

Mechanical and Surface Properties of Polyurethane/Fluorinated Multi-Walled Carbon Nanotubes Composites

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Received 10 April 2007; accepted 25 June 2007

DOI 10.1002/app.27625

Published online 4 February 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: To improve the mechanical and surface properties of poly(etherurethane) (PEU), multi-walled carbon nanotubes (MWCNTs) were surface grafted by 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol (TDFOL) (MWCNT-TDFOL) and used as reinforcing agent for PEU. Fourier-transform infrared spectroscopy revealed the successful grafting of MWCNTs. PEU filled with MWCNT-TDFOL could be well dispersed in tetrahydrofuran solution, and tensile stress-strain results and dynamic mechanical analysis showed a remarkable increase in mechanical properties of PEU by adding a small amount of MWCNT-TDFOL. Contact angle testing displayed a limited improvement

(just 9°) in the hydrophobicity of PEU surface by solution blending with MWCNT-TDFOL. However, a large improvement of surface hydrophobicity was observed by directly depositing MWCNT-TDFOL powder on PEU surface, and the water contact angle was increased from 80° to 138°. Our work demonstrated a new way for the modification of carbon nanotubes and for the property improvement of PEU. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2023–2028, 2008

Key words: polyurethane; fluorinated multi-walled carbon nanotubes; mechanical and surface properties

INTRODUCTION

Since their discovery by Iijima¹ in 1991, carbon nanotubes (CNTs) have been widely used in various fields, such as electronic materials, biological technology, multi-functional composites, and so on because of remarkable nanostructures combining high electrical conductivity, high surface area, significant mechanical strength, and good chemical stability.^{2–5} The break strength of CNTs was reported as high as 200 GPa and elastic modulus in the 1-TPa range.^{6–9} Thus, there exists a great deal of potentiality in using CNTs as a reinforcing agent for polymer matrices. However, CNTs are strongly affected by van de Waals attraction just due to their small size and large surface area. These forces give rise to the formation of aggregation, which in turn, make dispersion of CNTs in polymers difficult, resulting in rather poor mechanical and electro-conductive properties. Therefore, the key point to fully explore CNTs reinforcing potential or enhance the properties of a polymer matrix is a uniform dispersion, exfoliation, and orientation,^{10–11} and improving the interac-

tion between CNTs and a polymer matrix is also important.

Polyurethane (PU) with the two-phase structure of hard and soft domains: hard domains, composed of aromatic (or aliphatic) urethane or urea segments, and soft domains, composed of aliphatic polyether, polycarbonate, polyester, or poly(methylsiloxane) segments are widely used as biomedical materials because of their good blood compatibility.^{12–13} Recently, the preparation of CNT/PU composites has attracted a great attention, due to their enhanced mechanical and electrical properties and blood combinability.^{16–21} Self-organized single-walled carbon nanotubes (SWCNTs) in PU could be obtained by just simply dissolving SWCNTs in the solution of thermoplastic PUs and tetrahydrofuran (THF).²⁰ Super-hydrophobic surface was reported on SWCNTs film and its wrap by fluorinated PU.^{22–23} In our previous study, a three-step surface treatment of multi-walled carbon nanotubes (MWCNTs) was carried out to obtain MWCNT grafted to isophorone diisocyanate, which had a similar structure to the hard segment of poly(etherurethane) (PEU). And PEU/MWCNT membrane composites with well mechanical properties and great permeability have been obtained.²⁴ Following this line, in this article, MWCNT grafted by 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol (TDFOL) (MWCNT-TDFOL) was prepared for the first time and used as the filler for PEU modification. In this way, a remarkable increase of mechanical properties of PEU has been achieved by adding a

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Contract grant sponsor: the National Natural Science Foundation of China; contract grant numbers: 50673063 and 50533050.

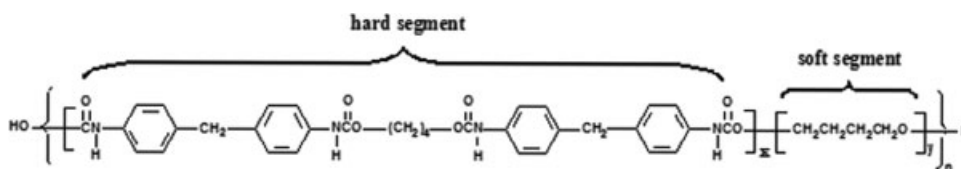


Figure 1 Chemical structural formulation of PEU used in the study.

small amount of MWCNT-TDFOL, on the other hand, a hydrophobic surface was also obtained by directly depositing MWCNT-TDFOL on PEU surface.

EXPERIMENTAL

Materials

MWCNTs having the length of $< 50 \mu\text{m}$ and the diameter of 10–20 nm were provided by Chengdu Timesnano Company, China. PEU was synthesized in our group and the structure is shown in Figure 1. Sulfuric acid, nitric acid, and THF were all from Kelong Chemical reagent plant, Chengdu, China. Thionyl chloride (SOCl_2) was from Bodi Chemical Company, Tianjin, China and in sealed preservation. TDFOL was purchased from Aldrich.

Preparation

The process of the treatment of MWCNTs is shown in Figure 2. Three grams of MWCNTs with the length of $< 50 \mu\text{m}$ and the diameter of 10–20 nm, were treated with 300 mL mixed solution of sulfuric acid and nitric acid (3 : 1 by volume, respectively) at room temperature for 24 h to obtain $-\text{COOH}$ grafted MWCNT (MWCNT-COOH). After that, MWCNT-COOH were filtrated and washed by distilled water until pH of the filtration was 7. Then MWCNT-COOH were dried at 80°C in vacuum oven for 24 h.

SOCl_2 (30 mL) and 0.3 g MWCNT-COOH were stirred at 65°C for 24 h to obtain MWCNT-COCl. After that MWCNT-COCl were washed with anhydrous THF and centrifuged at 10,000 r/m repeatedly, and then MWCNT-COCl were dried at 40°C in vacuum oven for 3 h. Then the dried MWCNT-COCl and 3 g TDFOL were mixed at 80°C for 48 h. Finally, the production was washed with THF and centrifuged at 12,000 r/m repeatedly, till the unreacted were removed, then they were dried at 40°C in vacuum oven for 3 h to obtain MWCNT-TDFOL.

PEU were dissolved in 20 mL THF for 1 day. Various amount of MWCNT-TDFOL with 15 mL THF were ultrasonicated for 15 min using ultrasonicate reaction (CF-300, Southwest applied Acoustics Institute, Sichuan, China), then they were poured into

PEU/THF solution. After it appeared uniform, the mixture was ultrasonicated for another 5 min. Finally, the composite film was cast in oven 45°C , till THF was completely volatilized and pure PEU film without any fillers was also prepared according to the same process for comparison. The proportions of MWCNT-IPDI were listed in Table I. And samples were prepared by dripping a single drop on the cover glass and then drying them at 40°C for about 3 h, then those samples were treated by vacuum extraction at 40°C for 2 days to remove the THF thoroughly and the fluorinated chain could migrate to the surfaces by this drive.

For the deposition of MWCNT-TDFOL on PEU film, the flat PEU membrane on the cover glass was put into the bottom of beaker, which contains well dispersed MWCNT-TDFOL (0.0030 g) in ethanol solutions (35 mL) (by ultrasonication). Finally, the deposit of MWCNT-TDFOL on PEU films was obtained in a vacuum oven 45°C after the solvent was completely volatilized.

Characterization

Grafted MWCNTs were characterized using Fourier-transform infrared (FTIR) spectra (Nicolet 560). Scanning electron microscope (SEM) was used to observe the surface morphology of grafted MWCNTs. Me-

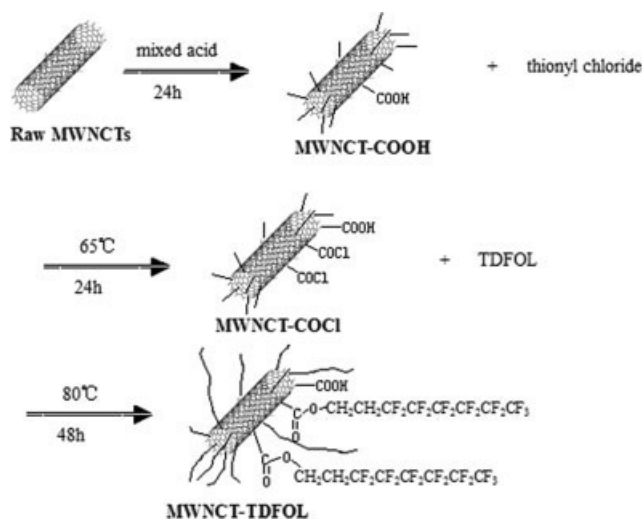


Figure 2 Step-by-step modification process of MWCNTs.

TABLE I
The Amount of MWCNTs and PEU in Experiment

Sample	MWCNTs-TDFOL (g)	PEU (g)	MWCNTs-TDFOL (wt %)
pure PEU	0.0000	2.0000	0
MWCNTs-TDFOL 0.05/PEU	0.0010	1.9990	0.05
MWCNTs-TDFOL 0.1/PEU	0.0020	1.9980	0.1
MWCNTs-TDFOL 0.3/PEU	0.0060	1.9940	0.3
MWCNTs-TDFOL 0.5/PEU	0.0100	1.9900	0.5
MWCNTs-TDFOL 0.8/PEU	0.0160	1.9840	0.8

chanical properties of pure PEU and composite membranes were represented by tensile testing (Instron Company, general tensile test) with the velocity of 500 mm/min and the membrane dimension was 7.24 mm in width, 2 cm in length and with the thickness of 0.1–0.2 mm, and by dynamic mechanical analysis (DMA) (Q800, TA Company) from -80 to 80°C with the calefactive rate of $3^{\circ}\text{C}/\text{min}$ and the frequency was 10 Hz, after the films were cut into 4 cm in length and 6 mm in width, and the thickness were 0.1–0.2 mm. Contact angles were measured on $3\ \mu\text{L}$ water with an OCA20 (Dataphysics Inc.) contact angle goniometer.

RESULTS AND DISCUSSION

FTIR spectra analyses and SEM

The FTIR spectra of the surface grafted MWCNTs are shown in Figure 3. One observes peaks at $1715\ \text{cm}^{-1}$ ($\gamma_{\text{C=O}}$) and $3436\ \text{cm}^{-1}$ ($\gamma_{\text{O-H}}$) for spectra **b**, suggesting the grafting of $-\text{COOH}$ group onto MWCNTs, compared with spectra **a** in which no obvious peak could be observed. The peaks at 1235 and $1194\ \text{cm}^{-1}$ in spectra **c** corresponding to the C-F stretching can be observed, which shows evidence that TDFOL is successfully grafted onto MWCNTs. Besides, it is also evident that functional group $-\text{COOH}$, could also exist on the surface of MWCNT-TDFOL, owing to the efficiency of the grafting reaction. The expanded and rough surface of MWCNT-TDFOL can be observed in SEM photos Figure 4(c), and the graphite layers in Figure 4(a) disappear with the acid treatment in Figure 4(b). Figure 5 illuminates the dispersion of raw MWCNTs and MWCNT-COOH, and MWCNT-TDFOL in THF. At the same concentration (0.0020 g MWCNTs and 20 mL THF), the dispersion of raw MWCNTs and MWCNT-COOH is poor and precipitated out in a few minutes after ultrasonicated mix. An improved dispersion is seen for MWCNT-TDFOL, which can be dispersed homogeneously in THF for several days without precipitation. However, from the dark color, instead of transparent, the size of MWCNT-TDFOL should be in micro scale.

Tensile testing

Figure 6 displays the tensile stress–strain curves of PEU membranes filled with different content of MWCNT-TDFOL. It's obvious that strength of PEU filled with MWCNT-TDFOL is increased with the increasing of MWCNT-TDFOL content. And when content reaches 0.8%, the strength gets to the highest (from 24 to 37.5 MPa), and the elongation is also increased about 350%. The improved stress and strain could be understood, in part, as caused by the improved dispersion of MWCNT-TDFOL in PEU matrix. Recently, molecular-dynamic studies have suggested that the mobility of the nanoparticles in the polymer might be crucial for introducing new energy-dissipating mechanism that lead to enhanced elongation in the nanocomposite.²⁵ Furthermore, Shah et al.²⁶ presented experimental evidence that nanoparticle orientation and alignment under tensile stress was responsible for this energy-dissipation mechanism, and the mobility of polymer matrix was a precondition for this mechanism to be effective. Due to the lowered surface free energy of MWCNTs by grafting of TDFOL, one expects an increased mobility of MWCNT-TDFOL during tensile deforma-

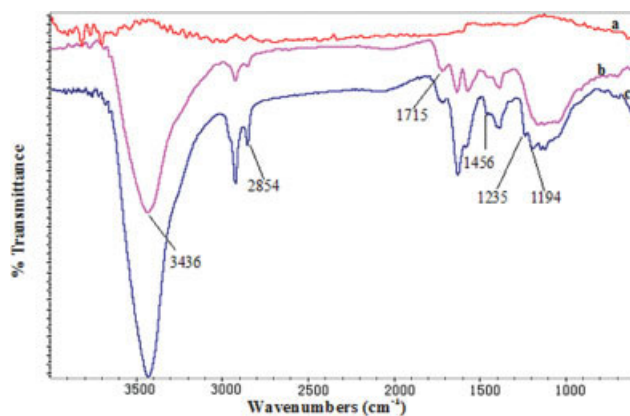
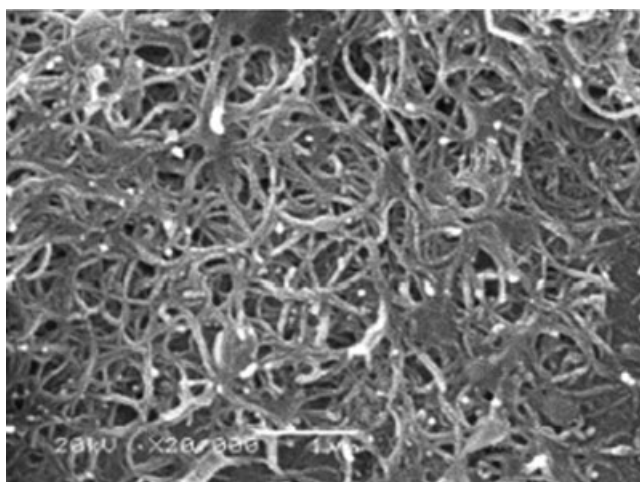
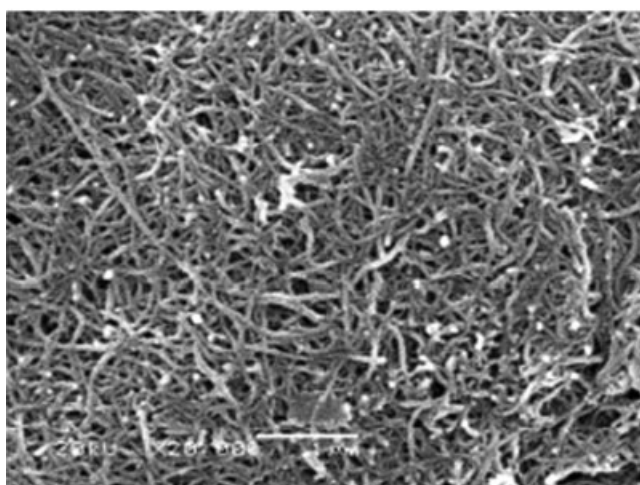


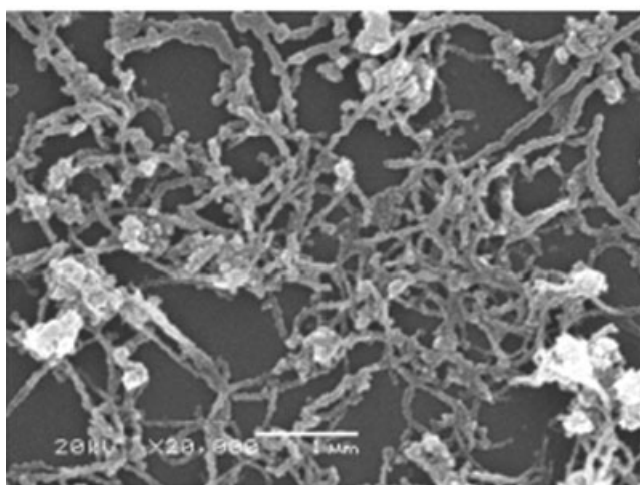
Figure 3 The FTIR spectras of the surface grafted MWCNTs. Lines **a**, **b**, **c** represents raw MWCNTs, MWCNT-COOH, MWCNT-TDFOL, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



(a)

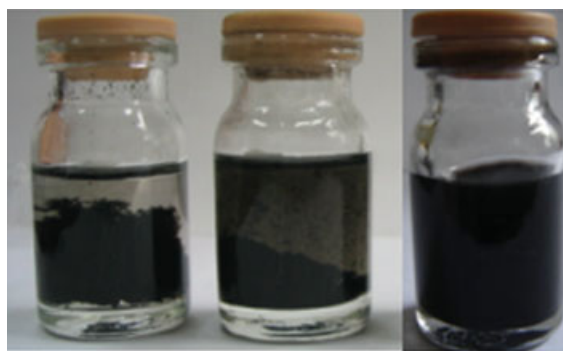


(b)



(c)

Figure 4 SEM of (a) raw MWCNTs, (b) MWCNT-COOH, and (c) MWCNT-TDFOL.



Raw MWCNT MWCNT-COOH MWCNT-TDFOL

Figure 5 The dispersion of various grafting MWCNTs in THF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tion, compared with the raw MWCNTs. This could be considered as the main reason for the largely improved elongation.

DMA data

The mechanical enhancement of PEU by grafted MWCNT can be further proved by the results of DMA analysis, which are shown in Figures 7 and 8. Storage modulus (E') vs. temperature curves of the PEU film and PEU/MWCNT membranes are shown in Figure 7. E' of the composites are greatly enhanced with the addition of MWCNT-TDFOL. When the content reaches 0.3%, E' of PEU/MWCNT-TDFOL film reaches the highest (from 2150 to 2500 MPa). But with the content of MWCNT-TDFOL increasing further, E' of the composite is decreased, which is probably due to the aggregation

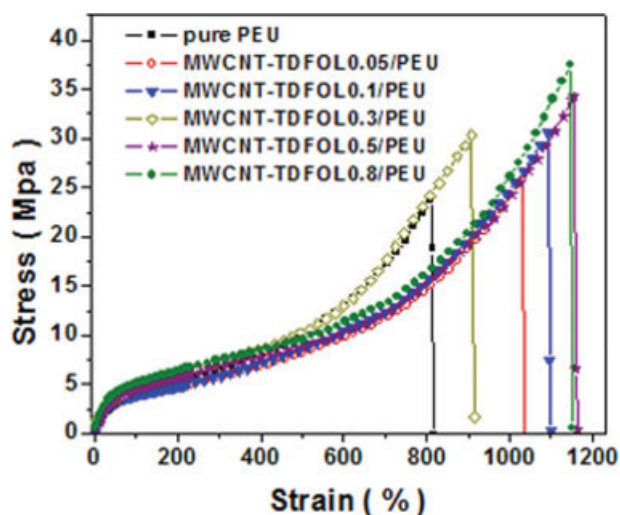


Figure 6 Tensile stress-strain curves of PEU and PEU/MWCNT-TDFOL composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

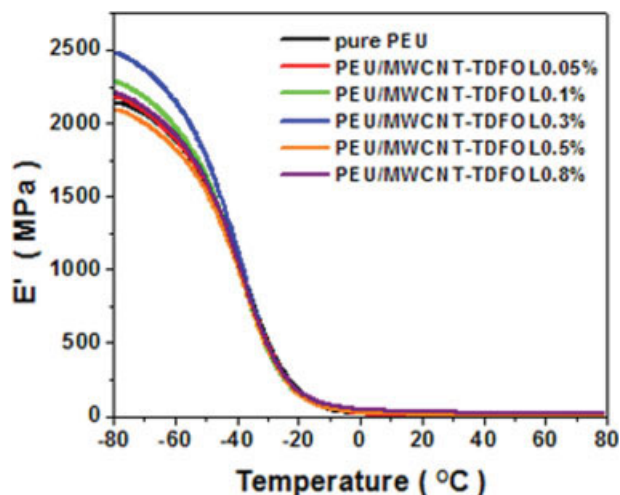


Figure 7 Storage modulus (E') versus temperature curves of PEU and PEU/MWCNT-TDFOL composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of MWCNT-TDFOL in PEU. On the other hand, the glass transition temperatures (T_g) in soft segments of PEU/MWCNT-TDFOL are changed unobviously within the experimental error (Fig. 8), which indicates a phase separated structure in PEU/MWCNT-TDFOL composites.

Contact angle testing

With the addition of MWCNT-TDFOL, the contact angle of PEU/MWCNT-TDFOL (with the content of 0.8 wt %) is enhanced from PEU 80°–89°, as shown in Figure 9(a,b), and the contact angles of composites with different content of MWCNT-TDFOL are

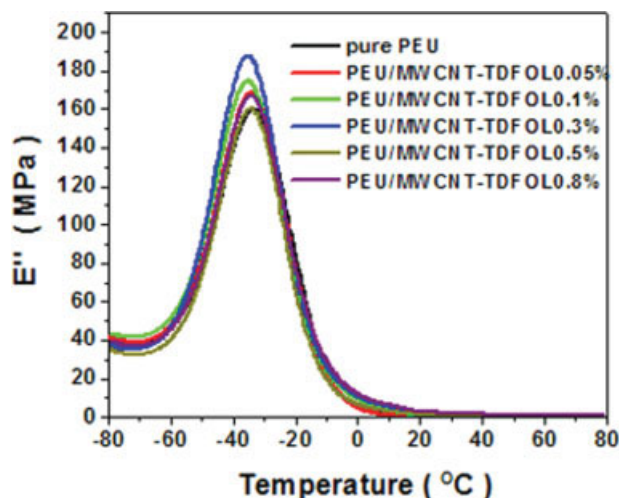


Figure 8 Loss modulus (E'') versus temperature curves of PEU and PEU/MWCNT-TDFOL composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

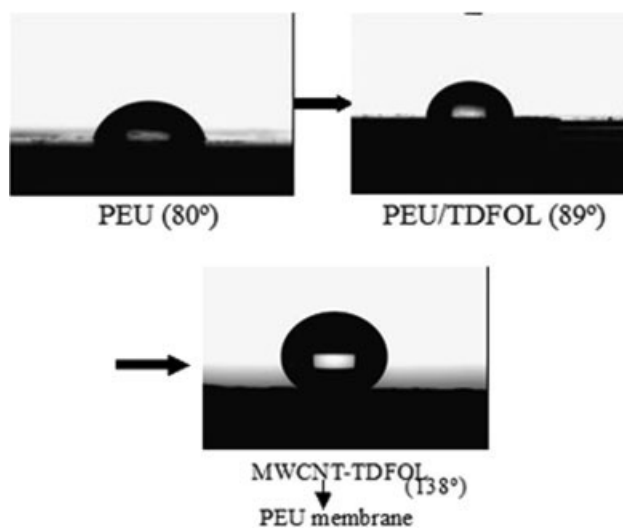


Figure 9 The contact angles of (a) PEU, (b) PEU/MWCNT-TDFOL, and (c) MWCNT-TDFOL deposited on PEU membrane.

almost constant, owing to the limited immigration of some long fluorinated chains of MWCNT-TDFOL close up to the surface of the film. However, a large improvement in surface hydrophobicity is observed by directly depositing MWCNT-TDFOL powder on PEU film surface, and water contact angle is increased from 80° to 138° [Fig. 9(c)]. Because the hydrophobic surface is necessary for improved blood compatibility for PEU used as a biomaterial,²⁷ our work also demonstrates a new and simple way to prepare bio-compatible PEU.

CONCLUSION

A successful grafting of TDFOL onto MWCNTs could be achieved by surface treatment of MWCNTs. PEU/MWCNT-TDFOL composite films have been prepared and their properties were investigated. Though a phase-separated structure could exist in the composites as indicated by dark color and the DMA result, a largely improved tensile strength and elongation of PEU were observed by adding a small amount of MWCNT-TDFOL. Besides, contact angle testing displayed a limited improvement in the hydrophobicity of PEU surface by solution blending with MWCNT-TDFOL. However, a large improvement in surface hydrophobicity was observed by directly depositing MWCNT-TDFOL powder on PEU surface, and this deposit experiment need further investigation in our future work.

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