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Influence of the addition of montmorillonite to the matrix of unidirectional glass fibre/epoxy composites on their mechanical and water absorption properties

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ABSTRACT

Epoxy nanocomposites were used as matrix of glass fibre-reinforced composites. The dispersion of the clay in the epoxy was studied by X-ray diffraction analyses given strong evidence that the clay formed an intercalated structure in the polymer. An increment in the mechanical properties after the addition of clay in the epoxy matrix was observed in the composites. The water absorption curves at 80 °C fitted a two-step diffusion model, where the first step was diffusion controlled and the second one was associated with the molecular motion and relaxation process of the polymer chains. The composites containing a nanocomposite matrix absorbed higher quantity of water at long times than the one with a pure epoxy matrix due to the diminution in the crosslinking density of the epoxy. A diminution in the mechanical properties after water submersion as well as a detrimental effect of the water on the matrix and interface of the composites was observed.

1. Introduction

Recently, the utility of inorganic particles such as layered silicates as additives to enhance the polymer performance has been established. Organically modified layered silicate nanocomposites have attracted much academic and industrial interest because of their significant enhancement, relative to an unmodified polymer, of a large number of physical properties including barrier, flammability resistance, thermal stability and solvent uptake. These improvements are generally attained at silicate content lower than 5 wt%. This fact makes the nanocomposites far lighter in weight than conventional composites and allows them to compete with other materials for specific applications [1,2]. The strong interfacial interactions between matrix and the well-dispersed silicate layers are the main reason for the improvement in the properties of the nanocomposites. Generally, the silicates are modified through ion exchange reactions with quaternary alkylammonium cations to facilitate the intercalation of polymers into the interlayer galleries and therefore favour the formation of an exfoliated nanocomposite. The presence of the organic modifiers lower the surface energy of the silicate, expand the interlayer spacing and in some cases they can react with the polymer matrix or initiate polymerization. Layered silicates such as fluorohectorite or montmorillonite have a remarkable ability to exchange ions.

A significant amount of research has been performed on nanocomposites based on different thermoset polymers [2] but especially on epoxy resins. In those studies, the epoxy polymerization reaction [3–5], thermal and mechanical properties [6–8] and the addition of different clay modifiers [5,9,10] were analysed. While significant progress has been made on the development of clay reinforced polymers, the use of nanocomposites as the matrix for fibre-reinforced composites has not been extensively studied. Epoxy resin nanocomposites were used as the matrix for glass [11–13] and carbon fibre composites [14–16]. Haque et al. [11] obtained an important increment on the mechanical properties of the composites reinforced with glass fibre mat using a very low silicate content. The laminates were obtained by resin infusion moulding. Kornmann et al. [12] obtained glass fibre/epoxy-layered silicate nanocomposites laminates by hand lay-up combined with vacuum bagging and hot pressing techniques. An improvement in the flexural modulus and strength with the addition of clay by 6% and 27%, respectively, was observed. Additionally, the presence of organosilicate causes a decrease of the glass transition temperature and this decrease seems to be responsible for the larger water uptake observed in the composites made with a nanocomposite matrix. Lin et al. [13] studied composites with the fibres placed in two directions using the vacuum-assisted resin transfer moulding process. Even though the mechanical properties of the composites deviated slightly with the direction of the fibres, the properties were improved with the clay content.

Among the studies made on carbon fibre-reinforced composites, Rice et al. [14] observed an improvement of 12% in the composite modulus compared with that of the pure resin. Siddiqui et al. [15] studied the fracture behaviour and mechanical properties of carbon reinforced composites using a nanoclay-filled epoxy matrix.

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They obtained an improvement in the flexural modulus with the addition of clay to the matrix as well as in the initiation and propagation values of mode I interlaminar fracture toughness. Miyagawa et al. [16] observed a diminution in the glass transition temperature with the addition of organoclay to a bio-based epoxy matrix. However, no change in the flexural modulus and strength was observed by adding clay to the composites reinforced with carbon fibres.

In general, polymers tend to absorb significant amounts of water when exposed to high humidity conditions. The absorbed moisture has many detrimental effects on the composite performance. Therefore, investigation of water aging of polymer/fibre composites is useful because these materials are usually designed for use in construction or transportation industry and they will be exposed to wet environments. Understanding the moisture diffusion mechanism in composites is essential to improve the material durability.

Pultrusion is among the most effective processes to fabricate composites that are being used nowadays in several and very diverse industrial applications such as construction, automotive, aerospace [17]. It is a continuous process where the matrix is cured "in situ" while the material is pulled through a mould. It is possible to obtain profiles of many different shapes by means of pultrusion.

The aim of this work is to study the influence of the addition of montmorillonite to the matrix of a unidirectional pultruded fibre-reinforced composite on their mechanical and water absorption properties. A non-modified and two modified montmorillonites were used to compare their behaviour.

2. Experimental

2.1. Materials

A commercial formulation based on epoxy (DER 383) and anhydride (Lindride 62) from Dow Chemicals was used as matrix of the composites. Two organically modified montmorillonites (MMT) Cloisite® 30B and Cloisite® 10A were used. Clays were supplied by Southern Clay Products (TX, USA). The characteristics of each montmorillonite are shown in Table 1.

E-type glass fibres (E-8204) with γ-Aminopropiltrietoxysilane (γ-APS) sizing were provided by Isotex® Argentina. Fibre volume fraction was 30%, measured following API 15LR specifications. The low fibre fraction was chosen in order to better evaluate the matrix behaviour. The fibres were washed with a ketone:methylethylketone solution (50:50 vol) for 2 h at room temperature and then dried in an oven at 80 °C up to constant weight prior to use. This treatment on the fibres was made in order to eliminate the excess of lubricant that the fibre's surface contains [18]. An improvement in the interfacial properties with an epoxy/phenolic matrix when the fibres were washed was obtained in a previous work [19].

The epoxy resin and the nanocomposites made with the montmorillonites previously mentioned were used as the matrix for the composites. The nanocomposites were prepared by mixing the epoxy resin with the corresponding percentage of MMT for 2 h at room temperature by means of a mechanical stirrer. Three nanocomposites were obtained by adding 3% and 5% (wt/wt) of C10A and 3% (wt/wt) of C30B to the epoxy resin, respectively.

Pultruded fibre-reinforced composites were obtained. Pultrusion preparation method consisted of pulling the fibres impregnated with the resin through a mould at room temperature. Then, the mould was introduced in an oven and the following curing cycle was applied: 120 min at 80 °C, 90 min at 120 °C and 120 min at 140 °C.

2.2. Methods

X-ray diffraction analyses (XRD) of the composites were performed in a Philips PW 1710 diffractometer (45 kV and 30 mA) at 2°/min, radiation of KCu_{α} (λ = 0.154 nm).

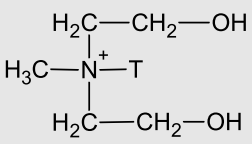
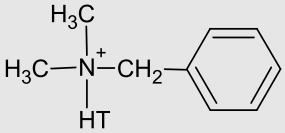
Water absorption measurements were made by immersing the samples in a distilled water bath at 80 °C, and the weight changes with time were recorded. Samples were carefully dried with an absorbent paper prior to be weighed. The dimensions of the samples were 112 mm × 10 mm × 3.5 mm. They were cut from the pultruded plaques.

Scanning electronic microscopy (SEM) was performed on the polished and fractured surfaces of the specimens. SEM micrographs of the samples before water absorption were taken from the fractured surface of the composites. However, after water absorption, the cross section of the samples was polished prior to analysis by SEM in order to clearly observe the interface between the fibre and the matrix as well as the presence of cracks in the matrix. Specimen surfaces were coated with a 30 nm gold layer and observed in a scanning electron microscope JEOL JSM-6460LV.

Flexural tests were performed using an Instron 4467 machine at a crosshead speed of 1.7 mm/min in three-point bending configuration (ASTM D 790). Impact tests (ASTM D256-93) were performed by means of a falling weight Fractovis Ceast. The speed of the test was set at 3.5 m/s. An average value of at least five specimens was determined for the mechanical tests. Mechanical tests were performed before and after submerging the specimens on water.

Interlaminar Shear Strength of the composites was calculated by Short-Beam method following ASTM D2344-84 by means of an Instron 4467 machine at a crosshead speed of 1.3 mm/min.

Table 1
Characteristics of the montmorillonites used

Clay	Organic modifier	Modifier concentration	Interlayer distance (d_{001}) (nm)
Cloisite® 30B (C30B)		125 meq/100 g clay	1.85
Cloisite® 10A (C10A)		90 meq/100 g clay	1.92

Where T is Tallow (~65% C18; ~30% C16; ~5% C14); anion: chloride and where HT is Hydrogenated Tallow (~65% C18; ~30% C16; ~5% C14); anion: chloride.

An average value of six specimens was used in the calculus of the shear strength value of each composite.

3. Results and discussion

X-ray diffraction analyses of the composites showed that the clay formed an intercalated structure in the epoxy matrix, without reaching complete exfoliation. The basal diffraction peak corresponding to the clay C30B was observed at $2\theta = 4.88$, and that peak appeared as a broad one in the region $2\theta = 4.47–6.8$ with a maximum at 5.7 for the composite with the matrix containing C30B (Fig. 1). The displacement of this peak could be due to an intra-gallery contraction during curing. This behaviour was previously reported in epoxy [7,10] and resol resins nanocomposites systems [20] where the *d*-spacing contraction was explained as a consequence of the different rates of intra- and extra-gallery polymerization. On other hand, XRD pattern of the composite containing epoxy+C10A as matrix showed an intercalated structure since the XRD trace gives a peak at $2\theta = 4.11$, while the pristine C10A exhibited its characteristic peak at $2\theta = 4.58$. However, another broad peak was observed in the region $2\theta = 4.47–6.85$ (Fig. 1) indicating the inhomogeneous clay distribution in the polymer. Surely, the mode of mixing was insufficient to allow the effective clay layer separation.

Flexural properties determined for the composites are shown in Figs. 2 and 3. An increment in the flexural modulus up to 20% for the composites containing montmorillonite C10A in the matrix (Fig. 2) was observed. The addition of MMT C30B did not cause an increment in the modulus of the epoxy. It could be due to the collapse of the clay. However, in general an increment in the modulus of thermoplastic polymers and rubbers by the addition of clay was observed, but the increment observed was not as high as in thermoset polymers [21]. The increment of the modulus is due to the addition of high modulus particles approximately equal to 170 GPa and due to the strong interfacial interaction between the matrix and clay [2]. On other hand, the flexural strength showed an increment up to 29% for the composites made with C10A (Fig. 3). This increase in the flexural strength may be due to the presence of the silicate layers at the surface of the glass fibres improving the interfacial adhesion between the matrix and the fibres. Another possible cause could be the increment in the compressive strength of the epoxy by the clay so improving the bending strength of the fibre-reinforced composite [5].

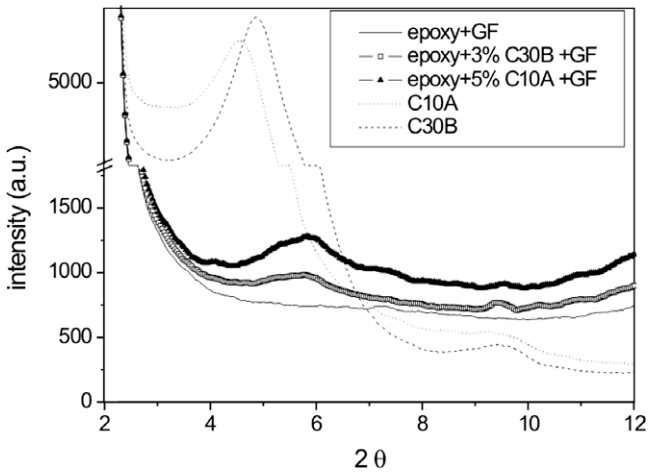


Fig. 1. XRD spectra of the two modified mantmorillonites and the glass fibre composites with epoxy and nanocomposite matrix.

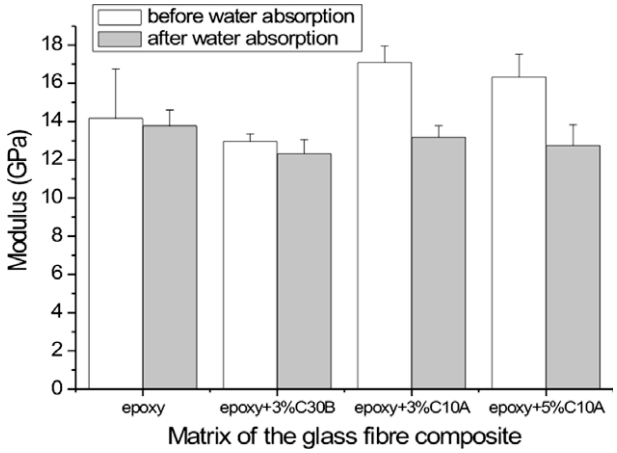


Fig. 2. Flexural modulus of glass fibre composites containing different matrix.

To evaluate the interlaminar shear strength of the composites Short-Beam test were performed on the specimens. A slightly increment in the interlaminar shear strength for the composites containing Cloisite 10A in the epoxy matrix compared with the ones containing the montmorillonite Cloisite 30B or without clay in the epoxy matrix (Table 2) was observed. These results are in accordance with the ones obtained from the flexural test where the high modulus and flexural strength were observed for the nanocomposites containing C10A. Additionally, it was observed in the micrograph obtained by SEM (Fig. 4) that the fibres in the composites made with matrix of pure epoxy and with the addition of C30B (Fig. 4a and b) showed less quantity of matrix adhere to their surface than the composites where C10A was added to the matrix (Fig. 4c and d). This could be due to the higher affinity between the C10A silicate layers and the fibres surface. In addition, in the pure epoxy composite a more brittle surface was observed in the micrograph whereas the surface of the nanocomposites ap-

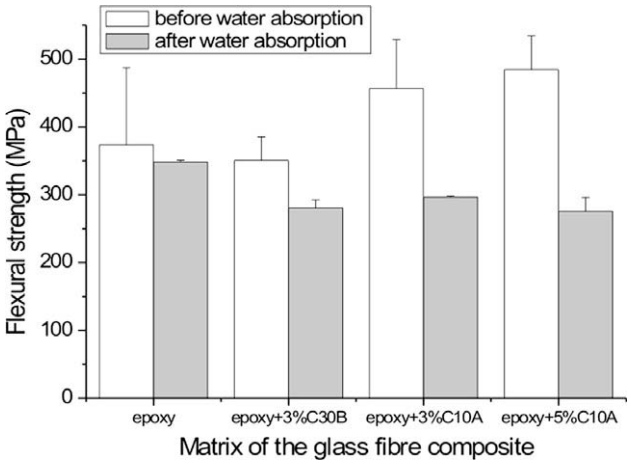


Fig. 3. Flexural strength of glass fibre composites containing different matrix.

Table 2
Shear strength measured by Short-Beam test and glass transition temperature measured by DSC, of the reinforced composites

Matrix of the glass fibre composites	Shear strength (MPa)	Tg (K)
Epoxy	51.6 ± 3.0	409.9
Epoxy+3% C30B	52.5 ± 2.4	398.7
Epoxy+3% C10A	55.1 ± 3.4	399.8
Epoxy+5% C10A	55.5 ± 1.4	399.4

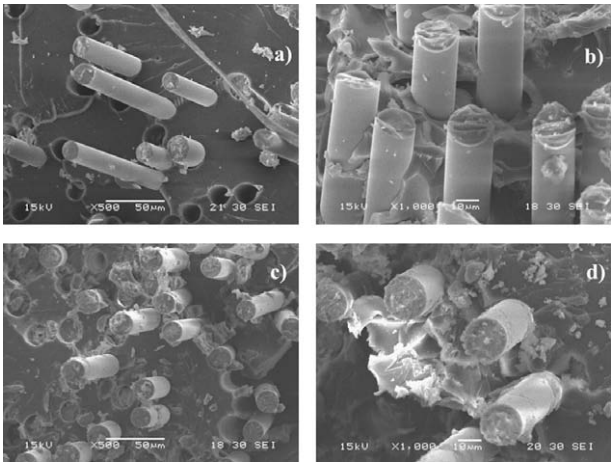


Fig. 4. SEM micrograph of the fractured surface of epoxy composites before water absorption, containing matrix of: (a) epoxy, (b) epoxy+3% C30B, (c) epoxy+3% C10A, (d) epoxy+5% C10A.

peared much rougher. This behaviour is in accordance with their increment in the strength measured by the impact test (Fig. 5). The composites made with the addition of clay showed a similar value of impact strength among them. However, this value of impact strength is higher than that of the composite without clay, reaching an increment of 23% for the composite made with the addition of 5% of C10A. In these composites, there are two factors to be taken into account that influence their strength behaviour: the matrix and the interface. The matrix properties are influenced by the MMT and it was reported that the addition of clay to a polymer enhanced the impact strength because the nanoparticle formed a tortuous fracture path [13] as well as the growth of micro-cracks are stopped by the MMT platelets [22,23]. On other hand, the stronger the interface formed between the matrix and the fibres in a polymer composite, the lower the impact strength. The properties of the composites used in this work should depend on the matrix behaviour because they contain low fibre percentage. Then, an increment in the impact strength was observed in the nanocomposite matrix composites. Regardless the type of clay the same behaviour was observed.

A diminution in the glass transition temperature (Tg) of the epoxy with the addition of MMT (Table 2) was observed. The value obtained was similar for the composites studied independent of the type and quantity of clay added to the epoxy. It was observed that the ammonium ions of the clays catalyse both the epoxy homopolymerization and the epoxy-amine reactions modifying the crosslinking reactions of the epoxy [10,21,24,25]. Park et al. [24] reported that the intra- and extra-gallery polymerization rates of an epoxy-amine system are different due to the presence of the organic modifiers in the clay. The rate of intra-gallery polymerization was faster due to the acidity of the modifiers inside the galleries. Apart from catalysing epoxy curing reactions quaternary ammonium ions were capable of plasticizing crosslinked epoxy chains. This effect was observed in the reduction of the Tg and in the values of storage modulus [25]. Chen et al. [21] studied the interlayer expansion mechanism and thermal-mechanical properties of epoxy-anhydride nanocomposites. They observed a drop in the Tg and in the rubbery modulus of the composites as the interlayer spacing increased due to the formation of an interface where the epoxy was plasticized by the surfactant chains.

The diminution observed in the Tg value could be related with the higher absorption of water observed in the composites made with a nanocomposite matrix compared with the ones containing pure epoxy matrix. The water absorption of the glass fibre composites at 80 °C was measured and the water uptake was calculated from:

$$M\% = \frac{M_t - M_0}{M_0} 100 \quad (1)$$

where M_0 is the dry initial weight, and M_t is the weight of the specimen at each time. The weight changes of the composites are shown in Fig. 6.

In general, the water uptake is influenced by: (i) the hydrophilic character of the matrix and the fibres, (ii) the adhesion between the fibres and the matrix, and (iii) the presence of voids in the material. It was observed that the maximum water uptake was higher in the fibre reinforced nanocomposites than in the ones made with pure epoxy matrix. The diminution in the crosslinking density seems to be one of the factors controlling the absorption of water. The presence of clay affects the polymer network and the higher free volume allows the water to diffuse throughout the material.

The water absorption curves shown in Fig. 6, revealed a two-step diffusion behaviour. The absorption at the first times is associated to a Fickian diffusion model and after that, a continuous and gradual increase in weight gain was observed. Bao et al. observed the same behaviour during the water absorption of a bismaleimide resin [26] as well as in its carbon reinforced composites [27]. They

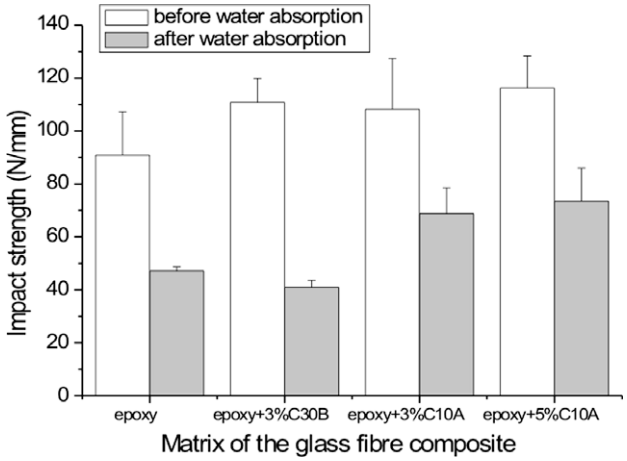


Fig. 5. Impact strength of the epoxy-glass fibre composite and their nanocomposites.

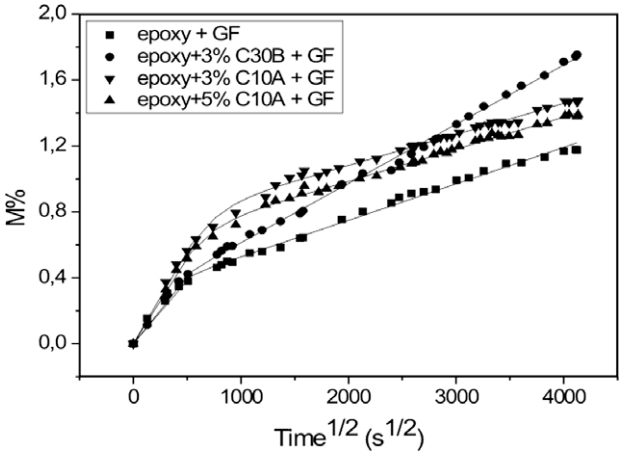


Fig. 6. Weight gain curves during water absorption at 80 °C, of the different matrix composites reinforced with glass fibre.

proposed a two-stage diffusion model that fits both the water absorption curves of the matrix and the composites, and is represented by Eq. (2):

$$M_t = M_{\infty 0}(1 + k\sqrt{t})\left\{1 - \exp\left[-7.3\left(\frac{D_x t}{h^2}\right)^{0.75}\right]\right\} \quad (2)$$

where D_x is the diffusion coefficient, h is the thickness of the specimen, t is the diffusion time and k is the parameter related to the rate of relaxation. The term $(1 + k\sqrt{t})$ characterizes the mentioned second-stage.

It was assumed that the first stage is diffusion controlled and the second one was associated with the molecular motion and relaxation process of the polymer chains. In that diffusion model, the structural relaxation was assumed to be much slower than the diffusion process. In the case of composite materials, the presence of the fibre constrains the segmental motions and affects the second-stage behaviour. The experimental measurements of weight gain as a function of time$^{1/2}$ were fitted using Eq. (2). The lines in Fig. 6 represent the composites fit curves and a good agreement between the experimental and fitted results was observed. The composites with C10A showed the lowest slope in the second-stage, indicating the lowest k parameter and as a consequence, a slower rate of polymer chains relaxation. This is surely due to the rigid fibre-matrix interface that was observed to be stronger for the composites containing C10A compared to the ones with pure epoxy and epoxy+C30B matrices. The composite with C30B showed the highest water absorption rate after the Fickian behaviour. This could be due to the weaker fibre-matrix interface compared to the other nanocomposites.

As the first-stage transport kinetics only depends on the local motions, the presence of the interface does not affect the diffusion of water at short times. Fick's law is applicable for homogeneous materials, and when no chemical interaction occurs between the materials and water. The composites studied are not homogenous due to the presence of some voids as well as some chemical interaction among the water, the matrix and the clay could occur. However, an effective diffusion coefficient (D_x) was considered, in order to compare the differences between the samples. It was observed in Table 3 that the D_x of the composites with C10A are lower than those of the composites with C30B and pure epoxy. The higher polarity of the C30B compared to the C10A could be the reason for the enhancement in the rate of diffusion of water in the composites containing C30B. In a previous work [28] we found that the maximum water uptake of a resol resin with different percentage of epoxy-amine depends on the void content of the sample, whereas the diffusion coefficient appears to be related to the polarity of the material. The void content of the glass fibre-reinforced composites studied in this work was measured from the SEM micrographs using the program Image-Pro plus. The ratio of voids area to total area was showed in Fig. 7. It was observed that the composite without clay in their matrix showed the least void content. On other hand, the composite containing C30B in the matrix contained higher quantity of voids than the ones containing C10A. Thus, the void content showed the same behaviour as the maximum water uptake of the composites.

Mechanical properties of the composites after submersion in water at 80 °C were measured. Water absorption affects the composite properties, especially at higher temperatures. The synergistic action of moisture penetration and high temperature strongly influences the matrix structure and the sorption mechanisms. The effects of water absorption have been associated with micromechanical damage in the resin and at the fibre-matrix interface as well as with internal stresses, relaxation of mechanical strength and plasticisation. The damage in the fibre-matrix interface was observed in the SEM micrograph of the composites after immersion in water (Fig. 8) if compared to the micrograph taken before immerse the composites in water (Fig. 9). In addition, cracks in the matrix were clearly observed in Fig. 8b. Water enters the composite by diffusion through the resin and by capillary action along the fibre-matrix interface. A diminution in the flexural modulus as well as in the flexural strength after immersion in water (Figs. 2 and 3) was observed. The main reason for the diminution in the flexural strength is because water can cause matrix swelling and plasticisation, interface debonding and hydrolysis of the material. In addition, the impact resistance was reduced after the water influence (Fig. 5). An increment in the impact energy due to the detriment of the interface after water immersion should be expected. However, the diminution on the impact energy was attributed to the diminution on the matrix modulus.

Table 3
Diffusion coefficient of the composites

Matrix of the glass fibre composites	D_x (mm^2/s)
Epoxy	$2 \times 10^{-5} \pm 2.91 \times 10^{-6}$
Epoxy+3% C30B	$2 \times 10^{-5} \pm 3.36 \times 10^{-6}$
Epoxy+3% C10A	$6.22 \times 10^{-6} \pm 3.77 \times 10^{-7}$
Epoxy+5% C10A	$5.23 \times 10^{-6} \pm 3.09 \times 10^{-7}$

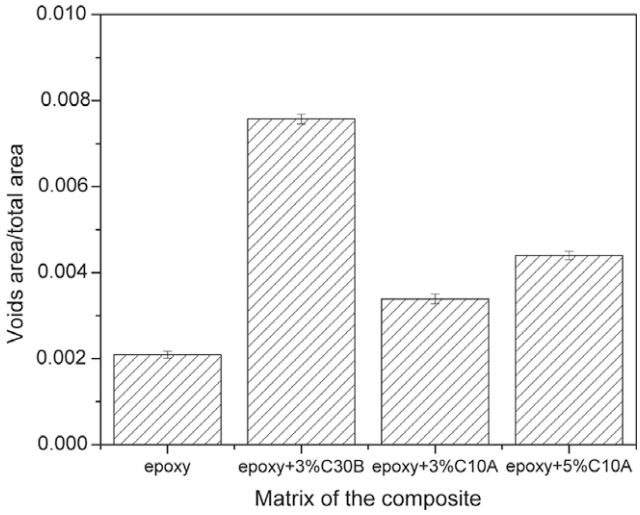


Fig. 7. Ratio of voids area to total area of the epoxy/glass fibre composite and their nanocomposites.

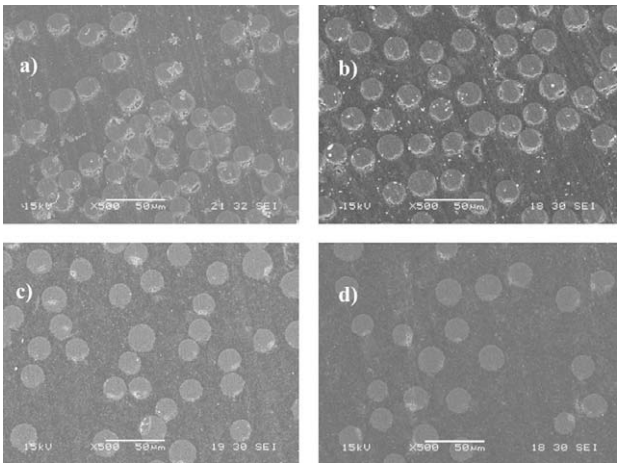


Fig. 8. SEM micrograph of the polished cross section of epoxy composites after water absorption, containing matrix of: (a) epoxy, (b) epoxy+3% C30B, (c) epoxy+3% C10A, (d) epoxy+5% C10A.

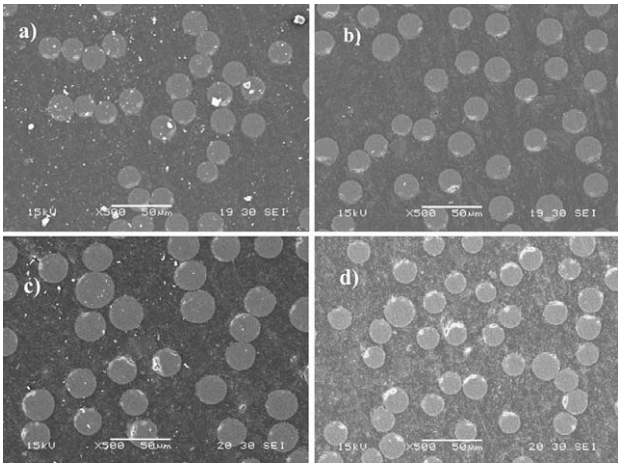


Fig. 9. SEM micrograph of the polished cross section of epoxy composites before water absorption, containing matrix of: (a) epoxy, (b) epoxy+3% C30B, (c) epoxy+3% C10A, (d) epoxy+5% C10A.

4. Conclusions

It was observed by XRD analyses that the clays formed an intercalated structure in the epoxy matrix, without reaching complete exfoliation. Mechanical properties of the composites were enhanced by the addition of clay to the epoxy matrix. The clay C10A, containing the less hydrophilic modifier, showed a higher compatibility with the matrix and the glass fibres. So, the composites with C10A showed the highest increment in their mechanical properties compared with the neat epoxy matrix composites. The water absorption curves measured at 80 °C fitted to a two-step diffusion model. The first step was faster and diffusion controlled, whereas the second one was associated with the molecular motion and relaxation process of the polymer chains. The addition of clay to the epoxy matrix caused higher maximum water absorption and this was related with the diminution in the crosslinking density of the polymeric matrix. On other hand, it was observed that water and temperature affected both the matrix and the fibre-matrix interface causing micromechanical damage. As consequence, a diminution in the mechanical properties after water immersion was observed.

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