

Effects of Graphene Nanosheets on the Dielectric, Mechanical, Thermal Properties, and Rheological Behaviors of Poly(arylene ether nitriles)

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ABSTRACT: Poly(arylene ether nitriles) (PEN) containing various contents of graphene nanosheets (GNs) was prepared via solution-casting method and investigated for their dielectric, mechanical, thermal, and rheological properties. For PEN/GNs nanocomposite with 5 wt % GNs, the dielectric constant was increased to 9.0 compared with that of neat PEN (3.1) and dielectric losses of all nanocomposites were in the range of 0.019–0.023 at 1 kHz. The tensile modulus and strength were increased about 6 and 14% with 0.5% GNs, respectively. The fracture surfaces of the all PEN/GNs nanocomposites revealed that GNs had good adhesion to PEN matrix. The thermal properties of

the nanocomposites showed significant increase with increasing GN loading. For 5 wt % GNs-reinforced PEN nanocomposite, the temperatures corresponding to a weight loss of 5 wt % ($T_{d5\%}$) and 30 wt % ($T_{d30\%}$) increased by about 20 and 13°C, respectively. Rheological properties of the PEN nanocomposites showed a sudden change with the GN fraction and the percolation threshold was about 1 wt % of GNs. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1723–1730, 2012

Key words: dielectric properties; high performance polymers; nanocomposites; mechanical properties; rheology

INTRODUCTION

In comparison with conventional composites based on micro-fillers, incorporation of nano-fillers such as carbon nanotubes (CNTs) into polymers has received tremendous interest in material science to develop multifunctional nanocomposites with enhanced properties. Much of the excitement is due to the interesting properties those nano-fillers can exhibit, including high aspect ratio, high modulus, and excellent physical and electrical performances.¹ Potential applications of nanocomposites are also numerous, including aerospace and automotive materials (high temperature and light weight), packaging (films and containers), and dielectric materials (high dielectric constant and low dielectric loss).²

Nevertheless, previous investigations mainly focus on polymer/CNT composites. Since a new member of carbon family graphene combines the low cost of clay and the superior properties of CNT,³ graphene is a potential alternative to CNT as nano-fillers.¹ Graphene was first obtained through peeling single-

layer samples from graphite by Novoselov and coworkers.⁴ Afterwards, tremendous researches have been done on the preparation of graphene or modified graphene.^{5,6} Another interest focuses on polymer/graphene nanocomposites. Different polymer/GNs nanocomposites have been prepared by incorporating GNs into various polymer matrices, such as polyethylene^{7–9} polypropylene,^{2,10,11} epoxy,¹² poly(vinylidene fluoride),¹³ and poly(3,4-ethylenedioxythiophene).¹⁴ Previous results indicated that a small addition of GNs into polymer can realize good dispersion and increase thermal, mechanical, electrical and other properties. However, works on the rheological properties of the polymer/GNs systems are quite limited and no thermoplastic poly(arylene ether nitriles) (PEN)/GNs nanocomposites have been reported. PEN, as an engineering thermoplastic, exhibits excellent mechanical strength, radiation resistance and strong chemical inertia.^{15–17} The potential crosslinking nitrile groups on the aromatic ring in PEN promotes adhesion of the polymer to many substrates¹⁸ and PEN can easily be readily processed into shaped forms. Thus, PEN is a good polymer matrix which can be used to prepare advanced materials. Up to now, several attempts have been made in our lab to further multi-functional PEN composites for special areas such as aerospace and military,^{19–24} for example, PEN/CNT nanocomposites.

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Thus in this study, to expand various advantages and applications of GNs and PEN materials, especially in the fields required for high performances in dielectric, mechanical, and thermal properties, we report a facile method to prepare PEN-based nanocomposites containing GNs. For this purpose, we first prepared GNs via acid treatment and rapid thermal expansion followed by long-time exfoliation, and then prepared the PEN/GNs via a facile solution-casting method. The rheological, mechanical, thermal, and morphological properties of as-prepared nanocomposites were investigated.

EXPERIMENTAL

Materials

PEN was synthesized from 2, 6-dichlorobenzonitrile with bisphenol A in our laboratory. Its viscosity is 1.22 dL/g (0.005 g/mL in *N*-methyl-2-pyrrolidinone (NMP)). NMP was obtained from Tianjin BODI chemicals. Natural graphite was purchased from Qingdao Yanxin Graphite, China. The mean diameter is about 500 μm .

Preparation of GNs

GNs were fabricated by acid-intercalated expanded natural graphite (EG) followed by applying a cost- and time-effective exfoliation process in a microwave environment as described in the previous report.⁸⁻¹²

Synthesis of PEN/GNs nanocomposites

PEN nanocomposites with various GNs loadings were prepared via solution casting method. First, a certain weight of GNs was added in NMP under sonication for 30 min. Meanwhile, weight-measured PEN was dissolved in NMP with a mechanical stir. The mixture was refluxed at 200°C for 30 min after PEN was totally dissolved. Second, first-ultrasonic GNs was added to PEN under sonication and mixed with a high-speed mechanical stir for 60 min. And then the mixture was put on a clean preheated glass plate and cast solvents using a sequential mode of temperature program at 60, 80, 100, 120, 140, 160, and 200°C for 1 h, respectively. Then it was cooled to room temperature gradually and the PEN/GNs nanocomposite films were obtained.

Measurements and characterizations

Morphological characterization

The morphology of GNs and fracture surfaces of the PEN/GNs 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.

Dielectric measurements

Dielectric properties for the PEN/GNs nanocomposite films were performed by using a dielectric analyzer (DEA 2970, TA Instruments). The experiments were performed at frequencies from 100 Hz to 100 kHz at 20°C with 40% humidity. For sample preparation, the nanocomposite films were cut into small pieces (length: 10 mm, width: 10 mm, and thickness: 70~90 μm), and coated with conductive silver paste on both surfaces.

Mechanical measurements

The tensile test of the PEN/GNs composites was 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. The final results were the average values of five replicate measurements.

Thermal measurements

Glass transition temperature (T_g) was measured on TA instrument DSC Q100, at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) of composites 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.

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'), loss modulus (G'') and complex viscosity (η^*) as a function of angular frequency range from 0.1 to 100 rad/s at 320°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 DISCUSSIONS

The SEM image of expanded natural graphite (EG) is shown in Figure 1(a). As described in the previous report,²⁵ EG has a worm-like structure. After a series of post-treatments, the worm-like structure was destroyed and EG could be effectively separated into very thin GNs [Fig. 1(b)]. The thickness of GNs is in the range from 10 to 30 nm and its diameter is

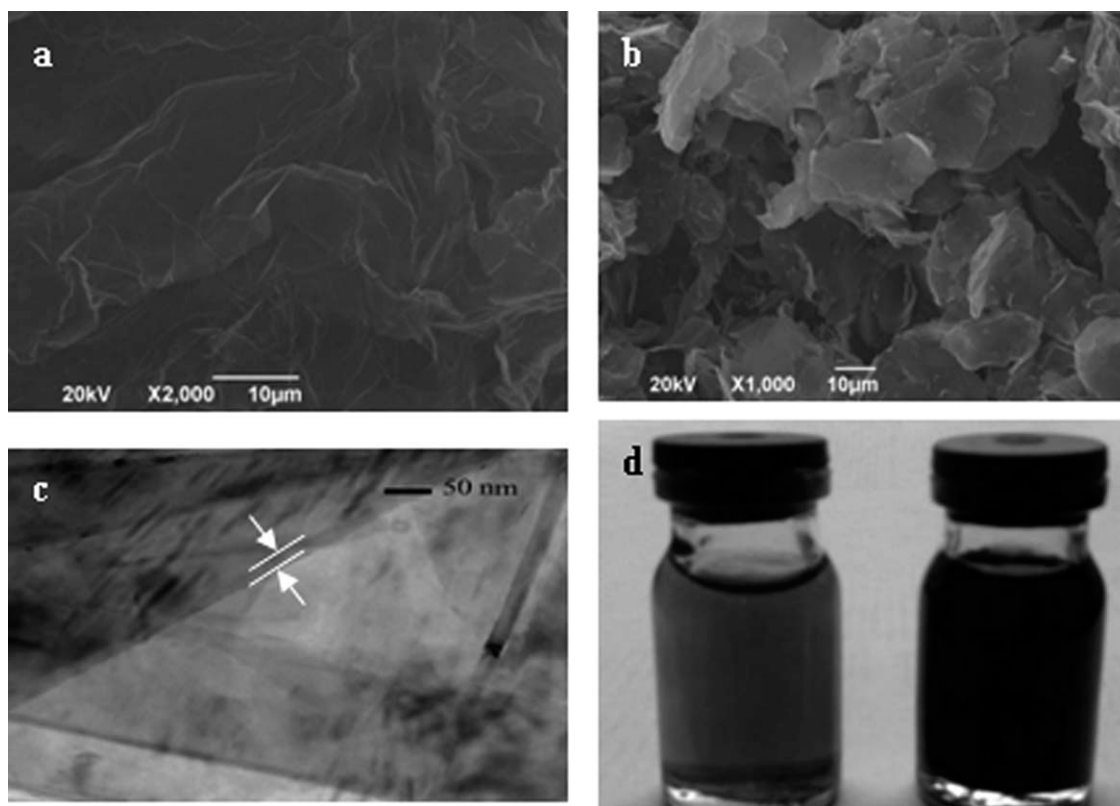


Figure 1 (a) SEM image of EG, (b) SEM image of GNs, (c) TEM image of GNs, and (d) photograph of GNs dispersed in NMP (0.5 and 5 mg/mL, respectively).

mostly from 1 to 20 μm [Fig. 1(c)]. Thus, GNs exhibit an aspect ratio (diameter to thickness) as high as around 100 to 500. Besides, the structure of the isolated GNs is very different from that of the EG. For graphene, the strong exfoliation energy of the *p*-stacked layers in graphite, that is, the high cohesive van der Waals energy (5.9 kJ/mol) makes GNs easily adhere to another and thus they are often indissoluble in many solvents.²⁶ However, it was found that GNs after preparation with a series of chemical and physical treatments could be well dispersed into NMP in different concentrations [Fig. 1(d)]. This offered convenience for preparing uniform PEN/GNs nanocomposite films.

As we know, PEN is an excellent insulating material, with volume resistivity of about 10^{13} $\Omega\cdot\text{m}$, whereas GNs have similar electrical characteristics to metallic/semimetallic materials. So the incorporation of GNs may increase dielectric constants of PEN. Figure 2(a) shows that dielectric constants increased linearly with the increase of GNs loading at 1 kHz as we expected. Typically, the dielectric constants of the PEN/GNs nanocomposite with 5 wt % GNs increased by 190.3% up to 9.0 compared with that of neat PEN (3.1). In addition, the dielectric losses of PEN/GNs films are all in the range from 0.019 to 0.023 at 1 kHz. Generally, dielectric properties are also related with frequencies. Therefore, studying

dielectric constant and loss versus frequency for high energy density films is necessary for application demand, and high energy density films should possess such typical characteristics as high dielectric constant and low dielectric loss.^{19–21} Figure 2(a) shows that dielectric constants of PEN/GNs nanocomposite with 5 wt % GNs decreased slightly from 9.0 at 100 Hz to 8.6 at 10 kHz, less than 0.5. The dielectric losses show similar trend. These results indicate that dielectric properties of PEN/GNs have little frequency dependence in the given frequencies, which is quite beneficial to their potential applications.

Figure 3(a) shows the influence of GNs content on mechanical properties of PEN/GNs composites. The tensile strength and modulus of 0.5 wt % GNs loading significantly are increased by about 6 and 14% compared with those of neat PEN, respectively. However; tensile strength decreases with the higher GNs content (>0.5 wt %) while tensile modulus reaches its maximum to 2493 MPa with 1 wt % GNs loading and then slightly drops, but they are still much higher than that of neat PEN. These results indicated that GNs showed higher effect on the tensile modulus than tensile strength. As shown in Figure 3(b), the elongation of the composites decreases; but elongation of 0.5 wt % GNs loading (5.3%) is still very similar to that of neat PEN (5.7%). Besides, the photograph in the Figure 3(c) demonstrates the

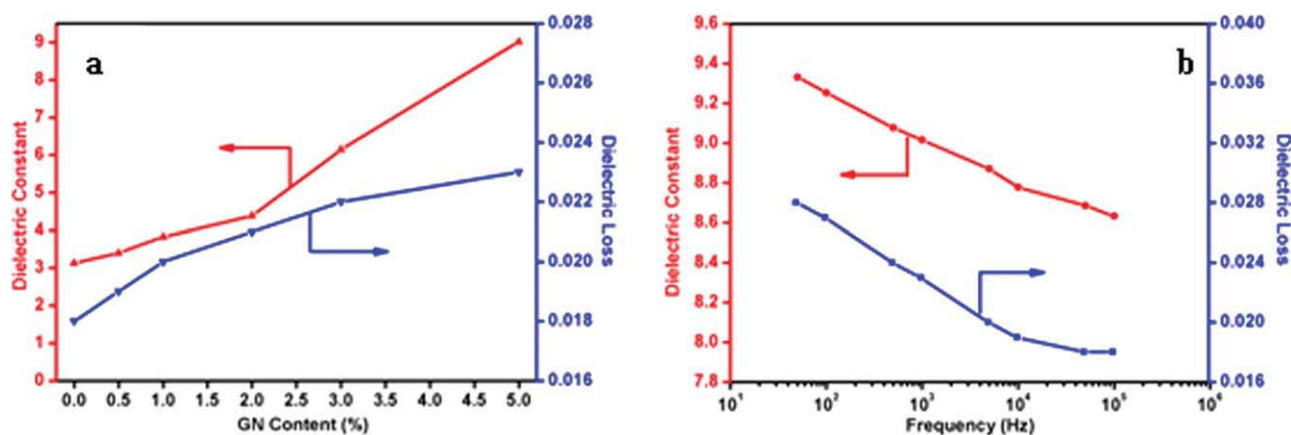


Figure 2 (a) Effects of GNs content on dielectric constant and dielectric loss of PEN at 1 kHz and (b) dielectric constant and dielectric loss versus frequency for the composites with 5% GNs concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

high degree of flexibility of the PEN/GNs nanocomposite thin film even with 5 wt % GNs loading. These results indicate that mechanical performance of PENs was strengthened with the addition of GNs.

It is now a consensus that the mechanical performances of polymer-based nanocomposites, espe-

cially the modulus, depend largely on the filler dispersion and interfacial interaction.²⁷ The dispersion of GNs that restricted the mobility of polymer chains of PEN improved the tensile modulus and the strength in low content. In addition, the high aspect ratio, high modulus and strength of GNs also

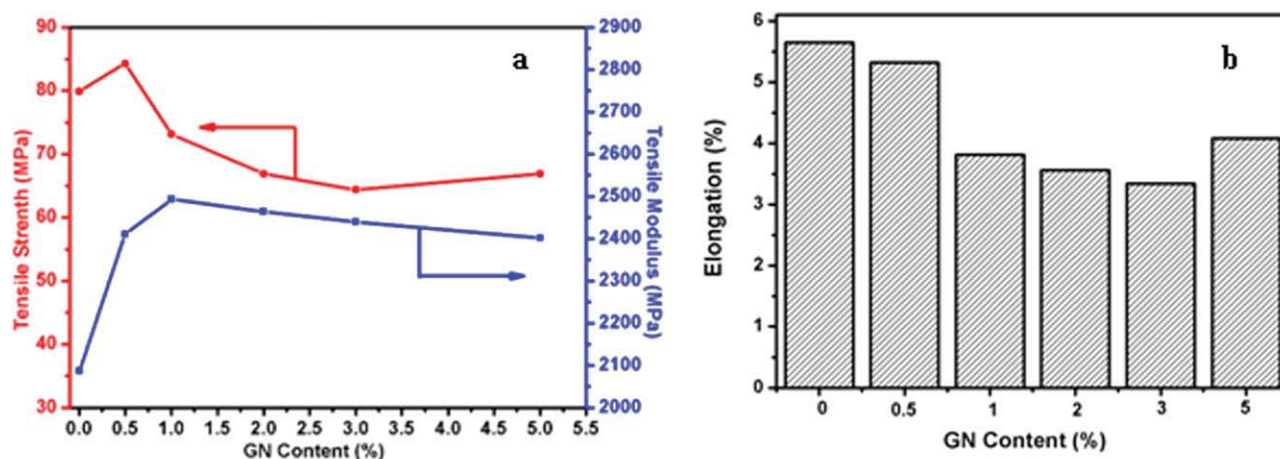


Figure 3 Mechanical properties of neat PEN and PEN/GNs composites: (a) tensile strength and modulus, (b) elongation at break, and (c) photograph of PEN/GNs composite film with 5 wt % GNs content (length: 15 cm, width: 5 cm, and thickness: 85 μm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

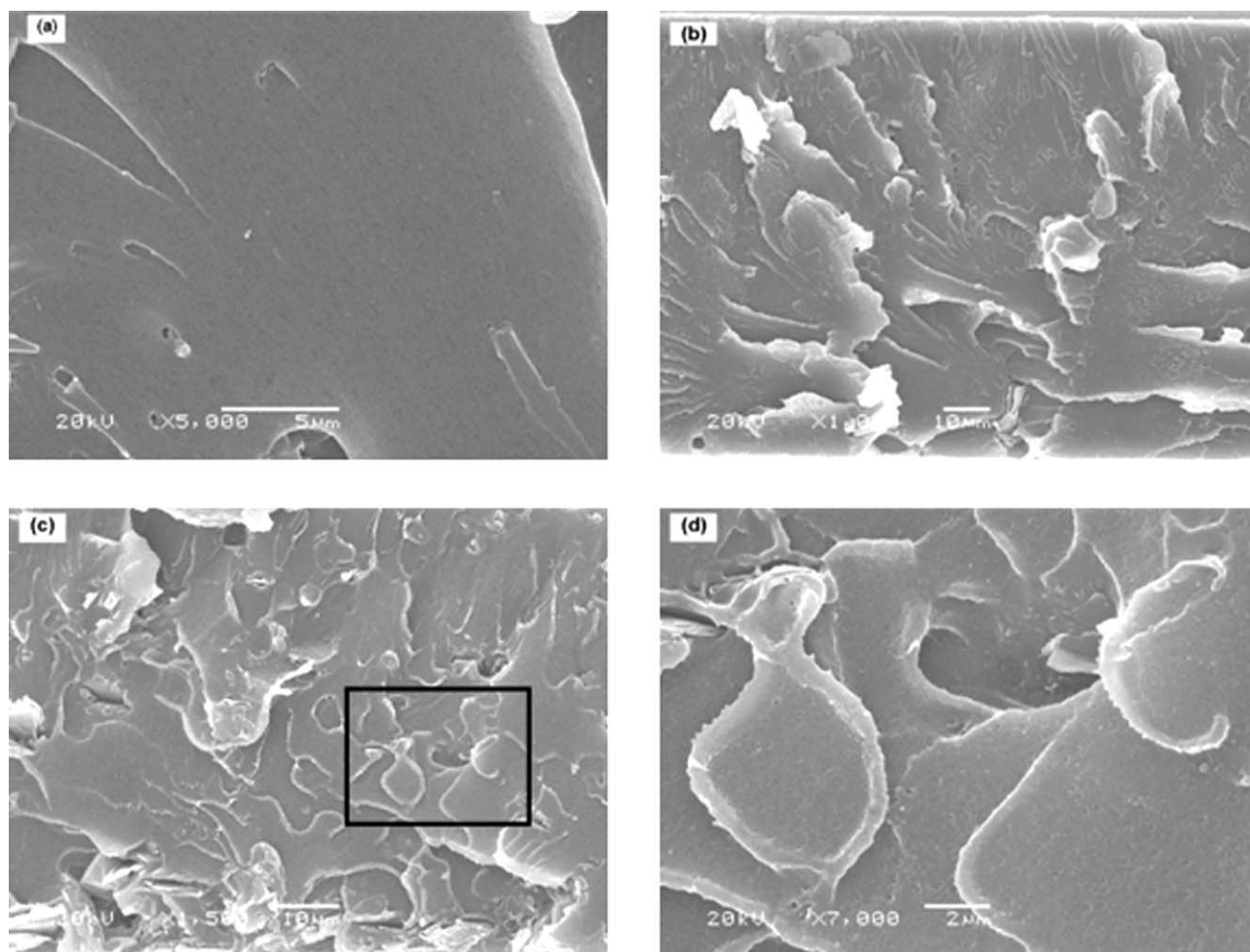


Figure 4 SEM images of fracture surfaces of (a) neat PEN, (b) PEN with 1 wt % of GNs, (c) PEN with 3 wt % of GNs, and (d) enlarged region of (c).

contributed to the reinforcement. However, the lessening of strength with higher GNs content may be ascribed to the not homogeneous dispersion of GNs in higher loading systems.

The mechanical properties of the PEN/GNs nanocomposites could be also explained by morphology to determine the dispersion of GNs in the PEN matrix. Figure 4 shows SEM images of fracture surfaces of the neat and GNs-phased specimens. The neat PEN [Fig. 4(a)] exhibits a relatively smooth fracture surface while fracture surface of nanocomposite with low GNs loadings [Fig. 4(b)] is wavelike and that of high GNs [Fig. 4(c)] loading is fish scaly probably due to nonuniform dispersion of GNs. From the enlarged SEM of Figure 5(d), it is clear that GNs exhibit good adhesion to neat PEN. Besides, no “pull-out” is observed in the nanocomposite. These results confirmed the enhancement of the mechanical performances investigated. Compared with the polymer/CF and polymer/GF composites with the appearance of fiber “pull-out,” GNs have relatively good adhesion to the polymer

matrix.²⁸ These results indicate that GNs are excellent fillers to provide excellent mechanical properties and decrease interface loss, which could probably improve thermal stabilities of PEN.

Therefore, DSC and TGA curves in Figure 5 were plotted to show the effects of different GNs loadings on the thermal properties of PEN/GNs composites and the main results were summarized in Table I, in which glass transition temperature (T_g), the initial decomposition temperatures at weight loss 5%, 30% ($T_{d5\%}$, $T_{d30\%}$) were displayed. Overall, compared with the neat PEN, $T_{d5\%}$ and $T_{d30\%}$ of composites ascend significantly. For example, $T_{d5\%}$ and $T_{d30\%}$ of the PEN/GNs nanocomposite with 5 wt % GNs increased by about 20 and 13°C, respectively. This improvement is mainly attributed to good matrix-GNs interaction, nice thermal conductivity of the GNs and also due to GNs’ barrier effect.²⁹ With the introduction of GNs into the PEN, GNs serve as the mass transfer barriers against the volatile pyrolyzed products in the PEN matrix, eventually retarding thermal degradation of the nanocomposites.

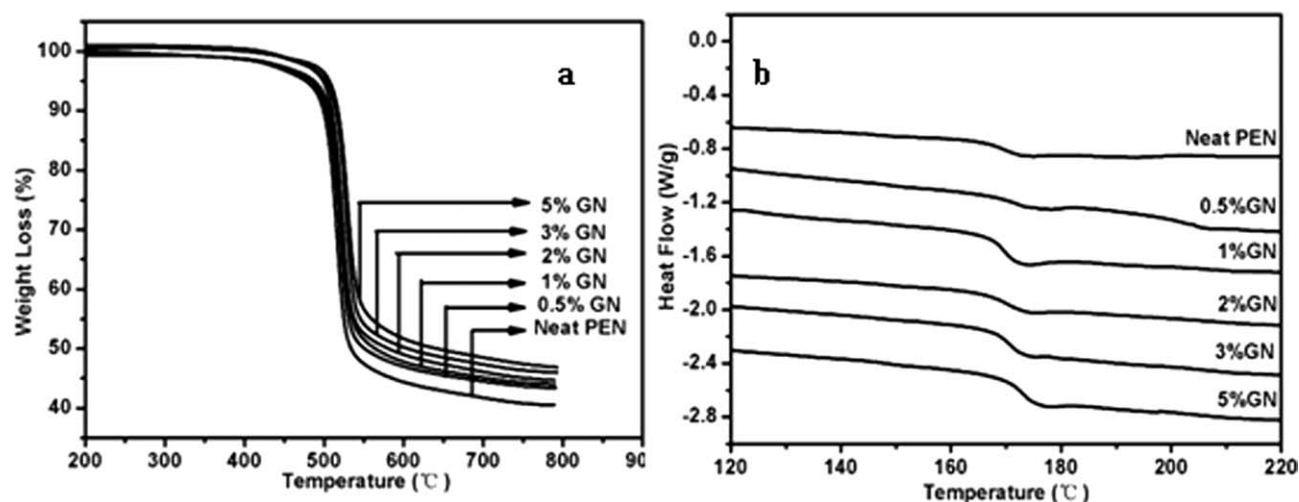


Figure 5 (a) TGA curves of neat PEN and PEN/GNs composites and (b) DSC curves of neat PEN and PEN/GNs composites.

However, GNs have little effective effect on the T_g of PEN. Furthermore; in comparison with PEN/CNT composites,²⁴ the glass transition temperature of PEN/GNs composites increased by over 10°C with the same filler content. This may be largely due to the different shapes of GNs and CNT: CNT is bar-like while GNs is flake-like. The contact area is larger among GNs as they contact by means of plane-to-plane, leading to strong molecular interactions.³⁰ Therefore, we believe that PEN/GNs composites with increased T_g will surely enlarge their applying scope.

Dynamical rheological measurements are also used to investigate the rheological behaviors of the PEN/GNs nanocomposites with various GNs loadings. The storage modulus (G') and loss modulus (G'') of the neat PEN and PEN/GNs composites with different GNs contents as a function of shear frequencies at 320°C are plotted in Figure 6. G' of PEN/GNs composites are increased with an increase in the oscillatory frequency. As the GN loading increases, higher G' are obtained, indicating that the large scale polymer relaxation was restrained by the presence of GNs effectively. This behavior has also been observed for other polymer/GNs systems.^{10,11} Moreover, the composites below 1 wt % GN loading shows almost the same slope of G' versus frequency with that of neat PEN in the terminal region. However, when GNs content is over 1 wt %, the flow

regime of PEN/GNs composites was significantly altered at low frequencies and a pseudosolid like behavior was more visible.^{10,28} This solid-like behavior can be due to the existence of interactions between GNs and polymer resin.³¹ It was also reported that fillers with small sizes are very likely to produce strong particle-polymer interactions even at very low filling rates.²⁸ In this paper, the preparation process of GNs made them into small and separate pieces. So, the high aspect ratio and huge surface area of GNs also increased the storage modulus of PEN/GNs composites.

Loss modulus (G'') of the neat PEN and PEN/GNs composites in Figure 6(b) shows the similar tendency with the G' . Interestingly, when GNs content is higher than 1 wt %, the flow regime of PEN/GNs composites once again was significantly altered at low frequencies and the slope of G'' decreased. From the results of the Figure 6, it is also observed that the increase of the G' of the PEN/GNs composites is greater than that of the G'' of the PEN/GNs composites in the specified frequency. Thus the effect of GNs on rheological behaviors of PEN is more sensitively reflected on the G' than on the G'' .³²

Figure 7 shows complex viscosity (η^*) of the neat PEN and PEN/GNs composites with different GNs contents at 320°C. Consequently, η^* values are increased with an increase of GNs loadings in the given frequencies. In addition, all PEN/GNs

TABLE I
Thermal Properties of PEN and PEN/GNs Nanocomposites

GN content (wt %)	0	0.5	1	2	3	5
T_g (°C)	168.5	169.9	169.3	169.5	170.9	172.7
$T_{d5\%}$ (°C)	481.4	489.1	487.6	494.1	493.8	501.3
$T_{d30\%}$ (°C)	515.8	520.2	522.8	523.4	525.2	528.1

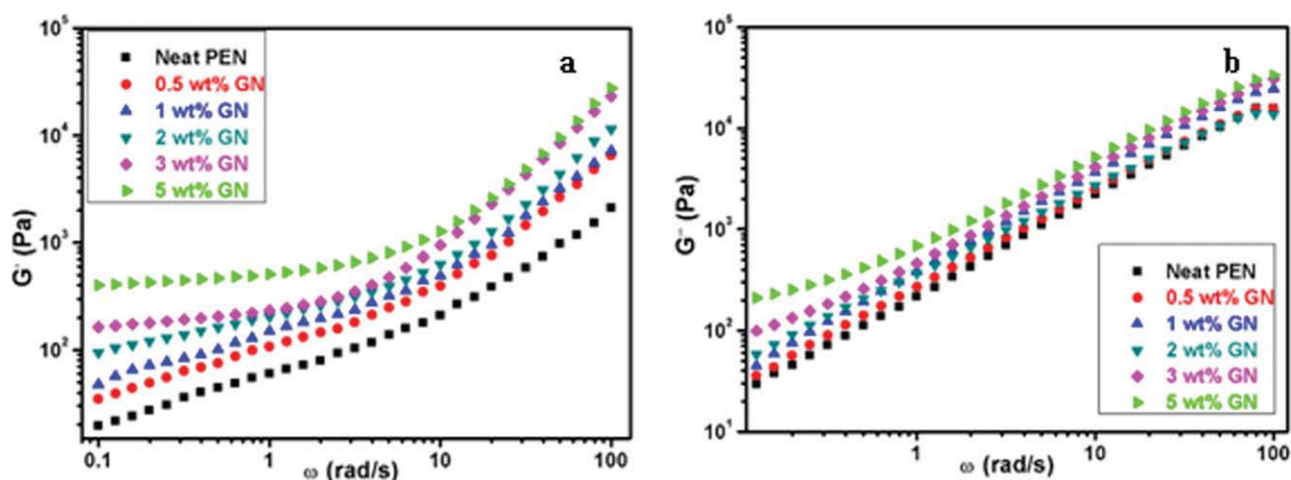


Figure 6 (a) Storage modulus (G') and (b) loss modulus (G'') of neat PEN and PEN/GNs composites with different GNs contents at 320°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composites exhibit a very strong shear thinning behavior and then nearly become independence of frequencies whereas the neat PEN almost behaves like a Newtonian fluid.¹¹ Moreover, the Newtonian region disappeared even if very low content of GNs (0.5 wt %) was added into the PEN resin. This implies that strong particle–particle interaction of GNs is one major factor that leads to an increase in shear viscosity of the PEN/GNs composites.

The low shear rate range is useful for discerning differences in the structure of the systems. From Figures 6 and 7, for the PEN/GNs composites, it has shown that the rheological properties such as storage (G') and loss modulus (G''), and complex viscosity (η^*) increase with the GNs content. Combined with the mechanical and thermal studies on PEN/GNs composites, we believe that the changes of rheological behaviors were mainly attributed to

interactions between fillers and polymer matrices. All these interactions can be detailed as follows. First, the existence of GNs occupied a specified space for movement of polymer chain. Second, GNs acted as bars in the process of the polymer motion. Third, the polymer chains can get stuck among the gaps of separate GNs layer. In addition, the decreased diameter of GNs after fabrication [Fig. 1(b)] provides huge surface area to react with polymer chains. Moreover, PEN/GN composites with small GN amount have well dispersions and thus lead to stronger effects above, which exhibited more obvious changes of rheological behaviors.

CONCLUSION

PEN/GNs nanocomposite films with significantly improved dielectric, mechanical, and thermal properties were successfully fabricated via solution-casting method. The results showed that dielectric constants were relatively high while dielectric losses were low and stable. Moreover, GNs exhibited higher effect on tensile modulus than tensile strength. The SEM images of fracture surfaces confirmed the enhancement of the mechanical performances and revealed that GNs had good adhesion to PEN. The thermal improvements were mainly attributed to good matrix-GNs interaction, nice thermal conductivity of the GNs, and GNs' barrier effect. Linear dynamic rheological measurements revealed that storage modulus (G') and loss modulus (G'') values of resin suspensions as a function of angular frequency increased with respect to GNs loadings. All PEN/GNs composites exhibited a very strong shear thinning behavior whereas the neat PEN almost behaved like a Newtonian fluid. In addition, there was a sudden change in rheological behaviors when the GNs loading content was around 1 wt %.

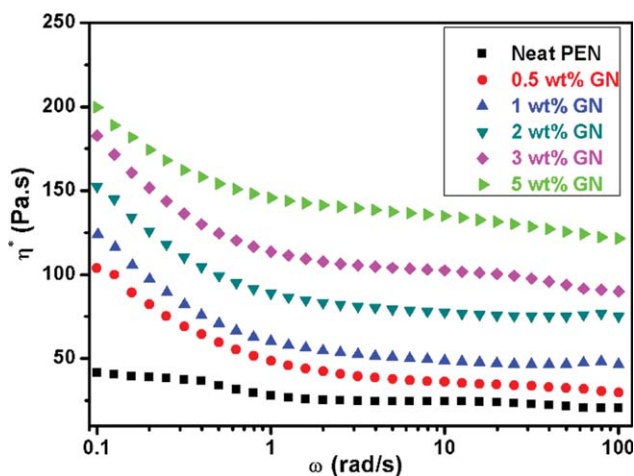


Figure 7 Complex viscosity (η^*) of neat PEN and PEN/GNs composites with different GNs contents at 320°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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