

Thermal Properties and Flame Retardancy of Polycarbonate/Hydroxyapatite Nanocomposite

Quan-Xiao Dong, Qian-Jin Chen, Wei Yang, Yi-Lei Zheng, Xin Liu, Yuan-Li Li, Ming-Bo Yang

College of Polymer Science and Engineering, Sichuan University, State Key Laboratory of Polymer Materials Engineering, Chengdu, 610065, Sichuan, People's Republic of China

Received 31 October 2007; accepted 11 January 2008

DOI 10.1002/app.28053

Published online 1 April 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The thermal degradation of polycarbonate (PC) and polycarbonate/hydroxyapatite (PC/HAP) composite was investigated by the thermogravimetric analysis (TGA) and the decomposition activation energy was calculated by Kissinger method. It was found that the first step decomposition activation energy (E_{a1}) was higher than that of pure PC while the second step decomposition (E_{a2}) decreased a little. The limiting oxygen index (LOI) of PC/HAP composite with 0.5 wt % HAP reached 34. The carbon char of PC and PC/HAP composite after combustion was analyzed by scanning electron microscopy (SEM), X-

ray photoelectron spectroscopy (XPS), and fourier transform infrared spectroscopy (FTIR) and similar morphology, components, and the same functional groups were found in the char residues. Based on these results, it can be concluded that a low content of HAP in PC matrix can significantly improve the thermal properties and flame retardancy of the composite. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 659–663, 2008

Key words: polycarbonate; hydroxyapatite; nanocomposite; thermal property; flame retardancy

INTRODUCTION

Polymer nanocomposites have attracted much attention recently. With low additional levels, the mechanical or thermal property of polymers can be significantly enhanced.^{1–7} Polycarbonate (PC) is an important thermoplastic and one of the best studied is bisphenol A PC. Bisphenol A PC is an engineering thermoplastic with excellent mechanical properties, high heat distortion temperature, excellent transparency, and electrical properties, which is widely used in the fields such as electrical and electronic devices, automobiles, and construction. PC shows a high limiting oxygen index (LOI) due to relatively high tendency to charring during combustion. However, for electronic and electric applications, even higher flame retardancy is required. To meet such requirement, flame retardant technologies of PC have been continuously expanding for decades.

Resorcinol bis(diphenyl phosphate) and bisphenol A bis(diphenyl phosphate) are very efficient in PC and PC-based blends, which can provide the system

a high flame retardancy with low loading.⁸ Phosphate of alkali and alkaline earth metals could interfere with the reaction of methyl radicals as a flame retardant suggested by Ref. 9. Hydroxids, such as $Mg(OH)_2$ and $Al(OH)_3$, were widely used in polymer composite by virtue of its high decomposition temperature, innocuity, and the ability to restrain smoke.^{10,11} Many studies based on polycarbonate nanocomposites have been carried out and both promoting and hindering effects of nanofillers on the thermal or flame retardant properties have been found.^{12–16} Zong et al.¹⁴ reported that PC/acrylonitrile-butadiene-styrene/montmorillonite nanocomposite showed a higher thermal stability and lower flammability. In contrast, Zhao et al.¹⁵ observed a decrease of T_g for PC nanocomposite with liquid trisilanolisooctyl-polyhedral oligomeric silsesquioxane. Carrión et al.¹⁶ also observed both the T_g and decomposition temperature of the composite were lower than pure polycarbonate in the presence of the ZnO nanoparticles, which was interpreted the existence of large aggregate nanoparticles.

Calcium hydroxyapatite (HAP) represented by the formula $Ca_{10}(PO_4)_6(OH)_2$ is a kind of ceramic biomaterial that has been widely used in medical and biomaterial areas, such as bone,^{17,18} metal orthopedic implants,¹⁹ and coating process. To the best of our knowledge, there has been no public report on the study of polycarbonate composites containing calcium hydroxyapatite nanoparticles.

In this study, nano-HAP was used to prepare PC/HAP nanocomposite by conventional melt blending

Correspondence to: M.-B. Yang (yangmb@scu.edu.cn).

Contract grant sponsor: Student Innovation Foundation of Sichuan University; contract grant number: 2006 G001.

Contract grant sponsor: National Nature Science Found of China; contract grant number: 10590351.

Contract grant sponsor: Special Funds for Major Basic Research; contract grant number: 2005CB623808.

Journal of Applied Polymer Science, Vol. 109, 659–663 (2008)
© 2008 Wiley Periodicals, Inc.

method to enhance the flame redundancy of PC. With the addition of HAP to the matrix PC, a noticeable improvement of LOI was observed. The study on the thermal degradation behavior of the PC with HAP was carried out by using the thermogravimetric analysis (TGA). The Kissinger method²⁰⁻²² was used to estimate the thermal decomposition activation energy for PC and PC/HAP (0.5 wt %) composites. In addition, the flame retardant mechanism is speculated based on the results of X-ray photoelectron spectroscopy (XPS) and fourier transform infrared spectroscopy (FTIR).

EXPERIMENTAL

Material and sample preparation

The PC pellets were obtained from Chongqing Changfeng Chemical Co. Ltd (China) and used as received, with a melt flow rate (300°C and 1.2 kg load) of 2.857 g/10 min. The number average molecular weight is 26,786 g/mol with a molecular weight distribution index of 2.56. The nano-HAP with an average diameter of 80 nm was obtained from Nanjing High Tech. Co. Ltd (China) and used as received. The pellets were dried at 100°C in a blast oven over 12 h prior to process. After simple mixing, the PC pellets and HAP powder were put into a corotating twin-screw extruder (SHJ-20, Nanjing Gaint Machine Co. Ltd, China) with a diameter of 20 mm and a length/diameter ratio of 35 to compound in the melting state, with a temperature profile of 245, 250, 260, 255°C from the hopper to die. After drying to remove any moisture picked up during the extrusion the pellets were injection molded into dumb-bell tensile sample and impact sample in a precise injection-molding machine (PS40E5ASE, Nissei Plastic Industry Co. Ltd, Japan), with a temperature profile of 270, 280, 285, and 280°C from the feeding zone to the nozzle. The injection pressure and holding pressure were 35 MPa. The pure PC sample was dried and directly injection molded under the same condition.

TGA analysis

TGA was carried out on a thermoanalyser (WRT-2P, Shanghai Instrument Factory, China). Samples of about 8 mg were heated from 200°C up to 650°C with flowing air atmosphere at a heating rate of 5, 10, 15, and 20°C/min. The temperature reproducibility of TGA is $\pm 3^\circ\text{C}$ and the error range of the mass is $\pm 3\%$.

LOI test

The LOI value was measured on an oxygen index instrument (JF-3 Jiangning Analysis Instrument Fac-

tory, China), according to ISO4589-1984. The dimensions of all samples are 160 mm \times 10.28 mm \times 4.26 mm.

FTIR analysis

The solid combustion substrate char was collected and analyzed using the standard KBr-pellet technique by a fourier transform infrared (FTIR) analyzer (NIOLET-560, Nicolet Co., USA) to determine the functional groups presented in the residue.

XPS analysis

The X-ray photoelectron spectroscopy (XPS) measurements were carried out using XSAM800 (KRATOS Co. Ltd, England) with Mg Ka exciting source in ultra-high vacuum condition. The sensitivity factor were 0.493, 0.914, 0.831, and 2.87 for C1s, O1s, N1s, and Br 3d, respectively.

SEM analysis

Scanning electron microscopy (SEM) analysis was performed using a JSM-5900LV (JEOL Co. Ltd., Japan). The samples were cryo-fractured in liquid nitrogen and then sputtered with gold and examined in the microscope. The accelerated voltage was 20 kV.

RESULTS AND DISCUSSION

Thermal properties

Typical TGA curves of PC and PC/HAP composite obtained at different heating rates under the air environment are shown in Figures 1 and 2. It was found that all the samples showed a two-step decomposition process and the mass loss temperature of PC/HAP was higher than that of PC with the increase of heating rate.

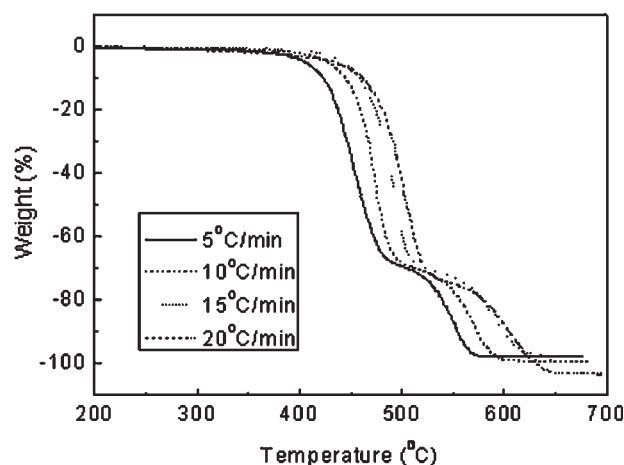


Figure 1 TGA curves of pure PC at different heating rate.

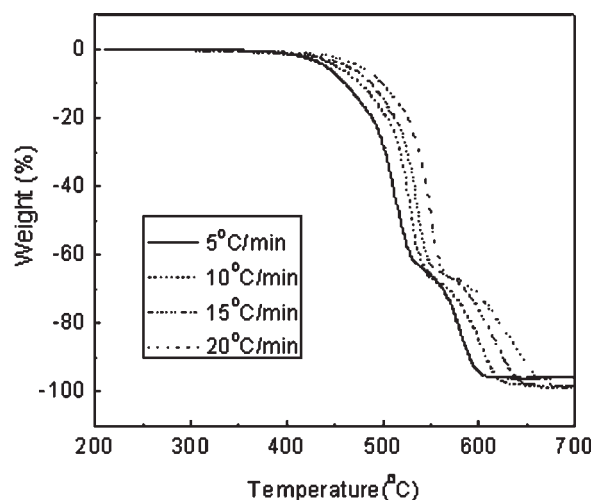


Figure 2 TGA curves of 0.5 wt % PC/HAP at different heating rate.

The degradation trend of PC/HAP is similar to that of neat PC under the air environment. It is visible that the PC/HAP nanocomposites start to degrade at a higher temperature than that of pure PC. The onset degradation temperature $T_{10 \text{ wt } \%}$ at which the mass loss is 10%, the 50% mass loss temperature ($T_{50 \text{ wt } \%}$), the first max. mass loss temperature ($T_{\text{max}1}$) and the second max. mass loss temperature ($T_{\text{max}2}$) of PC and PC/HAP were summarized in Tables I and II, respectively. It was found that with the addition of 0.5 wt % HAP to the matrix, the $T_{\text{max}1}$ increased almost 30°C and there was more residue left at 600°C than that of pure PC.

It is well known that the thermo-oxidation is an important factor to cause aging and degradation of PC in the presence of air. The results obtained indicate that the existence of HAP may hinder the thermo-oxidation of PC in the earlier degradation stage,⁹ and thus increases the thermal stability of the nanocomposites.

The activation energy (E_a) value for the degradation under air can be estimated using the Kissinger method²² without a precise knowledge of the reaction mechanism^{23–24}

$$\ln \frac{\beta}{T_{\text{max}}^2} = -\frac{E_a}{R} \left(\frac{1}{T_{\text{max}}} \right) + \ln \frac{nAR(1-a_m)^{n-1}}{E_a}$$

TABLE I
TG Data of PC Obtained in Air Atmosphere at Different Heating Rate

Heating rate (C/min)	$T_{10\%}$	$T_{50\%}$	$T_{\text{max}1}$	$T_{\text{max}2}$	Residue at 600 C
5	424	462	453	551	1.97
10	445	479	474	571	0.81
15	459	494	493	593	2.09
20	462	505	507	608	12.14

TABLE II
TG Data of PC/HAP 0.5 wt % Obtained in Air Atmosphere at Different Heating Rate

Heating rate (C/min)	$T_{10\%}$	$T_{50\%}$	$T_{\text{max}1}$	$T_{\text{max}2}$	Residue at 600 C
5	433	484	483	567	4.2
10	461	507	509	592	9.04
15	472	517	518	617	18.05
20	481	528	531	629	21.29

where A is the pre-exponential factor, E_a the apparent activation energy of the degradation reaction, R the universal gas constant, β the heating rate, n the reaction order, a_m the maximum conversion, T_{max} the absolute temperature at different heating rates under the maximum mass loss.

In this method the activation energy is calculated from the T_{max} , the temperature at which the maximum degradation occurs for different heating rates by assuming that a_m or weight loss percent at T_{max} is constant. Thus, the activation energy can be calculated from the slope of the linear correlation between $\ln(\beta/T_{\text{max}}^2)$ and $1/T_{\text{max}}$ plot (Fig. 3) for various heating rates as the following the relationship of $E_a = -R \times \text{slope}$. The activation energy of PC and PC/HAP (0.5 wt %) composite are shown in Table III. For the first stage degradation at 420–500°C is a thermo-oxidation process and the second stage is the char oxidation.²⁵ The E_{a1} of PC/HAP was 139 kJ/mol higher than that of pure PC (107 kJ/mol), which suggested that the nano-HAP interfere with the early stages of the thermal-oxidation reaction⁹ and increased the thermal stability of PC under air atmosphere. While the E_{a2} of PC/HAP was 126 kJ/

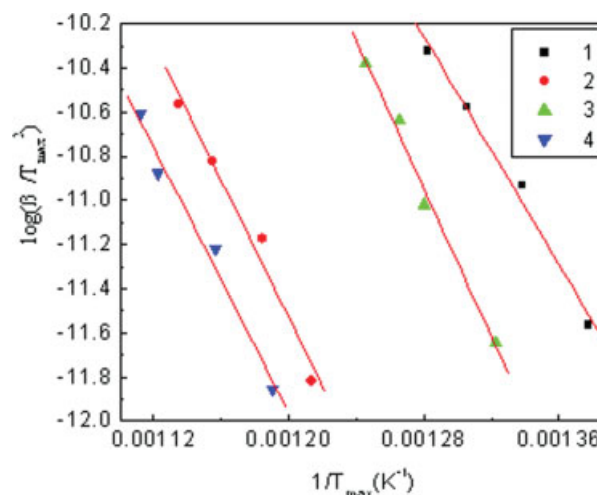


Figure 3 Kissinger plots of PC and PC/HAP at different the two stages: 1-PC $T_{\text{max}1}$; 2-PC $T_{\text{max}2}$; 3-PC/HAP $T_{\text{max}1}$; 4-PC/HAP $T_{\text{max}2}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Activation Energies of PC and PC/HAP 0.5% by Kissinger Method

Samples at different stages	Slop	E_a (KJ/mol)	Correlation coefficient r
PC at the first stage degradation	-12920.7	107	0.993
PC at the second stage degradation	-15575.9	129	0.987
PC/HAP at the first stage degradation	-16700.8	139	0.994
PC/HAP at the second stage degradation	-15096.9	126	0.991

mol, a little lower than that of PC (129 kJ/mol), suggesting that the carbon char oxidation was a little easily formed in the presence of HAP.

Flame retardancy

LOI test is widely used for determination of the relative flammability of polymeric materials. An improvement in LOI could give us an indication of potential flame retardancy of a polymer. When 0.5 wt % HAP was added to the PC matrix the LOI value increased from 26 of pure PC to 34. This

increase indicated that the nano-HAP could be an efficient flame retardant for PC.

Figure 4 shows the SEM images of the char after the LOI test. There is no obvious difference between the PC sample and PC/HAP sample suggesting that similar carbon char was formed during the LOI test. The residue of both PC and PC/HAP samples after the LOI test was measured by XPS and Figure 5 reveals that the residue of pure PC contains 91% carbon and 9% oxygen, while the residue of PC/HAP contains 89.2% carbon and 10.8% oxygen. This confirmed that similar carbon char was formed during the LOI test.

FTIR was used to determine the functional group of the samples before and after the LOI test. The FT-IR curves of pure PC, carbon char of pure PC and PC/HAP were showed in Figure 6, which exhibits quantitative changes of the PC nanocomposite char prior to and after the ignition during the LOI test. The similar curves of the carbon char suggest the same functional group were generated after the LOI test. Curve A revealed a very broad O—H absorption band between 3700 and 3200 cm^{-1} . The O—H absorption bands appeared to be due to moisture on the sensitized PC surface after the specimens were exposed to the atmosphere. The increase of O—H bands of curve B and curve C based on the virgin PC sample implied that alcohol or phenol groups were generated during the degradation. Similarly,

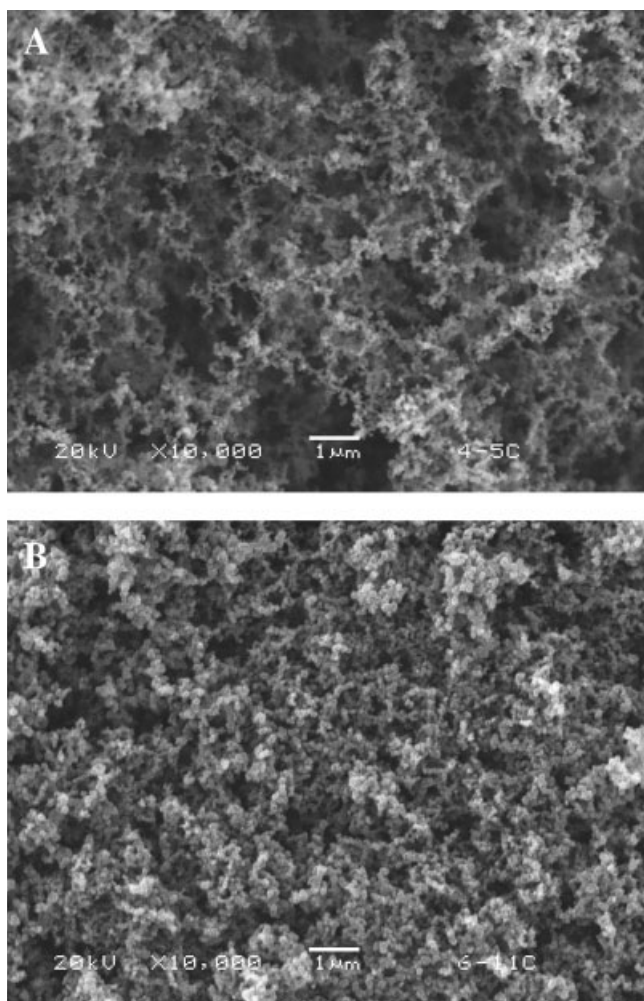


Figure 4 SEM images of LOI tested carbon char: A-PC B-0.5 wt % PC/HAP.

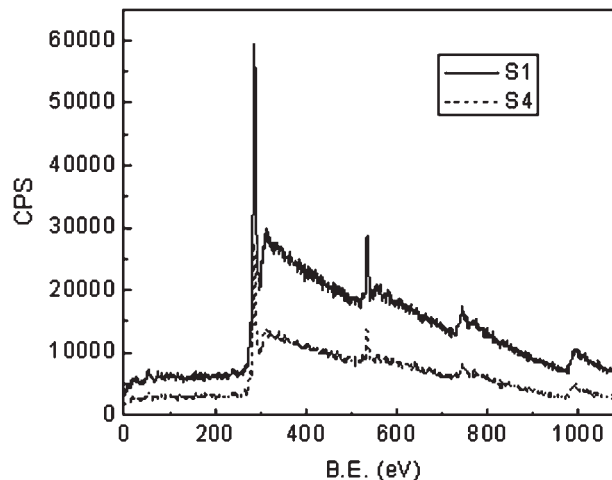


Figure 5 XPS of the LOI tested carbon char: S1-PC and S4-0.5 wt % PC/HAP.

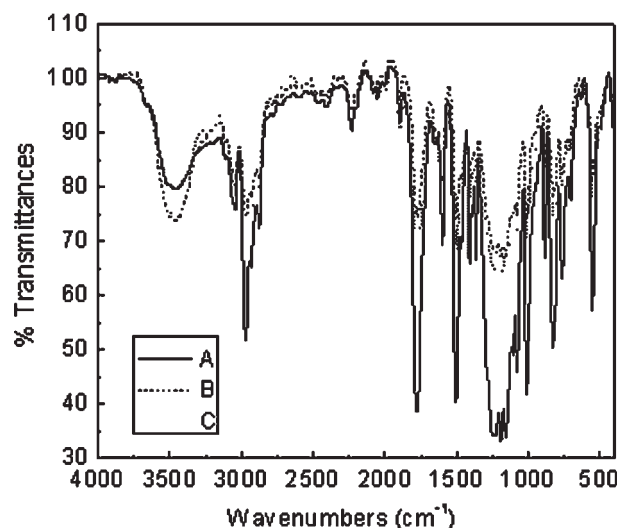


Figure 6 FTIR of Pure PC (A), carbon char of Pure PC (B) and PC/HAP composite.

the diminishment of the ester band also showed the scission of C—O. The decrease of the bands in $2800 \sim 3200 \text{ cm}^{-1}$ region, which is C—H stretching vibrations, shows a fraction of alkyl is exhausted after the LOI test. This result is also consistent with the changes of isopropylidene flexural vibrations peaks at 1365 cm^{-1} and 1409 cm^{-1} as shown in Figure 6. As is known, the absorption at 1365 cm^{-1} and 1409 cm^{-1} should be identical for single isopropylidene and HAP interfered with the reaction of methyl radicals and inhibited the first reactions.

CONCLUSIONS

The thermal properties and flame retardancy of PC and PC/HAP have been investigated. The improvement in thermal properties of PC/HAP composite is due to the existence of HAP. It may hinder the thermo-oxidation of PC in the earlier degradation, thus increases the thermal stability of the nanocomposites. HAP improved the flame retardancy of PC

and future work should focus on the flame retardancy mechanism.

We extend our gratitude to Mr. Li from the Center of Analysis and Test of Sichuan University for careful SEM analysis.

References

- Kim, S. W.; Jo, W. H.; Lee, M. S.; Ko, M. B.; Jho, J. Y. *Polym J* 2002, 34, 103.
- Mohanty, S.; Nayak, S. K. *Polym Compos* 2007, 28, 153.
- Sinha Ray, S.; Okamoto, M. *Prog Polym Sci* 2003, 28, 1539.
- Leszczynska, A.; Njuguna, J.; Pielichowski, K.; Banerjee, J. R. *Thermochim Acta* 2007, 453, 75.
- Chu, C. C.; Lin, J. J.; Shiu, C. R.; Kwan, C. C. *Polym J* 2005, 37, 239.
- Sato, H.; Ohtani, H.; Harada, R.; Tsuge, S.; Kato M.; Usuki, A. *Polym J* 2006, 38, 171.
- Liu, X.; Zou, Y.; Cao, G.; Luo, D. *Mater Lett* 2007, 61, 4216.
- Levchik, S. V.; Weil, E. D. *Polym Int* 2005, 54, 981.
- Marcano, J. S.; Mirodatos, C.; Wolf, E. E.; Martin, G. A. *Catal Today* 1992, 13, 227.
- Cui, W. C.; Guo, F.; Chen, J. F. *Polym Compos* 2007, 28, 551.
- Chen, X. L.; Yue, J.; Guo, S. Y. *J Appl Polym Sci* 2006, 102, 4943.
- Yoon, P. J.; Hunter, D. L.; Paul, D. R. *Polymer* 2003, 44, 5323.
- Maity, A.; Biswas, M. *Polym J* 2004, 36, 812.
- Zong, R.; Hu, Y.; Wang, S.; Song, L. *Polym Degrad Stab* 2004, 83, 423.
- Zhao, Y.; Schiraldi, D. A. *Polymer* 2005, 46, 11640.
- Carrion, F. J.; Sanes, J.; Bermudez, M. D. *Wear* 2007, 262, 1514.
- Fujisaki, K.; Tadano, S. *J Biomech* 2007, 40, 1832.
- Velayudhan, S.; Anilkumar, T. V.; Kumary, T. V.; Mohanan, P. V.; Fernandez, A. C.; Varma, H. K.; Ramesh, P. *Acta Biomater* 2005, 1, 201.
- Yang, H.; Zhang, L.; Xu, K. W. *Appl Surf Sci* 2007, 254, 425.
- Wan, C. Y.; Tian, G. H.; Cui, N.; Zhang, Y. X.; Zhang, Y. *J Appl Polym Sci* 2004, 92, 1521.
- Liu, S. M.; Ye, H.; Zhou, Y. S.; He, J. H.; Jiang, Z. J.; Zhao, J. Q.; Huang, X. B. *Polym Degrad Stab* 2006, 91, 1808.
- Kissinger, H. E. *Anal Chem* 1957, 29, 1702.
- Zhao, H.; Wang, Y. Z.; Wang, D. Y.; Wu, B.; Chen, D. Q.; Wang, X. L.; Yang, K. K. *Polym Degrad Stab* 2003, 80, 135.
- Li, J.; Tong, L. F.; Fang, Z. P.; Gu, A. J.; Xu, Z. B. *Polym Degrad Stab* 2006, 91, 2046.
- Zhou, W.; Yang, H. *Thermochim Acta* 2007, 452, 43.