



EFFECT OF DISPERSION, FUNCTIONALIZATION AND ORIENTATION OF CARBON NANOFIBERS ON THE PROPERTIES OF NANOREINFORCED EPOXY RESINS

Alejandro Ureña, María Burón, Rubén Chaos, Mónica Campo, Dolores Escalera, Silvia G. Prolongo,
Dpt. Ciencia e Ingeniería de Materiales. Universidad Rey Juan Carlos
C/ Tulipán s/n 28935 Móstoles, Madrid (SPAIN)

Keywords: *nanocomposite, carbon nanofibers, epoxy matriz, functionalization*

Abstract

The present work analyses the efficiency of the different techniques of dispersion, functionalization and even orientation of carbon nanofibers in epoxy resin for nanocomposite manufacturing. For it, different thermomechanical properties were studied (storage modulus, E' , and temperature associated to α -relaxation, T_α). The most important relative increase of E' was measured for epoxy composite reinforced with 0.25 wt % of functionalized surface CNFs with the cure agent for the epoxy resin, 4,4'-methylenedianiline (DDMs). The better strategy found to enhance the mechanical properties of epoxy resin was to limit the contents of added nanofibers, but using functionalized ones. The enhancements obtained of modulus reach up to 37 % regard to neat epoxy resin.

1 Introduction

The epoxy resins usually present good mechanical properties and high thermal and chemical resistance. Therefore, they are commonly used in numerous applications as matrix of composite materials. The reinforcement improves their main limitations, such as its low toughness and low electrical conductivity.

The most recent researches about epoxy composites are centred on the introduction of nanoreinforcements, such as carbon nanofibers and nanotubes, silica nanoparticles, nanoclays, etc [1]. Their main advantage is the low reinforcement content necessary, avoiding an important increase of its density and price. Also, the use of carbon nanofibers would enhance the electric and thermal conductivity.

Theoretically, these nanoreinforcements present excellent mechanical properties, such as very high elastic modulus and mechanical strength. Therefore, epoxy resins reinforced with carbon nanofibers (CNFs) should present enhanced mechanical properties compared with the pure resin and even with micro-reinforced resins. However, the published results for the moment are quite modesties [2]. These limitations are related to problems with the dispersion of nanofibers and with a poor interaction reinforcement-matrix.

Different techniques and procedures of dispersion are being actually researched, such as thermal, mechanical and ultrasonic stirring techniques, use of organic solvent, between them. [3]. To enhance the matrix-reinforcements interaction, the main applied procedure consists on the modification of nanofibers [3–7]. This modification can be carried out by physisorption of different compounds, generally oligomers and polymers, or by chemical modification of fibers surface. The chemical functionalization of carbon nanofibers usually contains several steps. First, it is necessary a previous step of surface activation by oxidation of fibers through chemical or thermal processes. Then, the functionalization itself consists on the introduction functional groups on the fibers surface by chemical reaction.

The present work analyses the efficiency of the different techniques of dispersion, functionalization and even orientation of carbon nanofibers. For it, different properties were studied. The homogeneity of the non-cured nanofibers-epoxy mixtures was observed by optical transmission microscopy while the final morphology of cured epoxy nanocomposites was analyzed by transmission electron microscopy. Finally, it was determined the

effect of the different reached morphologies on the thermal and mechanical properties of these nanocomposites.

2 Experimental Procedures

2.1 Materials

CNFs were prepared by chemical vapour deposition (provided by Grupo Antolin, Spain) with diameters ranging from 20 to 47 nm and an average length of 35 μm . The epoxy monomer used was diglycidyl ether of bisphenol A (DGEBA), supplied by Sigma-Aldrich with 178 g / epoxy equivalent. As curing agent, 4,4'-methylenedianiline (DDM) was used, purchased from Sigma Aldrich.

2.2 Nanofiber funcionalization

To functionalize the CNFs were treated with concentrated nitric acid at 70 °C for 3h. After washing with distilled water until the filtrate reached a pH value of 7, the nanofibers were dried in vacuum at room temperature. The surface-oxidized CNFs were acylated by chemical reaction with thionyl chloride at 70 °C for 24h. Then the mixture was cooled, washed with tetrahydrofurane (THF) and vacuum filtered. Finally, surface-acylated CNFs were reacted with DDM at 60 °C for 96 h. After vacuum filtration and washing with THF, the DDM-derivatized CNFs were dried at reduced pressure overnight. The different stages of the treatment are collected in Figure 1.

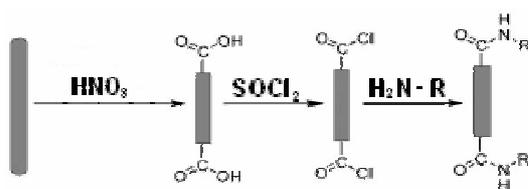


Fig. 1. Functionalization scheme

The characterization of treated CNFs was carried out by infrared spectroscopy (FTIR), to determine the presence of functional groups, and by transmission electron microscopy (TEM) in order to analyze the possible modification on the geometry and morphology of carbon nanofibers. With them, we probed the presence of the corresponding functional groups showed in Fig 1. Also, we observed that the length of graphitic nanofibers decreases up to 10 – 20 μm with the oxidation treatment.

2.3 Composite Fabrication

Carbon nanofibers/epoxy composites were prepared using two different CNFs: CNFs without any surface treatment and surface DDM-derivatized CNFs (abbreviated as DDM-CNFs). Both composites were prepared following the same procedure, adding nanoreinforcement loads of 0.25, 0.5, 1 and 5 wt %.

Several methods of nanocomposites preparation were applied to analyze the effect of different synthesis parameters on the nanofibers dispersion, on the reinforcement / matrix interaction and, therefore, on the final properties of nanocomposites. The final objective is to determine the optimum conditions of preparation of nanofibers/epoxy composites. Two methods of nanocomposites preparation were applied: concentrated method [4–9], where the carbon nanofibers were directly dispersed on epoxy precursor, and diluted method [3,10], using a solvent to decrease the epoxy viscosity and to enhance the nanoreinforcement dispersion. Figure 2 shows a scheme of the applied processing methods.

On diluted method, the graphitic nanofibers were first dispersed in a distilled solvent. Two different solvents, THF and chloroform (CHCl_3), were used in order to determine the optimum solvent to get a homogeneous dispersion of CNFs and DDM-CNFs. These solvents are ones of the most used dispersion agents of carbon nanofibers / nanotubes [3, 10]. The nanofibers suspension was stirring at 50 °C for 30 min and then mildly sonicated for 15 min using a 50-60 Hz sonicator. Next, DGEBA was mixed with the nanofibers suspension and sonicated for 1 h. The resultant solution was then subjected to high shear mixing (200 rpm) for 30 min at 70 °C. After slowly evaporating the solvent with continuous stirring at 70°C, a stoichiometric amount of DDM was added into the mixture, followed by stirring at 150°C to dissolve the hardener. The resulting mixture was then taken into a steel mould, whose walls were previously treated with an anti-adherent demould agent, Marbocote 445. Afterwards, the mould was inserted into heater, applying a curing treatment consisting on a heating at 150 °C during 3 hours and then a postcuring process of 180 °C for 1h.

As an alternative to the moulding processing, to analyze the effect of the nanofiber orientation on the nanocomposite properties, injection processing were also applied. Injection moulding consisted on adding the non-cured sample into the syringe and injecting it into the mould. To avoid the air bubbles,

the mould is sited in vertical and the injection direction is contrary to the gravity effect.

2.4 Characterization Techniques

Nanofibers dispersion in the epoxy monomer was studied using transmission optical microscopy (Leica DMR), placing a few drops of the nanofibers/resin mixture on a microscope slider and using a heat deck for high temperature. The density of the cured nanofibers/epoxy composites was measured by the gravimetric method of water immersion, using a Mettler Toledo balance with ± 0.001 mg. Dynamic mechanical measurements were carried out on a DMA Q800 V7.1 analyser from TA Instruments. The frequency used was 1 Hz and the heating rate was 2 °C / min between 30 and 250 °C. The samples used were parallelepipedic bars (1.5 x 12.5 x 35 mm³).

The morphology of cured nanocomposites was studied by SEM (Phillips XL30) on fracture surface

3 Results and Discussions

3.1 Structure of the nanocomposites

Figure 3 shows optical micrographs, collected at 100x magnification, of the uncured nanofibers / DGEBA mixtures obtained by different dispersion processes. The direct dispersion of nanofibers on epoxy (fig. 3a) precursor gives heterogeneous mixtures, showing aggregates, whose size is higher than 20 μm in length. The use of a dissolvent enhances the nanofibers dispersion due to the viscosity decrease of mixture. Chloroform (fig. 3b) seems to be better solvent than THF, meaning that the high solvent polarity enhances the graphitic nanofibers dispersion. This behaviour was observed for non-treated CNFs and derivatized DDM-CNFs.

The temperature increase to 60 °C (fig. 3c) during the dispersion stages of magnetic stirring and high shear mechanical mixing causes an important decrease of the size of nanofibers agglomerates.

Regarding the application of different dispersion techniques, it has been observed that the

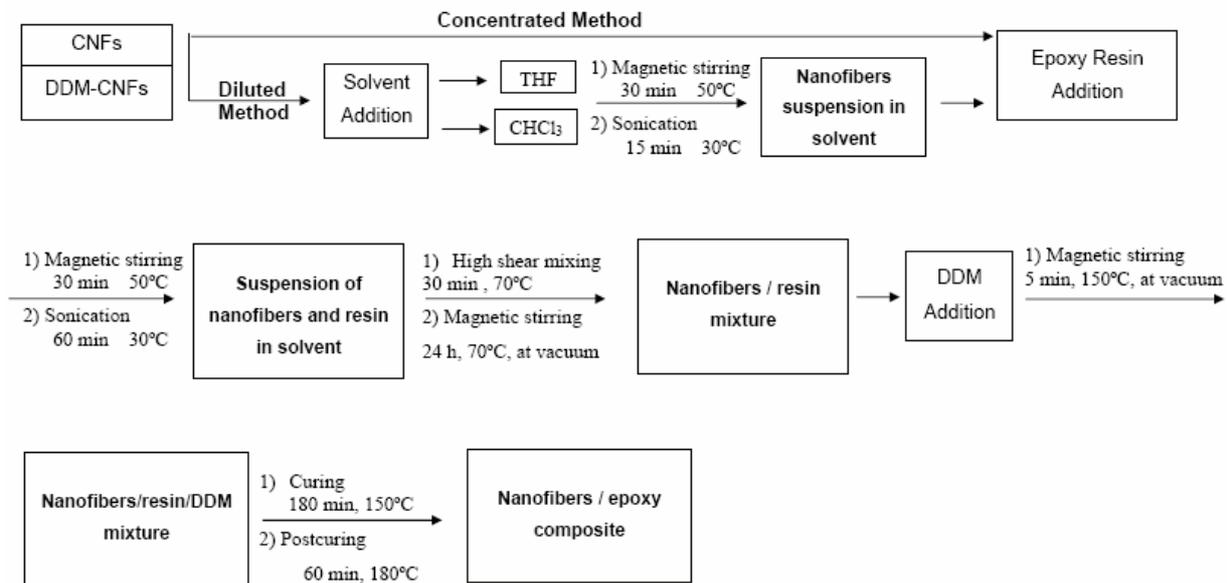


Fig. 2. Scheme of the processing stages of CNF / epoxy nanocomposites.

at room temperature. To reduce charging, these were coated with a thin sputtered layer of Au/Pd. TEM (Phillips Tecnai 20) was used to analyse the morphology of nanofiber / epoxy interface and the nanofibers dispersion on the studied nanocomposites. Samples were cut at room temperature using an ultramicrotome (Leica EMFCS) equipped with a diamond knife and the resulting ultrathin sections were picked up on copper grids.

sonication is not enough process, being necessary the application of high shear mixing to get a uniform dispersion. The same observation was reported by Winey et al [11]. They obtained a homogeneous epoxy nanocomposites reinforced with 0.01 wt % carbon nanotubes. The combination of sonication technique and high shear mechanical stirring was effective to separate bundles. However, despite of the improvement, not total homogeneity is achieved on our epoxy / nanofiber mixtures. Small aggregates,

whose size is smaller than 1 μm , are observed on the uncured mixtures processed with the best conditions, following the diluted method with chloroform and mixing at 60°C using both, magnetic stirrer, sonicator and shear mechanical mixer. These small heterogeneities could be associated to the high nanofibers concentration and the high length of themselves. Also, these nanofibers did not suffer any chemical surface treatment.

Finally, in order to enhance the nanofiber / epoxy interaction, the carbon nanofibers were chemical treated to introduce functional groups on their surface. The epoxy mixtures with acylated-CNFs are very heterogeneous, due to the self-association between acid groups forming hydrogen bonds. The functionalized nanofibers, DDM-CNFs, seem to show greater homogeneity because of the positive interaction between epoxy groups of precursor and amine groups of the nanofibers surface.

Taking into account all these results, the optimum conditions of preparation of noncured carbon nanofibers / epoxy mixtures involves the prior surface nanofibers functionalization with an amine linker agent, the use of chloroform as dissolvent and the application of several dispersion techniques in stages, magnetic stirring at 60°C, ultrasonication and high shear mechanical mixing.

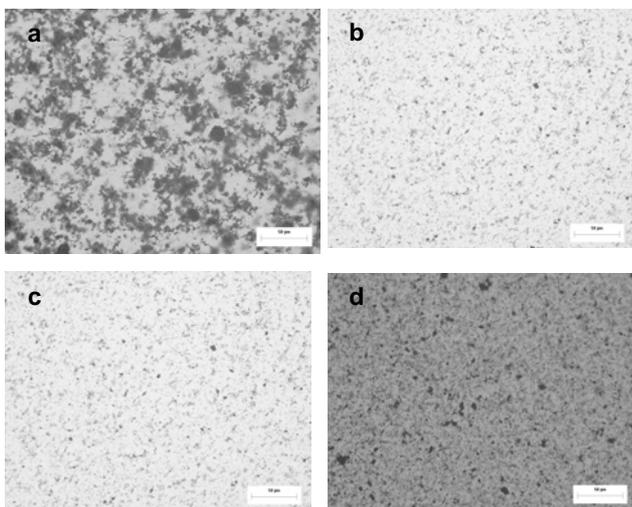


Fig. 3. Micrographs showing the effects of different dispersion methods: a) concentrated method, b) diluted method with CHCl_3 c) temperature: 60°C, d) magnetic stirring, sonication and high shear mixing.

The morphology of cured epoxy/nanofibers composites was observed by SEM in order to

confirm that the obtained dispersion on the preparation of nanofiber / epoxy mixtures determines the homogeneity of the final nanocomposites. The absence of any agglomerates indicated a uniform dispersion of the carbon nanofibers into the epoxy matrix at the micron and submicron level for the nanocomposite prepared with the optimum conditions previously determined.

Spite of the apparent homogeneity observed by SEM in the DDM-CNFs/epoxy nanocomposites processed with the optimum conditions, its observation by TEM shows small nanofibers aggregates (Figure 4). The applied dispersion techniques are effective to separate bundles into small braids and homogeneously dispersed them into the epoxy matrix. However, the carbon nanofibers tend to wind up and to braid forming aggregates. On these micrographs, it is possible to observe the presence of treated carbon nanofibers with different lengths, from 500 nm to several micrometers. However, the initial length of used CNFs was close to 35 μm . This confirms that the oxidation process shortens the nanofibers, which cause a decrease of its aspect ratio and therefore could decrease its effectiveness for increasing the epoxy mechanical properties.

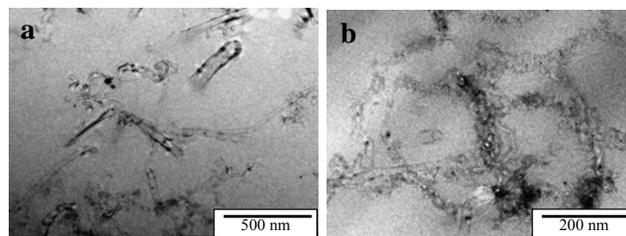


Fig. 4. TEM images of the nanofibers / epoxy nanocomposites with 0.5 wt % DDM-CNFs, manufactured by diluted method using the optimum conditions.

Neither by SEM nor by TEM, it was possible to determine if the studied nanocomposites present voids and other kind of defects.

3.2 Thermo-mechanical properties

The effect of the dispersion grade reached through the different processing methods applied on the thermo-mechanical properties of the nanocomposites was studied by DMTA. Figure 5 shows the change of storage modulus (E') as a function of temperature for different specimens of

EFFECT OF DISPERSION, FUNCTIONALIZATION AND ORIENTATION OF CARBON NANOFIBERS ON THE PROPERTIES OF NANOREINFORCED EPOXY RESINS

epoxy nanocomposites with 0.5 wt % CNFs. This dynamic property reflects the amount of energy stored in the composites as elastic energy, which is affected by the presence of nanofibers: their geometrical characteristics, volume fractions, dispersion in the matrix, and adhesion between fibers and the matrix [6]. The first observation is that the temperature associated to α -relaxation (T_α), determined by the abrupt drop of E' , does not depend on the experimental conditions of processing. This means that the glass transition temperature remains constant and it does not depend on the grade of CNFs dispersion obtained or the nature of interface bonding. While the CNFs content is constant, the formation of CNFs agglomerates or, on the contrary, homogeneous nanofibers dispersion into epoxy matrix does not modify the T_α value of resin. In fact, the T_α value remains constant with the introduction of non-treated CNFs and surface derivatized DDM-CNFs. This means that the epoxy/amine ratio is scarcely affected by the functionalization process. It implies that the amount of amine groups introduced in CNFs

surface is quite low [3,12].

The homogenisation grade reached during the CNFs dispersion process mainly affects to the value of storage modulus at room temperature of the studied nanocomposites. In Fig 5a, DMTA curves were measured with specimens of nanocomposites processed by different dispersion methods, concentrated and diluted. The highest modulus was obtained for the sample manufactured through the suspension of CNFs/DGEBA diluted in chloroform. These experimental conditions were classified as the optimum ones to obtain homogeneous composites during the morphological characterization by TEM. Therefore, it is confirmed that the homogeneity of the final nanocomposites is directly related with the homogeneity of non-cured CNF/epoxy solutions and that a higher grade of CNFs dispersion implies an increase of the storage modulus of material. These results prove the great importance of applying a right dispersion method, which directly influences on the final morphology of the nanocomposites and therefore on their mechanical properties.

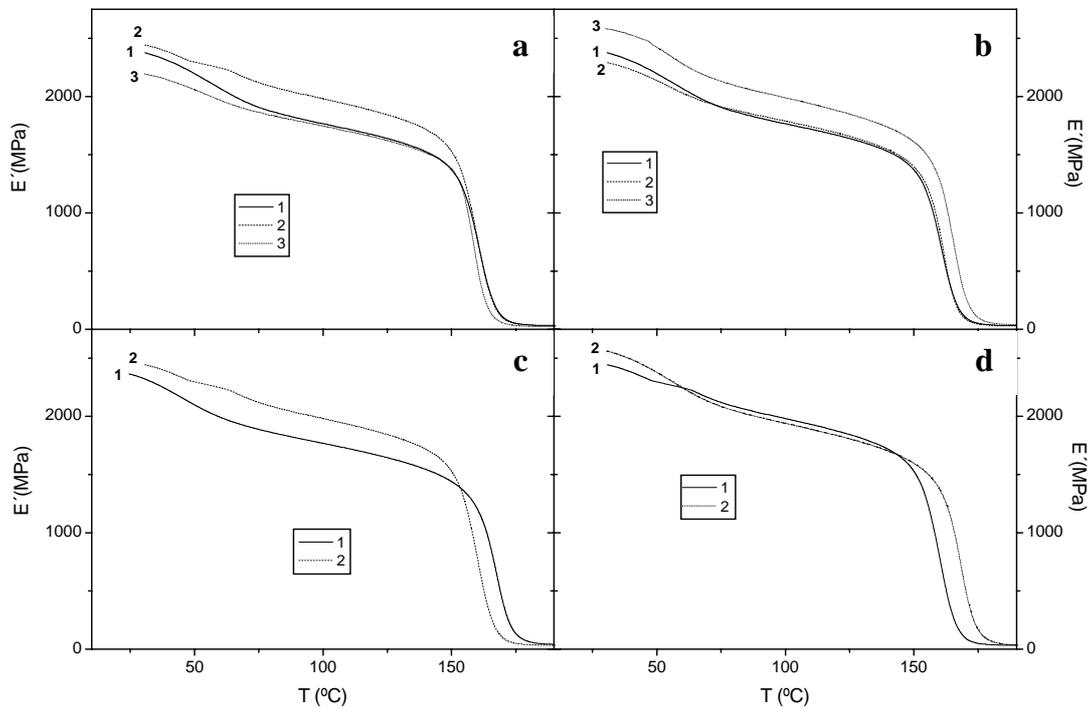


Fig. 5. DMTA curves of epoxy nanocomposites with 0.5 wt % CNFs processed by different procedures: a) Solvent effect: 1. concentrated, 2. diluted in chloroform, 3. diluted in THF; b) CNF functionalization effect: 1. CNF, 2. Oxidized-CNF 3. DDM-CNF; c) Dispersion effect: 1. mechanical stirring, 2. mechanical stirring and sonication; d) Orientation and processing effect: 1. molding, 2. injection.

Fig 5c shows the E' versus temperature curves for epoxy nanocomposites reinforced with 0.5 wt % CNFs, which were processed modifying the dispersion stage of nanofibers/resin solution. To manufacture the sample 1, the CNFs dispersion was carried out by mechanical stirring while the dispersion stage of the sample 2 also implies the use of sonication. A moderate increase of the E' at room temperature is measured for sample 2, indicating that the sonication treatment enhances the CNFs dispersion, obtained more homogeneous nanocomposites. This increase also implies that the length of nanofibers does not seem to be modified by the ultrasonic treatment.

The effect of functionalization on the thermal-mechanical properties is determined in Fig 5b, where they are represented the corresponding DMTA curves of epoxy nanocomposites reinforced with non-treated CNFs, oxidized-CNFs and DDM-CNFs. Like the previous DMTA results, T_α value is the same for all studied samples; the main difference is the E' value at room temperature. This value changes from 2.2 GPa for epoxy nanocomposites reinforced with CNFs and oxidized-CNFs, to 2.5 GPa for epoxy/DDM-CNF sample. The E' increase of epoxy resin reinforced with functionalized-DDM CNFs can be due to two reasons. One of them is the higher uniformity obtained during DDM-CNFs dispersion into the epoxy matrix, which was confirmed by TEM on uncured epoxy/nanofiber mixtures. On the other hand, the increase of modulus on the nanocomposites with functionalized DDM-CNFs reflects the immediate effective load transfer of nanofibers through strong interfacial bonding due to the free terminal amino groups covalently attached to the side chain on the CNFs, which reacts with the epoxy matrix [3].

Finally, Figure 5d shows the effect of processing method applied to manufacture the epoxy nanocomposite: molding or injection process. The main difference between both is the orientation of nanoreinforcement. In principle, the nanocomposite processed by molding method should be anisotropic with the nanofibers randomly oriented. In contrast, the carbon nanofibers on injected nanocomposites should be a preferential orientation. Not great differences are observed on the values of storage modulus of molding and injected probes. It is due to DMTA test was carried out in single cantilever mode, applying the load on the transversal direction to the preferential direction of nanofibers on injected nanocomposite. On the other hand, an increase of the α -relaxation temperature (T_α), around 8 °C, is

measured for the injected nanocomposite. The increase of T_α on epoxy nanocomposite is associated to the restriction of macromolecular motions due to the presence of nanofibers. Therefore, this could indicate that the orientation of nanofibers on injected probes causes a more effective package.

In order to determine the orientation of nanofibers on injected epoxy nanocomposites, the coefficient of linear thermal expansion (CTE) was measured by DMA. At room temperature the isotropic moulding nanocomposite with 0.5 wt % nanofibers presents an α value of $77 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. This value is constant in the three spatial dimensions. In contrast, the injected composite with the same nanofibers content has two different thermal expansion coefficients: CTE_L in the longitudinal direction and CTE_T in the transverse direction. The measured values of CTE_L and CTE_T are $86 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ and $53 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, respectively. These measurements confirm that the injection processing method generates a preferential orientation of the carbon nanofibers. To justify the obtained results, the neat epoxy resin was also measured, determining an CTE value of $58 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ in each spatial direction.

The tendency of measured thermal expansion coefficients of the nanocomposites is different to the expected for traditional composites. Traditional fibers generally have a lower expansion coefficient than that of the matrix; therefore the CTE value of laminate composites is lower than that of the epoxy resin. Also, the value of L is smaller than CTE_T for the unidirectional laminate composites. This apparent anomaly was already observed by Wei C et al. [13] and it is explained for the different behaviour of the fibers of nanometric dimensions regard to the micrometric traditional fibers.

Figure 6 shows the DMTA curves of neat epoxy resin and epoxy nanocomposites with different nanofibers contents, from 0.25 to 5 wt %. The curves of epoxy nanocomposites reinforced with non-treated CNFs are plotted in Fig 6a while Fig 6b shows the obtained results for the composites with functionalized DDM-CNFs. The introduction of nanofibers causes an enhancement of the storage modulus in the glassy state while the α -relaxation temperature remains constant. The E' increase is higher as the CNFs content increases up to reaching a maximum value [14]. This optimum value is different for epoxy nanocomposites reinforced with non-treated CNFs, 1.0 wt %, and with functionalized DDM-CNFs, 0.5 wt %.

It is interesting to observe that the maximum content of CNFs is higher for non-treated carbon

nanofibers than the functionalized ones. In contrast, the previous results indicated that the nanofibers functionalization enhanced the dispersion process. This indicates that the functionalization process is necessary for the processing of epoxy nanocomposites with relative low nanofibers contents. In contrast, to manufacture composites with CNF contents higher than 1 wt % is not necessary the previous functionalization stage of the reinforcement.

For the same nanofibers content, the glassy storage modulus of the nanocomposites is higher when the nanofibers are functionalized, indicating that the covalent bonding between the matrix and nanofibers enhances the load transfers, increasing the mechanical properties of the composite. In fact, the most important relative increase of E' is measured for epoxy composite reinforced with 0.25 wt % DDM-CNFs. Therefore, the better strategy to enhance the mechanical properties of epoxy resin is not added great nanofibers contents, but it is to add low amounts of functionalized nanofibers. This is justified by the high aspect ratio of graphitic nanofibers and the better dispersion get with low nanofibers percentages added. The enhancements obtained of modulus reach up to 37 % regard to neat epoxy resin.

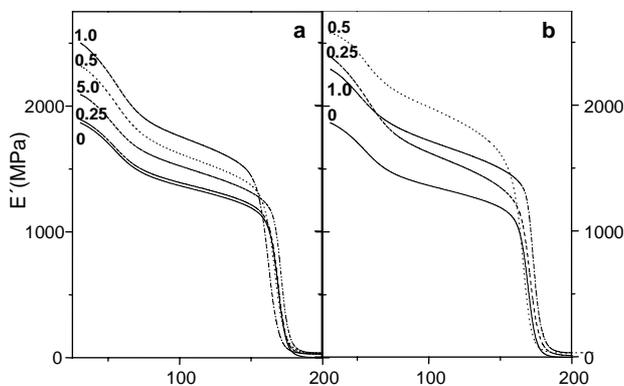


Fig. 6. DMTA curves of epoxy nanocomposites with 0, 0.25, 0.5, 1 and 5 wt %: a) non-treated CNFs; b) DDM-CNFs.

4 Conclusions

In this study, the epoxy based nanocomposite materials were reinforced with carbon nanofibers (CNFs). The experimental processing conditions were optimized to separate bundles into small braids and homogenously dispersed them into the epoxy matrix. For it, it was necessary to apply several consecutive stages of dispersion, including dilution, sonication, mechanical mixing, thermal treatment

and stirring at vacuum. Also, the CNFs had to be chemical amino-derivatized with reactive linker molecules in order to enhance their adhesion to epoxy matrix. The functionalization applied consists on the oxidation of carbon sites to carboxylic groups, which later were acylated by chemical reaction with thionyl chloride. Then the acylated-CNFs were covalently bound to diamine linker molecules, using carboxylate amidation chemistry.

The use of derivatized CNFs does not modify excessively the amino-epoxy ratio, indicating that the amount of amino groups added into the CNF surface must be low.

Using the optimum processing conditions, CNFs were dispersed relatively well into the matrix but there were some agglomerates and voids on the nanocomposites with high CNFs content, from 1 wt %.

While the α -relaxation temperature remains constant, the glassy storage modulus of epoxy resin increases by the introduction of CNFs. The E' enhancement significantly increased with increasing CNFs loading and with the functionalization of CNFs. This indicates good nanofibers dispersion and a high interfacial adhesion between the reinforcements and the epoxy matrix, enhancing the load transfer.

Acknowledgements

The authors would like to acknowledge the financial support of *Comunidad de Madrid* and *Universidad Rey Juan Carlos*, through the program ESTRUMAT-CM (reference MAT/77) and the project MYN-031-1 and URJC-CM-2006-CET-0634.

References

- [1] Zhu, S. *Fundamentals of nanocomposites*. Springer, 2006.
- [2] Coleman, J.N., Khan, U, Blan, W.J, Gun'ko, Y.J. T. "A review of the mechanical properties of carbon-nanorube-polymer composites". *Carbon*, Vol. 44, No. 9, pp. 1624, 2006.
- [3] Zhu, J, Peng, H, Rodriguez-Macias, F, Margrave, J. L., Khabashesku, V. N., Imam, A. M., Lozano, K., Barrera, E. V. "Reinforcing epoxy polymer composites through covalent integration of functionalized nanotubes". *Advanced Functional Materials*. Vol. 14, No. 7, pp. 643-648, 2004.
- [4] Xu, L. R., Bhamidipati V., Zhong W. H., Li J., Lukehart C. M., Lara-Curzio E., Liu K. C., Lance M. J. "Mechanical Property Characterization of A

- Polymeric Nanocomposite Reinforced by Graphitic Nanofibers with Reactive Linkers". *Journal of Composites Materials*. Vol. 38, No. 18, pp. 1563-1582, 2004.
- [5] Coleman, J. N., Khan, U., Gunko, Y. K. "Mechanical reinforcement of polymers using carbon nanotubes". *Advanced Materials*. Vol. 18, pp. 689-706 2006.
- [6] Wang, J., Fang, Z., Gu, A., Xu, L., Liu, F. "Effect of amino-functionalization of multi-walled carbon nanotubes on the dispersion with epoxy resin matrix". *Journal of Applied Polymer Science*. Vol. 100, No. 1, pp. 97-104, 2006.
- [7] Li, J., Vergne, M. J., Mowles, E. D., Zhong, W. H., Hercules, D. M., Lukehart, C. M. "Surface functionalization and characterization of graphitic carbon nanofibers (GCNFs)". *Carbon*. Vol. 43, pp. 2883-2893, 2005.
- [8] Li, Q.Q., Zaiser, M., Koutsos, V. "Carbon nanotube/epoxy resin composites using a block copolymer as a dispersing agent". *Physica Status Solidi A-Applied Research*. Vol. 201, No.13, pp. R89-R91. 2004.
- [9] Choi, Y. K., Sugimoto, K., Song, S. M., Gotoh, Y., Ohkoshi, Y., Endo, M. "Mechanical and physical properties of epoxy composites reinforced by vapor grown carbon nanofibers". *Carbon*. Vol. 43, pp. 2199-2208, 2005.
- [10] Liu, L., Wagner D. "Rubbery and glassy epoxy resins reinforced with carbon nanotubes". *Composites Science and Technology*. Vol. 65, pp. 1861-1868, 2005.
- [11] Moniruzzaman, M., Du, F., Romero, N., Winey, K. I. "Increased flexural modulus and strength in SWNT/epoxy composites by a new fabrication method" *Polymer*. Vol. 47, pp.293-298. 2006.
- [12] Miyagawa, H., Drzal, L. T. "Thermo-physical and impact properties of epoxy nanocomposites reinforced by single-wall carbon nanotubes". *Polymer*. Vol. 45, pp.5163-5170, 2004.
- [13] Wei, C., Srivastava, D. Cho, K. Thermal Expansion and Diffusion Coefficients of Carbon Nanotube-Polymer Composites". *Nano Letters*. Vol. 2, No. 6 pp. 647- 650, 2002.
- [14] Fidelus, J. D., Wiesel, E., Gojny, F. H., Schulte, K., Wagner, H. D. "Thermo-mechanical properties of randomly oriented carbon/epoxy nanocomposites" *Composites: Part A*. Vol.36, pp. 1555-1561, 2005.