

Available at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/carbon

A graphite nanoplatelet/epoxy composite with high dielectric constant and high thermal conductivity

Chao Min ^{a,b}, Demei Yu ^{a,b,*}, Jingyu Cao ^c, Guolong Wang ^b, Lihua Feng ^b

^a Department of Applied Chemistry, School of Science, Xi'an Jiaotong University, Xi'an 710049, PR China

^b State Key Lab of the Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an 710049, PR China

^c Department of Computer Science & Technology, School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, PR China

ARTICLE INFO

Article history:

Received 22 July 2012

Accepted 8 December 2012

Available online 19 December 2012

ABSTRACT

A simple strategy for the preparation of composites with high dielectric constant and thermal conductivity was developed through a typical interface design. Graphite nanoplatelets (GNPs) with a thickness of 20–50 nm are fabricated and homogeneously dispersed in the epoxy matrix. A high dielectric constant of more than 230 and a high thermal conductivity of 0.54 W/mK (a 157% increase over that of pure epoxy) could be obtained for the composites with a lower filler content of 1.892 vol.%. The dielectric constant still remains at more than 100 even in the frequency range of 10^5 – 10^6 Hz. When loaded at 2.703 vol.%, GNP/epoxy composites have a dielectric constant higher than 140 in the frequency range of 10^2 – 10^4 Hz and a high thermal conductivity of 0.72 W/mK, which is a 240% increase over that of pure epoxy. The high dielectric constant and low loss tangent are observed in the composite with the GNPs content of 0.949 vol.% around 10^4 Hz. It is believed that high aspect ratio of GNPs and oxygen functional groups on their basal planes are critical issues of the constitution of a special interface region between the GNPs and epoxy matrix and the high performance of the composites.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

For smaller, faster, more flexible and higher performance embedded passives such as resistors, capacitors and inductors in integrated circuit, high dielectric constant (high- κ) polymer materials with high thermal conductivity is required [1]. Desirable and high-performance energy storage devices are needed to enable efficient, versatile, and environmentally friendly uses of energy including electricity. Hence, problems associated with electric charge storage, transportation and heat dissipation in these materials have been aggravated [2–6]. Normally, ferroelectric ceramic and metallic particles are incorporated into polymer matrix to achieve high- κ composites, which also present a number of limitations such as

high weight, low flexibility, and poor mechanical performance [2,7–10]. However, due to the low thermal conductivities of ferroelectric ceramics, large enhancement in thermal conductivity of the resulted polymer-based composites might not be easily realized. Meanwhile, the high volume fraction of traditional micro-scale spherical and rod-like thermal conductive fillers such as aluminum nitride (AlN), silicon nitride (Si_3N_4) and copper particles, which was necessary to achieve the high thermal conductivity of the composites, cannot afford excellent dielectric properties for the composites [11,12]. Therefore, the composites with combination of high dielectric constant and high thermal conductivity, though not easy to be achieved, possess great potential in the application of energy storage devices.

* Corresponding author at: Department of Applied Chemistry, School of Science, Xi'an Jiaotong University, Xi'an 710049, PR China. Fax: +86 29 82668559.

E-mail address: dmyu@mail.xjtu.edu.cn (D. Yu).
0008-6223/\$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
<http://dx.doi.org/10.1016/j.carbon.2012.12.017>

The existence of interface regions at polymer-filler interfaces has been revealed, and a concept of the multi-core model suggesting the importance of interface regions was proposed. The appropriate design of interface region becomes a critical issue for achieving high-performance materials [13–19]. Recently, several efforts have been performed with focus on interfacial controlling of polymer based composites. Core-shell structured barium titanate (BaTiO_3)/poly(methyl methacrylate) nanocomposites were successfully prepared through in situ atom transfer radical polymerization of methyl methacrylate from the surface of BaTiO_3 nanoparticles [20]. It was observed that all the nanoparticles were embedded in the polymer matrix due to strong interfacial bonding and excellent dispersion of the BaTiO_3 nanoparticles. The dielectric permittivity of the core-shell structured hybrid nanoparticles can be tailored by interface region design, that is, varying the polymer shell thickness, but with rare influence upon the relaxation process. Non-covalent and covalent functionalization of boron nitride (BN) nanoplatelets were performed by octadecylamine (ODA) and hyperbranched aromatic polyamide (HBP), respectively, and the effect of functionalized BN nanoplatelets on the thermal properties of epoxy composites was investigated [21]. The chemical reaction of HBP functionalized BN with epoxy matrix formed a strong interface, resulting in the best dispersion of nanoplatelets in matrix and the most increment of thermal properties. The physical molecular entanglements between ODA from non-covalent functionalized BN with epoxy matrix produced an intermediate interface interaction, which resulted in relatively good dispersion of nanoplatelets and the moderate improvement of thermal properties. The BN nanoplatelets showed weak interface for the BN/epoxy composites because neither chemical bonding nor molecular entanglement occurred between nanoplatelets and matrix.

In addition, owing to high aspect ratio, outstanding physical properties and cost efficiency, graphite nanosheets are considered to be effective filler for dielectric or thermal conductive enhancement in polymer matrix as compared to carbon nanotubes [5,22,23]. The morphology and dielectric properties of layered graphene nanosheet (GNS)/polyvinylidene fluoride composites were intensively investigated, and the composites exhibited much higher dielectric constant and lower percolation threshold than materials filled with carbon nanotubes, which was attributed to the orientation and homogeneous dispersion of GNS [24]. Epoxy resin showed poor thermal conductivity but the inclusion of graphite sheets resulted in significant improvements. A 5 wt.% graphite oxide-filled epoxy resin showed a thermal conductivity of $\sim 1 \text{ W/mK}$, which is approximately four times higher than that of the neat epoxy resin [25]. Despite of many researches on the graphite nanosheet/polymer composites, it is still interesting to explore an approach to obtaining a novel composite with high dielectric constant and high thermal conductivity through interface design. In this present work, we reported a simple strategy to fabricate very thin graphite nanoplatelets (GNPs) with unique characteristics. The aspect ratio of GNPs and the content of oxygen functional groups on basal planes are easily adjustable, which facilitate the interface designing when incorporated with epoxy matrix. A composite with high dielectric constant and high thermal conductivity could be achieved through an appropriate interface region design.

2. Experimental

2.1. Preparation of GNPs

Natural crystalline graphite flakes (80 mesh, Kuntai Graphite Co. Ltd., China) were intercalated by acid treatment (sulfuric acid and acetic acid). After thermal shock, the graphite was added into the acetone bath and sonicated in the ultrasonic equipment for exfoliation, and then the very thin GNPs were obtained in acetone solvent.

2.2. Preparation of GNP/epoxy composites

After heating the bisphenol type epoxy resin (D.E.R.331, DOW Chemicals) to 60°C , the curing agent (methyltetrahydrophthalic anhydride, MTHPA, DOW Chemicals) and GNP-acetone mixture were added into the epoxy resin under ultrasonication and continuously stirring for 1 h to obtain a uniform dispersion. Then the mixed epoxy system containing a certain content of accelerator (2,4,6-tri(dimethylaminomethyl) phenol, DMP-30, DOW Chemicals) was poured into a preheated mold at 90°C and cured with standard procedure. The weight ratios of epoxy, curing agent and accelerator were 100, 70, and 1, respectively. The volume contents of GNPs were employed in the range from 0.270 to 2.703 vol.%.

2.3. Characterization

The GNPs and fracture morphology of GNP/epoxy composites were examined using JSM 7000F scanning electron microscopy (SEM). The thermal conductive properties of the composites were measured with Netzsch LFA 457 Laser Flash Apparatus. The X-ray photoelectron spectroscopy (XPS) data was acquired on a Kratos Axis Ultra X-ray photoelectron spectrometer. Raman spectroscopy (LabRAM, T6400) was used to characterize the GNPs.

3. Results and discussion

3.1. Surface chemistry of GNPs

Fig. 1(a) illustrated that after the oxidation and ultrasonication, the graphite flakes completely exfoliated into very thin platelets, forming oxygen-containing GNPs. As shown in Fig. 1(b), the D band of GNPs becomes stronger and broader, suggesting a higher level of disorder of the graphene layers and defects introduced during the functionalization process. The ratio of the intensities (I_D/I_G) for GNP was slightly increased, indicating the formation of some sp^3 carbon after acid oxidation. The XPS results in Fig. 1(c) showed that the initial oxygen concentration on graphite was only a small proportion of 5.68%, but after oxidation and ultrasonication, it drastically increased to 27.15% along with the reduction in carbon content. High-resolution core-level C 1s spectra for GNPs was present in Fig. 1(d), and this band indicated that a considerable degree of oxidation with four major signatures corresponding to carbon atoms in different functional groups. The generation of oxygen functional groups, such as epoxide, hydroxyl, carboxyl and carbonyl groups would render the

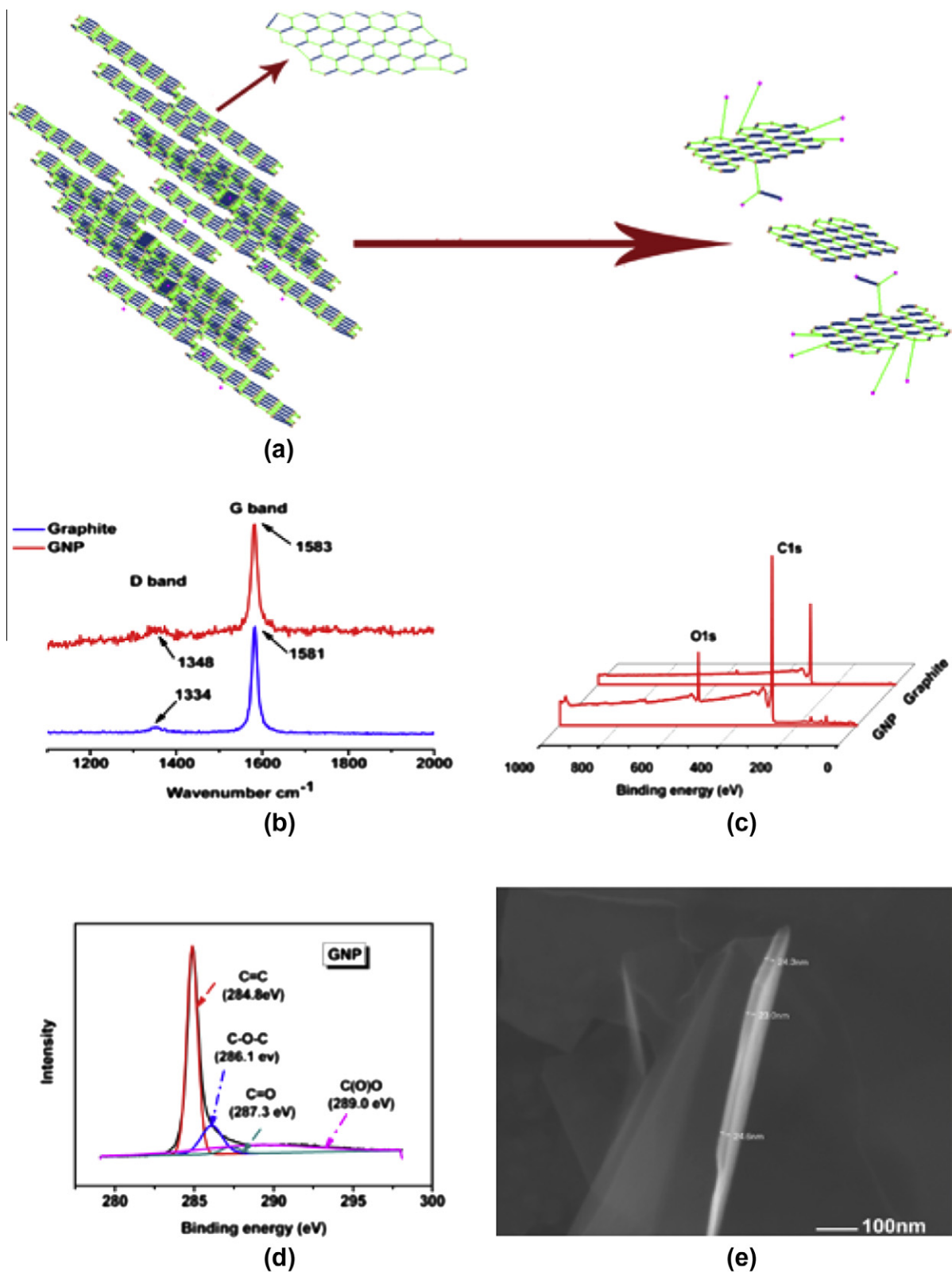


Fig. 1 – (a) A schematic of the surface change of Graphite nanoplatelets after oxidation and ultrasonication; (b) Raman spectra of graphite and GNP; (c,d) XPS general spectra and high resolution C_{1s} spectra of graphite and GNP; and (e) SEM image of GNPs.

GNPs somewhat hydrophilic and better compatibility with polymer matrix. After ultrasonic treatment, the expanded

graphite worms were fragmented into GNPs with the thickness of 20–50 nm, as shown by Fig. 1(e).

3.2. Morphology of GNP/epoxy composites

For the purpose of interface region designing, the controllable formation of oxygenic functional groups on the basal planes of GNPs was considered to be a critical issue. In order to realize the functionalization, the intercalated graphite flake was treated by thermal shock and ultrasonication. During the curing process of epoxy matrix, strong interfacial adhesion and chemical reaction were speculated to occur between functionalized GNPs and epoxy molecular chains, as illustrated in Fig. 2.

As revealed in Fig. 3, isolated GNPs were homogeneously dispersed in epoxy matrix and almost no large agglomerates or bundles were observed. The strong interfacial adhesion between oxygenic groups on the basal planes of GNPs and epoxy molecular chains led to high embedding and tight binding of GNPs in the matrix. For this reason, these wrinkled and isolated GNPs effectively prevents direct contact between graphite nanoparticles in the composite, which give advantages for forming a large microcapacitor network and suppressing the leakage current.

3.3. Dielectric properties of GNP/epoxy composites

The variations of the dielectric properties with increased frequency ranging from 10^2 to 10^6 Hz for pure epoxy and GNP/epoxy composites are shown in Fig. 4. At a lower frequency range (10^2 – 10^4 Hz), the dielectric constant of GNP/epoxy composite improved dramatically, and up to higher than 230 when the filler content was 1.892 vol.%. Moreover, this value still remained at more than 100 even in the frequency of 10^6 Hz. It was notable that at the filler content of 0.949 vol.%, the dielectric constant of the composite was almost frequency independent

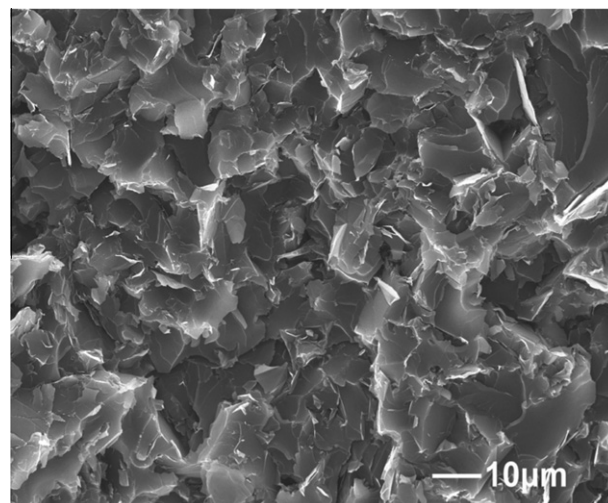


Fig. 3 – SEM fractographs of GNP/epoxy composite (the content of GNPs is 1.892 vol.%).

and reached above 60 over the frequency range of 10^2 – 10^5 Hz. The loss tangent of the composite, however, kept values lower than 0.3 around 10^4 Hz, which indicated a promising composite with high dielectric constant and low dielectric loss. As mentioned in the percolation theory, both the dielectric constant and loss tangent exhibit a transition behavior in the vicinity of percolation threshold. Thus, considerably high loss tangent of the composites with higher volume fraction of GNPs could be observed in Fig. 4(b). Normally, the conductivity of GNP/epoxy composites originated two mechanism: (1) Ohmic conduction (frequency independent), through direct contact

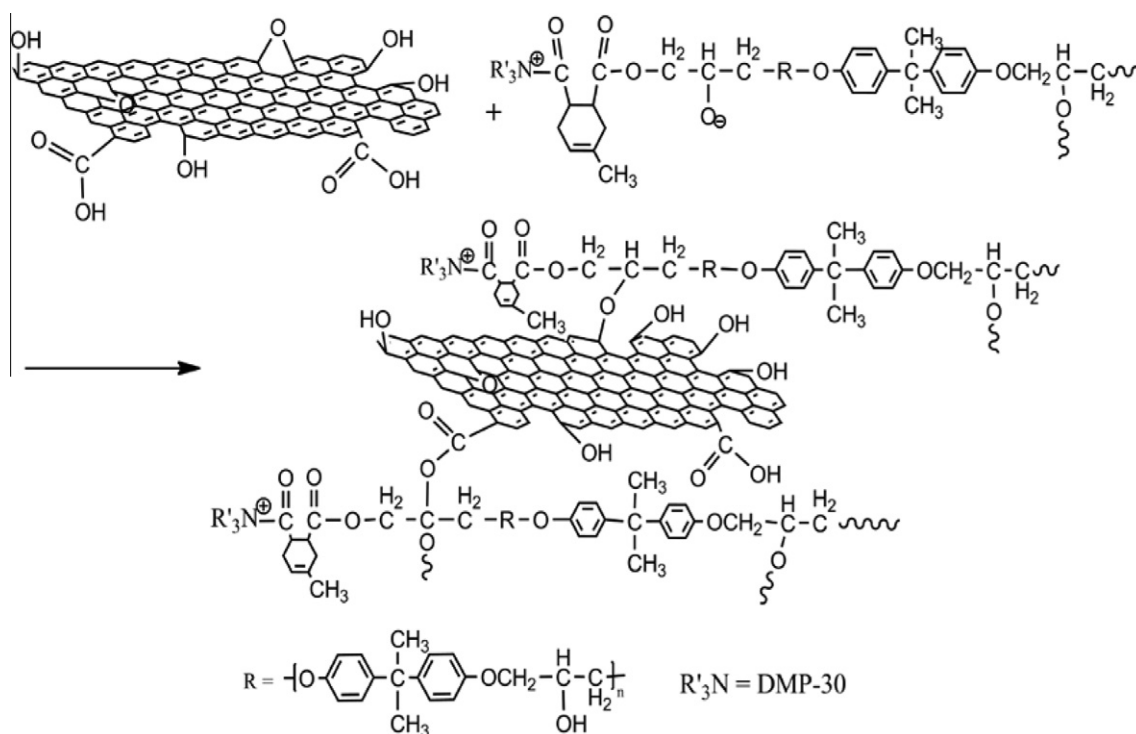


Fig. 2 – Chemical reactions between GNPs and epoxy matrix.

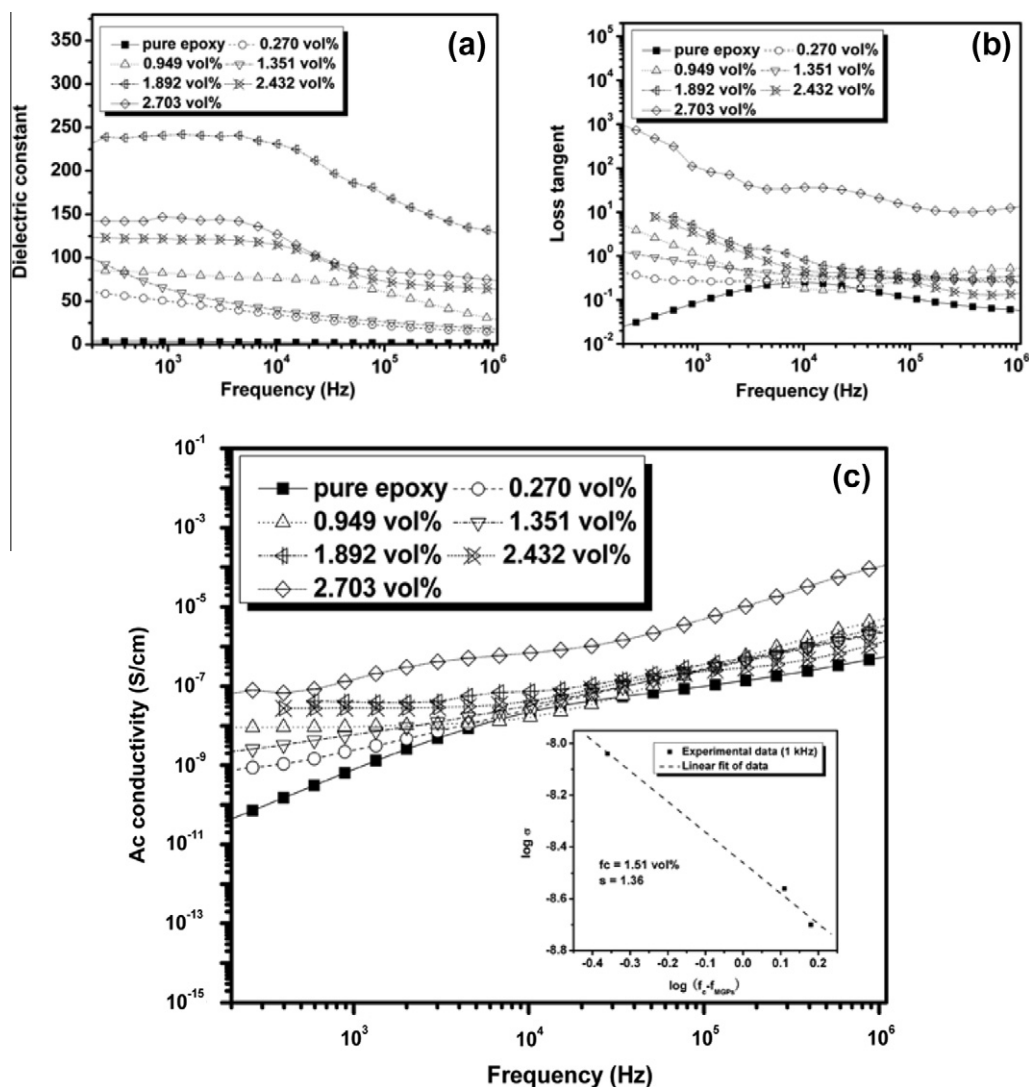


Fig. 4 – Dependence of (a) the dielectric constant, (b) dissipation factor and (c) ac conductivity of the GNP/epoxy composites on frequency at room temperature. The inset of (c) shows the best fit of the ac conductivity at 1 kHz to power law.

of GNPs, and (2) non-Ohmic conduction (frequency dependent), through the barrier-tunneling effect between GNPs separated by an epoxy layer. As revealed in Fig. 4(c), the percolation transition can be considered as the transition from non-Ohmic conduction to Ohmic conduction. When the filler content exceed a critical value (higher than 1.351 vol%), the variation of ac conductivities of the composites are frequency independent when the external field frequency is lower than 1 kHz. With further increase of external field frequency, the dipoles and charge carriers have less time to orient in the direction of the alternating field and the conduction mechanism comes back to the non-Ohmic conduction through tunneling effect. Therefore, the percolation threshold need to be calculated in the frequency range that the insulator-to-conductor transition occurs. According to the literature [26–29], the ac conductivities of the composites at 100 and 1 kHz were the mostly used data to calculate the percolation threshold. However, due to the large leakage current in the GNP/epoxy composites at lower frequency (i.e., at 100 Hz), we had to choose the latter frequency of 1 kHz. The ac conductivity σ of the

GNP/epoxy composites near the percolation threshold can be predicted by power law as follows:

$$\sigma(f_{\text{GNPs}}) \propto (f_c - f_{\text{GNPs}})^{-s} \text{ for } f_{\text{GNPs}} \leq f_c$$

where f_c is the percolation threshold, f_{GNPs} is the volume fraction of GNPs, and s is the critical exponents. The best fit of the experimental ac conductivity values to the plot of power laws give $f_c = 1.51$ vol.% and $s = 1.36$, and the critical exponent value is close to the value of PVDF/exfoliated graphite nanosheets [30]. Besides, it is notable that a high dielectric constant of more than 230 and a high thermal conductivity of 0.54 W/mK could be achieved simultaneously for the composite with the GNPs content of 1.892 vol.%.

The significant increase of dielectric constant can be mainly attributed to the interfacial polarization in heterogeneous epoxy system filled with GNPs and to the mini-capacitor principle. The former phenomenon is known as the Maxwell-Wagner-Sillars (MWS) mechanism which is caused by the large difference in dielectric constant between the polymer matrix and the fillers [26,27]. A large increase in permittivity

is observed at the percolation limit as in the case of electrical conductivity. The mini-capacitor principle can be invoked as being responsible for such increment [31]. With increase of GNPs content in polymer phase, the isolation distances between neighboring GNPs are continuously reduced. Finally, a network of mini-capacitors with the GNPs as electrodes and a very thin epoxy layer in between as dielectric can be formed in the composite near percolation threshold. Each mini-capacitor contributes an abnormally large capacitance, which can then correlate with the significant increase in the dielectric permittivity. At the percolation point, conductive paths are limited and the contribution of mini-capacitors to the conductivity is of large importance and becomes dominant after a critical frequency. Furthermore, a thin insulating layer of epoxy is combined with the GNPs to form a nanoscale structure in the composites, which can fully realized the advantages of GNPs (i.e., large specific surface area) and result in a huge interfacial area between GNPs and polymer in the nanocomposite, which in turn provides numerous sites for the reinforced MWS effect. As can be seen in the calculation of critical exponent, the value of s is higher than universal ones ($s = 0.8$ – 1) were explained by unusual models, such as the inverse Swiss-cheese model. The inverse Swiss-cheese model, which is based on a medium made of conducting particles embedded in an insulating matrix, where the conduction process is controlled by inter-particle tunneling. This in turn proves that the large increase of dielectric constant is mainly attributed to the formation of mini-capacitors in the composite. Besides, inhomogeneous composites were found to show better dielectric properties than the homogeneous composites [32,33]. Therefore, the inhomogeneous nature may be another reason for the large deviation of dielectric constant from the Maxwell relation. In our study, the GNPs obtained from thermal shock and ultrasonication may have different thicknesses and aspect ratios, which can lead to inhomogeneity. Thus, the fillers are not well dispersed, but rather stay touching other platelets forming interfaces between GNPs. The interface dipoles associated with GNP/GNP interfaces are thus apparently responsible for the increased permittivity. These interface dipole moments are thought to arise from the electronic that are trapped at the GNP/GNP interface electronic states, and the energy levels of these states are different from those of GNP/epoxy interface states.

The multi-core model of the interface has been prominent in a number of contributions concerning the dielectric behavior of composites [13,34,35], and the effective dielectric constant of the composite may be influenced through the variation of any of the interface characteristics [13,22,23]. Since the chemical structure of the interface region is a function of the polymer and its interaction with the surface of the filler particles, changes of the bonding situation between these two phases will alter the effective dielectric constant of the composite [20,36–39]. Therefore, the controlling of aspect ratio and surface chemistry of GNPs could be an effective way to realizing the interface designing, thereby achieving the composites with both high dielectric constant and high thermal conductivity. In this research, large diffusion cloud and out of phase dipole movement offered an explanation of the unusual high permittivity of GNP/epoxy composites at lower frequency range. With further increasing frequency of applied

field, the diffusion cloud lessened and with it the out of phase dipole movement. Meanwhile, when the filler concentration was sufficiently high, it would be possible for the diffusion clouds and ultimately the double layers to overlap, which give the explanation of large leakage current within the composites. Referred in the multi-core model, the structures of the second and third layers were presumed crucial in characterizing physical performances. Due to the high aspect ratio and multi-layered structure of GNPs, charges could easily diffuse through the inside graphene layers of GNPs, which functioned as highly conductive channels in the first layer. Besides, the oxygenic groups on the basal planes of GNPs afford sufficient covalent and non-covalent bonds with epoxy matrix molecule chains in the second and third layer, which decrease the carrier traps and increase the hole mobility. Coupling with the high conductivity of GNPs, the collaborative effects of multi-layers in the interface region brought about the composites with high dielectric constant even at very low filler content. Thus, the strategy of interface design is feasible in our research. Fig. 5 illustrates the multi-core model of the interface region of GNP/epoxy composites.

3.4. Thermal properties of GNP/epoxy composites

As expected, the thermal conductivities of the polymeric composites were strongly dependent on the GNPs content, with higher volume fractions consistently resulting in higher thermal conductivities of the composites, shown in Fig. 6. When the filler content was 2.703 vol.%, the thermal conductivity of the epoxy resin achieved 0.72 W/mK a 2.4-fold improvement, which showed large advantages comparing to that of composites filled with AlN, Si₃N₄ and copper particles [11,12,40]. Meanwhile, with the incorporation of 2.703 vol.% GNPs, the dielectric constant of the composites was higher than 140 at 10^2 – 10^4 Hz, accompanied by considerably dielectric loss.

Recently, it was found that fillers with high aspect ratio, such as whiskers and platelets, can form more continuous thermally conductive pathways in the polymer matrix and thus are more effective in enhancing the thermal transfer [41]. Combined with the high intrinsic thermal conductivity of GNPs, these offered reasonable explanations for the larger increment of thermal conductivity of GNP/epoxy composites with increasing filler content than traditional thermally conductive fillers. It has been acknowledged that the thermal conductivity of polymeric composite is mechanistically limited by the polymer-filler interfacial thermal resistance, resulting from the presence of a weak interfacial interaction between soft epoxy layer and rigid GNP hinders the phonon transport [42–44]. With the oxygenic groups on the basal planes of GNPs, a homogeneous GNP network in the epoxy matrix could be achieved under relatively higher filler content, as also can be seen in the SEM fractographs of the composite. Thus the thinner polymer layers on the surface would decrease the scattering for the phonon transfer and promote the diffusion of phonons in the overall composites, which has been proved in the polymeric systems filled with carbon nanotubes or GNP/carbon nanotubes [45–48]. Surface modification of the particles had already been proved to be a wide applicable technique to prevent from the filler aggregation and enhance particle-matrix interfacial interaction, and enhanced interfacial

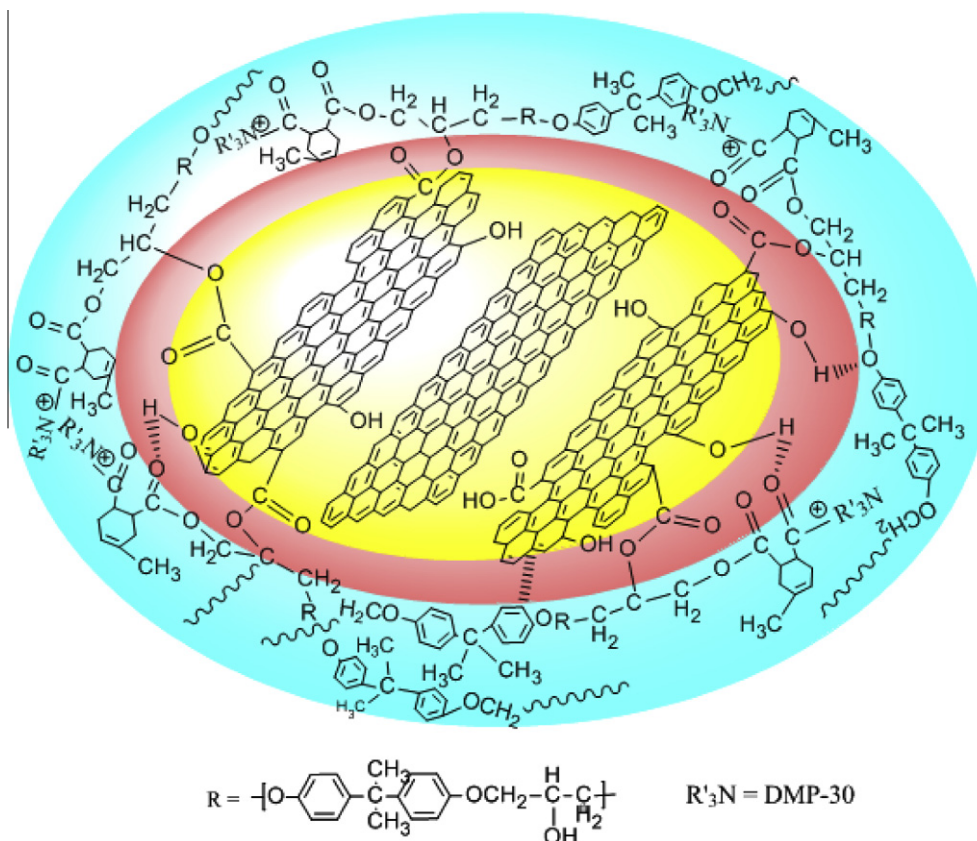


Fig. 5 – The multi-core model of the interface region of GNP/epoxy composites.

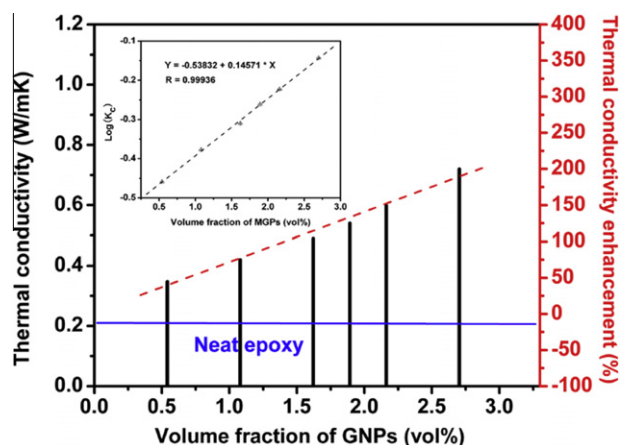


Fig. 6 – Thermal conductivity of pure epoxy and the composites with different GNPs content. The inset graph is the variation of logarithm value of thermal conductivity with different GNPs content.

adhesion by chemical bonding is an effective way to decrease interfacial thermal resistance [49–51]. The short and rigid interfacial bonding (covalent bonds) can cause significant reduction of the acoustic impedance mismatch and minimization of interfacial phonon scattering in the overall composites [52,53]. In GNPs, the inside graphene layers functioned as highly conductive channels for thermal transport, while the chemically functionalized outside layers could afford suffi-

cient covalent and non-covalent bonding with the matrix molecule chains, and facilitated the phonon transfer from the graphene oxide to the polymer matrix [5]. With the oxygenic groups on the surface of GNPs, the covalent bridge bonds between GNPs and epoxy molecular chains minimized the interfacial phonon scattering and decreased the interface heat resistance by interpenetrating particles-resin interface. Considering the multi-core model, the functional groups reacting with the epoxy molecule during the curing process built up the first layer through covalent bonds, which facilitate the phonon transportation. In addition, a collaborative effect among fillers through the second and third layer would work for better thermal conductivity, either, which had been illustrated in silica-polyimide composites [54].

Agari's semi-empirical model is based on the generalization of series and parallel conduction models in the composite and correlates thermal conductivity with the ability of fillers to create particle conductive chains. The logarithmic equation of Agari is [55]:

$$\log k_c = \phi C_2 \log k_f + (1 - \phi) \log(C_1 k_p)$$

where k_c , k_p and k_f are respectively the thermal conductivity of the composite, of the polymer matrix and of the fillers. ϕ is the filler volume fraction, and C_1 and C_2 are obtained by fitting experimental data. A logarithmic plot of thermal conductivity values as a function of the filler volume concentration is presented in the inset graph of Fig. 6, and the two parameters C_1 and C_2 were calculated to be 0.73 and -0.186 . The value of 0.73 for C_1 suggested that the GNPs with abundant functional

groups could affect the curing process of epoxy resin chains and decrease the cross-linking degree of the matrix. The low value of C_2 suggested that the GNPs have strong ability to create continuous thermal conductive chains, and the formation of conductive network becomes much easier with the incorporation of GNPs. As mentioned in recent results, when the size of fillers decreases from micro-scale to nano-scale, the C_2 value might have a negative value representing the overwhelming ability of GNPs to create continuous chains [12]. Besides, Agari and his co-workers assumed that there is a relationship between C_2 parameter obtained from the fitting of thermal conductivity data and the concentration at electrical percolation threshold when the polymeric matrix is filled with metallic particles. This assumption is possible if the crystallinity of the polymer does not change in the presence of filler particles. In this case, the Agari's model becomes:

$$\log(k_c/k_p) = \varphi C_2 \log(k_f/k_p)$$

Finally, Agari et al. showed that C_2 remains a curve fitting parameter that can be used to determine the electrical percolation threshold using:

$$C_2 = \log(1/\varphi_c)$$

where φ_c is determined as the volume concentration at the inflection point in the electrical resistivity versus filler concentration curve, i.e. concentration of electrical percolation. When C_1 is defined as unity and C_2 values from linear fitting of thermal conductivity of the composites ($C_2 = -0.186$), the value of φ_c is calculated to 1.53 vol.%. According to the analysis of dielectric properties, the percolation threshold of the GNP/epoxy composites was found to be 1.51 vol.%. Besides, one important assumption is that the crystallinity of the polymer does not change in the presence of filler particles. The GNPs took part in the curing process of epoxy resin and caused a lower C_1 value, which resulted in a higher C_2 value and lower φ_c value. Thus, the percolation threshold calculated from linear fitting of thermal conductivity showed accordance with that of dielectric experiment data.

4. Conclusion

A simple strategy to fabricate thin GNPs with unique characteristics was reported and the GNP/epoxy composites were successfully prepared. The thickness of GNPs was 20–50 nm and the presence of oxygen functional groups on GNPs were evidenced by the results of XPS and Raman spectroscopy. It was found that the homogeneous dispersion of GNPs in the epoxy matrix could significantly improve the dielectric properties of the composites with a low percolation threshold. A high dielectric constant of more than 230 could be obtained for the composites with filler content of 1.892 vol.% at a lower frequency range of 10^2 – 10^4 Hz. The dielectric constant still remained at more than 100 even in the frequency range of 10^5 – 10^6 Hz. Meanwhile, a high thermal conductivity of 0.54 W/mK, a 157% increase over that of pure epoxy, was observed for the composite with the same filler content. The composite with the GNPs content of 0.949 vol.% showed significantly increased dielectric constant and low dielectric loss in the vicinity of 10^4 Hz simultaneously, and had a weak frequency dependence of dielectric properties over a wide range of

frequencies. When embedded into epoxy matrix, the GNPs demonstrated a remarkable enhancement of the thermal conductivity at low-volume loadings (0.72 W/mK at 2.703 vol.% a 2.4-fold enhancement) and significantly outperformed traditional thermal conductive fillers. Simultaneously the dielectric constant was higher than 140 in the frequency range of 10^2 – 10^4 Hz for the composite with the GNPs content of 2.703 vol.%. In GNPs, the inside graphene layers functioned as highly conductive channels for thermal transport, while the chemically functionalized outside layers facilitated the phonon transfer from the platelets to polymer matrix through covalent bonding in the interface region. The multi-core model of the interface was used as a guidance of tailoring interface region of the composites and offered an explanation for both high dielectric constant and high thermal conductivity of the composites with low GNPs volume fraction. The interface design through the controlling of aspect ratio and the content of oxygen functional groups on basal planes of GNPs was proved to be feasible to obtain composites with high- κ and high thermal conductivity.

REFERENCES

- [1] Wang Z, Nelson JK, Hillborg H, Zhao S, Schadler LS. Graphene oxide filled nanocomposite with novel electrical and dielectric properties. *Adv Mater* 2012;24:3134–7.
- [2] Lu JX, Moon KS, Kim BK, Wong CP. High dielectric constant polyaniline/epoxy composites via in situ polymerization for embedded capacitor applications. *Polymer* 2007;48:1510–6.
- [3] Poot M, van der Zant HSJ. Nanomechanical properties of few-layer graphene membranes. *Appl Phys Lett* 2008;92:063111–63113.
- [4] Jeong HK, Lee YP, Lahaye RJ, Park MH, An KH, Kim IJ, et al. Evidence of graphitic AB stacking order of graphite oxides. *J Am Ceram Soc* 2008;130:1362–6.
- [5] Yu AP, Ramesh P, Itkis ME, Bekyarova E, Haddon RC. Graphite nanoplatelet-epoxy composite thermal interface materials. *J Phys Chem C* 2007;111:7565–9.
- [6] Wang SR, Tambraparni M, Qiu JJ, Tipton J, Dean D. Thermal expansion of graphene composites. *Macromolecules* 2009;42:5251–5.
- [7] Li Y, Pothukuchi S, Wong CP. Development of a novel polymer-metal nanocomposite obtained through the route of in situ reduction and its dielectric properties. In: *Proceedings of the 54th IEEE electronic components and technology conference*. Nevada, USA: Las Vegas; 2004. p. 507–13.
- [8] Psarras GC, Manolaki E, Tsangaris GM. Electrical relaxations in polymeric particulate composites of epoxy resin and metal particles. *Compos Part A* 2002;33:375–84.
- [9] Bai Y, Cheng ZY, Bharti V, Xu HS, Zhang QM. High-dielectric-constant ceramic-powder polymer composites. *Appl Phys Lett* 2000;76:3804–6.
- [10] Wang JW, Wang Y, Wang F, Li SQ, Xiao J, Shen QD. A large enhancement in dielectric properties of poly(vinylidene fluoride) based all-organic nanocomposite. *Polymer* 2009;50:679–84.
- [11] He H, Fu RL, Han YC, Shen Y, Song XF. Thermal conductivity of ceramic particle filled polymer composites and theoretical predictions. *J Mater Sci* 2007;42:6749–54.
- [12] Boudenne A, Ibos L, Fois M, Majeste JC, Gehin E. Electrical and thermal behavior of polypropylene filled with copper particles. *Compos Part A* 2005;36:1545–54.

- [13] Tanaka T, Kozako M, Fuse N, Ohki Y. Proposal of a multi-core model for polymer nanocomposite dielectrics. *IEEE Trans Dielectr Electr Insul* 2005;12:669–81.
- [14] Tanaka T. Dielectric nanocomposites with insulating properties. *IEEE Trans Dielectr Electr Insul* 2005;12:914–28.
- [15] Min C, Yu DM. Simultaneously improved toughness and dielectric properties of epoxy/graphite nanosheet composites. *Polym Eng Sci* 2010;50:1734–42.
- [16] Zhou WY, Yu DM. Thermal and dielectric properties of the aluminum particle/epoxy resin composites. *J Appl Polym Sci* 2010;118:3156–66.
- [17] Liang HL, Yu DM, Xie YC, Min C, Zhang J, Hu GH. Preparation of nano-Ag particles and their modification on the mechanical and dielectric properties of epoxy resin. *Polym Eng Sci* 2009;49:2189–94.
- [18] Wan WT, Yu DM, He J, Xie YC, Huang LB, Guo XS. Simultaneously improved toughness and dielectric properties of epoxy/core-shell particle blends. *J Appl Polym Sci* 2008;107:1020–8.
- [19] Zhou WY, Yu DM, Min C, Fu YP, Guo XS. Thermal, dielectric, and mechanical properties of SiC particles filled linear low-density polyethylene composites. *J Appl Polym Sci* 2009;112:1695–703.
- [20] Xie LY, Huang XY, Wu C, Jiang PK. Core-shell structured poly(methyl methacrylate)/BaTiO₃ nanocomposites prepared by in situ atom transfer radical polymerization: a route to high dielectric constant materials with the inherent low loss of the base polymer. *J Mater Chem* 2011;21:5897–906.
- [21] Yu JH, Huang XY, Wu C, Wu XF, Wang GL, Jiang PK. Interfacial modification of boron nitride nanoplatelets for epoxy composites with improved thermal properties. *Polymer* 2012;53:471–80.
- [22] Liu Q, Liu ZF, Zhang XY, Yang LY, Zhang N, Pan GL, et al. Polymer photovoltaic cell based on a solution processable graphene and P3HT. *Adv Funct Mater* 2009;19:894–904.
- [23] Raghu AV, Lee YR, Jeong HM, Shin CM. Preparation and physical properties of waterborne polyurethane/functionalized graphene sheet nanocomposites. *Macromol Chem Phys* 2008;209:2487–93.
- [24] Shang JW, Zhang YH, Yu L, Shen B, Lv FZ, Chu PK. Fabrication and dielectric properties of oriented polyvinylidene fluoride nanocomposites incorporated with graphene nanosheets. *Mater Chem Phys* 2012;134:867–74.
- [25] Zhan YQ, Yang J, Zhou YK, Yang XL, Meng FB, Liu XB. Nitrile functionalized graphene for poly(acrylene ether nitrile) nanocomposite films with enhanced dielectric permittivity. *Mater Lett* 2012;78:88–91.
- [26] Dang ZM, Nan CW, Xie D, Zhang YH, Tjong SC. Dielectric behavior and dependence of percolation threshold on the conductivity of fillers in polymer-semiconductor composites. *Appl Phys Lett* 2004;85:97–9.
- [27] Li YC, Tjong SC, Li RKY. Electrical conductivity and dielectric response of poly(vinylidene fluoride)-graphite nanoplatelet composites. *Synth Met* 2010;160:1912–9.
- [28] Dang ZM, Lin YH, Nan CW. Novel ferroelectric polymer composites with high dielectric constants. *Adv Mater* 2003;15:1625–9.
- [29] Yuan JK, Yao SH, Dang ZM, Sylvestre A, Genestoux M, Bai JB. Giant dielectric permittivity nanocomposites: Realizing true potential of pristine carbon nanotubes in polyvinylidene fluoride matrix through an enhanced interfacial interaction. *J Phys Chem* 2011;115:5515–21.
- [30] He F, Lau S, Chan HL, Fan J. High dielectric permittivity and low percolation threshold in nanocomposites based on poly(vinylidene fluoride) and exfoliated graphite nanoplates. *Adv Mater* 2009;21:710–5.
- [31] Deng Y, Zhang YJ, Xiang Y, Wang GS, Xu HB. Bi₂S₃-BaTiO₃/PVDF three-phase composites with high dielectric permittivity. *J Mater Chem* 2009;19:2058–61.
- [32] Soulintzis A, Kontos G, Karahaliou P, Psarras GC, Georga SN, Krontiras CA. Dielectric relaxation processes in epoxy resin-ZnO composites. *J Polym Sci: Part B: Polym Phys* 2009;47:445–54.
- [33] Hong JJ, Winberg P, Schadler LS, Siegel RW. Dielectric properties of zinc oxide/low density polyethylene nanocomposites. *Mater Lett* 2005;59:473–6.
- [34] Todd MG, Shi FG. Characterization of the interphase dielectric constant of polymer composite materials: effect of chemical coupling agents. *J Appl Phys* 2003;94:4551–6.
- [35] Chew WC, Sen PS. Dielectric enhancement due to electrochemical double-layer: thin double layer approximation. *J Chem Phys* 1982;77:4683–93.
- [36] Li Z, Fredin LA, Tewari P, Dibenedetto SA, Lanagan MT, Ratner MA, et al. In situ catalytic encapsulation of core-shell nanoparticles having variable shell thickness: dielectric and energy storage properties of high-permittivity metal oxide nanocomposites. *Chem Mater* 2010;22:5154–64.
- [37] Zhang Y, Wang Y, Deng Y, Li M, Bai JB. Enhanced dielectric properties of ferroelectric polymer composites induced by metal-semiconductor Zn-ZnO core-shell structure. *ACS App Mater Interfaces* 2012;4:65–8.
- [38] Yuan JK, Yao SH, Dang ZM, Sylvestre A, Genestoux M, Bai JB. Giant dielectric permittivity nanocomposites: realizing true potential of pristine carbon nanotubes in polyvinylidene fluoride matrix through an enhanced interfacial interaction. *J Phys Chem C* 2011;115:5515–21.
- [39] Todescato F, Capelli R, Dinelli F, Murgia M, Camaioni N, Yang MJ, et al. Correlation between dielectric/organic interface properties and key electrical parameters in PPV-based OFETs. *J Phys Chem B* 2008;112:10130–6.
- [40] Yu SZ, Hing P, Hu X. Thermal conductivity of polystyrene-aluminum nitride composite. *Compos Part A* 2002;33:289–92.
- [41] Kemaloglu S, Ozkoc G, Aytac A. Properties of thermally conductive micro and nano size boron nitride reinforced silicon rubber composites. *Thermochim Acta* 2010;499:40–7.
- [42] Winey KI, Kashiwagi T, Mu M. Improved electrical conductivity and thermal properties of polymers by the addition of carbon nanotubes as fillers. *MRS Bull* 2007;32:348–53.
- [43] Gojny FH, Wichmanna MHG, Fiedler B, Kinloch IA, Bauhofer W, Windle AH, et al. Evaluation and identification of electrical and thermal conduction mechanisms in carbon nanotube/epoxy composites. *Polymer* 2006;47:2036–45.
- [44] Veca LM, Mezziani MJ, Wang W, Wang X, Lu FS, Zhang PY, et al. Carbon nanosheets for polymeric nanocomposites with high thermal conductivity. *Adv Mater* 2009;21:2088–92.
- [45] Yang SY, Ma CC, Teng CC, Huang YW, Liao SH, Huang YL, et al. Effect of functionalized carbon nanotubes on the thermal conductivity of epoxy composites. *Carbon* 2010;48:592–603.
- [46] Shenogin S, Xue L, Ozisik R, Keblinska P, Cahill DG. Role of thermal boundary resistance on the heat flow in carbon-nanotube composites. *J Appl Phys* 2004;95(12):8136–44.
- [47] Shenogin N, Shenogin S, Xue L, Keblinska P. On the lack of thermal percolation in carbon nanotube composites. *Appl Phys Lett* 2005;87:133106–1–3.
- [48] Yu A, Ramesh P, Sun X, Bekyarova W, Itkis MW, Haddon RC. Enhanced thermal conductivity in a hybrid graphite nanoplatelet-carbon nanotube filler for epoxy composites. *Adv Mater* 2008;20:4740–4.
- [49] Zhou TL, Wang X, Mingyuan GU, Liu XH. Study of the thermal conduction mechanism of nano-SiC/DGEBA/EMI-2,4 composites. *Polymer* 2008;49:4666–72.

-
- [50] Rong MZ, Zhang MQ, Ruan WH. Surface modification of nanoscale fillers for improving properties of polymer nanocomposites: a review. *Mater Sci Technol* 2006;22:787–96.
- [51] Clancy TC, Gates TS. Modeling of interfacial modification effects on thermal conductivity of carbon nanotube composites. *Polymer* 2006;47:5990–6.
- [52] Ganguli Sabyasachi, Roy Ajit K, Anderson David P. Improved thermal conductivity for chemically functionalized exfoliated graphite/epoxy composites. *Carbon* 2008;46:806–17.
- [53] Xingyi Huang, Tomonori Iizuka, Pingkai Jiang, Yoshimichi Ohki, Toshikatsu Tanaka. Role of interface on the thermal conductivity of highly filled dielectric epoxy/AlN composites. *J Phys Chem C* 2012;116:13629–39.
- [54] Irwin PC, Cao Y, Bansal A, Schadler LS. Thermal and mechanical properties of polyimide nanocomposites. In: 2003 Annual report of conference on electrical insulation and dielectric phenomena; 2003. P. 120–3.
- [55] Agari Y, Uno T. Estimation on thermal conductivities of filled polymers. *J Appl Polym Sci* 1986;32:5705–12.