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Ceramics International 36 (2010) 33–38

CERAMICS INTERNATIONAL

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Effects of thermal and chemical treatments on physical properties of kaolinite

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Received 10 November 2008; received in revised form 20 November 2008; accepted 26 June 2009
Available online 17 July 2009

Abstract

Kaolinite clay from a natural deposit was processed to remove impurities and submitted to thermal and chemical treatments. Based on thermogravimetry/differential thermal analysis data, the samples were submitted to a thermal treatment at 500 °C, for 8 h, to remove organic components and turn the clay color lighter. The chemical treatment was conducted first using hydrogen peroxide and then, an acid attack using nitric acid and sulfuric acid. Chemical compositions of the nanoclay after the chemical treatment indicated that the hydrogen peroxide treatment removed part of the organic matter without any other significant effect on the chemical composition of the clay, while the acid attack reduced significantly the contents of MgO, CaO and Fe_2O_3 turning the clay color lighter. A small increment in cation exchange capacity was also observed after hydrogen peroxide treatment and acid attack. BET surface area measurements indicated an increment in surface area after the thermal and chemical treatments. The thermal treatment produced only a slight increase in surface area, from about 35.3 to 37.8 m^2/g, while the chemical treatment using hydrogen peroxide promoted an increase in specific surface area from 35.3 to 53.0 m^2/g. The acid attack did not produce any further increment in surface area. X-ray diffraction patterns of the clay corresponding to various treatments proved that the chemical treatment did not affect the clay structure, while the thermal treatment favored the formation of an amorphous material. Thus, the chemical treatment of kaolinite proposed in this work may be a promising approach to process this clay for the production of advanced materials.

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

1. Introduction

Producing synthetic nanoparticles in large amounts for technological applications is not a simple task and may not be cost-effective for many applications. Thus, there is a special interest in nanoparticles obtained from natural deposits. Nanoclays are minerals, which have at least one dimension in the range of 1–100 nm. Interest in nanoclays for the production of polymer-based nanocomposites has increased significantly in recent years [1]. Many studies have indicated that the mechanical, thermal, and other properties of polymer matrices, such as dimensional stability, may be significantly improved by the incorporation of nanoclays [2–13]. These improvements in properties have been attributed to the very large specific surface area of the nanoparticles [12,13], which greatly affects their interactions with the polymer chains [14].

Montmorillonites (MMT) have very large surface areas – in the range of 750 m^2/g [6] – and thus, have been the subject of most studies involving clay nanocomposites. However, montmorillonite deposits worldwide are limited and often contain contaminants such as Fe-oxides, which may be detrimental to some of the nanocomposites properties. Alternatively, kaolinite is a more frequent material in earth and some of the natural kaolinite deposits present low contamination. Therefore, they may be a good option for the production of polymer–clay nanocomposites.

Kaolinite ($Al_2Si_2O_5(OH)_4$) is a phyllosilicate containing a gibbsite octahedral layer and a silicon oxide tetrahedral sheet. This asymmetric structure produces hydrogen bonds of large cohesive energy between adjacent layers. Therefore, the material forms agglomerates and the intercalation of polymer

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doi:10.1016/j.ceramint.2009.06.017

chains in between the platelets is greatly impeded. However, it is possible to accommodate electrically neutral molecules, either organic or inorganic, within the clay structure, thus expanding the basal spacing [15,16]. Chemical treatments have been used to facilitate intercalation and exfoliation of the clay within the polymer matrix when processing polymer–kaolinite nanocomposites. The treatment usually consists of an intercalation of chemical agents to increase the clay basal spacing [15].

The use of natural nanoclays in advanced applications is often limited by the lack of uniformity in chemical composition and physical properties. Purity is a particularly important characteristic of nanoclays to the mechanical properties of nanocomposites since impurities may act as stress concentrators, thus reducing impact resistance and strength. In addition, in film applications where optimum clarity is desired, the presence of impurities contributes to increased haze. High surface area kaolinite crystals are normally found as plastic clays. These clays include high organic contents, which must be removed before they can be used in polymer and paper industries.

In the present study, kaolinite obtained from a natural deposit is processed to remove impurities and submitted to thermal and chemical treatments, to remove organic matter and reduce iron oxide content. The treatments are investigated as an alternative to facilitate clay deagglomeration and promote color lightening when processing large amounts of materials. The clay characteristics and the effects of the treatments were examined through the determination of chemical composition and by the techniques of X-ray diffraction, thermogravimetry/differential thermal analysis (TG/DTA) and Brunauer, Emmett, and Teller (BET) nitrogen adsorption technique. Cation exchange capacity (CEC) and SEM micrographs of the nanoclays are also presented.

2. Experimental

2.1. Material

The kaolinite sample used in this investigation was collected from a natural deposit, located in the city of Goianinha – RN, Brazil. This region is rich in high plasticity kaolinites, which are notorious for high surface areas.

2.2. Clay preparation procedure

Initially, the crude clay was washed in water to remove large size impurities. Then, 250 g of the purified clay was divided into five portions of about 50 g each. Subsequently, each portion was suspended in 1 l of distilled water and placed in a planetary ball mill, where it was milled for 10 min, using 800 g of alumina balls of various diameters, in a 600 ml vial. Once the milling procedure was complete, the five portions were again combined in a plastic recipient and the mixture was allowed to settle, for seven days. After this period, two phases could be clearly observed in the recipient: a clay suspension and a sediment deposited on the bottom of the recipient.

The clay suspension was siphoned off and placed in separate glass containers. The sediment was also collected and taken apart. A glass container with the clay suspension was placed on a hot plate at 80 °C to evaporate the water. After drying, an average yield of 55 wt.% of clay was obtained.

The dry material collected was then dispersed in ethylic alcohol and deagglomerated in a ball mill for 3 h, using 1000 g of zirconia balls of an average diameter of 3 mm, in a 500 ml vial. Afterward, the material was collected and placed on a glass hot plate at 200 °C to permit quick evaporation of the alcohol, thus reducing the formation of agglomerates.

After the procedure was completed, the clay was analyzed by X-ray diffraction and thermogravimetry/differential thermal analysis (TG/DTA). Subsequently, the clay was submitted to thermal and chemical treatments. The effects of the thermal treatment on the surface area were analyzed by BET nitrogen adsorption technique and scanning electron microscopy (SEM). In addition, the effects of the chemical treatment on the chemical composition and cation exchange capacity of the clays were also evaluated.

2.3. Thermal analysis and thermal treatment

Thermal analyses were conducted on samples after the preparation procedure. The simultaneous thermogravimetry/differential thermal analysis (TG/DTA) measurements were carried out with a Shimadzu DTG-60H, using a scan rate of 10 °C/min, over the range of 25–900 °C. Mass loss (in percents) was calculated from TG curve, based on the initial mass of the sample.

Based on the TG data collected, a sample of the nanoclay was thermally treated to evaluate the procedure as an approach to reduce the content of organic matter and to turn the clay color lighter. The sample was placed in an oven at 500 °C, for 8 h.

2.4. Chemical treatment

Chemical treatment was conducted on samples collected from the clay after the preparation procedure. The samples were first treated with hydrogen peroxide (p.a., 30%) to eliminate organic matter. This treatment was conducted using a magnetic shaker (Tecnal TE-085) for 6 h at 60 °C. Then, the samples were submitted to an acid attack using nitric acid 65 wt.% and sulfuric acid 98 wt.% to reduce iron oxide content. For this treatment, 10 g of clay were mixed for 24 h with 20 ml of nitric acid, 20 ml of sulfuric acid and 100 ml of distilled water in a magnetic shaker (Tecnal TE-085) for 24 h at 30 °C.

2.5. Chemical composition

Samples collected before and after the hydrogen peroxide treatment and acid attack were analyzed for the determination of the chemical composition. Silicon content was determined using gravimetric analysis, while the content of carbon and sulfur were determined by inductively coupled plasma optical emission spectrometry (ICP OES). Other elements were quantified by atomic absorption spectroscopy (AAS).

2.6. Cation exchange capacity

Cation exchange capacity (CEC) of samples collected from the untreated clay and also after the hydrogen peroxide treatment and acid attack was measured using the methylene blue adsorption technique (ASTM C837-99, 2003), based on the relationship that exists between the methylene blue index (MBI) and cation exchange capacity.

2.7. BET, SEM and particle size analysis

Clay samples were collected before and after the thermal treatment and also after the chemical treatments and the surface areas were measured by nitrogen adsorption technique (BET) using a QUANTACHROME NOVA 2000. For the scanning electronic microscopy (SEM) analysis, a drop from the clay suspension in distilled water was placed on a carbon tape. Samples were analyzed by SEM using a Philips XL-30-ESEM. Particle size distribution was determined for samples collected before the thermal treatment and after the chemical treatment using a CILAS 920 particle size analyzer with measurement range from 0.3 to 400 μm. Prior to the particle size analysis, the samples were dispersed in a solution of distilled water and neutral detergent.

2.8. X-ray diffraction

X-ray experiments were conducted using a Shimadzu XRD-6000. Intensity vs. scattering angle (2θ) were recorded at room temperature in the range 5–75° (2θ), with step size of 0.02° and scanning rate of 2°/min. X-ray experiments were conducted in samples before and after the thermal treatment and also after the chemical treatments to evaluate the effects of the treatments on the kaolinite structure.

3. Results and discussion

3.1. Thermal analysis and thermal treatment

Thermogravimetry/differential thermal analysis (TG/DTA) measurements were used to examine the thermal stability of the nanoclays and define the conditions for the thermal treatment. Weight reduction is observed in two steps (Fig. 1). In the TG curve, a weight loss of about 1% on average was observed, under 110 °C, which corresponds to loss of adsorbent water. A greater weight loss – about 14% – was observed over the temperature range of 350–550 °C, corresponding to elimination of organic matter of the clay and water from the structure. The DTA shows an endothermic peak curve, at about 480 °C, which is associated to the dehydroxylation of the clay [17]. Based on the thermal analysis data, the thermal treatment was defined as 8 h at 500 °C to eliminate organic matter from the clay. After the thermal treatment, the clays changed color from a dark brown to a light gray due to the removal of organic matter.

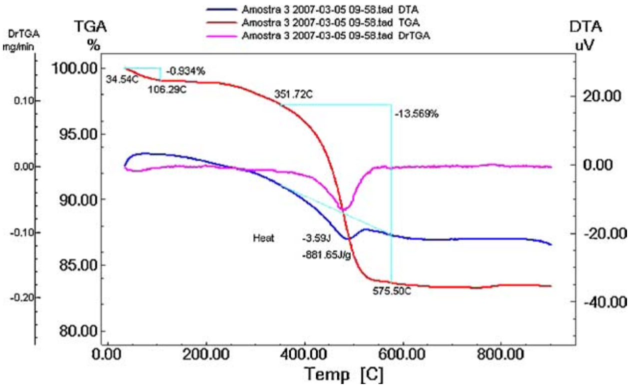

Fig. 1. TG-DTA of untreated kaolinite.

3.2. Chemical composition

Chemical compositions of the nanoclay before the chemical treatment, after hydrogen peroxide treatment and after chemical treatment using nitric acid and sulfuric acid are presented in Table 1. The low content of MgO, CaO, Fe_2O_3, K_2O, TiO_2, Na_2O, MnO_2, proves the low contamination level of this kaolinite. It can be observed that hydrogen peroxide treatment removed part of the organic matter without any other significant effect on the chemical composition of the clay, based on loss-on-ignition wt.%. According to the data presented in Table 1, carbon content was reduced from 2.11 to 0.42 wt.% after hydrogen peroxide treatment. However, the acid attack reduced significantly the contents of MgO, CaO and Fe_2O_3. The loss-on-ignition wt.% was slightly increased after the acid attack, which indicates acid adsorption on the clay surface, since the organic matter had been already removed during the hydrogen peroxide treatment.

In addition to changes in composition, it was verified that the sample presented a lighter color after the chemical attack. This was related to the reduction in Fe_2O_3 and organic matter contents, which indicates that the chemical treatment was effective.

Table 1
Composition of kaolinite before and after chemical treatments.

wt.%	Before treatment	H_2O_2 attack	Acid attack
SiO_2	44.30	46.41	46.80
Al_2O_3	35.28	36.40	36.01
MgO	0.56	0.45	0.09
CaO	0.11	0.10	Traces
Fe_2O_3	0.78	0.80	0.17
K_2O	0.20	0.23	0.10
TiO_2	0.18	0.15	0.19
Na_2O	0.09	0.02	Traces
MnO_2	Traces	Traces	Traces
C	2.11	0.42	0.47
LOI	16.09	14.48	16.03

LOI: loss-on-ignition.

3.3. Cation exchange capacity

A small increment in cation exchange capacity is observed after hydrogen peroxide treatment and acid attack. The estimated cation exchange capacity increased from 16 $cmol_c$/kg (centimol positive charge per kg of clay), for the untreated clay, to 19.5 $cmol_c$/kg after acid attack. Organic matter is known to have a 4 to 50 times higher CEC per given weight than clay [18]. Therefore, a reduction in cation exchange capacity would be expected after the chemical treatment due to the reduction in organic matter content. However, the small increment in cation exchange capacity observed after the chemical treatment may be related to the deagglomeration of clay platelets.

3.4. Surface area measurements

Nitrogen BET surface area measurements indicate an increment in surface area after the thermal and chemical treatments (hydrogen peroxide and acid attack). The thermal treatment produced only a slight increase in surface area, from about 35.3 to 37.8 m^2/g. However, when the samples were submitted to a chemical treatment using hydrogen peroxide, the specific surface area increased from 35.3 to 53.0 m^2/g. The acid attack using nitric acid and sulfuric acid, after treatment using hydrogen peroxide, did not produce any further increment in surface area, which was maintained in 53.0 m^2/g.

It has been stated that the BET surface area determined for nanoclays represents interactions with only particle surfaces that can be reached by N2 [19]. Therefore, the increase in specific surface area observed is the result of a reduction on the agglomerating effect of the organic matter on the clay surface. The thermal treatment produced only a slight increase in specific surface area because it was not effective in deagglomerating the material, even though organic matter content was reduced. However, after the treatment using hydrogen peroxide, the organic matter is removed and the clay platelets are separated, thus significantly increasing the specific surface area.

The acid attack using nitric acid and sulfuric acid, after the treatment using hydrogen peroxide, was effective only in reducing iron oxide content. The specific surface area was not modified, which indicates that the organic matter had been removed during the treatment using hydrogen peroxide and the clay platelets were already separated.

3.5. SEM

SEM micrograph of the untreated clay sample suggests a very cohesive material (Fig. 2). The micrograph confirms that the material is forming micron-size agglomerates. A higher magnification micrograph of the same structure shows that the micro-size particles are composed of individual platelets, which conglomerate into larger size particles (Fig. 3).

SEM micrograph of the material after the chemical treatment using hydrogen peroxide shows separation of some discrete platelets (Fig. 4). This is related to the removal of organic matter, which contributes to reduce the agglomerating effect. The separation of the platelets significantly increased the specific surface area, as it was previously discussed. Acid attack using nitric acid and sulfuric acid, after the chemical treatment,

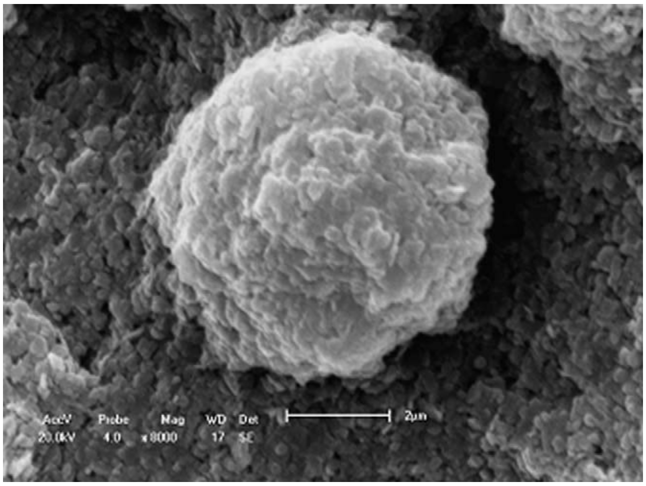

Fig. 2. SEM micrograph of untreated kaolinite.

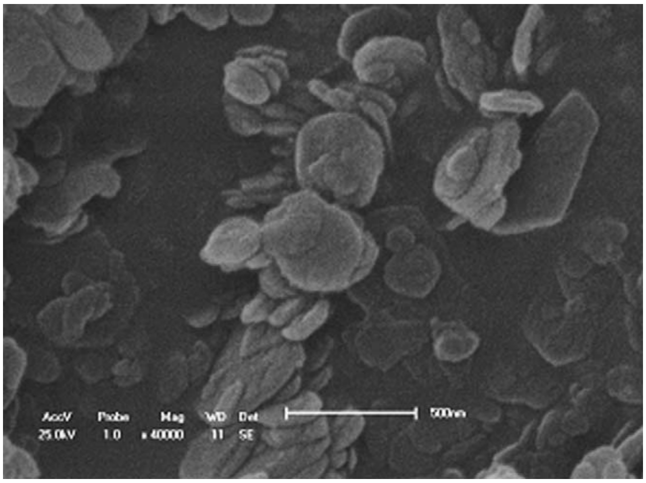

Fig. 3. SEM micrograph of untreated kaolinite at higher magnification.

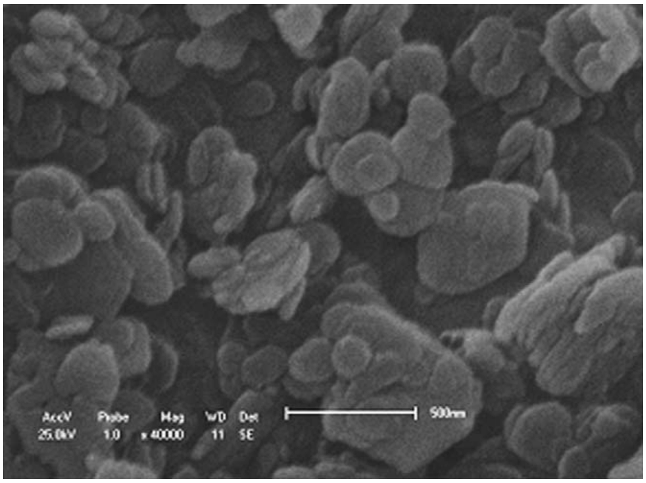

Fig. 4. SEM micrograph of kaolinite after chemical treatment using H_2O_2.

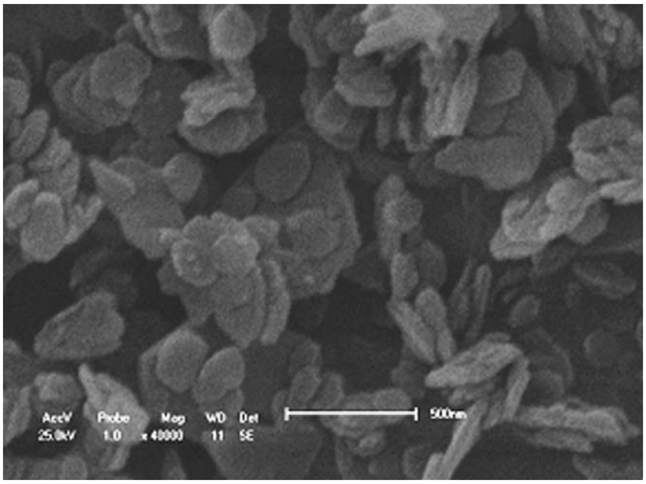

Fig. 5. SEM micrograph of kaolinite after chemical treatment using H_2O_2 and acid attack.

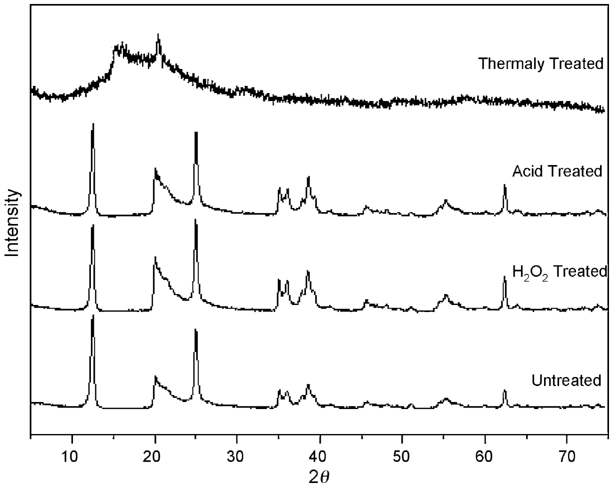

Fig. 7. Effect of treatments on X-ray diffraction pattern of kaolinite.

did not produce any further increment to the separation of the platelets (Fig. 5), as it was also verified in BET measurements.

Treatments able to reduce the agglomerating effect in clays and increase platelets separation are particularly important for the production of polymer matrix nanocomposites, to facilitate the dispersion of the clay within the polymer matrix. Agglomerates of inorganic material within the polymer matrix are known to limit improvement in nanocomposite properties [20]. Therefore, chemical treatment using hydrogen peroxide holds promise as a viable approach to facilitate the dispersion of nanoclays within polymer matrices.

3.6. Particle size analysis

The particle size distribution for samples collected before the thermal treatment and after the chemical treatment are presented in Fig. 6. It was verified a reduction in content of the small size fraction of the clay after the chemical treatment, which is related to the removal of organic matter after hydrogen peroxide treatment and dissolution of the kaolinite fine fraction due to the acid attack.

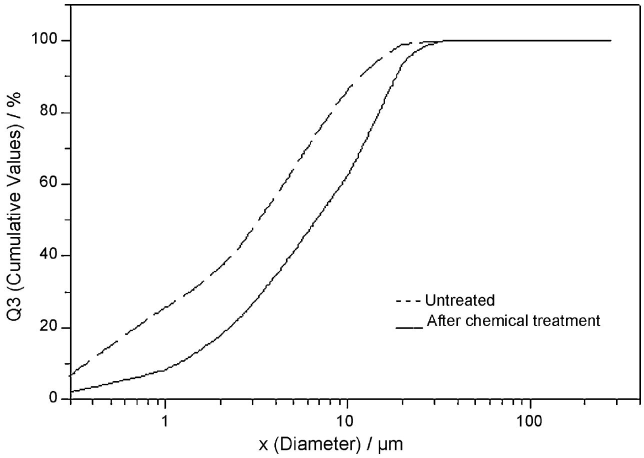

Fig. 6. Particle size distribution of kaolinite untreated and after chemical treatment using acid attack.

3.7. X-ray diffraction

X-ray diffraction patterns of the nanoclay corresponding to various treatments are presented in Fig. 7. Based on X-ray diffraction patterns, it can be verified that, after the preparation procedure, the clay does not contain quartz, which confirms the efficiency of the procedure used. The crystal structure of the clay before the thermal treatment confirms that the clay is basically kaolinite.

However, the clay structure was significantly modified after the thermal treatment. X-ray diffraction pattern of the thermally treated clay shows the formation of an amorphous material (Fig. 7), due to the loss of hydroxyl groups, which caused a rearrangement of the original structure of kaolinite. A completely amorphous structure was not obtained since a temperature level of 550 °C would be necessary for this to occur, as indicated in the TGA curve.

The chemical treatment with hydrogen peroxide did not produce any noteworthy change in X-ray diffraction patterns, as presented in Fig. 7. Similarly, the additional acid attack did not produce any further effect on the clay structure. The small difference in intensity peaks indicates the addition or removal of atoms between basal planes, produced by the treatment with hydrogen peroxide and acid attack. Thus, according to the X-ray diffraction patterns, the kaolinite structure is basically preserved after the chemical treatment with hydrogen peroxide and acid attack.

4. Conclusions

Kaolinite may be a good option for the production of polymer-based nanocomposites. However, it has a strong tendency to form agglomerates due to its asymmetric structure, which produces hydrogen bonds of large cohesive energy between adjacent layers. This requires additional procedures to improve exfoliation and dispersion within a polymer matrix. In this investigation, kaolinite from a natural deposit was purified and submitted to a thermal treatment at 500 °C for 8 h and a chemical treatment, first using hydrogen peroxide and then an acid attack using nitric acid and sulfuric acid. X-ray diffraction patterns indicated that the clay purification procedure was able to remove quartz contamination. The subsequent thermal treatment conducted proved able to remove part of the organic components which turned the clay a lighter color. It also favored the formation of an amorphous material. However, the thermal treatment produced only a slight increase in specific surface area because it was not effective in deagglomerating the material even though organic matter content was reduced. After the treatment using hydrogen peroxide, organic matter was removed and the clay platelets were separated, thus significantly increasing the specific surface area—from 35.3 to 53.0 m^2/g. The succeeding acid attack did not produce any further increment in surface area, but reduced significantly the contents of MgO, CaO and Fe_2O_3 turning the clay lighter in color. A small increment in cation exchange capacity was also observed after hydrogen peroxide treatment and acid attack, which was related to the deagglomeration of clay platelets. Therefore, the chemical treatment using hydrogen peroxide followed by acid attack proved effective in reducing organic matter and iron oxide contents, which turned the clay a lighter color, and promoting deagglomeration of clay platelets, which increased specific surface area. Future work will study the addition of small fractions of the chemically treated clay with functionalization on the physical and mechanical properties of polymer-based nanocomposites.

Acknowledgments

The authors gratefully acknowledge the financial support of the Brazilian financing agencies MCT, CNPq, FINEP, CAPES and FAPERN.

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