Flame Retardancy of Hollow Glass Microsphere/Rigid Polyurethane Foams in the Presence of Expandable Graphite

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ABSTRACT: Rigid polyurethane foams (RPUF) filled with various loadings of expandable graphite (EG) or/and hollow glass microspheres (HGM) were prepared by cast molding. The flame retardant properties of these composites were investigated by limiting oxygen index (LOI), horizontal and vertical burning tests. The composite with 10 wt % HGM and 20 wt % EG had the best flame retardant properties, and its LOI value reached 30 vol %. The addition of an appropriate loading of HGM improved the compressive strength and modulus of RPUF and EG/RPUF. When the HGM content arrived at 10 wt %, the compressive strength and modulus of the composites reached the maximum value. The dynamical mechanical analysis (DMA) showed that the addition of EG and HGM made the glass transition temperature shift to a higher temperature, and 10 wt % EG and 10 wt % HGM filled RPUF had the highest storage modulus. The scanning electronic microscope (SEM) observation indicates that the additives led to the decrease in the cell size. In addition, the flame retardant mechanism, the thermal properties, the burned surfaces and the interface surfaces were elucidated. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1935–1943, 2008

Key words: polyurethane foams; expandable graphite-hollow glass microsphere; flame retardant; mechanical properties

INTRODUCTION

Polyurethane foams (PUF) have been used in a wide diversity of consumer and industrial applications, including insulating materials, construction panel sandwich structures, cushions of furniture, encapsulating stock of nuclear weapons, etc.[1,2] Being organic by nature, PUF easily ignites when subjected to a source of intense energy and releases toxic gases during burning which limits its application.[3,4] As a consequence, how to improve the flame retardancy of PUF is attracting more and more attention. The flammability of PUF strongly depends on the physical properties of the foams which are closely linked to its chemical ingredients such as polyol, isocyanate, catalyst systems, etc. The most important and simplest way of improving the flammability of PUF is to add flame retardant additives in the matrix. The common flame retardant additives are such compounds including halogen,[5–7] phosphorus,[8–10] nitrogen,[11–14] etc. But these flame retardant compounds have correspondingly weak ability to retard flame or emit toxic gases and smoke in the process of burning, and which can erode equipments and even choke people.[15–19] More and more attention has been paid to intumescent systems, since they are quite effective in flame retardancy materials and release few toxic smokes during burning.[20–22] The action of intumescent flame retardant is due to the formation of a compact char layer deriving from its expansion which covers the surface of polymer matrix and prevents further decomposition of the material. Expandable graphite (EG) is a novel intumescent flame retardant system and has successfully been used in PUF.[16,23] Modesti et al.[15,24] studied the flame retardant properties of low density EG/PUF and concluded that good flame retardant composites could be obtained through increasing EG content. At the same time, they also found that the compression strength of EG/PUF composites gradually fell with increasing EG content. The authors' group studied the factors influencing the flame retardant ability of EG/PUF foam, such as EG particle diameter,[25,26] the density of EG/PUF composites,[27] etc. We have prepared high-density EG/PUF composites whose limit-

ing oxygen index (LOI) could reach 39.5 vol % when the EG content was 20 wt %. The compression strength of these high-density EG/PUF composites, however, dropped with increasing EG content.[28] These results demonstrate that improving flame retardant ability of PUF with EG will simultaneously weaken the material's mechanical properties. Naturally, the next target is to improve the flame retardancy with the least sacrifice of the mechanical properties.

Hollow glass microsphere (HGM) was often used to reinforce polymer for its high compression strength and good fluidity.[29–31] Chalivendra et al.[31] found that the enhanced effects of HGM were better than glass fiber in PUF matrix. Furthermore, the presence of HGM hardly affected the density of HGM/PUF because of its low density[32]. Gupta et al.[33] found that keeping other conditions consistent and varying inner radius of HGM, the density and mechanical properties of PUF would be varied accordingly.

In this work, we added both EG and HGM particles to rigid polyurethane foams (RPUF), and successfully obtained RPUF composites with good flame retardant and mechanical properties.

EXPERIMENTAL

Materials

(1) Polyether polyol, GR-4110G, obtained from Gaoqiao Petro. Co. (Shanghai, China). The manufacturer provides the following properties: density (25°C), 1.1 g/cm³; typical hydroxyl number, 430 mg potassium hydroxide (KOH) equiv/g of resin; viscosity (25°C), 3283 cps; functionality, 4.1; average molecular weight, 550 g/mol. (2) Isocyanate, N200, PAPI available from ChangFeng Chemical Co. (ChongQing, China). Main properties for N200: Isocyanate equivalent weight, 126.5 g; —NCO weight percent, 30%; viscosity (25°C), 215 cps; functionality, 2.2. (3) Triethanoladiamine, crosslink catalyst, available from Shanghai Chemical Reagent Co. (Shanghai, China); density (25°C) 1.122 g/cm³. (4) Dibutyl tin dilaurate, a catalyst with a Sn content of 18% available from Sichuan Chemical Reagent Co. (Chengdu, China); density, 1.052 g/cm³. (5) Distilled water, used as blowing agent in this work, made by ourselves. (6) Silicone glycol copolymer, a surfactant. (7) Expandable graphite (EG), flame retardant, available from Haida Graphite Co. (QingDao, China). Sulfuric acid is inserted as blowing agent between its layers. The expanding of EG is originated by the reaction between sulfuric acid and the graphite. Main properties: ash, 1.0%; moisture, 1.0%; volatile, 15%; PH value, 3.0; average diameter, 200 μm; expansion rate, 200mL/g. (8) Hollow glass microsphere (HGM), re-

TABLE I
The Equilibrium Ratio of NCO to OH groups and the Weight Ratio of Polyol to PAPI

Density (g/cm³)	The equilibrium ratio of NCO to OH groups	The weight ratio of Polyol to PAPI
0.08	1.40	100/180

inforced additives, received from Shanghai Zhengmeiya Chemical Co.(Shanghai, China). Main properties: cumulate density, 0.7 g/cm³; average particle diameter, 10 μm.

The reaction ratio of NCO to OH and the weight ratio of polyol to PAPI are listed in Table I.

Foam preparation

In this work, all foam composites were prepared by cast molding and the densities of these composites were controlled at 0.08 ± 0.004 g/cm³. All components except additives and PAPI were mixed and stirred together with an electric stirrer for 10 min. Then added PAPI and the remaining additives, EG and HGM particles, into the mixture and stirred for an additional 30 s. The HGM particles are needed to modify by silane coupling agent beforehand.[31] PAPI reacts with distilled water and generates carbon dioxide which inflates the reactants. The final mixture was quickly poured into a mold with a lid completely. Then the impregnate mold was placed in an oven for 4 h at 100°C. The specimen was obtained through taking out the foam from the mold and removing the hard coat before characterization. All the foam composites were prepared with the same way. The weight content of EG was from 0 to 20 wt % and the weight loading of HGM was also from 0 to 20 wt %.

In this article, 10 wt % EG filled RPUF was shortened as EG10 RPUF, 10 wt % HGM filled RPUF was shortened as HGM10 RPUF, 10 wt % EG and 10 wt % HGM filled RPUF was shortened as EG10-HGM10 RPUF, the series of EG filled RPUF composites in which EG content was from 0 to 20 wt % was shortened as EG0-20 RPUF, the series of HGM filled RPUF composites in which HGM content was from 0 to 20 wt % was referred as HGM0-20 RPUF, the series of EG (EG content from 0 to 20 wt %) filled RPUF composites which contained 10 wt % HGM was referred as HGM10-EG0-20 RPUF.

Characterization

Horizontal and vertical burning test

The horizontal and vertical burning tests were performed on a CTF-2 horizontal and vertical burning instrument (made in Jiangning, China) according to the standard horizontal burning test, ASTM D 635-98, and the standard vertical burning test, ASTM D

3801-96. The specimens for measurement were machined into sheets of size 127 × 13 × 10 mm³.

Limiting oxygen index test

The limiting oxygen index (LOI) test was performed with an HC-2 oxygen index test instrument (made in Jiangning, China) in terms of the standard LOI test, ASTM D 2863-97. The specimens for measurement were sheets of size 127 × 10 × 10 mm³.

SEM observation

The morphology of the samples including original and burned samples was investigated by means of a JSM-9600 (JEOL, Japan) scanning electron microscopy (SEM) with an accelerating voltage 20kV. All the samples were obtained by impact fracture at room temperature and the surfaces were coated with a layer of a conductive material to make them conduct.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out in air at a heating rate of 10°C/min using a WRT-2P instrument thermogravimetric analyzer (Shanghai, China). In each case, an 8 mg sample was examined with an air flow rate of 50 mL/min at temperatures ranging from 50 to 700°C.

Mechanical measurement

Uniaxial compression tests have been performed on a universal electronic tensile machine (Shimadzu, Japan) with a compressive rate of 2 mm/min according to ASTM D 1621-94.

Dynamic mechanical analysis

Dynamical mechanical analysis (DMA) was carried out using a Q800 DMA instrument (TA, USA). The samples tested are parallelepipeds of 35 mm length, 10 mm width, and 4mm thickness. A temperature ramp is performed during the test from 50 up to 240°C with a heating rate of 3°C/min and a frequency of 1 Hz.

RESULTS AND DISCUSSION

Morphology of RPUF composites

Figure 1 shows SEM images of the fractured surfaces of RPUF composites. All the cells are oriented along
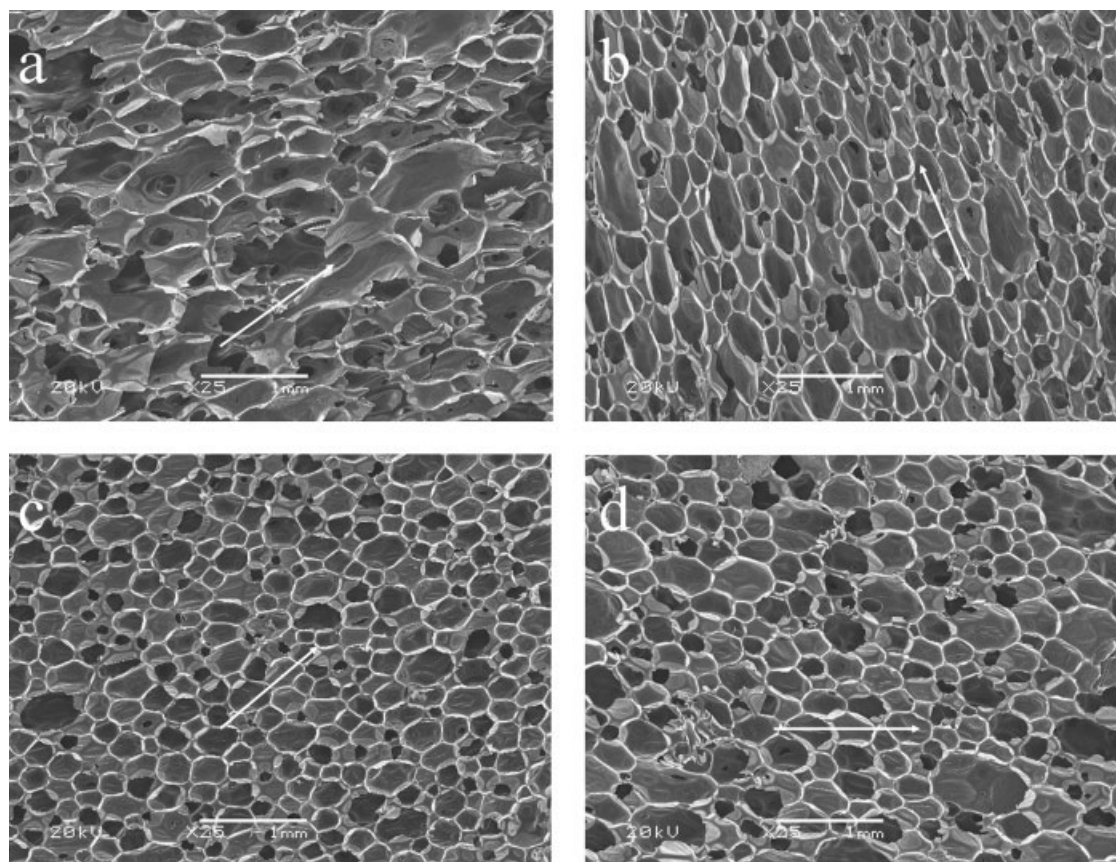

Figure 1 SEM micrographs of pure RPUF, EG10 RPUF, HGM10 RPUF, and EG10-HGM10 RPUF with the density of 0.08 g/cm³. (a) pure RPUF; (b) EG10 RPUF; (c) HGM10 RPUF; (d) EG10-HGM10 RPUF.

the foaming direction (arrowhead direction) and basically assume polyhedron. While foaming, the gas gives the resin a force to lead to resin flow and orientation. Furthermore, these RPUF composites have a low density (0.08 g/cm^3); thus, the resin has lower viscosity which leads to less resin resistance to foam. For the pure RPUF [Fig. 1(a)], many cells are collided each other and perforative. In contrast, the cells of the filled RPUF composites [Fig. 1(b–d)] are almost integrated. The additives are solid and cannot flow, which causes correspondingly great resistance while foaming. The addition of additives can reduce the average equivalent diameter of cells. The average equivalent diameter of pure RPUF is 187.70 μm, while that of EG10 RPUF, HGM10 RPUF, EG10-HGM10 is 136.86, 128.80, 132.53 μm, respectively. This indicates that the addition of small size additives has nucleation for cell formation.[28] But different-sized particles result in the ununiformity of cell size, especially for the hybrid composite as shown in Figure 1(d).

Compressive strength and compressive modulus of RPUF composites

Figures 2 and 3 show compressive strength and compressive modulus of EG0-20, HGM0-20, and HGM10-EG0-20 RPUF. Increasing EG amount causes a decrease in compressive strength and compressive modulus of EG0-20 RPUF. When the EG content increases from 0 to 20 wt %, the compressive strength decreases from 0.58 to 0.17 MPa, and the compressive modulus reduces from 14.10 to 9.30 MPa. This is due to the poor compatibility of EG with RPUF matrix, EG's structure, and its large particle size (average diameter, 200 μm) worsen the mechanical properties of the composites. EG is

Figure 3 Compressive modulus of EG0-20 RPUF, HGM0-20 RPUF, HGM10-EG0-20 RPUF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

composed of graphite sheets and gaps exist between graphite sheets. Its large size EG particles can traverse several cells and thus destroy the integrality of cells, causing an inhomogeneous cellular structure. As a consequence, the compressive strength and modulus decrease in the presence of EG.[15,28]

Figures 2 and 3 also indicate that with increasing the HGM content from 0 to 20 wt %, the compressive strength and modulus gradually rise until the HGM content reaches 10 wt %, then fall. When the HGM content is 10 wt %, the maximum of compressive and modulus is obtained, which are 0.69 and 21.4 MPa, respectively. When RPUF has low HGM content, HGM particles can be dispersed uniformly in matrix. When the matrix is compressed, the stress can be transferred to the HGM particles from the matrix. HGM particles share the external stress. Furthermore, the breakage of material mainly occurs on the surface between HGM particles and resin. Thus, with increasing the HGM content, the surface area becomes larger and more energy is needed to destroy RPUF.[30–34] For the introduction of more HGM content (> 10 wt %), the resin amount gradually decreases and the HGM particles agglomerate; therefore, the mechanical properties begin to decrease.

When the HGM content was fixed at 10 wt % in the RPUF matrix, HGM10-EG0-20 RPUF composites were prepared through changing EG content from 0 to 20 wt %. Comparing the compressive strength and modulus of HGM10-EG0-20 RPUF with only EG filled RPUF, the mechanical properties are improved apparently. As the EG content is 10 wt %, the compressive strength increases from 0.33 to 0.50 MPa, and the compressive modulus increases from 11.07 to 17.79 MPa. This should be contributed to the reinforced effect of HGM particles. In the compressed process, the HGM particles can share the stress.
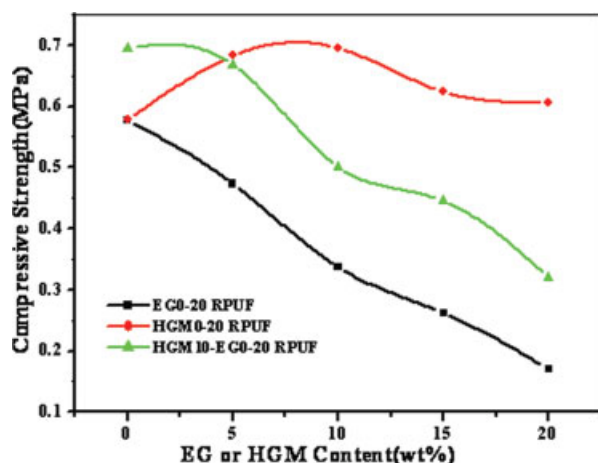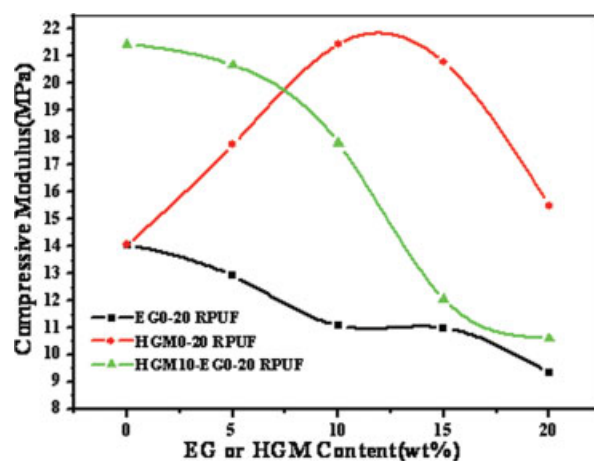

Figure 2 Compressive strength of EG0-20 RPUF, HGM0-20RPUF, HGM10-EG0-20 RPUF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

HGM (wt %)	EG (wt %)	H-V rating or linear burning rate
0	0	6.76×10^{-3} m/s
0	5	1.53×10^{-3} m/s
0	10	H-1
0	15	V-0
0	20	V-0
5	0	2.59×10^{-3} m/s
10	0	3.54×10^{-3} m/s
15	0	3.69×10^{-3} m/s
20	0	3.89×10^{-3} m/s
10	5	0.69×10^{-3} m/s
10	10	H-1
10	15	V-0
10	20	V-0

Flame retardant properties of RPUF composites

To evaluate the flame retardant properties of the RPUF composites with different fillers, horizontal and vertical (H-V) burning tests were performed, and the obtained data are listed in Table II. With increasing EG content, the burning classification of the composites changes from horizontal burning test to vertical burning test. When EG content is below 15 wt %, EG/RPUF composite can be classified only by horizontal burning test. When the EG content reaches 15 wt %, the composites can be classified by vertical burning test and achieve V-0 rating.

HGM0-20 RPUF can be only classified by horizontal burning test. The burning rate of these composites is slightly improved with HGM content. As the HGM content increases from 0 to 20 wt %, the linear burning rate of these composites increases from 6.76×10^{-3} to 3.89×10^{-3} m/s, showing very limited improvement. This is because the HGM particles has no flame retardancy, i.e., absorbing heat,[35] decreasing the concentration of oxygen,[5,14] etc. Though the addition of the HGM particles does not induce any modification of the flame retardance, but it decreases the resin fraction in the composite with a fixed density. It has, hence, slightly improved the linear burning rate of the composites.

The H-V burning properties of HGM10-EG0-20 RPUF are also listed in Table II. Compared to EG/RPUF, there is no apparent improvement on classification at the same EG concentration. Only the linear burning rate has been more or less improved.

Figure 4 shows the LOI data of the RPUF composites. As the EG content changes from 0 to 20 wt %, the LOI values of EG/RPUF increase linearly from 20.5 to 28 vol %. It is well known that EG particles can expand upon heating above 200°C and form worm-like structure in the process of burning.[15,24] The higher the EG content, the higher volume expansion is, so it needs higher oxygen content for burning.

The LOI values of HGM filled RPUF remain at 20.5 vol % with HGM content changing from 0 to 20 wt %. It indicates that the presence of HGM has little improvement of flame retardancy, even for quite high filler content. The result is consistent with H-V burning test. This is also due to the HGM particles do not possess the flame-retardant properties.

In contrast, the LOI values of HGM10-EG0-20 RPUF show an interesting phenomenon. When the EG content is below 15 wt %, its LOI values are the same as EG/RPUF. However, the EG content goes up to 20 wt %, the LOI value increases from 28 vol % (EG/RPUF) to 30 vol %. This should be due to the fact that the presence of HGM reduces the resin content, i.e., reduces flammable material. When EG content is 20 wt %, the decrease of resin has a synergistic effect on LOI with EG.

Thermogravimetric analysis

Figures 5 and 6 show the thermogravimetric and derivative thermogravimetric behavior of the RPUF composites under a flow of air. Both pure RPUF and filled RPUF show a two-stage degradation process. The first step of mass loss occurs at 290–400°C and the peak rate temperature (the maximum mass loss rate) is at 342°C. The second step of mass loss occurs at 520–700°C and the temperature of the maximum mass loss rate is at 590°C. However, at the same temperature, the filled RPUF composites have more residual weight than the pure RPUF because the fillers have better thermal properties than the resin. Moreover, the residual weight of EG10 RPUF and EG10-HGM10 RPUF is more than HGM10 RPUF from 290°C. It is because that EG particles will
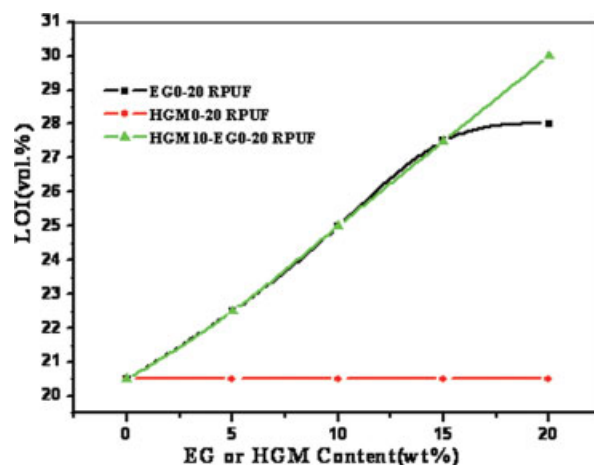

Figure 4 LOI of EG0-20 RPUF, HGM0-20 RPUF, HGM10-EG0-20 RPUF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
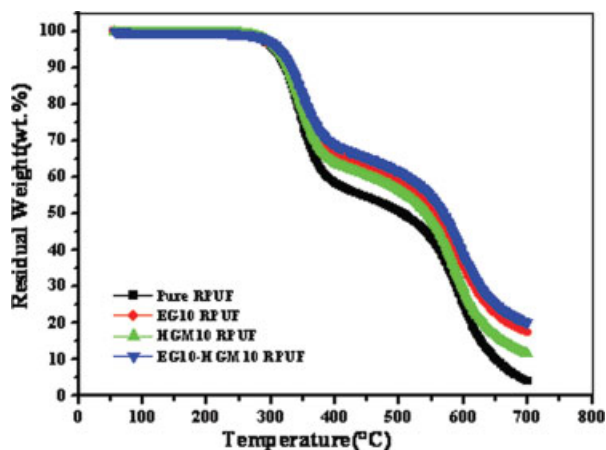
expand by heating above 200°C and their degradation products slightly react with RPUF matrix.[23] HGM particles are circular which means the meeting area with the resin is larger than EG. Figure 6 also shows that the maximum weight loss rate of the filled RPUF composites also occurs at 342 and 590°C. This suggests the adding of HGM or/and EG has no effective improvement on the thermal stability of the polyurethane matrix.

Dynamic mechanical analysis

Because RPUF is often used as package materials, the damping performance of the RPUF composites is of high significance. The dynamical mechanical properties of the RPUF have been examined in this work. The evolution of the storage modulus (E') as a
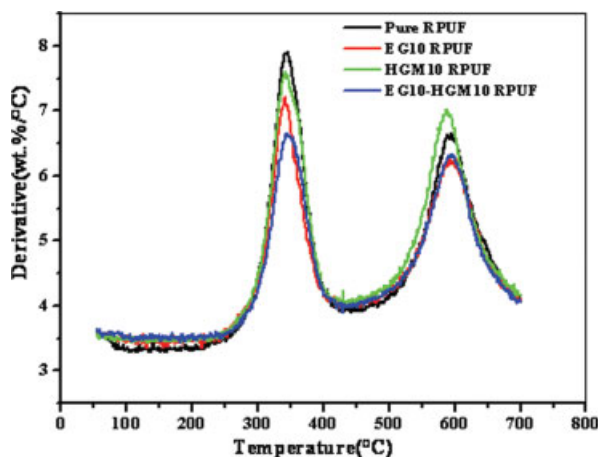
function of temperature measured by DMA is shown in Figure 7. An evident falling trend can be found for all the samples with the increase of the temperature, because the molecular mobility increases with temperature. The E' value of pure RPUF is higher than that of 10 wt % EG or HGM filled RPUF from 50 to 160°C, and beyond 160°C the reverse is true. There are two points which are needed to mention. First, the composites were prepared with high molar NCO/OH value (1.40), so the crosslinking degree is higher and the E' of all formulations is also comparatively higher.[36] Second, the addition of HGM particles increases the E' of the composites for its stiffness, while the presence of EG particles decreases the E' of the composites for its interstice between graphite flakes. Both HGM and EG particles can restrict the molecules mobility and consequently may decrease the crosslinking degree of PUF. From 50 to 160°C, the effect of the HGM particles on E' of cannot compensate for their effect on the decrease of E' by dropping crosslinking degree. For EG10 RPUF, the introduction of EG particles can only decrease E' value in this temperature range. After 160°C, the stiffness of the fillers (HGM and EG particles) is higher than PU matrix. So, their storage modulus values are higher than pure RPUF. Compared with the pure RPUF, the E' value of EG10-HGM10 RPUF is better throughout the temperature range. While heating, polymer chain segments become easier moving, that induce the decrease of E'. But the E' values of the additives are not sensitive to the temperature, thus, the decrease of EG10-HGM10 RPUF is less. Moreover, with the decrease of the resin, the fillers' effect on E' is the controlling factor all through the process of increasing temperature.

Figure 8 shows the loss modulus (E'') spectra of pure RPUF, EG10 RPUF, HGM10 RPUF, EG10-

Figure 8 Loss modulus of Pure RPUF, EG10 RPUF, HGM10 RPUF, and EG10-HGM10 RPUF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
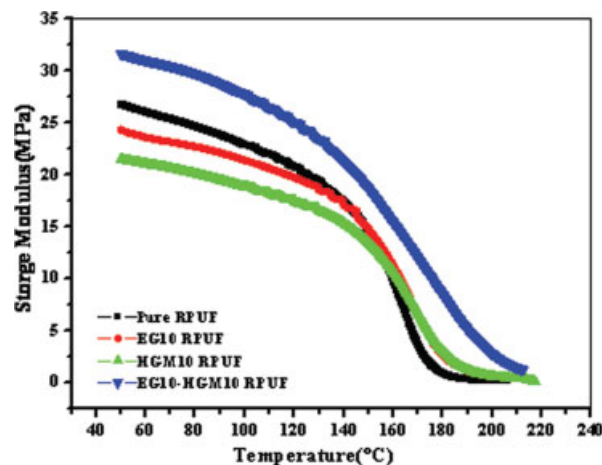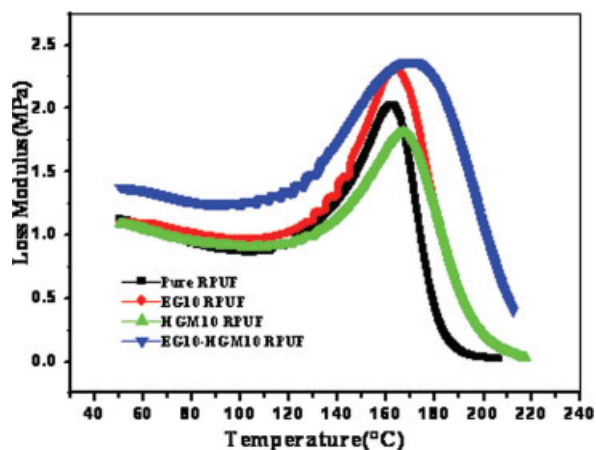
Figure 9 Tan δ of Pure RPUF, EG10 RPUF, HGM10 RPUF, and EG10-HGM10 RPUF. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]
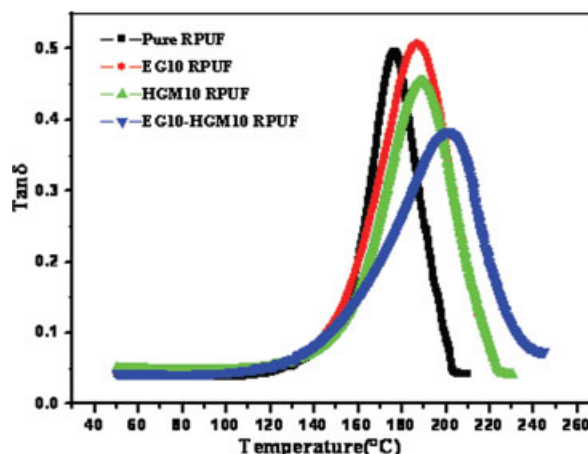
HGM10 RPUF, and one major transition of E'' for all formulations can be seen. The E'' values of EG10 RPUF and EG10-HGM10 RPUF are higher than pure RPUF, while the E'' value of HGM10 RPUF is lower than pure RPUF on account of the shape of the additive particles. That is, the EG particles are sheet structure and generate greater friction while molecular chain moves, which results in higher E'' value; however, the HGM particles are circular and generate less friction, leading to a lower E'' value.[37]
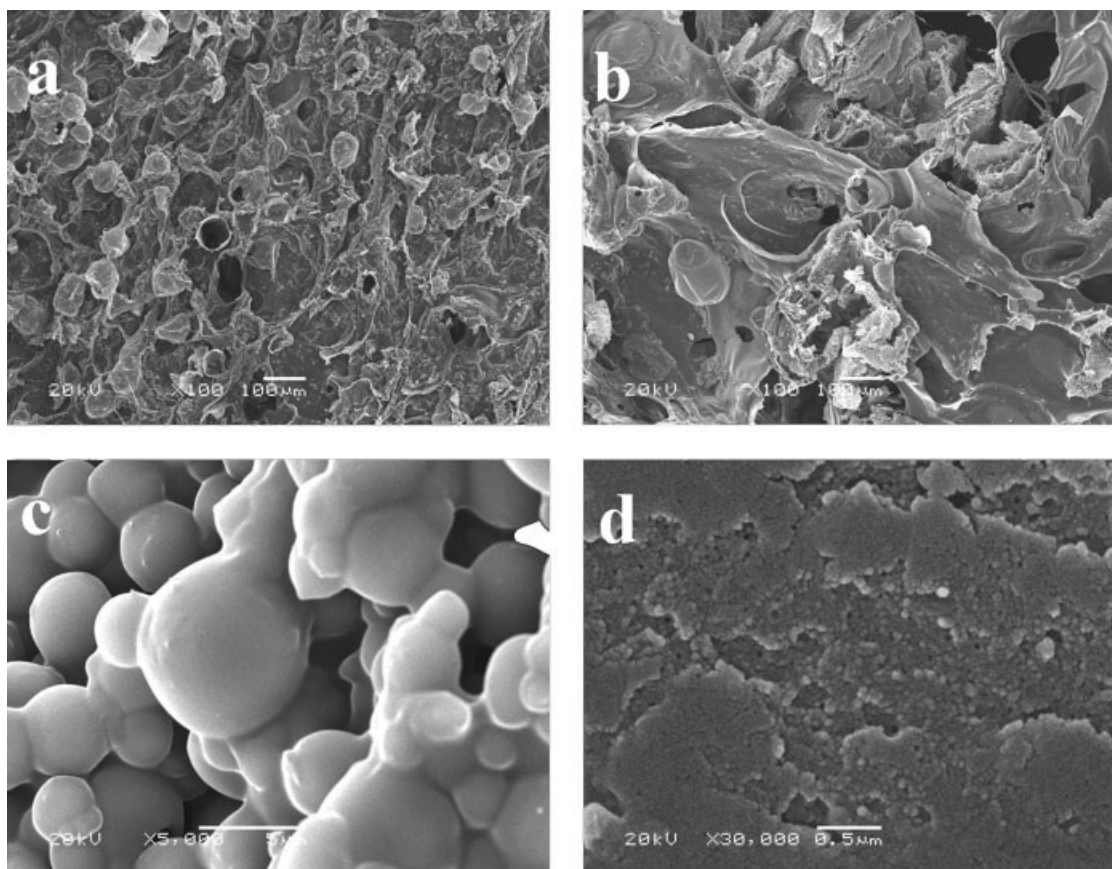

Figure 10 SEM micrographs of the burned char: (a) low magnification of HGM10 RPUF; (b) low magnification of EG10-HGM10 RPUF; (c) high magnification of HGM10 RPUF; (d) high magnification of EG10-HGM10 RPUF.

Figure 11 SEM micrographs of the fractured surfaces: (a) low magnification of HGM10 RPUF; (b) low magnification of EG10-HGM10 RPUF; (c) high magnification of HGM10 RPUF; (d) high magnification of EG10-HGM10 RPUF.
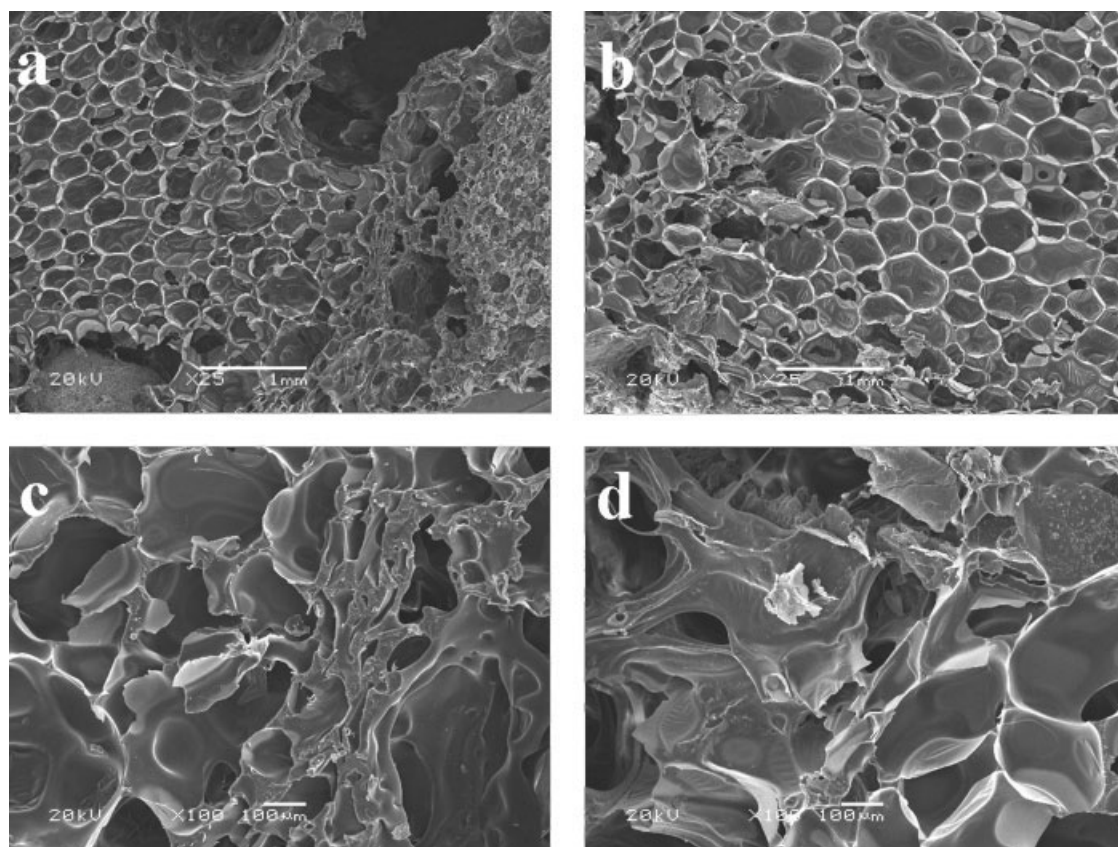
The loss tangent (tan δ) spectra of pure RPUF, EG10 RPUF, HGM10 RPUF, EG10-HGM10 RPUF are presented in Figure 9. From this figure, it can be found that the glass transition temperature (T_g) values and the temperature range for damping effect (tan δ > 0.3) of all the filled composites are improved in comparison with that of pure RPUF. The Tg value of pure RPUF, EG10 RPUF, HGM10 RPUF, and EG10-HGM10 RPUF is 176, 187, 189, and 200°C, respectively. Generally, the material of which tan δ value is beyond 0.3 can be considered having damping effect. According to this rule, the temperature range for each formulation having damping effect, respectively, is that pure RPUF 165.5–187.7°C, EG10 RPUF 168.5–203.5°C, HGM10 RPUF 172.5–203°C, EG10-HGM10 RPUF 184–212°C. The increase of the temperature range for damping effect is caused by the limit to molecular motion because of the incorporation of additives.[38] The maximum tan δ (tan δ_{max}) value for each formulation is also different. The tan δ_{max} of pure RPUF, EG10 RPUF, HGM10 RPUF, and EG10-HGM10 RPUF is 0.50, 0.51, 0.46, and 0.38, respectively. Among these composites, the tan δ_{max} of EG10 RPUF is the best. Furthermore, the damping factor (tan δ) provides information on the relative contributions of the viscous and

elastic components of a viscoelastic material. Lower tan δ indicates that the formulations exhibit more elastic than viscous nature.[39] So, EG10-HGM10 RPUF has more elastic nature. It should be contributed to that the adding of HGM and EG decreases the crosslinking degree of RPUF.

Morphology of the burned surfaces of RPUF composites

The burned layer SEM micrographs of HGM10 RPUF and EG10-HGM10 RPUF are presented in Figure 10 with various magnifications. From Figure 10(a), only charred layer can be found due to the small size of HGM particles. Figure 10(b) shows the expanded graphite sheets and charred layer. With a higher magnification, the HGM particles which have been covered by charred layer can be found clearly [Fig. 10(c)]. Moreover, there are many gaps between HGM particles. Hence, the addition of HGM particles cannot effectively prevent flame but only decrease the resin content. For EG10-HGM10 RPUF, the HGM particles cannot be found on the burned surfaces. With higher magnification, there is charred layer except expanded graphite sheets. It further proves that the HGM particles cannot prevent flame.

Morphology of the interfaces of RPUF composites

Figure 11 shows the overall regions from unburned region to burned region for HGM10 RPUF and EG10-HGM10 RPUF. Figure 11(a,b) are for the low magnification, and that 11(c,d) are for the high magnification. Figure 11(a,c) show vague interface region between unburned layer and burned layer. This is because that the HGM particles have no flame-retardant properties. Figure 11(c) clearly illustrates that the heat distortion appears in the interface region. Comparing Figure 11(b) with Figure 11(a), the interface regions of EG10-HGM10 RPUF are larger than that of HGM10 RPUF. From Figure 11(d), more serious distortion and collapse of the cells can be found. It is because that the increase of flame retardant properties is a key factor which insulates the flame and heat resource.[28]

EG has excellent flame retardant ability for RPUF.[15-17,28] More EG content goes with better flame retardant properties. But the mechanical properties of RPUF fall with the EG content rising.[15,28] In many applications, the mechanical properties are as important as flame retardant properties. HGM is a useful type of enhanced additive for RPUF.[31] The mechanical properties of EG/RPUF composites can be improved with adding 10 wt % HGM particles. At a certain EG content (EG content = or > 20 wt %), the flame retardant properties can be improved simultaneously.

CONCLUSIONS

1. The adding of HGM particles can improve the compressive strength and modulus of RPUF. When the HGM content reaches 10 wt %, the optimal result is obtained. But the adding of HGM particles cannot improve the flame-retardant properties of RPUF.
2. 10 wt % HGM filled RPUF composites which contain various EG particles content can improve their mechanical properties. Moreover, when the EG content arrives at 20 wt %, the flame-retardant properties can also be improved.
3. The adding of EG or/and HGM particles make Tg of the RPUF composites shift to the high temperature and the damp temperature range magnify. Furthermore, 10 wt % EG and 10 wt % HGM filled RPUF has the higher storage modulus than other formulations.
4. Through TGA, it can be found that the adding of HGM and EG will not reform the thermal properties of RPUF matrix.

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