

Layered Nanoparticles Modified by Chain End Functional PE and Their Nanocomposites with PE*

Zhong-chuan Peng^{a, b}, Qian Li^{a*}, Hua-yi Li^{a*} and You-liang Hu^a

^a Beijing National Laboratory of Molecular Sciences, CAS Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

Abstract Layered materials (MMT, LDH) were successfully modified by chain end functionalized polyethylene *via* an ion exchange method. The samples were characterized by using elemental analysis, Fourier transform infrared (FTIR) spectrum, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). The XRD results demonstrated that MMT was successfully exfoliated with the disappearance of [001] peak. For the LDH, the peak [003] moved to a low angle and greatly weakened, indicating that LDH was successfully functionalized and completely intercalated or exfoliated. HDPE/layered nanocomposites were obtained between HDPE and different content of functional layered materials. The SEM and TEM results of nanocomposites showed the layered materials were well dispersed in the HDPE matrix, with a particle size of 100–200 nm.

Keywords MMT; LDH; Polyethylene; Modify; Nanocomposites

INTRODUCTION

In recent decades, the layered nanomaterials, such as layered double hydroxides (LDH)^[1] and montmorillonite (MMT)^[2–5], have been considered as an emerging class of nanofillers for the preparation of multifunctional polymer nanocomposites. Both LDH and MMT have exchangeable ions in the interlayers. Anions including CO₃²⁻, NO₃⁻, Cl⁻ and SO₄²⁻ can be incorporated into the interlayer for LDH, while the ions in the interlayer of montmorillonite are cations, such as Na⁺, Mg²⁺, Ca²⁺, which can be exchanged by ammonium group (NH₄⁺).

Polymer/MMT and polymer/LDH nanocomposites have attracted great interest both in fundamental research and practical applications. Many papers^[6, 7] have reported the synthetic methods and the properties of polymer/layered material nanocomposites. Adding a small amount of layered nanomaterials in polymer matrix can dramatically enhance the physical, thermal and mechanical properties of polymer. For example, with 2 wt% of MMT, nylon-6 nanocomposites^[8] show double of tensile strength and modulus as compared with the parent polymer. Hu^[9] and Yang^[10] reported that layered-nanoclay could improve the rheology of polymer and flame retardant performance of polymeric materials. Their combustion experiments exhibited that the composite with 5 wt% MMT burned in the same way as pure PE; however, the heat release rate was reduced by 32%. Gao *et al.*^[11] reported the synthesis of HDPE/LDH nanocomposites with high efficient flame retardance. After adding LDHs, the flame retardant performance was significantly improved. The 50% weight loss temperature increased

* This work was financially supported by the National Natural Science Foundation of China (No. 51403216) and Petro China Innovation Foundation.

* Corresponding authors: Qian Li (李倩), E-mail: liqian2010@iccas.ac.cn

Hua-yi Li (李化毅), E-mail: lihuayi@iccas.ac.cn

Received December 6, 2016; Revised December 30, 2016; Accepted January 3, 2017

doi: 10.1007/s10118-017-1931-8

67 °C by the addition of 15 wt% Zn₂Al-Cl LDH. With 40 wt% of LDH loading, the heat release rates were reduced by 24%, 41%, 48%, and 54% for HDPE/Zn₂Al-Cl, HDPE/Zn₂Al-CO₃, HDPE/Zn₂Al-NO₃, and HDPE/Zn₂Al-SO₄, respectively.

High-density polyethylene (HDPE) is an important thermoplastic material with excellent properties, including fluidity, flexibility, transparency and a glossy surface. However, the main drawbacks of HDPE are the low thermal stability and poor mechanical properties^[12], which limit its application. A less expensive and more practical strategy to improve the properties of HDPE, such as mechanical strength, flame retarding and crystallization behavior is to blend it with clay, *e.g.* blending with montmorillonite^[3, 12–14].

The good dispersion of nanoparticles in polymer matrix is crucial for the preparation of blends mentioned above. Usually, the nanolayers of LDH and MMT cannot be dispersed in polymers because of the ion interactions, especially for polyolefin containing no polar group in its backbone structure. As we know, the electrostatic force is in inverse proportion to the distance. If the distance between the layers of LDH and MMT is increased, the interaction between the layers will decrease. As reported for the composites of polymer and LDH and MMT, layered materials are intercalation-modified by ion exchange to increase the distance between the layers for improving dispersion in the polymer matrices. It has been a challenging issue to reform the interaction between nanolayer and polymer matrix for obtaining the nanocomposites with good properties.

In most cases, polyolefin/MMT composites were prepared by using modified MMT with small molecules of organic quaternary ammonium salt (*o*-MMT) and functional polyolefin *via* melt blending. For example, Kato *et al.*^[15] prepared PP/*o*-MMT nanocomposites through the melt intercalation of PP chains modified by either maleic anhydride (PP-*g*-MA) or hydroxyl groups (PP-OH). For both matrices, intercalated nanocomposites were recovered after melt blending at 200 °C for 15 min. However, the PP-*g*-MA matrix with a lower maleic anhydride content did not intercalate under the same conditions, indicating that a minimal functionalization of PP chains was required for the intercalation. Using reactive chain transfer agents, Chung^[16] discovered a facile route to prepare end-functionalized polypropylene containing a terminal functional group (OH, NH₂, COOH, anhydride, *etc.*). They used PP-*t*-NH₃⁺Cl[−] to modify MMT *via* ion exchange^[17]. The result showed that the hydrophobic high molecular weight PP and semicrystalline PP “tail” effectively exfoliated the clay platelets and the exfoliated structure was maintained even after further mixing with neat PP. Dong *et al.*^[18] prepared polyethylene/MMT nanocomposite by *in situ* polymerization. The copolymerization of ethylene and 10-undecen-1-ol was carried out using the metallocene catalyst of Et[Ind]₂ZrCl₂/MAO that was intercalated in the organically modified montmorillonite. The obtained hydroxyl-functionalized polyethylene enhanced the interaction between PE and MMT.

It is well known that LDH has unique anion exchange property. The high charge density of LDH layers results in strong interlayer electrostatic interactions between the sheets and significantly hydrophilic properties. Thus, if the stronger electrostatic interaction between the LDH layers is weakened, exfoliated or intercalated polymer/LDH nanocomposites can be synthesized successfully. The modification of LDH *via* ion-exchange widens the *d*-spacing value, which is a facile way to decrease the electrostatic interactions between LDH layers. Pugazhenth and coworkers^[19] used sodium dodecyl sulfate (SDS) to modify Ni-Al-LDH and afforded the intercalated LDH. The XRD analysis revealed that the *d*-spacing value of the modified LDH increased from 0.80 nm to 1.35 nm. Chen^[20] prepared exfoliated nanocomposites by solution intercalation of polyethylene-grafted-maleic anhydride (PE-*g*-MA) into the galleries of organo-modified MgAl layered double hydroxide (OMgAl-LDH) under refluxing in xylene. They found that the exfoliated LDH single layers with the thickness of 4.64 nm were dispersed disorderly in the polymer matrix. The rate of thermal oxidation of PE-*g*-MA chains in the nanocomposites is much slower than that in the pure PE-*g*-MA in the temperature range from 200 °C to 320 °C.

It is obvious that the best modification agents for ionic exchange of MMT and LDH to prepare polyolefin nanocomposites are the chain end functional polyolefin with high molecular weight. It can greatly increase the *d*-spacing of the nano-sheets and has best miscibility with polyolefin matrix. The preparation of chain end functional polyolefin has been extensively investigated^[21–24]. In our previous work^[25–27], we successfully

synthesized many functionalized polyolefins with different chain end groups *via* click chemistry. In this work, polyethylene with the chain end of quaternary ammonium salt and sodium sulfonate was prepared and firstly used to modify MMT and LDH by ion-exchange, respectively. HDPE nanocomposites with different content of the modified layered materials were prepared by solution mixing, and the properties of nanocomposites were characterized by SEM, TEM, DSC, TG, *etc.* The layered materials modified by the chain end functionalized polyethylene are prone to prepare exfoliated polymer/layered nanocomposites.

EXPERIMENTAL

Materials

High density polyethylene (HDPE) was supplied by Yanshan Petrochemical Co., Ltd., Beijing, China. Sodium montmorillonite (Na-MMT) was purchased from Zhangjiakou Qinghe Chemical Factory, China. 2-Hydroxy-*N,N,N*-trimethylethanaminiumchloride [$\text{HOC}_2\text{H}_4\text{N}^+(\text{CH}_3)_3\text{Cl}^-$, choline chloride, denoted as CC], 3-chloroperbenzoic acid (*m*-CPBA), 1-hexyl-1,4,5,6-tetrahydropyrimidine [$\text{C}_9\text{H}_{16}\text{N}_2$, designed as DBU], magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and sodium lauryl sulfonate (SDS) were purchased from Aladdin. Xylene, toluene and aminobenzene were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Vinyl-terminated polyethylene was synthesized according to the literature^[26] (ν -PE, $M_n = 500$ g/mol). The chain end functionalized polyethylene with the group of sulfonate (PE-SO₃Na) was synthesized according to the literature^[25].

Characterization

Differential scanning calorimetry (DSC) was conducted using a TA Q2000 thermal analyzer under nitrogen atmosphere with a heating rate of 10 K/min in the temperature range of 50–200 °C for dynamic scanning. Melting temperature (T_m) was determined in the second scan. Thermogravimetric analysis (TGA) was performed with Perkin-Elmer TG at a heating rate of 10 K/min under nitrogen atmosphere. Wide-angle X-ray diffraction (XRD) analysis was performed on a Japan Rigaku D/max-2500 diffractometer with Cu K α radiation ($\lambda = 0.154$ nm) at a generator voltage of 40 kV and generator current of 100 mA; scanning was conducted from 1° to 80° at a speed of 4 (°)/min. Scanning electron microscopy (SEM) (Jeol JEM6700) was used to observe the size, shape and dispersability of nanoparticles in HDPE matrix. Scanning electron microscope (SU1510, Hitachi High-Tech Corporation, Japan) equipped with electron-dispersive X-ray spectroscopy (EDS) was used to obtain the elemental analysis. For SEM observation, the samples were fractured in liquid nitrogen and the fracture surfaces for observation were coated with gold. Transmission electron microscopy (TEM) was carried out on a Jeol JEM2200 transmission electron microscope using an acceleration voltage of 100 kV. Samples for TEM were prepared by ultramicrotomy.

Preparation of HDPE/MMT Nanocomposites

Synthesis of choline chloride end functional polyethylene

Firstly, the functional polyethylene with epoxy end group was synthesized according to the literature^[26]. The polyethylene with epoxy end group (5 g), choline chloride (5.5 g) and the catalyst of DBU (0.8 mL) were added in a 500 mL flask which contained 150 mL of xylene. The mixture was heated at 120 °C under stirring for 5 h, and then cooled and filtered. The solid was washed with the mixed solvent of ethanol-water (1:1, *V:V*) twice. The product was dried at 50 °C for 6 h in vacuum and designated as PE-CC.

Modification of Na-MMT by PE-CC

The functional montmorillonite was prepared *via* ion-exchange reaction and the general procedure was as following: PE-CC and Na-MMT (1 g) were added in 50 mL of xylene at 120 °C for 10 h under agitation. The product was cooled and filtered, and then washed with ethanol-water (1:1, *V:V*) until no Cl^- was detected in the filtrate by a 0.1 mol/L AgNO_3 solution. The crude product was purified by successive Soxhlet extraction of unreacted PE-CC using boiling hexane for 24 h. The products were dried for 12 h at 50 °C in vacuum, and denoted as PE-MMT.

Preparation of HDPE/MMT nanocomposite

The HDPE/MMT composites were prepared *via* solution mixing. A certain amount of HDPE and MMT or PE-MMT were added in a flask containing 100 mL of xylene. The mixture was heated at 125 °C for 5 h under agitation with nitrogen gas. The product was precipitated in large amounts of ethanol, washed with ethanol and dried for 12 h at 50 °C in vacuum.

Preparation of HDPE/LDH Nanocomposite

Synthesis of SDS-LDH and Mg-Al-LDH

The Mg-Al-LDH was prepared by the co-precipitation method and the Mg/Al molar ratio was 3^[28]. 1.8 g of NaOH (0.20 mol) and 6.8 g of SDS (0.025 mol) were dissolved in 135 mL of deionized water as base solution. 19.2 g of Mg(NO₃)₂·6H₂O (0.075 mol) and 9.4 g of Al(NO₃)₃·9H₂O (0.025 mol) were dissolved in 135 mL of deionized water. The nitrate solution and base solution were added dropwise together to a 1000 mL flask which contained 135 mL of deionized water under 85 °C with stirring. After the addition of all the solutions, the mixture was aged at 85 °C and refluxed crystallization for 12 h. The slurry was then filtered until all the unreacted liquid was removed. The products were washed for several times by deionized water and denoted as SDS-LDH. In order to minimize contamination with atmospheric CO₂, the preparation of SDS-LDH was under a nitrogen atmosphere. Mg-Al-LDH was prepared using the same method without SDS.

Preparation of PE-intercalated LDH

The desired proportion of SDS-LDH and PE-SO₃Na were added in a 250 mL flask containing xylene/aniline (12 mL/60 mL) under stirring at the temperature of 110 °C for 24 h. The mixture solution was centrifuged at high speed and then poured out supernatant liquor. The original product was dried under vacuum at 50 °C for 24 h. And then, the crude sample was purified by successive Soxhlet extractions to remove unreacted PE-SO₃Na using boiling hexane. The products were denoted as PE-LDH.

Preparation of HDPE/LDH nanocomposite

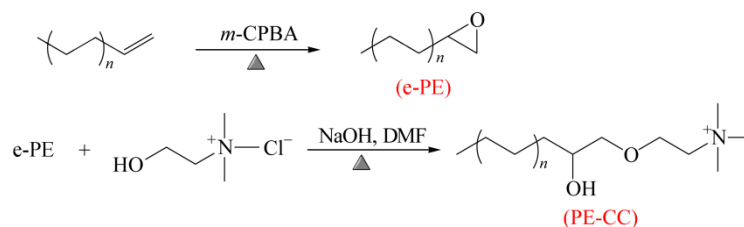
A certain amount of PE-LDH and HDPE were added in a 100 mL flask containing 60 mL of xylene at the temperature of 130 °C and stirred for 4 h. The solution was then poured out into 100 mL of ethanol under fast stirring. The precipitates were filtered and dried under vacuum at 50 °C for 24 h.

RESULTS AND DISCUSSION

PE-MMT and HDPE/MMT Nanocomposites

Synthesis of choline chloride end functional polyethylene

Polyethylene with quaternary ammonium group was synthesized by the ring opening reaction between polyethylene with epoxy end group^[26] and choline chloride catalyzed by of DBU. Scheme 1 shows the synthetic reactions of the choline chloride end functional polyethylene (PE-CC).



Scheme 1 The synthetic route to choline chloride end functional polyethylene

The structure of the PE-CC is clearly evidenced by NMR and FTIR. ¹H-NMR spectrum (Fig. 1) clearly shows that e-PE is quantitatively reacted, which is evidenced by the disappearance of the epoxy group. In the ¹H-NMR spectrum of PE-CC, new peaks emerge around $\delta = 3.55$ corresponding to CHOH and CH_2 protons'

resonances, and the proton signals at $\delta = 2.0$ – 2.3 correspond to the methyl adjacent to the atom nitrogen. Furthermore, the detailed chain end structure of PE-CC is also confirmed by ^{13}C -NMR spectrum (Fig. 2) with peaks at $\delta = 67.3$ and 72.6 corresponding to $-\text{CH}(\text{OH})$ and $-\text{CH}_2\text{O}-$, respectively. In the FTIR spectrum (Fig. 3), the peaks at 1160 – 1000 , 3670 – 3230 , 2917 and 2845 cm^{-1} are observed, which correspond to $\text{C}-\text{O}-\text{C}$ (in PE-CC), $-\text{OH}$ stretching, and the stretching of $\text{C}-\text{H}$ in the alkyl chain of PE. The results from the measurements of ^1H -NMR, ^{13}C -NMR and FTIR demonstrate the successful synthesis of PE-CC.

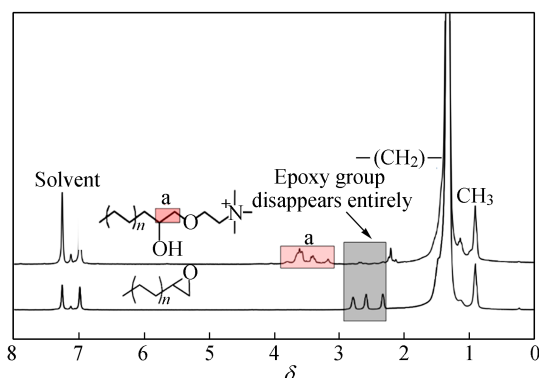


Fig. 1 ^1H -NMR spectra (1,2-dichlorobenzene- d_4) of e-PE and PE-CC

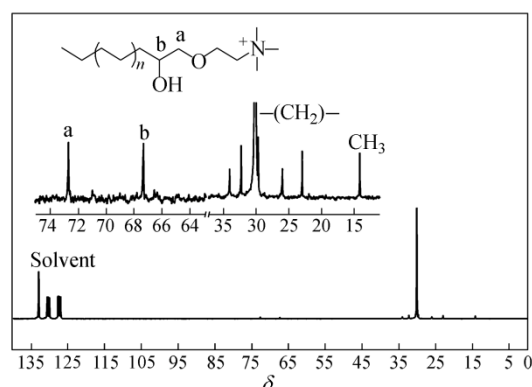


Fig. 2 ^{13}C -NMR spectrum (1,2-dichlorobenzene- d_4) of PE-CC

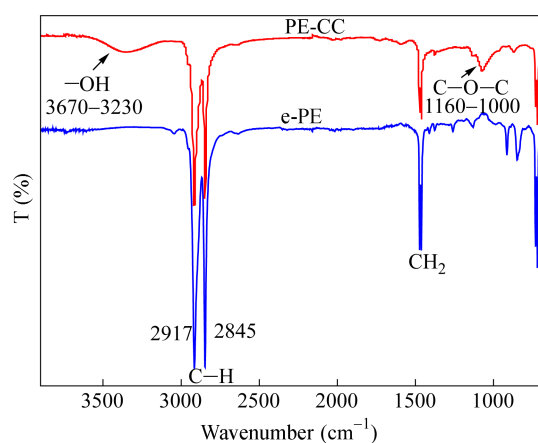


Fig. 3 FTIR spectra of e-PE and PE-CC

Modification of Na-MMT by PE-CC

Sodium montmorillonite was modified by PE-CC in the solvent of xylene *via* ionic exchange reaction. Different weight of PE-CC was used to react with 1 g of Na-MMT. After the reaction, the unreacted PE-CC was removed by solvent extraction. Table 1 shows the reaction conditions and the compositions of the modified MMT. The content of PE-CC in the modified MMT was determined by TGA (Fig. 4). XRD was used to examine the changes of the interlayer distances of MMT. Figure 5 shows the XRD patterns of the modified MMT. It is found that the $[001]$ diffraction peak disappears gradually with the increase of PE-CC content, which represents the successful intercalation of PE-CC in the layer of Na-MMT.

Table 1 Composition of PE-MMT

Sample	PE-CC in feed (g)	PE-CC in the modified MMT (wt%)
PE-MMT-1	0.8	50
PE-MMT-2	1.0	52
PE-MMT-3	1.2	61

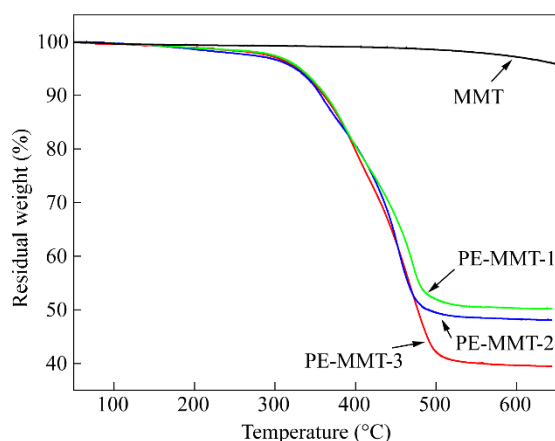


Fig. 4 TGA curves of MMT and PE-MMT

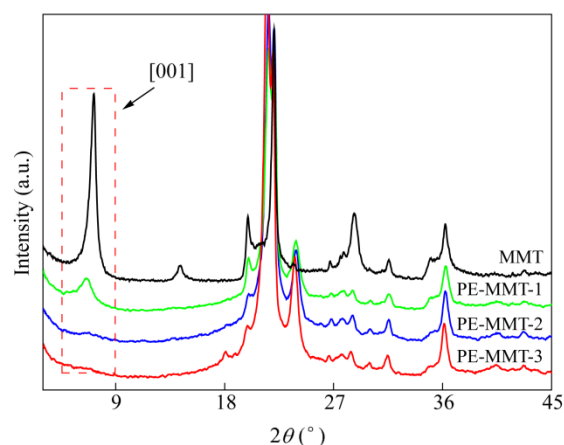


Fig. 5 XRD patterns of MMT and PE-MMT

HDPE/PE-MMT nanocomposites

The sample of PE-MMT-3 was used to prepare HDPE nanocomposites *via* solution mixing in xylene. Five HDPE/MMT nanocomposite samples were prepared and the compositions are listed in Table 2. The dispersion of MMT in HDPE was analyzed by SEM. The samples were fractured in liquid nitrogen and the fracture surfaces for observation were coated with gold. As shown in the SEM image (Fig. 6), the exfoliated MMT particles with the size of 100–200 nm were dispersed in the matrix of HDPE.

Table 2 Composition of HDPE/PE-MMT nanocomposite

Sample	HDPE (g)	PE-MMT-3 (g)	MMT (wt%)
HDPE/MMT-1	1.96	0.04	1.0
HDPE/MMT-2	1.92	0.08	2.1
HDPE/MMT-3	1.84	0.16	4.2
HDPE/MMT-4	1.80	0.20	5.2

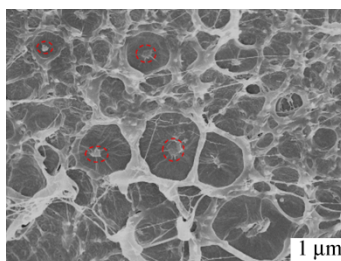


Fig. 6 SEM image of HDPE/MMT-4 (5.2 wt%) nanocomposite

DSC and TGA were used to detect the thermal properties of HDPE/PE-MMT nanocomposites. The DSC curves (Fig. 7) of the HDPE/PE-MMT nanocomposites with different PE-MMT contents show that the melting temperature and crystallization temperature almost remain unchanged. Table 3 summarizes the data of the thermal properties of the nanocomposites. Figure 8 provides the TGA curves of the HDPE/PE-MMT composites and the pure HDPE. The result shows that the decomposition temperature decreases with the addition of modified PE-MMT in pure HDPE matrix. Many reports^[29–31] have analyzed the reason of the degradation. Their results showed that the initial degradation of the organoclay follows a Hoffman elimination mechanism (Fig. 9) with the release of long chained α -olefins. In our case, the reason of degradation of HDPE/PE-MMT nanocomposite may follow a Hoffman elimination mechanism with the release of long chained α -olefins, and the exfoliated lamella MMT particles may promote or catalyze the degradation of HDPE/PE-MMT nanocomposite of HDPE matrix^[32].

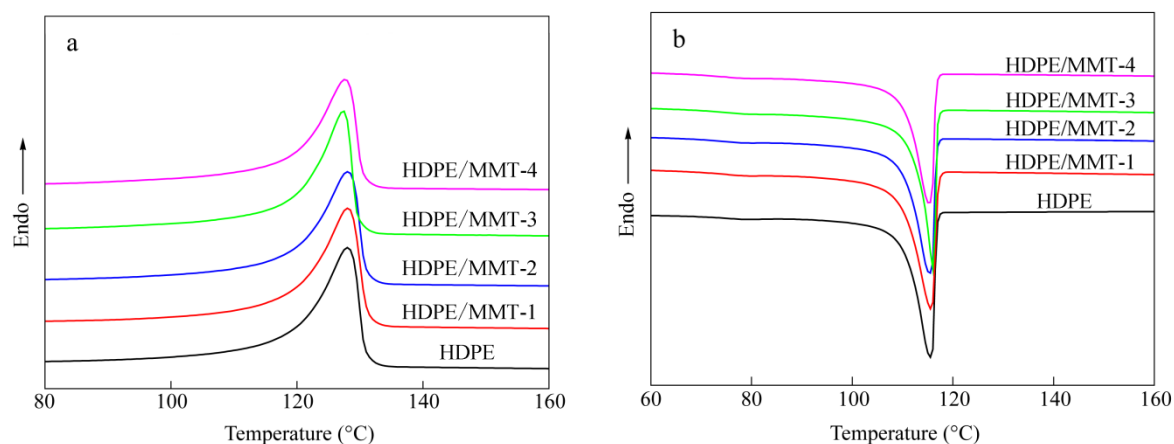


Fig. 7 DSC curves of HDPE/PE-MMT nanocomposites for various MMT contents: (a) heating and (b) cooling

Table 3 Thermal properties of HDPE/PE-MMT nanocomposites for various MMT contents

Sample	T_m^a (°C)	T_c^b (°C)	T_{95}^c (°C)
HDPE	128.06	115.55	452.00
HDPE/MMT-1	128.10	115.58	448.03
HDPE/MMT-2	128.01	115.37	447.80
HDPE/MMT-3	127.37	116.18	443.71
HDPE/MMT-4	127.69	115.22	452.54

^a Melting temperature; ^b Crystallization temperature; ^c Temperature at 5% weight loss

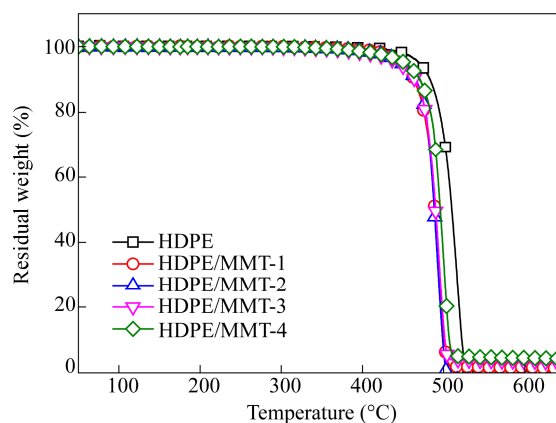


Fig. 8 TGA curves of HDPE/PE-MMT nanocomposite and pure HDPE in nitrogen atmosphere

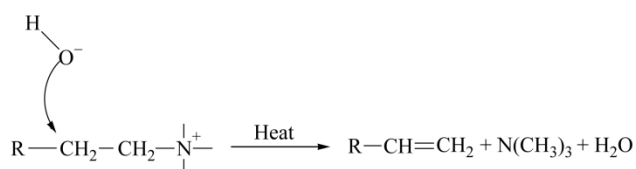


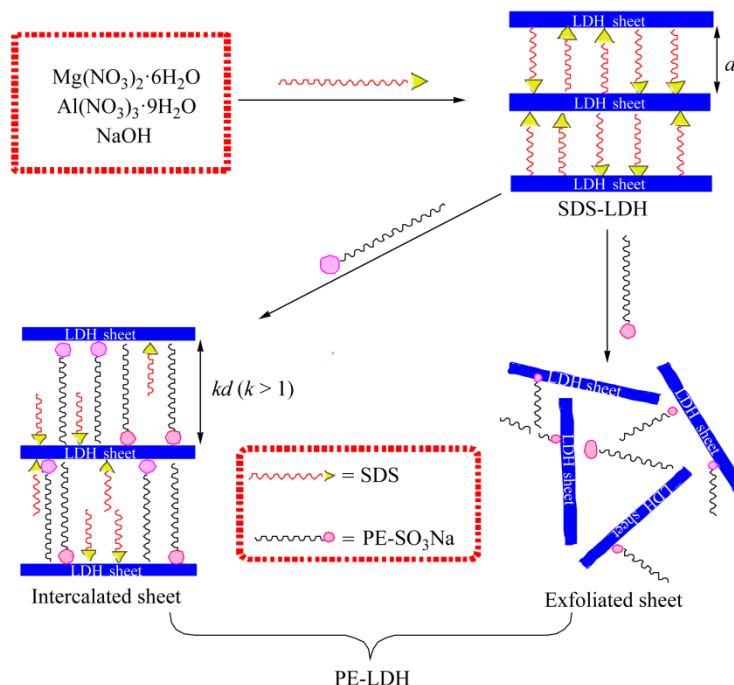
Fig. 9 Hoffman elimination mechanism

Functional LDH and HDPE/PE-LDH Nanocomposites

Modification of LDH by PE-SO₃Na

Mg-Al-LDH was synthesized and reacted with PE-SO₃Na in toluene. Unfortunately, PE-SO₃Na could not be exchanged into the layers of LDH. Then sodium dodecyl sulfonate intercalated LDH (SDS-LDH) was prepared

via co-precipitation. SDS-LDH (0.5 g) was used to react with PE-SO₃Na (5.0 g) and the unreacted PE-SO₃Na was removed by solvent extraction. The exfoliated PE-LDH was prepared successfully. Scheme 2 shows the modification procedure of LDH by PE-SO₃Na. Table 4 shows the compositions of the PE-LDH samples.



Scheme 2 The preparation of PE-LDH

Table 4 Composition of the PE-LDH

Sample	PE-SO ₃ Na (g)	SDS-LDH (g)	TG loss (wt%)
LDH	—	—	41.1
SDS-LDH	—	—	47.2
PE-LDH	5.0	0.5	52.4

The XRD patterns in the range of $2\theta = 1^\circ$ – 70° for LDH, SDS-LDH and PE-LDH samples are shown in Fig. 10. The diffraction peak [003] at $2\theta = 11.3^\circ$ corresponds to a basal spacing of 0.78 nm, consistent with the result reported by Chen *et al.* A new peak at $2\theta = 7.3^\circ$ emerges in the XRD patterns of SDS-LDH and PE-LDH, which represents that the peak [003] moves to a low angle. The basal spacing ($2\theta = 7.3^\circ$) was 1.20 nm as calculated *via* the Bragg equation: $2d\sin\theta = n\lambda$. As a result from the moving of [003], we may conclude that the SDS anions have been intercalated into the LDH layers. From Fig. 10, we can find that the diffraction face peak ($2\theta = 7.3^\circ$) of PE-LDH is greatly weakened, which indicates that the LDH is intercalated or exfoliated with the adding of PE-SO₃Na.

TGA curves of the intercalation compounds are displayed in Fig. 11. The content of the inorganic component and the degradation temperature have been determined by recording the thermal decomposition of LDH and the relative composites up to 700°C in air. The TGA curve of LDH shows two steps of endothermic weight loss between 50 and 250°C , which relate to the loss of co-intercalated water and water derived from dehydroxylation of the inorganic layers sheet. The main weight loss between 250 and 700°C may be ascribed to endothermic nitrate and to exothermal combustion of the residual organic part. The TGA curve of SDS-LDH displays one main degradation step in the range of 50 – 250°C and the onset temperature is similar to that of the modified PE-MMT, which indicates that the degradation of SDS-LDH is mainly due to the alkyl group. The weight loss of SDS-LDH increases to 47.2% from 41.1% for LDH. The results indicate that LDH is successfully

exchanged by anions (SO_3^{2-}). Besides, the curve displays one small degradation step in the range of 350–700 °C as well. The TGA curve of PE-LDH also displays one main degradation step in the range of 50–700 °C. The weight loss of PE-LDH increases to 52.4%. The results from XRD and TGA indicate the successful modification of LDH by PE- SO_3Na .

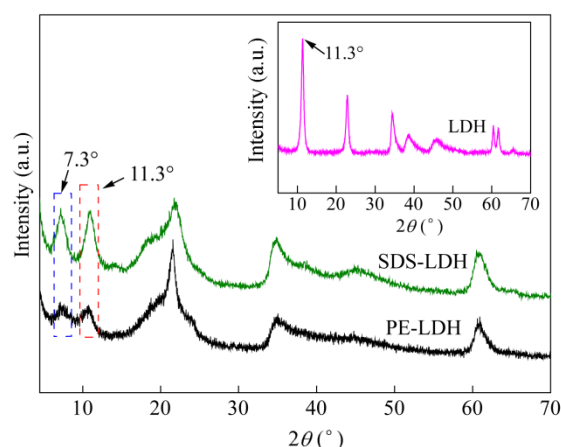


Fig. 10 XRD patterns of LDH, SDS-LDH and PE-LDH

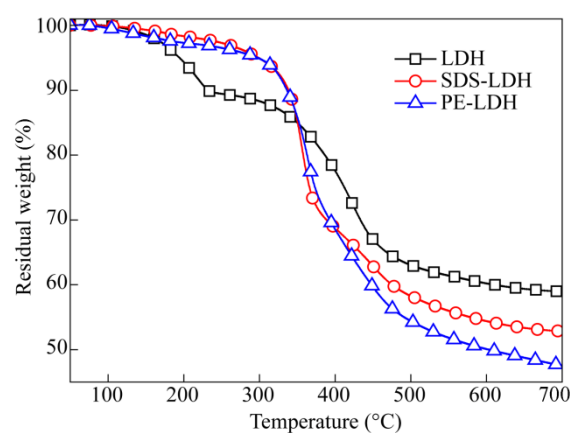


Fig. 11 TGA curves of LDH, SDS-LDH and PE-LDH

Morphology and dispersion of LDH in the nanocomposites

The nanocomposites of HDPE/PE-LDH with different contents of LDH were prepared by melt-mixing method using a HAAKE Minilab-II internal mixer at 190 °C with a screw speed of 50 r/min for 5 min. Table 5 shows the compositions of HDPE/PE-LDH nanocomposites.

Table 5 The composition of HDPE/PE-LDH nanocomposite

Sample	HDPE (g)	PE-LDH (g)	PE-LDH (wt%)
HDPE/PE-LDH-2	4.9	0.1	2
HDPE/PE-LDH-4	4.8	0.2	4
HDPE/PE-LDH-6	4.7	0.3	6

SEM and TEM were used to evaluate the dispersion of LDH particles in the HDPE matrix. Figure 12 shows the SEM images of HDPE/PE-LDH-6 and HDPE/SDS-LDH. LDH particles with the size of 100–200 nm are well dispersed in the matrix of HDPE. The TEM (Fig. 13) results also show that the PE-LDH layers display fine dispersion and distribution in the HDPE matrix with uniform exfoliated nano-sheets (Fig. 13a) as compared with the SDS-LDH layers (Fig. 13b). The EDS mapping (Fig. 14) shows that the Mg, Al elements from LDH are uniformly dispersed in the HDPE matrix. The results from SEM image, TEM micrograph and EDS mapping indicate that PE functional LDH are able to well-distribute in polymer matrix.

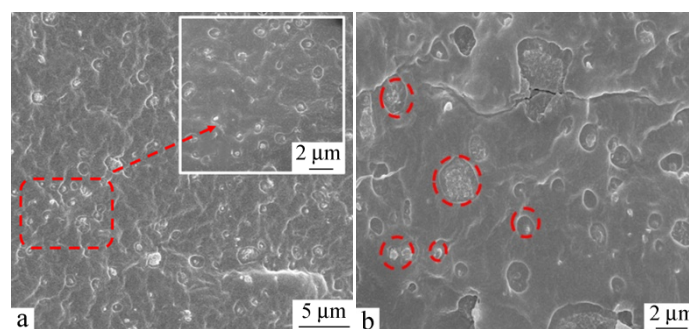


Fig. 12 SEM images of (a) HDPE/PE-LDH-6 and (b) HDPE/SDS-LDH

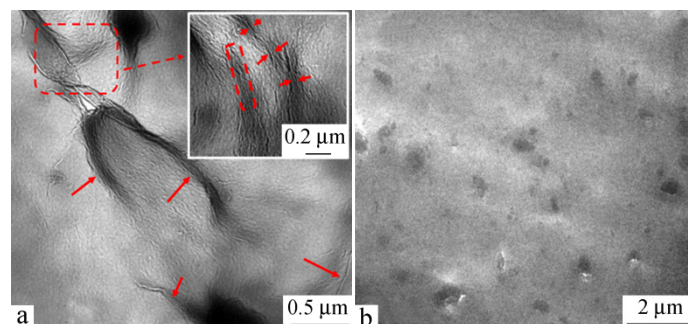


Fig. 13 TEM micrographs of (a) HDPE/PE-LDH-6 composites with 6 wt% loading of PE-LDH and (b) HDPE/SDS-LDH composites with 6 wt% loading of SDS-LDH

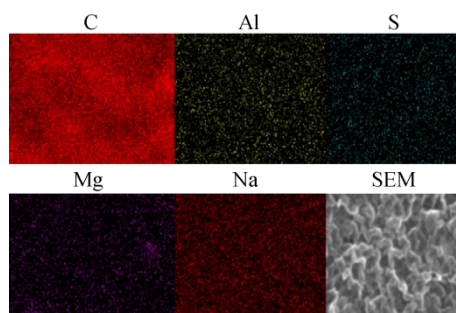


Fig. 14 EDS mapping of HDPE/PE-LDH-6 nanocomposite
The mapping was taken from area shown in the SEM image.

Thermal properties of HDPE/PE-LDH nanocomposites

Figure 15 shows the DSC curves of HDPE/PE-LDH nanocomposites with different PE-LDH contents. The thermal properties of the nanocomposites are listed in Table 6. The melting temperature and crystallization temperature almost remain unchanged. The TGA curves of HDPE/PE-LDH composites and pure HDPE are

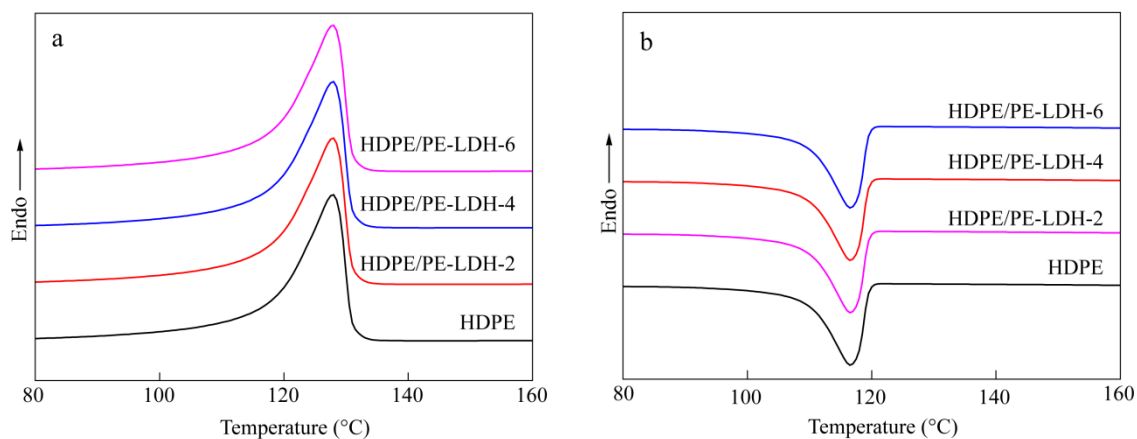


Fig. 15 DSC curves of HDPE/PE-LDH nanocomposites for various PE-LDH contents: (a) heating and (b) cooling

Table 6 Thermal properties of HDPE/PE-LDH nanocomposites for various PE-LDH contents

Sample	T_m (°C)	T_c (°C)	T_{95} (°C)
HDPE	127.90	116.54	452.30
HDPE/PE-LDH-2	127.37	115.63	447.06
HDPE/PE-LDH-4	127.26	116.05	445.70
HDPE/PE-LDH-6	127.62	115.47	441.11

shown in Fig. 16. About 5% weight loss of HDPE/PE-LDH and pure HDPE was observed in the temperature range from 440 °C to 452 °C, which was due to a small amount of PE-SO₃Na in the HDPE/PE-LDH sample. From the TGA curve, we can find out the decomposition temperature decrease with the addition of the modified PE-LDH in pure HDPE matrix.

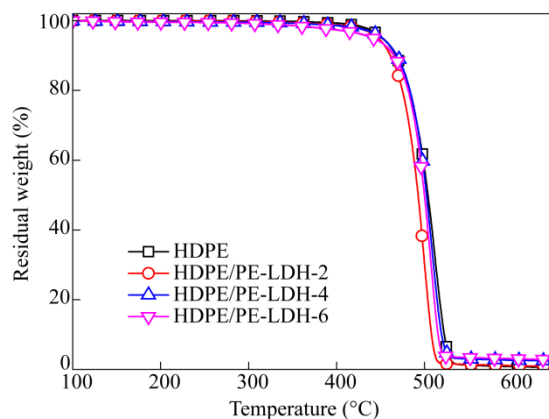


Fig. 16 TGA curves of HDPE/PE-LDH nanocomposite and pure HDPE in nitrogen atmosphere

CONCLUSIONS

In summary, choline chloride end functional polyethylene (PE-CC) was successfully synthesized *via* the epoxide ring-opening reaction, and used to modify MMT by cation ion-exchange. The intercalated LDH was obtained through anion ion-exchange between LDH and PE-SO₃Na. The XRD results indicated the successful intercalation of PE in the layers of MMT and LDH. The nanocomposites of HDPE/MMT, HDPE/LDH were prepared respectively. The properties of the nanocomposites and stable homogeneous dispersion of MMT and LDH particles were investigated. The SEM and TEM results showed that the nanoparticles were exfoliated nano-sheets and dispersed uniformly in the HDPE nanocomposites with a particle size of 100–200 nm.

REFERENCES

- 1 Gueho, T.C., Feng, Y., Faour, A. and Leroux, F., Dalton Trans., 2010, 39(26): 5994
- 2 Liu, P., Appl. Clay Sci., 2007, 38(1-2): 64
- 3 Ray, S.S. and Okamoto, M., Prog. Polym. Sci., 2003, 28(11): 1539
- 4 Peponi, L., Puglia, D., Torre, L., Valentini, L. and Kenny, J.M., Mat. Sci. Eng., R, 2014, 85: 1
- 5 Kumar, A.P., Depan, D., Tomer, S.N. and Singh, R.P., Prog. Polym. Sci., 2009, 34(6): 479
- 6 Paul, D.R. and Robeson, L.M., Polymer, 2008, 49(15): 3187
- 7 Pettarin, V., Frontini, P.M., Pita, V.J.R.R., Dias, M.L. and Diaz, F.V., Compos. Part A, 2008, 39(12): 1822
- 8 Jiang, T., Wang, Y.H., Yeh, J.T. and Fan, Z.Q., Eur. Polym. J., 2005, 41(3): 459
- 9 Wang, S., Hu, Y., Qu, Z., Wang, Z., Chen, Z. and Fan, W., Mater. Lett., 2003, 57(18): 2675
- 10 Qin, H., Zhang, S., Liu, H., Xie, S., Yang, M. and Shen, D., Polymer, 2005, 46(9): 3149
- 11 Gao, Y., Wang, Q., Wang, J., Huang, L., Yan, X., Zhang, X., He, Q., Xing, Z. and Guo, Z., ACS Appl. Mater. Interfaces, 2014, 6(7): 5094
- 12 Lomakin, S.M., Dubnikova, I.L., Shchegolikhin, A.N., Zaikov, G.E., Kozlowski, R. and Michler, G.H., J. Therm. Anal. Calorim., 2008, 94(3): 719
- 13 Šebenik, G., Huskić, M., Vengust, D. and Žigon, M., Appl. Clay Sci., 2015, 109-110: 143
- 14 Muksing, N., Magaraphan, R., Coiai, S. and Passaglia, E., Express Polym. Lett., 2011, 5(5): 428

- 15 Kato, M., Usuki, A. and Okada, A., *J. Appl. Polym. Sci.*, 1997, 66(9): 1781
- 16 Chung, T.C., *Macromolecules*, 1999, 32(25): 8678
- 17 Wang, Z.M., Nakajima, H., Manias, E. and Chung, T.C., *Macromolecules*, 2003, 36(24): 8919
- 18 Huang, Y., Yang, K. and Dong, J.Y., *Macromol. Rapid Commun.*, 2006, 27(15): 1278
- 19 Chakraborty, S., Kumar, M., Suresh, K. and Pugazhenth, G., *Powder Technol.*, 2014, 256: 196
- 20 Chen, W. and Qu, B., *Chem. Mater.*, 2003, 15(16): 3208
- 21 Passaglia, E., Coiai, S., Cicogna, F. and Ciardelli, F., *Polym. Int.*, 2014, 63(1): 12
- 22 Zhang, W., Wei, J. and Sita, L.R., *Macromolecules*, 2008, 41(21): 7829
- 23 Dong, J.Y., Wang, Z.M., Hong, H. and Chung, T.C., *Macromolecules*, 2002, 35(25): 9352
- 24 Lu, B. and Chung, T.C., *Macromolecules*, 1998, 31(17): 5943
- 25 Li, Y., Zhang, Y., Li, Q., Li, H., Zheng, S. and Hu, Y., *Macromol. Chem. Phys.*, 2015, 216(5): 569
- 26 Zhang, Y., Li, H., Dong, J.Y. and Hu, Y., *Polym. Chem.*, 2014, 5(1): 105
- 27 Zhang, Y., Li, H., Xu, Z., Bu, W., Liu, C., Dong, J.Y. and Hu, Y., *Polym. Chem.*, 2014, 5(13): 3963
- 28 Tao, Q., He, H., Frost, R.L., Yuan, P. and Zhu, J., *Appl. Surf. Sci.*, 2009, 255(7): 4334
- 29 Davis, R.D., Gilman, J.W. and VanderHart, D.L., *Polym. Degrad. Stab.*, 2003, 79(1): 111
- 30 Fornes, T.D., Yoon, P.J. and Paul, D.R., *Polymer*, 2003, 44(24): 7545
- 31 Wei, X., Gao, Z., Pan, W.P., Hunter, D., Singh, A. and Vaia, R., *Chem. Mater.*, 2001, 13(11): 2979
- 32 Shah, R.K. and Paul, D.R., *Polymer*, 2006, 47(11): 407