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Research paper

Preparation and characterization of soy lecithin-modified bentonites

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ABSTRACT

In this work, a study of exchange of soy lecithin, a natural product, in bentonite was performed in order to synthesize bio-organoclays. The effects of initial amount of modifier and reaction time were studied at a fixed reaction temperature. Organoclays thus obtained were characterized by means of X-ray diffraction (XRD) analysis, X-ray fluorescence spectrometry (XRF), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and water absorption tests. An effective intercalation of soy lecithin between the clay layers was obtained. The ionic exchange reaction was completed at short times whereas variations in the initial amount of modifier produced organoclays with different final properties. At low ratios of soy lecithin to bentonite, a slight increment in basal spacing of organoclays was observed due to intercalation of the organic modifier between the clay layers and a significant diminution on water absorption was achieved. When the organic content increased, the interlayer spacing increased but thermal stability of organoclays decreased compared to the samples with low organic content, whereas the water absorption was not affected. The obtained bio-organoclays are potential environmental-friendly fillers for the development of clay/biopolymer nanocomposites.

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1. Introduction

Clays have been used for the last 30 years as nanometric fillers to reinforce polymeric matrices (Fornes et al., 2001; Hedley et al., 2007) with the aim of improving specific properties, mainly thermal, barrier, impact and mechanical, for an important number of applications (Limpanart et al., 2005; Roelofs and Berben, 2006; Xie et al., 2002). Bentonite (Bent) is one of the most commonly used clays in polymer nanocomposites technology due to its low cost and natural abundance (Bergaya et al., 2012). Montmorillonite, a clay mineral of the smectite group, is the primary component of Bent and determines its defining properties, such as high specific surface area and swelling capability (Bergaya et al., 2011). It is composed of layers of about 1 nm which are held apart mainly by electrostatic forces. Each layer is characterized by a 2:1 structure with a central octahedral sheet of alumina which is attached to two external tetrahedral sheets of silica (Alexandre and Dubois, 2000; Mandalia and Bergaya, 2006; Picard et al., 2007). The net negative charge of the layers, which is generated due to isomorphic substitutions of Al^{+3} with Fe^{+2} or Mg^{+2} in the octahedral sites and of Si^{+4} with Al^{+3} in the tetrahedral sites, is compensated by the presence of cations, mainly as Na^{+} and Ca^{+2}, situated in the interlayer space (Bergaya et al., 2011).

It is known that in the pristine state, Bent is compatible only with hydrophilic polymers, such as poly(vinyl alcohol) (Ollier et al., 2013). However, a large number of polymeric matrices are hydrophobic. In those cases, in order to increase chemical compatibility between both components, and then, improve the dispersion of Bent inside the polymer matrix, it is necessary to modify one of them (Čapková et al., 2006; Pavlidou and Papaspyrides, 2008). Generally, this can be accomplished by the appropriate conversion of these hydrophilic clays in organophilic ones, via ion exchange reactions (Picard et al., 2007; Xi et al., 2007; Xie et al., 2002). Modified clays prepared by cation exchange with long-chain quaternary alkylammonium or phosphonium salts have been widely studied and the resulting organoclays have been used in the preparation of clay/polymer-nanocomposites, mainly for industrial applications (Ruiz-Hitzky and Van Meerbeek, 2006). Nevertheless, the application of these clays in biological fields is limited by the toxicity and poor biocompatibility presented by these kinds of modifiers (Wicklein et al., 2010). However, during the last years, the application of organoclays has been extended to these fields including drug delivery systems (Dong and Feng, 2005; Lin et al., 2002; Park et al., 2008; Zheng et al., 2007), excipient and active substances in pharmaceutical products (Lee et al., 2005; Wang et al., 2008), antithrombogenic materials (Zhou et al., 2009), immobilization host for biological species like enzymes, amino acids, proteins, nucleic acids and phospholipids (Mallakpour and Dinari, 2012, 2013; Nagy et al., 2013; Ruiz-Hitzky and Van Meerbeek, 2006; Songurtekin et al., 2013; Wicklein et al., 2011; Yu et al., 2013).

Moreover, phospholipids have been scientifically studied since the 1700's and became commercially available as lecithin in the 1930's (Szuhaj, 2003). They have a basic structure of a diacylglycerol backbone with a phosphate ester on the α or third carbon of the glycerol molecule (Szuhaj, 2003). Usually, another compound is attached that

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characterizes the phospholipid. The main commercial source of lecithin today is the soya bean, but phospholipids can be found in all living cells as part of the cellular membranes. The International Lecithin and Phospholipid Society defines lecithin as “a complex mixture of glycerophospholipids obtained from animal, vegetable or microbial sources, containing varying amounts of substances such as triglycerides, fatty acids, glycolipids, sterols, and sphingophospholipids” (Szuhaj, 2003). However, the composition of lecithins and their phospholipids will vary depending on their source. Vegetable lecithins are high in phosphatidylcholine, phosphatidylethanolamine, phosphatidylinositol, and phosphatidic acid, but very low in phosphatidylserine and sphingomyelin (Macrae et al., 1993; Szuhaj, 2003). Phosphatidylethanolamine and phosphatidylcholine are neutral, zwitterionic phospholipids with an amphiphilic character. These possess a net positive charge at pH lower than the isoelectric point (Nagy et al., 2013), which allows the cationic ion exchange with clays and, on the other hand, the presence of the hydrophobic chains allow interactions via Van der Waals forces with the other components of soy lecithin. For these reasons, soy lecithin (SL) could act as a natural bio-surfactant and environment-friendly bio-modifier that can be used for the preparation of organoclays. Thus, the resulting bio-organoclays are potential reinforcements of biodegradable polymers for the development of bionanocomposites applicable to cosmetic, biomedical and food industry, among other fields. In the specific case of melt compounding and injection molding of thermoplastic polymer nanocomposites at high processing temperatures, it is important to know the thermal stability of the clay to avoid its thermal degradation during the processing of the material. When the organoclay is degraded during processing, the compatibility with the polymer matrix, as well as the final performance of the nanocomposite are affected (Ludueña et al., 2013).

In this work, Bent was modified via cation exchange reactions with SL and the effect of reaction time and the initial amount of SL on the modification of Bent were analyzed. The effectiveness of each modification was discussed in the light of the characterization results by X-ray diffraction analysis (XRD), X-ray fluorescence spectrometry (XRF), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and water absorption tests. In order to choose the most potential organoclays for the preparation of clay/polymer nanocomposites, the organic content, the degree of hydrophobicity, the interlayer space and the degradation temperature of the organoclays were studied. These parameters will determine the type of polymer to be employed and also the processing conditions (or processing window).

2. Experimental

2.1. Materials

The clay employed in this work was a bentonite supplied by Minarmco S.A. (Neuquén, Argentina); it was used as received. The cation exchange capacity (CEC) of bentonite, measured by the methylene blue method, was found to be 105 meq/100 g clay. Granular soy lecithin was obtained from Melar S.A (Buenos Aires, Argentina).

2.2. Modification of bentonite with soy lecithin

A 4 g sample of Bent was dispersed in 100 ml of distilled water and the adequate content of aqueous solution of SL, acidified with hydrochloric acid (pH = 1), was added in order to obtain samples with g SL/g bent = 0.25, 0.50, 0.75, 1.00 and 1.20. The dispersion was kept under stirring at 75 °C for different times. The exchanged clay was then filtered and washed several times with a 1:2 mixture of ethanol-distilled water. Finally, the wet product was frozen for 24 h and then lyophilized at 100 mTorr and −50 °C for 72 h using a VirTis 2KBTES-55 freeze dryer in order to obtain a free flowing product.

2.3. Characterization

X-ray diffraction (XRD) tests were performed on the clay powder using an X-Pert Pro diffractometer, operating at 40 kV and 40 mA, with CuK$_\alpha$ radiation ($\lambda = 1.54$ Å). Powders of finely ground samples were put in horizontal glass holders, then passed over several times with a glass slide in order to eliminate texture. Diffractograms were recorded at a scanning speed of 1°/min from $2\theta = 2°$ to 15° in steps of 0.0167°; 0.5° was selected for the divergent slit and scatter slit.

X-ray Fluorescence spectroscopy (XRF) was performed for elemental analysis, by using a PANalytical MiniPal 2, equipped with CrKα radiation ($\lambda = 0.2291$ nm) and a Si-PIN detector. Measurements were carried out at 20 kV and 5 μA, in helium flow. Light elements (below Na in periodic table) could not be detected. Samples were analyzed in powder form without any additional preparation. Each powder was put into a XRF plastic sample cup with a thin polypropylene window measuring 76 mm in diameter.

Thermogravimetric analysis (TGA) was carried out with a TG HI-Res thermal analyzer (TA Instruments) at a heating rate of 10 °C/min from room temperature to 900 °C in air flow. The specimen weight was in the range of 7–15 mg. Organic mass contents were determined subtracting the mass loss between 150 °C and 500 °C from the bentonite to the modified clays. Degradation temperatures were obtained from the maximum of each event at the derivative curves of TG (DTG).

Fourier transform infrared (FTIR) spectra were acquired with a Nicolet 6700 Thermo Scientific instrument equipped with a diamond ATR probe, over the range 400–4000 cm^{-1} from 32 co-added scans at 4 cm^{-1} resolution. About 10 mg of finely ground clays were placed on the sample holder.

Water absorption tests were carried out at 90% RH (relative humidity). To control the humidity level during testing, clay samples were enclosed in a small chamber containing an aqueous solution of glycerine (34 wt.%) which fixes the relative humidity (RH) within 90% ± 1% (Greenspan, 1977). Before tests, all the samples were dried under vacuum until constant weight. Samples were weighted at prefixed times until the equilibrium mass (M_{eq}) was achieved and water absorption at each time was calculated as:

$$M_t(\%) = \frac{M_t - M_0}{M_0}.100 \quad (1)$$

where M_t is the mass of the sample at a time t and M_0 is the initial mass of the sample (dried). Triplicate measurements were conducted for each sample and the average values were used for water absorption calculation.

3. Results and discussion

The bentonite used in this study consisted predominantly of montmorillonite as evidenced by XRD analysis (D'Amico et al., 2014). Also, it contained quartz and feldspar as major impurities, as well as traces of gypsum and sepiolite. The main chemical composition was obtained by XRF and the results are shown in Table 1. This Bent has high content of Fe, which can be attributed to the location of the deposit from which it was extracted (Murray, 2006).

Table 1
Chemical composition of Bent.

Sample	Composition (wt.%)							
	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	TiO_2	Others[a]
Bent	52.3	13.1	22.1	1.9	4.7	1.3	2.0	2.4

[a] Others = % SO_3 + % Cl.

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