

# Properties of Anionic Polymerized $\epsilon$ -Caprolactam in the Presence of Carbon Nanotubes

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**ABSTRACT:** The results of the investigations of the relations between structure, physical and usage properties of polyamide 6 (PA6) reinforced with multiwall carbon nanotubes (MWNTs) are presented. A method of *in situ* anionic bulk polymerization of  $\epsilon$ -caprolactam in the presence of MWNTs was used for the preparation of reinforced PA6. The polymerization product was crushed, and the pellets of PA6 and PA6/MWNTs composites were injection molded to produce the standard test specimens for various measurements. The surface morphology (SEM), thermal (DSC, TGA, DMTA), and mechanical properties (tensile strength, Charpy's notched impact strength) of these materials were examined. Some differences between our specimens and those obtained by hydrolytic polymerization of  $\epsilon$ -caprolactam (CL) were found. It was found that a small amount of carbon nanotube decreases the

crystallinity degree of PA6 matrix in the composites. The thermal stability was higher than that for neat PA6. DMTA results showed that the magnitudes of the storage modulus are higher for the PA6/MWNTs composites than for the unmodified PA6 in the temperature range between  $-90$  and  $200^\circ\text{C}$ . The tensile strength and tensile modulus are higher compared with the neat PA6. The elongation at break showed no noticeable change in the range of MWNTs loading considered, while the Charpy's notched impact strength slightly decreased. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3010–3017, 2007

**Key words:** anionic polymerization of  $\epsilon$ -caprolactam; multiwalled carbon nanotubes; polyamide 6; nanocomposites

## INTRODUCTION

In recent years, organic–inorganic nanoscopic scale composites have attracted a great interest since they frequently exhibit unexpected hybrid properties synergistically derived from two components.<sup>1–4</sup> Since Iijima<sup>5</sup> reported discovery of carbon nanotubes (CNTs), intensive study of nanocomposites polymer/CNTs is going on in many laboratories and research facilities, for their unique properties. Multiwalled carbon nanotubes (MWNTs) show a tensile strength as high as 200 GPa and a tensile modulus as high as 1 TPa, in addition to high thermal and electrical conductivities.<sup>6,7</sup> MWNTs have very large aspect ratios (length to diameter), as high as 100–1000 and high specific surface areas. Such properties make CNTs excellent candidates for high strength and electronically conductive, polymer composite applications. By employing minimal addition levels, CNTs enhance tensile strength, elastic modulus, fire retardancy, and

electrical conductivity of the polymers.<sup>8–15</sup> The effective application of CNTs depends strongly on two factors: homogeneous dispersion of CNTs throughout the polymer matrix without destroying the integrity of the tubes and the adequate interfacial adhesion between the phases.<sup>9</sup> However, the main issue in the fabrication of CNTs-filled composites is the prevention of their agglomeration in the matrix. Polymer/CNTs nanocomposites have been produced by a variety of processing routes. They may be prepared by a direct mixing, by melt blending or solution blending, or by an *in situ* polymerization process. While direct mixing is generally applied only to thermosetting polymers, all the other methods can be used for thermoplastic polymers. The main idea in all processing methods is to use fluid shear forces to break nanotubes aggregates or prevent their formation.<sup>3,9,11,15</sup>

Among engineering thermoplastic polymers, polyamide 6 (PA6) is a polymer of great industrial importance due to its favorable properties such as chemical and mechanical resistance, low permeability respect to gases and vapors, high optical transparency, printability, etc. One of the most important features of the PA6 and the other polymers is the possibility of controlling their macroscopic physical–chemical properties by tailored manipulation of their structures at a micro- and nanoscopic scale.<sup>1,2</sup>

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Several attempts have been made to introduce of pristine and functionalized CNTs into the PA6 matrix. Mencken et al.<sup>16</sup> reported the preparation of PA6/CNTs composites, at low filler loadings (4–6 wt %), by melt compounding on a corotating twin-screw extruder. Tensile tests of the CNT-composites show an increase in the tensile modulus by 27%, however the elongation at break of these materials dramatically decreases because of the ductility of the PA6.<sup>16</sup>

An increase of 115% in elastic modulus and 124% in tensile strength of PA6 has been reported for the melt mixed composites of PA6 and MWNTs (purified and COOH and OH functionalized MWNTs) at 1 wt % carbon nanotubes level.<sup>17</sup> 1 wt % poly(*n*-butyl acrylate) encapsulated MWNTs melt mixed with PA6 could be used<sup>18</sup> to enhance the interfacial adhesion between PA6 and MWNTs. This leads to the increased yield strength and tensile modulus compared with both neat PA6 and PA6/unmodified MWNT composites, whereas, elongation at break, ultimate tensile strength, and impact strength decreased considerably.

Zhao et al.<sup>19</sup> studied synthesis of MWNTs reinforced polyamide 6 via *in situ* hydrolytic polymerization of  $\epsilon$ -caprolactam (CL). PA6/MWNTs composites have been prepared in the presence of pristine and carboxylated MWNTs (MWNTCOOH). Compared with neat PA6, the yield strength of PA6 composites loaded with 0.5 wt % MWNTs is almost unchanged, and the tensile strength is increased slightly. Dynamic mechanical analysis demonstrates that both the storage modulus ( $E'$ ) and glass transition temperature ( $T_g$ ) of the PA6/MWNTs composites increase, particularly for PA6/MWNTCOOH, indicating there is some chemical bonding between PA6 and carboxylated multiwalled carbon nanotubes.<sup>19</sup>

To our knowledge, there are no reports on the synthesis of MWNTs-reinforced PA6 via *in situ* anionic polymerization of CL. Compared with the classical hydrolytic polymerization of CL, the use of the anionic route in the preparation of PA6 has considerable advantage. The latter allows lower polymerization temperature (160–180°C) and shorter times (total conversion within only few minutes,<sup>20–28</sup> compared with the hydrolytic polymerization which takes about 12 to 24 h, depending on the conditions used. It is well known that the polymerization method can influence on the properties of PA6 and PA6/CNTs composites. Dispersion of inorganic additives within a medium of low viscosity  $\epsilon$ -caprolactam could cause some particle aggregation for a very short time. The aggregation and/or sedimentation could depend on the particle size and the specific surface area of the additive, as well as on its purity. Hence, the use of finely dispersed CNTs during the anionic polymerization process could be expected to be a very attractive method for obtaining a composite or nanocomposite materials.

In this paper, a two-step approach with a combination of bulk anionic polymerization of CL, in the presence of multiwalled carbon nanotubes and injection molding was used for the preparation of PA6/MWNTs composites. The structure, thermal, and mechanical properties of these materials were examined.

## EXPERIMENTAL

### Materials

Crystalline  $\epsilon$ -caprolactam, (melting point  $\sim 70^\circ\text{C}/760$  mmHg; boiling point  $\sim 137^\circ\text{C}/10$  mmHg, made by Nitrogen Chemistry Plant, Tarnow, Poland), was used without additional purification. Sodium bis[(2-methoxyethoxy)caprolactam]-aluminate (initiator), made by Chemopetrol Spolana Neratovice, Czech Republic was used as received. 2,4-toluene diisocyanate (activator), having a density ( $20^\circ\text{C}$ ) of  $1.2175\text{ g/cm}^3$ , was made by Nitrogen Chemistry Plant Zachem in Bydgoszcz (Poland). Multiwalled carbon nanotubes (MWNTs) were delivered by Heat and Mass Transfer Institute, Minsk, Belarus.

### *In situ* polymerization and preparation of specimens

PA6 homopolymer and PA6/CNTs composites containing 0.05, 0.1, and 0.3 wt % of MWNTs were synthesized by anionic bulk polymerization of CL, under normal conditions in the presence of air. No process stabilizer was used. The concentration of initiator was kept constant at 0.3 mol %, and the amount of activator was kept at 0.15 mol %, based on the total monomer feed. The polymerization was carried out in a thermostatic chamber (bath with silicone oil), electrically heated to the constant temperature  $175 \pm 2^\circ\text{C}$ . The polymerization of CL was carried out in the vessel; CL and MWNTs were placed and the mixture was heated at  $100 \pm 2^\circ\text{C}$  in an oil bath. After homogenization (at 15,000 rpm) of the molten monomer and MWNTs using homogenizer (DISPERMAT<sup>®</sup> CV-SIP, VMA-GETZMANN GMBH), the initiator was introduced. The mixture was heated at  $135 \pm 2^\circ\text{C}$  and the activator was added with vigorous stirring, and then the mixture was immediately poured in the glass test tube molds (length 160 mm,  $\varnothing$  12 mm, wall thickness 0.5 mm), and were placed into the thermostatic chamber.

The products were removed from the glass tube, mechanically crushed, and the particles were extracted five times with fresh portions of boiling water for 20 min (to extract the unreacted monomer and the oligomers) and dried in vacuum at  $80^\circ\text{C}$  to constant weight.<sup>20</sup> The test specimens for thermal analysis and mechanical properties were formed by an Engel injection molding machine at a barrel temperature of  $270^\circ\text{C}$ , mold temperature of  $65^\circ\text{C}$ , injection

**TABLE I**  
**Polymerization Time ( $\tau$ ), Monomer Content ( $M_{\text{con}}$ ),  
 and Melt Flow Index (MFI) for PA6  
 and PA6/MWNTs Composites**

MWNTs content (wt %)	$\tau$ ( $\pm 0.5$ min) (min)	$M_{\text{con}}$ (%)	MFI (230°C; 2.16 kg) (g/10 min)
0	4.5	4.5 $\pm$ 0.5	2.50 $\pm$ 0.06
0.05	3.5	3.9 $\pm$ 0.5	2.58 $\pm$ 0.04
0.1	4.5	4.3 $\pm$ 0.6	2.60 $\pm$ 0.05
0.3	4.0	4.1 $\pm$ 0.3	2.53 $\pm$ 0.07

pressure of 110 bars and holding pressure of 30 bars. Since the MFI of PA6/MWNTs composites was almost equal to that of neat PA6 (Table I), PA6/MWNTs composites could be molded under the same conditions as PA6.

### Characterization and tests

#### Monomer conversion

To determine the monomer conversion, the ground specimens (about 5–10 g) were extracted with methanol, using a Soxhlet, for 20 h. After extraction, the specimens were dried at 85°C for 24 h under low pressure, and stored in a desiccator over phosphoric oxide. Then, the monomer and oligomers content was calculated according to:

$$M_{\text{con}} = \frac{m_0}{m_1} \times 100(\%)$$

where:

- $m_1$  – polymer weight before extraction, (g),
- $m_0$  – polymer weight after extraction, (g).

An average value of five specimens of each material were taken as experimental data for further analysis.

#### Melt flow index

Melt flow index (MFI) of materials was measured by using a MP-IIRT-M plastometer (RU) at 230°C, and load 2.16 kg.

#### Scanning electron microscopy

The morphology of the fracture surfaces of the PA6/MWNTs composites were observed in a scanning electron microscope (SEM: JOEL type JMS-50A, Japan) at an accelerating voltage of 25 kV. The specimens were broken in liquid nitrogen and the fracture surfaces were coated with a thin layer of gold before examinations.

#### Crystallization properties

Differential scanning calorimetric (DSC) measurements were conducted on a Mettler Toledo DSC 821

apparatus, using 6–8 mg specimen sealed into aluminum pans. The specimens for thermal analysis were excised from injection molded (perpendicular to direction of flow) especially cylindrical specimens (length 0.8 mm,  $\varnothing$  0.4 mm). To avoid any effect of moisture, all the test specimens were dried using vacuum oven at 80°C for 48 h before the measurements. The specimens were heated from 25 to 250°C, and maintained for 3 min to minimize differences in their thermal history; then were cooled to 25°C and reheated to 250°C. A scan rate of 10°C/min was used for all the runs. All DSC analyses were performed under nitrogen atmosphere. The exothermal curves of heat flow as a function of time were recorded. The values of melting temperature  $T_m$  and degree of crystallinity were obtained from the second heating scan.

The DSC degree of crystallinity was calculated according to the formula:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \quad (\%)$$

where:

- $\Delta H_m$  – the enthalpy of melting of a tested specimen, J/g,
- $\Delta H_m^0$  – the enthalpy of melting for a 100% crystalline standard of PA6.

In literature, several values were proposed for the enthalpy of melting for the different 100% crystalline polymorphic forms of PA6. In this paper, an intermediate value of 190 J/g has been chosen<sup>29</sup> for calculations.

#### Thermogravimetric analysis (TGA)

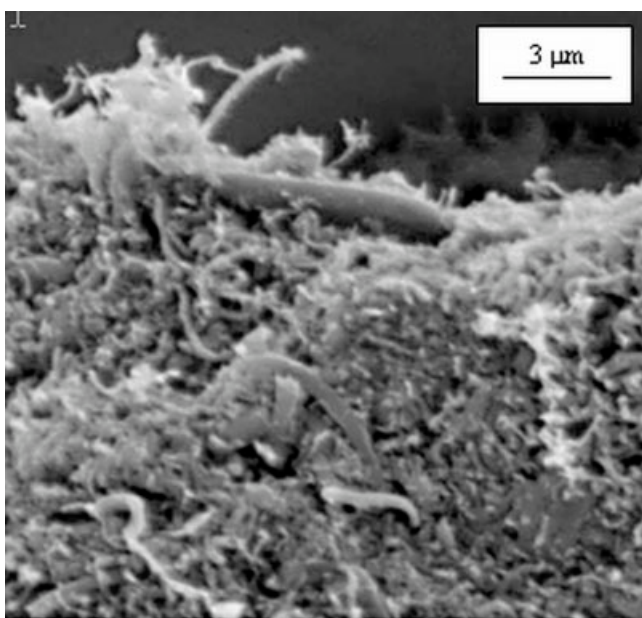
The analyzer STA 409C (Netzsch, Germany) was used to investigate the thermal stability of the PA6 and PA6/MWNTs composites. The specimens (about 10 mg) were heated under nitrogen atmosphere from ambient temperature to 600°C, at the heating rate of 10°C/min in all cases. The thermal degradation temperature ( $T_d$ ) was taken as the onset temperature at which 5 wt % of weight loss occurs.

#### Dynamic mechanical thermal analysis (DMTA)

The dynamic mechanical tests were done using the MK III DMTA Polymer Laboratories instrument operating in the bending mode. Measurements were taken at a frequency of 1 Hz. The temperature was raised from –100 to 240°C at a scanning rate of 4°C/min, under nitrogen atmosphere.

#### Mechanical properties

The tensile tests were carried out using an Instron tensile machine (Model 1115, UK). All tests being



**Figure 1** SEM microphotograph of MWNTs powder.

done at a crosshead speed of 5 cm/min and a temperature of  $20 \pm 3^\circ\text{C}$ . Charpy impact strength was measured at room temperature using an Instron pendulum tester, Type PW-5. For measurements of mechanical properties, 10 specimens of each polymer were tested and average values were taken as experimental data for further analysis.

## RESULTS AND DISCUSSION

### Polymerization

The color of PA6/MWNTs composites was black, even though  $\leq 0.3$  wt % MWNTs was added. The rate of polymerization process for PA6/MWNTs for the unmodified PA6 is shown in Table I. Since CL polymerizes by a ring-opening mechanism, the ring-chain equilibrium prevails and the conversion of the mono-

mer to polymer does not reach 100%.<sup>30</sup> Therefore, it is important to know the percent of monomer conversion. In the range of MWNTs concentration examined, monomer and oligomers content was stable and takes out average 4 wt %. These experimental results showed that MWNTs does not act as an inhibitor of the polymerization process.

Because of the low loading (0.3 wt % and below) the introduction of MWNTs has minimal effect on the melt flow index of PA6 (Table I).

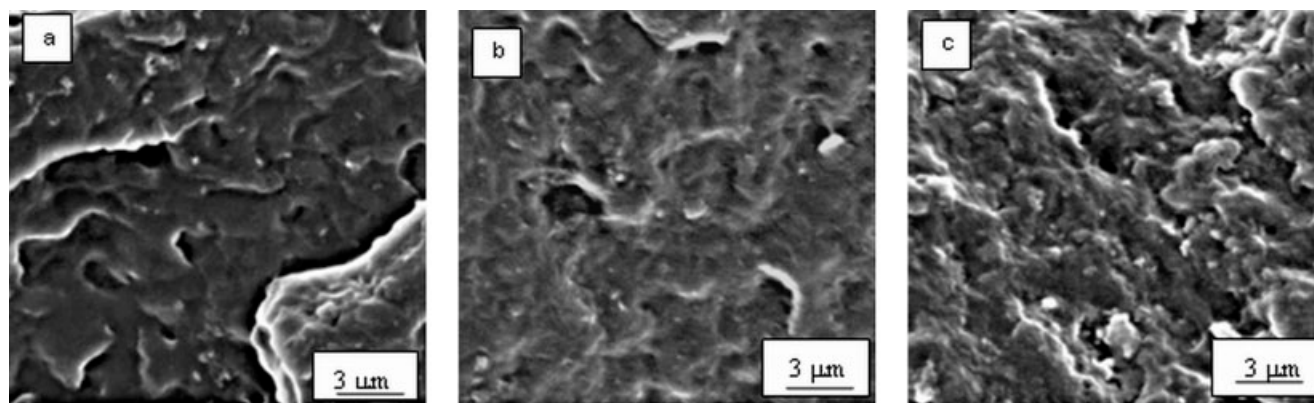
### SEM observations

Figure 1 shows scanning electron photomicrograph of MWNTs powder. The nanotubes bundles, which have an average diameter of about 0.4–0.8  $\mu\text{m}$  are visible. Figure 2(a–c) shows the SEM photomicrograph of fracture surface of PA6/MWNTs composites. For the PA6/MWNTs composites, if a good dispersion of MWNTs is attained in the polymer matrix, the individual nanotubes will not be observable with SEM, due to their small size and the level of magnification achieved. In fact, SEM observation of fracture surfaces of composites did not show any considerable amount of MWNTs.

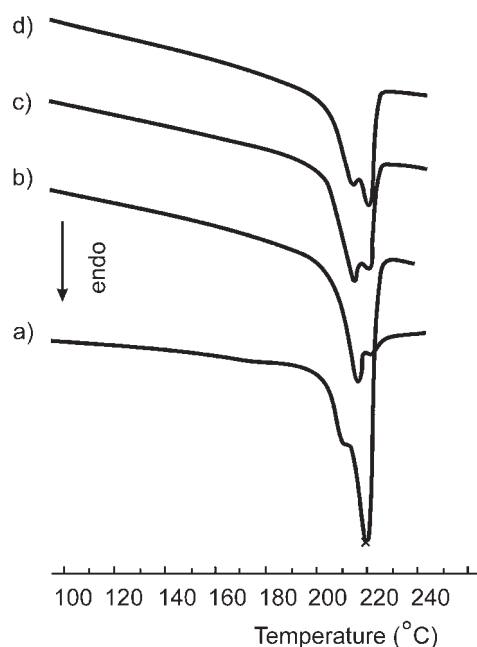
### Crystallization properties

For semicrystalline polymers, such as PA6, and its nanocomposites, processing methods and history define the thermal properties, which in turn determine the mobility and extent of chain extension, as well as nucleation, growth, and orientation of crystallites.<sup>31</sup> To obtain reproducible thermal history of the specimens, it is useful to study the second heating.

The DSC thermograms of neat PA6 and PA6/MWNTs composites are presented in Figure 3. The results of investigations of the melting peak and crystallinity degree are given in Table II. It is clear that all the DSC thermograms possess two melting endo-



**Figure 2** SEM microphotographs of PA6/MWNTs composites containing: 0.05 wt % (a), 0.1 wt % (b), and 0.3 wt % (c) of MWNTs.



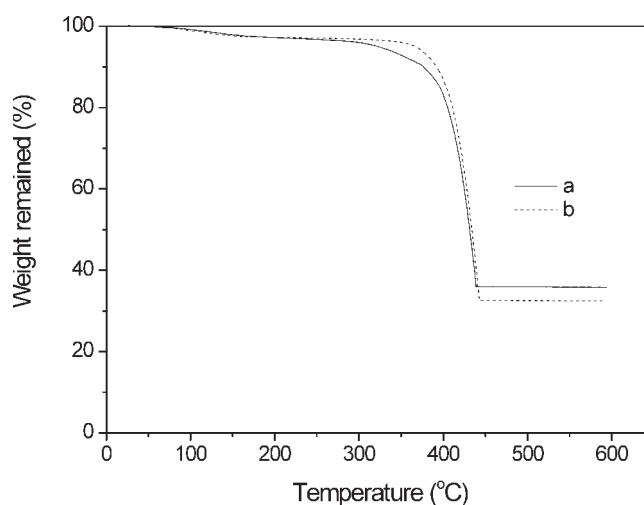
**Figure 3** DSC thermograms of materials investigated from second heating: the neat PA6 (a), PA6/MWNTs composites containing 0.05 wt % (b), 0.1 wt % (c), and 0.3 wt % (d) of MWNTs.

therms: around 210–215°C and 218–220°C. For the composites with 0.05 and 0.1 wt % of MWNTs, the height and breadth of low temperature peaks around 213°C increase, at the expense of the major peak. The origin of double melting peaks has been the subject of debate for PA6 and its nanocomposites. There are contradictory explanations on the nature of such endotherms. It is generally believed that different thermal history leads to crystals with different perfection.<sup>31–35</sup> Probably, the addition of the MWNTs might hinder the motion of the PA6 chains, leading to less perfection of the crystals.

It can be concluded (Table II) that the crystallinity degree of PA6/MWNTs is lower than that of the neat PA6, which is contrary to a previous result obtained by Zhao et al.<sup>19</sup> for hydrolytic polymerization of CL. Our study suggests that the lower crystallinity seen in the PA6/MWNTs composites is due to the inability of polymer chains to be fully incorporated into growing crystalline lamella.<sup>7</sup>

**TABLE II**  
Melting Peak and Crystallinity Degree Determined by the DSC for PA6 and PA6/MWNTs Composites

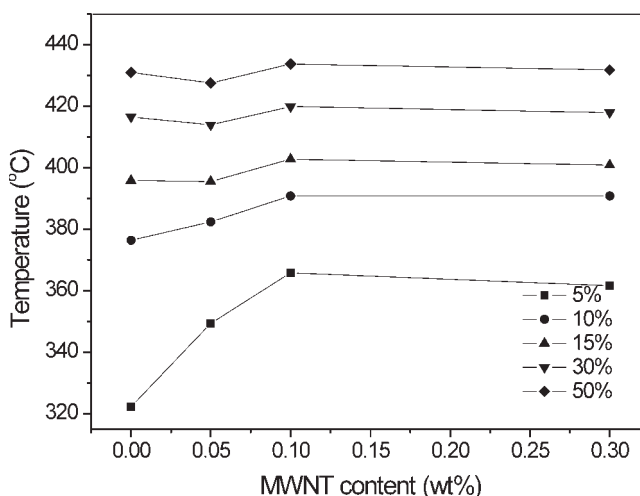
MWNTs content (wt %)	Melting peak (°C)		Crystallinity degree (%)
	Low	High	
0	210.0	218.0	42.3
0.05	212.5	219.0	37.3
0.1	213.0	220.0	36.9
0.3	215.0	218.5	40.3



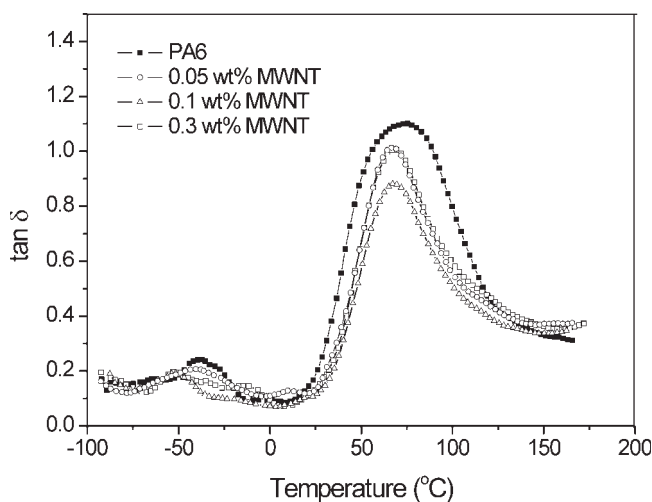
**Figure 4** TGA curves of the neat PA6 (a), PA6/MWNTs specimens containing 0.1 wt % (b) of MWNTs.

### Thermogravimetric analysis

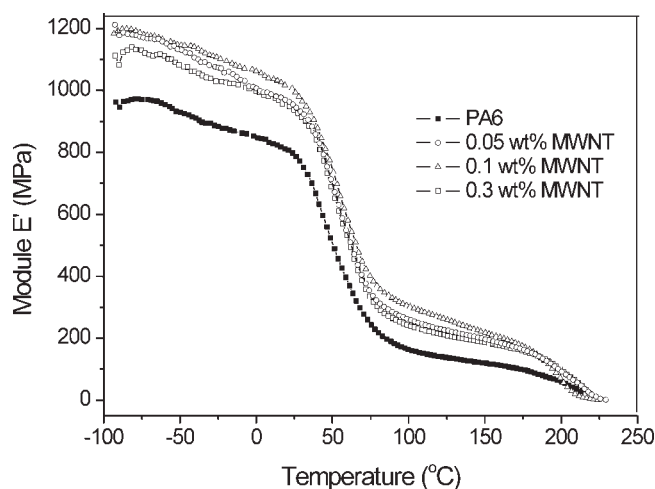
CNTs can stabilize polymer matrix.<sup>10,11,15,36,37</sup> Our observation is similar. The TGA curve of PA6 and example curve of PA6/MWNTs composite and the variation of the degradation temperatures at different weight losses are shown in Figures 4 and 5, respectively. Neat PA6 starts to degrade in a nitrogen atmosphere at about 322°C. The incorporation of MWNTs into PA6 offers a stabilizing effect since the onset of degradation ( $T_d$ ) occurs at a higher temperature (see curves for 5, 10 and 15% in Fig. 5). For example, the composite containing 0.1 wt % MWNTs starts to degrade at 366°C, which is 44°C higher than that for PA6. The improved thermal stability of the composites may come from the enhanced distribution of MWNTs raising the surface area in the polymer matrix. However, as the temperature continues to



**Figure 5** Degradation temperature (°C) at different loss weight versus MWNTs content (wt %).



**Figure 6** Dynamic mechanical loss  $\tan \delta$  of neat PA6 and PA6/MWNTs composites.



**Figure 7** Dynamic storage modulus of neat PA6 and PA6/MWNTs composites.

increase, the MWNTs itself started to oxidize, resulting in the degradation of the stabilizing effect of MWNTs on the matrix (see curves 30 and 50% in Fig. 5). The stabilization effect of MWNTs is probably similar to that of other carbon fillers such as fullerene ( $C_{60}$ ) and carbon black. Troitskii et al.<sup>38</sup> studied the thermal degradation of poly(methyl methacrylate) (PMMA) in the presence of  $C_{60}$  by isothermal thermogravimetry. Fullerene retards the thermal degradation of PMMA and the retardation effect was attributed to interactions between  $C_{60}$  and macroradicals generated during the thermal degradation process.

### Dynamic mechanical properties

The dynamic mechanical properties of PA6 and PA6/MWNTs composites are shown in Figures 6 and 7. The results of DMTA experiments are summarized in Table III. The PA6 and composites show two loss angle tangent ( $\tan \delta$ ) peaks in the above temperature range, which have been labeled  $\alpha$ - and  $\beta$ -relaxation transitions.<sup>39,40</sup> The maximum of the  $\alpha$ -relaxation is assigned to the glass transition temperature ( $T_g$ ) of the PA6, which involves the motion within the amorphous region and depends on the polymer crystallinity.<sup>39</sup> The  $\beta$  damping peak is attributed to the carbonyl group of the polyamide forming hydrogen bonds, and depends on the moisture content.<sup>40,41</sup> The interesting

feature from DMTA results is that the  $\tan \delta$  peaks (Fig. 6) of the PA6/MWNTs composites move to a slightly lower temperature, showing that the  $T_g$  of the composite is depressed by the addition of nanotubes, which is contrary to a result obtained by Zhao et al.<sup>19</sup> for hydrolytic polymerization of CL.

The  $E'$  curves (Fig. 7) indicate a high material stiffness at low temperatures, which decreases considerably with the appearance of certain relaxation processes. The first decrease of  $E'$  corresponds to the  $\beta$ -relaxation transitions. With increasing temperature, another significant decrease in  $E'$  is observed at the glass transition of the amorphous region of the PA6. The magnitudes of storage modulus are higher for the composites than for the unmodified PA6 throughout the temperature range (Fig. 7). The improvement in storage modulus of the PA6/MWNTs composites is mainly due to the stiff nature of the MWNTs and due to the combined effect of the high aspect ratio and fine dispersion of the nanotubes. This increase in the storage modulus agrees with the results of the tensile experiments discussed below.

### Mechanical properties

Because of high elastic modulus, CNTs increase the stiffness of composites.<sup>7</sup> Therefore, we have investigated the tensile properties of the neat PA6 and PA6/

**TABLE III**  
Dynamic Mechanical Data for PA6 and PA6/MWNTs Composites

MWNTs content (wt %)	Storage modulus at $23 \pm 2^\circ\text{C}$ (MPa)	$\alpha$ Peak location ( $^\circ\text{C}$ )	$\alpha$ Peak magnitude	$\beta$ Peak location ( $^\circ\text{C}$ )	$\beta$ Peak magnitude
0	840	73.0	1.10	-37.5	0.25
0.05	990	67.5	1.02	-37.5	0.2
0.1	1050	66.5	0.90	-50.0	0.2
0.3	980	67.0	1.02	-50.0	0.2

**TABLE IV**  
**Tensile Properties and Charpy Impact Strength of PA6 and PA6/MWNTs Composites**

MWNTs content (wt %)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Charpy impact strength (kJ/m <sup>2</sup> )
0	40.1 ± 4.5	1100 ± 12	25.8 ± 2.0	29.2 ± 2.1
0.05	42.1 ± 4.9	1190 ± 11	24.8 ± 2.5	26.3 ± 0.9
0.1	70.7 ± 5.5	1340 ± 12	24.1 ± 1.5	27.1 ± 1.3
0.3	60.2 ± 7.0	1280 ± 10	18.7 ± 2.1	22.0 ± 1.6

MWNTs composites. Good nanotubes dispersion is necessary for effective reinforcement. The tensile strength and tensile modulus of the PA6/MWNTs composites are higher compared with the neat PA6, Table IV. For instance, the tensile modulus increased from 1100 MPa for neat PA6 to 1340 MPa for the composite that contains 0.1 wt % of MWNTs, but decreases for 0.3 wt %. This could be explained by worsening of nanotubes dispersion within polymer matrix in case of concentration of about 0.3 wt %. Such explanation is in agreement with DMTA data.

The elongation at break for this composite revealed no noticeable change (Table IV). The notched Charpy impact strength slightly decreases in PA6/MWNTs composites.

## CONCLUSIONS

By the method of anionic bulk polymerization, we have successfully polymerized  $\epsilon$ -caprolactam in the presence of MWNTs. It has been demonstrated that polymerization method influences the properties of PA6; some differences between results our specimens and obtained by hydrolytic polymerization of CL were found. In our case a small amount of MWNTs in the composite decreases the crystallinity degree. The thermal stability of the PA6/MWNTs was higher than that for neat PA6. DMTA results showed that the magnitudes of the storage modulus are higher for the composites than for the unmodified PA6 in the temperature range of  $-90$  to  $200^{\circ}\text{C}$ . All investigated PA6/MWNTs composites show an increased the tensile strength and tensile modulus compared with the neat PA6. The elongation at break of the composites revealed no noticeable change in the range of MWNTs loading considered. The Charpy's notched impact strength slightly decreases in PA6/MWNTs composites.

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