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Hybrid nanocomposites prepared by *in situ* photopolymerization using photoinitiator-modified montmorillonite

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ABSTRACT

A series of hybrid nanocomposite coatings were prepared by UV curing of the urethane dimethacrylate monomers with various amounts of photoinitiator-modified montmorillonite (1, 3 and 5 wt.%, respectively). First, two different types of free-radical generating photoinitiators, a Type I – Irgacure 2959 (alpha cleavage type) and a Type II – benzophenone derivative (hydrogen abstraction type) were synthesized and bounded on Cloisite Na^+ layers. The homogeneous thin films were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), UV–vis spectrophotometry, thermogravimetric analysis (TGA) and mechanical testing. The XRD pattern of organic/MMT nanocomposite with 3 wt.% PI-1-MMT (Type I) hybrid photoinitiator displays a small peak at 6.36° (1.39 nm) characteristic to an intercalated structure, while in the XRD diffraction spectra of polymeric nanocomposites with PI-2-MMT (Type II) photoinitiator, no diffraction peaks were visible, suggesting the formation of an exfoliated structure. These outcomes were further confirmed by TEM and UV analyses, and can be attributed to the binding pathways (grafting/intercalation) of the photoinitiator molecules on the nanoclay surface. Also, the *in situ* photogeneration of silver nanoparticles ($5 \div 10$ nm diameter) triggered by photoinitiator-MMT systems was proved, when small well dispersed Ag NPs were formed.

1. Introduction

Today, the combination of organic and inorganic components has become an important pathway for the production of new materials with superior properties over pure constituents, reason for that they have found numerous applications in nanoscience and nanotechnologies [1,2]. Generally, the literature reports have shown that the incorporation of inorganic components with nanometric dimensions into common organic polymers generates a new class of hybrid nanocomposite materials with tuned structure and physico-chemical properties (hydrophilicity, chemical, thermal and mechanical stability). Therefore, a broad range of polymer nanocomposites starting from different inorganic components such as clays [3], hydroxyapatite [4], metals [5] and metal oxides [6] or silica [7] included in a polymer host were presented, but the most investigated composites are those based on silica-clays due to their abundance, low cost and well-known intercalation chemistry [8]. Given the inherent immiscibility between the clays and polymer matrix (except for water soluble polymers), an important issue that should not be neglected is the realization of polymer nanocomposites with proper dispersion of the nanoparticles in the network. The complete dispersal of the inorganic phase will lead to the development of large interfacial area, which optimizes the organic–inorganic interactions responsible for the significant improvements of the final material properties. So, the majority of the research efforts in this domain have been focused on achieving higher compatibility between clays and various organic polymers promoting thus better matrix–nanoparticle interactions. Taking into account that the main difficulty related to the dispersion of clays in polymer matrices during the preparation of polymer nanocomposites is caused by the hydrophilic nature of clay minerals [9], a good solution seems to be the organic modification of the clays prior their use. In fact, the clay modification provides not only the compatibility with various organic polymers, but also increases the interlayer distance (d_{001} spacing) facilitating the access of polymer chains during the dispersion process. Since the Toyota researchers reported for the first time the dispersion of montmorillonite (MMT) into nylon-6 matrix [10], these layered silicate particles were used in combination with various polymer matrices. The clay modification was accomplished mainly through the cationic exchange [11–14] or silanization [15,16], and the nanocomposites can be obtained by four principal methods, namely solution exfoliation, melt intercalation, *in situ* polymerization, and template synthesis. Subsequently, three distinct morphologies of

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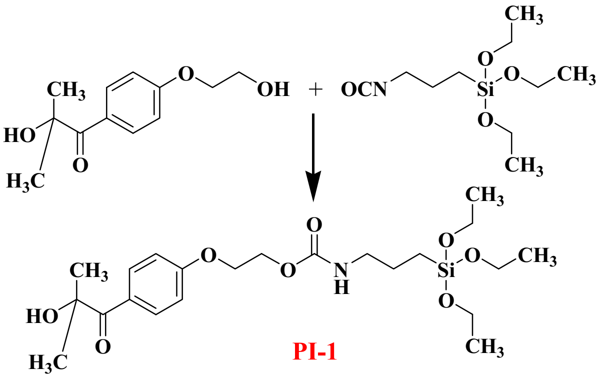
the systems could be obtained: conventional microcomposites, intercalated and exfoliated nanocomposites. The best final properties of the nanocomposites are attained when the clay mineral platelets are fully exfoliated [17], but frequently, a mixture of intercalated and exfoliated structures are present in materials with both single platelets and stacked tactoids. Due to the obvious advantages compared to other synthesis methods, the *in situ* polymerization is the most used technique to yield this type of nanocomposites. *In situ* polymerization is initiated by external stimulation (thermal, photochemical or chemical activation), the suitable initiator can be free in the system or anchored within the silicate layers, while the chain growth takes place in the interlayer space and generates the particle exfoliation and nanocomposites formation. The literature data reported various *in situ* polymerization techniques, such as conventional free radical polymerization [18–21], controlled radical polymerization [22–25], ring-opening polymerization [26–29], ring-opening metathesis polymerization [30,31], cationic polymerization [32–34], and anionic polymerization [35,36]. All these methods are usually solvent-based processes, so in order to eliminate this drawback, the formation of clay-nanocomposites through UV-curing technology, which is a solvent-free procedure, was also considered [37–42]. Moreover, the photopolymerization process offers additional benefits: efficiency, energy saving, economics (short time processing at room temperature, high production speed) and greenability (no emission of volatile organic compounds and waste reduction), and it can be easily controlled by simply turning on and off a light [43,44].

In the present work, we describe the attachment on montmorillonite layers of two different free-radical generating photoinitiators, a Type I – Irgacure 2959 (alpha cleavage type) and a Type II – benzophenone derivative (hydrogen abstraction type). Further, the photopolymerization process of some acrylic monomer mixtures in the presence of various amounts of photoinitiator-modified MMT (1, 3 and 5 wt.%, respectively) was investigated, as well as their influence on the formation and properties of the resulting polymer nanocomposites. Besides, the ability of photoinitiator-functionalized clay to photoinduce the formation of silver nanoparticles (NPs) *via* the reduction of metal salt simultaneously with the photopolymerization of monomers was also studied. This solvent free environmental friendly approach allows the achievement of polymer coatings enclosing both clay nanoplatelets and noble metal nanoparticles easily produced by a green technique. Supplementary, the Ag nanoparticle agglomeration is overcoming through the stabilization provided by the organic matrix and their good dispersion is furnished by the initiation of the photopolymerization process in the vicinity of silicate layers.

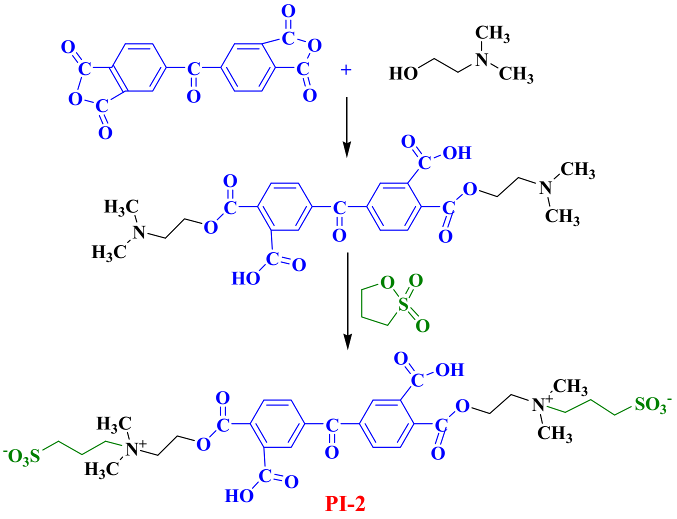
2. Experimental

2.1. Materials

2-Hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (IRG2959), 3-(triethoxysilyl) propyl isocyanate, benzophenone-3,3′,4,4′-tetracarboxylic dianhydride, 2-dimethylaminoethanol, 1,3-propanesultone, poly(butylene adipate) (PBA, $M_n = 1000$), trimethyl-1,6-diisocyanatohexane, the mixture of 2,2,4- and 2,4,4-isomers, 2-hydroxyethyl methacrylate (HEMA), castor oil, isophorone diisocyanate and 4-(dimethylamino) phenylacetic acid (DMPheAA) were used as received (from Sigma Aldrich Chemical Co.) without any purification. The unmodified sodium montmorillonite (MMT) Cloisite® Na$^+$ was purchased from Southern Clay.



Scheme 1. Synthetic route of the PI-1 photoinitiator.



Scheme 2. Synthesis of the PI-2 photoinitiator bearing benzophenone core.

2.2. Intermediates and monomers synthesis

For the preparation of 2-(4-(2-hydroxy-2-methylpropanoyl) phenoxy) ethyl 3-(triethoxysilyl) propylcarbamate (PI-1) (Scheme 1), 3.43 g (15 mmol) IRG2959 were dissolved in 50 mL chloroform and 3.91 mL (15 mmol) 3-(triethoxysilyl) propyl isocyanate were dropwise added, in the presence of few drops of dibutyltin dilaurate used as catalyst. The system temperature was raised at 40 °C and the stirring was continued for 24 h. The solvent of the resulting solution was evaporated under vacuum and the PI-1 compound was collected as a pale yellow solid.

2.2.1. PI-1

Yield: 6.65 g (94.1%). ^{1}H NMR ($CDCl_3$, δ ppm): 7.97 (2H, Ar—C=O); 6.82 (2H, Ar—O); 5.36 (1H, NH); 4.28 (2H, $-C\underline{H}_2-OCO-NH$); 4.07 (2H, $Ar-O-C\underline{H}_2-$); 3.69 (6H, $Si-O-C\underline{H}_2-CH_3$); 3.05 (2H, $-OCO-NH-C\underline{H}_2-$); 1.48 (8H, $-C\underline{H}_2-CH_2-Si$ and $-C\underline{H}_3-C-OH$); 1.1 (9H, $Si-O-CH_2-C\underline{H}_3$); 0.51 (2H, $-C\underline{H}_2-Si$). FTIR (KBr, cm^{-1}): 3373 (NH); 2886-2975 (C—H); 1705 (C=O); 1670 (amide I); 1600 (Ar); 1535 (amide II); 1248; 1166 (C—O—C); 1078 (Si—O).

For the synthesis of PI-2 photoinitiator (Scheme 2), 5.1 g (15.5 mmol) benzophenone-3,3′,4,4′-tetracarboxylic dianhydride were dissolved in 30 mL dimethylformamide and 3.18 mL (31 mmol) 2-dimethylaminoethanol were dropwise added, the mixture being stirred at 65 °C for 8 h. Afterwards, the solution containing the benzophenone intermediate (BP-I) was concentrated