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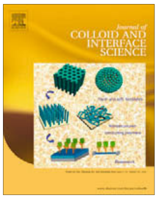

New synthesis strategies for effective functionalization of kaolinite and saponite with silylating agents

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ABSTRACT

Functionalization of Brazilian São Simão kaolinite and Spanish Yunclillos saponite with the alkoxysilanes 3-aminopropyltriethoxysilane and 3-mercaptopropyltrimethoxysilane is reported. The resulting hybrids were characterized by X-ray diffraction, thermal analysis, infrared absorption spectroscopy, and scanning electron microscopy, which demonstrated the effectiveness of the interlamellar grafting process. The X-ray diffractograms revealed incorporation of the alkoxide molecules into the interlayer space of the clays. The displacement of the stretching bands of interlayer hydroxyls in the infrared spectra of the modified kaolinites and the increased intensity of the Mg–OH vibrations in the spectra of the modified saponites confirmed the functionalization of the clays. The thermal behavior of the organoclays confirmed the stability of the hybrids, which was dependent on the clay used for preparation of the materials.

1. Introduction

Inorganic and organic components can be mixed at the nanometer scale, in virtually any ratio, leading to the so-called hybrid organic–inorganic nanocomposites. These materials have attracted considerable attention in the past years [1–3]. Zeolites, silica, and other matrices are being used as inorganic hosts to prepare hybrid nanocomposites [4–10]. These materials are extremely interesting because they combine the properties of their components in the interface, thus giving rise to composites with unique magnetic, photoluminescent, mechanical, optical, optoelectronic, conducting, and catalytic properties for specific applications in areas such as optoelectronics, catalysis, and biomaterials, among others [11–14].

These materials have been mainly prepared by surface modification of the inorganic matrix with organic molecules like polymers, biomolecules, alkoxides, and macromolecules. Functionalization of the inorganic surface can occur via weak bonds (hydrogen, van der Waals, or ionic bonds) or through strong chemical bonds (covalent or iono–covalent bonds). The conditions employed in the preparation of these materials depend on the inorganic matrix [15–23]. On the other hand, various organofunctional alkoxysilanes have been extensively employed for functionalization of inorganic matrices, such as aminoalkoxysilane [20,24–26], methacrylatealkoxysilane [16,27], glycidylalkoxysilane [9,26], polydimethylsiloxanes [28,29], and others [30–33]. The so-called silanization process occurs by the reaction between the inorganic matrix and the alkoxysilanes, whose alkoxy groups react with the OH groups present on the surface of the solids producing the hybrid organo–inorganic material after hydrolysis and condensation [34,35].

Among the potential nanocomposite precursors, those based on layered clays are the most widely investigated, probably because the starting materials are easily available and their intercalation chemistry has long been studied [33]. Natural and synthetic clay materials have been modified by intercalation or functionalization with organosilanes, leading to the production of new hybrid organo–inorganic materials with large surface areas and relatively high cation exchange capacities, which may find numerous applications [36–40].

This paper describes the functionalization of natural kaolinite and saponite clays with the alkoxysilanes 3-aminopropyltriethoxysilane (APTS) and 3-mercaptopropyltrimethoxysilane (MPTMS), in the case of the kaolinite by treatment of previously prepared clay–DMSO complexes. The synthesized solids are characterized by infrared spectroscopy (FTIR), thermal analysis (TG/DTA), X-ray diffraction (XRD), and scanning electron microscopy (SEM).

2. Experimental

2.1. Starting materials

Two clay minerals were used in this study: a kaolinite obtained from the municipality of São Simão, State of São Paulo, Brazil,

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kindly supplied by Darcy R.O. Silva & Cia. (São Simão-SP, Brazil), and a saponite collected from Yunclillos (Toledo, Spain), kindly supplied by TOLSA (Madrid, Spain). Both samples were purified according to standard sedimentation techniques, and the experiments were conducted on the <2 m fractions; in both cases, the mineralogical impurities are almost completely removed by purification; only traces of them are detected in the extracted fractions. Characterization of the original clay minerals has previously been reported [35,41]. Purified kaolinite and saponite were designated as Ka and Sa, respectively.

3-Aminopropyltriethoxysilane and 3-mercaptopropyltrimethoxysilane were supplied by Sigma–Aldrich, with 99% purity. Toluene, from Fisher Scientific, at 99% purity, was used as solvent.

2.2. Kaolinite organofunctionalization

First, kaolinite intercalated with dimethyl sulfoxide, Ka-DMSO, was prepared following the methodology described in the literature [42,43]. Twenty grams of the purified kaolinite was suspended in a mixture of 180 mL of DMSO and 20 mL of H_2O, which was maintained at 60 °C under agitation for 10 days. The solid was then centrifuged, washed with ethanol, and oven-dried at 60 °C. This precursor was then employed for the preparation of the organofunctionalized solids using the following procedure: 5.0 g of Ka-DMSO, previously dried by heating at 90 °C for 2.5 h, was placed in a 100 mL flask, which was closed and filled with dried nitrogen atmosphere. The silylating agent (APTS or MPTMS, 25 mL) was added by means of a syringe, stirred continuously (no solvent was used; the silanes give the liquid medium needed for suspending the clays). The mixture was heated at 200 °C for 48 h in a thermostatic bath containing silicone oil. After cooling, the product was filtered and washed several times with toluene, in order to remove the excess of the silanes [44], and then dried in vacuum at 110 °C for 14 h. The resulting samples were designated Ka-APTS and Ka-MPTMS.

2.3. Saponite organofunctionalization

For the syntheses of the two organofunctionalized saponites, purified saponite (5.0 g) and distilled water (100 mL) were placed in a reaction flask under stirring, for 1 h, followed by addition of the silylating agent, APTS or MPTMS, 2 mL (intercalation of saponite is easy and this small amount of the silylating agents is enough, contrary to the large excess needed in the case of kaolinite). The suspension was then stirred at room temperature for 48 h. In the case of MPTMS, HCl was also added to the reaction at a 1/1 MPTMS/HCl molar ratio. The grafted saponite was filtered, extensively washed with toluene, and dried in vacuum at 110 °C for 14 h. The resulting samples were designated Sa-APTS and Sa-MPTMS.

2.4. Characterization techniques

The X-ray diffractograms of the solids were registered on a Siemens D-500 diffractometer operating at 40 kV and 30 mA (1200 W), using filtered Cu Kα radiation. The angle 2θ varied from 2° to 65°. All the analyses were undertaken at a scan rate of 2° per minute.

Thermal analyses (TG/DTA/DSC) were carried out in a TA Instruments SDT Q600 Simultaneous DTA-TGA thermal analyzer, in the 25–1000 °C temperature range, at a heating rate of 20 °C/min and under air flow of 100 mL/min.

The FTIR absorption spectra were obtained with a Perkin–Elmer 1739 spectrophotometer with Fourier transform, using the KBr pellet technique, with a KBr:sample ratio of 300:1.

Scanning electron microscopy (SEM) of the materials was performed in a digital scanning microscope DSM 960 Zeiss. The samples were coated with a thin gold layer using a Bio-Rad ES100 SEN coating system.

3. Results and discussion

Fig. 1 shows the XRD patterns of natural kaolinite and the derivatives Ka-DMSO, Ka-APTS, and Ka-MPTMS. The 001 reflection of the original kaolinite appears at 7.14 Å. This reflection shifts to a higher spacing, 11.30 Å, after DMSO addition to this clay mineral, confirming the insertion of this molecule between the clay layers, in agreement with literature reports [34,45]. The shift in the basal diffraction peak of an organoclay toward higher basal spacings is well known. The repetitive multilayer structure is usually well preserved in such intercalated nanocomposites, giving rise to an intense basal reflection and allowing easy determination of the interlayer spacing. In contrast, the extensive layer separation associated with exfoliated structures disrupts the coherent layer stacking and results in a featureless diffraction pattern [33].

On reaction with APTS and MPTMS, the XRD patterns of the resulting materials exhibit well developed basal reflections, indicating that the kaolinite layer structure is preserved after the functionalization process. XRD patterns of the resulting materials exhibit well developed basal reflections, which appear at 18.42, 9.96, and 11.30 Å in the case of Ka-APTS, and 8.66 Å in the case of Ka-MPTMS. Compared to original kaolinite, both solids are swollen. In the case of Ka-APTS, if compared to Ka-DMSO, it can be observed that the peak at 11.30 Å remains relatively intense, which suggests that a certain number of layers maintain DMSO between them. This is further confirmed by thermal analysis, which gives evidence of a mass loss between approximately 180 and 290 °C, attributed to the presence of residual DMSO molecules. Besides, two new peaks appear at 18.42 and 9.96 Å, clearly showing the expansion of the layers by APTS molecules. The second peak has a spacing approximately half of that of the first one, and behavior characteristic of first-order and second-order reflections of the basal diffraction, although the intensity ratios does not follow the usual behavior. Alternatively, it can be proposed that both basal spacings correspond to two very different arrangements of the silane molecules in the interlayer region. In the case of the solid functionalized with MPMTS, the basal spacing of 8.66 Å is clearly higher than that of the original kaolinite, but lower than that of

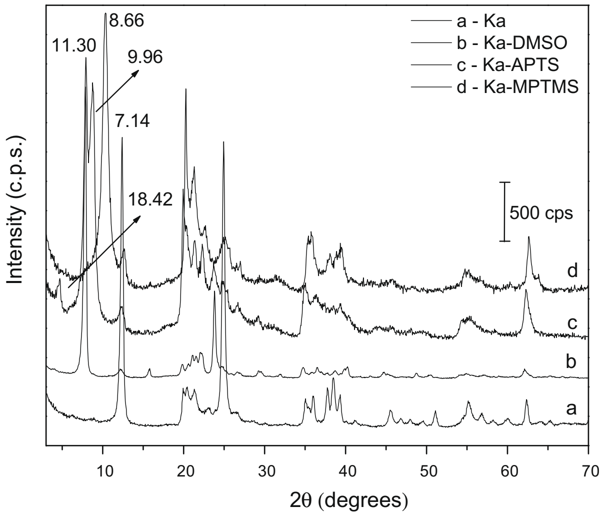

Fig. 1. X-ray powder diffraction patterns of Ka (a), Ka-DMSO (b), Ka-APTS (c), and Ka-MPTMS (d) solids.