

Research Article

Preparation of Graphene Nanoplatelets by Thermal Shock Combined with Ball Milling Methods for Fabricating Flame-Retardant Polymers

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Graphene nanoplatelets were successfully prepared from graphite powder by simple and scalable thermal shock combined with ball milling methods. The formation of the graphene nanoplatelets were observed by field-emission scanning electron microscopes and Brunauer–Emmett–Teller methods with the much smaller number of layers and the considerable increase of specific surface area in comparison to the initial expanded graphite material. The other characterizations such as Fourier transform infrared spectroscopy and X-ray powder diffraction methods of graphene nanoplatelets showed unchanged structure. These graphene nanoplatelets were combined with aluminum trihydroxide and zinc borate to prepare flame-retardant polycarbonate plastic and chlorine-sulfonated polyethylene rubber. The prepared composites showed the improvement of flame resistance properties with V0 level according to the UL-94 test method, and the limiting oxygen index value was higher than 27.

1. Introduction

Graphene nanoplatelets (Gnps) and their derivatives are potential flame-retardant additives applied for preparation of flame-retardant polymers [1]. It can be combined with polymer matrix as a nanofiller for the case of plastic [1–4], rubber [5, 6], or coating agent for the case of fabric [7–9]. The flame resistance effect of Gnps depends mainly on their dispersity in polymer matrix. Beside the factor of compatibility between Gnps and polymers, the size and layer number of Gnps also play an important role. Gnps can be prepared by two main methods, the bottom-up and top-down methods [10, 11]. The bottom-up methods, such as chemical vapor deposition and epitaxial growth, are expensive and cannot meet the requirement of big quantitative production of Gnps. On the contrary, the top-down methods are expected to meet large-scale production of graphene with low cost. Graphite material can be cracked and exfoliated using a very useful mechanical method reported by Babak Alinejad et al. [10]. This method simply

used NaCl as an exfoliation agent because this salt is harder than graphite. The mixture of graphite powder and NaCl salt particles were grinded by using a planetary ball mill for 2–5 hours to crack graphite flakes to nanosized pieces. In this paper, we apply another simple method to produce Gnps material by using thermal shock combined with ball milling methods. An expanded graphite (EG) is firstly prepared from graphite powder. Next, a planetary ball milling machine is used for EG exfoliation to form Gnps. The ball milling of the EG instead of graphite powder is expected to improve the exfoliation effectiveness. Properties of the obtained Gnps are characterized by fourier transform infrared the spectroscopy (FTIR), X-ray powder diffraction (XRD), field-emission scanning electron microscope (FE-SEM), and Brunauer–Emmett–Teller (BET) methods. The prepared Gnps are used to fabricate the plastic and rubber flame-retardant materials. The obtained flame-retardant materials are measured the fire resistance property by UL-94 and limiting oxygen index (LOI) methods.

2. Materials and Methods

2.1. Chemicals. Graphite powder (<20 μm , synthetic, Sigma-Aldrich), hydrogen peroxide (H_2O_2 , AR, 30–32%, Xilong Scientific), sulfuric acid (H_2SO_4 , 98%, AR, Xilong Scientific), sodium chloride (NaCl, AR, 99.5%, Xilong Scientific), aluminum trihydroxide (AR, Xilong Scientific), zinc borate (99%, Kayseri, Turkey), polycarbonate plastic (Lotte Chemicals, Korea), and chlorine-sulfonated polyethylene rubber (CSM-3304, KunLun Co. Ltd, China) were used.

2.2. Gnps Preparation. Gnps were prepared from graphite powder via two steps. In the first step, graphite powder was undergone a thermal treatment. Typically, graphite powder was pretreated by being added to the mixture of H_2O_2 (30%): H_2SO_4 (98%) = 1 : 1.5 (v/v) at 20°C for 2 h. The solid was filtered and washed by DI water to have the pH = 7. The obtained solid was dried at 80°C for 24 h. This solid was thermal shocked by using a microwave at 800 W for 60 s. The solid was subjected to the pretreatment and the thermal shock once again by the same procedure described above to obtain EG sample. In the second step, the EG was grinded by using NaCl salt as discussed in [10]. 5 g EG sample was mixed with NaCl salt (EG : NaCl = 3 : 1 in molar ratio). A planetary ball milling machine (Pulverisette 5) with ball to powder weight ratio of 20 : 1 was used to grind the obtained mixture with a rotational speed of 350 rpm for 2 h in argon inert gas medium. NaCl salt was removed from the obtained powder by DI water using an ultrasonic bath. The final sample was centrifuged and dried at 80°C under vacuum to get the final sample.

2.3. Flame-Retardant Polymers Preparation. Gnps were used as nanofiller additive for flame-retardant polycarbonate (PC) plastic and chlorine-sulfonated polyethylene (CSPE) rubber preparation. Typically, a mixture of Gnps, conventional flame-retardant aluminum trihydroxide (ATH), and/or zinc borate (ZB) was melt-compounded with PC plastic or CSPE rubber in a Brabender closed mixing machine. PC plastic or CSPE rubber was melted in the first 4 min with a rotor speed of 50 rpm at 200°C (PC) and 85°C (CSPE). The above mixture with different percentage of Gnps, ATH, and/or ZB was then added to the compound with PC plastic or CSPE rubber for 10 min. The compounded sample was hot-pressed in a Brabender molding machine at 210°C (PC) and 95°C (CSPE) for 7 min to obtain the sample.

2.4. Materials Characterizations. The FTIR spectra were recorded using an IMPACT-410 (Nicolet, Germany) infrared spectrophotometer at room temperature in the range 4000–400 cm^{-1} on thin wafer of KBr in which 1% (w/w) of sample was dispersed. XRD diffraction patterns were recorded on a HUT-PCM-Bruker D8 Advance instrument diffractometer system equipped with Ni-filtered Cu Ka radiation (operating at 40 kV; 40 mA; wavelength $k = 0.154 \text{ nm}$). FE-SEM was carried out using a Jeol JSM-7500F instrument. Sample was dried, mounted on a thin plate, and coated by a thin

gold layer before recording. The BET method was measured by ASAP2010 equipment (Micrometrics-USA). The sample was treated in vacuum of 106 mmHg, at 120°C for 4 h and at 350°C for 9 h.

The fire resistance property of flame-retardant PC plastic and CSPE rubber was tested by the UL-94 method on Atlas Electric HVUL-94 flame test station and LOI analysis on a JF-3 instrument according to GB/T 10707-2008 standard.

3. Results and Discussion

3.1. Characterization of Gnps

3.1.1. FTIR and XRD Methods. The FTIR spectra of the graphite and GNPs samples are shown in Figures 1(a) and 1(b), respectively. Both FTIR spectra show the peaks at about 1635 cm^{-1} and 1450 cm^{-1} assigned to C=C skeletal band of aromatic domains [12] and the peak at 3430 cm^{-1} assigned to OH groups [13]. These OH groups may be corresponded to O–H stretching vibrations of adsorbed water molecules and structural OH groups which do not allow a distinction between C–OH and H_2O peaks. In the FTIR spectrum of Gnps sample, there are more peaks at 2975.09 cm^{-1} assigned to CH_2 (the symmetric and antisymmetric vibrations of methylene) [14] and peaks at 1089.48 and 1048.86 cm^{-1} assigned to OH stretching vibrations [15]. This result shows that by the pretreatment process using H_2O_2 and H_2SO_4 , more OH groups and CH_2 were formed. The intercalation of OH groups may help improve the ball milling effectiveness.

In addition, there is no considerable change between the XRD patterns of graphite and Gnps samples by using XRD method (Figure 2). There is a peak with high intensity at 2-theta of 26.4° assigned to the layer-by-layer structure of both graphite and Gnps samples [10, 12]. This result shows that by using thermal shock and ball milling, the Gnps sample was formed without structural transformation in comparison to the graphite sample.

3.1.2. FE-SEM and BET Methods. The FE-SEM images (Figure 3) show clearly that the structure of Gnps is layer-by-layer assembly. This structure is similar to the initial graphite structure. However, in comparison to the FE-SEM image of the EG sample (Figure 3(a)), the FE-SEM of the Gnps sample (Figures 3(b)–3(d)) shows clearly the exfoliation of EG to obtain Gnps with a monolayer or a few layers in its morphology.

The exfoliation of EG to Gnps is further demonstrated with the increase of specific surface area by BET result that is shown in Figure 4 and Table 1. The similarity of nitrogen adsorption/desorption curves shows the unchanged structure between EG and Gnps samples (Figure 4). The data in Table 1 show that the EG sample obtained by thermal shock has a BET specific surface area of 5.33 m^2/g . After the ball milling process of EG mixed with NaCl salt, BET specific surface area of the obtained GNPs is increased to 638.11 m^2/g (Table 1). It is 130 times higher in comparison to BET specific surface area of the EG sample and also higher than the reported result (524.4 m^2/g) that used virgin graphite powder for the ball milling [10]. In addition, the pore volume of Gnps sample is decreased to 0.02 cm^3/g from 0.04 cm^3/g (the pore

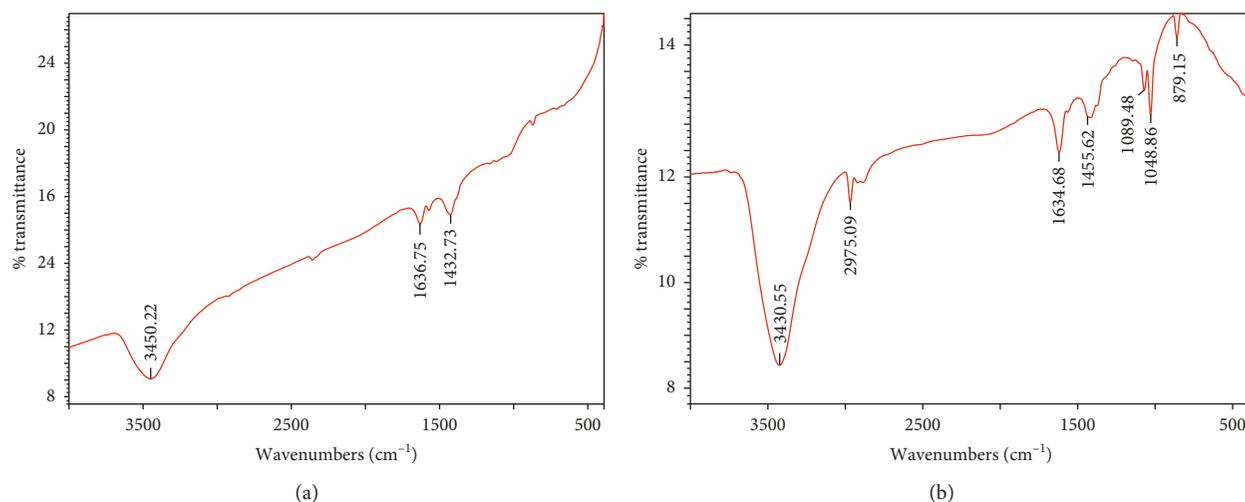


FIGURE 1: FTIR spectra. (a) Graphite sample; (b) Gnps sample.

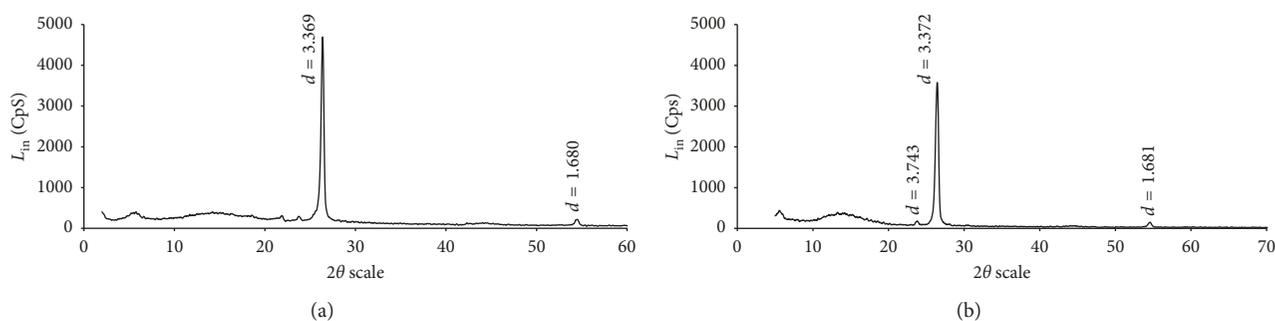


FIGURE 2: XRD patterns. (a) Graphite sample; (b) Gnps sample.

volume of EG sample before the ball milling). This result is in agreement with the FE-SEM result that showed the exfoliation of EG to obtain Gnps material with a few layers.

Gnps have been well known as an effective nanofiller flame-retardant additive with only small amount compounded with polymers (<5 wt.%) [1]. However, to improve the self-extinguishing property of polymers, it is better to use Gnps combined with conventional flame retardants. In this study, the ATH and ZB conventional flame retardants were applied. The compositions of the composite samples are shown in Table 2.

The results in Table 2 show that by using the same content (5 wt.%) of graphite and Gnps as nanofillers to PC material, their flame resistance abilities are UL-94 V2 and V1 levels, respectively. This result shows that the Gnps material is better flame retardant than the graphite material. However, at high content of Gnps, it may result in the agglomeration of Gnps and the decrease of the flame resistance ability. The experiments of decreasing Gnps content have been performed. The observed results show that by decreasing Gnps content to 1.5 and 1.0 wt.%, the UL-94 V0 level is attained. The lower content (0.5 wt.%) of Gnps did not show the good result (UL-94 V2 level).

The self-extinguishing property was improved by combining the Gnps material with the ATH and ZB

conventional flame retardants. The ATH and ZB conventional flame retardants were measured to get the UL-94 V1 level of the PC-ATH and PC-ZB composites. The idea is that by adding more Gnps combined with the PC-ATH and/or PC-ZB composites, the Gnps can help improving PC flame resistance ability to the UL-94 V0 level. The obtained results reach the expectation. By adding Gnps 1.5 wt.% combined with ATH (25 wt.%) or ZB (15 wt.%) to PC, the obtained composites attain the UL-94 V0 level. However, the LOIs of these composite samples are lower than 27% (PC-Gnps-ATH: 22.9%; PC-Gnps-ZB: 24.0%). The LOI of 27% is needed for a flame-retardant composite to become a self-extinguishing material [16]. Thus, the LOI of the composite sample was improved by adding Gnps, ATH, and ZB with the measured optimal contents (1.5 wt.% Gnps, 25 wt.% ATH, and 15 wt.% ZB) to the PC plastic. The result shows that the obtained composite sample (PC-Gnps-ATH-ZB) reaches the UL-94 V0 level and LOI of 29.7%. This shows the role of Gnps to increase the LOI of this sample. Besides the fire resistance measurement, the mechanical property of the samples was also evaluated. The result indicates that the flame-retardant PC (PC-Gnps-ATH-ZB sample) has higher tensile strength (39.5 MPa) in comparison to the virgin PC plastic sample (34 MPa). This shows that adding Gnps can enhance the mechanical property of PC plastic [1].

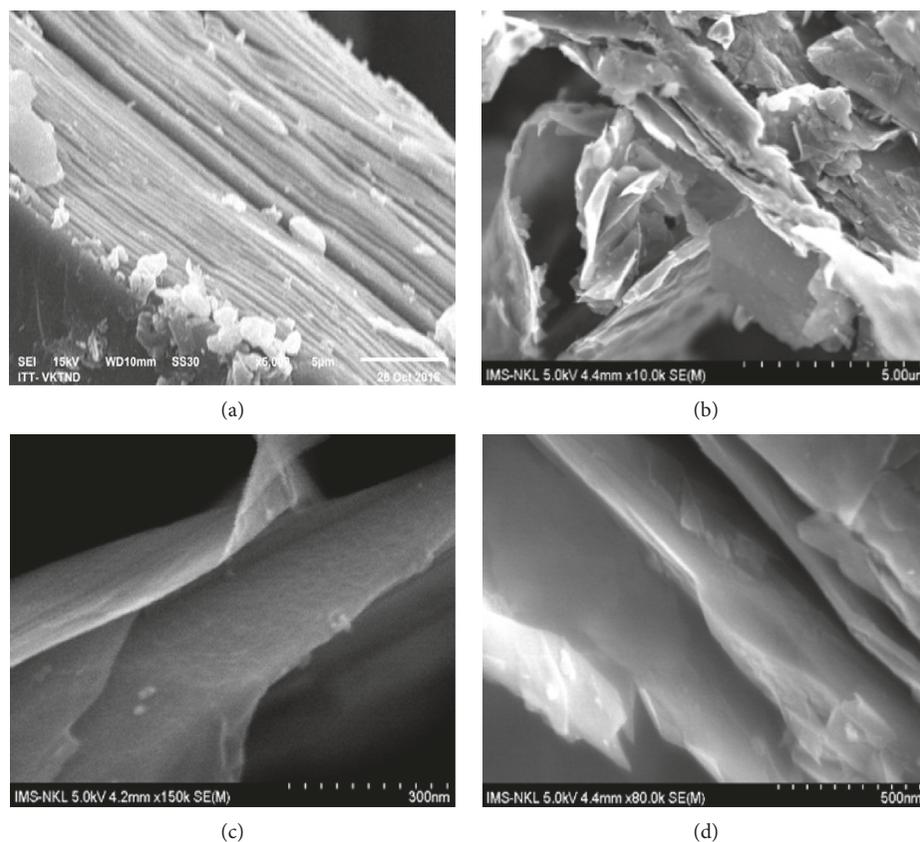


FIGURE 3: FE-SEM images. (a) EG sample; (b–d) Gnps sample.

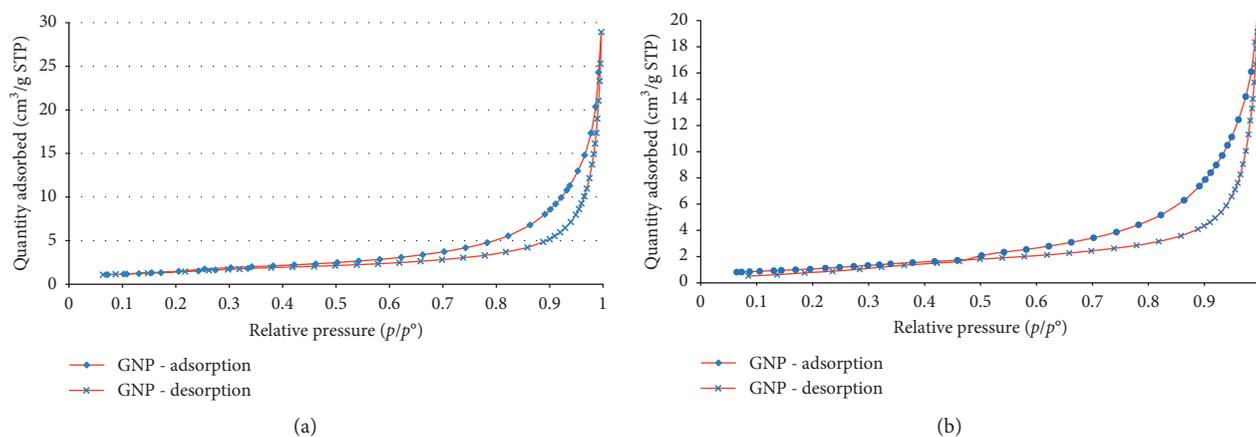


FIGURE 4: Nitrogen adsorption/desorption curves. (a) EG sample; (b) Gnps sample.

TABLE 1: BET data.

Sample	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
EG	5.16	0.04	26.58
Gnps	638.11	0.02	27.36

Fire resistance test result of prepared flame-retardant polymers.

Another CSPE rubber polymer was used to illustrate the flame resistance effectiveness of Gnps. ZB has been well known as flame-retardant filler for rubber [17, 18]. The contents

of Gnps (1.0 wt.%) and ZB (15 wt.%) were measured to add to CSPE rubber. The result in Table 2 shows that both the CSPE-Gnps and CSPE-ZB composites attain the UL-94 V1 level. In addition, by combining Gnps and ZB with the contents mentioned above, the CSPE-Gnps-ZB composite (84.0-1.0-15.0 wt.%) sample attains the UL-94 V0 level. However, the LOI of this composite sample attains only 23.1%. This LOI has been improved by increasing Gnps content up to 1.5 wt.%, and the LOI of the CSPE-Gnps-ZB composite (83.5-1.5-15.0 wt.%) reaches the value of 28.6%. This result once again shows that Gnps can be used very effectively as flame-

TABLE 2: Effectiveness of Gnps in combination with the ATH and ZB conventional flame retardants.

Polymer	Filler	Content (wt.%)	UL-94 test	LOI (%)	Tensile strength (MPa)
PC	—	0.0	V2	21.1	34.0
	Graphite	5.0	V2	—	—
		5.0	V1	—	—
		2.0	V1	—	—
	Gnps	1.5	V0	—	—
		1.0	V0	—	—
		0.5	V2	—	—
		25.0	V1	—	—
	ATH	20.0	V2	—	—
		15.0	V2	—	—
		15.0	V1	—	—
	ZB	15.0	V1	—	—
		10.0	V2	—	—
	Gnps-ATH	1.5–25.0	V0	22.9	—
	Gnps-ZB	1.5–15.0	V0	24.0	—
Gnps-ATH-ZB	1.5–25.0–15.0	V0	29.7	39.5	
CSPE	—	0.0	V2	22.1	—
	Gnps	1.0	V1	—	—
	ZB	15.0	V1	—	—
	Gnps-ZB	1.0–15.0	V0	23.1	—
1.5–15.0		V0	28.6	—	

retardant additive, especially for increasing the self-extinguishing property of polymer composite by combining with conventional flame retardants.

4. Conclusions

The Gnps material was successfully prepared with the simple and scalable method of thermal shock combined with ball milling. The characterization methods (FTIR, XRD, FE-SEM, and BET) showed that the initial graphite material was exfoliated to obtain the Gnps material with few layer numbers and unchanged structure. The obtained Gnps material was applied as flame retardant for PC plastic and CSPE rubber. The results obtained by UL-94 and LOI measurement methods showed that by combining the Gnps material with ATH and ZB with suitable content, the PC-Gnps-ATH-ZB and CSPE-Gnps-ZB composite materials can be prepared with highest fire resistance properties (UL-94 V0 level and LOI is higher than 27%). The results also showed that Gnps have important role in improving the LOI of composite material with small added amount (1.5 wt.%).

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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