



## Research paper

## Preparation and characterization of montmorillonite modified with 3-aminopropyltriethoxysilane

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## ABSTRACT

The modification of montmorillonite clay mineral (Mt) was performed using the 3-aminopropyltriethoxysilane ( $\gamma$ -APS) silylation agent in different synthesis solutions. The modified products (S-Mt) were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectroscopy. The XRD demonstrated that silane was intercalated in the interlayer space of Mt due to the increase in basal spacing. The basal spacing shown by some S-Mts suggests the presence of a double layer of aminopropyl molecules in the interlayer space of the clay mineral modified in water and in a hydroalcoholic media at both synthesis temperatures (50 °C and 80 °C). The TGA revealed the presence of peaks in the range of 200 °C to 600 °C due to the presence of adsorbed silanes, intercalated silanes and silanes chemically bonded between the clay mineral layers and/or the edges. Evidence showed that the presence of water in dispersant is essential for intercalation of the silane in the interlayer space of the Mt such that the S-MMT<sub>water</sub>, S-Mt<sub>E/A(50)</sub> e S-Mt<sub>E/A(80)</sub> showed higher amount of silane and higher basal spacing in its structure. Qualitative evidence of the presence of  $\gamma$ -APS in the modified clay minerals was obtained by FTIR spectroscopy.

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## 1. Introduction

Montmorillonite clay mineral (Mt) is an inorganic phase frequently used to obtain polymeric nanocomposites due to its aspect ratio, capacity for swelling and ion exchange, softness, high solvent resistance, good mechanical strength and high capacity for delamination (Alexandre and Dubois, 2000; Bergaya and Lagaly, 2001; Paiva et al., 2008).

The structure of the Mt consists of two tetrahedral sheets of silica and a central sheet of alumina octahedrons, connected by oxygen atoms common to both sheets. The Mt has 1-nanometer-thick layers, stacked on each other and loosely bound by van der Waals forces, which allow the penetration of water and/or other polar molecules. To compensate for the negative charges generated by the isomorphic substitutions which occur in the tetrahedral and octahedral sheets of the Mt, exchangeable cations such as Na<sup>+</sup>, Ca<sup>2+</sup> and Li<sup>+</sup> are electrostatically fixed in the interlayer space of the clay minerals (Alexandre and Dubois, 2000; Paul and Robeson, 2008; Pavlidou and Papaspyrides, 2008; Ray and Okamoto, 2003).

The clay mineral in its natural state has a hydrophilic character and when added to a polymer matrix it tends to form agglomerates. This occurs because the surface energy of the clay mineral is greater than that of the polymer, generating a particle–particle interaction

(cohesion) stronger than the particle–polymer interaction (adhesion) (Zulfiqar et al., 2008).

To cause complete dispersion of the Mt in the polymeric matrix, it is necessary for the layers to be individually separated or exfoliated. Due to the high electrostatic attraction between the Mt layers and because the clay mineral has a surface energy greater than that of the polymer, it is necessary for the clay mineral to be modified organically to increase the interlayer spacing. This modification allows the intercalation of the polymer inside the interlayer space of the clay mineral. The modification procedure of the Mt in organically modified clay mineral is called cation exchange (Alexandre and Dubois, 2000; Paul and Robeson, 2008; Pavlidou and Papaspyrides, 2008; Ray and Okamoto, 2003).

Quaternary ammonium salts have been used during the cation exchange of the metal ions present in structure of the Mt, producing clay mineral with a hydrophobic character and a greater interlayer space (Bergaya and Lagaly, 2001; Paiva et al., 2008; Pavlidou and Papaspyrides, 2008). However, due to the quaternary ammonium salt degradation at high temperatures, the thermal instability of the organoclay becomes a strong limitation in the processing of clay mineral/polymer nanocomposites (Bikiaris, 2011; Wang et al., 2012; Xie et al., 2002). Therefore, the grafting reaction of the Mt with organosilanes has attracted interest from researchers (Guimarães et al., 2009; He et al., 2005; Park et al., 2009; Piscitelli et al., 2010; Shanmugaraj et al., 2006; Shen et al., 2007, 2009; Wu et al., 2012).

The grafting reaction is a reaction in which the molecule of the modifier is chemically bonded to the layers of clay mineral, providing new functions for the compound. The ion exchange is a reversible process,

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but the grafting reaction is an irreversible process because chemical bonds with a covalent character occur between the clay mineral surface and the molecules of the modifier compound (Wypych, 2004). The presence of water on the surface of the clay mineral causes the formation of silanol, allowing the silicon atoms present in the structure to bond chemically with the hydroxyl groups adsorbed on the surface (Gianni et al., 2008; Guimarães et al., 2009; Xie et al., 2010). Studies investigating the modification of the clay mineral with different types of silanes and different routes of synthesis have been performed by several researchers (Huang et al., 2011; Mishra et al., 2012; Park et al., 2009; Paul et al., 2011; Piscitelli et al., 2010; Shen et al., 2007; Yang et al., 2012).

The interaction of the clay mineral with the organosilane through the silanols facilitates the surface treatment of the Mt. The molecular bond of the silane with the clay mineral can occur on the external surface of the clay mineral without altering the basal spacing, or it may occur in the interlayer space and/or edges of the clay mineral, providing expansion of the basal spacing (He et al., 2005; Shanmugharaj et al., 2006).

In this work, we studied the modification of the Mt with 3-aminopropyltriethoxysilane ( $\gamma$ -APS) in different dispersion media using different functionalization conditions. X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectroscopy were employed to characterize the modified clay minerals.

## 2. Experimental

### 2.1. Materials

The materials used to accomplish the modification of the clay mineral were montmorillonite (Mt) Cloisite®Na<sup>+</sup> provided by Southern Clay Products, 3-aminopropyltriethoxysilane ( $\gamma$ -APS) with a purity of 99% provided by Aldrich Chemical Company, ethylene glycol (EG) provided by Nuclear, tetrahydrofuran (THF) provided by Nuclear and ethanol P.A. provided by Nuclear.

### 2.2. Clay mineral modified with silane

The modification of the Mt with  $\gamma$ -APS followed the procedure described by Shanmugharaj et al. (2006): 1 g of the Mt previously dried at 60 °C for 24 h was dispersed in 100 mL of solvent, and the dispersion was maintained under magnetic stirring until complete dispersion of the clay mineral. Separately, a solution with 1 g of  $\gamma$ -APS was dissolved in 100 mL of solvent. This solution was added to the dispersion containing the Mt.

For the THF, EG and distilled water, the clay mineral dispersion was stirred at 20 °C for 30 min. The solid was separated and dried at 60 °C for 24 h.

For the hydroalcoholic solution (25/75 by volume), the clay mineral dispersion was stirred for 8 h. One procedure was performed at 50 °C, and another was performed at 80 °C. The dispersion was left to stand for 1 h to separate out the solid, which was dried at 60 °C for 24 h.

The modified clay mineral samples (S-Mts) in various solvents – THF, ethylene glycol, distilled water and hydroalcoholic solution at 50 °C and 80 °C – were called S-Mt<sub>THF</sub>, S-Mt<sub>EG</sub>, S-Mt<sub>Water</sub>, S-Mt<sub>E/A(50)</sub> and S-Mt<sub>E/A(80)</sub>, respectively.

### 2.3. Characterization

XRD measurements of the samples of Mt and S-Mts were performed in a Shimadzu-XRD 6000 diffractometer, using copper as the source for generating X-rays with a  $K\alpha_1$ Cu wavelength = 1.54178 Å, a voltage of 40 kV, a current of 30 mA and a diffraction angle of  $2\theta$  scanning from 1° to 12°. The XRD experiment was performed with a step scan of 0.05°/5 s<sup>-1</sup>.

FTIR spectroscopy was performed on Nicolet IS10 Thermo Scientific equipment using the ATR technique, in the range of 400–4000 cm<sup>-1</sup>.

TGA was performed on Shimadzu TGA-50 equipment between 25 °C and 500 °C at a rate of 10 °C min<sup>-1</sup> with an inert gas flow of 50 mL min<sup>-1</sup> from nitrogen (N<sub>2</sub>) and from 500 °C to 800 °C in a synthetic air atmosphere. Using TGA data, it was possible to calculate the percentage of the loaded silane that corresponds to the percentage of silane molecules with respect to the total inorganic weight, using Eq. (1) (Piscitelli et al., 2010), where  $W_{200-600}$  is the percentage of lost weight between 200 °C and 600 °C.

$$\text{Silane loaded amount (\%)} = \frac{100 \times W_{200-600}}{100 - W_{200-600}} \quad (1)$$

## 3. Results and discussion

### 3.1. X-ray diffraction

The XRD patterns obtained for the Mt and the S-Mts are shown in Fig. 1. The significant increase in the interlayer space of the Mt was observed after the modification with silane. The Mt showed a peak at  $2\theta = 7.3^\circ$  corresponding to a basal spacing of 12.1 Å, in agreement with the values reported in the literature (Shanmugharaj et al., 2006; Shen et al., 2007, 2009). The incorporation of the  $\gamma$ -APS shifted the peak corresponding to the basal spacing  $d_{001}$  of the Mt to the left (lower values of  $2\theta$ ), indicating an increase in the basal spacing  $d_{001}$  of 12.1 Å for values of up to 20.5 Å, as shown in Table 1. The appearance of a second peak in some of the S-Mts is attributed to the (002) reflection (Su et al., 2012).

The S-Mts showed a basal spacing greater than the Mt, indicating that the silane molecules were intercalated or grafted in the interlayer region and/or at the edges of the clay (He et al., 2005; Piscitelli et al., 2010; Shanmugharaj et al., 2006; Shen et al., 2007).

According to Shen et al. (2007), the height of the interlayer space can be estimated with the basal spacing and the thickness of the sheet of phyllosilicate of 9.6 Å, calculated by Eq. (2).

$$\text{Interlayer spacing height (\AA)} = \text{Distance}(d_{001}) - 9.6 \text{ \AA} \quad (2)$$

The interlayer space of the Mt has a height of approximately 2.5 Å and can reach a maximum value of 10.9 Å after modification. Table 1 shows the values of the heights of the interlayer space for the S-Mts prepared in different media.

According to the literature (He et al., 2005; Shen et al., 2007, 2009), the height of the aminopropyl group is approximately 0.4 nm (4 Å). The basal spacing shown by some S-Mts suggests the presence of a double layer of aminopropyl molecules in the interlayer space of the clay

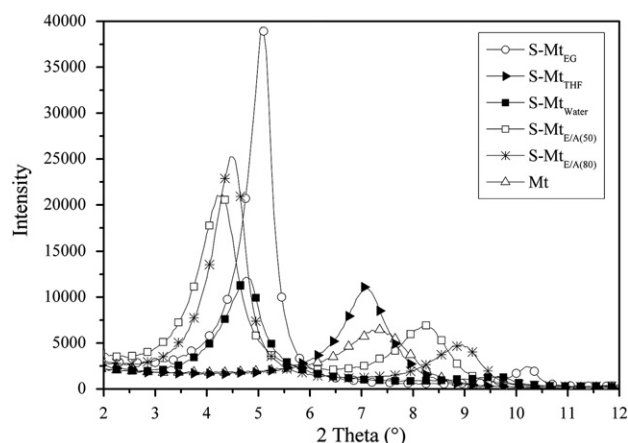


Fig. 1. Overlap of the X-ray diffractograms of the Mt and the S-Mts.

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