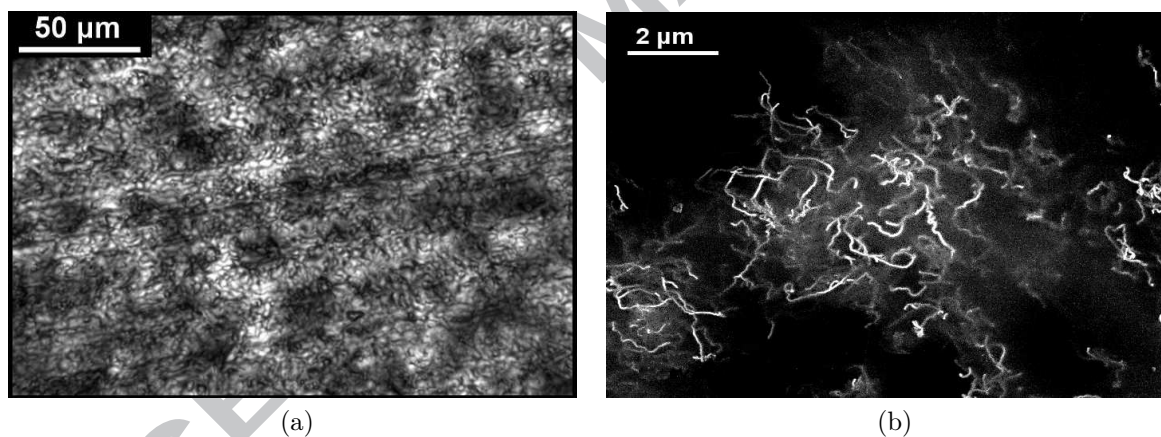


Figure 3: Nanocomposite containing 0.15 wt. % of carbon nanotubes: (a) transmission light micrograph (b) charge contrast imaging.

Figure 3a shows the microstructure of the cured nanocomposite containing 0.15 wt. % . This loading has been selected to show and to compare reaggregation at microscale and nanoscale, as the best compromise between high conductivity required

for contrast charge imaging and optical transmission required for optical microscopy. The existence of an heterogeneous structure comprising areas of high and low nanotube content is observed with optical microscopy. The low brightness regions, corresponding to relatively higher nanotube content, cover a significant percentage of the sample area indicating the existence of aggregates of a different nature to those originally mixed with the resin. These aggregates, which are formed during the cure of the material, are not as tightly packed as the original clusters. Charge contrast imaging can be used to visualise the morphology of the reaggregated nanotubes embedded in the resin in the proximity of the sample surface [31, 32]. Figure 3b is a representative example of the structure of such secondary agglomerate. Its size is about $10\ \mu\text{m}$ and it comprises an assembly of loosely packed nanotubes. Since the tubes are wavy and entangled, a precise evaluation of their length is not possible. However, most of the visible nanotubes appear to be longer than the nominal length of $1.5\ \mu\text{m}$, suggesting that carbon nanotubes have not been damaged during processing.

3.3. Electrical behaviour

Impedance spectroscopy has been used to evaluate the AC conductivity of composites at the end of cure, as shown in figure 4. The neat cured resin follows a purely capacitive behaviour at all frequencies. The nanocomposite with loading of 0.05 wt. % exhibits a frequency independent conductivity up to $10^4\ \text{Hz}$, which changes to a capacitive response at high frequencies. The nanocomposites with nanotubes loading greater than 0.1 wt. % show a predominantly resistive electrical behaviour, with constant conductivity over the whole range of frequencies investigated.

The effect of filler loading on the DC conductivity of the solid composites is shown in figure 5a. The neat resin is an insulating material, with an electrical

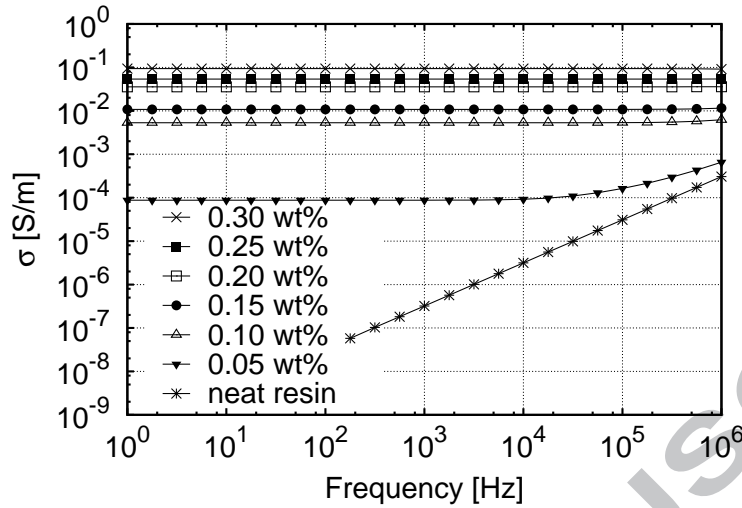


Figure 4: AC conductivity at the end of curing as a function of frequency for different filler loadings.

conductivity in the order of 10^{-12} S/m. Addition of 0.05 wt. % of filler increases the electrical conductivity by eight orders of magnitude, to the value of $2.7 \cdot 10^{-4}$ S/m. Conductivity increases further with higher loading, up to $1.3 \cdot 10^{-1}$ S/m at the highest loading tested. The values of DC conductivity are in agreement with the values of AC conductivity measured by impedance spectroscopy. The conductivity of the liquid suspensions at the end of processing is compared with the conductivity of the nanocomposite in figure 5a. The values in the two cases differ by a factor of about 10^4 . It is interesting to note that the two trends imply a positive correlation between liquid and solid conductivity. This specific subject has not been developed within this study and will be the subject of further investigation. However, the experimental data suggest that the electric behaviour of liquid suspensions and solid nanocomposites are controlled by percolation in similar manners. Liquid conductivity measurements during processing might potentially be exploited to predict the final conductivity of

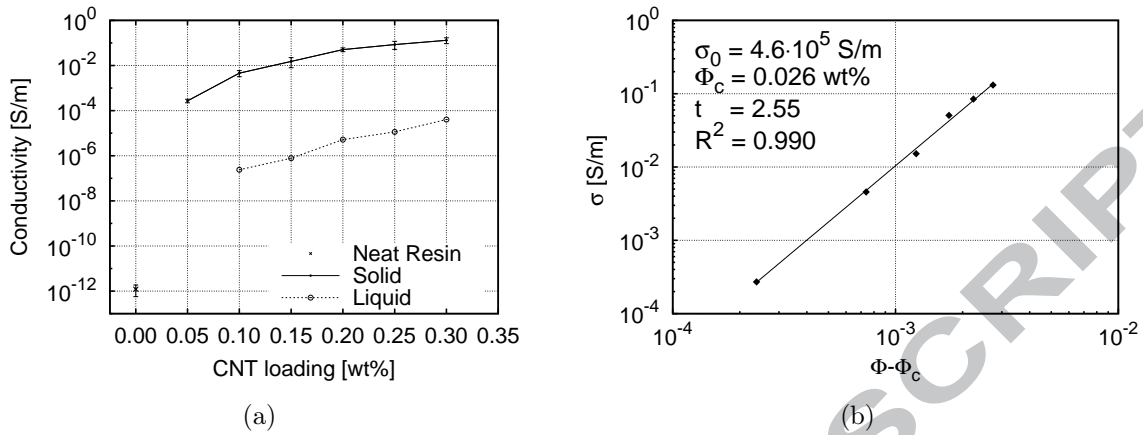


Figure 5: (a) DC conductivity as a function of filler loading. Error bars denote three times the standard deviations of nanocomposites and one time the standard deviation of neat resin. Circles denote the liquid conductivity of suspensions at the end of mixing. (b) Fitting of DC conductivities according to equation 1.

the corresponding nanocomposite. The solid nanocomposites show the characteristics of a percolating system. Conductivity at various loading has been fitted to the model of statistical percolation described by equation 3, resulting in a percolation threshold of 0.026 wt. % and a critical exponent of 2.55. The value of percolation threshold is significantly lower than the value predicted by statistical percolation theory (0.96 wt. %). This suggests that the electrical properties of the CNT-unsaturated polyester composite are enhanced by the spontaneous reaggregation of filler particles during cure, as previously reported for CNT/epoxy systems.

The electrical properties of the material described in this study have been compared with the data published in literature. The percolation threshold observed compares well with the best results obtained with entangled MWNT in different polymers, i.e. epoxy, polyurethane and vinyl esters [9, 10]. The value is forty times lower than the 1 wt. % previously observed for entangled MWNT/unsaturated

polyester systems and four times lower than the 0.1 wt. % observed for non-entangled MWNT/unsaturated polyester systems [8]. Given the simple preparation process, the low cost of the resin and the electrical conductivity achieved, CNT/unsaturated polyester nanocomposites hold potential for the production of electrically conductive composites.

4. Conclusion

The preparation of microscopically uniform unsaturated polyester nanocomposites based on industrial grade multi-walled nanotubes has been carried out successfully using a combination of triple roll milling and shear mixing. The resistivity of the liquid composite has been measured to monitor the evolution of dispersion during processing. The on-line data showed that, after an incubation period that is correlated to the filler loading, the resistivity of the suspension decreases steadily until the end of the process. The magnitude of the drop is also positively correlated to the filler loading. This is followed by a gradual decrease which is attributed to the existence of residual undispersed clusters of nanotubes. The value of conductivity of the liquid suspension at the end of mixing is directly correlated to the filler loading and the final value of conductivity of the nanocomposites.

The final level of dispersion achieved was adequate to create a conductive network whilst preserving the high aspect ratio of filler particles. Well dispersed suspensions of nanotubes in unsaturated polyester form a spatial structure of agglomerates during cure which results in a percolation threshold of 0.026 wt. %. The cured nanocomposite has maximum conductivity of 0.13 S/m for 0.3 wt. % CNT loading.

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