



## Note

# New chemical treatment of bentonite for the preparation of polypropylene nanocomposites by melt intercalation



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## ARTICLE INFO

## Article history:

Received 8 October 2014

Received in revised form 2 April 2015

Accepted 3 April 2015

Available online 16 April 2015

## Keywords:

Bentonite

Nanocomposite

Polymer

Polypropylene

## ABSTRACT

In the present work, sodium bentonite was chemically modified with alkyl aluminum compounds to prepare polypropylene nanocomposites containing nanosized clay with homogeneous morphology. The compounds were compared with PP/commercial organoclay containing alkyl ammonium ions. Both unmodified and modified bentonite compounds were incorporated in a commercial PP matrix and maleated PP (PP-MA) as coupling agent was also mixed by melt intercalation using a mini-extruder. The obtained clay/polymer nanocomposites (CPN) were characterized by differential scanning calorimetry, X-ray diffractometry, thermodynamic–mechanical analysis and thermogravimetry. According to the results of the method developed in this study, the prepared PP-nanocomposites containing clays with different chemical treatments exhibited an increase of the d-value of the clay in the XRD, and resulted in much better properties, like increased degradation temperature and mechanical parameters, compared with those of the polymer without clay and of the materials with untreated clay. Also, treatment with triethylaluminum was most efficient.

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## 1. Introduction

Polymer nanocomposites have attracted a wide scientific and technological interest due to their high performance compared with pure polymer and regular composites. These materials have small quantities of filler that are dispersed in the polymer matrix in nanometric dimensions (Hambir et al., 2001; Paul and Robeson, 2008; Mingliang and Demin, 2009). The improvement of the properties depends on the type of nanofiller. Clay, carbon nanotubes, graphite and others have been used as fillers to obtain polymer nanocomposites. Clays are one of the most common fillers for polypropylene (PP) nanocomposites (Okamoto and Ray, 2003). This is because clays are plentiful in nature and their chemical intercalation has been studied for a long time (Zhang et al., 2008; Sanchez et al., 2009). The melt intercalation technique is the most common and economical to obtain clay PP nanocomposites (Wang et al., 2004; Kiliaris and Papispyrides, 2010). The incorporation of clay in the polymer in an extruder, for example, leads to dispersion of the clay particles in the polymer matrix in the molten state, providing significant improvements in mechanical, physical and chemical properties of the polymer (Paiva et al., 2008; Paul and Robeson, 2008; Abdallah and Yilmazer, 2011). However, it is very difficult to produce a

clay PP nanocomposites with uniform morphology through this technique, because generally some microparticles are present and intercalated and exfoliated morphologies are obtained (Maiti et al., 2002; Garcia et al., 2003; Ziaei et al., 2011). The production of a PP/clay nanocomposite with intercalated/exfoliated morphology requires the use of modified clays due to the incompatibility between the hydrophobic PP and hydrophilic clay (Kodgire et al., 2001; Maiti et al., 2002). However, there are only a few studies of treatments of clays other than ion exchange to obtain clay PP nanocomposites with uniform morphology by the melt intercalation method. The most widely used modification agents are ammonium or alkyl ammonium salts with long chains, which enable interaction between the highly hydrophilic polymer and highly hydrophobic clay, especially in the case of PP and other polyolefins (Pavlidou and Papispyrides, 2008; Oliveira and Marques, 2011; Ziaei et al., 2011; Mittal, 2012). Compounds containing silane are also widely used for clay treatment (Lee et al., 2006; Joo et al., 2008; Mittal, 2009). Treatment with compounds of imidazole and phosphonium is also a good alternative, leading to an increase in thermal resistance of the clay, although they are very expensive (Mittal, 2009).

Hence, there is a need to conduct research into new clay treatments to obtain clay/polymer nanocomposites (CPN) with more homogeneous morphology and absence of microparticles (Lee et al., 2006; Kato et al., 2011). The aim of developing new clay treatments is to modify the regular stacking of the clay lamellae and increase the interlayer spacing, to facilitate intercalation of polymer chains between

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the clay lamellae and achieve CPN with the highest possible fraction of exfoliated morphology (Kato et al., 2011). The overall aim is to increase the mechanical, physical and other properties, expanding the application of these materials (Rong et al., 2001; Kiliaris and Papispyrides, 2010; Ziaei et al., 2011). Moreover, to make intercalation of organoclay in the matrix easier and promote a strong interaction between clay and PP, a compatible agent is usually employed (Hambir et al., 2002; Maiti et al., 2002; Li et al., 2003).

Therefore, the objective of the present work was to treat commercial sodium clay with alkyl aluminum compounds in order to disrupt the crystalline structure of the material, to enable blending it with the PP matrix in the melted state.

## 2. Experimental

### 2.1. Materials

Sodium clay Argel 40 was provided by Bentonit União Nordeste S.A.; organoclay Cloisite 15A (dimethyl-diHT ammonium chloride, where HT contains around 65% C<sub>18</sub>; 30% C<sub>16</sub> and 5% C<sub>14</sub>) was provided by Southern Clay Products, Inc.; methylaluminoxane (MAO) was supplied by Crompton GmbH (10% by mass in toluene); triethylaluminum was acquired from Akzo Nobel; hexadecyl ammonium bromide was supplied by Aldrich; toluene was obtained from Ipiranga; the commercial polypropylenes HP550K (MFI = 3.5 g/10 min) and HHP516MK (MFI = 8 g/10 min) were provided by Quator/Braskem; and polypropylene grafted with 1% mol of maleic anhydride (PP-MA) was provided by Chemtura (Crompton-Uniroyal Chemicals).

### 2.2. Methods

After treating the sodium clay with triethylaluminum (TEA), TEA and ammonium salt, and methylaluminoxane (MAO), masterbatches (25% by mass) of commercial polypropylenes (two different grades: HP550K for automotive industry and HHP516M for packaging) and the treated clays were prepared in a mini-extruder. All CPN were prepared with 5% by mass of the compatibilizer PP-MA. These materials

were then diluted with the corresponding commercial PP to 5% by mass of clay in the same processing conditions.

#### 2.2.1. Treatment of sodium clay with triethylaluminum

Clays were treated in solution of triethylaluminum in hexane at 7.5 mmol of TEA per gram of clay. The addition of TEA in the clay was carried out in a Schlenk apparatus under inert atmosphere. After the addition, the clay was kept under stirring for 24 h at 50 °C. The samples were then washed three times with hexane and subsequently washed with wet ethanol.

#### 2.2.2. Treatment of clay/TEA with ammonium salt

Samples of Argel 40 previously treated with TEA were subjected to a second treatment with aqueous salt of trimethylhexadecyl ammonium bromide. After clay drying, 7 mmol of the 0.5 M ammonium salt solution was added to the clay. The clay was kept under stirring for 72 h and then was filtered and washed with water. For testing, 1 ml of 1% AgNO<sub>3</sub> solution was used in the clay washing water to evaluate the presence of ammonium salt.

#### 2.2.3. Treatment of sodium clay with methylaluminoxane

The Argel 40 was treated with 5 mmol of methylaluminoxane. The concentration of MAO solution employed was 1.72 M. Sixty milliliters of toluene was added and then the Argel 40 was impregnated with 29 ml of MAO solution at 70 °C for 4 h. The clay was washed with toluene at 90 °C. Then wet ethanol was added in the clay and the clay was dried at 120 °C for 24 h. The structures proposed for sodium clay after treatments are shown in Fig. 1.

#### 2.2.4. Preparation of masterbatches and dilutions

To obtain the masterbatches and dilutions, two commercial polymers were used: HP550K and HP516M. The masterbatches containing 25% by mass of clay and 25% by mass of compatibilizing agent PP-MA were obtained in Haake mini-extruder at 180 °C, 60 rpm, and 15 min, in the contra-rotational mode. The dilutions containing 5% by mass of clay were prepared by mixing 1 g of masterbatch with 4 g of each corresponding commercial PP under the same extrusion conditions as

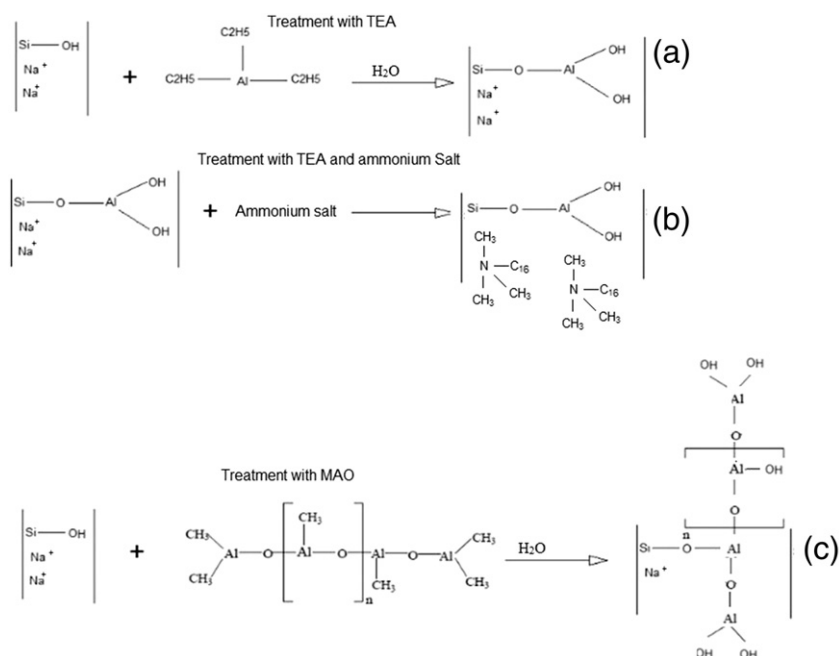


Fig. 1. Structures proposed for sodium clay after treatments. (a) with TEA; (b) with TEA and ammonium salt; (c) with MAO.

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