Research paper

Sodium montmorillonite modified with methacryloxy and vinylsilanes: Influence of silylation on the morphology of clay/unsaturated polyester nanocomposites

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Unsaturated polyester resins are widely used in the automotive, construction and naval industries. To further widen their application, they may be combined with clay minerals, which are advantageous due to their thermal, barrier, inflammability and stiffness characteristics. In order to avoid agglomeration and improve the interaction of Cloisite® Na + montmorillonite (Mt) with an unsaturated polyester matrix, this study focused on clay minerals modified with compatible silanes, vinyltriethoxysilane (VTES) and γ-methacryloxypropyltrimethoxysilane (MPS), and their use in composites in comparison with nanocomposites prepared using commercial clays (Cloisite® 30B and Cloisite® 15A). Functionalization of Cloisite® Na with MPS and VTES was confirmed by the appearance of characteristic infrared bands and the increase in the basal spacing. The nanocomposites containing silane-modified clays prepared in hydro-alcoholic solution showed the best result compared with ethanol solution. The presence of iron changed the color of the CNa and C30B samples and all of those prepared with silane modified Na-Mt-clays.

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1. Introduction

Montmorillonite (Mt) is a 2:1 clay mineral composed of aluminosilicate layers with exchangeable, hydrated cations in the interlayer spaces. Each aluminosilicate layer consists of two Si–O tetrahedral sheets sandwiching an Al–OH or Al–O octahedral sheet by means of –Si–O–Al–O–Si– bonds. Isomorphous substitution in the Mt layers generates a net negative surface charge on the layers, which is balanced by exchangeable inorganic cations (e.g., Na⁺, Ca2⁺, and Mg2⁺) (Bergaya and Lagally, 2013; Wu et al., 2014; Zhu et al., 2015). Mt is the most popular among the 2:1 layered silicates used in thermoset nanocomposites due to its high aspect ratio, high expansion capacity between layers, abundance and low cost (Silva et al., 2011).

Regarding thermoset composites, unsaturated polyester resins and fibers are already widely applied in the automotive, construction and naval industries (Chieruzzi et al., 2013). For instance, if combined with clay minerals that promote thermal, barrier and flammability-control characteristics, these resins may be used to produce multifunctional three-component composites, and their performance optimization would enhance their range of applications even further (Thostenson et al., 2005). Resin transfer molding (RTM) is one of the most common processes used by the automotive industry to produce glass fiber composites. In order to obtain a well-dispersed three-component composite, the affinity between Mt and the unsaturated polyester (UP) matrix is vital.

Organic ammonium or phosphorus salts are commonly incorporated in the clay structure through cation exchange within the interlayer space (e.g., for Na⁺ and Ca2⁺). This modification enables improvement of dispersion and interaction of the clay with the polymeric matrix, allowing the preparation of high-performance composites (Bordes et al., 2009; Silva et al., 2011; Thostenson et al., 2005). However, it cannot provide an effective clay/polymer matrix bond and, depending on the processing temperature, it may even degrade the quaternary ammonium salt through the well-known Hofmann degradation (Silva et al., 2011). Another possibility for the chemical modification comprises functionalization of clay and silanes, which interacts with the polymeric matrix through reactions with clay mineral OH groups, which are located at the edges and at the structural defects situated at the external surfaces at the interlayer. In this last case, it is possible to increase the interlayer spacing of a clay mineral (Gianni et al., 2008; Silva et al., 2011). Successful silylation depends on the reactivity of clay surfaces (e.g., density of surface hydroxyls) (He et al., 2013), the
silane characteristics (e.g., number of functional groups and configuration) (Piscitelli et al., 2010; Salon and Belgacem, 2010), and the reaction conditions, e.g., polarity of the solvent (Posthumus et al., 2004; Su et al., 2013), time (Daniel et al., 2008) and temperature (He et al., 2013).

Studies investigating modification of clay with different silanes have been performed by several researchers (Bertuoli et al., 2014; Daniel et al., 2008), among others. For example, Bertuoli et al. (2014) studied the modification of Mt with γ-aminopropylsilane (APS) using different dispersion media. The grafting of the silane was more predominant in water and hydro-alcoholic solution compared to tetrahydrofuran and ethylene glycol solutions. Daniel et al. (2008) examined the edge modification of laponite with dimethyl-oxymethoxysilane. According to the authors, the amount of grafted silane increased for higher silane to clay ratio and maintaining the reaction mixture for less than 24 h to avoid removal of grafted silane due to equilibrium effects.

However, few studies have focused on clays modified with polyester compatible silanes, for example vinyltriethoxysilane (VTES) and methacryloxypropyltrimethoxysilane (MPS). For instance, a study performed by Albdiry and Yousif (2013) in polyester resin and halloysite nanotubes (HalNT) untreated and treated with vinyltrimethoxysilane (VTMS) showed lower specific wear rate compared with those without treatment. The VTMS and the HalNT were prepared in ethanol/water solution, mixed together for 2 h at 60 °C, filtered, oven-dried, ground and sieved. To the best of our knowledge, no study has evaluated the silylation of sodium montmorillonite modified with methacryloyloxy and vinylsilanes and their influence on the morphology of two-component UP matrix nanocomposites. This has encouraged the development of the clay silylation methodology based on those studies already discussed, but varying the silane functionality (methacryl and vinyl) and the dispersion media (ethanol–water and ethanol), in order to achieve an ideal silane modified Mt-clay to apply, in future studies, in multifunctional three-component clay/polymer/glass fiber composites prepared by RTM.

The present work investigates the modification of sodium montmorillonite with γ-methacryloxypropyltrimethoxysilane (MPS) and vinyltriethoxysilane (VTES) to obtain polyester/silane-modified montmorillonite nanocomposites focusing on their morphological comparison with composites prepared with commercial Cloisite 30B and Cloisite 15A clays.

2. Experimental

2.1. Materials

Montmorillonite clays Cloisite® Na⁺ (Na-Mt), Cloisite® 30B (30B-Mt) and Cloisite® 15A (15A-Mt) were purchased from Southern Clay Company Products. The unsaturated orthophthalic polyester resin UCEFLEX UC 5530-M (styrene content up to 45 vol.% and viscosity at 25 °C of 90–120 cP) was provided by Elekeiroy S.A., the initiator methyl-ethyl-ketone peroxide in diisobutyl phthalate (Butanox LPT) was purchased from Akzo Nobel and the accelerator dimethylaniline (DMA) was purchased from Rudnik. The vinyltriethoxysilane (VTES) and γ-methacryloxypropyltrimethoxysilane (MPS) were purchased from Aldrich. The chemical structure of the silanes is shown in Fig. 1.

2.2. Preparation of the clay modified with ethanol–water or ethanol solution

Silane (5 g) and anhydrous 99% ethanol (200 mL) were mixed by magnetic stirring for 1 h. Cloisite® Na⁺ clay (10 g) was dispersed into ethanol P.A. (150 mL)/distilled water (150 mL) solution by mechanical stirring for 40 min at 750 rpm. Both the silane solution and the clay dispersion were then mixed (final ethanol/water ratio of 70:30) and kept under magnetic stirring for 24 h at 60 °C. The ethanol:water ratio of 70:30 was chosen based on the results obtained by Salon and Belgacem (2010), who concluded that for VTES and MPS, higher water amount decreased the hydrolized species, thus producing condensed structures. The reported optimum amount of water in hydro-alcoholic solutions was 20% for MPS and 40% for VTES.

After mixing for 24 h at 60 °C, the modified clay was vacuum filtered on a Buchner funnel with a sintered glass filter plate (porosity 4, 10–16 μm) and washed with ethanol to remove excess silane. A similar process was performed with the samples prepared with a pure ethanol solution. The only difference was that the clay was dispersed in 300 mL of ethanol solution PA in the first stage of preparation. The modified clay was oven-dried for 10 h at 100 °C, ground and sieved (325 mesh). The modified Na-Mt was denoted according to the silane and solvent used in the silylation, i.e., Na-Mt-VTES(E/A) was prepared with VTES silane in ethanol/water solution.

2.3. Preparation of the nanocomposites

The clays were oven-dried for 60 min at 100 °C and then added to the polyester resin (3 wt.%). Homogenization was performed by mechanical stirring at 750 rpm for 40 min followed by three sonication cycles (at 20% amplitude) for 10 min under magnetic stirring, and finally degassing for 20 min at 25 °C and 0.4 bar in a vacuum oven. The filled resin was transferred to a mold and left to cure for 24 h at room temperature (20–25 °C) and post-cured for 6 h at 80 °C and then 2 h at 120 °C. The nanocomposites were denoted according to the clay used, i.e., CNa-VTES(E/A) and CNa-MPS(E/A) were prepared with silane-modified clays, C30B and C15A with Cloisite 30B and Cloisite 15A commercials organic-modified clays, respectively, and CNa was prepared with commercial Cloisite® Na⁺.

2.4. Characterization

Thermogravimetric analysis (TGA — Shimadzu TGA-50) was performed at a heating rate of 10 °C·min⁻¹ with nitrogen gas flow (50 mL·min⁻¹) between 25 and 900 °C. The amount of grafted and intercalated silane was calculated according to Eq. (1):

\[ \text{Silane grafted amount (mequiv/g)} = \frac{10^2 \times W_{200-600}}{\left(W_{200-600} \times 400 - W_{200-600}\right) \times M} \]  \hspace{1cm} (1)

where \( W_{200-600} \) corresponds to the weight loss between 200 and 600 °C and M (g·mol⁻¹) is the molecular weight of the grafted silane molecules (Piscitelli et al., 2010). The percentage of grafted silane, which corresponds to the percentage of organic silane moieties with respect to the total inorganic mass (Piscitelli et al., 2010; Su et al., 2013), was calculated as follows:

\[ \text{Silane grafted amount(%) = } \frac{100 \times W_{200-600}}{W_{200-600}} \]  \hspace{1cm} (2)

Fourier-transform infrared spectroscopy (FTIR — Nicolet IS10-Thermo Scientific) was performed in the 400–4000 cm⁻¹ range using
the KBr pressed disc technique (5 mg of sample and 95 mg of KBr). For each sample 32 scans were recorded with a resolution of 4 cm⁻¹.

X-ray diffraction (XRD — diffractometer XRD 6000-SHIMADZU) was performed with copper source and operating at a scan rate of 2°·min⁻¹ and a step of 0.01°·s⁻¹, 40 kV and 30 mA in the 2θ range of 1.5–12°. The scatter and divergence slit used was 0.5° and a receiving slit of 0.15 nm. The distance between clay layers in the nanocomposites was estimated by following the characteristic reflection in the 1° < 2θ < 10° range and considering the thickness of the phyllosilicate sheet (9.6 Å) (Bertuoli et al., 2014).

Color values of the nanocomposites were determined with a spectrophotometer (Konica Minolta — CM-2500D). The chromaticity coordinates L*, a* and b* were collected and reflectance curves versus the wavelength were plotted. In L*, a* and b* color space, L* indicates lightness, its value extended from 0 (black) to 100 (white), and a* and b* are the chromaticity coordinates, that is, +a* is the red direction, −a* is the green direction, +b* is the yellow direction and −b* is the blue direction. The center is achromatic, and as the a* and b* values increase and the point moves out from the center, the saturation of the color increases (Korifi et al., 2013).

Transmission electron microscopy was performed using JEOL JEM 1200ExII microscope at an accelerating voltage of 80 kV. The samples were cut by ultramicrotomy with a diamond knife for a final thickness of 50–70 nm. The CNa, C15A and C30B nanocomposites elements were analyzed by Energy Dispersive Spectroscopy (EDS) and performed using a Leo 1450 VP SEM apparatus operating at 20 kV. The nitrogen-fractured samples were gold-sputtered prior to SEM observation.

3. Results and discussion
3.1. Silylation of the clays

The FTIR analysis of the Na-Mt, Na-Mt-MPS(E) and Na-Mt-MPS(E/A) clays and the MPS silane is shown in Fig. 2. For the Na-Mt clay, the band at 3630 cm⁻¹ corresponds to the stretching vibration of the hydroxyl groups bonded to aluminum atoms of the clay mineral (Gates, 2005). The broad band at 3440 cm⁻¹ and a sharp band at 1645 cm⁻¹ are assigned to hydroxyl stretching and H–O–H bending vibrations, respectively, of the free and interlayer water molecules on montmorillonite clay, and the band at 1050 cm⁻¹ is associated with the stretching vibrations of the Si–O and Si–O–Si groups (Bertuoli et al., 2014; Mishra et al., 2012). For the MPS silane, the band at 1630 cm⁻¹ is related to the C≡C stretching vibration and the band at 1720 cm⁻¹ is related to the C=O stretching vibration. Finally, the bands in the 1070–1100 cm⁻¹ range are associated with the stretching vibrations of Si–O–Si groups (Mishra et al., 2012; Posthumus et al., 2004).

In relation to the Na-Mt-MPS(E/A), functionalization was evidenced by the 2955 and 2895 cm⁻¹ bands, related to the asymmetric stretching of the CH₃ and the stretching of the CH₂ groups of the silane (Mishra et al., 2012; Park et al., 2009). However, low intensity bands at 2926 and 2854 cm⁻¹, corresponding to the antisymmetric and symmetric stretching vibrations of CH₂ (Shen et al., 2007), are found for both Na-Mt-MPS(E/A) and Na-Mt-MPS(E) samples, implying the presence of silane in both samples, but with increased grafted MPS silane for those prepared in hydro-alcoholic solution.

![Fig. 2. FTIR spectra of the Na-Mt, Na-Mt-MPS(E) and Na-Mt-MPS(E/A) clays and the MPS silane.](image-url)
The shoulder at 1700 cm\(^{-1}\) (highlighted) and the band at 1720 cm\(^{-1}\) are due to the presence of the C=O functional group of the MPS (Park et al., 2009), being the one at 1720 cm\(^{-1}\) more pronounced for Na-Mt-MPS\(_{(E/A)}\) sample than for the Na-Mt-MPS\(_{(E)}\) sample. The increase in intensity at 1050 cm\(^{-1}\) is related to the stretching vibration of Si–O–Si. The bands at 523 cm\(^{-1}\) and 467 cm\(^{-1}\) related to the bending vibration of and Si–O–Si and Si–O–Al showed increased intensity for the Na-Mt-MPS\(_{(E/A)}\) and, according to Mishra et al. (2012), these observations suggest the successful grafting of the silane on the surface of the clay.

FTIR analyses of the Na-Mt, Na-Mt-VTES\(_{(E)}\) and Na-Mt-VTES\(_{(E/A)}\) clays and the VTES silane are shown in Fig. 3, in which the band intensity was very low, when compared with Na-Mt modified with MPS silane. The bands in the 2800–3063 cm\(^{-1}\) range refer to the C=H organic bonds (Yi et al., 2010) and the band at about 775 cm\(^{-1}\) is due to the symmetric stretching of the Si–O–Si bond (Eo et al., 1998) of the VTES, being more pronounced for the Na-Mt-VTES\(_{(E/A)}\), implying increased grafted VTES silane in this sample.

The 2960 cm\(^{-1}\) band is due to the asymmetric stretching vibrations of the aliphatic CH\(_3\) group (Yi et al., 2010), and the 1410 cm\(^{-1}\) band indicates the presence of C=C bonds in the modified clay (Dean et al., 2007). The increased intensities at 1050, 523 and 467 cm\(^{-1}\), as already discussed for the Na-Mt-MPS\(_{(E/A)}\) bands, confirmed graphitization of the VTES silane.

In all cases, intensities were more pronounced for the Na-Mt-MPS\(_{(E/A)}\) and Na-Mt-VTES\(_{(E/A)}\) in comparison with Na-Mt-MPS\(_{(E)}\) and Na-Mt-VTES\(_{(E)}\), respectively. The amount of incorporated silane and the swelling capacity of the clay are related to the surface energy of the solvent. According to Shanmugharaj et al. (2006), solvents with surface energy similar or lower than Mt (surface energy of 44 mN/m), such as ethanol (22 mN/m) and hydro-alcoholic solution (32 mN/m at 50 °C), can easily wet this clay, allowing the silane to interact with the hydroxyl groups present on the edges of the clay. On the contrary, solvents with high surface energy (e.g., water, 72 mN/m) show less significant interactions, thereby allowing silane to diffuse between the clay layers. This explains the more pronounced intensities for the modified Na-Mt-MPS\(_{(E/A)}\) and Na-Mt-VTES\(_{(E/A)}\) clays.

The TGA results of the Na-Mt modified with MPS silane (Fig. 4) show that, when the silane was functionalized, new stages of mass loss were observed in the range of 200 to 600 °C due to the evaporation and/or
decomposition of silane (He et al., 2005; Su et al., 2013). For the Na-Mt, the DTG curve displayed a peak at 646 °C related to the dehydroxylation of the Mt (He et al., 2005; Shen et al., 2007). A small weight loss (~1%) in the 200–550 °C region occurred due to water removal from the interlayer region (Daniel et al., 2008).

For the silane-modified clays, other stages of mass loss were observed within 200–600 °C. For the Na-Mt-MPS(E) clay, there was a peak around 335 °C due to the silanes covalently bonded to the edges of the clay and/or adsorbed on the clay surface (Su et al., 2013). The DTG curve of Na-Mt-MPS(E/A) displayed a shoulder at 283 °C attributed to the loss of intercalated water in the clay or silane bound to the edges and surface of the clay, a peak at 403 °C due to intercalated silane between the clays and a shoulder in the 530–650 °C range due to silane covalently bonded to the clay (Piscitelli et al., 2010; Su et al., 2013). The mass loss related to dehydroxylation of Na-Mt (peak at 640 °C) decreased considerably, partly due to the consumption of hydroxyl groups with the silylation reactions (Su et al., 2013), but also due to the presence of a new species in the Na-Mt.

The Na-Mt-VTES(E/A) clay (Fig. 5) showed peaks at 350 °C and 580 °C related to the mass loss of the intercalated silane in the clay mineral layers, and related to the decomposition of the silane chemically bonded to the clay mineral layers, respectively (He et al., 2005; Shen et al., 2007), with a larger amount of grafted silane (6.4%) compared to Na-Mt-VTES(E) clay (Table 1). The Na-Mt-VTES(E) samples did not show significant differences in the DTG curve when compared with the Na-Mt sample and achieved a similar silane grafted amount as Na-Mt-MPS(E).

The silane-grafted amount was influenced by the solvent. For samples containing ethanol, the mass lost within 200–600 °C was similar for both MPS and VTES silanes. However, for samples that used hydro-alcoholic solution, the values increased considerably, especially for the Na-Mt-MPS(E/A) clay, corroborating the FTIR results. In the work of Bertuoli et al. (2014), aminopropyltriethoxysilane modified Na-Mt prepared in hydro-alcoholic ethanol/water (75:25) solution and in water (12.3%) showed a larger amount of grafted silane than those using ethylene glycol (6.1%) and THF (3.5%) solvents.

The Na-Mt-MPS(E/A) sample showed higher silane grafted amount than Na-Mt-VTES(E/A) silane. For example, increased water content in the solvent solution induced a reduction of hydrolyzed species producing condensed structures and the optimum amount of water–ethanol solution tested was 20% for MPS and 40% for VTES (Salon and Belgacem, 2010). Furthermore, the MPS silane showed lower reactivity in comparison with VTES silane, taking more time to hydrolyse and further condensation. For this reason, the combination of the conditions proposed in the methodology (e.g., pH, temperature and time) and the characteristics of MPS silane, e.g., number of functional groups and configuration (Fig. 1), were determinants for the success of MPS silylation.

In the XRD analysis of the clays (Fig. 6), Na-Mt displayed a reflection at 7.35° assigned to the (001) crystalline plane or basal spacing of the clay, reported also by other authors (Bertuoli et al., 2014; Piscitelli et al., 2010). The samples modified with MPS and VTES silanes in ethanol solution presented very similar reflection for both silanes, with some displacement to the left. Reflections at 5° and 6.7° were observed for the samples prepared in hydro-alcoholic solution, especially Na-Mt-MPS(E/A) and Na-Mt-VTES(E/A) samples indicating a significant expansion of the interlayer space due to intercalation. The broadening of the curves are characteristic of a more disordered structure (Tjong, 2006), and the presence of two reflections for Na-Mt-MPS(E/A) and Na-Mt-VTES(E/A) samples indicates two families of modified Na-Mt with different interlayer space. This could be related to distinct interactions between the silane and the clay mineral structure, as previously demonstrated by Bertuoli et al. (2014). This could justify the presence of two distinct stages of

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass loss (%) 200–600 °C</th>
<th>Silane grafted amount (%)</th>
<th>Silane grafted amount (mequiv/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Mt-MPS(E)</td>
<td>3.0</td>
<td>3.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Na-Mt-MPS(E/A)</td>
<td>18.4</td>
<td>22.6</td>
<td>0.9</td>
</tr>
<tr>
<td>Na-Mt-VTES(E)</td>
<td>3.0</td>
<td>3.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Na-Mt-VTES(E/A)</td>
<td>6.1</td>
<td>6.4</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Fig. 5. TGA of the Na-Mt, Na-Mt-VTES(E) and Na-Mt-VTES(E/A) clays.

Fig. 6. XRD analysis of the silane-modified clays.
mass loss in TGA analysis, which were less pronounced for the samples modified with silanes in ethanol solution.

According to He et al. (2013), for expanded clays, all inner surfaces (interlayer region), external surfaces and edges are prone to grafting with silanes. However, successful grafting may not increase the basal spacing if the edges and external surfaces of the clays are the most reactive sites. Considering that the length of the silane chain of γ-MPS is 1.0–1.1 nm (Isoda et al., 2000), and the interlayer space height of Na-Mt is ≈0.24 nm (2.4 Å), the silane modification in Na-Mt-MPS increased the interlayer space to 0.30 nm (Table 2). In this situation, silane appears to have attached to the edges or to the clay surface, as expected based on the TGA results and furthermore, MPS could be responsible for an increased interlayer space if there are flat lying silane chains. Similar conclusions can be drawn for the Na-Mt-VTES clay.

For the Na-Mt-MPS(E/A) and Na-Mt-VTES(E/A), a reflection at ~5° suggests an increase in basal spacing from 12 Å (Na-Mt) to ~13 Å and 17.7 Å (close to 18.3 Å found for 30B-Mt), corroborating the TGA results in which the silane may now be intercalated and/or graphitized between the clay layers. These results relate with those reported for aminopropylsilane (APS), that is, an increase in d001-value from 12 Å to ~20 Å (Bertuoli et al., 2014; Piscitelli et al., 2010).

### 3.2. Preparation of the nanocomposites polyester/clays

The diffractograms for the nanocomposites with different clays are shown in Fig. 7. Incorporation of the silane into the sodium clays slightly shifted the (001) reflection to the left in comparison with the Na-Mt clay (Table 2), and lower 2θ values were found for the samples prepared in ethanol/water solution, confirming the previous clay results. The best result was found for CNa-MPS(E/A) due to the presence of a reflection shoulder between 4° and 5°, different from the CNa-VTES(E/A) sample (reflection at ~5.7°). The nanocomposites with C30B and C15A showed lower 2θ values when compared with those with silane-modified clays. The reflection at ~2.3° for C15A indicates an intercalated structure. In this case, the appearance of the second reflection at ~4.6° is attributed to the (002) crystalline plane (Bertuoli et al., 2014).

In the TEM micrographs for CNa, CNa-MPS(E/A), CNa-VTES(E/A), C30B and C15A nanocomposites, the chemical silane treatment on CNa sample contributed to the rearrangement and delamination of the clay particles in the unsaturated polyester matrix. Besides, the difference between untreated (Fig. 8.1) and MPS and VTES silane-treated particles (Fig. 8.2 and 8.3) indicates that substantial clusters of pristine CNa agglomerates have been separated due to the silane treatment. Nevertheless, the presence of tactoids was, in general, more pronounced in silane-modified clays. According to the XRD results, the C30B sample presented a shoulder around 2°–3°, possibly due to the intercalated structure as confirmed by TEM analysis (Fig. 8.4), and C15A a reflection at 2.3°, evidencing an organized intercalated structure (Fig. 8.5).

Reflectance curves as a function of the wavelength for the various nanocomposites and a distinct profile are seen for C15A nanocomposites in Fig. 9. Different clays have different chemical structures and different cation concentrations, which explains the different colors obtained for these samples. The montmorillonite containing only Si, Al, Mg, O and H ions has a colorless unit cell, the exchangeable cation

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### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>2θ (°)</th>
<th>d001-Values (Å)</th>
<th>Interlayer space (Å)</th>
<th>Sample</th>
<th>2θ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Mt</td>
<td>7.3</td>
<td>12.0</td>
<td>2.4</td>
<td>CNa</td>
<td>~6.3</td>
</tr>
<tr>
<td>Na-Mt-MPS(E)</td>
<td>~7.0</td>
<td>12.6</td>
<td>3.0</td>
<td>CNa-MPS(E)</td>
<td>~5.7</td>
</tr>
<tr>
<td>Na-Mt-MPS(E/A)</td>
<td>6.7–4.9</td>
<td>13.1/17.7</td>
<td>3.5/8.1</td>
<td>CNa-MPS(E/A)</td>
<td>Shoulder 4.0–5.0</td>
</tr>
<tr>
<td>Na-Mt-VTES(E)</td>
<td>~7.0</td>
<td>12.6</td>
<td>3.0</td>
<td>CNa-VTES(E)</td>
<td>~5.7</td>
</tr>
<tr>
<td>Na-Mt-VTES(E/A)</td>
<td>6.7–5.0</td>
<td>13.0/17.7</td>
<td>3.4/8.1</td>
<td>CNa-VTES(E/A)</td>
<td>~5.3</td>
</tr>
<tr>
<td>30B-Mt</td>
<td>4.8</td>
<td>18.3</td>
<td>8.7</td>
<td>C30B</td>
<td>5.3</td>
</tr>
<tr>
<td>15A-Mt</td>
<td>2.7</td>
<td>33.0</td>
<td>23.4</td>
<td>C15A</td>
<td>2.3</td>
</tr>
</tbody>
</table>

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**Fig. 7.** Diffractogram of the nanocomposites prepared with different clays.

**Fig. 8.** TEM of the (1) CNa, (2) CNa-MPS(E/A), (3) CNa-VTES(E/A), (4) C30B and (5) C15A samples with (a) 60 k, (b) 100 k and (c) 400 k magnification.
values, followed by the samples modified with MPS and VTES, and the lowest values were found for CNa.

The values of L*, a* and b* for the nanocomposites are shown in Table 3. According to Fornes et al. (2003), there is a strong correlation between the L* parameter and the degree of organoclay exfoliation in polymer matrix nanocomposites. The CNa-MPS(E/A) sample showed very close L* values compared with C30B, followed by CNa-VTES(E/A), CNa-MPS(E) and CNa-VTES(E). The lowest L* value was found for CNa sample. These findings corroborate the XRD results, in which the reflection values for the nanocomposites (Table 2) followed a similar trend.

The C15A showed positive a* and b* values, indicating yellow color, and the other nanocomposites showed negative a* and positive b* values, resulting in green color. The nanocomposites were also analyzed by Energy Dispersive Spectroscopy (EDS), and those containing commercial clays (CNa, C30B) showed the presence of iron, while the C15A sample did not show (Table 4). For this reason, the presence of iron changes the color of the resulting nanocomposites. It is possible that the difference in the iron amount is due to the different batches of raw material used to prepare the organic modified clay. Another possibility is the autotransformation mechanism (Rhodes and Brown, 1995) responsible for the migration of metal ions from the lattice to exchange sites. Furthermore, the silane-modified samples displayed a color similar to C30B.

In all cases, the results were more pronounced for samples prepared in ethanol/water solution compared to those prepared with ethanol solution. Solvents with high surface energy, such as water, show less significant interactions with the edges of the clay due to the low-wetting phenomena, thereby causing the silane to diffuse between the clay platelets.

The nanocomposites containing silane-modified clays and prepared using hydro-alcoholic solution showed the best results (intercalated and exfoliated structure). However, they displayed tactoids, which were less evident in the Cloisite 30B and Cloisite 15A nanocomposites (intercalated and exfoliated structure). The variation in L* spectroscopy parameter was related to the state of clay dispersion and corroborated the XRD results. Finally, the presence of iron changed the color of CNa, C30B and of all nanocomposites prepared with silane modified Na-Mt clays.

Acknowledgments

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Eo, Y.J., Kim, D.J., Bae, B.S., Song, K.C., Lee, Y.T., Song, S.W., 1998. Coating of tetrahydrofuransilicate (TEOS)/vinyltriethoxysilane (VTES) hybrid solution on poly


Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNa</td>
<td>39.19</td>
<td>-21.41</td>
<td>5.90</td>
<td>Colorless</td>
</tr>
<tr>
<td>CNa-MPS(E)</td>
<td>53.43</td>
<td>-5.35</td>
<td>16.19</td>
<td>Colorful</td>
</tr>
<tr>
<td>CNa-MPS(E/A)</td>
<td>58.80</td>
<td>-5.61</td>
<td>18.14</td>
<td>Silicate</td>
</tr>
<tr>
<td>CNa-VTES(E)</td>
<td>51.90</td>
<td>-9.77</td>
<td>17.50</td>
<td>Clay</td>
</tr>
<tr>
<td>CNa-VTES(E/A)</td>
<td>55.94</td>
<td>-6.24</td>
<td>17.22</td>
<td>Organoclay</td>
</tr>
<tr>
<td>C30B</td>
<td>58.91</td>
<td>-5.82</td>
<td>23.79</td>
<td>White</td>
</tr>
<tr>
<td>C15A</td>
<td>65.52</td>
<td>1.07</td>
<td>30.30</td>
<td>Brown</td>
</tr>
</tbody>
</table>

4. Conclusions

In this study, the analyses carried out confirmed silane functionalization by the appearance of characteristic FTIR bands, by the percentage of grafted silane and by the increase in basal spacing. The Na-Mt-MPS(E/A) sample showed the best results, possibly due to the improved interaction between the methacryl group (MPS) and the vinyl group of the polyester resin, which was also responsible for a greater dispersion.

Table 4

<table>
<thead>
<tr>
<th>Element atomic (%)</th>
<th>CNa</th>
<th>C30B</th>
<th>C15A</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>32.91</td>
<td>57.97</td>
<td>80.03</td>
</tr>
<tr>
<td>O</td>
<td>47.30</td>
<td>32.1</td>
<td>18.41</td>
</tr>
<tr>
<td>Na</td>
<td>0.81</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Mg</td>
<td>0.50</td>
<td>0.31</td>
<td>–</td>
</tr>
<tr>
<td>Ca</td>
<td>0.25</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Si</td>
<td>12.91</td>
<td>6.83</td>
<td>0.40</td>
</tr>
<tr>
<td>Al</td>
<td>4.40</td>
<td>2.39</td>
<td>1.00</td>
</tr>
<tr>
<td>Fe</td>
<td>0.50</td>
<td>0.28</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 4. Nanocomposites CNa, C30B and C15A analyzed by Energy Dispersive Spectroscopy (EDS).

Fig. 9. Reflectance as a function of wavelength for the various nanocomposites.


