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Poly(epsilon caprolactone)/clay nanocomposites via host–guest chemistry

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ABSTRACT

Cyclodextrin-modified montmorillonite (MMT-CD) has been prepared from commercial montmorillonite clay (Cloisite 30B) containing two hydroxyl groups by reacting succinic anhydride through esterification. Poly(epsilon caprolactone) (PCL)/clay nanocomposites are prepared by host–guest chemistry between MMT-CD as host and PCL, hydrophobic polymer as guest. The structures of the intermediates and final nanocomposite are investigated in detail by FT-IR XRD, TEM, DSC and TGA measurements. The intercalated/exfoliated morphologies are determined by combined XRD and TEM analyses. Thermal stabilities of all nanocomposites are improved by the addition of MMT-CD compared to the neat polymer. The DSC data confirm that the crystallinity of PCL is slightly increased by increasing clay loading.

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1. Introduction

Combination of organic and inorganic structures within a single material at nanoscopic level is one of the most effective approaches for producing new materials with advanced properties [1]. Generally, inorganic nanoparticles have been incorporated into common organic polymers to generate a new class of hybrid nanocomposite materials that combine the desirable properties of inorganic nanoparticles (e.g. rigidity, high strength, electrical conductivity, thermal and oxidative stability) with the advantages of organic polymers (e.g., processability, flexibility, toughness and cost). The significant improvements are due to the strengthened interfacial interactions between polymer chains and nanoparticles, which are well dispersed in the polymer matrix. A wide range of nanoparticles such as, clays, carbon nanotubes, graphites, polyhedral oligomeric silsesquioxane (POSS) and metal oxides are currently available and used for preparing polymer nanocomposites. The silicate-based clays are among the most widely studied inorganic nanoparticles because of their abundance, price and well-known intercalation chemistry [2–4]. Up to date, several strategies have been considered for the preparation of polymer/clay nanocomposites with homogenous dispersion of clay layers, namely, solution exfoliation, melt intercalation, in-situ polymerization, and template synthesis [5]. Depending on the interfacial interactions and mode of mixing of the polymer and clay layers, three distinct morphologies can be obtained in the system; unintercalated (or microcomposite), intercalated (and/or flocculated), or exfoliated (or delaminated) [6]. In-situ polymerization involves the swelling of the organomodified

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clays in liquid monomers, which diffuse in between the clay platelets [7]. The subsequent polymerization, which can be initiated by external stimulations such as thermal [8–15], photochemical [12–22], or chemical activation [22–26], triggers the delamination of clay layers and hence the nanocomposite formation containing intercalated or exfoliated structures. This approach provides better exfoliation compared to melt and adsorption methods [27]. Recently, click chemistry reactions, and in particular the copper-mediated 1,3-dipolar [3 + 2] cycloaddition between azides and alkynes (CuAAC) have been applied for the preparation of polymer/clay nanocomposites. In this approach, the exfoliation is rooted in the functional units of the intercalant that readily react with the antagonist groups of the preformed polymers [28–31]. The azide and alkyne partners can each be incorporated in either the clay surface or polymer chain. The quantitative efficiency of click reaction coupled with tolerance to a wide variety of functional groups and reaction conditions make this coupling process highly attractive for the nanocomposite preparation. Not only but also, the thiol-ene and atom transfer nitroxide radical coupling click reactions have been employed to prepare polymer/clay nanocomposites. Spectroscopic and microscopic investigations revealed that nanocomposite formations with mixed morphologies including intercalated layers with a non-uniform separation and exfoliated single layers isolated from any stacks were successfully attained. The multiple hydrogen-bonding interactions based on 2-ureido-4[1H]pyrimidinone system have been also utilized to fabricate exfoliated silicate polymer/clay nanocomposites [32]. The multiple hydrogen-bonding interactions between intercalated 2-ureido-4[1H]pyrimidinone (UPy)-functionalized organoclay and UPy-end functionalized polymers have been exploited to delaminate the clay tactoids resulting in the formation of nanocomposites.

Cyclodextrins (CD)s are cyclic oligosaccharides and classified according to their number of glucopyranose units (α -cyclodextrin (6 units of glucopyranose), β -cyclodextrin (7 units of glucopyranose) and γ -cyclodextrin (8 units of glucopyranose)) [33]. The most important feature of such cyclic structures is a hydrophobic inner cavity and a hydrophilic outer surface, hence their ability to form non-covalent inclusion complexes with organic [34], inorganic [35], biological molecules [36] or supramolecular aggregates [37,38]. The main factors acting as driving force to form host-guest complexes and their stabilities are hydrophobic forces, the sizes of molecules/cavity and the guest properties. The host-guest chemistry provides a valuable platform for the synthesis of various supramolecular macromolecular architectures [39] including stars [40], hydrogels [41], polymer brushes [42] with other molecules and polymers [43–45]. There are few reports on the preparation of organomodified clays containing cyclodextrin units in the literature [46–53]. However, in these study only inclusion complexes with various low-molecular-weight compounds such as benzene [50], benzoic acid [46], toluene [46,49,50], cetylpyridinium chloride [47], crystal violet [48], ethylbenzene [50], menthone [49], mimonene [49], naphthalene [50] pyrene [52], tetrachloroethylene [50], 1,2,3trichlorobenzene [50], trichloroethylene [50] and o-xylene [50] were investigated. To the best of our knowledge, no report is currently available in the literature regarding the preparation of polymer/clay nanocomposites using host-guest type complex system.

In this study, firstly the cyclodextrin as host has been introduced to the hydroxyl groups of commercial montmorillonite clay (MMT-(CH₂CH₂OH)₂) by reacting a cyclic anhydride through esterification [54]. Poly(ϵ -caprolactone) (PCL), a well-known biodegradable polymer, is employed as guest polymer, which is able to form inclusion complexes with cyclodextrin. The host-guest type complex formation of the intercalated cyclodextrine-functionalized clay (MMT-CD) and PCL could gradually push the layers apart, leading to delamination of clay tactoids. The obtained PCL/MMT nanocomposites have been characterized by X-ray diffraction (XRD) spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and transmission electron microscopy (TEM). The influence of molecular weight of PCL and clay loadings on the microstructure and thermal properties of PCL/MMT composites is also investigated. The mild reaction condition coupled with tolerance to a wide variety of convenient polymers make this process highly attractive for the nanocomposite preparation.

2. Experimental

2.1. Materials

An organo-modified clay, Cloisite 30B [MMT-(CH₂CH₂OH)₂] was purchased from Southern Clay Products (Gonzales, TX, USA). The organic content of organo-modified MMT, determined by thermogravimetric analysis (TGA), was 21 wt%. The clay was dried under vacuum at 110 °C for 1 h before use. Succinic anhydride (SA, Merck, 99%), 4-(*N,N*-dimethylamino) pyridine (DMAP, Merck, 99%) were purchased from Merck. Chloroform-*d* (CDCl₃, 99.8 atom% D), deuterium oxide (D₂O, 99.9 atom% D) and dicyclohexylcarbodiimide (DCC) were provided by Sigma-Aldrich. Tetrahydrofuran (THF, VWR Chemicals, 99.7%), *N,N*-dimethylformamide (DMF, Merck), pyridine (J.T. Baker, 99%), diethyl ether (VWR Chemicals, 99.5%) were used as received. Dichloromethane (DCM, VWR Chemicals, 99.9%) was dried and stored over 4 Å molecular sieves before use. Triethylamine (TEA, 98%) was purchased from J.T. Baker. The poly(ϵ -caprolactone)s with different molecular weights (M_n = 6000 or M_n = 12,000) were prepared according to the literature procedure [32].

2.2. Characterization

All ¹H NMR spectra were recorded on an Agilent NMR System VNMRS 500 spectrometer at room temperature in CDCl₃ with Si(CH₃)₄ as an internal standard. Molecular weights were determined by gel permeation chromatography (GPC) using

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