

Properties and microstructure of expandable graphite particles pulverized with an ultra-high-speed mixer

Lei Shi ^a, Zhong-Ming Li ^{a,*}, Wei Yang ^a, Ming-Bo Yang ^a, Qiu-Ming Zhou ^b, Rui Huang ^a

^a College of Polymer Science and Engineering, Sichuan University, State Key Laboratory of Polymer Materials Engineering, Chengdu, 610065, Sichuan, People's Republic of China

^b Institute of Chemical Materials, Engineering Physical Academy of China, Mianyang, 621900, People's Republic of China

Received 28 June 2005; received in revised form 21 June 2006; accepted 25 August 2006

Available online 9 September 2006

Abstract

The expandable graphite (EG) particles were pulverized to achieve different and smaller sizes using an ultra-high-speed mixer. The microstructure of particles was observed by a scanning electron microscope (SEM). The as-received EG particles showed an irregular flake shape. With the increase of the mixing time, the EG particles tended to be circular and the collapses and cracks in the EG surfaces appeared, and their average diameter and average area rapidly reduced. At the same time, their expansion volume after thermal treatment greatly decreased, resulting from the reduction of particle sizes and the direct release of the oxidant inside the EG particles instead of exfoliating the particles. The expanded EG particles revealed the typical wormlike structure.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Expandable graphite; Expanded graphite; Fine particle; Microstructure; Particle size

1. Introduction

Expandable graphite (EG) is a graphite intercalation compound in which some oxidants, such as sulfuric acid, potassium permanganate, etc., are inserted between the carbon layers of the graphite [1–4]. When experienced a heat source, EG, occupies hundred times its initial volume and generates a voluminous structure, thus providing fire-retardant performance for the polymeric matrix [4,5]. Some studies implied that EG can produce good fire-retardant properties for some polymers, such as polyolefins [6,7], polyurethane foam [5,8,9], coating [10], etc. In addition, EG after expansion can be used as biomedical materials due to its pore structure and absorptive capacity [3]. And for its high electrical conductivity and a unique layered nano-structure, it was compounded with some polymers, such as polymethyl methacrylate (PMMA) [11], poly(styrene-co-acrylonitrile) [1], etc., to fabricate the so-called nano-composites with excellent electrical conductivity. In our previous study

[5], EG can efficiently improve the fire-retardant properties of high-density rigid polyurethane foam (RPUF) as a halogen-free fire-retardant additive. However, in the open literature, little attention has been paid to the EG pulverization, and the microstructures of finer EG particles before and after expansion, and their influences on the flame behaviors of polymers, etc. Usually a material as a filler for polymers should be fine and uniformly dispersive, that is, the finer and the more uniformly dispersive and distributive filler particles bring out better properties of composites [12–15]. As sheet fire-retardant additives, the fine and uniform dispersion of EG is believed to give a considerable effect on the fire-retardant properties of RPUF. In this series studies, accordingly, the EG particles were crushed into fine ones, and subsequently added to RPUF for further improvement of fire behaviors. In the present work, an ultra-high-speed mixer, which was specially designed for dispersion of nano fillers in polymers depending on its high shear and intense mixing [15], was used for pulverization of the EG particles. After pulverization, EG particles with various sizes were obtained. The structure before and after expansion, size distribution and expansion volume of these particles have been investigated.

* Corresponding author. Fax: +86 28 8540 5324.

E-mail address: zm_li@263.net.cn (Z.-M. Li).

2. Experimental

2.1. Materials

Expandable graphite (Model KP9932300) was purchased from Haida Graphite Co. (QingDao, China). The manufacturer specifies the following properties: ash, 1.0%; moisture, 1.0%; weight loss after expansion, 15%; pH value, 3.0; expansion rate, 300 ml/g.

2.2. Pulverization of expandable graphite particles

EG particles were broken up into smaller ones using an ultra-high-speed mixer whose configuration is shown in Fig. 1. This mixer can provide high speed (as high as 6000 rpm) and high shear force, with a special rotor designed to cut glomerate particles. It has been demonstrated that this mixer can effectively reach dispersion of nano- CaCO_3 in polypropylene, and lead to a considerable increase in mechanical properties of nano- CaCO_3 /polypropylene composite [15]. The shear mixing time is 4 and 13 min, and the EG particles thus obtained are signed as EG4 and EG13 for simplicity, respectively. Correspondingly, the initial EG particles (as received) are referred to as EG0.

2.3. Characterization

The morphology of EG particles before and after expansion was observed by a JSM-9600 (JEOL, Japan) scanning electron

microscope (SEM). The EG particles were suspended in water by stirring, and then some suspension mixture was dripped on the sample stage. After the water volatilizes completely, the surface of the sample was coated with a conductive material and then used for observation. The accelerating voltage was 20 kV. Sizes of EG particles were estimated using SEM micrographs and an image analysis system (some quite small scraps in the EG4 and EG13 were neglected).

The expansion multiple of different EG particles was measured after they were expanded at $950 \pm 10^\circ\text{C}$ for 15 s according to GB 10698-89 (China standard).

The apparent density of various EG particles was tested according to ASTM D2854.

Thermogravimetric analysis (TGA) was carried out in air at a heating rate of $10^\circ\text{C}/\text{min}$ using a SEIKO EXSTAR6000 instrument thermogravimetric analyzer. In each case, a 4.0 mg sample was examined at an air flow rate of 100 L/min at temperatures ranging from room temperature (25°C) to 700°C .

3. Results and discussion

3.1. Morphology of EG particles

Fig. 2 shows the SEM micrographs of EG particles. All the EG particles assume irregular flake shape. And the size of processed EG particles (Fig. 2b and c) is much smaller than that of the unprocessed one (Fig. 2a). With the increase of the mixing time, the EG particles become circular, and their size smaller (see Fig. 2c). Fig. 3 shows the surface microstructure of

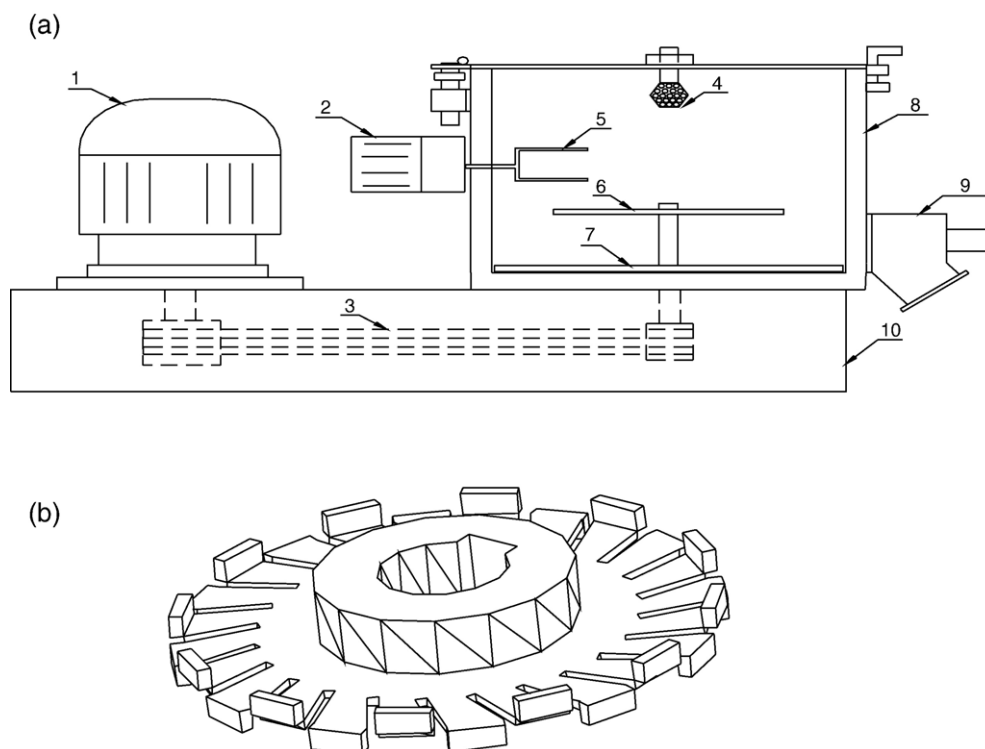


Fig. 1. Structural illustration of ultra-high-speed mixer: (a) overall schematic, (b) shape of upper gear type blade wheel. (1) Main engine, (2) Engine for cutting tool, (3) Driving belt, (4) Atomization nozzle, (5) Cutting tool, (6) Upper blade wheel, (7) Lower blade wheel, (8) Mixing kettle, (9) Discharge, (10) Base.

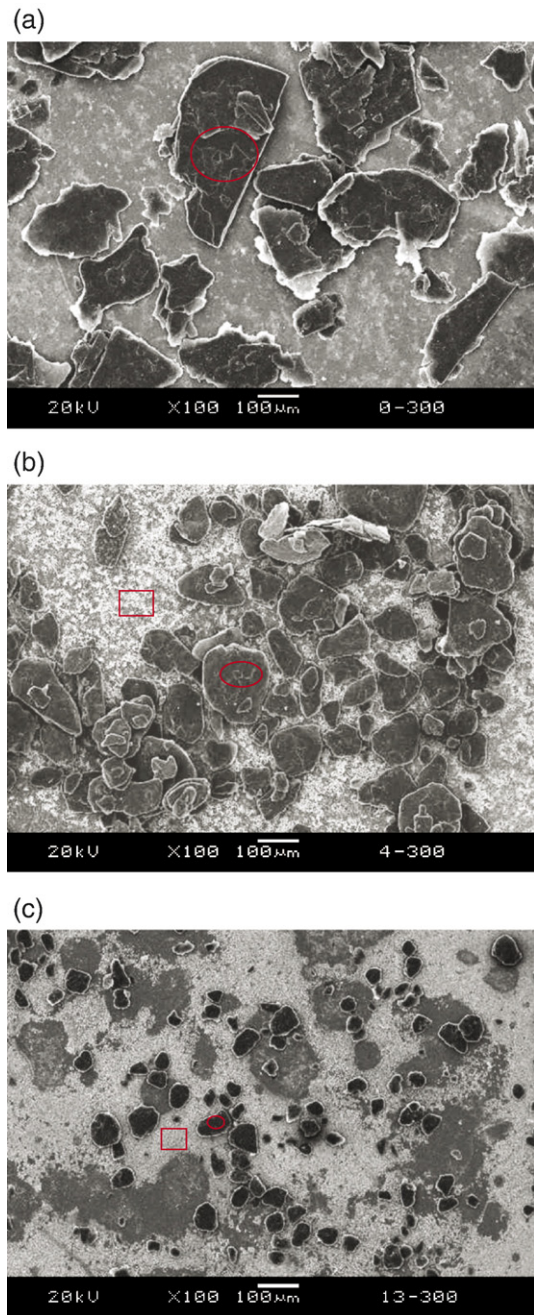


Fig. 2. SEM micrographs of different EG particles. (a) EG0, (b) EG4, and (c) EG13.

EG particles. Some graphite flakes exist in the surface of EG0 (Fig. 3a). These graphite flakes are well absorbed together without any separation. However, after high shear mixing, many EG particles collapse and flaws can be found as shown in Fig. 3b for EG4, in which some graphite flakes in the surface start to be divided. With further increasing the mixing time, Fig. 3c for EG13 shows that the collapses and cracks become more and more, and many divided graphite flakes are observed. The divided graphite flakes produced some scraps with quite small sizes around the EG particles as shown in Fig. 2b and c. The SEM micrographs with higher magnifications of these powders (Fig. 4) exhibit some scraps of graphite flakes, whose

sizes reduce with increasing the pulverization time. One can think that these scraps are exfoliated from the host EG particles under the influences of the high shear during pulverization. Due to the high shear of ultra-high speed mixer, the graphite flakes can be split into smaller ones. The morphological observation implies that this tendency becomes more pronounced with increasing the mixing time.

3.2. Sizes, density and expansion volume of EG particles

Sizes of EG particles were estimated through SEM micrographs and an image analysis system. Due to the irregular sheet

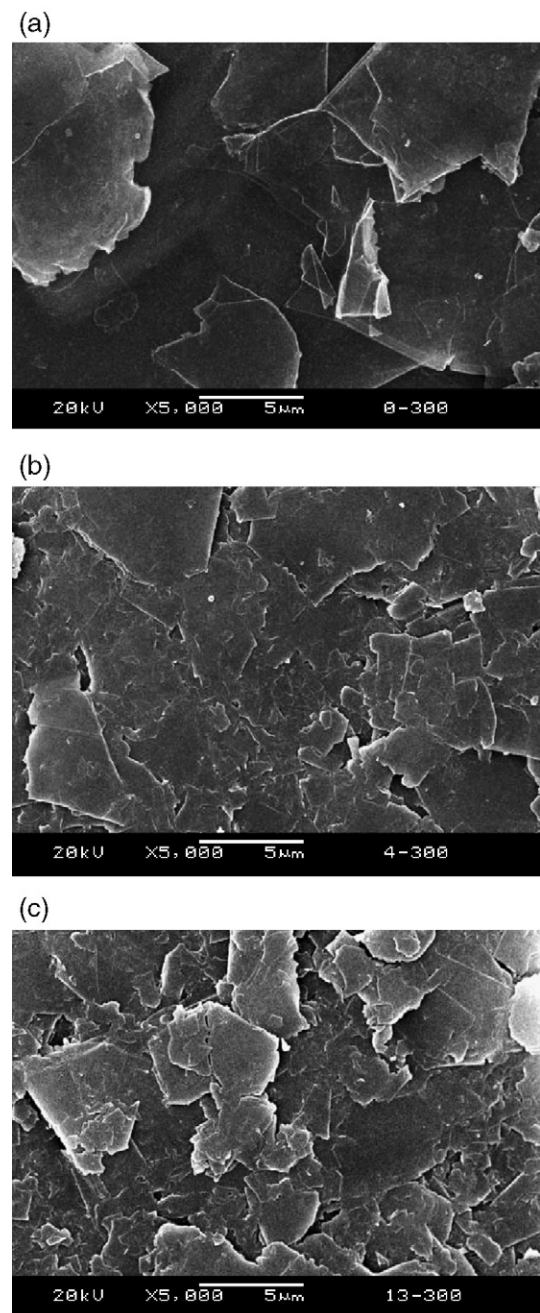


Fig. 3. SEM micrographs of the surfaces for EG particles as shown in Fig. 2 with a high magnification. (a) EG0, (b) EG4, and (c) EG13.

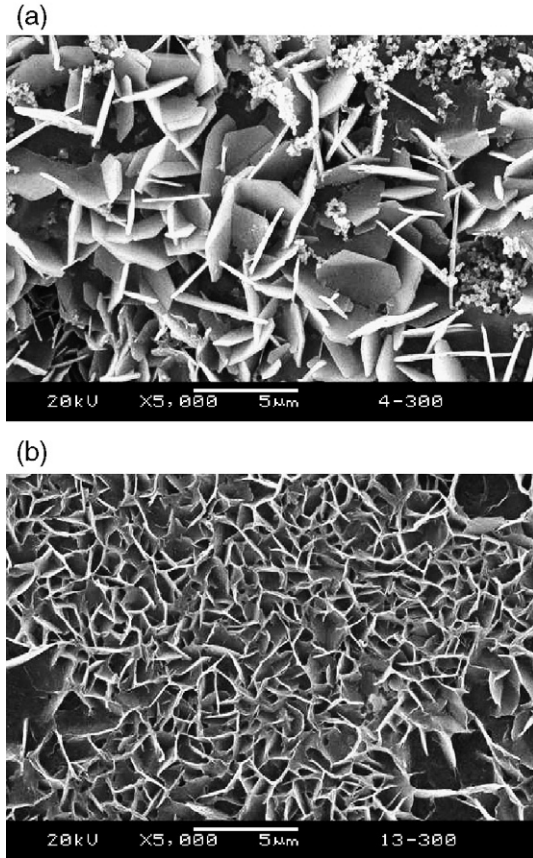


Fig. 4. SEM micrographs of graphite flakes exfoliated during high shear pulverization. (a) EG4, (b) EG13.

structure of EG particles as shown in Fig. 2, we use the diameter, average diameter and area to describe their sizes according to Eqs. (1), (2) and (3):

$$S_a = \left(\sum_{i=1}^N S_i \right) / N \quad (1)$$

where N is the total particle number, S_i is the area of the particle i , and S_a is the number average area.

$$D_i = 2 \times \sqrt{S_i / \pi} \quad (2)$$

where D_i is the equivalent diameter of the particle i .

$$D_a = \left(\sum_{i=1}^N D_i \right) / N \quad (3)$$

where D_a is the number average diameter.

The average diameter (D_a) and area (S_a) are listed in Table 1. Apparently, the average diameter and area rapidly decreases as the mixing time increases. For example, the average area of EG4 is decreased from 39661.5 to 7424.4 μm^2 after 4 min, and further to 1422.4 μm^2 after 13 min. Fig. 5 shows the area distribution of three EG particles. The area for EG0 particles (Fig. 5a) ranges from 0 to $3.0 \times 10^5 \mu\text{m}^2$. The percent of particles below $1.0 \times 10^5 \mu\text{m}^2$ is above 80%. After mixing for

Table 1

Average diameter and average area of EG0, EG4 and EG13

EG particles	Average diameter (μm)	Average area (μm^2)
EG0	196.6	39661.5
EG4	83.7	7424.4
EG13	39.8	1422.4

4 min, the area distribution of EG4 is shown in Fig. 5b. Apparently, almost all the particles have an area below $0.5 \times 10^5 \mu\text{m}^2$. The area distribution is mainly below $0.2 \times 10^5 \mu\text{m}^2$,

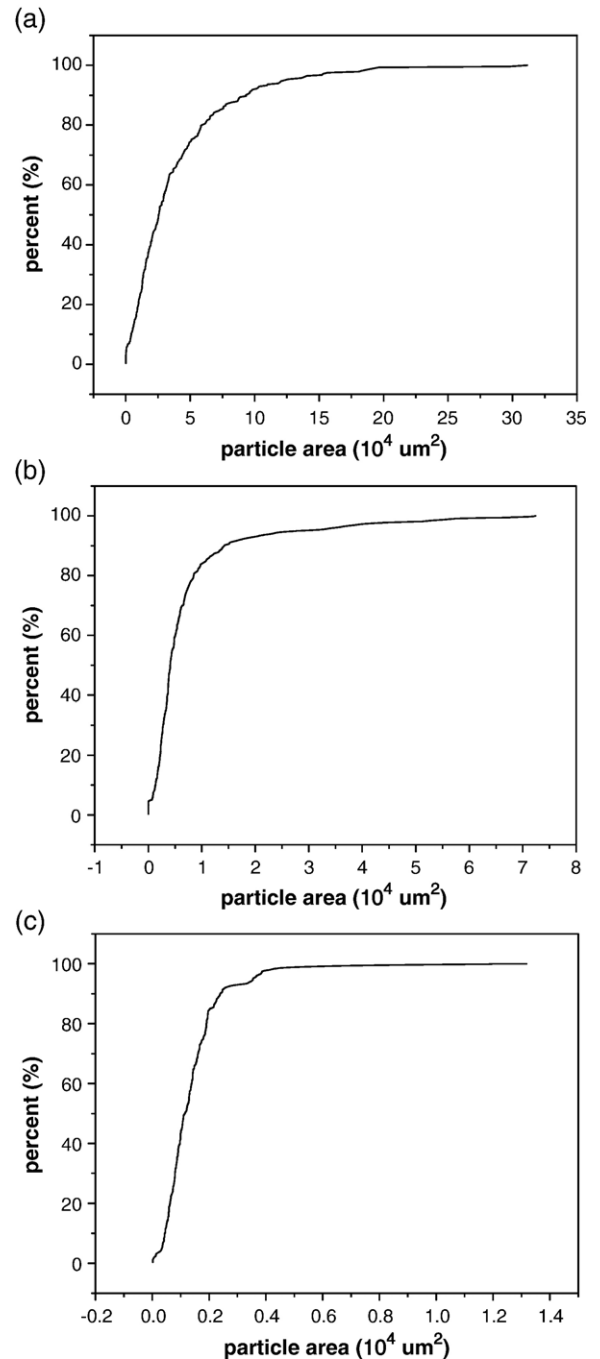


Fig. 5. Area distributions curves of different EG particles. (a) EG0, (b) EG 4, and (c) EG13.

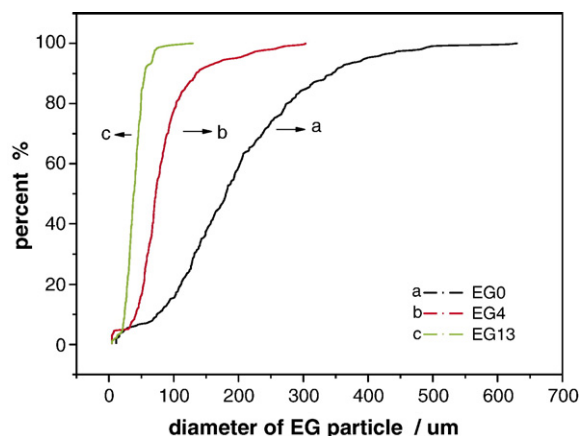
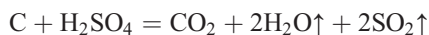


Fig. 6. Diameter distribution curves of EG0, EG4, and EG13.

whose fraction reaches 85.0%. It can be seen from Fig. 5c that almost all of the particles are below $0.04 \times 10^5 \mu\text{m}^2$. These results agree with the data in Table 1. The diameter distribution for the three-sized EG particles are shown in Fig. 6. The diameter for EG0 particles is mainly below 400 μm and the percentage is close to 100%, and below 150 μm for almost all EG4 particles. The diameter of EG13 is mainly below 50 μm and the percent is as high as 83.1%, and especially, the percent of the particles below 100 μm is almost 100%.

The influences of mixing time on the apparent density of different EG particles are shown in Table 2. The density for EG4 increases from 0.468 to 0.693 g/cm^3 for EG0 and further to 0.771 g/cm^3 for EG13. Usually, finer particles tend toward a lower apparent density. But here the contrary result appears, which is presumably due to the fact that the larger size particles form the larger and more space among them. For finer particles, the space reduces and is filled by the exfoliated flakes at the same time.

The expandable graphite that underwent a rapid thermal treatment produces a high volume expansion, and is thus turned into expanded graphite [2,4,5,16–18]. As shown in Fig. 2, the virgin EG particles appear to be sheet agglomerates and are structurally composed of some carbon flakes. When it expanded after treated at 950 $^\circ\text{C}$ for 15 s, a redox process between H_2SO_4 and the graphite generates the blowing gases according to the reaction:



The blowing effect causes an increase of the volume by about many times upon heating, the lamellar structure of EG particles were transformed to a vermicular structure by expansion and

Table 3

Expansion volume of EG0, EG4 and EG13

EG particles	Expanded volume (ml/g)
EG0	300
EG4	140
EG13	40

exfoliation along the *c*-axis of graphite crystal. Expansion volume of various EG particles is shown in Table 3. It can be concluded from Table 3 that the longer the mixing time, the smaller the expanded volume is. This implies that finer EG particles tend to decrease their expansion volume. The similar phenomena has been observed by Schilling [4], who found that the flake size is crucial to the expandability of EG, that is, the smaller flake size brings out the smaller expanded volume. It is because that cutting the EG particles resulted in the splitting of the airproof EG flakes. When the EG4 and EG13 are heated, some oxidant volatilized and the gas that originated from reaction between oxidant and graphite escaped from the edge of flakes with heating. As a result, the expansion volume decrease with the decrease of the particle sizes of EG. In addition, the weight ratio of the graphite to oxidant quite possibly decreases, and thus gives rise to a negative effect on the expansion volume [2]. This can be, to a great degree, confirmed by the data in Fig. 7 which shows the thermogravimetric analysis (TGA) results for three expandable particles at a heating rate of 10 $^\circ\text{C}/\text{min}$. After pyrolysis, the remains percentage of the EG0 was 80.4 wt.%, less than that of EG4 and EG13, both about 87.0 wt.%. This difference should be due to the loss of the oxidant during shear mixing.

3.3. Morphology of EG particles after expansion

Fig. 8 shows the SEM micrographs of three EG particles after expansion. The worm-like structures of the expanded graphite are revealed, as observed in other literature [1,11]. The differences in sizes of three expanded EG particles can be clearly identified. The expanded EG0 (Fig. 7a) is larger than

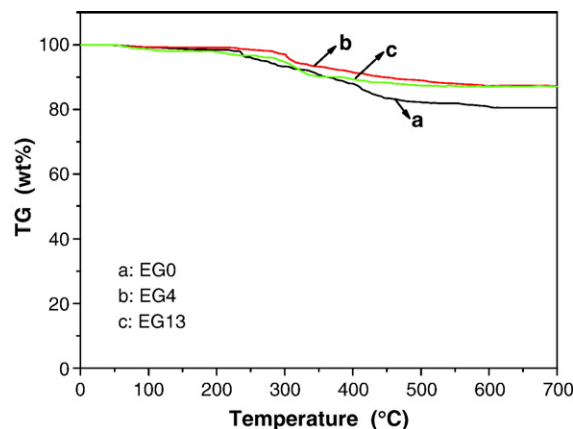


Fig. 7. Thermogravimetric analysis (TGA) curves of EG particles in air at a heating rate of 10 $^\circ\text{C}/\text{min}$. (a) EG0, (b) EG4, and (c) EG13.

Table 2

Apparent density of EG0, EG4 and EG13

EG particles	Apparent density (g/cm^3)
EG0	0.468
EG4	0.693
EG13	0.771

EG4 (Fig. 7b), while the expanded EG13 (Fig. 7c) is the smallest. This also indicates that the expansion multiple reduces with the increase of mixing time. Higher magnification SEM images (Fig. 9) show layered structures and clear layer spacing. Moreover, a few graphite sheets bounded together by Van der Waals forces have expanded completely and there are many apertures. The volume of expanded graphite is many times larger than that of the original EG. Based on these features, EG can be employed as the fire-retardant additive, as shown in the other article [5–10]. Following the present work, the fire retardant efficiency of different-sized EG

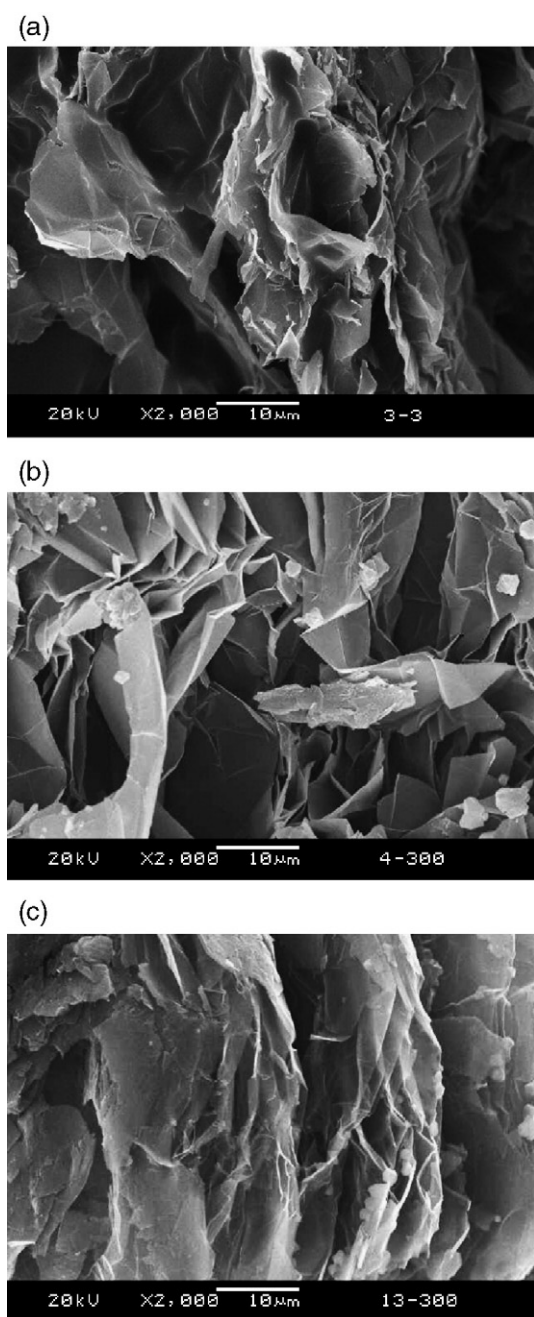


Fig. 8. SEM micrographs of EG particles after expansion with a high magnification. (a) EG0, (b) EG4, (c) EG13.

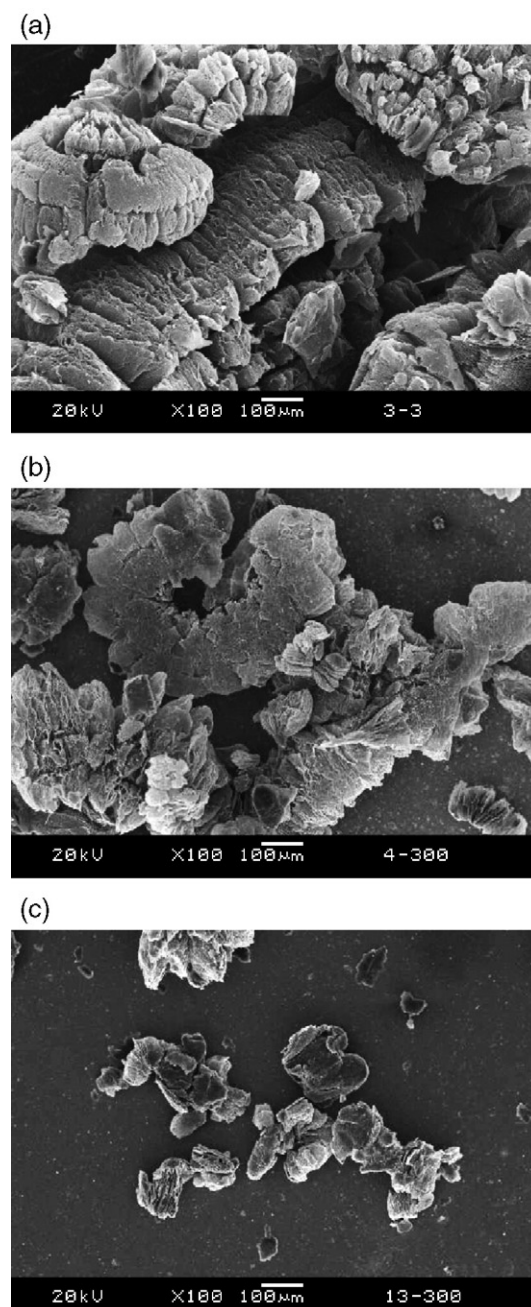


Fig. 9. SEM micrographs of EG particles after expansion. (a) EG0, (b) EG4, and (c) EG13.

particles in polyurethane foam has been evaluated and reported elsewhere [19].

4. Conclusions

The original EG particles show an irregular flake shape. The increase of the mixing time results in more circular EG particles. More scraps of EG flakes around the EG particles produced, and their size reduced with increasing the pulverization time. The average diameter and area rapidly decreased as the shear mixing time increases. The finer particles have a higher apparent density for EG particles due to the smaller and less spaces

formed among the smaller size particles. The expansion volume of EG particles decreased with the increase of mixing time, the reduction of particle sizes and the easy escape of the oxidant from the EG particles instead of exfoliating the particles. Expanded graphite shows wormlike structure for all the EG particles. But the particles size of expanded graphite decreases with increasing the pulverization time. The finer EG particles are a promising intumescent flame retardant for polymers with less sacrifice of the mechanical properties.

Acknowledgments

The authors gratefully acknowledge the financial support of this subject by National Natural Science Foundation of China and Engineering Physical Academy of China (Contract No.10276024). We are also indebted to Mr. Zhu Li from Analytical and Testing Center, Sichuan University, for his careful measurement.

References

- [1] G.H. Zheng, J.S. Wu, W.P. Wang, C.Y. Pan, Characterizations of expanded graphite/polymer composites prepared by in situ polymerization, *Carbon* 42 (2004) 2839–2847.
- [2] X.L. Chen, K.M. Song, J.H. Li, Preparation of lower-sulfur content and expandable, *Carbon* 34 (1996) 1599–1603.
- [3] W.C. Shen, S.Z. Wen, N.Z. Cao, L. Zheng, W. Zhou, Y.J. Liu, J.L. Gu, Expanded Graphite-A New Kind of Biomedical Material, *Carbon* 37 (1999) 351–358.
- [4] B. Schilling, Expandable graphite, *Kunstst. Plast Eur.* 87 (1997) 16–17.
- [5] L. Shi, Z.M. Li, M.B. Yang, B. Yin, Q.M. Zhou, J.H. Wang, Expandable graphite for halogen-free flame-retardant of high-density rigid polyurethane foams, *Polym.-Plast. Technol. Eng.* 44 (2005) 1323–1337.
- [6] R.C. Xie, B.J. Qu, Expandable graphite systems for halogen-free flame-retardant of polyolefins I. flammability characterization and synergistic effect, *J. Appl. Polym. Sci.* 80 (2001) 1181–1189.
- [7] R.C. Xie, B.J. Qu, Expandable graphite systems for halogen-free flame-retardant of polyolefins II. Flammability characterization and synergistic effect, *J. Appl. Polym. Sci.* 80 (2001) 1190–1197.
- [8] S. Duquesne, L.B. Michel, S. Bourbigot, R. Delobel, H. Vezin, G. Camino, et al., Expandable graphite: a fire retardant additive for polyurethane coatings, *Fire Mater.* 27 (2003) 103–117.
- [9] S. Duquesne, R. Delobel, L.B. Michel, G. Camino, A comparative study of the mechanism of action of ammonium polyphosphate and expandable graphite in polyurethane, *Polym. Degrad. Stab.* 77 (2002) 333–344.
- [10] M. Modesti, A. Lorenzetta, F. Simioni, G. Caminon, Expandable graphite as an intumescent flame retardant in polyisocyanurate-polyurethane foams, *Polym. Degrad. Stab.* 77 (2002) 195–202.
- [11] W.G. Zheng, S.C. Wong, Electrical conductivity and dielectric properties of PMMA/expanded graphite composites, *Compos. Sci. Technol.* 63 (2003) 225–235.
- [12] N. Gospodinova, P. Mokreva, T. Tzanov, L. Terlemezyan, A new route to polyaniline composites, *Polymer* 38 (1997) 743–746.
- [13] O. Peitl, R.L. Oréfice, L.L. Hench, A.B. Brennan, Effect of the crystallization of bioactive glass reinforcing agents on the mechanical properties of polymer composites, *Mater. Sci. Eng., A Struct. Mater.: Prop. Microstruct. Process.* 372 (2004) 245–251.
- [14] J.S. Chung, H.J. Sohn, Electrochemical properties of amorphous comb-shaped composite PEO polymer electrolyte, *J. Power Sources* 112 (2002) 671–675.
- [15] G. Wang, X.Y. Chen, R. Huang, L. Zhang, Nano- CaCO_3 /polypropylene composites made with ultra-high-speed mixer, *J. Mater. Sci. Lett.* 21 (2002) 985–986.
- [16] J.H. Han, K.W. Cho, K.H. Lee, H. Kim, Porous graphite matrix for chemical heat pumps, *Carbon* 36 (1998) 1801–1810.
- [17] A. Celzard, S. Schneider, J.F. Maréché, Densification of expanded graphite, *Carbon* 40 (2002) 2185–2191.
- [18] A. Celzard, J.F. Maréché, G. Furdin, Surface area of compressed expanded graphite, *Carbon* 40 (2002) 2713–2718.
- [19] L. Shi, Z.M. Li, B.H. Xie, J.H. Wang, C.R. Tian, M.B. Yang, Flame retardancy of different-sized expandable graphite particles for high-density rigid polyurethane foam, *Polym. Int.* 55 (2006) 862–871.