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Electrical, dielectric and surface wetting properties of multi-walled carbon nanotubes/nylon-6 nanocomposites*

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This paper reports that the multi-walled carbon nanotubes (MWCNT)/nylon-6 (PA6) nanocomposites with different MWCNT loadings have been prepared by a simple melt-compounding method. The electrical, dielectric, and surface wetting properties of the CNT/PA6 composites have been studied. The temperature dependence of the conductivity of the CNT/PA6 composite with 10.0 wt% CNT loading ($\sigma_{\rm RT} \sim 10^{-4}$ S/cm) are measured, and afterwards a charge-energy-limited tunnelling model ($\ln \sigma(T) \sim T^{-1/2}$) is found. With increasing CNT weight percentage from 0.0 to 10.0 wt%, the dielectric constant of the CNT/PA6 composites enhances and the dielectric loss tangent increases two orders of magnitude. In addition, water contact angles of the CNT/PA6 composites increase and the composites with CNT loading larger than 2.0 wt% even become hydrophobic. The obtained results indicate that the electrical and surface properties of the composites have been significantly enhanced by the embedded carbon nanotubes.

Keywords: carbon nanotubes, composites, electrical conductivity, dielectric property
PACC: 7280, 7720, 8120T

1. Introduction

Since the discovery of carbon nanotubes (CNT) in 1991,[1] they have attracted much attention in many fields because of their unique electronic, thermal, optical, and mechanical properties,[2−5] and potential applications in field-effect transistor, full-colour display, chemical actuator, tip of scanning-probe microscope, and molecular computer.[6−9] In recent years, scientists have demonstrated that the combination of CNT and polymeric matrix is an effective method for taking full advantages of both CNT and polymers.

By now, a large number of papers have been published about the synthesis and properties of composite films and nanostructures based on CNT and conjugated polymers.[10−19] For instance, the strength and modulus of a polystyrene coated carbon nanofibre composites are higher than those of uncoated composites.[10] Long *et al*[11−13] have observed an enhancement of conductivity of the CNT/polymer nanocables by two orders of magnitude with increasing CNT weight percentage and studied the low-temperature magnetoresistance of these CNT/polymer composites. Liu *et al*[14] found that the CNT/SCPU composites exhibited strong microwave absorption in the microwave range of 2–18 GHz. Nylon-6 (PA6), also known as polyamide-6 and polycaprolactam, is one of the most widely used synthetic polymers for fibres due to excellent physical and mechanical properties. Multi-walled CNT reinforced PA6 composites have been explored intensively in recent years. For instance, in comparison with pure PA6, the elastic modulus and the yield strength of the 2.0 wt% MWCNT/PA6 composite are greatly improved by about 214% and 162%, respectively.[15,16] Significant improvements in tensile modulus, strength, and toughness relative to nylon have also been achieved in nylon nanocomposites using functionalized single-walled CNT.[17,18] In addition, Gao *et al*[19] reported an interesting continuous spinning of a single-walled CNT/nylon composite fibre. However, their temperature-dependent electrical

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conductivity, dielectric loss and wettability have not been reported extensively. In the present study, we have synthesized multi-walled CNT/PA6 composites by a simple melt-compounding method, and studied their temperature-dependent electrical conductivity, dielectric, and surface wetting properties as a function of CNT loading. It is interesting to find that these physical properties have been enhanced evidently by the embedded nanotubes and nanostructures of the composites.

2. Experimental section

PA6 in pellet form (relative viscosity ∼3.2 in 98% H_2SO_4 solvent, and diameter 2–3 mm) was supplied by Yue-Yang Petro-Chemical Engineering Factory. Multi-walled CNT used in this work were prepared by ethylene chemical vapour deposition (CVD) using Al_2O_3 supported Fe catalysts.[12] The outer diameter of MWCNT was about 30 nm, and the inner diameter was 5–10 nm. The products were washed with concentrated hydrochloric acid to remove the catalyst and the carrier of catalyst, and then were purified with concentrated HNO_3 to remove the amorphous carbon particles. PA6 nanocomposites containing different MWCNT loadings (0, 0.5, 1.0, 2.0, 5.0 and 10.0 wt%) were prepared by a melt-compounding method using a twin-screw mixer at 260°C for 10 min with a screw speed of 100 rpm. Pellet samples (with thickness of about 1.5 mm) were prepared by compression molding in a press at 260°C.

A scanning electron microscope (SEM; JEOL JSM-6390) operating at 20 kV was used to observe the morphology of the cross-sections of the CNT/PA6 composites. The infrared (IR) spectra of the composites were recorded by using a MAGNA-IR 550 spectrometer. The temperature-dependent electrical conductivity of the 10.0 wt% composite was measured by a four-probe method using Keithley-220 current source and Keithley-181 nanovoltmeter. The dielectric constant and dielectric loss at room temperature were measured by a TH2819 Precision LCR Meter (Changzhou Tonghui Electronic Co. LTD). The water contact angle values were acquired on a Dataphysics OCA-20 contact angle system at room temperature in ambient atmosphere. For each measurement, a 5 μL droplet was dispensed onto the sample under investigation.

3. Results and discussion

3.1. Structure and morphology

The structure of the PA6 was identified through the IR spectrum, as shown in curve *A* in Fig.1. The sharp peak at 1650 cm^{-1} corresponds to the stretching vibration of the C–O group of the amide functionality,[20−22] and the strong peak around 1560 cm^{-1} could be attributed to a combination of the bending vibration of the N–H bond and the stretching vibration of the C–N bond of the amide group.[19,23] In addition, the broad bands between 3000 and 3300 cm^{-1} are assigned to the hydrogen-bonded –COOH and –NH– groups of the PA6, while the C–H stretching vibrations take place at 2860 and 2940 cm^{-1}.[19,23] Curves *B*–*F* in Fig.1 are the IR spectrum of the CNT/PA6 composites with 0.5, 1.0, 2.0, 5.0 and 10.0 wt% CNT loadings, respectively. These IR spectra of the CNT/PA6 composites with different loadings are nearly the same. In comparison with the curve *A*, the peaks and bands of function groups still appear in the IR spectra. However, the peaks at 1560 cm^{-1}, 1650 cm^{-1}, 2860 cm^{-1} and 2940 cm^{-1} and the broad bands between 3000 and 3300 cm^{-1} in curves *B*–*F* are evidently weaker than those of curve *A*, which may be attributed to the influence of the embedded CNT on the PA6 matrices.

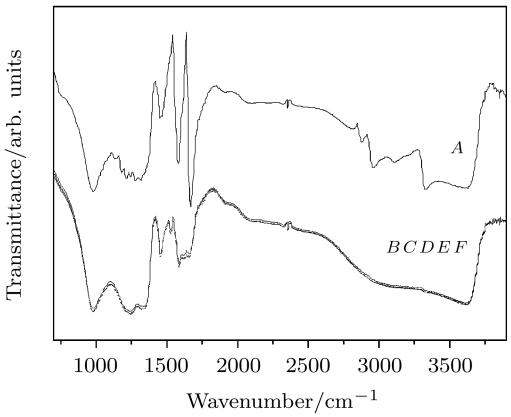


Fig.1. IR spectrum of the CNT/PA6 composites: (curve *A*) pristine PA6; (curve *B*) 0.5 wt%; (curve *C*) 1.0 wt%; (curve *D*) 2.0 wt%; (curve *E*) 5.0 wt% and (curve *F*) 10.0 wt%.

The morphology of the composites was verified by using SEM. Cross sections of the composites were prepared by breaking off the CNT/PA6 composites to give a fracture surface, and the resulting SEM image is shown in Fig.2, which displays the disordered dispersion of the CNT in the host PA6 matrices. The

bright dots and wires in the image are the MWCNT due to their relatively high electrical conductivity and the other parts are PA6 matrices.

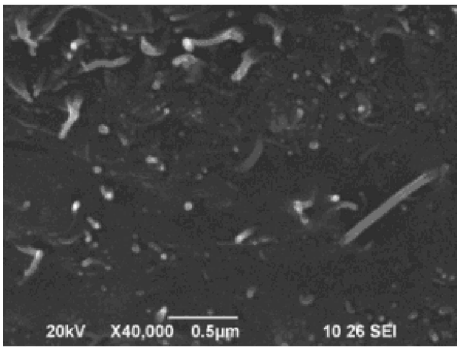


Fig.2. Typical SEM image of the cross section of the 5.0 wt% CNT/PA6 composite.

3.2. Electrical conductivity

It is reported that the room-temperature conductivities (σ_{RT}) of the CNT/PA6 composites are 3.2×10^{-5} S/cm and 5.9×10^{-4} S/cm for the composites with 5.0 wt% and 10.0 wt% CNT, respectively.[24] In comparison with the room temperature conductivity of the pure PA6, which has the order of magnitude of 10^{-14} S/cm, it is obvious that the room temperature conductivity of the composites is enhanced significantly.

In order to further explore how the composite's conductivity is affected by the embedded CNT, we measured the temperature dependence of the conductivity of the 10.0 wt% CNT/PA6 composite, as shown in Fig.3.

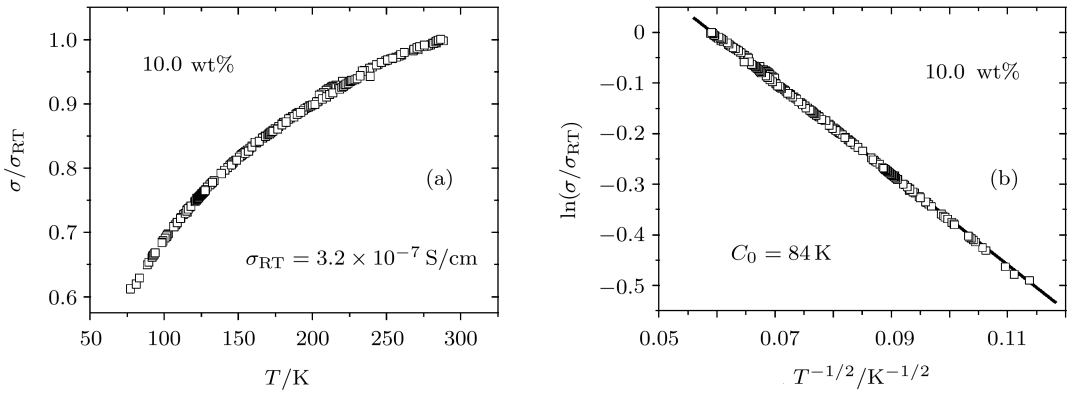


Fig.3. Temperature dependence of the electrical conductivity of the 10.0 wt% CNT/PA6 composite plotted as (a) σ/σ_{RT} versus T, and (b) $\ln(\sigma/\sigma_{RT})$ versus $T^{-1/2}$.

It is obvious that the conductivity data of this sample can be well fitted with the relation $\ln \sigma(T) = A + B \cdot T^{-1/2}$, namely, $\ln \sigma(T)$ is linear in $T^{-1/2}$.[25] The temperature dependence can be interpreted in terms of the charge-energy-limited tunnelling model, which describes the charge transport in a system of metallic particles embedded in a dielectric matrix:[26]

$$\sigma(T) = \sigma_0 \exp[-(C_0/T)^{1/2}], \qquad (1)$$

where C_0 is a constant and depends on the barrier height for the charge carriers and the charging energy. The value of $C_0 = 84$ K for this sample is calculated from the slope of the $\ln \sigma(T)$ versus $T^{-1/2}$ plot. Here, it is noted that different methods and techniques of incorporation of CNT in the polymer matrix will influence strongly on the electrical and mechanical properties of the composite by modifying the dispersion of CNT and the interfacial interactions between the two components.[10–12,24,27] For example, homogeneous CNT/polymer composites, which are fabricated by using functionalized soluble CNT, show dramatic improvements in electrical conductivity with very low percolation threshold owing to significantly improving the dispersion of CNT in the polymer matrix.[27] Long *et al*[11,12] also reported that a cationic surfactant directed *in situ* chemical oxidative polymerization can also improve the dispersion of MWCNT in conducting polymers and electrical properties of the resulting composites. In addition, it is also reported that a plasma polymerization (coating) treatment can enhance carbon nanofibre dispersion and interfacial bonding in polystyrene composites, and thus enhance their strength and modulus significantly.[10]

3.3. Dielectric properties

Dielectric constant and dielectric loss are also important parameters of the composite materials. The complex permittivity is $\varepsilon^* = \varepsilon' - i\varepsilon''$, where ε' and ε'' represent the real and imaginary parts, and the

dielectric loss tangent is $\tan\delta = \varepsilon''/\varepsilon'$. The dielectric properties of the CNT/PA6 composites have not been reported intensively yet. This paper reports that we have measured the dielectric constant and dielectric loss of the composites at room temperature. Compared with the Liu's work,[16] the dielectric properties of CNT/PA6 are explored at low frequencies. Figure 4 exhibits the relative dielectric constant ε ($\varepsilon = \varepsilon'/\varepsilon_0$, ε_0 is the permittivity of vacuum) of the CNT/PA6 composites as function of the CNT concentration and the frequency. It is evident that the dielectric constant increases by several times with increasing CNT weight percentage from 0 to 10.0 wt%. For example, $\varepsilon = 4.1$ for the pure PA6 pellet, and $\varepsilon = 51.7(f = 0.5\,\text{kHz})$, 19.3 ($f = 10\,\text{kHz}$) and 11.0 ($f = 200\,\text{kHz}$) for the 10.0 wt% CNT/PA6 composite. When the conductive fillers and CNT are incorporated into an insulating PA6 matrix, a large interfacial polarization occurs. And the enhancement of the dielectric constant at low frequencies can be attributed to this large interfacial polarization.[28] In addition, for the CNT/PA6 composite with a fixed CNT concentration (e.g., especially for the 10.0 wt% composite), the dielectric constant decreases with the enhancement of the frequency. This indicates that at high frequencies the mobility of polar groups at the CNT/PA6 interfaces is too slow to contribute to the dielectric constant.[29,30]

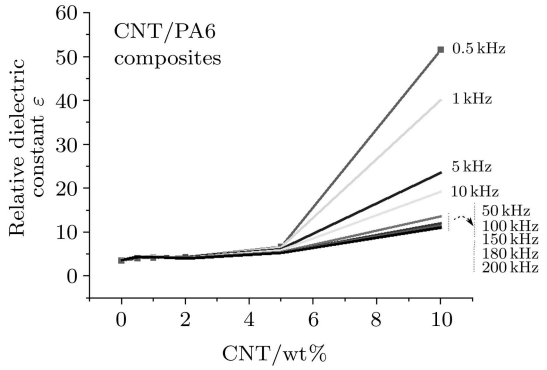


Fig.4. Relative dielectric constant of the CNT/PA6 composites, which increases with increasing CNT loading.

Figure 5 shows the dielectric loss tangent of the CNT/PA6 composites as function of the CNT loading and the frequency. It is clearly seen that the dielectric loss tangent of the composites increases by one to two orders of magnitude with increasing CNT weight percentage. In the meantime, the dielectric loss tangent becomes less frequency-dependent at the range of 50–200 kHz. Our results indicate that the dielectric properties of the CNT/PA6 composites have been enhanced significantly by the embedded CNT.

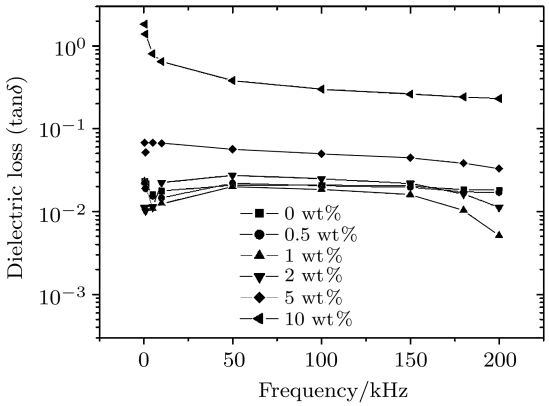


Fig.5. Dielectric loss tangent of the CNT/PA6 composites, which increases two orders of magnitude with increasing CNT weight percentage.

3.4. Surface wetting property

Wettability is one of the important properties of solid surface from both fundamental and practical aspects. A static water contact angle (WCA) is usually used as a criterion for the evaluation of hydrophilicity (WCA< 90°) or hydrophobicity (WCA> 90°) of the surface. In this article, the surface wetting property of the CNT/PA6 composites was evaluated by WCA measurements, as shown in Fig.6. According to the WCA results (Fig.7), it is proved that the pure PA6 surface is hydrophilic, with the WCA of about 51°. Surprisingly, there is evident increase of the WCA values which can even reach to about 101.1°) (Fig.6) when the CNT loading was increased to 2.0 wt%. Namely, there is a transition from hydrophilicity to hydrophobicity.

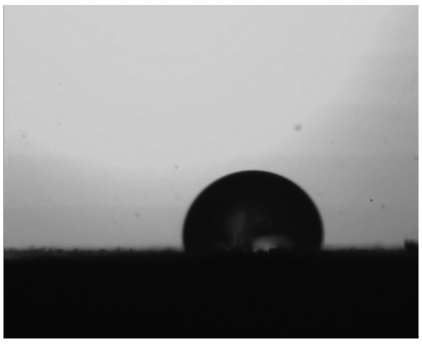


Fig.6. Water droplet on the 2.0 wt% CNT/PA6 composite surface.

As we know, the wettability of a surface is determined by a combination of its chemical properties and topographical microstructure. If a surface is rough or

microtextured with a low interfacial free energy, the WCA can reach a value larger than 160°. For example, although Kakade and Pillai[31] reported that CNT exhibited intrinsic hydrophilic behaviour (contact angle $< 90°$) because of their perfect graphitic network of sp^2 carbon, however, superhydrophobic phenomenon (WCA$> 150°$) has been observed in aligned CNT due to their particular nanostructures.[32] For the present case, the embedded CNT have modified the inner structures and surface morphologies of the CNT/PA6 composites evidently (as shown in Fig.2). As a result of their nanostructures, the WCA of the composites

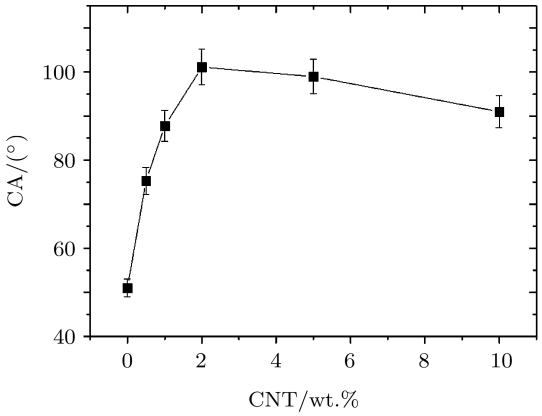


Fig.7. Water contact angles of the CNT/PA6 composites with different CNT loadings.

increases significantly from 51° to 101.1°. Here we note that the CNT were disorderedly dispersed into the PA6 matrix, if the nanotubes are aligned in the polymer matrix and aligned on the surface, the WCA may reach a much larger value. Figure 7 also shows when the CNT loading continues increasing from 2.0 to 5.0 and 10.0 wt%, the WCA does not enhance but seems to decrease a little (91° for the 10.0 wt% composite). This is possibly related with the disordered dispersion of the nanotubes and water seepage into the voids of the composite's surface because it has been reported that the droplets on CNT were not stable and eventually seeped into the voids after a few minutes due to a hydrophilic surface of the CNT graphitic surface.[33,34] Therefore, it is evident that the surface wetting property of the CNT/PA6 composites is strongly dependent on the embedded CNT and the nanostructures of the composites.

4. Conclusions

Multi-walled CNT/PA6 nanocomposites with different CNT loadings from 0 to 10.0 wt% have been prepared by a simple melt-compounding method. The structure, morphology and physical properties of the composites have been characterized by infrared spectra, SEM, electrical conductivity, dielectric constant, dielectric loss, and wettability measurements. It is found that the temperature dependence of the conductivity of the CNT/PA6 composite with 10.0 wt% CNT loading follows a charge-energy-limited tunnelling model ($\ln \sigma(T) \sim T^{-1/2}$). The CNT/PA6 composites dielectric constant and the dielectric loss tangent increase by one to two orders of magnitude. Particularly, the 2.0, 5.0, and 10.0 wt% CNT/PA6 composites show hydrophobicity. These results indicate that the electrical, dielectric and surface wetting properties of the CNT/PA6 composites have been enhanced significantly by the filled MWCNT. Dealing with the mechanical properties of the resulting composites, we shall make further investigation on this topic.

References

[1] Iijima S 1991 *Nature* **354** 56

[2] Fan S S, Chapline M G and Franklin N R 1999 *Science* **283** 512
Zhang Y, Cao J X and Yang W 2008 *Chin. Phys.* B **17** 1881

[3] Lin M F, Shu F L and Chen R B 2000 *Phys. Rev.* B **61** 14114

[4] Pan Z W, Xie S S and Lu L 1999 *Appl. Phys. Lett.* **74** 3152
Yuan Y H, Miao R C, Bai J T and Hou X 2006 *Chin. Phys.* **15** 2761

[5] Tsui F, Jin L and Zhou O 2000 *Appl. Phys. Lett.* **76** 1452
Zhou X Y and Lu H J 2007 *Chin. Phys.* **16** 0335

[6] Baughman R H, Cui C X and Zakhidov A A 1999 *Science* **284** 1340

[7] Frank S, Poncharal P, Wang Z L and de Heer W A 1998 *Science* **280** 1774

[8] Rueckes T, Kim K and Joselevich E 2000 *Science* **289** 94
Fang J H, Liu L W, Kong W J, Cai J Z and Lu L 2006 *Chin. Phys.* **15** 1071

[9] Stanislaus S W, Adam T W and Ernesto J 1998 *Nature* **394** 52
Long Y Z, Yin Z H, Hui W, Chen Z J and Wan M X 2008 *Chin. Phys.* B **17** 2707

[10] Shi D L, Lian J, He P, Wang L M, Xiao F, Yang L, Schulz M J and Mast D B 2003 *Appl. Phys. Lett.* **83** 5301

[11] Long Y Z, Chen Z J, Zhang X T, Zhang J and Liu Z F 2004 *J. Phys.* D: *Appl. Phys.* **37** 1965

[12] Long Y Z, Chen Z J, Zhang X T, Zhang J and Liu Z F 2004 *Appl. Phys. Lett.* **85** 1796
[13] Long Y Z, Yin Z H and Chen Z J 2008 *J. Phys. Chem.* C **112** 11507
[14] Liu Z F, Bai G, Huang Y, Li F F, Ma Y F, Guo T Y, He X B, Lin X, Gao H J and Chen Y S 2007 *J. Phys. Chem.* C **111** 13696
[15] Zhang W D, Shen L, Phang I Y and Liu T X 2004 *Macromolecules* **37** 256
[16] Liu T X, Phang I Y, Shen L, Chow S Y and Zhang W D 2004 *Macromolecules* **37** 7214
[17] Gao J, Zhao B, Itkis M E, Bekyarova E, Hu H, Kranak V, Yu A and Haddon R C 2006 *J. Am. Chem. Soc.* **128** 7492
[18] Moniruzzaman M, Chattopadhyay J, Billups W E and Winey K I 2007 *Nano Lett.* **7** 1178
[19] Gao J, Itkis M E, Yu A, Bekyarova E, Zhao B and Haddon R C 2005 *J. Am. Chem. Soc.* **127** 3847
[20] Chen J, Hamon M A, Hu H, Chen Y, Rao A M, Eklund P C and Haddon R C 1998 *Science* **282** 95
[21] Hamon M A, Chen J, Hu H, Chen Y, Itkis M E, Rao A M, Eklund P C and Haddon R C 1999 *Adv. Mater.* **11** 834
[22] Hu H, Zhao B, Hamon M A, Kamaras K, Itkis M E and Haddon R C 2003 *J. Am. Chem. Soc.* **125** 14893
[23] Rodriguez-Rios H, Nuno-Donlucas S M, Puig J E, Gonzalez-Nunez R and Schulz P C 2004 *J. Appl. Polym. Sci.* **91** 1736
[24] Saeed K and Park S Y 2007 *J. Appl. Polym. Sci.* **106** 3729
Meincke O, Kaempfer D, Weickmann H, Friedrich C, Vathauer M and Warth H 2004 *Polymer* **45** 739
[25] Long Y Z, Chen Z J, Liu Z X, Zhang Z M, Wan M X and Wang N L 2003 *Chin. Phys.* **12** 0433
Long Y Z, Chen Z J, Peng H L and Liu Z F 2008 *Chin. Phys.* B **17** 2251
Long Y Z, Duvail J L, Chen Z J, Jin A Z and Gu C Z 2008 *Chin. Phys. Lett.* **25** 3474
[26] Abeles B, Sheng P, Coutts M D and Arie Y 1975 *Adv. Phys.* **24** 407
[27] Ramasubramaniam R, Chen J and Liu H Y 2003 *Appl. Phys. Lett.* **83** 2928
[28] Bunget I and Popesco M 1984 *Physics of Solids Dielectrics* (New York: Elsevier Science)
[29] Popielarz R, Chiang C K, Nozaki R and Obrzut J 2001 *Macromolecules* **34** 5910
[30] Tsuchiya K, Shibasaki Y, Aoyagi M and Ueda M 2006 *Macromolecules* **39** 3964
[31] Kakade B A and Pillai V K 2008 *J. Phys. Chem.* C **112** 3183
[32] Li S, Liu H, Wang X, Song Y, Liu Y, Jiang L and Zhu D 2002 *J. Phys. Chem.* B **106** 9274
[33] Lau K K S, Bico J, Teo K B K, Chhowalla M, Amaratunga G A J, Milne W I, McKinley G H and Gleason K K 2003 *Nano Lett.* **3** 1701
[34] Huang L, Lau S P, Yang H Y, Leong E S P, Yu S F and Prawer S 2005 *J. Phys. Chem.* B **109** 7746