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Effects of dispersion techniques of carbon nanofibers on the thermo-physical properties of epoxy nanocomposites

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ABSTRACT:

The influence of the dispersion states of carbon nanofibers (CNFs) on the structure and thermo-physical properties of the epoxy nanocomposites has been investigated. Two main different methods for dispersion of nanoreinforcements into an epoxy matrix have been tested: 1) directly mixing the CNFs and the epoxy monomer, and 2) previous addition of CNFs to a solvent to produce a stable suspension which later was mixed with the epoxy resin. For it, solvents of different nature were tested. Also, several dispersion techniques were evaluated, such as high shear mechanical stirring and sonication at high frequency. In order to improve the compatibility with epoxy matrix, CNFs were amino-functionalizated through the acid-thionyl chloride way.

It was found that the experimental conditions applied for CNFs dispersion are critical to obtain homogeneous nanocomposite. It was probed that it is necessary to carry out several stages of CNFs dispersion, including the chemical modification and functionalization of CNFs, the dilution of non-cured epoxy/CNF mixture into a relative polar solvent and to combine different dispersing techniques (magnetic stirring, high shear mixing and sonication) for relative long periods of time at high temperature. In this way, homogeneous nanocomposites were manufactured with important increases of storage modulus.

Key words: carbon nanofibers, nano composite, dynamic mechanical thermal analysis (DMTA), infrared spectroscopy, scanning /transmission electron microscopy

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1. INTRODUCTION

Vapour grown carbon nanofibers (VG–CNFs) are widely interesting because they have unique combination of mechanical, electrical and thermal properties. CNFs also possess high flexibility, low mass density and large aspect ratio. CNFs, grown from the vapour phase, usually present diameters on the order of 20 - 100 nm and lengths between 10 and 100 μm [1]. They tend to have outstanding mechanical properties, with Young modulus in the range 100-1000 GPa and tensile strength between 2.5 and 3.5 GPa [2]. Another important advantage of CNFs is their lower costs with regard to carbon nanotubes. For all these reasons, VG–CNFs are being investigated as potential candidates of being used for reinforcing polymer matrices to improve their properties.

Some recent investigations show that the length of nanofibers/nanotubes plays an important role in the toughening mechanism of nanocomposites [3, 4]. The effective toughening may not be energetically favourable at nanolength scale, being generally necessary filler lengths greater than 100 nm [5, 6]. Therefore, in this work, long graphitic carbon nano-fibers, whose length reaches 10-30 μm, have been added as reinforcement on epoxy resins. However, these large lengths difficult the CNFs separation necessary to reach a homogeneous distribution in the matrix, avoiding entanglement and clustering effects.

It is well recognized that, to take full advantage of the enhanced properties of nanoreinforcements it is necessary that they are homogeneously dispersed in the polymeric matrix [7-11]. Different dispersion methods are being researched [12-14], including the dilution method, the use of ultrasonication, high shear mixing, the addition of sulfactant and the alignment techniques, between others.

Beside, it is necessary the optimization of nanofiber-matrix interface properties to reach an efficient load transfer between both constituents of the nanocomposite [1]. Due to the smooth surface of carbon nanofibers/nanotubes, lack of interfacial bonding limits load transfer from the matrix to the reinforcement [14, 15]. Numerous efforts are being carried out to enhance the matrix-nanoreinforcement interactions [14-17]. Two strategies are commonly employed to modify carbon nanostructure surfaces: covalent functionalization of surface carbon atom sites and non-covalent wrapping of carbon nanostructures with sulfactants, polymers or ceramic coatings. Covalent functionalization consists on covalent attachment of reactive linker molecules to carbon nanostructure surface and later, chemical reaction between linker and matrix functional

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groups, generating carbon/matrix interfaces of high covalent integrity. There is a vast literature reporting surface functionalization of carbon nanotubes and nanofibers, adding different functional groups, such as aromatic and aliphatic amine, carboxylic acid, etc [14-17]. However, the success of the reported results has a very high variability, and not always consistent results are reported. In general, covalent functionalization of carbon nanoreinforcements generally increases the chemical interaction with polymer matrix but, can cause the break of continuous carbon structure, decreasing their good intrinsic properties. On the other side, the non-covalent treatments of CNFs do not modify the atomic structure of reinforcement but they are usually unable to get a strong interface with the matrix.

In this investigation, chemical functionalization of nanofibers surfaces is employed to enhance attractive fiber/polymer interactions. A chemical modification of surface carbon sites is carried out introducing acid groups. The subsequent reaction between surface-derivated CNFs and bifunctional linker molecules provides functionalized CNFs which can form covalent bonds with the epoxy groups of the resin. Beside, different alternatives and processing conditions were explored to get a homogeneous dispersion of nanofibers into the epoxy matrix. Both high-power mechanical mixing and ultrasonic dispersion were investigated. The specimens of CNF-epoxy nanocomposites were prepared following two different methods, by directly mixing [9-10, 15-16] and by means diluted dispersions [14,18]. Also, different nature solvents were evaluated to produce stable dispersions of carbon nanofibers. The dispersion degree between CNF and polymer resin was analysed both in the uncured stage, by optical microscopy using heat deck, and after completing the curing reaction, by scanning and transmission electron microscopy. The effect of the obtained dispersion on the properties of nanocomposite was analysed through density measurements and Dynamic Mechanical Thermal Analysis (DMTA).

2. EXPERIMENTAL

2.1 Materials

VGCNFs (provided by Antolin, Spanish company), were used as nanoreinforcements. Their diameters are in the range from 20 to 47 nm and its average length is 35 μm. The polymer matrix is an epoxy resin based on diglycidyl ether of bisphenol A (DGEBA), with 178 g / epoxy equivalent, manufactured by Ciba under the commercial name of

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Araldite F. As curing agent, 4,4´-methylenedianiline (DDM) was used, purchased from Sigma Aldrich.

2.2 Surface oxidation and functionalization of carbon nanofibers

The applied functionalization process consisted of three stages treatment: oxidation, acylation and amino-functionalization with DDM. To oxidize the CNFs, they were treated with concentrated nitric acid at 70 ºC for 4h. After washing with distilled water until the filtrate reached a pH value of 7, the nanofibers were dried in vacuum at 60 ºC. The surface-oxidized CNFs were acylated by chemical reaction with thionyl chloride at 70 ºC for 24h. Then the mixture was cooled, washed with tetrahydrofurane (THF) and vacuum filtered. Finally, surface-acylated CNFs were reacted with DDM at 60 ºC in ethanolic solution 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 CNF surface modification are schematized in Figure 1.

The characterisation 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 analyse the possible modification on the dimensions and morphology of carbon nanofibers. We observed that the lengths of graphitic nanofibers decrease up to 10 – 20 µm with the oxidation treatment. The study of functionalization process and its effect on the morphology, stability and surface characteristics of CNFs is being published in other paper [19]. In that research work, we have shown the presence of the corresponding functional groups showed in Fig 1.

2.3 Preparation of the nanocomposites

CNF/epoxy composites were prepared using neat CNFs, as received, without any surface treatment, and surface DDM-derivatized CNFs (abbreviated as DDM-CNFs). Also, several methods of nanocomposites preparation were evaluated. The effect of different synthesis parameters on the nanofibers dispersion, on the reinforcement / matrix interaction and, therefore, on the final properties of nanocomposites were analysed. The final objective is to determine the optimum conditions of preparation of nanofibers / epoxy composites.

Two methods of nanocomposites preparation were applied: concentrated method, where the CNFs were directly dispersed into the epoxy precursor, and diluted method, using a solvent to decrease the epoxy viscosity and, in principle, to enhance the

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nanoreinforcement dispersion. Figure 2 shows a scheme of the processing methods applied. The CNFs content added is 0.5 wt % respect to epoxy monomer mass added.

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 [14,18]. The nanofibers suspension was stirred at 50 ºC for 45 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 45 min at 85 ºC. After slowly evaporating the solvent with continuous stirring at 85ºC, only in the case of the functionalized DDM-CNFs, the resultant mixture was pre-cured at 130 ºC for 1 h, in the in order to enhance the chemical reaction between the amino groups of DDM-CNFs and DGEBA. Then, a stoichiometric amount of DDM was added into the mixture, followed by stirring at 150ºC to dissolve the hardener. The resulting mixture was then taken into a steel mould, whose walls were previously treated with an anti-adherent demoulding agent, Marbocote 445. Afterwards, the mould was inserted into a oven, applying a curing treatment consisting on a heating at 150 ºC during 3 hours and then a postcuring process of 180 ºC for 1h.

2.4 Characterization of nanocomposites

The homogeneity of CNFs dispersion into the epoxy monomer, before curing, was studied by transmission optical microscopy (TOM), placing a few drops of the nanofibers / resin mixture on a microscope slider and using a heat deck for high temperature. After curing, resultant nanocomposites were microstructural characterized by means of scanning and transmission electron microscopy (SEM and TEM). So, the effectiveness in the CNFs dispersion in the cured nanocomposites was studied by SEM (Phillips XL30) on fracture surface at room temperature. To reduce charging, the surfaces were coated with a thin sputtered layer of Au / Pd. Beside, TEM (Phillips Tecnai 20) was used to obtain additional information on the dispersion grade and mainly to analyse the morphology of nanofiber / epoxy interfaces. In this case, specimens 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.

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Fourier Transform Infrared Microscopy (FTIR) was applied to analyse the interaction between untreated and DDM-CNFs with the polymer resin. For it, samples of neat epoxy resin and nanocomposites had to be grinded, obtaining fine powders, which were mixed with dry potassium bromide and pressed on thin disk form. These disks were dried in vacuum at 80 ºC during one hour. IR spectra were collected in a Nicolet Magna IR-750 apparatus, at 2 cm^{-1} resolution in a wavenumber range 400 – 4000 cm^{-1}. Additional measurements of density were carried out on the cured nanofibers/epoxy composites by the gravimetric method of water immersion, using a Mettler Toledo balance with ±0.001 mg.

Finally, the effect of the dispersion grade and functionalization of CNFs on the final properties of epoxy/CNF composite was determined by dynamic mechanical thermal analysis (DMTA). These tests 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 ºC / min between 30 and 250 ºC. The samples used were parallelepiped bars (1.5 x 12.5 x 35 mm^3).

3. RESULTS AND DISCUSSIONS

3.1 Dispersion of CNFs into non-cured epoxy monomer

Figure 3 shows optical micrographs, collected at 100 x magnifications, of the uncured CNF / DGEBA mixtures obtained by different dispersion processes. The added amount of CNFs is 0.5 wt % regard to DGEBA mass. The micrographs 3a1, 3a2 and 3a3 show the effect of the dispersion method applied, concentrated or diluted. The directly dispersion of nanofibers with the epoxy precursor gives highly heterogeneous mixtures, showing large aggregates, whose size is higher than 20 μm in length. The use of solvents enhances the nanofibers dispersion due to the decrease of the mixture viscosity. For the tested conditions, chloroform seems to be better solvent than THF, meaning that its relative high polarity enhances the graphitic nanofibers dispersion. Other potential solvents, such as water and acetone, were tested but the obtained dispersions were very unstable.

The effect of the temperature applied during the dispersion is observed in micrographs 3b1 and 3b2. Both correspond with mixtures prepared with the same procedure, using chloroform, sonication and magnetic and high shear mixing. The difference between them is the temperature at which this procedure is applied, at room temperature and 60ºC. The temperature increase up to 60 ºC during the application of magnetic stirring

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and high shear mechanical mixing causes an important decrease of the average size of nanofibers agglomerates. Higher temperature could not be applied during this dispersion stage due to the early evaporation of chloroform.

The micrographs 3c1, 3c2 and 3c3 show the uncured CNF / epoxy mixtures obtained changing the dispersion techniques. The sonication of filled resin at relative high frequencies enhances the dispersion of CNFs. However, it was observed that sonication is was insufficient to obtain an optimum dispersion, being also necessary the use of high shear stirring to get a more uniform dispersion [20]. The combination of sonication technique and high shear mechanical stirring seems to be enough effective to separate bundles. However, despite of this improvement, no total homogeneity was achieved in the studied epoxy / nanofiber mixtures. Small aggregates, whose average length is smaller than 1 μm, are still observed on the uncured mixtures processed with the best studied conditions; that is using the diluted method with chloroform and mixing at 60ºC using both, magnetic stirrer, sonicator and shear mechanical mixer. These small heterogeneities could be associated to the high nanofibers concentration and their great length. Beside, it must be taken into account that these nanofibers were not subjected to any chemical surface treatment.

Finally, in order to enhance the nanofiber / epoxy interaction, the carbon nanofibers were chemically treated to incorporate functional groups attached to their surface (micrographs 3d1, 3d2 and 3d3). The uncured 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. The dispersion is enhanced when the prepared epoxy / DDM-CNF mixtures are heated at 130 ºC for 1 hour (micrograph 3e1), after removing solvent, to induce the pre-curing reaction between oxirane rings of DGEBA and amino groups of DDM-functionalized CNF. In fact, this mixture seems totally homogenous at the limited resolution of optical microscopy. Therefore, it is possible to affirm that applying the optimized conditions of processing of epoxy / CNF mixtures, there are not agglomerates or bundles higher than 1 μm. All the mixtures are macroscopically darks due to the great length of CNFs used. It is also worthy to stand out that the CNFs content added is very high, 0.5 wt %, which corresponds to approximately 5 % in volume, calculated from the density of DGEBA and CNFs.

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Taking into account all these results, the optimum conditions of preparation of 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 60ºC, sonication at high frequency, high shear mechanical mixing and pre-curing treatment.

3.2 Dispersion degree of CNFs in cured nanocomposites

Figure 4 shows SEM images of the fracture surfaces of several nanofibers / epoxy nanocomposites manufactured with different processing conditions. The absence of any agglomerates in fig 4c and 4d could indicate an uniform dispersion of the carbon nanofibers into the epoxy matrix at the micron and submicron level. These micrographs correspond to the nanocomposite prepared with the optimum conditions previously determined. By contrast, the CNF / epoxy nanocomposite manufactured without using any solvent (fig 4a and 4b) shows nanofibers agglomerates. In this nanocomposite, at very high magnification, it can be observed the presence of unstuck nanofibers. This indicates a lack of adherence between the reinforcement and matrix, confirming the necessity of the surface nanofibers treatment [18].

In 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 (Figures 5a and 5b). The applied dispersion techniques are effective to separate bundles into small braids and homogenously dispersed them into the epoxy matrix. However, the carbon nanofibers tend to wind up and to braid forming aggregates (Fig 5b). On the TEM micrographs, it is also possible to observe the presence of treated carbon nanofibers with different lengths, from 500 nm to several micrometers [20]. 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 to increase the mechanical properties of the polymer matrix.

TEM micrographs at very high magnifications (fig 5d, 5e and 5f) show that the walls of treated surface DDM-CNFs keep smooth and its thickness does not seem to modify after chemical treatment. This could mean that the chemical functionalization must occur in a low proportion. In fact, Lukehart et al. [17] studied the functionalization of carbon nanofibers applying similar experimental conditions and they reported that the

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number basic amine-sites on the CNF surfaces is around (0.4 -1.4) x 10^{-4} mol/g using a diamine-aromatic linker molecules as linker.

Also, in TEM micrographs, it is observed a high continuity level between the matrix epoxy matrix and DDM-CNFs which could be considered as an evidence of good interfacial adhesion. At lengthwise of nanoreinforcements, any cracks, unstuck zones or other characteristic evidence of bad adhesion are observed.

In order to study the possible chemical interactions between the epoxy matrix and CNFs, the nanocomposites was analysed by FTIR. Figure 6 shows the FTIR spectra obtained for cured DGEBA/DDM resin and CNFs. Neat epoxy resin presents numerous bands (fig 6b), associated to vibrations of stretch and deformation of its chemical bonds (C-C, C-O, C-H, etc), which have been already reported by other authors [21-23]. It is only worthy to indicate the very low intensity of the band at 917 cm^{-1}, which is related to the symmetric stretching of C-O-C bonds of the oxirane rings. This means that the epoxy resin is almost totally cured. The same conclusion was obtained for the manufactured epoxy nanocomposites. In contrast, the spectrum of CNFs (fig 6a) scarcely presents bands due to the high purity and its simple carbon structure [24, 25]. The sharp band at 1382 cm^{-1} is associated to the stretching of C-O bonds, which means that non-treated CNFs are partially oxidized.

The cured epoxy/CNF nanocomposites, manufactured using different dispersion techniques, were also studied by FTIR. Figure 7 shows a magnification of the interested region of the spectra (1400 – 1320 cm^{-1}). In this area of IR spectrum the epoxy resin presents two bands, at 1382 and 1362 cm^{-1}, both associated to asymmetric deformation of C-H bonds of methyl groups. These bands are inert, their corresponding functional groups, formed by aliphatic bonds, do not interact with other functional groups. Therefore, remaining the same concentration of epoxy and CNFs, the intensity of these bands should not vary. Similar behaviour must present the band at 1382 cm^{-1} associated to CNFs. If the added nanofibers amount does not change, the intensity of this band should be constant. However, the relative intensity of these bands varies with the dispersion technique applied for manufacturing the epoxy/CNF nanocomposites. The sample processed following the concentrated method, without using solvents, presents a higher intensity of the band at 1382 cm^{-1}. In contrast, the band at 1362 cm^{-1} is higher for the case of nanocomposites manufactured using chloroform as solvent. Both bands present similar intensity in the case of epoxy nanocomposite processed with THF.

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Therefore, the relative intensity of the band at 1382 cm^{-1} decreases with regard to the one of band at 1362 cm^{-1} in this order: epoxy resin < concentrated < THF < $CHCl_3$.

Taking into account the previous conclusions about the dispersion grade of these nanocomposites, it is possible to affirm that the intensity of band at 1382 cm^{-1} decreases with the enhancement of dispersion of carbon nanoreinforcements. This behaviour can be explained in this way: the enhancement of CNFs dispersion implies a higher chemical interaction of the carbonyl groups of CNFs with the epoxy and hydroxyl groups of epoxy resins, causing a decrease of the intensity of its band.

Neither by SEM, nor TEM (fig 4 and 5), it was possible to observe if the studied nanocomposites present voids and other kind of defects of processing. For it, measurements of density of epoxy nanocomposites were carried out in order to analyse the density changes associated to presence of voids.

Table 1 collects the values of density of epoxy nanocomposites reinforced with 0.5 wt % CNFs, which were manufactured applying different techniques of nanoreinforcements dispersion. The theoretical density is also shown, which was calculated by rule of mixtures, using the CNF density value supplied by the manufacturer. It is observed that the nanocomposites synthesised by diluted method, using chloroform or tetrahydrofurane as dissolvent, present values of density higher than theoretical density. In contrast, the nanocomposites obtained without solvent have lower densities. The diluted methods must enhance the wetting of CNFs with epoxy monomer, which indeed results in a higher density because of less free volume around the CNFs. Also, comparing the density of epoxy/CNF samples obtained by the concentrated method, its value increases with the use of techniques which enhance the nanoreinforcements dispersion. The lowest density was measured for the nanocomposite obtained through the magnetic stirring, without using solvent, sonication or other stirring techniques. Therefore, seeing these results and taking into account the morphologic analysis carried out by TEM and SEM, it is confirmed that the samples which present a good dispersion of CNFs have values of density higher than the theoretical one. The less homogeneity of the nanocomposites, the less is its value of density. The lower density of poor-dispersed nanocomposites could be related with the higher intrinsic free volume in the CNFs bundles.

The experimental density of homogeneous nanocomposites is higher than the theoretical one due to the introduction of CNFs on the free volume of epoxy resin. In contrast, the density of nanocomposites with heterogeneous dispersion of CNFs is lower. This drop

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is usually associated to the presence of voids. These defects must have appeared by dispersion problems during the processing, indicating the formation of agglomerates of great dimensions.

3.3 Thermo-mechanical properties of the nanocomposites

The effect of the dispersion state reached through the different processing methods on the thermo-mechanical properties of the nanocomposites was studied by DMTA. Figure 8 shows the variation of storage modulus (E´) as a function of temperature for different specimens of epoxy nanocomposites with 0.5 wt % CNFs. A summary of the numeric results is collected in Table 2. 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 interfacial adhesion between nanofibers and matrix [15].

The first observation is that the temperature associated to α-relaxation (T_α), determined by the abrupt drop of E´, is higher for neat epoxy resin than the ones of the all processed nanocomposites. This effect has been already reported for other authors [26,27]. The possible cause could be the preferential adsorption of one of the matrix constituent [27]. This leads to non-stoichiometric balance, which would result in depression of glass transition temperature. This would also justify the fact of the T_α of epoxy nanocomposite reinforced with DDM-CNFs is higher than the ones of the non-treated CNF/epoxy nanocomposites. The amino-functionalization of CNFs would partially compensate the non-balance stoichiometry, increasing the T_α value. This would imply that the compound which is preferentially adsorbed by nanofibers is the amino-crosslinker instead of epoxy monomer. This preferential adsorption of DDM could be justified by the lower size of the DDM molecules regard to DGEBA.

On the other hand, the glass transition temperature does not seem to depend on the experimental conditions of processing, the use of solvents or dispersion techniques. This means that the glass transition temperature remains constant and it does not depend on the state of CNFs dispersion obtained. 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 the epoxy resin.

As expected, the glassy storage modulus of the nanocomposites is higher than the one of neat epoxy resin. Comparing the values of E'_G obtained for the different processed

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nanocomposites, it is possible to affirm that it is affected by the homogenisation grade reached during the CNFs dispersion process. In Figure 8a, 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 TOM, SEM and 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 8b shows the E´ versus temperature curves for epoxy nanocomposites reinforced with 0.5 wt % CNFs, which were processed modifying the used dispersion technique of nanofibers/resin solution. To manufacture the sample 1, the CNFs dispersion was carried out by mechanical stirring while the dispersion method applied for the sample 2 also implies several stages, using mechanical stirring, high shear mixing and sonication at high frequency. A moderate increase of the E´ at room temperature is measured for sample 2, indicating that the sonication treatment enhances the CNFs dispersion, obtained nanocomposites more homogeneous.

Finally, the effect of functionalization on the thermal-mechanical properties is determined in Fig 8c, where they are represented the corresponding DMTA curves of epoxy nanocomposites reinforced with non-treated CNFs, oxidized-CNFs and DDM-CNFs. The value of E´ at room temperature changes from 2.3 GPa for epoxy nanocomposites reinforced with CNFs and oxidized-CNFs, to 2.6 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 previously confirmed by morphologic analysis of the nanocomposites. On the other hand, the increase of modulus on the nanocomposites with functionalized DDM-CNFs reflects the increase in effectiveness in the load transfer to the nanofibers because the formation of a stronger interfacial bonding by the reaction among the free terminal amino groups covalently

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attached to the side chain on the CNFs with the epoxy groups of the composite matrix [14].

Table 2 also collects the values of storage modulus in the rubbery region. An important increase is observed in the E´ above the glass transition temperature of epoxy nanocomposite comparing with the rubbery storage modulus of neat epoxy resin. This behaviour can be explained by the reduction of the mobility of the epoxy matrix around the nanoreinforcements, which leads to the observed increase in thermal stability. The strong interaction between DDM-CNFs and epoxy resins by chemical grafting causes higher restriction in the mobility of matrix, leading higher increase of the rubbery storage modulus.

With the DMTA results, it is confirmed that the mechanical properties of nanocomposites depend on dispersion state of nanofibers and the interfacial adhesion between nanoreinforcements and the matrix. To improve the modulus, it is necessary to get a uniform dispersion of nanofibers into the matrix and a relative strong bonding between them. Both can be partially achieved applying several stages of CNFs dispersion, including dilution in an optimum solvent, sonication dispersion and high shear mechanical stirring, and carrying out the previous functionalization process of the nanofibers.

4. CONCLUSIONS

In summary, this paper proposed and investigated an efficient procedure of the dispersion of CNFs on epoxy resins. In order to obtain well dispersed CNF/epoxy nanocomposites is necessary to carry out the chemical surface modification of the nanoreinforcements and several consecutive stages of CNFs dispersion using different techniques, including dilution into chloroform solvent, stirring with mechanical and high shear mixers and the dispersion with ultrasonication.

Morphology of CNF/epoxy nanocomposites was studied by TOM, SEM and TEM. Density measurements and FTIR were also used in order to study the homogeneity of the samples. The measurement of the density of the samples allows obtaining information about the presence or absence of porous and defects. On the other hand, by FTIR it is possible to analyse the possible chemical interactions between epoxy matrix and added CNFs.

As results, the experimental conditions used for epoxy / CNF nanocomposites fabrication are critical. Important differences on the dispersion grade of CNFs are

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observed depending of manufacture process applied and these affect to the thermo-physcial properties of nanocomposites. The epoxy resin containing well dispersed CNFs exhibits higher storage modulus. Also, this sample presents low density, indicating the absence of porous and defects and the introduction of CNFs into the free volume of epoxy matrix.

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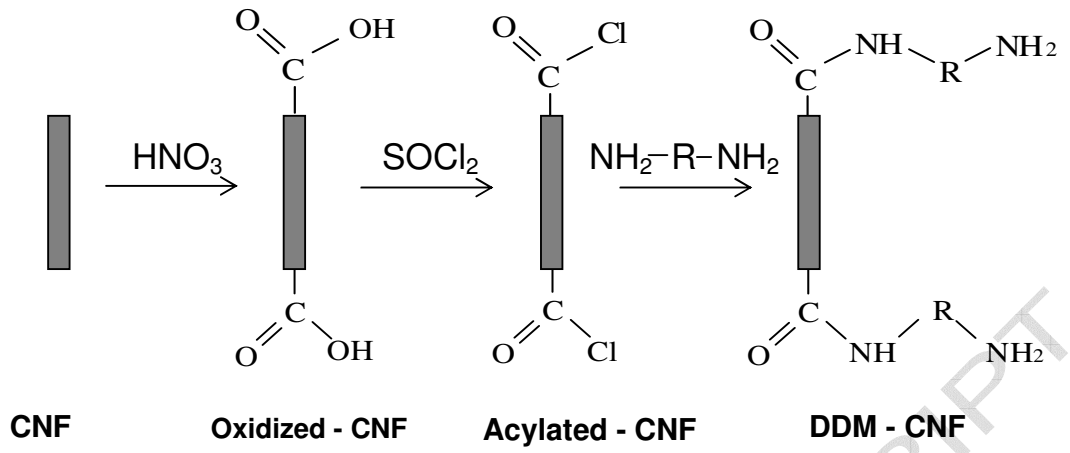

Figure 1. Surface oxidation, acylation and functionalization of carbon nanofibers

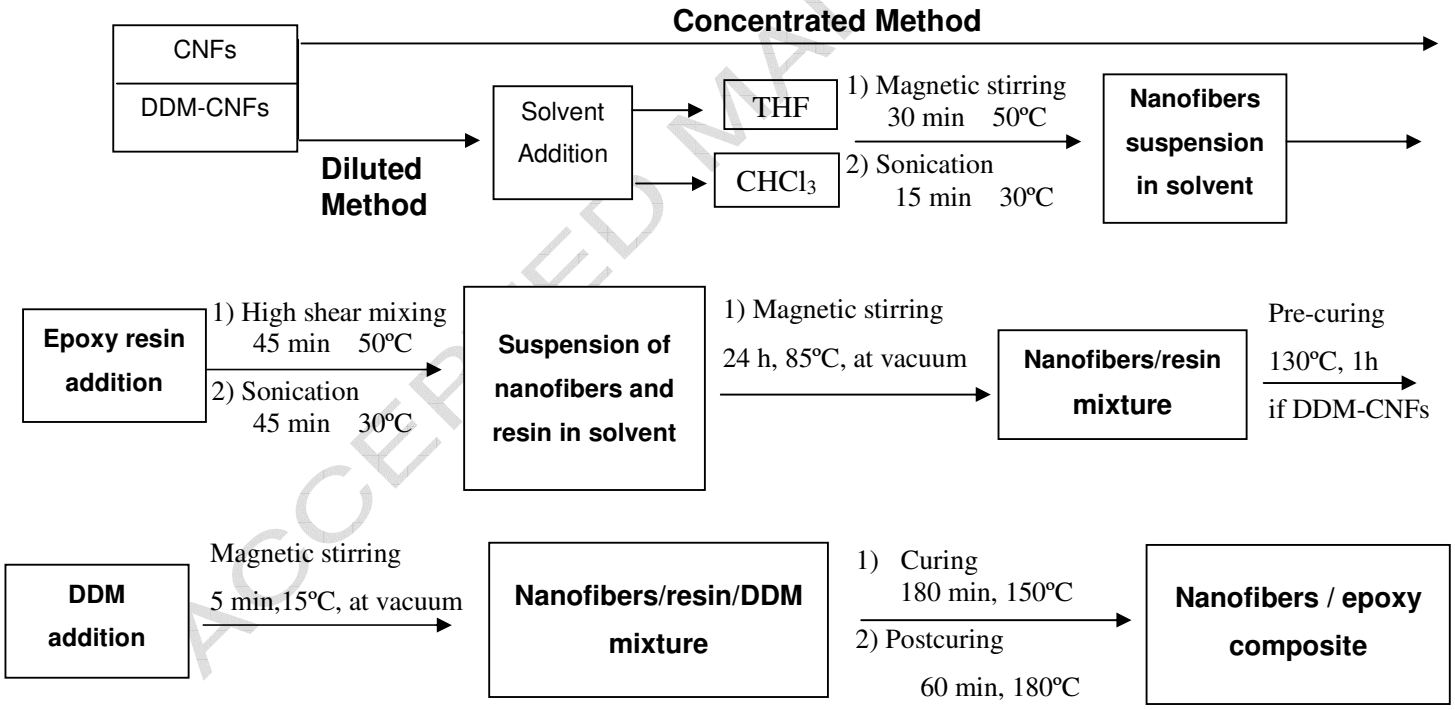

Figure 2. Scheme of the processing stages of CNF / epoxy nanocomposites.

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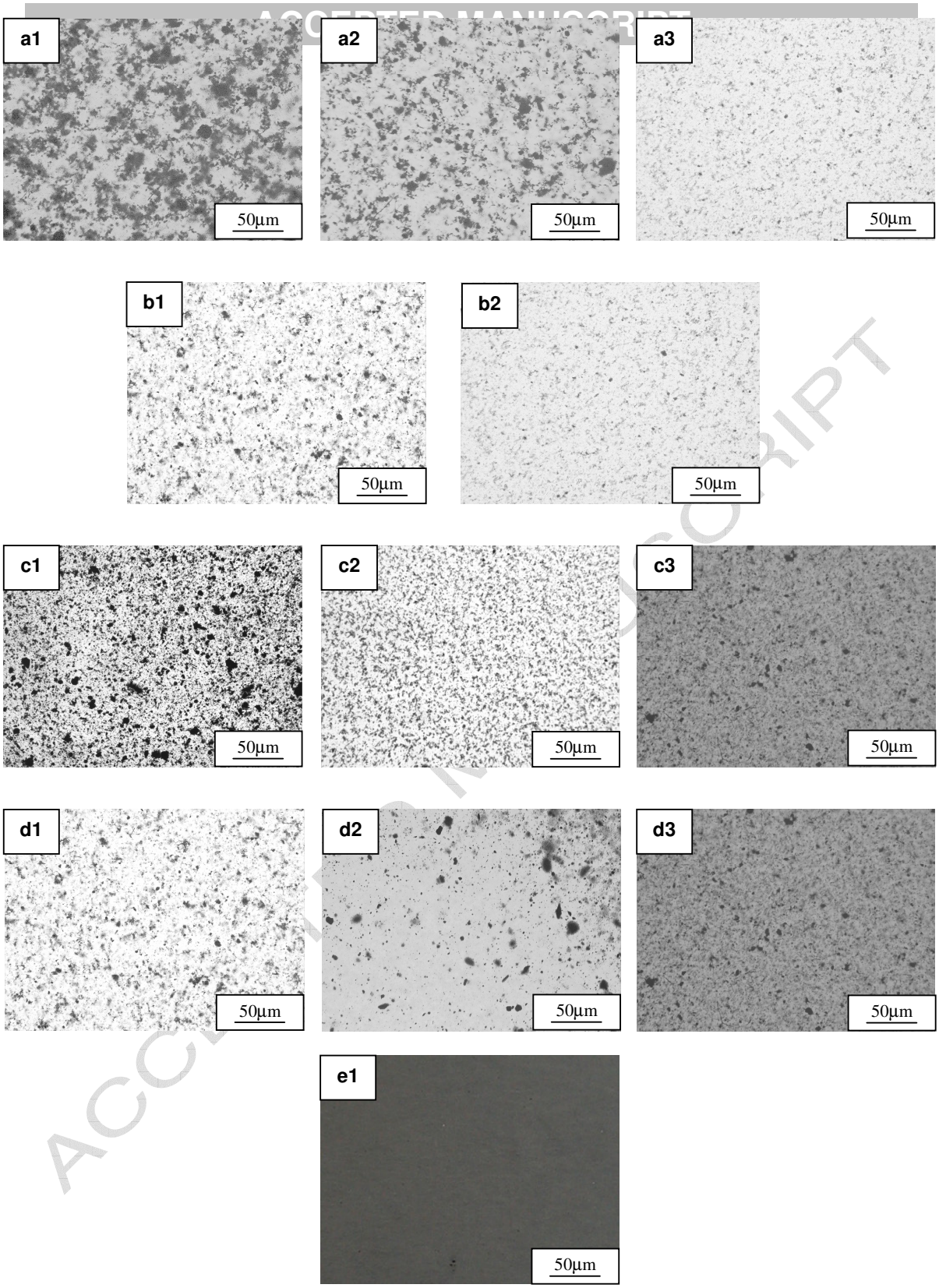

Figure 3. Optical micrographs showing the effects of different dispersion methods. a) Solvent: (a1) concentrated method, (a2) diluted method with THF (a3) diluted method with $CHCl_3$ b) temperature: (b1) room temperature, (b2) 60ºC, c) Dispersion technique:

(c1) only magnetic stirring, (c2) magnetic stirring and sonication, (c3) magnetic stirring, sonication and high shear mixing, d) Nanofibers functionalization: (d1) CNFs, (d2) acylated-CNFs (d3) DDM-CNFs. e) Precuring treatment: (e1) precuring at 130ºC for 1 hour.

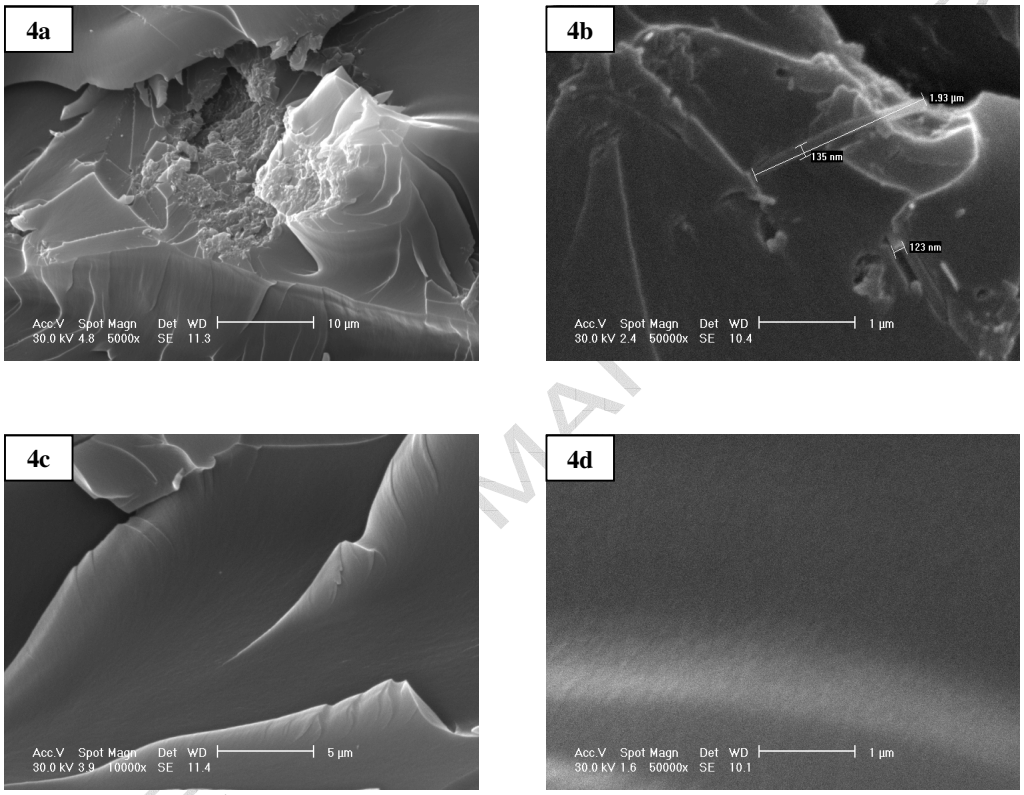

Figure 4. SEM images of the fracture surfaces of nanofibers / epoxy nanocomposites with 0.5 wt % CNFs, prepared by concentrated method (4a, 4b) and 0.5 wt % DDM-CNFs, manufactured by diluted method using the optimum conditions (4c, 4d).

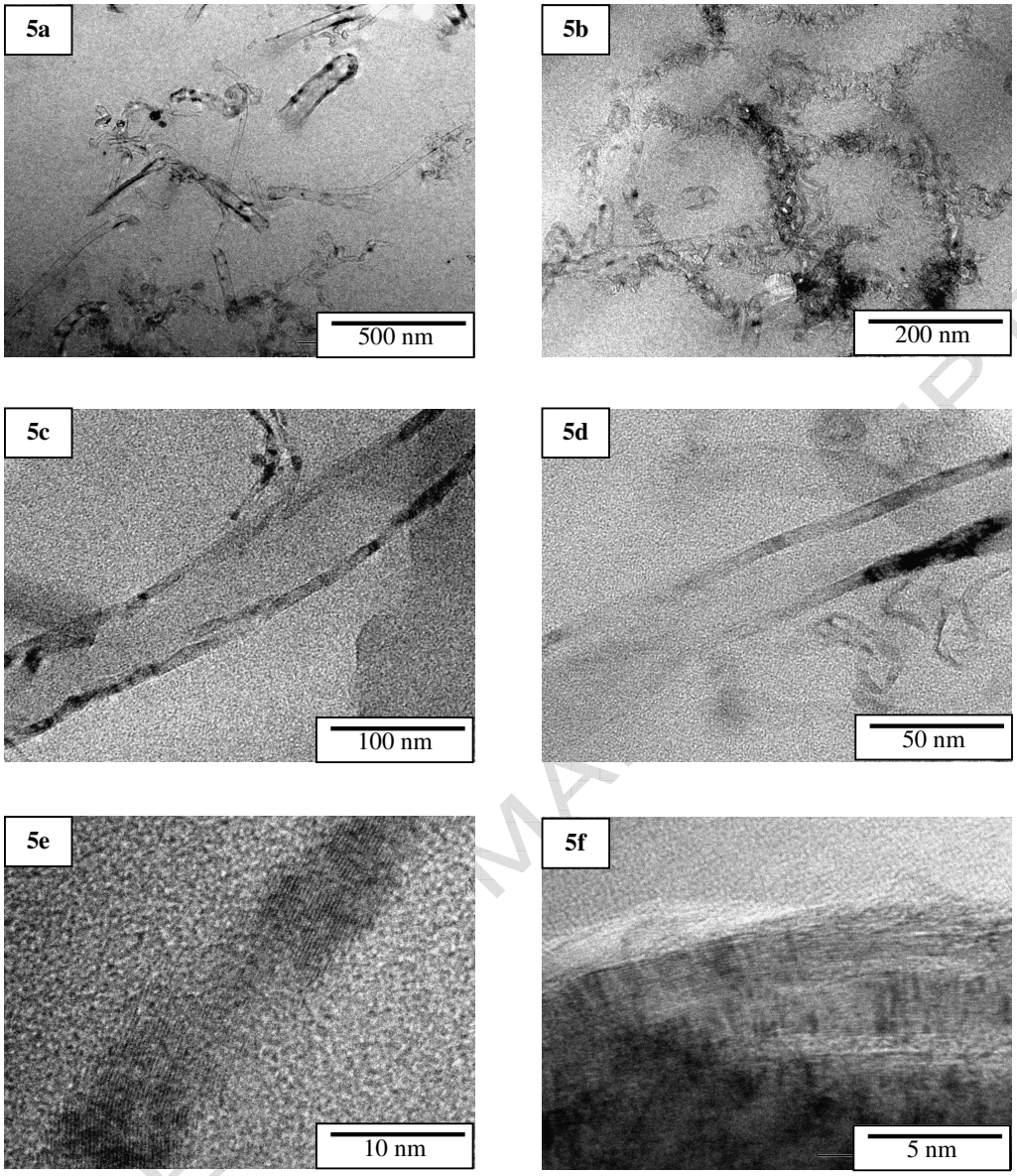

Figure 5. TEM images of the nanofibers / epoxy nanocomposites with 0.5 wt % DDM-CNFs, manufactured by diluted method using the optimum conditions.

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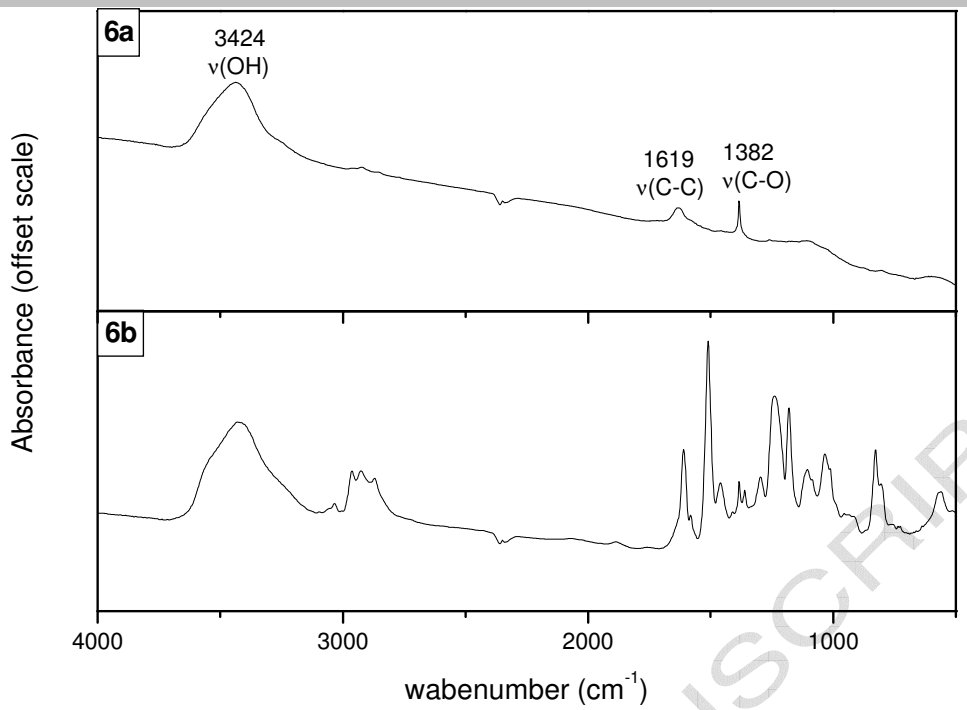

Figure 6. FTIR spectra for 6a) CNFs and 6b) neat epoxy resin.

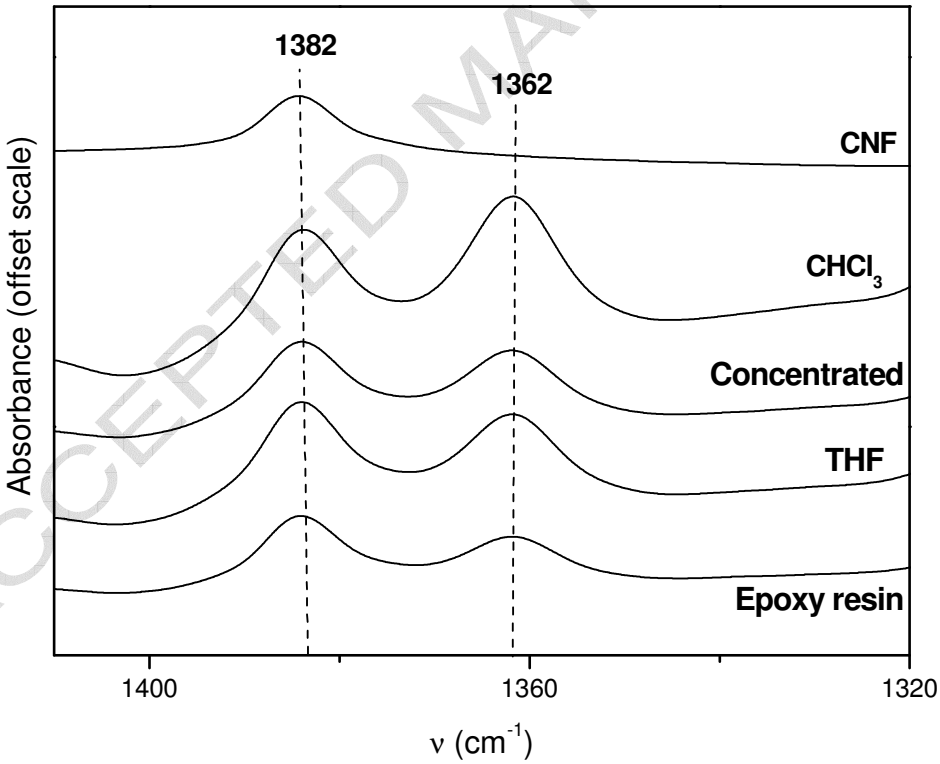

Figure 7. Absorbance region (1400 -1320 cm^{-1}) of FTIR spectra for pure CNFs, neat epoxy resin and epoxy nanocomposites with 0.5 wt % CNFs, which were manufactured by concentrated method and using solvents, THF or chloroform.

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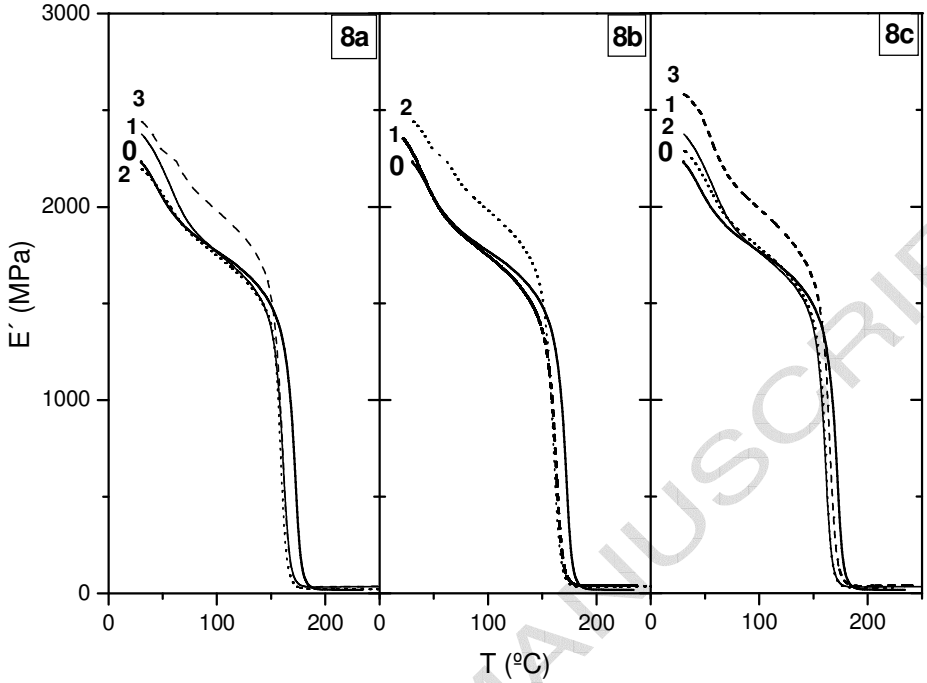

Figure 8. DMTA curves of neat epoxy resin (0) and epoxy nanocomposites with 0.5 wt % CNFs processed by different dispersion procedures: 8a. Solvent effect: 1) concentrated, 2) diluted in THF, 3) diluted in chloroform; 8b. Dispersion effect: 1) mechanical stirring, 2) mechanical stirring, high shear mixing and sonication; 8c. CNF functionalization effect: 1) CNF, 2) Oxidized-CNF, 3) DDM-CNF.

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Dispersion conditions	ρ (g / cm^3)
Concentrated method Magnetic stirring	1.174 ± 0.002
Concentrated method Magnetic stirring and sonication	1.185 ± 0.002
Concentrated method Magnetic stirring, sonication and high shear mixing	1.182 ± 0.003
Diluted Method with $CHCl_3$ Magnetic stirring, sonication and high shear mixing	1.192 ± 0.003
Diluted Method with THF Magnetic stirring, sonication and high shear mixing	1.191 ± 0.003
Theoretical density	1.185

Table 1. Density of CNF / epoxy nanocomposites manufactured through the use of different conditions of nanoreinforcement dispersion

Dispersion procedure	T_α (ºC)	E'_G (GPa) at 30ºC	E'_R (MPa) at 200ºC
None	171	2.2	19.6
SOLVENT EFFECT			
Concentrated	161	2.4	34.2
Diluted THF	161	2.2	40.8
Diluted in chloroform	159	2.5	34.2
DISPERSION EFFECT			
Mechanical stirring	160	2.3	40.8
Mechanical stirring, high shear mixing and sonication	161	2.5	34.2
FUNCTIONALIZATION EFFECT			
CNFs	161	2.4	34.2
Oxidized-CNFs	160	2.3	30.8
DDM-CNFs	166	2.6	40.1

T_α = α-relaxation temperature
E'_G = Glassy storage modulus at 30ºC
E'_R = Rubbery storage plateau modulus at around 200ºC

Table 2. Summary of key DMTA properties