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Preparation of waterborne hyperbranched polyurethane acrylate/LDH nanocomposite

Haibo Hu, Yan Yuan, Wenfang Shi*

CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Jinzhai Road 96, Hefei, Anhui 230026, PR China

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A series of novel waterborne hyperbranched polyurethane acrylate (WHPUA)/layered double hydroxide (LDH) nanocomposites based on hyperbranched aliphatic polyester Boltorn H20 (H20) and MgAl-LDH were successfully synthesized by *in situ* polymerization approach. The MgAl-LDH was firstly modified by sodium dodecyl sulfate (SDS) through the coprecipitation method, and then grafted by isophorone diisocyanate (IPDI), forming a complex with NCO groups at the surface and interlayer of LDH (LDH-DS-NCO). The residual hydroxyl groups after modification with succinic anhydride were crosslinked by the semi-adduct of IPDI reacted with HEA, and LDH-DS-NCO, followed by a neutralization reaction with triethylamine. The resulting water dispersible hyperbranched polyurethane acrylate WHPUA/LDH hybrid oligomer was then exposed to a medium pressure mercury lamp, forming a partially exfoliated WHPUA/LDH nanocomposite in the presence of a fragmental photoinitiator. The chemical structure, crystal configuration, morphology of WHPUA/LDH nanocomposite were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, thermogravimetric analysis, and high resolution transmission electron microscopy. The experimental results indicated that both the intercalated and exfoliated structures were formed in the UV cured polymer/LDH nanocomposite. The TGA results showed that the thermal stability was improved. Moreover, the pencil hardness was greatly increased, and the flexibility remained at an acceptable level for the UV cured polymer/LDH nanocomposites.

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1. Introduction

Organic/inorganic nanocomposites have been considered as a novel class of materials, and extensively studied as a hot topic in polymer material field in recent years. Their enhanced thermal and mechanical properties, improved barrier properties, and reduced flammability have been widely recognized [1–3]. The use of different kinds of inorganic nanoparticles such as Ag [4], Au [5], SiO_2 [6], TiO_2 [7], montmorillonite [8], and kaolinite [9] to prepare organic/inorganic nanocomposites was reported in previous work.

The layered double hydroxide (LDH), known as a hydrotalcite-like material, is a kind of anion clay. It can be represented by the ideal formula $[M_{1-x}{}^{2+}M_x{}^{3+}(OH)_2]^{x+}A_{x/n}{}^{n-}\cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, such as Mg^{2+}, Al^{3+}, respectively, and A^{n-} is an exchangeable anion, such as $CO_3{}^{2-}$, $SO_4{}^{2-}$, and $NO_3{}^{-}$. Due to the highly tunable properties, LDHs are considered as a new class of the most favorable layered crystals for preparing polymer/layered crystal nanocomposites [10]. However, the interlayer electrostatic force resulting from the high charge density and strong polarity of a large number of hydroxyl groups at the surface make the intercalation and exfoliation of LDH difficult [11–13]. To improve the affinity of LDH toward organic materials, much effort has been focused on the modification of LDH with organic or polymeric anions, such as alkyl sulfates, alkyl sulfonates, phenyl phosphates, poly(propylene carbonate), and polystyrene [14–17]. Furthermore, several silane coupling agents have successfully been used to intercalate into LDH layers successfully by the covalent linkage formation through the reaction of hydroxyl group on LDH sheet with alkyloxysilane group of silane coupling agent [18–20]. Qiu et al. [21] prepared the exfoliated polystyrene/LDH nanocomposites through the *in situ* atom transfer radical polymerization of styrene in the presence of an initiator after the intercalation of dodecyl sulfate into LDH galleries.

Waterborne polyurethanes (WPUs) have evoked great academic and commercial interests due to their “clean, green and efficient” performance. However, their thermal stability, dispersibility and mechanical properties are usually lower than those of organic solventborne PUs [22]. It has been found that using inorganic nanoparticles as additives is an effective way to enhance the properties of WPU. Various types of fillers, such as clay [23–25], multiwalled carbon nanotubes [26–28] and Au [29], have been introduced, showing the significant improvement in performance

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* Corresponding author. Tel.: +86 551 3606084; fax: +86 551 3606630.
E-mail address: wfshi@ustc.edu (W. Shi).

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of the nanocomposites such as mechanical properties, thermal stability and others. The polyurethane/LDH nanocomposites prepared by blending LDH with polyurethane have also been reported recently [30–33]. In this case, the physical interaction and noncovalent linkage bond between LDH and polyurethane occurred, and resulted in a small enhancement in the properties of materials.

The conventional UV curable waterborne polyurethane acrylates (UV-WPUA) are usually prepared by end-capping linear polyurethane prepolymers with monohydroxyl (meth)acrylates, which results in low unsaturation density, and thus low crosslinking density. Consequently, the mechanical properties, and solvent and water resistance of cured films are not good enough [34–36]. Using pentaerythritol diacrylate as an extension agent, a novel UV-WPUA incorporating acrylate double bonds as side chains of polyurethane has been reported, showing the excellent solvent resistance and mechanical properties for a UV cured film [37–39]. Recently, UV-WPUA with different functionality were prepared using various chain extension agents, and it was shown that the mechanical properties and solvent resistance increased along with the increase of functionality of modified polyurethane [40]. Hyperbranched polymers are characterized by large amounts of end-groups, and can be used to prepare the UV-WPUA with high functionality [41]. The waterborne hyperbranched polyurethane (WHPUA) prepared by modifying the commercial hyperbranched polyesters (Boltorn H20, H30 and H40), and hyperbranched prepolymer (HPE-OH) were synthesized in our group, showing low viscosity, and good water resistance and mechanical properties of the UV cured films [42,43]. However, there has been little report on the preparation of WHPUA/LDH nanocomposites used for coatings.

In the present work, the preparation of UV-cured partially exfoliated WHPUA/LDH nanocomposites is presented. To obtain an exfoliated nanostructure, the adopted method is firstly to prepare an organically modified LDH with sodium dodecyl sulfate, and urethanate with isophorone diisocyanate (IPDI), obtaining the grafted LDH containing isocyanate group (LDH-DS-NCO) as a crosslinker. Then the LDH-DS-NCO was further photopolymerized with WHPUA in the presence of a photoinitiator to form the WHPUA/LDH nanocomposite. The molecular structures of LDH-DS and LDH-DS-NCO are characterized by Fourier transform infrared spectroscopy (FT-IR). The microstructure and morphology of nanocomposites are investigated by X-ray diffraction (XRD) analysis and high resolution transmission electron microscopy (HR-TEM) observation. The thermal property, pencil hardness and flexibility of the UV cured polymer/LDH nanocomposites were investigated.

2. Experimental

2.1. Materials

$Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, sodium hydroxide, sodium dodecyl sulfate (SDS), isophorone diisocyanate (IPDI), di-*n*-butyltin dilaurate (DBTDL), stannous chloride, succinic anhydride, triethylamine (TEA), p-hydroxyanisole, toluene, 1,4-dioxane, acetone were all purchased from Shanghai Sinopharm Chemical Reagent Co. (China). Hydroxyethyl acrylate (HEA) was provided by Eternal Chemical Co. (Taiwan). The hyperbranched aliphatic polyester, Boltorn® H20 (H20), a dendritic polymer with theoretically 16 primary hydroxyl groups and a molecular weight of 1747 g mol^{-1}, was provided by Perstorp Specialty Chemicals AB (Perstorp, Sweden). HEA was distilled and collected as a purified reactant and used after drying over 4-Å molecular sieves. IPDI was distilled before use. Acetone was dried over 4-Å molecular sieves before use. 1,4-Dioxane was dried over potassium hydroxide and then distilled. 1-Hydroxy-2-methylpheny-propane-1-one (Runtecure 1103), used as a photoinitiator, was provided by Runtec Chemicals Co. (Changzhou, China). All other materials were used as received without any further purification.

2.2. Synthesis

2.2.1. Modification of LDH with SDS

The coprecipitation method was used to prepare the SDS-modified LDH. 7.35 g SDS was dissolved into 150 mL of deionized water in a 500 mL three-neck round-bottom flask at the pH 10.5 which was adjusted by concentrated NaOH solution, under stirring at 90 °C. 9.38 g $Al(NO_3)_3{\cdot}9H_2O$ and 19.23 g $Mg(NO_3)_2{\cdot}6H_2O$ were dissolved into 50 mL of deionized water, and then dropped into the above SDS solution under vigorous stirring at 90 °C. The pH value of reactant was kept at 10.5 by adding 4.0 M NaOH solution *via* a peristaltic pump. The formed homogenous suspension was then aged for 24 h at 90 °C. The formed slurry was filtered until all supernatant liquid was removed, and then washed extensively with deionized water to remove unreacted SDS, obtaining a SDS-modified MgAl-LDH, named LDH-DS as a milk-white suspension. The powder for measurements was collected by centrifugation and dried at 65 °C in a vacuum oven for 24 h.

2.2.2. Modification of LDH-DS with IPDI

Before modifying LDH-DS with IPDI, an appropriate amount of aqueous suspension containing 10.90 g LDH-DS was dispersed into 200 mL of toluene in a 500 mL three-neck round-bottom flask. Then water was removed by azeotropic distillation, and a toluene suspension of LDH-DS was obtained. 26.00 g (117 mmol) IPDI with a catalytic amount of DBTDL was added into the flask which was then sealed to form an airtight system, and reacted under ultrasonic agitation at 50 °C for 3 h. Subsequently, the flask was equipped with a condenser and the mixture was refluxed at 85 °C for 60 h under magnetic stirring in a N_2 atmosphere. After cooling to room temperature, the IPDI-modified LDH-DS (LDS-DS-NCO) was collected as a pale yellow powder (yield 90.8%) by centrifugation at 3000 rpm, then thoroughly washed with acetone, and dried in a vacuum oven at 65 °C for 24 h.

2.2.3. Preparation of WHPUA/LDH dispersions

The ideal molecular formula of H20 and a schematic presentation for the reaction procedure are shown in Scheme 2. Firstly, 20.00 g (11.45 mmol, 183.2 mmol OH groups) H20 was dissolved in 50 mL of 1,4-dioxane at 100 °C, and then 6.88 g (68.7 mmol) succinic anhydride and a catalytic amount of stannous chloride were added. The reaction was conducted in dry N_2 atmosphere at 100 °C to ensure an acceptable reaction rate until the anhydride peak at 1786 cm^{-1} in the FT-IR spectrum disappeared.

For preparing the semi-adduct IPDI-HEA, into a 50 mL round-bottom flask equipped with a dropping funnel and a drying tube, 20.00 g (90.0 mmol) IPDI was dissolved into 15 mL of 1,4-dioxane at 0 °C. 10.45 g (90.0 mmol) HEA in 10 mL of 1,4-dioxane with catalytic amount of DBTDL and *p*-hydroxyanisole (1000 ppm over total amount of reactant) was dropped slowly into the IPDI solution of 1,4-dioxane under efficient stirring at 0 °C, and then reacted at 25 °C until the theoretical isocyanate (NCO) content reached to half of the original value determined by the di-*n*-butyl-amine titration method.

Then different amount of LDH-DS-NCO powder (1%, 3%, and 5%) was added in batches into the mixture of succinic anhydride modified H20 by succinic anhydride and IPDI-HEA adduct under vigorous stirring, and reacted at 40 °C until the peak at 2268 cm^{-1} for NCO group completely disappeared. An excess of TEA was added and stirred vigorously at 40 °C for 2 h to ensure completion of the neutralization reaction. Finally, 1,4-dioxane was evaporated under vacuum, and deionized water was added slowly under vigorous

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