Flame-Retardant Epoxy Resin from a Caged Bicyclic Phosphate Quadridentate Silicon Complex

Li-Li Zhang, An-Hua Liu, Xing-Rong Zeng

College of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China

ABSTRACT: The synergistic effects of phosphorus–silicon in a caged bicyclic phosphate quadridentate silicon complex (CPQS) on the flame retardancy of epoxy resin (EP) were studied with the limiting oxygen index, the UL-94 test, thermogravimetric analysis, real time Fourier transform infrared spectroscopy, X-ray powder diffraction, and scanning electron microscopy. The limiting oxygen index data, UL-94 test, and thermogravimetric analysis results showed that the use of phosphorus and silicon together had a synergistic effect on the flame retardancy of EP. The Fourier transform infrared results and X-ray powder diffraction measurements provided evidence that CPQS could promote the formation of char with silicophosphate and phosphocarbonaceous structures. The morphological structures observed by scanning electron microscopy demonstrated that more compact charred layers were formed in samples with CPQS than in those with 1-oxo-1-phospha-2,6,7-trioxabicyclo[2.2.2]-4-hydroxymethyl octane and tetraethoxysilane. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 168–174, 2009

Key words: composites; kinetics (polym.); pyrolysis; resins; silicones

INTRODUCTION

Organophosphorous flame retardants (FRs), which generate little toxic smoke under combustion, have shown the most potential to replace halogen-containing FRs for epoxy resins (EPs) in recent years.[1] Among organophosphorous FRs, caged bicyclic phosphates have attracted much interest;[2–4] they can serve as effective intumescent FRs in many polymers, especially in EPs. Incorporating silicon into EPs with phosphorus has a high synergistic effect on flame retardance.[5–8] Liu and his colleagues have done a lot of work on the synergistic effect of P—Si on the flame retardancy of EPs, and they have developed those systems by the sol–gel reaction[9] and the fusion reaction.[10] This literature is all based on cyclic aromatic phosphorus compounds and silicon chemicals used in establishing P—Si synergistic systems. In this study, we used a caged bicyclic phosphate quadridentate silicon complex (CPQS) in which the caged bicyclic phosphate was linked to the siloxane, and we investigated the synergistic effect of P—Si on the flame retardancy of EP in comparison with the conventional caged bicyclic phosphate 1-oxo-1-phospha-2,6,7-trioxabicyclo[2.2.2]-4-hydroxymethyl octane (PEPA) and tetraethoxysilane (TEOS) FR system.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A (DGEBA) EP E-51 was obtained from Guangzhou Yuehua Chemical Factory (Guangdong, China). The epoxide equivalent weight of the resin was 203.19 g/mol, as determined by the HBr/acetic acid titration method.[11] Triethylene tetramine (TETA; analytical reagent) was obtained from Tianjin Damao Chemical Reagent Factory (Tianjin, China); TEOS (analytical reagent) was obtained from Guangzhou Chemical Reagent Factory (Guangdong, China). All the reagents were used as received.

Preparation

PEPA and CPQS (Fig. 1) were synthesized according to refs. 12 and 13, respectively.

The preparation of the EP hybrid materials is shown in Figure 2. Certain amounts of PEPA, TEOS, PEPA/TEOS, and CPQS were added to DGEBA. The mixture was stirred for 10 min and then dispersed to produce a homogeneous solution with a sonifier for another 20 min; the amplitude of the sonifier was set at 30%. The temperature of the solution was about 70°C, and it was then cooled to room temperature in half an hour; a stoichiometric amount of TETA (13 g/100 g of DGEBA) was added under
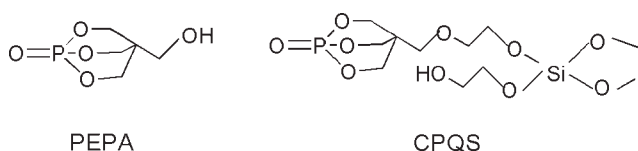
Figure 1 Chemical formulas of PEPA and CPQS.

stirring. Once a homogeneous solution was obtained, the solution was poured into a self-made Teflon mold after being degassed for 10 min and cured at room temperature for 7 days, and then it was post-cured at 80°C for 2 h. The compositions of the cured EP/FRs samples are tabulated in Table I.

Instruments

A Branson 450A sonifier (Shanghai, China) was used to disperse the compounds in the EP.

The limiting oxygen index (LOI) value was measured with a ZRY-type instrument (Nanjing Jiangning Analytic Instrumental Factory, Nanjing, China) on $120 \times 6 \times 3$ mm^3 sheets according to the standard LOI test (ASTM D 2863-77).

The vertical test was measured with a CZF-3-type instrument (Nanjing Jiangning Analytic Instrumental Factory, Nanjing, China) on $127 \times 12.7 \times 3$ mm^3 sheets according to the American National UL-94 test (ASTM D 635-77).

Differential scanning calorimetry (DSC) thermograms were recorded with a Netzsch DSC 204 analyzer (Bavarian, Germany) at a heating rate of 10°C/min from 25 to 200°C under a continuous nitrogen purge (50 mL/min). The instrument was calibrated with indium and tin standards. Samples of 10 mg were used for the measurements.

Thermogravimetric analysis (TGA) was carried out with a Netzsch TG 209 thermogravimetric analyzer (Bavarian, Germany) at a heating rate of 10°C/min from 25 to 700°C under a continuous air purge (50 mL/min). Samples of 10 mg were used for the measurements.

Infrared (IR) spectra were obtained on a Nicolet (USA) 205 Fourier transform infrared (FTIR) spectrometer; all the samples were kept in the muffle furnace at setting temperatures for 5 min, and then they were ground and examined in KBr discs.

The X-ray powder diffraction (XRD) diffractograms of the samples were taken on a D/max-IIIA automatic powder diffractometer (Rigaku Corporation, Tokyo, Japan). The Cu Kα radiation was monochromatized with a Ni filter and an amplitude analyzer and recorded with a scintillation counter. The diffractograms were recorded in the diffraction angle (2θ) range of 3–70°. The samples were obtained from the charred residues of TGA.

The morphologies of samples obtained from the char residue in the UL-94 test were examined with a

Philips XL series XL-30 scanning electron microscope (Eindhoven, Netherlands). The surfaces of the samples were coated with gold.

RESULTS AND DISCUSSION

Flame retardancy

The EPs blended with FRs with a series of additives, which are cataloged by the amount of phosphorus or silicon, the LOI values, the UL-94 test results, and the glass-transition temperatures (T_g's), are shown in Table I. For the compounds with only silicon FR elements (TEOS), the enhancement of LOI values is limited. Figure 3 presents the LOI values versus the weight concentration of phosphorus in the EP/FR samples. The y-coordinate values of the plots on curve AB indicate the LOI values contributed by the addition of phosphorus according to the ratio. Curve AC is above curve AB, and this indicates that the LOI values on AC are larger than those on AB. This shows that the FRs containing phosphorus and silicon FR elements (PEPA/TEOS) can simultaneously confer larger LOI values to the samples than those with only phosphorus-containing FRs. An identical scenario (AD above AC) pertains to CPQS, which contains intramolecular phosphorus and silicon FR elements, and the LOI values increase to 26.5 when the FR contains 1.72 wt % phosphorus and 1.56 wt % silicon. This suggests a better synergistic effect between the two elements on the flame retardancy of EP. The UL-94 data for the CPQS FR systems are obviously better than those for the TEOS, PEPA, and PEPA/TEOS FR systems. Only CPQS/EP can reach the UL-94 V-0 grade with the same weight loading of phosphorus and silicon.

These phenomena can be explained as follows. The samples consisting of phosphorus and silicon simultaneously, because of the low surface energy of
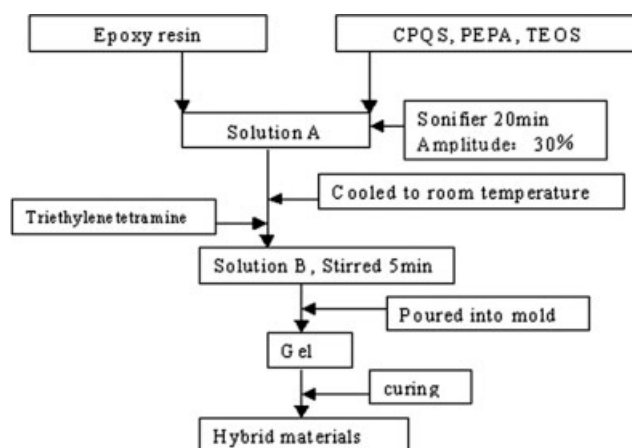

Figure 2 Preparation of the EP hybrid materials with the *in situ* sol–gel process.

<div align="center">

TABLE I
LOI Values, Results of UL-94 Testing, and T_g Values for FR EPs

</div>

FR	Sample	Additive amount (wt %)	Phosphorus (wt %)	Silicon (wt %)	LOI	UL-94	T_g (°C)
Not applicable	1	0	0	0	19	Burning	79
CPQS	2	5	0.43	0.39	23	Burning	79
	3	10	0.86	0.78	24	Burning	78.5
	4	15	1.29	1.17	25.5	V-1	78
	5	20	1.72	1.56	26.5	V-0	78
PEPA	6	2.5	0.43	0	21	Burning	82
	7	5	0.86	0	22.5	Burning	89
	8	7.5	1.29	0	23	Burning	95
	9	10	1.72	0	24	V-2	98
TEOS	10	2.91	0	0.39	20	Burning	100
	11	5.82	0	0.78	21	Burning	105
	12	8.73	0	1.17	21.5	Burning	108
	13	11.64	0	1.56	22	Burning	110
PEPA/TEOS	14	2.5/2.91	0.43	0.39	22.5	Burning	110
	15	5/5.82	0.86	0.78	23.5	Burning	115
	16	7.5/8.73	1.29	1.17	23.5	Burning	122
	17	10/11.64	1.72	1.56	24.5	V-2	127

the silicon-containing compounds, can transport to the surface of the EP,[14] and the ignition temperature of the samples is elevated. When they are ignited, the phosphorus-containing compounds influence the degradation behaviors of EP by self-decomposition at relatively low temperatures. This is due to the weak linkage of P—O—C structures in the polymers; they are very susceptible to chain scission during thermal degradation. Then, protective phosphorus–carbon layers are formed to increase the thermostability, and these layers can hold back the flammable gases of pyrolysis that arrive at the fire and isolate the heat away from the unburned matrix. However, these phosphorus–carbon layers might decompose further during the processing of burning. High-temperature thermal stability can be increased with the addition of the silicon-containing compounds because their decomposed products are silica or silicate, which cannot be oxidized further. If the FR element is used as an individual FR in the materials, it can offer only one kind of flame-retarding function during a fire. The phosphorus–carbon layer will be burnt without the protection of the silicate layer, and the silicon-containing TEOS cannot alone afford the protective phosphorus–carbon layer needed to meet the requirements in a fire. When they (PEPA/TEOS and CPQS) are simultaneously used in the same materials, their functions for the FR property are correlated. Furthermore, as for the CPQS/EP systems, phosphorus and silicon are incorporated in one molecule, and the reaction between the phosphorus-containing group and silicon-containing group in CPQS might take place during the heating; the formed heat-resistant compounds can rapidly stabilize phosphorus species and

protect the char from oxidation, then prevent the continuing development of flame,[6] and finally contribute to the enhancement of the UL-94 level.

Thermal properties

DSC analysis

The T_g values of CPQS/EP are noteworthy (Table I). As CPQS contains only one hydroxyl group, it can react with the epoxide groups at higher temperatures, and it can lower the original crosslink density; this will reduce the T_g values of cured samples.
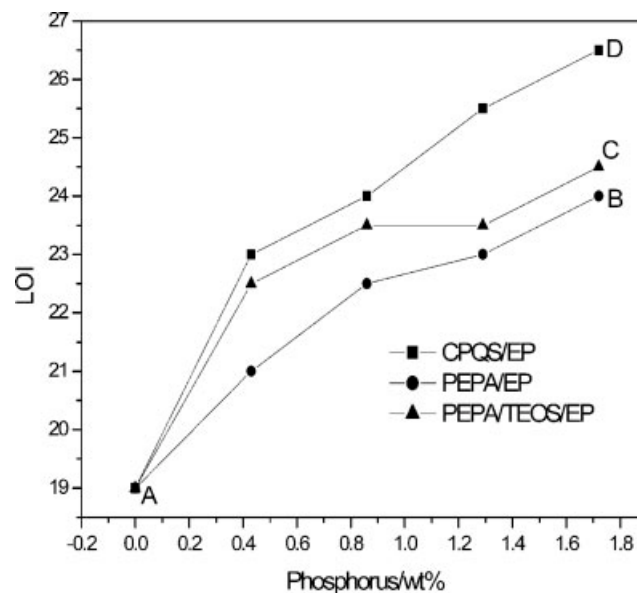

Figure 3 Plots of LOI versus the weight percentage of phosphorus in the samples.

However, an interesting tendency in the T_g values of CPQS/EP has been observed in this research. The T_g values of CPQS/EP are almost the same as that of the pristine EP. The results of the CPQS effect on T_g may be explained as follows: the hydroxyl-terminated CPQS certainly reduces the crosslinking density of the cured EPs, thereby reducing the T_g values. However, the bulky, rigid caged bicyclic phosphate group incorporated into the epoxy chain will increase the rotational barrier of the EPs[15] and show a counteraction with an increase in T_g. Therefore, the decrease in T_g is slight.

The T_g values of PEPA/EP increase with the increasing addition of PEPA because PEPA can serve as a curing agent of EP.[16] The T_g-enhancing effect of TEOS is also quite significant. The reason that T_g increases with the content of TEOS can be explained by the higher crosslink density of the cured TEOS/EP. Besides, the bulky caged bicyclic phosphate group also hinders the mobility of molecular chains and thus further increases T_g of PEPA/TEOS/EP.

TGA

Thermogravimetric (TG) behaviors of pristine EP, PEPA/EP, TEOS/EP, PEPA/TEOS/EP, and CPQS/EP samples under a flow of air are presented in Figure 4. The curve for pristine EP shows one step of total weight loss, in which the thermooxidative degradation takes place in the range of 300–450°C. The TG behavior of PEPA/EP does not fall into this situation. First, there is a step of about 5% weight loss from the evolution of some volatiles in the blends between 100 and 250°C. Second, there is about a 45–50% weight loss between 250 and 400°C. Finally, there is about a 38% weight loss between 400 and 700°C because of further decomposition of residual carbonaceous materials. The whole stage of weight loss of PEPA/TEOS/EP is lower than that of PEPA/EP, and this means that the incorporation of TEOS into PEPA/EP can reduce the amounts of evolving combustible gases during degradation; this phenomenon is consistent with previous reports.[17] The weight loss of TEOS/EP before 300°C arises from the dehydration condensation reaction between silanol groups left from the uncompleted gel reaction. It appears to be sustained weight loss above 300°C because of the loss of the silicon dioxide products in the air stream; this suggests that the silicon compounds do not provide enough carbon to protect the unburned material during fire, although its products cannot promote burning.

The amount of weight loss for CPQS/EP is somewhat larger than that for other samples before 300°C, and this weight loss might be from the degradation of the organic glycol moiety of CPQS. The
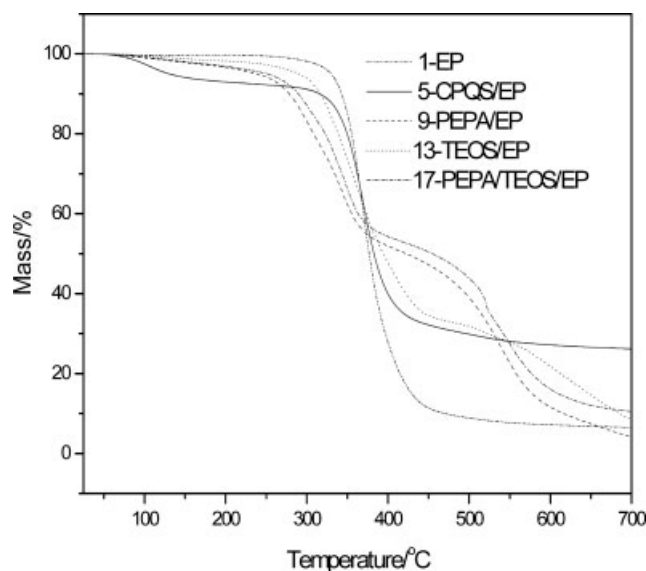

Figure 4 TG behavior of pristine EP, PEPA/EP, TEOS/EP, PEPA/TEOS/EP, and CPQS/EP systems.

char residues of PEPA/EP, TEOS/EP, and PEPA/TEOS/EP are higher than that of CPQS/EP from 380 to 530°C, and this can also be understood by the degradation of the organic part of CPQS. In addition, the combination of PEPA or TEOS into EP can increase the crosslink density, and this will reduce the production of volatile fuel and thus will also increase the char yield. As the temperature rises to 550°C, these kinds of char become easily cracked and oxidized, and the captured gases and volatile fuel escape; thus, the char yield decreases rapidly. The charred layer from the CPQS/EP system remains as high as 26.3% in the temperature range of 500–700°C, whereas that from the PEPA/TEOS/EP system continues to degrade to 10.1%; this means that the CPQS/EP system has better thermal stability than the PEPA/TEOS/EP system at temperatures higher than 500°C.

Thermooxidative degradation: FTIR analysis

To investigate the chemical and structural changes of the samples containing both phosphorus and silicon, we chose the thermooxidative degradation temperatures from the TGA results. The FTIR spectra at different pyrolysis temperatures of the pristine EP, CPQS/EP, and PEPA/TEOS/EP systems are shown in Figure 5(a–c), respectively. They can be divided into two regions. One is located at 2800–3000 cm^{-1}. The intensities of the peaks at 2920 and 2850 cm^{-1} assigned to the CH$_2$ or CH$_3$ asymmetric and symmetric vibrations and of the peaks at 1461 and 1375 cm^{-1} assigned to the CH$_2$ or CH$_3$ deformation vibrations of the aliphatic group in the polymer chains all
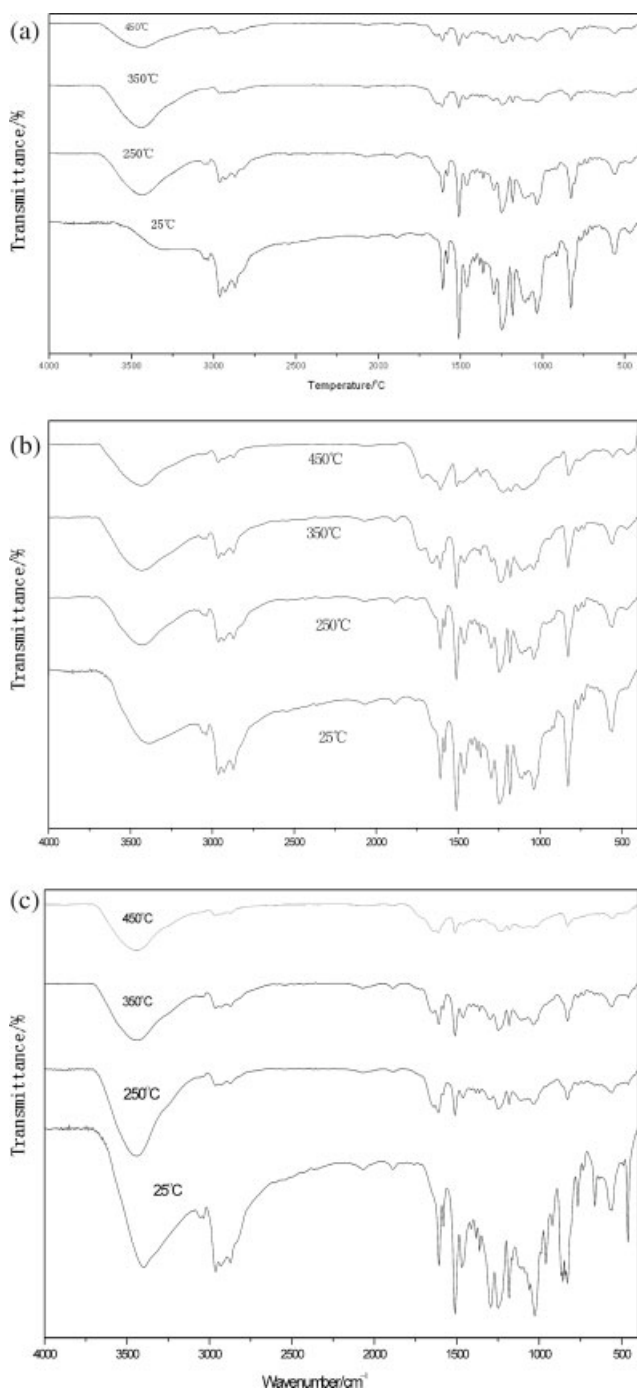
Figure 5 IR spectra of EP hybrid materials: (a) EP, (b) CPQS/EP, and (c) PEPA/TEOS/EP.

decrease rapidly with increasing pyrolysis temperatures. The disappearance temperatures of the aliphatic groups for different samples have been observed at 350°C for pristine EP and at 250°C for the PEPA/TEOS/EP systems, and this indicates that the degradation of EP is easier in the PEPA/TEOS/ EP systems because of the cleavage of the O=P—O group in the backbone. However, the aliphatic groups can be distinguished easily even at 350°C in

the CPQS/EP systems, although they also have the same caged bicyclic phosphate; this indicates that the cleavage of the O=P—O group in the CPQS/EP systems may have been delayed.

The second interesting region is at 800–1500 cm^{-1} for the CPQS/EP and PEPA/TEOS/EP systems. The overlapping peaks at 1350–1360 cm^{-1} have been assigned to the stretching mode of P=O. The peaks at 1250 cm^{-1} have been assigned to the stretching mode of P—O—C in the phosphocarbonaceous complex.[6] The peaks at 1088 and 880 cm^{-1} are assigned to the P—O vibration in the P—O—P groups.[18] Because of the steric hindrance and electronegativity of the siloxane group, the P=O and P—O—C stretching vibrations have a higher absorption frequency than usual. The peaks at 1010 and 948 cm^{-1} are assigned to the symmetric vibration of Si—O—Si groups. The absorptions of O—P=O and P—O—C in the caged bicyclic phosphate become very weak at temperatures above 250°C in the PEPA/TEOS/EP systems. However, these assignments provide positive evidence that the charred layers have P—O—P, P—O—C, and Si—O—Si structural groups above 350°C in the CPQS/EP systems. These phenomena can be explained by the degradation of silicon-containing TEOS and phosphorus-containing PEPA, which are not synchronous in the PEPA/TEOS/EP systems. The flowability of thermosetting EP is very poor, so the nanosilica formed by TEOS[6] cannot protect the phosphocarbonaceous complex as effectively as the continuous siloxane network and heat-resistant silicophosphate formed by CPQS, in which phosphorus and silicon are incorporated in one molecule. This is consistent with the TGA results discussed previously.

All the IR absorptions become weaker and simple as the temperatures rise; only the absorptions of 833, 1090, 1230, and 1610 cm^{-1} remain at 450°C. These are fire-resistant silicates and aromatic compounds resulting from carbonization of the char.

XRD phase analysis

The charred residue of the CPQS/EP system is a hard, compact, and laminated structure that has been demonstrated to be a good fire barrier. It is very different from the fluffy charred residue obtained from the PEPA/TEOS/EP system. The XRD spectra of the TGA charred residues from pristine EP, CPQS/EP, and PEPA/TEOS/EP systems are shown in Figure 6. A silicate phase [2θ (d/Å): 19.4 (4.572), 28.32 (3.149), and 50.18(1.817)] and a silicophosphate phase [2θ(d/Å): 40.52 (2.224)] appeared in the CPQS/EP sample,[16] and these can increase the thermal stabilization of the charred layer. It is surprising that there is not a silicon dioxide phase appearing in the PEPA/TEOS/EP system. The

charred residue spectrum of PEPA/TEOS/EP is almost the same as that of the pristine EP system; only some amorphous char and a little minicrystal graphite remain, and this might be the result of a loss of nanosilica in streams of air[14] and the emission of gases during TGA. This suggests that the silica particles cannot provide enough protection for the phosphorus–carbon layers during a fire.

Morphological structures of char from CPQS/EP and PEPA/TEOS/EP

Figure 7 shows the morphological structures of the charred layers obtained from CPQS/EP and PEPA/TEOS/EP. The surface of the CPQS/EP sample is relatively smooth and compact versus that of the PEPA/TEOS/EP sample. The PEPA/TEOS/EP sample shows irregular swollen structures and clusters of flocculent nanosilica deposited on the surface of the char. The swollen cells are easily broken, and the flocculent nanosilica is easily blown away, as shown by the results of XRD and TGA; although this kind of silica might raise the char yields, it cannot completely inhibit the flame and the vaporization of small molecules and ultimately enhances the flame retardancy of EP. For CPQS, in which phosphorus and silicon are incorporated, the caged bicyclic phosphate group and silicon-containing group decompose during heating, and then silicate is formed or reacts immediately with phosphate to yield silicophosphate, which is known to stabilize phosphorous species.[19] The closed and smooth structural cells provide a good barrier to the transfer of heat and
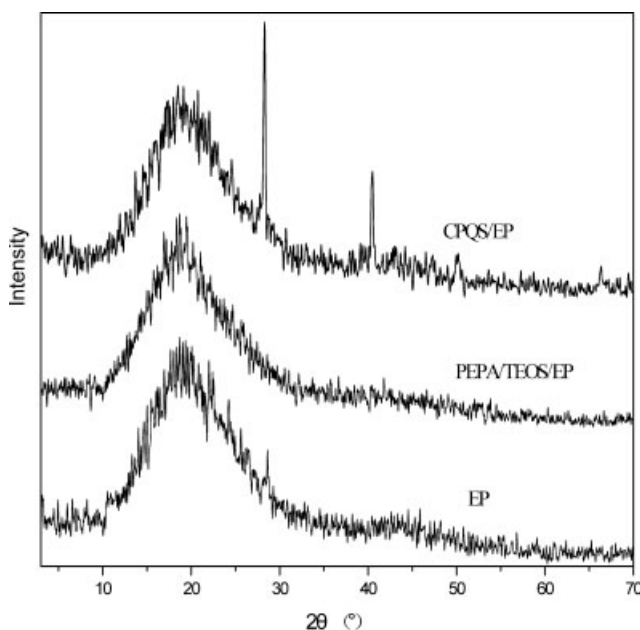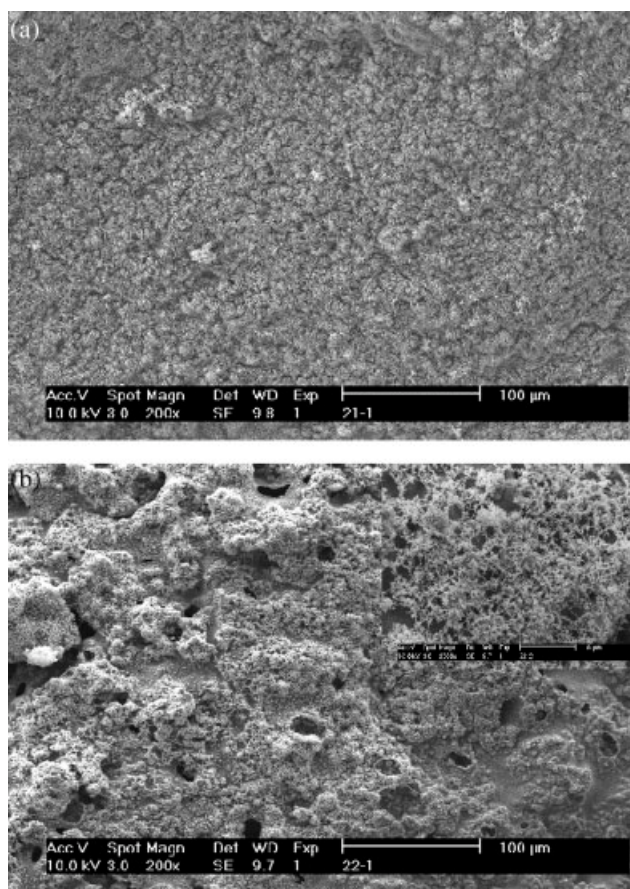

Figure 7 Scanning electron microscopy photographs of the charred layer of the EP hybrid materials: (a) CPQS/EP and (b) PEPA/TEOS/EP.

mass during a fire and promote the thermal protection properties of charred layers.

CONCLUSIONS

The incorporation of phosphorus, silicon, or both into EP can produce halogen-free FR EP. TG, FTIR, and XRD results have demonstrated that the use of phosphorus and silicon together has a synergistic effect on the flame retardancy of EP, especially when phosphorus and silicon are incorporated in one molecule. The flame retardancy of EP increases with the CPQS content, and an LOI of 26.5 and UL-94 V-0 grade have been achieved with a content of 20 wt %. The TGA and thermooxidative degradation FTIR data show that the thermal stability of CPQS/EP is better than that of the other FR systems at temperatures higher than 500°C. The improvement of the flame retardancy and thermal stability is attributed to the compact silicate and silicophosphate charred layers formed by CPQS.

Figure 6 XRD spectra of the char residues.

References

1. Levchik, S. V.; Weil, E. D. Polym Int 2004, 53, 1901.

2. Li, X.; Ou, Y. X.; Zhang, Y. H.; Lian, D. J. Chin Chem Lett 2000, 11, 887.
3. David, W. A.; Edwyn, C. A.; Leslie, E. S. Polym Degrad Stab 1995, 47, 67.
4. David, W. A.; Edwyn, C. A.; Leslie, E. S. Polym Degrad Stab 1994, 45, 399.
5. Hsiue, G. H.; Liu, Y. L.; Tsiao, J. J Appl Polym Sci 2000, 78, 1.
6. Hsiue, G. H.; Liu, Y. L.; Liao, H. H. J Polym Sci Part A: Polym Chem 2001, 39, 986.
7. Chiang, C. K.; Wallace, W. E.; Lynn, G. W.; Feiler, D.; Xia, W. Appl Phys Lett 2000, 76, 430.
8. Wu, C. S.; Liu, Y. L.; Chiu, Y. S. Polymer 2002, 43, 4277.
9. Liu, Y. L.; Wu, C. S.; Chiu, Y. S.; Ho, W. H. J Polym Sci Part A: Polym Chem 2003, 41, 2354.
10. Liu, Y. L.; Chiu, Y. C.; Wu, C. S. J Appl Polym Sci 2003, 87, 404.
11. Bassindale, A.; Liu, Z.; Parker, D.; Taylor, P.; Horton, P.; Hursthouse, M.; Light, M. J Organomet Chem 2003, 687, 1.
12. Halpern, Y.; Denna, M. M.; Niswander, R. H. U.S. Pat. 4,454,064 (1984).
13. Zhang, L. L.; Liu, A. H.; Zeng, X. R.; Wen, Y. X. Chin J Org Chem 2006, 26, 1125.
14. Li, Q.; Jiang, P. K.; Su, Z. P.; Wei, P.; Wang, G. L.; Tang, X. Z. J Appl Polym Sci 2005, 96, 854.
15. Cai, S. X.; Lin, C. H. J Polym Sci Part A: Polym Chem 2005, 43, 2862.
16. Li, X.; Ou, Y. X.; Shi, Y. S. Polym Degrad Stab 2002, 77, 383.
17. Liu, Y. L.; Chou, C. I. Polym Degrad Stab 2005, 90, 515.
18. Wu, Q.; Qu, B. J. Polym Degrad Stab 2001, 74, 255.
19. Bourbigot, S.; Le Bras, M.; Duquesne, S.; Rochery, M. Macromol Mater Eng 2004, 289, 499.