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Research Article

Synergistic Flame Retardant Effects of Expandable Graphite and Ammonium Polyphosphate in Water-Blow Polyurethane Foam

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In this research, expandable graphite (EG) and ammonium polyphosphate (APP) were incorporated into water-blow semirigid polyurethane foam (SPUF) as flame retardants. The synergistic flame retardant effects of EG with APP in SPUF had been studied by thermogravimetric analysis (TGA), limiting oxygen index (LOI), horizontal burning test, polarizing microscope, and scanning electron microscopy (SEM). The results indicated that APP and EG used together in SPUF could effectively improve the flame retardancy of SPUF. When the EG to APP ratio reached 2 : 1 under the total content of flame retardants was kept constant as 20%, the LOI value was increased by about 51% compared to pure SPUF, 2.9% to SPUF/EG and 16.3% to SPUF/APP. Besides, the residual char was increased up to 27.7% displayed by TG test results. SEM shows that burned residues of EG/APP/SPUF present more compact char and worm-like structure. Furthermore, EG shows negative effect on the mechanical property of SPUF with 21.7% decrease in compression modulus, but the mechanical property can be improved by the addition of appropriate content of APP.

1. Introduction

Water-blown polyurethane foam (WPUF) has been attracting more attention especially in the application closely related to human beings because the foaming agent, water, is cheap, safe, nontoxic, and free from any pollution [1–7]. Water-blown rigid polyurethane foam with high crosslinking density resulted by the high hydroxyl value of polyol is suitable to make the material of construction and insulation in building industry. By lowering the hydroxyl value, the crosslinking density and hardness of WPUF decrease, and the semirigid foam and the soft foam can be obtained. Water-blown semirigid polyurethane foam (SPUF) of hardness between 55 and 75 HA is widely used to make the inertial decorating parts, such as dashboard, inner door of automobile, or other transports [8]. According to the data about vehicle fire accidents in China, the amounts of auto spontaneous combustion have been increasing year by year; lots of people suffer injuries or deaths in these accidents because the rapid combustion rate of the interior parts and the toxic volatile gas from the polymer materials [9–11]. In fact, water-blown SPUF has low thermal stability and is inflammable because its molecules contain more easily decomposed urea bond structure; as a result, the improvement of the fire behavior of water-blown SPUF has been an important subject [12–15].

Typically, the main flame retardants of polyurethane (PU) foam are compounds containing halogen, alone or in conjunction with antimony trioxide [16]. Because of the problems related to the large amount of toxic and corrosive gases and smoke released during PU decomposition, halogen-free flame retardants have been facilitated rapidly. Over the past decades, halogen-free flame retardants have been increasingly applied in polymeric systems [17, 18]. The phosphorus-nitrogen intumescent flame retardants (IFR) are widely used as halogen-free additives because they provide excellent fire protection with less smoke and lower toxicity [19–22]. As an environment-friendly halogen-free flame retardant, ammonium polyphosphate (APP) has the advantages of low volatility, facilitating the release of toxic

gas and smoke, and easier to synthesis [23], compared to the halogenated and phosphorus-based compounds. In recent years, the effect of soluble ammonium polyphosphate (SAPP) on the thermal degradation, the flame resistance, and the mechanical properties of the SPUF has been studied [24]. However, APP/SPUF has a low flame retardant efficiency and thermo stability, which limits the application of it [19, 25].

Expandable graphite (EG) is a "particular" intumescent additive known to impart fire retardant to various materials and in particular to PU foam [15]. The temperature range of major thermal decomposition is expanded by addition of the graphite [13, 26, 27], and because of the developed voluminous "worm-like" structure, the increase of volatiles evolved in the presence of graphite in the major step of PU decomposition is prevented. Yi et al. incorporated different particle size of EG into water-blown SPUF and found that the larger particle size of EG could effectively enhance the retardant properties, but exhibited a poor compression performance compared with the others [28]. Some metal hydroxide or inorganic particles are added in the flame retardant system of EG as the synergistic flame retardants, which could also enhance the mechanical properties of the compound [29–31]. Phosphorus-based or nitrogen-based flame retardant is also found to have the reinforcement effect on the mechanical properties in some compounds [24, 32].

The aim of this study is to increase the flame retardant property of water-blown SPUF without sacrifice of mechanical properties. Because of the high flame retardant efficiency of EG and the reinforcement effect of APP, semirigid WPUF with EG/APP of different content was prepared. Not only the synergistic flame retardant effect of EG and APP on SPUF is studied but also the most important is that the effects of EG and APP on the pore formation and the cell structure of semirigid WPUF are also studied by polarizing microscope (POM) and scanning electron microscopy (SEM). The mechanism for synergistic flame retardancy and mechanical properties enhancement of APP was proposed in detail.

2. Experimental

2.1. Materials. Polyether polyol (330 N, average functionality 3.0, OH content 33~37 mg KOH/g; 3630, average functionality 3.0, OH content 25~29 mg KOH/g) was obtained from Jv Yi Polymeric Materials Co., China. Isocyanate (MDI, NCO wt%, 26~27%) was obtained from Jv Yi Polymeric Materials Co., China. Triethanolamine (TEA) was supplied by Beijing Chemical Plant, China. Silicone oil (8631), amine catalysts, and organic tin catalyst were supplied by Jv Yi Polymeric Materials Co., China. Ammonium Polyphosphate (APP) with a polymerization degree<20 was supplied by Zhenjiang Star Flame Retardants Co.Ltd., China. Expansible graphite (EG) (E300) was bought from Yanhai Graphite Co. (Qingdao, China); its main property, i.e., expansive rate>270 ml/g. Distilled water was obtained in laboratory. All reagents and chemicals were used without further purification.

2.2. Preparation of SPUF and Its Composites. Polyol (330 N, 3630) was mixed with distilled water, catalysts (TEA, amine catalysts, and organic tin catalyst), foam stabilizer (silicone oil 8631), and flame retardant (EG, APP or EG/APP) and then fully stirred for 60 s in a 1 L plastic beaker. MDI was then added into the beaker with vigorous stirring for 5 s. MDI reacted with distilled water to generate carbon dioxide, of which carbon dioxide inflated the reactants. After that, the mixture was immediately poured into a laboratory-made foaming mold ($15 \times 15 \times 6\ \text{cm}^3$) to produce foam for 15 min. The foam was cured for 24 h under 50°C to increase the cross-link density and to make the reaction more sufficient. Total content of flame retardants used in SPUF was kept constant as 20%; the proportion of EG and APP in SPUF is shown in Table 1.

3. Measurement

3.1. Limiting Oxygen Index (LOI). The LOI values of the WPUF samples were measured according to ISO4598, using a flammability testing technology instrument (JF-3, Jiangsu, China). The dimensions of the specimen were $100\ \text{mm} \times 10\ \text{mm} \times 10\ \text{mm}$ ($L \times W \times T$).

3.2. UL-94 Horizontal Burning Test. The horizontal burning tests were performed with a burning test instrument (H1011D, Changchun, China) according to UL-94. The specimens for measurement were machined into sheets of $130 \times 70 \times 10\ \text{mm}^3$.

3.3. Thermogravimetric Analysis (TG). The thermal stability of WPUF samples were studied using a NETZSCH STA TG instrument (449F3, Germany) and a sample mass of 2–5 mg in a nitrogen environment at a heating rate of 10°C/min from 25°C to 800°C.

3.4. Scanning Electron Microscopy (SEM). The morphology of the samples, including the original and the burned samples, were examined under a ZEISS EVO18 (Germany) scanning electron microscope (SEM) with an accelerating voltage of 20 kV.

3.5. Polarized Light Microscope Observation (POM). The foam cross section specimen was observed by 59XC optical microscope of Xiamen McEdio Manufacturing Co., LTD.

3.6. Mechanical Properties. The hardness of bulks was tested according to QC/T 29089-1992 with Shore A-type durometer, and the results were the average of ten tests. The compressive strength and the compressive modulus were measured with universal electronic tensile machine (WSM-5 KN, Changchun Intelligent Instrument Equipment Co., LTD, China) with compression rate of 25%, compression speed 10 mm/min according to ISO 604. The apparent density was measured according to GB/T6343-1995. The sample size was $50\ \text{mm} \times 50\ \text{mm} \times 50\ \text{mm}$, and six samples were tested and averaged.

Table 1: Parameters of flame retardant SPUF.

Materials	Parts by weight (pbw)
Polyether polyol (330 N)	50
Polyether polyol (3630)	50
Triethanolamine	2
Amine catalysts	0.5
Organic tin catalyst	0.1
Silicone oil	1.2
Distilled water	3.5
Isocyanate (MDI)	79
Fire retardant	20

4. Results and Discussion

4.1. Flammability. The LOI value and UL-94 horizontal combustion test results of SPUF, APP/SPUF, EG/SPUF, and EG/APP/SPUF are shown in Table 2. SPUF without any flame retardant is easy to combust, the LOI value is 18.9%, and the combustion rate is 49.01 mm/min, while SPUF containing flame retardant in Table 1 can pass the HF-1 rating in the UL-94 HBF test. EG/SPUF has higher LOI values and shorter self-extinguish time than APP/SPUF, which indicates that EG has better flame retardant effects in SPUF than APP. When the content of EG is higher than APP in synergistic flame retardant system, the LOI value of SPUF composites reach above 28%, which are higher than the values by EG and APP individually, and once the EG to APP ratio reaches 2 : 1, the LOI value is increased by about 51% compared to pure SPUF, 2.9% to SPUF/EG, and 16.3% to SPUF/APP. Besides, when the ratio of EG and APP are higher than 2 : 1, the composite sample cannot be ignited any more. That indicates that due to the combined effect of EG and APP, the SPUF composites exhibit outstanding flame retardant properties, and synergistic flame retardant effect depends on the proportion of EG and APP.

4.2. Thermal Properties. Thermogravimetric analysis (TGA) is widely used to evaluate the thermal stability of polyurethane [33–36]. TG and DTG curves of SPUF composites with different flame retardants under nitrogen atmosphere are presented in Figure 1. The initial degradation temperature (5% mass loss temperature, T_d), the maximum degradation temperature (which corresponds to the depolymerization of polyurethane, T_{max}), the maximum thermal weight loss rate (V_{max}), different decomposition stage (T_{stage}), and the char residue at 800°C of flame retardants and SPUF composites are listed in Table 3. It can be seen that the SPUF without flame retardant has two degradation processes at 215~450°C and 450~600°C, respectively [37]; the first degradation step was mainly due to the depolymerization of polyurethane chains to form isocyanate, polyol, primary or secondary amine, olefin, and carbon dioxide; after this degradation process, the residue mass is about 20%, the maximum mass loss temperature of SPUF is 388°C, and only 13.1% char residue remains at 800°C. Thermal decomposition of APP/SPUF shows three processes, and its T_d is 110°C. The first stage is the decomposition of APP; polyphosphoric acids are formed during this stage, which accelerate the decomposition of SPUF by reaction between an acid function of polyphosphoric acid and hydrogen function of urethane [38]; thus the T_{max} of APP/SPUF decreased to 358°C, but the decomposition rate of SPUF is lower, and char residue at 800°C is bigger compared to the pure SPUF. EG/SPUF composite shows two decomposition step; its T_d increased to 280°C, decomposition rate decreased 0.81%/°C, and the char residue increased to 27.9% at 800°C. This confirms that the degradation of EG makes a big contribution to form the compact char residue, which slows down the decomposition of SPUF.

However, the decomposition of APP/EG/SPUF takes place at two independent stages: 120–215°C and 270–450°C. The degradation of SPUF with flame retardant of both APP and EG at 120–215°C was attributed to the initial weight loss of APP. The second degradation step at 270–450°C was caused by the decomposition of EG and the depolymerization of polyurethane to form isocyanate, polyol, primary or secondary amine, olefin, and carbon dioxide. Due to the decomposition of APP and carbonization of EG under lower temperature, the decomposition rate of APP/EG/SPUF is decreased to 0.79%/°C, but the T_{max} and char residue at 800°C are slightly lower than the value of EG/SPUF composite. These results indicate that the combination of EG and APP used in water-blow SPUF can slow down the decomposition of SPUF effectively.

4.3. Char Morphology of SPUF Composites. The char layers' micrographs of SPUF, APP/SPUF, EG/SPUF, and EG/APP/SPUF are shown in Figures 2(a)–2(d). Clearly, the surface of APP/SPUF is more compact than SPUF from Figures 2(a) and 2(b). This elucidates the char residue of APP/SPUF is higher than SPUF. The burning charcoal layer of SPUF composites containing EG is relatively tight, and the "popcorn" phenomenon arises in the process of combustion from Figures 2(c) and 2(d). This is because the heated EG expanded and generated "worm" carbon layer [35]. This can insulate heat and oxygen during combustion effectively. After mixing APP, the size of "popcorn" becomes smaller. This is due to the fact that as the EG expands, the degradation product of APP catalyzes PU decomposition, resulting in an intermediate product with a relatively high viscosity. And the carbon layer is adhered and gets more compact. This is conducive to insulating oxygen from reducing droplets and increasing the LOI value.

4.4. Mechanical Properties of SPUF. The mechanical properties of SPUF composites are listed in Table 4. The apparent density, Shore's hardness, compression strength, and modulus of compression of neat SPUF are 46.60 kg/m^3, 55.64 HA, 0.056 MPa, and 0.75 MPa, respectively. The addition of EG and APP results in an increase of apparent density by approximately 47% and 32%, respectively, compared to the neat SPUF. The flame retardant SPUF of higher apparent density must have the lower volume since the addition weight of EG and APP are same, which reveals that EG has more effect on the foam forming process than

Table 2: Flammability of SPUF containing various concentrations of flame retardants.

Samples	EG (wt.%)	APP (wt.%)	Ratio of EG/APP	LOI (%)	UL-94 HBF	Combustion rate (mm/min)/self-extinguish time (s)
SPUF	0	0	—	18.9	—	49.01 mm/min
EG/SPUF	20	0	—	27.7	HF-1	14.825 s
APP/SPUF	0	20	—	24.5	HF-1	27.25 s
EG/APP/SPUF-1	3.33	16.67	1 : 5	25.3	HF-1	15.80 s
EG/APP/SPUF-2	4	16	1 : 4	27.7	HF-1	12.98 s
EG/APP/SPUF-3	5	15	1 : 3	27.6	HF-1	12.42 s
EG/APP/SPUF-4	6.67	13.33	1 : 2	27.8	HF-1	11.42 s
EG/APP/SPUF-5	8	12	2 : 3	27.2	HF-1	11.26 s
EG/APP/SPUF-6	10	10	1 : 1	27.4	HF-1	11.02 s
EG/APP/SPUF-7	12	8	3 : 2	28.1	HF-1	10.79 s
EG/APP/SPUF-8	13.33	6.67	2 : 1	28.5	HF-1	10.00 s
EG/APP/SPUF-9	15	5	3 : 1	28.3	HF-1	Non-ignitable
EG/APP/SPUF-10	16	4	4 : 1	28.2	HF-1	Non-ignitable
EG/APP/SPUF-11	16.67	3.33	5 : 1	28.6	HF-1	Non-ignitable

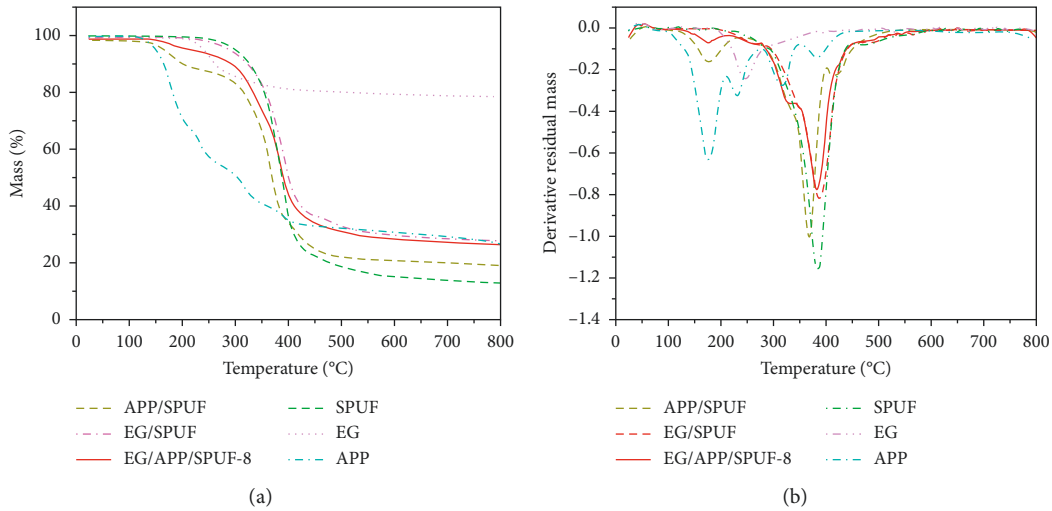

Figure 1: TG and DTG curves of EG, APP, SPUF, and SPUF composites.

Table 3: Thermal properties of flame retardants and SPUF composites.

samples	T_d (°C)	T_{max} (°C), V_{max} (%/°C)	T_{1stage} (°C)	T_{2stage} (°C)	T_{3stage} (°C)	T_{4stage} (°C)	Char residue (%)
SPUF	215	388, 1.16	280~450	450~600	—	—	13.1
EG	200	—	200~380	—	—	—	78.7
APP	110	—	110~215	220~280	280~358	360~437	27.8
EG/SPUF	280	392, 0.81	215~450	450~600	—	—	27.9
APP/SPUF	110	358, 1.05	110~230	260~400	400~488	—	19.2
EG/APP/SPUF-8	120	385, 0.79	120~215	270~450	—	—	27.7

APP. Polarizing microscope of the foam morphology gives the detail of the foam cell structure, as shown in Figure 3. There are many smaller pores in APP/SPUF compared with neat SPUF. As a result, the volume of the whole foam is decreased and density is increased in APP/SPUF. For the SPUF containing EG, the morphology of cell structure is inhomogeneous. In the SPUF with lower content of EG, EG lamellas with dark color are located between adjacent holes of the foam, and the cell wall sticks together around EG lamella. With the increasing of EG content, EG lamellas are inclined to aggregate by the van der Waals interactions. The EG aggregation with big size adhered to more polyurethane matrix, which induces the high viscosity around EG, and pore forming becomes difficult. As a result, the foam cells are filled by cohered EG instead of gas; other cells without EG are very big and full of gas. The sticky polyurethane matrix makes the foaming incomplete; therefore, the whole volume of the SPUF decreased, and the apparent density of EG/SPUF is higher than APP/SPUF.

The compressive strength and modulus are increased by 13.4% and 66.7%, respectively, in APP/SPUF sample, which can be explained by its high apparent density. For the sample

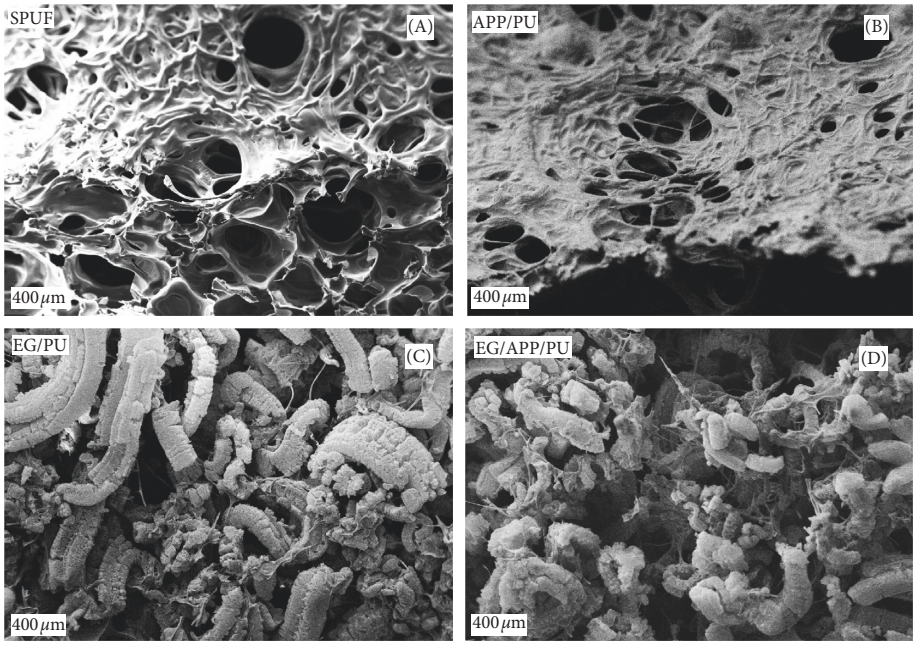

Figure 2: SEM micrograph of SPUF composites' char residue obtained from LOI test.

Table 4: Influence of EG/APP proportion on the performances of SPUF.

Samples	Ratio of EG/APP	Apparent density (kg/m^3)	Shore's hardness (HA)	Compression strength (MPa)	Modulus of compression (MPa)
SPUF	\	46.60 ± 0.76	55.64 ± 1.32	0.056 ± 0.002	0.75 ± 0.04
APP/SPUF	\	61.56 ± 0.97	64.77 ± 2.10	0.064 ± 0.004	1.25 ± 0.06
EG/SPUF	\	68.06 ± 1.43	58.82 ± 1.33	0.051 ± 0.001	0.59 ± 0.05
EG/APP/SPUF-2	1 : 4	59.60 ± 0.36	56.63 ± 1.12	0.053 ± 0.003	0.70 ± 0.04
EG/APP/SPUF-4	1 : 2	66.52 ± 1.02	59.54 ± 0.65	0.047 ± 0.002	0.45 ± 0.02
EG/APP/SPUF-8	2 : 1	61.88 ± 0.63	58.08 ± 0.53	0.044 ± 0.002	0.40 ± 0.02

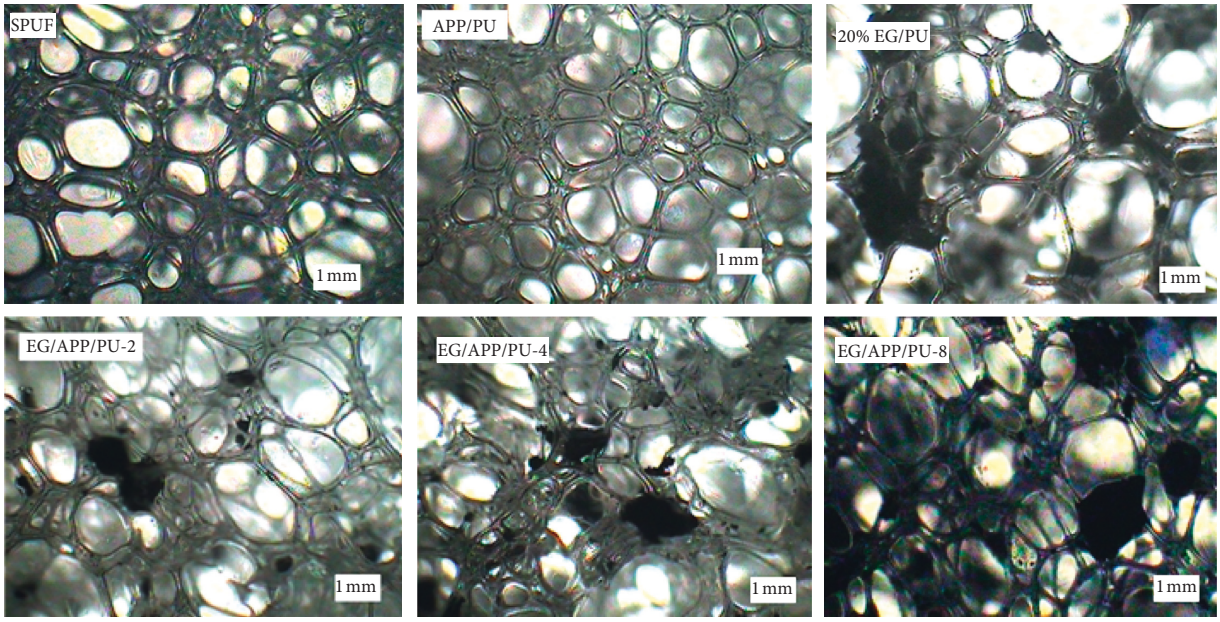

Figure 3: POM morphology of SPUF composites.

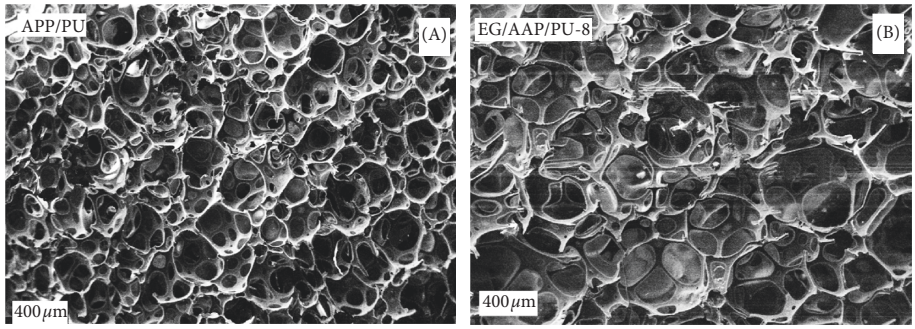

Figure 4: SEM micrograph of SPUF composites before burning.

with EG, although the apparent density is also high, the compressive strength and modulus are decreased, and the values are lower with the content of EG increasing. The sample of EG/APP/SPUF-2 shows better compressive strength and modulus than EG/SPUF. This is caused by the damage of the cell structure by EG, as we discussed in the apparent density paragraph. Besides the apparent density, the cell morphology is another important factor that affects the mechanical properties of foam [7]. The morphology of cell structure is shown in Figure 4. The cell size of the foam is small and well distributed in APP/SPUF sample. In the sample of SPUF containing EG, the cells shows random sizes and shapes, and the wall of the cell is not continuous, which reduces the support capacity of the cells and affecting the foam's ability to resist compression. Besides, the compatibility of water soluble APP and polyurethane matrix is better than that of EG, and APP has little effect on the forming of the foam.

Compared with neat SPUF, Shore's hardness of SPUF containing flame retardants is increased. The surface of the foam became harder because SPUF foam is flexible, while the additives are rigid. All SPUF containing flame retardants in this research with hardness within the range of 55 to 75 HA can be used as the interior parts of automobile.

5. Conclusion

This research investigated the synergistic effect between EG and APP on flammability and thermal behavior of water-blow SPUF. The study shows that the addition of APP and EG improved the flame retardancy and thermal stability of SPUF effectively. SPUF added EG/APP obtained higher LOI value and carbon residue than that with the same loading of EG or APP. TG results show that the addition of APP accelerates the decomposition of SPUF but slows down the decomposition rate of SPUF; the combination of EG with APP improved the thermal stability significantly. SEM morphology of char residue shows the "worm-like" structure developed by EG form the more compact char layer, which proved that EG acts as the main protective role in the improvement of thermal stability. The presence of EG destroys the completeness of the hole in the foam; as a result, the compression property of SPUF composites decreased. While, APP has positive effect on the mechanical properties of SPUF, and the addition of APP with small amount to the EG/SPUF can improve the compression property to a certain extent.

Data Availability

The data (limiting oxygen index (LOI); UL-94 horizontal burning test; mechanical properties) used to support the findings of this study are included within the article. The data (thermogravimetric analysis (TG); scanning electron microscopy (SEM); polarizing microscope) used to support the findings of this study have been deposited in the figshare repository (https://figshare.com/account/home#/data; e-mail address: 2920771312@qq.com; password: wsns19941026).

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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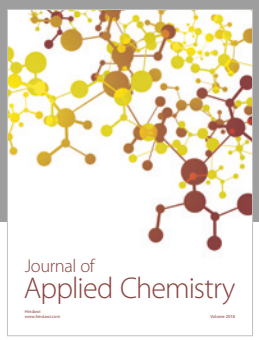

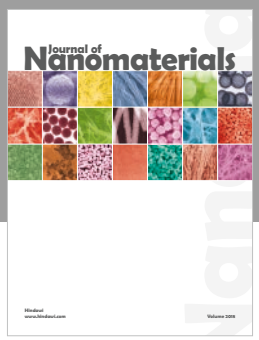

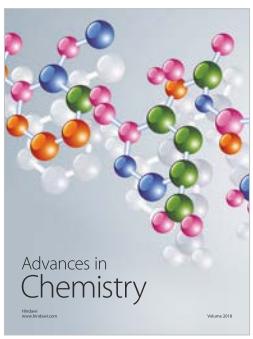

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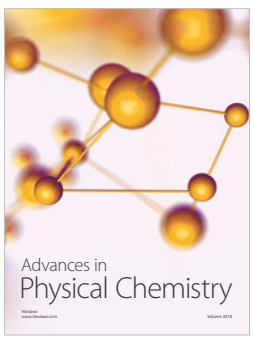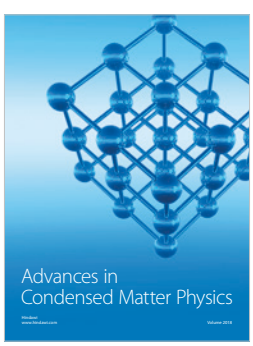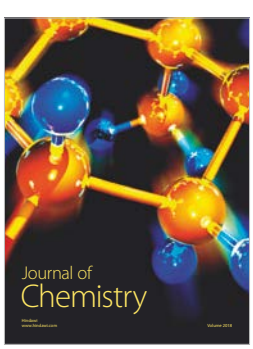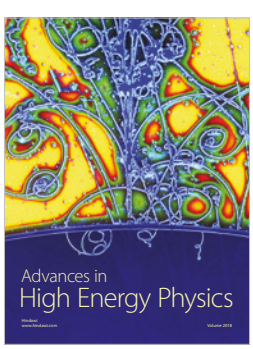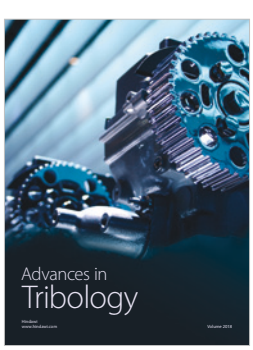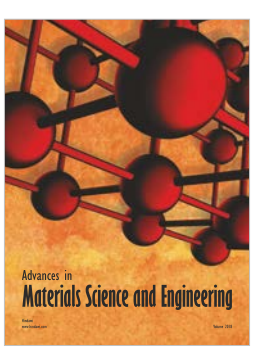
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