Effect of the addition of nanoclays on the water absorption and mechanical properties of glass fiber/up resin composites

N Rull, RP Ollier, G Francucci, ES Rodriguez and VA Alvarez

Abstract

Mechanical performance of composite materials must remain satisfactory during their life in service. However, composite structures such as wind blades are usually exposed to humid and severe environments, and the absorbed water can degrade the fiber–matrix interface decreasing the composite overall performance. Dual scale (nano-micro) composites can be obtained by adding nanoparticles to the polyester resin and reinforcing that nanomaterial with a glass fiber mat. These materials have good potential in the production of composite parts such as wind blades because nanoparticles dispersed in the polymer matrix could lower the water absorption of the composites and improve their performance in humid environments. However, nanosized reinforcing particles have high internal surface and therefore they tend to agglomerate and are difficult to disperse homogeneously in the polymeric matrix. Moreover, the final properties of the nanocomposites are strongly influenced by clay particles' morphology and dispersion. In this work, the effect of the addition of pristine and organomodified nanoclays on the water absorption and mechanical properties of glass fiber/ unsaturated polyester resin composites was studied. Results showed that the chemical treatments were effective in improving clay dispersion, reducing water absorption, and increasing the composites' performance in humid environments. In addition, this work presents a procedure to use water absorption tests as means of accelerated humidity absorption tests.

Introduction

Nowadays, the production of wind turbines is growing fast, because they produce clean energy from a free and renewable resource, reducing fossil fuel consumption and contaminant gasses emission, which in turn contributes to reduce the global warming. Wind blades are manufactured of composite materials, usually using glass fibers as reinforcement and a thermosetting polymeric matrix. The low weight, high stiffness, high strength and resistance to corrosion and fatigue of composites allow increasing the size of the blades and therefore, the power generated by the turbines. In addition, these materials can be processed to produce huge finished parts like wind blades by simple and inexpensive manufacturing methods such as vacuum infusion.

Wind mills are designed for a service life of 20 years. During that period they are exposed in some cases to high humidity conditions (e.g. in offshore applications). It is known that humidity absorption can degrade composite materials and this can reduce the expected lifetime of wind mills.[1] It has been reported that water

Composite Materials Group (CoMP), Research Institute of Material Science and Technology, INTEMA-CONICET, Engineering Faculty, National University of Mar del Plat, Mar del Plata, Argentina

Corresponding author:
G Francucci, Composite Materials Group (CoMP), Research Institute of Material Science and Technology, INTEMA-CONICET, Engineering Faculty, National University of Mar del Plata, Solís 7575, B7608FDQ Mar del Plata, Argentina.
Email: gfrancucci@fi.mdp.edu.ar

absorption reduces the mechanical properties of turbine blades, especially fatigue, which is the most common failure mode in these components.[2–4] Water sorption mechanisms in fiber reinforced composites are diffusion of water molecules inside the micro gaps between polymer chains, capillary transport into the gaps and flaws which interfaces between fiber and matrix, and transport of microcracks in the matrix.[5] Water absorption also depends on the void content in the resin, the relaxation of the resin in the presence of moisture and elevated temperature, and the binding of water molecules to the molecular structure of the resin.

Layered silicates are widely used as nanoreinforcements of polymeric materials to improve the mechanical properties of composite materials and also to increase its barrier properties to water/humidity. Because of the nanoscale of these reinforcements, these improvements can be achieved using very small amounts of reinforcing particles. Their crystalline network consists of bi-dimensional layers where a central octahedral layer of either alumina or magnesia is joined to two external tetrahedrons of silica in such a way that the oxygen ions of the octahedral layer also belong to the tetrahedral layers.[6,7]

It is understood that the dimension of the reinforcement should be at the molecular or atomic scale in order to effectively reinforce the matrix, so, if clay particles are used, the dispersion of the platelets is crucial to obtain the optimal properties. In the exfoliated state, the silicate layers are completely and uniformly dispersed in a continuous polymeric matrix.[8] However, the tendency of the particles to agglomerate is difficult to overcome. Therefore, the interlayer structure of intercalated clays is the crucial factor affecting the exfoliation energy necessary for the splitting of the silicate structure to the individual silicate layers.[9] Moreover, most of the polymers are hydrophobic, so it is necessary to make a previous treatment to the clay or to the polymer so as to make them more compatible. The most popular method consists on converting these hydrophilic silicates to organophilic ones via cation exchange reactions, in which the interlaminar Na^+ cations are replaced by other positively charged surfactants such as alkyl ammonium or phosphonium cations with long alkyl chains.[10,11] Depending on the functionality, packing density, and length of these modifiers, the organically modified clay may optimize compatibility with a given polymer and intercalated or exfoliated clay minerals may be obtained.[12] In this way, the optimal structure configuration can be achieved as the polymer chains are introduced inside the galleries of the silicates under certain processing conditions.[7,13]

Bentonite is a type of smectite clay that presents some advantages over other layered silicates because of its natural abundance, low cost, excellent swelling behavior, and high mechanical properties.[14,15] This type of clay is characterized by a moderate cation exchange capacity (CEC).[16,17]

Kim et al.[18] have found that the humidity barrier properties of epoxy resins were enhanced by the addition of clays. Many authors have found improvements in mechanical properties of composite materials caused by the addition of nanoparticles. Jen et al.[19] reported an improvement on the ultimate strength of 12.48% and on the elastic modulus of 19.93% in quasi-isotropic AS-4/PEEK APC-2 nanocomposite laminates, by the addition of SO_2 nanoparticles (1% by total weight). Haque et al.[20] have manufactured S2-glass/epoxy-clay nanocomposites by the vacuum assisted resin infusion method and they reported an improvement of 44, 24, and 23% in interlaminar shear strength, flexural strength, and fracture toughness, respectively, in comparison to conventional S2-glass/epoxy composites. In addition, they found the thermal decomposition temperature of the nanocomposites to be approximately 26°C higher than that of conventional composites. They attributed these improved properties of the nanocomposites to increased interfacial surface areas, improved bond characteristics, and intercalated/exfoliated morphology of the epoxy-clay nanocomposites. Rice et al.[21] found a 12% improvement in modulus by adding a 2 wt% of organosilicate to aerospace composite materials, but they observed no improvement in other mechanical properties. The use of glass fiber as the reinforcement, however, has yielded improved results compared to carbon,[22] which has been attributed by Brunner et al.[23] to the affinity between the silicate organoclay and the silicate glass fibers that enhances the fiber matrix adhesion.

In this work, composite materials were manufactured with a commercial unsaturated polyester (UP) resin reinforced with a glass fiber mat. In addition, 5% by weight of unmodified and modified bentonite was added to the polyester matrix and the effect of these nanoreinforcements on the mechanical properties and water absorption behavior of the composites was analyzed. In addition, the possibility of using water absorption tests as means of accelerated humidity absorption tests was analyzed. The effect of the unmodified and modified clays on the polyester matrix was previously studied by Ollier et al.[24] in a previous work published by our research group. It was demonstrated that whereas the original bentonite is highly hydrophilic, chemical modifications with alkylammonium and alkylphosphonium salts drove to hydrophobic (or organophilic) clays which make them more compatible with the polymeric matrix. The interlaminar spacing clearly increased after cation exchange reaction. This increase contributes to the feasibility of intercalation of polymer chains between clay platelets.

It was also shown by transmission electron microscopy (TEM) images that due to the low compatibility of the original bentonite with the polyester resin, the separation of the layers was poor and the clay formed agglomerates along UP matrix. On the other hand, the increase in the interlaminar spacing and the hydrophobic nature of the treated clays improved the compatibility with the matrix, resulting in a much higher dispersion degree in the polymer.

Experimental

Materials

Unsaturated polyester resin (Dolplast®) was used as the polymeric matrix. Its density was $1.07 \pm 0.02 \, \text{g/cm}^3$ and the styrene content was 32–38%. The total reaction heat was 190 J/g, determined from a test in a dynamic scanning calorimetry (DSC-50 Shimadzu). The reinforcement used was a chopped strand mat of glass fibers (M123, from Saint Gobain) with a surface density of $484 \pm 34 \, \text{g/m}^2$. Surface density was measured by weighting 10 square samples (10 cm by 10 cm) which were cut from the glass fiber mat. The reported value corresponds to the average of the 10 weight/area results. The bentonite was supplied by Minarmco S.A. (Neuquén, Argentine). Two different organic modifiers were used: tributyl hexadecyl phosphonium bromide (TBHP) and octadecyl ammonium chloride (ODA).

Preparation of organoclays

Two organoclays were prepared by cation exchange reaction by using aqueous solutions of TBHP and ODA. The quantity of modifier was three times the CEC of the pristine bentonite (which was 28.76 meq/ 100 g clay). A more detailed explanation of these clay modifications can be found in a previous work.[25]

Samples preparation

Plaques of 15 cm $\times$ 15 cm $\times$ 0.3 cm (length $\times$ width $\times$ thickness) of UP matrix were prepared by casting using 0.4% of Co, 0.1% dimethylacetamide (DMA), and 1.2% of methyl ethyl ketone peroxide which was added to the formulation after the Co and DMA were thoroughly mixed with the resin. The mold consisted of two glass layers separated by a 3-mm rubber ring. The curing was carried out in an oven at 70°C for 90 min and a postcuring at 120°C for another 90 min. In addition, plaques of UP resin with 5% by weight of modified and unmodified bentonite were obtained using the same resin formulation and curing cycle. The clay was

previously dried in a vacuum oven until constant weight was achieved. Then, an ultrasonic bath at 25°C was used to disperse the clays in the polymer resin until a homogeneous dispersion was accomplished. Subsequently, the catalyzer was added and the plaques were molded.

Resin viscosity was 408 cP (at 25°C) measured by means of a Brookfield DV–II+ cone and plate viscometer (precision ± 2.5 cP). The added bentonite increased the resin viscosity to about 440 cP, but it remained suitable for composite processing by liquid composite molding techniques.

Composites with and without clay were prepared using six mats of glass fibers by vacuum bagging using the same matrix/catalyst/accelerator ratio as for the matrix. In this technique, hand lay-up process is performed to impregnate layers of glass fiber mat. Then, the laminate is covered by a porous film, a bleeder cloth, and everything is sealed with a vacuum bag. Steel spacers and a heavy clear acrylic top face were used to ensure constant thickness throughout the plate. Vacuum is applied causing the bag to compact the laminate and the resin to be drained through the porous film. The excess of resin is finally absorbed by the bleeder. This simple method allows obtaining parts with low excess resin and air bubbles. Panels of 30 cm $\times$ 30 cm (length $\times$ width) were obtained and left to cure under vacuum for 24 h at room temperature ($\sim$25°C). The final thickness of the cured plates was around 0.3 cm, established by the thickness of the spacers minus the thickness of the stack of peel ply, porous film, and bleeder cloth. Postcuring was carried out in an oven at 120°C for 90 min. The fiber and clay content obtained for each composite plaque was measured by incineration of the plaques using a two-stage thermal cycle: 250°C for 2 h followed by 565°C for 4 h. Fiber content was 62.85 wt% in the composite without clay, 64.7 wt% in the composite containing bentonite, and 64.65 and 64.32 wt% in the composite containing TBHP and ODA modified bentonite, respectively. Final clay content was found to be around 4.3 wt% in all composites. Void content was determined from density measurements and found to be 3 ± 0.5% in all the composites. Complete curing of both, matrix and composites, was confirmed by dynamic scanning calorimetry (DSC-50 Shimadzu), running from room temperature to 250°C at 10°C/min in nitrogen atmosphere.

The composites without clay will be referred as Composite A (CA), the composite containing unmodified bentonite will be referred as Composite B (CB), and the materials containing phosphonium and ammonium modified bentonite as Composite C (CC) and Composite D (CD), respectively. In all cases, the matrix was UP, the fibers were mat glass, and the clay content was 4.3 wt%.

Characterization of composites

Fiber and clay content were determined from thermogravimetric analysis (TGA) and calcinations. TGA tests were carried out by using a TA Auto-MTGA Q500 Hi-Res from room temperature to 1000°C under air flow with a heating rate of 10°C/min. In the case of UP/glass fiber composites, composition could be calculated directly from calcinations. On the other hand, for UP-bentonite/glass fibers composites, the residual mass obtained after the calcinations was attributed to the glass fibers plus the inorganic part of the clay. Therefore, TGA measurements were used to determine the organic part of the clay and the residual mass of each component at 1000°C allowing calculating the UP, clay, and glass fibers contents.

The fiber–matrix interface was analyzed by scanning electron microscopy (SEM, model JEOL JSM 6460 LV) to samples that were previously coated with a thin layer of gold.

Water and humidity absorption tests were performed on composites samples of $15\,cm \times 15\,cm \times 3\,mm$ (ASTMD 570 standard). Test samples were first dried at 60°C in a vacuum oven until constant weight was achieved. Then they were situated in different aqueous environments. The samples were weighed periodically using an analytical scale accurate to $10^{-4}\,g$ and the time of each weight measure was controlled with a chronometer. Before the weight measurements, the specimens were withdrawn from the water and wiped dry to remove the surface moisture. In order to become independent of the weight of the specimen tested, the relative water absorption was calculated with equation (1), where M_t (%) is the relative water absorption of the specimen, M_t is the specimen weight at each time, and M_0 is the initial specimen weight. Three specimens were tested for each sample

$$M_t(\%) = \frac{M_t - M_0}{M_0} \cdot 100 \qquad (1)$$

Mechanical properties of the samples were measured before the water absorption tests and periodically in order to correlate the effect of the water uptake on the mechanical performance of the composites. Three point bending tests were performed in the Instron dynamometer 4467 according to ASTM D790-03 standard. At least five specimens were tested for each sample.

Results and discussion

Humidity and water absorption tests data correlation

The following procedure is proposed to predict the water content of the composites immersed in environments with different relative humidities by performing water immersion tests. This allows obtaining results in a considerable less amount of time than the required in the humidity absorption tests. This analysis was performed on CA samples (without clay).

First, water and humidity absorption tests were performed. The water content M (%) was then plotted against the exposure time and the curves were fitted using the following expression,[26] where M_t is the specimen weight at each time, M_0 is the initial specimen weight, M_{max} is the maximum observed uptake of each sample, D_{eff} is the diffusion coefficient, t is the immersion time, and h is the sample thickness

$$\frac{M_t - M_0}{M_{max} - M_0} = 1 - e^{\left[-7.3 \cdot \left(\frac{D_{eff} \cdot t}{h^2}\right)^{0.75}\right]} \qquad (2)$$

Figure 1(a) shows the experimental data fitted with equation (2) applied to the different conditions, and the fitting parameters are presented in Table 1.

The time difference between the water absorption curve and the others was calculated for each $M_t(\%)$ value, as shown as an example in Figure 1(a) for $M_t(\%) = 0.3$. It can be seen that the time needed by the samples to reach that absorption value is 10.000 min when immersed in water, 80.000 min in 90% relative humidity (RH), 240.000 min in 70% RH, and 290.000 min in 65% RH.

Afterwards, the time difference against the water absorption curve was plotted against time of immersion in water, as shown in Figure 1(b). Then, the curves were fitted with equation (3), and the fitting parameters are presented in Table 1 for each experimental condition. This equation is an empirical model that was found to fit almost perfectly the observed experimental behavior

$$Dif(t) = y_0 + A \cdot e^{t/b} \qquad (3)$$

Finally, knowing the parameters of equation (3), the exposure time of a sample tested in an environment of the selected relative humidity (x) to obtain the same water absorption from the immersion tests can be estimated by applying the following relationship

$$t_{x\,\%HR} = t_{water} + Dif_x(t_{water}) \qquad (4)$$

It would be possible to find empirical relationships between any of the parameters and the %RH tested. Then, the parameters for any %RH could be estimated by interpolation. Regardless, the usefulness of the procedure presented lies on the possibility of predicting the water content of the composites immersed in environments with different relative humidities by performing water immersion tests. For example, some properties could have not been considered at the time when the humidity absorption tests were carried out, and slow
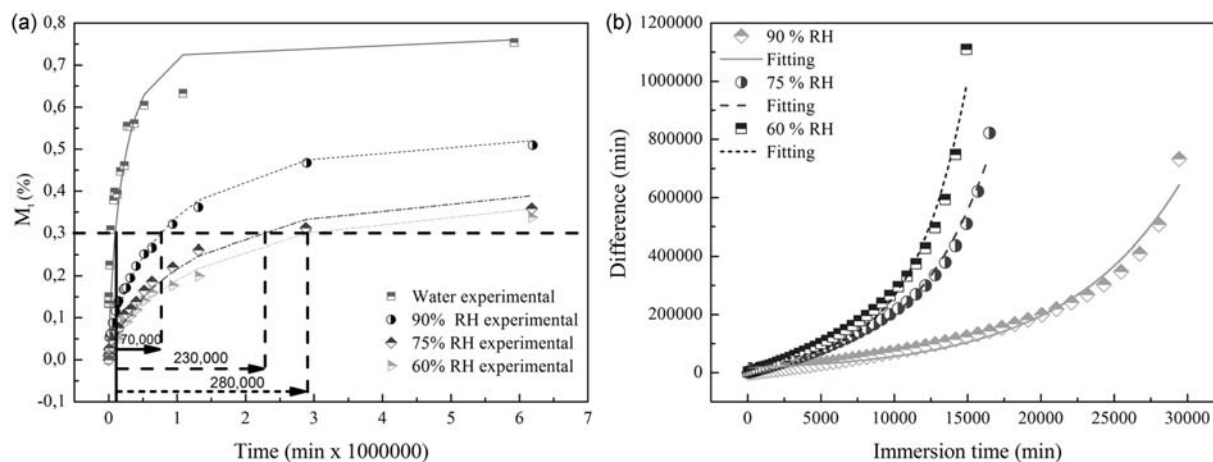
Figure 1. (a) Water and humidity absorption data fitted with the proposed models and determination of the time difference between the absorption curves for UP/glass fibers composites and (b) Determination of the time difference between the absorption curves.

Table 1. Modeling parameters for equations (2) and (3) obtained for UP/glass fiber composites.

Medium	Parameters equation (2)		Parameters equation (3)		
	$M_{max}-M_0$ (g)	D_{eff}/h^2 (s^{-1})	y_0 (s)	A (s)	B (s)
60 %RH	0.39	4.22×10^{-7}	15,718	15,747	3619
75 %RH	0.41	4.84×10^{-7}	29,277	10,856	5063
90 %RH	0.52	7.10×10^{-7}	15,364	15,306	7887
Water	0.76	2.90×10^{-6}	–	–	–

humidity absorption tests should have to be performed again in order to evaluate them. However, the degradation of different mechanical properties of these composite materials immersed in 90, 70, and 65% RH can be studied in a very short amount of time just by performing water immersion tests.

This procedure is only valid if the water transport mechanisms do not change when the composite is exposed to different humidity conditions and water. In order to prove this, SEM images of the composites were taken after the immersion tests, as shown in Figure 2. These images correspond to the fracture surface of specimens that were previously subjected to flexural tests. It can be observed that the fiber–matrix interface looks almost identical after the exposure to 60, 75, and 90% RH, where no significant debonding occurs. Although some degree of debonding occurs between the fiber and matrix of the composite that had been immersed in water (Figure 2(d)), the microstructure looks reasonably similar to that of the composites exposed to different relative humidities. Therefore, it can be assumed that the water transport mechanisms do not change significantly, and, thus, the

results obtained using the proposed correlation method should be reliable.

Water absorption tests

In the previous section, it was shown that water absorption tests can be used as means of accelerated humidity absorption tests. Therefore in this section, immersion tests in distilled water were performed to obtain water absorption results in a shorter period of time than the one needed to perform humidity absorption tests. These results can be used to predict the water absorption curves of the samples exposed to different relative humidity following the correlation method proposed previously. Furthermore, it was proved that the relative flexural modulus E/E_0 (where E is the flexural modulus of the sample exposed to the aqueous media and E_0 is the dry sample flexural modulus) is the same for a given value of water content in the composite ($M\%$) regardless the samples were immersed in water or exposed to a humid environment (Figure 3).

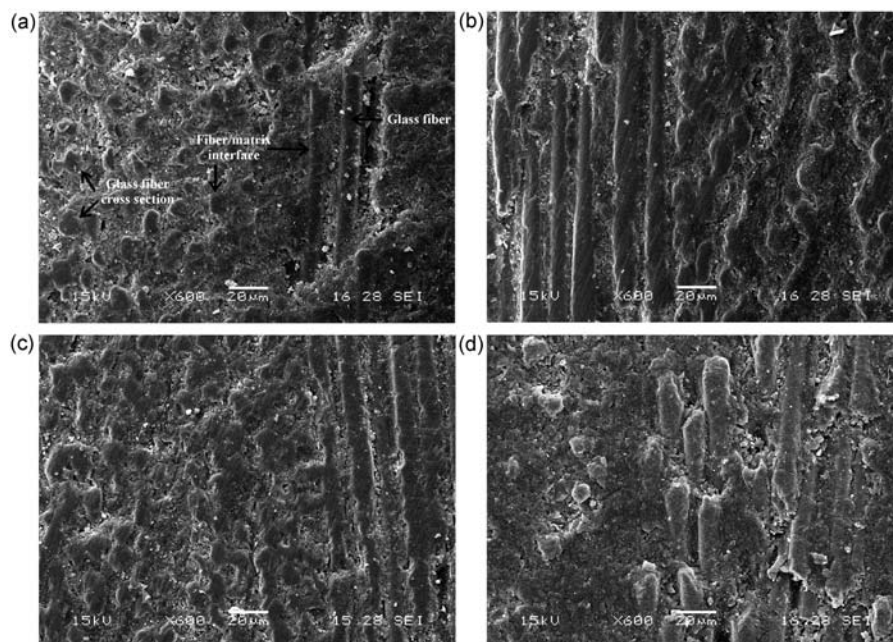There are two known factors affecting water absorption of clay filled polymeric matrices, and each one has

Figure 2. SEM images of the UP/glass fibers composites microstructure after different exposure conditions: (a) at 60% RH, (b) at 75% RH, (c) at 90% RH and (d) water.
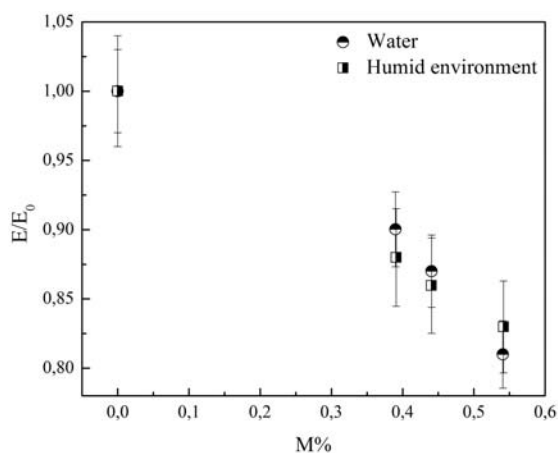

Figure 3. Flexural modulus ratio (E/E_0) between the dry samples (E_0) and samples that were exposed to aqueous media (E) as a function of the water content ($M\%$).

an opposite effect on the water uptake. The first one is the intrinsic hydrophilic nature of the clay and its ability to retain water molecules. This effect increases the water absorption of the composites as a function of the bentonite content.[27] On the other hand, several authors suggested that clay layers dispersed at the nanometer scale in the matrix can decrease the mean free path of water molecules to pass through the nanocomposite network compared to the pure matrix, which leads to lower water absorption.[28,29]

Voids present in the laminate also affect water absorption of the material, because they can give a preferential path to the infiltrated water. These voids are usually generated during the composite manufacturing process, i.e. resin mixing and reinforcement impregnation. However, void content was found to be identical (3%) for all the samples used in this work, as expected since the same resin preparation procedure and processing technique was used.

It was shown in a previous work that the incorporation of phosphonium and ammonium modified clays had no important influence on the neat polyester matrix water absorption, whereas the original bentonite increased its water absorption.[24] The high intrinsic hydrophilic character of the bentonite caused both high water absorption and bad dispersion inside the matrix. Apparently, the higher hydrophobicity and better clay morphology obtained after the chemical treatments could reduce the water absorption of clay filled composites.

It can be seen in Figure 4 that the composites containing unmodified bentonite displayed the highest amount of water uptake of all the samples, 75% more than the composites without clay, which were taken as the reference material (100%). As seen for the neat matrix, treatments were effective in reducing water absorption of the samples. The addition of TBHP modified clay had no effect in the water absorption behavior of the composite, whereas the addition of ODA modified clay reduced water absorption of the
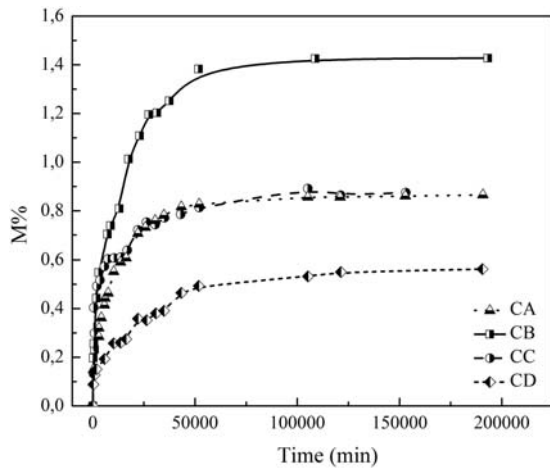
Figure 4. Water content ($M\%$) of all the composites studied as a function of the immersion time.

Figure 5. Flexural modulus ratio (E/E_0) between the dry samples (E_0) and samples that had been immersed in distilled water (E) as a function of the water content.

composites by 37%. These results can be interpreted using the explanations given previously for the clay filled neat polymeric matrix. However, results showed that the addition of ammonium modified clay was more effective in reducing water absorption than the addition of phosphonium modified clay, despite the fact that the latter presented higher interlaminar spacing and lower water absorption than the former. This suggests that the best composite performance is not necessarily obtained by using the best clay in terms of water absorption and interlaminar spacing.

Composites flexural performance

Flexural properties of the dry composite samples were found to be almost the same regardless of the clay type and content. The composite containing no clay (CA) showed a flexural modulus of 9.3 ± 1.0 GPa and a flexural strength of 274 ± 30 MPa. Similarly, the flexural modulus and strength of CC and CD were found to be 10.0 ± 1.5 GPa and 279 ± 20 MPa; and 9.6 ± 1.3 GPa and 261 ± 31 MPa, respectively. Hence, the addition of 5 wt% of these clays has a negligible effect (less than 10%) on the mechanical properties of the dry composites.

Figure 5 shows the flexural modulus ratio ($E/E0$) between the dry samples (E_0) and samples that had been immersed in distilled water (E) as a function of the water content in the composites. This plot was constructed using the water absorption test data. No significant differences can be observed between the behavior of the composites CA, CB, and CC. The relative modulus (E/E_0) decreased as the water content increased in all those materials, showing that neither the bentonite nor the phosphonium modified bentonite is effective in reducing the detrimental effect of water on the materials performance. On the other hand, the
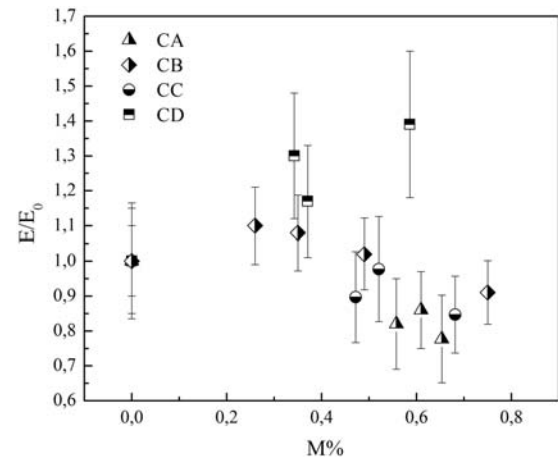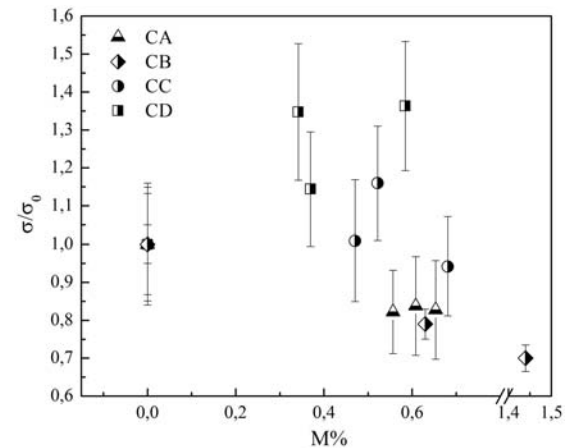

Figure 6. Relative flexural strength (σ/σ_0) between the dry samples (σ_0) and samples that had been immersed in distilled water (σ) as a function of the water content ($M\%$).

ammonium modified bentonite seems to be effective in reducing the degradation of the flexural modulus as the water content in the sample increases. This result suggests that this treatment was effective in improving the clay compatibility with the polymeric matrix, generating an exfoliated structure of the clay and improving its dispersion in the polymer, in accordance to the results shown in the previous sections.

In the same way, the relative flexural strength (σ/σ_0) of the composites was plotted against the water content in Figure 6. As expected, a clear detriment in the mechanical properties due to water absorption could be observed in CA, CB, and CC samples. Water affects the mechanical properties of the composites as it plasticizes the polymer matrix,[30–32] it interacts with it

chemically (hydrolysis),[32] and it also degrades the fiber–matrix interface, resulting in the loss of integrity and a significant drop of the mechanical properties. In addition, it has been reported that the absorption of water induces the generation of interfacial micro cracks that weaken the composite and debond the fiber from the matrix.[33,34] These mechanisms are believed to affect the composite overall performance much more significantly than matrix plasticization or hydrolyzation.[35] Although the material containing phosphonium modified bentonite seems to be slightly more resistant to degradation than the composite without bentonite and the composite with unmodified bentonite, the differences fall within error bars, and therefore no clear conclusions can be extracted from the results. On the other hand, the addition of ammonium modified bentonite seems to help the material to hold its mechanical performance even after water absorption occurs. This observation is in accordance to the water absorption results suggesting that the ammonium modified bentonite is more compatible with the polymer matrix, and the nanocomposite presents an exfoliated morphology.[24] This favorable morphology helps reducing water transport through the composite material, preventing the damage caused by water on its mechanical properties.

Conclusions

In this work, dual scale fiber glass reinforced UP-bentonite composites were made by the vacuum bagging technique. Pristine and organomodified bentonites were used. Mechanical properties and water absorption behavior of the composites were analyzed and compared to those of conventional UP/glass fiber reinforced composites. The pristine clay increased water absorption rate of the composite and decreased the mechanical performance of the material due to its hydrophilic nature and low compatibility with the UP resin. Water absorption behavior and mechanical performance of the UP-TBHP modified bentonite/glass fiber composites were found to be almost identical to those of the conventional UP/glass fiber reinforced composites. In addition, both composites showed a detriment in the mechanical properties during the water absorption tests. The best results were obtained when the ODA modified bentonite was used as nanoreinforcement because the higher compatibility with the polymeric matrix improved the dispersion of the clay in the polymer and reduced the water absorption of these composites (37% with respect to the UP/glass fiber composites) and retained the mechanical properties almost equal to the dry composites. Furthermore, the ODA modified clay was very effective in the mitigation of the damage caused by water absorption, because the material was observed to hold its mechanical performance even after water absorption occurs.

In addition, this work presented a procedure to use water absorption tests as means of accelerated humidity absorption tests. This correlation method can be used to estimate the evolution of the water content with time of composites that will be exposed to a certain relative humidity by performing water absorption tests, which reduce dramatically the laboratory testing time.

References

1. Apicella A, Migliaresi C, Nicolais L, et al. The water ageing of unsaturated polyester-based composites: Influence of resin chemical structure. *Composites* 1983; 14: 387–392.
2. Caprile C, Sala G and Buzzi A. Environmental and mechanical fatigue of wind turbine blades made of composites materials. *J Reinf Plast Compos* 1996; 15: 673–691.
3. Kensche CW. Fatigue of composites for wind turbines. *Int J Fatigue* 2006; 28: 1363–1374.
4. Shan Y and Liao K. Environmental fatigue behavior and life prediction of unidirectional glass–carbon/epoxy hybrid composites. *Int J Fatigue* 2002; 24: 847–859.
5. Akil HM, Cheng LW, Mohd Ishak ZA, et al. Water absorption study on pultruded jute fibre reinforced unsaturated polyester composites. *Compos Sci Technol* 2009; 69: 1942–1948.
6. Alexandre M and Dubois P. Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials. *Mater Sci Eng R* 2000; 28: 1–63.
7. Picard E, Gauthier H, Gérard JF, et al. Influence of the intercalated cations on the surface energy of montmorillonites: Consequences for the morphology and gas barrier properties of polyethylene/montmorillonites nanocomposites. *J Colloid Interface Sci* 2007; 307: 364–376.
8. Roelofs JCAA and Berben PH. Preparation and performance of synthetic organoclays. *Appl Clay Sci* 2006; 33: 13–20.
9. Čapková P, Pospíšil M, Valášková M, et al. Structure of montmorillonite cointercalated with stearic acid and octadecylamine: Modeling, diffraction, IR spectroscopy. *J Colloid Interface Sci* 2006; 300: 264–269.
10. Xie W, Xie R, Pan W-P, et al. Thermal stability of quaternary phosphonium modified montmorillonites. *Chem Mater* 2002; 14: 4837–4845.

11. Xi Y, Frost RL and He H. Modification of the surfaces of Wyoming montmorillonite by the cationic surfactants alkyl trimethyl, dialkyl dimethyl, and trialkyl methyl ammonium bromides. *J Colloid Interface Sci* 2007; 305: 150–158.

12. Xie W, Gao Z, Pan W-P, et al. Thermal degradation chemistry of alkyl quaternary ammonium montmorillonite. *Chem Mater* 2001; 13: 2979–2990.

13. Drown E, Mohanty A, Parulekar Y, et al. The surface characteristics of organoclays and their effect on the properties of poly (trimethylene terephthalate) nanocomposites. *Compos Sci Technol* 2007; 67: 3168–3175.

14. Silva SML, Araújo PER, Ferreira KM, et al. Effect of clay/water ratio during bentonite clay organophilization on the characteristics of the organobentonites and its polypropylene nanocomposites. *Polym Eng Sci* 2009; 49: 1696–1702.

15. Santiago F, Mucientes AE, Osorio M, et al. Preparation of composites and nanocomposites based on bentonite and poly (sodium acrylate). Effect of amount of bentonite on the swelling behaviour. *Eur Polym J* 2007; 43: 1–9.

16. Mandalia T and Bergaya F. Organo clay mineral-melted polyolefin nanocomposites effect of surfactant/CEC ratio. *J Phys Chem Solids* 2006; 67: 836–845.

17. He H, Duchet J, Galy J, et al. Influence of cationic surfactant removal on the thermal stability of organoclays. *J Colloid Interface Sci* 2006; 295: 202–208.

18. Kim J-K, Hu C, Woo RSC, et al. Moisture barrier characteristics of organoclay–epoxy nanocomposites. *Compos Sci Technol* 2005; 65: 805–813.

19. Jen M-HR, Tseng Y-C and Wu C-H. Manufacturing and mechanical response of nanocomposite laminates. *Compos Sci Technol* 2005; 65: 775–779.

20. Haque A, Shamsuzzoha M, Hussain F, et al. S2-Glass/epoxy polymer nanocomposites: Manufacturing, structures, thermal and mechanical properties. *J Compos Mater* 2003; 37: 1821–1837.

21. Rice BP, Chen C, Cloos L, et al. Carbon fiber composites: Organoclay-aerospace epoxy nanocomposites. Part I. *SAMPE J (USA)* 2001; 37: 7–9.

22. Quaresimin M and Varley RJ. Understanding the effect of nano-modifier addition upon the properties of fibre reinforced laminates. *Compos Sci Technol* 2008; 68: 718–726.

23. Brunner AJ, Necola A, Rees M, et al. The influence of silicate-based nano-filler on the fracture toughness of epoxy resin. *Eng Fract Mech* 2006; 73: 2336–2345.

24. Ollier R, Rodriguez E and Alvarez V. Unsaturated polyester/bentonite nanocomposites: Influence of clay modification on final performance. *Compos Part A* 2013; 48: 137–143.

25. Ollier R, Vazquez A and Alvarez V. Biodegradable nanocomposites based on modified bentonite and polycaprolactone. In: Bartul Z and Trenor J (eds) *Advances in nanotechnology*. New York: Nova Publishers, 2011, pp.281–301.

26. Springer GS. Numerical procedures for the solutions of one-dimensional Fickian diffusion problems. In: Springer GS (ed.) *Environmental effects on composite materials*. Westport, CT: Technomic Publishing Co, Inc, 1981, pp.166–199.

27. Abu-Jdayil B, Al-Malah K and Sawalha R. Study on bentonite-unsaturated polyester composite materials. *J Reinf Plast Compos* 2002; 21: 1597–1607.

28. Liu X, Wu Q, Berglund LA, et al. Polyamide 6-clay nanocomposites/polypropylene-grafted-maleic anhydride alloys. *Polymer* 2001; 42: 8235–8239.

29. Ward W, Gaines G Jr, Alger M, et al. Gas barrier improvement using vermiculite and mica in polymer films. *J Membr Sci* 1991; 55: 173–180.

30. Chu W, Wu L and Karbhari VM. Durability evaluation of moderate temperature cured E-glass/vinylester systems. *Compos Struct* 2004; 66: 367–376.

31. Won J-P, Lee S-J, Kim Y-J, et al. The effect of exposure to alkaline solution and water on the strength–porosity relationship of GFRP rebar. *Compos Part B* 2008; 39: 764–772.

32. Tsenoglou CJ, Pavlidou S and Papaspyrides CD. Evaluation of interfacial relaxation due to water absorption in fiber–polymer composites. *Compos Sci Technol* 2006; 66: 2855–2864.

33. Morii T, Ikuta N, Kiyosumi K, et al. Weight-change analysis of the interphase in hygrothermally aged FRP: Consideration of debonding. *Compos Sci Technol* 1997; 57: 985–990.

34. Weitsman Y and Guo Y-J. A correlation between fluid-induced damage and anomalous fluid sorption in polymeric composites. *Compos Sci Technol* 2002; 62: 889–908.

35. Liao K, Schultheisz CR and Hunston DL. Effects of environmental aging on the properties of pultruded GFRP. *Compos Part B* 1999; 30: 485–493.