Effect of Expandable Graphite on the Properties of Intumescent Flame-Retardant Polyurethane Foam

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ABSTRACT: Water-blown rigid polyurethane foam (PUF) with two different particle sizes (180 and 300 μm) of expandable graphite (EG) as a flame-retardant additive were prepared, and the effects on the mechanical, morphological, water absorption, thermal conductivity, thermal, and flame-retardant properties were studied. In this investigation, EG content was varied from 5 to 50 php by weight. The mechanical properties of PUF decreased with increasing EG loading in both cases. The water absorption of the PUF increased with an increase in the EG loading mainly because of the collapse of foam cells, as evidenced from the scanning electron microscopy pictures. The thermal conductivity of the EG-filled PUF showed that the insulation properties decreased with EG loading. The flame-retardant properties (limiting oxygen index and char yield measurement) of the PUF improved with increasing EG loading. PUF filled with the higher particle size EG showed better mechanical properties and fire-retardant properties than the PUF filled with the lower particle size EG. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2586–2594, 2008

Key words: flame retardance; intumescence; polyurethanes; thermal properties

INTRODUCTION

Rigid polyurethane foams (PUFs) are widely used in industry because of their excellent mechanical properties, insulation properties, and so on. In general, PUF is flammable and releases toxic gases during burning, which limits its applications in fire-resistant materials. Flame retardants are added to PUFs to reduce their flammability. The most widely used flame retardants in rigid PUFs are based on halogenated or phosphate compounds or a combination of both.[1–3] In the event of fire, halogenated additives release corrosive and toxic smoke, which erodes instruments, pollutes the environment, and therefore, threatens the safety of people. In recent years, there has been worldwide concern over their use, and the stringent conditions set by statutory governmental regulations for the use of flame retardants has demanded the development of halogen-free, flame-retardant materials. As a result, flame-retardant additives with good flame-retardant efficiency and low pollution potential are particularly needed. Recently, attention has been paid to char-forming flame retardants, such as phosphorus and intumescent systems, as it is known that they are quite effective in the flame protection of materials and do not produce toxic smoke.[4] Intumescent flame-retardant systems were first developed for application in the field of coatings in the 1960s, whereas the incorporation of intumescent additives in polymeric materials is a relatively recent development.[5] These materials when exposed to flame give a swollen multicellular char capable of protecting the underlying material from the action of the flame. On burning, these additives develop a foamed char on the surface of the polymeric material. During combustion of polymers, there is a relationship between char formation and flammability. The flame retardancy of foams can be improved by the promotion of the formation of a carbonaceous char layer during combustion. The char can serve as a solid insulating layer, which may protect the polymer from the heat of combustion, limit the access of oxygen to the polymer, and reduce smoke production.

Recently, there have been a few reports of the application of expandable graphite (EG) as a flame-retardant material in PUF. EG is a special type of graphite flake in which sulfuric acid (H_2SO_4) is intercalated between the carbon layers. EG is an intumescent flame-retardant material. At high temperatures, the graphite gets oxidized on reaction with H_2SO_4:
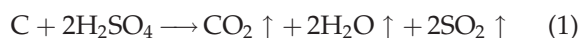
$$C + 2H_2SO_4 \longrightarrow CO_2 \uparrow + 2H_2O \uparrow + 2SO_2 \uparrow \quad (1)$$

TABLE I
Characteristics of the Raw Materials Used for Making PUF

Material	Equivalent weight	Functionality	Role/characteristics
PMDI	136.6	2.7	NCO content = 30.8%
Polyether polyol	127.5	3.0	OH value = 440 mg of KOH/g
PMDETA	—	—	Catalyst
Polyether dimethyl siloxane (Tegostab B 8460)	—	—	Surfactant
Distilled water	9.0	2.0	Blowing agent
EG	—	—	Flame retardant

The evolved gases cause the expansion of the material; this expanded volume suffocates the flame and acts as physical barrier for heat and mass transfer. The effect of such flame-retardant additives has been studied for polyolefin blends,[6,7] polyurethane coatings,[8] high-density PUF, and polyurethane–polyisocyanurate (PIR–PUR) foam.[9–15] These reports have mainly explained the mechanical and fire-retardant properties of EG-filled rigid or PIR–PUR foams, generally at lower loadings of EG. Because high-density rigid PUF or PIR–PUR foams already have good thermal stability and good fire-retardant performances, lower loadings of EG were used to enhance the further flame retardancy of these foams. Low-density and water-blown low-density PUF occupies a lion's share of the PUF market in the world. Although Bian et al.[15] reported that the flame-retardant performance depends on the foam density, its studies have been mainly restricted to high-density PUF. In this article, we report the application of two different particle sizes of EG as flame-retardant materials in water-blown, low-density PUF. In this case, we used 5–50 php of EG and studied the effect of particle size on the different properties of PUF, such as the mechanical, thermal conductivity, water absorption, thermal stability, and flame-retardant properties. The structure–property relationships were compared between PUF filled with EG of different particle sizes and neat PUF with scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and limiting oxygen index (LOI) studies.

EXPERIMENTAL

Materials

Polymeric methane diphenyl diisocyanate (PMDI) and polyether polyol were obtained from Huntsman International Pvt., Ltd. (Mumbai, India). Distilled water was generated in our laboratory and was used as a chemical blowing agent. N,N,N′,N′,N″-Pentamethyl diethylene triamine (PMDETA) was obtained from Aldrich (St. Louis, MO) and was used as a cat-

alyst. Polyether dimethyl siloxane (TEGOSTAB B 8460), supplied by Goldschmidt (Essen, Germany) was used as a surfactant. EG (particle size = 180 or 300 μm, density = 1.25 g/cm^3), supplied by Graph Tech International (Cleveland, OH), was used as a flame-retardant additive. The characteristics of the different materials used in the preparation of the PUF are shown in Table I. All of the chemicals were used as received.

Preparation of the foam

The EG-filled PUF samples were prepared by a one-shot, free-rise method. Their chemical compositions are shown in Table II. The amount of raw materials, except that of EG, were chosen as optimum after a series of test experiments. Raw materials were first well mixed in a plastic beaker, and then, the flame retardant was added and mixed with a mechanical stirrer. The amount of PMDI required for the reaction with polyether polyol and distilled water was calculated from their equivalent weights. For the completion of the reaction, excess PMDI (NCO/OH = 1.1) was used. To this homogeneous mixture, PMDI was added with vigorous stirring for 10 s. The resulting mixture was immediately poured into an open paper mold (30 × 25 × 15 cm^3) to produce free-rise foams. Foam blocks so obtained were kept in an oven at 70°C for 24 h to complete the polymerization reaction. Samples were cut into the desired shape and size by rubbing with fine emery paper, and these test species were used for the evaluation of different properties.

TABLE II
Chemical Compositions of EG-Filled, Water-Blown, Rigid PUF

Material	php
Polyether polyol	100
PMDETA	0.5
Tegostab B 8460	2.0
Distilled water	0.3
EG	5–50
PMDI	122

TABLE III
Effect of EG on the Viscosity of the Polyol Mixture

Sample	Amount of EG (php)	Viscosity at 25°C (Pa s)
1	0	3.1
2	5	3.2
3	15	4.8
4	25	4.9
5	50	5.5

Measurement of different properties

The viscosity of the polyol and its mixture were measured with a Bohlin Visco 88 BV model instrument (Muhlacker, Germany) at 25°C. The apparent densities of the PUF samples were measured as per ASTM D 1622-03, and the average value of three measurements is reported. The mechanical properties of the PUF samples were measured under ambient conditions with an Instron Hounsfield universal testing machine (model H10KS Horsham, PA). The compressive stress at 10% strain in parallel to foam-rise direction was performed as per ASTM D 1621-00. The size of the specimen was $55 \times 55 \times 30$ mm^3 (length $\times$ width $\times$ thickness), the rate of crosshead movement was fixed at 2.5 mm/min for each sample, and the load cell used was 10 kN. The strengths of five specimen samples were measured, and the average of these values are reported. The morphology of the PUF samples were studied with a Jeol JSM 5800 scanning electron microscope (Tokyo, Japan). The samples were gold-coated before scanning to provide an electrically conductive surface. The accelerating voltage was 20 kV to prevent degradation of the sample. Fourier transform infrared (FTIR) spectra were recorded with a PerkinElmer FTIR spectrometer (Spectrum RX 1 model). The samples were prepared in the pellet form by mixture of the powder sample with KBr at a ratio of 1 : 10 or in the filler form. The water absorption of the PUF samples was measured as per ASTM D 2842-01. The size of the specimen was $40 \times 40 \times 20$ mm^3 (length $\times$ width $\times$ thickness). The water absorption of three specimens per sample were measured, and their average values are reported. The thermal conductivity of the PUFs were measured between the two plates on a guarded hot-plate apparatus as per ASTM C 177-97. The size of the specimen was $100 \times 100 \times 25$ mm^3 (length $\times$ width $\times$ thickness). The thermal properties of the foams were evaluated on a thermogravimetry analyzer (TGA) Q50 (TA Instruments, New Castle, DE) under an air environment at a heating rate of 20°C/min. The flammability test was performed an the LOI test instrument (Stanton Redcroft FTA unit (East Grinstead, UK)) as per ASTM D 2863-97. The specimens for the LOI measurement were $120 \times 12 \times 10$ mm^3 (length $\times$ width $\times$ thickness). The LOI values of five specimens per sample were measured, and their average values are reported. The char yields of the foams were measured on a muffle furnace at 550°C for 30 min.

RESULTS AND DISCUSSION

The viscosity of the reaction mixture plays a crucial role in the processing and preparation of PUF by the one-shot, free-rise method. Table III shows the effect of viscosity on the addition of the EG particles into the polyol mixture. It indicates that there was rise in viscosity with the addition of EG particles. So, it was still suitable to make rigid foams; Jin et al.[16] reported that the upper limit of the viscosity of polyols for the preparation of PUFs might be less than 6 Pa s. With the addition of PMDI (lower viscosity = 0.25 Pa s), the polyol mixture became easy processable. Foam density is a very important parameter, which affects the mechanical properties of PUFs.[17] In general, the foam density is dependent on degree of foaming, which in turn, depends partly on the type and amount of foaming (blowing) agent. In this study, the amount of chemical blowing agent (distilled water) was kept constant. Table IV shows the densities of the PUFs filled with two different particle sizes. Initially, there was drastic reduction in density in both cases and then an increase with increasing EG loading. The density of the PUF filled with the higher particle size EG was greater than

TABLE IV
Effects of EG on the Density and Compressive Strength of PUF

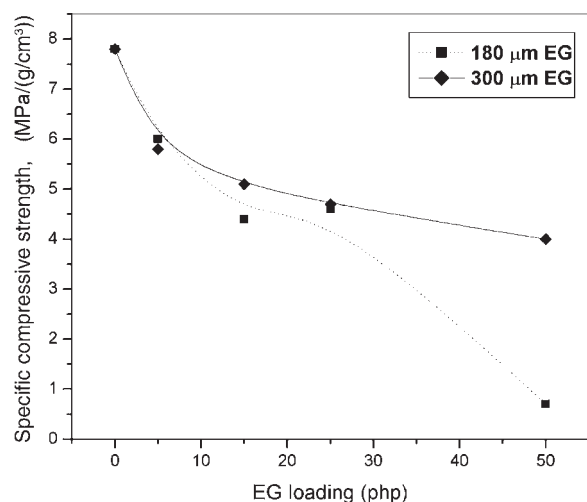| Sample	EG content (php)	Density (kg/m^3)		Compressive strength at 10% strain (kg/cm^2)	
		EG: 180 μm	EG: 300 μm	EG: 180 μm	EG: 300 μm
1	0	103	103	8.1	8.1
2	5	58	67	3.5	3.9
3	15	54	61	2.4	3.1
4	25	63	83	2.9	3.9
5	50	143	103	1.0	4.1

Figure 1 Effect of EG on the specific compressive strength of PUF.

that filled with the lower particle size EG. The decrease in density of the EG-filled PUFs might have been due to an increase in the cell size/volume (as shown by the SEM picture and discussed later). There was an increase in the density of the PUFs with higher loading (50 php) of EG, which was probably because the density of EG (1250 kg/m^3) was higher than that of the neat PUF.

Mechanical properties

The mechanical properties of PUFs are important parameters that determine their applications, such as in load bearing and as packaging materials. The achievement of good mechanical properties in filled-polymer composites depend on the distribution and dispersion of filler in the polymer matrix.[18] To study the effect of EG on the compressive properties of the PUFs and to eliminate the effect of foam density, we normalized the compressive strength of different foams were by dividing them by their respective densities. Figure 1 and Table IV show the effect on the specific compressive strength (normalized compressive strength) and compressive strength at 10% strain of the PUFs filled with two different particle sizes of EG. It was clear that the specific compressive strength and compressive strength at 10% strain decreased with increasing EG loading. This observation was in good agreement with Modesti and Lorenzetti's report[11] on low-density PIR–PUR foams filled with EG. They observed that EG flakes did not locate in the cell strut but were observed between the cell walls when the particle size of EG was of the same order as the cell size of the PUF. However, the compressive strength of PUF filled with the higher particle size EG was better than that of the PUF filled with the lower particle size EG. This was

because of the smaller EG particles were poorly dispersed and formed aggregates. This led to an inhomogeneous cell structure and resulted in poor mechanical properties. Shi et al.[14] also observed a similar kind of behavior for high-density PUFs filled with EG.[14]

Figure 2 shows a broad peak at 3408 cm^{-1}, which indicated the presence of —OH on the surface of EG. PMDI reacted with the —OH group of EG instead of reacting with —OH group of the polyol. This affected the cell structure. The complete disappearance of the peak intensity of the —OH group (3408 cm^{-1}) and the decrease in the peak intensity of the —NCO group at 2274 cm^{-1} indicated its chemical reactions with the —OH group of EG. Duquesne et al.[19] also confirmed that the interaction of EG with the polyurethane matrix. The effect of the interaction of the —OH group with PMDI on cell formation in PUFs was also confirmed from studies of the morphology of the PUFs, as shown by SEM pictures.

Morphology

In general, the physical properties of foam not only depend on the rigidity of the polymer matrix but also are related to the cellular structures of the foam. Thus, it is of interest to observe the morphology of foam specimens with SEM. Figure 3(a–e) shows microphotographs of the fracture surfaces of the PUFs with EG at different loadings. The shape of the cells in neat PUF and in the EG-filled PUFs was approximately spherical. As shown in Figure 3, the incorporation of EG caused an increase in the cell volume and tearing of cell walls in both cases. This was because EG releases some gases during the highly exothermic reaction between polyol and PMDI and the surface —OH group of EG. Also, the lower particle size (180 μm) EG resulted in the tearing or collapse of the cellular structure and agglomerated in the PUFs, as revealed in Figure 3(b,c). Figure 3(d,e) indicates that the cell sizes were larger the PUF with the larger particle size EG. It also shows that the EG was located mainly in the struts, that is, the intersection of several
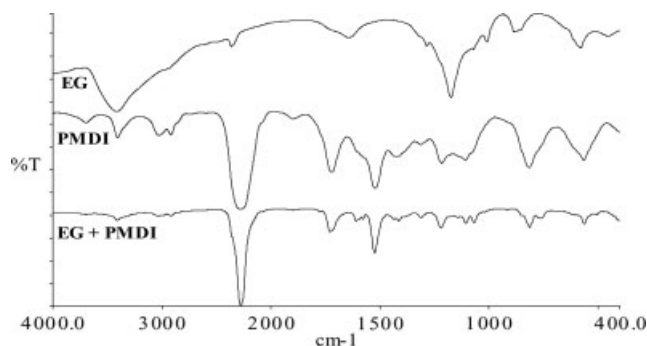

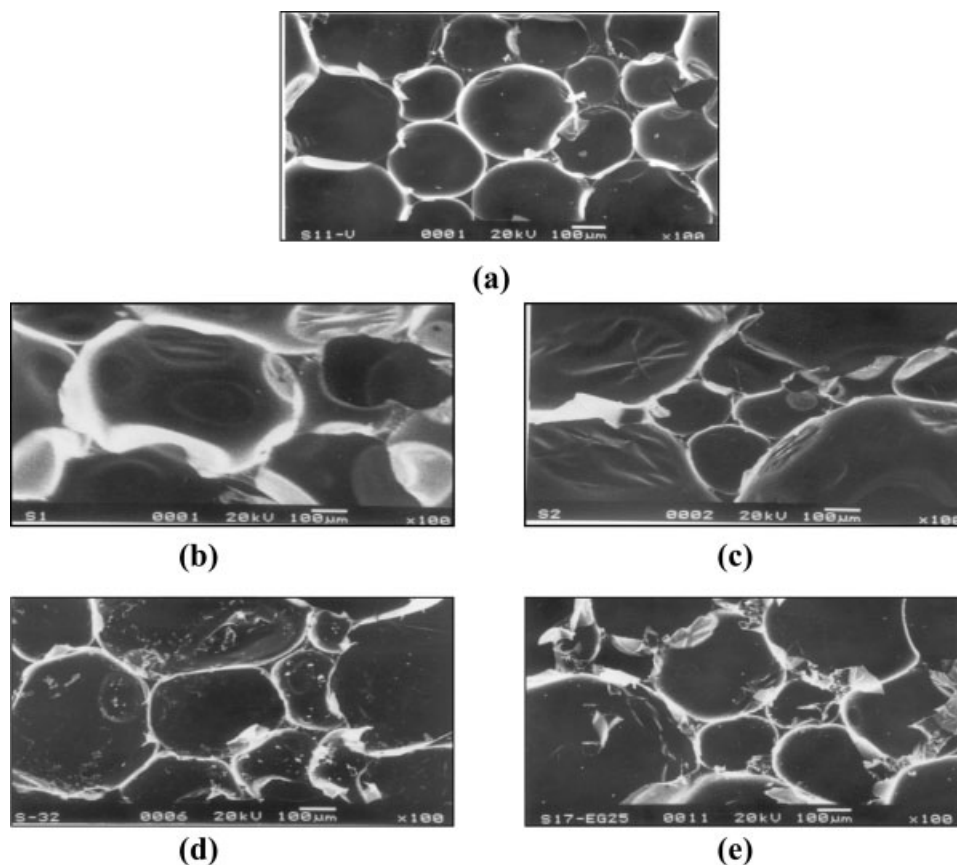**Figure 2** FTIR spectra of EG before and after its reaction with PMDI.

Figure 3 Microphotographs of EG-filled PUF samples: (a) neat, (b) 5 php EG (180 μm), (c) 25 php EG (180 μm), (d) 5 php EG (300 μm), and (e) 25 php EG (300 μm).

cells, but the same behavior was not observed in with the PUF filled with the lower particle size EG. This was probably because of the lower particle size of the EG compared to the average cell size (255 μm) of the neat PUF.

Water absorption

It is generally known that the amount of water absorption of a cellular material mainly depends on the cell size and cell structure, whether it is closed or open.[20] Figure 4 shows the effect of EG on the water absorption behavior of the PUFs. It is clear from the figure that the water absorption behavior of the EG-filled PUFs did not follow the any regular trend with the addition of EG. However, the EG-filled PUFs showed more water absorption than the neat PUF. This was mainly because of the larger cell formation and interconnection of various cells due to the tearing and collapse of the cells, as shown in Figure 3. At a very high loading of EG of 50 php, the water absorption was very high (Fig. 4). Residual —OH groups also led to H bonding with water molecules and, hence, resulted in increased water absorption. It is well known that bigger PUF cells have thinner cell wall thicknesses.

Thermal conductivity

The thermal conductivity of PUFs depends on the foam density, cell size, cell orientation, ratio of closed to open cell content, thermal conductivity of the gases (blowing agent), and filling materials.[18]
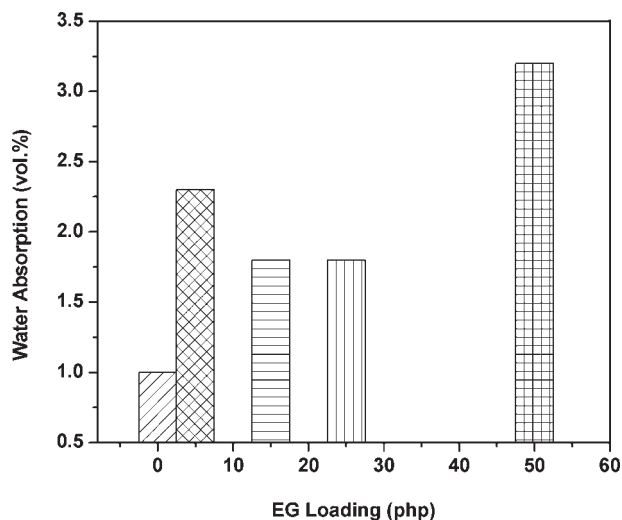

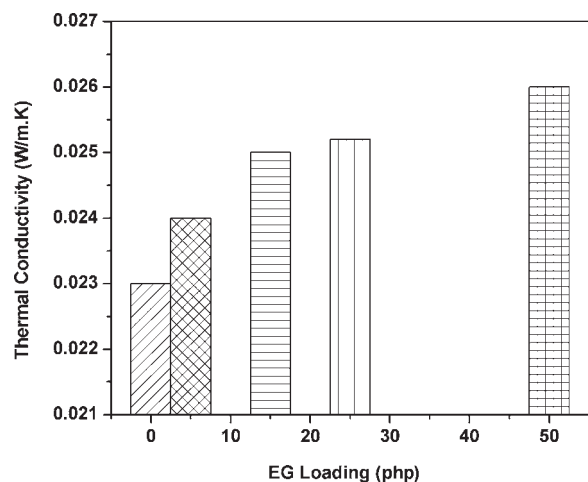**Figure 4** Effect of EG (300 μm) on the water absorption of PUF.

Figure 5 Effect of EG (300 μm) on the thermal conductivity of PUF.

Figure 5 shows the effect of EG on the thermal conductivity of the PUFs. It indicates that with increasing EG loading in the PUFs, the thermal conductivity increased. EG itself has a high thermal conductivity because the main constituent of EG is a highly conducting carbon. The thermal conductivity behavior had the same analogy with electrical conductivity. It is known that, when a conductive additive is added to an insulating matrix, the conductivity of the matrix increases slowly, which is followed by an abrupt change, and then, the conductivity attains a constant value equal to that of the conductive additive. This signifies that a conductive network is found in the insulating matrix through the aggregation of the conductive filler. Applying the same analogy here, we found that the incorporation of EG had a higher thermal conductivity compared to neat PUF. The increase in average cell size
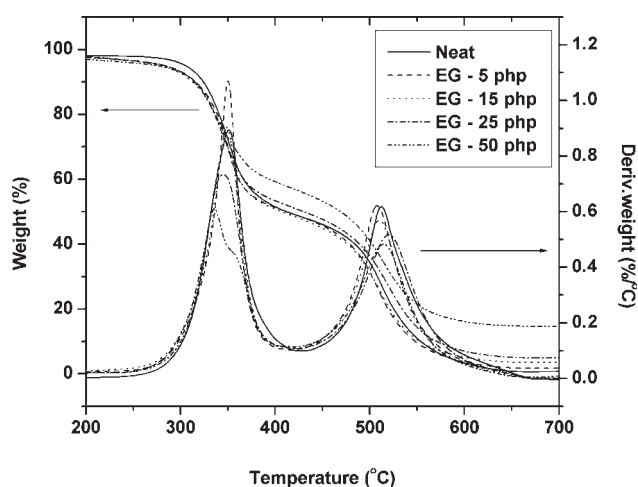

Figure 6 Effect of EG (300 μm) on the degradation behavior of PUF in air.

TABLE V
Effect of EG on the Degradation Temperature of PUF in Air

Sample	EG (300 μm) content (php)	T_{1max} (°C)	T_{2max} (°C)
1	0	351	511
2	5	350	508
3	15	349	510
4	25	345	520
5	50	336	515

and broken cell walls in the EG-filled PUFs was also responsible for its increased thermal conductivity.

Thermal properties

Figure 6 shows the thermograms of PUFs with different loadings of EG and also of neat PUF. Both the neat and EG-filled samples showed a two-step degradation. Table V shows both maximum degradation temperatures at each step of the degradation. It reveals that the first and second degradations of the neat PUF took place at 351°C [first maximum degradation temperature (T_{1max})] and 511°C [second maximum degradation temperature (T_{2max})], respectively. The first step of degradation was due to the formation of alcohol and isocyanate groups. The isocyanates from this depolycondensation reaction are very reactive to dimerise to form carbodiimide with the evolution of carbon dioxide at higher temperatures. This carbodiimide can further react with alcohol or water vapor to impart the substituted urea. This is more thermally stable and is formed in the second-step degradation of PUFs.[21]

There was no significant change in T_{1max} at the initial loading of EG (Table V). This was because EG and its degradation products did not react with polyurethane and, consequently, did not affect the degradation at the lower loading of EG under air. However, at higher loadings of EG, T_{1max} decreased, and the DTG curve showed broad and bimodal peaks at 300–400°C. This may have been due to the degradation of EG, which started at about 300°C (please see the TGA curve of EG in the supplementary material). T_{2max} was not much affected by the initial loading of EG. However, at higher loadings, there was a slight increase in T_{2max}. This may have been due to more char formation at that temperature (515°C), as shown in Table VI. This char layer could have acted as a thermal barrier for the unburnt polymer and prevented further decomposition and, therefore, limited the mass loss. Shi et al.[14] also observed a similar trend in the degradation profile in high-density PUFs filled with EG under an air atmosphere.

TABLE VI
Effect of EG on the Char Yield in the Muffle Furnace and TGA of PUF

Sample	EG content (php)	Char yield at 550°C/ 30 min in a muffle furnace (%)		Char yield at 515°C by TGA in air (%)
		180 μm	300 μm	
1	0	0.12	0.12	25
2	5	1.3	1.5	22
3	15	2.4	3.2	23
4	25	4.5	6.0	30
5	50	12.3	14.0	34

Flame-retardant properties

The fire-resistant behavior of water-blown rigid PUFs filled with different sizes of EG at different loadings was analyzed through the measurement of the LOI and char yield. Figure 7 shows the effect of the loading of EG and its particle size on the LOI of the PUFs. It was clear that the LOI increased linearly with increasing EG loading. At high temperatures, graphite reacts with sulfuric acids (intercalated between the carbon layers in EG) and forms CO_2, SO_2, and H_2O gases [shown in eq. (1)]. These evolved gases diluted the concentration of oxygen near the flame zone during burning, and thus, the LOI increased.

Figure 8 shows the pictures of the LOI test samples of neat PUF and the EG-filled PUFs. It clearly indicates that the EG-filled samples had more voluminous carbon-rich char on the burnt surface than the neat PUF. This was mainly because of the reaction between graphite and sulfuric acid, which generated gases at high temperatures. On the other hand, upon heating, sulfuric acid boiled and released vapors, causing a significant expansion of the graphite. This voluminous charring prevented the filled PUF from burning further and led to the
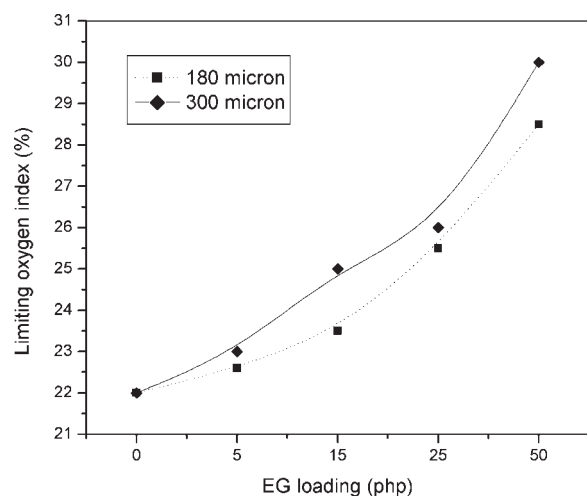
increase in LOI values. Figure 7 shows that the LOI values of the PUF with the higher particle size EG were much higher than those of the PUF with the lower particle size EG. This was because of the formation of a greater amount of char residue in the PUF with the larger particle size EG, as shown in Table VI. This observation was in good agreement with Shi et al.'s study of high-density PUFs with different times of pulverizing for EG; they observed that the LOI values were lower for longer pulverized EG-filled PUFs (smaller particle size) than shorter pulverized EG-filled high-density PUFs.[14]

There is a strong correlation between char yield and fire resistance. This is mainly because char is formed at the expense of combustible gases, and this char inhibits further spread of flame by acting as a thermal barrier around the unburnt material.[22] When subjected to high temperature, a polymer passes through several steps in the formation of
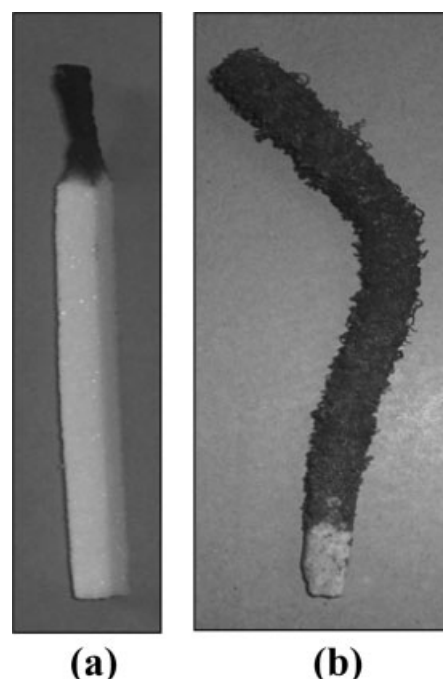

Figure 8 Images of burnt neat PUF and EG-filled PUF: (a) neat and (b) 50 php EG.

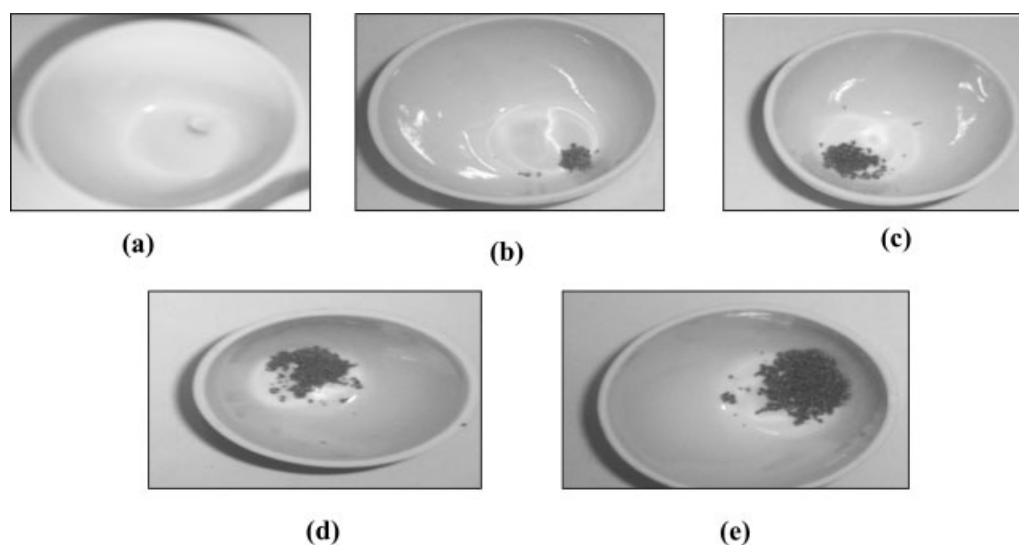**Figure 7** Effect of EG on LOI of PUF.

Figure 9 Char images of EG-filled PUF at 550°C after 30 min: (a) neat, (b) 5 php EG, (c) 15 php EG, (d) 25 php EG, and (e) 50 php EG.

char. These include chemical decomposition, cross-linking, aromatization, fusion of aromatics, turbostratic char formation, and graphitization. Table VI shows the effect of EG with two different particle sizes on the char yield measured by the heating of the same amount of EG-filled PUFs in a muffle furnace and also as measured by TGA under an air atmosphere. The results show that the char yield increased with increasing EG content (Fig. 9). The smaller particle size EG imparted less char residue than the larger size EG. This was caused by the uneven distribution of EG in the PUF.
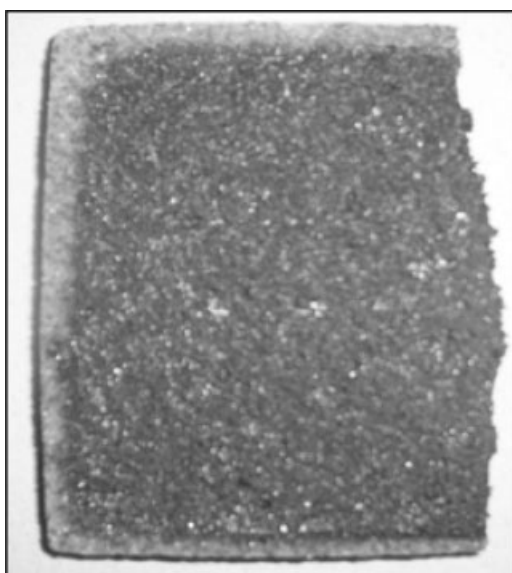
EG is an intumescent flame-retardant material. It is composed of flake graphite, in which sulfuric acid is intercalated between the carbon layers of graphite. When exposed to temperatures higher than 160°C, carbon is oxidized with H_2SO_4 to form gaseous products [as shown in eq. (1)]. This blowing effect of the evolved gases causes an increase in the volume of the material. It also causes a wormlike structure in the PUF (shown in Fig. 10), which suffocates the flame. The compact char layer limits heat transfer and mass transfer from the polymer source. It also acts as a physical barrier against heat transfer and the diffusion of oxygen toward the polymer. Fire cannot spread further because of a dearth of oxygen. Thus, it acts as an intumescent flame-retardant material.

CONCLUSIONS

Rigid PUFs were prepared with EG with two different particle sizes and at different concentrations. The studies clearly showed that

1. The viscosity of the polyol mixture increased with increasing loading of EG.
2. The mechanical properties of the EG-filled PUFs decreased with increasing EG loading. However, the mechanical properties were better for the PUFs filled with the higher particle size EG than for those filled with the lower particle size EG.
3. The thermal conductivity of the EG-filled PUFs increased with increasing EG loading.
4. The water absorption of the EG-filled PUFs increased with EG loading because of the damage to the cell wall and the EG particles located between the cell walls.

Figure 10 Image of the burnt wormlike structure of EG (50 php)-filled PUF.

5. At higher loadings of EG, there was a decrease in the first decomposition temperature. However, interestingly, the char residue was higher for higher loadings of EG. The second decomposition temperature of the EG-filled PUFs increased because of the formation of thermally stable char residue, which depleted the oxygen/air concentration.

6. The flame resistance properties of the PUF increased with increasing loading of EG. The higher particle size EG led to better flame-retardance properties. This was probably because the higher particle size EG imparted more char residue. Finally, it followed the condensation mechanism and formed the loose and needle-like char. This wormlike char protected the unburnt polymeric material by preventing heat transmission and the diffusion of air toward the unburnt polymer source trapped in the bulk of the PUF.

7. The 25-php EG (300 µm) was the optimum loading for the optimum properties.

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