

AMMONIUM SULFAMATE FLAME RETARDED POLYAMIDE 6: MORPHOLOGY AND THERMAL DEGRADATION*

Lei Xia, Hai-long Wang, Bao-qing Shentu** and Zhi-xue Weng

State Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering,
Zhejiang University, Hangzhou 310027, China

Abstract The effect of ammonium sulfamate (AS) content on the flame retardancy of polyamide 6 (PA6) was studied. It is found that the limiting oxygen index (LOI) of PA6 increases with the increase of AS content and the flame retardancy of PA6 is significantly improved. The morphology of the residues after combustion was examined by means of scanning electron microscopy (SEM). SEM results show that AS facilitates the formation of the intumescent char layer with honeycomb-like structure, which inhibits the transfer of heat and mass, and thus improves the flame retardancy of PA6. The thermal degradation of AS flame retarded PA6 was studied by thermogravimetric analysis (TGA). The Kissinger method was applied to estimate the activation energy (E_a) of the degradation. The activation energy of the thermal degradation of PA6 decreases by adding AS, indicating that AS can promote the degradation of PA6.

Keywords: Polyamide 6; Ammonium sulfamate; Flame retardancy; Morphology; Thermal degradation.

INTRODUCTION

PA6 is one of the important engineering plastics and has been widely used in various fields due to its excellent mechanical properties, oil resistance and abrasive resistance^[1]. However, neat PA6 with low limiting oxygen index (LOI) value can easily burn, which limits its application in electric and electronic industry. Therefore, how to improve the flame retardancy of PA6 becomes an important research topic^[2, 3].

Several types of flame retardants (FRs), such as halogen FR and phosphorus FR, have been used to improve the flame retardancy of PA6^[4]. However, the application of halogen FR is being greatly limited due to the possible production of dioxin, large amount of smoke and corrosive gases during the combustion of the halogen flame retarded materials. Phosphorus FR also has some drawbacks such as heavy color, toxicity and high exudation^[2–4].

Sulfur based flame retardants such as sulfamic acid and sulfamate were originally used in the flame retardancy of cotton, paper and wood^[5–7]. Ammonium sulfamate (AS) decomposes at elevated temperatures and releases some non-combustible gases, such as NH_3 and H_2O . Therefore, the combination of AS and polyol (carbon source) is expected to be a promising intumescent flame retardant of polyamide. Lewin *et al.*^[8, 9] found that the addition of AS and dipentaerythritol resulted in the improvement of flame retardancy of PA6 and the AS flame retarded PA6 (AS-FR-PA6) had excellent mechanical properties.

Generally speaking, the flame retardancy of polymeric materials is closely related to the morphology of the residue formed during combustion and the thermal degradation behavior^[3, 10, 11]. The morphology of char layer and thermal degradation are also very important for AS-FR-PA6. Lewin *et al.*^[8] mainly concentrated on the

* This work was financially supported by Science and Technology Department of Zhejiang Province (No. 2009C11127).

** Corresponding author: Bao-qing Shentu (申屠宝卿), E-mail: shentu@zju.edu.cn

Received September 7, 2009; Revised November 2, 2009; Accepted November 16, 2009

doi: 10.1007/s10118-010-9116-8

flame retardancy and chemical reaction of the polyamide/sulfamate/dipentaerythritol system. The present paper attempts to complement their previous work. The combination of AS and dipentaerythritol was used to improve the flame retardancy of PA6. Morphology of the residues obtained from neat PA6 and AS-FR-PA6 after combustion in a muffle furnace was examined by means of SEM. The thermal degradation behavior of AS-FR-PA6 was evaluated by TGA and the kinetic parameters of thermal degradation were also estimated.

EXPERIMENTAL

Materials

PA6 (M12403) was obtained from Guangdong Xinhui Meida Nylon Co. Analytically pure AS and industrial grade dipentaerythritol were supplied by Shanghai Hengxing Chemical Reagent Co. and Jiangsu Ruiyang Chemical Reagent Co., respectively.

Sample Preparation

AS-FR-PA6 with various AS (1.5 wt%, 3.0 wt% and 4.5 wt%, respectively) and dipentaerythritol (0.75 wt%, 1.5 wt% and 2.25 wt%, respectively) contents was prepared using the following procedure. PA6, AS and dipentaerythritol were first mixed by a high speed mixer at room temperature and then the mixture was fed into a twin-screw TE35 extruder (Keya Plastic Mechanical Factory of Jiangsu, China) at the temperature of 225–245°C with a screw speed of 600 r/min. The resulting pellets were dried for 4 h at 80°C and then injection moulded into test specimens using an Arburg Allrounder 221-55-250 injection moulding machine. The barrel had a flat temperature profile of 250°C and the mould temperature was kept at 40°C with an injection pressure of 8.5 MPa.

Characterization and Measurements

The limiting oxygen index (LOI) value was measured on an oxygen index instrument (Nanjing Jiangning Instrument Co., HC-2).

The TGA measurements were performed on a Perkin-Elmer Pyris 1 thermogravimetric analyzer to study the thermal degradation of PA6. The sample (2.0 ± 0.2 mg) was heated from room temperature to 700°C at various heating rates under air or nitrogen atmosphere at a flowing rate of $30 \text{ mL} \cdot \text{min}^{-1}$.

The fracture surface of the residue after combustion in a muffle furnace at 600°C for 2 min was coated with a conductive gold layer and the morphology was observed by a Hitachi S-5700 scanning electron microscope (SEM). The changes of PA6 and AS-FR-PA6 in morphology during thermo-oxidative degradation in a muffle furnace were also observed by a Canon Powershot A650 digital camera.

RESULTS AND DISCUSSION

The Influence of AS Content on the Flame Retardancy of PA6

The effect of AS content on the LOI of PA6 was studied, and the result is shown in Fig. 1. Various AS contents

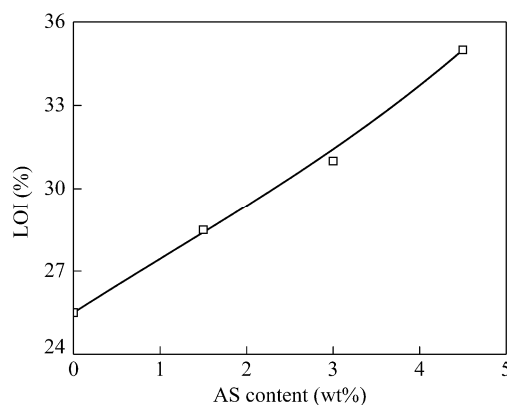


Fig. 1 Relationship between AS content and LOI of AS-FR-PA6

have been attempted and it is found that adding 4.5 wt% AS is sufficient for the required flame retardancy of PA6. The LOI of AS-FR-PA6 increases with the increase of AS content. When AS content is 4.5 wt%, the LOI value of PA6 reaches 35, which indicates that the flame retardancy of PA6 is significantly improved by adding AS.

The Morphology of the Residue after Combustion

The morphology of char layer has great impacts on the flame retardancy of polymeric materials^[3]. In addition, intumescence and char formation play important roles in flame retardancy of the intumescent flame retardant^[12]. Although the LOI value of AS-FR-PA6 increases with the increase of AS content, the mechanical properties decrease with AS content. When AS content is 3 wt%, the comprehensive properties of AS-FR-PA6 are the best. Therefore, we select to analyze the morphology of the sample with AS content of 3 wt%. Figure 2 shows the morphology of neat PA6 and AS-FR-PA6 with the same mass before and after combustion in a muffle furnace at 600°C for 2 min. It can be observed that in comparison with neat PA6 the volume of AS-FR-PA6 after combustion dramatically increases, indicating that the presence of AS is helpful for PA6 to produce the intumescent char. The formed intumescent char may inhibit the transfer of heat and mass, which results in the improvement of the flame retardancy of PA6.

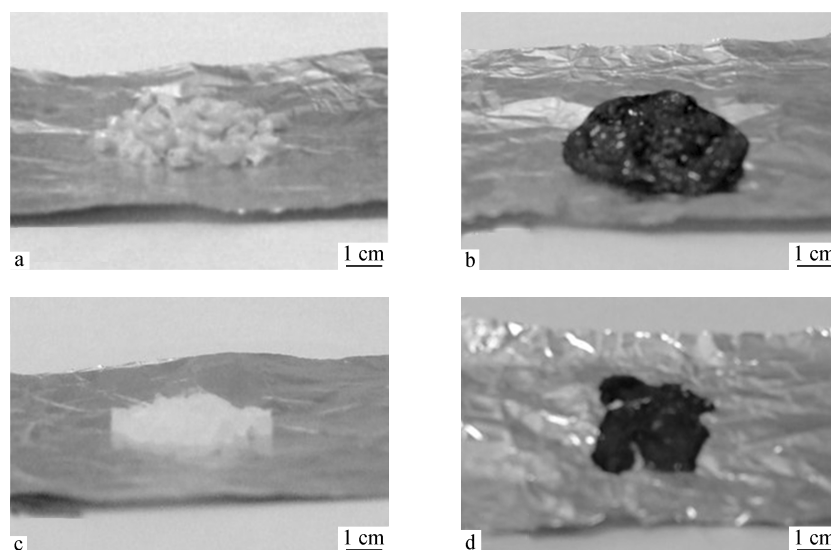


Fig. 2 Morphology of neat PA6 and AS-FR-PA6 (3.0 wt%) before and after combustion in a muffle furnace at 600°C for 2 min: (a) AS-FR-PA6 before combustion, (b) AS-FR-PA6 after combustion, (c) neat PA6 before combustion and (d) neat PA6 after combustion

The fracture surface of the residues for neat PA6 and AS-FR-PA6 after combustion was observed by a Hitachi S-5700 SEM, and the results are shown in Fig. 3. As presented in Figs. 3(a) and 3(d), the residues for both PA6 and AS-FR-PA6 are divided into two layers. The outer layer is the non-combustible char, whereas the inner layer is the incompletely decomposed resin.

An obviously honeycomb-like structure in the outer layer for AS-FR-PA6 after combustion can be seen from Figs. 3(a, b). It is the honeycomb-like structure that provides a good barrier to the transfer of heat and mass, which results in the improvement of the flame retardancy of PA6. The formation of the honeycomb-like structure may be attributed to NH_3 and other non-combustible gases released from AS. The dense structure of the inner layer as seen from Fig. 3(c) indicates that the honeycomb-like structure provides a considerable protection for the inner resin against decomposition during combustion. On the contrary, as shown in Fig. 3(f), the inner layer of the residue for PA6 after combustion is loose, indicating that the inner resin is easy to decompose. As presented in Fig. 3(e), the cracks can be observed in the outer layer of PA6, which may be

produced by gas molecules released from the decomposition of the inner resin. The presence of cracks is in favor of the transfer of mass and energy, resulting in the poor flame retardancy of PA6.

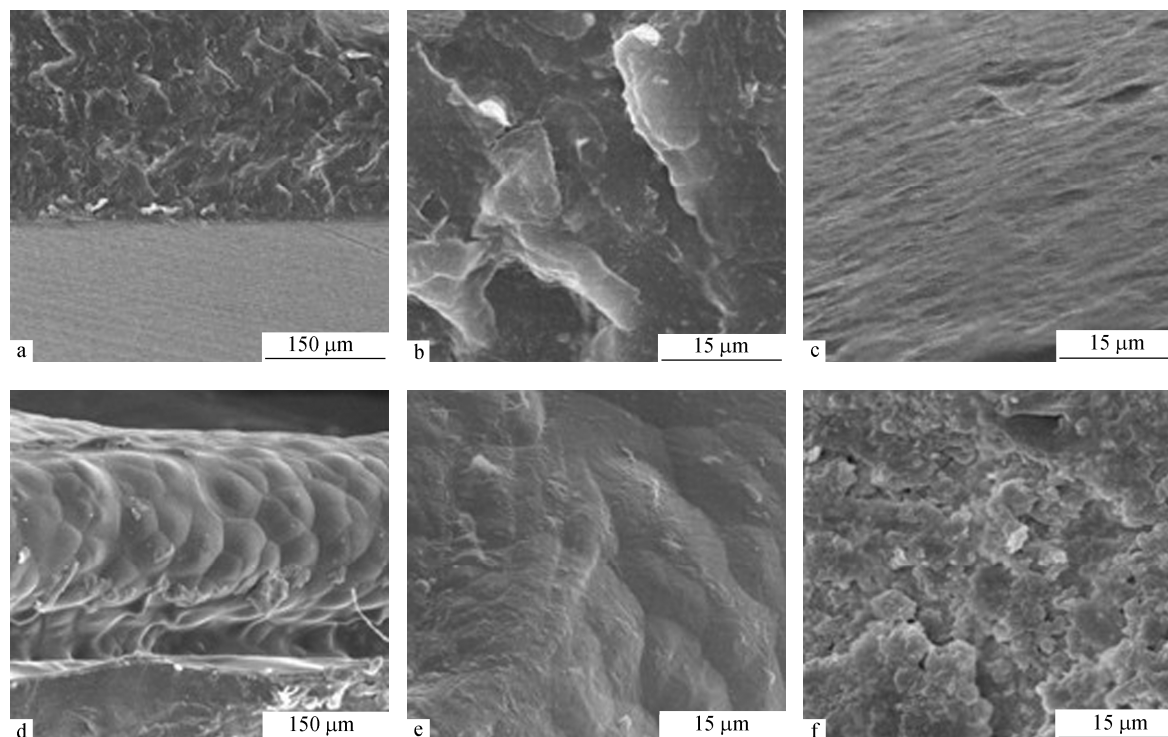


Fig. 3 Micrographs of the fracture surface of the residues for AS-FR-PA6 (a, b, c) and neat PA6 (d, e, f) after combustion in a muffle furnace at 600°C for 2 min: (a), (d) the whole section; (b), (e) the outer layer; (c), (f) the inner layer

The Change of Morphology for PA6 and AS-FR-PA6 at Various Temperatures

The change of morphology during thermo-oxidative degradation in a muffle furnace for neat PA6 and AS-FR-PA6 was investigated at a heating rate of 20 K·min⁻¹, and the results are shown in Fig. 4.

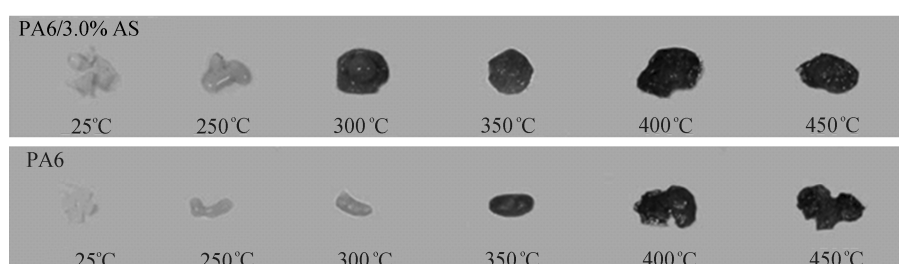


Fig. 4 Change of morphology for AS-FR-PA6 and neat PA6 at various temperatures

AS-FR-PA6 changes to black when the temperature reaches 300°C, indicating the occurrence of the notable thermo-oxidative degradation. Simultaneously, incombustible gases (NH₃ etc.) evolved from the decomposition of AS^[8] lead to the intumescence of the specimen. When the temperature rises to 400°C, an intumescent char layer is formed on the surface of AS-FR-PA6. Meanwhile neat PA6 still retains its original color until 350°C and no intumescent phenomenon was observed during the whole process. The results indicate that the presence of AS accelerates the degradation of PA6 and produces an intumescent char layer.

Thermal Degradation Behavior of AS-FR-PA6

The thermal degradation behavior is extremely important for flame retarded materials^[13]. The degradation behavior of neat PA6 and AS-FR-PA6 (3.0 wt%) was studied by a thermogravimetric analyzer under nitrogen atmosphere at a heating rate of 20 K·min⁻¹, and the results are shown in Fig. 5.

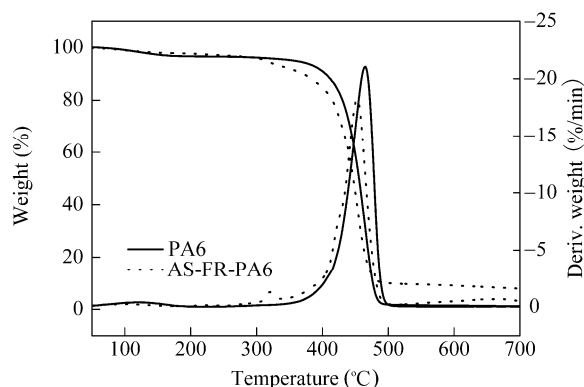


Fig. 5 TGA and DTG curves for neat PA6 and AS-FR-PA6 under N₂

The software of TGA was used to check the initial weight loss temperature (T_{onset}) for both AS-FR-PA6 and neat PA6. T_{onset} for AS-FR-PA6 is 423°C, which is 11°C lower than that for neat PA6 (434°C), indicating that AS facilitates the degradation of PA6. Furthermore, PA6 has completely decomposed at 500°C, whereas the weight percentage retained for AS-FR-PA6 is about 9.8 wt%, which demonstrates that AS is in favor of the formation of non-combustible char layer which results in the incomplete degradation of PA6.

One-step decomposition is observed for neat PA6 under nitrogen atmosphere, while two-step decomposition (as indicated by a small peak at 320°C) is found under nitrogen atmosphere for AS-FR-PA6 (Fig. 5). The small peak for AS-FR-PA6 is attributed to the following reactions between AS and dipentaerythritol^[8].

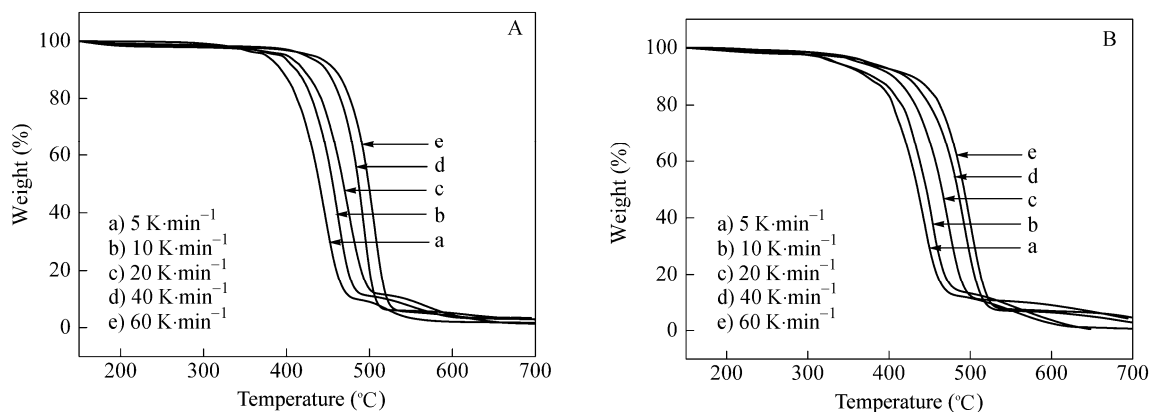
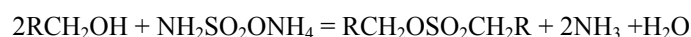
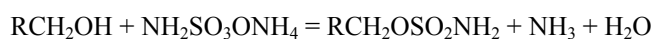


Fig. 6 TGA curves for neat PA6 (A) and AS-FR-PA6 (B) at various heating rates under air

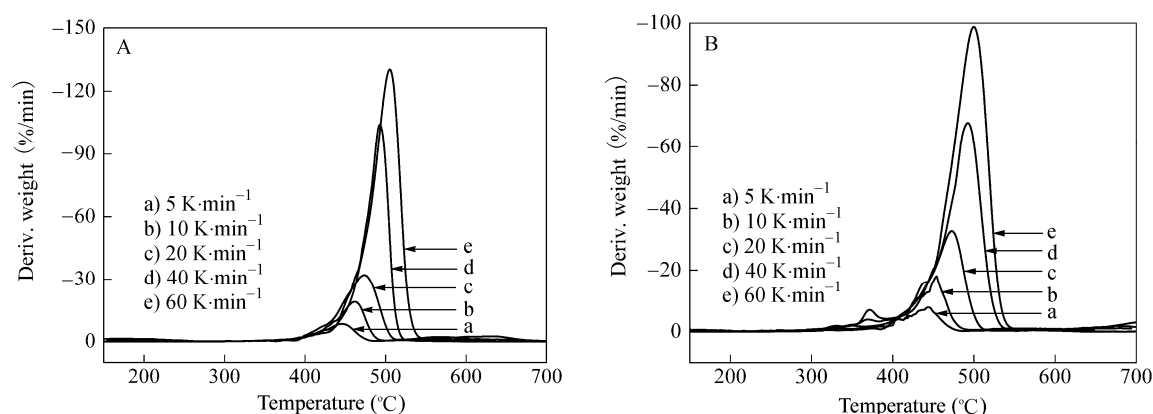


Fig. 7 DTG curves for neat PA6 (A) and AS-FR-PA6 (B) at various heating rates under air

TGA and DTG curves for PA6 and AS-FR-PA6 at heating rates of 5, 10, 20, 40, 60 K·min⁻¹ under air atmosphere are shown in Figs. 6 and 7. The degradation trends for both AS-FR-PA6 and neat PA6 under air atmosphere are similar to those under nitrogen atmosphere. For a closer analysis, the detailed characteristic temperature of degradation, for example, 5% and 10% weight loss temperatures ($T_{5\%}$ and $T_{10\%}$) and maximum decomposition temperature ($T_{\max}$) for PA6 and AS-FR-PA6 at various heating rates, are summarized in Table 1. The characteristic temperature ($T_{5\%}$, $T_{10\%}$, and $T_{\max}$) increases gradually with the increase of the heating rate. At the same heating rate, the characteristic temperature of AS-FR-PA6 is lower than that of PA6, which also confirms that AS facilitates the thermal degradation of PA6.

Table 1. The characteristic temperature of degradation for neat PA6 and AS-FR-PA6 at various heating rates under air

β (K·min ⁻¹)	PA6			AS-FR-PA6		
	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{\max}$ (°C)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{\max}$ (°C)
5	347	387	446	322	366	443
10	371	408	461	318	368	454
20	390	412	475	346	396	472
40	426	449	493	373	419	492
60	428	457	503	374	426	501

The Thermal Degradation Kinetics of AS-FR-PA6

The kinetic parameters of thermal degradation are beneficial in characterizing thermal stability of polymers and thus clarifying the mechanism of flame retardants^[11]. The Kissinger method is the most widely used method to estimate the kinetic parameters of thermal degradation.

The activation energy (E_a) for the thermal degradation under air is calculated according to the Kissinger method (Eq. (1))^[14, 15].

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \left\{ \ln \frac{AR}{E_a} + \ln[n(1 - \alpha_{\max})^{n-1}] \right\} - \frac{E_a}{RT_{\max}} \quad (1)$$

Where β is the heating rate, $T_{\max}$ is the temperature at which the maximum degradation occurs at various heating rates, A is the pre-exponential factor, R is the universal gas constant (8.314 J/(mol·K)), E_a is the apparent activation energy of the degradation reaction (kJ·mol⁻¹), n is the order of the degradation reaction, $\alpha_{\max}$ is the conversion degree at $T_{\max}$.

In this method the activation energy can be calculated from the linear dependence of $\ln(\beta/T_{\max}^2)$ versus $1/T_{\max}$ plot (Fig. 8).

The correlation coefficient and the calculated E_a values are listed in Table 2. Based on the high correlation

coefficient (R), the activation energy is well described by the Kissinger method. The E_a value of AS-FR-PA6 is lower than that of neat PA6, indicating that AS facilitates the thermal degradation of PA6 and accelerates char formation.

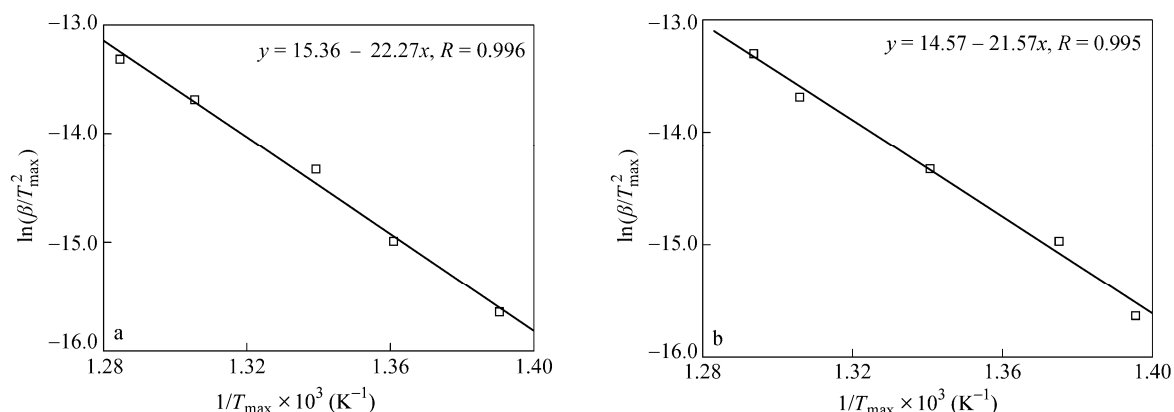


Fig. 8 Determination of activation energy based on Kissinger method for neat PA6 (a) and AS-FR-PA6 (b)

Table 2. Thermal degradation kinetics results for neat PA6 and AS-FR-PA6 by the Kissinger method

Samples	Correlation coefficient, R	Activation energy, E_a ($\text{kJ}\cdot\text{mol}^{-1}$)
PA6	0.996	185
AS-FR-PA6	0.995	179

CONCLUSIONS

The LOI value of PA6 significantly increases with the increase of AS content, representing the improvement of flame retardancy of PA6. The SEM results show that AS facilitates the formation of the intumescent char layer with honeycomb-like structure, which prevents the transfer of heat and mass, and thus improves the flame retardancy of PA6. TGA and DTG results show that at the same heating rate the characteristic temperatures of AS-FR-PA6 are lower than those of PA6, which also confirms that AS facilitates the thermal degradation of PA6. The E_a value of AS-FR-PA6 is lower than that of neat PA6, indicating that AS facilitates the thermal degradation of PA6 and accelerates the formation of char layer.

REFERENCES

- Wu, Z.Y., Xu, W., Xia, J.K., Liu, Y.C., Wu, Q.X. and Xu, W.J., Chinese Chem. Lett., 2008, 19(2): 241
- Chen, Y.H., Wang, Q., Yan, W. and Tang, H.M., Polym. Degrad. Stab., 2006, 91(11): 2632
- Fei, G.X., Liu, Y. and Wang, Q., Polym. Degrad. Stab., 2008, 93(7): 1351
- Markarian, J., Plast. Addit. Compd., 2005, 7(2): 22
- Mostashari, S.M. and Mostashari, S.Z., J. Therm. Anal. Calorim., 2008, 91(2): 437
- Liodakis, S., Vorisis, D. and Agiovlasis, I.P., Therm. Chim. Acta, 2006, 444(2): 157
- Dobele, G., Urbanovich, I., Zhurins, A., Kampars, V. and Meier, D., J. Anal. Appl. Pyrolysis, 2007, 79(1-2): 47
- Lewin, M., Brozek, J. and Martens, M.M., Polym. Adv. Technol., 2002, 13(12): 1091
- Lewin, M., Zhang, J., Pearce, E. and Gilman, J., Polym. Adv. Technol., 2007, 18(9): 737
- Paik, P. and Kar, K.K., Polym. Degrad. Stab., 2008, 93(1): 24
- Hu, Z.R. and Shi, Q.Z., "Thermal analysis kinetics"(in Chinese), Science Press, Beijing, 2007, p.79
- Jimenez, M., Duquesne, S. and Bourbigot, S., Ind. Eng. Chem. Res., 2006, 45(13): 4500
- Zhao, C.X., Liu, Y., Wang, D.Y., Wang, D.L. and Wang, Y.Z., Polym. Degrad. Stab., 2008, 93(7): 1323
- Kissinger, H.E., Anal. Chem., 1957, 29(11): 1702
- Chen, Y.H. and Wang, Q., Polym. Degrad. Stab., 2007, 92(2): 280