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Research paper

Preparation of photopolymerized nanocomposites through intercalating multifunctional acrylated siloxane into montmorillonite

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ABSTRACT

The multifunctional acrylate-intercalated montmorillonite (TA-Mt) was prepared by intercalating the cetyltrimethyl ammonium bromide (CTAB)-modified Mt (CTAB-Mt) with a trifunctional acrylated siloxane (TAS). The TA-Mt was further formulated with epoxy acrylate and 1,1,1-propanetrimethanol tris(3-mercaptopropionate) (PTTM) in an equimolar ratio of thiol group to acrylate double bond, and a trace amount of 0.5 wt.% photoinitiator. This formulation was then exposed to UV light to form the polymer/Mt nanocomposites through the thiol-ene click reaction. The FT-IR, XRD, and TGA analysis confirmed the successful grafting of TAS to the Mt interlayers. The TEM and HR-TEM micrographs together with further XRD measurement indicated that the UV-cured nanocomposites possess an intercalated structure. The TGA and DMA analyses demonstrated the better thermal stability and excellent compatibility. The T_g increased with the TA-Mt content increasing in the nanocomposites.

1. Introduction

UV curing technology has been widely used in various industrial fields in the last decades, such as coatings, inks, adhesives, fabricated plastics and electrical/electronics manufacturing due to the 5E's benefits: efficiency, excellent properties, energy saving, economics, and environmentally friendliness. UV curable formulations consist mainly of three components, that is, oligomers, multifunctional monomers, and photoinitiators. Photoinitiators are usually used in a small percent amount but play a decisive role in photopolymerization process. However, the inherent disadvantages, such as oxygen inhibition in curing process and migration of photolysis species to the film surface, which cause coating yellowing and unpleasant odors, restrict their applications in high-tech areas and food contact fields (Davidson et al., 1995; Wang et al., 2010). Moreover, some of them may even be harmful to human beings, such as carcinogenic effects and endocrine disrupting (Grosse et al., 2011; Reitsma et al., 2012). Therefore, the self-initiated photopolymerization systems, such as thiol-ene (Cramer et al., 2002, 2004), N-substituted maleimide (Ahn et al., 2007; Bongiovanni et al., 2005; Morel et al., 1999), β-diketone based (Gaudl et al., 2003; Zhang et al., 2007), and vinyl acrylate (Jönsson et al., 2005; Lee et al., 2003), have been extensively studied, recently. On the other hand, reducing the amount of photoinitiator in UV curing systems has become an important issue for advancing UV coating industry.

From the previous studies (Xie et al., 2012; Zhang et al., 2011), the thiolether group in UV curing systems was demonstrated to restrain the surface oxygen inhibition, and simultaneously promoted the photoinitiating efficiency. Consequently, as an alternative of photoinitiator, thiol-ene resins can self-initiate photopolymerization. In most instances a trace amount (lower than 1 wt.%) of photoinitiator is used for UV curing compared with traditional UV curing systems (Cramer and Bowman, 2001; Cramer et al., 2002, 2004). This is beneficial for the environment and reduces the cost. Moreover, excellent chemical resistance, water absorption resistance, thermal stability, and mechanical properties with the UV cured thiol-ene based films were obtained (Sangermano et al., 2002; Woods, 1995; Yang et al., 2009).

The thiol-ene system is the so-called “click chemistry” for its high reaction efficiency and mild reaction conditions (Hoyle and Bowman, 2010; Hoyle et al., 2004). Especially the thiol-ene polymerization can be UV light-initiated at room temperature, providing high conversion in air. Recently, thiol-ene systems have been used for synthesis of complex structural macromolecules and organic/inorganic hybrid materials (Hoyle et al., 2010; Lowe, 2010).

In a hybrid material, there are two kinds of interface interaction: the weak bond (hydrogen, van der Waal or ionic bond) and the strong chemical bond (covalent or iono-covalent bond) (Judeinstein and Sanchez, 1996; Sanchez et al., 2005). Moreover, the chemical bond is the most important for the properties of a hybrid material, providing better compatibility of inorganic component with polymeric chains. Many researchers have made full use of thiol-ene chemistry to graft polymer chains onto inorganic particles for its high efficiency (Connal et al., 2009; Li et al., 2010; van der Ende et al., 2009).

Recently, montmorillonite/polymer-based nanocomposites have been paid great attention due to its easy organic modification (Pagacz and Pielichowski, 2009; Zou et al., 2008). In this work, the Mt/polymer

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nanocomposites were prepared by first intercalating the triacrylated siloxane into the Mt layers, and then conducting the thiol-ene reaction by UV irradiation of the formulation based on bisphenol A epoxy acrylate and tri-functional thiol. After intercalated with multifunctional acrylated siloxane, the Mt became organophilic and UV curable. This intercalation is followed by the thiol-ene click reaction between the double bond and tri-functional thiol. This resulted in a uniform dispersion of Mt layers in the polymer matrix. To the best of our knowledge, it is the first example of a thio-ene system in the preparation of polymer/Mt nanocomposites. The 1H NMR, FT-IR, XRD and TEM analyses were utilized to determine the structures of intercalated Mt and UV cured products. The photo-DSC and DMA analyses were used to evaluate the self-initiating activity of thiol-ene system and the compatibility of Mt with polymeric chains.

2. Experimental

2.1. Materials

Dichloromethane, petroleum ether (bp. 30 °C to 60 °C), toluene, *p*-toluene sulfonic acid (PTSA), sodium bicarbonate, cetyltrimethyl ammonium bromide (CTAB), trimethylolpropane (TMP) and dibutyltin dilaurate (DBTDL) were supplied by Sinopharm Chemical Reagent Co. (China). Sodium montmorillonite (Na-Mt) with cationic exchange capacity (CEC) of 90 mEq/100 g was kindly provided by Fenghong Co., Zhejiang (China). Pentaerythritol tetraacrylate (PET4A) and EB605, a standard bisphenol A epoxy acrylate containing 25 wt.% tripropyleneglycol diacrylate (TPGDA), were offered by Eternal Chemical Co. (Taiwan) and Cytec (USA), respectively. 2-Hydroxy-2-methyl-1-phenylpropane-1-one (1173) was provided by Runtec Chemicals Co., Changzhou (China). 3-Mercaptopropionic acid and 3-triethoxysilylpropylamine (APTES) were purchased from Sigma-Aldrich (USA). 4-Dimethylaminopyridine *p*-toluenesulfonate (DPTS) was prepared according to the literature reported by Moore and Stupp (1990). All reagents were of reagent grade and used without further purification.

2.2. Measurements

The Fourier transfer infrared (FT-IR) spectra were recorded using a Bruker Tensor 27 FT-IR spectrometer with a KBr disk. The Proton Nuclear Magnetic Resonance (^{1}H NMR) analyses were carried out with a DMX-300 MHz instrument (Bruker, Switzerland). The photopolymerization rate (R_p) was monitored in air at 25 °C with a differential scanning calorimeter (DSCQ 2000) equipped with a UV spotcure system from TA Instruments (USA). The incident light intensity at the sample pan was measured to be 100 mW cm^{-2} using a UV powermeter. The DSC curves were normalized by the weight (g) of samples. The R_p is defined as the heat of polymerization per second for 1 g samples (J g^{-1} s^{-1}). The final unsaturation conversion (P^f) in the cured film was calculated by the formula, $P^f = H_t/H_\infty$, where H_t was the heat effect within *t* s, and H_∞ was the heat effect of 100% unsaturation conversion (Scott et al., 2002, 2003).

The X-ray diffraction (XRD) analysis was performed using a Rigaku D/Max-rA rotating anode X-ray diffractometer equipped with Cu Kα tube and Ni filter ($\lambda = 0.1542$ nm). The transmission electron microscope (TEM) and high resolution TEM (HR-TEM) micrographs were obtained using Hitachi (Tokyo, Japan) H-800 and JEOL-2011 instruments, respectively, operating 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 thermogravimetric analysis (TGA) was performed on a thermoanalyzer (TGAQ60) from TA Instruments (USA). In each case a 10-mg sample was examined under a N_2 flow rate of 75 ml min^{-1} at a heating rate of 10 °C min^{-1} from room temperature to 700 °C. The tensile storage modulus (E') and tensile loss factors (tan δ) were measured on a dynamic mechanical thermal analyzer (Diamond DMA, PE Co., USA) at a frequency of 10 Hz and heating rate of 10 °C min^{-1} in the range of -60 °C to 80 °C with the sheet of 25.0 mm × 4.00 mm × 1.00 mm.

2.3. Synthesis and preparation

2.3.1. Synthesis of 1,1,1-propanetrimethanol tris(3-mercaptopropionate) (PTTM)

Trimethylolpropane (50.0 g, 0.373 mol), 3-mercaptopropionic acid (122.2 g, 1.152 mol) and DPTS (5.17 g, 3 wt.%) were dissolved in 200 ml of toluene, and heated to reflux in Dean Stark condenser in nitrogen atmosphere until no water was produced. After cooling to room temperature, saturated $NaHCO_3$ aqueous solution (3 × 120 ml) and distilled water (3 × 120 ml) were used to wash the product, successively. Then, the upper organic phase was dried over anhydrous $MgSO_4$. After filtration, the filtrate was evaporated to remove toluene and further purified by silica gel column chromatography using CH_2Cl_2 and petroleum ether as eluents. After removing the solvents with a rotary evaporator, the product, 1,1,1-propanetrimethanol tris(3-mercaptopropionate) (PTTM), was obtained as a viscous liquid (124.4 g, yield: 83.7%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 4.08 (s, 6H, –COO–CH$_2$–), 2.81–2.74 (m, 2H, –CH$_2$–***CH$_2$***–SH), 2.69–2.64 (t, 2H, –***CH$_2$***–CH$_2$–SH), 1.65–1.60 (t, 1H, –SH), 1.55–1.47 (q, 2H, –***CH$_2$***–CH$_3$), 0.93–0.88 (t, 3H, –CH$_2$–***CH$_3$***)

FT-IR (KBr plate, cm^{-1}): 2967, 2944, 2885 (–CH$_2$–CH$_3$), 2570 (–SH), 1731 (C = O of ester moiety)

2.3.2. Synthesis of triacrylated siloxane (TAS)

PET4A (30.0 g, 0.0851 mol) and APTES (18.84 g, 0.0851 mol) were separately dissolved in 60 ml and 20 ml of CH_2Cl_2. Then the APTES solution was added dropwise into the PET4A solution in icewater bath within 30 min, and further reacted for 10 h at room temperature. After CH_2Cl_2 was removed with a rotary evaporator, the product, triacrylated siloxane (TAS), was obtained as a viscous liquid.

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.44–5.85 (m, 3H, CH$_2$ = CH–COO–), 4.29–4.14 (m, 2H, –COO–CH$_2$–), 3.84–3.77 (q, 2H, CH$_3$–***CH$_2$***–O–), 2.90–2.88 (m, 2H, –***CH$_2$***–CH$_3$–COO), 2.63–2.51 (m, 5H, Si–CH$_2$–CH$_2$–***CH$_2$***– and –CH$_2$–***CH$_3$***–COO), 1.64–1.54 (m, 2H, Si–CH$_2$–***CH$_2$***–CH$_2$–), 1.24–1.19 (t, 3H, ***CH$_3$***–CH$_2$–O–), 0.64–0.59 (t, 2H, Si–***CH$_2$***–CH$_2$–CH$_2$–).

FT-IR (KBr plate, cm^{-1}): 2974, 2927, 2885 (–CH$_2$–CH$_2$), 1734 (C = O of ester moiety), 1410 (CH$_2$ = CH–COO–), 1080 (–Si–O–), 810 (C–H of CH$_2$ = CH–).

Table 1
Photo-DSC, DMA results at different TA-Mt loadings.

Sample	Formulation composition (wt.%)			R_p^{max} (Jg^{-1} s^{-1})	t^{max} (s)	P^f (%)	T$_g$ (°C)	V_e (mmol/mm^3)
	TA-Mt	1173	EB605/PTTM					
PM0	0	0.50	99.50	22.00	8.38	83.44	16.1	2.09
PM1	1.0	0.50	98.50	19.82	11.58	79.87	17.8	2.30
PM3	3.0	0.50	96.50	17.51	13.98	74.83	18.1	2.46
PM5	5.0	0.50	94.50	13.40	15.88	69.36	20.0	2.59