

# Flame Retardancy and Nondripping Properties of Ammonium Polyphosphate/Poly(butylene succinate) Composites Enhanced by Water Crosslinking

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**ABSTRACT:** Ammonium polyphosphate (APP)/poly(butylene succinate) (PBS) composites were prepared with a unique water-crosslinking technique to improve the flame retardancy and nondripping properties of the composites and to maintain the main structure of the composites during flame tests. The composites were treated with a coupling agent (tetraethoxysilane) and then were compounded in a twin-screw extruder. The compound was moisture-crosslinked. Fourier transform infrared spectra were used to monitor the water-crosslinking reaction. The composites via the water-crosslinking treatment exhibited improved mechanical properties because of the interfacial bonding between the APP and PBS matrix. Scanning electron microscopy of the fractured surfaces of the water-cross-

linked composites showed that the void size increased with increasing water-crosslinking time. Composites with 15 wt % APP were classified as UL-94 V-2; however, the ones with only a 0.5-h water-crosslinking reaction were classified as UL-94 V-0. Thermal analyses of the water-crosslinked composites indicated that the thermal degradation temperature of the composites increased with increasing water-crosslinking time. Differential scanning calorimetry results revealed that the water-crosslinking reaction could limit the crystallization rate of PBS. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2935–2945, 2006

**Key words:** biodegradable; composites; crosslinking; crystallization; flame retardance

## INTRODUCTION

Biodegradable polyester is one of the most important environmentally friendly materials. Recently, poly(butylene succinate) (PBS) has received extensive attention for polymers and copolymers<sup>1–5</sup> and for blending with other polymers.<sup>6,7</sup> To improve the physical properties of PBS, some methods have been reported, such as the addition of nanoclay<sup>8–10</sup> and crosslinking reactions.<sup>11–13</sup>

To improve the flame retardancy of biodegradable polymers, some efforts<sup>14–18</sup> have been made via the addition of various flame retardants. Ammonium polyphosphate (APP, City of Industry, CA) is an effective flame retardant for improving the flame retardancy of polymers, fibers, and other organic materials.<sup>19–29</sup> In this study, APP was used as the flame retardant to improve the flame retardancy of PBS. The proposed degradation mechanism<sup>21</sup> of APP is illustrated in Scheme 1.

Halogen-free flame retardation and silane crosslinking have been investigated for polyethylene.<sup>30</sup> In this study, a water-crosslinking method is proposed to achieve an improved interface between APP and PBS. This process is via condensation by water, leading to

the crosslinking of the polymer matrix. The resultant composite also possesses enhanced flame retardancy and nondripping properties. The main advantage of this technique is to maintain the main structure of the composites during flame tests.

The objective of this study is to investigate the effects of the contents of flame-retardant APP and the water-crosslinking time on the mechanical properties and flame-retardancy properties of APP/PBS composites. A crosslinking mechanism is proposed for this system, as described in Scheme 2. The dynamic mechanical properties and crystallization behavior of the composites are also investigated.

## EXPERIMENTAL

### Materials

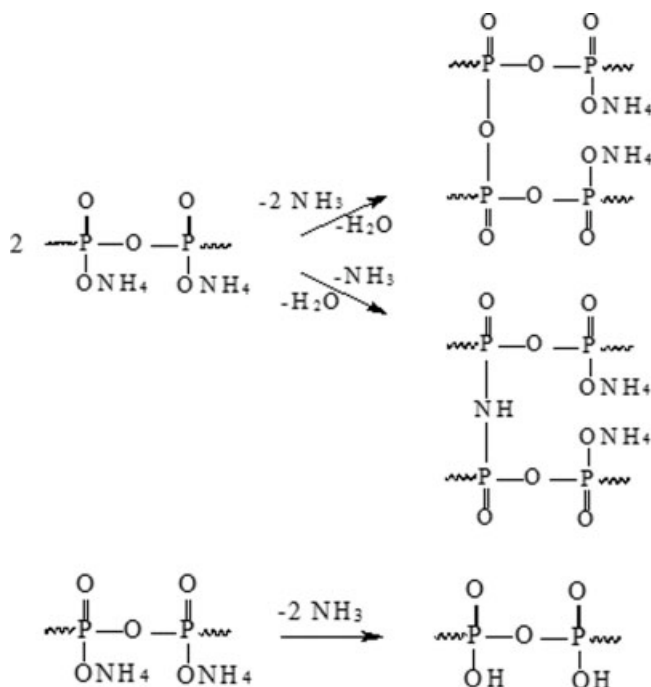
PBS (Bionolle 1001; melt flow index  $\sim 1.0$ , weight-average molecular weight =  $2.6 \times 10^5$ ) was supplied by Showa Highpolymer Co., Ltd. (Tokyo, Japan). APP (trade name PNP1) was produced by JLS Chemical, Inc. (United States). Tetraethoxysilane (TEOS) was supplied by Acros Organics Co. (Geel, Belgium). Di-*n*-butyltin dilaurate (T12) was supplied by Air Products Co. (Allentown, PA).

### Sample preparation

APP was treated with 1–10 phr TEOS, was mixed with a Henschel mixer (Chiao-wei Co., Taichung, Taiwan),

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Scheme 1 Degradation mechanism of APP.<sup>21</sup>

and then was mixed with Bionolle 1001 pellets in a plasticizing extruder (a corotating-type twin-screw extruder with a length/diameter ratio of 43.5 and a high-shear-rate configuration). The compositions of the APP/PBS composites are listed in Table I. The barrel temperature ranged from 110 to 180°C. Extruded materials were cut into small pellets in a granulator. Dumbbell-shaped specimens were then injection-molded with a Battenfeld Ba750 CD Plus injection-molding

machine (Meinerzhagen, Germany) at mold temperatures of 160–190°C. The maximum injection pressure was 100 bar, and the hold pressure was 10 bar.

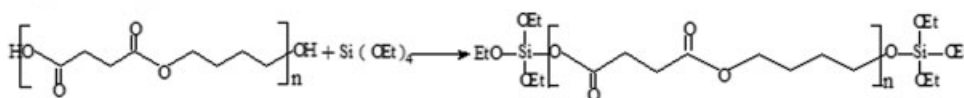
Some of the specimens were subsequently subjected to water crosslinking with different crosslinking times; they were placed in an isothermal water bath at 70°C for 0.5, 1, 2, or 4 h to advance the water-crosslinking reaction further.

### Property measurements

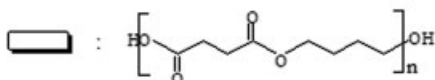
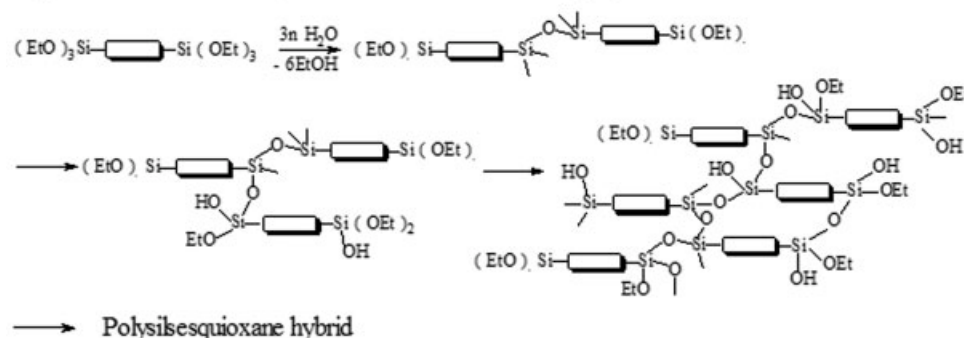
Fourier transform infrared (FTIR) spectra of water-crosslinked APP/PBS blends were recorded between 4000 and 600  $\text{cm}^{-1}$  with a Nicolet Avatar 320 FTIR spectrometer (Nicolet Instrument Corp., Madison, WI). Samples were placed on the attenuated-total-reflection attachment, and a minimum of 32 scans were averaged with a resolution of 2  $\text{cm}^{-1}$  within the 4000–600- $\text{cm}^{-1}$  range. The characteristic absorption peaks of functional groups were detected and monitored during the water-crosslinking reaction.

The mechanical properties of dumbbell-shaped specimens were measured on an Instron model 4468 universal testing machine (Norwood, MA). Tensile test procedures followed the ASTM D 638-82 method with a crosshead speed of 20 mm/min. The dimensions of the samples were 25.0  $\times$  10.0  $\times$  1.4  $\text{mm}^3$ . Six specimens were tested in each case. Flexural tests followed the ASTM D 790 method with a span-to-depth ratio of 40 and a crosshead speed of 1.0 mm/min. The notched impact strength was tested according to ASTM D 256, and a TMI testing machine (TMI Co., Ronkonkoma, NY) was used. The dimensions of these samples were

#### Step 1: PBS grafted with TEOS



#### Step 2: Water-crosslinking reaction of functionalized polymer



Scheme 2 Water-crosslinking reaction mechanism of APP/PBS composites proposed in this study.

**TABLE I**  
Formulations of PBS and Flame-Retardant-Containing PBS Samples (g)

Sample <sup>a</sup>	PBS	APP	TEOS
APP10	90	10	0
APP15	85	15	0
APP20	80	20	0
APP30	70	30	0
APP15T1	85	15	1
APP15T2.5	85	15	2.5
APP15T5	85	15	5
APP15T10	85	15	10

<sup>a</sup> APP represents APP, and T represents TEOS.

63.0 × 12.7 × 3.2 mm<sup>3</sup>. All tests were performed at the ambient temperature (25 ± 2°C).

For a melt-crystallization study, samples were first placed in a vacuum oven at 100°C for 24 h before being sealed in an aluminum sample cell, and they then were kept at 150°C for 10 min and cooled to room temperature at a cooling rate of 5°C/min. All data were obtained on a TA Instruments DSC 10 (DuPont, New Castle, DE).

The dynamic mechanical properties were measured with a TA Instruments DMA 2980 dynamic mechanical analyzer operating in the three-point-bending mode at an oscillation frequency of 1.0 Hz. The amplitude was 10 μm. Data were collected from -50 to 90°C at a heating rate of 5°C/min. At least three specimens of each composition were tested.

Limiting oxygen index (LOI) values were measured with a Toyoseiki S-6M type instrument (Tokyo, Japan). LOI is defined as the minimum fraction of O<sub>2</sub> in a mixture of O<sub>2</sub> and N<sub>2</sub> that will just support combustion. The LOI test was performed according to the testing procedure of the ASTM D 2836 oxygen index method with a test specimen bar 7–15 cm long, 6.5 ± 0.5 mm wide, and 3.0 ± 0.5 mm thick. The sample bars, suspended vertically, were ignited by a Bunsen burner. The flame was removed, and the timer was started. The concentration of oxygen was raised if the specimen was extinguished before burning 3 min or 5 cm. The oxygen content was adjusted until the limiting concentration was determined.

The UL-94 vertical test was performed according to the testing procedure of ASTM D 3801 with a test specimen bar 127 mm long, 12.7 mm wide, and about 1.27 mm thick. Five sample bars suspended vertically over surgical cotton were ignited by a Bunsen burner. A flame was applied twice to the lower end of each specimen for 10 s. The class of UL-94 V-0 was achieved if each afterflame time did not exceed 10 s, and the sum of the afterflame times for the five samples did not exceed 50 s. Meanwhile, for UL-94 V-0, the surgical cotton below the specimen could not be ignited with the flaming drippings. The class of UL-94 V-1 was achieved if each afterflame time did not exceed 30 s, and the sum of the afterflame times for the five samples did not exceed

250 s. Meanwhile, for UL-94 V-1, the surgical cotton below the specimen could not be ignited with the flaming drippings. If the surgical cotton below the specimen was ignited with the flaming drippings, the sample was assigned to the UL-94 V-2 class.

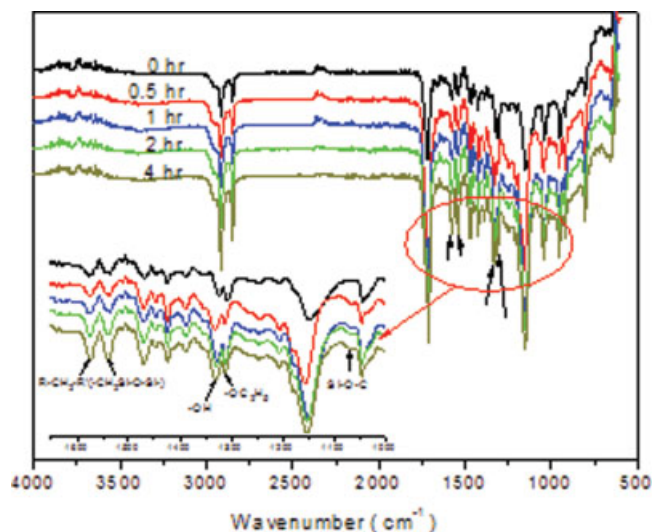
Thermal degradation of these composites was measured with a thermogravimetric analysis (TGA) instrument (951, DuPont) coupled to a 1050 thermal analyzer. The measurements (10 ± 3 mg) were stacked in an open platinum sample pan, and the experiment was conducted under N<sub>2</sub> gas at various heating rates (i.e., 5, 10, 20, and 40°C/min). Although machine-selected heating rates were reported and used in the calculations, the actual heating rates were determined from the appropriate plots. For the multiple-heating-rate kinetic experiments, each sample was placed in a TGA pan and heated until the sample reached thermal degradation in N<sub>2</sub> gas.

The gel content (insoluble fraction) produced in silane-crosslinkable APP/PBS composites by crosslinking was determined according to ASTM D 2765. It was determined by two extractions of the water-crosslinked sample (*m*<sub>1</sub>) in boiling chloroform for 24 h. After being dried, the insoluble residue (*m*<sub>2</sub>) was weighed. The average gel content was calculated as *m*<sub>2</sub>/*m*<sub>1</sub>. Three samples were analyzed to determine the average gel content for a given set of water-crosslinking times.

## RESULTS AND DISCUSSION

### FTIR spectroscopy analysis of the APP/PBS composites

Figure 1 shows the FTIR spectra of composites with various water-crosslinking times. The changes in the



**Figure 1** FTIR spectra of 15 wt % APP/PBS composites for various water-crosslinking times (1 phr TEOS). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



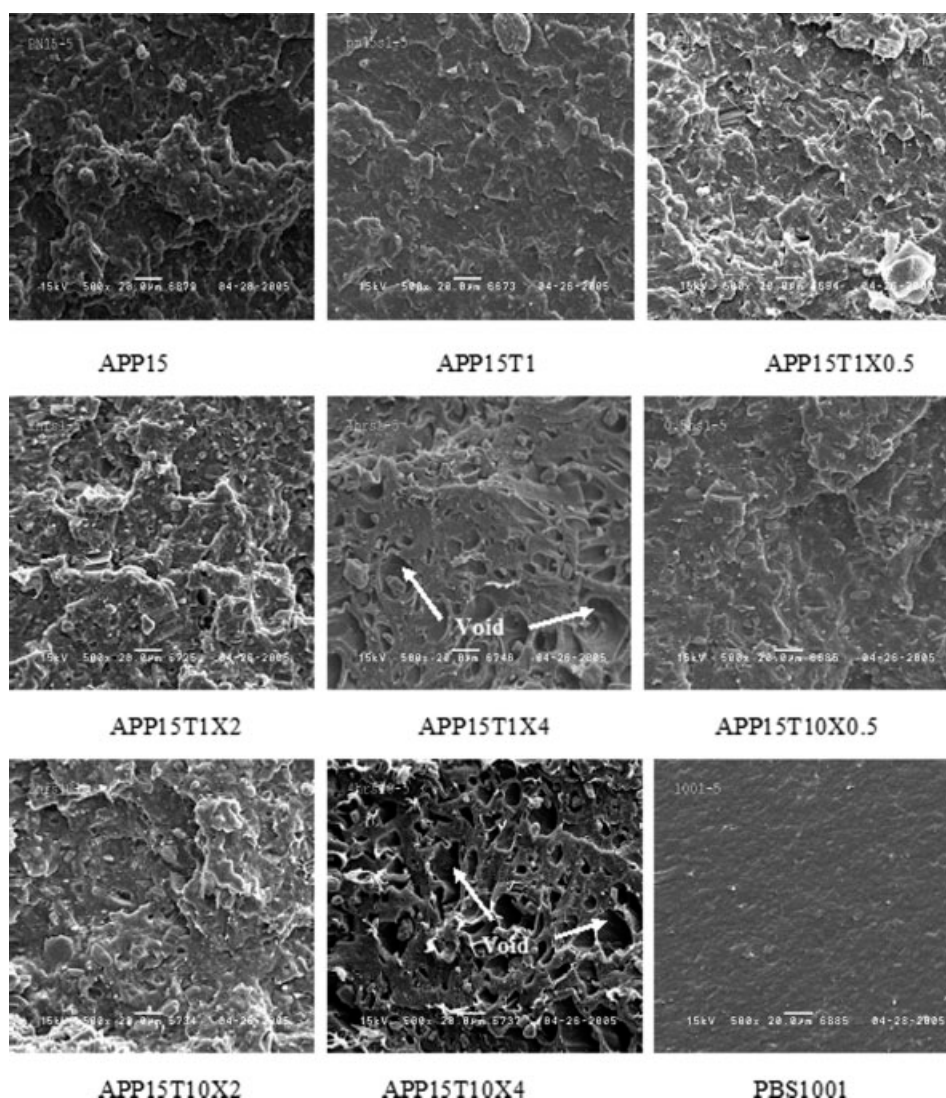
**TABLE II**  
**Mechanical Properties of PBS and Flame-Retardant-Containing PBS Samples**

Sample	Tensile strength (MPa)	Elongation (%)	Flexural strength (MPa)	Flexural modulus (MPa)
PBS	38.8 ± 0.1	391.2 ± 7.5	38.6 ± 0.1	607.6 ± 9.2
APP10	34.4 ± 0.1	341.4 ± 6.5	38.7 ± 0.1	660.4 ± 5.2
APP15	31.1 ± 0.1	327.0 ± 5.7	39.8 ± 0.1	725.0 ± 8.5
APP20	30.4 ± 0.2	306.8 ± 3.2	40.8 ± 0.2	799.2 ± 4.7
APP30	23.2 ± 0.1	177.7 ± 9.3	41.3 ± 0.2	963.5 ± 8.2
APP15T1	32.5 ± 0.2	351.9 ± 7.1	42.0 ± 0.1	739.0 ± 6.4
APP15T2.5	32.3 ± 0.1	340.7 ± 9.5	41.3 ± 0.2	696.4 ± 7.6
APP15T5	32.2 ± 0.1	346.3 ± 8.5	41.2 ± 0.1	689.3 ± 8.1
APP15T10	29.2 ± 0.1	351.1 ± 5.2	36.7 ± 0.3	615.7 ± 6.5

<sup>b</sup> APP represents APP, and T represents TEOS.

FTIR absorption peak heights were due to actual changes in the chemical composition of the composite. In Figure 1, the absorbance bands appearing at 1540, 1576, 2914, and 2847  $\text{cm}^{-1}$  can be considered the

R—CH<sub>2</sub>—R' bonds (—CH<sub>2</sub>Si—O—Si—) introduced into PBS during the water-crosslinking process. Another absorption peak is at 1075  $\text{cm}^{-1}$ , representing the asymmetric stretch of the Si—O—C group.



**Figure 2** SEM microphotographs (500 $\times$ ) of the fractured surfaces of APP/PBS composites (in the sample names, APP represents APP, T represents TEOS, and X represents the crosslinking time).

The absorption peak at  $1312\text{ cm}^{-1}$  ( $-\text{OCH}_2\text{H}_5$ ) decreased with increasing water-crosslinking time because it converted to the  $-\text{CH}_2\text{Si}-\text{O}-\text{Si}-$  functional group. The absorption peak at  $1334\text{ cm}^{-1}$  increased with increasing water-crosslinking time, representing the formation of the  $-\text{OH}$  group during the water-crosslinking process.

## Mechanical properties

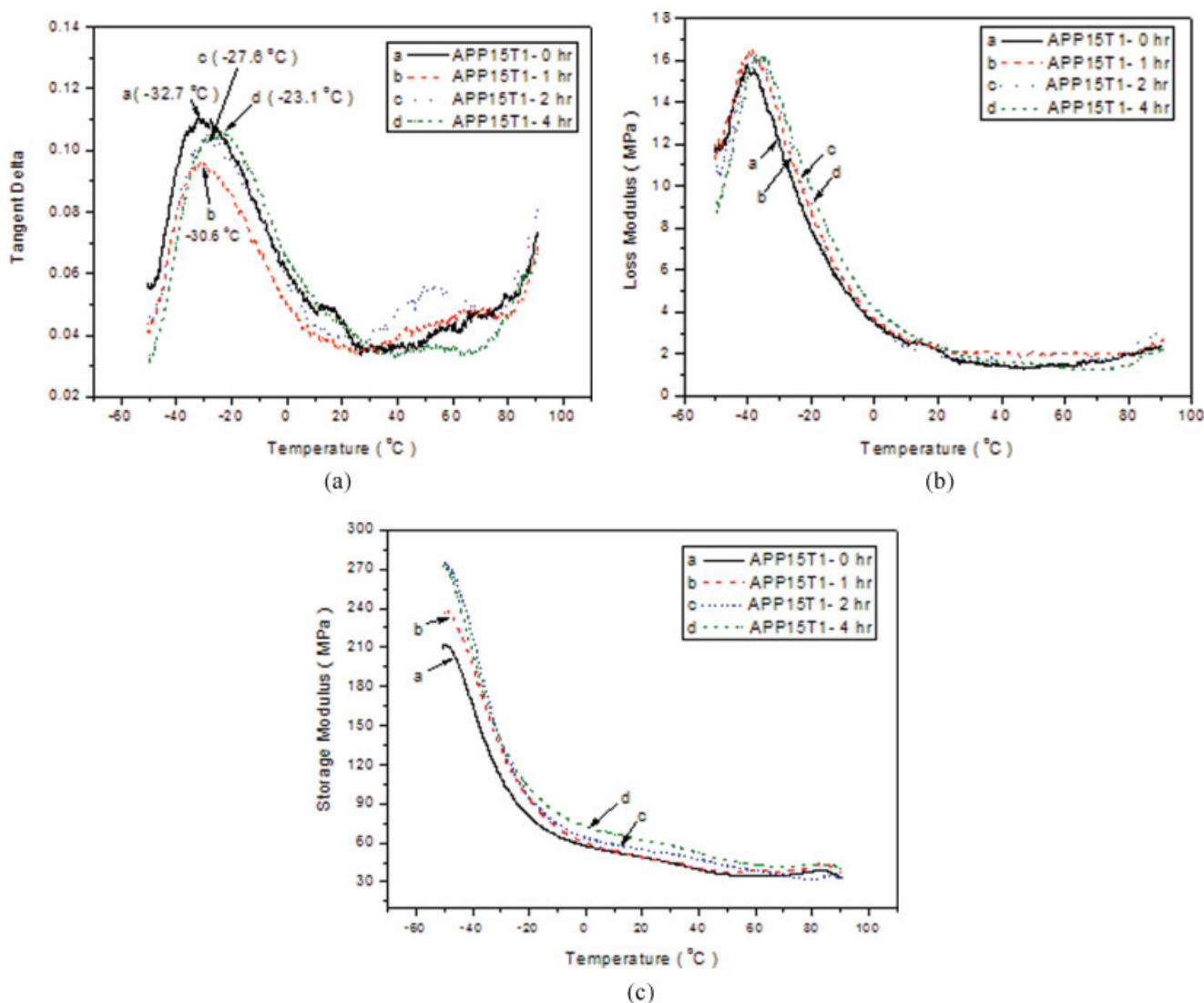
### Tensile properties

Table II illustrates the mechanical properties of APP/PBS composites with and without TEOS treatment and with various APP contents. Table II shows that adding APP reduced the tensile strength of the composites from 38.8 to 23.2 MPa as the APP content increased from 0 to 30 wt %. APP is a powder; hence, the tensile strength could be reduced by the addition of such a

flame-retardant filler. Composites treated with TEOS exhibited better tensile strength than the untreated ones because better interfacial bonding was achieved. The tensile elongation also decreased from 391.2 to 177.7% as the APP content increased from 0 to 30 wt %. Composites treated with TEOS exhibited better tensile elongation than the untreated ones. The results suggested that the modified APP surface could enhance the compatibility between the polymer and filler.

### Flexural properties

The flexural strength and modulus of the APP/PBS composites are listed in Table II. Adding APP to the PBS matrix increased the flexural strength and markedly increased the initial flexural modulus of the composites. The flexural strength of the APP/PBS composite increased from 38.6 to 41.3 MPa when the APP



**Figure 3** (a)  $\text{Tan } \delta$ , (b) loss modulus, and (c) storage modulus of 15 wt % APP/PBS composites with various water-crosslinking times (in the sample names, APP represents APP, and T represents TEOS). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

content increased from 0 to 30 wt %. The flexural modulus of the APP/PBS composites also increased from 607.6 to 963.5 MPa (increase by 58.6%). The composites treated with interfacial modifiers exhibited even better flexural strength than the untreated ones. The flexural strength of the 2.5 phr TEOS-modified APP/PBS composite was 41.3 MPa when the APP concentration was 15 wt %. However, adding more TEOS to the composites could reduce the flexural modulus of the APP/PBS composites. The results suggested that excess TEOS in the resin matrix could play the role of a plasticizer, reducing the flexural modulus of the composites.

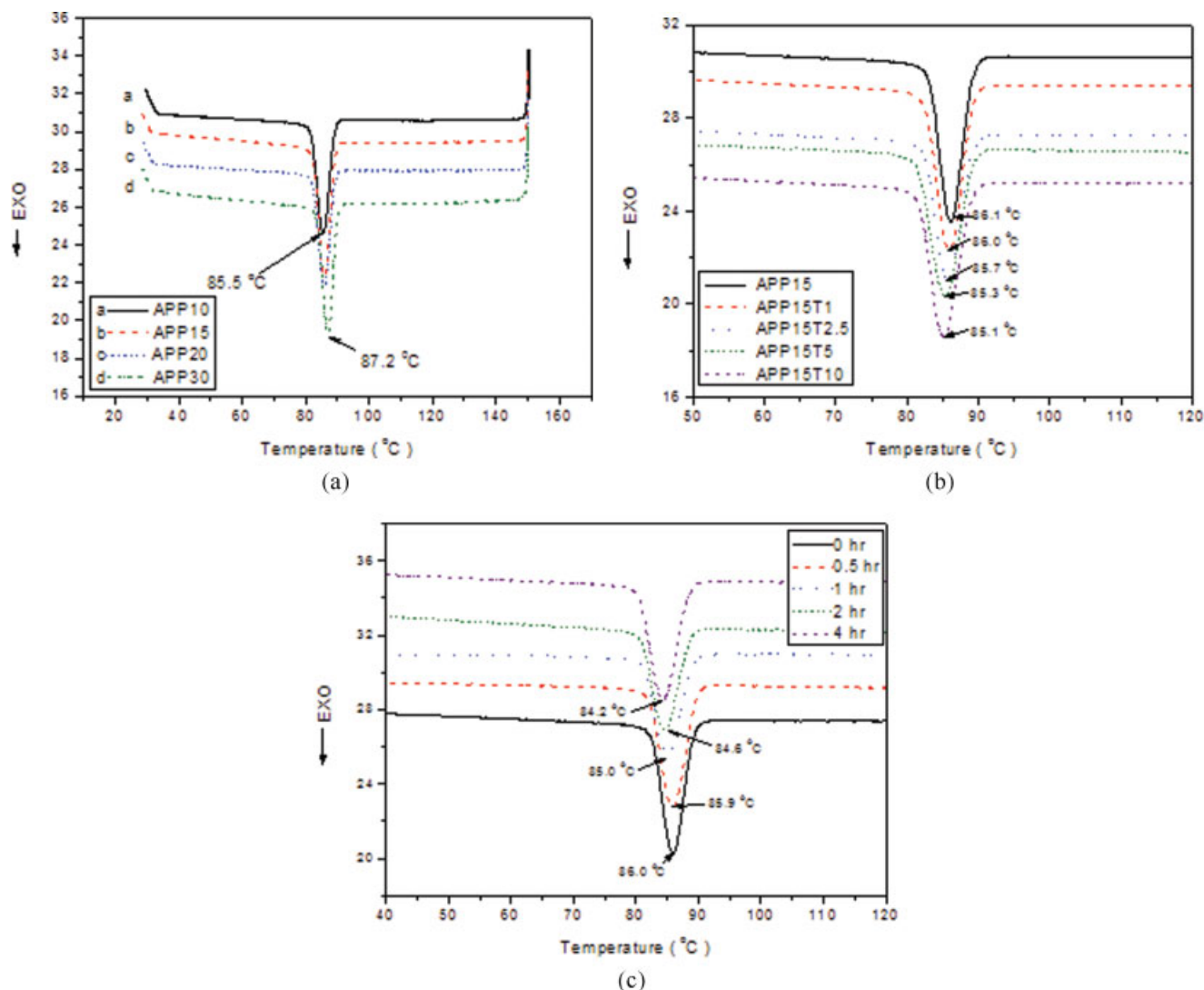
### Morphology of the fractured surfaces

Figure 2 presents that the morphology of the fractured surfaces of APP/PBS composite before and after the

water-crosslinking reaction. Scanning electron microscopy (SEM) microphotographs show that APP was pulled out and broken during the fracture of the composites. The SEM micrographs in Figure 2 show that the void size increased as the water-crosslinking time increased. This water-crosslinking reaction formed a PBS molecular network, which probably caused the phase separation of PBS and APP with the dissolution of the latter, yielding more numerous and larger voids in the matrix.

### Dynamic mechanical analysis (DMA)

DMA was performed for pristine PBS and its composites to obtain further information on the mechanical properties and molecular motions. DMA is a method that measures the stiffness and mechanical damping of



**Figure 4** DSC curves of (a) APP/PBS composites with various APP contents, (b) 15 wt % APP/PBS composites with various TEOS contents, and (c) 15 wt % APP/PBS composites with various water-crosslinking times (in the sample names, APP represents APP, and T represents TEOS). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

TABLE III  
Flame-Retardant Behavior of PBS Formulations with APP

Sample	APP (wt %)	LOI	UL-94					
			Ranking		Dripping		$T_f$ (s) <sup>a</sup>	
			3.2 mm	1.6 mm	3.2 mm	1.6 mm	3.2 mm	1.6 mm
APP10	10	22	V-2	V-2	Yes	Yes	113.5	75.0
APP15	15	24	V-2	V-2	Yes	Yes	53.7	39.3
APP20	20	28	V-0	V-0	No	No	12.2	14.3
APP30	30	37	V-0	V-0	No	No	8.6	9.4

<sup>a</sup> Total duration (five specimens) of flaming combustion.

a cyclically deformed material as a function of temperature. The identification of the glass-transition temperature ( $T_g$ ) is one of the most common uses of DMA, and generally  $T_g$  is determined as a maximum of the  $\tan \delta$  curve and is seen as a drop in the storage modulus or loss modulus curve. Figure 3(a) presents the dynamic mechanical properties of APP/PBS composites for various water-crosslinking times.  $T_g$  of the APP/PBS composites increased with increasing water-crosslinking time (from  $-32.7$  to  $-23.1^\circ\text{C}$ ). The water-crosslinking reaction could restrict the molecular motion of a PBS molecular chain, which increased  $T_g$  of the APP/PBS composites. The same trend can be seen in Figure 3(b,c); the transition peak of the loss modulus of the APP/PBS composites increased with increasing water-crosslinking time. Meanwhile, the storage modulus of the APP/PBS composites increased steadily with the water-crosslinking time. These results suggested that the water-crosslinking reaction could increase the stiffness of composites in both the glassy state and rubbery state of the composites.

### Crystalline behavior of the composites

Nonisothermal crystallization experiments were conducted with differential scanning calorimetry (DSC) cooling scans of the neat PBS and APP/PBS composites at a cooling rate of  $5^\circ\text{C}/\text{min}$ , and the results are shown in Figure 4(a–c). Only one exothermic peak temperature could be observed for each curve between  $80$  and  $100^\circ\text{C}$ . The crystallization temperature ( $T_c$ ) values illustrated in

Figure 4(a) indicate that the addition of APP raised  $T_c$  by about  $1.7^\circ\text{C}$ , and  $T_c$  did not change very much with different APP contents. The increase in the peak temperature indicated that APP served as a nucleating agent and increased the crystallization rate of PBS.

As shown in Figure 4(b), the addition of TEOS reduced  $T_c$  by about  $1.0^\circ\text{C}$ . The higher the TEOS content was, the lower the crystallization rate was of PBS, and this indicated that the addition of APP could reduce the crystallinity rate of PBS. This phenomenon may have resulted from TEOS restricting the chain mobility of PBS and leading to a lower crystallinity rate.

The water-crosslinking reaction reduced  $T_c$  by  $1.8^\circ\text{C}$ , as shown in Figure 4(c). The presence of a crosslinking network may have restricted the mobility of polymer chains of PBS when the crystallization process took place, resulting in the formation of small, imperfect crystallites with a lower melting point.

### LOI and UL-94 tests

The flame-retardant characteristics of APP/PBS composites were examined by the measurement of their LOIs. Table III reveals a considerable increase in LOI (from  $22$  to  $37$ ) when APP was added to PBS. This change suggests that incorporating APP significantly promoted the flame retardancy of PBS. On the other hand, adding TEOS to APP/PBS composites reduced LOI from  $26$  to  $22$ , as shown in Table IV. As shown in Table V, treating the composites with the water-crosslinking reaction could increase the LOI values of the

TABLE IV  
LOI and UL 94 Testing Results of Flame-Retardant-Containing PBS Samples with Various TEOS Treatments

Sample <sup>a</sup>	TEOS (wt %)	LOI	UL-94					
			Ranking		Dripping		$T_f$ (s) <sup>b</sup>	
			3.2 mm	1.6 mm	3.2 mm	1.6 mm	3.2 mm	1.6 mm
APP15T1	1	26	V-2	V-2	Yes	Yes	34.5	40.5
APP15T2.5	2.5	24	V-2	V-2	Yes	Yes	32.6	103.4
APP15T5	5	23	V-2	V-2	Yes	Yes	37.3	162.0
APP15T10	10	22	V-2	V-2	Yes	Yes	73.7	121.5

<sup>a</sup> APP represents APP, and T represents TEOS.

<sup>b</sup> Total duration (five specimens) of flaming combustion.



TABLE V  
LOI and UL 94 Testing Results of Flame-Retardant-Containing PBS  
Samples with Various TEOS Treatments

Sample <sup>a</sup>	Gel content (%)	LOI	UL-94 (3.2 mm)		
			Ranking	Dripping <sup>c</sup>	T <sub>f</sub> (s) <sup>b</sup>
APP15T1X0.5	18.8	26	V-0	No	33.1
APP15T1X1	25.6	27	V-0	No	11.4
APP15T1X2	31.4	27	V-0	No	21.0
APP15T1X4	34.2	28	V-0	No	13.8
APP15T2.5X0.5	11.7	24	V-2	Yes	16.2
APP15T2.5X1	13.5	24	V-2	Yes/no	18.9
APP15T2.5X2	17.1	25	V-2	Yes/no	29.2
APP15T2.5X4	20.2	25	V-0	No	12.2
APP15T5X0.5	9.5	22	V-2	Yes	38.5
APP15T5X1	12.6	23	V-2	Yes	40.5
APP15T5X2	14.2	22	V-2	Yes/no	34.5
APP15T5X4	16.3	24	V-0	No	33.8
APP15T10X0.5	9.2	20	V-2	Yes	40.2
APP15T10X1	10.4	21	V-2	Yes	40.7
APP15T10X2	12.3	22	V-2	Yes	60.1
APP15T10X4	13.8	22	V-2	Yes	56.5

<sup>a</sup> APP represents APP, T represents TEOS, and X represents the water-crosslinking time, the units of number after APP, T and X are wt%, wt% and h, respectively.

<sup>b</sup> Total duration (five specimens) of flaming combustion.

<sup>c</sup> Yes/no corresponds to the first and second flame applications.

composites. A longer water-crosslinking time enhanced the flame retardancy of the composites.

Furthermore, the UL-94 test was conducted to quantify and rank the flame retardancy of the composites. Table III shows that the composites could be placed in the UL-94 V-0 class (no dripping) when the APP concentration was greater than 15 wt %. The composites that contained TEOS could be classified as UL-94 V-2 grade, as shown in Table IV. When the water-crosslinking reaction was applied, the flame retardancy of the composites could be improved even with an APP concentration of 15 wt %. Table V shows that the 15 wt % APP composites with 1 phr TEOS could be classified as UL-94 V-0 (no dripping) grade after treatment with the water-crosslinking reaction. During the water-crosslinking reaction, the molecular structure was modified and turned into a network structure, and this suggested that the dripping characteristics of the samples could be reduced during the flame retardancy test. Table V shows that the gel content of the composites increased as the water-crosslinking time increased. These results agreed with the flame retardancy and nondripping properties of the composites.

### Thermal degradation properties

Figure 5 shows the TGA curves of pristine PBS and APP/PBS composites. Thermal analysis of the water-crosslinked composites indicated that the thermal degradation temperature of the composites increased with increasing water-crosslinking time. The thermal degradation temperature of maximum weight loss for pristine PBS and APP/PBS composites (after a 4-h water-

crosslinking reaction) were 429 and 384°C, respectively. The thermal stability of the APP/PBS composites was not superior to that of pristine PBS; however, the char yield of the APP/PBS composites was higher than that of pristine PBS at 500°C. This phenomenon revealed that the APP/PBS composites possessed better thermal stability during the high-temperature period. The char yield of pristine PBS was 0.76 wt %, and that of the APP/PBS composites was 9.71 wt % at 800°C. This behavior characterized all phosphorylated polymers and may have been due to the low degree of polymerization and the easy thermal degradation of the phos-

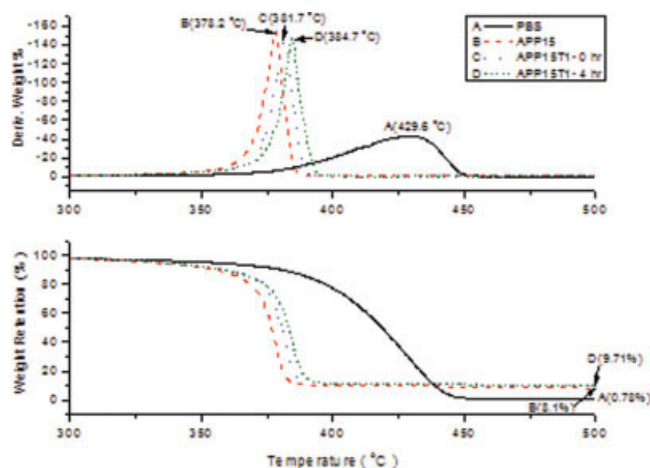
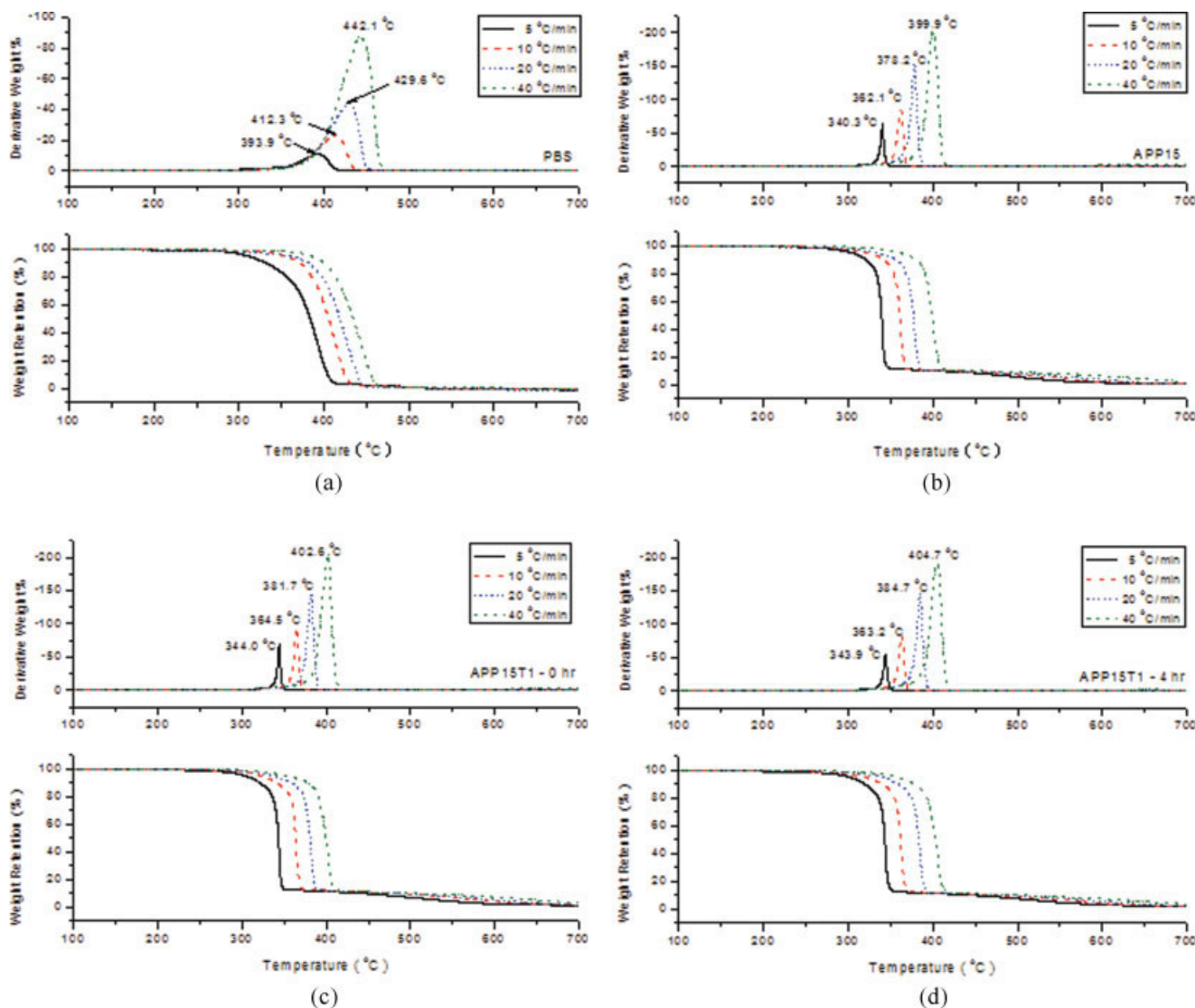


Figure 5 Comparison of the TGA curves of APP/PBS composites with various water-crosslinking times (in the sample names, APP represents APP, and T represents TEOS). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]





**Figure 6** TGA curves of (a) pristine PBS at various heating rates, (b) 15 wt % APP/PBS, (c) 15 wt % APP/PBS composites (without a water-crosslinking reaction) at various heating rates, and (d) 15 wt % APP/PBS composites (with a 4-h water-crosslinking reaction) at various heating rates (in the sample names, APP represents APP, and T represents TEOS). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

phorus segment.<sup>31</sup> Typical bond energies of P–C, C–C, C–O, and C–H are 260, 349, 286, and 370 kJ/mol, respectively.<sup>32,33</sup> The bonding of phosphorous and carbon (P–C) is susceptible to chain scission during thermal degradation and acts as a weak link.<sup>34,35</sup> Flame resistance can be evaluated from residual char upon pyrolysis. A linear relationship between the LOI value and char residue for halogen-free polymers was established by Kreylen.<sup>36</sup> Increasing char formation can limit the production of combustible carbon-containing gases, reduce the exothermicity due to pyrolysis reactions, and reduce the thermal conductivity of the surface of burning materials.<sup>37</sup> A higher char yield will enhance the flame retardancy. The LOI of the APP/PBS composites was 37. This indicated that the APP/PBS composites possessed better flame retardancy.

**Activation energy calculations**

One can apply the PerkinElmer standard program to obtain the characteristics of the TGA curves, as shown in Figure 6. The kinetic parameters are listed in Table VI.

**TABLE VI**  
**Activation Energy of Thermal Degradation for PBS and Flame-Retardant-Containing PBS Samples by Kissinger’s Method**

Sample <sup>a</sup>	PBS	APP15	APP15T1X0	APP15T1X4
Activation energy (kJ/mol)	156.8	110.9	117.5	107.4

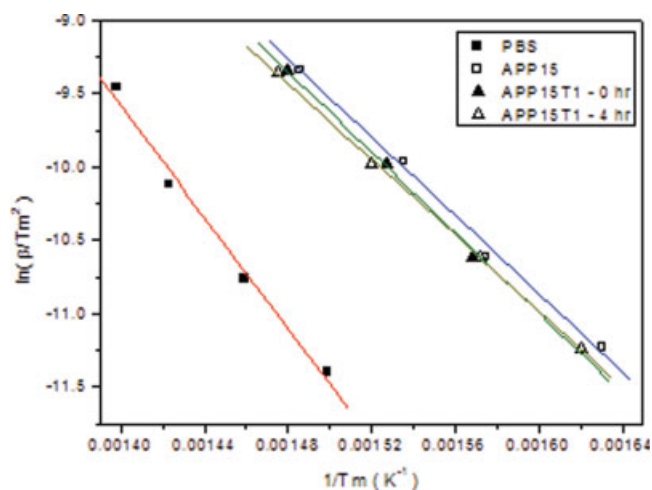
<sup>a</sup> APP represents APP, T represents TEOS, and X represents the water-crosslinking time (h).

Kissinger's method<sup>38</sup> involves the maximum temperature ( $T_m$ ) values of the first-derivative weight-loss curves. Therefore, eq. (1) was differentiated to the temperature, and the resulting expression was set to zero. With some rearrangements and heating rate  $\beta$ , the following expression was derived:

$$\frac{d[\ln(\beta/T_m^2)]}{d(1/T_m)} = \frac{-E}{R} \quad (1)$$

where  $E$  is activation energy and  $R$  is gas constant. Therefore, the activation energy could be determined from a plot of  $\ln(\beta/T_m^2)$  versus  $(1/T_m)$ . Figure 7 show Kissinger's plots of pristine PBS and APP/PBS composite degradation in an air atmosphere. Each straight line corresponds to a degradation stage of pristine PBS and APP/PBS composites. Table VI summarizes the activation energies of thermal degradation for pristine PBS and APP/PBS composites by Kissinger's method. The activation energy of thermal degradation calculated from the slopes was 158.6 kJ/mol for pristine PBS. The activation energy of thermal degradation calculated from the slopes was 110.9 kJ/mol for 15 wt % APP/PBS composites. The activation energies of thermal degradation for 15 wt % APP/PBS nanocomposites were less than those of thermal degradation for pristine PBS. This phenomenon indicated an important role in improving the flame retardancy of the composite. Although the resin was burning, the phosphorus-containing groups decomposed first and then formed a phosphorus-rich residue that prevented further decomposition of PBS.

After the addition of TEOS to the 15 wt % APP/PBS composite, the activation energy of thermal degradation increased to 117.5 kJ/mol because TEOS had better thermal degradation stability than APP. When the



**Figure 7** Plot of  $\ln(\beta/T_m^2)$  versus  $1/T_m$  (in the sample names, APP represents APP, and T represents TEOS). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

4-h water-crosslinking reaction was performed, the activation energy of thermal degradation was reduced to 107.4 kJ/mol. That might be the aggregation of APP after the water-crosslinking reaction increasing the degradation rate of APP, which reduced the activation energy of thermal degradation of the APP/PBS composites.

## CONCLUSIONS

APP/PBS composites were prepared successfully. All the mechanical properties slightly improved in the presence of APP, except for the flexural modulus, which showed a promising increase. After the water-crosslinking reaction, the thermal stability and flame-retardant properties of the composites were enhanced, and the nondripping behavior of the composites was improved significantly. The LOI values of 15 wt % APP composites ranged from 24 to 28 after a hot-water treatment for 4 h, and the flame retardancy was classified from UL-94 V-2 to UL-94 V-0. The activation energy of thermal degradation of 15 wt % APP/PBS composites was reduced from 117.5 to 107.4 kJ/mol after a 4-h water-crosslinking reaction. The water-crosslinking reaction could limit the crystallization rate of the composites and, moreover, increase  $T_g$  of the APP/PBS composites from  $-32.7$  to  $-23.1^\circ\text{C}$  (after a 4-h water-crosslinking reaction).

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