

Photo-oxidative degradation of polyethylene/montmorillonite nanocomposite

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Abstract

Photo-oxidative degradation is critical to polymer materials. It is even the case in polymer/layered silicate nanocomposites. A UV photo-oxidative degradation study on polyethylene/montmorillonite (PE/MMT) nanocomposite was carried out by FT-IR technique. It is indicated that the rate of photo-oxidative degradation of PE/MMT nanocomposite is much faster than that of pure PE. The acceleration of photo-oxidative degradation of PE/MMT nanocomposite is due to the effect of MMT and ammonium ion, in which the effect of ammonium ion is primary. It has been found that the dispersion state (either nano- or micro-) of MMT does not seem conclusive on the acceleration of degradation. Fe³⁺ modified MMT can also accelerate the photo-oxidative degradation of PE matrix.

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1. Introduction

In the past decade, polymer layered silicate (PLS) nanocomposites have received considerable attention whether in fundamental research or industry exploitation in the field of polymer. This new family of materials exhibits enhanced properties at very low filler content level, usually inferior to 5 wt.%, such as increased Young's modulus and storage modulus, increase in thermal stability and gas barrier properties and good flame retardancy [1]. Montmorillonite (MMT) belongs to the general family of 2:1 type layered aluminosilicates. The galleries (also referred to as interlayers) are occupied by exchangeable cations, typically Na⁺ and/or Ca²⁺, which balance the charge deficiency due to the isomorphous substitution of partial Al³⁺ by lower-valent metal ions. The ion exchange of the gallery cations by organic cations, particularly alkylammonium

ions, allows the modification of the gallery surfaces and enlarges the interlayer spacing for intercalation of polymer precursors or preformed polymers [2]. As a result of progress in this field, a new class of nanocomposites with involved matrices containing polar or non-polar polymers, such as polyamides [3], polystyrene [4], polypropylene [5] and polyethylene [6,7] (PE) has been developed. Recently, we successfully prepared an intercalated PE/MMT nanocomposite via a melt intercalation method.

Fire retarded materials are now expanding into new areas where permanent exposure to UV light might occur. It is important to investigate the photo-aging behavior of PLS nanocomposites [8]. In this paper, we report some results of the photo-oxidation of PE/MMT nanocomposite for the first time. It is shown that the rate of photo-oxidative degradation of PE/MMT nanocomposite is much faster than that of pure PE. The experiment results indicate that both ammonium ion and pure MMT can also accelerate the photo-oxidation of PE.

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2. Experimental

2.1. Materials

The polyethylene, LDPE 112A, was supplied by Yan-shan Petrochemical Co. LTD., Beijing, China. Cetyltrimethyl ammonium bromide ($\text{C}_{16}\text{H}_{33}\text{N}^+(\text{CH}_3)_3\text{Br}^-$, denoted with C16), *p*-aminophenol ($\text{NH}_2\text{C}_6\text{H}_4\text{OH}$) and dioctadecyldimethyl ammonium chloride ($(\text{C}_{18}\text{H}_{37})_2\text{N}^+(\text{CH}_3)_2\text{Cl}^-$, denoted with 2C18) were purchased from Beijing Chemical Reagent Co., China. Ferric chloride anhydrous (FeCl_3) was purchased from Beijing Medical Co., China. Sodium montmorillonite (Na-MMT), with cation exchange capacity (CEC) of 90 meq/100 g, was purchased from Zhangjiakou Qinghe Chemical Factory, China.

2.2. Modification of Na-MMT

Two kinds of organically modified montmorillonite were used in the present work. The first one is prepared by cation-exchange of Na-MMT with 2C18. The procedures were as following: Na-MMT (30 g) was cation-exchanged with 2C18 (19.32 g) in an ethanol–water (1:1 by weight) mixed solvent (500 ml) at 75 °C for 2 h under agitation. After being filtered and washed with the ethanol–water mixed solvent until no Cl^- was detected by 0.1 mol/l AgNO_3 solution, the product was dried for 8 h at 100 °C in vacuum, and then ground into powder with a particle size of 40–70 μm to get organophilic MMT. This organophilic MMT was termed OMMT.

The second organically modified montmorillonite, termed PMMT, was *p*-aminophenol treated by a similar manner to the OMMT, where a solution of *p*-aminophenol (3.3 g) in a 0.02 mol/l HCl solution (500 ml) was used and the treatment was operated at 30 °C.

Iron(III) montmorillonite, termed Fe-MMT, was prepared by treating Na-MMT (30 g) with FeCl_3 (2.974 g) in the de-ionized water (500 ml) at 55 °C for 1 h under agitation. The products were filtered and washed with de-ionized water until no Fe^{3+} was detected by 0.1 mol/l KSCN solution. The product was then dried and ground to get Fe^{3+} modified MMT at the same condition as OMMT.

2.3. Preparation of the PE/MMT compounds

Five types of PE compounds were prepared in this work: (1) PE/OMMT nanocomposite, (2) PE/Na-MMT microcomposite, (3) PE/PMMT microcomposite, (4) PE/Fe-MMT microcomposite and (5) PE/C16 blend. The mass fraction of MMT was 5 wt.% in compound 1–4 and the amount of C16 in PE/C16 blend is used according to the amount of 2C18 in PE/OMMT nanocomposite. A twin-screw extruder (Haake RC-90) was used for the preparation of these compounds in form of

pellets. The operation temperature was maintained at 120, 150, 160 and 160 °C from hopper to die of the extruder. The screw speed was maintained at 60 rpm. After drying at 50 °C for 6 h, the pellets were transformed to thin films with a thickness of 50 μm by a blow-moulding machine. Through XRD and TEM test, it was revealed that PE matrix formed an intercalated nanocomposite with OMMT and conventional microcomposites (no intercalation/exfoliation of the silicate layers) with Na-MMT, PMMT and Fe-MMT.

2.4. UV exposure test

UV exposure test was carried out in a WFH-201-B canned UV exposure instrument (Wenzhou Analytic Apparatus Co., China). The working temperature was controlled at 45 ± 2 °C and the wavelength of radiation was 300 nm. The rate of photo oxidation of the UV degraded films was followed by measuring carbonyl oxidation products through FT-IR per 20 h upon UV exposure, for a period from 40 to 200 h. The FT-IR measurements used was a Perkin-Elmer System 2000 infrared spectrum analyzer with the wave-number range of 4000–370 cm^{-1} .

3. Results and discussion

Fig. 1 shows the FT-IR spectra of PE/OMMT nanocomposite before and after 200 h UV irradiation. The absorption at 1034 and 1096 cm^{-1} is Si–O stretching ($\nu_{\text{Si-O}}$) of MMT. The bands at 516 and 463 cm^{-1} are Al–O stretching ($\nu_{\text{Al-O}}$) and Si–O bending ($\delta_{\text{Si-O}}$) of MMT. As shown in the figure a new broad band appears at about 1716 cm^{-1} after 200 h UV irradiation which belongs to a mixture of different carbonyl species [9].

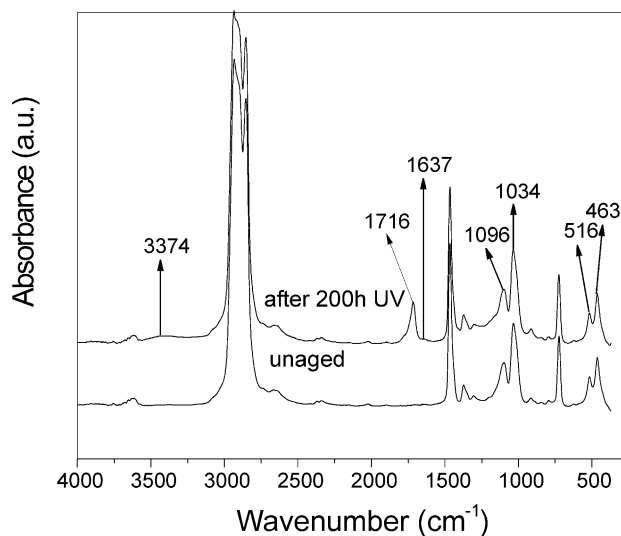


Fig. 1. FT-IR spectra of PE/OMMT nanocomposite before and after 200 h UV irradiation.

The second new band at 1637 cm^{-1} shows the resultant of the olefinic band. The third new band at 3374 cm^{-1} belongs to hydroxyl group, which indicates the resultant of hydroperoxides.

Fig. 2 shows the FT-IR spectra of pure PE before and after 200 h UV irradiation. After 200 h UV exposure, the appearance of new bands are similar to those of PE/OMMT nanocomposite, but the intensity of the carbonyl band of PE is far lower than that of PE/OMMT nanocomposite. The film samples were measured by FT-IR per 20 h upon UV exposure, from 40 to 200 h. Fig. 3 shows the evolution of the infrared spectra of PE/OMMT nanocomposite in the carbonyl region upon UV irradiation. It can be seen that with increasing the exposure time, the intensity of the carbonyl band grows. This behavior indicates that the material suffers

degradation. The shape of this band suggests that more than one functional group is formed that absorbs in the carbonyl region. It could be seen that there are four functional groups that contribute to the survey peak: the vibration of lactone (near 1780 cm^{-1}), ester (around 1735 cm^{-1}), ketone (at 1715 cm^{-1}) and carboxylic acid group (about 1700 cm^{-1}) [9].

Fig. 4 shows the evolution of the infrared spectra of pure PE in the carbonyl region upon UV irradiation. It could be seen that the spectra had little change until 60 h. The intensity of the carbonyl band grows slower in comparison with the PE/OMMT nanocomposite. The FT-IR spectra of PE/PMMT, PE/Na-MMT and PE/Fe-MMT microcomposites are similar to that of PE/OMMT nanocomposite. The FT-IR spectra of PE/C16 blend are similar to that of pure PE. The intensity of the carbonyl band of PE/C16 blend, PE/PMMT and PE/Fe-MMT microcomposites grows faster, while that of PE/Na-MMT microcomposite grows slower. The area of each FT-IR spectrum at carbonyl band was obtained separately [10]. Fig. 5 shows a varying tendency of the area with exposure time about different samples. The area of the carbonyl region band could be seen as the quantity of the carbonyl. It is the measurement of photo-oxidative degradation of samples.

As shown in the figure the rate of photo-oxidation of PE/OMMT nanocomposite is faster than that of pure PE. The effect of MMT and ammonium ion was reviewed separately. It was shown that the rate of photo-oxidation of PE matrix was accelerated by MMT and ammonium ion respectively. Distinctly, during the induction stage, the rate of photo-oxidation of PE/OMMT nanocomposite was the fastest. The rate of photo-oxidation of PE/Na-MMT microcomposite was a little faster than that of pure PE. It indicates that the

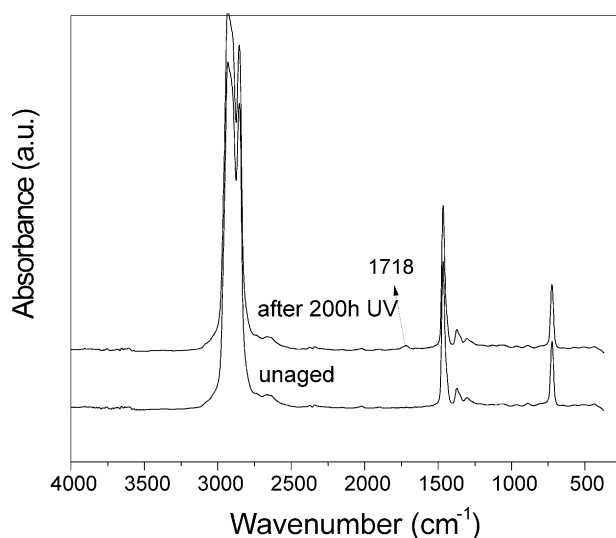


Fig. 2. FT-IR spectra of pure PE before and after 200 h UV irradiation.

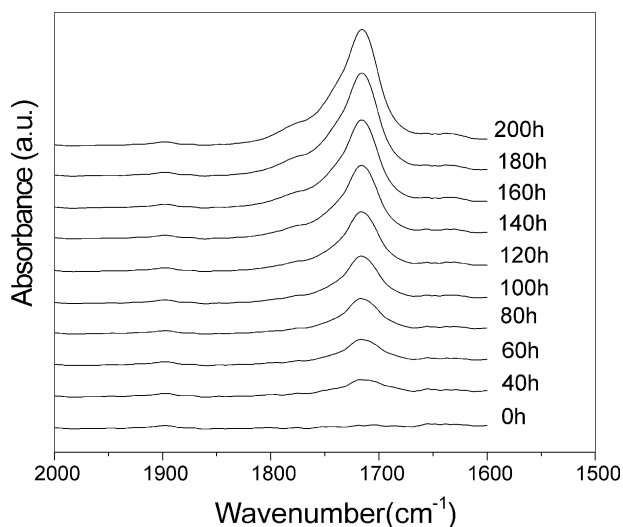


Fig. 3. Evolution of the FT-IR spectra at different times of UV irradiation of PE/OMMT nanocomposite in the carbonyl region (from bottom to top, the irradiation time varies from 0 to 200 h).

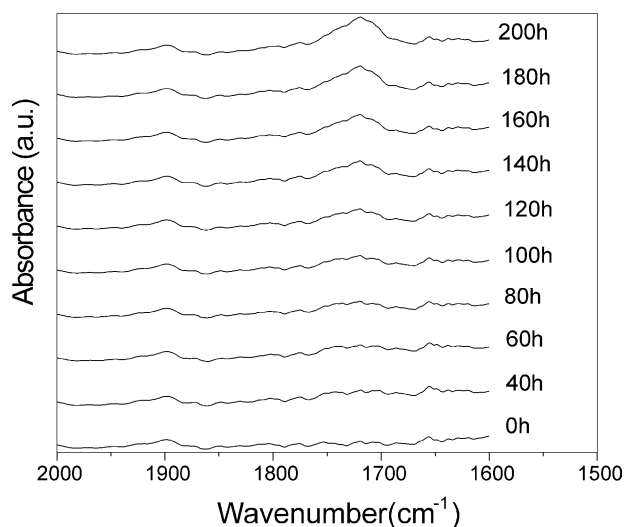


Fig. 4. Evolution of the FT-IR spectra at different times of UV irradiation of pure PE in the carbonyl region (from bottom to top, the irradiation time varies from 0 to 200 h).

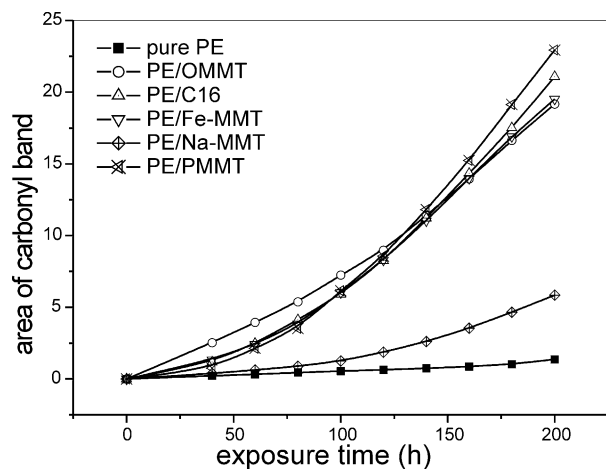


Fig. 5. Variations in the area of carbonyl band during the photo-oxidation of thin films.

effect of ammonium ion is principal. The exposure time was about 80 h and the photo-oxidative degradation of samples entered the stage of catalysis acceleration. The rate of photo-oxidation of pure PE had a little change. The rate of PE/Na-MMT microcomposite had a big increase relatively. The rate of PE/PMMT microcomposite had the fastest increase. After 140 h, the quantity of the carbonyl of PE/PMMT microcomposite preponderated over that of PE/OMMT nanocomposite. The samples upon UV exposure after 200 h showed that, the quantity of the carbonyl of PE/OMMT nanocomposite was about 14 times to that of pure PE, while the quantity of the carbonyl of PE/Na-MMT microcomposite was about 4 times to that of pure PE. Although the dispersion state of MMT in polymer matrix was different, the tendency of photo-oxidation of PE/PMMT microcomposite was similar to that of PE/OMMT nanocomposite. It suggested that the effect of the dispersion state of MMT seems not conclusive on the acceleration of degradation. However, the effects of different ammonium ions should be taken into account and will be considered in further work.

The rate of photo-oxidation of samples upon UV exposure during the two stages is listed in Table 1. The photo-oxidative of polymer matrix is due to the formation of free radical [9]. The effect of ammonium ion is at the bottom of its degradation leading to the formation of free radical. The influence of Fe-MMT results in the catalysis effect of transition metal ions (Fe^{3+}) [11]. This result suggests that the transition ions in Na-MMT can accelerate the photo-oxidation of PE matrix. Maybe it is also the reason for the catalysis effect of Na-MMT. In fact, few quantities of interlayer iron(III) were found in Na-MMT. The subject needs deep investigation.

Table 1

The rate of photo-oxidation of samples upon UV exposure during different stages

Oxidation stage	The rate of photo-oxidation (1/h)					
	PE/P-MMT	pure PE	PE/OMMT	PE/C16	PE/Na-MMT	PE/Fe-MMT
Stage 1 ^a	0.030	0.0051	0.065	0.036	0.010	0.036
Stage 2 ^b	0.186	0.0086	0.13	0.14	0.056	0.13

^aStage 1: Induction stage.

^bStage 2: Catalysis acceleration stage.

4. Conclusion

The experiment result indicates that the photo-oxidative degradation of PE/OMMT nanocomposite is faster than that of pure PE upon UV exposure. The acceleration of photo-oxidative degradation of PE/OMMT nanocomposite is due to the effect of MMT and ammonium ion, in which the effect of ammonium ion is primary. The effect of the dispersion state of MMT seems not conclusive on the acceleration of degradation. The transition metal ion Fe^{3+} modified MMT can accelerate the photo-oxidative degradation of PE matrix due to the catalysis effect.

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References

- [1] Alexandre M, Dubois P. *Mater Sci Eng* 2000;28:1–63.
- [2] Lan T, Pinnavaia TJ. *Chem Mater* 1994;6:2216–9.
- [3] Okada A, Kawasumi M, Kurauchi T, et al. *Polym Prepr* 1987; 28:447.
- [4] Chen G, Liu S, Zhang S, Qi Z. *Macromol Rapid Commun* 2000; 21:746–9.
- [5] Manias E, Touny A, Wu L. *Chem Mater* 2001;13:3516–23.
- [6] Heinemann J, Reichert P, Thomann R, Mulhaupt R. *Macromol Rapid Commun* 1999;20:423–30.
- [7] Wang KH, Choi MH, Coo CM, Choi YS, Chung LJ. *Polymer* 2001;42:9819–26.
- [8] Tidjani A, Wilkie CA. *Polym Degrad Stab* 2001;74:33–7.
- [9] Ranby B, Rabek JF. *Photodegradation, photo-oxidation and photostabilization of polymers*. John Wiley & Sons; 1975.
- [10] Shen D. *Application of infrared spectra in polymer study*. Beijing: Science Press; 1982.
- [11] Kaczmarek H, Sionkowska A, Kaminska A, et al. *Polym Degrad Stab* 2001;73:437–41.