

Effect of Annealing Treatment on the Structure and Properties of Polyurethane/Multiwalled Carbon Nanotube Nanocomposites

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ABSTRACT: The thermoplastic polyurethane/multiwalled carbon nanotube (TPU/CNT) nanocomposites with high conductivity and low percolation threshold value were prepared by melting blending and annealing treatment. The effect of annealing process on the microphase structure and the properties of TPU/CNT nanocomposites was studied. It has been shown that CNT flocculation can occur in TPU/CNT nanocomposites during the annealing process. At a critical CNT content, which defined the percolation threshold, CNTs could form conductivity network. The conductive percolation threshold value of TPU/CNT nanocomposites was decreased from 10 to 4% after annealing process, and the conductivity of TPU/CNT nanocomposites with 10 vol % of CNT could reach 1.1 S/m after an annealing time of 1 h. The significant enhance-

ment of electrical conductivity was influenced by the annealing time and the content of CNTs. The formation of CNT networks was also verified by dynamic viscoelastic characterization. The results of X-ray diffraction and differential scanning calorimetry indicated that annealing process reinforced the microphase separation of the nanocomposites. Mechanical properties test showed that the annealing treatment was in favor of improving the mechanical properties; however, further increase in the annealing time has negative effect on the mechanical properties. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: nanocomposites; thermoplastic polyurethane; multiwalled carbon nanotubes; annealing; electrical conductivity

INTRODUCTION

Since the innovative discovery of carbon nanotubes (CNTs) by Iijima in 1991, CNTs have attracted enormous attention for their excellent properties and for their use in a wide variety of applications.¹ With unique mechanical and physical properties, such as excellent strength, modulus, electrical and thermal

conductivities, and low density, CNTs have attracted much interest in the field of polymer/CNT composites.^{2–4} When compared with the enormous number of studies on the application of CNTs in epoxides, thermoplastics, and fiber, there were few reports dealing with the applications of CNTs in elastomers for reinforcement because of the high viscosity of the elastomeric polymer matrix.^{5–8} Thermoplastic polyurethane (TPU) is an important class of polymer materials with their unique properties such as excellent flexibility, elasticity, and damping ability. The PU properties can be easily tailored through changing their molecular chain structure of soft and hard segment. Therefore, it is believed that TPU can serve as an excellent matrix for polymeric carbon nanocomposite materials.^{9–11}

Various methods have been reported for the preparation of CNT-reinforced polymer composites such as solution mixing, melt mixing, and *in situ* polymerization.^{12–17} Among them, melt mixing is a favorable method for compounding of composites because it is environmentally friendly and widely available in the polymer industry. To obtain nanocomposites with high electrical conductivity, it is

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essential to choose suitable mixing conditions under which the deagglomeration and dispersion of CNTs in the polymer matrix can be controlled. In addition to the melt-mixing conditions, some studies reported that the electrical conductivity could be improved through annealing the composites above its melting temperature.^{18–20} It is presumed that the reaggregation of conductive fillers at elevated temperatures can enhance the electrical conductivity of the nanocomposites by promoting the formation of macroscopic conductive networks.²¹ At the same time, the CNTs have been aligned by the flow during processing and they relaxed to random orientations during annealing, which contribute to the network formation. To the best of our knowledge, the annealing process on the improvement of conductivities of nanocomposites with an elastomeric matrix has not been studied.

In this work, thermal annealing method has been adopted to improve the electrical conductivity of the nanocomposites by melt blending. Scanning electron microscope (SEM), transmission electron microscope (TEM), dynamic mechanical thermal analysis (DMTA), and rubber process analyzer (RPA) were used to study the effect of annealing treatment on the network formation of the CNTs in the annealed TPU/CNT nanocomposites. X-ray diffraction (XRD) and differential scanning calorimetry (DSC) were used to study the effect of annealing treatment on the microphase separation of the annealed nanocomposites. The effect of annealing treatment on the mechanical properties was also studied.

EXPERIMENTAL PART

Materials

TPU (9380A, supplied by Bayer, Germany) was a kind of polyether-based polyurethane thermoplastic elastomer, with a glass transition temperature of -50.5°C . CNTs with a diameter of 10–20 nm and length of 0.5–1000 μm were prepared by chemical vapor deposition and supplied by Tsinghua University, Beijing, China. The CNTs were used as received and without surface modification. Antioxidant 1010, pentaerythritol tetrakis 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (CAS# 6683-19-8) was purchased from Beijing Jiacheng Additive Research Institute (Beijing, China) and used without further purification.

Preparation of annealed TPU/CNT nanocomposites

The TPU/CNT nanocomposites were prepared as follows: TPU was dried at 110°C for 2 h and then preheated on a two-roll mill (SK-160B; Shanghai Rubber Machinery Works, Shanghai, China) at 160°C for 3 min. The roller size is Φ 155 mm \times L 350 mm.

The antioxidant 1010 was added with the TPU/antioxidant mass ratios of 100/1. The gap between the rolls was 2 mm, and the speed of the rolls was set as 20 r/min. CNT was then slowly added into the mixture. The mixing process was continued for 5 min. The obtained TPU compounds were compression molded at 170°C for 10 min under a pressure of 10 MPa.

The TPU/CNT nanocomposites with 10 parts per hundreds of rubber CNTs were melt annealed at 180°C for a predetermined time (varied from 10 min to 6 h) under 10 MPa. The samples were gradually cooled under pressure. All annealing experiments were performed in a nitrogen atmosphere to avoid oxidative degradation of TPU.

Characterization

The fracture morphologies of the samples were observed using SEM (S-4700, Hitachi, Japan) with an accelerating voltage of 20 kV. The specimens for SEM were prepared by fracturing the composites in liquid nitrogen. The morphologies and the distribution of CNTs in the nanocomposites were observed using H-800 TEM of Hitachi, Japan. The specimens for TEM observation were prepared by cryogenic microtoming using a Reichert Jung Ultracut Microtome and mounted on 200-mesh copper grids.

The crystal structure of the products was studied by XRD (D/Max 2500 VB2+/PC; Rigaku, Japan) with a Cu target radiation for a 2θ range of 5° to 90° at a scan speed of $0.02^{\circ}/\text{s}$. DSC traces were recorded on a NETZSCH 204 analyzer (Germany) at a heating rate of $10^{\circ}\text{C}/\text{min}$ under N_2 atmosphere.

The Payne effect of the nanocomposites was measured at 170°C and 1 Hz as a function of strain amplitude from 0 to 400% using the RPA-2000 apparatus (Alpha Technologies, Ohio, USA).

Mechanical properties were measured on the CMT4104 testing machine (Shenzhen SANS Testing Machine, Shenzhen, China) at the speed of 500 mm/min according to ASTM D-412 under room temperature (25°C). Storage modulus, loss modulus, and $\tan \delta$ were measured as a function of temperature with the DMTA VA3000 of 01dB-Metravib, France, under tension mode of the frequency of 10 Hz and temperature step of $3^{\circ}\text{C}/\text{min}$.

The electrical conductivity of the TPU/CNT nanocomposites was measured by using a digital multimeter when the resistance was below $2 \times 10^7 \Omega$ and a ZC43-type megger when the resistance was above $2 \times 10^7 \Omega$.

RESULTS AND DISCUSSION

The TPU/CNT nanocomposites were prepared by blending CNTs with TPU in a two-roll mill. Figure 1

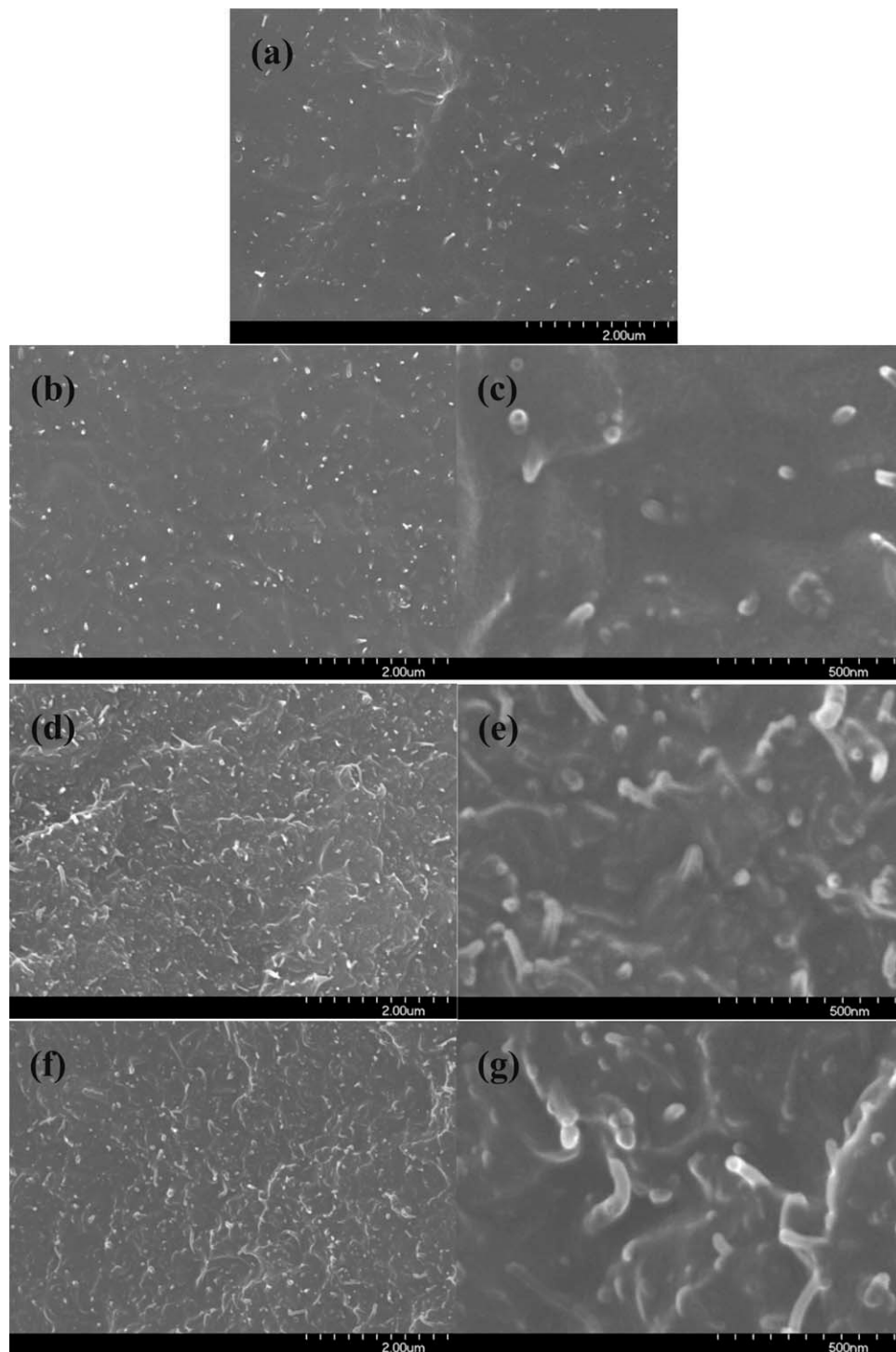


Figure 1 SEM images of (a) the TPU/CNT nanocomposites and annealed TPU/CNT nanocomposites with annealing time of (b) and (c) 10 min; (d) and (e) 40 min; and (f) and (g) 1 h.

shows the SEM images of fracture surface of the TPU/CNT nanocomposites and the annealed nanocomposites with different annealing time (the light section is CNT). When compared among different images, it could be seen that the space between CNT and CNT became smaller with the increment of annealing time, and the CNT in the TPU matrix gradually formed

CNT–CNT network. The viscosity of TPU decreased when it was at melt temperature in a pressure of 10 MPa, and the Brownian movement of nanoparticles increasing, which made for the rearrangement of CNTs, promoted the flocculation of CNTs and strengthened the filler network structure. Figure 2 shows the TEM images of TPU/CNT nanocomposites

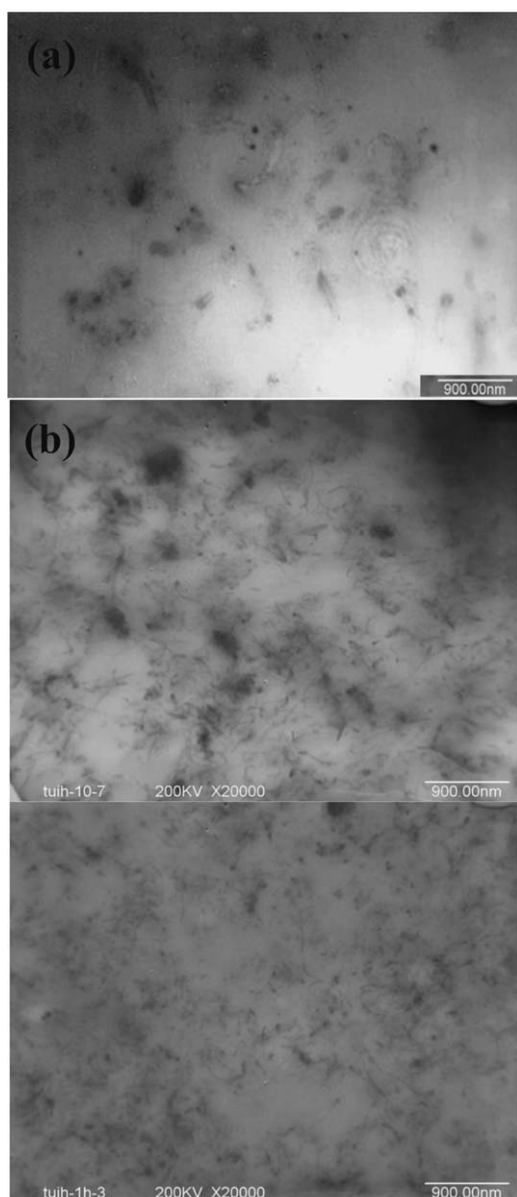


Figure 2 TEM images of (a) the TPU/CNT nanocomposites and the annealed TPU/CNT nanocomposites with annealing time of (b) 10 min and (c) 1 h.

and annealed nanocomposites with different annealing time (the dark section is CNT). It could be seen from Figure 2 that the networks formed between CNT and CNT after an annealing time of 1 h, and this kind of network may influence the properties of nanocomposites.

Effect of annealing process on the microphase of the nanocomposites

Figure 3 shows the XRD patterns of the TPU/CNT nanocomposites. The pure TPU had only one characteristic diffraction peak at 2θ of 20.0° , and the pure

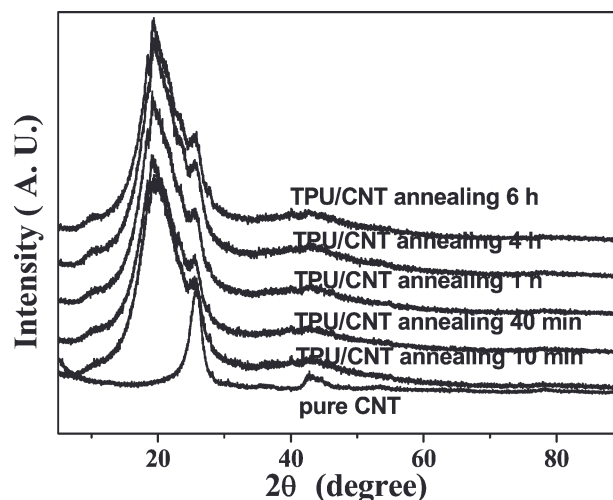


Figure 3 X-ray diffraction patterns of the pristine CNT and TPU/CNT nanocomposites with different annealing time.

CNT had two characteristic diffraction peaks at 2θ of 25.6° and 42.8° , respectively. All of the three peaks were present in the TPU/CNT nanocomposites, and the position of all the peaks kept unchanged after annealing treatment, which indicated that the microstructure type of TPU was not changed by the annealing treatment. It could be seen from the diffraction peak at 2θ of 20° that the characteristic diffraction peak became sharper and appeared as a small sharp peak gradually with the increment of annealing time, which indicated that annealing process made the microphase separation higher due to the rearrangement of the fixed macromolecules in the annealing process.

Figure 4 illustrates the DSC curves of the annealed TPU/CNT nanocomposites with different annealing time. It was seen that the glass transition temperature (T_g) of the annealed nanocomposites with annealing time of 10 min and 6 h were -55.3 and

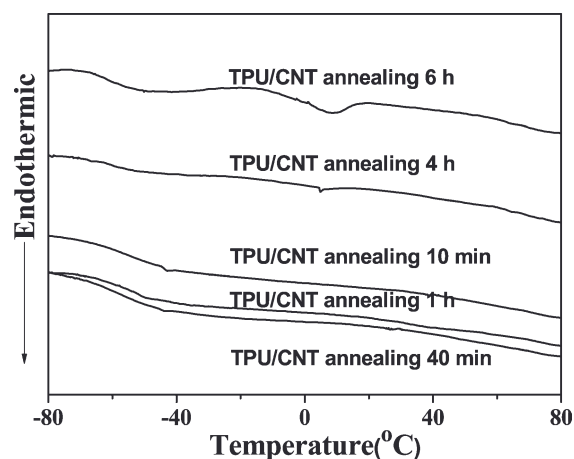


Figure 4 DSC curves of the annealed TPU/CNT nanocomposites with different annealing time.

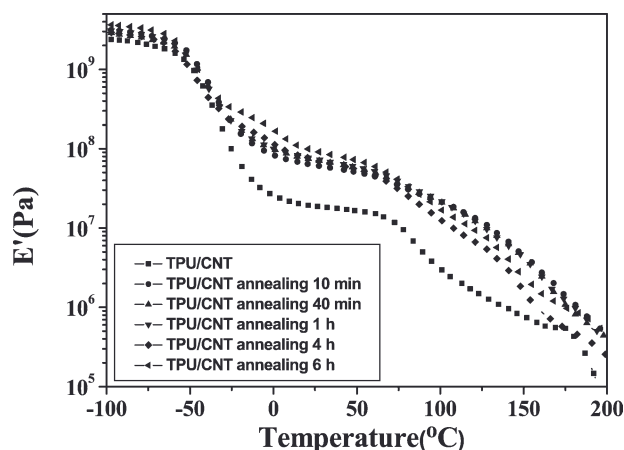


Figure 5 The temperature dependence of storage modulus of the TPU/CNT nanocomposites and the annealed TPU/CNT nanocomposites with different annealing time.

–62.1°C, respectively. The T_g of the annealed nanocomposites decreased with the increment of annealing time. In the cooling process, TPU had enough time to relax, and the macromolecular chains could reorient, which made some parts of amorphous chains rearranged to form more complete soft segments and hard segments. The above process improved the microphase separation. Therefore, the strength of filler networks also affected the T_g .

The melting peaks that belonged to hard segments appeared when the annealing time was more than 4 h, and the area of melt peak became larger when the annealing time was 6 h. This may be caused as some crystal melted in the annealing process and recrystallized in the cooling process to form higher order and larger crystal region, which was helpful for the microphase separation of TPU.

Dynamic mechanical analysis of annealed nanocomposites

The effect of the annealing time on the dynamic mechanical property of TPU/CNT nanocomposites was analyzed by DMA in the experiment. The elastic modulus (E') and the loss factor ($\tan \delta$) of the annealed TPU/CNT nanocomposites with different annealing time were characterized as a function of temperature.

The storage modulus of the annealed TPU/CNT nanocomposites with different annealing time versus temperature curves are shown in Figure 5. When compared with the unannealed TPU/CNT nanocomposites, the temperature viscous flow temperature (T_f) of the annealed TPU/CNT nanocomposites was slight higher. The storage modulus of the annealed TPU/CNT nanocomposites with different annealing time exhibited no obvious differences in glassy state. However, the storage modulus of annealed TPU/CNT nanocomposites obviously increased in rubbery

state and increased slightly with the increment of annealing time. The above results concluded that the flocculation of CNT–CNT networks after annealing increased the elasticity and prevented the movement of molecules under small deformation.

Figure 6 shows the loss factor as a function of temperature for annealed TPU/CNT nanocomposites with different annealing time and exhibited the effect of annealing time on the loss factor. The position of the $\tan \delta$ peak in the loss factor versus temperature curve can be used to identify the T_g of the elastomer materials. All the curves contained two peaks due to soft segments and hard segments in the TPU. The $\tan \delta$ peak at –25°C slightly shifted to low temperature with the increment of annealing time, which indicated that the T_g of soft segments of TPU slightly decreased with the increment of annealing time. The hydrogen bonding of TPU was destroyed at high temperature in the annealing process and the macromolecular chain was rearranged. In the cooling process, the TPU molecule chains could be rearranged, which made some part of amorphous chains rearrange, and gradually fixed orderly to form complete soft segments and hard segments. The above process was helpful to obtain higher degree of microphase separation, which led to the decrease of T_g at about –25°C.

The interaction between CNT and TPU was one of the important factors to impact the loss factor. The position of $\tan \delta$ peak at 200°C kept unchanged; however, the maximum of $\tan \delta$ peak decreased with the increment of annealing time. This was because that the interface between CNT and TPU was the major component of $\tan \delta$ and that the smaller interface area due to the flocculation of filler networks made the friction smaller, which led to decrease in $\tan \delta$.

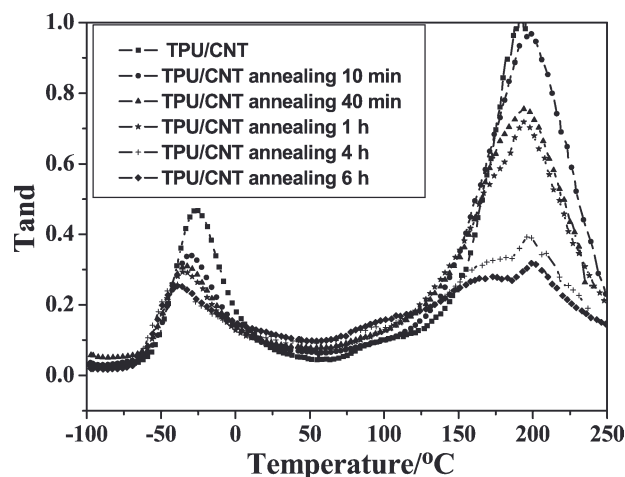


Figure 6 The temperature dependence of $\tan \delta$ of the TPU/CNT nanocomposites and the annealed TPU/CNT nanocomposites with different annealing time.

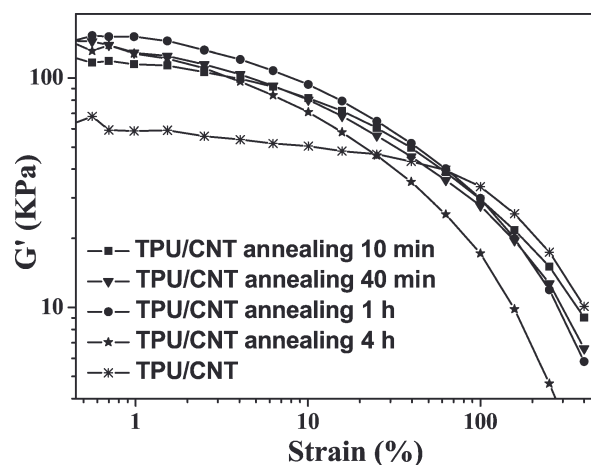


Figure 7 Strain dependence of the shearing storage modulus of the TPU/CNT nanocomposites and the annealed TPU/CNT nanocomposites with different annealing time.

Effect of annealing process on the Payne effect

The shearing storage modulus (G') of unfilled rubbers is independent of the deformation amplitude. In contrast, G' for the filled rubber shows a significant dependency on the dynamic deformation; here, the value considerably decreases with the increment of strain amplitude. This nonlinear behavior of filled rubbers is known as “Payne effect”²² and has been explained by the existence of a filler network in the rubber matrix above the percolation threshold.

Figure 7 shows the strain dependence of the shearing storage modulus of the annealed TPU/CNT nanocomposites with different annealing time. It could be seen that the plateau region of TPU/CNT nanocomposites was long, which indicated that its dynamic modulus did not change with the increment of strain in certain range. After exceeding the amplitude corresponding to the percolation threshold of the filler network, this structure was broken down resulting in the lowering of the G' value. The G' value of annealed TPU/CNT nanocomposites was larger than the TPU/CNT nanocomposites in the small strain region due to the increment of filler networks, and the G' reached maximum when the annealing time was 1 h. However, as shown in Figure 7, with further increase in the annealing time to 4 h, the TPU molecular may be decomposed to some extent, resulting in the decrease of the G' value. When compared with the TPU/CNT nanocomposites, the plateau of annealed TPU/CNT nanocomposites region became shorter.

Figure 8 shows the strain dependence of loss factor ($\tan \delta$) of the TPU/CNT nanocomposites and the annealed TPU/CNT nanocomposites with different annealing time. It could be seen that $\tan \delta$ of the annealed TPU/CNT nanocomposites decreased with the increment of annealing time within certain strain

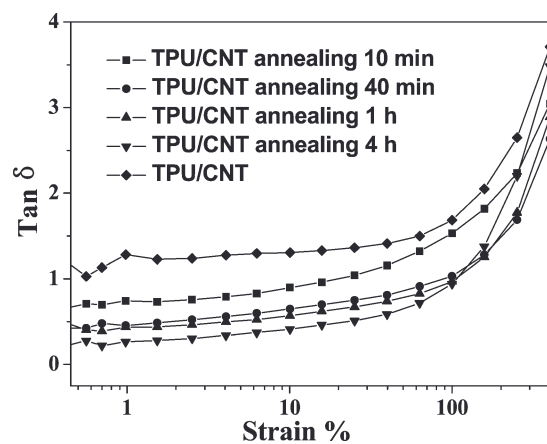


Figure 8 Strain dependence of the loss factor of the TPU/CNT nanocomposites and the annealed TPU/CNT nanocomposites with different annealing time.

region. TEM micrographs showed that CNT dispersion is improved during annealing because of the relaxation and redistribution of the CNT, and therefore, the CNT network become a more integrity structure. On the other hand, reduced mobility of the chains because of better dispersion of the CNT may also have contribution to the decrease of the $\tan \delta$. The above reason interpreted the decrease of $\tan \delta$.

Effect of annealing process on the mechanical properties

The tensile stress-strain curves of the annealed TPU/CNT nanocomposites with different annealing time are shown in Figure 9. The mechanical properties of the nanocomposites are tabulated in Table I. TPU is composed of soft segments and hard segments, which can act as rubber phase and plastic phase, respectively. TPU is a kind of self-reinforced

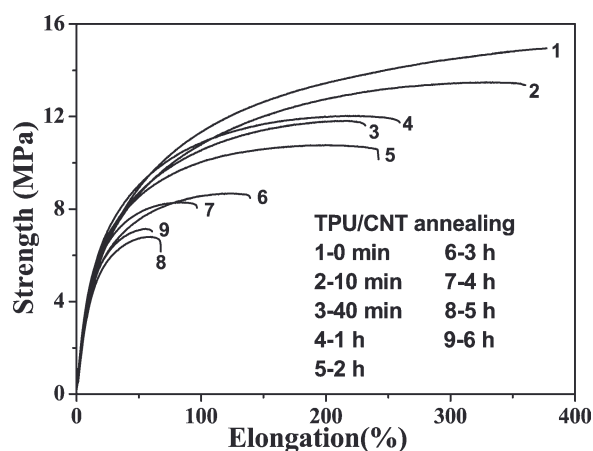


Figure 9 Mechanical properties: tensile stress versus strain curves of the TPU/CNT nanocomposites and the annealed TPU/CNT nanocomposites with different annealing time.

TABLE I
Mechanical Properties of the TPU/CNT Nanocomposites

Annealing time	Tensile strength (MPa)	Elongation at break (%)	Modulus at 100% elongation (MPa)
0 min	23.6	574	9.9
10 min	15.2	415	11.33
20 min	13.5	364	10.81
40 min	11.8	235	10.54
1 h	12.03	265	10.88
2 h	10.77	250	10.02
3 h	8.67	152	8.55
4 h	8.28	107	–
5 h	6.79	68	–
6 h	7.15	74	–

polymer because of its hard segment. As shown in Figure 9, the tensile strength and the elongation at break decreased with the increment of annealing time; however, the modulus at low strain increased slightly with the increment of annealing time. The TPU main chain may undergo decomposition during the annealing process,²³ which will result in the decrease of tensile strength and elongation. The data in Table I indicated that the modulus at 100% elongation increased slightly with the increment of annealing time in certain time. When the annealing time was more than 2 h, the modulus at 100% elongation decreased. The soft segment of TPU made it flexible, and the hard segment played a role as physical crosslinking points and reinforcement. The microphase separation became more obvious after annealing treatment, which led to the deterioration of the mechanical properties, as shown in Table I.

Effect of annealing process on the electrical conductivity

The conductivity of TPU/CNT nanocomposites was strongly affected by the concentration of CNTs. There is a critical volume fraction known as the percolation threshold at which the conducting inclusions form an interconnecting filler network leading to a sharp increase in the electrical conductivity. The effects of the concentration of CNTs and the annealing time on the electrical conductivity were studied as follows. It is proposed that before annealing, CNTs are dispersed individually in the polymer matrix and that there is no interconnection of CNTs, except some highly packed agglomerates. When the CNTs do not have effective contacts or interconnections, no conductive pathways are formed inside the composites. Under such conditions, the composites are nonconductive or possess very low electrical conductivity. After annealing, there is considerable numbers of loosely packed CNT agglomerates formed through thermal diffusion of individual nanotubes. These loosely packed CNT agglomerates

contribute to the formation of conductive networks by acting as the junctions or connections.

Figure 10(a) shows the effect of CNT loading on the electrical conductivity of TPU/CNT nanocomposites and annealed TPU/CNT nanocomposites, and the annealing time was 4 h. The electrical conductivity of TPU/CNT nanocomposites and annealed TPU/CNT nanocomposites increased with the increment of CNT loading, and the percolation threshold of the annealed TPU/CNT nanocomposites was lower than TPU/CNT nanocomposites. TPU was in molten state at 180°C, and therefore, the CNTs could rearrange in the molten TPU matrix. CNTs were easy to flocculate under the thermodynamic driving force, which made the CNTs easy to form filler networks, improved the probability of electron tunneling effect, and decreased the percolation threshold value. When the CNT loading was low, the space between fillers was large; however, there was interaction between aggregates. The CNT is difficult to move and form networks, so it could only form partial networks. The above reasons led to unobvious difference on electrical conductivity

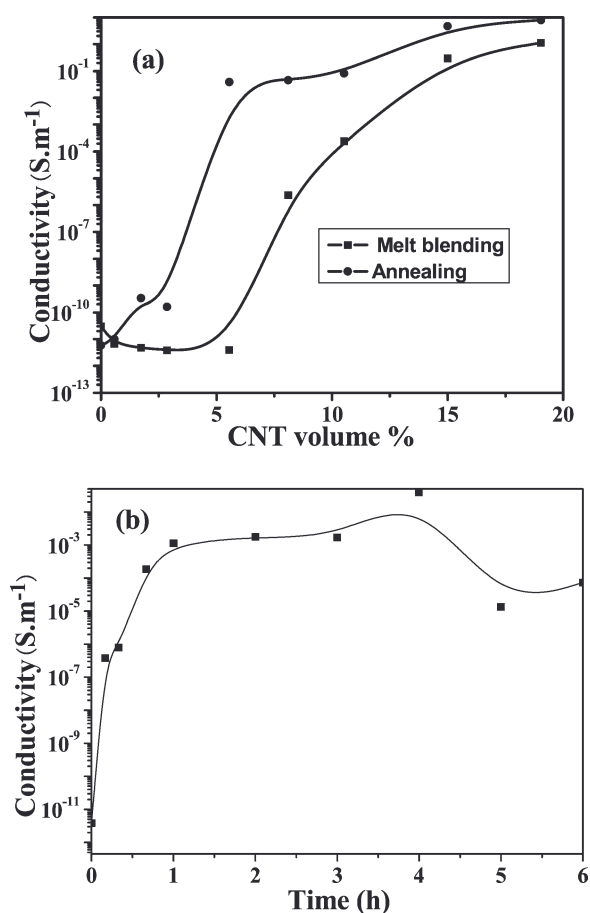


Figure 10 Electrical conductivity of (a) the TPU/CNT nanocomposites and annealed nanocomposites with different CNT volume fraction and (b) the annealed TPU/CNT nanocomposites with different annealing time.

between TPU/CNT nanocomposites and annealed TPU/CNT nanocomposites. When the CNT loading was high, the fillers themselves were easy to form networks, and therefore, the annealing process could improve the networks only in small extent. However, networks were most sensitive when the filler loading was near the critical volume fraction, which led to lower percolation threshold value of annealed TPU/CNT nanocomposites.

Figure 10(b) shows the effect of annealing time on the electrical conductivity of annealed TPU/CNT nanocomposites. The conductivity of nanocomposites increased rapidly with the increment of annealing time within 1 h. However, the conductivity of nanocomposites had no obvious change when the annealing time was more than 1 h. The CNT network was completely developed after annealing for a certain time (1 h), which made the electrical conductivity have no obvious change. We could also interpret this from the TEM morphology shown in Figure 2. The space of CNTs in TPU/CNT nanocomposites was large, and the CNT networks were formed after annealing for more than 1 h.

CONCLUSIONS

The TPU/CNT nanocomposites with high conductivity and low percolation threshold value were prepared by melt blending and annealing. Post-thermal annealing above the melting temperature of TPU could lead to the formation of CNT network and thus a significant enhancement of electrical conductivity. The conductive percolation threshold value of TPU/CNT nanocomposites was decreased after annealing process, and the conductivity of nanocomposites with 10% of CNT was greatly improved after annealing treatment. The SEM, TEM, DMTA, and RPA results indicated that the annealing process improved the network structure of the CNT in the nanocomposites, which was in favor of increasing the conductivity and decreasing the percolation threshold value. XRD and DSC results indicated that annealing process reinforced the microphase separation of the nanocomposites. Mechanical properties

test showed that the annealing treatment was in favor of improving the mechanical properties; however, further increase in the annealing time has negative effect on the mechanical properties.

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