Flame-Retardant and Mechanical Properties of High-Density Rigid Polyurethane Foams Filled with Decabrominated Dipheny Ethane and Expandable Graphite

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ABSTRACT: The article reported the flame-retardant and the mechanical properties of expandable graphite (EG), an intumescent type, and decabrominated dipheny ethane (DBDPE), a gas-phase type of flame-retardant-containing high-density rigid polyurethane foams (RPUF) with a constant density of $0.5 \mathrm{g/cm^3}$. The results indicated that both EG and DBDPE could effectively interdict the burning of RPUF, besides, the EG exhibited more effective flame retardancy than the DBDPE. When the flame-retardant loadings were 20 wt %, the LOI value of DBDPE-filled RPUF increased to 33 vol %, while, surprisingly, the EG-filled RPUF reached 41 vol %. Unfortunately, when they were both simultaneously added into RPUF, there was not any flame-retardant synergistic effect. Although EG had outstanding flame retardancy, the compressive strength and modulus of 20 wt % EG-filled RPUF dropped to only 9.1MPa and 229.7MPa respectively, which were lower than those of DBDPE (12.4 MPa and 246.8 MPa). The phenomena were ascribed to the different flame-retardant mechanisms of EG and DBDPE, which were verified by scanning electronic microscope (SEM) observation of the burned surfaces. Besides, the dynamical mechanical analysis (DMA) demonstrated that the additions of EG and DBDPE made the glass transition temperature shift to the high temperatures, and the EG-filled RPUF had the higher storage modulus. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2372–2380, 2009

Key words: rigid polyurethane foams; expandable graphite; decabrominated dipheny ethane; flame-retardant property; mechanical property

INTRODUCTION

Polyurethane (PU) forms a very wide family of polymeric materials (paints, adhesives, elastomers, flexible, and rigid foams, etc.) and thus plays an important and increasing role in our daily life.[1,2] The rigid polyurethane foams (RPUF) are commonly used as structural and insulating materials,[3,4] and particularly, as an excellent encapsulant to isolate and support heat-sensitive components for electrical engineering, electronics, and weapon systems with good physical and mechanical properties.[5]

Like other organic materials, one of the major drawbacks of RPUF is their flammability, and therefore flame-retardant additives are usually needed, among which halogenated compounds are most widely used. It is reported that brominated additives represent 25–30% of the total flame retardant consumption in the United States and the Western Europe,[6] which work by suppressing ignition and by slowing flame spread. In the point of flame retardancy, the halogenated flame retardants are most effective and cannot be substituted in many applications to date, but, in certain cases, they may give rise to environmental problems. For instance, the decabromo diphenyloxide (DBDPO) used in conjunction with antimony trioxide (Sb_2O_3) is one of the universally used flame-retardant systems for fire-retardant polymers. Nevertheless, the use of diphenyl oxide (DPO) based on flame retardants is of growing environmental concern because studies have shown that small amounts of brominated dioxins and furans can produce during processing DBDPO-containing polymers.[7] Therefore, the aim of gradually limiting brominated DPOs has led to the development of new brominated substituted products to answer the current ecological needs.[8] To substitute the traditional flame retardants, decabrominated dipheny ethane (DBDPE) is employed which does

not possess any ether bonds with regard to the chemical structure. Consequently, there are no brominated dioxins or furans to produce. Thereby, in our study, we added DBDPE/Sb$_2$O$_3$ as one kind of flame retardant into high-density RPUF.

Nowadays, the progressive shift away from halogenated flame retardants particularly in the North European countries, because of the potential risks related to their decomposed products, has led to a new interest in specific mineral fillers and has accelerated the development of intumescent formulations, which represents a potential interesting way to impart fire performance to polymeric materials.[9] Once exposed to a heat source, the intumescent systems will develop a voluminous, stable carbonaceous layer on the surface of the material. The layer limits heat and mass transfer as well as oxygen diffusion between the heat source and the virgin polymer thus interrupting the self-sustaining combustion of the polymer.[10] As an intumescent additive, expandable graphite (EG) is used in a growing number of fire-retardant applications as a blowing agent and suppressor for smoke, and its efficiency in PU has been reported in a large amount of literature.[11,12]

However, with the addition of EG particles into RPUF, the mechanical properties of this matrix will be deteriorated, according to our previous works.[13] Therefore, the other kind of flame retardant, DBDPE, was filled into the RPUF system and its mechanical properties were investigated. Meanwhile, the flame retardancy of these composites was evaluated in this work. In addition, the synergistic flame-retardant effect of EG and DBDPE was also estimated.

EXPERIMENTAL

Materials

1. Polyether polyol, GR-4110G, originated from polypropylene oxide and sucrose/glycerin base, was obtained from Gaoqiao Petro. Co. (Shanghai, China). The 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, a crosslink catalyst with a density (25°C) of 1.122 g/cm^3, was purchased from Shanghai Chemical Reagent Co. (Shanghai, China).
3. Dibutyl tin dilaurate, a catalyst with a density of 1.052g/cm^3, was available from Sichuan Chemical Reagent Co. (Chengdu, China); Sn content, 18 wt %.
4. Distilled water, a blowing agent, was made by us.
5. Silicone glycol copolymer, a surfactant for foams was saved in our laboratory.

6. EG, a flame retardant, was bought from Haida Graphite Co. (Qingdao, China). Main properties of EG: ash, 1.0%; moisture, 1.0%; volatile, 15%; PH value, 3.0; expansive rate, 200 mL/g.
7. Isocyanate, N200, PAPI was gotten from Changfeng Chemical Co. (Chongqing, China). Main properties of N200: Isocyanate equivalent weight, 126.5 g; -NCO weight percent, 30%; viscosity (25°C), 215 cps; functionality, 2.2.
8. DBDPE, decabromated dipheny ethane, a flame retardant, purity: 97%, melting point: 345–350°C, was prepared in our laboratory.
9. Sb$_2$O$_3$, antimony trioxide, a synergist, purity: 98%, was gained from Xinggang Chemical Co. Guangzhou, China.

DBDPE preparation

A new type of flame retardant, decabromodiphenyletbane (DBDPE), forming not-dloxin-related compounds when oxidized or burned, was prepared by bromination of 1,2-diphenylethane which was synthesized with 1,2-dichlorcethane in course of which benzene was used as a reactant and AlCl$_3$ as a catalyst. Then the crude product was dried for 1 h at 110°C and heat-treated for 4 h at 200–220°C. Finally, a white retardant was prepared with a yield of 94.2% and purity of 97%.

Foam preparation

The preparation of the RPUFs has been reported in our previous works.[14–16] In this work, the density of the foams was controlled to ∼ 0.50 ± 0.01 g/cm^3. The RPUFs filled with 5, 10, 15, and 20 wt % of EG were prepared respectively, and DBDPE/Sb$_2$O$_3$ (3 : 1)-filled RPUFs were prepared similarly. We abbreviate 5, 10, 15, and 20 wt % EG-filled RPUF to EG5 RPUF, EG10 RPUF, EG15 RPUF, and EG20 RPUF, respectively. And similarly, 5, 10, 15, and 20 wt % DBDPE/Sb$_2$O$_3$ (3 : 1)-filled RPUF are abbreviated to DBDPE5 RPUF, DBDPE10 RPUF, DBDPE15 RPUF, and DBDPE20 RPUF.

Characterization

Horizontal and vertical burning tests

The horizontal and the vertical burning tests were performed using a CTF-2 horizontal and a vertical burning instrument (made in Jiangning County, 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 127 × 13 × 10 mm^3. The procedures of the standard vertical
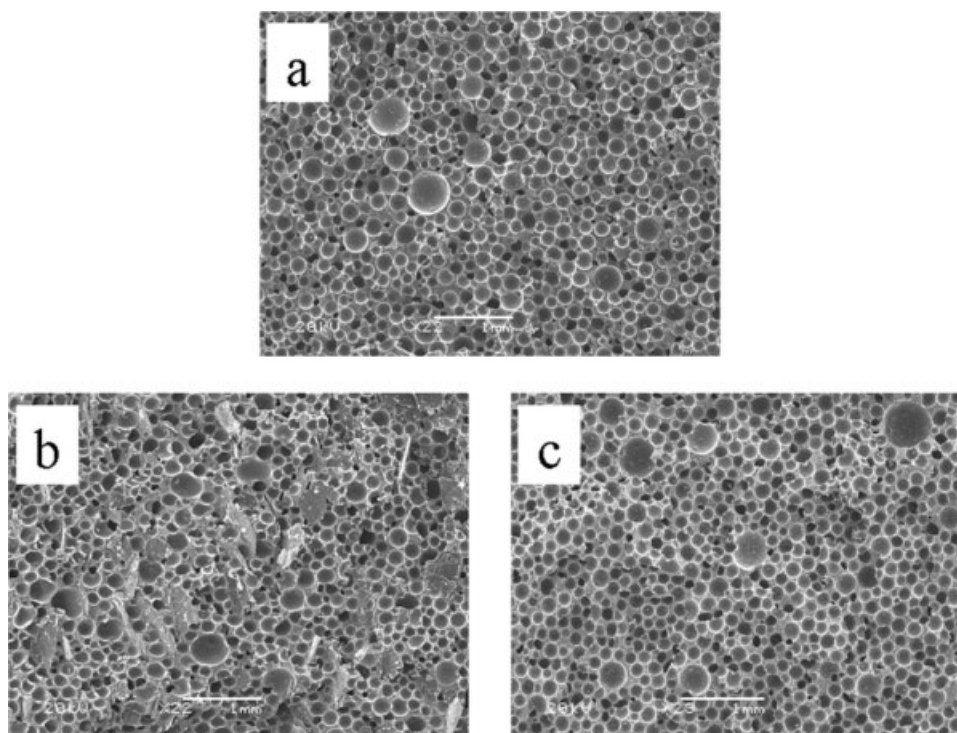
Figure 1 SEM micrographs of pure RPUF (a), EG10 RPUF (b), DBDPE10 RPUF (c).

burning test and the horizontal burning test as well as the definitions and units of Vertical and Horizontal burning rate were referred to what were expatiated in the literature 16.

Limiting oxygen index test

The limiting oxygen index (LOI) test was performed with an HC-2 oxygen index test instrument (made in Jiangning County, China) in terms of the standard LOI test, ASTM D 2863-97. The specimens for measurement were sheets of $127 \times 10 \times 10$ mm^3.

SEM observation

The morphology of the samples, including the original and the burned samples, was observed under a JSM-9600 (JEOL, Japan) scanning electron microscope (SEM) with an accelerating voltage 20 kV.

Mechanical measurement

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

Dynamic mechanical analysis

The dynamical mechanical analysis (DMA) was carried out using a Q800 DMA instrument (TA, America)

with a heating rate of 3°C/min. The samples were constituted of sheets of $35 \times 10 \times 4$ mm^3. The temperature range was 50–250°C.

RESULTS AND DISCUSSION

Morphology of RPUF composites with different additives

Figure 1 shows the SEM micrographs of pure RPUF, EG10 RPUF, and DBDPE10 RPUF. As observed from Figure 1(a), the cell shape of the pure high-density RPUF is approximately spherical and the size of the cell is symmetrical on the whole. Besides, no signs of collapse or collisions in the cell system are observed, too, indicating a homogeneous integral in the unfilled RPUF matrix and cells.

As presented in Figure 1(b), the EG flakes, which are built up with multiple layers of graphite sheets, are intercalated in the RPUF matrix. The dispersion of EG in the matrix is poor, and many agglomerates are formed. Furthermore, owing to the thickness and the width of EG flakes, they span several cells in the foam matrix and therefore make these cells collapse [as shown in Fig. 2(a)]. On the contrary, Figure 1(b,c) displays an absolutely different microstructure. Compared with the pure RPUF [Fig. 1(a)], the shape of cells almost does not change for the DBDPE-filled RPUF, namely, the cell system is integrated as no collapse or collision happens. However, the size of cells decreases and the homogeneity improves after adding the DBDPE into RPUF.
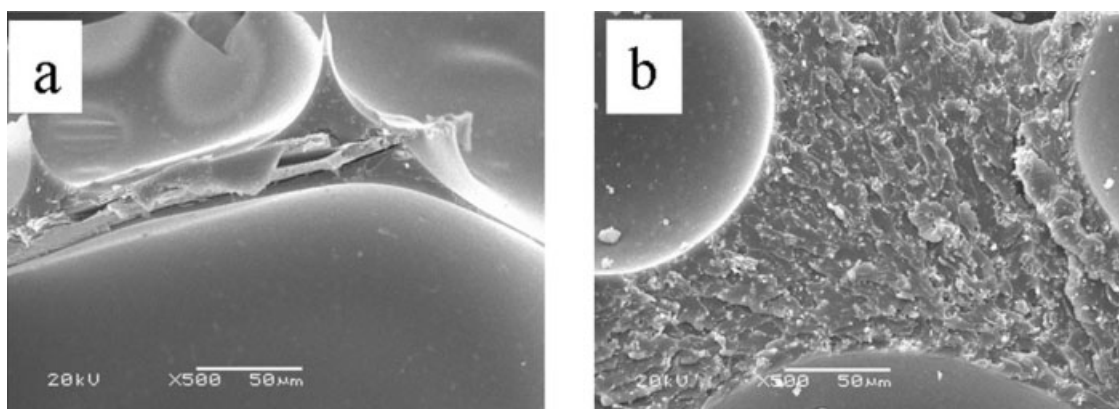
Figure 2 SEM micrographs of high magnification of EG10 RPUF (a), DBDPE10 RPUF (b).

Figure 2(b) demonstrates that the small-sized powders of DBDPE are mostly distributed homogeneously to the walls and the struts of cells. From Figure 3, the average cell diameter of EG10 RPUF and pure RPUF are similar (186.13 μm and 185.13 μm, respectively), larger than that of DBDPE10 RPUF (141.23 μm), indicating the nucleation of the small-sized additives in the process of foaming. Besides, the cell-sized distribution of EG10 RPUF is the widest of the three kinds of materials, also revealing that the cells of EG10 RPUF are asymmetrical because of the collapse and collision of the cells while the smallest cell-sized distribution of DBDPE10 RPUF shows the most symmetrical cell structure.

Flame-retardant properties of RPUF composites

As shown in Figure 4, both EG and DBDPE are effective fire retardants for RPUF. The curves of the LOI versus EG and DBDPE contents show a substantial increase in the LOI values. The LOI value increases drastically from 21 vol % for pure RPUF to 33 vol % for DBDPE20 RPUF, and even to 41 vol % for EG20 RPUF, implying that the incorporation of sufficient EG and DBDPE into RPUF can make these RPUFs flame-retardant upgrade. Besides, Figure 4 indicates that, compared with the LOI values of DBDPE-filled RPUF, the EG-filled RPUF presents more excellent effect on flame retardacy with the same weight content. It may be ascribed to EG, an effective intumescent fire retardant, developing a voluminous, stable, and compact carbonaceous layer when exposed to a heat source. However, as a gas-phase flame retardant, DBDPE will release Br_2 and HBr needed to limit heat and mass transfer, and dilute the content of oxygen, between the heat source and the virgin polymer, thus interrupting the self-sustaining combustion of the polymer. The vertical and the horizontal burning tests also confirm the results of LOI, as shown in Tables I and II.

From Tables I and II, it is seen that the after-flame time (i.e., after the first flame impingement) for pure
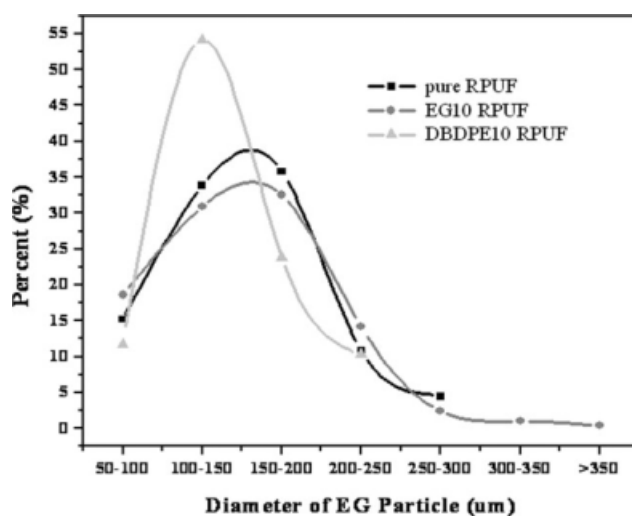

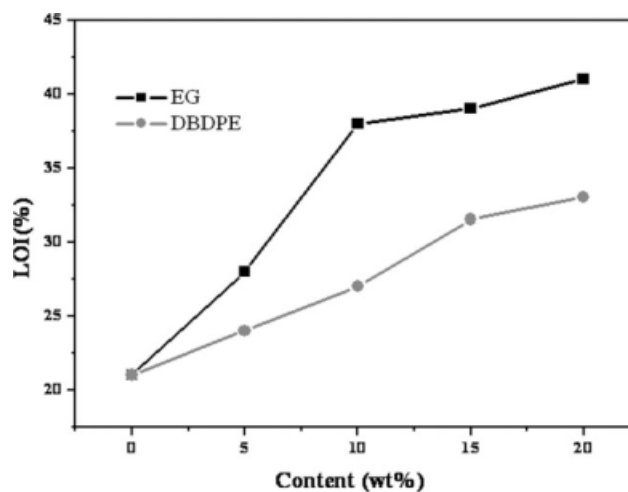**Figure 3** The size distribution of pure RPUF, EG10 RPUF, and DBDPE10 RPUF.

Figure 4 The effects of EG, DBDPE contents on the LOI values.

TABLE I
Formulas of EG-Filled RPUF Composites That Passed the Vertical and the Horizontal Burning

Content of EG (wt %)	The after-flame time after the first flame impingement (t_1/s)	The after-flame time after the second flame impingement (t_2/s)	Horizontal burning rate	Vertical burning rate
0	201	–	6.76×10^{-3} m/s	–
5	3.1	13.0	HB-1	V-1
10	2.0	3.7	HB-1	V-0
15	1.3	2.4	HB-1	V-0
20	1.2	1.7	HB-1	V-0

V, vertical burning; H, horizontal burning.

RPUF is longer than 30 s; thus pure RPUF cannot be classified by the vertical burning test but by the horizontal burning test, suggesting that the pure RPUF is a quite combustible polymer. After the addition of EG or DBDPE, the flame-retardant properties of these composites are improved, so that the vertical burning rate turns into V-0 rate. Although the vertical burning rate of the composites can achieve the V-0 rate when the content of EG or DBDPE reaches 10 wt %, the first and the second after-flame time of EG-filled RPUF are 2.0 s and 3.7 s, shorter than those of DBDPE-filled RPUF (3.1 s and 4.5 s), demonstrating the EG-filled RPUF possesses more effective anticombustible capability.

In the flame-retardant system of RPUF, the synergistic effect of two or several flame retardants has been reported. In our study, EG is the intumescent flame retardant, and DBDPE belongs to the gas-phase flame retardant. Whether these two types of flame retardants can carry out the synergistic effect arouses our interest. However, the synergistic effect does not occur when we add EG and DBDPE into RPUF simultaneously in our study. As shown in Figure 5, the broken line represents the critical curve. When a curve lies under the critical curve, it indicates that there is no synergistic, and vice versa. The LOI values reduce as the content of EG decreases. From Figure 5—we fix the total content of

additions (20 wt %)—it is indicated that not only do the two kinds of flame retardants have no synergistic effect on RPUF, but the EG can also more effectively improve the flame-retardant property of RPUF than DBDPE. For instance, when the weight ratio of EG/DBDPE is 15 wt %:5 wt %, the LOI value is 38%, and the LOI value turns down to 34% as the weight ratio of EG/DBDPE becomes 5 wt %:15 wt %.

Compressive strength and compressive modulus of RPUF composites

To verify the function of EG or DBDPE-filled RPUF, the compressive strength and the compressive modulus of the composites with different contents in the matrices were measured. Figures 6 and 7 present the variations of the compressive strength and the compressive modulus of various EG or DBDPE contents.

From Figures 6 and 7, it can be seen that both the compressive strength and the compressive modulus reduce with the addition of EG or DBDPE into the RPUF matrix, and with the contents of these additions increasing, the curves drop gradually. For instance, the compressive strength of pure RPUF is 18.3 MPa; however, it drops to 13.9 MPa and 16.7 MPa with 5 wt % EG and 5 wt % DBDPE into RPUF, respectively. This is due to the incompatibility of these additives and the matrix. From these

TABLE II
Formulas of DBDPE-Filled RPUF Composites That passed the Vertical and the Horizontal Burning

Content of DBDPE (wt %)	The after-flame time after the first flame impingement (t_1/s)	The after-flame time after the second flame impingement (t_2/s)	Horizontal burning rate	Vertical burning rate
0	201	–	6.76×10^{-3} m/s	–
5	8.3	14.0	HB-1	V-1
10	3.1	4.5	HB-1	V-0
15	2.0	3.6	HB-1	V-0
20	1.8	2.0	HB-1	V-0

V, vertical burning; H, horizontal burning.
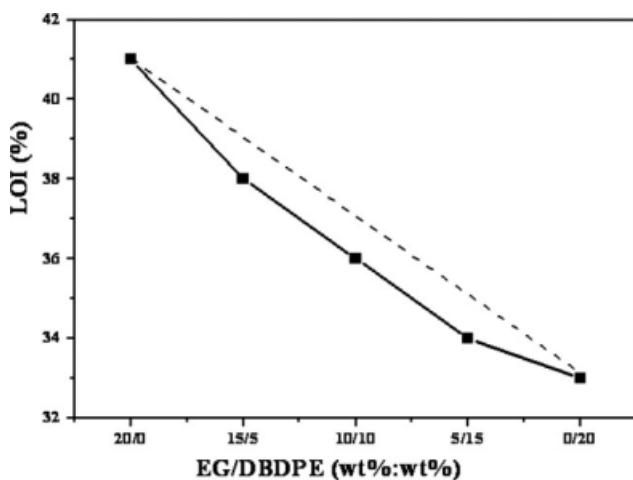
Figure 5 The effects of EG/DBDPE (wt %:wt %) complex systems on the LOI values.

Figure 7 Compressive modulus of EG, DBDPE-filled RPUF with various contents.

two figures, it is demonstrated that the decreasing degree of DBDPE-containing RPUF is smaller than that of EG-containing RPUF. For example, when the added contents are 20 wt %, the compressive strength and modulus of DBDPE-filled RPUF are 12.4 MPa and 246.8 MPa, while only 9.1 MPa and 229.7 MPa for EG-filled RPUF, which are the low-level marks of all the four curves. This is owing to the relatively large size of sandwich EG. In contrast, for the DBDPE powders, they are tiny, therefore, the collapse of the matrix cells does not take place, so the integrality of RPUF is well preserved.

Dynamic mechanical analysis of RPUF composites

The dynamic mechanical analysis is a precise technique that provides the information about the viscoelastic properties like the stiffness and the energy dissipation of soft and hard materials. Therefore,
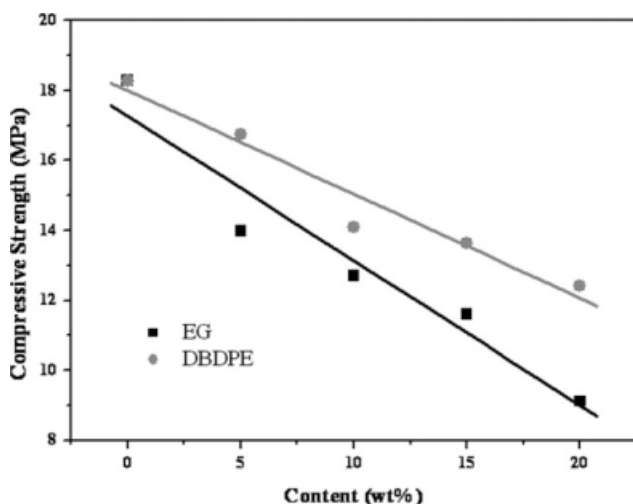
DMA is a widely used technique to examine the viscoelastic features of PU foams.[17–19] The storage modulus (E'), loss modulus (E'') and loss factor (tanδ) curves obtained from the DMA measurement of pure RPUF, and EG10 and DBDPE10 RPUF are shown in Figures 8–10.

Figure 8 shows the variations of the storage modulus (E') as the functions of the temperature of pure RPUF, and EG10, DBDPE10-filled RPUF. At around 160°C, the glass transition appears. Below the glass transition temperature, the storage modulus values drop as the temperature increases. In the vicinity of glass transition temperature, a very considerable drop is observed, which indicates that the material is going through a glass transition.[20] Within all the temperature range used in this study, a general monotonically falling trend can easily be observed for all formulations, and a considerable improvement in the storage modulus values is seen when
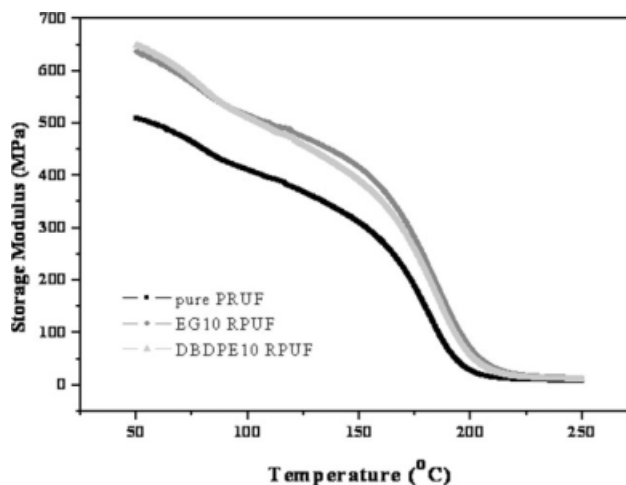

Figure 6 Compressive strength of EG, DBDPE-filled RPUF with various contents.

Figure 8 Dependence of the storage modulus of composites on temperature.
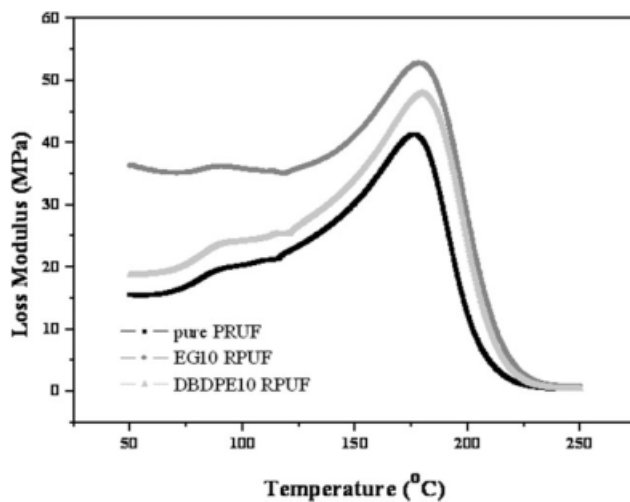
Figure 9 Dependence of the loss modulus of composites on temperature.

EG or DBDPE is added. From this figure, it is also observed that the E' of EG10 RPUF shows slightly more predominant than that of DBDPE10 RPUF. It is also important to known that the glass transition determined from the storage modulus spectrum generally differs from what is determined from the loss modulus spectrum, because they actually show two different stages in transition. In the storage modulus spectrum, the onset of the transition is observed, while in the loss modulus spectrum, the peak point is considered.

Figure 9 shows the dependence of the loss modulus (E'') of pure RPUF, and EG10 RPUF, DBDPE10 RPUF on temperature. The transition, which is seen at around 176°C, is the glass transition. As mentioned above, the glass transition temperature observed in the loss modulus curve is about 15°C higher than what is determined from the storage modulus curve. Moreover, in the case of the storage modulus, the same trend is observed of both pure RPUF and the composites, but the intensities of the transitions and their locations are different in the loss modulus curve. Namely, all the composite formulations exhibit higher loss modulus values than pure RPUF. The curves also demonstrate the loss modulus of EG10 RPUF is higher than that of DBDPE10 RPUF, which is because the EG particles are the sheet structure and generate greater frictions with the molecular chains moving. However, the DBDPE particles are finer powders and generate less frictions while the molecular chains are moving, which leads to a lower E'' value.[21,22]

The glass transition temperature is an important indicator for applications of polymeric materials. The peak tanδ is the most prevalent criterion appearing in the literature because it corresponds more closely to the transition midpoint, while the peak E''

more closely denotes the initial drop from the glassy state into the transition.[21,23,24]

Damping (loss factor, tanδ) expresses the ability of converting the mechanical energy into the heat energy when a material is subjected to an external loading. It is generally defined as the equality as follows:

$$\tan \delta = E''/E'$$

Here δ is the phase angle between stress and strain, and E' and E'' are the elastic storage modulus and the elastic loss modulus respectively. As a result, tanδ is an important parameter characterizing material's viscoelasticity.[25,26] From Figure 10, we can see that the values of tanδ increase first and then decrease with the temperature increasing, which means that the increase in E' is slower than that in E'' when the temperature is under the glass transition temperature (T_g), but the case is reversed when the temperature increases to over T_g. As shown in Figure 10, the peak values of tanδ of the composites with EG10 (0.41), DBDPE10 (0.40) in the matrices are lower than that of the composite with pure RPUF (0.46), which proves that the addition of EG or DBDPE cannot enhance the dynamic mechanical property of RPUF. Lower tanδ of the composite formulations clearly indicates that these formulations exhibit more the elastic (spring-like) than the viscous (dashpot-like) nature as compared with pure RPUF.

The burned char layers of RPUF composites after combustion

SEM micrographs illustrated in Figure 11 show the microscopic structures of inside layers, interfaces and char layers of EG10 and DBDPE10 RPUF. In the
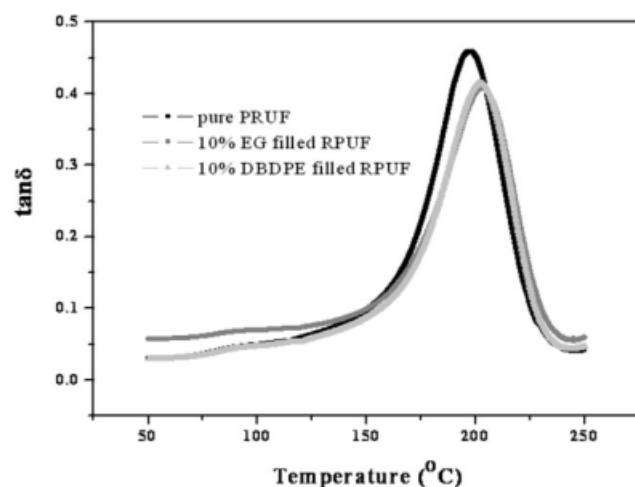

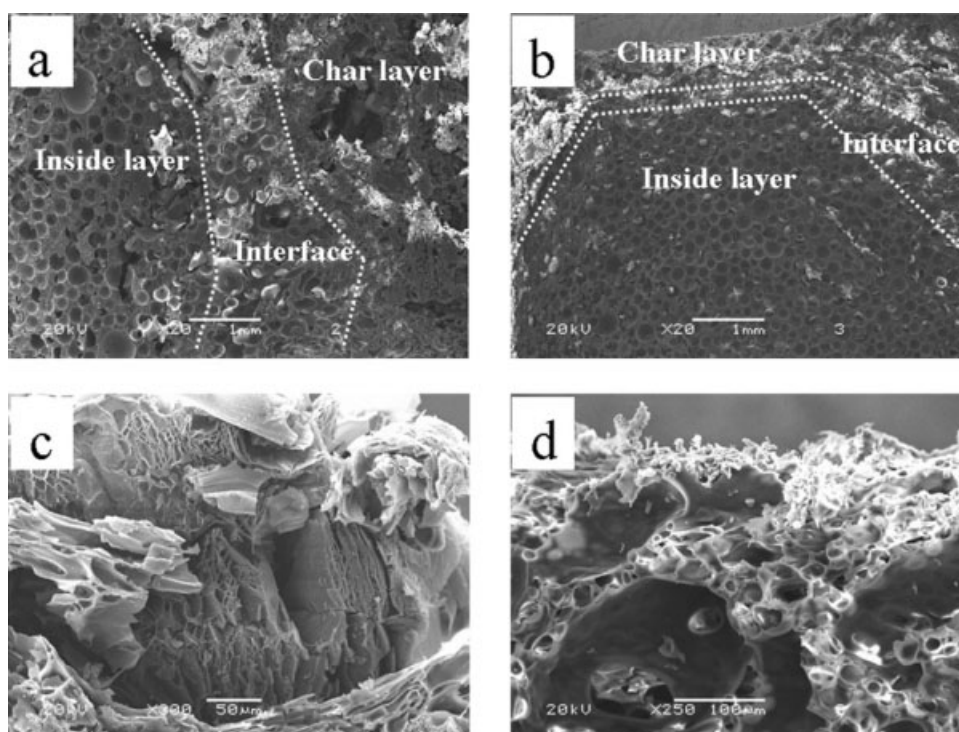**Figure 10** Dependence of the tanδ of composites on temperature.

Figure 11 SEM micrographs of the burned char: (a) low magnification of EG10 RPUF, (b) low magnification of DBDPE10 RPUF, (c) high magnification of EG10 RPUF, (d) high magnification of DBDPE10 RPUF.

low magnified micrographs, the cell structure of the interfaces is anamorphic, and at the same time, the interfaces and the char layers outside the matrix are very clear for both EG10 and DBDPE10 RPUF [Fig. 11(a,b)], indicating that the additions of EG and DBDPE, can prevent the combustion of RPUF effectively. In addition, as shown in Figure 11(a,b), EG10 RPUF [Fig. 11(a)] possesses thicker char layer than DBDPE10 RPUF [Fig. 11(b)] due to the different mechanisms of the flame retardants of EG and DBDPE. For EG, it belongs to the intumescent flame retardant, therefore, when exposed to a heat source, it will experience a great volume expansion to form a loose structure whose thickness of monolayer is estimated to be less than 100 nm, and eventually it appears to be many times larger than the original graphite flakes, as shown in Figure 11(c). As a sort of gas-phase flame retardant, DBDPE will release HBr covering the RPUF and then dilute the oxygen concentration when it is heated. After burning, the char layers of DBDPE10 RPUF [Fig. 11(d)] appear many irregular holes indicating the deformation of RPUF.

As described above, Both EG and DBDPE can effectively interdict the burning of RPUF, besides, EG displays more outstanding flame-retardant property, but worse mechanical property compared with DBDPE. Therefore, EG and DBDPE are filled into RPUF simultaneously to observe the synergetic effect of them. However, the result shows that the addi-

tions of the EG and DBDPE will not exhibit a synergetic effect on flame-retardant property, which can be due to the different mechanism of the flame retardants. At the same time, adding EG and DBDPE into RPUF simultaneously, owing to the lack of EG concentration, makes the flame-retardant property of it not bear compared with that of the EG-filled RPUF with the same content.

CONCLUSIONS

In this study, we have characterized the flame-retardant properties through the horizontal, the vertical burning test and the LOI, the mechanical properties of EG, DBDPE-filled RPUF through compressive tests, the damping properties through dynamic mechanical analysis, etc., and have made some progress. As the flame retardants, both EG and DBDPE could improve the flame-retardant property of RPUF effectively. At 20 wt % content, the LOI value of EG was 41%, higher than that of DBDPE (33%), from which it was also known that EG possesses more effective anticombustible capability than DPDPE, as could be well explained from their microstructures. However, in our study, no flame-retardant synergistic effect produced, as was shown from the curve of the LOI values lay under the critical curve when EG and DBDPE were added simultaneously into RPUF. Moreover, although EG showed more outstanding flame-retardant property, it

displayed worse compressive strength and modulus than DBDPE. The additions of EG and DBDPE particles could make T_g of the RPUF composites shift to the high temperature. Furthermore, EG10 RPUF and DBDPE10 RPUF had the higher storage modulus than other formulations. Finally, the SEM micrographs of the burned char layers demonstrated that the mechanism of the flame retardant, namely the compact and condensed burned char layers of EG-filled RPUF, possessed better flame-retardant property.

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