



Research paper

Characterization of montmorillonites modified with organic divalent phosphonium cations



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ABSTRACT

Montmorillonite was surface modified by the cation exchange method with *o*-xylylenebis(triphenylphosphonium bromide) (Dim-Br), a compound consisting of two phosphonium groups. The modification yield of the exchange reaction was characterized by means of several analytical methods (Fourier-transformed infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and thermogravimetry analysis (TGA)). The obtained organoclays (OC) exhibited higher thermal stability than the pristine montmorillonite due to the hydrophobization effect that produced the organic modification with Dim-Br. The basal space determined by means of X-ray diffraction (XRD) increased gradually with surfactant concentration, until it reached a maximum, and was well correlated with the organic content of the modified montmorillonites. Moreover, EDX results showed that with increasing surfactant concentration, the sodium content corresponding to the unmodified surface decreased and the phosphorus content related to the modifier increased. EDX technique is proposed as an additional analytical tool that might be applied in the chemical characterization of modified nanoclays.

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1. Introduction

Surface modification of clay minerals received significant attention during the last years because of the opportunity to create new materials and new applications. One of the main interesting advantages of surface modification was its use in polymer science since the organic modification of clays was necessary in order to increase the compatibility between the polymer and the clay, and to get higher enhancement in the properties (de Paiva et al., 2008; Bergaya et al., 2011; Beltrán et al., 2013).

Important improvements in mechanical, thermal or flame retardant properties (Okada et al., 1990; Vaia et al., 1993; Hasegawa et al., 1998; Gong, 2004; Kiliaris and Papaspyrides, 2010; Bikiaris, 2011; Chrissafis and Bikiaris, 2011) were reported in nanocomposites prepared with organoclays. Among the clay minerals, smectites and especially montmorillonite (abbreviated as Mt) were extensively used to prepare organoclays because of its excellent properties, such as high cation exchange capacity, swelling behavior, adsorption properties and large surface area.

To achieve the highest enhancement of properties, good dispersion of the filler at the nanolevel must be accomplished when processing

the nanocomposite. Consequently, the surface characteristics (presence of reactive/functional groups and wettability) of the particles were one of the key factors to improve compatibility with the polymer chains. The organic modification not only improved the compatibility of the clay with the polymer but also increased the distance between the silicate layers, which may facilitate the insertion of the polymer chains and thus producing an exfoliated or intercalated nanocomposite.

Several routes were employed to modify clays (Bergaya and Lagaly, 2001), although the most convenient and straightforward method to prepare organoclays was cation exchange. The first generation of modified montmorillonites was developed during the 1990s and employed quaternary alkylammonium salts (Vaia et al., 1994). The observed low thermal stability of ammonium surfactants represented a problem for melt compounding and processing of polymer nanocomposites, where high processing temperatures exceeding 200 °C were commonly employed and by which the degradation of the modifier of the clay could be initiated (Wu and Lerner, 1993). To overcome this difficulty, montmorillonites were also modified with other group of compounds with higher thermal stability such as imidazolium (Bottino et al., 2003; Bourbigot et al., 2003; Awad et al., 2004), stibonium (Wang and Wilkie, 2003) and phosphonium surfactants (Yu et al., 2004; Patel et al., 2007; Calderon et al., 2008; Avalos et al., 2009; Mishra et al., 2012). Several studies found that the thermal stability of phosphonium organoclays was superior to that of ammonium organoclays (Xie et al., 2002; Calderon et al., 2008; Abdallah and Yilmazer, 2011; Mittal, 2012).

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The present study describes the surface modification and subsequent characterization of montmorillonite with a special type of phosphonium compound, *o*-xylylenebis(triphenylphosphonium bromide) (Dim-Br), where a xylylene bridge connects two phosphonium groups. To the best of our knowledge, this type of surfactant with two phosphonium groups in the same molecule for the modification of montmorillonite has not been previously described in the literature. It is expected that both the higher size of Dim cation in comparison with other phosphonium compounds and the presence of two phosphonium groups in the same molecule will result in a higher basal space in comparison with that of other phosphonium organoclays, which might lead to more exfoliated structures when processing nanocomposites. In addition, thermal stability properties might also be enhanced with Dim montmorillonites because of the presence of two phosphorus atoms on the same molecule. The modification yield of the exchange reaction as function of surfactant concentration in terms of interlayer spacing, organic, sodium and phosphorus content was assessed by means of FTIR, TGA, XRD and SEM-EDX techniques.

2. Materials and experimental methods

2.1. Materials

Sodium montmorillonite (Na-Mt), trade name Cloisite Na⁺, with a cation exchange capacity (CEC) of 0.92 mEq/g was kindly provided by Southern Clay Products. Surface modification was performed with *o*-xylylenebis(triphenylphosphonium bromide) (Dim-Br), supplied by Alfa Aesar (Fig. 1).

2.2. Experimental procedure

The intercalation of the phosphonium surfactant (Dim-Br) into the montmorillonite galleries was carried out by the cation exchange reaction following the method previously described by Patel et al. (2007). Briefly, 1.0 g of Na-Mt (Cloisite Na⁺) was dispersed into 100 mL of deionized water and subsequently heated to around 80 °C under continuous stirring. When the clay was completely dispersed, the phosphonium compound was slowly added, and stirring was maintained during 24 h. Several concentrations or amounts of Dim-Br, as proportion of the CEC of the organoclay, were tested: 0.5CEC (193 mg), 1.0CEC (386 mg), 1.5CEC (578 mg), 2.0CEC (771 mg), 2.5CEC (964 mg), 3.0CEC (1157 mg) and 4.0CEC (1542 mg). Subsequently, the organoclay was recovered by vacuum filtration and washed several times with deionized water until no halide anions were detected by the silver nitrate test. The product was dried at 105 °C overnight and finally ground manually in an agate mortar.

2.3. Characterization of modified montmorillonites

2.3.1. Fourier transform infrared spectroscopy (FTIR)

The phosphonium modified Mt were characterized by Fourier transform infrared spectroscopy (FTIR) in a Perkin-Elmer Spectrum One FTIR Spectrometer equipped with an UATR in order to obtain qualitative evidence about the extent of the intercalation.

2.3.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was applied to assess both the thermal stability of the montmorillonites and the performance of the intercalation in terms of the organic content and yield. Samples were heated to 800 °C at a heating rate of 10 °C/min in a nitrogen flow of 40 ml/min with a Perkin-Elmer Pyris1 TGA instrument. The organic content was calculated as the percentage of organic mass with respect to the dried mass of organoclay. The dried mass of organoclay (initial mass) was obtained at 200 °C from thermogravimetric curves in order to avoid the contribution of water, which could introduce error if samples were not dried correctly. On the other hand, the

mass of organic compounds was calculated from the mass loss registered between 200 °C and 800 °C, so that the organic content would be calculated as:

$$\text{Organic content (not corrected)} = \frac{m_i - m_f}{m_i} \cdot 100 \quad (1)$$

where m_i and m_f are the masses of organoclay at 200 °C and 800 °C, respectively. Note that, although the decomposition of organics indeed takes place in the range 200–500 °C, the final temperature was chosen at 800 °C since some overlap with the dehydroxylation of silicate layers was observed at 500 °C. For that reason, Eq. (1) was corrected with the mass loss observed in the same region of temperature for the unmodified sample Na-Mt and the organic content was finally calculated from Eq. (2):

$$\text{Organic content} = \left(\frac{m_i - m_f}{m_i} \cdot 100 \right) - \% \Delta m_{\text{Na-Mt}} \quad (2)$$

where $\% \Delta m_{\text{Na-Mt}}$ is the percentage of mass loss between 200 °C and 800 °C registered in the unmodified sample Na-Mt.

In addition to the organic content, the yield was also calculated from TGA curves. The yield represents the percentage of surfactant cations, from the total added to the reaction media, that were finally incorporated in the organoclay. It can be calculated considering the ratio of experimental and theoretical or expected organic content:

$$\text{Yield} = \frac{\text{exp. organic content}}{\text{theo. organic content}} \cdot 100 \quad (3)$$

The experimental organic content was calculated from Eq. (2). The theoretical organic content was calculated assuming that all surfactant cations were incorporated to the final organoclay:

$$\text{theo. organic content} = \frac{m_{\text{Dim}}}{m_{\text{Dim}} + m_{\text{Mt}}} \cdot 100 \quad (4)$$

where m_{Dim} and m_{Mt} represent the total mass of Dim cations and clay layers added to the reaction media. The total mass of surfactant cations was calculated from the amount of surfactant added to the reaction media through Eq. (5):

$$m_{\text{Dim}} = m_{\text{Dim-Br}} \frac{\text{MW}_{\text{Dim}}}{\text{MW}_{\text{Dim-Br}}} \quad (5)$$

where $m_{\text{Dim-Br}}$ is the mass of Dim-Br added to the reaction media, whereas MW_{Dim} and $\text{MW}_{\text{Dim-Br}}$ are the molecular weights of Dim cations (468.95 g/mol) and Dim-Br surfactant (628.75 g/mol), respectively. On the other hand, the total mass of clay layers was calculated subtracting the mass of sodium cations from the mass of Na-Mt added to the reaction media as was indicated in Eq. (6):

$$m_{\text{Mt}} = m_{\text{Na-Mt}} (1 - \text{MW}_{\text{Na}} \cdot \text{CEC}) \quad (6)$$

where $m_{\text{Na-Mt}}$ is the mass of Na-Mt added to the reaction media (1.0 g), MW_{Na} is the molecular weight of sodium (23.10 g/mol) and CEC is the cation exchange capacity of the Na-Mt (0.92×10^{-3} Eq/g). Here it was assumed, as a reasonable approximation, that all exchangeable cations of the montmorillonite were composed of sodium (other metal cations might be in trace amounts).

2.3.3. X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis was used to measure the interlayer distance. The corresponding basal spacings were derived from the first-order reflections (001) by applying the Bragg's law. Analyses were carried out with a Phillips powder X'Pert Pro diffractometer using PW3373/00 curved Cu-filtered Cu-K α radiation at the wave length

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