Thermal Degradation Behaviors of Polypropylene with Novel Silicon-Containing Intumescent Flame Retardant

Qiang Li, Hanfang Zhong, Ping Wei, Pingkai Jiang

School of Chemistry and Chemical Engineering, Shanghai Jiaotong University, Shanghai 200240, People's Republic of China

Received Received 1 March 2005; accepted accepted 23 March 2005
DOI 10.1002/app.21944

ABSTRACT: The *N*-[3-(dimethoxy-methyl-silanyl)-propyl]-*N'*- (9-methyl-3,9-dioxo-2,4,8,10-tetraoxa-3,9-diphospha-spiro-[5.5]undec-3-yl)-ethane-1,2-diamine/dimethoxy dimethyl silane copolymer (PSiN II), which simultaneously contains silicon, phosphorus, and nitrogen, is synthesized and incorporated into polypropylene (PP). The flame retardancy is evaluated by the limiting oxygen index value, which is enhanced to 29.5 from 17.4 with 20% total loading of PSiN II. The thermal degradation behavior of PP/PSiN II is investigated by thermogravimetric analysis under N_2 and air. The PP/PSiN II sample degrades at 400°C for different amounts of time, and the process of degradation is studied by Fourier transform IR. The morphology of the char formed at 400°C for 10 min is investigated by scanning electron microscopy. The swollen inner structure, close, and smooth outer surface provide a much better barrier for the transfer of heat and mass during fire and good flame retardancy. The thermal stability of PP is improved by incorporation of PSiN II. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2487–2492, 2005

Key words: thermal degradation; flame retardancy; thermogravimetric analysis; scanning electron microscopy; Fourier transform IR

INTRODUCTION

Past studies have incorporated intumescent flame retardant (IFR) systems into polymers to provide fire protection.[1–7] IFRs have the advantages of low smoke, low toxicity, low corrosion, no molten dropping, and being halogen free.[3–7] Generally, IFRs contain three main ingredients: an acid source, a carbon source, and a gas source. They offer polymer flame retardancy through modifying the decomposition mode. Phosphorus-containing compounds are often used as an acid source in IFRs, and they degrade to form char layers during a fire. Gas sources in IFR systems, which are often nitrogen-containing compounds, produce incombustible gases when they degrade. The heat gases swell the formed char layer, and the swollen char isolates the transfer of mass and heat during a fire. It can protect unburned materials from degradation.[8–14]

In IFRs, not only the amount of char that is formed but also the thermal stability of the char plays an important role in flame retardancy. However, the char that is formed by phosphorus-containing compounds loses weight at a high temperature region in air (>700°C).[15] This indicates that the stability of the char is reduced. When silicon is incorporated into the polymers, the weight loss of the char at above 500°C is retarded and its stability of char at high temperature is improved.[15–18] IFRs and silicon-containing compounds exhibit a synergistic effect on the flame retardancy of polymers when they are used together.[3,7,19,20] In contrast, the three ingredients often come from different compounds in IFRs, and the silicon-containing compounds also come from other compounds. There are four kinds of additives in polymers incorporated into polypropylene (PP) through blending. In our work, a silicon-containing IFR (PSiN II), which contains an acid source, a gas source, a char source, and silicon-containing groups simultaneously, has been synthesized. In this article, PSiN II is incorporated into PP and the thermal degradation behaviors of PSiN II and PP/PSiN II are studied.

EXPERIMENTAL

Materials

Phosphorus oxychloride ($POCl_3$) was purchased from Tingxin Chemical Industry Company of China (Shanghai). Dimethyl methanephosphonate (DMMP) was procured from Tian Cheng Chemical Corp. Tetrahydrofuran (THF), ethyl acetate (EtAc), pentaerythritol (PER), and sodium methylate were purchased from Shanghai Chemical Reagent Co. Ltd. α,ω-Dihydroxide poly(dimethylsiloxane) (PDMS) was received from Shanghai Resin Industries Corp., and *N*-β-(aminoethyl)-γ-aminopropyl methyl dimethoxysilane (HD-103) was obtained from Shanghai Yehao Chemical Industries Corp. The PP

Correspondence to: P. Jiang (pkjiang@sjtu.edu.cn).

Journal of Applied Polymer Science, Vol. 98, 2487–2492 (2005)

used here was Novatel H57541 supplied by Japan Polychem Corp. with a melt index (GB 368283) of 2 g/10 min and a density of 0.918 g/cm^3.

Synthesis of PSiN II flame retardant

We added 13.6 g (0.1 mol) of PER, 13.6 g (0.11 mol) of DMMP, and 0.05 (0.01 mol) of sodium methylate into a 150-mL three-necked round-bottomed flask with a stirrer. The temperature in the flask was heated to 180–200°C and kept constant for 2 h. The obtained products were separated though chromatographic separation. One of the products was 5,5-dihydroxymethyl-2-methyl-2-oxo-[1,3,2]dioxaphosphinan, whichwas crystallized in EtAc to obtain a white crystal. Mass spectrometry and Fourier transform IR (FTIR) instrumental analysis revealed the following: mp 117–119°C. Mass spectrometry: M + 1 = 197. FTIR (KBr, cm^{-1}): 3437–3400 (C—OH), 2980–2875 (—CH_2—, —CH_3), 1324–1240 (P=O), 1046–839 (P—O—C). ^{1}H-NMR (DMSO-d_6, δ): 4.9–4.7 (2H, HO—C), 4.1–4.0 (4H, —CH_2—O—P), 3.5–3.3 (4H, —CH_2—O—C), 1.5–1.4 (3H, CH_3—P).

5,5-Dihydroxymethyl-2-methyl-2-oxo-[1,3,2]dioxaphosphinan (19.6 g, 0.1 mol) and 1000 mL of THF were added into a three-necked flask with a stirrer. The THF was heated to 65°C to dissolve the white crystal. Then, 15.4 g (0.1 mol) of $POCl_3$ was slowly added dropwise while the temperature of the solution was kept at about 65°C during the process. After $POCl_3$ had been added, the temperature was changed to 20–40°C and kept for 2 h. Then, the THF was removed to obtain a white solid, which was 3-chloro-9-methyl-2,4,8,10-tetraoxa-3,9-diphospha-spiro[5.5]undecane (DPCl). Instrumental analysis was performed. FTIR (KBr, cm^{-1}): 2980–2875 (—CH_2—, —CH_3), 1300–1320, 1240 (P=O), 1046–1100, 839 (P—O—C).

PDMS (74 g) and HD-103 (206 g) were mixed with KOH as the catalyst in a three-necked round-bottomed flask with a stirrer under nitrogen, and the temperature of the mixture was controlled between 80 and 100°C. Two hours later, 1–5 mL of water was added into the flask. After 1 h, the by-products were removed under vacuum for 6 h at around 80°C. The product obtained was termed Si—N, and it was characterized by FTIR. FTIR (KBr, cm^{-1}): 3200–3340 (—NH_2, —NH—), 2884–2963 (—CH_2—, —CH_3), 1260 (Si—O), 1000–1100 (Si—O—Si), 800 (Si—C).

DPCl was dissolved in THF. The solution was put into the three-necked round-bottomed flask with a stirrer at 18–25°C. The Si—N was also dissolved in THF and the solution was added slowly into the flask with the nitrogen stream to bring out HCl. When the solution had been added, the temperature was kept at 18–25°C for 2 h. Then, the temperature was raised to 120°C and the solvent was removed under vacuum for several hours. The flame retardant was obtained (PSiN II), which contains phosphorus, nitrogen, and silicon. The structure of PSiN II is presented in Figure 1.

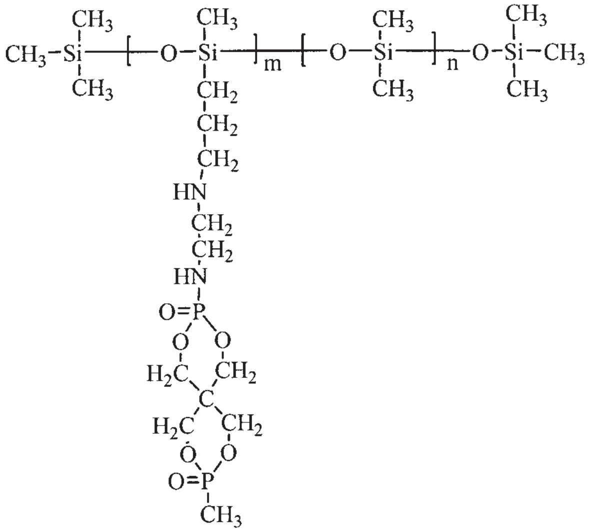

Figure 1 The chemical structure of PSiN II.

Preparation of PP/PSiN II blends

PP (40 g) and PSiN II (10 g) were mixed in a Haake Rheocord 90 internal mixer at 180°C for 8 min.

Characterization

FTIR spectroscopy was performed with a Perkin–Elmer Paragon 1000. The ^{1}H-NMR analysis was conducted with a Mercuryplus 400. Mass spectrometry was performed with an inductively coupled plasma mass spectrometer (Agilent 7500A).

Thermogravimetric analysis (TGA) was conducted with a Netzsch TG209 thermal analyzer at a heating rate of 20°C/min from room temperature to 800°C under an air atmosphere. The thermal degradation experiments were the following: the weighted samples were put in porcelain cups and placed in the muffle furnace (under air) at the required temperatures. The weight losses were monitored manually as a function of the heating time.[21] The morphologies of the samples being degraded at 400°C for 10 min were examined by scanning electron microscopy (SEM, Hitachi S520). The limiting oxygen index (LOI) values were used to evaluate the flammability of PP/PSiN II samples, and they measured on a Stanton–Redcroft LOI FTA II type instrument following ASTM D 2836.

RESULTS AND DISCUSSION

Thermal behaviors characterized by TGA

TGA and derivative thermogravimetry (DTG) of PP, PSiN II, and PP/PSiN II under nitrogen and air are

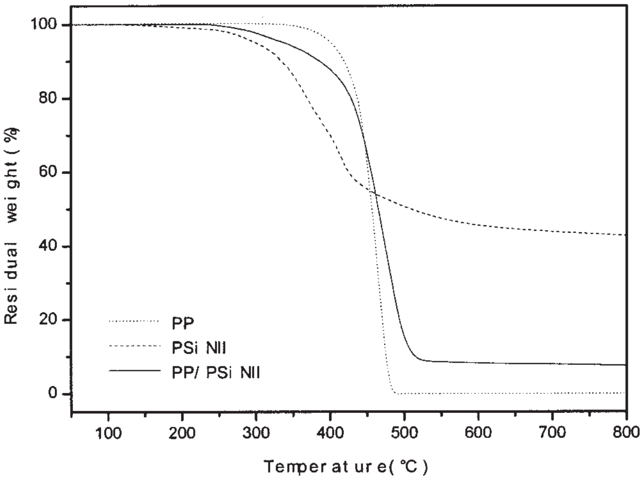

Figure 2 TGA curves of PP, PSiN II, and PP/PSiN II in N_2.

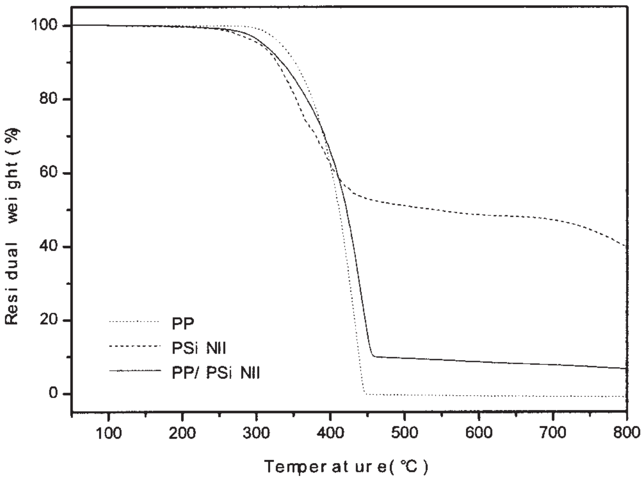

Figure 4 TGA curves of PP, PSiN II, and PP/PSiN II in air.

illustrated in Figures 2–5. The temperature at which 5 wt % weight loss occurs is defined as the initial decomposition temperature (IDT).[22] In N_2, the IDT of PSiN II is 320°C.

There are two rapid weight loss peaks ascertained by DTG of PSiN II ($T1_{max}$ = 366°C, $T2_{max}$ = 424°C), as shown in Figure 3. When PSiN II is tested in air by TGA, the IDT is reduced to 302°C and DTG shows a single peak (T_{max} = 363°C, Fig. 5). There is another small weight loss for PSiN II when the temperature is over 700°C in air in Figure 4. It indicates that the char formed by PSiN II degrades at high temperature in air. High char yields (42.0 and 40.9%) are obtained for PSiN II at 800°C in both N_2 and air. The degradation of PP is quite simple in N_2 and air. The IDT and T_{max} are 401 and 464°C in N_2 and 328 and 428°C in air, respectively. There is a single peak on the DTG curve in N_2 or air. When PSiN II is incorporated into PP, the thermal degradation behavior is changed. The IDT of PP/PSiN II reduces to 335°C in N_2; rapid weight loss occurs at 474°C, which is higher than that of PP; and about 8% char yield is obtained at 800°C. The decrease of the IDT, enhancement of the rapid weight loss temperature, and residue char at 800°C play an important role in improving the thermal stability and flame retardancy of PP/PSiN II materials. The phosphorus-containing groups in PSiN II first decompose to hydrate the char source containing groups in a fire or heating at high temperature. Then, they form a continuous and protective carbon layer. The gases produced by the nitrogen-containing groups form the carbon layer. The barrier properties of the expanded char are most effective in resisting the transport of heat and mass.[23] The char retards the production of flammable gas at high temperature. The silicon-containing groups decompose during heating and then SiO_2 is formed. This kind of char layer has better high temperature stability with silicon dioxide.[13,14] It re-

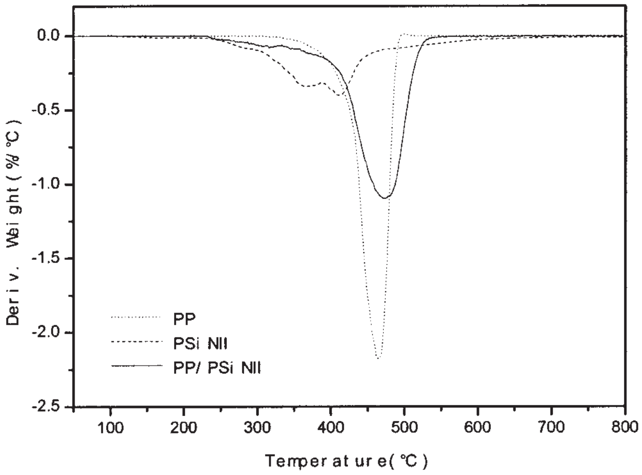

Figure 3 DTG curves of PP, PSiN II, and PP/PSiN II in N_2.

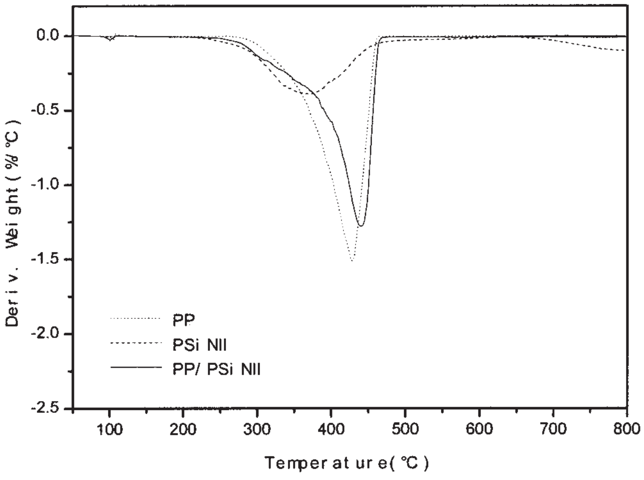

Figure 5 DTG curves of PP, PSiN II, and PP/PSiN II in air.

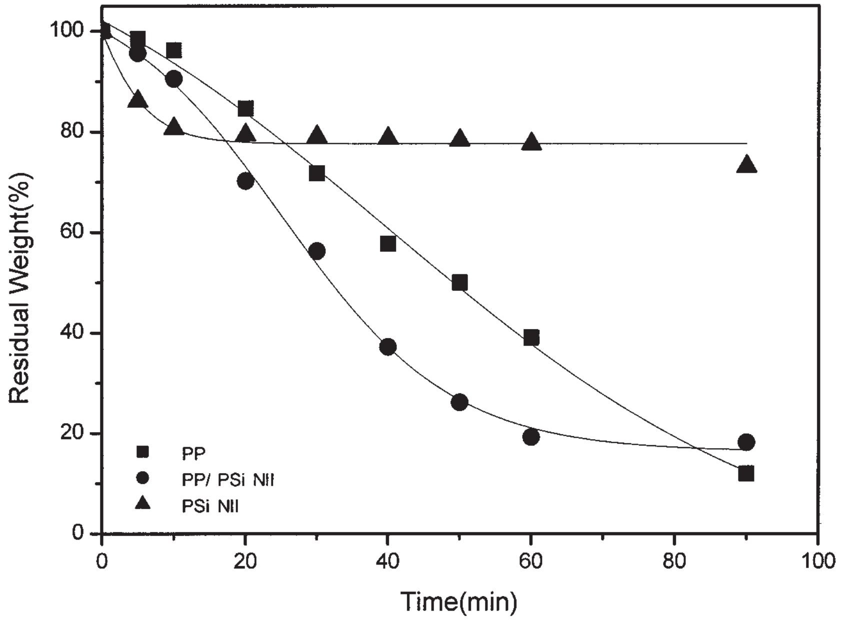

Figure 6 The char yield of PP/PSiN II heated at 400°C for different amounts of time.

sults in the slowing of the degradation of the PP matrix. In air, the degradation behavior of PP/PSiN II is similar to that in N_2. There is either no or less weight loss for PP/PSiN II when the temperature is above 500°C in N_2 or air as shown in Figures 2 and 4, and 8% char yield is obtained as shown in Figure 4 at 800°C. The char yields being obtained in air are near those obtained in nitrogen at 800°C. It indicates that the thermal stabilities of PP are improved by introducing PSiN II.

Degradation of PP/PSiN II at 400°C

Figure 6 presents the char yield of PP/PSiN II heated at 400°C for 0–90 min. The residue weight decreases with increasing time.

The residues of PSiN II hardly decrease after being heated for 10 min further, and the residue is about 79% afterward. The weight loss of PP increases with the increasing heating time. When PSiN II is incorporated into PP, the degradation is similar to that of pure PP before 50 min. Moreover, the char yield of PP/PSiN II is smaller than that of PP after being heated for the same time at 400°C because PSiN II degrades more easily than PP as investigated by TGA in air. The PSiN II degrades to form the silicon- and phosphorus-containing intumescent protective char layer. The char can retard the weight loss to continue at high temperature. This results in the residues of PP/PSiN II being larger than that of PP.

FTIR characterization of PP/PSiN II degraded at 400°C

Figure 7 presents the FTIR spectra obtained from the PP/PSiN II pyrolyzed at 400°C for different degradation times in air. The intensities of the peaks at 2840–2953 cm^{-1} are assigned to the CH_2 or CH_3 asymmetric and symmetric vibrations, and 1374 and 1455 cm^{-1} are assigned to the CH_2 or CH_3 deformation vibration of aliphatic groups that decrease with increasing the thermooxidative degradation time.[3,24,25] These peaks disappear after heating for 30 min at 400°C. This indicates that the C—H and C—C chains of PP are being broken, and most of them have decomposed 30 min later. The peaks at 1714 cm^{-1} are assigned to the carbonyl (C═O) groups formed from thermooxidative degradation products of the polymer.[3,24] The absorption peak at 1627 cm^{-1} appears after 4 min, which indicates the formation of carbon–carbon double bonds resulting from the cleavage of the main chains after thermal oxidation.[24,26] The broad absorption bands at 800–1400 cm^{-1} are assigned to the P—O groups. The peaks as 1090 and 995 cm^{-1} are attributable to the asymmetric and symmetric vibrations of P—O in P—O—P groups.[3,25]

Morphology of chars from PP/PSiN II

The SEM micrographs in Figures 8 and 9 show the morphological structures of the char heated at 400°C for 10 min. Figure 8 contains a micrograph of the outer surface of the char layers. Its surface is smooth. Its

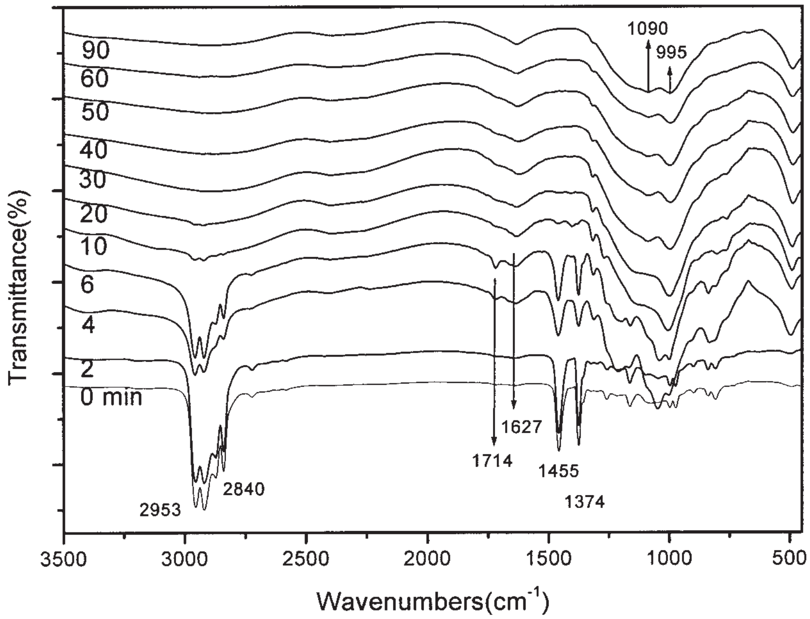

Figure 7 FTIR of PP/PSiN II for various heating times at 400°C.

inner surface is shown in Figure 9. Cells are formed by the gases in the process of heating. The char layer, which is a swollen inner structure as well as a close and smooth outer surface, provides a much better barrier to the transfer of heat and mass during a fire. Thus, the thermal behavior is improved by both the outer surface and inner structure of the char structure.

Flame retardant property of PP/PSiN II

The flame retardant properties of materials are often evaluated by the LOI values. The LOI value of PP/PSiN II is enhanced to 29.5 from 17.4 with 20 wt % PSiN II. When the PP/PSiN II is ignited or heated, the swollen char on the polymer surface is formed according to the SEM in Figures 8 and 9. The inner surface of the char is alveolate (Fig. 9), the outer surface is close (Fig. 8), and the char is thermally stable according to its thermal parameters in air. The kind of char structure slows down the transfer of gases and mass when the samples are burning. This results in improved fire performance for PP/PSiN II.

CONCLUSION

The thermal behavior of PP was improved by introducing a silicon-containing IFR (PSiN II), which was studied by TGA and degradation at 400°C. The char yield at 400°C was similar to that shown by TGA. The FTIR on the structure of the char formed at 400°C for different amounts of time showed that there were P—O products in the charred layer. This demon-

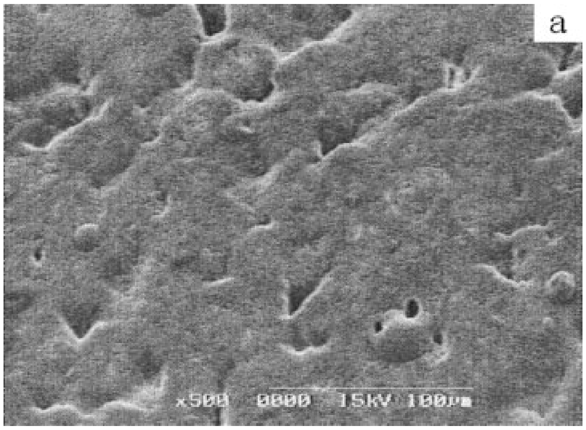

Figure 8 An SEM micrograph of the outer surface of the intumescent char.

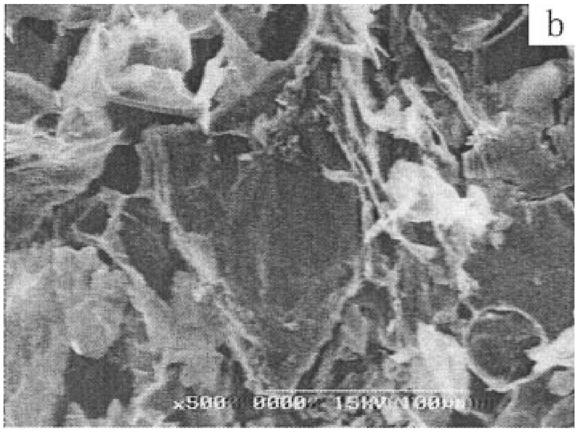

Figure 9 An SEM micrograph of the inner surface of the intumescent char.

strated that the phosphorus groups function in the process of forming char. The morphological structure of the char with PSiN II afforded PP with swollen cells in the inner and smooth outer surfaces, which improved the flame retardancy of PP. The flame retardant properties of PP were enhanced to 29.5 from 17.4 with 20 wt % PSiN II.

References

1. Zhang, S.; Horrocks, A. R. Prog Polym Sci 2003, 28, 1517.
2. Lu, S. Y.; Hamerton, I. Prog Polym Sci 2002, 27, 1661.
3. Wu, Q.; Qu, B. Polym Degrad Stabil 2001, 74, 255.
4. Ma, Z. L.; Zhao, M.; Hu, H. F.; Ding, H. T.; Zhang, J. J Appl Polym Sci 2002, 83, 3128.
5. Zhu, W.; Weil, E. D.; Mukhopadhyay, S. J Appl Polym Sci 1996, 62, 2267.
6. Horacek, H.; Pieh, S. Polym Int 2000, 49, 1106.
7. Chen, Y.; Liu, Y.; Wang, Q.; Yin, H.; Aelmans, N.; Kierkels, R. Polym Degrad Stabil 2003, 81, 215.
8. Chiu, S. H.; Wang, W. K. Polymer 1988, 39, 1951.
9. Camino, G.; Costa, L.; Tenza, S.; Marchetti, E. Polym Degrad Stabil 1984, 7, 221.
10. Banks, M.; Ebdon, J. R.; Johnson, M. Polymer 1994, 35, 3470.
11. Annkutty, K. S.; Kishore, K. Polymer 1988, 29, 756.
12. Banks, M.; Ebdon, J. R.; Johnson, M. Polymer 1993, 34, 4547.
13. Liu, Y. L.; Hsiue, G. H.; Chiu, Y. S.; Jeng, R. J.; Perng, L. H. J Appl Polym Sci 1996, 61, 613.
14. Liu, Y. L.; Hsiue, G. H.; Lan, C. W.; Chiu, Y. S. Polym Degrad Stabil 1997, 56, 291.
15. Hsiue, G. H.; Liu, Y. L.; Tsiao, J. J Appl Polym Sci 2000, 78, 1.
16. Ravadits, I.; Tóth, A.; Marosi, G.; Mráton, A.; Szép, A. Polym Degrad Stabil 2001, 74, 419.
17. Ebdon, J. R.; Hunt, B. J.; Jones, M. S.; Thorpe, F. G. Polym Degrad Stabil 1996, 54, 395.
18. Masatoshi, L.; Shin, S. Polym Adv Technol 1998, 9, 593.
19. Bourbigot, S.; Le Bras, M.; Duquesne, S.; Rochery, M. Macromol Mater Eng 2004, 289, 499.
20. Anna, P.; Marosi, G.; Csantos, I.; Le Bras, M.; Delobel, R. Polym Degrad Stabil 2002, 77, 243.
21. Jahromi, S.; Gabriëlse, W.; Braam, A. Polymer 2003, 44, 25.
22. Wu, C. S.; Liu, Y. L.; Chiu, Y. C.; Chiu, Y. S. Polym Degrad Stabil 2002, 78, 41.
23. Granzow, A.; Savides, C. J Appl Polym Sci 1980, 25, 2195.
24. Xie, R. C.; Qu, B. J. Polym Degrad Stabil 2001, 71, 395.
25. Bugajny, M.; Borbigot, S. Polym Int 1999, 48, 264.
26. Pagès, P.; Carrasco, F.; Saurina, J.; Colom, X. J Appl Polym Sci 1996, 60, 153.