

# PREPARATION AND CHARACTERIZATION OF THERMOPLASTIC POLYURETHANE/CARBON NANOTUBE NANOCOMPOSITES

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## Abstract

Thermoplastic polyurethane (TPU) nanocomposites with multi-walled carbon nanotubes (MWNT) were melt compounded to estimate the effects of carbon nanotubes (CNT) on the nanostructure morphology and material properties of the TPU matrix. The field emission scanning electron microscopy (FESEM) observations indicated that the CNTs were uniformly dispersed within the TPU matrix. The thermogravimetric analysis (TGA) study revealed that the thermal stability of the TPU matrix is noticeably enhanced with increase in CNT content. The dynamic mechanical analysis (DMA) showed that the storage modulus ( $E'$ ) and glass transition temperature ( $T_g$ ) of the TPU matrix were improved by the addition of MWNTs. The differential scanning calorimetry (DSC) study was employed to measure the melting point ( $T_m$ ) and  $T_g$  of the soft and hard segments of the TPU matrix, which was found to shift towards higher temperature with the incorporation of CNTs. The rubber process analyzer (RPA) test showed that the storage modulus ( $G'$ ) and complex viscosity ( $\eta^*$ ) significantly increased by the addition of MWNTs. The tensile strength and modulus of the nanocomposites were enhanced significantly with increasing in CNT content.

## 1 Introduction

The MWNT has received a great attention in science and engineering field because of its excellent properties since its discovery in 1991 by Iijima [1]. The first ever preparation of polymer/CNT nanocomposites was reported in literature by Ajayan et al. in 1994 [2]. MWNT is considered to be the most promising nanomaterial due to its high flexibility, low mass density, high aspect ratio (typically  $>10^3$ ), and exceptional mechanical and electrical properties. Further, a significant number of

papers are dedicated to the processing and characterization of materials properties of the fabricated polymer/CNT nanocomposites for high performance and multi-functions [3–7].

For most technologically important polymers, a direct melt blending method is the most versatile and environmentally benign among all the methods of preparation of polymer–nanotube nanocomposites. It shifts nanocomposites production downstream, thereby giving end-use manufacturers many degrees of freedom with regard to final product specifications (e.g. selection of polymer grade, choice of nanotube, level of reinforcement, etc.). At the same time, melt processing minimizes capital costs due to its compatibility with the existing processing techniques. The advantages of forming nanocomposites by melt processing are quite appealing, which makes this technique a promising one that would greatly enhances the commercial application of nanocomposites technology. The chemical structure and melt viscosity of polymers influence the molecular diffusion and shear stress during melt mixing, which governs the nanostructure morphology of the polymer nanocomposites.

The literature survey revealed that the research works based on the effect of functionalization and different types of multi-walled carbon nanotube (MWNT) on the mechanical, thermal, and electrical properties of the TPU/MWNT nanocomposites prepared through melt blending technique are in their nascent stage and there lies a large scope for considerable research. Chen et al. have concluded that the homogeneous dispersion of MWNTs within the TPU matrix and the strong interfacial adhesion between the functionalized MWNTs and the TPU matrix are responsible for the significantly enhancement of mechanical properties [8]. Pötschke et al. have focused on the effect of different types of MWNTs and carbon blacks as well as different melt

mixing methods on the electrical volume resistivity and tensile test behavior of TPU nanocomposites [9]. Raja et al. have observed that the tensile modulus and thermal stability of the nanocomposites were improved while the  $T_g$  of the TPU was slightly decreased by the addition of functionalized CNTs, which is attributed to the better dispersion of functionalized CNTs and development of interactions between CNTs and TPU matrix [10]. Abdullah et al. have comparatively evaluated the mechanical and electrical properties of the carbon fiber (CF) and CNT based TPU nanocomposites. The storage modulus, thermal stability, and thermal conductivity of the TPU nanocomposites were significantly improved due to good adhesion between the TPU matrix and the fillers [11]. Jiang et al. have indicated that the unmodified MWNT were uniformly dispersed within the TPU matrix and the microphase separation structures of the TPU nanocomposites were slightly affected by the presence of MWNT. The mechanical properties of the TPU nanocomposites were prominently increased at both room temperature and at 120 °C as well as the electrical and thermal properties were greatly improved with increase in MWNT content [12]. Zhang et al. have reported the effect of network formation in polymer melt on the conductivity of TPU/MWNT nanocomposites. The relationship between the processing conditions and dynamic percolation behaviour was established with an objective to reduce the percolation threshold and to improve the conductivity of the TPU nanocomposites [13].

The main aim of the paper is to obtain carbon nanotube (CNT) based novel thermoplastic polyurethane (TPU) nanocomposites with good material properties. The objective of the work confined to the preparation and characterization of TPU/CNT nanocomposites by a simple melt mixing method. The characterization of MWNT based TPU nanocomposites were carried out with special reference to evaluate the influence of the dispersion of nanotubes on resultant morphology, mechanical, dynamic mechanical, thermal, and rheological properties. Especially, the combined effect of the nanotubes on the material properties of the resulting nanocomposites has been also investigated.

## 2 Experimental

### 2.1 Materials

Commercial biomedical grade aliphatic, polyether based thermoplastic polyurethane (Tecoflex<sup>®</sup> EG

80A injection grade) used as the matrix material for this work was supplied by Lubrizol Advanced Materials Inc., Thermedics<sup>™</sup> Polymer Products, Ohio, USA. Tecoflex EG 80A (around 35% of hard segments) having Shore A hardness = 72, density = 1.04 gm/cm<sup>3</sup> and its constituent formulation contains methylene bis(cyclohexyl) diisocyanate (HMDI) hard segment, polytetramethylene glycol (PTMG) soft segment (molecular weight = 1000 g/mol) and chain extender 1,4 butane diol (BD).

The hydroxyl (–OH) functionalized multi-walled carbon nanotube (OH–MWNT) of 95 weight percent (wt%) purity contains 5.58 wt% OH groups used for the research work was supplied by Cheap Tubes Inc., Vermont, USA. OH–MWNT having bulk density: 0.27 gm/cm<sup>3</sup>, true density: ~ 2.1 gm/cm<sup>3</sup>, outer diameter: < 8 nm, inner diameter: 2–5 nm, length: 10–30 μm, ash content: < 1.5 wt%, specific surface area (SSA): 500 m<sup>2</sup>/gm, and electrical conductivity (EC): > 10<sup>2</sup> S/cm. From the material data sheet, the energy dispersive X-ray spectroscopy (EDXS) analysis shows that OH–MWNT contains carbon (C), aluminium (Al), chlorine (Cl), cobalt (Co), and sulfur (S) elements of 97.44, 0.19, 1.03, 1.10, and 0.24% contents, respectively. The Raman spectra of MWNT shows two modes of vibrations i.e. D-band (defect/disorder induced mode) and G-band (tangential mode) at around 1360 and 1580 cm<sup>-1</sup>, respectively [14].

### 2.2 Preparation of TPU/MWNT nanocomposites

TPU/CNT nanocomposites of 0.5, 2.5, and 5.0 wt% MWNT loading were prepared by melt mixing method in an internal batch mixer. The mixing of samples were carried out at temperature of 185 °C with a rotor speed of 100 rpm and mixing time of 8 min. TPU pellets and MWNTs were dried before processing to remove the water content if any in the supplied materials at 80 and 120 °C in a preheated vacuum oven for 6 and 24 hr, respectively. The sample sheets of 2 mm thick were prepared using compression molding machine and specimens for mechanical testing were punched from the compression-molded sheets. The virgin sample is coded as 'TPU' and TPU nanocomposite samples are designated as 'TPUXMO, where 'X' stands for wt% of CNT in TPU matrix and 'MO' stands for MWNT–OH carbon nanotubes.

### 2.3 Measurements and characterization

Field emission scanning electron microscope (model Supra 40, Carl Zeiss SMT AG, Oberkochen, Germany) study was carried out using the Zeiss

Everhart-Thornley secondary electron detector for evaluation of the nanostructured morphology of the cryofractured surface of the TPU/CNT nanocomposites. The sample surfaces were gold (Au) coated by means of manually operated sputter coater (model SC7620, Polaron Brand, Quorum Technologies Ltd, East Sussex, UK) machine. Thermal stability and composition of TPU and TPU/CNT nanocomposites were measured by thermogravimetric analysis (Q50 V6.1 series, TA Instruments, Delaware, USA). The  $T_g$  and  $T_m$  of nanocomposite samples were evaluated by means of differential scanning calorimetry (Q100 V8.1 series, TA Instruments). Dynamic mechanical thermal analyzer (2980 V1.7B series, TA Instruments) was used to measure the dynamic mechanical properties of nanocomposites. The melt rheological properties of the samples were carried out using rubber process analyzer (RPA 2000, Alpha Technologies, Ohio, USA). The tensile properties of the samples were determined according to the test procedure of ASTM D-412-98 using dumbbell shaped specimens with a universal testing machine (Model 4468, Instron Corporation, Massachusetts, USA).

### 3 Results and discussion

#### 3.1 FESEM

From the Fig. 1, it is concluded that the bright white dots shown in the micrograph are assigned to the uniformly dispersed CNT stubs or broken CNT tips exposed from the TPU matrix and grayish white color of the image surface attributed to the wetting of the CNTs by the TPU matrix [15]. The cryfractured surface is free from hole, void, parting line, porous structure, etc., which indicated that at the time of fracturing process the CNTs are broken down into two part and not pulled out. This result concluded that the good adhesion bonding is developed between MWNT and TPU matrix, which is arises due to the presence of hydrogen bonding between  $-OH$  of MWNT with urethane ( $-NHCO-$ ) group of the TPU matrix.

#### 3.2 TGA

Fig. 2 shows the TGA plots of pristine TPU and MWNT filled TPU nanocomposites. The temperature at maximum thermal degradation rates for hard and soft segments of the virgin TPU matrix are around 321 and 408 °C that increased to approximately 330 and 417 °C, respectively at 2.5 wt% MWNT filled TPU matrix because of the higher stability of the CNT and interfacial

interactions exist between TPU matrix and CNT [16]. The hydrogen bond formed between MWNT and TPU adequately transfer thermal energy among them that significantly promotes the homogeneous heat distribution of the heat without causing any accumulation of extra heat on the nanocomposites surface as a result rate of thermal decomposition process is significantly suppressed.

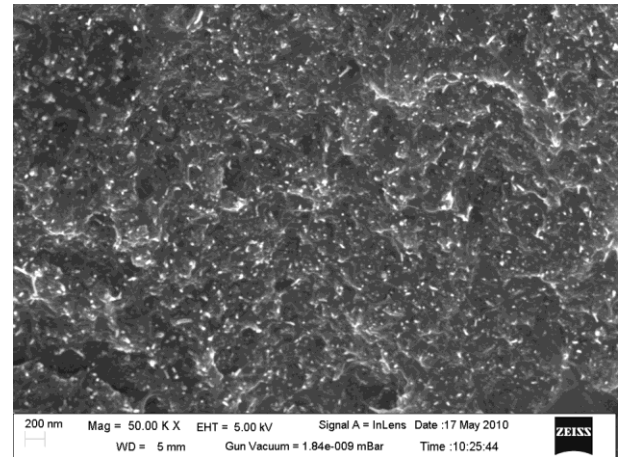


Fig. 1. FESEM microphotograph of 0.5 wt% MWNT based TPU nanocomposite.

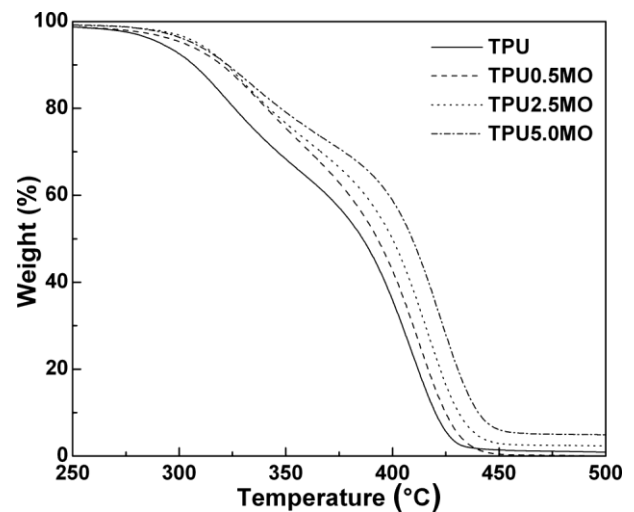


Fig. 2. TGA thermograms of neat TPU and 0.5, 2.5, and 5.0 wt% MWNT based TPU nanocomposite.

#### 3.3 DMA

Fig. 3 shows the variation of  $E'$  of neat TPU and MWNT based TPU nanocomposites with temperature. The magnitude of the elastic modulus increases significantly at lower temperature region (below  $T_g$ ), whereas it increases slightly at higher temperature region (above  $T_g$ ) because the TPU matrix become more stiff at low temperature but it become soft at high temperature. The significant

enhancement of  $E'$  of TPU matrix is contributed to the reinforcing effect of the CNTs [7].

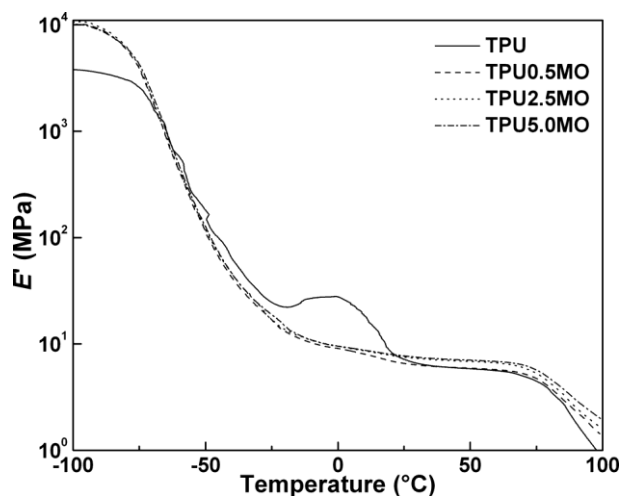


Fig. 3. The dependence of  $E'$  as function of temperature of neat TPU and 0.5, 2.5, and 5.0 wt% MWNT based TPU nanocomposite.

The variation of  $\tan\delta$  as a function of temperature of neat TPU and MWNT based TPU nanocomposites are shown in Fig. 4. The introduction of MWNT into the TPU matrix causes shifting of  $T_g$  values to higher temperature of about  $-49.3$  °C for pure TPU to  $42.5$  °C for the TPU/2.5 wt% CNT nanocomposites. It indicates that the main chain segmental mobility of the TPU matrix is significantly restricted by the incorporation of CNT due to the interfacial interaction arises between the polar groups [17].

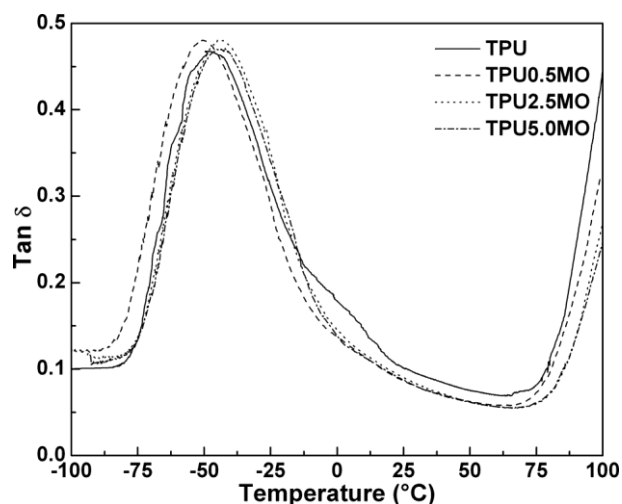


Fig. 4. The dependence of  $\tan\delta$  as function of temperature of neat TPU and 0.5, 2.5, and 5.0 wt% MWNT based TPU nanocomposite.

### 3.4 DSC

Fig. 5 represents the DSC traces of pure TPU and different wt% of MWNT reinforced TPU

nanocomposites. The  $T_g$  of the soft segment phase of pure TPU is found at about  $-71$  °C. The values of  $T_g$  of the 2.5 wt% MWNT filled TPU nanocomposites are  $-72$  °C. The  $T_g$  value did not change appreciably with nanotube loading because the heat capacity change at the  $T_g$  region is very low and the DSC experiment is carried out in static mode. The TPU matrix shows a endothermic peak at around  $22$  °C, which is assigned to the crystalline melting point of the short range regular arrangement of the soft segment present in it. The peak value of  $T_m$  is not changed by the incorporation of the MWNTs. The area of the peak which represents the enthalpy of the melting ( $\Delta H_{m(\text{soft})}$ ) enhanced with increase in wt% of MWNT loading that concluded that the crystallinity of the TPU matrix improved by the addition of MWNT because it imparted positive nucleating effect [18]. Small endothermic peak is observed at around  $250$  °C is referred to the melting of the very small regular order hard domain of the TPU matrix and the heat of melting ( $\Delta H_{m(\text{hard})}$ ) associated with it is very low due to the small amount of hard segment content. The peak temperature is not altered by the addition of MWNT because it may not affect the hard segments [19].

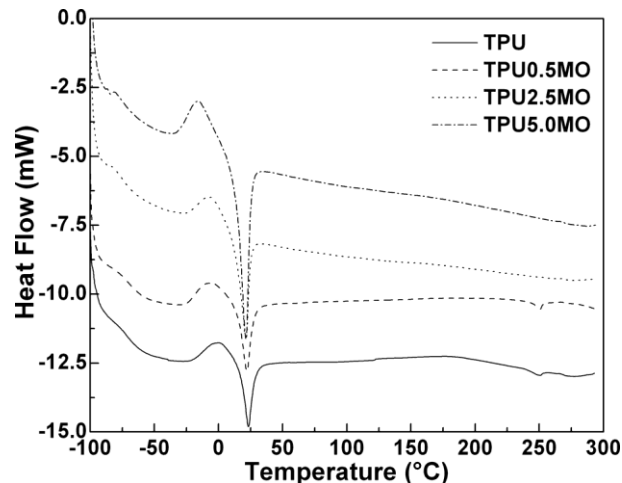


Fig. 5. DSC thermograms of neat TPU and 0.5, 2.5, and 5.0 wt% MWNT based TPU nanocomposite.

### 3.5 RPA

Fig. 6 shows the variation of  $G'$  as a function of applied frequency. The value of  $G'$  significantly increased with increase in wt% of MWNT content due to the strong nanotube–TPU interactions. Furthermore, the increase in  $G'$  is more pronounced especially at low frequency region as compared to the high frequency region because samples get enough time for dynamic relaxation process. A plateau region is developed with increase in

nanotube loading at low frequency. The transition of the viscoelastic response from ‘liquid-like’ to ‘solid-like’ at low frequency region is attributed to the high stiffness of the dimensionally stable nanotubes. The cross over frequency shifted to the higher frequency region with nanotube loading indicates the slow dynamic relaxation mechanism of the filled system, which is termed as *pseudo-solid-like* behavior [20].

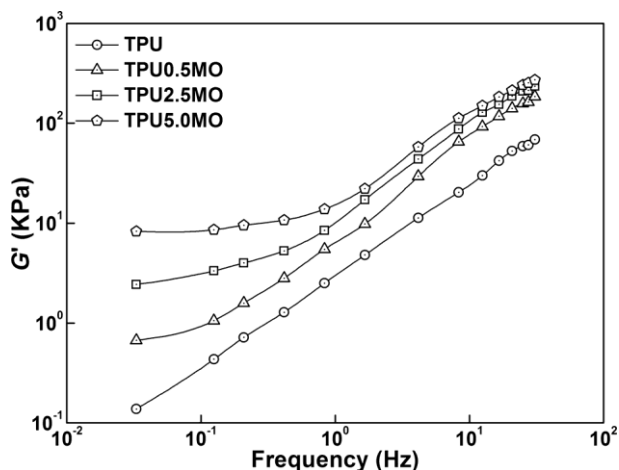


Fig. 6. The dependence of  $G'$  as function of frequency of neat TPU and 0.5, 2.5, and 5.0 wt% MWNT based TPU nanocomposite.

The variation of  $\eta^*$  with applied frequency is shown in Fig. 7. The magnitude of  $\eta^*$  for TPU/CNT nanocomposites increased substantially with increase in MWNT loading due to the developments of TPU–CNT and CNT–CNT attractive interactions that considerably counter act the segmental molecular chain mobility of the TPU matrix. The rate of increase in value of  $\eta^*$  is prominent at lower frequency region as compared to the higher frequency region. The dependency of  $\eta^*$  on applied frequency showed a linearly decrease in  $\eta^*$  with applied dynamic frequency, which is called as shear thinning behavior or pseudo-plasticity characteristic [21]. At higher frequency region, the polymer melt along with the MWNTs are aligned along the direction of the flow regime.

### 3.6 Tensile Properties

The initial modulus, tensile strength, and elongation at break of the TPU/MWNT nanocomposites were significantly increased with increase in wt% of MWNT loading due to the reinforcing effect exhibited by the nanotubes and strong adhesion bonding between CNT and TPU matrix [22]. At 5.0 wt% nanotube loading, the tensile properties decreased due to the increase in aggregation tendency of the CNTs.

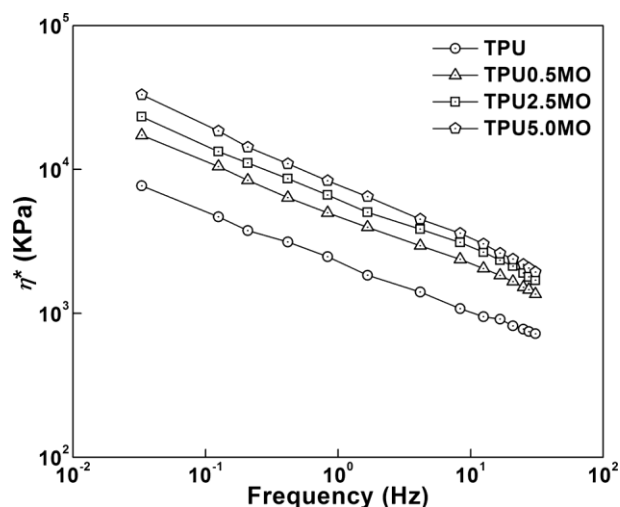


Fig. 7. The dependence of  $\tan\delta$  as function of frequency of neat TPU and 0.5, 2.5, and 5.0 wt% MWNT based TPU nanocomposite.

## 4 Conclusions

The MWNT based TPU nanocomposites was successfully prepared by melt intercalation technique. The thermal, mechanical, and rheological properties of the TPU matrix were significantly enhanced by the incorporation MWNT. The FESEM images observed that the –OH functionalized MWNTs are uniformly dispersed within the TPU matrix at low MWNT loading. TGA test concluded that the addition of CNTs substantially enhanced the thermal stability of the TPU matrix. DSC study showed that the melting temperature,  $T_g$ , and crystallinity of the TPU matrix slightly increased by the incorporation of MWNT, which suggested that the modified MWNT affect both crystalline and amorphous structural part of the TPU matrix. DMA study determined that the  $E'$  and  $T_g$  of the nanocomposites increased with increase in wt% of MWNT loading. RPA study revealed that the  $G'$  improved with increase in MWNT content and variation of  $\eta^*$  with frequency indicated a shear-thinning behavior. Tensile tests showed that the addition of MWNT significantly improved the tensile strength and modulus of the TPU matrix without sacrificing the elongation at break by incorporation of MWNTs. The homogeneous dispersion of MWNTs throughout the TPU matrix and presence of strong interfacial adhesion between the functionalized MWNTs and the TPU matrix are responsible for the significant improvement of overall material properties of the TPU/MWNT nanocomposites.

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