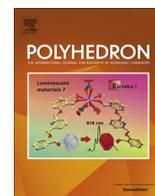




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Surface-initiated polymerization of styrene from one-step prepared thiol-functionalized organoclays

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ABSTRACT

A polystyrene–organoclay composite material was prepared by surface-initiated radical polymerization of styrene from the surface of thiol-functionalized organoclays synthesized in a one-step process. Characterizations of the composite by infrared spectroscopy (FTIR) and powder X-ray diffraction (PXRD) confirmed a direct covalent bonding between the polystyrene and the clay layers and an essentially exfoliated structure. The significant amount of SH reactive sites present in the organoclay resulted in a high grafting percentage (PG%, 49.8%) and in a high content of grafted polystyrene in the material (35.8 wt%), indicating that such polystyrene-grafted organoclays could be easily used as polymer fillers for incorporation in various polymeric matrices.

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1. Introduction

Despite extensive studies, research in the field of polymer–inorganic nanocomposites is still very active and growing, as the range of applications for these engineered plastics has been continuously expanding [1–3]. The value added to existing pure polymeric matrices by the incorporation of inorganic fillers is multifold. Compared to pure polymers, polymer–inorganic nanocomposites exhibit several enhanced properties such as mechanical properties [4,5] (e.g. stiffness, strength), corrosion resistance [6], ionic [7], electrical [8] and thermal [9] conductivity, gas barrier [10,11], inflammability [12,13] and antimicrobial [11] activity, which makes them very attractive for a variety of applications in the aerospace, automotive, energy, electronics, food packaging and biomedical industries.

Numerous investigations have been conducted on polymer-layered silicate nanocomposites using organically modified clay materials prepared via intercalation of long-chain alkyl ammonium cations into the interlayer space of natural clays [3]. However, this method has shown several drawbacks including a multi-step syn-

thesis and the lack of direct covalent bonding between the polymer and the clay layers, often resulting in macroscopic phase separation. Surface-initiated polymerization reactions, in which polymerization takes place from polymerizable monomers chemically grafted onto the silicate surface have been reported [14,15]. In this process [15], a coupling agent, generally an organoalkoxysilane with polymerizable end groups reacts with the silicate surface hydroxyl groups acting as anchoring sites, thus creating a covalent bond between the silicate filler and the polymer. While this method has been successfully used with low aspect ratio materials, such as SiO₂ [16–19] and TiO₂ [20–22] nanoparticles, its applications to clay materials has shown moderate success [23–25], as the coupling reaction with the anchoring OH groups is limited by the small amounts of these groups available on the surface of clay layers and by their accessibility.

The organoclay materials used in this work differ from organically modified layered silicates commonly used as polymer fillers, since they are prepared in a one-step process [26] from direct precipitation of metal ions (i.e. Mg²⁺) with organoalkoxysilanes (i.e. mercaptopropyltrimethoxysilane) in basic medium (Fig. 1).

Our previous work [27] showed that these one-step prepared organoclays exhibited a layered structure and elemental composition consistent with those of the natural talc material. Compared to chemically grafted clays, these directly prepared organoclays also displayed higher amounts of organic functional groups pending into the interlayer space. It can then be anticipated that, if these

Abbreviations: MTMS, mercaptopropyltrimethoxysilane; Mg–MTMS, thiol-functionalized organoclay material; AIBN, 2,2'-azobisisobutyronitrile; PSg, grafted polystyrene; PSf, free (non-grafted) polystyrene; PSg–Mg–MTMS, polystyrene-grafted Mg–MTMS material.

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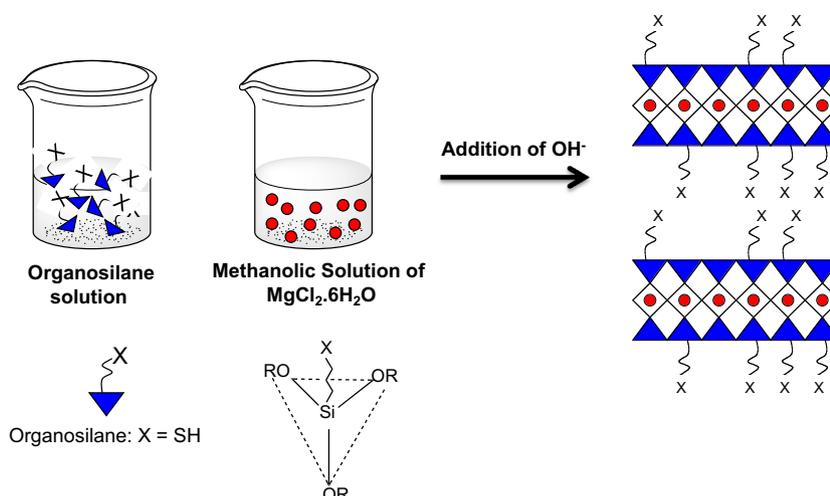


Fig. 1. Schematic representation of the one-step preparation of thiol-functionalized organoclays (Mg-MTMS).

pending organic groups were to bear functions from which polymerization could take place, the number of synthetic steps necessary for the preparation of polymer–clay nanocomposites would be significantly reduced, no phase separation should occur between the clay material and the polymer matrix, and the exfoliation of the clay layers into the polymer matrix would be promoted as the polymerization would progress from the layers as schematically represented on Fig. 2.

Here, we report on the surface-initiated radical polymerization of styrene from the surface of thiol-functionalized organoclays (Mg-MTMS) to produce polystyrene-grafted organoclay nanocomposite materials. Fig. 3 represents the reaction mechanism proposed for the preparation of such materials.

2. Experimental

2.1. Materials

Mercaptopropyltrimethoxysilane (MTMS) was obtained from Gelest and was kept under nitrogen prior to use. Methanol, magnesium chloride hexahydrate, anhydrous sodium sulfate and sodium hydroxide were purchased from Fisher Scientific and were used without prior purification. The polymerization inhibitor

(4-*tert*-butylcatechol) was removed from styrene (Aldrich) by washing styrene with a dilute (10%) sodium hydroxide aqueous solution and then drying it over anhydrous sodium sulfate. 2,2'-azobisisobutyronitrile (AIBN) was purchased from Aldrich and was purified by recrystallization from methanol. Toluene (Fisher Scientific) was degassed prior to use.

2.2. Synthesis of thiol-functionalized organoclay, Mg-MTMS

The thiol-functionalized organoclay, Mg-MTMS, material was prepared in a one-step silylation process as previously described [1]. Typically, mercaptopropyltrimethoxysilane (22.0 mmol, 4.3 g) was added to a methanolic (100 mL) solution of magnesium chloride hexahydrate (16.5 mmol, 3.4 g). Aqueous sodium hydroxide (0.05 M, 400 mL) was then slowly added to the solution and the mixture was stirred for about 18 h, at room temperature. A white precipitate formed that was filtered and washed thoroughly with distilled water and ethanol, then dried in air at 50 °C for 12 h.

2.3. Preparation of polystyrene-grafted Mg-MTMS composites

Mg-MTMS (1.00 g) was added to a Schlenk flask, and submitted to at least three vacuum pump-Ar-fill cycles. Degassed toluene

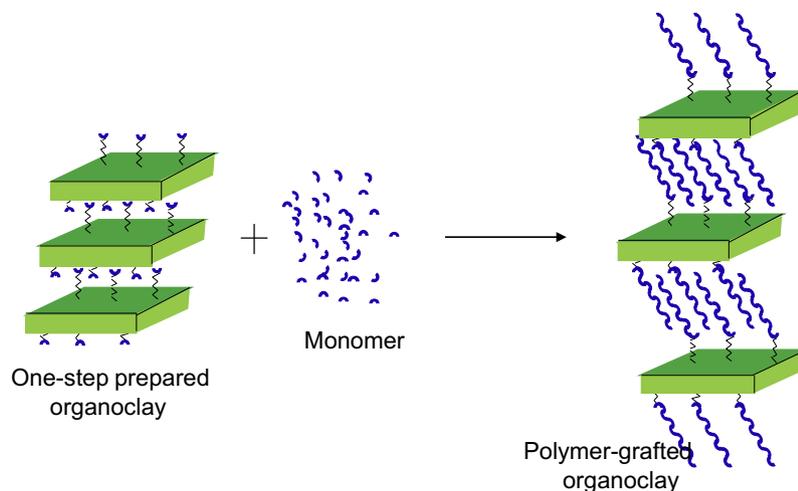


Fig. 2. Schematic representation of surface-initiated polymerization from one-step functionalized organoclays.

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