



A novel LDH nanofiller intercalated by silsesquioxane for preparing organic/inorganic hybrid composites

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ABSTRACT

A novel layered double hydroxide nanofiller (LDH-SA) was synthesized through intercalating the silsesquioxane-based aminoundecanoic acid (SAD) into MgAl-based LDH, following by grafted with the semiadduct of IPDI and 2-hydroxyethyl acrylate (IPDI-HEA). SAD was obtained by the reaction of semiadduct isophorone diisocyanate-aminoundecanoic acid (IPDI-AD) with the pre-synthesized silsesquioxane hybrid polyol (SOH). The molecular structures were characterized by FT-IR and ^1H NMR spectroscopy. LDH-SA was blended into an acrylic resin and UV irradiated, obtaining an exfoliated polymer/LDH nanocomposite which possesses the combined enhancement in thermal stability brought by both LDH and silsesquioxane. The formed UV cured nanocomposite possessed the exfoliated microstructure from the transmission electron microscope (TEM) and HR-TEM observations. The thermal and mechanical properties were greatly enhanced. The onset decomposition temperature of nanocomposite with 5% LDH-SA loading increased by 45 °C from TGA analysis, while the tensile strength and pencil hardness were enhanced to 9.4 MPa and 2 H from 7.2 MPa and 3B, respectively, compared with the pure polymer.

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1. Introduction

Polymer/layered crystal inorganic nanocomposites have drawn major attention among organic/inorganic nanocomposites for their advantaged mechanical and thermal properties, wonderful chemical stability, reduced flammability and so on (Becker et al., 2011; Costache et al., 2006; Maag et al., 2000; Pojanavaraphan and Magaraphan, 2010; Qiu et al., 2006). Therefore, the organic-intercalated layered double hydroxide (LDH) nanomaterials have become a hot topic and have been widely studied in scientific and industrial fields in recent years, for example, used as photoinitiator complexes in UV curing systems, flame retardant additives in coatings, as well as drug containers and catalyst carriers (Chakraborti et al., 2011; Evans and Duan, 2006; Frache et al., 2011; Hu et al., 2011; Tong et al., 2010; Yuan and Shi, 2010). The formed polymer/LDH nanocomposites possess the combined advantages of LDH and polymers. The LDHs are a class of anion clay materials containing hydroxides of different kinds of metal cations and anions intercalated into hydrated interlayer for supplying the balanced negative charge (Khan and O'Hare, 2002). They can be represented by the ideal formula $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}\text{A}^{n-}_{x/n}\cdot m\text{H}_2\text{O}$, where x means the

content of M^{3+} in the total element weight of the formula divided by the molar mass of M^{3+} when OH^- 's value set as 2, 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^- (Zhao et al., 2011).

Recent years, a new hybrid reagent, silsesquioxane complex, was introduced to prepare organic/inorganic nanocomposites for its enhancement in physical and chemical properties, and especially in thermal properties (Cheng et al., 2009; Choi et al., 2003; Li et al., 2001; Pyun and Matyjaszewski, 2001; Yoshimoto and Takahiro, 2004; Zhao and Schiraldi, 2005). Silsesquioxane refers a term of matters with the empirical formula of $\text{R}_n\text{Si}_n\text{O}_{1.5n-x}(\text{OH})_{2x}$, and can form ladder and cage-like or polymeric structure (Cheng et al., 2009). There are some studies combining LDH with silsesquioxane as a dual-nanofiller in nanocomposites. Yei and coworkers used aminopropylisobutyl polyhedral oligomeric silsesquioxane (POSS) as a surfactant to prepare polystyrene/montmorillonite (MMT) nanocomposites (Yei et al., 2004). However, the limited distance of 0.5 nm between Si-Si in POSS resulted in a small increase of 0.4 nm in d-spacing between layers after intercalated by POSS, almost acting as the traditional long chain alkyl ammonium salt surfactant. Furthermore, the complicated and time-consuming procedure in the synthesis of POSS makes its application limited in laboratory research.

Therefore, several large-scale silsesquioxane-based hybrid reagents have been produced in a brief process with lower cost (dell'Erba and Williams, 2007; dell'Erba et al., 2003, 2004). Mori and coworkers described the synthetic route for a kind of cage-type

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silsesquioxane with hydroxyl groups on the outermost surface, possessing 12–18 Si atoms and an average particle size of 2.7 nm (Mori et al., 2003, 2004, 2007). In this regard, the larger scale silsesquioxane is priority to be chosen as a surfactant for preparing polymer/LDH nanocomposites with unique properties. Firstly, a common surfactant, aminoundecanoic acid (AD), was reacted with isophorone diisocyanate (IPDI) to obtain the semiadduct IPDI-AD, followed by reacted with the pre-synthesized silsesquioxane hybrid polyol (SOH), obtaining a new anion surfactant silsesquioxane-based aminoundecanoic acid (SAD). Then SAD was intercalated into MgAl-LDH through the coprecipitation method, preparing LDH-SAD with expanding layer spacing.

Moreover, the UV irradiation technology was introduced to prepare polymer/LDH nanocomposites for its “clean, green and efficient” advantages (Zahouily et al., 2001, 2002; Zammarrano et al., 2005). In our group, a novel UV cured acrylated silane-intercalated polymer/LDH nanocomposite was prepared by modifying LDH with both sodium dodecyl sulfate (SDS) and [3-(methyl-acroloxy)propyl]trimethoxysilane (KH570), followed by UV irradiation after blended into an acrylate system (Yuan and Shi, 2011). Compared with the pure polymer, the mechanical and thermal properties of UV cured nanocomposites showed enhancements in different extents, as well as hardness. Herein, LDH-SAD was further reacted with the semiadduct of IPDI and 2-hydroxyethyl acrylate (IPDI-HEA), obtaining UV curable acrylate-modified LDH and named as LDH-SA. The LDH-SA was blended into an acrylic resin in the presence of 1-hydroxycyclohexyl-phenyl ketone as a photoinitiator, and then exposed to a medium pressure mercury lamp, forming a completely exfoliated polymer/LDH nanocomposite. The photopolymerization kinetics, mechanical and thermal properties, and microstructures of nanocomposite were all examined in details.

2. Experimental

2.1. Materials

Glycidol and aminoundecanoic acid (AD) were purchased from Sigma-Aldrich Co. (USA) and used as received. 3-Aminopropyltriethoxysilane (KH550) supplied by Nanjing Yudeheng Fine Chemical Co. (Nanjing, China), isophorone diisocyanate (IPDI) supplied by Shanghai First Reagent Co. (Shanghai, China), and 2-hydroxyethylacrylate (HEA) supplied by Eternal Chemical Co. (Taiwan) were distilled under reduced pressure before use. Hydrofluoric acid (46–48% HF aqueous solution), di-n-butyltindilaurate (DBTDL), p-hydroxyanisole, N,N-dimethylacetamide (DMAC), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, sodium hydroxide (NaOH), toluene were all purchased from Sinopharm Chemical Reagent Co. (Shanghai, China) and used as received except for DMAC, which was used after drying over 4-Å molecular sieves. The detailed synthesis and characterization of semiadduct (IPDI-HEA) of IPDI and HEA were described in our laboratory (Asif and Shi, 2003). EB270, an aliphatic urethane diacrylate with an unsaturation concentration of 1.33 mmol g^{-1} and a molar mass of 1500 g mol^{-1} , tripropylene glycol diacrylate (TPGDA) and 1,6-hexamethyldiol diacrylate (HDDA) were supplied by Cytec Industries Inc. (USA). 1-Hydroxycyclohexyl-phenyl ketone (Runtecure 1104) used as a photoinitiator was provided by Runtex Chemicals Co. (Changzhou, China).

2.2. Measurements

The Fourier transfer infrared (FT-IR) spectra were recorded using a Nicolet MAGNA-IR 750 spectrometer with a KBr disk. The Proton Nuclear Magnetic Resonance ($^1\text{H NMR}$) spectra were recorded with an AVANCE 300 Bruker spectrometer using tetramethylsilane as an internal reference and D_2O as a solvent. The X-ray diffraction (XRD) analysis was performed using a Rigaku D/Max-rA rotating anode X-ray diffractometer equipped with a Cu $\text{K}\alpha$ tube and Ni filter ($\gamma =$

0.1542 nm). The transmission electron microscope (TEM) and high resolution TEM (HR-TEM) micrographs were obtained using Hitachi (Tokyo, Japan) H-800 and JEOL-2011 instrument, respectively, operated both at an acceleration voltage of 200 kV. The samples were ultramicrotomed with a diamond knife on a LKB Pyramitome to give 60-nm thick slices.

The photopolymerization rate was monitored in air by a CDR-1 differential scanning calorimeter (DSC) (Shanghai Balance Instrument Co., Shanghai, China) equipped with a UV spot cure system BHG-250 (Mejuro Precision Co., Japan). The incident light intensity at the sample pan was measured to be 2.4 mW cm^{-2} with a UV power meter. The unsaturation conversion (P_t) was calculated by the formula, $P_t = H_t/H_\infty$, where H_t is the heat effect within t (s), the H_∞ is the heat effect of 100% unsaturation conversion. For calculating the H_∞ , the value, $H_0 = 86 \text{ kJ mol}^{-1}$, for the heat of polymerization per acrylate unsaturation was taken. The DSC curve was normalized by the weight (g) of sample. The polymerization rate is defined by $\text{J g}^{-1} \text{ s}^{-1}$, named the variation of enthalpy (J g^{-1}) per second.

The thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50 H thermoanalyzer. In each case a 10-mg sample was examined under a N_2 flow rate of $6 \times 10^{-5} \text{ m}^3 \text{ min}^{-1}$ at a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ from room temperature to $600 \text{ }^\circ\text{C}$. The tensile storage modulus (E') and tensile loss factors ($\tan\delta$) were measured by a dynamic mechanical thermal analyzer (Diamond DMA, PE Co., USA) at a frequency of 10 Hz and a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ in the range of -100 to $200 \text{ }^\circ\text{C}$ with the sheets of $25 \times 5 \times 1 \text{ mm}^3$. The crosslink density (ν_e) as the molar number of elastically effective network chain per cube centimeter of the film, was calculated from the storage modulus in the rubbery plateau region according to: $\nu_e = (E'/3RT)$, where E' is the elastic storage modulus, R is the ideal gas constant, and T is the temperature in K.

The mechanical properties were measured with an Instron Universal tester (model 1185, Japan) at $25 \text{ }^\circ\text{C}$ with a crosshead speed of 25 mm min^{-1} . The dumb-bell shaped specimens were prepared according to ASTM D412-87. Five samples were analyzed to determine an average value in order to obtain the reproducible result. The pendulum hardness was determined in Persoz mode in seconds by using a QBY pendulum apparatus (Tianjin Instrument Co., China). The pencil hardness was determined using a QHQ-A pencil hardness apparatus (Tianjin Instrument Co., China).

2.3. Preparation of acrylated silsesquioxane-intercalated LDH (LDH-SA)

2.3.1. Preparation of silsesquioxane hybrid polyol (SOH)

The SOH was prepared according to the procedure developed by Mori et al. (2003). 110.5 g (0.5 mol) KH550 was dropped slowly into 74.08 g (1.0 mol) glycidol at ice cooling, and reacted for 1 h at $25 \text{ }^\circ\text{C}$ under stirring. The formed adduct N,N-di(2,3-dihydroxypropyl)-(aminopropyl)triethoxysilane was then dissolved in 700 mL of methanol, following by added with 21.03 g HF aqueous solution (3.225 wt%), and then stirred for 4 h at $25 \text{ }^\circ\text{C}$. After removed methanol, ethanol and water, and dried at $80 \text{ }^\circ\text{C}$ in vacuum for 72 h, the silsesquioxane hybrid polyol (SOH) was obtained in a glassy solid at room temperature (yield 97%).

2.3.2. Preparation of silsesquioxane-based aminoundecanoic acid (SAD)

A mixture of 8.04 g (0.04 mol) AD, 8.88 g (0.04 mol) IPDI and a catalyst amount of DBTDL (0.1 wt%) were dispersed in 40 mL of dried DMAC with vigorously stirring for 5 h at $40 \text{ }^\circ\text{C}$, forming the intermediate semiadduct IPDI-AD. Then the IPDI-AD was dropped slowly in 73.4 g (0.02 mol) SOH solution of DMAC (1.5 wt%) at room temperature for 1 h, and reacted at $60 \text{ }^\circ\text{C}$ for 5 h. After dried at $80 \text{ }^\circ\text{C}$ in vacuum for 72 h to remove DMAC, a new anion surfactant silsesquioxane-based aminoundecanoic acid (SAD) was obtained.

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