

Contents lists available at ScienceDirect

Materials Research Bulletin



journal homepage: www.elsevier.com/locate/matresbu

Preparation of polymer/LDH nanocomposite by UV-initiated photopolymerization of acrylate through photoinitiator-modified LDH precursor

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ARTICLE INFO

Article history: Received 30 June 2010 Received in revised form 30 September 2010 Accepted 1 November 2010 Available online 5 November 2010

Keywords: A. Layered compounds A. Nanostructures B. Intercalation reactions C. X-ray diffraction D. Mechanical properties

ABSTRACT

The exfoliated polymer/layered double hydroxide (LDH) nanocomposite by UV-initiated photopolymerization of acrylate systems through an Irgacure 2959-modified LDH precursor (LDH-2959) as a photoinitiator complex was prepared. The LDH-2959 was obtained by the esterification of 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959) with thioglycolic acid, following by the addition reaction with 3-(2,3-epoxypropoxy)propyltrimethoxysilane (KH-560), finally intercalation into the sodium dodecyl sulfate-modified LDH. For comparison, the intercalated polymer/LDH nanocomposite was obtained with additive Irgacure 2959 addition. From the X-ray diffraction (XRD) measurements and HR-TEM observations, the LDH lost the ordered stacking-structure and well dispersed in the polymer matrix at 5 wt% LDH-2959 loading. The glass transition temperature of UV-cured exfoliated nanocomposites increased to 64 °C from 55 °C of pure polymer without LDH addition. The tensile strength was improved from 10.1 MPa to 25.2 MPa, as well the Persoz hardness enhanced greatly, while the elongation at break remained an acceptable level.

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1. Introduction

The polymer/inorganic nanocomposites have attracted much attention for research and industrial uses in recent decades, because of their enhanced thermal and mechanical properties, improved barrier properties, and reduced flammability [1–3]. Moreover, the majority of previous studies have been focused on polymer/clay nanocomposites, especially based on montmorillon-ite-type layered silicates (MMTs) due to the lower charge density of clay layer which is in favor of the formation of exfoliated structure. However, the variability in the chemical composition of naturally occurred layered clay make the control in properties of the formed polymer/clay nanocomposite difficult.

The layered double hydroxide (LDH), known as a hydrotalcitelike material, is a so-called anion clay. The idea chemical structure can be represented by the formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}A^{n-}_{x/}$ $n \cdot mH_2O$, 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 [4]. However, the hydrophilic layer surface and the strong interaction between LDH layers both impede organic components to enter into the galleries, resulting in difficult exfoliation LDH layers [5–7]. In order to increase the compatibility of inorganic LDH filler with organic phase, some organic or polymeric anions, such as alkyl sulphonate [8], polyacylate [9], poly(styrene sulfonate) [10] and poly(propylene carbonate) [11] are used to modify LDH particles. Furthermore, several silane coupling agents have 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 [12–14]. Qiu et al. [15] prepared the exfoliated polystyrene/LDH nanocomposite through the *in situ* atom transfer radical polymerization of styrene under the presence of an initiator after the intercalation of dodecyl sulfate into the LDH galleries.

In recent years, much work are concerning with UV cured polymer/clay nanocomposites [16–19]. However, only little work has been done for preparing polymer/LDH nanocomposites by using UV irradiation [20,21]. In our laboratory, Lv et al. [22] prepared the UV cured polymer/LDH nanocomposites, and proposed that the intercalation of reactive groups into LDH interlayers results in the formation of exfoliated structure of LDH.

In the present work, the exfoliated UV cured polymer/LDH nanocomposite was prepared by using a novel photoinitiatormodified LDH precursor. A fragmental photoinitiator, 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959) was used to react with thioglycolic acid, 3-(2,3-epoxypropoxy)propyltrimethoxysilane (KH-560), and the sodium dodecyl sulfatemodified LDH to form the LDH-2959 used as a photoinitiator complex for acrylate systems. For comparison, the formulations

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^{0025-5408/\$ -} see front matter \circledcirc 2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.materresbull.2010.11.002

with additive Irgacure 2959 were also prepared. The photopolymerization kinetics of acrylate systems initiated by LDH-2959, and both LDH-2959 and Irgacure 2959 was investigated in detail. The mechanical and thermal properties, and microstructures of the formed nanocompsites were examined.

2. Experimental

2.1. Materials

Sodium dodecyl sulfate (SDS), Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O and sodium hydroxid were all purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Thioglycolic acid was purchased from Aldrich Chemical Co. 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959) and 1,6hexamethyldiol diacrylate (HDDA) were supplied by Ciba Specialty Chemicals and Eternal Chemical Co., Taiwan, respectively. 4-Dimethylamino pyridine (DMAP), p-toluene sulphonic acid (PTSA) and dimethylacetamide (DMAC) were purchased from Shanghai First Reagent Co. 4-Dimethylaminopyridine ptoluenesulfonate (DPTS) was prepared from the reaction of DMAP with PTSA according to the literature reported by Moore and Stupp [23]. 3-(2,3-Epoxypropoxy)propyltrimethoxysilane (KH-560) was purchased from Nanjing Yudeheng Chemical Co. EB270, which is an aliphatic urethane acrylate with a molar mass of 1500 g mol⁻¹ and an unsaturation concentration of 1.33 mmol g⁻¹, was offered by Cytec Industries Inc., USA. All chemicals were used as received without further purification except for KH-560, which was purified by distillation under reduced pressure before use.

2.2. Synthesis

2.2.1. Synthesis of thioglycolic acetate-modified 2959 (TA-2959)

Thioglycolic acid (11.04 g, 0.12 mol), Irgacure 2959 (22.4 g, 0.1 mol) and DPTS (0.672 g) were mixed with 50 mL of toluene in a 150 mL three-neck flask with a Dean-Stark trap, and stirred overnight at 125 °C under refluxing in nitrogen atmosphere. Then toluene was removed by rotary evaporation under reduced pressure. The crude product was diluted with 60 mL of CH_2Cl_2 , washed with saturated NaHCO₃ aq. (5× 100 mL) and distilled water (3× 100 mL). The organic phase was dried with anhydrous MgSO₄ overnight, and then filtrated and distilled, obtaining the product, named TA-2959, as a yellowish liquid (yield: 91%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.04–7.98 (–CH=CH–C–CO–), 6.93–6.87 (–O–C–CH=CH–), 4.49–4.43 (–COO–CH₂–CH₂–), 4.24–4.19 (–COO–CH₂–), 3.27–3.23 (HS–CH₂–), 2.0–1.94 (HS–CH₂–), 1.57 (CH₃–C–CH₃).

FTIR (NaCl plate, cm⁻¹): 3600–3100 (–OH), 2571 (–SH), 1735 (C=O of ester group), 1667 (C=O abutted on the aromatic ring), 1600 (C=C of the aromatic ring).

2.2.2. Synthesis of trimethoxysilane-modified 2959 (TMS-2959)

In a typical synthesis, into a 50 mL round-bottom flask equipped with a mechanical stirrer, a mixture of KH-560 (4.727 g, 0.02 mol), TA-2959 (5.96 g, 0.02 mol), triethylamine (0.179 g) as a catalyst and CH_2CI_2 (30 mL) was added, and stirred at 40 °C under nitrogen atmosphere. Completion of the reaction was confirmed by the disappearance of characteristic –SH peak at 2570 cm⁻¹ in the FT-IR spectrum. Finally, a modified Irgacure 2959 by KH-560, named TMS-2959, was obtained as a yellowish liquid (yield: 97%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.09–8.06 (–CH=CH–C–CO–), 6.98–6.94 (–O–C–CH=CH–), 4.54–4.45 (–COO–CH₂–CH₂–), 4.29–4.26 (–COO–CH₂–), 4.01–3.88 (–CH–CH₂–S–), 3.76–3.31 (CH₃–O–Si–, –CH₂–CH₂–O–CH₂–, –S–CH₂–COO–), 3.13–3.09

 $(-CH-CH_2-S-), \ 1.62 \ (CH_3-C-CH_3), \ 1.46-1.33 \ (-Si-CH_2-CH_2-), \ 1.46-1.33 \ (-Si-CH_2-CH_2-).$

FTIR (NaCl plate, cm^{-1}): 3600-3100 (–OH), 1735 (C=O of ester group), 1667 (C=O abutted on the aromatic ring), 1600 (C=C of the aromatic ring), 1046 (Si–O).

2.2.3. Modification of LDH with SDS

The coprecipitation method was used to prepare the SDSmodified LDH. 17.3 g SDS, 11.3 g $(0.03 \text{ mol}) \text{ Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 23 g $(0.09 \text{ mol}) \text{ Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved into 300 mL of deionic water, and stirred vigorously at 70 °C. The pH value of 10 was maintained by adding 1.0 M NaOH aqueous solution via a peristaltic pump. The formed homogenous suspension was aged at 75 °C for 24 h, and then washed by deionic water to remove unreacted SDS, obtaining a SDS-modified MgAl-LDH, named LDH-DS, as a milk-white suspension.

2.2.4. Intercalation of TMS-2959 into LDH-DS

For intercalating TMS-2959 into LDH, a proper amount of water suspension containing 3.0 g LDH-DS was dispersed into 200 mL of toluene, and then distilled by azeotropy to remove water, obtaining a LDH-DS suspension in toluene. Then 200 mL of DMAC was mixed with 200 mL of LDH-DS toluene suspension, and vigorously stirred at 100 °C until LDH-DS uniformly dispersed in DMAC. After toluene was removed under vacuum, 15 g TMS-2959 was added, stirred at 120 °C for 30 h under nitrogen atmosphere. The product, named LDH-2959, was collected by filtrating washed repeatedly with toluene to remove the unreacted TMS-2959, and finally dispersed in toluene for further use.

2.2.5. Preparation of formulations for UV curing

The primary formulation utilized in this study was consisted of a 7:3 (w/w) mixture of EB270 as an oligomer to HDDA as a monomer, and LDH-2959 loadings of 1, 3, 5 wt% as toluene suspensions, respectively. The formulation was stirred until a complete dispersion was achieved, and then distilled to remove toluene under vacuum. For preventing any unexpected polymerization, all the operations were performed in the dark. Every formulation was divided into two samples, including one with only LDH-2959 addition, referred as a-1, a-3 and a-5 (series A), and the other added with additional 3 wt% Irgacure 2959 based on series A, and referred as b-1, b-3 and b-5 (series B). And the formulation for preparing the pure polymer film as a reference was consisted of a 7:3 (w/w) mixture of EB270 to HDDA and 3 wt% Irgacure 2959.

2.2.6. Preparation of UV-cured polymer/LDH nanocomposite

The above formulations were exposed to a medium pressure mercury lamp (2 KW, Fusion UV Systems, USA) situated at 10 cm above the moving belt in air to form tack free films (Scheme 1).

2.3. Measurements

The ¹H NMR spectra were recorded with a DMX-300 MHz instrument (Bruker, Germany) using CDCl₃ as a solvent. The FTIR spectra were obtained with a Nicolet MAGNA-IR 750 spectrometer. The UV–Vis spectra were measured with a SHIMADZU UV-2401pc instrument in dichloromethane with the concentration of 1.25×10^{-2} g L⁻¹. The X-ray diffraction (XRD) patterns were recorded using a Rigaku D/Max-rA rotating anode X-ray diffractometer equipped with a Cu K α tube and Ni filter (λ = 0.1542 nm). The high resolution transmission electron microscope (HR-TEM) images were obtained with JEOL-2011 instrument, operated 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 kinetics analysis was carried out on a modified CDR-1 DSC apparatus (Shanghai Balance Instrument



Scheme 1. Synthetic route of LDH-2959 and illustration of polymer/LDH nanocomposites.

Co., China) with a UV spot cure system BHG-250 (Mejiro Precision Co., Japan). The incident light intensity at the sample pan was measured to be 2.4 mW cm^{-2} by a UV power meter. The final unsaturation conversion (P^{f}) was calculated by the formula, $P^{f} = H_{t}$ / H_{∞} , where H_t is the heat effect within *t* seconds, H_{∞} is the heat effect for 100% unsaturation conversion. The DSC curve was unified by the weight of sample (g). The polymerization rate was defined by $Jg^{-1}s^{-1}$, namely, the heat of polymerization per second for 1 g samples. For calculating the unsaturation conversion, the value of polymerization heat $\triangle H_0 = 86 \text{ J mmol}^{-1}$ per acrylic double bond was considered. The thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50H thermoanalyzer with 5-mg sample under a N₂ flow rate of 8×10^{-5} m³ min⁻¹ at a heating rate of 10 °C min⁻¹ from room temperature to 600 °C. The tensile storage modulus (E') and tensile loss factors (tan δ) of UV cured films were measured by a dynamic mechanical thermal analyzer (Diamond DMA, PE Co., USA) at a frequency of 5 Hz and a heating rate of $5 \,^{\circ}\text{Cmin}^{-1}$ in the range of -100 to $250 \,^{\circ}\text{C}$ with 25 mm \times 5 mm \times 1 mm specimens. The crosslink density (ν_e), as the molar number of elastically effective network chain per cube centimeter of the film, was calculated from the lowest storage modulus in the rubbery plateau region according to: $v_e = (E'_{rubb})$ 3RT), where E'_{rubb} is the lowest elastic storage modulus, R is the ideal gas constant, and T is the temperature in K corresponding to the lowest storage modulus. The mechanical properties were measured with an Instron Universal tester (model 1185, Japan) at 25 °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 using a QBY pendulum apparatus (Tianjin Instrument Co., China), while for the pencil hardness a QHQ-A pencil hardness apparatus (Tianjin Instrument Co., China) was used.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic route of LDH-2959 and the structural illustration of polymer/LDH nanocomposite are shown in Scheme 1. As depicted, TA-2959 was firstly prepared by the esterification reaction of thioglycolic acid with Irgacure 2959. Fig. 1a shows the ¹H NMR spectrum of TA-2959. The peaks at 2.0–1.94 ppm are assigned to the proton of –SH, while other proton-corresponding peaks can be also distinguished clearly. KH-560 reacted with TA-2959 for introducing trimethoxysilane group into TA-2959 to



Fig. 1. ¹H NMR spectra of (a) thioglycolic acetate-modified 2959 (TA-2959) and (b) trimethoxysilane-modified 2959 (TMS-2959) in CDCl₃.



Fig. 2. FTIR spectra of TA-2959 and TMS-2959.

obtain the TMS-2959. The peaks at 2.0-1.94 ppm disappeared completely in the ¹H NMR spectrum of TMS-2959 (Fig. 1b), which indicates that -SH groups of TA-2959 have been consumed and TMS-2959 was synthesized successfully. Fig. 2 represents the FTIR spectra of TA-2959 and TMS-2959. The peak at 2571 cm⁻¹ for –SH group in the spectrum of TMS-2959 disappeared compared with the spectrum of TA-2959. Contrariwise, the peaks for the C=O group of ester at 1735 cm⁻¹, C=C group of the aromatic ring at 1600 cm⁻¹, and Si–O group at 1046 cm⁻¹ appeared. The results of FTIR analysis further confirmed the molecular structures of TA-2959 and TMS-2959.

The UV–Vis spectra of Irgacure 2959 and TMS-2959 were measured in ethanol with the concentration of 1.25×10^{-2} g L⁻¹, as shown in Fig. 3. It can be seen that TMS-2959 has the similar absorbance spectra, but smaller molar extinction coefficient compared with Irgacure 2959. This indicates that the obtained TMS-2959 can initiate the photopolymerization of acrylate systems but with low photoinitiating efficiency due to its lower molar percentage of chromophore moiety.

Fig. 4 shows the FTIR spectra of LDH-DS and LDH-2959. Both samples display a broad absorption peak between 3600 and 3100 cm^{-1} , which is attributed to the O–H stretching vibration. And the peaks at 2920 and 2850 cm⁻¹ assigned to the aliphatic C–H stretch vibration are also found in both spectra. Moreover, the absorption peak at 1220 cm^{-1} attributed to the stretching



Fig. 4. FTIR spectra of LDH-DS and LDH-2959.

vibration of sulfate is observed in LDH-DS spectrum, demonstrating that SDS was intercalated into the LDH interlayer. The absorption peaks at 1735 cm⁻¹ for C=O group of ester group, and at 1044 cm⁻¹ for Si–O group are observed from the FTIR spectrum of LDH-2959, indicating that TMS-2959 has been grafted into the LDH-DS interlayer. In addition, the stretching vibration of sulfate for LDH-DS at 1220 cm⁻¹ shifted to 1112 cm⁻¹ for LDH-2959 after grafting TMS-2959 into the LDH-DS interlayer due to the change of chemistry environment around SDS.

The XRD patterns for MgAl-LDH and LDH-DS are shown in Fig. 5. The starting scattering angle 2θ was set as 2°. The unmodified MgAl-LDH shows a basal spacing of 0.78 nm ($2\theta = 11.4^{\circ}$), while the LDH-DS shows 2.67 nm ($2\theta = 3.3^{\circ}$). The enlarged spacing of LDH-DS indicates the intercalation of SDS into MgAl-LDH. The starting scattering angle 2θ for Fig. 6 was set as 0.8°.As shown in Fig. 6, after TMS-2959 reacted with LDH-SDS, the basal spacing greatly increases from 2.67 nm to 5.2 nm, indicating that a new complex photoinitiator LDH-2959 was successfully prepared. Furthermore, for the samples a-5 and b-5, containing 5 wt% LDH-2959 and additional 3 wt% Irgacure 2959, respectively, no XRD diffraction was observed, compared to LDH-2959 with the basal spacing of 5.2 nm ($2\theta = 1.7^{\circ}$). Though the absence of XRD diffraction peak doesn't imply that the exfoliation has happened, it indicates the occurrence of random orientation for a-5 and b-5.

 $\begin{array}{c} 1.0 \\ 0.8 \\ 0.6 \\ 0.4 \\ 0.2 \\ 0.0 \\$

Fig. 3. UV–Vis spectra of Irgacure 2959 and TMS-2959 (ethanol, $1.25\times10^{-2}\,g\,L^{-1})$.

The contents of organo-modifiers and other volatile materials (e.g. water) in the samples were determined by TGA in N_2



Fig. 5. XRD patterns of MgAl-LDH and LDH-DS.



Fig. 6. XRD patterns of LDH-2959 and UV cured polymer/LDH nanocomposites.

atmosphere. As shown in Fig. 7, the weight loss of 13.9% for MgAl-LDH, 12.7% for LDH-DS, and 11.6% for LDH-2959 below 200 °C were attributed to the loss of physically adsorbed and interlayer water. At above 200 °C, the weight loss of 42% for LDH-DS and 38.4% for LDH-2959 were resulted from the decomposition and combustion of intercalated organo-modifiers. After heating to 600 °C, the weight residuals for LDH-DS and LDH-2959 were 45.3% and 54.2%, respectively. The more residuals for the latter than the former was interpreted to due to the incorporation of silane group, forming more char.

3.2. Photopolymerization behavior initiated by LDH-2959

The photoinitiating performance of LDH-2959 was investigated by Photo-DSC measurement in air at room temperature (25 °C). Figs. 8 and 9 show the photopolymerization rates at the peak maximum (R_p^{max}) and the final unsaturation conversion (P^{f}) for series A samples, respectively. It can be seen that the formulation containing photoinitiator Irgacure 2959 has the highest R_p^{max} and P^{f} , as well the shortest irradiation time to reach the R_p^{max} , compared with the formulations using LDH-2959. This can be interpreted as follows: the photoinitiating chromophore group of LDH-2959 was linkaged to the LDH interlayer, which weakens the remotion of formed photoinitiating radicals, and thus decreases the reactivity of double bond. However, the R_p^{max}



Fig. 7. TGA curves of MgAl-LDH, LDH-DS and LDH-2959.



Fig. 8. Photopolymerization rates of the formulations without and with LDH-2959 addition (series A).

and $P^{\rm f}$ increase distinctly with increasing the LDH-2959 loading, due to the increased content of photoinitiating chromophore group. It can be concluded that the LDH-2959 can be used as a photoinitiator complex to initiate the photopolymerization of acrylate resin.

As shown in Figs. 10 and 11, the R_p^{max} and P^f for series B samples are comparable with those for the pure resin without LDH addition. This can be explained that the additional Irgacure 2959 plays a dominative role in initiating the photopolymerization. Otherwise, the R_p^{max} and P^f increase slightly as the LDH-2959 loading increased.

3.3. Morphology of the UV cured nanacomposite

Fig. 12 shows the HR-TEM micrographs of cured films with 5 wt% LDH-2959 and adding additional Irgacure 2959. The dark lines are the intersections of LDH platelets. It can be seen that for both samples a-5 and b-5 LDH dispersed in the polymer matrix. However, for sample a-5, the LDH layers lost the ordered stacking-structure and show the completely exfoliation after UV curing. This can be explained by the fact that the sample a-5 only containing LDH-2959 exhibited a relative lower photopolymerization rate (Fig. 8), which was propitious to further expand the LDH intergallery to form the exfoliated structure. The cured sample b-5 film shows a different morphology. The LDH layes were not



Fig. 9. Unsaturation conversion in the UV cured polymeric film and nanocomposites (series A).



Fig. 10. Photopolymerization rates of the formulations without and with LDH-2959 addition (series B).

completely exfoliated, showing the partly intercalation into the thin tactoids. The sample b-5 containing not only LDH-2959 but also additional 3 wt% Irgacure 2959 was provided with higher photopolymerization rate (Fig. 10), resulting in the formation of cross-linking network at early stage, and thus retardance of the interlayer spacing enlarging. As a results, the intercalated structure for the sample b-5 was formed.

3.4. Thermal properties of the UV cured nanocomposites

Figs. 13 and 14 show the TGA curves of UV cured pure polymer and polymer/LDH nanocomposites. It can be found that the nanocomposites have the similar thermal behavior as the pure polymer. However, for the nancomposite as the LDH loading increased, the onset temperature of thermal decomposition slightly raised. Moreover, the char residue also increased along with LDH-2959 added, indicating that the LDH promoted the charring process. On the other hand, as LDH-2959 loading increased, the crosslinking density increased, resulting in the enchancement in the thermal property.

The dynamic mechanical thermal analysis (DMTA) was used to investigate the mechanical properties of polymer/LDH nanocom-



Fig. 11. Unsaturation conversion in the UV cured polymeric film and nanocomposites (series B).

posites. The storage modulus (E') curves and loss factor (tan δ) curves are shown in Figs. 15 and 16. The data are listed in Table 1. The temperature associated with the peak position of tan δ curve is defined as the glass transition temperature (T_g) . E', which is a measurement of material stiffness, can be used to provide the information regarding the degree of cure and cross-linking density. For series A, as the content of LDH-2959 increased from 1 wt% to 5 wt%, the $T_{\rm g}$ value increased from 56.7 to 63.9 °C, the storage modulus increased from 39.1 to 58.3 MPa. These results can be attributed to the exfoliation morphology with well dispersion of LDH in the polymer matrix. The bulky LDH inorganic core might restrict the segmental motion of polymer chain, and thus higher temperature was required to provide the requisite thermal energy for the occurrence of glass transition in the nanocomposite. In addition, the nanoreinforcement effect from the LDH core on the polymer matrix also enhanced the storage modulus. The same results were obtained for the series B nanocomposites with lower values than series A samples (Fig. 16), as listed in Table 1. This can be explained that the series A samples propossess the exfoliation structure, and thus more uniformly dispersion in the polymer matrix compared to series B samples with the intercalated structure.



Fig. 12. HR-TEM micrographs of UV cured nanocomposites at 5 wt% LDH loading for a-5 (a) and b-5 (b).



Fig. 13. TGA curves of UV cured polymer and nanocomposites (series A) under N_2 flow.



Fig. 14. TGA curves of UV cured polymer and nanocomposites (series B) under $\ensuremath{\mathsf{N}}_2$ flow.

The influence of LDH content on the mechanical properties and hardness of UV cured polymer/LDH nanocomposites are listed in Table 2. The tensile strength increases along with the increase of LDH-2959 loading. Furthermore, the tensile strength of series A samples are higher than that of series B. This is consistent with the results obtained by DMTA. However, the elongation at break of all the nanocomposites decreases slightly compared with that of the pure polymer. This can be attributed to that the polymer chains in the nanocomposites are restricted by the LDH, resulting in the decreased degree of freedom. The pendulum and pencil hardness of series A and series B samples both increase with increasing LDH loading due to the nanoreinforcement effect of LDH.

1E9 -	0.2
	anõ
	0.1
-50 0 50 100 150] _{0.0}
Temperature (°C)	

03

Fig. 15. DMTA curves of UV cured polymer and nanocomposites (series A).



Fig. 16. DMTA curves of UV cured polymer and nanocomposites (series B).

Table 1 $E'_{\rm rubb},\,T_g$ and ν_e of UV cured polymer and nanocomposites from DMTA.

Sample	$E'_{\rm rubb}$ (MPa)	$T_{\rm g}$ (C)	$\nu_{\rm e}~(10^{-3}{\rm mol}{\rm cm}^{-3})$
Pure polymer	36.1	55.1	3.78
a-1	39.1	56.7	4.09
a-3	51.2	59.1	5.36
a-5	58.3	63.9	6.11
b-1	38.6	56.1	4.04
b-3	42.5	57.5	4.45
b-5	49.1	59.2	5.14

Table 2									
Mechanical	properties	and ha	ardness	of UV	cured	polymer	and	nanocom	posites.

Sample	Tensile strength (MPa)	Elongation at break (%)	Persoz hardness (s)	Pencil hardness (H)
Pure polymer	10.1(1.1)	16(0.2)	91(1.5)	2(0)
a-1	13.3(1.3)	14(0.3)	99(1.8)	2(0.5)
a-3	17.8(1.2)	13(0.2)	110(1.3)	4(0.4)
a-5	25.2(1.1)	13(0.4)	124(1.4)	4(0.4)
b-1	10.9(1.4)	16(0.6)	96(2.0)	2(0.5)
b-3	11.6(1.2)	15(0.3)	104(2.5)	3(0)
b-5	13.1(1.3)	13(0.5)	115(1.9)	3(0.5)

Standard deviation listed in parenthesis.

4. Conclusion

The UV cured polymer/LDH nanocomposites were prepared through the photopolymerization initiated by the photoinitiatormodified LDH precursor, LDH-2959. The LDH-2959 showed the acceptable photoinitiating activity for acrylate systems. The exfoliated UV cured nanocomposites were achieved in the presence of LDH-2959 only. However, the UV cured nanocomposites prepared using both LDH-2959 and Irgacure 2959 showed the intercalated structure. Compared with the pure polymer, the exfoliated polymer/ LDH nanocomposite showed remarkable enhanced thermal stability and mechanical properties because of their well dispersion in the polymer matrix. On the contrary, the intercalated structure of polymer/LDH nanocomposite led to the limited improvement in the thermal and mechanical properties. Moreover, the hardness of nanocomposites was higher than that of the pure polymer. It can be concluded that the exfoliated polymer/LDH nanocomposite was provided with the enhancement in mechanical and thermal properties through the photoinitiating polymerization by intercalating a photoinitiator into LDH interlayers.

Acknowledgements

The financial support of National Natural Science Foundation of China (No. 50973100) is gratefully acknowledged.

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