

Mechanical and Thermal Properties of Graphite Nanoplatelets Reinforced Polyarylene Ether Nitriles/Bisphthalonitrile IPN System

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ABSTRACT: A new type of graphite nanoplatelets (GN) reinforced polyarylene ether nitriles (PEN)/bisphthalonitrile (BPh) interpenetrating polymer network with high strength and high toughness was synthesized and characterized. The results showed that GN and PEN had obvious synergistic effect on its properties of resulted BPh composites. Compared to pure BPh, with a loading of 10 wt % PEN and 10 wt % GN, the obtained composites exhibited excellent mechanical properties. In these systems, the flexural toughness and strength of BPh resin could be enhanced with the incorporation of PEN; meanwhile, GN could further improve the flexural modulus and thermal stability lowered by PEN. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Over the years, phthalonitrile polymers have attracted tremendous attention due to their outstanding rigidities, thermal and thermo-oxidative stabilities, excellent mechanical properties, superior moisture, and fire resistances.^{1–3} To date, phthalonitrile monomers with various structures have been synthesized and polymerized into thermosets.⁴ Among them, 4, 4'-bis-(3,4-dicyanophenoxy) biphenyl (BPh) is one of key monomers used for composite formulation. Due to its low melt viscosity (0.1–0.2 Pas), composites based on BPh exhibit excellent processability, which are amenable to processing by cost-effective resin transfer molding method. The mechanical properties, thermal and oxidative stability of BPh-based composites are superior to that of many state-of-the-art high-temperature composites.

However, the performances of this BPh-based system are limited by the intrinsic brittleness of the network structure that adversely affects its mechanical properties. To overcome this limitation, the thermoset–thermoplastic interpenetrating polymer networks (IPN) tend to be effective. The IPN, with an intimate combination of two kinds of polymers in network formation,^{5–7} can exhibit synergistic properties of both the component polymers, which is often more excellent than single component. As a kind of engineering thermoplastic, polyarylene ether nitrile (PEN) has attracted much interest from both industry and academia due to its excellent property similar to polyether ether

ketone (PEEK). Owing to its rigid molecular structure, PEN exhibits high mechanical strength, high toughness, good radiation resistance, and high thermo-oxidative stability,^{8–10} which make it very attractive for the composites used at toughening mechanism, aggressive chemical environments, and so on. Herein, we chose PEN as the guest polymer in BPh system. However, the introduction of thermoplastic resin always increases the tenacity but decreases the modulus and thermal stability of the thermoset resin. Therefore, it is necessary to introduce a third component to offset losses of the flexural modulus and thermal stability lowered by PEN. Graphite nanoplatelet (GN) exhibits unique structural features and physical properties. It is known that GN has high mechanical strength (Young's modulus of 1060 GPa) and excellent thermal stability. It is a potential alternative to other nano-reinforcements such as nanoclays and carbon nanotubes since it combines the low cost and layered structure of nanoclays and the superior thermal and electrical properties of carbon nanotubes.^{11,12}

In this work, PEN-BPh IPN system was prepared and investigated for the effects of the PEN content on the mechanical and thermal properties of the system. The results shown the toughness and strength of BPh resin could be enhanced with the incorporation of PEN, but modulus and thermal stability of the IPN composites were decreased. Then the GN reinforced PEN-BPh IPN system was prepared and the results demonstrated that GN could improve the flexural strength of BPh and also

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offset losses of the flexural modulus and thermal stability lowered by PEN. The high performance GN reinforced PEN-BPh IPN composite is believed to have potential application in military industry, aerospace, and other places where solvent resistance and/or exposure to high temperature is necessary.

EXPERIMENTAL

Materials and Instruments

Natural graphite was purchased from Qingdao Yanxin Graphite, China. The mean diameter is about 500 μm . Diphenyl diamine sulfoxide (DDS) was purchased from Yangzhou Tianchen Meticulous Chemical, China. All the chemicals and reagents were used without further purification. Phthalonitrile monomer and the phenolphthalein-based PEN were synthesized in our laboratory, the synthetic procedure and raw materials were reported previously.^{10,13}

The Fourier transform infrared spectrophotometer (FTIR) spectra were recorded on Shimadzu FTIR-8400S spectrometer. The thermal decompositions of copolymers were determined by TA Instruments TGA-Q50 thermogravimetric analyzer with a heating rate of 20 °C/min under nitrogen. The flexural tests of the composites were performed with a SANS CMT6104 Series Desktop Electromechanical Universal Testing Machine at room temperature, with a crosshead rate of 2 mm/min for flexural tests. The final results were the average values of six replicate measurements. The structure of GN and fracture surfaces morphology of the composites was observed with scanning electron microscope (SEM) (JEOL JSM-5900LV) and transmission electron microscope (Hitach H600).

Preparation of PEN-BPh IPN System

BPh monomer was first melted in a beaker with the chamber volume of 200 mL at 250 °C (the melting point of BPh is 235 °C), and PEN powder was added to the BPh monomer after 10 min stirring then 2 wt % of DDS (curing agent) was added. The resultant melting liquid was transferred into the moulds and cured in the oven by the sequential mode of temperature program as follows: 250 °C, 4 h; 280 °C, 4 h; 300 °C, 4 h; 350 °C, 6h; 375 °C, 2h. Finally, PEN-BPh IPN system with different weight ratios (PEN wt % = 0, 5, 10, and 15) were obtained.

Preparation of Graphite Nanoplatelet

According to Ref. 14, GN was prepared by intercalation of natural graphite followed by rapid exfoliation in a microwave environment. The graphite rapidly heats as a result of coupling with the microwave radiation and the entrapped intercalates vaporize. The exfoliated graphite particles undergo significant expansion (500 μm) forming a worm-like structure. This worm-like structure is then mechanically grounded to form the individual GN.

Preparation of GN Reinforced PEN-BPh IPN System

The preparation method of GN/PEN-BPh composites was shown in Figure 1 which is similar to the preparation of PEN-BPh IPN system. The BPh monomer was first melted at 250 °C then PEN (10 wt%) were added to the BPh monomer melt and after 10 min stirring 10 wt% of GN was added, at last 2 wt% of DDS was added. Then the resultant melting liquid was transferred into the moulds and cured in the oven by the same mode as shown in PEN-BPh IPN system. Finally, GN/PEN-BPh

nanocomposites with weight ratios of BPh/PEN/GN=100/10/10 were obtained.

RESULTS AND DISCUSSION

FTIR Spectra of the PEN-BPh IPN System

The FTIR spectra were performed to monitor the formation of the PEN-BPh IPN system. In Figure 2(a,b), the absorption at 2231 cm^{-1} is the characteristic symmetrical stretching of -CN group. Figure 2(c) shows the FTIR spectra of PEN-BPh blend after curing. Clearly, the peaks at 2230 cm^{-1} shuttles down and another new peaks at 1360, 1520, and 1010 cm^{-1} can be observed, indicating the formation of phthalocyanine ring and triazine ring,¹⁴ respectively. The results showed the polymerization of BPh monomer had happened and the crosslink density of PEN was also increased. Both PEN and BPh have -CN groups, so the -CN groups in PEN chain segment may participate in the cyclization reaction of BPh. Meanwhile, the increasing absorbance from 3450 to 3500 cm^{-1} indicated the presence of hydroxyl groups with incorporation of PEN. It may be one factor that affects the flexural modulus and thermal stability of resulted composites.

Thermal Properties of the PEN-BPh IPN System

Figure 3 displays the TGA curves of pure BPh, PEN and PEN-BPh system with various PEN contents. To explore the effect of PEN on the thermal stability of BPh polymer, the thermal degradation temperatures of 5 and 10% weight losses ($T_{5\%}$ and $T_{10\%}$) and the carbon yield at 800 °C were summarized. The pure BPh is rather thermally stable [curve (a)]. However, the thermal stability of the PEN-BPh IPN system is reduced with increasing PEN content. The $T_{5\%}$, $T_{10\%}$ and carbon yield of pure BPh polymer at 800 °C were about 543 °C, 595 °C, and 79% respectively. In cases of PEN-BPh IPN system, the $T_{5\%}$ and $T_{10\%}$ of the composites occurred at lower temperatures than these of pure BPh. For 15 wt % of PEN-BPh IPN system, the $T_{5\%}$ and $T_{10\%}$ and carbon yield at 800 °C were decreased by about 67 °C, 77 °C, and 16% respectively. That is largely because soft polymer chains of PEN reduce the thermal stability of the PEN-BPh system, which is confirmed by TGA curve (e) that pure PEN exhibits poorer thermal stability than that of pure BPh.

Mechanical Property of the PEN-BPh IPN System

The mechanical properties of pure BPh, PEN, and PEN-BPh system with various PEN contents are shown in Figure 4. Figure 4(a) shows that PEN exhibit excellent toughness with fracture flexural strain as high as 9.1%. Because of the intrinsic brittleness of the network structures, the flexural strength and fracture flexural strain of pure BPh polymer are only 83 MPa and 2.1%. But its flexural modulus is 3.6 GPa, about 0.9 GPa higher than that of PEN. Compared to pure BPh polymer, addition of 5 wt % PEN resulted in about 1.0% and 12 MPa increase in the flexural strain and flexural strength, but 0.2 GPa decrease in flexural modulus. Flexural strain and flexural strength exhibit maximum values at 10 wt% PEN content, about 2% and 25 MPa above those of pure BPh, respectively. This result is due to the good compatibility and high interpenetrating degree between BPh and PEN. In this system, BPh network provided rigid frame while flexible PEN chains wind around the framework,

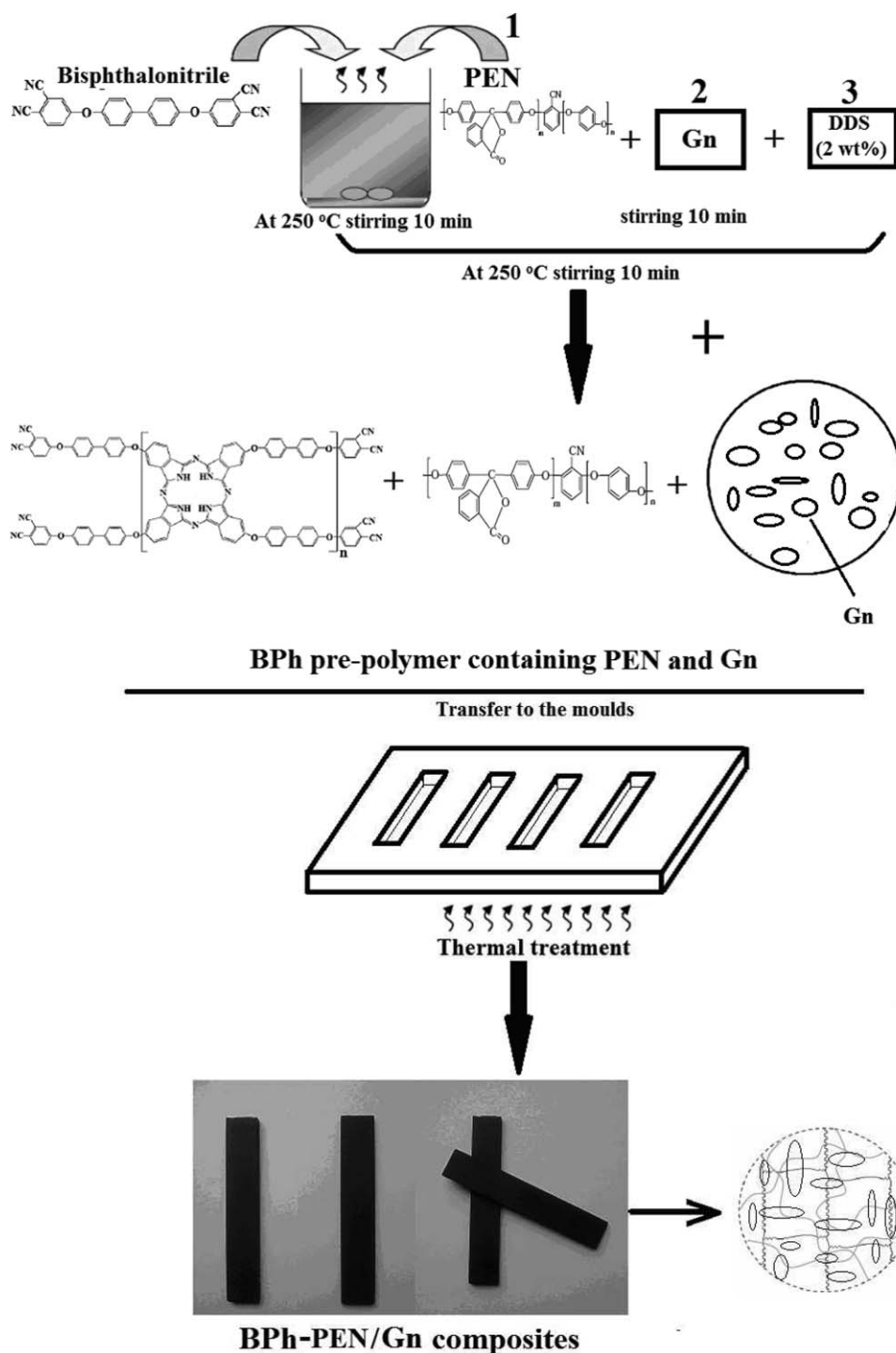


Figure 1. Preparation of GN/PEN-BPh composites.

serving as buffer zone for ambient pressure. Therefore, the strength and tenacity were enhanced largely. Meanwhile, with the introduction of flexible PEN chains, the system tended to soften up to some extent and thus the modulus of BPh is decreased. The flexural modulus of the PEN-BPh IPN system with 10 wt% PEN content is only 3.2 GPa, about 0.4 GPa decrease than pure BPh. Moreover, the mechanical properties of PEN-BPh IPN system with 15 wt% PEN content were poorer

than the composites with 10 wt% PEN content. This may due to the problems of phase segregation and low interpenetrating degree between BPh and PEN chains.

The fracture surfaces of the PEN-BPh composites with various PEN contents in Figure 5 also confirmed the mechanical performances investigated above. The fracture surfaces of the pure BPh indicated a smooth, glassy, and homogeneous microstructure without any plastic deformation. But the fracture surfaces

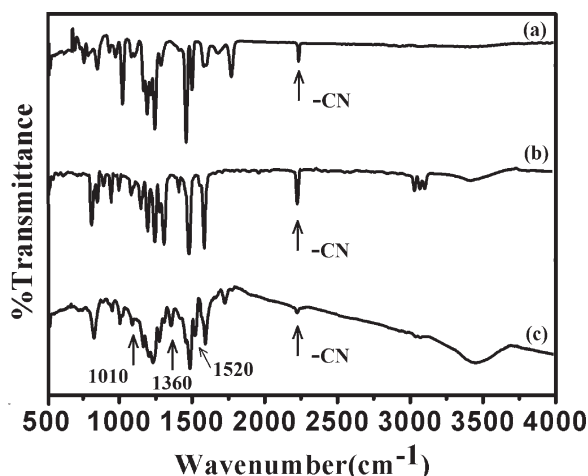


Figure 2. FTIR of (a) pure PEN, (b) pure BPh, and (c) BPh with 10 wt % of PEN.

of PEN-BPh composites reflect different degree of plastic deformation and tearing behavior. These are compelling proof of toughness increasing. The homogeneous morphology exhibited by the PEN-BPh IPN system with 10 wt% PEN is due to the good compatibility and interpenetrating between the BPh and PEN chains.

From the above, the PEN-BPh IPN system with 10 wt% PEN exhibit highest strength and toughness, so we choose this ratio for the subsequent research.

Structure of Graphite Nanoplatelet

It was known that expanded graphite (EG) consists of graphite sheets with thickness of less than 100 nm [Figure 6(a)]. After mechanical agitation, EG was torn to fully GN, as described in the previous report.¹⁵ The plane dimension of the GN was mostly in the range of 5–20 μm , as shown in the Figure 6(b). Figure 6(c) shows the TEM images of GN, it could be seen that the thickness of GN was less than 50 nm. Thus, they exhibited an aspect ratio (diameter to thickness) as high as around 200–

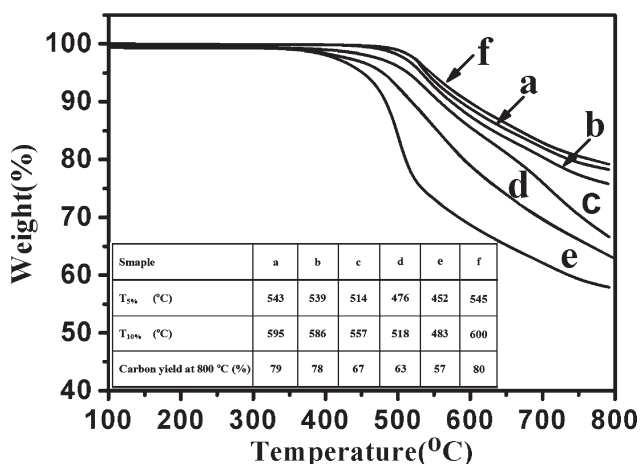


Figure 3. TGA curves of (a) pure BPh, (b) BPh with 5 wt% of PEN, (c) BPh with 10 wt% of PEN, (d) BPh with 15 wt% of PEN, (e) pure PEN, and (f) BPh with 10 wt% of PEN and 10 wt% of GN.

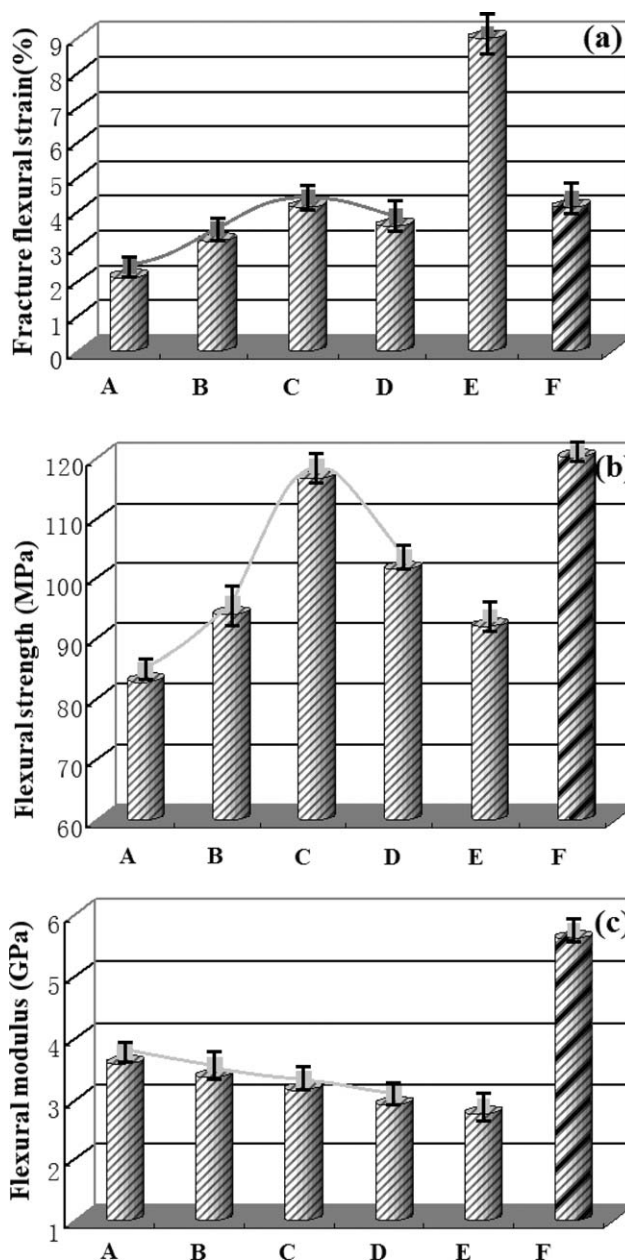


Figure 4. Mechanical properties of (a) fracture flexural strain of, (b) flexural strength of, (c) flexural modulus of (A) pure BPh, (B) BPh with 5 wt% of PEN, (C) BPh with 10 wt% of PEN, (D) BPh with 15 wt% of PEN, (E) pure PEN, and (F) BPh with 10 wt%.

500. Besides, the structure of the isolated GN was very different from that of the EG.

Thermal Properties of GN/PEN-BPh Composite

Based on the study of the PEN-BPh IPN system, GN/PEN-BPh composites with weight ratios of BPh/PEN/GN = 100/10/10 were prepared. Figure 3, curve (f) shows TGA thermograms of GN/PEN-BPh composites. The $T_{5\%}$, $T_{10\%}$, and carbon yield of GN/PEN-BPh composites at 800 °C were about 545 °C, 600 °C, and 80 respectively. Comparing with the PEN-BPh IPN system (10 wt% PEN content), the thermal property of the GN/PEN-BPh composites was improved. With the incorporation of GN,

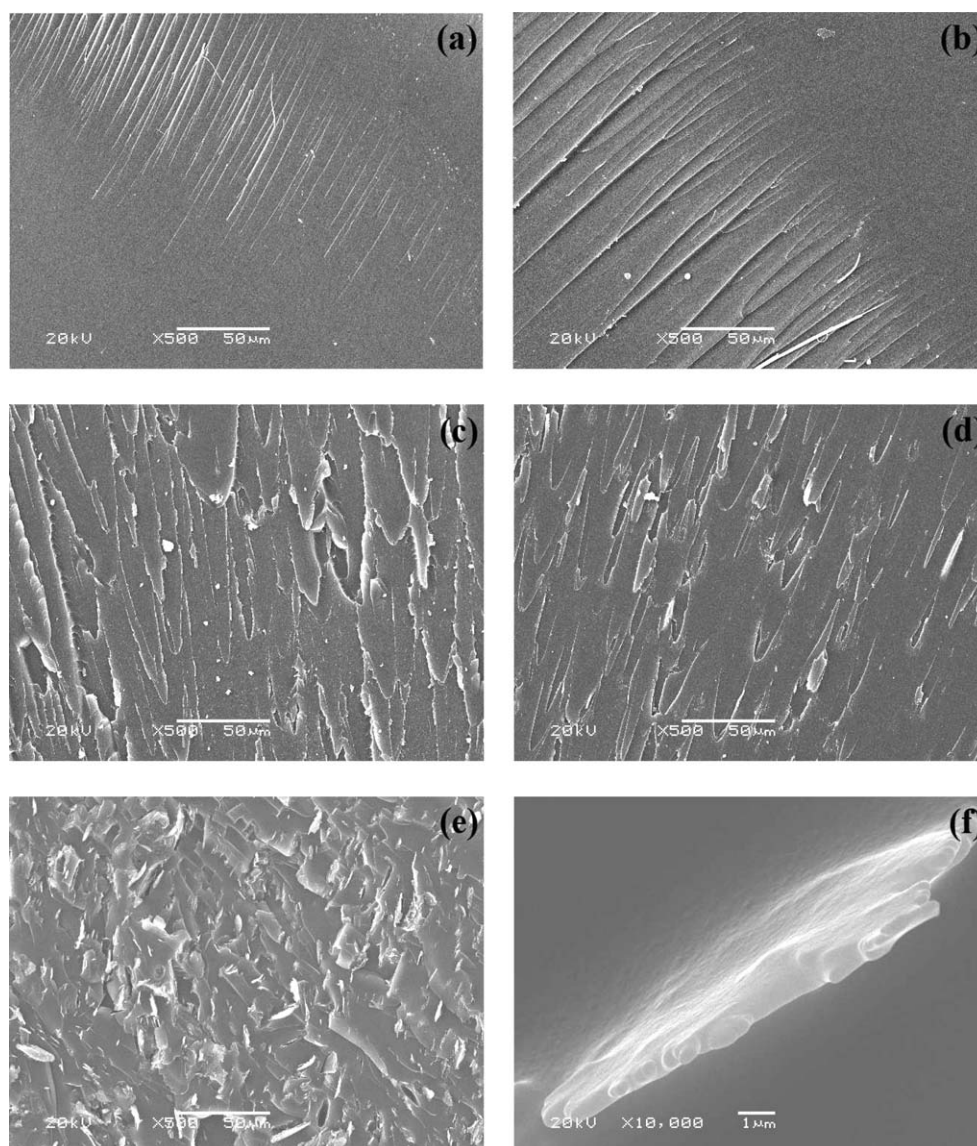


Figure 5. SEM images of fracture surfaces of (a) pure BPh, (b) BPh with 5 wt% of PEN, (c) BPh with 10 wt% of PEN, (d) BPh with 15 wt% of PEN, (e) BPh with 10 wt% of PEN and 10 wt% of GN, and (f) BPh with 10 wt% of PEN and 10 wt% of GN in high magnification.

the thermal property of the composites reached even a little higher level as pure BPh polymer. This was believed to originate from the fact of GN, which were dispersed homogeneously in the PEN-BPh network, serving as the mass transfer barriers against the volatile pyrolyzed products in the matrix, eventually retarding thermal degradation of the composites.

Mechanical Property of GN/PEN-BPh Composites

The overall performances of PEN-BPh composites were further enhanced by the incorporation of GN component. According to Figure 4 (b,c), the flexural strain and modulus of the GN/PEN-BPh composites were increased to 127 MPa and 5.6 GPa, respectively. It is worth emphasizing that the modulus of the GN/PEN-BPh composites is 2 GPa higher than pure BPh and 2.4 GPa higher than PEN-BPh system (10 wt% PEN content) by the incorporation of GN; the soft materials return to hard. It is well known and commonly admitted that the mechanical

properties of polymer nanocomposites, especially the modulus, depend to a great extent on filler dispersion and interfacial interaction, and are increased only when good dispersion of the nanofiller and effective stress transfer at the polymer/filler interface are guaranteed.¹⁶ In this sense, the improvements in the mechanical properties can also verify the uniform dispersion of GN in the PEN-BPh networks. The fracture surfaces of the nanocomposites in Figure 5(e) also confirmed the enhancement of the mechanical performances investigated. It can be seen clearly that much vertical GN were dispersed uniformly in the PEN-BPh matrix. In addition, SEM photo with high magnification [Figure 5(f)] shows that the GN is well coated by PEN-BPh resin and effective stress transfer at the GN/resin interface are thus guaranteed. According to the previous researches,¹⁷ good dispersion states can increase average aspect ratio of the nanofillers in the polymer matrix; as a consequence, mechanical properties were improved. Here apparently, GN effectively

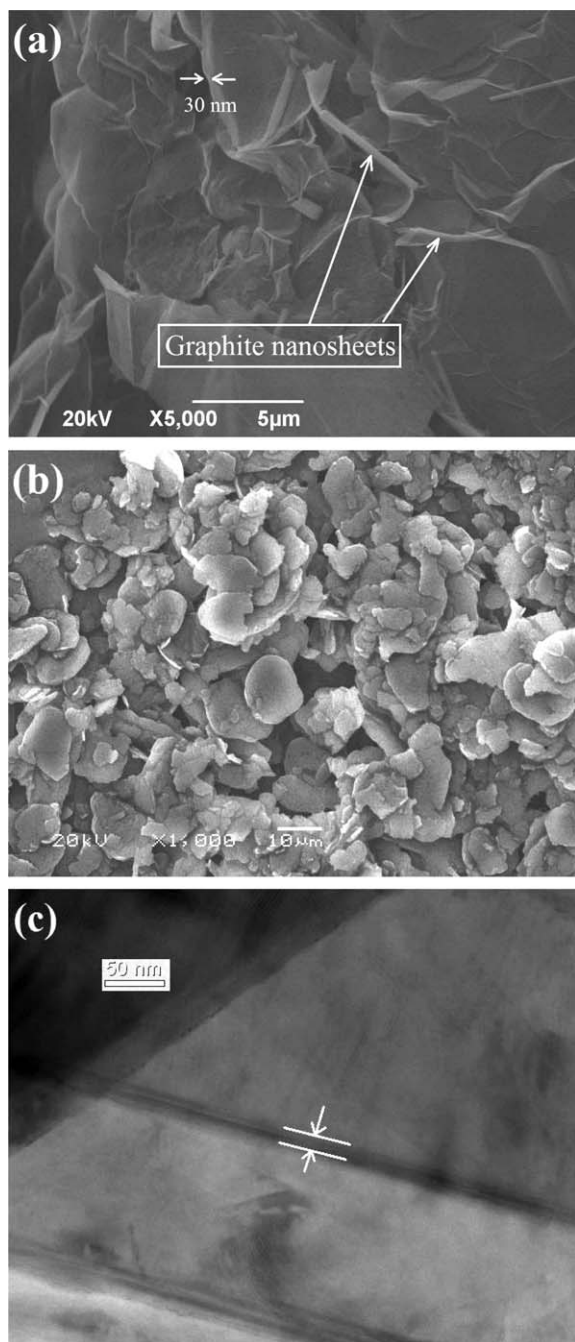


Figure 6. SEM images of expanded graphite and graphite nanoplatelets: (a) expanded graphite, (b) graphite nanoplatelets, and (c) TEM images of graphite nanoplatelets.

reinforced mechanical properties of the PEN-BPh matrix due to their good dispersion states, large aspect ratio, combined with excellent mechanical properties of GN itself. Moreover, the fracture flexural strain of GN/PEN-BPh composites was 4.1 which is same as PEN-BPh system (10 wt% PEN content) and about 2.0% higher than that of pure BPh. The contradiction between the strength and toughness of a material is that higher strength usually leads stress concentration and thus lower toughness. In the GN/PEN-BPh composites, GN can restrain the welding

cracks effectively during the crack process. As a result, its strength is enhanced and toughness is maintained.

CONCLUSION

The GN/PEN-BPh composites as a type of thermoset–thermoplastic nanofiller blend system were successfully prepared via a cost-effective method and characterized for mechanical, thermal, and morphological properties. It was found that the strength and toughness of the GN/PEN-BPh composites was much better than that of pure BPh. Compared with BPh, for 10 wt% of PEN and 10 wt% of GN reinforced BPh composite, the flexural strength, modulus, and fracture flexural strain increased by about 44 MPa, 2 GPa, and 2.0 respectively. The induced PEN enhanced the strength and toughness of BPh polymer while GN improved the flexural strength and also offset losses of the flexural modulus and thermostability lowered by the PEN. The high performance GN/PEN-BPh composites are believed to have potential application in military industry, aerospace, and other places.

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