Unsaturated polyester/bentonite nanocomposites: Influence of clay modification on final performance

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ABSTRACT

In this work, unsaturated polyester/bentonite nanocomposites were obtained and characterized. The bentonite used was unmodified and with different chemical treatments. The effects of these different chemical modifications (cation exchange reactions with quaternary ammonium and phosphonium salts) of this clay as well as the effect of clay content on the thermal, barrier (water absorption), mechanical (flexural) and dynamic-mechanical properties of unsaturated polyester matrix were analyzed. The results clearly show that the chemical modifications of the clay cause a desired effect on its final properties improving the performance of the nanocomposites. The enhancements could be directly related to the dispersion of the clay inside the matrix, as shown by transmission electron microscopy.

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1. Introduction

For decades, polymeric materials have been reinforced to improve different properties such as mechanic, thermal and impact resistance ones, or to decrease others such as electric conductivity and gas permeability, depending on the application [1]. For example, unsaturated polyesters (UPs) are commonly reinforced with short or continuous glass fibers and also filled with mineral particles. UP composites have been widely used in industrial applications such as the marine, automotive and building industries due to their low cost, high chemical resistance and good processability [2]. Unsaturated polyesters are an economical thermoset materials extensively used due to their excellent processability and good crosslinking tendency as well as good mechanical properties when cured [3]. With over 60 years of history in commercial development, the use of these resins continues growing globally at robust rates because of the versatility of UP resins in industrial applications. Whereas the chemical constituents of the resin preparations can modify its performance, equally important are the performance attributes created through the use of additives, fillers and reinforcements [4]. However, microscopic reinforcements and fillers generally have imperfections. Structural perfection improves if these elements are smaller: it is believed that the last properties of the reinforcement would be achieved if they were of molecular size order [1]. Clay particles, which are about 1 nm thick, have a perfect

crystalline structure and have been successfully used in thermosetting polymer matrices for improving mechanical properties [5–8]. However, the smaller these reinforcement elements are, the larger internal surface will be, and consequently its tendency to agglomerate in a matrix, rather than to disperse homogenously [9]. Among the great variety of clays, the use of bentonite is an interesting option because beyond the environmental and economic factors, its mechanical and chemical resistance makes it very useful as reinforcement for polymeric materials [10]. Also, bentonite is an abundant natural resource which can be found in many regions of Argentina. This clay is characterized by a moderate negative charge, known as cation exchange capacity, CEC, and expressed in meq/100 g [11,12].

One of the main problems that arise when adding nanoclays to polymers is the dispersion of the particles. A totally exfoliated structure (i.e., that the silicate layers are completely and uniformly dispersed in a continuous polymeric matrix) is necessary to maximize the mechanical properties, but the tendency of the particles to agglomerate is, in general, difficult to overcome. This is because most polymers are hydrophobic while silicates are hydrophilic, so it is necessary to make a previous treatment to the clay or to the polymer so as to make them more compatible [13,14]. One of the most reliable methods for increasing compatibility consists in converting the hydrophilic silicates into organophilic ones. The hydrated cations that are in the galleries are replaced by positively charged surfactants like alkyl or hydroxyl ammonium cations [15–19]. When this occurs, the basal spacing of the clay layers increases and the surface energy decreases. Thus, the compatibility

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with hydrophobic polymers is improved, and polymer chains are able to enter inside the galleries under defined processing conditions [18]. A less studied organic modification consists in using quaternary phosphonium salts instead of ammonium salts. One of the advantages of this modification is that phosphorous compounds may increase the thermal and fire resistance [13,20–24].

Several studies in which clays were incorporated to UPs can be found in literature. Kornmann et al. doubled the fracture energy of UP by adding only 1.5 vol.% of montmorillonite (MMT) [25]. Xu and Lee improved the shrinkage control of low profile UPs by adding up to 3% of MMT [2]. Also, Dhakal et al. reported the use of organoclays to improve of some mechanical properties of polyesters [7]. By using the nanoindentation technique, these authors observed an increase of 29% in the hardness of nanocomposites with 1% of clay in comparison with the pristine resin. Esfahani et al. [26] reported that UP resin containing only 1.5 wt.% of nanoclay displayed the best performance for tensile modulus and Izod impact strength. Tribological properties can be increased as well. Jawahar et al. demonstrated that nanocomposites with 3% of bentonite content exhibit an improvement of 85% in wear resistance and a decrease of 35% in the friction coefficient [27]. Bentonite has also been used in combination with UPs to improve other properties like thermal conductivity and chemical stability [28,29]. In general, clays can increase mechanical properties and thermal resistance of thermosetting resins. Some works have also shown that humidity and water absorption can be reduced by the incorporation of nanoclays [5,28,30]. Nevertheless, the effects of clay modification on the level of water uptake as well as the mechanisms that govern the diffusion processes have not been fully clarified. As regards nanocomposites with thermoset matrices reinforced with phosphonium treated clays, few research works can be found. Saitoh et al. studied the epoxy/clay nanocomposites by incorporating phosphonium modified MMT [23]. The dispersibility was improved by incorporating carboxyl-phosphonium modified MMT and high-performance materials with optimal thermal and thermal mechanical properties were obtained.

The main objective of the present work was to analyze the effect of chemical modifications of bentonite on the final performance of UP/bentonite nanocomposites. Specifically, water absorption and thermal degradation were studied as a function of clay treatment and content. The mechanical and dynamic-mechanical properties of the nanocomposites were also studied.

2. Materials and methods

Unsaturated polyester resin (Dolplast®) was used as polymer matrix. This type of resin has a density of 1.8–2.2 g/cm³, a viscosity of 300–400 cPs and a styrene content of 32–42%. MEKP OX 483 (Médano) was used as catalyst. Neat bentonite (Clay 1) was supplied by Minarmco S.A. (Neuquén, Argentina). Tributyl hexadecyl phosphonium bromide (TBHP) and octadecyl ammonium chloride (ODA), both obtained from Sigma Aldrich, were used as organic modifiers.

A Na⁺-saturated bentonite (Clay 2) was obtained by saturation of pristine clay with a NaCl solution for 20 days. After this process, the suspension was centrifuged, washed with deionized water several times to remove the chloride ions (negative AgNO₃ test) and then freeze dried [31]. In addition, two organoclays were prepared by cation exchange reaction by using aqueous solutions of TBHP and ODA. Phosphonium and ammonium modified clays were named Clay 3 and Clay 4 respectively. A more detailed explanation of these clay modifications can be found in a previous work [32].

Preparation of the nanocomposites: Adequate quantities of UP resin were weighed and different amounts (1, 2.5, 5, 7.5 and 10 wt.%) of the selected clays (previously dried in a vacuum oven) were

added. The mixture was stirred in an ultrasonic bath at room temperature for the time needed to obtain a homogeneous dispersion. Then, 1.5 wt.% of catalyst was incorporated and the mixture was manually homogenized. After that, plaques were prepared by pouring the mixture in a mold which consisted of two glass layers separated by a 3 mm rubber o ring. The curing cycle was carried out in an oven, first for 1 h at 50 °C to remove trapped air, then for 1 h at 80 °C to produce the crosslinking and finally for 1 h at 130 °C to ensure the complete conversion.

X-ray diffraction patterns (XRD) (for clays and nanocomposites) were obtained from a PW1710 diffractometer equipped with a Cu Kα generator (λ = 1.5406 Å) operating at 45 kV, 30 mA and at room temperature.

Water absorption tests were performed by immersing the samples in distilled water at room temperature. All the samples were previously dried under vacuum until constant weight. Samples were removed from water, carefully dried with a tissue paper and weighed at prefixed times. The absorption at each time was calculated as:

$$M_t(\%) = \frac{M_t - M_0}{M_0} \times 100 \tag{1}$$

were M_t is the mass of the sample at time t and M_0 is the initial mass of the sample (dried).

The effective diffusion coefficient (D_{eff}) was obtained from the next equation:

$$D_{eff} = \pi \cdot \left(\frac{h}{4 \cdot M_{max}}\right)^2 \cdot \left(\frac{dM}{d\sqrt{t}}\right)^2 \tag{2}$$

where $\left(\frac{dM}{d\sqrt{t}}\right)$ is the slope of the initial (linear) part of the curve $M_t(\%)$ vs $t^{1/2}$, M_{max} is the maximum water uptake at which the linear relationship is kept and h is the thickness of the sample.

Thermogravimetric analysis (TGA) was carried out by means of a Shimadzu thermal analyzer from room temperature to 1000 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

Transmission Electron Microscopy (TEM) was performed at JEOL CX II using an acceleration voltage of 80 kV, to observe the dispersion of clay platelets within the polymer matrix.

Flexural tests were carried out at room temperature in a Universal Testing Machine INSTRON 4467 following the recommendations of the ASTM D790M-03 standard. At least five specimens were tested.

Dynamic Mechanical tests (DMA) were performed in a Perkin Elmer dynamical mechanical analyzer (DMA-7). The tests were carried out in temperature scan mode from −25 °C to 220 °C, with a three-point bending measuring system. The test conditions were 1 Hz of frequency, a heating rate of 10 °C/min, dynamic stress of 300 kPa and static stress of 500 kPa. Specimens were rectangular (20 mm × 3.5 mm × 1.5 mm) and the span was 15 mm. At least five specimens were tested.

3. Results and discussion

In a previous work humidity adsorption (19.71% for Clay 1; 23.33% for Clay 2; 2.73% for Clay 3 and 3.19% for Clay 4 measured at 90% relative humidity) and contact angle measurements of clays demonstrated that whereas Clays 1 and 2 are highly hydrophilic, both modifications produced hydrophobic (or organophilic) clays (Clays 3 and 4), which might be more compatible with the polymeric matrix. In addition, the interlaminar spacing (d_{001} determined from XRD spectra: Fig. 1) clearly increased after cation-exchange reaction (from 1.3 nm for unmodified clays to 2.5 nm for Clay 3 and 1.9 nm for Clay 4) [32]. This increase contributes to the feasibility of intercalation of polymer chains between clay platelets. On the other hand, the thermal stability obtained by
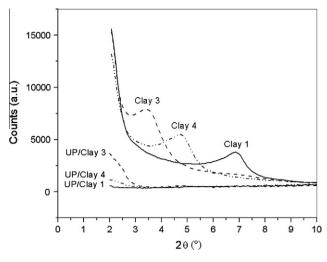
Fig. 1. XRD patterns of clays and nanocomposites.

Fig. 2. TEM images of 5 wt.% UP/clay nanocomposites with: (a) Clay 1; (b) Clay 3; (c) Clay 4.

TGA was reduced in both cases being the degradation peak centered at 380 °C (starting at 250 °C) for Clay 3 and near 300 °C (starting at 190 °C) for Clay 4 [26]. This must be taken into account especially when the processing temperatures are quite high (or longer times are required to cure the resin).

3.1. Characterization of the nanocomposites

The XRD patterns (shown in Fig. 1) confirmed the absence of clay diffraction peak suggesting an intercalated-exfoliated mixed structure. Clay 2 was considered as an intermediate step to obtain the organophilic clays, and was thus not considered for the preparation of nanocomposites. It is believed that the dispersion is facilitated by the lower size and higher mobility of the styrene, which can enter the clay galleries more easily than UP oligomers [33]. Then, when the curing reaction starts, the styrene has two possible reactions, with other styrene monomers and with UP instaurations [34]. The former reactions cause chain extension and the latter network cross-linking. Then, chain extension reactions are more probable to happen inside the clay galleries, causing the separation of the silicate layers and, thus, promoting the intercalation of the clay. These styrene–styrene linear chains can then react with the active points in the surrounding resin.

To better understand the clay morphology inside the matrix and to evaluate the degree of dispersion, TEM studies were conducted. Fig. 2a–c show the images obtained for the systems studied. In view of the fact that the silicate platelets are dark, the presence of tactoids which are composed of un-separated clay layers, was manifested for non-modified clays (morphology typically observed when there is no compatibility between the clay and the polymer) but also for organophilic ones with high clay concentrations (in accordance with mechanical properties). For Clays 3 and 4 with low clay contents (1, 2.5 and 5 wt.%), a higher number of disordered structures and exfoliated layers were observed, especially for the former. The higher exfoliation observed for the nanocomposite prepared with Clay 3 could be related to the higher interlayer spacing but also to the increased degradation temperature (some degree of organic modifier degradation could have taken place during the processing of UP/Clay 4 nanocomposites).

3.2. Mechanical and dynamic-mechanical characterization

The flexural modulus of nanocomposites as a function of clay content is displayed in Fig. 3. In general, all the bentonites caused an increase in the flexural modulus of the samples. By comparing
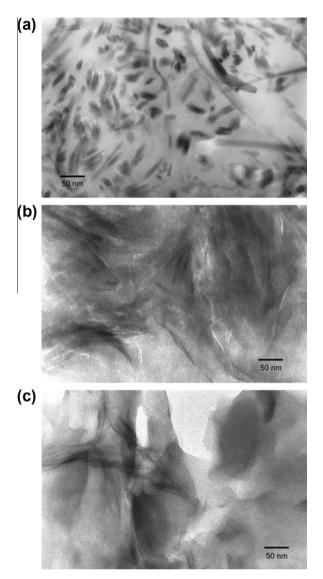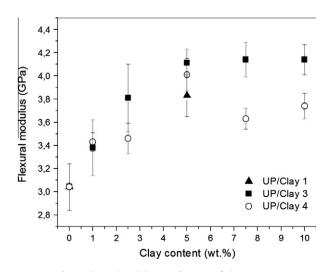

Fig. 3. Flexural modulus as a function of clay content.

the same clay content, at the commonly used percentage of 5 wt.%, it can be seen that the modified clays (Clays 3 and 4) caused an improvement in the mechanical behavior of the UP matrix, being slightly higher than that obtained for the untreated clay. Even when the difference was not high, the different values can be explained by the higher interlayer spacing as well as by the enhanced polymer/clay compatibility. Clay 3 seemed to be better than Clay 4. On the other hand, it is interesting to note that the modulus increased until 5 wt.% of clay and then either remained almost constant (Clay 3) or decreased (for Clay 4). This could be related to a possible agglomeration of clay platelets forming tactoids. The latter was confirmed by the observation of TEM micrographs (see Fig. 2).

To have a more detailed insight of the effect of adding the modified clays to the polymer resin, and explain the trend observed in the flexural tests, dynamic-mechanical analysis experiments were carried out. Fig. 4 shows an example of the curve obtained for the UP/7.5 wt.% Clay 4 system.

From DMA results, several parameters were analyzed. Table 1 summarizes the variation in the glass transition temperature of the materials (Tg), which is the temperature of the maximum of tan δ, storage modulus (E' glass at 25 °C) with the clay content for the organophilic clays composites.

The variation in Tg is very slight for both materials. The same behavior was observed by Ngo et al. who showed that the presence of a commercial organoclay did not significantly affect the Tg of the epoxy systems regardless of the clay loading [35]. In general, when particles are added to thermosetting resins the amount of interphase increases as the dispersion of the particles is enhanced and as its size is reduced. For nanocomposites, small amounts of reinforcement produce a large amount of interphase. If the Tg of the interphase region changes, the behavior of the whole material is affected, but the glass transition at the interphase can be affected in
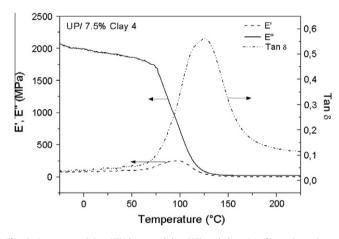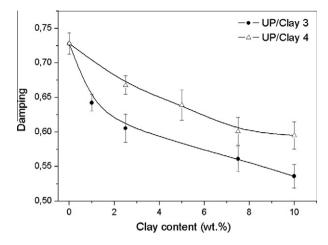

Fig. 5. Damping values of the UP/organophilic clays composites as a function of the clay content.

two opposite manners. Chemical bonding of the silicate and UP matrix could lead to hindered relaxational mobility in the polymer segments near the interface, which leads to an increase in Tg. However, a lack of surrounding entanglements and reduced crosslink density at the interface are also important, which may decrease the Tg. The Tg observed is the combination of these opposite factors.

The damping (height of the tan δ peak) is related to the capacity of the material for dissipating energy. During glass transition, long-range polymer chains gain mobility dissipating energy through viscous movement [36]. Then, any reduction in the height of tan δ is related to a decrease in the number of mobile chains during the glass transition. Fig. 5 shows that for both modified bentonites, dumping decreases as the clay content increases. In composite materials, the damping has two main contributions: the matrix and the interphase. A decrease in the damping in the nanocomposites can be explained in terms of the formation of an immobilized region around clay platelets, at the interphase. The ammonium-modified clay composite showed lower dumping values than the phosphonium-modified one, which indicates the presence of a stronger interphase in the former.

The rubber modulus (E' at $Tg + 50$ °C) can be correlated with the crosslinking of the network. Fig. 6 shows that E'_{rubber} increased as the clay content increased. This is due because nanoparticles can

Fig. 4. Storage modulus (E'), loss modulus (E'') and damping factor (tan δ) as a function of temperature for UP/7.5% Clay 4 nanocomposite.

Table 1
Properties of UP and UP/organoclay nanocomposites obtained from DMA analyses as a function of clay content.

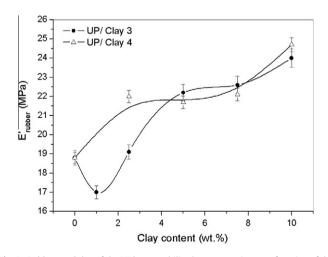| Clay content (wt.%)	UP/Clay 3		UP/Clay 4	
	Tg (°C)	E' glass (GPa)	Tg (°C)	E' glass (GPa)
0	120.5 ± 4.5	2.45 ± 0.8	120.5 ± 4.2	2.45 ± 0.8
1.0	120.6 ± 3.5	1.82 ± 0.1	120.2 ± 3.7	2.05 ± 0.3
2.5	117.9 ± 2.5	2.46 ± 0.3	119.5 ± 2.1	2.69 ± 0.2
5.0	120.5 ± 1.0	2.25 ± 0.2	122.3 ± 1.4	2.46 ± 0.3
7.5	123.5 ± 2.0	1.92 ± 0.3	121.6 ± 1.9	2.78 ± 0.2
10.0	119.1 ± 1.0	2.52 ± 0.1	122.3 ± 2.0	2.86 ± 0.3

Fig. 6. Rubber modulus of the UP/organophilic clays composites as a function of the clay content.

Fig. 7. Weight loss as a function of temperature for neat UP and 5 wt.% UP/clay nanocomposites.

and glass modulus has been reported by other authors in micron- and nano-sized filled composites [37,38]. The better reinforcement efficiency of the nanoparticles above and below the Tg of each material can be explained in terms of the comparative stiffness of the particles and the matrix in the glassy and rubbery state. Above Tg, the clay particles are much more rigid than the polymer, and therefore there is a more significant effect on the modulus than at low temperatures, when the matrix and particles stiffness are similar.

3.3. Thermal characterization (TGA)

The thermal stability of the nanocomposites was characterized by TGA. Fig. 7 shows the residual mass as a function of temperature for the neat resin and the UP/5% bentonite nanocomposites. It can be seen that the addition of bentonite increases the thermal stability of the UP resin. Moreover, the chemically modified bentonites did not have a significant influence on the degradation temperatures of the nanocomposites in comparison with untreated bentonite nanocomposite. The variations in thermal degradation of the bentonites with different chemical treatments observed in a previous work was not determinant for the degradation process observed in the composites [32]. The degradation of the organic modifiers contained in the bentonites was not detected, probably because the clay content in the UP matrix is very low (up to 10 wt.%) and from that just a part is the clay modifier (30% in the case of phosphonium salt and 22% in the case of ammonium one). In general, regarding the effect of clay incorporation on the

act as physical crosslinks for the UP molecular chains in the nanocomposites. On the other hand, the storage modulus at temperatures below Tg (E′ glassy, measured at 25 °C) is related to the flexural modulus obtained in static conditions. In this case, the value of the modulus remained almost unchanged as the clay content increased (Table 1). This difference in the behavior of the rubber
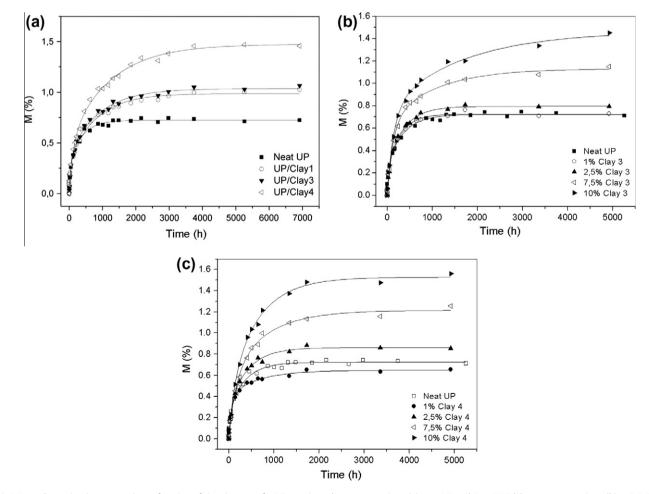

Fig. 8. Water absorption (percentage) as a function of time in water for UP matrix and nanocomposites: (a) neat UP and 5 wt.% UP/clay nanocomposites; (b) 1, 2.5, 7.5 and 10 wt.% Clay 3; (c) 1, 2.5, 7.5 and 10 wt.% Clay 4.

Table 2
Equilibrium water content (M_∞) and effective diffusion coefficient (D_{eff}) for UP and UP/organoclay nanocomposites immersed in water as a function of clay content.

Clay content (wt.%)	UP/Clay 3		UP/Clay 4	
	$M_{\infty\text{ water}}$ (%)	$D_{eff\text{ water}}$ (mm^2/seg)	$M_{\infty\text{ water}}$ (%)	$D_{eff\text{ water}}$ (mm^2/seg)
0	0.723 ± 0.010	$2.86 \times 10^5 \pm 1.84 \times 10^4$	0.723 ± 0.010	$2.86 \times 10^5 \pm 1.84 \times 10^4$
1.0	0.715 ± 0.008	$6.31 \times 10^5 \pm 8.24 \times 10^4$	0.634 ± 0.001	$5.36 \times 10^5 \pm 2.85 \times 10^5$
2.5	0.786 ± 0.004	$5.84 \times 10^5 \pm 1.94 \times 10^5$	0.855 ± 0.046	$3.10 \times 10^5 \pm 1.11 \times 10^5$
7.5	1.069 ± 0.016	$4.55 \times 10^5 \pm 8.98 \times 10^3$	1.161 ± 0.004	$2.43 \times 10^5 \pm 7.76 \times 10^4$
10.0	1.295 ± 0.021	$3.80 \times 10^5 \pm 7.07 \times 10^2$	1.506 ± 0.036	$2.00 \times 10^5 \pm 8.27 \times 10^3$

thermal stability of thermosetting matrices, different results can be found in the literature. Bharadwaj et al. showed that the incorporation of commercially modified MMT to unsaturated polyester was detrimental for the thermal stability of the nanocomposites [39]. Becker et al. also observed a slight decrease in the onset temperature of the degradation process of epoxy resin with increasing organoclay content [40]. Carrasco and Pagès showed that, at low clay contents (up to 5 wt.%) the addition of clay had no effect on the thermal stability of the epoxy matrix, whereas for higher contents (10 wt.%) a clear increase on this parameter was observed [41]. Other authors demonstrated that the thermal stability of the epoxy based nanocomposite is dependent upon the dispersion of the organoclay in the epoxy matrix but that all the epoxy nanocomposites had enhanced thermal stability compared with the neat epoxy resin [42]. In addition, Lakshmi et al. reported an improvement in thermal stability of epoxy resins with the incorporation of MMT with the same chemical treatments used in this work [43]. Saitoh et al. found that the phosphonium cations used to obtain the organoclays influenced the thermal resistance of the resulting epoxy/clay nanocomposites [23]. The explanation for this behavior is that the dispersed MMT-Clay nanolayers can act as a barrier protecting the epoxy polymer matrix degradation gaseous products from volatilizing. A similar mechanism could be present in the materials studied in this work.

3.4. Water absorption

Figs. 8a–c shows the water absorption curves of the neat UP matrix and nanocomposites with different clays in water. The curves for 90% relative humidity were similar to those for water absorption, but the values of M_∞ were found to be smaller. This is because the driving force for the water diffusion process inside the material is lower.

Table 2 shows that the incorporation of Clays 3 and 4 had no important influence on water absorption, whereas the original bentonite (Clay 1) increased the water absorption of the neat matrix. This is due to its intrinsic hydrophilic character which causes both higher water absorption and bad dispersion inside the matrix (previously demonstrated by TEM). Diffusion coefficients are also included in Table 2.

Several authors have reported that the water absorption of clay/polymeric matrix nanocomposites is mainly influenced by two factors. The first one is based on the fact that the clay body itself is water rich, and, thus, absorbs more water than nearly all the polymers used as matrix, leading to an increase in the equilibrium water content as a function of the clay content. The other factor is that clay layers dispersed in 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 [44,45]. So, it is difficult to predict the global effect of nanoclay incorporation to the water absorption behavior of polymeric matrices. Although some studies have demonstrated that humidity and water absorption can be reduced by the incorporation of nanoclays into thermosetting

matrices, the effects of clay modification on water uptake, as well as the mechanisms that govern the diffusion processes have not been fully clarified [5,28,30]. For instance, Abu-Jdayil et al. have explained that the ability of composites to absorb water is low and increases as a function of the bentonite content [28]. This increase in water absorption is due to the ability of bentonite to retain water molecules.

4. Conclusions

Unsaturated polyester (UP)/bentonite nanocomposites were obtained. The bentonites used were unmodified and chemically modified by cation exchange reactions with quaternary ammonium and phosphonium salts. The nanocomposites were obtained and characterized by analyzing its thermal (TGA), barrier (water absorption), mechanical (flexural) and dynamic-mechanical (DMA) properties.

The proposed chemical modification of clay (with quaternary ammonium and phosphonium salts) seems to be adequate to improve the thermal, mechanical and dynamic-mechanical properties of the UP matrix without causing a detriment on the barrier properties (measured by water absorption), which is very important for several applications.

The results of the present work demonstrate that phosphonium salts can be used instead of ammonium ones to modify bentonites, which are the commercially used ones. The resultant clay was organophilic as well as compatible with the UP matrix and seems to be very useful to improve the mechanical performance of the UP matrix without detriment on the water uptake or thermal properties. These results are based on the higher interlayer spacing of clay platelets which is related to the better dispersion of clay platelets among polymeric chains (clearly observed in the TEM micrographs).

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