Effects of Expandable Graphite and Ammonium Polyphosphate on the Flame-Retardant and Mechanical Properties of Rigid Polyurethane Foams

Xian-Yan Meng,[1] Ling Ye,[2] Xiao-Guang Zhang,[1] Pei-Mei Tang,[1] Jian-Hua Tang,[1] Xu Ji,[1] Zhong-Ming Li[2]

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

ABSTRACT: In this work, the effect of expandable graphite (EG) and ammonium polyphosphate (APP) on the flame retardancy and mechanical properties of the rigid polyurethane foam (RPUF) was studied. The results indicated that both EG and APP could effectively improve the flame retardancy of RPUF, while the retardancy of EG was better than APP. When the flame-retardant loading was 15 wt %, the limited oxygen index (LOI) values of APP- and EG-filled RPUF were 24.5 and 32 vol %, respectively. According to the LOI test , the optimal ratio of APP to EG in RPUF composites was 1 : 1 by weight, at which the LOI value of 15 wt % (APP + EG)/RPUF was 30.5 vol %. Thermal degradation test of RPUF composites by thermogravimetric analysis indicated that the addition of APP and EG to RPUF could lead to an increase in the amount of high-temperature residue. Under the same conditions, the residue amount of EG/RPUF was less than that of APP/RPUF at the same temperature. Compression test and dynamic thermal mechanical analysis indicated that both the compressive strength and modulus decreased at a certain extent with the EG- or APP-filled into RPUF, respectively, but with the mixture of EG and APP added into RPUF, the mechanical properties of these materials increased. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 853–863, 2009

Key words: polyurethane foam; ammonium polyphosphate; expandable graphite; flame retardance

INTRODUCTION

Polyurethanes (PU) form a very wide family of polymeric materials, such as paint, adhesive, elastomer, flexible, and rigid foam. Foams, either flexible or rigid, are the most common commercial products and play an important and an increasing role in our daily life.[1–3] Especially, the rigid polyurethane foam (RPUF) is extensively used as an excellent encapsulant to isolate and support thermal-sensed components in many systems with good physical and mechanical properties.[2,4] Unfortunately, like the majority of organic materials, RPUF is combustible, consequently, their use is particularly limited.[5,6] So, nowadays, more and more attention has been paid to improve its flame-retardant properties.

Usually, a major method to interdict the burning of polymers is adding flame retardant. In particular, intumescent additives exhibit high efficiency in polymeric materials.[7,8] Intumescence is a process in which, in a fire, a suitable combination of various components generates a cellular charred layer on the surface of the material that protects the underlying material from the action of the heat flux or flame and acts as a physical barrier limiting the diffusion of combustible volatile products toward the flame and oxygen toward the polymer.[6] Ammonium polyphosphate (APP) is an effective intumescent fire retardant for several kinds of polymer-based materials,[9,10] and in particular, for PU.[5] Phosphorus-containing compounds are involved in altering the pathway of the thermal degradation of the substrate by promoting solid-state reaction leading to carbonization, and their vapor-phase activity is also reported.[5,11] The efficiency of APP is generally attributed to increase in the char formation through a condensable-phase reaction.[6,12]

Expandable graphite (EG) is another typical of the intumescent flame retardant, which is an intrinsical graphite intercalation compound. It is a layered crystal consisting of sheets of carbon atoms tightly bound to each other. Chemicals such as sulphuric acid may be inserted between the carbon layers.

TABLE I
Specifications of the Materials

Materials	Specifications
Isocyanate (PAPI)	N200, provided by Changfeng Chemical Co. (Chongqing, China). Main properties: Isocyanate equivalent weight, 126.5 g; NCO wt %, 31.8%; viscosity (25°C), 215 cps; functionality, 2.2
Polyester polyol	GR-4110G, prepared by polypropylene oxide and sucrose/glycerin, obtained from Gaoqiao Petro. Co. (Shanghai, China). Main properties: density (25°C), 1.1 g/cm³; typical hydroxyl number, 430 mg potassium hydroxide (KOH) equiv/g; viscosity (25°C), 3.283cps; functionality, 4.1; average molecular weight, 550 g/mol
Triethanoladiamine	Crosslinked catalyst, provided by Shanghai Chemical Reagent Co. (Shanghai, China); density, 1.122 g/cm³
Dibutyl tin dilaurate	Catalyst for the prolongation of molecular chains.Main properties: density, 1.052 g/mol; Sn content, 18 wt %; provided by Sichuan Chemical Reagent Co. (Chengdu, China)
Silione glycol copolymer	Surfactant
Distilled water	Blowing agent
APP	Flame retardant, obtained from Tongli Additive Co. (Chengdu, China). Main properties: degree of polymerization, 80; PH value (1% aqueous solution), 6.5–7.0
EG	Flame retardant, obtained from Haida Graphite Co. (Qingdao, China). Main properties : ash, 1.0%; moisture, 1.0%; volatile, 15%; PH value, 3.0; particlesize, 80%; expansion rate, 200 mL/g

When exposed to heat, EG expands and generates a voluminous insulative layer thus providing fire-retardant performance to the polymeric matrix.[1] EG is used in a growing number of fire-retardant applications as a blowing agent and as a smoke suppressor.[7,13] Its efficiency in PU has been reported in the literature.[14,15]

APP and EG can be used as intumescent flame retardants for RPUF.[1,6,16] We have also done some correlative work on EG as a flame retardant for RPUF.[2,3,17,18] We found that the flame retardancy of EG was very good, but meanwhile EG could deteriorate the mechanical properties of RPUF. In addition, according to our work, the combustion of EG/RPUF released heavy smoke. Therefore, APP and EG were filled into the RPUF system together, and its flame-retardant and mechanical properties were investi-

gated. The aim of this work was to study the effects of APP and EG, whether or not they can synergistically improve the flame-retardant and mechanical properties of RPUF. We prepared RPUF composites with different APP and EG contents by cast molding and characterized the flame-retardant properties of these foams through limiting oxygen index (LOI) test, horizontal–vertical burning test, and discussed the thermal stabilization of them through thermogravimetric analyses (TGA), etc.

EXPERIMENTAL

Materials

The raw materials used were polyester polyol, isocyanate (PAPI), triethanolamine, dibutyl tin dilaurate, distilled water, APP, and EG, whose details are listed in Table I.

Foam Preparation

One-step expanding foam technology was used to prepare the flame-retardant RPUF by cast molding, a standard laboratory mixing and pouring procedure was used for making foams.[15,16] All components except PAPI were mixed and stirred with an electric stirrer until a uniform mixture was obtained. Then, PAPI was added into the mixture while stirring. PAPI reacted with distilled water to generate polymer and carbon dioxide, of which carbon dioxide inflated the reactants. Then, the mixture was poured into a mold with a lid completely and quickly, when frothy bubbles formed, the mold was put into an oven and heated for 4 h at 100°C to increase the cross-link density and to make the reaction more sufficient. Finally, the foam was took out from the mold and the hard coat was removed. The samples for measurements were machined according to the standard of the test. EG- or APP-filled RPUF was prepared in the same way, and EG or APP was added into the polyester polyol before the other components.

In this work, the density of the foams was controlled to approximately 0.08 ± 0.01 g/cm³.

TABLE II
Parameters of Flame-Retardant RPUF

Materials	Parts by Weight (pbw)
Polyester polyol	100
Isocyanate (PAPI)	180
Dibutyl tin dilaurate	0.1
Triethanoladiamine	0.1
Silione glycol copolymer	0.5
Water	3.5
Fire retardant	5–20
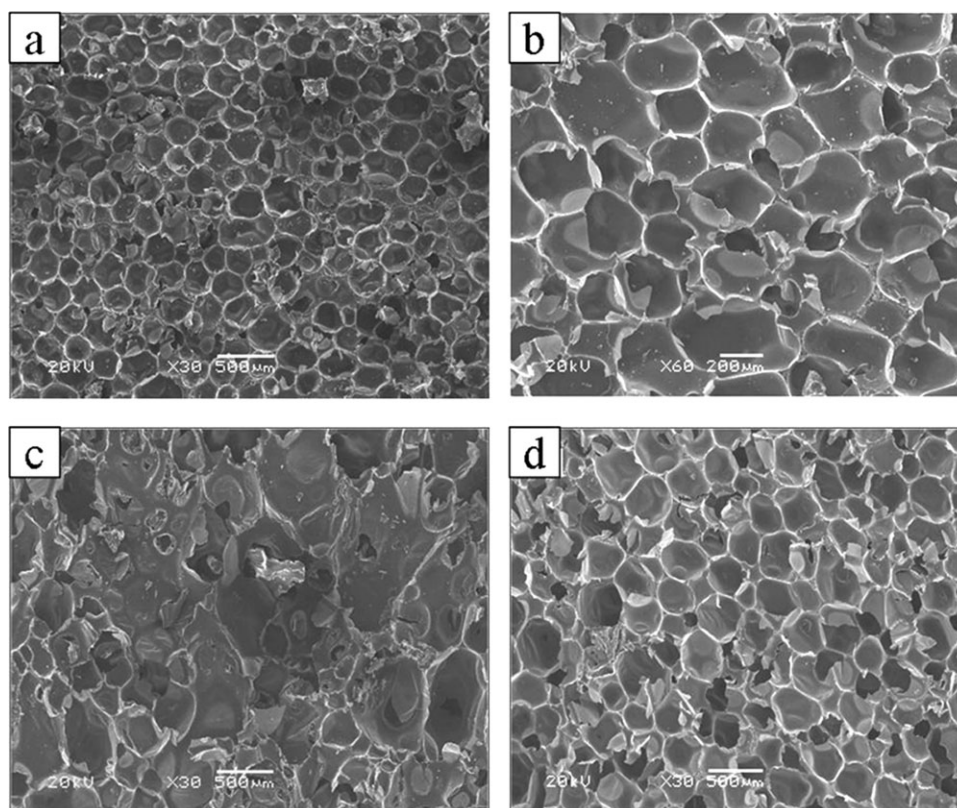
Figure 1 SEM micrographs of the pure RPUF and fire-retardants filled RPUF. (a) Pure RPUF; (b) 15 wt % APP/RPUF; (c) 15 wt % EG/RPUF; (d) 15 wt % (EG + APP)/RPUF, EG : APP = 1 : 1.

Formulations and technical parameters of flame-retardant RPUF were shown in Table II.

Characterization

LOI test

LOI (standard test method for measuring the minimum oxygen concentration to support candle-like combustion of plastics) was measured with an HC-2 oxygen index test instrument (made in Jiangning Company, China) on sheets $130 \times 10 \times 10$ mm^3 according to the standard "oxygen index" test ASTMD 2863-97.

Horizontal and vertical burning test

Horizontal and vertical burning tests were performed with a CTF-2 horizontal and vertical burning instrument (Jiangning County, China) on sheets of size $130 \times 15 \times 10$ mm^3 according to the standard vertical burning test ASTM D 3801-96 and horizontal burning test ASTMD 635-98.

Thermogravimetric analyses

TGA were carried out at 10°C/min under air (flow rate : 50 mL/min) with a SEIKO EXSTAR6000 thermogravimetric analyzer. In each case, the mass of the used sample powder was 7 to 10 mg, and the samples were heated from 50 to 800°C.

Dynamic thermal mechanical analysis

Dynamic mechanical measurements were taken on a Du Pont 983 dynamic thermal mechanical analysis (DMA) unit at a frequency of 1 Hz, ranging in temperatures from 50 to 250°C at a heating rate of about 5°C/min.The sample size was approximately $40 \times 10 \times 4$ mm^3.

Compression test

Compression test was carried out with an AGS-J all-purpose material test instrument (Shimaduz, Japan) on columns of size $\Phi 50 \times 50$ mm^3 according to the standard ASTMD1621-94. The rate of compression was 2 mm/min.

Scanning electron microscopy

Scanning electron microscopy (SEM) was performed with a JSM-9600 (JEOL Japan) SEM with an accelerating voltage of 20 kV. The samples were obtained by impacting into fractures at a room temperature, including original and burned samples.

TABLE III
Vertical Burning Tests Formulations

No.	Name/formula	Wt %	t (s)	V-Rating
1			–	–
2	APP	5	–	–
3	APP	10	–	–
4	APP	15	–	–
5	APP	20	–	–
6	EG	5	–	–
7	EG	10	6.3	V-0
8	EG	15	5.1	V-0
9	EG	20	1.9	V-0
10	APP : EG = 3 : 1	APP + EG = 15	2.1	V-0
11	APP : EG = 2 : 1	APP + EG = 15	2.7	V-0
12	APP : EG = 1 : 1	APP + EG = 15	1.9	V-0
13	APP : EG = 1 : 2	APP + EG = 15	1.8	V-0
14	APP : EG = 1 : 3	APP + EG = 15	2.9	V-0

t, average after-flame time after the first and second flame impingements;
V-Rating, rating of vertical burning tests.

RESULTS AND DISCUSSION

Morphology of RPUF composites

Figure 1 shows the SEM micrographs of the pure RPUF, EG- and APP-filled RPUF. As observed in Figure 1(a), the cell shape of the pure RPUF is closed cellular polyhedron, no collapse or collision in the cell system is observed except the damage during machining the samples, and the unfilled RPUF is a homogeneous integrality.

Figure 1(b–d) presents SEM micrographs of 15 wt % APP/RPUF, 15 wt % EG/RPUF and 15 wt % (APP + EG)/RPUF composites, respectively. Comparing (a) with (b), we can discover that the addition of APP does not change the homogeneous integrality of APP/RPUF, which may be because the APP particles are small, and most of the particles are in the cell wall or backbone of polymeric matrix. From Figure 1(c), we can see that the appearance of EG damages the RPUF matrix to a certain extent. The cell size of EG/RPUF becomes large and irregular shape compared with the pure RPUF with EG/RPUF. The addition of EG results in a viscosity increase and the increased viscosity makes it more difficult to disperse the graphite flakes. The EG agglomerates and the comparatively big flakes will destroy the closed regular cellular polyhedron.

Figures 1(d) shows the micrograph of the RPUF filled with APP and EG with a weight, ratio of 1 : 1. This micrograph is quite different from the EG/RPUF. The cell shape of the (APP + EG)/RPUF is also closed cellular polyhedron, and there is no collapse or collision in the cell system basically. Namely, with the same weight of fire retardants, adding the APP and EG mixture into RPUF can reduce the influence on the frame of the RPUF composite. This result can be explained as follows: the

spherical APP particles substitute for a part of EG flakes, thus reducing the breakage of closed regular cell; the APP isolates the graphite flakes at a certain extent, which can also reduce the breakage of cell.

Flammability properties

The flammability properties of composite RPUF are analyzed by horizontal–vertical burning tests and the LOI. The results of the horizontal–vertical burning tests of RPUF composites are presented in Tables III and IV.

In the vertical burning test, the pure RPUF, APP/RPUF, and 5 wt % EG/RPUF burn fast, even the flame reaches the clamp, and thus resulting in failure of classification. Table III shows the average after-flame time of the samples. For EG/RPUF, when the content of EG increases from 10 to 20 wt %, the average after-flame time decreases from 6.3 to 1.9 s. The after-flame time is less than 10 s, which means that the composite with more than 10 wt % EG reaches *V-0* rating. These results prove that EG can efficiently reduce the burning time of RPUF. Although the APP/RPUF composites cannot be classified by the vertical burning test, the addition of APP makes the average burning time of 15 wt % (EG + APP)/RPUF samples less than that of 15 wt % EG/RPUF. And the composite with EG and APP mixture can pass the vertical burning test of *V-0* rating at the ratio of APP and EG used in this work. Therefore, APP and EG presents a favorable flame-retardant synergistic effect.

As shown in Table IV, the burning rate of pure RPUF is 363 mm/min, and that of 5 wt % APP/RPUF and 10 wt % APP/RPUF decreases to 219 and 151 mm/min, respectively, indicating that with the increase of APP content, the burning rate reduces gradually. And the other additives filled RPUFs

TABLE IV
Horizontal Burning Tests Formulations

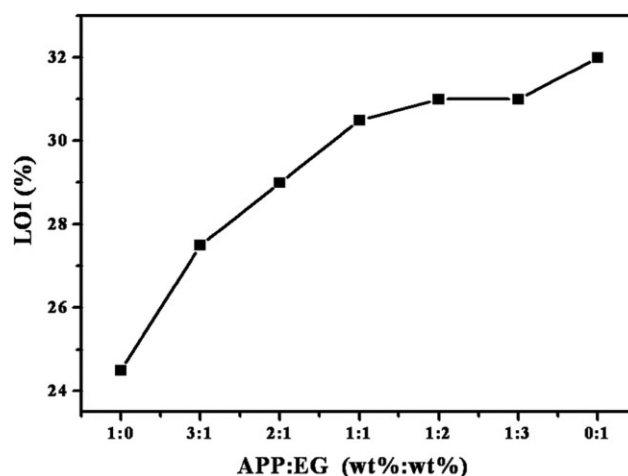| No.	Name/formula	Wt %	H-Rating
1			HB-4-363 mm/min
2	APP	5	HB-4-219 mm/min
3	APP	10	HB-4-151 mm/min
4	APP	15	HB-1
5	APP	20	HB-1
6	EG	5	HB-1
7	EG	10	HB-1
8	EG	15	HB-1
9	EG	20	HB-1
10	APP : EG = 3 : 1	APP + EG = 15	HB-1
11	APP : EG = 2 : 1	APP + EG = 15	HB-1
12	APP : EG = 1 : 1	APP + EG = 15	HB-1
13	APP : EG = 1 : 2	APP + EG = 15	HB-1
14	APP : EG = 1 : 3	APP + EG = 15	HB-1

H-Rating, rating of horizontal burning tests.
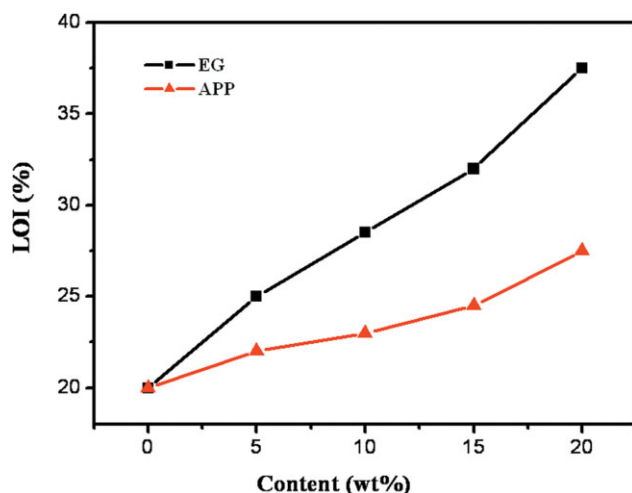
Figure 2 LOI curves of EG/RPUF and APP/RPUF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 3 LOI curves of 15 wt % (EG + APP)/RPUF.

burn slowly and are extinguished fast to reach *HB-1* rating. Although the horizontal burning tests are implemented, most RPUF composites are the same ratings, consequently, the LOI tests are maked out to further study. The LOI values can describe a procedure for measuring the minimum concentration of oxygen that will just support flaming combustion in a flowing mixture of oxygen and nitrogen.

Figure 2 shows the results of the LOI burning tests of APP/RPUF and EG/RPUF. The curve of the LOI versus EG content shows that the LOI value increases with the EG content. When the EG content is 20 wt %, the LOI value increases to 37.5 vol %. Commonly, the material whose LOI value is less than 21 vol % is flammable; between 22 and 25 vol % quenches automatically; more than 26 vol % burns difficultly. As presented in Figure 2, although the LOI values of the APP/RPUF composites are lesser than those of the EG/RPUF composites, they are still enhanced with increasing APP content, and the LOI value of the composite containing 20 wt % APP can reaches 27.5 vol %.

Figure 3 shows the results of the LOI tests of 15 wt % (APP + EG)/RPUF. The EG and APP mixture content of RPUF composites remains 15 wt %, and the ratios of APP and EG are 3 : 1, 2 : 1, 1 : 1, 1 : 2 and 1 : 3, respectively. The LOI value of the 15 wt % APP/RPUF is only 24.5 vol %, whereas the 15 wt % EG/RPUF increases to 32 vol %. In Figure 3, we can see that all the LOI values of the 15 wt % (APP + EG)/RPUF are more than 24.5 vol % and lesser than 32 vol %, and increase along with EG content, indicating that EG can more effectively improve the flame-retardant property of RPUF than APP.

To research the mutual influences of APP and EG on the flame retardancy of RPUFs, we define ΔLOI as the differences between the experimental LOI (LOI_a) and theoretical LOI (LOI_b). The ΔLOI curve shows an eventual increase or decrease in the LOI values of the composites.

LOI_b can be computed by linear combination between the data of EG and APP according to eq. (1):

$$LOI_b = \sum \% i \times LOI_i \qquad (1)$$

where % i is the weight percentage of material i in the initial material and LOI_i is the LOI value of 15 wt % i/RPUF. If ΔLOI > 0, there is a synergistic effect between the additives APP and EG and if ΔLOI < 0, there is an antagonistic effect between the additives APP and EG. The effects of the additives APP and EG on the LOI values are shown according to the curve ΔLOI (Fig. 4). From the data listed in Figure 4, it is clear that the ΔLOI values are higher than zero, which proves that EG and APP have a synergistic effect on flame retardancy of RPUF. And
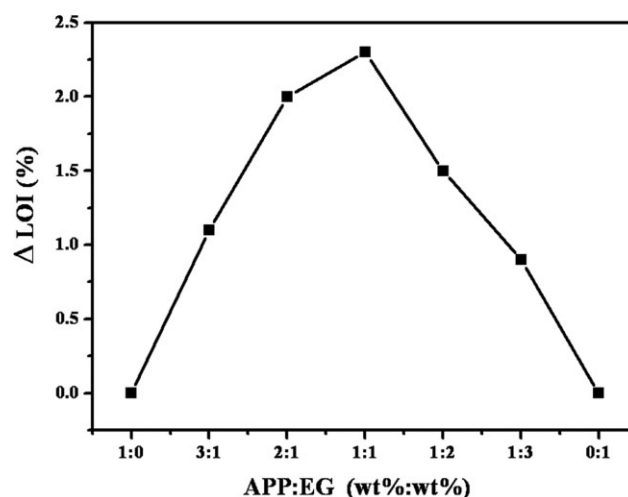
Figure 4 ΔLOI curves of 15 wt % (EG + APP)/RPUF.
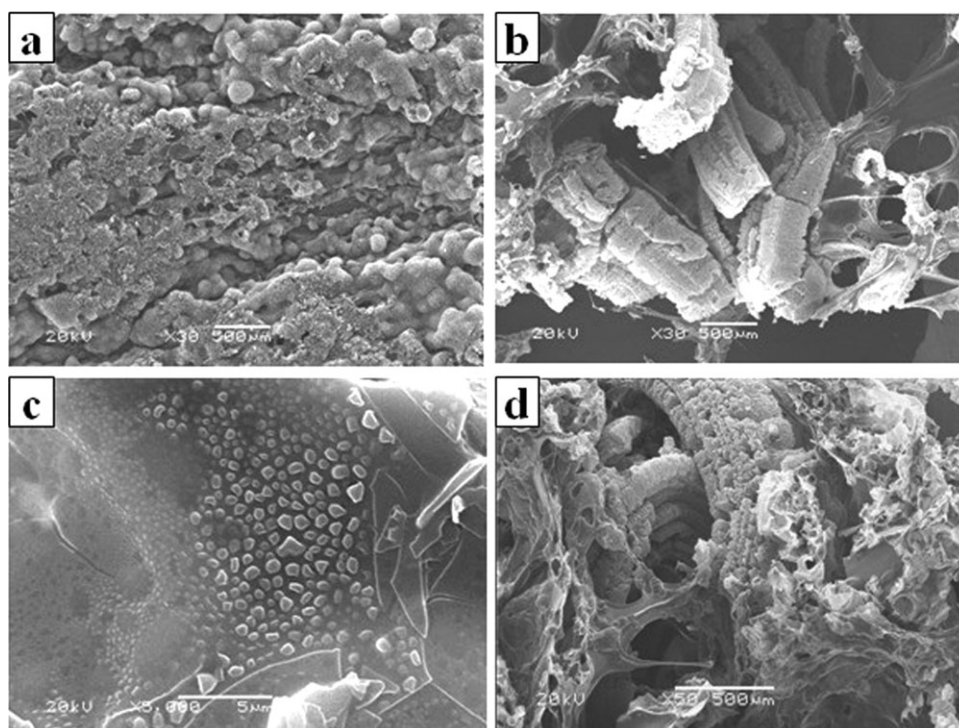
Figure 5 SEM micrograph of burned fire-retardants filled RPUF. (a) Pure RPUF; (b) 15 wt % EG/RPUF; (c) 15 wt % APP/RPUF; (d) 15 wt % (EG + APP)/RPUF, EG : APP = 1 : 1.

from the ΔLOI curve, we can see that the ΔLOI values increase first and then decrease, and attain the maximum when the percentage of EG is 50 wt %. The results show that APP and EG used together in RPUF does have good flame retardancy. When the ratio of APP : EG is 1 : 1, the synergistic effects seem the best.

There may be two reasons for the increase in the LOI value of the composite containing APP and EG. First, compared with the composite containing APP or EG only, The dispersion of the additive particles in the RPUF matrix is improved. And, the EG slices act as the blowing agent for APP in the intumescent flame-retardant system compared with APP/RPUF.

During the LOI test, the residues of pure RPUF are little after combustion, but the RPUF with 15 wt % APP or 15 wt % EG remains more. It suggests that a protective intumescent carbonaceous char is formed on the surface of the material. Figure 5 shows the images of the burned layer of samples after burning. Comparing (b) with (d) (Fig. 5), we can see that the expansion layers of 15 wt % EG/ RPUF are loose and lacunaris, whereas the layers of 15 wt % (EG + APP)/RPUF are compact. The compact layers may be developed by the worm-like structure of the graphite expansion agglutinated by the high-viscosity products of depolycondensation reaction, which is the other main reason for the increase in the LOI value possibly.

Thermal stability

For better understanding of the flame retardancy, the thermal decomposition behavior of the mixtures was studied through TGA.

Figure 6 shows the thermogravimetric (TG) curves of pure RPUF, 15 wt % APP/RPUF, 15 wt %EG/ RPUF, and 15 wt % (APP + EG)/RPUF under air. All samples show the two-step degradation. In
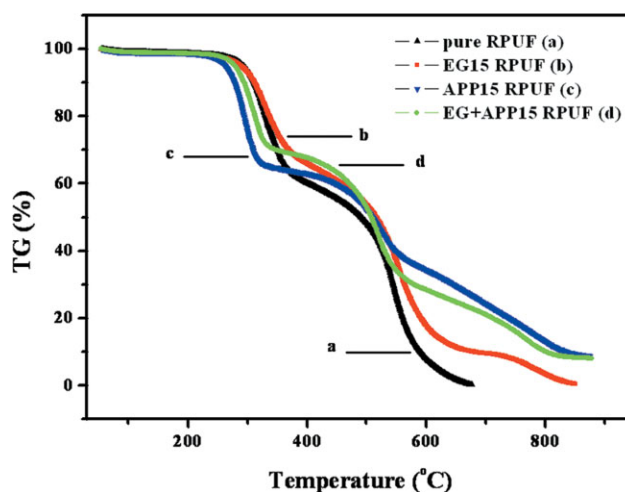
Figure 6 TG curves of pure RPUF and fire-retardants filled RPUF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
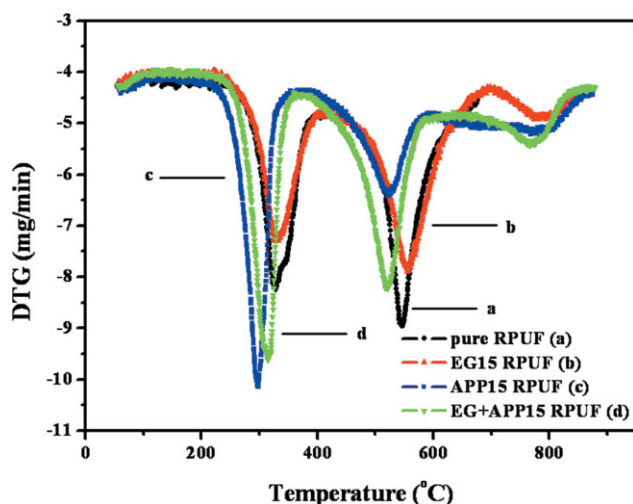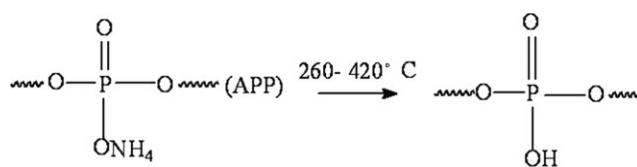
Figure 7 DTG curves of pure RPUF and fire-retardants filled RPUF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

regard to pure RPUF, the first step of degradation between 250 and 440°C attributes to the depolycondensation reaction.[19] The second step of degradation between 440 and 676°C leads to 0 wt % residues. The maximal rate of weight loss for two-step degradation is at 328 and 547°C according to the DTG curves (Fig. 7).

The two degradation steps of 15 wt % EG/RPUF were previously reported in the literature.[2,19] The first one occurs from about 230 to 450°C with a peak at 331°C corresponding to the expansion of EG. And the second appears at about 440°C with a peak at 560°C. The residue of 15 wt % EG/RPUF is always higher than pure RPUF from 230 to 850°C and the residue of degradation for pure RPUF leads to 0 wt % at 670°C and 15 wt % EG/RPUF is about 850°C. The second step is assigned to the thermooxidative degradation of the transient char that yields high-temperature residues. Within the high-temperature range, the astable and thick expanded layer is formed, it can act as the thermal insulative barrier between the flame and the virgin material, which proves that EG leads to the formation of a thermally stable material for RPUF.

The degradation of 15 wt % APP/RPUF is also composed of two steps. The first step begins at about 160°C with the weight loss of 1 wt %. In the presence of APP, the degradation of 15 wt %APP/ RPUF begins at a lower temperature than that of pure RPUF, which suggests that RPUF and APP react first.[6] The evolution products of APP at this step are mainly ammonia and water, and at the same time crosslinked polyphosphoric acids (PPA) are formed simultaneously (Scheme 1).[6,12] Then, an acceleration in the depolycondensation reaction takes place due to the acid catalysis by the phos-

phoric acid as shown in Scheme 2,[6,20] whereas the second step begins at about 500°C higher than pure RPUF. The temperature of the maximum mass loss rate (T_{max}) for the two steps is 297 and 527°C according to the DTG curves (Fig. 7). Within the high-temperature range, the amount of residue remains almost constant and equals to 8.7 wt %, higher than 0 wt % for the residue of pure RPUF degradation. All the above results indicate that the addition of APP to RPUF decreases the thermal stability of RPUF at the first stage and increases the thermal stability at the second stage. Therefore, the thermal degradation of RPUF may take place as follows: at the first stage, APP interacts with RPUF, leading to generation of volatile compounds and a phosphorus rich layer, which could protect the polymer matrix under heat, and then the protective layer would decompose to yield a compact char on the surface of the material to protect the polymer matrix effectively at the second stage.

Compared with the thermogravimetric curves of 15 wt % APP/RPUF, 15 wt % EG/RPUF and 15 wt % (APP + EG)/RPUF under air, the TG curve of 15 wt % (APP + EG)/RPUF lies between 15 wt % EG/ RPUF and 15 wt % APP/RPUF basically. The 15 wt % (APP + EG)/RPUF shows a two-step degradation. The first one occurs with a peak at about 200°C, whereas the second step at a temperature higher than 390°C with a peak at about 526°C. Within the high-temperature range, the amount of residue remains almost constant. From 550 to 850°C, the amount of residue is always higher than 15 wt %

Scheme 1 The thermal degradation of APP under 260–420°C.
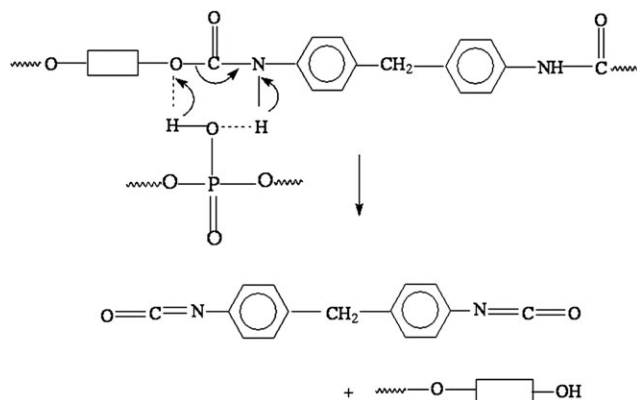
Scheme 2 Catalytic action of phosphoric acid on depolycondensation reaction.
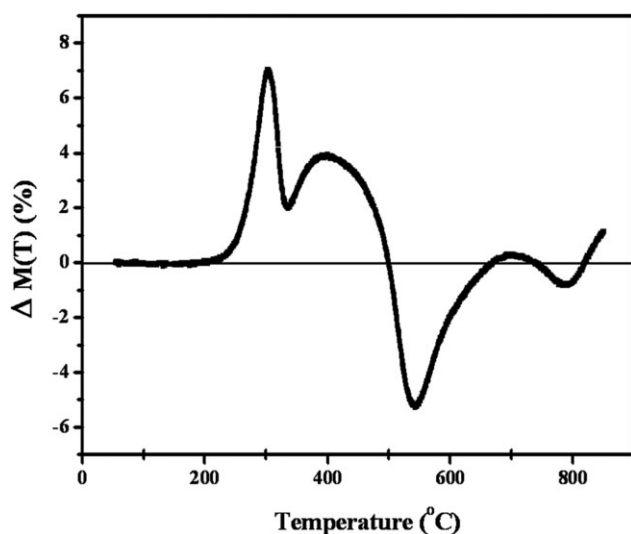
Figure 8 $\Delta M(T)$ curve of the 15 wt % (APP + EG)/RPUF, APP : EG = 1 : 1.

EG/RPUF and lower than 15 wt % APP/RPUF. And at about 850°C, the amount of residue approaches APP/RPUF. This suggests that the effect of mixture of APP and EG on the formation of a thermally stable material is better than EG.

To further assess the thermal decomposition of the polymer in the presence of EG and APP, the weight differences between the experimental and theoretical TG curves are obtained by combining TG data of 15 wt % APP/RPUF and 15 wt % EG/RPUF. The curves of the weight differences between the experimental and theoretical TG curves are computed according to eq. (2):

$$\Delta M(T) = M_{exp}(T) - M_{the}(T) \qquad (2)$$

where $M_{exp}(T)$ is from experimental TG curve of 15 wt % (APP + EG)/RPUF at, EG : APP = 1 : 1, $M_{the}(T)$ is from TG curve computed by linear combination between the TG curves of EG/RPUF and APP/RPUF as follows:

$$M_{the}(T) = \sum \% \, i \times M_i(T) \qquad (3)$$

where % i is the weight percentage of material i in the initial material and $M_i(T)$ is the residual weight of material i at temperature T. The $\Delta M(T)$ curve enables the observation of an eventual increase or decrease in the thermal stability of the polymer related to the presence of the additive. Synergistic effects are represented by a positive $\Delta M(T)$ value, and a negative $\Delta M(T)$ value represents antagonistic effects.[21]

The interaction of the EG and APP is shown in Figure 8 according to the curve $\Delta M(T)$. The different weight curve is positive from 200 to 500°C, which shows that there is a synergistic effect between APP

and EG. And the temperature range corresponds to the reaction between the polymer and APP. This result confirms the previous argument on the catalytic action of phosphoric acid on the degradation of RPUF (Scheme 2).

The reason for the positive interactions may be due to the phosphoric acid, which is produced by the expansion of APP. In the case of the 15 wt % EG/RPUF formulation, the expansion starts at 210°C, the maximum is 300°C and then slowly decreases between 300 and 500°C.[1] The worm-like structure developed by graphite expansion can act as a thermal insulative barrier for APP and the high-viscosity products of depolycondensation reaction can agglutinate graphite layers. All the above causes the positive interactions of APP and EG and can leads to more residual weight of material than theoretical.

From 500 to 820°C, the different weight curve is negative basically, which proves that there is an antagonistic effect between APP and EG. When the temperature is higher than 550°C, PPA evapor and/or dehydrate to P_4O_{10}.[6] At the same time, the worm-like structure of EG enlarges the interface between PPA and environment. So, the degradation is accelerated and the antagonistic effect appears.

When the temperature is higher than 820°C, the curve is positive. Within the high-temperature range, a stable and thick expanded layer is formed unceasingly. It can act as a thermal insulative barrier between the flame and the virgin material, which may explain the thermal stability of the material.
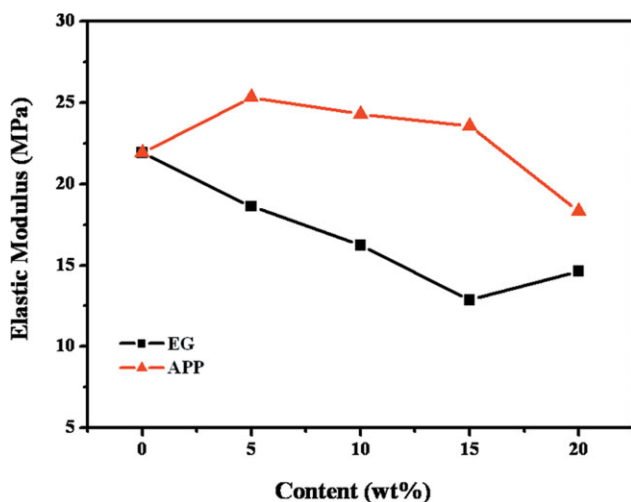
Compression properties

To verify the mechanical properties of the RPUF composite, the compressive strength and the
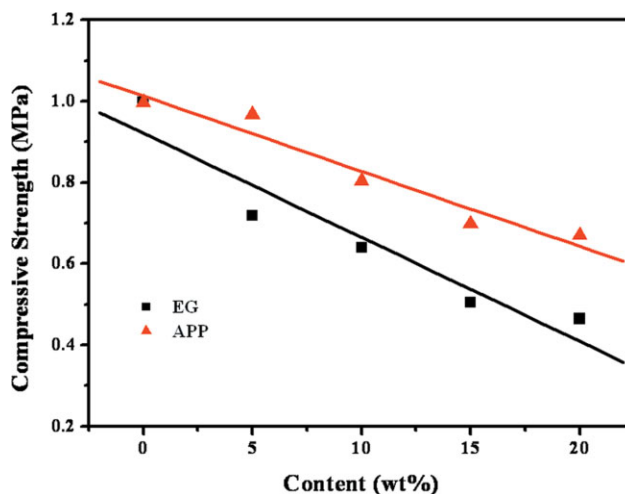
Figure 9 Effect of the flame retardants on the compressive strength of the RPUF composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 10 Effect of the flame retardants on the elastic modulus of the RPUF composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

compressive modulus of the composites were measured. Figures 9 and 10 show the results of the compression tests of pure RPUF and RPUF composites. It is known that the mechanical properties of materials depend mainly on their density.[3] In this experiment, the densities of the RPUF composites were set at 0.08 ± 0.01 g/cm^3 for each sample.

The compressive strength of a foam is the maximum compressive stress which the foam is capable of withstanding, based on the original area of the cross-section, for a short time at a fixed point in the compression-loading cycle. The samples were compressed parallel to the direction foam rises. Figure 9 shows the effect of the flame retardants on the compressive strength of the composite RPUF. As shown in Figure 9, the compressive strength of the RPUF composites decreases versus APP or EG content, and on the other hand, the compressive strength of APP/RPUF is higher than EG/RPUF.

Figure 10 shows the effect of the flame retardants on the elastic modulus of RPUF composites. For rigid foams, the definition of the elastic modulus is the maximum slope of the stress–strain curve. Its value is a hard index of a material. As shown in Figure 10, the elastic modulus of EG/RPUF always decreases versus EG content. But versus APP content, the elastic modulus of the APP/RPUF increases first and then decreases, and higher than EG/RPUF at the same content.

Figure 11 shows the compressive strength and elasticity modulus of 15 wt % (APP + EG)/RPUF. On the whole, the compressive strength and elastic modulus reduce versus EG content. The compressive modulus values of 15 wt % (APP + EG)/RPUF are higher than 15 wt % APP/RPUF when APP : EG =

2 : 1, 1 : 3. The compressive modulus values of 15 wt % EG/RPUF are lesser than 15 wt % (APP + EG)/RPUF except that APP : EG = 1 : 2. The elastic modulus of 15 wt % (APP + EG)/RPUF is higher than 15 wt % APP/RPUF when APP : EG = 1 : 3.

The different effects on mechanical properties could be explained by fire-retardant mechanism of APP and EG. The APP particles are smaller, but the EG particles are big slices. As shown in Figure 1, the appearance of EG damages the RPUF matrix to a certain extent, but APP does not. APP reacts with RPUF first (Scheme 2), which can produce high-viscosity products to agglutinate APP and RPUF. In addition, the asymmetrical dispersion of the additives and the poor interface performances of RPUF and fire retardants also reduce the mechanical properties. To synthesize a composite with good mechanical properties, a uniform dispersion of the additive is necessary.

Dynamic mechanical properties

The DMA is a widely used technique to examine the viscoelastic features of PU foams, which can provide the information about the viscoelastic properties like the energy dissipation of soft and hard materials.[22,23] The storage modulus (E'), loss modulus (E''), and loss factor (tan δ) curves obtained from the DMA measurement of RPUF composite are shown in Figures 12–14.

Figure 12 shows E' of the pure RPUF and RPUF composites with flame retardants. As shown in Figure 12, at around 150°C, the glass transition appears for the pure RPUF, EG/RPUF, (EG + APP)/RPUF, whereas, the glass transition of APP/RPUF appears at about 110°C. For 15 wt % APP/RPUF and EG/RPUF, the values of the storage modulus are the
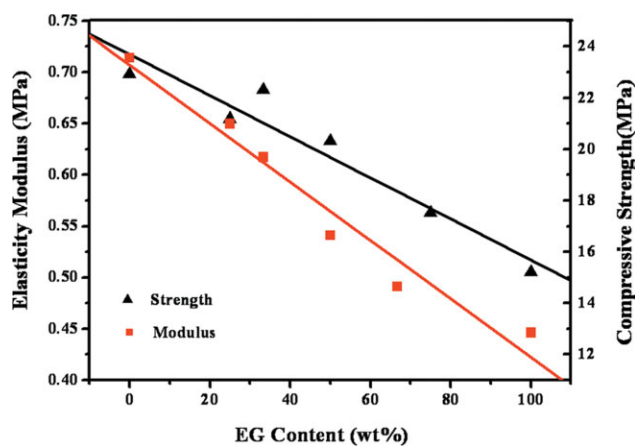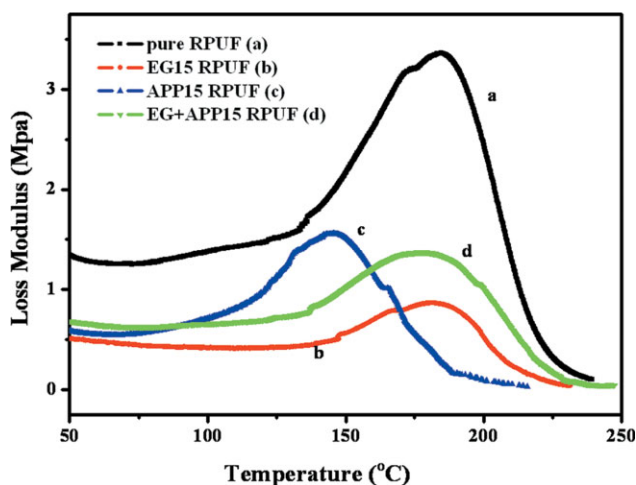

Figure 11 Compressive strength and elasticity modulus of 15 wt % (APP + EG)/RPUF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
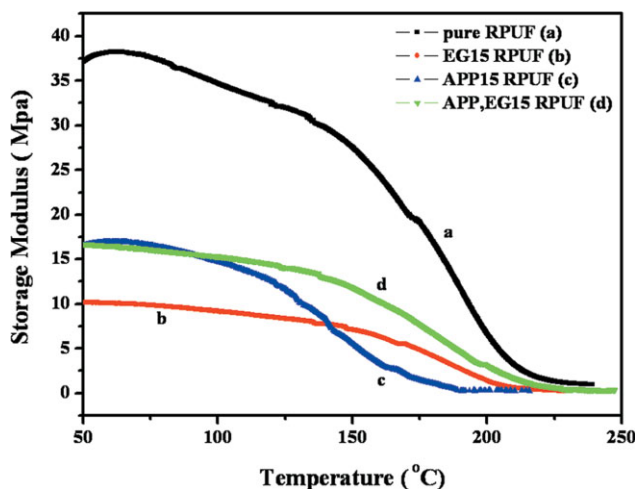
Figure 12 Effect of the flame retardants on the storage modulus of the composite RPUF. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

same when the temperature is about 140°C. The storage modulus values of 15 wt % APP/RPUF are higher than 15 wt % EG/RPUF below 140°C and lower than EG/RPUF when the temperature is over 140°C. From about 90°C, the storage modulus values of 15 wt % (APP + EG)/RPUF are always higher than EG/RPUF and APP/RPUF. The storage modulus of the pure RPUF and RPUF composites maintains a slow drop below the glass-transition temperature (T_g) and decreases sharply through the glass-transition process, which indicates that the material is going through a glass transition. Within the entire testing temperature rage, the E' of the RPUF composites is lower than the pure RPUF and that of

(APP + EG)/RPUF is higher than EG/RPUF and APP/RPUF.

Figure 13 shows the E'' versus the temperature for the pure RPUF and RPUF composites with flame retardants. E' of the RPUF composites is lower than the pure RPUF, and for 15 wt % APP/RPUF and EG/RPUF, the E'' is the same when the temperature is about 170°C. From about 160°C, the E'' of 15 wt % (APP + EG)/RPUF is always higher than that of EG/RPUF and APP/RPUF.

The glass-transition temperature (T_g) is an important indicator for applications of polymeric materials. The selection of the glass-transition temperature from the DMA data is usually either the peak E'' or tan δ and the glass-transition temperature is dependent on the frequency.[24] The peak tan δ is the most prevalent criterion appearing in the literature, because it corresponds more closely to the transition midpoint, whereas the peak E'' more closely denotes the initial drop from the glassy state into the transition.[25,26] So, the mechanical transition temperature of materials was measured by DMA at the maximum of tan δ, and can approximate to the T_g.

Figure 14 shows the shifted tan δ versus the temperature for the pure RPUF and RPUF composites with flame retardants. As shown in Figure 14, the T_g of the 15 wt % EG/RPUF and 15 wt % APP/RPUF decreases compared with that of pure RPUF, but the T_g of 15 wt % (APP + EG)/RPUF composites is higher than pure RPUF. From Figure 14, we can also see that the values of tan δ increases first and then decreases with the increasing temperature, which means that the increase in E' is slower than that in E'' when the temperature is smaller than T_g, but the case is reversed when the temperature is above T_g.
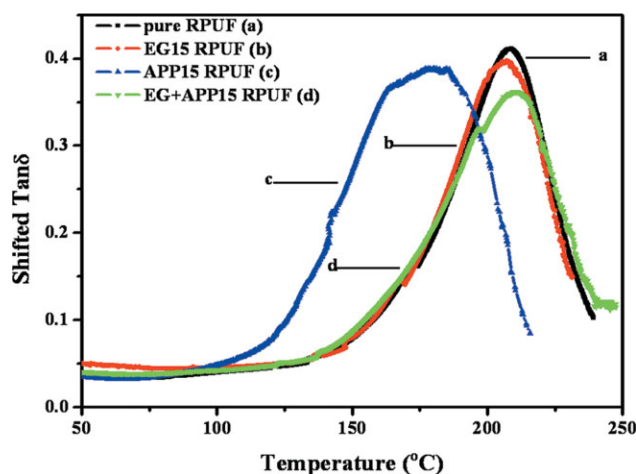

Figure 13 Effect of the flame retardants on the loss modulus of the composite RPUF. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

Figure 14 Effect of the flame retardants on the shifted tan δ of the composite RPUF. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

For pure RPUF and RPUF composites, the tan δ is the same when the temperature is about 190°C. The tan δ values of APP/RPUF are higher than pure RPUF, EG/RPUF, and (APP + EG)/RPUF when the temperature is below 140°C, and from 190 to 240°C, the tan δ of APP/RPUF, EG/RPUF, and (EG + APP)/RPUF is always higher than pure RPUF. The lower tan δ of the composite formulations clearly indicates that these formulations exhibit more elastic (spring-like) than the viscous (dashpot-like) nature as compared with pure RPUF. Above results of E', E'', and tan δ versus the temperature for the pure RPUF and RPUF composites imply that the addition of EG and APP together can enhance the dynamic mechanical property of RPUF at a certain extent.

CONCLUSIONS

In this work, the flame-retardant and the mechanical properties of APP- and EG-filled RPUF have been studied. The results indicated that both EG and APP could effectively interdict the burning of RPUF. When the flame-retardant loadings was 15 wt %, the LOI value of APP-filled RPUF was 24.5 vol %, whereas the EG-filled RPUF could reach 32 vol %. In contrast to APP or EG alone, the mixture of APP and EG was an efficient fire-retardant additive for RPUF. It increased the oxygen index and the rating of vertical and horizontal burning tests of RPUF composite. With the addition of APP and EG simultaneously into RPUF, the ratings of vertical and horizontal burning tests of RPUF composites increased obviously. When the flame-retardant loadings were 15 wt %, the rating of vertical RPUF composites was *V-0* and the rating of horizontal burning tests was *HB-1*. And according to the LOI test, when the ratio of APP to EG is 1 : 1, the value of ΔLOI reach maximum, namely, the optimal ratio of APP to EG in RPUF composites is 1 : 1. On the other hand, the addition of APP and EG to RPUF led to an increase in the amount of high-temperature residue, which acted as a protective thermal barrier during the fire-retardancy process. According to the compression tests, although the compressive strength and modulus decreased at a certain extent with the EG or APP filled into RPUF respectively, but with the mixture of EG and APP added into RPUF, the mechanical properties of these materials increased. Moreover, the dynamic properties of the RPUF composites with flame retardants are lower than pure RPUF. How-

ever, the RPUF adding the same content of APP and EG mixture shows higher dynamic properties. This result implies that the interaction of APP and EG improves the dynamic properties compared with APP or EG.

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