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Thermal and chemical treatments of montmorillonite clay

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Abstract

Montmorillonite clay from a natural deposit was processed to remove impurities and later submitted for thermal and chemical treatments. The sample was first subjected to a thermal treatment at 400 °C, for 1 h, to remove organic components. The chemical treatment was conducted first by using an acid attack with nitric acid and sulfuric acid, then, adding sodium acetate in ethylene glycol clay dispersion, and finally the clay was dispersed in xylene with subsequent addition of silane, N-(b-aminoethyl)-g-aminopropyil-trimethylsilane. The combined thermal and chemical treatment was found to have a significant effect on the final chemical composition of the nanoclay. X-ray diffraction patterns suggested that the combined thermal and chemical treatment resulted in increased interplanar distances, thus favoring exfoliation of the clay lamellae, which was also confirmed by SEM images. Fourier transform infrared (FTIR) spectroscopy analysis suggested that the combined thermal and chemical treatment resulted in removal of water from the montmorillonite, without any modification or destruction of the clay structure. Thus, the combination of thermal and chemical treatments proposed in this work may be a promising approach to process montmorillonite intended for the production of advanced materials.

Keywords: B. Impurities; C. Chemical properties; D. Clays; Raw materials

1. Introduction

Some materials are used as fillers for polymers to obtain composite materials, being applied from macro- to nanoscale. Some forms such as nanotubes, nanoparticles and nanoplatelets stand out among them. For example, carbon nanotubes display exceptional properties for specific applications. Nanotubes, however, have the disadvantage of being produced on a limited industrial scale at high prices. The addition of nanoparticles to polymers is already employed with beneficial results to their mechanical and physical properties.

Clays have been the most widely studied material used as nanofillers. This is partly due to the large natural reserves of these minerals and to many studies aiming at obtaining nanosized clays, which are increasingly mastered by researchers.

One major problem in studying and obtaining polymer/clay nanocomposites is the difficulty to achieve a high degree of exfoliation of the clay lamellae, which allows greater interaction with polymer matrices. In recent years, universities and industries have worked with various unconventional methods to facilitate the exfoliation of clays [1–9]. A strategy frequently adopted is to use organic additives to modify the clay surface, in an attempt to improve the compatibility between the hydrophobic polymer and hydrophilic clay, thereby facilitating clay exfoliation [10].

Among nanoclays, montmorillonite stands out, being classified as mineral clay, with lamellar structure of the smectite group belonging to family 2:1. It has elementary crystal forming structures consisting of layers of octahedra, with aluminum at the center and oxygen or hydroxyl at the vertices, between two tetrahedral layers, with silicon at the center and oxygen at the vertices [11].

Isomorphic substitutions of Al^{3+} by Mg^{2+} or Fe^{2+} can be observed in the octahedral structure, which generate a negative effective charge on their surface. This negative charge is compensated by the presence of cations in the interlayer space. Smectites are capable of accommodating water molecules or other polar molecules in the interlayer

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region, causing variation of the basal spacing, depending on the type of cation intercalated [12].

For better control of the intercalation of cations or molecules between layers, it is necessary to treat the montmorillonite clay with an attack of acids, thus promoting the removal of impurities from the clay surface and morphological changes in the montmorillonite structure [13]. These changes must not alter the crystalline structure of the mineral.

2. Experimental

2.1. Clay preparation procedure

A montmorillonite sample was initially screened on a 200 mesh sieve. After clay deagglomeration, a thermal treatment was performed, consisting of heating the sample up to 400 °C, at a heating rate of 5 °C/min, for 1 h. After this thermal treatment, the clay was submitted to a chemical attack with sulfuric and nitric acid, where 100 g of clay was dispersed in 800 ml of distilled water at 70 °C until complete dispersion occurred, adding 100 ml of sulfuric acid 98 wt%, stirring and controlling the temperature for 3 h, and then adding 100 ml of nitric acid 65 wt% under the same time and temperature conditions. The solution was kept at rest for 24 h. After this period, the clay sample was subjected to successive washes with distilled water until it reached pH 4. At the end of this process, the top and bottom phases were discarded, keeping only the clay between these two phases. The process of adding sodium to the clay was carried out by dispersing the clay in ethylene glycol with sodium acetate until homogenization, maintaining the temperature at 90 °C under magnetic stirring for 2 h. Soon after, the clay was dried in an oven with circulating air at 100 °C for 24 h, deagglomerated and heated again under magnetic stirring and the clay was dispersed in xylene. Then, silane, N-(b-aminoethyl)-g-aminopropyiltrimethylsilane was added under heating and magnetic stirring until total xylene evaporation occurred, leaving in the oven for more than 24 h. The resulting clay samples are described in Table 1.

The physical, chemical and morphological characterizations were carried out using X-ray diffraction (XRD), thermal analysis (TG), X-ray fluorescence (FRX), Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM).

Table 1
Nomenclature adopted for clay samples according to the process used.

Nomenclature	Treatments
Mont. Nat.	Natural montmorillonite
Mont. AA 400	Acid montmorillonite heated at 400 °C
Mont. AA 400 Na	Acid montmorillonite heated at 400 °C with sodium acetate
Mont. AA 400 Na Si	Acid montmorillonite heated at 400 °C with sodium acetate and silane

2.2. X-ray diffraction

X-ray diffraction experiments were conducted using a Shimadzu equipment model XRD-6000. Intensity *vs.* scattering angle (2θ) were recorded at room temperature in the range 2–75 (2θ), with a step size of 0.02° and scanning rate of 2°/min. X-ray diffraction experiments were conducted to evaluate the effects of treatments on the montmorillonite structure.

2.3. Thermal analysis

Thermogravimetric analyses were conducted on samples in various stages of the preparation procedure. Measurements were carried out with a BP model RB-3000, using a scan rate of 10 °C/min, over a temperature range from 25 to 1000 °C. Mass loss (in %) was calculated from the TG curve, based on the initial mass of the sample.

2.4. Chemical composition

Samples collected in the various stages of the preparation procedure were analyzed for chemical composition determination. Silicon content was determined using gravimetric analysis, while the content of other elements was determined by inductively coupled plasma optical emission spectrometry (ICP OES). The X-ray fluorescence analysis was performed by a semi-quantitative method. The equipment used was a Shimadzu model EDX 700.

2.5. FTIR

Fourier transform infrared (FTIR) spectroscopy analysis was performed on a Shimadzu equipment model IR Prestige-21 using absorbance mode, in the region of 400–4000 1/cm in KBr medium, and a proportion of 100 mg of 1% KBr sample.

2.6. SEM

Samples for scanning electron microscopy (SEM) were prepared and analyzed with a Shimadzu equipment model SSX-550, using an accelerating voltage VA of 20 kV.

3. Results and discussion

Fig. 1 shows X-ray diffraction results in accordance with the nomenclature previously mentioned in Table 1. This figure illustrates the changes promoted at each stage of the treatment, as well as treatment efficiency. Changes introduced by the treatment are observed by the main diffraction peak at 5.771°, corresponding to the interplanar spacing of 15.314 Å (Fig. 1a and Table 2). When the chemical and thermal processes are combined (AA Mont. 400), it was observed that with the removal of organic matter, there was an approximation of the montmorillonite lamellae, shifting the main peak to 9.212° corresponding to an interplanar

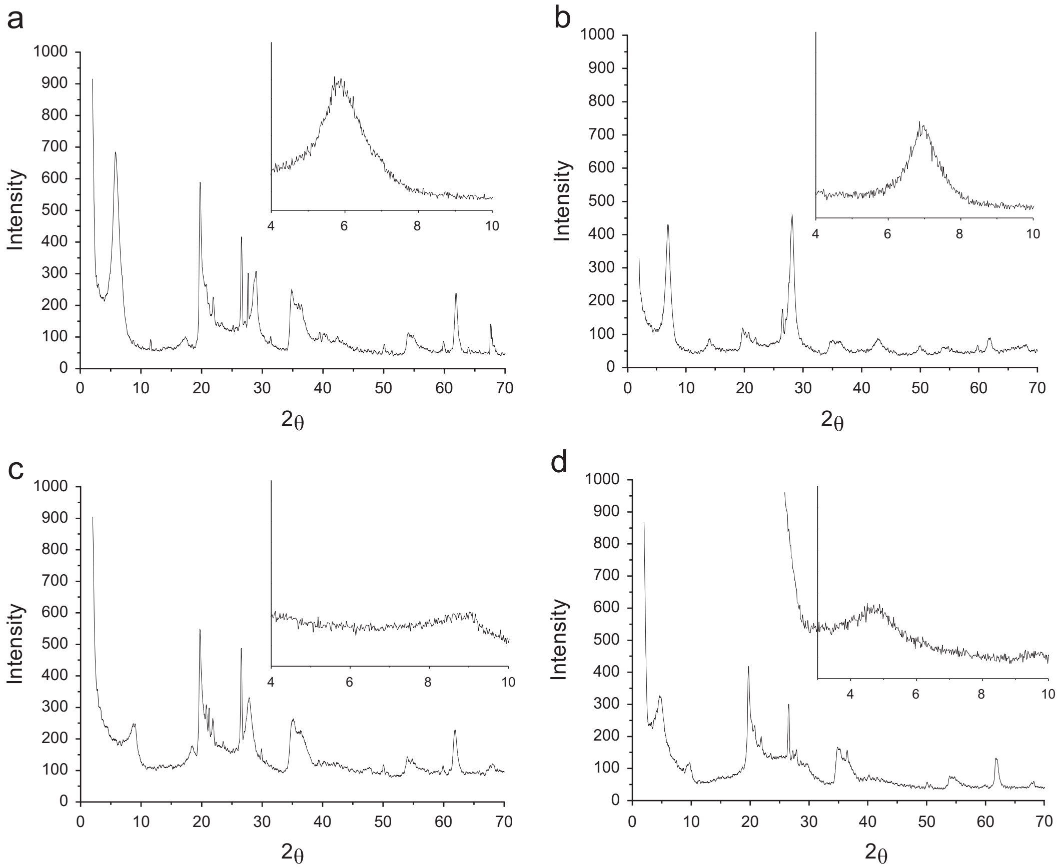

Fig. 1. XRD of clay samples: (a) natural montmorillonite, (b) acid montmorillonite heated at 400 °C, (c) acid montmorillonite heated at 400 °C with sodium acetate and (d) acid montmorillonite heated at 400 °C with sodium acetate and silane.

Table 2
Angles and changes of interplanar spacings of clays, both natural and chemically treated.

Samples	2θ (deg.)	Interplanar spacing d (Å)
Mont. Nat	5.771	15.314
Mont. AA 400	9.212	9.913
Mont. AA 400 Na	7.090	12.469
Mont. AA 400 Na Si	4.820	18.333

spacing of 9.913 Å (Fig. 1b and Table 2), suggesting an elimination of organic matter and water from the montmorillonite structure. When sodium acetate is added to the sample for combined treatment (Mont. AA 400 Na), the opposing phenomenon was observed, and the main peak shifted to 7.090°, reaching an interplanar spacing value of 12.469 Å (Fig. 1c and Table 2). After the incorporation of silane to the sample (Mont. AA 400 Na Si), the best result was obtained with the shift of the main peak to 4.820° and interplanar spacing of 18.333 Å (Fig. 1d and Table 2).

Although the chemical attack promoted the elimination of organic matter from Mont. Natural sample, the water existing in its structure was not removed by this treatment, as observed by thermogravimetry with 13% mass loss over the temperature range of 25–165 °C (Fig. 2). However, when chemical and thermal attacks are combined, the removal of water existing in the montmorillonite structure was clearly observed, with mass loss over the same temperature range dropping to a value lower than 4%. In the clay sample modified with silane (Mont. AA 400 Na Si), there was mass

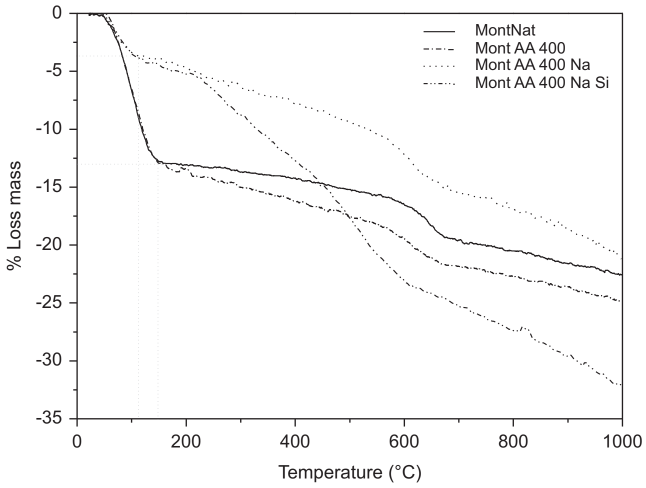

Fig. 2. TG analysis of clay samples, both natural and treated.

Table 3
Chemical composition of samples after each treatment.

Mont. Nat		**Mont. AA 400**		**Mont. AA 400 Na**		**Mont. AA 400 Na Si**	
Comp.	**%**	**Comp.**	**%**	**Comp.**	**%**	**Comp.**	**%**
SiO_2	61.60	SiO_2	51.94	SiO_2	49.75	SiO_2	47.21
Al_2O_3	20.96	Al_2O_3	33.35	Al_2O_3	30.9	Al_2O_3	22.61
Fe_2O_3	4.33	Fe_2O_3	2.58	Fe_2O_3	2.72	Fe_2O_3	2.55
CaO	1.38	CaO	0.18	CaO	0.15	CaO	0.12
MgO	2.44	MgO	2.79	MgO	2.36	MgO	1.60
Na_2O	1.25	Na_2O	–	Na_2O	1.07	Na_2O	0.88
SO_3	0.96	SO_3	0.73	SO_3	0.62	SO_3	0.50
K_2O	0.46	K_2O	0.33	K_2O	0.26	K_2O	–
TiO_2	0.36	TiO_2	0.26	TiO_2	0.27	TiO_2	0.22
ZrO_2	0.05	ZrO_2	0.05	ZrO_2	0.04	ZrO_2	0.03
LOI	**6.07**		**7.12**		**11.86**		**24.04**

LOI—loss-on-ignition.

loss over the temperature range of 200–600 °C, corresponding to the initial silane decomposition and another mass loss over the range of 610–1000 °C, corresponding to the final silane decomposition (Fig. 2).

Table 3 shows the results of the chemical analyses of the samples studied. Through comparison between Mont. Nat. and Mont. AA 400 samples, significant changes in the chemical composition of the Mont. AA 400 sample were observed such as reduction of SiO_2, confirming the elimination of quartz from the samples, reduction of Fe_2O_3 and CaO and complete elimination of Na_2O. In the Mont. AA 400 Na sample, the efficiency of this part of the process could be confirmed by introducing Na_2O in the clay. In Mont. AA 400 Na Si sample, despite a high reduction of SiO_2, the Si/Al ratio remained almost constant as compared with the Mont. Nat. sample, which confirmed the silane intercalation in the clay structure. The increased mass loss in all samples could be related to the elimination of organic matter. The loss on ignition (LOI) represents loss of water, hydroxyl groups from mineral clays, organic matter and carbonates [13]. For the samples studied, LOI showed values of 6.07% for Mont. Nat clay, 7.12% for Mont. AA 400 clay, 11.86% for Mont. AA 400 Na clay, and 24.04% for Mont. AA 400 Na Si clay. The highest LOI value was observed in the organically modified clay, indicating that silane was incorporated into the clay structure.

The spectrum infrared spectroscopy (FTIR) in Fig. 3 corresponds to pure clay and shows a typical band of OH stretching ($3634\,cm^{-1}$) absorbance. The broad bands at 3447 and $1640\,cm^{-1}$ can be attributed to water molecules adsorbed on the clay structure [15]. Bands of 1116, 1035 and $914\,cm^{-1}$ may be collectively allocated to the stretching and vibration of Si–O bonds [16]. The spectrum of the clay modified with thermal and chemical treatments shows the removal of water existing in the montmorillonite structure, without any modification or destruction of the clay structure, maintaining the same crystallographic pattern of the natural clay [10].

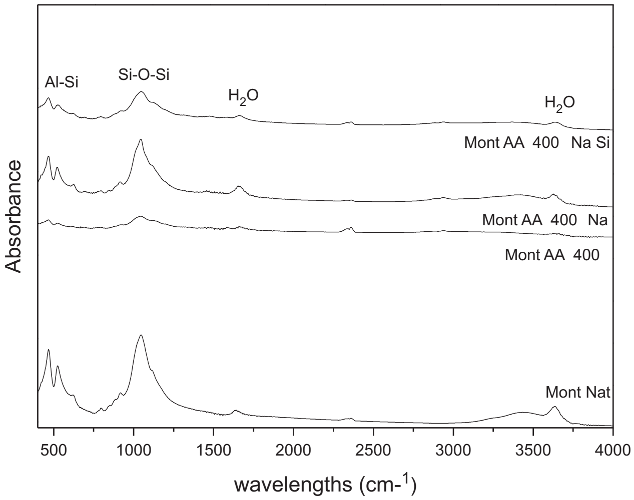

Fig. 3. FTIR analysis of clay samples both natural and treated.

Fig. 4 shows the scanning electron microscopy (SEM) analyses performed on samples with magnification of 10,000 ×. The micrograph of the Mont. Nat sample suggests a very cohesive clay, confirming that the material consists of micrometer-sized agglomerates composed of individual lamellae (Fig. 4a). The micrograph of the Mont. AA 400 sample shows the separation of some of these lamellae (Fig. 4b). This is due to the removal of organic matter and water existing within the clay structure, which contributes to reduce the effect of agglomeration. The micrograph of Mont. AA 400 Na sample confirms the X-ray diffraction of this sample, showing that the addition of sodium acetate in the clay structure promoted a new approximation in the clay lamellae (Fig. 4c). The micrograph of Mont. AA 400 Na Si sample confirms that the combination of thermal and chemical treatments, combined with the dispersion of silane into the clay, promoted a more refined exfoliation of the clay lamellae (Fig. 4d).

4. Conclusions

In this investigation, montmorillonite clay from a natural deposit was processed to remove impurities and later subjected to thermal and chemical treatments. The thermal treatment was conducted at 400 °C, for 1 h, followed by the chemical treatment which was conducted first by using an acid attack with nitric acid and sulfuric acid, then, adding sodium acetate with subsequent incorporation of silane. The characterization of the clay in various stages of the treatments was conducted by X-ray diffraction, thermogravimetry, Fourier transform infrared (FTIR) spectroscopy and X-ray fluorescence analysis. The results suggested that the chemical and thermal processes combined promoted the elimination of organic matter and water from the montmorillonite structure and resulted in increased interplanar spacing when compared to the natural montmorillonite clay, without any modification or destruction of the clay structure. Moreover, the elimination of quartz and incorporation

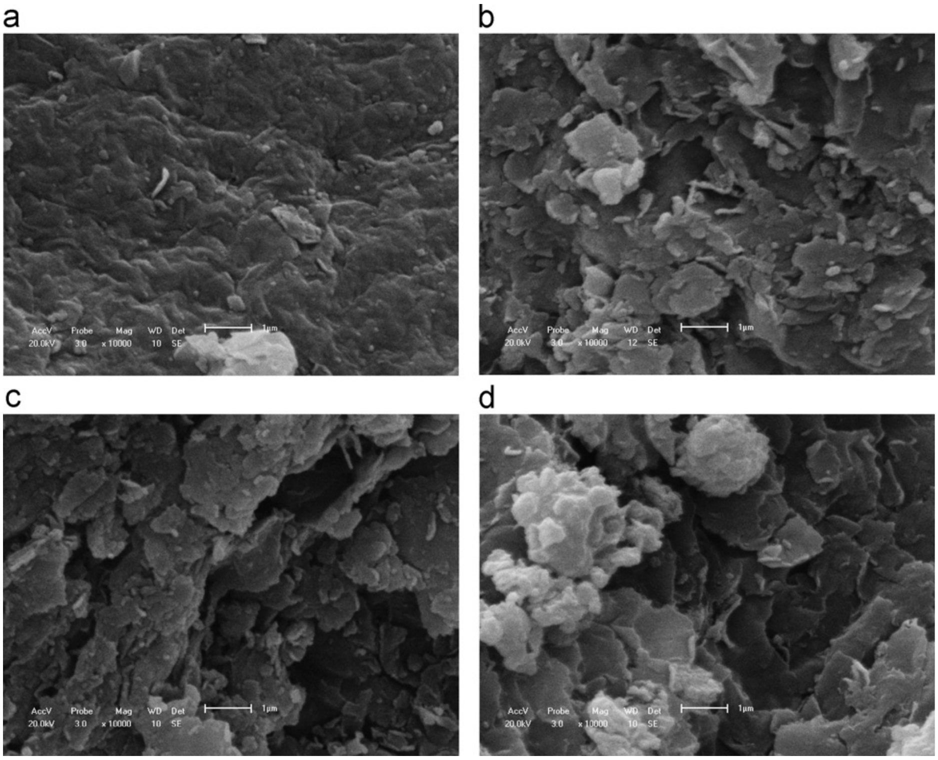

Fig. 4. SEM images of samples: a) Mont. Nat; b) Mont AA. 400; c) Mont. AA 400 Na; d) Mont. AA 400 Na Si.

of silane in the clay structure were confirmed. Therefore, the combination of thermal and chemical treatments of montmorillonite was found effective in removing impurities and promoting exfoliation of the clay lamellae.

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