

# Comparative Study on the Exfoliated Expanded Graphite Nanosheet-PES Composites Prepared via Different Compounding Method

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**ABSTRACT:** Composites made of polyethersulfone (PES) reinforced with exfoliated graphite nanoplatelets are fabricated by melt mixing, polymer solution, and coating. Coating is an efficient compounding method emphasized in this research, where expanded graphite (EG) and PES powder are premixed in isopropyl alcohol using sonication to disperse the EG by coating individual PES powder particles. The microstructure and property of EG/PES composites were investigated by X-ray diffraction, scanning electron microscope, thermal gravimetric analysis, differential scanning calorimetric, and electronic tensile tester. The electrical conductivity was confirmed using electrochemical tester. It is found that the coating method is more effective than the polymer solution and directly melt mixing methods widely used, in terms of increasing

the electrical conductivity and lowering the percolation threshold of thermoplastic composites, and enhancing the probability that the large platelet morphology of EG can be preserved in the final composite. The research reported here provides an understanding on how the compounding method used during the fabrication of composites is important to achieving the optimal mechanical properties, thermal properties, electrical conductivity, and percolation threshold. This method should have wide applicability to all thermoplastic matrix composite systems. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3547–3557, 2012

**Key words:** polyethersulfone; expanded graphite; composites; coating; mechanical properties; electrical properties

## INTRODUCTION

Composites of polymers reinforced with conductive fillers of nanometer size, in at least one dimension, have generated enormous interest for its possible implementation in a myriad of devices. These include light electromagnetic shielding, corrosion resistant coatings, and other functional applications.<sup>1–3</sup> The most common conductive reinforcements used are natural graphite flake, carbon black, carbon nanotubes, and metal powders. Among these, natural graphite may be preferred over other conventional nanofillers owing to high surface area, aspect ratio, thermal conductivity, and electrical conductivity (about  $10^4$  S/cm at ambient temperature).<sup>4</sup> In most cases, relatively large quantities of graphite were needed to reach a critical percolation value. However, large quantity of graphite could lead to materials

poor mechanical properties and high density of composite. Therefore, it is still a challenging work to obtain polymeric composites with superior properties with a quite low filler addition, in which processing methods in composites fabrication play an important role.<sup>2</sup>

Graphite shows layered crystal structure and the *d*-spacing between the carbon layers is 0.335 nm. As the van der Waals forces within the carbon layers are relatively weak, it is possible for a wide range of atoms, molecules, and ions to intercalate between graphite layers to form the graphite intercalation compounds (GICs). Expanded graphite (EG) is generally produced by subjecting H<sub>2</sub>SO<sub>4</sub>-GICs to rapid thermal treatment. EG was developed and proposed by Aylsworth<sup>5</sup> as reinforcement of polymers, phenolic resins in particular, in 1910s. The incorporation of intercalated graphite into an organic by using conventional processing techniques, such as extrusion, lay-up, injection molding, and pressing, was proposed by Lincoln and Claude<sup>6</sup> in 1980s. Since then, research has been conducted on exfoliated graphite reinforced polymers using graphite particles of various dimensions and a wide range of polymeric composites, such as EG/PMMA,<sup>7</sup> EG/PA-6,<sup>8</sup> EG/PE,<sup>9</sup>

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EG/Nylon 6,<sup>10</sup> EG/polystyrene (PS),<sup>11,12</sup> EG/aromatic polydisulfide,<sup>13</sup> and EG/poly(phenylene sulfide) (PPS),<sup>14</sup> have been extensively reported. In all the cases, the objective is to find the optimum processing method that will utilize graphite's superior properties and lead to composites with the desired properties. The processing methods used for graphite-polymer composites are similar to the ones used for clays as both materials have a layered structure. However, because they are chemically different, some modifications are required. Once the graphite is exfoliated (*ex situ* process), then the composites can be made by: (i) direct mixing, often used in case of low viscosity thermoset matrices.<sup>15</sup> (ii) Melt compounding, a method used mainly with polyolefins, i.e., exfoliated graphite/high-density polyethylene (HDPE)<sup>16</sup> and graphite/PS using a Brabender mixer,<sup>17</sup> graphite/nylon 6,6/ and graphite/polycarbonate using a twin screw extruder.<sup>18</sup> (iii) Solution intercalation, a method utilizing a solvent to dissolve the polymer and disperse the graphite. The solvent is evaporated once the mixing is completed. Composites made by the solution approach are graphite/poly(methyl methacrylate) (PMMA) using chloroform as solvent,<sup>19,20</sup> and graphite/maleic anhydride-grafted polypropylene in the presence of xylene.<sup>21</sup> This processing method results in composites with higher electrical conductivity and lower percolation threshold compared to composites made from the exactly same materials using the melt-mixing technique.<sup>21</sup> (iv) *In situ* polymerization, where the monomer is polymerized in the presence of monomer, initiator, and graphite nanosheets.<sup>22</sup> (v) Electrospinning of nanoscale fibers using polymer solution and melts at ambient conditions. If the graphite is not exfoliated before fabricating the composite, then an *in situ* exfoliation process can be used such as: (vi) polymerization filling technique, where *in situ* polymerization occurs in the presence of initiator-intercalated graphite,<sup>23</sup> it is found that graphite/polymer composites fabricated by this method have better properties compared to composites made by melt mixing method.

In summary, composites made by *in situ* processing have better mechanical properties compared to composites made by melt-mixing or other *ex situ* fabrication method due to better dispersion, prevention of agglomeration, and stronger interactions between the reinforcement and the polymer. *In-situ* exfoliation can also be achieved during melt mixing; however, since the temperature required for exfoliation is  $\sim 230^{\circ}\text{C}$ , only polymers that can be processed at high temperatures without being degraded can be used for *in situ* fabrication of composites.

Polyethersulfone (PES) is a typical engineering polymer that shows exceptional mechanical properties and good dimensional stability. Its high deflection temperature of about  $450^{\circ}\text{C}$ , flame retardancy,

and resistance to any solvents below  $200^{\circ}\text{C}$  endow it many special applications, such as electronics, automotive industry, and heat detector. Although much effort has been devoted to improve the mechanical and thermal properties of PES,<sup>24</sup> little information is available for the PES-based conductive materials. In this regard, EG/PES composites were prepared in this work via different processing methods. The focus of this research is to explore how the compounding method used to fabricate EG/PES composites alter their properties. The composites are fabricated by melt mixing or polymer solution method followed by compression or injection molding and their flexural properties, thermal properties, electrical conductivity, and percolation threshold are determined. A new compounding method, the coating of PES with EG by sonication in presence of isopropyl alcohol (IPA), is proposed as an alternative to the traditional melt-mixing method that results in poor dispersion and agglomeration of the reinforcements and to the commonly used polymer solution method that is used to improve dispersion and obtain electrically conductive polymer composites with low percolation threshold.

## EXPERIMENTAL

### Materials

PES was commercial product (injection grade), supplied from BASF (Germany). The melt flow index of the PES is 14 g/10 min measured according to Chinese GB/T 3682-2000 standard ( $260^{\circ}\text{C}$ , 2.16 kg, 1.0 mm). Expandable graphite with an expandable volume of 200 mL/g, was supplied by Qingdao Tianhe Graphite (Qingdao China).

### Sample preparation

EG was obtained by heating the expandable graphite in a muffle furnace at  $950^{\circ}\text{C}$  for 30 s. The detail process has been described in our previous work.<sup>25</sup> The expanded graphite was immersed in a 95% of aqueous alcohol solution and subjected to powdering in an ultrasonic bath for 2 h. The resulting suspension was then filtered and dried in the vacuum oven at  $60^{\circ}\text{C}$  for 12 h to obtain graphite nanosheets. PES was dried under vacuum at  $150^{\circ}\text{C}$  for 24 h before compounding.

### Processing of EG/PES composites

Three compounding methods were used to fabricate the EG/PES composites. Melt mixing, which is simple and compatible with existing polymer processing techniques such as extrusion and injection or compression molding (CM); using a twin screw extruder at  $250^{\circ}\text{C}$  with a screw speed of 100 r/min.

The second compounding method uses large amounts of solvents such as *N,N*-dimethylacetamide (DMAc) and high temperatures that are neither practical nor safe. However, to understand the effect of fabrication method on the electrical conductivity and percolation threshold of EG/PES composites a modified version of the solution method proposed by Shen et al.<sup>21</sup> was used. EG was dispersed in DMAc using sonication for 3 h, and the PES was dissolved in refluxing DMAc at 120°C for 1 h. The graphite suspension was added dropwise to the PES solution and kept refluxing for another 2 h. When the temperature dropped to about 70°C the solution precipitated by addition of acetone, filtered, and dried in vacuum oven. The resulting composite powder was used for compression or melt mixing or injection molding.

Coating of PES with graphite in presence of IPA is an efficient compounding method proposed in the work. The EG is first dispersed in IPA by sonication for 3 h at room temperature, then PES powder is added to above solution, and sonication is continued for 1 h. Finally, the solvent is evaporated at 80°C resulting in complete coverage of the powder particles with the EG. Alternatively, the IPA can be recycled by using filtration and reused. Thus, this new premixing method can be environmental friendly and more cost and time effective compared to the solution approach. The main advantage of this method is that sonication breaks down the EG agglomerates and the thick EG-IPA solution covers the PES particles very efficiently resulting in a homogeneous EG-coated PES powder that can be used for compression or injection molding. Micrographs of the uncompressed neat polymer powder, EG-coated PES at 2 wt % are shown in Figure 1(a–c), respectively. It clearly shows that EG has been exfoliated into thin sheets and coated homogeneously on the PES surface.

Once the compounding was completed, the composites standard specimens were made by melt mixing or CM or injection molding for testing.

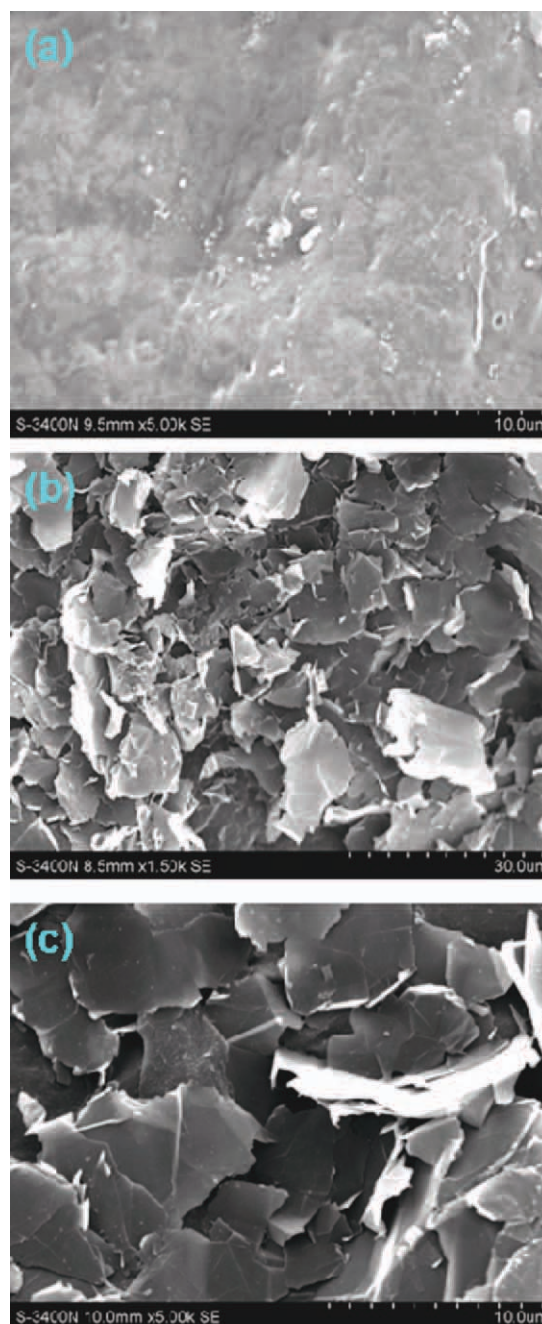
## Characterization

### Microscopy and structure

Morphologies of EG and EG/PES composites were examined using a JEOL JSM-820 scanning electron microscope (SEM). The fracture surfaces were gold coated before SEM investigation to avoid charging and were examined at 15 kV accelerating voltage.

### X-ray diffraction

X-Ray diffraction (XRD) test was performed on composites to evaluate the structure, and/or the degree of expansion and exfoliation of graphite particles in the composites. XRD was carried out on a Rigaku

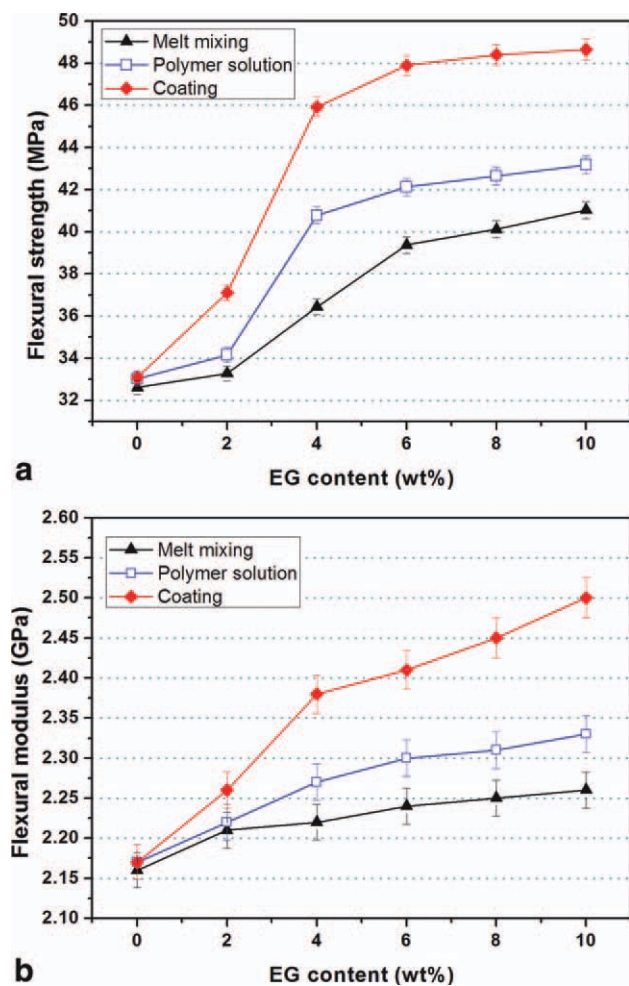


**Figure 1** SEM images of (a) PES particle (scale bar 10  $\mu$ m), (b) 6 wt % EG-coated PES (scale bar 30  $\mu$ m), and (c) 6 wt % EG-coated PES (scale bar 10  $\mu$ m). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

D/max-1200X diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 0.15406$  nm) with a scanning speed of 1.2°/min and operating at 40 kV and 30 mA.

### Thermogravimetric analysis

The thermal stability of materials was measured by thermogravimetric analysis (TGA) on a Perkin–Elmer TGA-7 instrument. The samples were gradually



**Figure 2** Effect of compounding method and EG content on the flexural strength (a) and flexural modulus (b) of EG/PES composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

heated at a rate of 20°C/min from 30 to 700°C under the N<sub>2</sub> flow with a flow rate of 20 mL/min.

#### Differential scanning calorimetric analysis

Differential scanning calorimetric (DSC) analysis was carried out on NETZSCH DSC-200PC under N<sub>2</sub> atmosphere. Samples were heated from room temperature to 320°C at a rate of 20°C/min and held at that temperature for 10 min to eliminate the heat history. The samples were then cooled to 50°C at a rate of 100°C/min. After keeping at 50°C for 5 min, samples were heated to 320°C at a rate of 20°C/min again. The thermal parameters were obtained from the cooling and reheating scans for the crystallization and melting behavior of PES composites.

#### Tensile test

Tensile properties were tested on an INSTRON3365 electronic tensile tester with a computer controlling

system. The rate of crosshead motion was 10 mm/min at 20°C. Five specimens of each composition were tested, and the average values were reported.

#### Electrical conductivity

The conductivity ( $\sigma$ ) of PES and composites were measured by electrochemical workstation (Solartron 1255B) at room temperature when the  $\sigma$  was less than 10<sup>-3</sup> S/cm. The circular specimens with a diameter of 10 mm and thickness of 2 mm were placed between two gold test electrodes, and then the resistance was measured. Removing the specimen, the resistance of test cell was measured again under the same condition to obtain the reference resistance. The resistance of the specimen was obtained by subtracting the reference resistance. The resistivity or conductivity of the specimen was determined by the following equation:

$$\rho = R_s \frac{A}{L} = \frac{(R_T - R_B)A}{L} \quad (1)$$

$$\sigma = \frac{1}{\rho} \quad (2)$$

where  $\rho$ ,  $\sigma$ ,  $A$ , and  $L$  are the resistivity, the conductivity, the cross-sectional area, and the thickness of the specimen, respectively.  $R_T$ ,  $R_B$ , and  $R_S$  are total resistance, reference resistance, and specimen's resistance, respectively. When  $\sigma$  of the specimen was greater than 10<sup>-3</sup> S/cm, it was tested by SDY-4 four-probe instrument (Guangzhou, China).

## RESULTS AND DISCUSSION

### Flexural properties of EG/PES composites

Figure 2(a,b) shows the comparison of flexural strength and modulus of EG/PES composites processed by (i) polymer solution mixing followed by melt mixing and injection molding, (ii) melt mixing and injection molding, and (iii) coating followed by melt mixing and injection molding. It can be seen that the flexural strength of pure PES is about 33 MPa and that the flexural strength of EG/PES composites increased with increasing EG content. The critical point at which the flexural strength began to sharply increase was about 2–4 wt % EG content. EG/PES composites (6 wt % of EG) prepared by melt-mixing method shows the best value of 39.4 Mpa and provides only ~19.4% increase in flexural strength, whereas the solution mixing and coating methods show the best value of 42.1 and 47.9 Mpa when 6 wt % EG was incorporated, which shows increase of 27.6 and 45.2%, respectively, over the pure PES. The maximum improvement by the coating method can be correlated to the improved

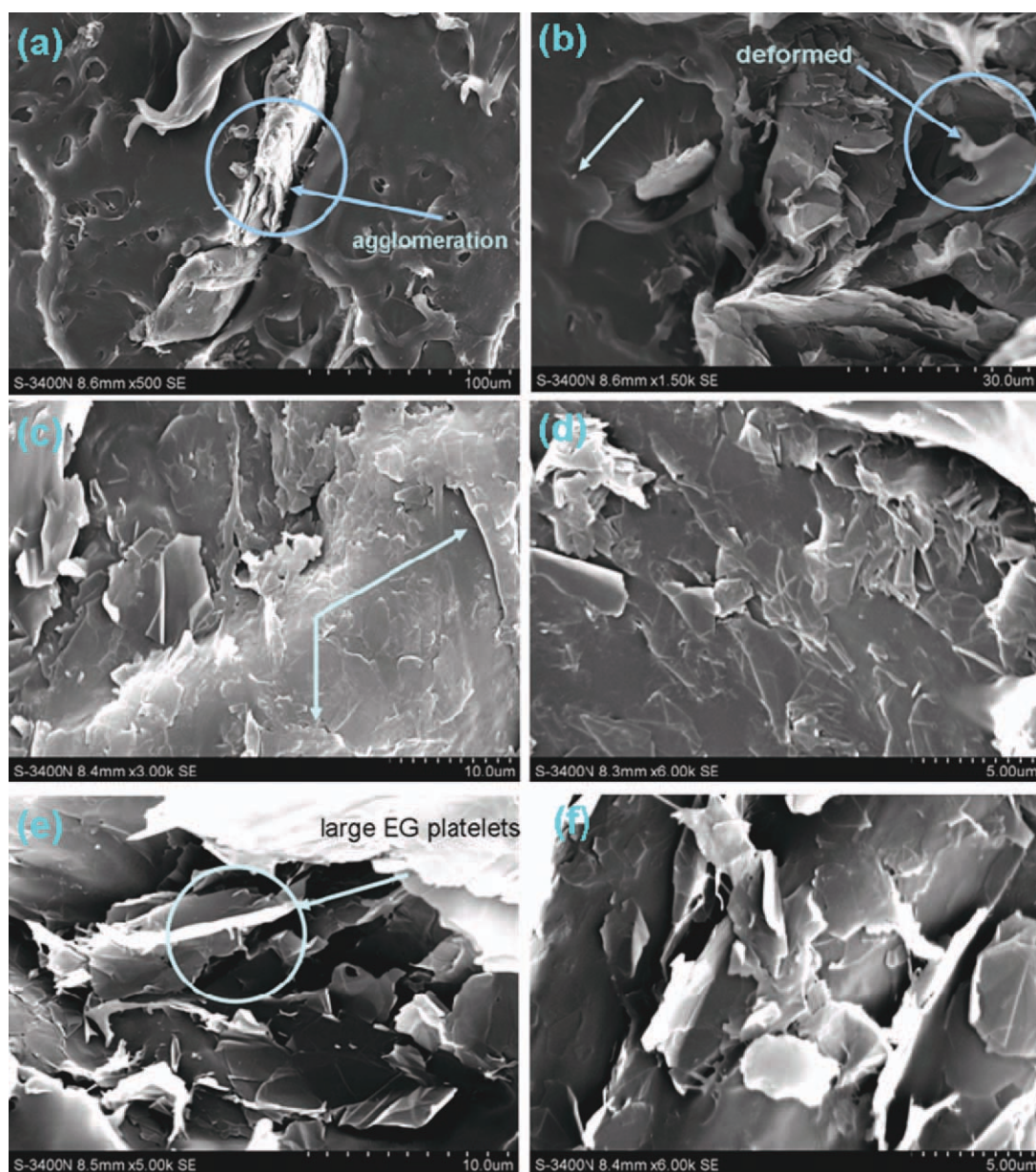
dispersion conditions due to the extra coating step. Flexural modulus of EG/PES composites [Fig. 2(b)] shows the similar trend to Figure 2(a). It can be seen that the flexural modulus of EG/PES composites prepared by coating method shows the highest value among the three routes reported. The flexural modulus of EG/PES composites increased with the increasing of EG content. The critical point at which the flexural modulus began to increase also was about 4 wt % EG content. It should be noted that the critical point for flexural strength and modulus to increase was about 2–4 wt % EG content. Perhaps, it corresponded to the point where the conductive network was completely formed, which will be confirmed and discussed later. This indicated that the variation trend of mechanical properties was correlated with the threshold filler concentrations. Similar phenomenon has been reported in the literature.<sup>2,26</sup> In summary, the flexural strength and modulus of EG/PES composites prepared by different methods were higher than that of pure PES within the experimental range of the EG content. Presumably, this is due to the well dispersion of EG within PES matrix, indicating a favorable reinforcement effect of EG to PES. The EG/PES composites prepared by coating method exhibited better flexural strength and modulus than other two methods because coating method can promote a better dispersion of EG nanosheets in polymer matrix.

### Morphology of EG/PES composites

The improvement in the physicochemical properties of the composites depends on the distribution of graphene layers in the polymer matrix as well as interfacial bonding between the graphene layers and polymer matrix. The morphology structure of polymer composites is a very important characteristic because it ultimately determines many properties of the polymer composites, such as thermal stability and mechanical properties. The fracture surfaces examined in this work were obtained during flexural testing. Agglomerates of EG are present in the samples made by melt mixing as shown by the arrows in Figure 3(a,b). In addition, the SEM study revealed that there are two distinguished types of morphology in the melt-mixed samples: (i) areas with big EG agglomerates, shown in Figure 3(a), and large flat graphite platelets buckled and deformed that are shown in Figure 3(b) and (ii) areas that are away from the specimen edges where no EG or only very small graphite particles can be seen on the surface as indicated by the arrows in Figure 3(b). Based on Figure 3(a,b) which are typical SEM images of melt mixed EG/PES morphology, it is concluded that during melt mixing, there is not enough shear to break down the EG agglomerates and homogene-

ously disperse the graphite platelets. Further analysis from Figure 3(c,d) show that polymer solution also afford dispersion of EG in comparison of melt-mixed composites, although not fine as coating one. Coating the PES powder with EG breaks the graphite agglomerates and results in a well-dispersed system free of particle agglomerations with the graphite platelets being well embedded in the PES matrix as shown by the arrows in Figure 3(e,f). It should be pointed out that coating enhances the probability that the large platelet morphology of EG can be preserved in the final composite, which will facilitate the formation of conductive network efficiently. The difference in EG dispersion in the preparation process may result in the various properties of EG/PES composites.

There are two complimentary techniques to characterize the structure of composites: scanning electron microscopy (SEM), and XRD, where the former shows the morphological structure of composites, whereas the later reveals the change of *d*-spacing of graphite gallery. Figure 4(a,b) shows the XRD patterns of samples. According to Figure 4(a), EG shows a (002) diffraction peak at  $2\theta = 26.5^\circ$ , which is corresponding to the *d*-spacing of 0.55 nm. While pure PES shows a group peaks in the range of  $2\theta = 18\text{--}22^\circ$ , indicating PES is semicrystal polymer. On compounding with PES, the characteristic diffraction peak of graphite shifts to low angle. For EG/PES composite prepared by polymer solution, it is observed at about  $2\theta = 26.4^\circ$ , corresponding to the interlayer spacing of 0.858 nm, whereas that of melt mixing and coating samples show a lower diffraction angle at  $2\theta = 26.34^\circ$  and  $2\theta = 26.31^\circ$ , and the corresponding *d*-value is increased to 1.17 and 1.71 nm, respectively. That is, the intercalation of PES chains increase the *d*<sub>002</sub> spacing of EG for about 1.2 nm for coating method. This result is ascribed to the intercalation of PES macromolecular chains into graphene layers, resulting in the enlargement of interlayer distance of EG. There is no obvious change for diffraction peak of PES in the range of  $2\theta = 18\text{--}22^\circ$  in the process of compounding, indicating that the EG addition and preparation method have little effects on crystal structure of PES. Further analysis for EG/PES composites with different EG contents prepared using coating method showed that the diffraction peaks of EG (002) also shifts to lower angle, accompanied by increasing in *d*-value [Fig. 4(b)]. This indicates that coating improve effectively the intercalation of PES into EG layers and also enhanced the dispersibility of EG nanosheets, which will be beneficial to improve the mechanical properties of composites. This conclusion is consistent with the former experiments results. The effects of enhancement in dispersibility on conductivity of composites will be further confirmed later.

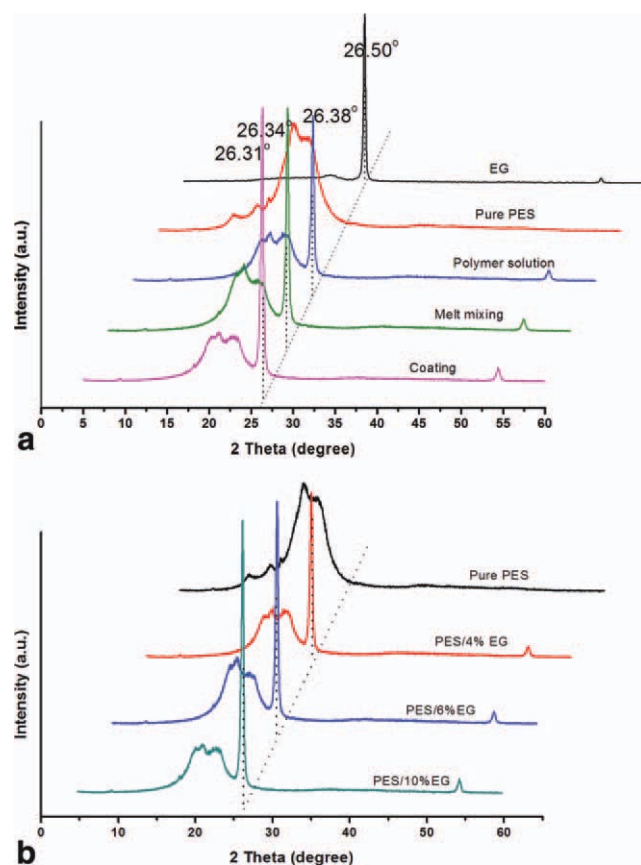


**Figure 3** SEM of fracture surface of 6 wt % EG/PES composites made by melt mixing: (a) and (b) (scale bar: 100 and 30  $\mu\text{m}$ , respectively), made by solution: (c) and (d) (scale bar: 10 and 5  $\mu\text{m}$ , respectively), and made by coating: (e) and (f) (scale bar: 10 and 5  $\mu\text{m}$ , respectively). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Thermal property of EG/PES composites

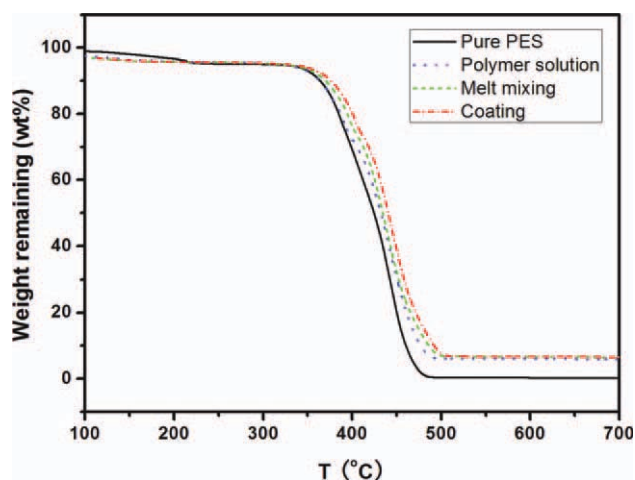
The effect of the three compounding methods: (i) melt mixing, (ii) polymer solution, and (iii) coating the PES powder with EG, on the thermal properties of EG/PES composites are shown in Figure 5. The thermal degradation parameters such as  $T_{\text{max}}$  (presents the temperature at which the maximum rate of degradation occurs) and  $T_{-5\%}$  (presents the onset temperature of thermal degradation when 5% weight lost) are listed in Table I. The weight loss curves (TGA curve) of filled and unfilled PES showed that degradation occurs in one step from

350 to 550°C. It is evident that the addition of EG can notably increase the thermal stability of PES. The  $T_{\text{max}}$  of the composites increased with increasing EG content. For example, the  $T_{\text{max}}$  of 6 wt % EG/PES composite prepared via polymer solution shows 12.2°C higher than that of the pure PES. The  $T_{\text{max}}$  of 6 wt % EG/PES composite is 14°C higher than that of the pure PES via melt mixing, whereas the  $T_{\text{max}}$  of 6 wt % EG/PES composite is 18°C higher than that of the pure PES via coating. The enhancement of thermal stability of PES can be ascribed to better thermal shielding effect of EG on the PES



**Figure 4** XRD patterns of (a) 6 wt % EG/PES composites prepared via different methods and (b) coating processed EG/PES composites with different EG content. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

matrix.<sup>2</sup> EG is believed to offer protection to the underlying PES from degradation process by acting as a physical barrier that limits the heat and mass transfer between the gas and condensed phase and thereby delaying degradation of PES. Moreover, the EG/PES composites prepared by coating shows higher thermal stability compared with polymer solution and melt mixing methods. Further analysis from Figure 5 and Table I, the EG/PES composites prepared by melt-mixing methods shows higher thermal stability compared with polymer solution. It seems that this result is not consistent with the mechanical properties and SEM observation. However, it should be noted that there are some factors in influence the properties (mechanical and thermal



**Figure 5** TGA curves of 6 wt % EG/PES composites prepared via different methods. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

properties) of polymer/fillers composites, including the dispersion of fillers, the interactions between fillers and polymer matrix, sample choosing and testing process, etc.

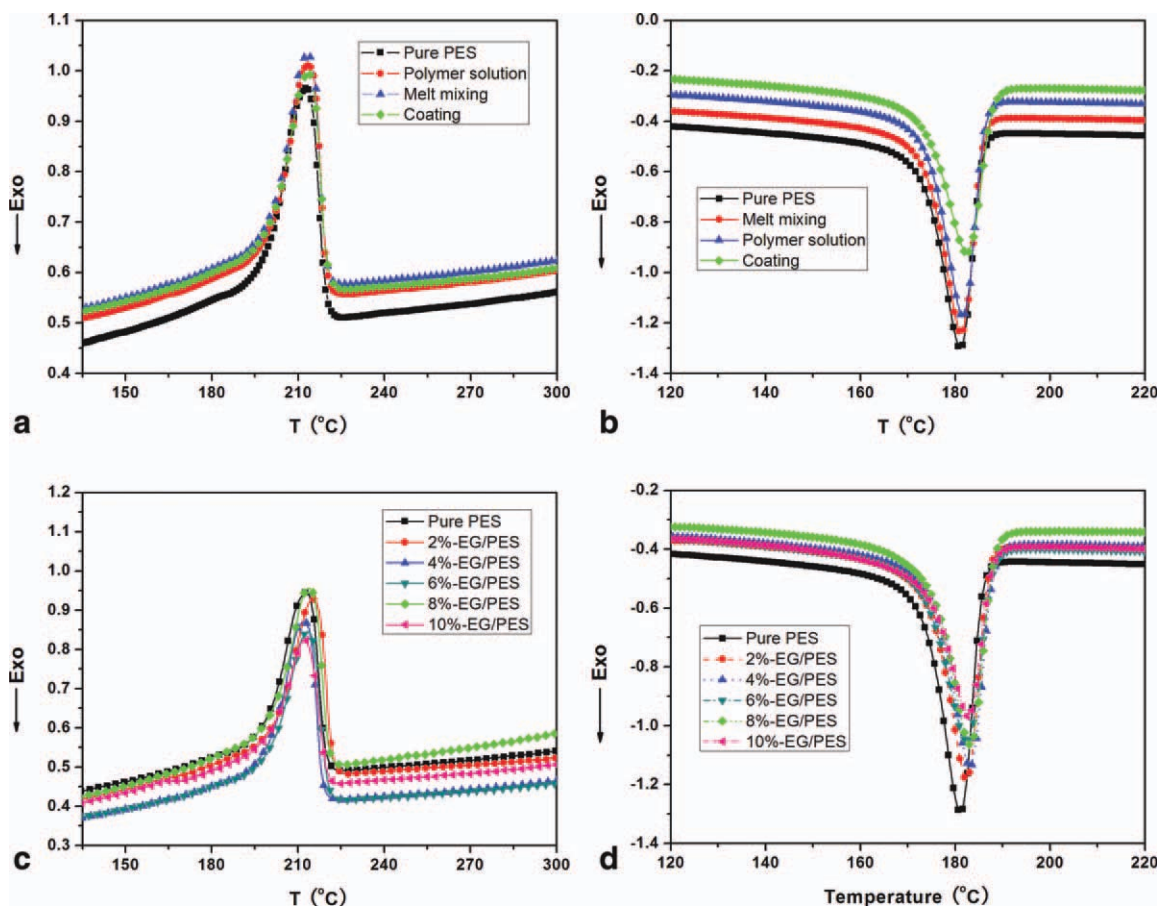
### Crystallization and melting behaviors of EG/PES composites

Figure 6 shows the comparison of DSC traces of EG/PES composites processed via different techniques [Fig. 6(a,b)] and with different EG content [Fig. 6(c,d)]. The crystallization and melting parameters determined are summarized in Tables II and III. From Figure 6(a), it can be observed that in the main melting region (200–250°C) of PES, there is only one melting peak ( $T_m$ ), at about 222°C, corresponding to the melting events of PES crystals. The  $T_m$  value increased with increasing EG concentration. From Figure 6(b), it can be clearly seen that only one exothermic peak is observed at about 180°C for all samples, indicating that crystal is formed in the cooling run. These results are well agreed with the XRD observations presented in Figure 3.

Further analysis from Tables II and III, the peak temperature of crystallization ( $T_{cp}$ ) and the peak temperature of melting ( $T_{mp}$ ) of pure PES is 181.1 and 213.0°C, respectively. Coating approach provides  $\sim 1.3^\circ\text{C}$  increase in  $T_{cp}$  for 6 wt % of EG,

**TABLE I**  
TGA Results for EG/PES Prepared via Different Methods and with Different EG Contents

EG content	Polymer solution						Melt mixing						Coating					
	0	2	4	6	8	10	0	2	4	6	8	10	0	2	4	6	8	10
$T_{-5\%}(\text{°C})$	306.2	311.3	317.0	319.6	323.4	325.4	305.2	309.8	312.9	319.6	323.4	327.4	305.7	315.8	322.9	309.6	331.4	328.4
$T_{\text{max}}(\text{°C})$	428.9	433.1	436.4	441.1	445.3	447.5	428.6	433.7	440.8	442.6	444.2	449.7	428.8	439.9	446.0	446.8	448.1	451.0



**Figure 6** DSC curves of: (a) heating run and (b) cooling run of 6 wt % EG/PES composites made via different methods. (c) Heating run and (d) cooling run of coating processed EG/PES composites with different EG contents. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

whereas the melting mixing and polymer solution methods show only  $\sim 0.2$  and  $0.5^\circ\text{C}$ , respectively, over the pure PES. The maximum improvement by the coating method can be correlated to the processing of composites into two steps. First, break up of EG into graphite nanosheets by sonication mixing. Second, uniform dispersion and coating of graphite nanosheets on the surface of PES particles during premixing. It has been confirmed by fractography that coating enable the fine dispersibility of graphite nanosheets. In contrast, melt mixing breaks the EG into smaller pieces by magnetic stirring but not into graphite nanosheets, as shown in SEM images. Overall, the DSC analysis clearly showed that incorporating EG in PES resulted in an increase in  $T_{cp}$  and  $T_{mp}$ . Moreover, coating shows slightly higher than those of other methods, and is attributed to the mixing method utilized. EG/PES obtained from coating mixing disrupts the graphite layers, separating them, and thus providing more surfaces for nucleation.

Based on the results above, EG/PES composites prepared via coating with different EG content were selected and further investigated to illustrate the

effects of EG content on crystallization and melting behaviors. As indicated in Figure 6(c,d) and Table III. Unfilled PES has a  $T_{co}$  of  $172.1^\circ\text{C}$  and a  $T_{mp}$  of  $213.0^\circ\text{C}$ . In the presence of EG, it was found that the onset temperature of crystallization ( $T_{co}$ ) and  $T_{cp}$  slightly increased on the addition of EG. When EG content was 4 wt %, the  $T_c$  of EG/PES was about  $2^\circ\text{C}$  higher than that of pure PES. Further analysis from Table III indicated that the crystallization process of PES was accelerated as evidenced by the narrowing of the crystallization peak width [Fig. 6(c,d), also can be indicated by  $D$  value listed

**TABLE II**  
Key Crystallization and Melting Parameters of 6 wt % EG/PES Nanocomposites Prepared via Different Methods

Results	6 wt % EG/PES nanocomposites		
	Melt mixing	Polymer solution	Coating
$T_{cp}$ ( $^\circ\text{C}$ )	181.3	181.6	182.4
$T_{mp}$ ( $^\circ\text{C}$ )	213.1	213.3	213.4
$T_{mp} - T_{cp}$ ( $^\circ\text{C}$ )	31.9	31.7	31.0



**TABLE III**  
Detailed Crystallization and Melting Parameters of Pure PES- and Coating-Processed EG/PES Nanocomposites with Different EG Content

EG content	$T_{co}$ (°C)	$T_{cp}$ (°C)	$T_{ce}$ (°C)	$D$ (°C)	$\Delta H_c$ (J/g)	$T_{mp}$ (°C)	$\Delta H_m$ (J/g)	$T_{mp} - T_{cp}$ (°C)
0	172.1	181.1	186.7	14.6	-56.5	213.0	68.1	31.9
2	173.6	182.2	187.0	13.4	-63.1	215.3	72.0	33.1
4	174.8	183.1	188.0	13.2	-62.6	212.2	64.8	29.1
6	173.2	182.4	187.5	14.3	-59.5	213.4	63.9	31.0
8	173.8	183.0	188.1	14.3	-64.4	213.8	64.5	30.8
10	173.5	182.7	187.8	12.3	-53.1	212.3	62.2	29.6

$T_{co}$  = Onset crystallization temperature (°C).

$T_{cp}$  = The peak temperature of crystallization (°C).

$T_{ce}$  = End crystallization temperature (°C).

$D$  = Temperature range of crystallization ( $T_{ce} - T_{co}$ , °C).

$\Delta H_c$  = The heat of crystallization (J/g).

$T_{mp}$  = The peak temperature of melting (°C).

$\Delta H_m$  = The heat of heating (J/g).

$T_{mp} - T_{cp}$  = Degree of supercooling (°C).

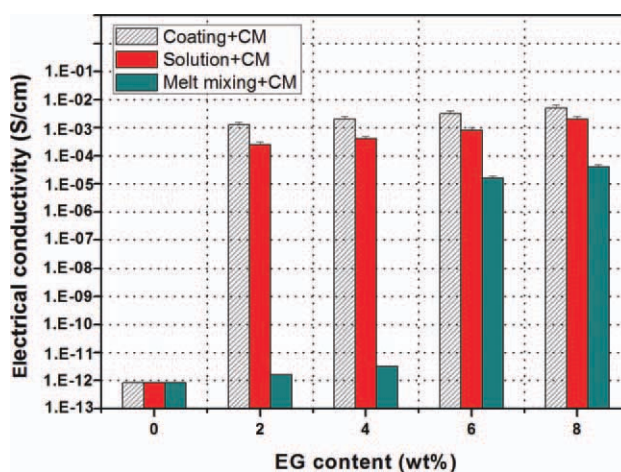
in Table III]. The results show that EG dispersed in PES matrix play the role of heteronucleating agent, which can facilitate the crystallization of PES. The supercooling degree ( $T_{mp} - T_{cp}$ ) as a thermodynamic driver of crystallization required for PES crystallization in the composites was lower compared with that required for pure PES. The drop in the supercooling degree indicated an accelerated nucleating process for PES in the presence of EG. Similar behaviors have been observed and reported in EG/PPS<sup>14</sup> and graphite/PA6<sup>10</sup> composites.

### Electrical conductivity of EG/PES composites

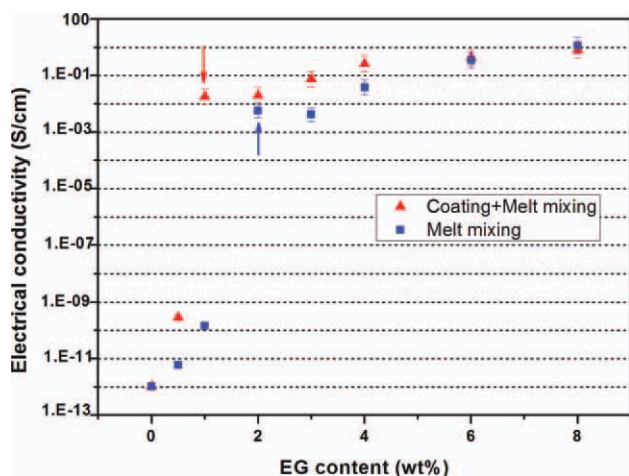
The important properties in electrical conductive composites are the electrical conductivity, reported as bulk conductivity (S/cm), and the percolation threshold, defined as the minimum volume content of the conductive reinforcement above which the polymer composite becomes electrically conductive. It is desirable for the conductive filler content to be as low as possible to achieve good processability, low cost, and satisfactory mechanical performance. Both the conductivity and the percolation threshold are affected by various factors such as the volume fraction and geometric characteristics of the conductive filler,<sup>3,27</sup> the filler orientation, and spacing within the polymer matrix,<sup>2,3,28</sup> as well as the crystallinity of the matrix.<sup>29</sup> The fabrication method and processing conditions of the composites play an important role in the percolation threshold and conductivity as they affect the orientation, dispersion, and interparticle spacing within the polymer matrix, and they may alter the filler's aspect ratio or enhance the interactions between filler and matrix and change the matrix crystallinity.

The effect of the three compounding methods; (i) melt mixing, (ii) polymer dissolution, and (iii)

coating the PES powder with EG, on the percolation threshold and electrical conductivity of EG/PES composites is shown in Figure 7. All the samples were compression molded, and the electrical conductivity was measured in the direction parallel to the sample's length. As shown the conductivity of EG/PES composites made by the coating method is as high as  $10^{-3}$  S/cm at a loading of 2 wt %, indicating that the percolation threshold which can be achieved by this method is much lower than the others. For both EG loadings used 2 and 4 wt %, the proposed coating method results in conductivity higher than the conductivity of the polymer solution and melt-mixing processed samples which is the method commonly used when composites with lower percolation threshold are required. This indicates that the coating method is at least as efficient in facilitating the formation of conductive network



**Figure 7** Effect of compounding on the percolation threshold and conductivity of EG/PES composites made by compression molding (CM). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 8** Effect of compounding on the percolation threshold and conductivity of EG/PES composites made by injection molding. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

as the commonly used solution method but avoids the problems with recovery of solvent.

In the case of coating, there are no agglomerates of EG due to the use of sonication as a result of the PES powder being homogeneously coated by EG. When the polymer melts under CM conditions, the EG platelet network formed on the exterior of the PES particles remains largely intact. In contrast, during the solution and melt-mixing process EG platelets have the opportunity to reaggregate and do not efficiently participate in the conductive network.

It is evident that combination of the coating and CM yields composites with lower percolation threshold and higher conductivity. However, it is of practical interest to explore what is the effect of coating in the case of injection-molded samples as injection molding is widely used in both research labs and large-scale production. Composites were made using (i) melt mixing and injection molding and (ii) coating, melt mixing, and injection molding, as it is not practical to injection mold the coated composite powder without passing it first through the extruder. The percolation threshold and electrical conductivity of EG/PES composites are shown in Figure 8. The premixed samples have a percolation threshold less than 1 wt %, whereas the melt-mixed ones have 2 wt % (as indicated by the arrows). As the EG content increases, the difference in electrical conductivity of the composites made with the two methods decreases. The reason is that coating breaks down the EG agglomerates and allows for formation of a continuous network at lower loadings; however, as the graphite concentration increases, the platelets can reaggregate. Further comparison of Figures 7 and 8, it can be seen that with similar compositions

the coating-melt mixing-injection molding EG/PES composites have higher electrical conductivity ( $10^{-2}$  S/cm) and lower percolation threshold (<1 wt %) than the composites prepared via coating-CM ( $10^{-3}$  S/cm and <2 wt %), indicating that processing method has obvious effects on the electrical conductivity and percolation threshold. Presumably, the significant effect is resulted from the difference in filler orientation during EG/PES composites formation.

## CONCLUSIONS

An efficient compounding method has been developed for optimizing the dispersion of nanoparticles in thermoplastic polymers. It consists of coating polymer particles with nanoparticles using a liquid phase nonsolvent under ultrasonication. In this research, EG nanoparticles were dispersed in IPA using sonication in the presence of PES powder at room temperature to produce a uniform coating on the PES. Subsequent melt mixing and injection molding produced composites with improved flexural strength and modulus. The enhancement of the flexural properties is attributed to the uniform dispersion of the nanoparticles in the solid state before melt processing.

The coating method is more effective at lowering the percolation threshold of composites than the widely used polymer solution and melt-mixing method. It may result that this is one of the only methods to insure that the large platelet morphology of EG can be preserved in the final composite.

Additional advantages of this method are that the experimental set up is very simple, no solvents are used, there is no need for high temperatures and the nonsolvent can be easily recycled making for a method that is practical, safe, cost and time effective, and environmentally friendly.

Composites made by melt mixing and injection molding show a higher percolation threshold because of limitations in the ability of the melt-mixing equipment to disperse the EG and maintain their platelet-type morphology. Furthermore, injection molding creates morphology with preferential alignment the platelets along the flow direction. As a result, no improvement in electrical conductivity resulting from the effect of larger EG aspect ratio was detected.

The lowest percolation threshold measured was less than 1 wt % for samples made by coating-melt mixing-injecting molding, whereas composites with similar compositions made by melt mixing-injection molding had a percolation threshold of 2 wt %.

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## References

1. Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. *Nature* 2006, 442, 282.
2. Kuilla, T.; Bhadra, S.; Yao, D. H.; Kim, N. H.; Bose, S.; Lee, J. H. *Prog Polym Sci* 2010, 35, 1350.
3. Sengupta, R.; Bhattacharya, M.; Bandyopadhyay, S.; Bhowmick, A. K. *Prog Polym Sci* 2011, 36, 638.
4. Du, X. S.; Xiao, M.; Meng, Y. Z.; Hay, A. S. *Polymer* 2004, 45, 6713.
5. Aylsworth, J. W. U.S. Pat.1,191,383 (1916).
6. Lincoln, V. F.; Claude, Z. U.S. Pat.4,414,142 (1983).
7. Wang, W. P.; Liu, Y.; Li, X. X.; You, Y. Z. *J Appl Polym Sci* 2006, 100, 1427.
8. Uhl Fawn, M.; Yao, Q.; Nakajima, H.; Manias, E.; Wilkie, C. A. *Polym Degrad Stab* 2005, 89, 70.
9. Shen, J. W.; Chen, X. M.; Huang, W. Y. *J Appl Polym Sci* 2003, 88, 1864.
10. Pan, Y. X.; Yu, Z. Z.; Ou, Y. C.; Hu, G. H. *J Polym Sci Part B Polym Phys* 2000, 8, 1626.
11. Xiao, M.; Sun, L. Y.; Liu, J. J.; Li, Y.; Gong, K. C. *Polymer* 2002, 3, 2245.
12. Chen, G. H.; Wu, D. J.; Weng, W. G.; Yan, W. L. *J Appl Polym Sci* 2001, 2, 2506.
13. Song, L. N.; Xiao, M.; Li, X. H.; Meng, Y. Z. *Mater Chem Phys* 2005, 3, 122.
14. Zhao, Y. F.; Xiao, M.; Wang, S. J.; Ge, X. C.; Meng, Y. Z. *Compos Sci Technol* 2007, 7, 2528.
15. Celzard, A.; McRae, E.; Marache, J. F.; Furdin, G.; Dufort, M.; Deleuze, C. *J Phys Chem Solid* 1996, 7, 715.
16. Wang, Y. S.; O'Gurkis, M. A.; Lindt, J. T. *Polym Compos* 1986, 7, 349.
17. Krupa, I.; Chodak, I. *Eur Polym J* 2001, 7, 2159.
18. Clingerman, M. L.; King, J. A.; Schulz, K. H.; Meyers, J. D. *J Appl Polym Sci* 2002, 3, 1341.
19. Zheng, W.; Wong, S.-C.; Sue, H.-J. *Polymer* 2002, 3, 6767.
20. Zheng, W.; Wong, S.-C. *Comp Sci Tech* 2003, 3, 225.
21. Shen, J.-W.; Chen, X.-M.; Huang, W.-Y. *J Appl Polym Sci* 2003, 8, 1864.
22. Pan, Y.-X.; Yu, Z.-Z.; Ou, Y.-C.; Hu, G.-H. *J Polym Sci Part B Polym Phys* 2000, 8, 1626.
23. Xiao, P.; Xiao, M.; Gong, K. *Polymer* 2001, 2, 4813.
24. Yumitori, S.; Wang, D.; Jones, F. R. *Compos* 1994, 25, 698.
25. Bian, J.; Xiao, M.; Wang, S. J.; Lu, Y. X.; Meng, Y. Z. *J Colloid Interface Sci* 2009, 334, 50.
26. Thongruang, W.; Spontak, R. J.; Balik, C. M. *Polymer* 2002, 3, 2279.
27. Banerjee, P.; Mandal, B. M. *Macromolecules* 1995, 8, 3940.
28. Fiske, T. J.; Gokturk, H. S.; Kalyon, D. M. *J Mater Sci* 1997, 2, 5551.
29. Chodak, I.; Krupa, I. *J Mater Sci Lett* 1999, 8, 1457.