Mechanical and Thermal Properties of Functionalized Multiwalled Carbon Nanotubes and Multiwalled Carbon Nanotube–Polyurethane Composites

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ABSTRACT: Multiwalled carbon nanotube (MWNT)–polyurethane (PU) composites were obtained by an *in situ* polycondensation approach. The effects of the number of functional groups on the dispersion and mechanical properties were investigated. The results showed that the functionalized MWNTs had more advantages for improving the dispersion and stability in water and N,N'-dimethylformamide. The tensile strength and elongation at break of the composites exhibited obvious increases with the addition of MWNT contents below 1 wt % and then decreases with additions above 1 wt %. The maximum values of the tensile strength and elongation at break increased by 900 and 741%, respectively, at a 1 wt % loading of MWNTs. Differential scanning calorimetry measurements indicated that the addition of MWNTs resulted in an alteration of the glass-transition temperature of the soft-segment phase of MWNT–PU. Additionally, new peaks near 54°C were observed with differential scanning calorimetry because of the microphase-separation structures and alteration of the segment molecular weights of the hard segment and soft segment of PU with the addition of MWNTs. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3407–3413, 2009

Key words: mechanical properties; morphology; nanocomposites; polyurethanes; TEM

INTRODUCTION

Carbon nanotubes (CNTs), because of remarkable properties such as excellent Young's modulus, good flexibility, and high electrical and thermal conductivity, have attracted considerable interest from the scientific community and industry.[1] CNTs are recognized as perfect reinforcements for high-performance, multifunctional composites.[2] Recently, there have been considerable achievements in CNT–polymer composites, which show extraordinary enhancements in their electrical and mechanical properties in comparison with monolithic polymers.[3–7] In many cases, these composites can be used not only as polymeric matrices but also as other matrix materials. Polymer composites reinforced with CNTs are believed to have many potential engineering uses ranging from battery electrodes, electronic devices, chemical/biological sensors, and catalysis to ultrastrong materials.[1,8–11] The advantages of CNTs as nanofibers include their light weight, high aspect ratio, and large surface area, which are good for physical absorption or chemical bonding. Many researchers have shown that the addition of only small fractions of CNTs can significantly change the properties of polymer materials. The atomic-scale structures of CNT composites, especially the relative structures at the interface between the polymer matrix and CNTs, are expected to explain many unique properties exhibited by nanotube-based composites.[12] In particular, this combination of properties makes CNTs ideal candidates for advanced filler materials in nanocomposites.

Polyurethanes (PUs) are an important and very versatile class of polymer materials with desirable properties, and they are used in a variety of products, such as coatings, adhesives, biomedical materials, elastomers, flexible and rigid foams, and tough solids.[13–15] However, the weak mechanical strength and poor durability of PUs have limited their practical applications. At present, some contributions have focused on physically crosslinked PU elastomers for long-term applications. A number of previous studies have demonstrated that the presence of CNTs
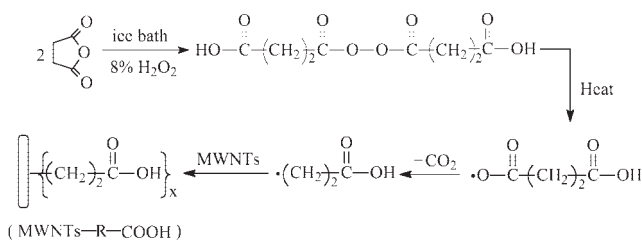
Scheme 1 Preparation of sidewall acid-functionalized MWNTs.

can improve the properties of a PU matrix.[16–24] Liu et al.[16] reported that the addition of multiwalled carbon nanotubes (MWNTs) to PU elastomer films can improve the permeability and conductivity of the PU elastomer. For PU–urea CNT composites prepared by the sol–gel process, the tensile strength and Young's modulus were improved by nearly 150 and 400%, respectively, whereas the elongation at break was retained completely, as reported by Xu et al.[20] The widespread applications of PU in different fields have brought about higher requirements for their properties. Therefore, exploiting high-performance PU is always of great importance.

We previously reported polymeric carbon nanocomposites via an *in situ* polycondensation approach.[25] In this work, the dispersion of functionalized MWNTs was studied, and the effects of the contents of MWNTs on PU were investigated. The mechanical and thermal properties of MWNT–PU composites were also evaluated.

EXPERIMENTAL

Materials

The pristine MWNTs used in this work were prepared by the chemical catalytic vapor deposition process.[26] The obtained products were oxidized with a mixture of concentrated nitric and sulfuric acid (1 : 3 v/v). Succinic acid peroxide was prepared by peroxidation of succinic anhydride in ice-cold 8 wt % hydrogen peroxide. Toluene 2,4-diisocyanate was distilled before use; polybutylene adipate (glycol) was dried *in vacuo* for 7 days; 1,4-butanediol (BDO) and N,N'-dimethylformamide (DMF) were dried over CaH_2; and thionyl chloride ($SOCl_2$), 1,6-diaminohexane, and other solvents were used as received.

## Functionalization of the MWNT sidewall and MWNT–PU composites

Generally, the degree of carboxylation is relatively low with ordinary strong oxidant treatment for CNTs. Here we used a convenient route to functionalized carbon nanotubes via the free-radical addition reaction of alkyl groups terminated with a carboxylic acid (Scheme 1). This method is scalable and provides a route to MWNTs functionalized by groups that are suitable for further elaboration. The aim of this step is to add —COOH. Subsequently, the amino-functionalized MWNTs (MWNT–R_1—NH_2) were prepared as shown in Scheme 2. MWNT–PU composites were prepared by an *in situ* polycondensation route. The synthetic procedures are described in Scheme 3. These procedures were previously studied.[25] For comparison, neat PU was synthesized by the same approach described previously, except that MWNT–R_1—NH_2 was added to PU. The compositions and corresponding MWNT contents in the composites are listed in Table I.

Characterization

Transmission electron microscopy (TEM) images were obtained on an H-800 transmission electron microscope (Hitachi Co., Japan) and a JEOL (Tokyo, Japan) 3010 ultrahigh resolution transmission electron microscope. Tensile testing on samples was performed at room temperature with an Instron 4464 universal tester (Changchun, China) according to standard procedures (GB standard 13022-91 for thin films). First, MWNT–PU composite films were obtained through the casting of an MWNT–PU solution into a mixed solvent of tetrahydrofuran and DMF at a 10 wt % concentration; then, the films (6.25 mm wide) with a dog-bone shape were fixed onto the testing station and subjected to an extension rate of 10 mm/min with a gauge length of 25 mm. To ensure data accuracy and repeatability, the results for five samples from different batches were averaged. Ultraviolet–visible (UV–vis)/near-infrared measurements were performed on a TU1901 apparatus (Pgeneral, Beijing, China); the concentration of samples was lower than 10^{-4} mol/L, and the wavelength ranged from 190 to 900 nm. Each sample was centrifuged at 4000 rpm for 30 min. Differential scanning calorimetry (DSC) measurements were performed with a PerkinElmer (Waltham, MA) DSC-7
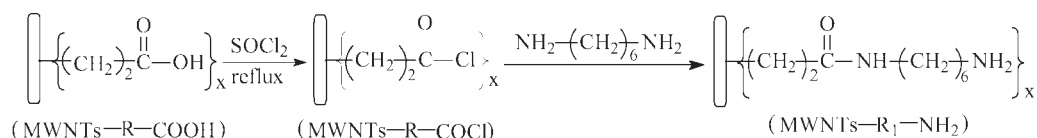
Scheme 2 Preparation of amido derivatives of MWNTs.
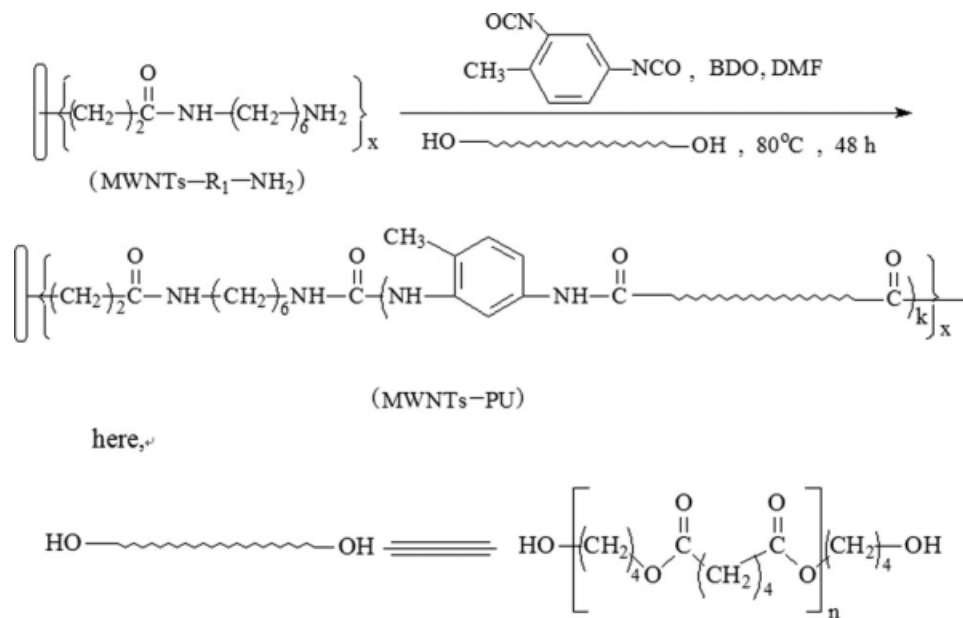
Scheme 3 Polycondensation for the preparation of PU-functionalized MWNTs (MWNT–PU).

Pyris 1 calorimeter within the temperature range of −100 to 200°C at a heating rate of 10°C/min under an N$_2$ atmosphere.

RESULTS AND DISCUSSION

Dispersion and stability of the functionalized MWNTs

The formation of stable suspensions of MWNTs is a critical target in the development of practical applications of some valuable materials.[27] A uniform distribution of fibers throughout the matrix is critical in producing materials with superior physical properties.[28] For various applications, obtaining a good dispersion of nanotubes is one of the critical issues. Indeed, efforts have been directed toward such a goal through the engineering of nanotube surfaces with either covalent or organic approaches. The goal of functionalized MWNTs is to have different organofunctional groups attached to the nanotube surface; this improves their chemical compatibility with specific polymers for producing new nanotube-based composites. MWNTs can be dispersed by aggressive chemical modification of the surface with acids or other functional groups. Here we report a covalent strategy for forming a stable dispersion of MWNTs

in aqueous and DMF solutions. To facilitate the study of suspension stability, we fixed the amounts of MWNTs and sonication time. After subsequent centrifugation, the supernatant was collected in a separate vial, and this ensured that no precipitate of nanotubes was incorporated into the final solution. The final solutions were examined with UV–vis spectroscopy and TEM. The types of samples, weights, solvents, and sonication times are listed in Table II. Figure 1 shows the UV–vis spectra of functionalized MWNT suspensions for samples 1–4 before and after centrifugation. In Figure 1, their spectra show an absorption peak at about 280 nm. The results are presented in Table III. In general, the sediment percentage of the suspension of MWNTs was smaller, and this meant that the suspension had better dispersion and stability under the same conditions. Therefore, the order of dispersion and stability for the four samples was 2 > 1 > 3 > 4. The results imply that the dispersion and stability of an MWNT suspension depends significantly on the amounts of the functionalized groups (here —COOH) on the surface of the MWNTs. Furthermore, the dispersion and stability of a suspension solution of MWNTs are

TABLE I
MWNT–PU Composites

			Sample				
	1	2	3	4	5	6	7
MWNT weight (g)	0	0.05	0.10	0.15	0.20	0.25	0.30
Content (wt %)	0	0.33	0.67	1.00	1.33	1.67	2.00

TABLE II
Sample Types and Weights, Solvents, and Sonication Times

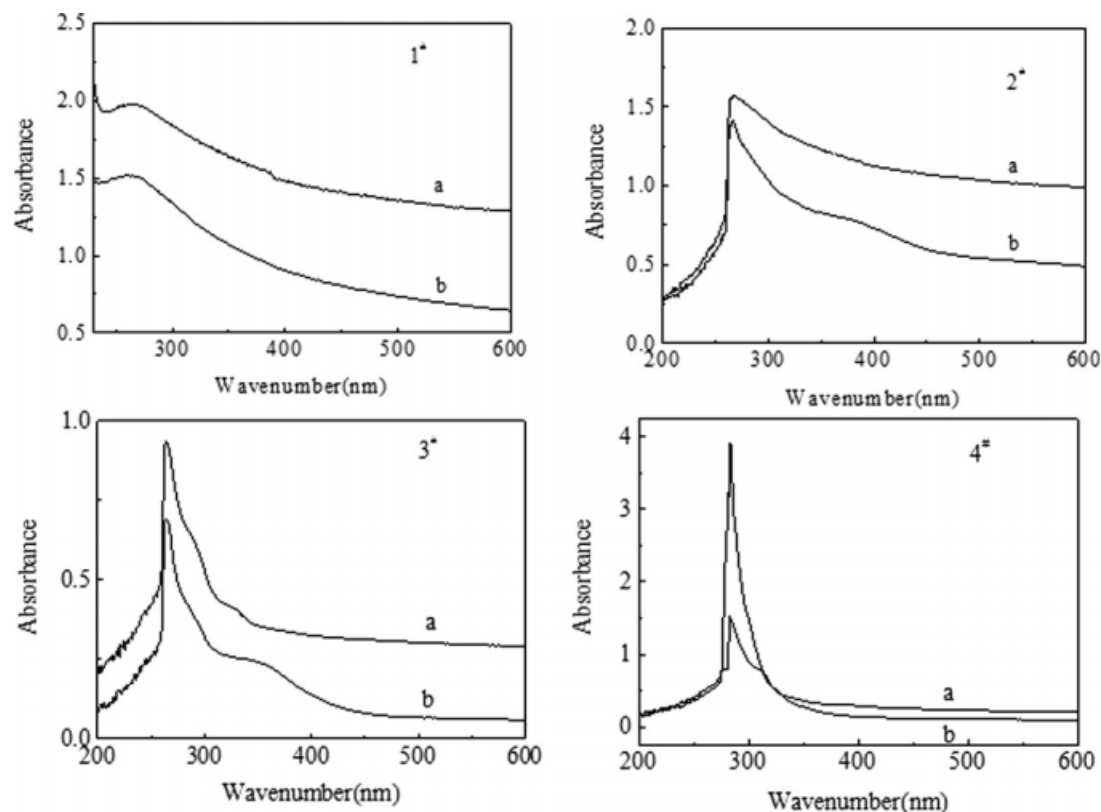| Sample	Type/weight	Solvent/volume	Sonication time
1	MWNT–R—COOH/10 mg	H$_2$O/50 mL	1 h
2	MWNT–R—COOH/10 mg	DMF/50 mL	1 h
3	MWNT–COOH/10 mg	H$_2$O/50 mL	1 h
4	Pristine MWCNTs/10 mg	H$_2$O/50 mL	1 h

Figure 1 UV–vis spectra of MWNT suspensions for samples 1–4: (a) before and (b) after centrifugation.

also associated with the polarity of the solvent. We have found that polar solvents are beneficial for the dispersion and stability of MWNTs. Direct measurements of the dispersion of these samples can be found in the TEM images. Figure 2 presents typical TEM images of these samples, which were prepared by the deposition of small droplet of a solution onto a carbon-coated copper grid followed by the evaporation of the solvent after centrifugation. The TEM image of sample 4 in Figure 2 shows that pristine MWNTs were entangled into large masses, and there were a lot of impurities on their surfaces. The entanglement degree of the other three samples was much lower in comparison with the pristine MWNT sample (4). On the other hand, the order of the entangle-

ment degree from high to low for the three samples was 3, 1, and 2. These results are in good agreement with the trends measured by UV–vis spectroscopy.

Mechanical properties of the MWNT–PU composites

The mechanical properties of the composite films were investigated. The results for the effect of the MWNT content (wt %) on the mechanical properties, including the tensile strength and elongation at break, are exhibited in Figure 3. The tensile strength remarkably increased from 1.8 to 18 MPa, which was 900% higher than that of neat PU, with the addition of MWNT contents within 1 wt %, and

TABLE III
Absorbance of the CNT Suspension Before and After Centrifugation and Sediment Percentage

Sample	Absorbance before centrifugation	Absorbance after centrifugation	Sediment percentage[a]	Effective particle diameter (nm)
1	1.983	1.522	23.25	600
2	1.573	1.408	10.49	280
3	0.984	0.649	34.04	1000
4	3.91	1.52	61.13	1200

[a] Sediment percentage = (Absorbance before centrifugation − Absorbance after centrifugation)/Absorbance before centrifugation × 100%.
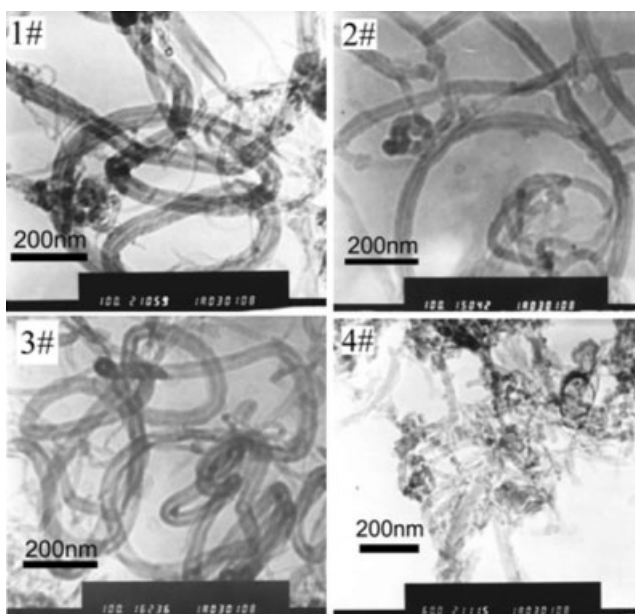
Figure 2 TEM pictures of MWNT suspensions for samples 1–4 after centrifugation.

then decreased with the addition of MWNT contents above 1 wt %. Very attractively, it was found that the MWNT–PU composite samples containing just a 1 wt % loading of MWNTs exhibited an increase in their ultimate tensile strength. The elongation at break also had a change tendency very similar to that of the tensile strength. The elongation at break increased about 741% at a 1 wt % loading of MWNTs in comparison with the neat PU system. This might indicate an upper limit to the content of MWNT–R_1—NH_2 that can be added directly to an MWNT–PU synthesizing system because of a significant increase in the viscosity and probably also a saturation of MWNT–R_1—NH_2 addition that needs to be addressed (because the DMF solution of MWNT–R_1—NH_2 was a stable dispersion even after 7 days at the same content with more than a 1 wt % addition of MWNT–R_1—NH_2 in this research). This is more proof of the strong reinforcement effect by MWNT–R_1—NH_2 when we consider the very high flexibility of MWNTs. Sen et al.[24] reported that single-wall nanotube (SWNT)–PU composite membranes prepared by an electrospinning process showed a significant enhancement in the mechanical properties. The tensile strength of AP–SWNT–PU composites increased by 46%, but the elongation at break did not show much change from the pure PU to the composite membranes. In our study, the mechanical properties, including the tensile strength and elongation at break, and thermal properties of MWNT–PU composites prepared by *in situ* polycondensation exhibited obvious increases with a 1 wt % loading of MWNTs. In general, the mechanical properties of fiber-reinforced composites strongly

depend on the extent of load transfer between the matrix and fiber. CNTs present a particular form of reinforcing fiber with a high aspect ratio and highly flexible elastic behavior during loading and are very different from micrometer-size fibers. In addition, because of intrinsic van der Waals forces, nanotubes are typically held together as bundles and have very low solubility in most solvents. When mixed into a matrix, nanotubes tend to exist as entangled agglomerates, and homogeneous dispersions are not easily obtained. Therefore, the ability to produce homogeneous dispersions of CNTs and strong interfacial interactions between CNTs and polymers will be a key issue in maximizing the advantages of CNT reinforcement. In this research, TEM images of the MWNT–PU composite films provide direct proof for this explanation, as shown in Figure 4. The samples were ultramicrotomed for TEM. The TEM images illustrate the dispersion of the MWNTs in the composites. The middle part of an ultrathin section of the composites with a 1 wt % loading of MWNTs showed an almost uniform dispersion [Fig. 4(A,B)]. However, as the content of MWNTs increased to more than 1.0 wt %, the composites exhibited a non-uniform dispersion and a tendency for the nanotubes to entangle as agglomerates [Fig. 4(C,D)]. As a result, the mechanical properties of the composite films decreased with the MWNT content increasing beyond 1 wt %. At high nanotube loadings, the extent of improvement in the mechanical properties might be limited by the high viscosity of the composite and the resulting void defects.[29]

Thermal properties of the MWNT–PU composites

The thermal properties of pure PU and MWNT–PU nanocomposites were measured by DSC, and the results are presented in Figure 5. The effects of
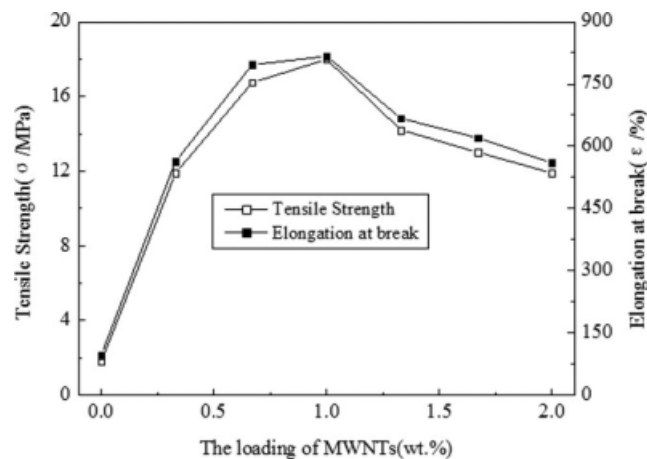

Figure 3 Effects of different loadings of MWNT–R_1—NH_2 on the tensile strength and elongation at break of the composites.
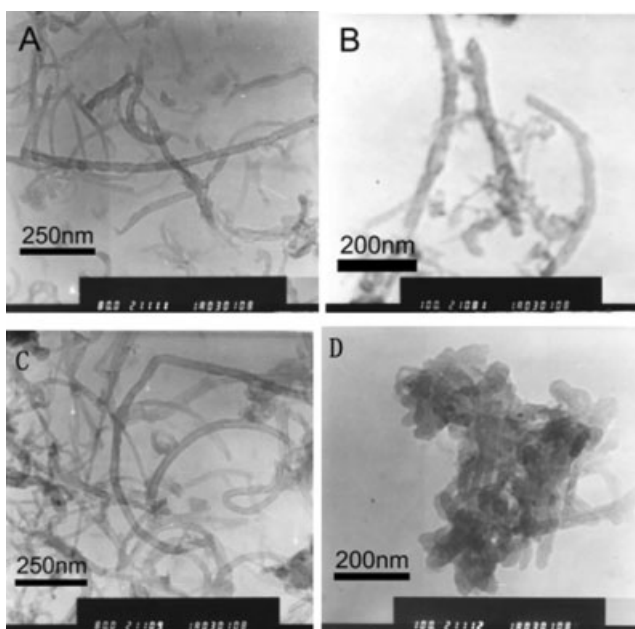
Figure 4 TEM images of MWNT–PU composites: (A,B) 1 wt % loading of MWNTs and (C,D) 1.67 wt % loading of MWNTs.

different contents of MWNTs on the glass-transition temperature (T_g) were studied as shown in Figure 6. The glass-transition temperature of the soft-segment phase ($T_{g,\mathrm{soft}}$) of pure PU was about $-28.2°C$, slightly higher than that of the MWNT–PU nanocomposites, and the glass-transition temperature of the hard-segment phase ($T_{g,\mathrm{hard}}$) of pure PU was not detectable in the DSC measurements because of the low hard-segment content and small heat capacity differences at the hard segment's glass transition.[30,31] Figure 6 shows that $T_{g,\mathrm{soft}}$ decreased with increasing MWNT content up to 1 wt % and then increased with increasing MWNT content beyond 1 wt %; $T_{g,\mathrm{soft}}$ was lowest at a 1 wt % loading of MWNTs.
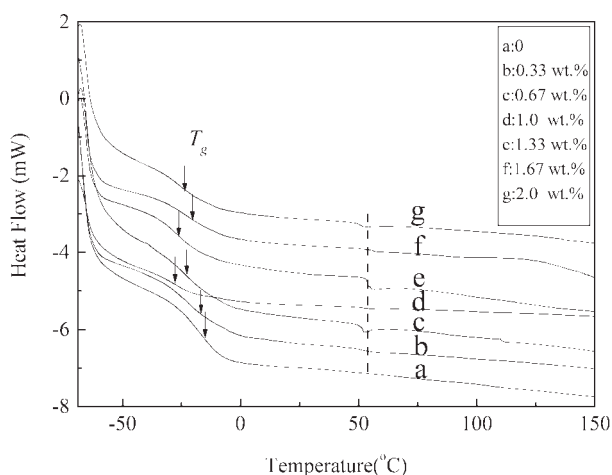

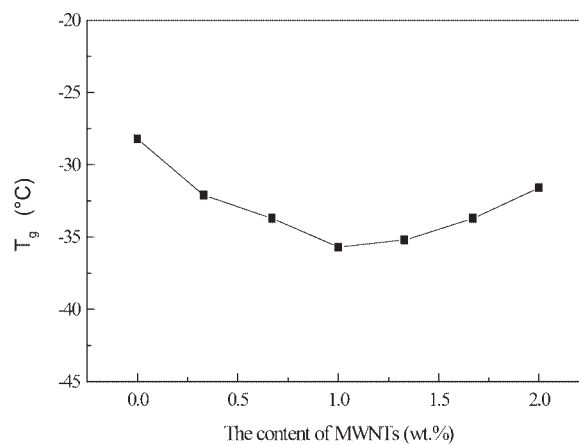**Figure 5** DSC curves of neat PU and MWNT–PU composites.

Figure 6 Effect of the MWNT loading on T_g.

This result seems to contradict the general phenomena for CNT-reinforced composites; that is, T_g increases distinctly when CNTs are added to the matrix. The reason for $T_{g,\mathrm{soft}}$ decreasing is not clear at this point in time. This might be attributed to the thin polymer confined between MWNTs, which tends to lower $T_{g,\mathrm{soft}}$ and enhance the segmental dynamics of the polymer chains.[32] Other possible reasons include an altered microphase morphology, excessive polymer–filler interaction, and an inhibition of the morphological change that accompanies deformation in segmented PUs (i.e., hard domain rotation, interchain slippage, fibrillation, and soft-segment crystallization). Future studies hope to elucidate the reason for the thermal properties. Furthermore, new peaks near 54°C were observed for the MWNT–PU nanocomposite samples, and they remained roughly constant as the MWNT content increased from 0.33 to 2.0 wt %. This result indicates that MWNTs in the MWNT–PU nanocomposite samples accelerated the microphase-separation structures and altered the segment molecular weights of the hard segment and soft segment of PU.

CONCLUSIONS

Functionalized MWNTs with carboxyl groups have more advantages for improving the dispersion and stability in water and DMF. The higher the amounts are of functionalized groups on MWNTs, the better the stability and dispersion are of suspensions of MWNTs. At the same time, polar solvents are beneficial for the dispersion and stability of MWNTs. The experimental results demonstrated that the tensile strength remarkably increased with the addition of MWNT contents within 1 wt % and then decreased with the addition of MWNT contents beyond 1 wt %. Therefore, both the tensile strength and elongation at break reached the maximum values at a 1 wt % loading of MWNTs, increasing 900 and 741%,

respectively. The results of DSC measurements indicated that $T_{g,\text{soft}}$ of MWNT–PU was altered, and new peaks near 54°C appeared because of the microphase-separation structures and alteration of the segment molecular weights of the hard segment and soft segment of PU with the addition of MWNTs.

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