

The Effects of Metallic Derivatives Released from Montmorillonite on the Thermal Stability of Poly(ethylene terephthalate)/Montmorillonite Nanocomposites

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Received 29 June 2005; accepted 29 September 2005

DOI 10.1002/app.23318

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: By *in situ* polycondensation, poly(ethylene terephthalate) (PET)/montmorillonite (MMT) nanocomposites were prepared, which were characterized via X-ray diffraction and transmission electron microscope. The processing stability of these nanocomposites was investigated by the change of number-average molecular weight and carboxyl terminal group content during injection molding, and the thermal stability of the nanocomposites was investigated via thermogravimetric analysis. It was found that some metallic derivatives released from MMT during polycondensation had a great influence on the processing and thermal

stabilities of the nanocomposites. The quantity of these metallic derivatives was determined by inductively coupled plasma. The stabilization effect of phosphorous compounds generated from MMT modified with phosphonium was observed. Processing stability and thermal stability of these nanocomposites exhibited similar trend because of almost the same causes. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1692–1699, 2006

Key words: nanocomposites; poly(ethylene terephthalate); polyesters; processing stability; thermal stability

INTRODUCTION

Recently, polymer/layered silicate nanocomposites (PLSN) have attracted much interest in academic and industrial studies, because of their expectable great improvement in mechanical and gas barrier properties, etc.^{1–6} Mica-type layered silicates, especially montmorillonite (MMT), are most widely used to prepare PLSN. To improve the dispersion of MMT, it had usually been treated with surfactants before polymer/MMT nanocomposites were prepared by *in situ* polymerization,^{1–4} solution mixing,⁵ or melt intercalation.^{6,7}

Because of its low cost and high performance, poly(ethylene terephthalate) (PET) finds extensive application in areas of fibers, films, beverage containers, and engineering plastics, etc. PET/layered silicate nanocomposites have also been a research focus in order to meet the practical needs to further improve its performance. However, the preparation of this kind of nanocomposites was not as successful as other PLSNs. Improvement of mechanical properties has been achieved by some researchers,^{2,8–10} but severe degra-

dation during processing was found in our recent research, because of the high processing temperature of PET. The poorer thermal stability of PET/layered silicate nanocomposites is a vital problem in its applications.

Usually, the decomposition of surfactants at higher processing temperature was thought as the main reason for the poorer thermal stability of PLSNs,^{11–15} which destroyed the unique chemical and physical properties of PLSNs. In our recent research, it was found that quantities of metallic derivatives released from MMT also have notable effects on the thermal stability of PET/MMT nanocomposites, besides the decomposition of surfactants. In this study, the quantity of metallic derivatives released from different kinds of MMT was determined, and the effects of metallic derivatives on the processing and thermal stabilities of PET/MMT nanocomposite were investigated in detail.

EXPERIMENTAL

Materials

Sodium-montmorillonite (Na-MMT) with a cation-exchange capacity of 100 mequiv/100 g and a nominal particle size of 40 μm was purchased from Zhangjiakou Clay Mineral Corp. (Hebei Province, People's Republic of China). Dimethyl terephthalate (DMT) was a

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Contract grant sponsor: Ministry of Science and Technology of China; contract grant number: 2003CB615605.

commercial product from Mitsubishi Chemical Corp. (Tokyo, Japan). Hexadecyltriphenylphosphonium (HTPP)¹⁶ bromide and 1-hexadecyl-2,3-dimethylimidazolium (HDMI)¹⁷ bromide were synthesized and purified with regular procedures in our lab, and 1-hexadecylpyridinium (HP) bromide was prepared with the same method as HDMI.

Preparation of organo-montmorillonites

Organo-montmorillonites (organo-MMTs) were acquired after Na-MMT had been treated with HTPP, HDMI, and HP salts, in 90°C water for more than 3 h. Then, these MMTs were separated by centrifugation and washed with distilled water repeatedly until no bromide ions could be detected by 0.01M silver nitrate aqueous solution. The acquired organo-MMTs are abbreviated as HTPP-MMT, HDMI-MMT, and HP-MMT, respectively. Other reagents were purchased from Beijing Chemical Reagent Company (Beijing, People's Republic of China) and used without further purification.

Preparation of PET/organo-MMT nanocomposites and pure PET

In the mixture of 100 parts of DMT by weight and 72 parts of ethylene glycol (EG) by weight, a zinc acetate catalyst (0.02 wt % with respect to DMT) was added. The temperature was raised to 190°C in nitrogen atmosphere, whereupon methanol was generated and removed by distillation. When the collected methanol exceeded the theoretical amount, a given weight of organo-MMT powder was added in, and an antimony trioxide catalyst (0.03 wt % with respect to DMT) was added into the reaction system. The pot temperature was increased to about 260°C, and the mixture was violently agitated for 1 h. Then, the temperature was raised to 280°C and a vacuum (<0.1 mmHg) was applied. EG was continuously removed by distillation. The polycondensation reaction was continued for 3 h, before PET/organo-MMT nanocomposite was finally formed. For comparison purpose, pure PET was also synthesized in our lab with the same method, but no organo-MMT powder was added.

Injection molding

The PET nanocomposites and pure PET were all dried in a vacuum oven at 140°C for at least 10 h, before injection molding. Then they were injected to form 40 mm × 40 mm × 0.5 mm slices on a plunger injection-molding machine at the processing temperature of 280°C.

Characterization

X-ray diffraction (XRD) was performed at room temperature by a Rigaku Model D/max-2B diffractometer using Cu K α radiation ($\lambda = 0.154$ nm) at a generator voltage of 40 kV and a generator current of 200 mA. Testing data were collected from 1.5° to 40° at a scanning rate of 2°/min. The type of transmission electron microscope (TEM) used was JEOL-100CX, and the acceleration voltage was 100 kV. All samples were microtomed into 50–80-nm thick slices by a diamond knife. Thermogravimetric analysis was performed on a Perkin-Elmer TGA7. Samples were heated at a rate of 20°C/min from 50 to 750°C in a nitrogen atmosphere. The standard uncertainty of decomposition temperature reported is $\pm 1^\circ\text{C}$. A Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) thermal analyzer was used for DSC analysis. Each sample, about 8 mg, was accurately weighted before being placed in DSC span. Under nitrogen atmosphere, it was heated from room temperature to 300°C with a heating rate of 20°C/min.

The intrinsic viscosity $[\eta]$ of all the samples was measured at $25 \pm 0.1^\circ\text{C}$ in a Ubbelohde viscometer, with the mixture of 50/50 (wt/wt) phenol/1,1,2,2-tetrachloroethane as solvent. The number-average molecular weight, M_n , was obtained from $[\eta]$ using the following relationship¹⁸

$$[\eta] = 2.1 \times 10^{-4} M_n^{0.82}$$

Carboxyl terminal group content ([COOH]) was measured by titration, according to the methods reported in literatures.^{19,20} In a nitrogen atmosphere, a sample of about 0.3 g of nanocomposite was dissolved in 10 mL of benzyl alcohol under heating and titrated with 0.01N KOH-EG solution with phenol red as an indicator. The titrations were carried out at a temperature higher than 100°C to avoid the reprecipitation of the polymer, and blank runs were carried out for correction.

In a nitrogen atmosphere, a given weight of organo-MMT was dispersed in 100 g of refluxing EG. The mixture was stirred for 6 h, before it was cooled to ambient temperature. Then, it was centrifuged with a speed of 5000 r/min for 30 min. The sediment cake was washed with EG, and then centrifuged for separation. This operation was performed for at least three times. All the upper, clear liquid from centrifugation was collected together, and EG was removed by vacuum distillation. The residue was carefully collected. About 0.1 g of residue was accurately weighted and then dissolved in concentrated sulfuric acid and hydrofluoric acid. The solution was analyzed on a Jobin Yvon Model Ultima ICP. Na-MMT was also analyzed with the same method.

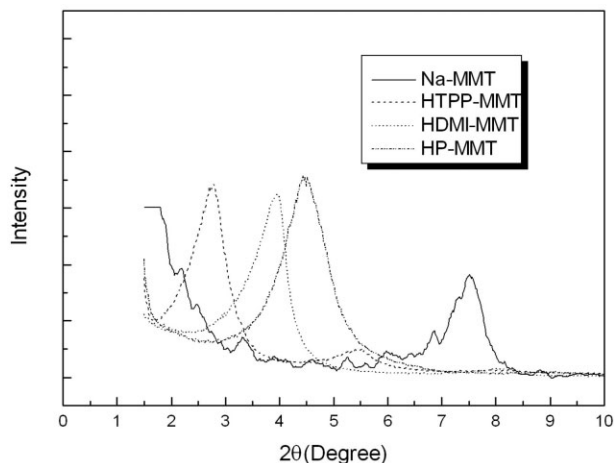


Figure 1 XRD patterns of untreated MMT and organically treated MMT.

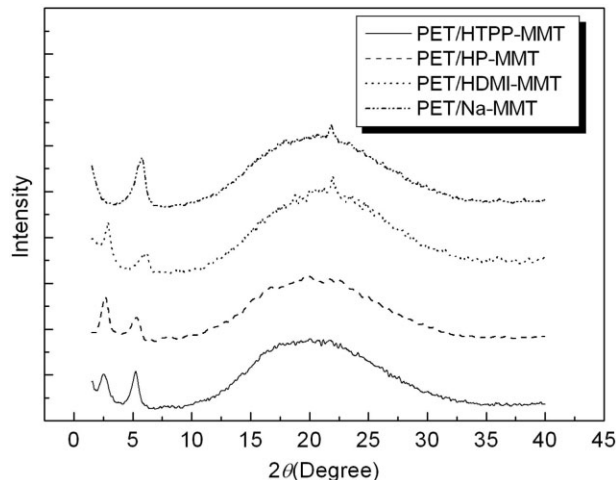


Figure 2 XRD patterns of PET/organo-MMT nanocomposites of 3 wt % MMT loading.

RESULTS AND DISCUSSION

Morphology of PET/organo-MMT nanocomposites

Three kinds of organic modifiers, HTPP, HDMI, and HP, were used to treat Na-MMT. Figure 1 shows the XRD patterns of Na-MMT and these organo-MMTs. After treatment, the gallery spacing of MMT was enlarged obviously, compared with that of Na-MMT. According to Bragg's equation, the gallery spacing of HTPP-MMT, HDMI-MMT, and HP-MMT reached 3.0, 2.1, and 1.9 nm, respectively, while the gallery spacing of Na-MMT was only about 1.2 nm.

PET/organo-MMT nanocomposites were prepared by *in situ* polycondensation of bis(2-hydroxyethyl) terephthalate with MMT loading of 3 wt %. As expected, the intercalation of macromolecules was achieved, which could be confirmed by the shift of 001 peak to lower 2θ value, according to the XRD patterns in Figure 2. The gallery spacing of PET/HP-MMT, PET/HDMI-MMT, and PET/HTPP-MMT reached 2.8, 2.9, and 3.4 nm, respectively. This indicated that nanocomposites, rather than simple incompatible blends, had formed. The gallery spacing of MMT in PET/Na-MMT composite was only enlarged to 0.3 nm compared with that of Na-MMT. This means that organic modification of MMT is necessary to favor the intercalation of macromolecules. Figure 3 shows the TEM images of selected sample (PET/HTPP-MMT nanocomposite with MMT loading of 3 wt %). Several single silicate layers could be observed, despite that MMT layers in polymer matrix mainly exhibited a face-to-face morphology.

Thermal and processing stabilities of PET/organo-MMT nanocomposites

The poorer thermal stability of PET/layered silicate nanocomposites is a vital problem that prevents them



Figure 3 TEM image of PET/HTPP-MMT nanocomposite with 3 wt % MMT loading.

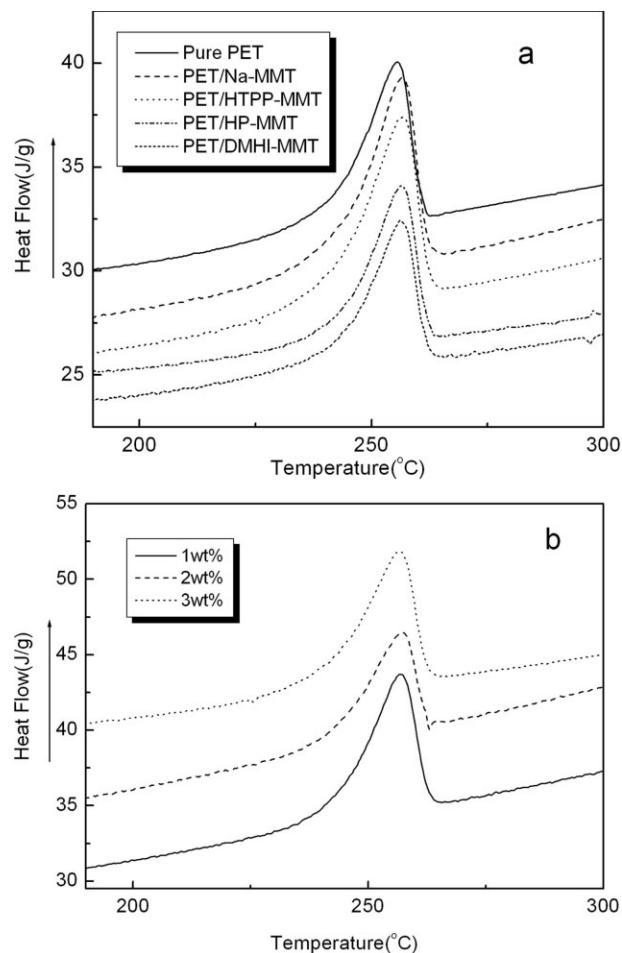


Figure 4 DSC melting exotherms of (a) pure PET and PET/MMT nanocomposites of 3 wt % MMT loading and (b) PET/HPP-MMT nanocomposites of 1, 2, and 3 wt % MMT loading.

from application; so, the study of thermal and processing stabilities of PET/organo-MMT nanocomposites is of great practical importance. The thermal and thermooxidative properties of PET are essentially affected by side-reactions taking place during polycondensation. These side-reactions are very complex,^{20–22} and many side-reactions are present in very small percentage and usually negligible, but two kinds of side-reactions have significant effect on the quality of PET, which are the formation of diethylene glycol (DEG) moieties in the backbone chains and the formation of carboxyl terminal groups.

A slight increase in DEG units usually results in remarkable lowering of melting point (T_m) and decay in thermooxidative stability during processing.²² DSC was used to determine the T_m in our research. From Figure 4, one can readily see that the T_m of all the samples, including pure PET and PET/MMT nanocomposites, is almost the same (about 255.5°C). This indicated that introduction of MMT had no influence on the content of DEG units under the present reaction

conditions. So, in this article, the disadvantages of DEG units will not be discussed.

Zimmerman and Kim had found that a low carboxyl terminal group concentration is crucial for the thermal and processing stabilities, because carboxyl terminal groups cause autocatalytic effect.^{22,23} Similar phenomenon had been observed during the investigation on the thermal properties of poly(propylene terephthalate).¹⁹ The cause for the generation of carboxyl terminal groups is very complex, depending on the starting monomers, the extent of reaction, the thermal history, and the catalysts employed, etc.²⁰ Since DMT and EG were starting materials in this research, which both had no carboxyl groups, and all the nanocomposites and neat PET were prepared under the same conditions, carboxyl terminal groups should mainly come from the side-reactions during polycondensation, especially thermal degradation side-reactions.²² Excessive catalytic substances in reaction system usually accelerate side-reactions during polycondensation because of their catalytic effect, which usually leads to more carboxyl terminal groups.

The change of number-average molecular weight (M_n) of these nanocomposites after processing is a direct evidence for degradation. Meanwhile, degradation reactions usually lead to increase in carboxyl terminal groups;²² so, change of [COOH] is another useful evidence for degradation. Here, the degradation reactions include thermal degradation and thermooxidative degradation. All the samples were molded to specimens on a plunger injection-molding machine at the processing temperature of 280°C. From the data listed in Table I, one can readily see that introduction of MMT caused processing stability deterioration of the nanocomposites except PET/HPP-MMT, for their M_n decreased notably, and their [COOH] increased remarkably.

The synthesis and processing temperature of PET is so high (near 300°C) that some most widely used organic modifiers such as alkyl ammoniums have decomposed far below this temperature.²⁴ This may cause some negative effects on products.^{11,12} So, thermal stability of organic modifier is also very important when preparing PET/organo-MMT nanocomposites. Thermogravimetric analysis in nitrogen atmosphere was used in our research to characterize the thermal stability of these organo-MMTs, and the results are shown in Figure 5. Their onset decomposition temperature (t_d) was around 320°C for HPP-MMT, 280°C for HDMI-MMT, and 250°C for HP-MMT. HPP-MMT showed much better thermal stability than the other two. This should be an advantage for it to resist the high temperature during polycondensation and processing. It seemed that poor thermal stability of the surfactants resulted in the severe degradation of PET/HDMI-MMT and PET/HP-MMT nanocomposites during processing. However, PET/Na-MMT system

TABLE I
Intrinsic Viscosity, Number-Average Molecular Weight and Carboxyl Terminal Group Content of the Nanocomposites (3 wt % MMT Loading) Before and After Processing

Sample	Before processing			After processing		
	$[\eta]$	M_n	[COOH] (mmol/Kg)	$[\eta]$	M_n	[COOH] (mmol/Kg)
PET	0.63	17,400	23.1	0.57	15,400 (-11.5%)	46.0
PET/Na-MMT	0.54	14,400	37.4	0.47	12,200 (-15.3%)	57.2
PET/HPPP-MMT	0.65	18,100	21.7	0.60	16,400 (-9.4%)	34.3
PET/HDMI-MMT	0.62	17,100	32.3	0.53	14,100 (-16.4%)	54.3
PET/HP-MMT	0.51	13,400	38.2	0.44	11,200 (-17.5%)	67.7

The data in parentheses indicate the relative change of M_n after the processing of the samples. Minus signs are used purely to indicate a decrease.

also experienced severe degradation during injection molding, although there was no surfactant at all. Obviously, attributing only poor processing stability to the lower thermal stability of surfactants was unreasonable. There must be other factors that affect the processing stability of PET/MMT nanocomposites markedly.

Derivatives of almost all metals are recommended as effective polycondensation catalysts for PET.^{20,22,25-26} However, such metallic derivatives usually accelerate the degradation reactions at the same time.^{22,27} The residual metallic compounds in nanocomposites will influence their thermal stability and processing stability. It is well known that the composing of MMT is quite complex. It is comprised of two silica tetrahedral sheets and a lumina octahedral sheet. Because of isomorphous substitution, which means an atom of lower positive valence replaces one of higher valence, negative charges are generated in these MMT layers. Exchangeable metal-ions existing in the interlayer space neutralize those negative charges distributing in the clay layers.²⁸ Inductively coupled plasma (ICP) analysis of Na-MMT was performed, and the result indicated that there are many kinds of metallic ele-

ments in it, such as Na, Mg, Al, Ca, Zn, Fe, Ti, Co, Ni, Cu, Mn, etc. Were these metallic elements likely to transfer into reaction mixture? After natural Na-MMT and organo-MMT were treated with refluxing EG in a nitrogen atmosphere, ICP was used to analyze the upper, clear liquids from centrifugation to determine if there was any metallic element released from MMT. It can be readily seen from Table II that many kinds of metallic elements were released from Na-MMT in refluxing EG.

How these metallic elements transferred from MMT to EG needs further research. It is general thought that, for an effective catalyst, it must be able to resolve in reaction mixture to form glycolates.²⁹ So, these released metallic elements were quite likely to exist in EG as glycolates. The content of the main elements released from organo-MMT are listed in Table III. From these data, one can find that these organo-MMTs released less metallic compounds than natural Na-

TABLE II
Metallic Elements Released from Na-MMT

Element	$\mu\text{g/g}$
Na	4281
Al	1357
Mg	244.1
Fe	165.4
Ca	55.8
Zn	55.6
Ti	11.78
P	7.72
Sr	2.08
Mn	1.14
Ni	1.03
Ba	0.93
Cr	0.80
Pb	0.74
Cu	0.40
V	0.076
B	0.073
Co	0.063
Mo	0.056
Cd	0.003

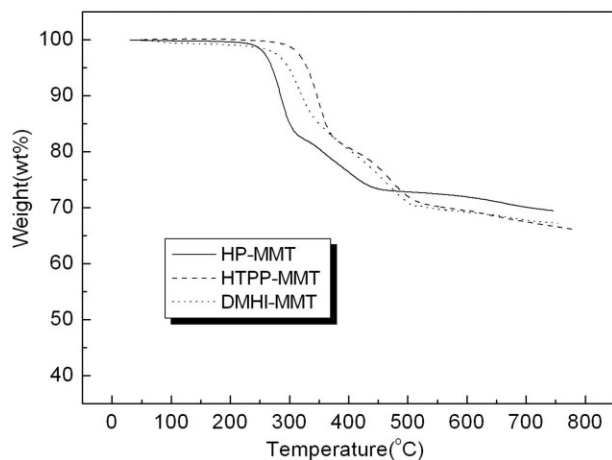


Figure 5 TGA thermograms of organically treated MMT.

TABLE III
Metallic Elements Released from Organo-MMTs (with Respect to the Inorganic Parts of Organo-MMTs)

Sample	Element ($\mu\text{g/g}$)						
	Zn	Mn	Fe	Mg	Ca	Ti	Al
HPPP-MMT	0.70	0.20	12.07	5.32	7.59	1.42	139.9
HDMI-MMT	6.37	0.17	138.6	7.55	13.19	15.91	573.5
HP-MMT	8.89	0.93	41.93	79.96	139.7	7.39	361.7

MMT did, and the tendency was extremely obvious when MMT was treated with HPPP salts. This phenomenon indicated that the content of metallic compounds released from MMT was concerned with the exposed surface area of MMT layers. Because these organically modified MMTs had less surface area exposed to medium, when being stirred in refluxing EG, they released less metallic compounds. HPPP cations had larger bulk size than the other two kinds of organic cations; so, the amount of metallic elements released from HPPP-MMT is least. Some other properties of these organic modifiers also can affect the release of metallic elements, and this aspect needs further research.

During polycondensation, MMT was dispersed in a mixture of diols of different polymerization degree. Some metallic compounds must have been released from MMT into reaction mixture. In our recent research, it was found that the upper clear liquids from centrifugation exhibited obvious polycondensation catalytic activity. This indicated that such catalytic activity had some relationship with the metallic derivatives released from MMT. Because polycondensation catalysts also can accelerate the degradation reactions during polycondensation and processing, these metallic derivatives must have an important influence on the thermal and processing stabilities of the nanocomposites prepared by in situ polycondensation.

Obviously, because some metallic derivatives were released from MMT, PET/Na-MMT, PET/HDMI-MMT, and PET/HP-MMT nanocomposites experienced excessive degradation side-reactions during polycondensation in comparison with pure PET. This resulted in higher [COOH] of these samples. Furthermore, overloaded metallic compounds also can catalyze the degradation reactions during injection processing. Thus, overloaded metallic compounds and higher carboxyl terminal group content of these nanocomposites were responsible for the deterioration of processing stability. PET/HDMI-MMT and PET/HP-MMT exhibited a little lower processing stability than PET/Na-MMT, despite both of them released less metallic compounds than Na-MMT. This may be a negative effect caused by poor thermal stability of HDMI and HP oniums during polycondensation and processing.

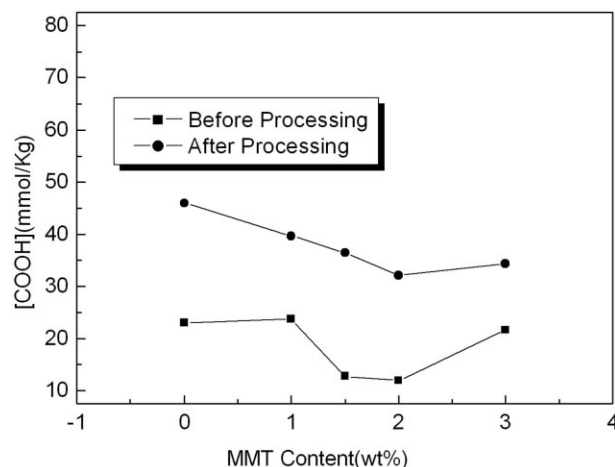


Figure 6 Change of carboxyl terminal group content ([COOH]) of PET/HTPP-MMT nanocomposites of different MMT loading during processing.

However, when HPPP-MMT was introduced, PET/HTPP-MMT nanocomposite exhibited improved processing stability in comparison with PET/Na-MMT and pure PET, although some metallic elements were still released. For further investigation purpose, a series of nanocomposites with different HPPP-MMT loading (1, 1.5, 2, and 3 wt %) were prepared, and all these samples were also processed on the injection-molding machine. It can be readily seen from Figure 6 that carboxyl terminal group content of the PET/HTPP-MMT nanocomposites was not higher than that of pure PET. After injection molding, their carboxyl terminal group content was much lower than that of pure PET, which indicated that PET/HTPP-MMT nanocomposites experienced less degradation reactions during injection molding and possessed better processing stability. The number-average molecular weight of the nanocomposites decreased less than that of pure PET, according to the data listed in Table IV, which confirmed the tendency indicated in Figure 6. Xie et al. thought that MMT modified with quaternary phosphonium may be advantageous for preparing polymer nanocomposites, because of the well-known

TABLE IV
Change of Number-Average Molecular Weight (M_n) During Processing

Sample	MMT loading (wt %)	M_n		Relative change extent (%)
		Before processing	After processing	
PET	0	17400	14700	-15.5
PET/HTPP-MMT	1	16700	14700	-12.0
PET/HTPP-MMT	1.5	17700	16100	-9.0
PET/HTPP-MMT	2	16700	15400	-7.8
PET/HTPP-MMT	3	18100	16400	-9.4

properties of phosphorous compounds, such as heat stabilization and flame retardancy.³⁰ It is quite obvious here that introducing proper quantity of HTPP-MMT can improve the processing stability of the nanocomposites. After MMT had been treated with HTPP salt, the metallic compounds released from MMT decreased greatly during polycondensation. Such phosphorous compound may act as a stabilizer to inhibit the side-reactions that caused the generation of carboxyl terminal groups. The ultimate result was the improvement of processing stability of the nanocomposites.

Thermogravimetric analysis (TGA) in nitrogen atmosphere was used to characterize the thermal stability of PET/organo-MMT nanocomposites. Figure 7 shows the TGA thermograms of PET/Na-MMT, PET/HDMI-MMT, PET/HP-MMT, and PET/HTPP-MMT nanocomposites with 3 wt % MMT loading, in comparison with that of pure PET. The weight loss onset temperature (t_{onset}) of pure PET in a nitrogen atmosphere was about 426°C, and t_{onset} of PET/HTPP-MMT had reached as high as 439°C, which was the highest. Compared with that of pure PET, PET/HDMI-MMT and PET/Na-MMT also exhibited improved thermal stability, and their t_{onset} was 434 and 432°C, respectively. However, PET/HP-MMT did not show any improvement in thermal stability. Its t_{onset} was only 425°C. This may also be caused by the poor thermal stability of HP cations at higher temperature, since HP-MMT and HDMI-MMT both released less metallic derivatives than that of Na-MMT. Like processing stability, thermal stability of PET/nanocomposites also depended on [COOH] and content of catalytic substances.

Figure 8 shows the TGA thermograms of PET/HTPP-MMT nanocomposites with MMT loading of 1, 2, and 3 wt %. It is generally recognized that higher

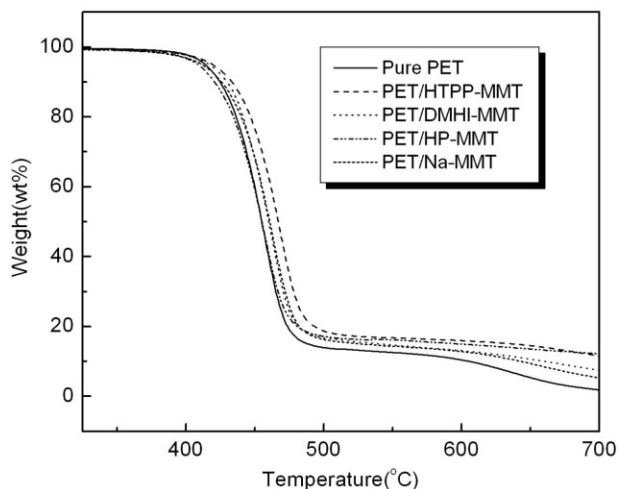


Figure 7 TGA thermograms of pure PET and PET nanocomposites with 3 wt % MMT loading.

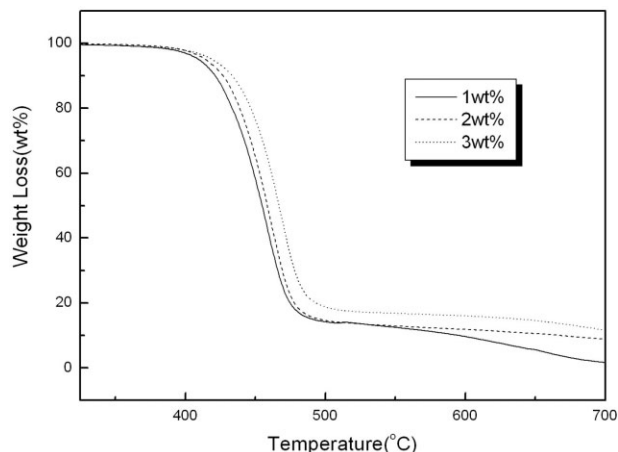


Figure 8 TGA thermograms of PET/HTPP-MMT nanocomposites of different MMT content.

MMT content will afford nanocomposites better thermal stability. Obviously, this trend was exactly observed in our research. The sample presenting best thermal stability was PET/HTPP-MMT of 3 wt % layered silicate loading, and the nanocomposite with a HTPP-MMT loading of 2 wt % exhibited better thermal stability than that of 1 wt % loading.

Thermal stability and processing stability of the materials have a very close relationship. In fact, they usually disclose the same essence, so they were both affected almost by the same factors.

CONCLUSIONS

Intercalated PET/MMT nanocomposites were prepared via *in situ* polycondensation, which was characterized by XRD and TEM. Metallic derivatives, which had catalytic activity on both polycondensation and degradation reactions, were released from MMT during polycondensation. The total quantity of these metallic derivatives decreased after Na-MMT had been organically modified, especially when HTPP was used as modifier. The overloaded catalytic substances caused excessive side-reactions during polycondensation, resulting in more carboxyl terminal groups, which had autocatalytic effect on degradation. Furthermore, overloaded catalytic substances would also accelerate the degradation during processing. The final result was the deterioration of processing stability of the nanocomposites.

However, when HTPP-MMT was introduced, the stabilization effect of phosphorous compounds was observed. Processing stability of PET/HTPP-MMT nanocomposites was improved when MMT loading was not more than 3 wt %. Affected by almost the same factors, thermal stability of the nanocomposites characterized by TGA exhibited similar trend as that of processing stability.

References

1. Yeh, J. M.; Liou, S. J.; Lin, C. Y.; Cheng, C. Y.; Chang, Y. W.; Lee, K. R. *Chem Mater* 2002, 14, 154.
2. Imai, Y.; Nishimura, S.; Abe, E.; Tateyama, H.; Abiko, A.; Yamaguchi, A.; Aoyama, T.; Taguchi, H. *Chem Mater* 2002, 14, 477.
3. Lepoittevin, B.; Pantoustier, N.; Devalckenaere, M.; Alexandre, M.; Kubies, D.; Calberg, C.; Jerome, R.; Dubois, P. *Macromolecules* 2002, 35, 8385.
4. Tripathy, A. R.; Burgaz, E.; Kukureka, S. N.; MacKnight, W. J. *Macromolecules* 2003, 36, 8593.
5. Krikorian, V.; Pochan, D. *J Chem Mater* 2003, 15, 4317.
6. Ray, S. S.; Yamada, K.; Okamoto, M.; Ogami, A.; Ueda, K. *Chem Mater* 2003, 15, 1456.
7. Giannelis, E. P. *Adv Mater* 1996, 8, 29.
8. Ke, Y.; Long, C.; Qi, Z. *J Appl Polym Sci* 1999, 71, 1139.
9. Imai, Y.; Inukai, Y.; Tateyama, H. *Polym J* 2003, 35, 230.
10. Zhang, G.; Shichi, T.; Takagi, K. *Mater Lett* 2003, 57, 1858.
11. Matayabas, J. C., Jr.; Turner, S. R.; Sublett, B. J.; Connell, G. W.; Barbee, R. B. (to Eastman Chemical Co.). *PCT Int Appl WO* 9829499, July 9, 1998.
12. Davis, C. H.; Mathias, L. J.; Gilman, J. W.; Schiraldi, D. A.; Shields, J. R.; Trulove, P.; Sutto, T. E.; DeLong, H. C. *J Polym Sci Part B: Polym Phys* 2002, 40, 2661.
13. Gilman, J. W.; Jackson, C. L.; Morgan, A. B.; Harris, R. H.; Manias, E.; Giannelis, E. P.; Wuthenow, M.; Hilton, P.; Philips, S. H. *Chem Mater* 2000, 12, 1866.
14. VanderHart, D. L.; Asano, A.; Gilman, J. W. *Chem Mater* 2001, 13, 3796.
15. Davis, R. D.; Gilman, J. W.; VanderHart, D. L. *Polym Degrad Stab* 2003, 79, 111.
16. Zhu, J.; Morgan, A. B.; Lamelas, F. J.; Wilkie, C. A. *Chem Mater* 2001, 13, 3774.
17. Gilman, J. W.; Awad, W. H.; Davis, R. D.; Shield, J.; Harris, R. H., Jr.; Davis, C.; Morgan, A. B.; Sutto, T. E.; Callahan, J.; Trulove, P. C.; DeLong, H. C. *Chem Mater* 2002, 14, 3776.
18. Conix, A. *Makromol Chem* 1958, 26, 226.
19. Berti, C.; Bonora, V.; Colonna, M.; Lotti, N.; Sisti, L. *Eur Polym J* 2003, 39, 1595.
20. Pilati, F.; Toselli, M.; Messori, M.; Manzoni, C.; Turturro, A.; Gattiglia, E. G. *Polymer* 1997, 38, 4469.
21. Plati, F. In *Comprehensive Polymer Science*; Allen, G.; Bevington, J. C., Eds.; Pergamon: Oxford, 1989; Vol. 5, Chapter 17.
22. Zimmerman, H. In *Developments in Polymer Degradation*; Grassie, N., Ed.; Applied Science Publishers: London, 1984; Vol. 5, Chapter 3.
23. Zimmerman, H.; Kim, N. T. *Polym Eng Sci* 1980, 20, 680.
24. Xie, W.; Gao, Z.; Pan, W. P.; Hunter, D.; Singh, A.; Vaia, R. *Chem Mater* 2001, 13, 2979.
25. Tomita, K. *Polymer* 1976, 17, 221.
26. Shah, T. H.; Bhatta, J. I.; Gamlan, G. A.; Dollimore, D. *Polymer* 1984, 25, 1333.
27. Chiu, S. J.; Cheng, W. H. *Polym Degrad Stab* 1999, 63, 407.
28. van Olphen, H. In *An Introduction to Clay Colloid Chemistry*; Wiley: New York, 1963; Chapter 6.
29. Ravindranath, K.; Mashelkar, R. A. *Chem Eng Sci* 1986, 41, 2197.
30. Xie, W.; Xie, R.; Pan, W. P.; Hunter, D.; Koene, B.; Tan, L. S.; Vaia, R. *Chem Mater* 2002, 14, 4837.