Journal of Applied Polymer Science

Effects of Inorganic Fillers on the Flame-Retardant and Mechanical Properties of Rigid Polyurethane Foams

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ABSTRACT: Rigid polyurethane foam (RPUF) composites filled with expandable graphite (EG), hollow glass microspheres (HGM), and glass fibers (GF) have been synthesized and characterized by limiting oxygen index, radiation ignition, compressing and torsion testing, and scanning electron microscopy. The results indicate HGM and GF benefit to the mechanical properties, while EG is good for flame retardancy. Proper ingredient of additive can lead to good flame retardancy and mechanical properties of the RPUF. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40253.

KEYWORDS: flame retardance; mechanical properties; polyurethanes

Received 12 August 2013; accepted 3 December 2013
DOI: 10.1002/app.40253

INTRODUCTION

Polyurethane materials, which have been widely used as thermal insulation materials, adhesives, coatings, etc., play a versatile role in our lives.[1–3] Especially, rigid polyurethane foam (RPUF) is extensively applied as encapsulant for thermal-sensed components in many cases due to its excellent properties such as high compressive strength, good heat resistance, low thermal conductivity, and light weight.[4,5] With the booming of functional materials, it raises a demand of developing novel RPUF with flame retardancy.[6–9] A most common way to improve the flame retardancy of RPUF is adding flame retardants.

Commonly used flame-retardant additives mainly include halogen,[10] phosphorus,[11,12] nitrogen,[13] etc. However, these traditional flame retardants cannot meet the public demands for good flame retardancy, mechanical properties, smoke suppression as well as low emission of toxic gas. Nowadays, as inorganic fillers such as chitin bentonite clay,[14,15] polyacryl clay,[16] calcium carbonate,[17,18] have been widely applied in modifying polymer materials, it provides an opportunity for the development of inorganic flame retardant. Large efforts have been made to find more effective and environmentally friendly flame retardants for decades.

A common halogen-free intumescent material for RPUF is expandable graphite (EG), which is a kind of flake graphite preprocessed with sulfuric acid. When heated to a certain temperature, EG will expand rapidly and generate insulative worm-like layer on the surface of the polymeric matrix that prevent the transfer of heat and oxygen. Shi et al.[19] have studied on the particle size effect of EG in high-density RPUF composites. They concluded appropriate particle size would improve flame retardancy. Besides, the influence of the EG content affected on flame retardant has been surveyed by Bian et al.,[20] and it revealed higher foam density and larger EG proportion were in favor of better flame retardancy. Hu et al.[21] and Meng et al.[22] also have systematically discussed the effect of EG on the flame retardancy and mechanical properties of RPUF, and they concluded that with the increasing of EG content, the flame retardancy would be improved, while the mechanical properties would be affected compared with original RPUF (Ref. RPUF).

Because the mechanical properties of the composites are sacrificed with the increase of EG content,[3] how to improve the mechanical properties of the EG/RPUF has attracted considerable attention. Glass fibers (GF) and hollow glass microspheres (HGM) are universally used to reinforce the mechanical properties of polymers. V. Yakushin and his fellows have investigated the effect of HGM on the properties of low-density RPUF.[25] They indicated compressive property of RPUF would be enhanced by increase of HGM content. Chalivendra et al.[26] found HGM had a great effect on compressive mechanical properties of RPUF, and the presence of HGM with intrinsic low density barely affected the density of HGM/RPUF.[27] However, HGM have a limited impact on tensile or torsional mechanical properties because of their spherical structures. Consequently, Lu et al.[28] looked into the tensile and compressive properties of RPUF

Table I. Specifications of the Materials Used in This Work

Materials	Specifications
Polyether polyol	450 mgKOH/g, obtained from Tianjin petrochemical company third petroleum chemical plants (Tianjin, China)
Polyisocyanate (PAPI)	Isocyanate 31 wt %, obtained from Rain Field Chemical (Shanghai, China)
33% of triethylene diamine solution and dibutyltin dilaurate	Available from OL chemical (Shanghai, China)
Silicon compound foam stabilizer	Provided by DE mercer and chemical company (Nanjing, China)
Phosphate (2,3-dichloro propyl) ester	Obtained from chunan qiandaohu longxiang chemical (Zhejiang, China)
Foaming agent HFC-365mfc	Boiling point: 40°C, ODP: 0, GWP: 0.21, purchased from Solvay company (Shanghai, China)
EG	Ash: 1.0%, volatile: 15%, pH value: 3.0, average diameter: 200 μm, expansion rate: 200 mL/g, obtained from Haida Graphite (Qingdao, China)
HGMs	Umulate density of 0.7 g/cm^3,average particle diameter of 10 μm, received from zhengmeiya chemical (Shanghai, China)
GF	Length of 4–6 mm, diameter of 10–125 μm, available from Haibo glass fiber (Nantong, China)

Table II. Composition of the Original RPUF (Ref. RPUF)

		Catalyst				
Polyether polyol (g)	Polyisocyanate (PAPI) (g)	33% of triethylene diamine solution (g)	Dibutyltin dilaurate (g)	Silicon compound foam stabilizer (g)	Phosphate (2,3-dichloro propyl) ester (g)	Foaming agent HFC-365mfc (g)
100	130	3.5	0.5	3	15	4

reinforced by GF, and drew a conclusion that the Young's modulus and strength of the materials could be improved by addition of GF. All the reports above have enlightened us on adding HGM and GF simultaneously with EG to RPUF.

We now report syntheses, flame retardancy, and mechanical properties of a class of RPUF composites with different formula of additives (EG, HGM, and GF). We aim to find a suitable ratio of these environmental friendly additives that cannot only give RPUF composites good flame retardancy but also compensate the loss of mechanical properties.

EXPERIMENTAL

Materials

The raw materials used were Polyether polyol, Polyisocyanate (PAPI), 33% of triethylene diamine solution, and dibutyltin dilaurate, silicon compound foam stabilizer, phosphate (2,3-dichloro propyl) ester, foaming agent HFC-365mfc, EG, HGM, GF, whose details are listed in Tables I and II.

Foam Preparation

In this work, all foam composites were prepared by cast molding. Polyether polyol, catalyst (triethylene diamine solution and dibutyltin dilaurate), silicon compound foam stabilizer, phosphate ester, and foaming agent (HFC-365mfc) were mixed together and stirred with an electric stirrer for 10 min. Then PAPI and inorganic fillers (of different content) were added with continuous stirring. After vigorous stirring for 30 s, the mixture was quickly poured into a mold. Then the impregnate mold was covered with a sealing lid and placed into an oven of 100°C. Four hours later, the specimen was obtained from the mold and cut into required size before characterization. All the RPUF composites were prepared according to the method

Table III. RPUF with Different Additives and Their Corresponding Short-Names

Content			
Short name (wt %)	EG	HGM	GF
EG10 RPUF	10		
HGM10 RPUF		10	
GF10 RPUF			10
EG16-HGM12-GF12 RPUF	16	12	12
EG0-24 RPUF	0–24		
HGM0-12 RPUF		0–12	
GF0-12 RPUF			0–12
EG16-HGM0-12 RPUF	16	0–12	
EG16-GF3-HGM0-12 RPUF	16	0–12	3
EG16-GF6-HGM0-12 RPUF	16	0–12	6
EG16-GF9-HGM0-12 RPUF	16	0–12	9
EG16-GF12-HGM0-12 RPUF	16	0–12	12
EG16-GF0-12 RPUF	16		0–12
EG16-HGM3-GF0-12 RPUF	16	3	0–12
EG16-HGM6-GF0-12 RPUF	16	6	0–12
EG16-HGM9-GF0-12 RPUF	16	9	0–12
EG16-HGM12-GF0-12 RPUF	16	12	0–12

Table IV. Independent Variables of the Process of Uniform Design

	Testing number				
Independent variables	1	2	3	4	5
HGM content (wt %)	0	3	6	9	12
GF content (wt %)	3	12	6	0	9

Figure 1. RI instrument. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mentioned above. The content of EG ranged from 0 to 24 wt % while those of HGM and GF were from 0 to 12 wt %. In this article, RPUF composites with different additives and their corresponding short-names are listed in Table III.

Uniform Experimental Design

Uniform design is a method that only takes into account the test points evenly spread within test range. This method, one of applications of quasi-Monte Carlo in number theory, is established by Fang and Ma[29] and Wang et al.[30] Generally, uniform design is appreciated since it cannot only evaluate multiple parameters and their relationships but also reduce the number of experiments significantly. Therefore, it is less laborious and time-consuming than other approaches required to optimize processes.[30] For uniform design, the software named Data Processing System (DPS Version 3.0) is used to generate the experimental designs.[31] In this article, there are two independent variables, namely X1 (HGM content, wt %) and X2 (GF content, wt %). Each of them has 5 variation levels (0, 3, 6, 9, and 12 wt %). The results of uniform design are shown in Table IV.

CHARACTERIZATION

Limiting Oxygen Index (LOI) Test

The LOI test was performed on an HC-2 oxygen index test instrument (made in Jiangning, China) in terms of the standard LOI test, ASTM D 2863-97. Specimens for measurement were sheets of size 127 × 10 × 10 mm^3.

Combustion Behavior Test

The combustion behavior test was conducted by radiation ignition (RI) instrument as shown in Figure 1.[32] This equipment can be considered as a mass loss calorimeter with a steadily changing heat flux ramp rather than a constant heat flux on the sample during the experiment. In this case, the thermal radiation will continuously increase with the time rising, which is more close to the most scenes of fire. In Figure 2, heat flow curves of various radiation powers are presented, where ignition temperature is defined as the temperature when the composite begins to burn, while combustion time is defined as the time that from the residual is 95% of the original weight to the residual weight changes very little (the loss of weight is <0.2% within 5 s). In our experiment, we set the output power of the apparatus 50% of the total power.

All the samples were cut into size of 100 × 100 × 20 mm^3 and enwrapped by silver paper leaving only one side exposed to heating mantle. In an experiment, sample was heated by a conical heating mantle, surface temperatures were recorded by the thermocouple on the samples at all times and the data were conveyed to computer by a data acquisition system. The sudden rising temperature indicated the ignition temperature. Meanwhile, mass variations were captured by an electronic balance under the samples.

Mechanical Measurement

Uniaxial compression tests were carried out on a universal electronic testing machine (made in Changchun, China) with a compressive rate of 2 mm/min according to ASTM D 1621-94. Torsion tests were performed on a torsion testing machine

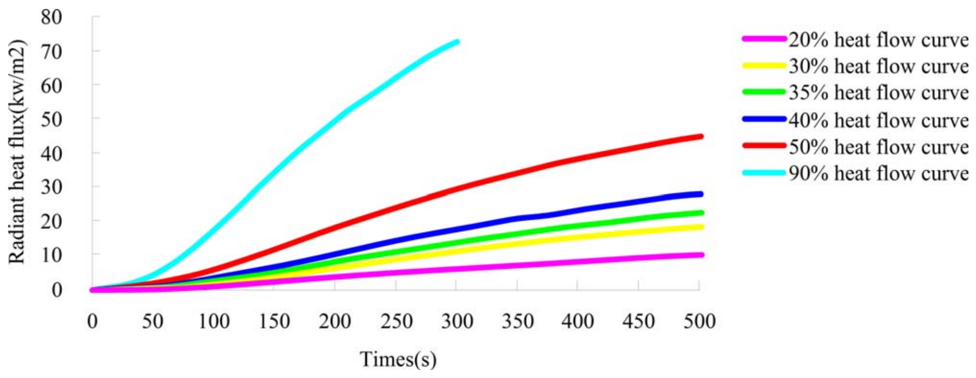

Figure 2. Heat flow curves of various output powers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

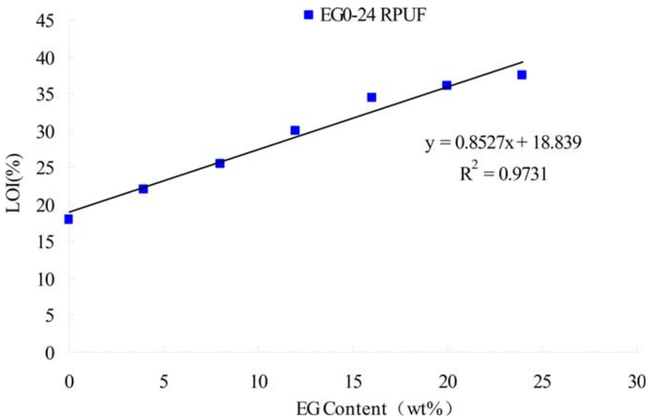

Figure 3. LOIs of EG0-24 RPUF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

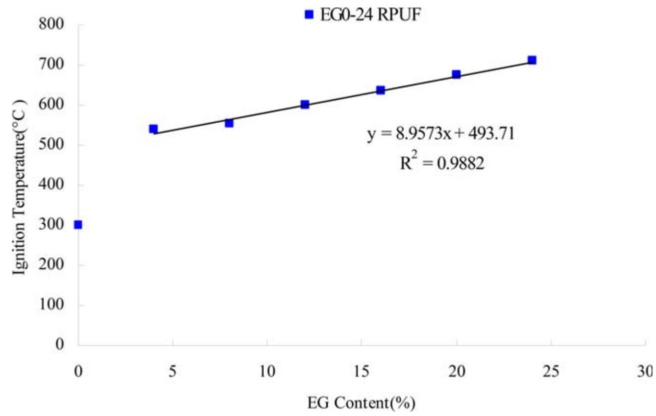

Figure 5. Ignition temperatures of EG0-24 RPUF composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(made in Changchun, China) with a rotational rate of 60°/min according to GBT 2567-2008.

Scanning Electron Microscopy (SEM) Observation

The morphology of the samples including original and some compressed samples were observed by FEI Quanta^{TM} 250 (FEI, America) SEM with an accelerating voltage of 30 kV. All the samples were obtained by impact fracture at room temperature and the surfaces were coated with layers of conducting materials to make them conductive.

RESULTS AND DISCUSSION

Flame Retardant Behavior

Figure 3 shows the LOIs of the RPUF composites of different EG content. It is obviously that the LOIs of composites have a linear relationship with EG content. The LOI changes from 18 vol % (without EG) to 37.5 vol % (EG content: 24 wt %). It can be partly attributed to the low heat release and smoke exhaust of EG. Furthermore, when the temperature rises up to 220°C, EG begin to expand, especially during the range of 230–280°C, EG expands rapidly and worm-like thermal insulating layers will be formed on the surface of the materials to prevent heat and oxygen transfer.[33–35] However, when the ratio of the EG exceeds 16 wt %, the growth rate of LOI will decrease.

Figure 4 points out the LOI maintained constantly around 35 vol % despite of the content of HGM and GF (Table IV) in EG16 RPUF, is similar to that of the original EG16 RPUF. The result indicates that GF and HGM affect little on the material flame retardancy.

Figure 5 shows the variation trend of ignition temperatures of EG0-24 RPUF composites, and it reveals the relationship between the ignition temperature and the EG content. While rising EG content from 0 to 24 wt %, the ignition temperature increases from 299.7 to 710.8°C. This phenomenon is mainly attributed to the high thermal conductivity of the EG/RPUF. When the material surface is exposed to heat radiation, the surface heat will transmit to the whole material immediately, thus reduce the rising rate of surface temperature. Furthermore, EG swelled at relatively low temperature after irradiation leads to appearance of pores in materials, and these pores are benefit to heat dissipation. EG will also cover the surfaces after expansion, and thus slow the increasing rate of temperature. Consequently, the flame retardancy is improved in the presence of EG.

The ignition temperatures of EG16 RPUF composites added HGM and GF change little and maintain around 630°C, which

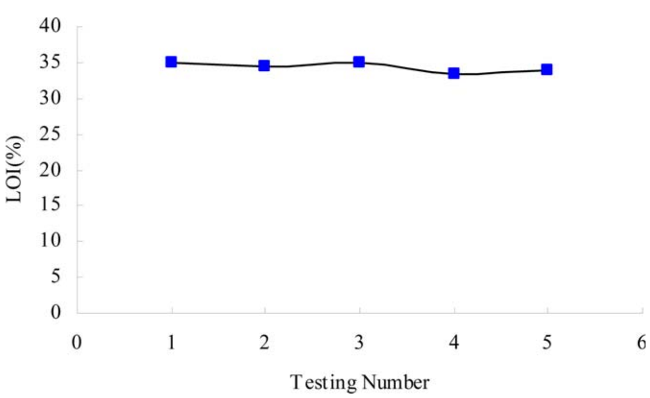

Figure 4. LOIs of different EG16 RPUF samples with HGM and GF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

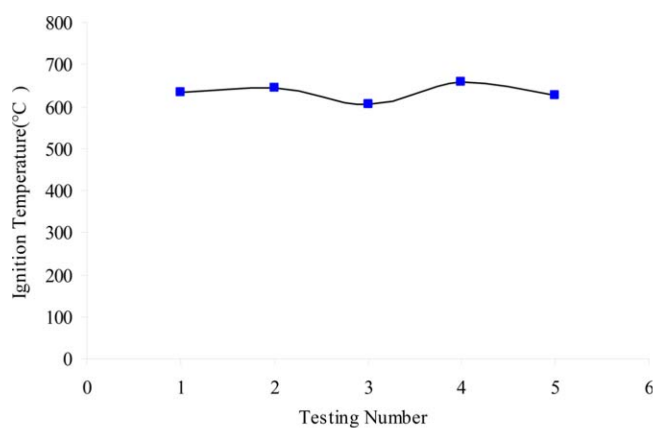

Figure 6. Ignition temperatures of different EG16 RPUF samples with HGM and GF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

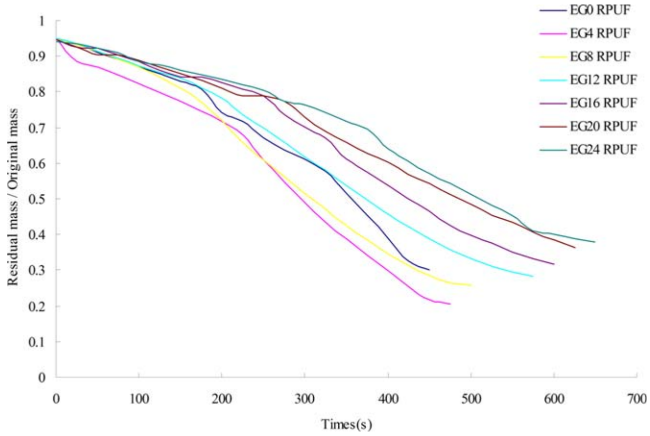

Figure 7. Residual mass of EG0-24 RPUF changing over time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

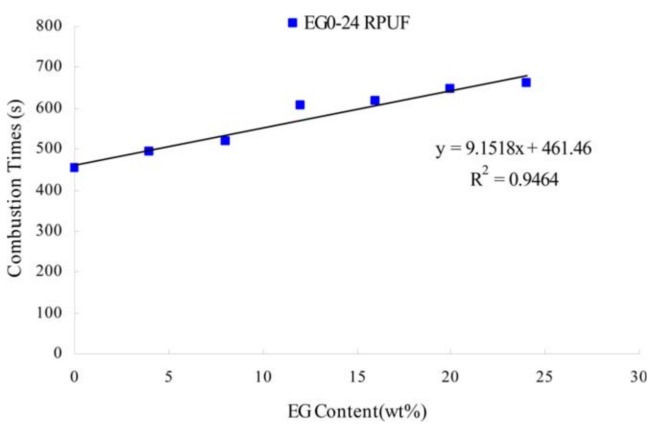

Figure 8. Combustion time of EG0-24 RPUF composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are similar to the ignition temperature of EG16 RPUF, regardless of HGM and GF content (Figure 6, Table IV). The result indicates that the addition of GF and HGM neither reinforce nor weaken the material flame retardancy.

Figure 7 shows the change of the weight of EG0-24 RPUF composites. In the beginning, oxidation process is slow. The decreasing rate of weight is relatively slow and gentle decline occurs in the curve. As temperature rise (>235°C), the weight loss caused by decomposition of polyurethane increases, therefore, in the curve knee point appears and the slope gets bigger. As mentioned before, EG expands fast during the range of 230–280°C, therefore, at the end of this period worm-like structure has already formed. At last, when temperature reaches to ignition temperature, the material begins to combust, however, worm-like covers reduce the combustion rate, and consequently the slope tends to be smaller. Before long the open fire is extinguished. It can be concluded that the longer the first period lasts, the later second period, the stage with the highest burning rate, appears. From the residual mass of EG0-24 RPUF samples changing over time (Figure 7), we can get the mass loss rate, which is in proportion to the heat release rate of our sample. The relationship between EG content and combustion time is presented in Figure 8. It is clear that the combustion time is directly proportional to EG content.

Physical-Mechanical Characterization

As seen from Figures 9 and 10, EG reduces the maximum torque significantly. This is due to the poor compatibility of EG with RPUF and the gaps between graphite sheets. When the composite is subjected to torsion force, graphite sheets will peel off from the matrix. Comparing Figures 9 with 10, we can see that GF have a better effect on reinforcing torsion resistance than HGM. In Figure 9, maximum torque decreases immediately on adding HGM into the EG16-GF0-12 RPUF. The increasing at the beginning can be probably attributed to the small quantity of gaps and pores introduced by HGM, which make bonding of materials more closely and composites difficult to fall off. However, with the increasing of additive amounts, the additives will agglomerate and thus lead to more gaps and loose of materials, which causes a decreasing of torsion resistance.

In contrast, in Figure 10, when adding GF into EG16-HGM0-12 RPUF, the maximum torque goes up initially but then decreases. When subjected to torsion force, tiny cracks will appear and GF on fractureface will share most of the torsional

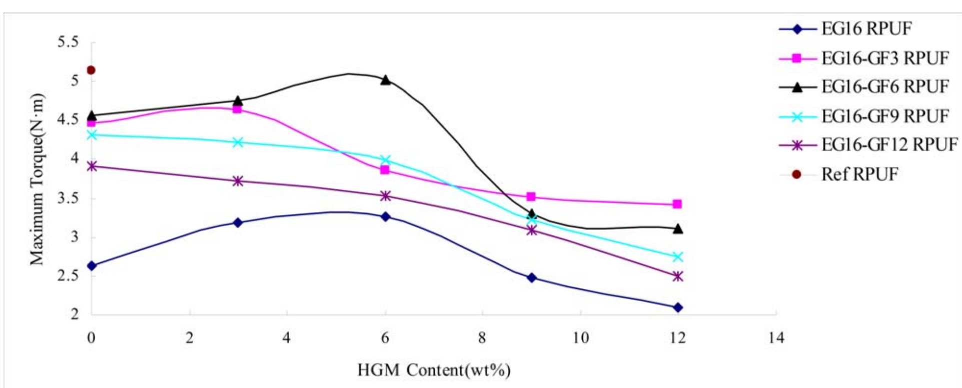

Figure 9. Maximum torques of Ref. RPUF, EG16-HGM0-12 RPUF, EG16-GF3-HGM0-12 RPUF, EG16-GF6-HGM0-12 RPUF, EG16-GF9-HGM0-12 RPUF, and EG16-GF12-HGM0-12 RPUF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

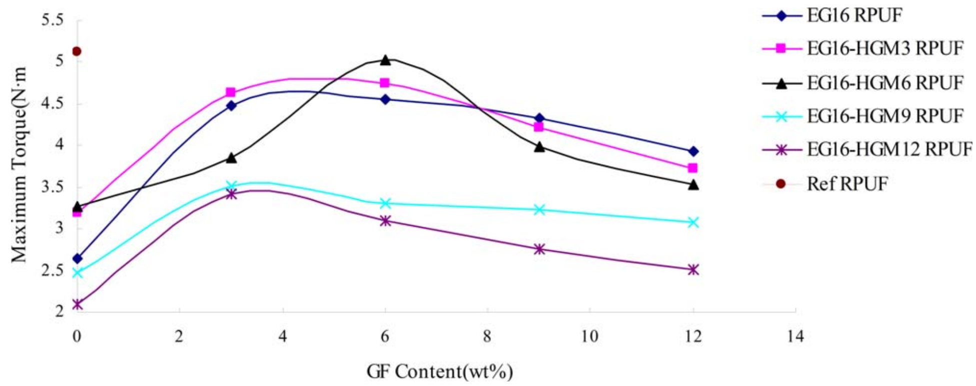

Figure 10. Maximum torques of Ref. RPUF, EG16-GF0-12 RPUF, EG16-HGM3-GF0-12 RPUF, EG16-HGM6-GF0-12 RPUF, EG16-HGM9-GF0-12 RPUF, and EG16-HGM12-GF0-12 RPUF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

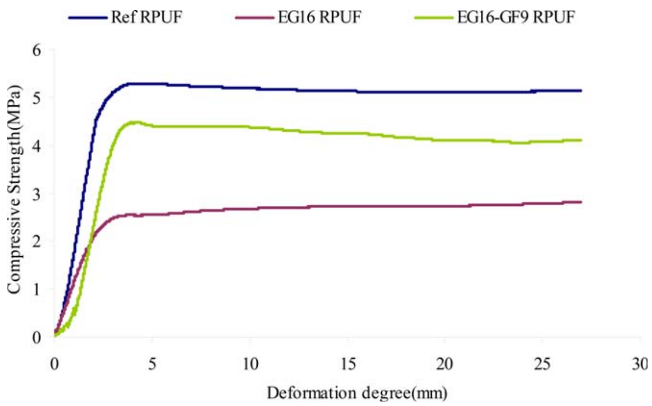

Figure 11. Stress-strain curves of Ref. RPUF, EG16 RPUF, and EG16-GF9 RPUF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

force, as a result, the maximum torque of the material will be improved. However, similar to the behavior of HGM, the maximum torque will decrease when excess GF are added. Furthermore, excess GF will increase the number of pores and low the cohesiveness between resins and additives, leading to a process of degradation.

As seen from Figure 11, similar to pure RPUF, there are three different areas in the stress-strain curves, namely elastic region, yield region, and compacting region. During the elastic region, in which compressive strain is <5%, the cell walls start to deform. Raising the pressure up to 5%, the pore units will begin to collapse, and debonding between additives and resin interfaces occur.[36] Finally, with continuous raising force, the pore units will be crushed and the material will deform completely.

By adding EG, which are composed of graphite sheets and gaps existed between these graphite sheets, in RUPF, the integrality of cells will be destroyed and inhomogeneous cellular structures will appear. Furthermore, the poor compatibility and large particle size of EG worsen the mechanical properties of the composites. Consequently, the compressive strength and modulus decrease in the presence of EG, compared with the pure RPUF, yield stress of EG16 RPUF even has a great drop.[37]

The yield stress of EG16-GF9 RPUF is obviously higher than that of EG16 RPUF, owing to the higher strength and modulus of GF. GF will endure most of the loading imposed on the matrix and reinforce the pore units, therefore, adding GF leads to higher stress-resisting ability.

Figures 12 and 13 show that the changes of compressive strength of samples can be divided into two stages, taking on the trend of rising first, then dropping with the increasing of inorganic fillers content. When a small amount of inorganic fillers are added, the compressive strength of RPUF will increase slowly. This is because the fillers wrapped by resin benefit to

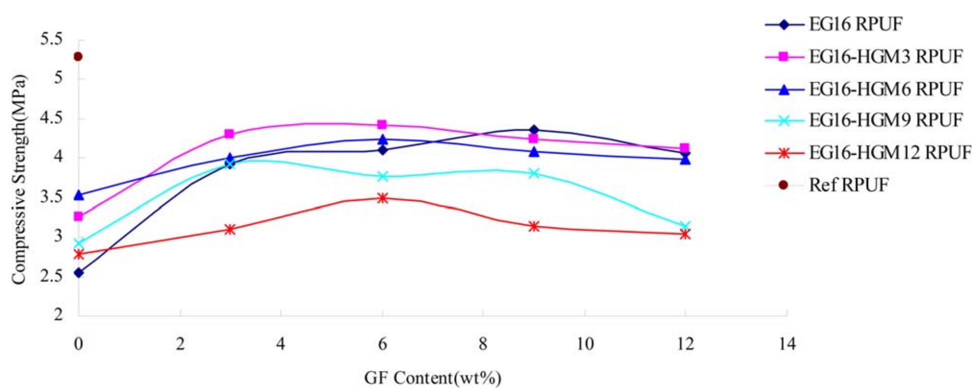

Figure 12. Compressive strength of Ref. RPUF, EG16-GF0-12 RPUF, EG16-HGM3-GF0-12 RPUF, EG16-HGM6-GF0-12 RPUF, EG16-HGM9-GF0-12 RPUF, and EG16-HGM12-GF0-12 RPUF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

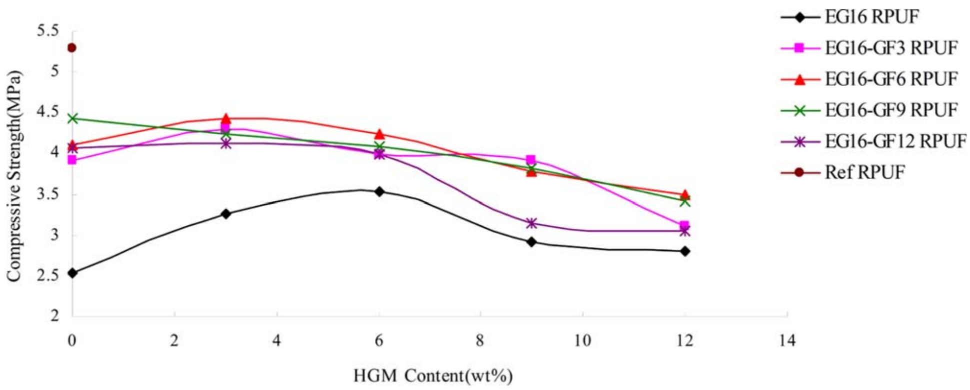

Figure 13. Compressive strength of Ref. RPUF, EG16-HGM0-12 RPUF, EG16-GF3-HGM0-12 RPUF, EG16-GF6-HGM0-12 RPUF, EG16-GF9-HGM0-12 RPUF, and EG16-GF12-HGM0-12 RPUF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

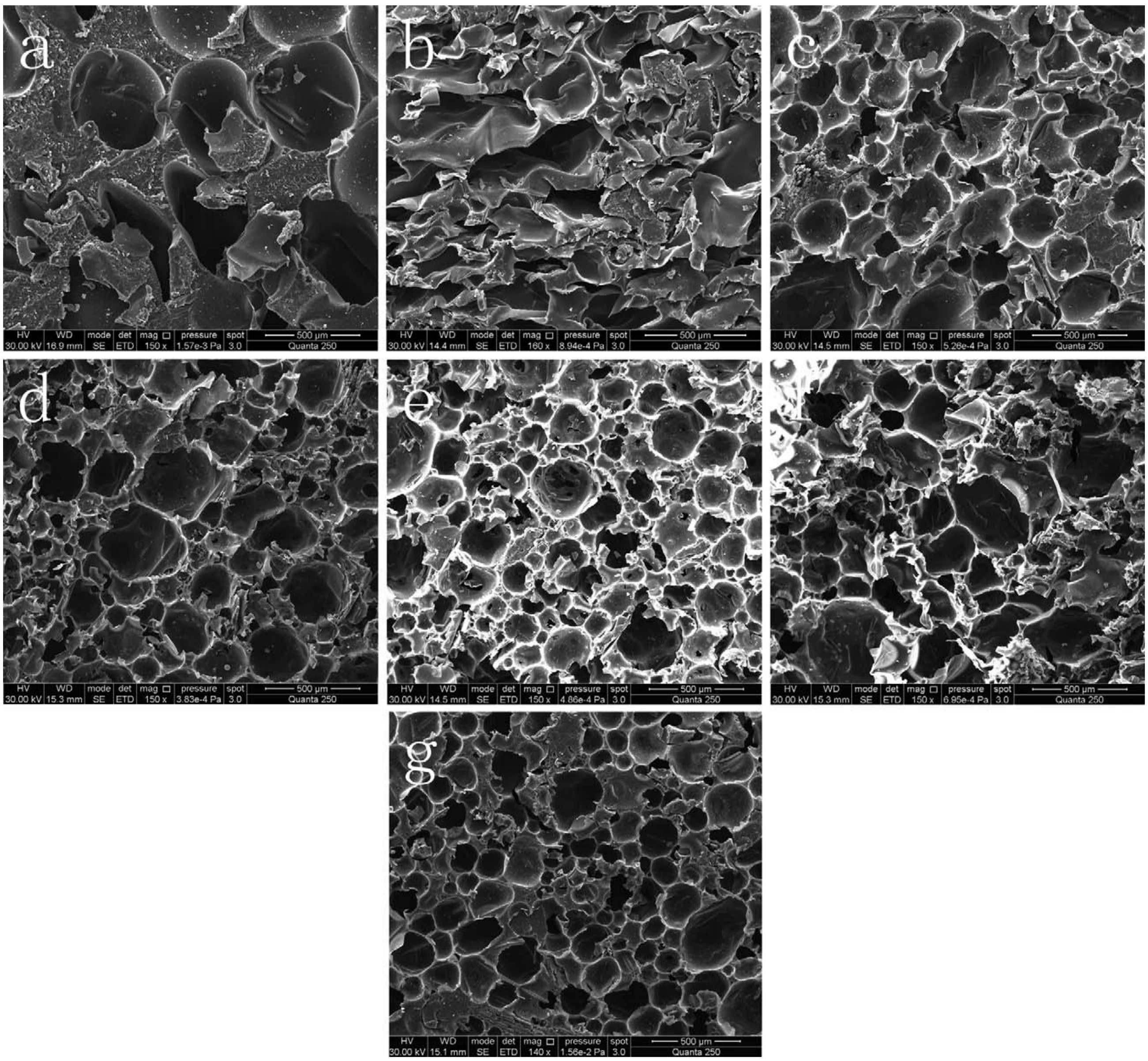

Figure 14. SEM micrographs of compressed RPUF composites (a) Ref. RPUF; (b) EG16 RPUF; (c) EG16-GF3 RPUF;(d) EG16-HGM3-GF12 RPUF; (e) EG16-HGM6-GF6 RPUF; (f) EG16-HGM9 RPUF; (g) EG16-HGM12-GF9 RPUF.

enhance adhesion. When the composite is compressed, stress transfers from the matrix to the uniformly dispersed additives. Especially, among these additives, HGM, which possess of sphere structures and capacity of resisting stress, does best in enhancing the mechanical properties of materials.[38] However, the compressive strength will decrease slowly when the inorganic fillers are continuously added. This phenomenon can be attributed to four aspects. Firstly, excess additives are inclined to agglomerate and hence cannot disperse uniformly. Secondly, according to foam colloid chemistry theory, excess of filler materials will cause cracking sinking, even collapse of the bubble. Thirdly, too many additives will not only weaken the adhesiveness but also thin the cell walls, so the RPUF matrix cannot wrap the additives totally. Consequently, the external stress cannot transfer through the composite and the foams around the additives are obliged to bear more stress. What is more, because the additive surfaces adsorb more air in the initial stage of foaming reaction, the fillers, which taper the bubble holes and deteriorate the strength of the cell walls are added as a part of the nucleating agent.

From what we have mentioned above, the addition of HGM and GF can improve the mechanical properties of EG16 RPUF. Thermal degradation test has been used by Xian-Yan Meng and his fellows for demonstrating that the addition of EG to RPUF could lead to an increase of the amount of high-temperature residues but a drop of the compressive strength.[22] To make up the loss of mechanical properties caused by EG, Xiang-Cheng Bian's group studied the RPUF added both EG and HGM, and found the resulting RPUF composites had the same flame retardancy but a better mechanical properties compared with the EG/RPUF.[23] However, only adding HGM cannot make a significant improvement to the compressive strength. As the results shown, there is a continuous drop of compressive strength with the increasing of EG content regardless of the HGM content. The addition of EG, GF, and HGM can increase flame retardancy on the premise of no serious damage to mechanical properties. We herein obtain materials with best flame retardancy and highest mechanical properties: 6 wt % HGM and 6 wt % GF filled EG16 RPUF has the higher compressive strength than others, which reaches to 4.42 MPa, in terms of torsion, the maximum torque goes to 5.03 N·m after 3 wt % HGM and 6 wt % GF filled in EG16 RPUF.

Morphological Characterization

Figure 14 displays the SEM micrographs of the fractured surfaces of various compressed RPUF composites. For the Ref. RPUF [Figure 14(a)], most of the cells are spherical and closed. Besides, the cells disperse uniformly in matrix and the cell diameters are similar. However, complete cell can hardly be found in compressed EG16 RPUF [Figure 14(b)], which is consistent with the compressive strength of samples measured by experiments. The special structure of EG and its poor compatibility with the matrix result in collapse of the cell units. Figure 14(c) shows that a part of GF, which are distributed between the cells, impale the cell walls, and reduce bearing capacity of the cells. When HGM are added into the EG/GF/RPUF [Figure 14(d)], the miscibility of HGM with matrix is better than that of GF; furthermore, HGM can fill the voids between GF and matrix. With the increasing addition of GF and HGM, the number of collapsed cells slightly increases [Figure 14(e)]. However, the fillers taking on the role in resisting stress improve the compressive strength of RPUF composites. Figure 14(f) shows a destroyed composite resulted from the incremental brittleness caused by the growing additive amount of HGM. When the additive amounts of HGM and GF reach limits [Figure 14(g)], most of the cells collapse. As a conclusion, the inorganic fillers play a key role in supporting structures. Besides, GF can maintain the integrity of the materials because of their filiform structures. Consequently, HGM and GF present favorable abilities of enhancing the mechanical properties of composites.

CONCLUSIONS

1. Adding EG can improve the flame retardancy of RPUF. On condition that the addition of EG is no more than 24 wt %, LOI ascends from 18.0 to 37.5 vol %, ignition temperature rises from 299.7 to 710.8°C, and combustion time increases from 453.0 to 661.0 s. However, adding EG weakens the mechanical properties of RPUF composites.
2. Appropriate additive contents of HGM and GF will improve the compressive strength and maximum torque of the EG/RPUF. The compressive strength and maximum torque of EG16 RPUF are 2.54 MPa and 2.64 N m, respectively. In contrast, the compressive strength reaches to 4.42 MPa and the maximum torque goes up to 5.03 N m after appropriate additions of HGM and GF. However, HGM and GF have little effect on flame retardancy.
3. The synergy of EG, HGM, and GF can improve both mechanical properties and retardant properties.
4. In conclusion, our results indicate that proper formula of additives (HGM: 3–6 wt %, GF: 6 wt %, and EG: 16 wt %) for RPUF favors good flame retardancy and mechanical properties.

ACKNOWLEDGMENTS

The authors thank the State Key Laboratory of Coal Resources and Safe Mining, CUMT (SKLCRSM12X04), the National Science fund for Distinguished Your Scholars (Grant No.51325403), the Natural Science Foundation of Jiangsu Province (SBK201021648), Program for Changjiang Scholars and Innovative Research Team in University (Grant No. IRT13098), and Jiangsu Province Outstanding Youth Scientific Fund (BK2012003), for financial support. This work is also a project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

REFERENCES

1. Shi, L.; Li, Z. M.; Yang, M. B.; Zhou, Q. M.; Wang, J. H. *Polym. Plast. Technol. Eng.* **2005**, *44*, 1323.
2. Duquesne, S.; Michel, L. B.; Bourbigot, S.; Delobel, R.; Vezin, H.; Camino, G. *Fire Mater.* **2003**, *27*, 103.
3. Duquesne, S.; Delobel, R.; Michel, L. B.; Camino, G. *Polym. Degrad. Stab.* **2002**, *77*, 333.
4. Shi, L.; Li, Z. M.; Xie, B. H.; Wang, J. H.; Tian, C. R.; Yang, M. B. *Polym. Int.* **2006**, *88*, 862.

5. Michael, L. H.; Kenneth, L. E.; Tze, Y. C. *Polym. Degrad. Stab.* **2000**, *69*, 47.
6. Borreguero, A. M.; Rodríguez, J. F.; Valverde, J. L.; Peijs, T.; Carmona, M. *J. Appl. Polym. Sci.* **2013**, *128*, 582.
7. Piszczyk, Ł.; Strankowski, M.; Danowska, M.; Haponiuk, J. T.; Gazda, M. *Eur. Polym. J.* **2012**, *48*, 1726.
8. Ye, L.; Meng, X. Y.; Ji, X.; Li, Z. M.; Tang, J. H. *Polym. Degrad. Stab.* **2009**, *94*, 971.
9. Usta, N. *J. Appl. Polym. Sci.* **2012**, *124*, 3372.
10. Duquesne, S.; Michel, L. B.; Bourbigot, S.; Delobel, R.; Vezin, H.; Camino, G.; Berend, E.; Lindsay, C.; Roels, T. *Fire Mater.* **2003**, *27*, 103.
11. Ravey, M. *J. Appl. Polym. Sci.* **1999**, *74*, 1317.
12. Ravey, M.; Keidar, I.; Weil, E. D. *J. Appl. Polym. Sci.* **1998**, *68*, 231.
13. Ravey, M.; Keidar, I.; Weil, E. D.; Pearce, E. M. *J. Appl. Polym. Sci.* **1998**, *68*, 217.
14. Mohammad, Z.; Khalid, M. Z.; Shahid, M.; Muhammad, H.; Ijaz, A. B. *Int. J. Biol. Macromol.* **2010**, *47*, 196.
15. Khalid, M. Z.; Mohammad, Z.; Mehdi, B.; Rizwan, H.; Tahir, J.; Sohail, A. *Int. J. Biol. Macromol.* **2011**, *49*, 1131.
16. Franci, M.; Bogdan, Z.; Urban, S.; Sasa, S.; Janvit, G.; Peter, V. *Prog. Org. Coat.* **2013**, *76*, 1471.
17. Chatterjee, A.; Mishra, S. *J. Polym. Res.* **2013**, *20*, 249.
18. Li, X. G.; Liu, Y. J.; Li, D. X.; Huang, Y. G. *J. Nanosci. Nanotech.* **2013**, *13*, 5924.
19. Shi, L.; Li, Z. M.; Xie, B. H.; Wang, J. H.; Tian, C. R.; Yang, M. B. *Polym. Int.* **2006**, *55*, 862.
20. Bian, X. C.; Tang, J. H.; Li, Z. M.; Lu, Z. Y.; Lu, A. *J. Appl. Polym. Sci.* **2007**, *104*, 3347.
21. Hu, X. M.; Wang, D. M. *J. Appl. Polym. Sci.* **2012**, *129*, 238.
22. Meng, X. Y.; Ye, L.; Zhang, X. G.; Tang, P. M.; Tang, J. H.; Ji, X.; Li, Z. M. *J. Appl. Polym. Sci.* **2009**, *114*, 853.
23. Bian, X. C.; Tang, J. H.; Li, Z. M. *J. Appl. Polym. Sci.* **2008**, *109*, 1935.
24. Bian, X. C.; Tang, J. H.; Li, Z. M. *J. Appl. Polym. Sci.* **2008**, *110*, 3871.
25. Yakushin, V.; Bel'kova, L.; Sevastyanova, I. *Mech. Compos. Mater.* **2012**, *48*, 579.
26. Chalivendra, V. B.; Shukls, A. *J. Mater. Sci.* **2003**, *38*, 1631.
27. Parameswaran, V.; Shukla, A. *J. Mater. Sci.* **2000**, *35*, 21.
28. Lu, Z. X.; Zou B.; Li Z. M.; Lu, A. J Beijing Univ Aeronaut Astronaut **2009**, *1*, 36. In Chinese.
29. Fang, K. T.; Ma, C. X. Orthogonal and uniform experimental design; Science Press: Beijing, **2001**; Chapter. *1*, pp 1–10. In Chinese.
30. Wang, Z.; Luo, D.; Ena, C. *Carbohydr. Polym.* **2007**, *69*, 311.
31. Luo, G. B. *Anal. Lett.* **2012**, *45*, 2493.
32. Zhang, G. W.; Zhu, G. Q.; Huang, L. L.; Han, R. S. *J. Build. Mater.* **2013**, *5*, 843. In Chinese.
33. Modesti, M.; Lorenzetti, A.; Simioni, F.; Camino, G. *Polym. Degrad. Stab.* **2002**, *77*, 195.
34. Modesti, M.; Lorenzetti, A. *Polym. Degrad. Stab.* **2002**, *78*, 167.
35. Zou, L. H.; Huang, B. Y. *Trans. Nonferrous Met. Soc. China* **1997**, *7*, 132. In Chinese.
36. Ma, C. G.; Rong, M. Z.; Zhang, Q. M. *J. Mater. Eng.* **2002**, *7*, 40. In Chinese.
37. Lu, Z. X.; Yan, H. B.; Wang, J. H. *China Plast.* **2004**, *18*, 31. In Chinese.
38. Uspenskaya, M. V.; Sirotinkin, N. V.; Yatsenko, S. V.; Masik, I. V. Russ. *J. Appl. Chem.* **2005**, *5*, 846.