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Research paper

Synthesis and characterization of organosaponites. Thermal behavior of their poly(vinyl chloride) nanocomposites

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ABSTRACT

The aim of this work was to synthesize and characterize the structural properties of the materials resulting from the combination of a synthetic saponite with several organic molecules, namely, Arquad 2HT-75, octadecylamine, 3-aminopropyltriethoxysilane, trimethyloctadecylammonium bromide and tetraethoxysilane, or combinations of them, and with or without the addition of HCl during synthesis. The ratios organic molecule/saponite and HCl/organic molecule were considered as synthesis variables. Structural characterization was based on X-ray diffraction (XRD), simultaneous thermogravimetric/differential thermal analysis (TG/DTA) and infrared spectroscopy (FTIR). The chemical composition of the materials was determined through X-ray fluorescence (XRF) and atomic absorption spectroscopy (AAS), and their morphology was analyzed through scanning electron microscopy (SEM). The values obtained for the basal spacings were a function of the type and amount of the organic molecule. Otherwise, HCl did not significantly influence the basal spacing, but it had the capacity to significantly modify the morphology and the chemical composition of the samples. From the results found, the solids modified with tetraethoxysilane and 3-aminopropyltriethoxysilane were selected to incorporate various titanium precursors. These new organo-modified saponites were used in the formulation of PVC nanocomposites and their thermal behavior was evaluated at two temperatures (70 and 180 °C).

1. Introduction

The utility of inorganic nanoparticles as additives to enhance polymer performance has been reported in the last years. The clay polymer nanocomposites (CPN) are of particular interest because of their enhancements, relative to an unmodified polymer, in a large number of physical properties including mechanical properties, gas permeability, fire and thermal resistance, environmental stability and solvent uptake (Pinnavaia and Beall, 2000).

Among the large number of inorganic layered materials that exhibit intercalation capabilities, layered silicates form one of the most typical groups because of their reaction versatility. In particular, clay minerals of the smectite group, such as montmorillonite, saponite and hectorite, have mainly been used because they have excellent intercalation abilities. Several reviews have recently appeared on CPN based on smectites (Bergaya et al., 2013; Chen et al., 2008; Galimberti et al., 2013; Giannelis, 1996; Lagaly, 1999; LeBaron et al., 1999; Pavlidou and Papaspyrides, 2008; Sinha Ray and Okamoto, 2003). Studies on layered silicate–polymer compounds based on other types of layered silicates have been conducted to a much lesser degree because of the relative difficulties in the preparation of the polymer-intercalated compounds.

Polymer and smectite are not miscible due to the hydrophilicity of the clay mineral layers and because most of the polymer is hydrophobic. Thus, the compatibility is not enough for the polymer chains to intercalate into the clay interlayer spaces. To solve this problem, inorganic smectites are modified with organic molecules by ion exchange resulting in organoclays (OC) (Lambert and Bergaya, 2013; Moghri and Akbarian, 2009). OC are essential to developed CPN, materials formed by the combination of two or more materials, producing unique and synergic properties, different from those of the individual components (Betega de Paiva et al., 2008).

Poly(vinyl chloride) (PVC) is one of the polymers with the highest production and applications (Dunlap and Desch, 1982) due to its characteristics such as easy modification and low cost. This polymer still has problems with its low thermal stability during manufacture and use. For that, the effect of the incorporation of additives as stabilizers, lubricants, plasticizers, fillers, etc. has been considered as topic in the PVC research. Among these possibilities, the use of layered clay minerals has been described by several investigators as an efficient method to modify and control the thermal stability of PVC (Awad et al., 2009; Gong et al., 2004; Liu et al., 2008; Peprnicek et al., 2006; Wu et al., 2010). The effect of the presence of titanium oxide has also been

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reported to reduce the photodegradation of this polymer (Gesenhues, 2000; Kemp and McIntyre, 2006).

The present study aims to synthesize and characterize the structural properties of materials resulting from the combination of a saponite with several organic molecules, namely Arquad 2HT-75, octadecylamine, 3-aminopropyltriethoxysilane, trimethyloctadecylammonium bromide and tetraethoxysilane, or combinations of them, that can be used as nanofillers of CPN. The OC with best properties will be selected to incorporate various titanium sources. These new organo-modified saponites will be used in the formulation of PVC nanocomposites and the thermal behavior will be evaluated at two temperatures (see Scheme 1).

2. Experimental

2.1. Raw material and preparation of organically modified saponite

The starting material was a synthetic saponite (Sap) from Kunimine, supplied by The Clay Science Society of Japan. The raw clay mineral is very pure, which allows a better identification by instrumental techniques. Its cationic exchange capacity (CEC) is 100 meq/100 g.

The organic molecules employed in this work to modify the clay mineral were: Arquad 2HT-75 (Fluka, H_2O 8–12%), mainly composed of dimethyldioctadecylammonium chloride, although it may also contain C_{16} chains; octadecylamine ($CH_3(CH_2)_{17}NH_2$, Aldrich, 90%); 3-aminopropyltriethoxysilane ($H_2N(CH_2)_3Si(OC_2H_5)_3$, Aldrich, 99%); trimethyloctadecylammonium bromide ($CH_3(CH_2)_{17}N(Br)(CH_3)_3$, Aldrich, 98%) and tetraethoxysilane ($Si(OC_2H_5)_4$, Alfa Aesar, 98%).

The syntheses of the modified Sap were carried out by cation-exchange. All samples were prepared by adding the necessary amount of surfactant to obtain 0.5, 1, 2 and 5 times the CEC of the clay mineral. The samples obtained and their nomenclature are summarized in Table 1.

Two methods were used to prepare the samples. In the first one, 5 g of Sap was stirred with the appropriate amount of surfactant and 250 cm^3 of deionized water in a centrifuge flask for 4 h at 50 °C. The solutions were separated from the solid by centrifugation for 20 min at 4500 rpm and washed three times with deionized water. Finally, the samples were dried for 14 h in air at 120 °C. The second method was only used to prepare the samples organofunctionalized with tetraethoxysilane (TEOS). This process was carried out in two steps: in the first step 5 g of Sap was dispersed in 15 cm^3 of 2-propanol with magnetic stirring, then deionized water and the necessary amount of TEOS was added until a homogeneous white gel was formed. This gel was dried at 60 °C in an oven to obtain S-TEOS. In the second step, 5 g of ground S-TEOS was stirred for 48 h with 3-aminopropyltriethoxysilane and 50 cm^3 of 2-propanol. Finally, the mixture was dried at 60 °C to obtain the final solid.

2.2. Preparation of titanium modified saponite and saponite PVC nanocomposite

A modification of the second method reported previously was used to prepare the samples with titanium. In the first step, 5 g of Sap was dispersed in 15 cm^3 of 2-propanol with magnetic stirring, then deionized water and 4.84 cm^3 of TEOS was added until a homogeneous white gel was formed. This gel was dried at 60 °C in an oven to obtain S-TEOS(5). In the second step, 5 g of ground S-TEOS(5) was stirred for 48 h with 50 cm^3 of 2-propanol, 3.19 cm^3 of 3-aminopropyltriethoxysilane and the titanium sources. The titanium sources were: titanium (IV) bis(ammonium lactate) dihydroxide ($[CH_3CH(O\text{-})CO_2NH_4]_2Ti(OH)_2$, $C_6H_{18}N_2O_8Ti$, Aldrich, 50 mass% in water); titanium (IV)-isopropoxide ($Ti[OCH(CH_3)_2]_4$, $C_{12}H_{28}O_4Ti$, Aldrich, 97%); titanium (IV) ethoxide ($Ti(OC_2H_5)_4$, $C_8H_{20}O_4Ti$, Aldrich) and titanium(IV) oxide (rutile, Aldrich, 99.99%). Finally, the mixtures were dried at 60 °C and calcined at 850 °C for 4 h to obtain the final solids. The samples obtained and their nomenclature are summarized in Table 2. The number of the C atoms of the titanium source was included in the nomenclature.

The formulation of Sap PVC nanocomposite was: 1 g of PVC, 0.8 g of $CaCO_3$, 0.03 g of stabilizing Ca/Zn, 0.8 g of plasticizer di-iso-nonyl phthalate and 0.08 g of titanium OC. All components are mixed with 25 cm^3 of tetrahydrofuran (HPLC purity) ultrasonically agitated for 1 h. After this time, a whitish homogeneous mixture is formed. This mixture is poured into a cylindrical mold, followed by evaporation of the solvent. Finally, plates with 1.5 × 1.5 cm square and 1 mm thick were obtained.

2.3. Characterization techniques

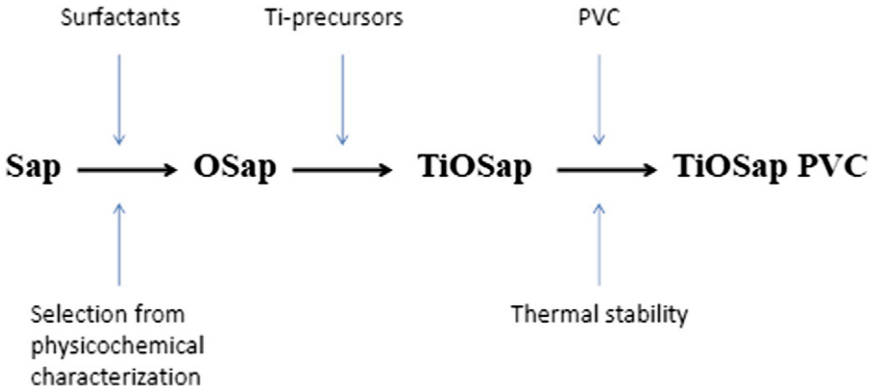
XRD patterns of the materials were obtained using a Siemens D-5000 diffractometer using Cu Kα filtered radiation ($\lambda = 0.1548$ nm). The working conditions employed were 30 mA, 40 kV and a scanning rate of 2° (2θ)/min.

Elemental analyses of the solids were carried out by the Instituto Geológico y Minero, Spain, using XRF and AAS, while special analyses were carried out for the determination of C.

Thermal analyses were performed on TA-Instruments, TGA2950. The measurements were carried out at a heating rate of 10 °C/min from room temperature to 800 °C under nitrogen atmosphere.

FT-IR spectra were recorded on a Perkin-Elmer 1730 Infrared Fourier Transform Spectrometer provided with a laser radiation source of He–Ne ($\lambda = 632.8$ nm). The spectra were performed using the KBr pellet technique, with a KBr:sample ratio of 300:1. The spectral region studied was between 400 and 4000 cm^{-1}.

SEM and Energy-Dispersive X-ray (EDX) analysis were performed using a Digital Scanning Microscope Zeiss DSM 940, operating at



Scheme 1. Synthesis steps of OSap PVC nanocomposites.