

Preparation and Characterization of Polyimide/Carbon-Nanotube Composites

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Abstract: Polyimide/carbon nanotube (CNT) composite films, for potential use in high performance microelectronics and aerospace applications, were prepared by mixing a polyisoimide (PII) solution and a CNT suspension in NMP, followed by casting, evaporation and thermal imidization. The CNTs were modified by a nitric acid treatment to improve the thermal and electrical properties, as well as to provide good dispersion of the CNTs in a polymer matrix. The formation of functional groups on the modified CNT was confirmed by Raman spectroscopy. Scanning electron microscopy revealed the modified CNTs to be well dispersed in the polyimide matrix, with a uniform diameter of ca. 50 nm. The thermal stability of the films containing the CNTs was improved due to the enhanced interfacial interaction and good dispersion between the polyimide matrix and modified CNTs. In addition, the thermal expansion coefficient of the composites films was slightly decreased, but the dielectric constants increased linearly with increasing CNT content.

Keywords: polyimide, polyisoimide, carbon nanotube, nanocomposite, thermal property, dielectric constant.

Introduction

Polyimide (PI) has been investigated for use as packaging materials, circuit boards, and interlayer dielectrics in various applications ranging from microelectronics to aerospace.¹⁻³ In particular, aromatic PIs have attracted significant scientific and technological interest for the development of candidate polymers for applications including packaging materials and FPCB on account of their useful properties such as high flexibility, high glass transition temperature, low thermal expansion coefficient, excellent thermal stability, and radiation resistance. Also for some application such as space durable aircrafts and their parts, it is desirable that the polymer film must possess optical transparency and sufficient electrical conductivity to mitigate electrostatic charge build-up. To provide electrical conductivity at a relatively low loading level to PI without detriment to other excellent properties, the introduction of carbon nanotube with good dispersion was postulated.⁴

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991,⁵ their incorporation in polymeric materials has attracted considerable attention.^{4,6-9} Polymer composites have potentially superior the thermal, electrical, and mechanical

properties than the pristine polymers. Unfortunately, pure CNTs are insoluble in organic solvents and tend to form aggregates due to the extremely high surface energy, which leads to a heterogeneous dispersion in the polymer matrix and has negative effects on the properties of the resulting composites. In order to improve the heterogeneous dispersion in a polymer matrix, Ausman *et al.* introduced a chemically functionalized CNT obtained by a strong mixed-acid treatment.¹⁰ The carboxyl groups on the resulting modified CNTs are expected to increase the interfacial interactions between the PI matrix and a CNT, which would be beneficial for the homogeneous dispersion of CNTs in a polymer matrix.

Previously we have reported on the preparation and properties of PI/organo-clay nanocomposite using soluble polyisoimide (PII), a precursor to PI.¹¹⁻¹³ PII, an isomeric form of PI, possess an improved solubility (or processability) and can be converted to PI without generating water byproduct. Homogeneous dispersion was obtained at a lower clay concentration (< 5 wt%) as confirmed by X-ray diffraction and transmission electron microscopy. The nanocomposites displayed improved thermal and mechanical properties. In this study, PI/CNT composites were prepared from the mixture of modified CNT and two different type of PII in NMP by dispersion with sonification and the thermal imidization of the cast films. The prepared composites were characterized

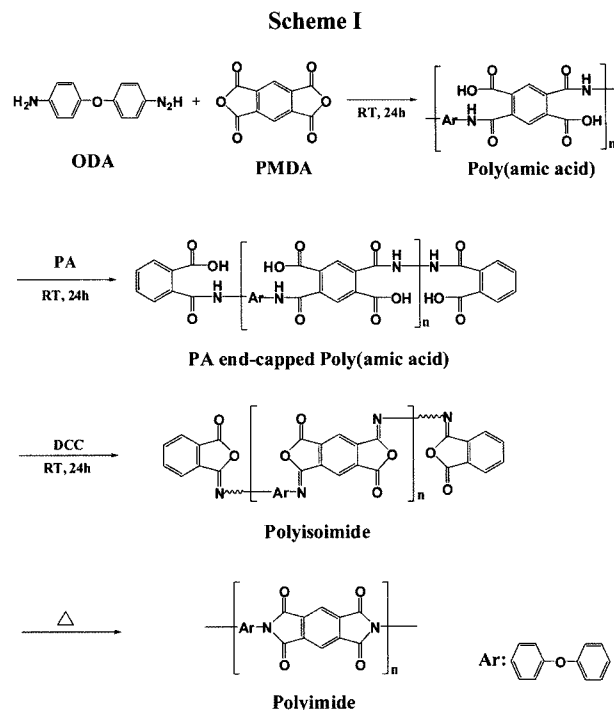
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by Fourier transform infrared (FT-IR), thermal gravimetric analysis (TGA), thermo mechanical analysis (TMA), scanning electron microscopy (SEM), Raman spectroscopy and a dielectric constant analyzer.

Experimental

Materials. The single-wall carbon nanotubes (CNTs) used in this study were produced by chemical vapor deposition and purified to > 90%. The purified CNT had a mean diameter of 30-50 nm and a length of 2-10 μm . The modified CNTs were prepared using the following steps: refluxing the CNT mixture in nitric acid at 70 °C for 3 h; filtering and washing with deionized water; drying in a vacuum oven at 100 °C for 24 h. The dried CNTs were sonicated to disperse them prior to use. Pyromellitic dianhydride (PMDA, 97%), 4,4'-oxydiphthalic dianhydride (ODPA, 97%) and 4,4'-oxydianiline (ODA, 97%) were obtained from Aldrich and purified by vacuum sublimation. Phthalic anhydride (PA, Aldrich 99%) and 1,3-dicyclohexyl carbodiimide (DCC, Aldrich 99%) were used as the end capping agent and a dehydrating agent, respectively. *N*-Methyl-2-pyrrolidinone (NMP, Aldrich 99%) was distilled over CaH_2 under reduced pressure and stored over 4 °C molecular sieves prior use.

Preparation of Polyimide/CNT Nanocomposite. Two types of PI with a different reactivity were prepared using two different aromatic dianhydride monomers. One was PMDA with a relatively high electron affinity ($E_a = 1.90$ eV) and strong rigidity, which can lead to a PI with a high glass transition temperature. The other is ODPA with a relatively low electron affinity ($E_a = 1.30$ eV) and flexibility. Initially, 40 mL NMP and the appropriate amount of modified CNT were placed in a flask and stirred vigorously under ultrasonication for 12 h at room temperature to obtain a homogeneous suspension. Second, 2.00 g (10 mmol) ODA and 40 mL NMP were placed in a flask and stirred for 30 min. 2.18 g (10 mmol) PMDA was then added to the solution in partition and stirred overnight at room temperature to prepare an approximately 20% poly(amic acid) (PAA) solution. After a viscous PAA solution was obtained, 0.06 g (0.40 mmol) phthalic anhydride (PA) was added to protect the reactive amine end groups and stirred for 24 h. Subsequently, 4.95 g (24 mmol) 1,3-dicyclohexyl carbodiimide (DCC), as a dehydrating agent, was added and stirred at room temperature for another 24 h. At this stage, the PAA was converted to the PII form. The solid, dicyclohexyl urea formed was removed by filtration and the PII solution collected was poured into a large excess of isopropanol. The precipitated PII was filtered, washed, and dried under vacuum at 80 °C. The PI/CNT composite films were prepared by thermal imidization of the PII/CNT cast films. Briefly, a PII solution in NMP at 2.5 wt% was added to the modified CNT/NMP suspension at 0.1, 0.3, 0.5, 1.0, 1.5 wt% (CNT)



based on the polymer, respectively. After stirring for several hours, the PII/CNT mixture was cast onto a glass plate and dried under vacuum at 50 °C for 48 h. For thermal curing of the PI, the cast composite films were heat-treated at 200 °C for 3 h followed by 300 °C for 2 h. Scheme I shows the structure and synthetic diagram. The ODPA/ODA-based PI/CNT composite films were also prepared using the same procedure, as described above.

Characterization. The FT-IR spectra were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. The particle size distribution of the CNT was obtained using a HELOS particle size analyzer (SYMPATEC). The presence of functional groups on the modified CNT was confirmed using a Reinshaw Raman Microspectrometer 1000 (780 nm excitation wavelength, 12 W/cm²) as a peak ratio D-1330 (defect) to G-1567 cm⁻¹ (graphite) band. The dielectric constant was measured using a Dielectric Interface Solatron (model 1296) at 1 MHz. The thermal stability and temperature variation of weight loss was measured using TGA, (Perkin-Elmer TGA-7) in air with a scan rate of 20 °C/min within the temperature range from RT to 900 °C. The coefficient of thermal expansion (CTE) was measured using TMA (Seiko Exstar 6000) as a dimension change as a function of temperature from RT to 450 °C. The morphology of the PI/CNT composite film was investigated by field emission scanning electron microscopy (FESEM, model JSM6700F, JEOL Inc.). Here the samples were fractured at liquid nitrogen temperature and were coated with gold via plasma sputtering to create a conductive surface layer that was necessary for SEM imaging.

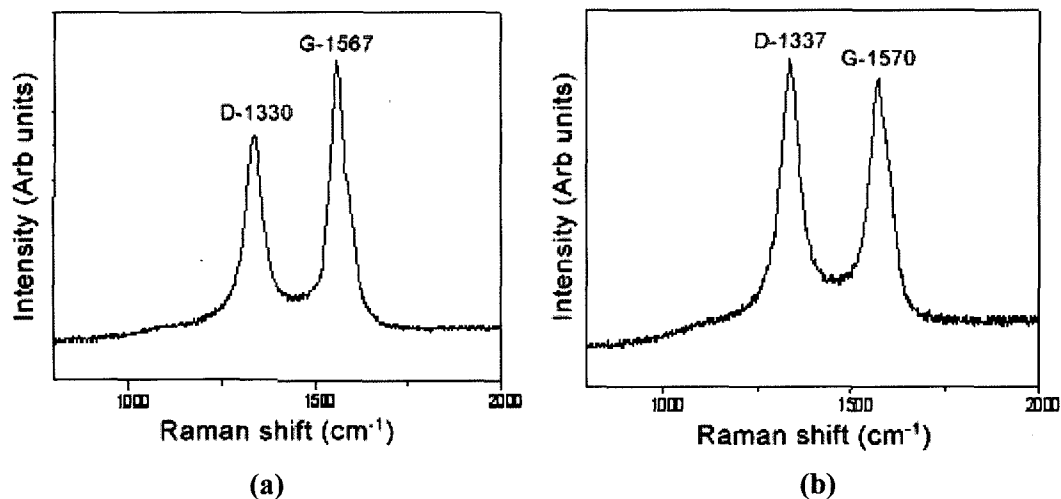


Figure 1. Raman spectra of CNT before (a) and after (b) the acid-treatment.

Results and Discussion

Chemical Functionalization of CNT and the Particle Size Distribution. Figures 1(a) and 1(b) show the Raman spectra of the untreated and nitric acid-treated CNTs, respectively. Each spectrum shows the characteristic D(defect)-band and G(graphite)-band peaks at 1330 and 1567 cm^{-1} of the CNTs, respectively. For the spectrum of the nitric acid-treated CNT, an increase in the intensity of the D-band at 1330 cm^{-1} was observed due to the formation of carboxyl groups on the CNT surface. The degree of carboxyl group formation was estimated from the peak ratio of 1330 to 1567 cm^{-1} . A higher the peak at 1330 cm^{-1} indicates a larger amount of carboxyl groups on the surface of the CNT.

Figure 2 shows the particle size distribution of the modified CNT using a HELOS particle size analyzer. The modified CNT had an outer diameter of 30-50 nm, an inner diameter 2-6 nm, and a length of 2-10 μm . The calculated average particle size was approximately 60 nm. After the

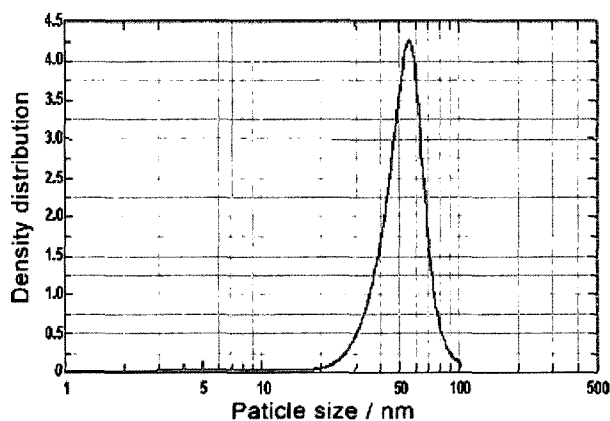


Figure 2. Particle size distribution of the modified CNTs.

nitric acid treatment, the CNTs appeared to be cut to a relatively short length with aggregation in the loose state in addition to chemical functionalization. Therefore, the lower level of aggregation in the modified CNTs can be attributed not only to the presence of functional groups such as carboxyl group but to their shorter length and aspect ratio. This transformation should contribute positively to the good dispersion of CNT in the PI matrix.

Characterization of Polyisoimide & Polyimide Synthesis. As described previously, poly(amic acid) (PAA) was prepared by a condensation reaction of ODA and PMDA (or ODPA) in NMP. After the PAA had been prepared, phthalic anhydride was added in order to prevent gelation by protecting the reactive amine end groups. 1,3-Dicyclohexyl carbodiimide, as a dehydrating agent, was used for chemical dehydration at room temperature to convert the

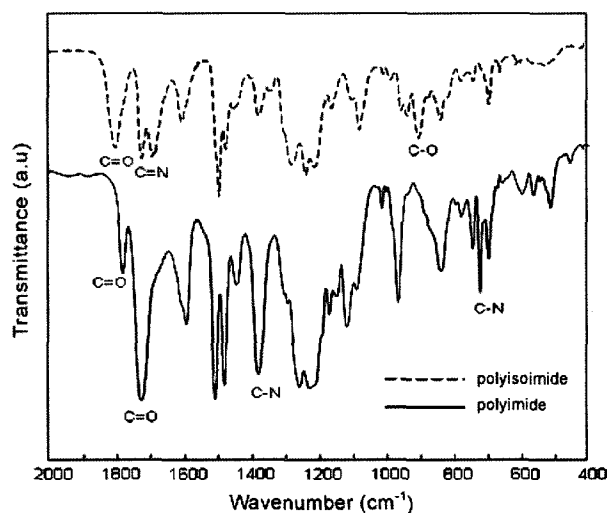


Figure 3. FT-IR spectra of polyimide/CNT composite films.

PAA into PII, which is another precursor for PI. The final PI/CNT composite films were prepared by the thermal imidization of PII/CNT at a programmed heating cycle in a nitrogen atmosphere. Figure 3 shows the FT-IR spectra of the PII and PI in the PMDA/ODA system. The characteristic bands due to PII absorption were observed near 1801 cm^{-1} (C=O asymmetrical stretching) and 905 cm^{-1} (C-O vibration), while the characteristic bands due to PI absorption were observed at approximately 1780 cm^{-1} (C=O asymmetrical stretching), 1724 cm^{-1} (C=O symmetrical stretching), 1380 cm^{-1} (C-N stretching), and 725 cm^{-1} (C=O bending).

Thermal Properties of Polyimide/CNT Composites.

Figure 4 shows the TGA curves of the pristine PI and PI (PMDA-ODA)/CNT composite films. The modified CNT decomposed slowly from 180°C and showed approximate 5

percent loss in weight before 500°C in TGA under nitrogen, probably due to the loss of carboxyl groups on the surface of the CNTs. On the other hand, pure PI has excellent thermal stability and does not decompose until 550°C . The thermal stability of the PI/CNT composite films increased linearly with increasing CNT content as the effect were clearly seen in the curves. From the other polymer system, a similar result in their TGA curves could be observed. The improvement in thermal stability of the films containing the CNTs will be resulted from the enhanced interfacial interaction and good dispersion between the PI matrix and modified CNTs.

Figure 5 shows the TMA curve of the pristine PI and PI (PMDA-ODA)/CNT composite films. The coefficient of thermal expansion (CTE) data can be explained by the intra-

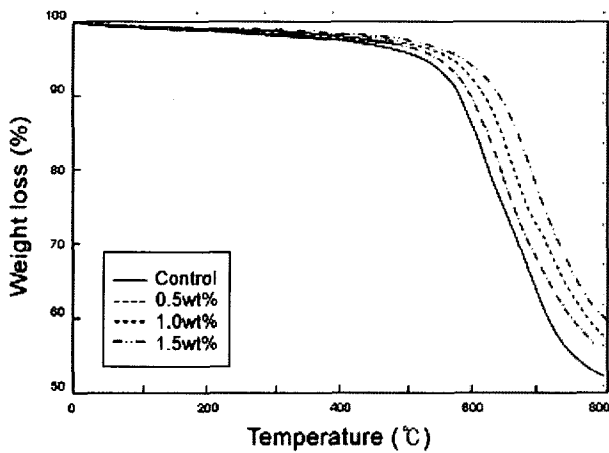


Figure 4. TGA thermograms of the polyimide/CNT composite films as a function of CNT content.

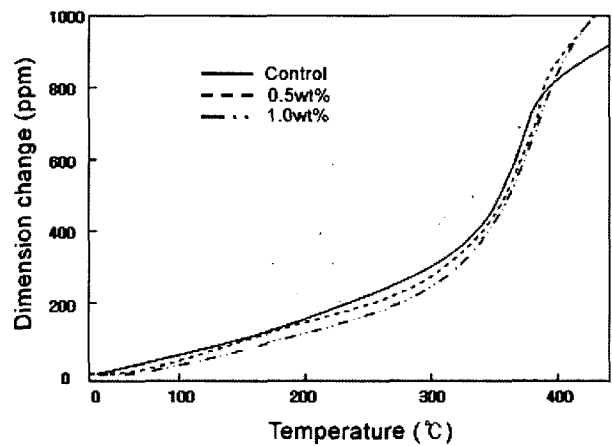


Figure 5. TMA curves of the polyimide/CNT composite films as a function of CNT content.

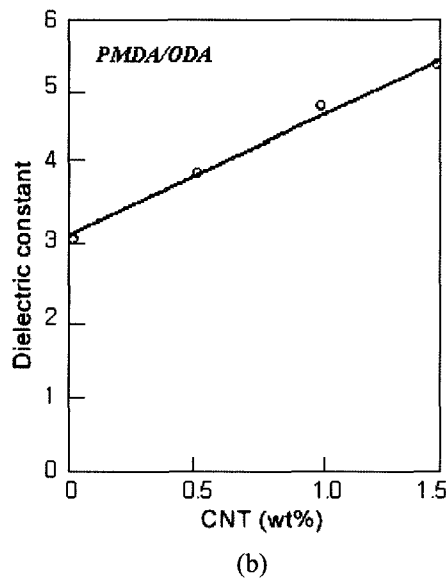
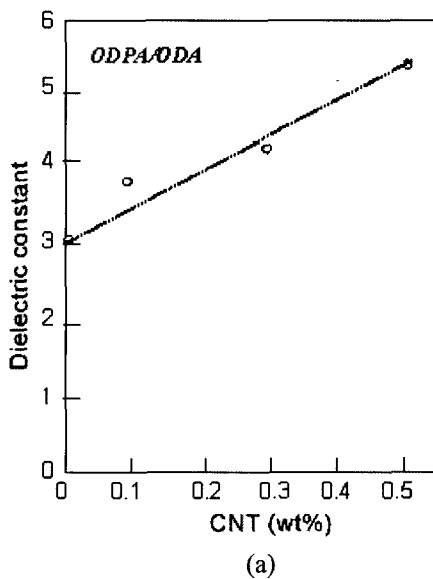


Figure 6. Dielectric constant change of the polyimide/CNT composite films as a function of CNT content.

and intermolecular forces of the polymer molecules. The CTE decreased with increasing CNT content, even though the difference appeared marginal. Nevertheless, CNT component must contribute to improve the level of dimensional stability over the given temperature range. The softening point (or glass transition temperature) of this composite system could be deduced to be around 300 °C, where the samples began to show an abrupt expansion in their dimension.

Electrical Properties of Polyimide/CNT Composites. Figure 6 shows the dielectric constant data of the PI/CNT composites with a different CNT content. The dielectric constant was calculated from the capacitance data using the following equation:

$$C = \epsilon_0 \epsilon_r A / t$$

where, ϵ_0 is the dielectric permittivity of free space, A is area of the electrical conductor, t is thickness of the film and ϵ_r is the relative dielectric permittivity of the film. The dielectric constants of the PI/CNT composite films ranged from 3.1 to 5.3 as shown in figure. The dielectric constant of the PI/CNT composite films increased linearly with increas-

ing the CNT content. This was expected because the dielectric constant of the CNT was larger than that of the PI matrix. The degree of increase in dielectric constant as a function of CNT content, however, was more pronounced from PI (ODPA-ODA) system compared to PI (PMDA-ODA), which might be caused by the relative chain rigidity of these two different polymers. Lee *et al.* reported that for the PI/BaTiO₃ composite system, the dielectric constants increased with increasing the BaTiO₃ content.¹⁴ Measured dielectric constants agreed with the calculated constants using the Maxwell-Garett approximation method.¹ Therefore, the change in the dielectric constant of the PI/CNT composite films can be estimated and controlled.

Morphology of Polyimide/CNT Composites. Figure 7 shows SEM images of the cross-sectional fractures of the PI without the CNT loading and the PI/CNT (1.5 wt%) nanocomposite films. The film cross-section was obtained by breaking the film in liquid nitrogen to expose the intact surface fracture and the intrinsic morphology. Here, the light and dark areas represent the PI matrix and CNTs, respectively. The CNTs in the PI matrix were observed as individual tubes. Yu *et al.* reported that most of the CNTs incorporated in the PI matrix existed as individual tubes or small nanotube bundles.¹⁵ Modified CNTs were well dispersed without any obvious aggregation, and the diameters of the CNTs were no larger than 50 nm. The greatly improved dispersion of CNTs in the PI matrix might be due to the strong interfacial interactions (covalent and hydrogen bonds) as well as to the chemical compatibility between the PI matrix and the modified CNTs.

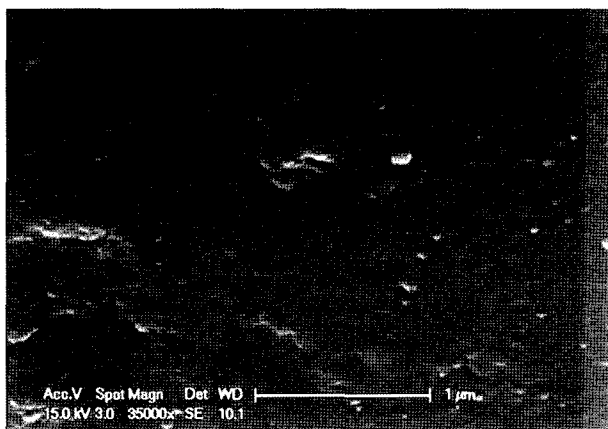
Conclusions

Polyimide/CNT composites were prepared using an efficient solution process. The good dispersion of CNTs in the polymer matrix was obtained by using a modified CNT with a nitric acid-treatment. The mean particle size of CNTs in the PI matrix was approximately 50 nm. The thermal stability of the composite films increased with increasing CNT content. The CTEs were decreased slightly, but the dielectric constants of these composite films increased linearly with increasing CNT content.

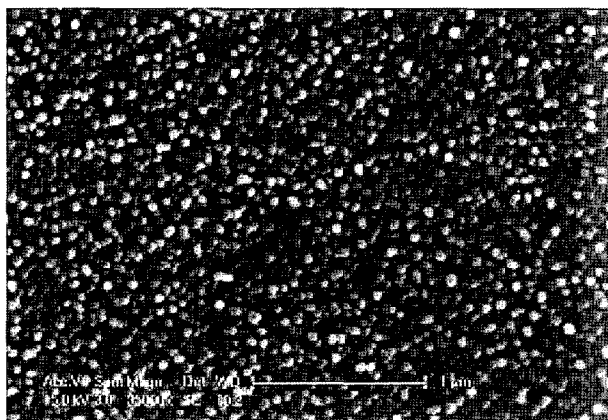
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References

- (1) M. K. Ghosh and K. L. Mittal, *Polyimides: Fundamental and Applications*, Marcel Dekker, New York, 1996.
- (2) G. Rabilloud, *Polyimide in Electronics: Chemistry and Applications*, Clemson Univ. Press, Clemson, 2000.
- (3) M. Lee, *Macromol. Res.*, **14**, 1 (2006).



(a)



(b)

Figure 7. Morphology of the polyimide/CNT composite films. (a) Control and (b) 1.5 wt%.

- (4) J. G. Smith, J. W. Connel, D. M. Delozier, P. T. Lillehei, K. A. Watson, Y. Lin, B. Zhou, and Y. Sun, *Polymer*, **45**, 825 (2004).
- (5) S. Iijima, *Nature*, **354**, 56 (1991).
- (6) Z. Ounaies, C. Park, K. E. Wise, E. J. Siochi, and J. S. Harrison, *Compos. Sci. Technol.*, **63**, 1637 (2003).
- (7) B. Zhu, S. Xie, Z. Xu, and Y. Xu, *Compos. Sci. Technol.*, **66**, 548 (2006).
- (8) Y. Zhang, Z. Dang, S. Fu, J. Xin, J. Deng, J. Wu, S. Yang, L. Li, and Q. Yan, *Chem. Phys. Lett.*, **401**, 553 (2005).
- (9) L. Qu, Y. Lin, D. E. Hill, B. Zhou, W. Wang, X. Sun, A. Kitagorodskiy, M. Suarez, J. W. Connell, L. F. Allard, and Y. Sun, *Macromolecules*, **37**, 6055 (2004).
- (10) K. D. Ausman, R. Piner, O. Lourie, R. S. Ruoff, and M. Korobov, *J. Phys. Chem. B*, **104**, 8911 (2000).
- (11) S. B. Oh, Y. J. Kim, and J.-H. Kim, *J. Appl. Polym. Sci.*, **99**, 869 (2006).
- (12) Y. J. Kim, J.-H. Kim, and J. C. Won, *High Perform. Polym.*, **17**, 19 (2005).
- (13) S. B. Oh, B. S. Kim, and J.-H. Kim, *J. Ind. Eng. Chem.*, **12**, 275 (2006).
- (14) B. I. Lee and N. G. Devaraju, *J. Appl. Polym. Sci.*, **99**, 3018 (2006).
- (15) A. Yu, H. Hu, E. Bekyarova, M. E. Itkis, J. Gao, B. Zhao, and R. C. Haddon, *Compos. Sci. Technol.*, **66**, 1187 (2006).