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Research Paper

Laponite RD/polystyrenesulfonate nanocomposites obtained by photopolymerization

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ABSTRACT

The present paper describes the synthesis and characterization by dynamic light scattering, X-ray diffraction, scanning electron microscopy and atomic force microscopy of Laponite RD/Sodium polystyrenesulfonate nanocomposites obtained by radical photopolymerization initiated by the cationic dye safranine. The presence of the clay mineral does not affect the hydrotropic aggregation of the monomers, but allows a better deaggregation of the initiator molecules, decreasing the quenching of the excited states that leads to the radicals that initiate polymerization. Increasing the amount of clay mineral loading in the polymerization mixture promotes higher monomer conversion and faster polymerization. The size of the nanocomposite particles, measured by light scattering decreases from 400 to 80 nm for clay mineral loadings of 1.0 wt.%. The X-ray diffraction patterns indicate that the clay mineral does not present a regular crystalline structure in the nanocomposite. Atomic force microscopy studies show films of sodium polystyrenesulfonate polymer with embedded Laponite platelets in its structure, forming 1–8 nm height and 25–100 nm diameter aggregates.

1. Introduction

Clay minerals are extensively used in a wide range of applications. They are key components in the formulation of ceramic products, cement, drilling fluids, paints, and paper, among others. An important characteristic that clay minerals are able to provide in such uses is an adequate particle dispersion which is necessary to obtain uniform and stable systems (Pacula et al. 2006). Smectites are aluminosilicate minerals that have layered structures, which allow the intercalation of other compounds forming novel materials that present nanostructures with new properties that might be interesting in several fields ((Annabi-Bergaya 2008; Lagaly 1986; Pinnavaia 1983).

The incorporation of clays in polymers for improving their physical and mechanical properties is an important trend in polymer chemistry. It is known that the fully exfoliated platelet structure of nanoclays dispersed in polymer matrices confers excellent mechanical and barrier properties (Okada and Usuki 2006; Shi et al. 1996; Tsai et al. 2008). A wide range of polymers derived from monomers like epoxides (Wang and Pinnavaia 1994), styrene (Fu and Qutubuddin 2000), ethers (Pinnavaia et al. 1994), and acrylamide (Muzny et al. 1996) has been used with raw or synthetic clay minerals for development of polymer layered silicate nanocomposites. Polymer-layered silicate nanocomposites are currently prepared in four ways: *in situ* polymerization, intercalation from a polymer solution, direct intercalation on polymer and sol–gel technology (Okada and Usuki 2006). The *in situ* polymerization technique was first developed by the Toyota Group to make Nylon-6 nanocomposites from caprolactam monomers (Usuki et al. 1993). A comprehensive review of the synthesis and mechanisms of *in situ* clay/polymer nanocomposites preparation has been published recently (Tasdelen et al. 2010).

Clay/polymer nanocomposites can be classified in three categories: conventional particulate composites (the clay mineral particles exist in their original aggregated state with no insertion of polymer matrix between the layers), intercalated nanocomposites (only a few molecular layers of polymer are incorporated in the clay mineral structure, which might alter the properties of the composite (Annabi-Bergaya 2008)) and exfoliated nanocomposites (the individual clay mineral layers are separated and dispersed in a continuous polymer matrix) (Qutubuddin and Fu 2001). The latter yield the maximum improvement in the nanocomposite properties, as maximal reinforcement is achieved.

The dispersion or exfoliation of clay mineral particles in monomers or polymer matrixes involves three steps: wetting of the surface, intercalation of monomers or polymers into the clay mineral interlamellar spaces, and exfoliation of the clay mineral layers (Qutubuddin and Fu 2001).

Polymerization in ordered domains results in different kinetic behaviour (Clapper and Guymon 2006; Uhl et al. 2004). Therefore, it may be assumed that the ordering of the platelets in the clay mineral particles may induce changes in the polymerization behaviour that could influence the final nanocomposite properties. In addition, the relatively large surface of the clay mineral particles could also affect

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the polymerization dynamics and induce interactions with other constituents of the polymerizing system (Polowinski 2002). The photopolymerization kinetics of clay–polymer nanocomposites using polymerizable quaternary ammonium surfactants as dispersants showed that higher free-radical photopolymerization rates are observed with increasing polymerizable surfactant concentration, while no significant changes occur when non-polymerizable surfactants are added. The increase on the photopolymerization rate was traced to the lower apparent termination rate due to the immobilisation of the surfactants. A significant increase in the polymerization rate was observed when increasing the degree of clay mineral exfoliation (Owusu-Adom and Guymon 2008).

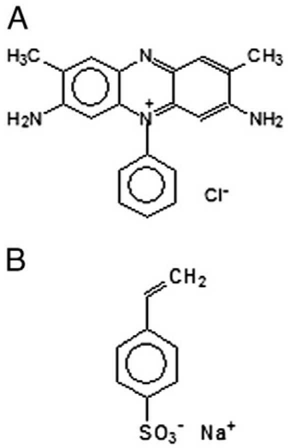
In the present work, *in situ* photopolymerization was used to obtain clay/polymer nanocomposites. The photopolymerization kinetics as a function of clay mineral loading was determined gravimetrically. In addition, the nanocomposites obtained were characterised by dynamic light scattering (DLS), X-ray diffraction (XRD) and atomic force microscopy (AFM). The clay mineral used in this study was a synthetic smectite (Laponite RD). These systems are potential candidates for forming regular nanocomposites, since the clay mineral is completely exfoliated when dissolved in aqueous solutions. Moreover, Laponite presents a high structural regularity and low level of impurities. Besides, it is almost completely dispersed when dissolved in aqueous solution, resulting in an increased accessible surface area, which favours the adsorption of substrates (Lagaly 1994).

2. Experimental

2.1. Materials

Laponite RD (Southern Clay Prods.) was used as received. Its cation exchange capacity (CEC) is 60 meq/100 g. All solutions were prepared in Milli-Q purified water. Laponite RD is synthetic trioctahedral hectorite composed of two tetrahedral silica sheets and a central octahedral sheet. Its chemical formula can be expressed as $Si_8[Mg_{5.5}Li_{0.4}O_{24.0}]^{-0.6}\ Na^{+0.6}_{0.6}$. Disk shaped layers of approximately 1 nm thickness and 25 nm diameter are formed when the clay mineral is dispersed in water.

Safranine (SfH^+, Aldrich) and the monomer sodium 4-styrenesulfonate (StyS, Aldrich) were used as received. The structure of these reactants is shown in Scheme 1.



Scheme 1. Structure of the reactants (A) safranine (SfH^+) and (B) sodium 4-styrenesulfonate (StyS).

2.2. Polymerization

The photopolymerization of sodium StyS (0.5 M) in the presence of SfH^+ (1×10^{-5} M) in Laponite RD dispersion (0.2–1.0 wt.%) was performed using four 100 W Phillips Daylight lamps (λ > 500 nm), at room temperature. PolyStyS (pStyS) and Laponite/polyStyS (Lap/pStyS) nanocomposites were precipitated with acetone and were washed several times with the same solvent.

The material was purified by dialysis for several days using cellulose membranes (14,000 D), until no fluorescence was detected in the 290–450 nm range (due to StyS), and dried by lyophilisation. Conversions were determined gravimetrically and the nanocomposites obtained were characterised by DLS, XRD, SEM and AFM.

2.3. Characterization

Fluorescence measurements were performed on a Hitachi F-4500 spectrofluorimeter and UV spectra were taken on UV-2550—Shimadzu spectrophotomer. All measurements were done at room temperature (25 ± 1 °C).

Silicate interlayer distance in the polymer matrix was obtained using an Enraf-Nonius Kappa CCD diffractometer (Cu, radiation λ = 0.154 nm) at 50 kV, 100 mA.

Particle sizes were analysed by DLS using a BI200-SM Brookhaven Instr. light scattering goniometer. The light source for the instrument is a JDS Uniphase, Model 4611-050-1000, 125 mW Nd-YAG laser (λ = 532 nm). The signal correlator from the amplifier/discrimination

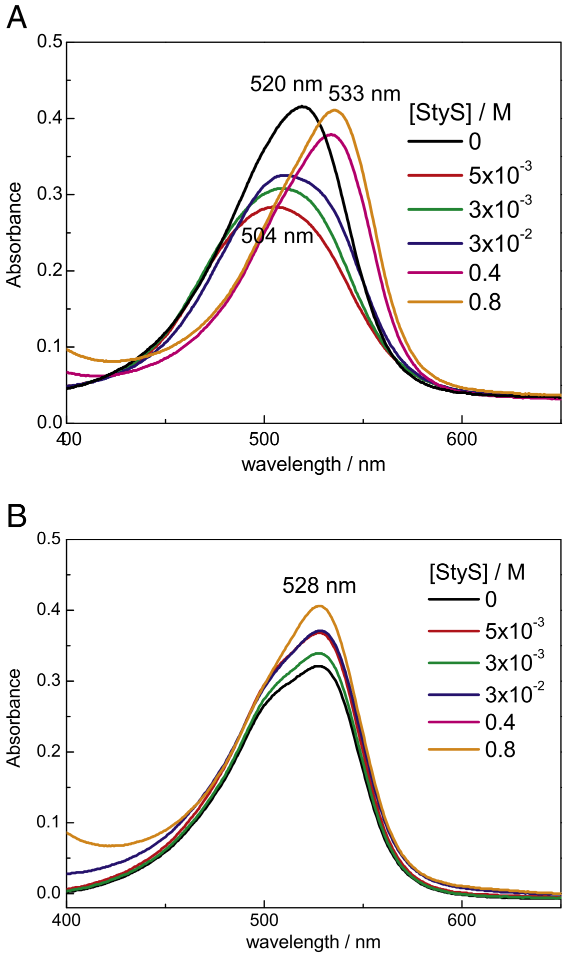


Fig. 1. Absorption spectra of SfH^+ (1×10^{-5} M) in the absence and presence of different concentrations of StyS. (A) Aqueous solution and (B) Laponite dispersion (0.5 g L^{-1}).