



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

Romina Ollier, Exequiel Rodriguez, Vera Alvarez*

Composite Materials Group (CoMP), Research Institute of Material Science and Technology (INTEMA), Engineering Faculty, National University of Mar del Plata, Solís 7575 (B7608FDQ), Mar del Plata, Argentina

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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 homogeneously [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

* Corresponding author. Tel.: +54 223 4816600; fax: +54 223 4810046.

E-mail address: alvarezvera@fi.mdp.edu.ar (V. Alvarez).

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 K α generator ($\lambda = 1.5406 \text{ \AA}$) 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:

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

where 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:

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

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 \times 3.5 mm \times 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

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