Flame Retardancy of Whisker Silicon Oxide/Rigid Polyurethane Foam Composites with Expandable Graphite

Xiang-Cheng Bian,[1,2,3] Jian-Hua Tang,[2] Zhong-Ming Li[1]

[1]*College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, People's Republic of China*
[2]*College of Chemical Engineering, Sichuan University, Chengdu 610065, People's Republic of China*
[3]*Center for Degradable and Flame Retardant Polymeric Materials, College of Chemistry, Sichuan University, Chengdu 610064, People's Republic of China*

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ABSTRACT: Rigid polyurethane foam (RPUF) composites filled with various expandable graphite (EG) or/and whisker silicon (WSi) loadings were prepared with the same density (0.08 g/cm^3). When the WSi content reached 10 wt %, the composite had the best mechanical properties, the values of compressive strength and modulus reached 0.74 and 21.0 MPa, respectively. Compared with only EG filled RPUF, the addition of 10 wt % WSi to EG/RPUF would also bring out improvement on their flame retardant and mechanical properties. Maintaining EG 20 wt %, the compressive strength increased from 0.17 (EG/RPUF) to 0.39 MPa (WSi/EG/RPUF), the compressive modulus increased from 9.32 (EG/RPUF) to 10.11 MPa (WSi/EG/RPUF), and the limiting oxygen index value increased from 28 vol % (EG/RPUF) to 32.5 vol % (WSi/EG/RPUF). The thermogravimetric analysis showed that the addition of EG and WSi particles improved the thermal stability of the composites. The dynamical mechanical analysis (DMA) showed that EG and WSi particles led to up-shift of the glass transition temperature. Moreover, 10 wt % EG and 10 wt % WSi filled RPUF had the highest storage modulus, as the EG and WSi exhibited a desirable synergetic effect on flame retardant properties and dynamic mechanical properties of RPUF composites. The morphologies of the composites were analyzed with scanning electron microscopy.
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Key words: polyurethane foams; expandable graphite; whisker silicon; flame retardant properties; mechanical properties

INTRODUCTION

Polyurethane can be classified into polyurethane foam (PUF), polyurethane elastomer, paint, adhensive, etc., and PUF is playing an important role in the industries and our lives. Because it is often used as structural and insulating materials, the good physical and mechanical properties are demanded.[1,2] Therefore, how to improve the strength and modulus of PUF attracts more and more attentions.

The direct way of improving mechanical properties of PUF is to change components or adjust the ratio of components. Some researchers had studied the effect of different blowing agents on the mechanical properties of PUF and found that the mechanical properties of PUF would rise with the reduction of residual blowing agent content.[3,4] To obtain PUF with good mechanical properties, different materials had also been developed.[5–7] The ratio of components also affects the mechanical properties of PUF, and higher toluene isocyanate index leads to better compression strength.[8] But these means have some defects, for example, the cost increases.

Adding additives to the PUF matrix is the simplest way to improve the mechanical properties of PUF and can obtain better results than changing components. Goods et al.[9] found that adding 30–50 wt % aluminum powder could improve the strength and modulus of rigid polyurethane foam (RPUF) obviously. Johnson and Shivkumar[10] filled PUF with green algae additions, and the best mechanical properties of PUF were obtained with the filler content in the range of 5–10 wt %. Cao et al.[11] found that the compressive strength and modulus of 5 wt % clay filled PUF were 6.5 and 7.8 times higher than that of pure PUF. Li and coworkers[12] reinforced RPUF with Nylon-1010. When the Nylon-1010 content was 5–10 wt %, the tensile strength and modulus of RPUF were improved because of the good compatibility between matrix and Nylon-1010. Other additives were also used to improve the mechanical properties of PUF, such as glass fiber,[13] mica,[14] silicon,[15,16] carbon black.[17] Currently, as a new style reinforced

Correspondence to: J.-H. Tang (jianhuatang@chuankepharm.com) or Z.-M. Li (zm_li@263.net.cn).
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TABLE I
The Main Formulations of Pure RPUF, EG10 RPUF, WSi10 RPUF, and EG10-WSi10 RPUF

	Polyol (g)	PAPI (g)	EG (g)	WSi (g)	H_2O (g)
Pure RPUF	63.7	114.7	0	0	1.73
EG10 RPUF	57.3	103.2	17.8	0	1.56
WSi10 RPUF	57.3	103.2	0	17.8	1.56
EG10-WSi10 RPUF	51.0	91.7	17.8	17.8	1.38

additive, whisker has also been used to reinforce polymers and obtained favorable results.[18–20] But there is few reports on the whisker filled RPUF. In this work, we attempt to reinforce RPUF with whisker silicon (WSi).

Although many reinforced additives can more or less improve the mechanical properties of PUF, there is little improvement on the flame retardant properties. So its flame retardant properties need to be enhanced too. The common flame retardant additives include halogen,[21] phosphorus,[22] nitrogen,[23] etc. However, compared with expandable graphite (EG), these flame retardant compounds have relative weak flame retardancy or emit toxic gases in the process of burning.[24–27]

In our previous works, we have thoroughly studied the flame retardant properties of EG filled high-density RPUF, and found that the addition of EG would improve the limiting oxygen index (LOI) of RPUF greatly,[28] and the flame retardant properties of EG/RPUF are affected by the size of EG particles.[29] The larger size EG particles lead to better flame retardant properties. We also found that the flame retardant properties of EG/RPUF are affected by the density of RPUF. At the same EG content, higher density leads to better flame retardant properties.[30] Unfortunately, the addition of EG particles decreased the mechanical properties of RPUF. Naturally, in this work, the EG and WSi particles are both incorporated into RPUF to simultaneously enhance the flame retardancy and the mechanical properties of the RPUF.

EXPERIMENTAL

Materials

The raw materials used in this work include the following:

1. Polyether polyol, GR-4110G, made from polypropylene oxide and a sucrose/glycerin base, was manufactured by GaoQiao Petro. Co. (Shanghai, China). The manufacturer lists the following properties: density (25°C), 1.1 g/cm^3; 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. Triethanolamine, crosslink catalyst with a density (25°C) of 1.122 g/cm^3, was produced by Shanghai Chemical Reagent Co. (Shanghai, China).
3. Dibutyltindilaurate, a catalyst with a density of 1.052 g/cm^3, was supplied by Sichuan Chemical Reagent Co. (Chengdu, China); Sn content, 18 wt %.
4. Distilled water, blowing agent, was prepared by ourselves.
5. Silicone glycol copolymer, a kind of surfactant for foams.
6. EG, used as flame retardant, was supplied by Haida Graphite Co. (QingDao, China). Main properties for EG are as follows: ash, 1.0%; moisture, 1.0%; volatile, 15%; pH value, 3.0; expansion rate, 200 mL/g; average diameter, 196.6 μm; average area, 39661.5 μm^2.
7. WSi, reinforced additives, was received from Shanghai Huijingya New Nanomaterials Co. (Shanghai, China). Main properties of WSi are as follows: main component, silicon dioxide; cumulate density, 1.3 g/cm^3; average particle diameter, 6 μm.
8. Isocyanate, N200, PAPI available from Chang-Feng Chemical Co. (ChongQing, China). Main properties to N200 are as follows: Isocyanate equivalent weight, 126.5 g; -NCO weight percent, 30%; viscosity (25°C), 215 cps; functionality, 2.2.

The molar ratio of NCO to OH is 1.40 and the weight ratio of polyol to PAPI is 100/180 in this work. The content of triethanolamine, dibutyltindilaurate, and silicone glycol copolymer is 0.3 wt %, 0.3 wt %, and 1.0 wt % of total weight of polyol and PAPI, respectively. The main formulations are listed in Table I.

Foam composites preparation

We prepared all foam composites, the densities of which were controlled at 0.08 ± 0.004 g/cm^3, by cast molding. To improve the compatibility of WSi particles with RPUF matrix, the WSi particles were

modified by silane coupling agent in advance. First, we mixed and stirred the Components 1–5 together with an electric stirrer for 10 min. Second, proper Components 6–8 were added into the above mixture and stirred fast for 30 s. Then this mixture was cast into a mold completely and the mold was closed with a lid quickly. Finally, put the impregnate mold into an oven which inner temperature was retained at 100°C for 4 h. The specimen was obtained by taking out the foam and removing the hard coat. We prepared all the foam composites used in this work with the same method. The content of EG and WSi by weight in the composites was from 0 to 20 wt % and from 0 to 30 wt %, respectively.

To express expediently, we abbreviated 10 wt % EG filled RPUF to EG10 RPUF, 10 wt % WSi filled RPUF to WSi10 RPUF, 10 wt % EG, and 10 wt % WSi filled RPUF to EG10-WSi10 RPUF. We abbreviated EG filled RPUF composites (the EG content was from 0 to 20 wt %) to EG0-20 RPUF, WSi filled RPUF composites (the WSi content was from 0 to 30 wt %) to WSi0-30 RPUF, the series of EG (EG content from 0 to 20 wt %) filled RPUF composites which contained 10 wt % WSi to WSi10-EG0-20 RPUF.

Measurements

According to the standard horizontal burning test, ASTM D 635-98, and the standard vertical burning test, ASTM D 3801-96, a CTF-2 horizontal and vertical burning instrument (made in Jiangning Courty, China) was used to test the horizontal and vertical burning classification. The specimens used for the measurement were processed into sheets 127 × 13 × 10 mm^3.

In terms of the standard LOI test, ASTM D 2863-97, an HC-2 oxygen index test instrument (made in Jiangning Courty, China) was used to test the LOI. The slices with the size of 127 × 10 × 10 mm^3 were needed for measurement.

The samples including original and burned samples were fractured at room temperature and coated with gold before scanning electron microscopy (SEM) investigation. The fracture surfaces of the samples were observed with a JSM-9600 (JEOL, Japan) SEM at an accelerating voltage of 20 kV.

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

The compression strength and modulus were measured with a universal electronic tensile machine (Shimadzu, Japan) at a compressive rate of 2 mm/min according to ASTM D 1621-94.

Dynamical mechanical analysis (DMA) was measured by means of a Q800 DMA instrument (TA, America) at a heating rate of 3°C/min. The samples constituted sheets of 35 × 10 × 4 mm^3. The temperature range was 50–240°C.

RESULTS AND DISCUSSION

Morphology of RPUF composites

SEM micrographs of the fractured surfaces of RPUF composites with EG and/or WSi are shown in Figure 1. Based on the image, we can find that all the cells of these composites are oriented along the foaming direction (arrow direction) and the cells' shape is approximately polyhedron. In the process of foaming, the gas forces the resin and leads resin to flow and orient. Because these RPUF composites have the same low density (0.08 g/cm^3), so there is less resin and lower viscosity to resist foaming. From Figure 1(a) (pure RPUF), most cells are collided and perforative each other. However, the cells of the RPUF composites filled with particles [Fig. 1(b–d)] are almost integrated. This should be attributed to the solid additives, which are difficult to flow leading to considerably greater resistance while foaming than that of pure resin component. The additives can also reduce the average equivalent diameter of cells. The average equivalent diameter is 187.70 μm, 136.86 μm, 124.40 μm, and 131.32 μm for pure RPUF, EG10 RPUF, WSi10 RPUF, and EG10-WSi10 RPUF, respectively. This indicates that the small size additives have nucleation effect during the process of foaming.[28] At the same time, different-size particles cause the wider distribution of cell size, especially for the hybrid RPUF composite just like shown in Figure 1(d). It is because the different size particles have different nucleation ability and unlike flow ability.

Compressive strength and modulus of composites

Because RPUF composites are often used as structural materials, the mechanical properties are very important for them. Compressive strength and modulus curves of EG0-20 RPUF, WSi0-30 RPUF, and WSi10-EG0-20 RPUF composites are shown in Figures 2 and 3. On the basis of the two figures, we can find compressive strength and modulus of EG filled RPUF decrease with the EG content increasing. With the EG content increasing from 0 to 20 wt %, the compressive strength drops from 0.58 to 0.17 MPa, and the compressive modulus drops from 14.1 to 9.30 MPa. As we known, EG is composed of graphite sheets, and many gaps exist between graphite sheets. Moreover, the compatibility of EG particles with RPUF matrix is poor. The large size of EG

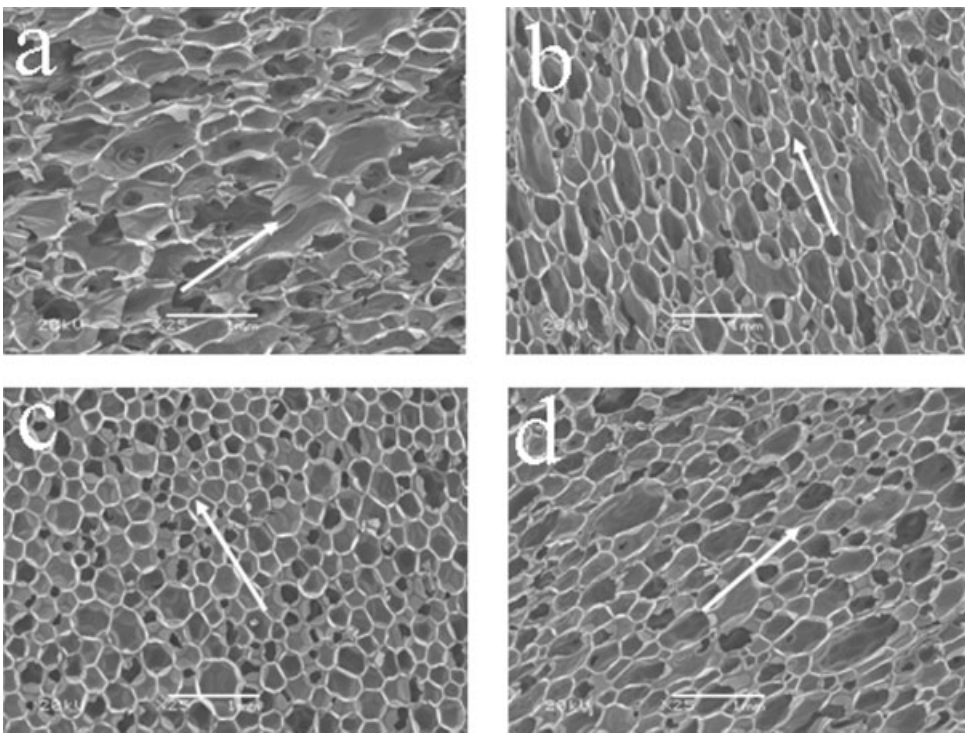

Figure 1 SEM micrographs of pure RPUF, EG10 RPUF, WSi10 RPUF, and EG10-WSi10 RPUF with the density of 0.08 g/cm^3. (a) Pure RPUF; (b) EG10 RPUF; (c) WSi10 RPUF; and (d) EG10-WSi10 RPUF.

particle makes it run through several cells and destroy the unity of cells, which causes an inhomogeneous cellular structure. All these factors worsen the mechanical properties of the composites.[28,31]

Based on Figures 2 and 3, we can also find that with the increase of WSi content from 0 to 30 wt %, the compressive strength and modulus rise first and then decrease. When the WSi content is 10 wt %, the values of compressive strength and modulus reach the maximum values which are 0.74 and 21.0 MPa, respectively. This is because that at low WSi content, WSi particles can be dispersed uniformly in the resin. When the composites are compressed, the external stress can be transferred from the resin to WSi particles.[32] Moreover, the breakage of materials mainly occurs on the interface between the additives and resin. So with the WSi content increasing (below 10 wt %), the interface area becomes larger and

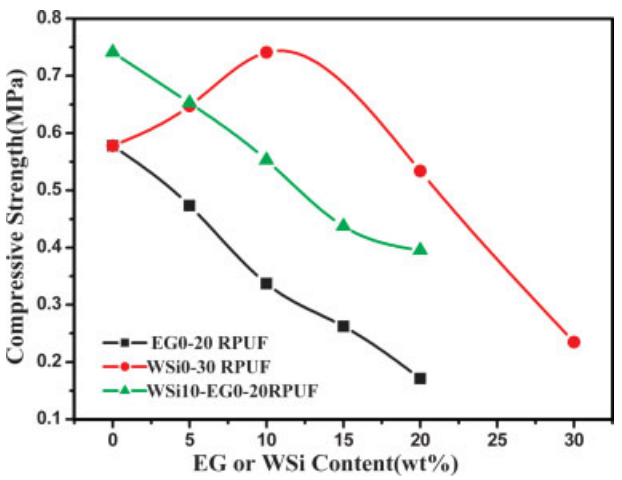

Figure 2 Compressive strength of EG0-20 RPUF, WSi0-30RPUF, and WSi10-EG0-20 RPUF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

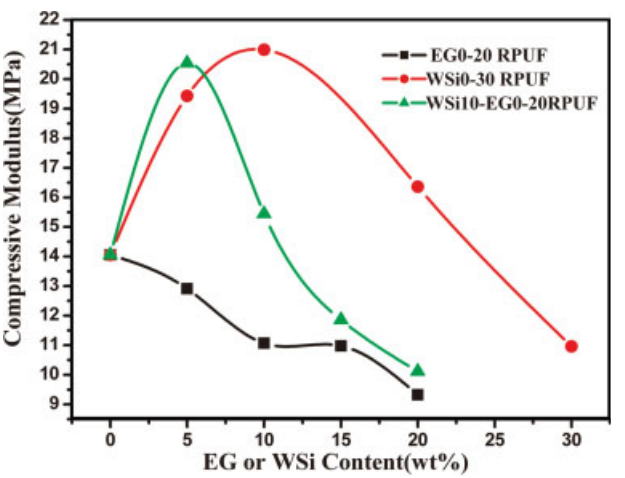

Figure 3 Compressive modulus of EG0-20 RPUF, WSi0-30 RPUF, and WSi10-EG0-20 RPUF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
H-V Rating or Linear Burning Rate of EG0-20 RPUF, WSi0-30 RPUF, and WSi10-EG0-20 RPUF

WSi (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	4.418×10^{-3} m/s
10	0	4.418×10^{-3} m/s
20	0	4.24×10^{-3} m/s
30	0	3.914×10^{-3} m/s
10	5	0.51×10^{-3} m/s
10	10	H-1
10	15	V-0
10	20	V-0

more energy is needed to destroy RPUF construction,[33–35] and the mechanical properties of the composites get better. However, with the WSi content continuously increasing (beyond 10 wt %), the resin amount dramatically decreases (the foam density is a constant) and the WSi particles begin to agglomerate and form defects which make the mechanical properties of the composites drop.[19,20]

For the RPUFs with EG content from 0 to 20 wt %, the compressive strength and modulus of the 10 wt % WSi particles filled EG/RPUF composites are apparently superior to that of the EG/RPUF composites without WSi particles. For example, as the EG content is 10 wt %, the addition of 10 wt % WSi particles leads to the compressive strength of the EG/RPUF composite increasing from 0.33 to 0.55 MPa, and the compressive modulus increasing from 11.10 to 15.40 MPa. This is definitely due to the reinforced effect of WSi particles which have shared the stress in the compressed process.[32]

Flame retardant properties of RPUF composites

To evaluate the flame retardant properties of these RPUF composites, we performed horizontal and vertical (H-V) burning tests on these composites, and list the results in Table II. The burning rating of the composites changes from horizontal burning rating to vertical burning rating while increasing the EG content. When the EG content is below 15 wt %, EG/RPUF composites cannot be classified by vertical burning test. It is because low EG content has low flame retardant ability. With the EG content up to 15 wt % and higher, the composites achieve V-0 rating.

From Table II, we can find that WSi0-30 RPUF can be only classified through linear burning rate. The linear burning rate of WSi0-30 is upgraded with the WSi content increasing. With the WSi content increasing from 0 to 30 wt %, the linear burning rate improves from 6.76×10^{-3} to 3.89×10^{-3} m/s. However, though WSi particles cannot induce much modification on the flame retardance of the composites in these systems, it can decrease the resin fraction in the composites at a fixed density, i.e., decrease the flammable material fraction. Hence, the linear burning rate of the composites increases.

In Table II, we also list the H-V burning rating of WSi10-EG0-20 RPUF. There is no apparent improvement on classification at the same EG concentration when comparing with EG/RPUF composite. Only the linear burning rate has little improved. But compared with WSi10 RPUF, the existence of EG can improve the burning rating to V-0 rating. This is because EG particles are excellent flame retardant for PUF.

Another method (LOI) for flame retardant properties test was performed, detailed data of which are shown in Figure 4. With the EG content increasing from 0 to 20 wt %, the LOI values of EG/RPUF enhance linearly from 20.5 to 28 vol %. As we known, EG particles can expand while heating above 200°C and form worm-like structure to retard flame.[31,36] High EG content results in high volume expansion, and thus more oxygen is needed to burn.

The WSi content has little effect on the LOI values of WSi filled RPUF. While the WSi content changing from 0 to 30 wt %, the LOI values improve only from 20.5 to 21 vol %. The result is consistent with the H-V burning test.

However, the LOI values of WSi10-EG0-20 RPUF show a significant improvement compared with EG0-20 RPUF at the same EG concentration. When the EG content is beyond 5 wt %, its LOI values get better than EG/RPUF. When the EG content goes up

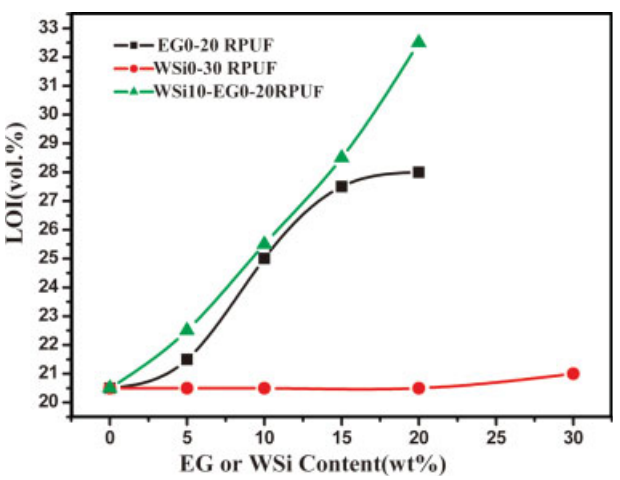

Figure 4 LOI of EG0-20 RPUF, WSi0-30 RPUF, and WSi10-EG0-20 RPUF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

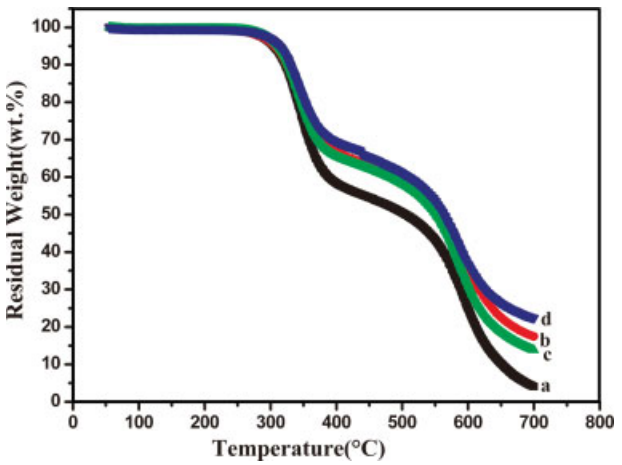

Figure 5 TGA: (a) Pure RPUF; (b) EG10 RPUF; (c) WSi10 RPUF and (d) EG10-WSi10 RPUF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

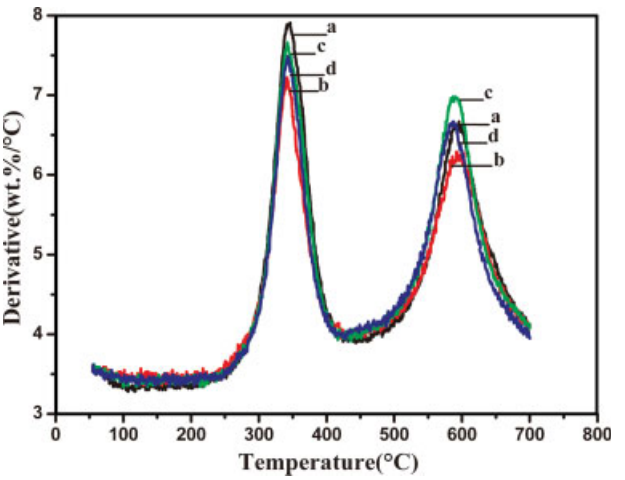

Figure 6 DTG: (a) Pure RPUF; (b) EG10 RPUF; (c) WSi10 RPUF; and (d) EG10-WSi10 RPUF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

to 20 wt %, the LOI value increases from 28 (EG/RPUF) to 32.5 vol %. With the EG content increasing from 0 to 20 wt %, the synergistic effect of WSi and EG becomes more and more obvious.

We all know, during the burning process, the resin decomposes and burns, then the particles come out. The WSi particles are little and a large amount is need for covering the surface of the matrix. The EG particles can expand and retard flame while heating, so the flame retardant properties of the composite filled with EG can be improved. The existence of WSi particles in the EG/RPUF can assist EG particles to cover the surface of matrix. This can be found in the later figures. In addition, the presence of WSi reduces the resin content, i.e., reduces flammable material.

Thermogravimetric analysis

To evaluate the thermal stability of these composites, the thermogravimetric and derivative thermogravimetric behavior was tested under a flow of air. The results are shown in Figures 5 and 6. All the composites mainly show a two-stage mass loss process. The first stage occurs at 290–400°C and the peak temperature (the maximum mass loss rate) is 342°C. The second one occurs at 520–700°C and the peak temperature (the maximum mass loss rate) is 590°C. From these figures, we can find that the filled RPUF composites have more residual weight than pure RPUF at the same temperature. This indicates that the addition of WSi or/and EG has improved the thermal stability of the composites. It is due to the better thermal stability of the fillers than the resin. We can also find that the residual weight of EG10 RPUF and EG10-WSi10 RPUF is more than WSi10 RPUF from 290°C. It is because that EG particles can expand by heating above 200°C and their degradation products will slightly react with RPUF matrix.[37] Moreover, the EG sheets may delay the thermal conduction. Figure 6 also shows that the maximum weight loss rate of all the RPUF composites happens at 342°C and 590°C.

Dynamic mechanical analysis

It is well known that the dynamical mechanical properties of package materials are important in applications. The storage modulus, loss modulus, and tan δ of the composites have been examined in this work. Figure 7 shows the relationship of the storage modulus (E') with temperature. With the increase of temperature, all the samples have an

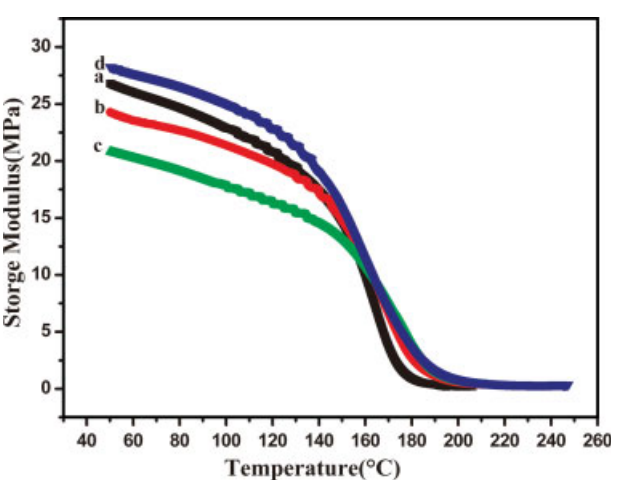

Figure 7 Storage modulus: (a) Pure RPUF; (b) EG10 RPUF; (c) WSi10 RPUF; and (d) EG10-WSi10 RPUF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

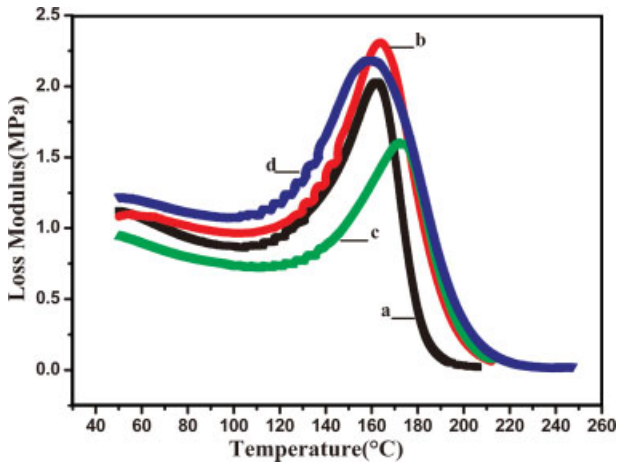

Figure 8 Loss modulus: (a) Pure RPUF; (b) EG10 RPUF; (c) WSi10 RPUF; and (d) EG10-WSi10 RPUF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

obvious falling trend because of the increase of the molecular mobility. From this figure, it can be obtained that the E' value of EG10 RPUF or WSi10 RPUF is lower than that of pure RPUF from 50 to 160°C. However, the reverse result obtains beyond 160°C. There are two important points. One is that higher molar NCO/OH value (1.40) results in higher crosslinking degree. Thus, the E' values of the composites are comparatively higher.[38] The other is that the addition of WSi particles increases the E' of the composites owing to its stiffness, whereas EG particles decrease the E' of the composites for its gaps between graphite flakes. Both WSi and EG particles can inhibit the molecules' mobility. As a consequence, the crosslinking degree of RPUF will decrease. In the range of 50–160°C, the effect of the WSi particles on the increase of E' cannot compensate for the effect on the decrease of E', which is caused by reduction of crosslinking degree. For EG10 RPUF, EG particles can only decrease E' value in this temperature range. Beyond 160°C, the stiffness of the fillers (WSi and EG particles) is much higher than that of PU matrix. So their storage moduli are higher than that of pure RPUF. The E' value of EG10-WSi10 RPUF is higher than pure RPUF throughout the temperature range. With temperature increasing, the movement of polymer chain segments becomes easier, thus the E' values drop. But the E' values of the additives are not sensitive to the temperature, thus, the decrease of E' of EG10-WSi10 RPUF is less than others. Furthermore, with the decrease of the resin fraction, the fillers' effect on E' becomes prominent during the process of heating.

The loss modulus (E'') spectra of pure RPUF, EG10 RPUF, WSi10 RPUF, and EG10-WSi10 RPUF are shown in Figure 8. It shows that all the formations have a major transition. The E'' values of EG10 RPUF and EG10-WSi10 RPUF are higher than that of pure RPUF, whereas the E'' value of WSi10 RPUF is lower than pure RPUF. It is because that EG particles are sheet-like structure, and when molecular chains move, greater friction will be generated between particles, which leads to higher E'' value. However, the WSi particles are pin and generate less friction whereas molecular chains move, which results in a lower E'' value.[39]

Figure 9 shows the loss tangent (tan δ) curves of pure RPUF, EG10 RPUF, WSi10 RPUF, and EG10-WSi10 RPUF. The glass transition temperature (T_g) values of all the filled composites are higher than that of pure RPUF. The T_g values of pure RPUF, EG10 RPUF, WSi10 RPUF, and EG10-WSi10 RPUF are 176°C, 187°C, 192°C, and 189°C, respectively. Generally, the material which tan δ value is beyond 0.3 can be considered to have damping effect. According to this rule, the temperature range for each composite having damping effect is 165.5–187.7°C, 168.5–203.5°C, 177.5–207.5°C, 171.5–207°C for pure RPUF, EG10 RPUF, WSi10 RPUF, and EG10-WSi10 RPUF, respectively. The maximum tan δ (tan δ_{max}) value for each formulation is also different. The tan δ_{max} of pure RPUF, EG10 RPUF, WSi10 RPUF, and EG10-WSi10 RPUF is 0.50, 0.51, 0.46, and 0.47, respectively. The tan δ_{max} of EG10 RPUF is the best. The increase of the temperature range for damping effect should be due to the restriction of molecular motion because of the incorporation of additives.[40] We can obtain the information of the viscous and elastic components of a viscoelastic material through tan δ value. Lower tan δ indicates that the formulations have more elastic nature than viscous nature.[41] Thus, WSi10 RPUF has more elastic nature. It is caused by two reasons. One is that the adding of WSi particles which decreases the

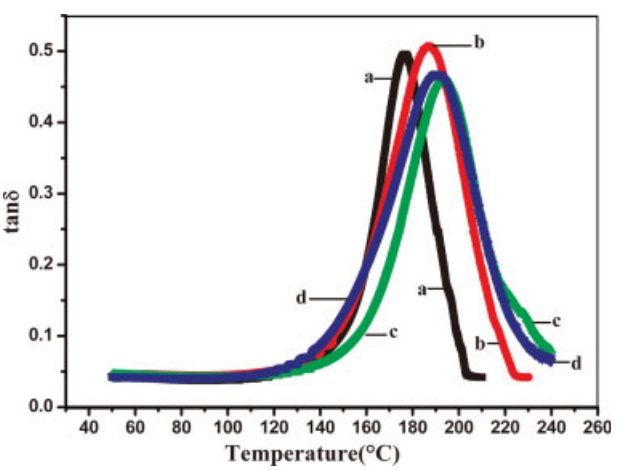

Figure 9 Tan δ: (a) Pure RPUF; (b) EG10 RPUF; (c) WSi10 RPUF; and (d) EG10-WSi10 RPUF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

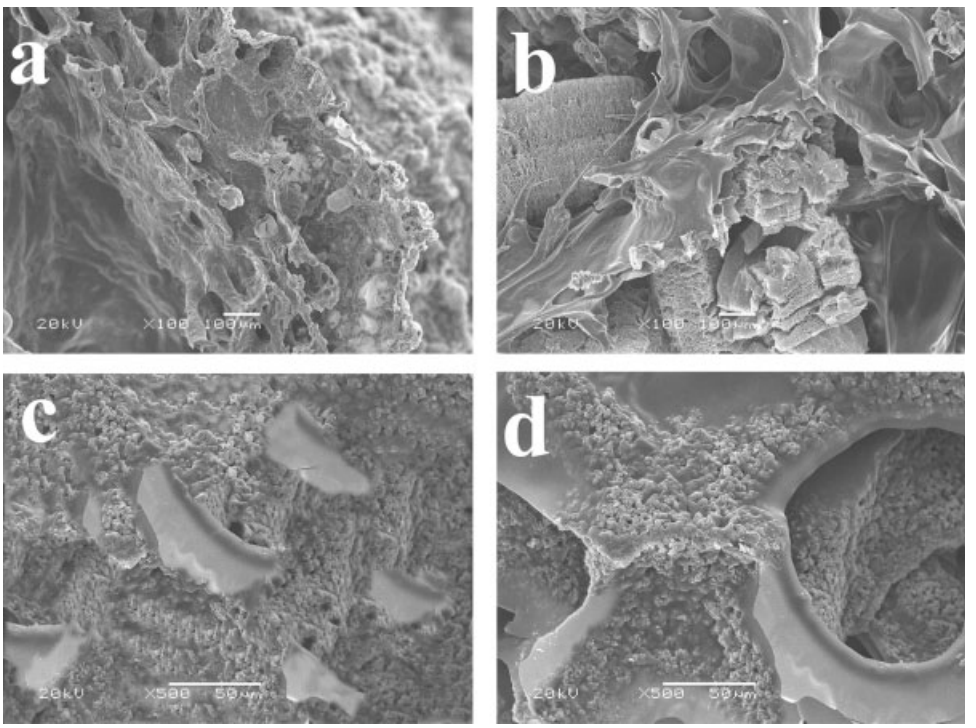

Figure 10 SEM micrographs of the burned char: (a) low magnification of WSi10 RPUF; (b) low magnification of EG10-WSi10 RPUF; (c) high magnification of WSi10 RPUF; and (d) high magnification of EG10-WSi10 RPUF.

crosslinking degree of RPUF, another is the shape and the rigidity of WSi particles leads to less friction.

Morphology of the burned surfaces of RPUF composites

Figure 10 shows the burned layer SEM micrographs of WSi10 RPUF and EG10-WSi10 RPUF with various magnifications. The burned layer of pure RPUF is residual charred layer.[30] The low-magnification micrograph of WSi10 RPUF [Fig. 10(a)] is similar with that of pure RPUF. Only charred layer can be observed because the size of WSi particles is small. From the high-magnification micrograph of WSi10 RPUF [Fig. 10(c)], the WSi particles and little charred layer can be found. This is because WSi particles cannot burn and do not have flame retardant property, so the particles and little charred layer are left. It is consistent with the analysis of flame retardant properties. Because EG particles are very larger than WSi particles, Figure 10(b) (low-magnification micrograph of EG10-WSi10 RPUF) presents the expanded graphite sheets and charred layer. With high magnification, more charred layer and less WSi particles can be found than that of WSi10 RPUF [Fig. 10(c)]. The result further proves that many WSi particles can assist EG particles to cover the burned surface of the matrix.

WSi particle is a useful addition to improve mechanical properties of RPUF. But the presence of WSi has little improvement on the flame retardant properties of RPUF. However, the flame retardant properties of RPUF are as important as the mechanical properties in many regions. As we known, EG is an excellent flame retardant additive for RPUF.[28–30] The adding of EG can improve the flame retardant properties of WSi/RPUF composites. With the EG content increasing, the flame retardant properties of the composites become better. But the mechanical properties of EG/RPUF composites fall. Adding 10 wt % WSi particles, the mechanical properties of EG/RPUF composites can be improved. At a certain EG content (EG content >5 wt %), the flame retardant properties can be improved too. So adding appropriate EG and WSi particles can improve the mechanical and flame retardant properties of RPUF simultaneously.

CONCLUSIONS

The adding of WSi particles can obviously improve the compressive strength and modulus of RPUF. When the WSi content goes up to 10 wt %, the enhanced effect is the best.

The mechanical properties of EG filled RPUF composites can be improved by filling 10 wt % WSi particles. Moreover, when the EG content is beyond 5 wt %, the flame-retardant properties of these composites can also be improved than that of only EG filled RPUF composites.

The adding of EG or/and WSi particles make T_g of the RPUF composites shift to the high temperature and magnify the damp temperature range. Furthermore, 10 wt % EG and 10 wt % WSi filled RPUF has the higher storage modulus than other formulations.

Through thermal analysis, it can be found that the adding of EG or/and WSi will improve the thermal properties of the composites.

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