

Development of Unsaturated Polyester Matrix – Carbon Nanofibers Nanocomposites with Improved Electrical Properties

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ABSTRACT: In this work, the dispersion of carbon nanofibers (CNFs) in an unsaturated polyester (UP) resin was performed by mean of the calendering process. The calendering process allows to obtain good dispersion of the nanoparticles, and, with respect to the other techniques, is also possible to scale it up at the industrial level. Optimization of the calendering conditions for the processing was carried out as a first step of this study. Optimization, in this case, means to reach the best dispersion level, as rapidly as possible and with the lowest amount of styrene evaporation. The dispersion level reached was investigated by the technique of scanning electron microscopy. The investigation on electric conductivity of the nanocomposites at different CNF

concentrations has revealed that the electrical percolation threshold exists at around 0.3 wt %, where electrical conductivity switches from 10^{-13} to 10^{-7} S/cm. The rheological characterization has been performed to verify if the improved electrical properties are obtained at the expense of loss of workability, that is a significant increase of viscosity. Eventually, a mechanical characterization was carried out. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1658–1666, 2010

Key words: unsaturated polyester resin; carbon nanofibers; electrical properties; calendering

INTRODUCTION

The possibility to modify and model materials at nanoscale level is leading modern society to developments that were unthinkable just a decade ago. For this reason, researchers all over the world have been focused on their studies in nanotechnology and nanomaterials: dispersion of even a low concentration of nanoparticles in a material can lead to a drastic enhancement of their performance.¹ Among the most common nanofillers used nowadays, carbon nanotubes and nanofibers have a particular role, because of their capability of significantly modifying the electrical properties of materials.^{2–6} The enhancement of the properties, which can be obtained, thanks to the introduction of nanotubes or nanofibers in a polymeric matrix, are possible only if the nanofillers are evenly dispersed into the matrix. Many techniques have been employed to improve the dispersion of nanoparticles inside the matrix.⁷ In the case of the processing of thermosetting-based nanocomposites, most of the approaches involve different steps that include mechanical stirring,^{4–8} high

energy sonication, and solution-evaporation processing.^{9–15} Most of these techniques, although valid, are limited by their scale up to produce larger amounts of nanocomposite material. In fact, only a technique which allows high rate and high volume production, can be really exploited for industrial applications.

Gojny et al.^{16–18} proposed a novel technique for nanoparticle dispersion that involves the use of calendering process. Calendering is nowadays used in many different applications, which need the dispersion of microsized particles in sectors, such as cosmetics, paints and coating, rubber, inks, and pigments. The insight was to apply this technique to disperse nanoscaled particles inside polymers with an extended degree of homogeneity. Basically, this method consists of forcing the fluid mixture of nanoparticles and resin to pass through adjacent cylinders separated by a very small gap. This flow is characterized by elevated shear stresses, which allow the breakage of the particles agglomerates and the dispersion of the nanometric particles. The advantage of using this approach is that this is a solvent-free, up-scalable technique, and furthermore, it produces homogeneous material properties as the whole fluid is uniformly stirred through the calender.

In this study, the calendering process was used to disperse carbon nanofibers in an unsaturated polyester resin, using a processing method that allowed to

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optimize the dispersion and the final properties of the nanocomposite. In the first part of this study, several calendaring conditions were investigated, to find which one produced the best results in terms of nanofibers dispersion.

Regarding the calendaring conditions, Gojny et al. in their papers proposed an approach in which the mixture of resin with nanofillers is divided in small batches, which are subsequently spread into the rolls for a dwelling time of 2 min and finally they are collected. However, this approach, suitable for epoxy resins, is barely applicable for UP resins as it causes the total evaporation of the styrene, compromising the possibility of collecting a reactive system.¹⁹ Thostenson et al.²⁰ suggested to perform different calendaring cycles, starting with larger gaps and progressively reducing them, to avoid the rupture of the nanoparticles, which involves a catastrophic reduction of their aspect ratio, and consequently, a decrease of the properties of the nanocomposites. The first cycles, in fact, break the bigger agglomerations, whereas during the last cycles, which are made using a smaller gap, the nanoparticles are homogeneously dispersed.

Once the best calendaring conditions were optimized, nanocomposites with different concentration were produced and studied.

Since the main goal of this study was to realize a thermoset-based nanocomposite with improved electrical properties, the key investigation was on electrical conductivity. However, the results on the electrical properties would be really attractive only if this improvement were not obtained at the expense of both, loss of workability and drop of other properties. In fact, it is well known that the presence of nanoparticles strongly affect the rheological behavior of a liquid resin (see for example, Ref. 21). For this reason a rheological characterization was also performed: in fact, many times the loss of workability for thermosets processing is strictly connected to the increase of viscosity. For the same reasons, a mechanical characterization was carried out. In fact, pristine carbon nanofibers, as the ones which were used in this study, could not have the strong surface interaction with the matrix, which they could have if compatibilized. If the interaction is too weak, the nanoparticles could act as defects and not as reinforcement, resulting in a drop of mechanical properties. Nonetheless, compatibilization is a quite expensive process, which is not feasible when a cost effective nanocomposite is produced, and therefore was not taken into account in this article.

EXPERIMENTAL

Polyester resin is one of the most used thermosetting matrix, because of its low cost and good properties.

The one employed in this study is a low-viscosity orthophthalic unsaturated polyester (UP) resin supplied by Cray Valley with the commercial name of Enydyne I 68835.

Vapor grown carbon nanofibers were purchased from Grupo Antolín (Spain). As claimed by the manufacturer, they have a highly graphitic structure (more than 70%) and, regarding to the dimension, an average diameter of 45 nm and a length of more than 30 microns that lead to an aspect ratio more than 600. They were employed as supplied by the manufacturer, without any other chemical process to increase the compatibility with the UP resin.

The cure reaction was activated by methyl-ethyl ketone peroxide (MEKP), in the percentage of 1.5 wt %, as recommended by manufacturer, and accelerated by 0.15 wt % of cobalt octoate (6%): first, the accelerator was mixed with the resin then the peroxide was added, to avoid the exothermic reaction between these two components. The reactive system was then held at room temperature for more than 600 min, and followed by a post-cure process at 55°C for an hour and 70°C for another hour.

Nanocomposites with different concentrations of nanofibers were produced and tested, and their properties were compared with those of the neat resin. Basically, six different percentages were chosen, namely 0.1, 0.3, 0.5, 1, 2, 3 wt %. Nonetheless, because of high viscosity of the 3% loaded mixture, the production of samples with this content without the presence of bubbles was inhibited. Consequently, at such filler percentage, electrical, mechanical, dynamic mechanical, and thermo-mechanical tests were not performed. Instead, the rheological study was faced even at 3%, as it was performed on the liquid system.

The following procedure was used to obtain the nanocomposite samples. First, the nanofibers were dispersed in the UP resin, then MEKP was added, the resin was manually mixed and put in a vacuum chamber for 10 min, in order to avoid the formation of bubbles in the final sample. Afterward, the mixture was poured into the molds and allowed to cure. After the cure finished, samples were removed from the molds and cut to get the desired sample shape.

To disperse nanofibers in the UP resin, a calendaring process was employed. First of all, nanoparticles were manually mixed into the resin and then the mixture was passed through the rolls of the calender until the desired dispersion was reached. The equipment used in this work was a three roll mill, consisting of three chrome-plated hardened steel rolls (80 mm in diameter), supplied from EXAKT Technologies model EXAKT 80E. This equipment can control both the velocities and the gaps among the rolls. In fact, the three rolls rotate with different angular velocities: the central roll rotates three times faster

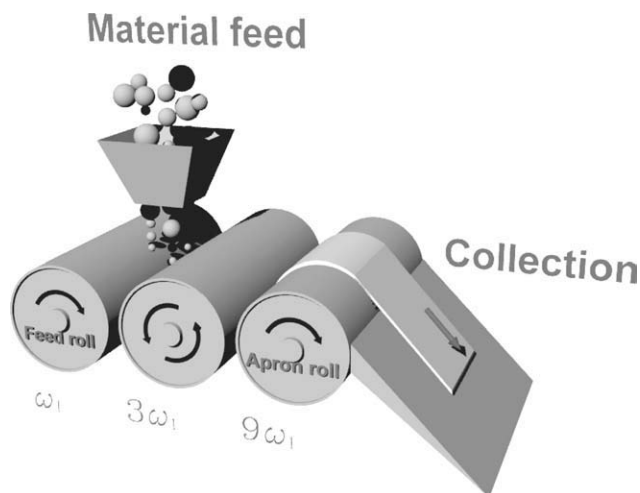


Figure 1 Schematic sketch of the calendaring process used in this work.

than the feed one and the third roll rotate three times faster than the central one (i.e. nine times faster than the feed one). This resulted in a very high shear stress between the rolls, and this stress is exploited to disperse nanoparticles. A schematic of the calendaring process used is depicted in Figure 1.

To optimize calendaring process for UP resins, experiments at different processing conditions were performed. To this aim the number of cycles and the gaps among the rolls were changed. Higher number of cycles enabled the nanoparticles to be better dispersed, conversely longer processing time involved the evaporation of a great amount of styrene causing a variation of the mixture composition and therefore of the characteristic of the final sample. Moreover, the elevated shear stress produces a consistent heating of the mixture, that produces further styrene evaporation. To minimize this heating the rolls were cooled by the internal cooling circuit of the equipment. In this work, the dispersion of the nanofibers was made by following cycles with smaller gaps every time.

The first processing condition tested consisted of five calendaring cycles, each one characterized by a different gap and just one final extraction from the calender. In the first four cycles the third roll was kept faraway, in order to leave the material rolling between the first two cylinders for 10 min. The gap between the first two rolls was, for the four cycles, 50, 25, 10, and 5 μm , respectively, and the extraction during the fifth cycle was done with the two gaps fixed both at 5 μm .

In the second process that was tested, different calendaring cycles were followed. More precisely four cycles were performed, each one having gaps of 50, 25, 10, and 5 μm between the first two rolls, respectively. Each cycle consisted in two steps; dur-

ing the first step, the mixture was kept rolling only between the first two rolls for 10 min, whereas the third roll was kept at a distance which avoided the extraction of the fluid. In the second step of each cycle the third roll was kept near the second one at a distance which allowed the extraction of the mixture.

Eventually, the third process involved four cycles, each one characterized by an extraction. The gaps used during each cycle and the modality of this process were the same of the second step of cycles of the previous process.

The speed of the rolls was set in a way that the residence time during the extraction was as short as possible: basically, the values were in the range of 150–400 rpm, depending on the viscosity of each mixture.

Thermal analysis was carried out in a differential scanning calorimeter (DSC) TA, model Q100. To determine the processing condition of the resin system, dynamic test were performed on the reactive system at different heating rates namely, 5, 10, and 20°C/min, between 0°C and 220°C. After a first scan, the sample was heated again in the same range of temperature at 10°C/min, in order to evaluate the T_g and the presence of a residual heat of reaction.

A survey on the morphological aspects was carried out on samples which contain 2 wt % of CNFs using both a field emission scanning electron microscope (FESEM) of ZEISS, model Supra 25, and a transmission electron microscope (TEM) Philips EM 208. No sputter coating treatment was needed for SEM images, because of the high electrical conductivity of CNFs.

Electrical characterization was carried out according to ASTM D257, which enables the measurement of bulk and surface electrical conductivity for materials with low conductivity. The equipment used is based on two independent units, both supplied by Keithley. One is the voltage supplier and conductivity gage, model Keithley 2410, the other is the resistivity test fixture (model Keithley 8009), which contains the samples.

Rheological properties were studied with the aim of investigating the influence of nanofibers on viscosity and on the viscoelastic behavior of the nanocomposites, and it consists in dynamic tests, with an oscillation frequency growing from 0.01 to 100 rad/s.

These tests were performed with a rotational rheometer Rheometric Scientific, model ARES N2, using the parallel-plate geometry. The temperature was set at 25°C and the strain at 1.5%, in order to keep the measurement in the linear viscoelastic range. The viscoelastic properties analyzed were the complex viscosity $\eta^*(\omega)$, and the storage (G') and loss (G'') moduli, studied as a function of oscillation frequency and stress.

Finally, mechanical characterization was carried out to verify if the introduction of the pristine carbon nanofibers leads to an improvement or, at least, does not lead to a drastic decrease on mechanical properties. Both tensile and flexural tests were performed according to the standards UNI EN ISO 527 and ASTM D790 respectively, using a dynamometer LLOYD Instruments, model LR30K.

Dynamic mechanical analysis was also carried out to better evaluate the effects of CNFs on the main transitions of the resin. Tests were performed with a rotational rheometer Rheometric Scientific, model ARES N2, according to the standard ASTM D 5279. The temperature range was set between 25°C and 150°C, to detect the peak of $\tan \delta$. Finally, thermo-mechanical analysis was performed to study the influence of the nanofibers on the dimensional stability of the polyester resin.

RESULTS AND DISCUSSION

Thermal analysis was used to investigate the cure reaction of the UP resin, and to study the influence of nanofibers on the thermal behavior of the nanocomposite. Figure 2 shows results for the sample heated at 5°C/min during the first scan. A double exothermic peak, characteristic of the UP resin catalyzed by cobalt octoate²² is clearly visible in the first scan. The second scan shows that no residual heat is observed and that the T_g of the system ranges around 65°C. These results allowed to define the cure cycles for the production of the samples. It is well known²³ that even small amounts of nanofillers can affect the cure process of nanocomposites, there-

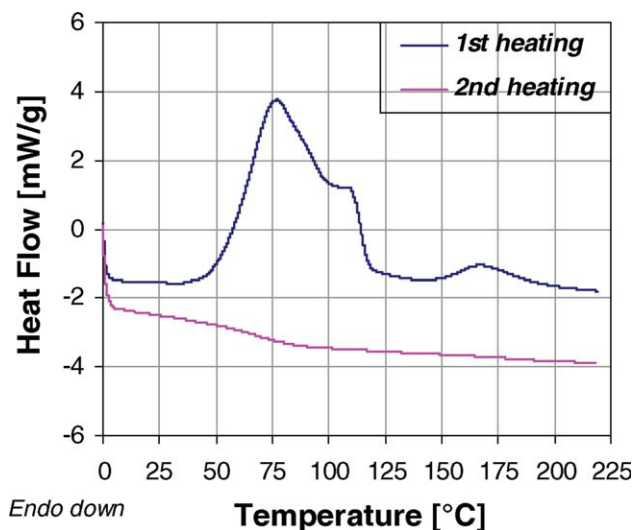


Figure 2 DSC dynamic thermogram for neat UP resin (first and second heating). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

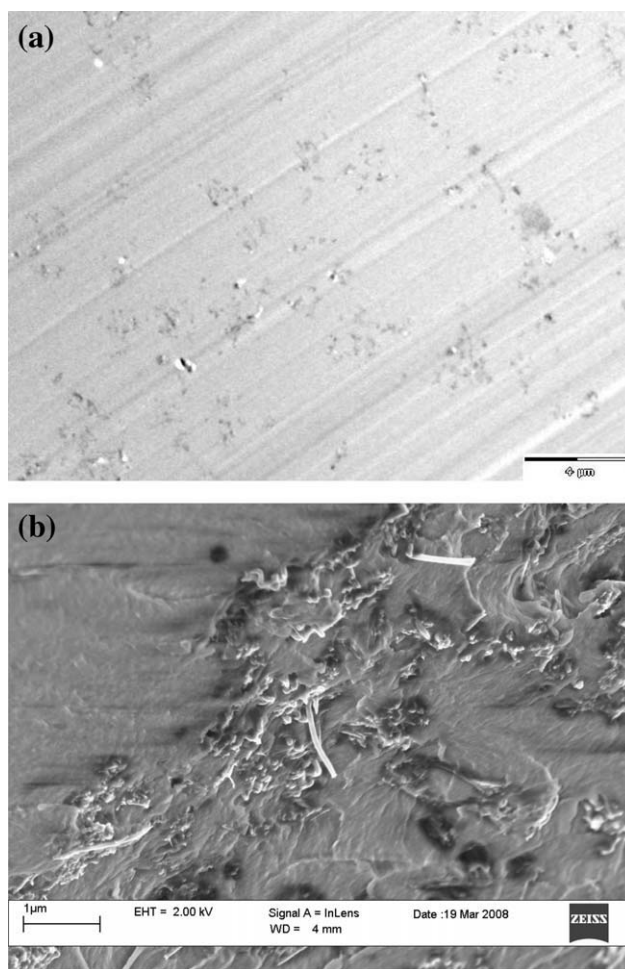


Figure 3 TEM (a) and SEM (b) images of the nanocomposites.

fore, every nanocomposite sample was tested after the curing process, to verify the cure state.

Dispersion tests on the samples produced with the three different calendaring cycles revealed that the third one was the more suitable for the polyester resin used. Adopting this processing condition, it has been possible to minimize the amount of styrene evaporated, without compromising the quality of the dispersion.

Some of the SEM and TEM images of the nanocomposite, are shown in Figure 3. As an outcome of this survey it is possible to affirm that a quite good dispersion of the nanofibers inside the matrix was reached: in fact, no big agglomerations were found in the surfaces, rather it is possible to see many fibers alone.

Electrical characterization involved different steps. The first tests on electrical properties were performed on nanocomposites produced with different calendaring processes, at the same CNF concentration (2 wt %), to investigate whether the process affected this property. It was observed that this parameter does not affect the values of electrical conductivity. The influence of CNF concentration was

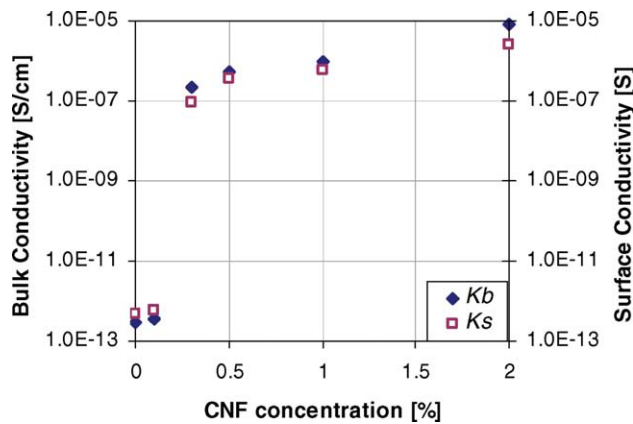


Figure 4 Bulk (K_b) and surface (K_s) electric conductivity for neat resin and nanocomposites as a function of CNF concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

also investigated. Figure 4 shows both the bulk and the surface conductivity of the nanocomposites produced as a function of CNF concentration. It is possible to observe the presence of a stepwise increase between 0.1 and 0.3 wt %, where conductivity switches from around 10^{-13} to 10^{-7} S/cm: such increase indicates that a percolation threshold for the electrical conductivity exists in this range. Beyond this concentration there is a constant but lower increase of the electrical conductivity as a function of CNF concentration.

Interesting results come from rheological characterization. Figure 5 shows the complex viscosity as a function of frequency for all the materials produced. The rheological properties were also reported for the neat resin as received, and for the neat resin processed through the calendering cycle to produce

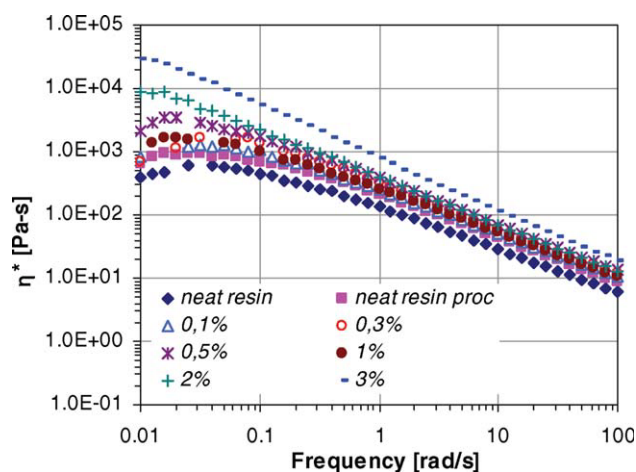


Figure 5 Complex viscosity as a function of frequency, for neat resin and for all the nanocomposites analyzed. The indication "Neat resin proc" stands for neat resin which has undergone the calendering process. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the nanocomposites. In Figures 5 and 6, plots related to this last sample are indicated as "neat resin proc". First of all, it is possible to get further confirmations about the changes induced by the calendering phase: in fact, viscosity of neat resin increases after the calendering cycle, because of styrene evaporation. Besides, it is possible to notice that the viscosity of the nanocomposites increases with increasing CNF concentration. In particular, the increase is more pronounced in the low frequency region and become less significant at higher frequency. It is important to note that a significant change in the rheological behavior occurs only at 2 and 3 wt %. In fact, till these concentrations the materials show the presence of the initial plateau and therefore a tendency to a zero-shear viscosity. Instead, for the materials with a CNF content of 2 and 3 wt % a tendency to a yield stress can be observed. These trends can be more visible if the viscosity is plotted as a function of the stress (Fig. 6). The tendency to a yield stress at the start up of the flow, can be explained by considering that at the higher concentration level, the percolation threshold could be reached.

The rheological curves of the resin and of the nanocomposites were modeled using a power-law-like equation, that is:

$$\eta^* = K\omega^{n-1} \quad (1)$$

In Figure 7 the experimental results obtained are compared with the model proposed: this equation fits well the experimental data in the range of frequency subsequent to the plateau, and, in the case of nanocomposites with 2 and 3 wt % of CNFs, that do not present this plateau, there is a perfect correspondence in the whole frequency range analyzed.

In Figure 8 the variation of the parameters K and n with the weight percentage of CNFs is shown. To

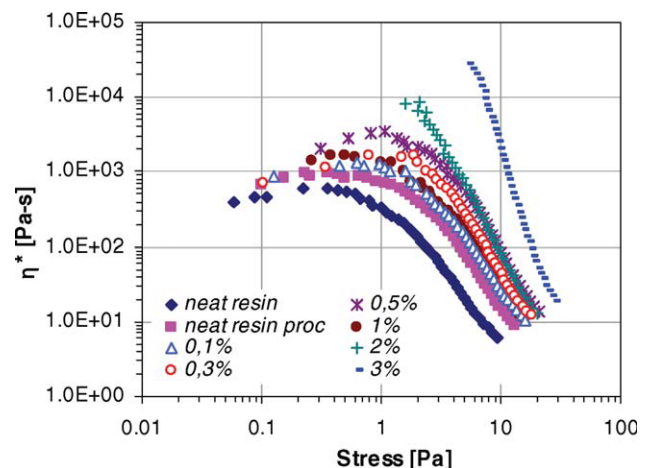


Figure 6 Complex viscosity as a function of stress, for neat resin and for all the nanocomposites analyzed. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

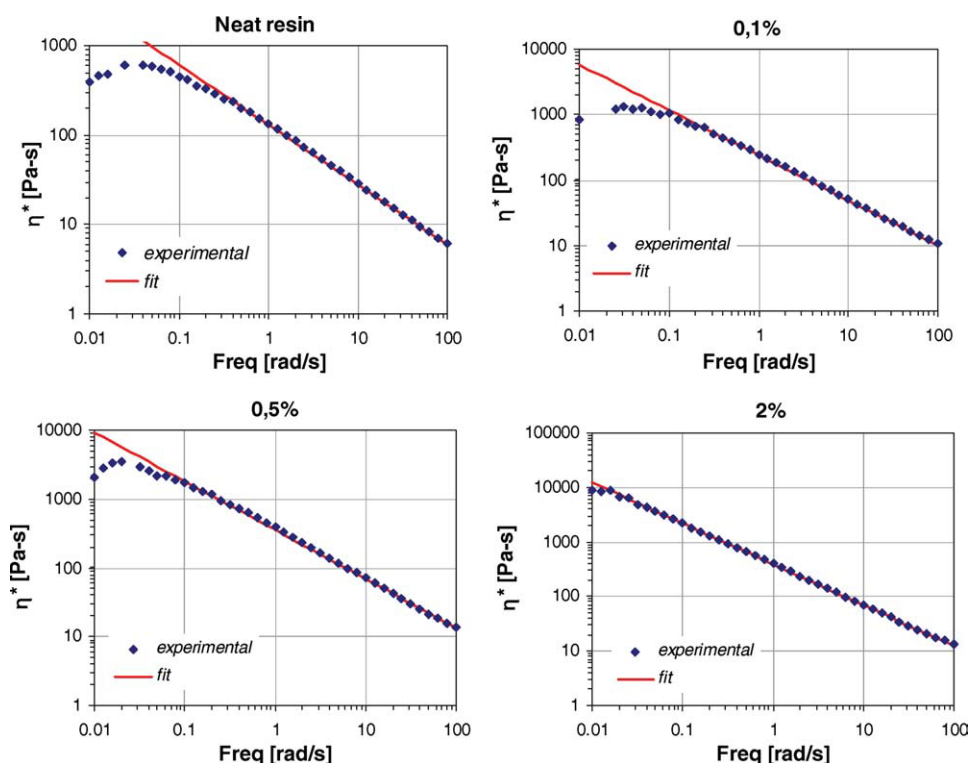


Figure 7 Viscosity as a function of frequency at different CNF concentrations, experimental data and model. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

isolate the effect of nanoparticles, the data reported for the neat resin referred to the resin after the calendaring cycle. The variation of CNF concentration affects in an exponential matter the values of K and n .

Storage and loss moduli were also studied. Figure 9 shows G' and G'' as a function of oscillation frequency for a selection of the studied mixtures. The presence of the crossover frequency at lower CNF concentrations provides important information about the viscoelastic behavior of these mixtures. In fact, this point shifts from around 0.2 rad/s to lower values of frequency as the CNF concentration increases,

and disappears for nanocomposites with 2 and 3 wt %. It is known that G' greater than G'' is related to a mainly elastic response to a solicitation, whereas the opposite is related to a mainly viscous response. For this reason, it is possible to affirm that the UP resin presents a mainly-viscous response at lower frequencies and mainly elastic response at higher frequencies, until it is charged with 1 wt % of CNFs. On the other hand, nanocomposites with 2–3 wt % of nanofibers present a mainly elastic response in the whole frequency range analyzed, providing further confirmation about the overcome of the percolation threshold.

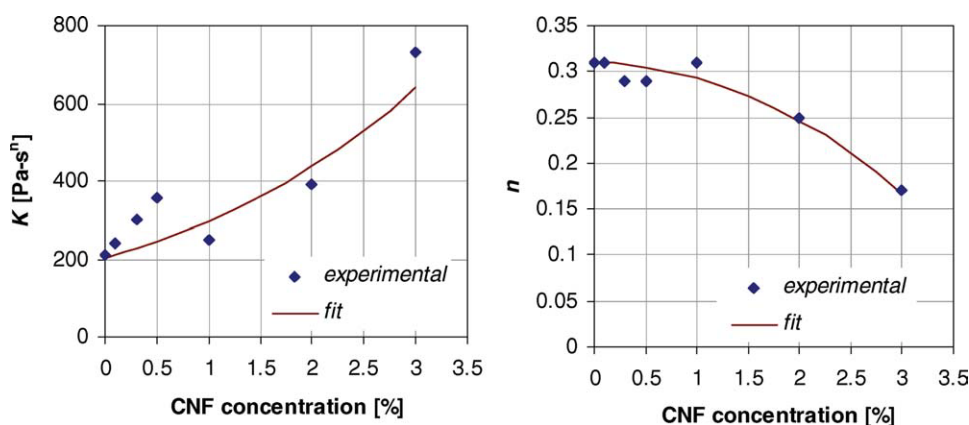


Figure 8 Experimental results and model prediction data as a function of CNF concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

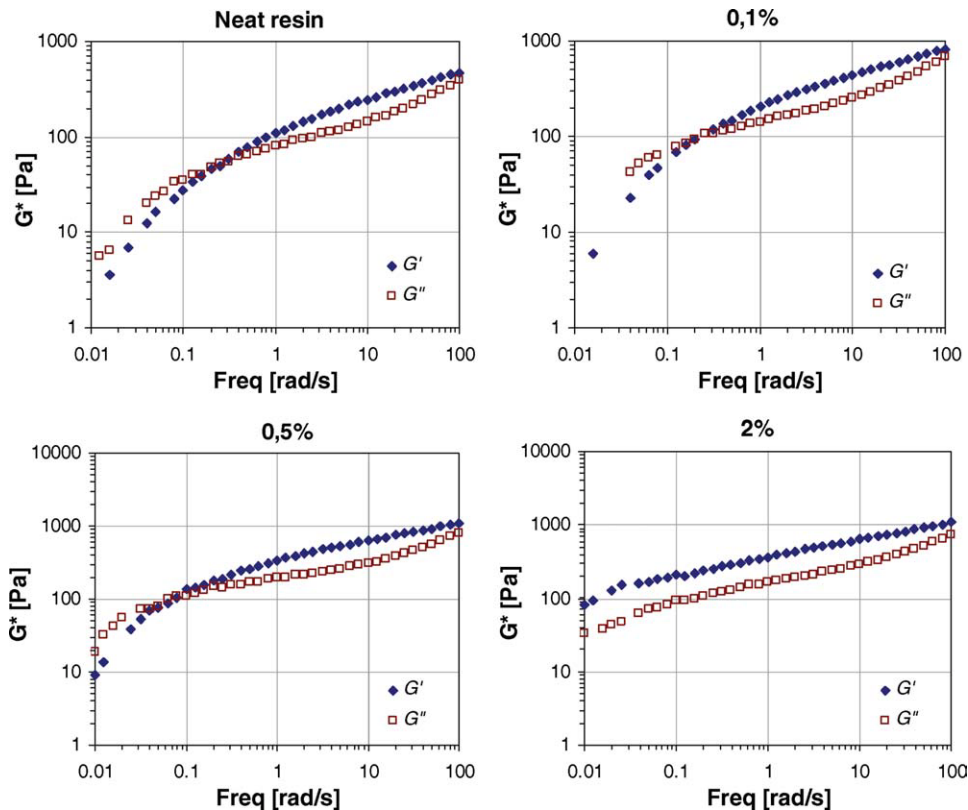


Figure 9 Storage and loss modulus trend at different nanofiber concentrations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In Figure 10, the variation of G' as a function of frequency is summarized for all the nanofiber concentration. It is possible to observe that all the mixtures with concentration lower than 1% experience a significant change of the slope of the curve at low frequency. This fact indicates that a less elastic behavior characterizes those mixtures, which is also confirmed by the presence of the crossover frequency discussed above. The sharp change of behavior with concentration suggest the presence of a “rheological percolation.” The fact that this rheological percolation occurs at CNF percentages, which are remarkably higher than those which produce electrical percolation may be explained considering that higher (surface) interaction between particles are needed to produce a rheological effect, conversely punctual interactions between conductive particles are enough to produce electrical effects.

Once figured out how nanofibers affect both electrical conductivity and rheology of the system, the study of mechanical performances was undertaken. As a result of tensile tests, Figure 11 shows the elastic modulus and the tensile strength as a function of CNF concentration: it is possible to observe that the elastic modulus slightly increases with CNF concentration, whereas tensile strength seems not to be affected by the presence of nanofibers. Moreover, the presence of the nanofibers affects neither the

stress nor the strain at break, which remains almost constant with the fiber concentration. Similar results were obtained performing flexural tests and are not reported in this article.

As a consequence of these results, it was found that the pristine nanofibers employed in this study do not influence the mechanical properties of the

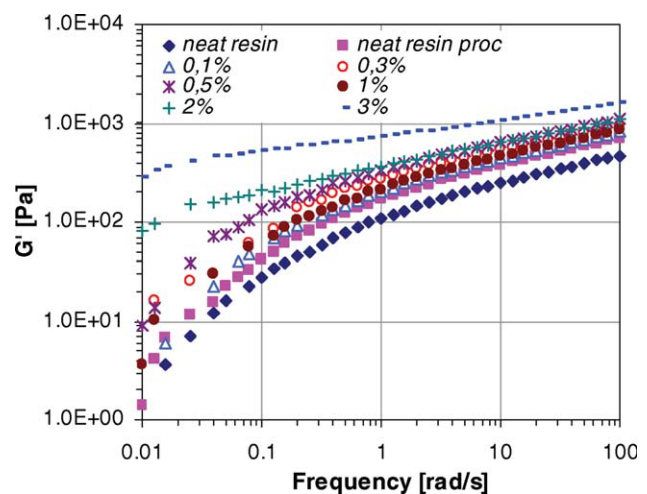


Figure 10 Storage modulus G' as a function of frequency for the neat resin and the nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

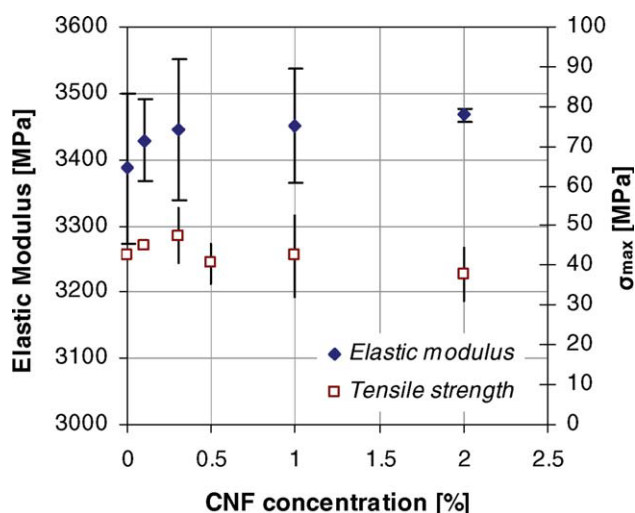


Figure 11 Elastic modulus and tensile strength of the resin and the nanocomposites as a function of CNF concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

unsaturated polyester resin: they do not produce a positive contribution on the mechanical properties, and therefore, they cannot be considered for reinforcing UP resin. Nonetheless, since they do not lead to a drastic reduction of such properties, it is still possible to employ these CNFs for other goals and applications (e.g., in this case, for their electrical properties).

Figure 12 shows the viscoelastic properties of neat resin as supplied by the manufacturer and of the resin that underwent the calendaring cycle. The peak of $\tan\delta$ visible in this range, being associated to a drop of G' , is directly linked with glass transition process. A lower value of T_g for the processed resin

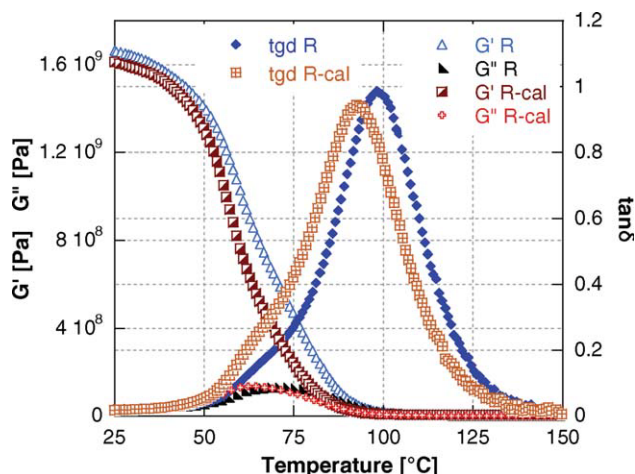


Figure 12 Influence of the calendaring process on neat resin properties. “R” stands for the neat resin as supplied by the manufacturer, “R-cal” for the neat resin that has undergone the calendaring process. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

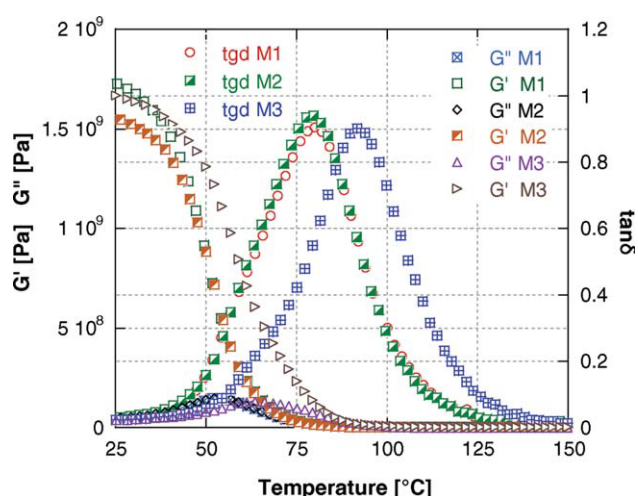


Figure 13 Influence of different calendaring cycles on 2 wt %-CNF nanocomposites. M1 stands for 1st calendaring condition, M2 for 2nd calendaring condition, and M3 for 3rd calendaring condition. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was observed, and this result confirmed the fact that there is an effect of the calendaring process on the properties of the resin. The decrease of the glass transition can be associated to the evaporation of styrene during the calendaring process, which leads to a resin with more unsaturation points and less crosslinks. This is also confirmed by the fact that G' is higher for not processed neat resin.

Regarding the influence of the nanofibers concentration on the glass transition and the modulus G' , the results have shown that there are no significant changes on these properties. Dynamic mechanical analysis was also performed on samples prepared by the different calendaring processes. Analyzing

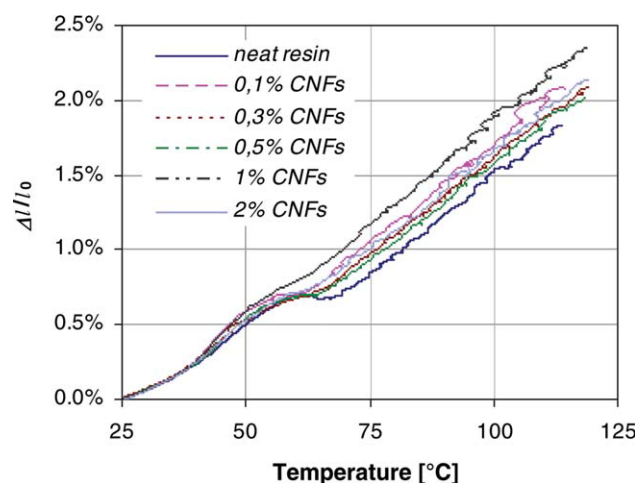


Figure 14 Linear thermal expansion for the neat resin and the nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Coefficients of Thermal Expansion for All the Materials Studied, in Two Different Temperature Ranges

Sample	CTE ($^{\circ}\text{C}^{-1}$)	
	30–40 $^{\circ}\text{C}$	70–90 $^{\circ}\text{C}$
Neat resin	1.71×10^{-4}	2.51×10^{-4}
0.1 wt % CNFs	1.68×10^{-4}	2.67×10^{-4}
0.3 wt % CNFs	1.74×10^{-4}	2.58×10^{-4}
0.5 wt % CNFs	1.53×10^{-4}	2.45×10^{-4}
1 wt % CNFs	1.89×10^{-4}	2.84×10^{-4}
2 wt % CNFs	1.80×10^{-4}	2.44×10^{-4}

the dynamic mechanical behavior of nanocomposites produced by the three different methods (Fig. 13), it is possible to notice that the third method produces samples with the highest glass transition temperature, confirming that this method is the one that minimizes the styrene lost.

Finally, a study on the thermal expansion of these nanocomposites was carried out, to verify whether the presence of nanofibers affect the dimensional stability of the polyester resin. Figure 14 shows the trend of thermal expansion as a function of temperature for the nanocomposites produced, while Table I summarizes the values of the coefficient of thermal expansion in two different temperature ranges, before and after the glass transition temperature. As it is possible to observe, the values of the linear expansion coefficient are in the order of $10^{-4} \text{ }^{\circ}\text{C}^{-1}$ for all the samples, therefore, it is possible to affirm that dimensional stability is not affected by the presence of the carbon nanofibers.

CONCLUSIONS

Calendering process was performed to disperse carbon nanofibers in an unsaturated polyester resin. The in depth study on the dispersion procedure and the TEM and SEM micrographs confirmed that calendering is a suitable tool to achieve good dispersion of nanoparticles even in an unsaturated polyester resin, provided that precautions are taken to minimize the styrene evaporation.

The study of electrical properties has shown that the addition of very small amounts of nanofibers produces significant enhancement of the electrical conductivity: six order of magnitude increase in the values of the electrical conductivities were obtained at 0.3% loading of CNFs. Conversely, mechanical properties do not show significant improvements as a result of the addition of carbon nanofibers. This could be associated to both the changes of reagent

percentages that occurs during the dispersion phase, which leads to mixtures with different concentration of reagents, and to a weak interface between CNFs and the UP resin.

Regarding the processing of such nanocomposites, rheological tests have shown that the presence of carbon nanofibers do affect the values of viscosity. In particular, rheological tests have shown that physical percolation occurs at loading of 2–3 wt % and it results in higher value of viscosity, presence of yield stress and absence of crossover.

In any case, it was noted that the electrical percolation occurs at lower loadings of CNFs. For concentrations in which there is the electrical percolation, the values of the viscosity do not increase remarkably, therefore the processing characteristics are not affected.

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