

## Glass Fiber Hybrid Composites Molded by RTM Using a Dispersion of Carbon Nanotubes/Clay in Epoxy

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Nanocomposites based on epoxy and a mixture of clays and multi-walled carbon nanotubes (MWCNT) were produced by casting, and also molded by RTM using glass fibers as reinforcement, yielding a hybrid multi-scale micro/nanocomposite material. Two types of montmorillonite clays were used, natural (MMT-Na) and organophilic (MMT-30B). Higher viscosity was obtained for the mixture with MMT-30B and it was observed that this clay did not perform as well as the MMT-Na in helping the dispersion of the carbon nanotubes (CNT). The glass transition temperature ( $T_g$ ) of the nanocomposites increased in up to 6 °C with the addition of MWCNT and up to 10 °C with the addition of MMT-30B, differently from the MMT-Na which did not alter the  $T_g$  of the material. By transmission electron microscopy, it was verified that more homogeneous dispersions and more intercalated structures were obtained with the MMT-30B than with the MMT-Na. Finally, the low clay content used and, especially, the very low MWCNT content, did not significantly alter the studied flexural properties.

**Keywords:** *hybrid composites, epoxy, clay, carbon nanotubes, glass fiber, RTM*

### 1. Introduction

Polymer matrix nanocomposites have been the subject of many recent studies in the literature. In the last eight years, a particular class of microcomposite/nanocomposite started being investigated, the combination of fibers, polymer and nanoparticles, a type of hybrid three-component material. Above a particular volume fraction, dispersion of carbon nanotubes (CNT) in a polymer matrix can produce percolated structures, promoting electrical conductivity<sup>1,2</sup>. Thus, the generally highly resistive polymer matrices can become suitable for applications that require electrostatic dissipation and/or electromagnetic shielding<sup>1,3</sup>.

The dispersion of clay nanoplatelets in polymer matrices<sup>4-8</sup> can increase stiffness<sup>4,7</sup>, tensile strength<sup>5,6,8</sup>, thermal resistance<sup>8</sup>, glass transition temperature<sup>4</sup>, besides reducing flame propagation<sup>7</sup> and gas permeability<sup>6</sup>. However, in its natural form, the montmorillonite clay is hydrophilic, being necessary to modify its surfaces with an organophilization reaction, providing better compatibility with non-polar polymer matrices. The matching of molecular polarity of matrix and clay helps the intercalation and exfoliation of the nanoplatelets<sup>9</sup>.

Tsai et al.<sup>10</sup> produced hybrids of epoxy/glass fibers and organoclay and an increase of up to 24% was verified in the transverse compression strength when using only 5 wt% of

organoclay. Lin et al.<sup>11</sup> also molded epoxy matrix hybrids with organoclays and glass fibers. The tensile modulus increased for clay content of up to 5 wt%, in both direction, parallel and normal to the fiber. Impact strength increased for clay contents higher than 3 wt% only perpendicularly to the fibers and impact resistance parallel to the fibers was reduced for clay fractions higher than 1 wt%.

Epoxy matrix hybrid micro/nanocomposites have already been produced and studied. Fan et al.<sup>12</sup> obtained an increase of up to 33% in interlaminar shear strength (ILSS) of an epoxy/glass fiber composite with the addition of 2 wt% of CNT. Bekyarova et al.<sup>13</sup> analyzed the effect of dispersing CNT functionalized with carboxylic groups in epoxy/carbon fiber composites, verifying an increase of up to 40% in ILSS when adding 0.5 wt% of CNT, though there was no change in flexural strength. In addition, Chang<sup>14</sup> evaluated the synergetic effect of multi-walled CNT, carbon fiber and glass fiber on the static and dynamic mechanical and thermal properties of their composites.

Another interesting potential not yet deeply exploited in the literature, is to make the clay act like a dispersing agent of electro-conductive carbonic phases, such as carbon black or CNT, enhancing some properties of interest, e.g. electrical conductivity<sup>15</sup>, mechanical properties<sup>15,16</sup> and flame retardance<sup>17</sup>. Liu and Grunlan<sup>15</sup> showed this effect when dispersing CNT and sodium montmorillonite clay in a

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DGEBF epoxy matrix. Haque et al.<sup>18</sup> fabricated epoxy matrix hybrid micro/nanocomposites with organoclay by vacuum assisted resin infusion method (VARIM) and reported that 1 wt% clay promotes an increase of 14, 24 and 23% in tensile modulus, flexural strength and toughness, respectively.

In this work, materials with one or two nanostructures were molded via casting and also using RTM (with glass fibers). The samples with the simultaneous dispersion of two nanostructures were produced for the purpose of analyzing potential synergic relations between montmorillonite clays and CNT, a subject still poorly studied at the literature.

## 2. Experimental

Initially, the nanoparticles were dispersed in DGEBA epoxy monomers using high energy sonication and without the aid of solvents. It is important to mention that the traditional dispersion method in solution was avoided, because it may result in reduced crosslinking degree of the polymer matrix if the solvents are not thoroughly removed<sup>19</sup>, and also due to environmental and labor safety concerns.

The epoxy monomer used, diglycidyl ether of bisphenol-A (DGEBA), is commercially known as Araldite® LY-1316, with an epoxy equivalent of 5.8-6.3 eq/kg. Due to its low viscosity compared to other liquid epoxy resins, it is suitable for resin infusion molding techniques. The hardener agent used for DGEBA is triethylenetetramine (TETA) - Aradur® HY-1208. Both chemicals were provided by Huntsman Co.

Two different kinds of clays supplied by Southern Clay were used in this work: Cloisite® Na<sup>+</sup> (MMT-Na), with interplanar spacing ( $d_{001}$ ) of 11.7 Å; and Cloisite® 30B (MMT-30B), an organoclay which was modified with a quaternary ammonium salt (MT2EtOH - T represents an alkyl group with 65% of C<sub>18</sub>H<sub>37</sub>, 30% of C<sub>16</sub>H<sub>33</sub> and 5% of C<sub>14</sub>H<sub>29</sub>), with  $d_{001}$  of 18.5 Å, according to the supplier datasheet. Both clays were previously oven-dried, for 48 h at 60 °C, under vacuum.

Multiwalled carbon nanotubes (MWCNT) were supplied by Chengdu Organic Chemicals Co., commercially known as TNIM4, with purity levels higher than 85% and electrical conductivity of 100 S/cm, according to the supplier data sheet. The non-woven E-CR glass fibers were provided by Owens Corning, with an aerial density of 450 g/m<sup>2</sup>.

All experiments were performed using 2 wt% of clay relative to the weight of epoxy monomers, except the neat system in cast and RTM samples. In some samples, a constant weight fraction of 0.1 wt% of MWCNT was used based on previous work, which showed the formation of CNT percolated structures when using weight fractions lower than 0.1 wt%<sup>15,20</sup>. The nanocomposite samples were obtained by casting and the hybrid samples were produced by RTM. The adopted nomenclature is shown in Table 1, where “L” indicates cast molded sample, “GF” indicates RTM sample; “Na” indicates the use of MMT-Na clay, “30” indicates the use of MMT-30B clay, and the subscript “c” indicates the use of MWCNT. It should be stressed out that two different clays were employed in this work.

First of all, the nanoparticles were weighed (precision of 10<sup>-4</sup> g) and added to 100.0 ± 0.5 g of epoxy monomers, manually stirring the system for about 1 min. The mixture

**Table 1.** Nomenclature and composition of the samples.

Cast samples	RTM samples*	MMT-Na	MMT-30B	MWCNT
LY	GF	---	---	---
LYNa	GFNa	2.0 wt%	---	---
LY30	GF30	---	2.0 wt%	---
LYc	GFc	---	---	0.1 wt%
LYNa,c	GFNa,c	2.0 wt%	---	0.1 wt%
LY30,c	GF30,c	---	2.0 wt%	0.1 wt%

\*Constant glass fiber volumetric fraction (~27 vol%).

was then sonicated for 30 min at 188 W using Sonics VCX 750 high energy sonication equipment. After cooling to room temperature, 0.3 wt% of degassing agent BYK A500 and 0.5 wt% of BYK A560 were added, following previous results of the group<sup>21</sup>. The resulting mixture was magnetically stirred for 40 min at room temperature, under vacuum, in order to remove entrapped air.

The hardener was added (at 13 wt% of epoxy monomers) to the degassed mixture, stirring for 3 min under vacuum. Part of this mixture was cast in opened molds and cured at room temperature (‘LY’ samples). The remaining mixture was used to produce hybrid micro/nanocomposites by RTM, infusing the mixture through four layers of glass fiber mats within a closed mold. The maximum infusion pressure was 1.2 bar and the average volumetric fraction of glass fibers was about 27.0 ± 1.9%. The curing reaction was allowed to occur for 24 h at room temperature, obtaining the ‘GF’ samples.

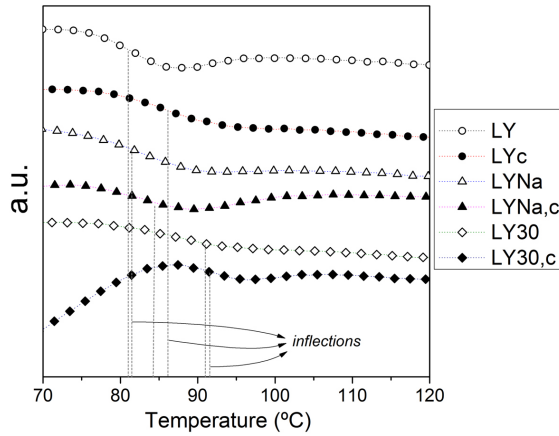
The glass transition temperature ( $T_g$ ) of the cast samples was obtained by differential scanning calorimetry (DSC), NETZSCH DSC 200 F3, with a heating rate of 10 K/min, from 30 to 300 °C (under nitrogen atmosphere) based on the inflection point of the second heating run. Viscometry tests were performed on a cone-plate viscometer – Brookfield CAP 2000 – at 50 °C. Transmission electron microscopy (MET) of the cast samples was carried out using a Philips CM-120 microscope and the specimens (nominal thickness of 40 nm) were obtained at room temperature on a Leica Ultramicrotome using a diamond knife. The RTM samples were submitted to three-point flexural tests according to ASTM D790, in a universal testing machine EMIC DL3000, using a load cell of 100 kN. The flexural modulus was obtained with the tangent method. Scanning electron microscopy (SEM) of the fractured surfaces of the RTM samples was performed on a Zeiss DSM 940A microscope.

## 3. Results and Discussion

Regarding the glass transition temperature ( $T_g$ ) obtained from DSC analyses (Figure 1), the neat epoxy cast sample (LY), the reference sample, exhibits a  $T_g$  of 81 °C, whereas the LYc sample exhibited a  $T_g$  of 86 °C. This increase of 5 °C may have occurred due to  $\pi$ - $\pi$  stacking interactions between the aromatic structure of CNT and bisphenol-A epoxy monomers<sup>22</sup>. The LYNa sample did not show any change in  $T_g$  when compared to the reference sample, suggesting that the molecular mobility of the matrix is not being

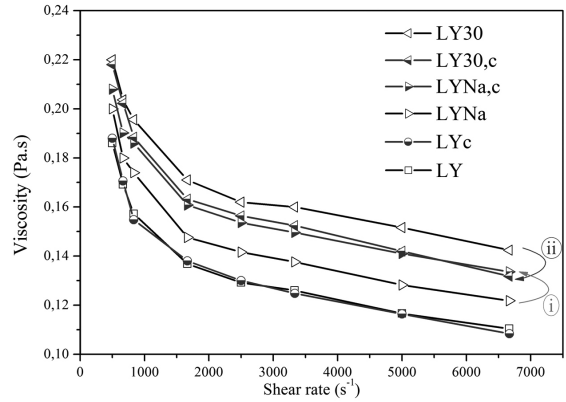
affected, even when adding 2 wt% of MMT-Na. In contrast, the MMT-30B dispersion increased the  $T_g$  in up to 10 °C, showing a  $T_g$  of 91 °C, which can be related to the higher compatibility of this organoclay with the epoxy matrix, restraining molecular dynamics in a more considerable way. The combined addition of MWCNT with any of these clays did not cause substantial changes in  $T_g$ , perhaps due to the lower fraction on MWCNT compared to the clay.

Figure 2 exhibits the viscosity as a function of the shear rate for different mixtures (previous to the addition of the

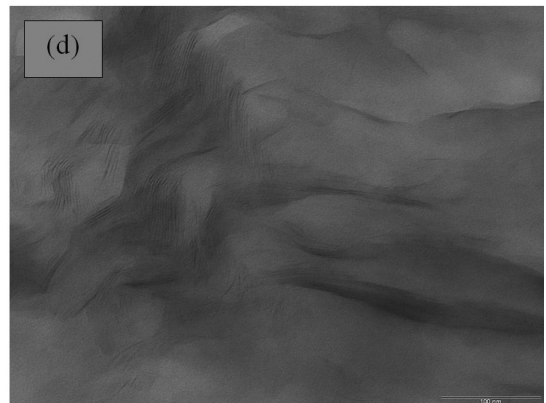
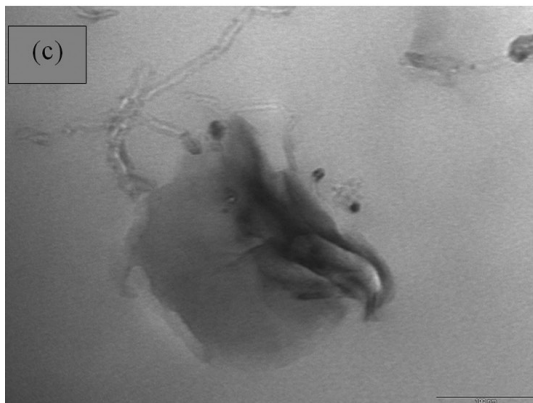
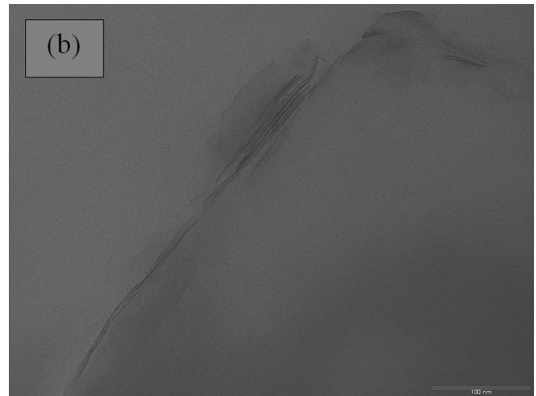
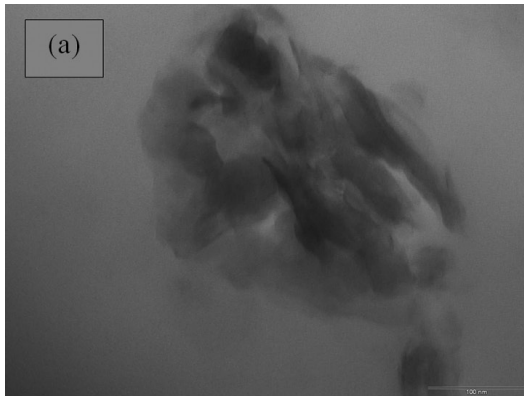


**Figure 1.** DSC results with the indication of the  $T_g$  found for each sample.

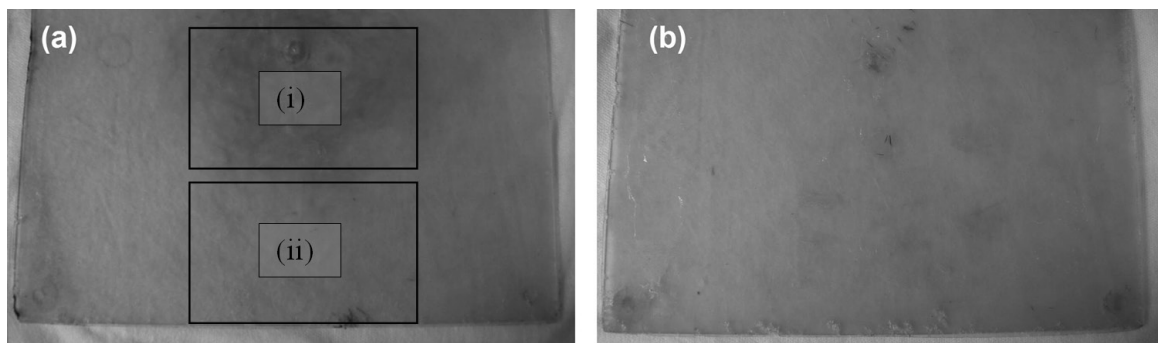
hardener). There is just a slight increase in viscosity after adding 0.1 wt% of MWCNT (sample LYc) probably due to the low weight fraction used. The dispersion of MMT-Na increased the viscosity of the medium, and MMT-30B promoted an even higher increase in viscosity for the same amount of clay (2 wt%). The organophilic nature of MMT-30B favored the intercalation of the platelets by the epoxy monomers, restraining the transfer of momentum through the viscous medium, corroborating the higher increase in  $T_g$  verified for the LY30 sample.



**Figure 2.** Viscometry data of the mixtures.



**Figure 3.** TEM of the cast samples: (a)LYNa; (b) LY30; (c) LYNa,c; (d) LY30,c.



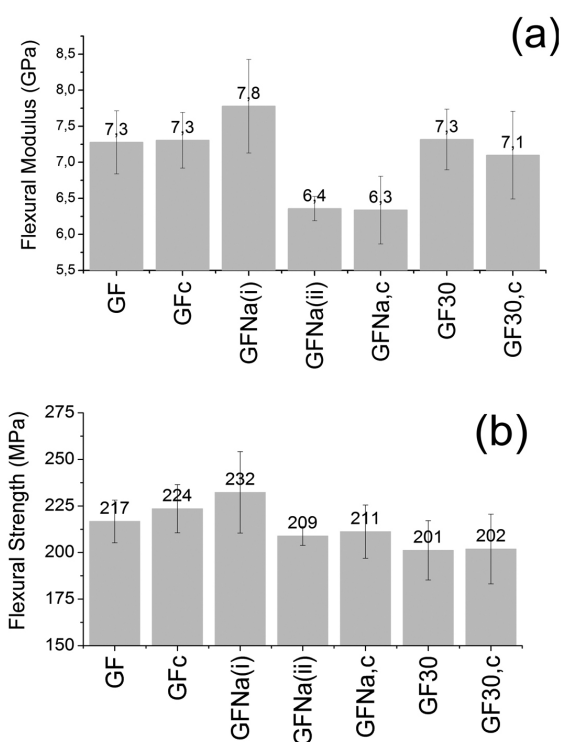
**Figure 4.** Samples molded by RTM. (a) GFNa(i) and GFNa(ii); (b) GF30.

The simultaneous dispersion of MWCNT with the clays yielded opposing effects on viscosity. The sample LYNa,c shows higher viscosity than LYNa sample (see indication 'i' in Figure 2). This effect suggests that MMT-Na and MWCNT dispersion is achieved<sup>23</sup>. The same was not verified between samples LY30 and LY30,c and the former showed increased viscosity after the addition of MWCNT, suggesting regrouping of MMT-30B or MWCNT in the epoxy monomers.

TEM images of the nanocomposite samples are shown in Figure 3. MMT-30B sample shows larger interplanar spacing (Figure 3b) than MMT-Na (Figure 3a), in agreement with the difference in viscosity between LY30 and LYNa samples (Figure 2). It was inferred that MWCNT is mainly located around MMT-Na tactoids (Figure 3c), but this effect was not obtained with the MMT-30B tactoids (Figure 3d), and not many CNT were observed around them. This observation also favors the correlation with the viscosity changes denoted by 'i' and 'ii' in Figure 2.

Hybrid micro/nanocomposites were molded by RTM with a maximum of 2 wt% clay fraction due to the increased viscosity of the mixtures with clay fractions above this limit and also because of the limited maximum pressure allowed by the RTM system used. In Figure 4, the RTM hybrid samples GFNa and GF30 are shown. Ordinary visual assessment suggests that the MMT-30B clay is more homogeneously dispersed through the epoxy/glass fiber composite (Figure 4b) than the MMT-Na (Figure 4a), possibly because of the greater interaction between the organoclay and the epoxide matrix than with the glass fibers surface. A more pronounced filtering effect through the glass-fiber porous media occurred for the MMT-Na, possibly related to the hydrophilic nature of this clay, which contributes to its poor compatibility with the epoxy matrix.

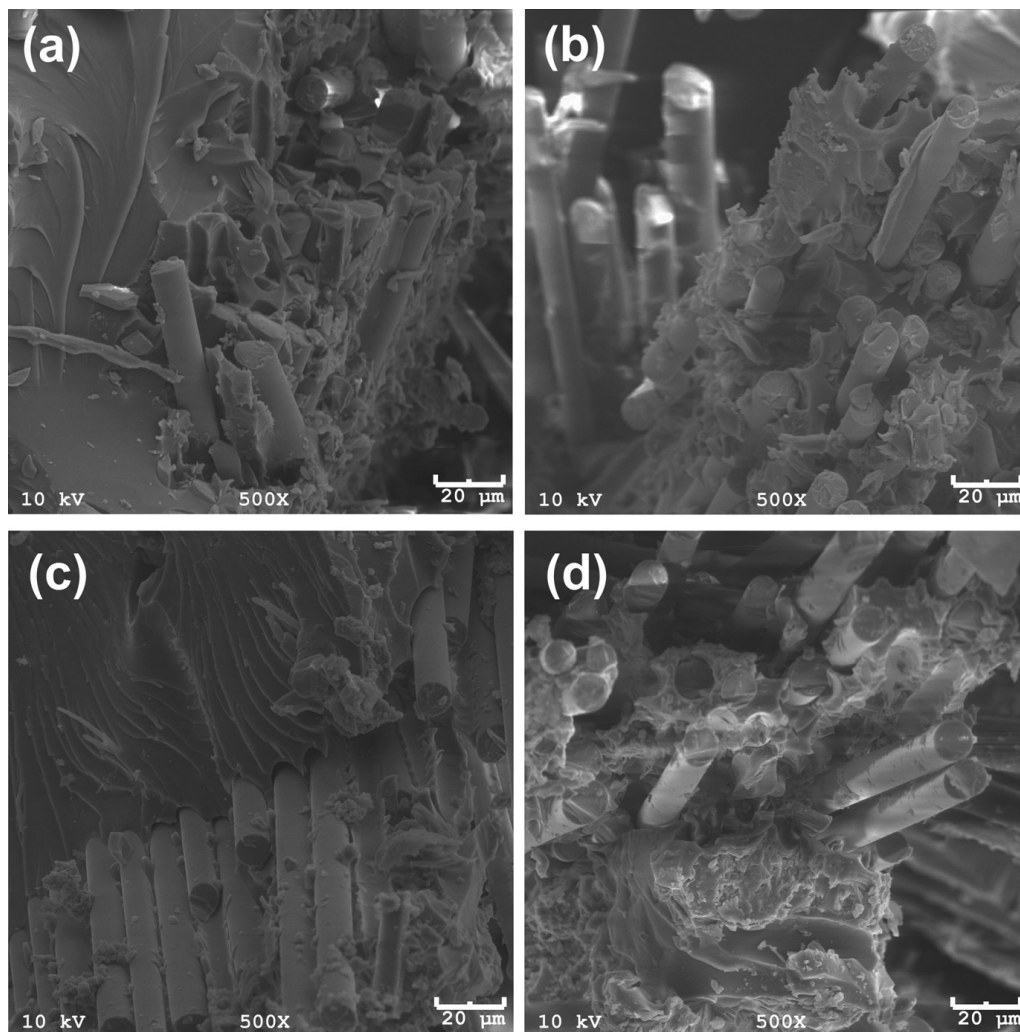
Because of the filtering effect noticed, samples were extracted from two different regions of the molded composite, as shown in Figure 4a. The GFNa(i) sample was taken close to the mold inlet, whereas the GFNa(ii) sample was taken from the outer edge of the plate, where clay concentration is lower. The results of the flexural tests of the hybrid micro/nanocomposites are shown in Figure 5. The low weight fraction of MWCNT practically did not influence the modulus and flexural strength of the hybrid GFc, because the high amount of glass fibers dominates these properties. The GFNa(i) sample showed a trend towards higher modulus



**Figure 5.** Flexural modulus (a) and flexural strength (b) of the hybrid micro/nanocomposites.

and strength, being attributed to the high concentration of clay in this sample. It may be inferred that the high content of MMT-Na in this region restrains deformation of the matrix in a more effective way, with higher stress transfer between matrix and clay. On the other hand, the GFNa(ii) sample showed a 12% decrease in modulus in relation to the reference sample (GF).

The GFNa,c sample was taken from the same region of the molded plate than the GFNa(i) and GF30 samples (Figure 4), and showed similar modulus than the GFNa(ii) sample, suggesting again the presence of the filtering effect, even though this could not be visually confirmed because the sample turned black when CNT was present. The GF30 sample showed similar modulus compared to the GF reference sample, which can be associated with the lower



**Figure 6.** SEM of the hybrid micro/nanocomposites: (a) GF; (b) GFc; (c) GFNa and (d) GF30.

weight fraction of clay compared to the glass fiber content. Indeed, considerable changes of modulus for hybrid micro/nanocomposites were only verified for clay content higher than 3 wt%<sup>12,13</sup>. Besides, the comparatively low CNT weight fraction in relation to the clay and glass fiber content in the GF30,c sample was also not able to significantly modify the evaluated properties.

SEM images of the flexural fracture surfaces of the hybrid micro/nanocomposite are shown in Figure 6. The fracture surface of the samples with CNT (GFc, GFNa,c and GF30,c) were similar to the analogous samples without CNT (GF, GFNa and GF30, respectively). SEM images suggest lower glass fiber wetting after clay dispersion in the epoxy matrix, indicating that the silanized glass fibers become less compatible with the clay-modified polymer matrix.

#### 4. Conclusions

Epoxy matrix nanocomposites with the combined dispersion of MWCNT and montmorillonite clays were produced by casting, without the aid of solvents. A more

intercalated structure was obtained for MMT-30B due to its organophilic nature and also because of the higher acidity of hydroxyethyl groups present in the adsorbed ammonium salts of the organoclay.

Based on TEM images, distinct interacting behaviors were observed between MWCNTs and the different clays. MWCNTs tend to agglomerate away from the organic clay (MMT-30B) particles due to intercalation/exfoliation, whereas in the nanocomposites with natural clay the MWCNTs tend to agglomerate around the clay particles, leading to an increase in the viscosity of the mixture.

In addition, hybrid micro/nanocomposites with glass fibers were produced by resin transfer molding. When MMT-30B was dispersed in the epoxy matrix used to infiltrate the reinforcement, a homogenous translucent hybrid material was obtained due to the improved compatibility of the organoclay with the polymer matrix. On the other hand, MMT-Na was filtered by the glass-fiber porous media during resin infusion, yielding a gradient of clay concentration towards the periphery of the mold. In the regions with higher content of MMT-Na (closer to the inlet), the material

exhibited slightly increased flexural modulus and strength. Besides, the addition of MWCNT did not change the overall properties of the hybrid micro/nanocomposites due to the low weight fraction used, even though this is already enough to produce a percolated structure.

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