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Electrical, thermal, and mechanical properties of polyarylene ether nitriles/graphite nanosheets nanocomposites prepared by masterbatch route

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Abstract Graphite nanosheets (GN) reinforced polyarylene ether nitriles (PEN) nanocomposites were successfully fabricated through masterbatch route and investigated for morphological, thermal electrical, mechanical, and rheological properties. The SEM images showed that GN were well coated by phthalonitrile prepolymer (PNP) and dispersed in the PEN matrix. Thermal degradation and heat distortion temperature of PEN/GN nanocomposites increased substantially with the increment of GN content up to 10 wt%. Electrical conductivity of the polymer was dramatically enhanced at low loading level of GN; the electrical percolation of was around 5 wt% of GN. The mechanical properties of the nanocomposites were also investigated and showed significant increase with GN loading. For 10 wt% of GN-reinforced PEN composite, the tensile strength increased by about 18%, the tensile modulus increased by about 30%, the flexural strength increased by about 25%, and the flexural modulus increased by 90%. Rheological properties of the PEN/GN nanocomposites also showed a sudden change with the GN loading content; the percolation threshold was in the range of 3–4 wt% of GN.

Introduction

As a type of engineering thermoplastic resin, polyarylene ether nitriles (PEN) have attracted much interest both from industry and academia because it has excellent properties similar to polyether ether ketone (PEEK). Owning to its rigid molecular structure, PEN exhibits high tensile strength, good radiation resistance, and high thermo-oxidative stability [1–3], which make it very attractive for the composites to use at elevated temperatures and aggressive chemical environments. Although PEN has the good mechanical properties and thermal stability, development of multifunctional PEN composites is still needed to pursue for special area such as aerospace and military. In some cases, a low electrical resistivity of PEN is required for the electrostatic and/or electromagnetic dissipation of advanced applications.

Polymer-based nanocomposites containing strong, durable, and multifunctional nanoparticles such as silicates [4–6], carbon nanotubes [7–10], and graphite sheets [11–16], have been considered as the promising advanced materials, because greatly improved properties of the nanocomposites can be achieved, compared with conventional composite counterparts, when nanoparticles are homogeneously dispersed in a polymeric matrix. In recent years, many studies on PEN-based nanocomposites have been performed to improve the properties of PEN by incorporating nanoparticles such as carbon nanotubes [17, 18]. However, research on PEN-based nanocomposites containing graphite sheets or graphite nanoplatelets has been carried out limitedly.

Graphite sheets exhibit unique structural features and physical properties. It has been known that graphite sheets have excellent mechanical strength (Young's modulus of 1060 GPa), electrical conductivity of 10^4 S/cm, and thermal stability. These properties observed at nanoscale have motivated many researchers to utilize graphite nanosheets (GN) as a new reinforcement in polymer composites [19–22]. Previous researches showed that GN are ideal

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filler for preparing polymer composites and promising application in polymer multifunctional composites. On these results, the development of GN as reinforcement for PEN matrix is expected to expand various applications with high performance in thermal, mechanical, and electrical properties. However, GN, whose thickness is in nanoscale, tend to accumulate when they are blended with polymer resins directly, and thus it is difficult to achieve good distribution in polymer matrices. In order to obtain high performance for PEN/GN nanocomposites with even low nanofiller content, it is desirable to modify the surface of the GN to enhance the dispersion of GN and PEN/GN′ interfacial adhesion. At present, main approaches for modifying the inorganic fillers are chemical covalent, plasma treatment, and electro-chemical, etc. It is well-known that masterbatch technique is also a simple and effective method to modify the inorganic fillers and presents potential application in thermoplastic industry.

In our lab, phthalonitrile prepolymer (PNP), which had the high initial decomposition temperature (>450 °C) and the low initial melt viscosity at 330 °C (<0.1 Pa·S) [23, 24], was successfully used as a kind of plasticizers to overcome the temperature resistance problem, and the blending materials maintained the high thermal and thermo-oxidative stability of PEN. Previous research also showed that PEN had favorable compatibility with PNP [25]. These excellent properties of PNP make it good candidate for modification of GN by masterbatch technique.

In this study, we first prepared the disorder GN via the intercalation of natural graphite followed by rapid exfoliation in a microwave environment. The as-prepared GN were then coated by PNP in order to prepare modified GN, called GN masterbatches, which contained different weight ratios of GN. The masterbatches were then blended with PEN via the extrusion process, resulting in good dispersion of GN throughout PEN matrix. Morphology, structures, thermal stability, mechanical, electrical, and rheological properties of PEN/GN nanocomposites were systematically investigated. The as-prepared PEN/GN nanocomposites with multifunctional properties are believe to have potential application in automotive area, aerospace, and other places where solvent resistance and/or exposure to high temperature is necessary.

Experimental

Materials

Natural graphite was purchased from Qingdao Yanxin Graphite Co. Ltd., China. The mean diameter is about 500 μm. Diphenyl diamine sulfoxide (DDS) was purchased from Yangzhou Tianchen Meticulous Chemical Co. Ltd., China. All the chemicals and reagents were used without further purification. Phthalonitrile monomer was synthesized in our laboratory, the synthetic procedure and raw materials were reported previously [26]. PEN were provided by Union Laboratory of Special Polymers of UESTC-FEIYA, Chengdu, China. It is a copolymer derived from 2,6-dichlorobenzonitrile with hydroquinone and resorcin with the inherent viscosity of 1.22 dL/g (0.005 g/mL in *N*-methylpyrrolidone).

Preparation of GN

According to Ref. [27], GN were 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×) forming a worm-like structure. This worm-like structure is then mechanically grounded to form the individual GN.

Preparation of PNP modified GN

The GN masterbatches were prepared through melt mixing process as shown in Fig. 1. The phthalonitrile monomer was first melted in a laboratory size internal mixer model thermo Haake poly-lab system with the chamber volume of 300 cm^3 at 230 °C, then GN were added to the phthalonitrile monomer melt and stirred for 10 min at 25 rpm, in the presence of 2 wt% of DDS as the curing agent. Thus different weight ratios of PNP/GN masterbatches (8/x wt%; $x = 0, 1, 3, 5, 8, 10$) were prepared.

Preparation of PEN/GN nanocomposites

A series of nanocomposites consisted of PEN/PNP/GN (92/8/x wt%; $x = 0, 1, 3, 5, 8, 10$) were melt-mixed in a TSSJ-2S co-rotating twin-screw extruder. The temperatures were maintained at 310, 320, 330, 330, 330, and 325 °C from the hopper to the die and the screw speed was about 120 rpm. Extruded strands of the molten blends were then pelletized and dried in vacuum oven at 120 °C for 24 h, followed by injection molding to prepare standard bars for mechanical tests with an injection and molding machine at 340 °C.

It should be clarified that a PEN/PNP (92/8 wt%) blend was used as the basal polymer (regarded as the neat PEN) for two reasons: (1) the good compatibility between PEN and PNP guarantees no obvious phase separation; (2) the estimation of the GN effect on properties and morphology will be drawn exactly, based on the basal polymer with the same composition.

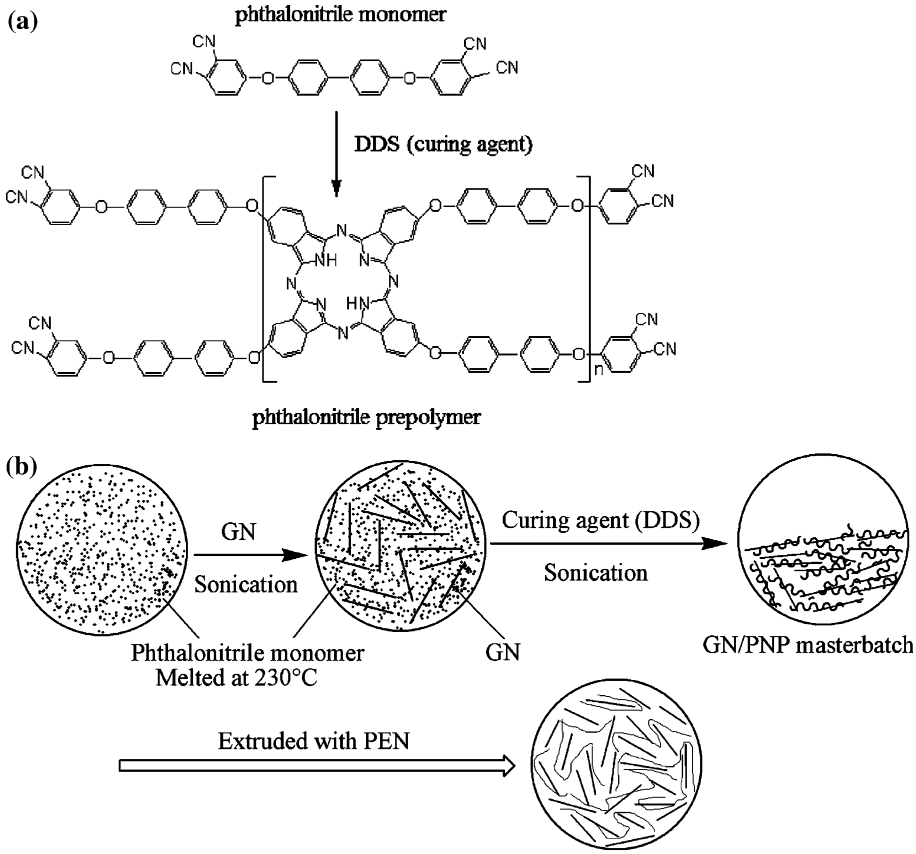

Fig. 1 **a** Synthesis of the phthalonitrile prepolymer. **b** Schematic illustration of preparation of masterbatch and the target composites

Morphological characterization

The morphology of the GN and fracture surfaces of the nanocomposites were observed with scanning electron microscope (JEOL JSM-5900LV) and transmission electron microscopy (Hitach H600). The SEM samples were coated with a thin layer of gold prior to examinations.

Thermal measurements

Glass transition temperature (T_g) and melting transition were measured on TA instrument DSC Q100, at a heating rate of 10 °C/min. TGA analysis of the composite was carried out under N_2 atmosphere at a heating rate of 10 °C/min using TA Q50 series analyzer system combination with data processing station. Heat distortion temperature (HDT) of the samples was measured according to ASTM D648-2007 at ZWK computer controlled HDT vikar tester (Shenzhen New SANS Materials Testing Machine Co., China).

Resistance measurements

The volume electrical resistivity of the final PEN/GN nanocomposites was determined by two probes method. The resistance of the samples was measured using High Resistance Meters (ZC36; 10^{-14} A and 10^{17} Ω) if the resistance was very high or using 4530 intelligent digital multimeter if the resistance was low. The resistivity of the nanocomposites was then calculated by Eq. 1:

$$\rho = \frac{RA}{t} \tag{1}$$

where ρ is the volume resistivity (Ω m), R is the volume resistance (Ω), A is the area of the sample contacting the electrode (m^2), and t is the thickness of the sample (m).

Mechanical measurements

The tensile and 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 5 mm/min for tensile tests and 2 mm/min for flexural tests, respectively. The final results were the average values of six replicate measurements.

Rheological measurements

Dynamical rheological measurements were carried out on a rheometer (TA Instruments Rheometer AR-G2) equipped with a parallel-plate geometry (25 mm diameter). Disk samples were prepared by compression molding with a thickness of 1.0 mm and diameter of 25 mm. Storage modulus (G') as a function of angular frequency (ω) range from 0.01 to 100 rad/s at 340 °C were measured. A fixed strain of 1% was used to ensure that measurements were carried out within the linear viscoelastic range of the materials investigated.

Results and discussion

Structure of GN and GN masterbatch

It is known that expanded graphite (EG) consists of graphite sheets with thickness of less than 100 nm (Fig. 2a). After mechanical agitation, EG was torn to fully exfoliated GN, as described in the previous report [28]. Figure 3 shows the TEM images of GN, it can be seen that the thickness of GN is in the range of 10–30 nm. The diameter of the GN was mostly in the range of 1–20 μm, as shown in Fig. 2b. Thus, they exhibited an aspect ratio (diameter to thickness) as high as around 100–500. Besides, the structure of the isolated GN is very different from that of the EG. Figure 2c shows the SEM image of the GN masterbatch with the weight ratio of PNP/GN (8/5 wt%). It can be seen that the GN in the masterbatch were well coated by PNP. The PNP wrapping around the GN effectively prevented the GN from agglomeration during the process of blending with PEN matrix. On the other hand, PNP has the similar molecular structure, aromatic ether bonds and cyano groups to that of PEN, which could also enhance the interfacial adhesion between the GN and PEN matrix.

Thermal properties

Figure 4a shows TGA thermograms of PEN/GN nanocomposites with various GN contents. Thermal degradation profiles of PEN/GN nanocomposites displayed that thermal stability of the nanocomposites was improved with the increment of GN content up to 10 wt%. To explore the effect of GN contents on the thermal stability of PEN/GN nanocomposites, the thermal degradation temperatures of 5 and 30% weight losses ($T_{5\%}$ and $T_{30\%}$) were evaluated from the TGA thermograms of Fig. 4a and summarized in Table 1. $T_{5\%}$ and $T_{30\%}$ of PEN homopolymer were determined to be about 460 and 515 °C, respectively. In cases of PEN/GN composites, the $T_{5\%}$ and $T_{30\%}$ of the nanocomposites occur at higher temperatures than that of neat PEN. For 10 wt% of GN-filled PEN composite, the $T_{5\%}$ and $T_{30\%}$ of PEN/GN composites increased by about 14 and 101 °C, respectively. This improved thermal stability of PEN/GN nanocomposites is believed to originate from the fact that GN, which were dispersed homogeneously in the PEN matrix, serve as the mass transfer barriers against the volatile pyrolized products in the PEN matrix, eventually retarding thermal degradation of the nanocomposites.

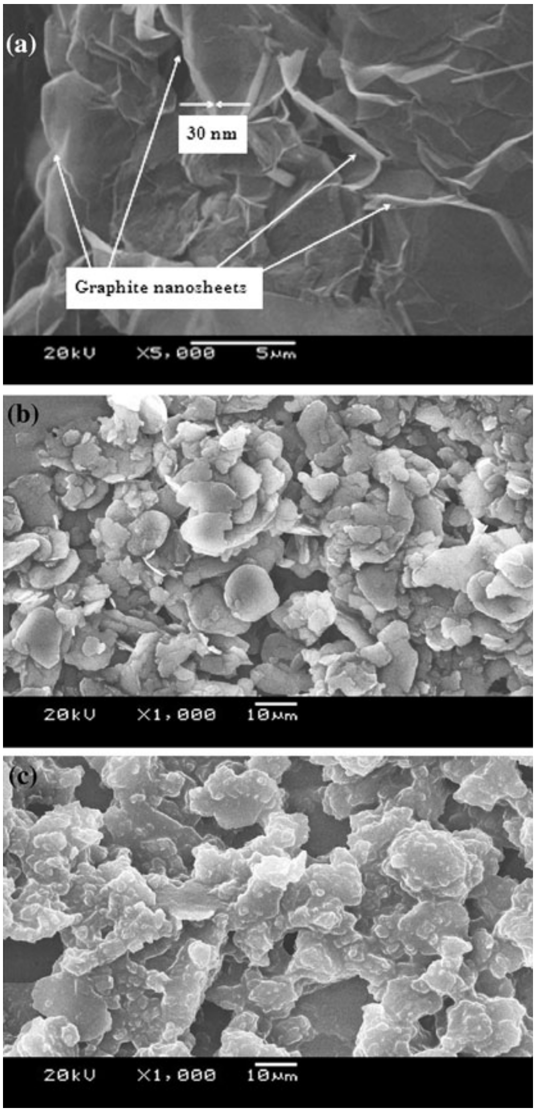

Fig. 2 SEM images of expanded graphite, graphite nanosheets, and GN masterbatch: **a** expanded graphite, **b** graphite nanosheets, **c** GN masterbatch

Figure 4b shows the HDT for PEN/GN composites with various GN contents. Compared with the neat PEN, the HDT of the PEN/GN nanocomposite with 10 wt% GN increased by about 10 °C, indicating that the formation maintenance capability of PEN/GN composite was enhanced compared to the neat PEN. It also can be seen from Table 1 that glass transition temperature (T_g) increases slightly with the increasing GN content in the PEN/GN nanocomposites. However, compared with the neat PEN matrix, melting temperature is not influenced by the addition of GN.

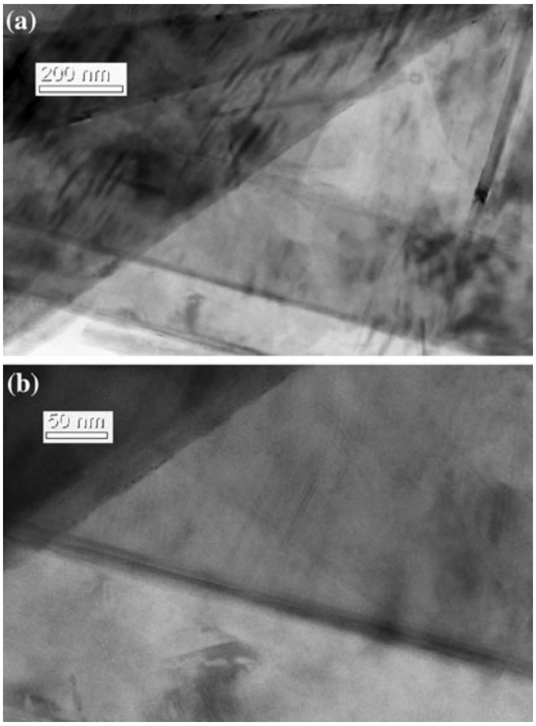

Fig. 3 TEM images of graphite nanosheets at two magnifications

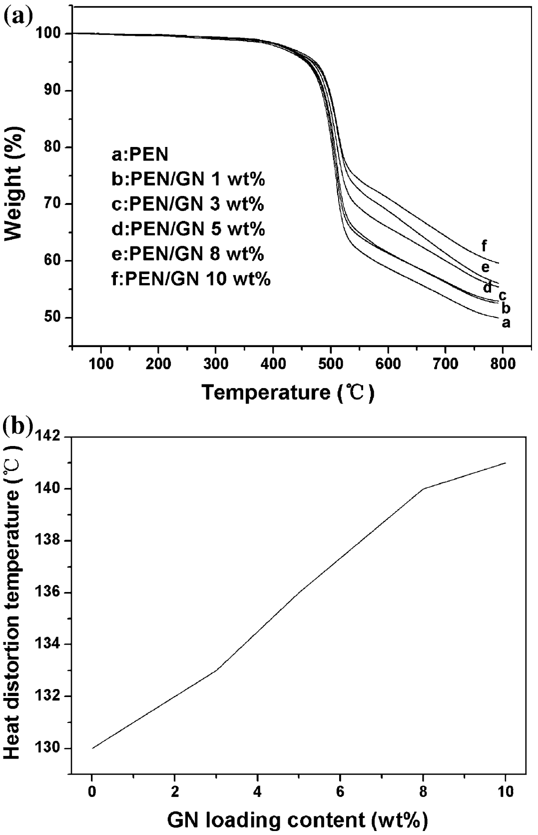

Fig. 4 **a** TGA curves of PEN and PEN/GN nanocomposites. **b** Effect of GN content on the heat distortion temperature of PEN/GN nanocomposites

Table 1 The thermal properties of PEN and PEN/GN nanocomposites

GN content (wt%)	0	1	3	5	8	10
T_g (°C)	158	160	162	162	162	164
T_m (°C)	330	329	331	329	330	330
$T_{5\%}$ (°C)	460	462	460	468	470	474
$T_{30\%}$ (°C)	515	519	522	544	583	616

Electrical properties of PEN/GN nanocomposites

PEN is an excellent insulating material, with electrical resistivity of about 10^{13} Ω cm, whereas GN have similar electrical characteristics to metallic/semimetallic materials. The resistivity of the PEN/GN nanocomposites measured at room temperature as a function of GN loading is shown in Fig. 5. The incorporation of GN could greatly decrease the resistivity of composites with a sharp transition from an electrical insulator to an electrical conductor. The percolation threshold of PEN/GN nanocomposite prepared from masterbatch route was around 5 wt%, which was much lower than that of composites filled by conventional method.

The percolation threshold for the resistivity depends very much on the dispersion and geometry of the conducting fillers [19]. We believed the low graphite content of electrical percolation threshold for PEN/GN nanocomposites is associated with the result that the GN were dispersed homogeneously in the PEN matrix by wrapping of PNP on GN, in agreement with the SEM observations. On the other hand, fillers with elongated geometry such as sheets can be used to achieve a very low percolation threshold value, due to the fact that sheets with higher aspect ratios have great advantage over spherical or elliptical fillers in forming conducting networks in polymer matrix [29]. The resistivity slowly decreased when the GN content was above 5 wt%. This is because once the

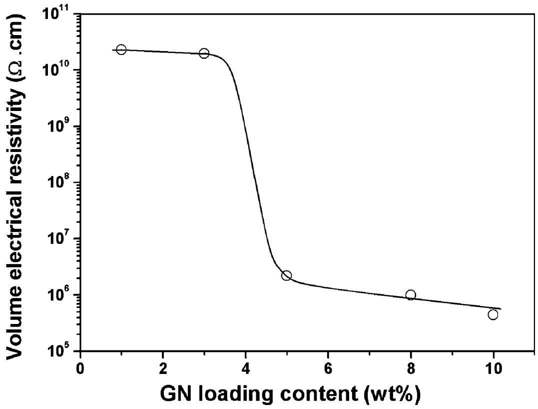

Fig. 5 Effect of GN content on the resistivity of PEN/GN nanocomposites

conductive network formed; a further increase of the GN loading had no obvious influence on the resistivity of the composite. It is noticeable that the electrical resistivity of 10^6 Ω cm of PEN/GN nanocomposites is low enough to attain the electrostatic dissipation and/or partial electromagnetic dissipation for thermoplastics and fibers.

Mechanical properties

The tensile strength and modulus of the composites are shown in Fig. 6a. It was found that the tensile strength and modulus of composites dramatically increased with GN content. The tensile strength and modulus of the 10 wt% GN loading increased by 18 and 30% compared to those of neat PEN, respectively. GN was effective to increase tensile strength in PEN matrix. However, tensile strength of 10% GN loading was similar to that of 8% GN loading which is a critical point of tensile strength for PEN/GN nanocomposite. Figure 6b shows the strain–stress curves of PEN/GN nanocomposites with various GN loading contents. It can be seen that the elongation of GN-reinforced PEN nanocomposites reduces with the increasing GN loading content. The 10 wt% GN loaded nanocomposite did not affect the elongation a lot, though the stress increased. GN showed higher effect on modulus increase than tensile strength.

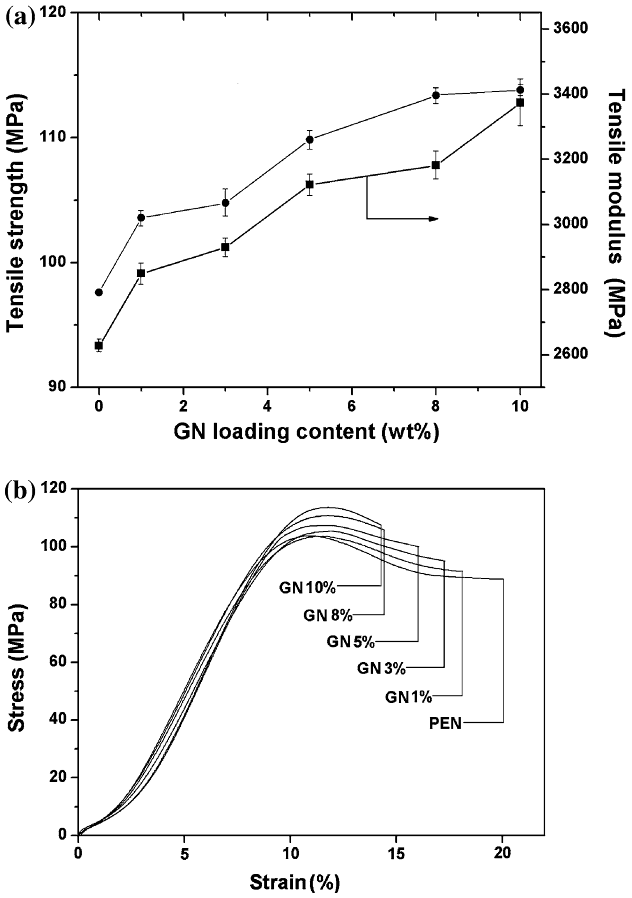

Fig. 6 **a** Effect of GN content on the tensile strength and tensile modulus of PEN/GN nanocomposites. **b** Stress–strain curves of PEN/GN nanocomposites

The flexural strength and modulus of PEN/GN nanocomposites are shown in Fig. 7. It can be seen that flexural strength and flexural modulus increase significantly with the increasing GN loading content. Comparing the mechanical properties of 10 wt% GN-reinforced composite with neat PEN, the modulus increases by about 90% and flexural strength increases by about 25%, respectively. It is now 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 [30]. In this paper, the increase of the modulus and strength are due to the fact that PNP improves the dispersion of GN in PEN matrix, and PNP due to the coating of GN modifies drastically the interface leading to the interfacial interaction enhancement and thus promotes a better stress transfer between GN and PEN matrix. On the other hand, according to the previous researches [31], the improvement of the dispersion also increases the average aspect ratio of the nanofillers in the polymer matrix and, as a consequence, mechanical properties also improved. Here apparently, GN are able to reinforce the PEN matrix due to their large aspect ratio combined with high mechanical properties. The improvements in the mechanical properties also verify the uniform dispersion of GN in the PEN matrix.

Figure 8 shows SEM images of fracture surfaces of the neat PEN resin and the nanocomposite containing 5 wt% of GN. It can be seen clearly that GN disperse uniformly in the PEN matrix, indicating that the GN masterbatch

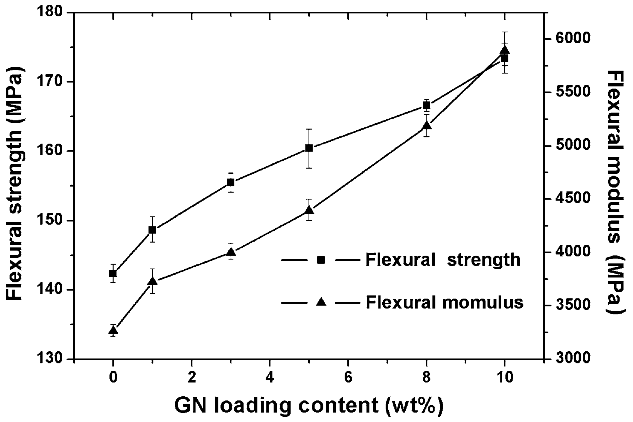

Fig. 7 Effect of GN content on the flexural strength and flexural modulus of PEN/GN nanocomposites

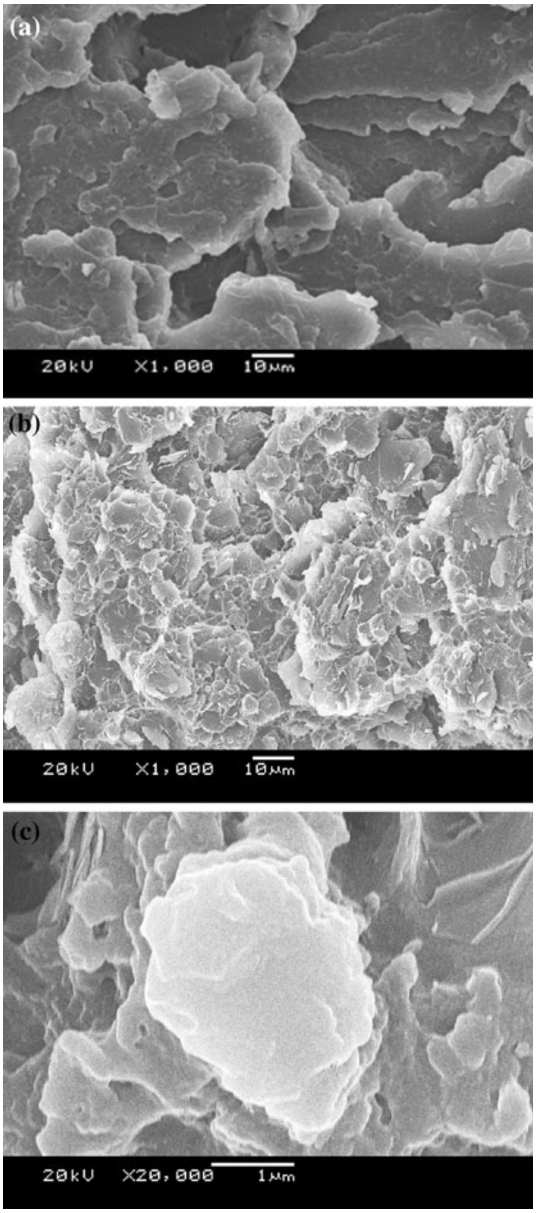

Fig. 8 SEM images of fracture surfaces of **a** neat PEN, **b** PEN with 5 wt% of GN, and **c** enlarged **b**

technique under the process conditions used in this study is effective in compounding GN with PEN. Besides, no "pull-out" was observed in the nanocomposite. Compared with the polymer/CF and polymer/GF composites with the appearance of fiber "pull-out", the GN have relatively good adhesion with the polymer matrix [27].

Rheological characterization

According to linear viscoelastic theory, the dynamic storage modulus G' for homogenous polymer system is proportional to ω^2 at low frequencies (terminal zone). However, for heterogeneous polymer systems, G' is no longer proportional to ω^2. Such deviation from the linear viscoelastic properties is significant, especially for particulate-filled polymer system.

The dependence of the dynamic storage modulus (G') on ω for neat PEN and PEN/GN nanocomposites is shown in Fig. 9. At low frequencies, PEN chains are fully relaxed and present typical terminal behavior with the scaling properties of about $G'\alpha\,\omega^2$, which is consistent with Cox–Merz rule [32]. With addition of GN, the dependence of low frequency G' on ω weakens. This indicates that the large scale polymer relaxations are restrained by the presence of GN effectively. As the GN loadings increase, the particle–particle interactions come to play a dominant role in the viscoelastic behavior. As a result, a transient network, the so-called rheological percolation structure, can be formed which is attributed to a filler network formed in the nanocomposites.

To further determine the threshold of the rheological percolation, the relation between G' at 0.01 rad/s and GN loading for PEN/GN nanocomposites was investigated, as shown in Fig. 10. Clearly, G' increases sharply between 3

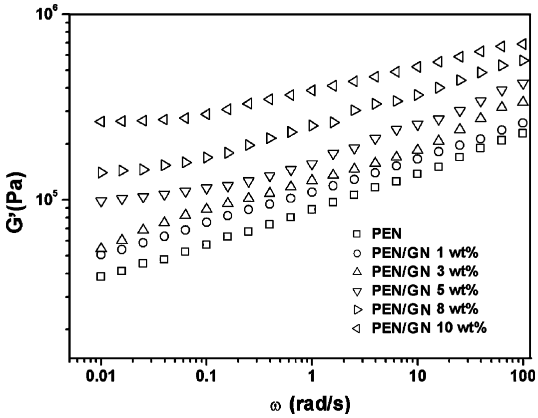

Fig. 9 Dynamic storage modulus (G') for the neat PEN and PEN/GN nanocomposites obtained in dynamic frequency sweep

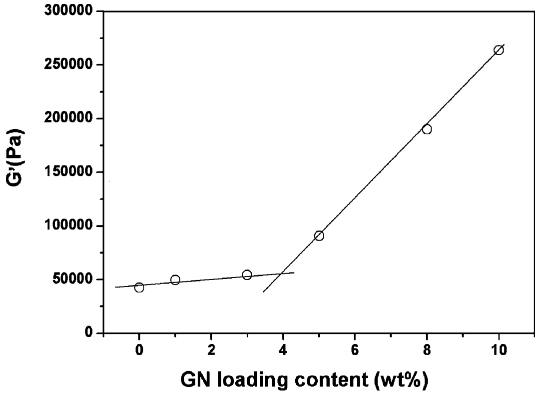

Fig. 10 The plots of dynamic storage modulus at 0.01 rad/s vs. GN loadings

and 4 wt% loadings, indicating that there is a sudden change in the material structure. At this loading level, the GN have formed a rheological percolation network, highly impeding the motion of polymer chains. Compared with our previous work, the addition of PNP would allow developing favorable interaction between PEN and GN, and thus, better interconnected and percolated structure of GN was produced in PEN matrix.

Conclusions

GN reinforced PEN nanocomposites with significant improved electrical, thermal, and mechanical properties were successfully fabricated via masterbatch route with a twin-screw extruder. The morphological characterization confirmed that GN were distributed uniformly, indicating a good dispersion of nanosheets in the PEN matrix by coating PNP on the GN surface. The incorporation of GN into PEN showed the significant improvement in thermal stability and HDT of nanocomposites. Electrical conductivity of the polymer was dramatically enhanced at low loading level of GN; the electrical percolation of was around 5 wt% of GN. The addition of GN into the PEN also had great impact on the mechanical properties of the nanocomposites. For 10 wt% of GN-reinforced PEN composite, the tensile strength increased by about 18%, the tensile modulus increased by about 30%, the flexural strength increased by about 25%, and the flexural modulus increased by 90%. The improvements of mechanical properties are due to the good adhesion between GN and PEN matrix and a certain degree of load transfer from resin to the GN. Rheological properties of the PEN/GN nanocomposites also showed a sudden change with the GN loading content; the percolation threshold was in the range of 3–4 wt% of GN.

Furthermore, these results reveal that using PNP/GN masterbatch to manufacture plastic parts is a very promising route. Such a route allows keeping the functional benefits of well-dispersed GN, whereas limiting the handling difficulties in plastics processing industrial workshops.

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