

Fabrication and Characterization of Solution Cast MWNTs/PEI Nanocomposites

Lu Shao,¹ Yong-Ping Bai,¹ Xu Huang,¹ Ling-Hui Meng,¹ Jun Ma²

¹Department of Polymer Science and Engineering, School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, People's Republic of China

²School of Municipal and Environmental Engineering, Harbin Institute of Technology, 202 Haihe Road, Harbin 150090, People's Republic of China

Received 18 July 2008; accepted 26 January 2009

DOI 10.1002/app.30197

Published online 17 April 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Under mild conditions with the aid of ultrasonic, multi-walled carbon nanotubes (MWNTs) have been functionalized by mixed acid treatment which was proved by FTIR and XPS. According to SEM, acid treatment on MWNTs decreased the thickness of the membrane. However, no devastating damage and fracture happened on MWNTs after acid treatment under mild conditions. Precipitation observation illustrated that the enhanced solubility of MWNTs in water, ethanol, and dimethylformamide (DMF). Further, MWNTs/polyetherimide (PEI) nanocomposite films have been prepared by the simple solution casting method. The dispersion of MWNTs in polyetherimide (PEI) matrix was observed by Atomic Force Microscopy (AFM) which illustrated the improved dispersion for acid

treated MWNTs in PEI. The adding of MWNTs in PEI decreased the dispersive component of surface energy and increased the polar component of surface energy, which resulted in the decrement of film surface energy. Differential scanning calorimetry showed that the glass transition temperature of PEI increased by about 4°C after the introduction of MWNTs. This improvement was related to the better affinity between MWNTs and PEI matrix, which also resulted in the improvement of mechanical strength in MWNTs/PEI nanocomposites. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1879–1886, 2009

Key words: multi-walled carbon nanotubes; polyetherimide acid modification; solution casting; nanocomposites

INTRODUCTION

Since the clear observation by Iijima¹ in 1991, carbon nanotubes (CNTs) have attracted considerable attention due to the unique structural, electrical, and mechanical properties.^{2–7} One of the most intriguing applications of CNTs is the CNTs/polymer nanocomposites.^{8–10} CNTs-based nanocomposites derived from various polymer matrixes such as polyethylene, polypropylene, poly(methyl methacrylate), poly(furfuryl alcohol), and polyurethane^{11–14} have been widely studied and typically showed the promising properties. Polyimide (PI) is the high-performance

polymer which bears with the advantages of high-temperature stability, excellent dielectric properties, and good chemical resistance. Therefore, polyimides has been widely used in the composite, microelectronics industries, and other advanced technologies.^{15,16} CNTs can further enhance the properties of polyimides, which currently attract great attention on CNTs/PI nanocomposite applications in various fields.^{17–20}

Liu et al. prepared multi-walled carbon nanotubes (MWNT)/PI composites by in-situ polymerization.¹⁷ The fine dispersion of MWNTs throughout PI matrix as well as the strong interfacial adhesion between MWNTs and matrix had been obtained by this approach. Mechanical characterizations showed that, with incorporating only 1 wt % MWNTs, the elastic moduli of nanocomposites was significantly improved about 248% while the tensile strength was comparable to that of neat PI matrix. Jiang et al. also fabricated PI-CNT composites by in-situ polymerization using MWNTs as fillers.²¹ Although in-situ polymerization^{22,23} can make a good dispersion of CNTs into matrixes, the process is complicated which hurdles its further development and wide applications.

Up to now, there have been several strategies to fabricate CNTs/polymer nanocomposites, including

Correspondence to: L. Shao (odysseynus@hotmail.com).

Contract grant sponsor: Specialized Research Fund for the Doctoral Program of Higher Education; contract grant number: 20070213004.

Contract grant sponsor: China Postdoctoral Science Foundation Funded Project; contract grant number: 20080430916.

Contract grant sponsor: Heilongjiang Postdoctoral Grand; contract grant number: LRB07-253.

Contract grant sponsor: Scientific Research Foundation for the Returned Oversea Chinese Scholars, State Education Ministry.

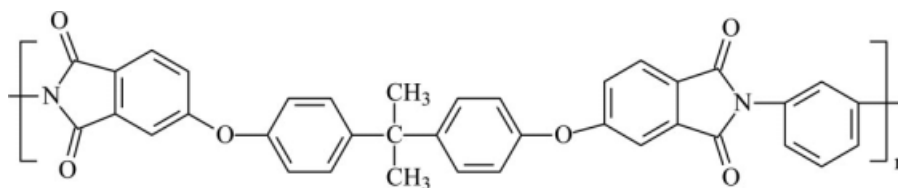


Figure 1 Chemical structure of polyetherimide.

solution casting,²⁴ melt blending,²⁵ melt spinning,²⁶ and in-situ polymerization. Each of these approaches has its advantages and disadvantages. The crucial point for the success of each approach is attributed to the chemical compatibility among different components in nanocomposites. In this study, the MWNTs were chemically modified by acid mixture under mild conditions to improve the compatibility between CNTs and commercial PI (Ultem[®]-1000). The original and acid-modified MWNTs were characterized by FTIR, XPS, SEM, TGA, and precipitation observation in different solvents. Furthermore, the MWNTs with and without modifications were added into polyetherimide (Ultem-1000) for fabricating MWNTs/PEI nanocomposites by the simple method of solution casting. Morphologies and thermal properties of nanocomposites were investigated by Atomic Force Microscopy (AFM) and DSC. Tensile strength and surface energy were further analyzed and discussed in details.

EXPERIMENTAL

Materials

Multi-walled carbon nanotubes (purity > 95%) were obtained from the Nanotech Port Company, Shenzhen, China. The diameter of MWNTs was 40 ~ 60 nm and the length was 5 ~ 15 μm . Polyetherimide (Ultem-1000) was purchased from GE Company used as received and the chemical structure of Ultem-1000 was demonstrated in Figure 1. Other reagents were purchased from local companies and used without further purification.

Acid modification of MWNTs under mild conditions

MWNTs were treated by a mixture of H_2SO_4 and HNO_3 with a weight ratio of 3 : 1 (H_2SO_4 : HNO_3) according to the references.^{26,27} In brief, MWNTs/acid solution with the weight ratio 500 : 1 (mixed acids: MWNTs) was treated by ultrasonic (100W) with different durations at 50°C to obtain acid-modified MWNTs. After acid treatment, MWNTs were washed using deionized water, filtered and dried in

120°C in vacuum.^{28–30} Resultant products were ready for further usage.

Preparation of MWNTs/PEI nanocomposites

Unmodified or modified MWNTs with prescribed weight were added to 2% PEI/chloroform solution (by weight) with vigorous stirring. The suspension was further dispersed by ultrasonic for 1 h and stirred at room temperature for 12 h. The suspension was cast onto a glass plate at room temperature. After controlled evaporation, the nascent films were dried in vacuum at 100°C for 48 hrs to remove the residual solvent. Finally, MWNTs/PI nanocomposite membranes were prepared for testing and characterizations.

Characterization

Fourier transform infrared spectroscopy (FTIR) spectra of MWNTs were recorded between 400 cm^{-1} and 4000 cm^{-1} using a Nicolet-Nexus 670 FTIR spectrometer. The sample was dried overnight in a vacuum oven at 120°C before tested. MWNTs were mixed with KBr and the mixture was pressed into plate form for FTIR characterization. X-ray photoelectron spectroscopy (XPS) was used to determine the surface chemical composition of original and acid-modified MWNTs. The XPS measurements were made on an AXIS HSi spectrometer using the monochromatized Al $\text{K}\alpha$ X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and a pass energy of 40 eV. All core-level spectra were obtained at a photoelectron take-off angle of 90° with respect to the sample surface. TGA was performed using TGA2050 in air with a heating rate of 10°C/min. SEM was carried out by FEI Sirio (scanning electron microscope) with the 10s coating time. Precipitation observation was performed by mixing MWNTs with different solvents by ultrasonic dispersion. Then, MWNTs/solvent solutions were positioned without disturbance for precipitation observation. Tensile tests were performed by a WD-1 type universal testing machine (Changchun Second Material Testing Machine Factory, PR China). The cross-head speed was 20 mm/min and a span-to-

TABLE I
Components of Surface Energy of Wetting Liquids Used

	(mJ/m ²)	(mJ/m ²)	(mJ/m ²)
Ultrapure water	22.1	50.7	72.8
Bromonaphthalene	44.4	0	44.4

depth ratio was 5 : 1. The tensile strength of films was calculated by the following eq. (1):

$$\delta = \frac{F}{D \times S} \quad (1)$$

where δ is the tensile strength of film (MPa); F is the force when broken (N); D is the thickness of film (μm); and S is the width of films (mm). The surface energy of films was tested at 22 ± 2 °C by an SB312-II Dynamic Wetting Determination Equipment from (Beijing) KeEn company. The Owens–Wendt approach was used to determine the total surface energy including dispersive and polar components. The expressions to combine dispersive and polar components of the wetting liquids and solid surface energy are as follows:

$$\gamma_1(1 + \cos \theta_1) = 2(\gamma_f^d \gamma_1^d)^{1/2} + 2(\gamma_f^p \gamma_1^p)^{1/2} \quad (2)$$

$$\gamma_2(1 + \cos \theta_2) = 2(\gamma_f^d \gamma_2^d)^{1/2} + 2(\gamma_f^p \gamma_2^p)^{1/2} \quad (3)$$

where θ is the contact angle between film and liquid; γ is the surface energy, subscripts 1, 2, and f refer to two different wetting liquids and film, respectively, and superscripts d and p refer to dispersive and polar components, respectively. The Owens–Wendt approach expresses the total surface energy as the contributions from both dispersive and polar components:

$$\gamma_f = \gamma_f^p + \gamma_f^d \quad (4)$$

When contact angles of the two wetting liquids on the film surface were measured, dispersive and polar components of surface energy of silica glass surface can be calculated from eqs. (2) and (3), and then total surface energy were obtained from eq. (4). The two liquids used are ultrapure water and bromonaphthalene, the basic data of which are shown in Table I.

Differential scanning calorimetry (DSC: NETZSCH STA449^C) was performed to characterize the thermal properties of nanocomposites. The samples were heated with a scanning rate of 10°C /min under nitrogen atmosphere to diminish oxidation. The surface morphology of purified PEI membrane and PEI/MWNTs nanocomposites was observed by atomic force microscope (NT-MDT, Zelenograd Research Institute of Physical Problems, Moscow,

Russia). The test was performed at room temperature and scanned with 12×12 μm area. Images were obtained in non-contact mode with a silicon cantilever (nominal spring constant of 3 N/m, minimum tip radius of 10 nm).

RESULTS AND DISCUSSION

Characterization of MWNTs before and after acid modification

FTIR results of original MWNTs and acid-modified MWNTs are shown in Figure 2. For FTIR test, the amount of MWNTs relative to KBr should be strictly controlled around 0.3% because MWNTs significantly absorb infrared rays. According to Figure 2, the band at 1573 cm^{-1} corresponds to C-deformation vibrations, which shows in both original and modified MWNTs. Compared with original MWNTs, acid-modified MWNTs show the new bands of C=O stretching vibration at 1720 cm^{-1} and C–O stretching vibration at 1220 cm^{-1} of carboxylic groups stretching (COOH) and the –OH stretching vibrations 3440 cm^{-1} indicating the presence of carboxylic groups on the surface of MWNTs. Because MWNTs are modified under very mild condition (ultrasonic treatment at 50°C), the surface functionalization of MWNTs is detectable, however, not very obvious. The benefits of this approach of mild modification are the less damage and breakage of MWNTs during modifications, which is crucial for nanocomposite applications. For further confirmation of the functionalization, XPS analysis also is employed to characterize the surface state of chemically modified MWNTs.

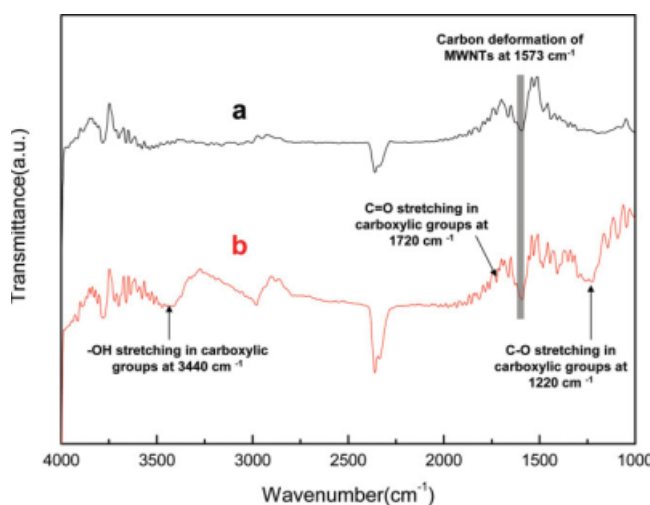


Figure 2 FTIR spectra of (a) original MWNTs and (b) 6 hrs acid-modified MWNTs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

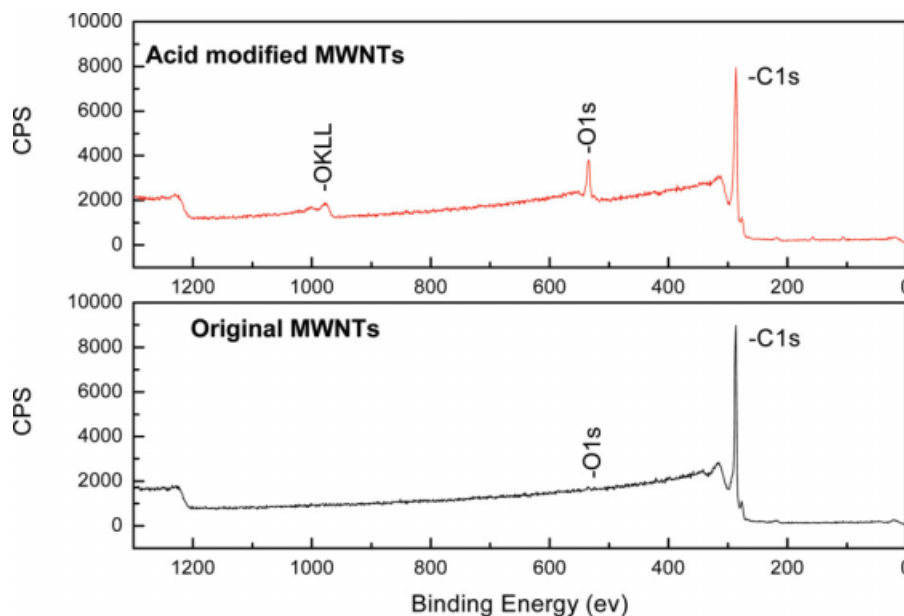


Figure 3 XPS wide spectra of original and 6 hrs acid-modified MWNTs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

XPS wide spectra of original and acid-modified MWNTs are demonstrated in Figure 3, and Table II lists the elemental composition. The ratio of oxygen to carbon on the surface of original MWNT is around 0.011, which is consistent with reference report.^{31,32} The induction of polar oxygen on the surface of acid-modified MWNTs is mainly contributed by $-\text{COOH}$ and $-\text{OH}$ groups corresponding to FTIR analysis.³³ Further analysis based on the curve fitting of C 1s peaks is performed and the result is illustrated in Figure 4 and Table III. Based on the possible reaction, the C_{1s} peak region of MWCNTs has been deconvoluted into four fitting curves at 284.6 eV, 286.1 eV, 288.3 eV, and 290.5 eV, which are correspondent to C–C, C–O, C=O, and O–C=O, respectively.³³ The decrease of sp^3 C–C groups and increase of other oxygen content functional groups on the surface of MWNTs after acid treatment, from another side, proves the successful functionalization of MWNTs, which is consistent with the FTIR results. Although the chemical effect of acids on MWNTs is illustrated by FTIR and XPS characterizations, what is the physical effect of acids on MWNTs?

TABLE II
Surface Elemental Composition of MWNTs Before and After Acid Modification

Sample	C (%)	O (%)	O/C
Original MWNTs	98.98	1.02	0.011
6 hrs acid-modified MWNTs	86.06	13.94	0.162

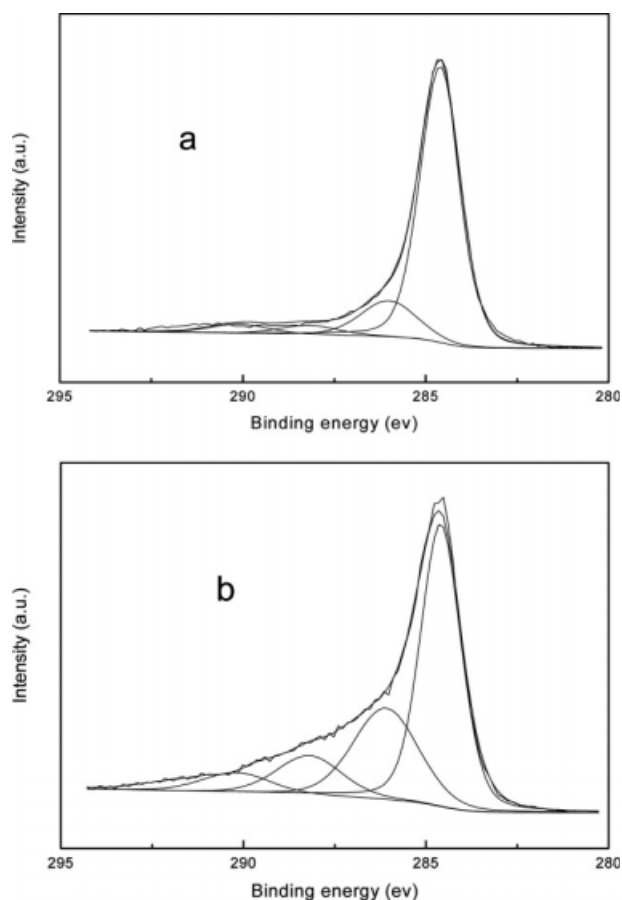


Figure 4 Curve fitting of C_{1s} peak area to surface functional groups of (a) original MWNTs and (b) 6 hrs acid-modified MWNTs.

TABLE III
Functional Group Content Based on Curve Fitting of C1s
Peak Area to Surface Functional Groups

	Functional group content (%)			
	C—C	C—O	C=O	O=C—O
Pristine MWNTs	78.33	14.08	3.79	3.79
6 hr acid-modified MWNTs	54.27	27.60	11.87	6.26

The reflux of MWNTs in acid mixture at elevated temperatures typically results in the devastating fracture. However, in this study, MWNTs are treated at mild condition with the aid of ultrasonic. To illustrate the physical effect of acids on MWNTs, SEM is performed and the result is shown in Figure 5. Based on SEM pictures, the thickness of MWNTs decreases a little after acid treatment, and no devastating breakage happens during this process. The above result indicates that the mild ultrasonic treatment is a suitable approach to functional CNTs without significantly damaging the physical properties.

The thermal property is characterized by TGA in Figure 6. The degradation temperature (defined as 5% weight loss in this study) decreases from 585°C to 441°C, which should be due to the vulnerability of —COOH groups to the thermal treatment. Although the final residual weight of acid-modified MWNTs (around 3.6%) is less than that of pristine MWNTs (around 5.7%), the interesting point is that the residual weight of acid-modified MWNTs is higher during 640°C–720°C. One possible reason is that the acid treatment purifies MWNTs by eliminating the impurities such as amorphous carbons, which makes it “stronger” than pristine MWNTs during 640°C–720°C. Furthermore, the solubility of MWNTs before and after acid modifications is observed and demonstrated in Figure 7. Although the well dispersion is shown up for both pristine and acid-modified MWNTs after ultrasonic disper-

sion, the obvious dispersion stability of acid-modified MWNTs after 30 days illustrates the enhanced solubility of MWNTs by acid treatment.

Characterization of MWNTs/PEI nanocomposites fabricated by solution casting

FTIR was performed on the pure PEI and acid 6 hrs modified MWNTs/PEI as shown in Figure 8. According to Figure 8, the PI has the characteristic bands³⁴ at around 1775 cm⁻¹ (attributed to C=O asymmetric stretch of imide groups), 1715 cm⁻¹ (attributed to C=O symmetric stretch of imide groups)³⁵, and 1375 cm⁻¹ (attributed to C—N stretch of imide groups), which are shown in both samples. It is obvious that the FTIR spectra of acid-modified MWNTs/PEI nanocomposites are almost the same as that of pure PEI. These phenomena reveal that adding MWNTs into the PI matrix did not have obvious effect on the chemical structure of polyetherimide because of the low loading of MWNTs.

The surface energies of different nanocomposites are examined and the results are listed in Table IV. According to Table IV, the surface characteristics of PEI film fabricated by solution casting have been changed after the introduction of MWNTs. Generally, the surface energy of different MWNTs/PEI films are all lower than that of pure PEI film and acid 6 hrs modified MWNTs/PEI film possesses the lowest surface energy. The declined surface energy of MWNTs/PEI is mainly due to the significant reduction of dispersive component. Although both surface energy and dispersive component of surface energy decrease after adding MWNTs to PEI, the polar component enhancement should arise from the water solubility of MWNTs and the surface polar groups of MWNTs as XPS and FTIR indicated. Therefore, the introduction of MWNTs to PEI contributes to the decline of the dispersive component and the enrichment of polar component of surface energy in films, which may be important for the

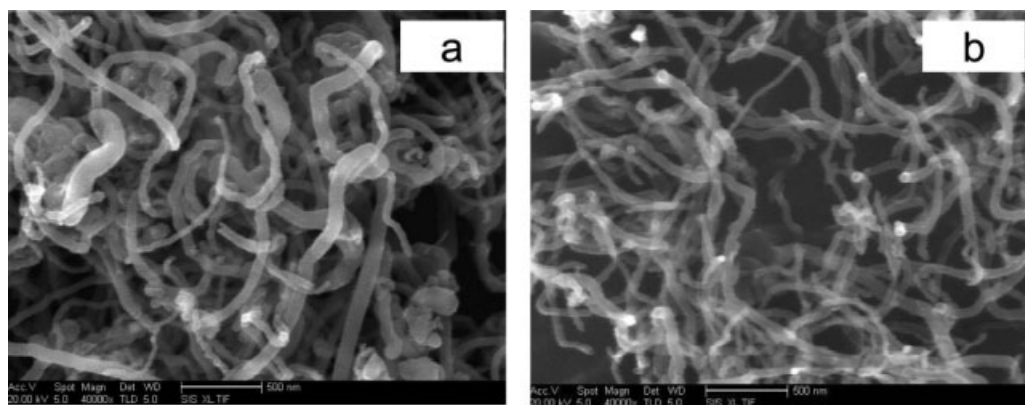


Figure 5 SEM pictures of (a) original MWNTs and (b) 6 hrs acid-modified MWNTs.

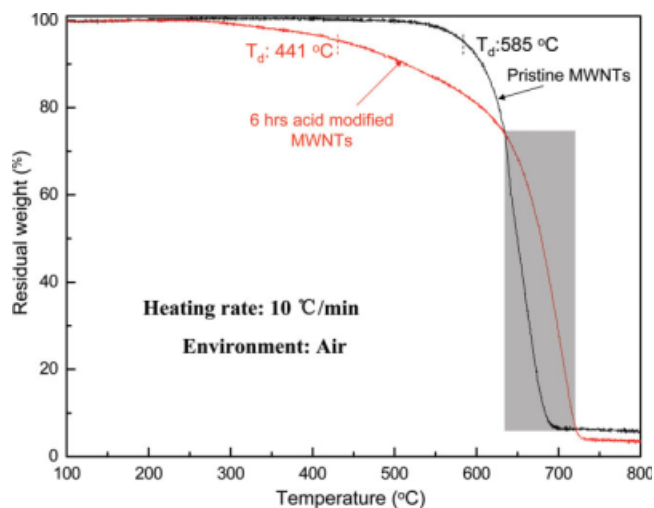


Figure 6 TGA result of MWNTs before and after acid modification. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

prospective biomedical applications of MWNTs/PEI nanocomposites.

The typical microstructure of MWNTs/PEI nanocomposites investigated by AFM is presented in Figure 9. Figure 9(b,c) are the AFM observations of the dispersion of the original and acid-modified MWNTs on the surface of MWNTs/PEI (the content of MWNTs is 1 wt%), respectively. Although not very good, compared with pristine MWNTs dispersed in PEI matrix, acid-modified MWNTs can be dispersed fairly throughout the bulk of PI matrix

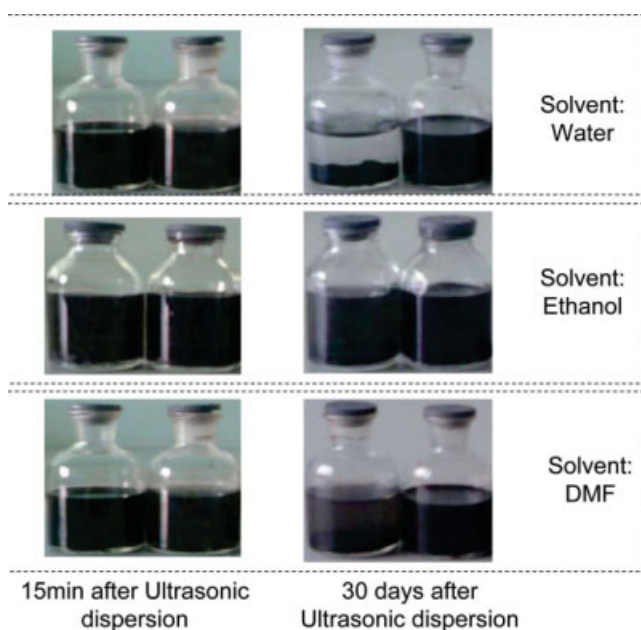


Figure 7 Precipitation observation of MWNTs in different solvents (left: pristine MWNTs; right: 6 hr acid-modified MWNTs).

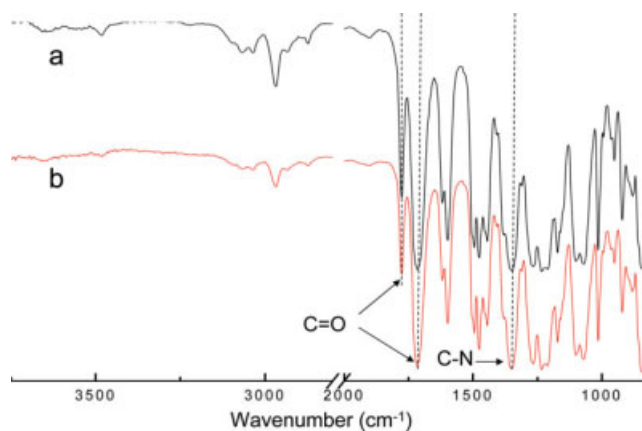


Figure 8 FTIR spectra of (a) pure PEI and (b) 6 hrs acid-modified MWNTs/PEI nanocomposite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

when the contents of MWNTs are low (wt% = 1%). The improved dispersion of MWNTs should be due to interfacial interactions and better chemical compatibility between the PI matrix and acid-modified MWNTs. As a result, the solution casting method can fabricate MWNTs/PEI nanocomposites with the acceptable MWNTs dispersion by using acid-modified MWNTs, which is further proved by the following mechanical test.

It is reported that tensile strength of carbon nanotubes can reach as high as 1 TPa with an aspect ratio of around 1000.³⁶ In this study, it is expected that MWNTs may improve the tensile strength of nanocomposites. Therefore, mechanical tests of different MWNTs/PEI samples are carried out and the results are listed in Table V. According to Table V, the tensile strength of pure PEI is 77.4 MPa. However, after the induction of pristine MWNTs in PEI matrix, the tensile strength of nanocomposites decreases to 60.2 MPa, which is due to the incompatibility between original MWNTs and PEI. However, if acid-modified MWNTs are applied to fabricate nanocomposites instead of pristine MWNTs, the tensile strength becomes better. The longer acid modification duration results in MWNTs with more polar groups to be compatible with PEI matrix. When the acid modification duration reaches 6 hrs, the tensile strength of nanocomposites becomes 77.9 MPa which is higher than that of pure PEI film. Therefore, the simple solution casting can

TABLE IV
Surface Energy and its Different Components of Films

Samples	(mJ/m ²)	(mJ/m ²)	(mJ/m ²)
Pure PEI	41.3	34.23	7.07
Original MWNTs/PEI	34.91	19.61	15.30
6 hrs acid-modified MWNTs/PEI	31.17	12.55	18.62

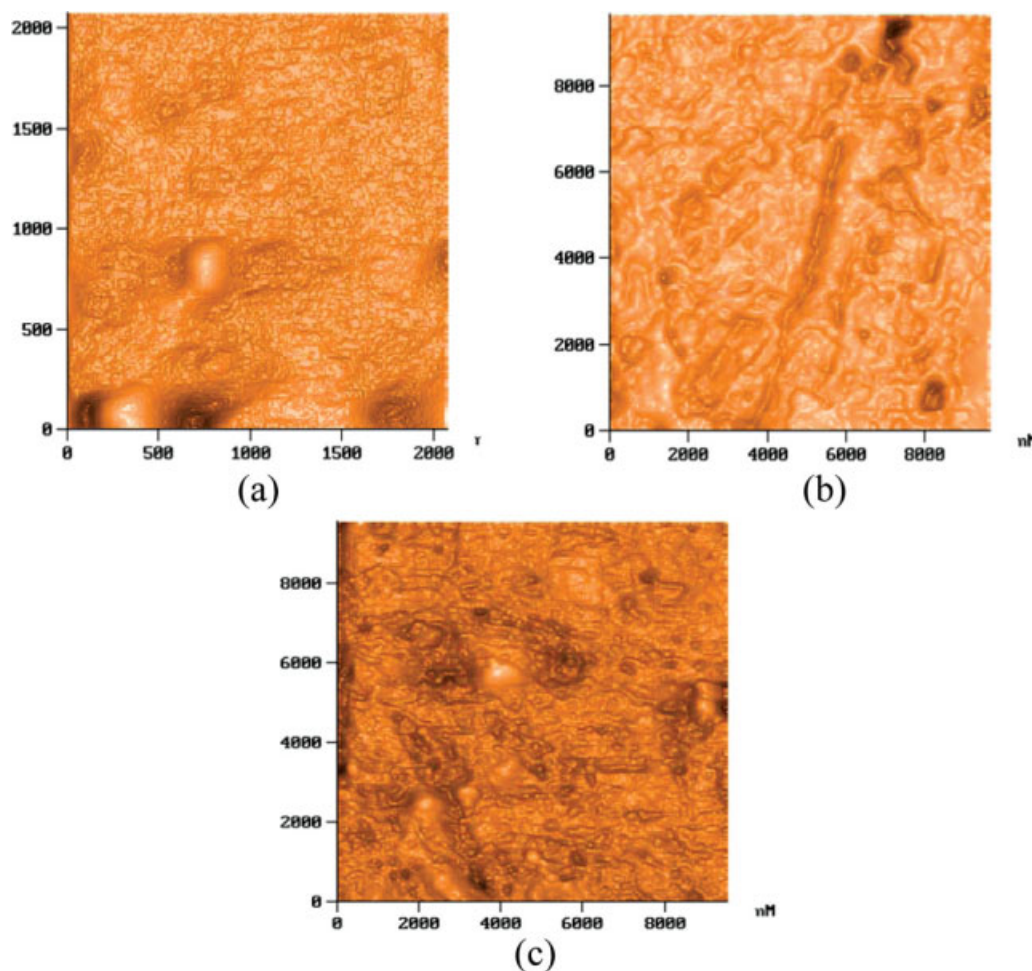


Figure 9 AFM images of (a) pure PEI, (b) original MWNTs/PEI, and (c) 6 hrs acid-modified MWNTs/PEI. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

fabricate nanocomposites with good mechanical properties by using acid modified MWNTs at mild conditions.

Figure 10 demonstrates DSC results of pristine PEI and 6 hrs acid-modified MWNTs/PEI (MWNTs content is 1% by weight) nanocomposites. It can be seen that, by incorporating only 1 wt % MWNTs into PEI matrix, T_g of films increases from 203.9°C to 207.3°C. This indicates that the mobility of polymer chains in nanocomposites is hindered due to the constraint effect of MWNTs arising from the improved compatibility between 6 hrs acid-modified MWNTs and PEI, which is consistent with the enhancement

in tensile strength of nanocomposites. Therefore, adding MWNTs to PEI by solution casting can enhance the thermal property of PEI.

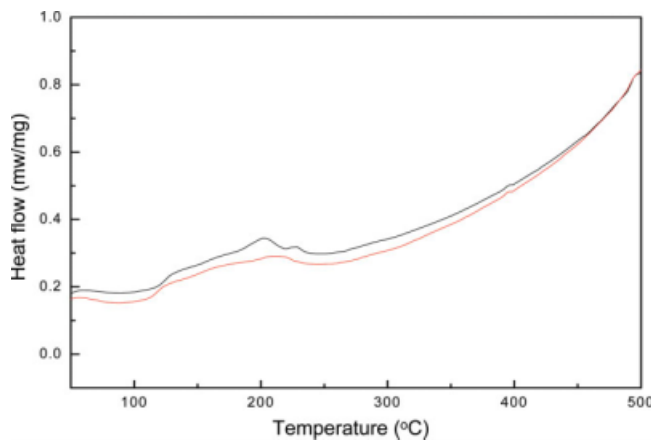


Figure 10 DSC curves of (a) pure PEI and (b) 6 hrs acid-modified MWNTs/PEI nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE V
Tensile Strength Comparison of Different Films

Samples	Tensile strength (MPa)
Pure PEI	73.4
Original MWNTs/PEI	60.2
2 hrs acid-modified MWNTs/PEI	64.7
4 hrs acid-modified MWNTs/PEI	68
6 hrs acid-modified MWNTs/PEI	77.9

CONCLUSIONS

FTIR and XPS analysis illustrates that mixed acid modification can effectively graft polar groups on the surface of MWNTs, which mainly includes —COOH and —OH. The grafted polar groups can enhance the stability of MWNTs in water, ethanol, and DMF. At the same time, because the acid modification is performed at mild conditions (by ultrasonic at 50°C), no significant fracture is observed by SEM. Although the degradation temperature becomes lower, acid-modified MWNTs still can bear with temperature up to 441°C only with around 5% weight loss. Although not perfect, acid-modified MWNTs still can be fairly dispersed in PEI matrix fabricated by solution casting, which is indicated by the enhancement in the tensile strength and glassy temperature of MWNTs/PEI nanocomposites. The adding of MWNTs to PEI contributes to the decline of the dispersive component and the increment of polar component of surface energy in film, which may be important for the prospective biomedical applications of MWNTs/PEI nanocomposites.

References

- Iijima, S. *Nature* 1991, 354, 56.
- Lin, M.; Tan, J.; Boothroyd, C.; Loh, K. P.; Tok, E. S.; Foo, Y. L. *Nano Lett* 2007, 7, 2234.
- Peigney, A.; Laurent, C.; Flahaut, E. *Synth Met* 2001, 3, 507.
- Chen, J.; Du, D.; Yan, F. *Chem Eur J* 2005, 13, 1467.
- Pedano, M. L.; Rivas, G. A. *Electrochem Commun* 2004, 6, 10.
- Frackowiak, E.; Jurewicz, K.; Szostak, K. *Fuel Process Technol* 2002, 14, 213.
- Geng, H.; Rosen, R.; Zheng, B.; Shimoda, H.; Fleming, L.; Liu, J.; Zhou, O. *Adv Mater* 2002, 14, 1387.
- Yang, B. X.; Pramoda, K. P.; Xu, G. Q.; Goh, S. H. *Adv Funct Mater* 2007, 17, 2062.
- Liu, P. *Eur Polym J* 2005, 41, 2693.
- Wang, C. C.; Guo, Z. X.; Fu, S. K.; Wu, W.; Zhu, D. B. *Prog Polym Sci* 2004, 29, 1079.
- Chang, T. E.; Ensen, L. R.; Kisliuk, A.; Pipes, R. B.; Pyrz, R.; Sokolov, A. P. *Polymer* 2005, 46, 439.
- Men, X. H.; Zhang, Z. Z.; Song, H. J.; Wang, K.; Jiang, W. *Appl Surf Sci* 2008, 254, 2563.
- Yuen, S. M.; Ma, C. C. M.; Lin, Y. Y.; Kuan, H. C. *Compos Sci Technol* 2007, 67, 2564.
- Yu, H. H.; Cao, T.; Zhou, L. D.; Gu, E.; Yu, D. S.; Jiang, D. S. *Sens Actuators B Chem* 2006, 119, 512.
- Shao, L.; Chung, T. S.; Pramoda, K. P. *Microporous Mesoporous Mater* 2005, 84, 59.
- Rubianes, M. D.; Rivas, G. A. *Electrochem Commun* 2007, 9, 480.
- Liu, T. X.; Tong, Y. J.; Zhang, W. D. *Compos Sci Technol* 2007, 67, 406.
- Sun, K. J.; Wincheski, R. A.; Park, C. J. *Appl Phys* 2008, 103, 023908.
- Peng, F. B.; Hu, C. L.; Jiang, Z. Y. *J Membr Sci* 2007, 297, 236.
- Yu, A.; Hu, H.; Bekyarova, E.; Itkis, M. E.; Gao, J.; Zhao, B.; Haddon, R. C. *Compos Sci Technol* 2006, 66, 1190.
- Jiang, X. W.; Bin, Y. Z.; Matsuo, M. *Polymer* 2005, 46, 7418.
- Wise, K. E.; Park, C.; Siochi, E. J.; Harrison, J. S. *Chem Phys Lett* 2004, 391, 207.
- Shieh, Y. T.; Yang, Y. F. *Eur Polym J* 2006, 42, 3162.
- Foster, J.; Singamaneni, S.; Kattumenu, R.; Bliznyuk, V. *J Colloid Interface Sci* 2005, 287, 167.
- Zhang, W. D.; Phang, I. Y.; Shen, L.; Chow, S. Y.; Liu, T. X. *Macromol Rapid Commun* 2004, 25, 1860.
- Park, S. J.; Lim, S. T.; Cho, M. S.; Kim, H. M.; Joo, J.; Choi, H. *J Curr Appl Phys* 2005, 5, 302.
- Goyanes, S.; Rubiolo, G. R.; Salazar, A.; Jimeno, A.; Corcuera, M. A.; Mondragon, I. *Diam Relat Mater* 2007, 16, 412.
- Li, J. Z.; Tang, T.; Zhang, X. B.; Li, S. Y.; Li, M. *Mater Lett* 2007, 61, 4351.
- Wang, Y. B.; Iqbal, Z.; Malhotra, S. V. *Chem Phys Lett* 2005, 402, 96.
- Gabriel, G.; Sauthier, G.; Fraxedas, J.; Moreno-Manas, M.; Martinez, M. T.; Miravittles, C.; Casabo, J. *Carbon* 2006, 44, 1891.
- Shen, J. F.; Huang, W. S.; Wu, L. P.; Hu, Y. Z.; Ye, M. X. *Mater Sci Eng A* 2007, 464, 151.
- Xu, T.; Yang, J. H.; Liu, J. W.; Fu, Q. *Appl Surf Sci* 2007, 2532, 8945.
- Okpalugo, T. I. T.; Papakonstantinou, P.; Murphy, H.; McLaughlin, J.; Brown, N. M. D. *Carbon* 2005, 43, 153.
- Shao, L.; Chung, T. S.; Wensley, G.; Goh, S. H.; Pramoda, K. P. *J Membr Sci* 2004, 244, 77.
- Shao, L.; Liu, L.; Cheng, S. X.; Huang, Y. D.; Ma, J. *J Membr Sci* 2008, 312, 174.
- Li, F.; Cheng, H. M.; Bai, S.; Su, G.; Dresselhaus, M. S. *Appl Phys Lett* 2000, 77, 3161.