J Polym Eng 32 (2012): 1–5 © 2012 by Walter de Gruyter • Berlin • Boston. DOI 10.1515/polyeng-2011-0118

Unsaturated polyester-clay slurry nanocomposites

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Abstract

In this work, nanocomposites were produced with an unsaturated polyester resin and sodium montmorillonite (MMT) slurry. Upon increasing the clay content [from 1 to 5 parts per hundred resin (phr)] increments of 57% and up to 120% were found in the flexural modulus, with respect to that of the resin alone. Using clay slurry, the cross-linking reaction was affected by the clay, in such a way that the gelation temperature and the thermal stability increased. Using transmission and scanning electron microscopy, resin intercalation into the MMT silicate layers was observed and the fracture morphology revealed the effect of the clay slurry on the nanocomposite morphology. Furthermore, shear and oscillatory rheological tests revealed the formation of a structure between resin and clay at low shear rates, and the presence of this structure was evidenced by X-ray photoelectron spectroscopy (XPS) measurements.

Keywords: montmorillonite slurry; nanocomposites; polyester resin.

1. Introduction

Unsaturated polyester resins are produced by a cross-linking reaction initiated with peroxides of a pre-polymer dissolved in styrene. This curing reaction renders an insoluble and infusible cross-linked matrix with high rigidity, but fragile. This resin is usually reinforced with glass fibers or fillers of micrometric size. Since the mechanical properties of such materials depend strongly on the interaction among phases, attention has been given to the analysis of matrix-filler interactions. On this field, it is well-known that nano-layered silicates and nanoclays possessing high surface to volume ratio, may improve the mechanical properties of the polymer-nanoclay system, if they achieve an optimum degree of intercalation or exfoliation. For instance, the effect of high-shear mechanical mixing and sonication methods on the physical properties of the nanocomposites has been analyzed [1] using modified clays with a quaternary ammonium salt and calcium carbonate [2], and also using silane-treated clays [3]. Although the nanoclay is usually chemically-modified to make it organophilic and compatible with the polymer matrix, untreated MMT was also used, taking advantage of its high swelling capacity in polar liquids like water or alcohol, allowing the expansion of the interlaminar spacing and the subsequent monomer and/or polymer intercalation or exfoliation of the clay after polymerization. Exfoliation of MMT in the polymer matrix has been shown to occur through a process called "slurry compounding", in which the montmorillonite swells in water, and is then mixed with a polymer [4]. Other techniques include the addition of MMT to water and subsequently, the replacement of water by an alcohol or acetone, with further addition of a silane agent to modify the clay and make it compatible with the polymer matrix [5–7].

In this work, this slurry preparation method is implemented to obtain polyester resin-clay nanocomposites. This work includes the analysis of the influence of MMT slurry on the cross-linking reaction with the unsaturated polyester resin, and the effect of the clay on the thermal, mechanical and rheological properties of the resulting nanocomposites.

2. Experimental procedure

2.1. Materials

An isophthalic neopentylic unsaturated polyester resin MI 49 (UP) with a viscosity of 5 Pa.s, specific gravity of 1.1 at 25°C and with 75 wt% solids content was used. The cross-linking agent (styrene monomer), the initiator [50 wt% solution of methyl ethyl ketone peroxide (MEKP)] and catalyst (6 wt% solution of cobalt octoate). All reagents from Poliformas Plasticas, S.A (D.F., Mexico) were used as received. Sodium MMT clay from Nanocor Inc. (Arlington Heights, IL, USA) with ionic interchange capacity of 135 meq/100 g, specific gravity of 2.6 and mean particle size of 22 μm [8] was employed as the dispersed phase. This clay contained 15 wt% adsorbed water (water molecules solvating Na^+ cations).

2.2. Equipment

Transmission electron micrographs were taken with a (Carl Zeiss NTS, LLC, Thornwood, New York, USA) EM910 apparatus at an acceleration voltage of 120 kV. Flexural mechanical tests were carried out in an Instron-1125 machine (Instron, Norwood, Massachusetts, USA) under the ASTM D790 norm. The interlayer distance among the clay platelets was determined in a Brucker-AXSD8-advanced X-ray diffractometer (Bruker AXS, Siemens Industrial Park, Karlsruhe, Germany) with a wavelength of CuK_α 1.5418 A at 35 kV and 30 mA. The rheological tests were carried out in a TA-AR-1000 (TA, New Castle, Delaware, USA) controlled stress rheometer equipped with 25 mm parallel plates of 0.75 mm gap and a cone and plate fixture of 40 mm diameter and 2° cone angle. The thermal analysis determinations were performed in a TA-Instruments-2910 differential scanning calorimeter (Dupont, Wilmington, Delaware, USA). The chemical analysis was performed using X-ray photoelectron spectroscopy (XPS). This equipment has an ultra-high vacuum system (UHV) of VG Microtech ESCA2000 Multilab (VG Microtech, East Grinstead, UK), with a CLAM4 detector analyzer and Al K_α (hv=1486.6 eV) X-ray source. The energy position is calibrated with the orbital of Ag $3d^{5/2}$ at 367.3 eV with a resolution (FWHM) of 1.10 eV and with C 1s at 285.00 eV. Deconvoluted spectra were obtained with the SDPv4.1 software (XPS International, LLC, Mountain View, California, USA).

2.3. Sample preparation procedure

The reference sample (labeled "UP") was prepared by adding 15 parts per hundred of resin (phr) styrene monomer and 1 phr of initiator (MEKP) to the unsaturated polyester resin under stirring (22000 rpm) for 5 min under vacuum. To this sample, 0.5 phr of catalyst (cobalt octoate) were added under stirring and the resulting solution was poured into a mold and left curing at room temperature. Two samples of the resin and MMT (labeled "UP-MMT") were prepared with 1 and 5 phr of MMT content in the resin. To each sample, 15 phr of styrene and subsequently 1 phr of initiator (MEKP) were added under stirring and vacuum. To each solution, 0.5 phr of cobalt octoate were poured, placed in a mold and left curing at room temperature. Also, two samples using MMT slurry (labeled "UP-MMT/W") were prepared following a similar procedure as before, adding 1 phr of MMT to 1.5 phr of water and 5 phr of MMT to 7.5 phr of water. The polyester resin was subsequently added to each clay slurry sample under continuous stirring. Then, 15 phr styrene and 1 phr initiator (MEKP) were poured in the mixtures. Finally, 1.1 phr of catalyst (cobalt octoate) was added to each solution. The final solutions were poured into a mold and each solution was left curing at room temperature. The sample UP-water (without clay) was prepared following the same UP-MMT/W procedure. For all samples, the same stirring time and speed were applied. It is important to point out that the cross-linking reaction efficiency depends strongly on the preparation procedure as reported elsewhere [1, 9].

3. Results and discussion

3.1. Flexural properties

With respect to the reference polyester sample (UP), which exhibited a flexural modulus of 830 MPa, samples of UP-MMT with 1 and 5 phr clay content showed increases of 6% and 43%, respectively (see Table 1). The moduli of UP-MMT/W samples improved above those of the reference sample (UP), with increases of 57% and 120% in the systems prepared with 1 and 5 phr clay slurry, respectively. Also, the reinforcement effect of the clay particles was observed in the augmented flexural strength at 5 phr for UP-MMT and 1 phr for UP-MMT/W. These improvements may be related to the dispersion state and intercalation of the clay. The improved properties obtained at these filler contents, reflect lower stress concentrations due to few clay agglomerates and to the homogeneus distribution of nanoclay within the matrix. Furthermore, intercalation of the resin in the clay galleries also reflects higher clay-polymer interactions. Larger contact areas promote an efficient stress transfer between the phases, resulting in improved flexural strength [10] and flexural modulus.

Table 1 Flexural modulus and flexural strength of the samples made with polyester resin, resin-montmorillonite and montmorillonite slurry.

Clay concentration (phr)	UP-MMT	
	Flexural strength (MPa)	Flexural modulus (MPa)
0	31.3 (±0.6)	830.6 (±1.0)
1	33.4 (±1.9)	884.7 (±0.5)
5	39.8 (±2.4)	1189.2 (±3.7)
		UP-MMT/W
0	31.3 (±0.6)	830.6 (±1.0)
1	41.3 (±2.2)	1296.8 (±7.2)
5	35.5 (±3.4)	1821.0 (±0.8)

3.2. Transmission electron microscopy

In the MMT clay, ordered structures consist of individual alumino-silicate layers, namely, the basic structural units. These layers form agglomerate stacks named tactoids, which break, disperse and distribute under processing. Figure 1 shows a transmission electron microscopy (TEM) image of the UP-MMT/W with 5 phr clay slurry content. In this image, the dark lines are MMT silicate layers, with about 1 nm thickness, some of which have been intercalated and dispersed in the polymeric matrix. Water induces separation of the clay

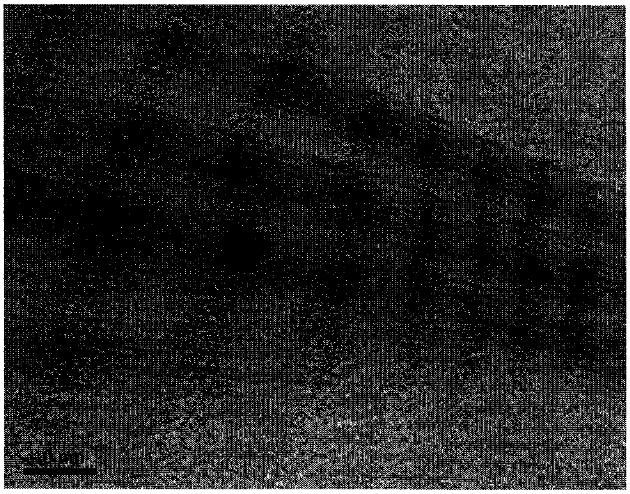

Figure 1 Intercalated UP-MMT/W with 5 phr clay.

platelets that facilitate the diffusion of the resin between galleries. The cross-linking reaction of the resin occurring in the galleries produces swelling and dispersion, inducing formation of intercalated structures.

3.3. X-ray diffraction

Samples of UP-MMT (5 phr), UP-MMT/W (5 phr), and MMT clay were tested. Figure 2 shows a diffraction peak at 2θ=6° with basal spacing of 1.46 nm, indicating one or more water layers located between the MMT layers. The XRD patterns of the UP-MMT and UP-MMT/W composites depict a very weak and broad peak at 2θ=5.7° with basal spacing of 1.55 nm and 1.56 nm, respectively, indicating an intercalated-exfoliated nanocomposite with reduced layer stacking content [11].

3.4. Thermogravimetric analysis

UP-MMT (5 phr), UP-MMT/W (5 phr) and pure UP were considered for this test. As seen in Figure 3, thermal degradation of UP, UP-MMT and UP-MMT/W is similar, with the exception of the rate of mass loss of UP-MMT/W, which is the lowest of the three systems. This retardation in the thermal degradation suggests formation of nano-composites [12]. Upon UP intercalation, increased interaction between UP and the clay surface may be induced through carboxylic groups in the chain ends and van der Waals interactions among the UP ester group and the clay surface. These interactions lead to reductions in the mass loss rate and better thermal stability.

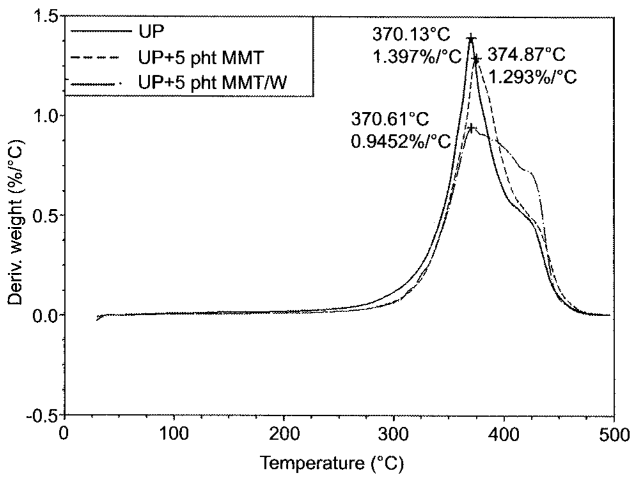

Figure 3 Thermograms of the three systems indicated in the inset.

3.5. Rheological analysis

In Figure 4, results of the complex viscosity under a flow-temperature sweep test are presented for a heating ramp of 15°C/min. Under small-amplitude oscillatory flow, the imposed strain was set at 1% (within the lineal viscoelastic regime) and a constant frequency of 5 rad/s was used in the tests. These conditions ensure that structure is preserved throughout the experiment. As observed, the temperature for the onset of the gel formation process shifted to a higher temperature, due to the effect of the clay slurry. Additional experiments were carried out under simple shear flow to analyze the effect of the flow on the structure of the material (not shown). Continuous shear retards the gel formation process, in such a way that the gelation temperature increases even more, while under oscillatory flow, structure is undisturbed, thus promoting the onset for gelation at a lower temperature.

The gelation temperature (here identified as the temperature of the steep increase of viscosity) augments in the UP-MMT sample (with 5 phr of clay) with respect to the UP reference (from 76°C to 85°C). The presence of MMT modifies the gelation time of the resin, mainly due to the absorption of the initiator and catalyst by the clay. Moreover, the layered structure

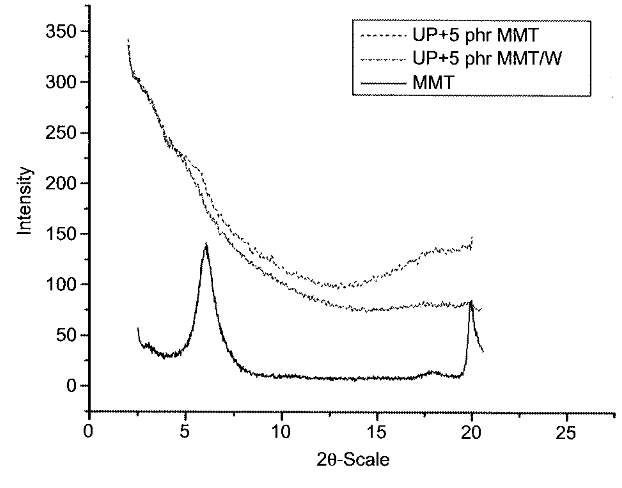

Figure 2 X-ray diffraction plot for MMT, UP-MMT and UP-MMT/W samples.

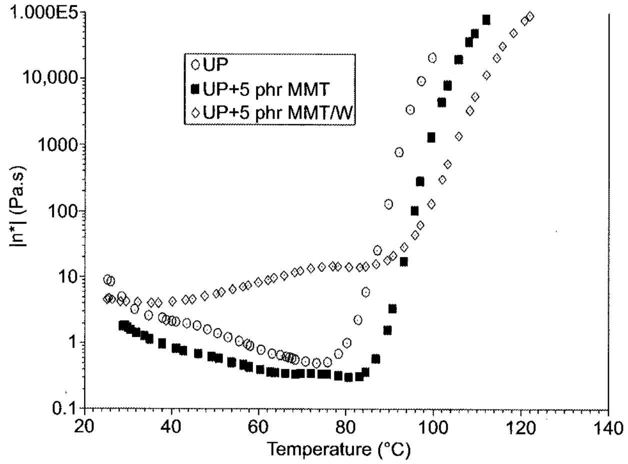

Figure 4 Complex viscosity vs. temperature for the different systems, revealing the temperature for the onset of the gelation reaction.

of MMT may prevent gel generation [13]; otherwise, when the MMT is exfoliated, a network structure is formed, reflecting increased polymer-particle interactions, and thus the onset temperature for gelation is increased considerably from 76°C to 93°C (when the clay slurry (MMT/W) content is 5 phr as compared to the pristine UP system). A longer gelation time generates more stable, expanded, intercalated structures [14].

Figure 5 shows the shear viscosity of the UP system and the effect of adding water, MMT and slurry at ambient temperature. The addition of MMT has little effect on the viscosity of pure UP resin and the curves of viscosity almost overlap in the system with clay. The effect of adding only water to the pure UP resin reduces the viscosity, i.e., water only acts as a lubricant. However, the addition of the clay slurry changes the rheological behaviour of the system drastically increasing the viscosity at low shear rates from 3 to 100 Pa.s, revealing the presence of yield stress and pronounced shear-thinning phenomena. At high shear rates, the viscosity of the UP-MMT/W system decreases and becomes a little lower than that of the pure UP resin. This is also evidence of a structure formed by the exfoliated clay; this structure is easily destroyed by flow, and at high shear rates the nanoclay becomes aligned to the flow and acts as a lubricant decreasing the viscosity to values even lower than that of pure UP. This exfoliated nanoclay structure is formed in the presence of water.

The behavior of the loss modulus shows a predominantly viscous behavior in all systems (same low-frequency slope, approx. 1) except in the UP-MMT/W system (Figure 6). For decreasing frequency, the viscous modulus of the UP-MMT/W system becomes frequency independent. This is more evident in the elastic modulus (Figure 7) which shows a gel-like behavior independent of the frequency throughout the frequency range, related to the weak solid-like behavior of the system in the presence of exfoliated clay structures. Interestingly, in this system both the loss and storage modulus show a rheological gel-like behavior (weak solid) at ambient temperature, although the gelation temperature is much higher (93°C). The other systems achieve the limiting slopes of one and two for the loss and storage modulus, respectively.

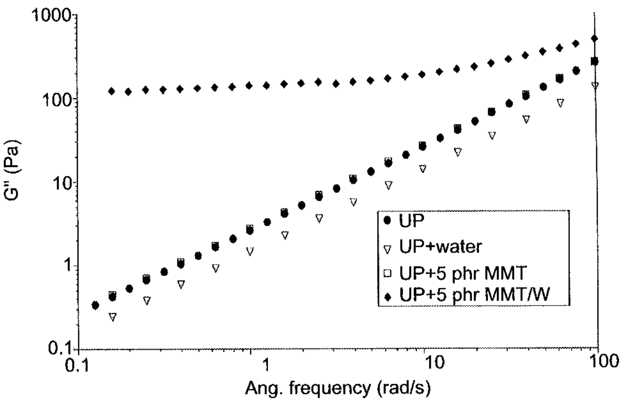

Figure 6 Viscous modulus as a function of frequency for the systems shown in Figure 4 T=25°C.

3.6. XPS

X-Ray photoelectron spectroscopy (XPS) is a convenient tool for surface analysis. Data obtained hereby provide information about the chemical constitution and bonding of the surface elements. Generally, only photoelectrons generated within the outermost 10 nm surface layer are detected. The C1s peaks of organic polymers have energies ranging from 284.7 eV for aromatic CH to 290.4 eV for the OCOO carbon [15]. As shown in Figure 8(A) (UP), the C1s spectrum is composed of a main peak at 284.6 eV and three small peaks at 285.4, 286.6 and 288.6 eV. The spectra of the samples results from contributions assigned to the C-H aromatic carbon, CH_2 aliphatic carbon at 284.6 eV, C-O carbon at 285.4 eV, and the C=O carbon at 288.8 eV. Slight changes in the relative peak areas (0.8%) of the UP as compared to UP-MMT [Figure 8(B)] were observed, revealing interactions between the C=O···HO and C-O···HO groups. These changes are more evident in the UP-MMT/W system with added clay slurry [Figure 8(C), up to 1.1%] attributed to UP resin hydrogen bonds between the UP functional groups and hydroxyl groups at the clay edges.

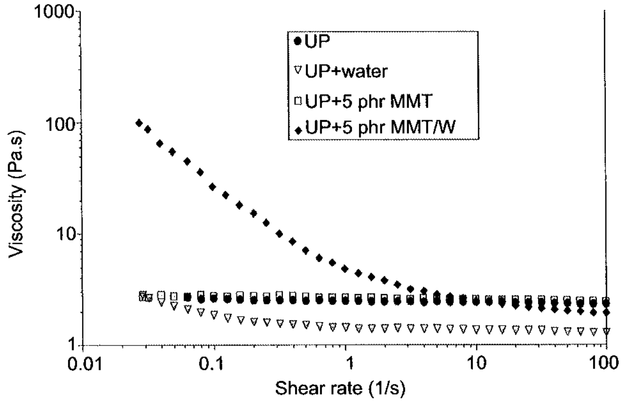

Figure 5 Shear viscosity vs. shear rate for various UP systems. Data taken at 25°C.

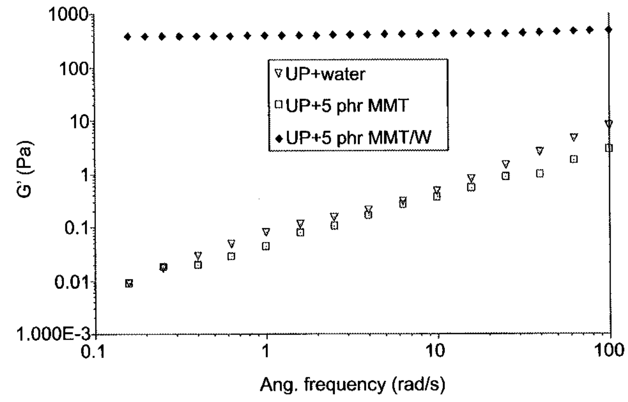

Figure 7 Elastic modulus as a function of frequency for the systems shown in Figure 4 T=25°C.

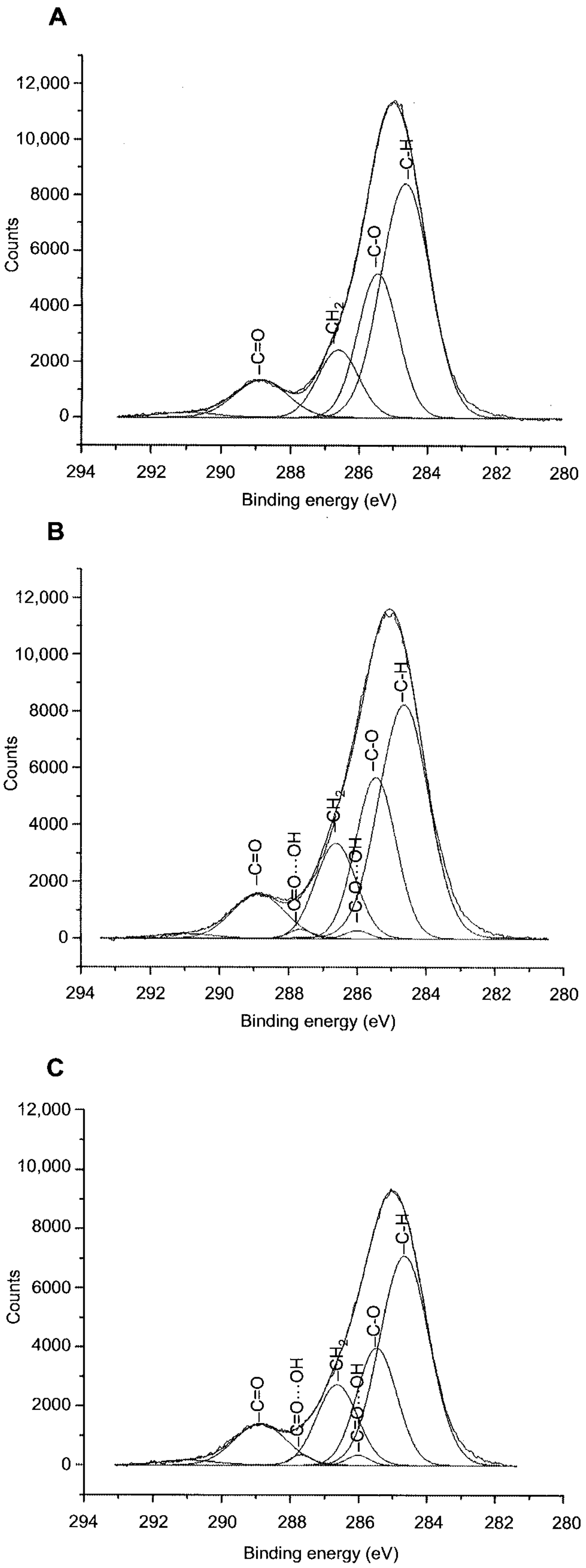

Figure 8 X-Ray Photoelectron Spectroscopy (XPS) of the samples: (A) UP; (B) UP-MMT; and (C) UP-MMT/W.

4. Conclusions

The procedure to obtain nanocomposites, based on unsaturated polyester resins-clay slurry illustrated in this work, leads to improvements of the order of 120% in the flexural modulus and 14% in flexural strength for UP-MMT/W (with 5 phr of clay slurry content). Thermal stability augments and the gelation temperature increases 17°C, as compared to that of the resin. It is apparent that the addition of water to MMT clays allows better intercalation of polymer chains in the inter-lamellar space. Because clay is first suspended in water, and this improves dispersion and distribution of the particles in the resin matrix, longer gelation times lead to more uniform and mechanically stronger structures. As observed, UP-MMT/W showed a shear-thinning viscosity, the presence of yield stress and moduli behavior indicative of a gel-like structure arranged between clay and polymer. XPS determinations evidenced interactions arising between the carboxyl groups of the resin and hydroxyl groups at the clay edges.

Acknowledgements

We acknowledge the financial support from the project IN116510 (DGAPA-UNAM) and a PhD grant (202517) from CONACYT. Also, authors wish to thank E. Sánchez, E. Fregoso. M. Canseco, O. Novelo, A. Tejeda and L. Huerta for their work in the mechanical, thermal, morphological, rheological, DRX and XPS measurements, respectively.

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