Research Article

Qianwei Xu* and Weijia Zhang

Improvement of the electromechanical properties of thermoplastic polyurethane composite by ionic liquid modified multiwall carbon nanotubes

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Abstract: Carbon nanotubes (CNTs) were non-covalently modified by two categories of ionic liquids (ILs), including 1-vinyl-3-ethylimidazole bromide (VEIMBr) and 1-vinyl-3-hexylimidazole bromide (VHIMBr) in the ratio of 1:1 and 1:4, respectively. The surface interaction between CNTs and ILs was well-characterized by FTIR, Raman spectra, XPS, etc. Thermoplastic polyurethane (TPU) containing different amounts of CNTs/ILs was fabricated by melting blending method. TPU-CNTs/ILs composites exhibited simultaneously enhanced electromechanical properties with improved dielectric constant and lowered elastic modulus. The electromechanical sensitivity of sample TPU-3CNT/12VHIMBr increased by approximately 45 times in comparison with that of pure TPU at 200 Hz. Besides, improved dispersion of CNTs/ILs in the TPU matrix was also exhibited.

Keywords: carbon nanotubes, ionic liquids, thermoplastic polyurethane, dielectric property, electromechanical property

1 Introduction

The dielectric elastomers (DEs) always deform under the drive of an external electric field and convert electrical energy to mechanical energy (1,2) and have received widespread attentions in the past two decades. Due to the advantages of large deformation, high electromechanical coupling efficiency and fast response, etc., DEs

show enormous application prospects in artificial muscles, prostheses, bionic robots, and wearable tactile devices (3). To fulfill these applications, low electric field and high actuated strain are necessary. According to previous studies (1), high electromechanical sensitivity (β) is required to endow DEs with low electric field and high actuated strain, which is the ratio of dielectric constant (ϵ') to elastic modulus (Y). Therefore, increasing the dielectric constant and decreasing the elastic modulus have been attempted as effective ways to increase electromechanical sensitivity in previous literatures (4).

Different from the low dielectric constant of most polymer elastomers, thermoplastic polyurethane (TPU) has the advantages of higher dielectric constant ($\epsilon' > 7$) (5,6) and good processing performance. However, large quantities of hydrogen bonds in TPU limit the movement of polar molecular chains and thus hinder the dipolar polarizability of polar groups, and further restrict the increase in dielectric constant (7).

A method to increase the dielectric constant of elastomer is to add conductive fillers such as carbon nanotubes (CNTs) and graphene (8–10). Due to its excellent conductivity, small loading of CNTs leads to great increase of the dielectric constant of the elastomers. However, CNTs are poorly dispersed in the elastomers because of the tendency to curl and entangle (11). In addition, the high modulus of CNTs is not conducive to the high actuated strain of DEs. Therefore, surface modification of CNTs by covalent (12) or non-covalent (13) methods has been attempted. Compared with covalent modification, non-covalent modification has the advantage of retaining most of the excellent properties of CNTs. Jiang et al. used carboxylated ionic liquid (CMI) to non-covalently modify carboxylated multiwalled carbon nanotubes (m-MWCNT), which improved the dispersion of multiwalled carbon nanotubes and thereby increased the real part of the dielectric constant of polychloroprene (CR)/m-MWCNT composites to some extent (14). Silva et al. found that the CNTs functionalized by ionic liquid led to an increase of the conductivity and a lower percolation threshold of the polystyrene/poly

* Corresponding author: Qianwei Xu, Department of Polymeric Materials, School of Materials Science and Engineering, Tongji University, No. 4800 Caoan Road, Shanghai, 201804, China, e-mail: xu_qw@tongji.edu.cn, tel: +86-133-0168-8786

Weijia Zhang: Department of Polymeric Materials, School of Materials Science and Engineering, Tongji University, No. 4800 Caoan Road, Shanghai, 201804, China

(butylene adipate-*co*-terephthalate) (PS/PBAT) composites (15).

Ionic liquid is a room temperature molten salt consisting of organic cations and inorganic/organic anions. Due to the characteristics of wide electrochemical window, high conductivity, nonvolatility, and good thermal and chemical stability (16), ILs have wide prospects in conductive polymer, polymer-based solid electrolyte and polymer antistatic, and plasticization (17,18). In previous literature, ILs have been introduced to improve the dielectric constant of polymer composites. For example, Abraham et al. reported SBR composites with a high shielding efficiency and a high dielectric constant by incorporating ILs modified MWCNTs into SBE matrix (19). Wang et al. used 1-vinyl-3-ethylimidazole tetrafluoroborate ([VEIM][BF₄]) to non-covalently modify CNTs to obtain nanofillers with good dispersion in the PVDF matrix, and the resultant materials had the advantages of high dielectric constant and good flexibility (20). Liu et al. found that ILs modified CNTs exhibited stronger interactions than ILs modified carbon black, and thus showed a better dispersion in the silicone rubber (SR)/polyolefin elastomer (POE) matrix (21). However, few works reported the introduction of ILs to improve the electromechanical sensitivity of polymer composites by the extra plasticizing effect to reduce the elastic modulus simultaneously.

In this work, the pristine CNTs and two categories of ILs including 1-vinyl-3-ethylimidazole bromide (VEIMBr) and 1-vinyl-3-hexylimidazole bromide (VHIMBr) were ground and blended. The obtained mixture was blended with TPU to prepare TPU-CNTs/ILs composites by the melt processing method. Raman spectroscopy, XPS, FT-IR, SEM, and XRD were used to investigate the structure of the obtained TPU-CNTs/ILs composites. Finally, the effect of modified CNTs on the electromechanical properties of TPU-CNTs/ILs composites was investigated.

2 Experimental

2.1 Materials

The thermoplastic polyester polyurethane (TPU 5377A) was provided by Covestro Polymers Co., Ltd. and was dried at 60°C for 6 h before use. Multiwalled carbon nanotubes (CNTs, internal diameter: 10–30 nm, length: 10~30 μm) were purchased from Nanjing Xianfeng Nanomaterials Technology Co. Ltd (China). Two kinds

of ionic liquids (ILs), named 1-vinyl-3-ethylimidazole bromide (purity >99%, VEIMBr) and 1-vinyl-3-hexylimidazole bromide (purity >99%, VHIMBr), were supplied by Shanghai Chengjie Ionic Liquid Company. Ethanol (99.5%), toluene (99.5%), and acetone (99.5%) were obtained from Sinopharm Chemical Reagent Co., Ltd.

2.2 Preparation of CNTs/ILs

VEIMBr modified CNTs were prepared by grinding in an agate mortar with the mass fraction ratios of 1:1 and 1:4, respectively. VHIMBr modified CNTs were prepared in the same way with the same ratio. Black paste was obtained after grinding.

2.3 Preparation of TPU-CNTs/ILs composites

A certain amount of CNTs/ILs and 100 phr of TPU were melt blended in an internal mixer at 180°C for 6 min. The resultant mixture was compressed at 180°C and under 10 MPa for 10 min, then cut into specimens with different size for subsequent performance testing. The experimental components and corresponding sample names are shown in Table 1, where CNTs were non-covalently modified by two categories of ILs, including 1-vinyl-3-ethylimidazole bromide (VEIMBr) and 1-vinyl-3-hexylimidazole bromide (VHIMBr), in the ratio of 1:1 and 1:4, respectively. The pure TPU was processed in the same way without the addition of CNTs as comparison sample. TPU containing different amounts of CNTs solely was also fabricated for comparison.

Table 1: Composition of TPU-CNTs/ILs composites

Samples	CNTs (phr)	ILs (phr)
Pure TPU	0	0
TPU-0.25CNTs/0.25ILs (1:1)	0.25	0.25
TPU-0.5CNTs/0.5ILs (1:1)	0.5	0.5
TPU-1CNTs/1ILs (1:1)	1	1
TPU-2CNTs/2ILs (1:1)	2	2
TPU-3CNTs/3ILs (1:1)	3	3
TPU-0.25CNTs/1ILs (1:4)	0.25	1
TPU-0.5CNTs/2ILs (1:4)	0.5	2
TPU-1CNTs/4ILs (1:4)	1	4
TPU-2CNTs/8ILs (1:4)	2	8
TPU-3CNTs/12ILs (1:4)	3	12

2.4 Characterization and measurements

2.4.1 Characterization of CNTs/ILs

The degree of graphitization of CNTs and CNTs/ILs was measured by Raman test on a Raman spectrometer (Raman, LabRam HR Evolution, HORIBA Ltd., Japan) with laser excitation at 532 nm. A Fourier transform infrared spectroscopy instrument (FTIR, EQUINOX 55, Bruker, Germany) was used to study characteristic group of CNTs/ILs and hydrogen bonds of TPU composites. All samples were scanned in a wavenumber range of 400–4,000 cm^{-1} at a resolution of 2 cm^{-1} . The XPS spectra were collected on an X-ray photoelectron spectroscope (XPS, K-Alpha™, Thermo Scientific, USA) equipped with X-ray source of Al K α . The binding energy scale was corrected with the C 1s peak at 284.8 eV. A transmission electron microscopy instrument (TEM, JSM-6360, JEOL, Japan) with an operating voltage of 200 kV was used to investigate the dispersion of CNTs/ILs, and the samples dispersed in methylbenzene solution with a concentration of 0.5 mg/mL after ultrasonic dispersing were placed on the copper mesh and dried under ambient temperature before observation. The thermogravimetric analysis (TGA, STD Q600, TA Instruments Inc., United States) tests were performed to study thermal stability of nanofillers under nitrogen flow with a heating rate of 10°C/min from 35°C to 800°C. Differential scanning calorimetry (DSC, Q100, TA Instruments Inc., United States) measurements were carried out to study the melting endotherm of CNTs/ILs in the temperature range of 30–180°C.

2.4.2 Characterization of structure of TPU-CNTs/ILs

X-ray diffraction (XRD, DX-1000, Fangyuan Co., Ltd., China) analysis was carried out with Cu K α radiation to study the effect of nanofillers on the crystallinity of TPU composites. Morphologies of the TPU-CNTs/ILs composites were observed by a scanning electron microscopy instrument (SEM, Nova Nano SEM 450, FEI, United States) with all the samples fully frozen and cryogenically fractured in liquid nitrogen. The etched surfaces were cleaned with ethanol and were sputtered with gold in vacuum.

2.4.3 Characterization of properties of TPU-CNTs/ILs

The dielectric behaviors of TPU-CNTs/ILs composites were investigated by a Broadband Dielectric/Impedance Spectrometer (E4980A LCR meter, Agilent, Palo Alto, CA,

USA) in the frequency range of 10^2 – 10^6 Hz at room temperature. The tensile strength, elongation at break, and tensile modulus were accomplished on a Universal Testing Machine (CMT4104, Shenzhen SANS Testing Machine Co., Ltd., China) with the dimensions of dumb-bell specimen $115 \times 6 \times 2 \text{ mm}^3$ according to GB 528-1998.

3 Results and discussion

3.1 Structure of CNTs and CNTs/ILs

The degree of graphitization of CNTs CNTs/VEIMBr and CNTs/VHIMBr was measured by Raman spectra in Figure 1. The D band around 1,350 cm^{-1} originates from amorphous carbon and lattice defects in the structure and is attributed to sp^3 -bonded (tetrahedral) carbons. The G band near 1,580 cm^{-1} originates from the C=C stretching vibration in the ordered graphite carbon layer and belongs to the sp^2 -bonded (triangular) carbons (22). The ratio of the integrated peak area of the D band to the G band (I_D/I_G) is used to characterize the degree of crystallinity and purity of CNTs. As shown in Table 2, this ratio of pristine CNTs is 0.6, while the ratios of CNTs/VEIMBr and CNTs/VHIMBr are increased to 1.0 and 1.8, respectively, which is attributed to the increase of the amorphous carbon and lattice defects of CNTs. Longer carbon chains of VHIMBr lead to more defects in CNTs/VHIMBr, compared to VEIMBr with shorter carbon chains. The changes in Raman bands after modification are caused by the cation- π or π - π interaction between the imidazole ring of ILs and the surface of CNTs.

Figure 1: Raman shift of CNTs, CNTs/VEIMBr, and CNTs/VHIMBr.

Table 2: Raman shift and the ratio of the integral area value of the D and G peaks of CNTs, CNTs/VEIMBr, and CNTs/VHIMBr

Sample	D band (cm^{-1})	G band (cm^{-1})	I_D/I_G
CNTs	1,350	1,577	0.6
CNTs/VEIMBr	1,360	1,579	1.0
CNTs/VHIMBr	1,360	1,580	1.8

FT-IR is used to further explore the interaction between ILs and CNTs. Figure 2a is the FT-IR spectrum of CNTs/VEIMBr. The peak of $3,425\text{ cm}^{-1}$ is attributed to H_2O . The stretching vibration peaks of $3,064$ and $1,660\text{ cm}^{-1}$ are assigned to $=\text{C}-\text{H}$ and $\text{C}=\text{C}$, respectively. The stretching vibration peaks of $1,546$ and $1,168\text{ cm}^{-1}$ are, respectively, ascribed to $\text{C}=\text{N}$ and tertiary amine $\text{N}-\text{C}$ of the imidazole ring in VEIMBr. Figure 2b shows the FT-IR spectrum of CNTs/VHIMBr. The stretching vibration peak of $3,064\text{ cm}^{-1}$ is due to $=\text{C}-\text{H}$, while the stretching vibration peaks of $2,927$ and $2,860\text{ cm}^{-1}$ together prove the existence of $-\text{C}-\text{H}$. The stretching vibration peaks of $1,54$ and $1,168\text{ cm}^{-1}$ are owing to $\text{C}=\text{N}$ and tertiary amine $\text{N}-\text{C}$ of imidazole ring in VHIMBr, respectively (23). Combined with Raman analysis, the results of FT-IR characterization further prove that complex interactions existed between ILs (VEIMBr/VHIMBr) and CNTs (24).

The XPS test is used to further analyze the chemical compositions and elements state of ILs modified CNTs. Figure 3c exhibits the XPS spectra of CNTs, CNTs/VEIMBr, and CNTs/VHIMBr. The peak located at 284.1 eV is associated with the C 1s of CNTs/VEIMBr and CNTs/VHIMBr, while the peaks appeared at 400.6 and 67.0 eV are related to N 1s and Br 3d, respectively. The N and Br elements in

CNTs/VEIMBr and CNTs/VHIMBr are originated from VEIMBr and VHIMBr attached on the surface of CNTs, suggesting the successful surface modification of CNTs by ILs through the cation- $\pi/\pi-\pi$ effect. Figure 3d depicts the C 1s peak of CNTs, CNTs/VEIMBr, and CNTs/VHIMBr. The comparison indicates that the binding energy of C 1s decreased from 284.1 eV of CNTs to 283.2 eV of CNTs/VEIMBr and 283.3 eV of CNTs/VHIMBr, which confirms that CNTs were successfully non-covalently modified by ILs (25). The above multiple characterizations indicate that ILs successfully were adsorbed to the surface of CNTs.

Figure 4 shows the TGA and DTG curves of CNTs/VEIMBr (Figure 4a) and CNTs/VHIMBr (Figure 4b). In Figure 4a, the weight loss of VEIMBr at 228.2°C is owing to the degradation of the imidazole ring (26), and the weight loss of CNTs/VEIMBr at 245.7°C is also ascribed to the decomposition of the imidazole ring. The increase of the decomposition temperature confirms that the stability of VEIMBr is increased by the cation- π or $\pi-\pi$ interaction between the imidazole ring of VEIMBr and the surface of CNTs. A similar phenomenon is also demonstrated in Figure 4b. The TGA curves of CNTs/ILs indicate the good thermal stability of the cation- π or $\pi-\pi$ interaction between the imidazole ring of ILs and the surface of CNTs at a processing temperature of 180°C .

The DSC curves of VEIMBr, CNT/VEIMBr and VHIMBr, and CNT/VHIMBr are shown in Figure 5a and b. The curve of VEIMBr shows an obvious melting endothermic peak near 87.7°C , shown in Figure 5a. For CNTs/VEIMBr, the melting endothermic peak shifts to a higher temperature of 119.8°C . A similar situation appears in Figure 5b: the presence of CNTs makes the melting peak of VHIMBr shift from 65.4°C to 106.4°C .

Figure 2: FT-IR spectra of CNTs: (a) CNTs/VEIMBr; (b) CNTs/VHIMBr.

Figure 3: XPS spectra of CNTs: (a) CNTs/VEIMBr and CNTs/VHIMBr; (b) comparison of C 1s XPS spectra of CNTs, CNTs/VEIMBr, and CNTs/VHIMBr.

The changes of melting temperatures suggest interaction exists between CNTs and ILs (27).

TEM images of unmodified CNTs, CNTs/VEIMBr, and CNTs/VHIMBr are exhibited in Figure 6. Unmodified CNTs are poorly dispersed with many black entangled areas, as presented in Figure 6a. After modification, Figure 6b and c show that the entanglement of CNTs modified by ILs are significantly reduced, which reveals the improved dispersion. The reason for that is ILs adsorbed to the surface of CNTs assists CNTs to unwind during the grinding.

3.2 Microstructure of TPU-CNTs/ILs composites

The SEM images of the brittle fracture section of TPU-3CNTs and TPU-CNTs/ILs composites are shown in the

Figure 7. In Figure 7a, the bright whiskers protruding from the polymer surface are CNTs, and the circled areas are the obvious aggregation of CNTs. Figure 7b–e show SEM images of TPU-3CNTs/3VEIMBr, TPU-3CNTs/12VEIMBr, TPU-3CNTs/3VHIMBr, and TPU-3CNTs/12VHIMBr composites, respectively. CNTs/ILs are uniformly dispersed in TPU matrix, indicating that the interaction between IL and CNT reduces the aggregation of CNTs (28). When the ratio of CNTs to ILs is 1:1, the dispersion state of CNTs in TPU-CNTs/VHIMBr composites is significantly better than that in TPU-CNTs/VEIMBr composites (Figure 7b and d). The reason is that a larger steric hindrance from the longer side segments of VHIMBr prevents CNTs from agglomeration. With the increasing amount of ILs, the accumulation of more ILs appears on the brittle fracture surface, which may deteriorate the mechanical properties of the composites (Figure 7c and e) (29).

Figure 4: TGA curves of: (a) CNTs/VEIMBr; (b) CNTs/VHIMBr.

Figure 5: DSC curves of: (a) VEIMBr and CNT/VEIMBr; (b) VHIMBr and CNT/VHIMBr.

Figure 6: TEM images of: (a) unmodified CNTs; (b) CNTs/VEIMBr; (c) CNTs/VHIMBr.

Figure 8a and b show the XRD patterns of pure TPU, CNTs, CNTs/ILs, TPU-CNTs, and TPU-CNTs/ILs composites. The XRD pattern of CNTs demonstrates a sharp peak at 25.6° and a broad peak at 42.8° , corresponding to the characteristic diffraction peak of (002) and (100), respectively, which is ascribed to the orderly arrangement of carbon atoms in CNTs. The pattern profiles of CNTs/ILs in Figure 8a and b are basically similar to those of CNTs, while the intensity of the diffraction peak at 25.6° becomes lower and the profile gets wider, which is owing to the destruction of the ordered structure of CNTs by ILs to a certain extent. An amorphous peak at 20.0° of pure TPU is relevant to the existence of ordered structure of both hard and soft domains of the TPU. With the addition of CNTs and CNTs/ILs, the peak becomes broadening and the intensity decreases, suggesting that CNTs and CNTs/ILs significantly affect the ordered structure of the hard segments of the TPU matrix. The tendency of disordering is attributed to the strong interface interaction between CNTs (CNTs/ILs) and the TPU matrix.

In addition, for TPU-CNTs/ILs composites, the plasticization of ILs also influences the accumulation of the soft and hard phases of the TPU matrix (30).

FT-IR is usually used to characterize the strength of N-H/C=O hydrogen bonds between TPU molecular chains. Figure 8c indicates the changes of hydrogen bonds in the TPU-CNTs/ILs composites before and after adding CNTs/ILs. The stretching vibration peak of the hydrogen-bonded N-H groups of pure TPU locates at $3,297\text{ cm}^{-1}$. When CNTs/ILs are introduced into TPU matrix, the peak becomes weaker and shifts to higher wavenumbers. The stretching vibration peaks of the hydrogen-bonded N-H groups of TPU-3CNTs/12VEIMBr and TPU-3CNTs/12VHIMBr are located at $3,313$ and $3,330\text{ cm}^{-1}$, respectively. The blue shift of hydrogen-bonded N-H groups proves that CNTs/ILs destroy the N-H/C=O hydrogen bonds in the TPU matrix (31). It is confirmed that the disruption of the hydrogen bonding was beneficial to increase the mobility of the TPU molecular chain and thereby increased its dipolar

Figure 7: SEM images of: (a) TPU-3CNTs; (b) TPU-3CNTs/3VEIMBr; (c) TPU-3CNTs/12VEIMBr; (d) TPU-3CNTs/3VHIMBr; and (e) TPU-3CNTs/12VHIMBr; (f) element distribution diagram of TPU-3CNTs/12VHIMBr.

Figure 8: (a) X-ray diffraction (XRD) patterns of pure TPU, CNTs, CNTs/VEIMBr, TPU-CNTs, and TPU-CNTs/VEIMBr composites; (b) X-ray diffraction (XRD) patterns of pure TPU, CNTs, CNTs/VHIMBr, TPU-CNTs, and TPU-CNTs/VHIMBr composites; (c) FT-IR spectra of pure TPU, TPU-3CNTs/12VEIMBr, and TPU-3CNTs/12VHIMBr.

polarizability under an electric field, which ultimately increased the dielectric constant of the composites (7).

3.3 Electromechanical properties of TPU-CNTs/ILs composites

3.3.1 Dielectric properties

As shown in Figure 9a, the dielectric constant (ϵ') of TPU-CNTs composites increases with the increment content of CNTs by the excellent electrical performance of CNTs. The increasing amount of CNTs/ILs produces a more obvious effect on improving the ϵ' of the TPU-CNTs/ILs

composites, compared to the TPU-CNTs composites with the same content of CNTs. The significant increasing of the ϵ' is attributed to the fact that the improved dispersion of CNTs/ILs increases the number of interfaces between CNTs/ILs and TPU, which enhanced the interfacial polarizability of the composites. In addition, according to the previous FT-IR analysis of Figure 9c, CNTs/ILs disrupt the hydrogen bonds of the TPU matrix, leading to the enhancement of the dipolar polarizability of TPU, and thus the ϵ' increases. On the other hand, the dielectric loss (ϵ'') of the TPU-CNTs/ILs composites also increases greatly with the addition of ILs (Figure A1), which is different from the previous reports (32). The unexpected increasing is probably due to the generation of ion polarizability by more ILs in the TPU matrix (33). In

Figure 9a, CNTs/VHIMBr result in a greater increase in the ϵ' of the composites compared to CNTs/VEIMBr with the same content, because the steric hindrance caused by the long side segments of VHIMBr is more conducive to the dispersion of CNTs/VHIMBr in TPU. A better electrical performance of TPU-CNT/VHIMBr is also reflected in the AC conductivity of TPU-CNT/VHIMBr in Figure A2.

In addition, the plateau area of the AC conductivity curve of TPU-CNT/VHIMBr at low frequencies is attributed to the formation of a network structure of CNT/VHIMBr with an increased dispersion in TPU. For example, the ϵ' of TPU-3CNTs/12VHIMBr at 200 Hz is 163.90, while the ϵ' of TPU-3CNTs/12VEIMBr at 200 Hz is only 76.76. As shown in Figure 9, the dielectric properties show a strong

Figure 9: Dielectric constants of TPU-CNTs/ILs composites.

Table 3: Summary of electromechanical properties of pure TPU, TPU-CNTs, TPU-CNTs/VEIMBr, and TPU-CNTs/VHIMBr composites

Samples	Tensile strength (MPa)	Elongation at break (%)	Dielectric constant (ϵ')@200 Hz	Dielectric constant (ϵ')@1 kHz	Elastic modulus (Y) (MPa)	Electromechanical sensitivity @200 Hz ($\beta = \epsilon'/Y$) (MPa ⁻¹)
Pure TPU	>17.0	>700	4.9	4.7	9.4 ± 0.3	0.5
TPU-3CNTs	14.1 ± 0.4	390	34.1	32.0	15.7 ± 0.3	2.2
TPU-3CNTs/3VEIMBr (1:1)	8.6 ± 0.2	413	35.5	25.9	12.9 ± 0.4	2.8
TPU-3CNTs/12VEIMBr (1:4)	7.7 ± 0.2	510	76.8	47.1	10.7 ± 0.3	7.2
TPU-3CNTs/3VHIMBr (1:1)	9.9 ± 0.3	577	64.1	37.3	9.5 ± 0.3	6.8
TPU-3CNTs/12VHIMBr (1:4)	8.0 ± 0.2	649	163.9	84.8	7.0 ± 0.3	23.6

frequency dependence (34). When the frequency is higher than 10^5 , the dielectric constant (ϵ') and dielectric loss (ϵ'') of the TPU-CNTs/ILs composites are close to those of pure TPU. It can be inferred that the interfacial polarizability and ion polarizability are mainly concentrated below the frequency 10^5 , except for the dipolar polarizability.

3.3.2 Mechanical properties

Table 3 shows the tensile strength, elastic modulus, dielectric constant, and electromechanical sensitivity of TPU, TPU-CNT, TPU-CNTs/VEIMBr, and TPU-CNTs/VHIMBr composites. Pure TPU possesses a high tensile strength (>17 MPa). The addition of CNTs/ILs reduces the strength of the composites; the tensile strength of TPU-3CNTs/12VEIMBr and TPU-3CNTs/12VHIMBr reaches 7.7 and 8.0 MPa, respectively. It can be seen from Table 3 that at the same CNTs content, the elastic modulus (Y) of the composites decreases with the increase of VEIMBr, which is resulted from the good plasticity of VEIMBr. Similar behavior also appears in TPU-CNTs/VHIMBr composites. Overall, the Y of TPU-CNTs/VHIMBr composites is lower than that of TPU-CNTs/VEIMBr composites with the same filler content due to the stronger plasticity of VHIMBr. The low elastic modulus of the composites contributes to its electromechanical sensitivity (electromechanical sensitivity = dielectric constant/modulus of elasticity, $\beta = \epsilon'/Y$). When the frequency is 200 Hz, the β of the TPU-3CNTs/12VHIMBr sample is improved from 0.5 of pure TPU to 23.6 by approximately 45 times.

4 Conclusion

In this work, ILs modified CNTs were obtained by non-covalent modification, and TPU-CNTs/ILs composites with electromechanical sensitivity were prepared by the melting blending method. Due to the cationic- π/π - π interaction between the surface of CNTs and the imidazole ring of ILs, CNTs/ILs are well-dispersed in the TPU matrix, and more interfaces are produced accordingly. The increase in the number of interfaces is conducive to the accumulation of interface charges, thereby enhancing the interfacial polarizability of TPU composites. Simultaneously, CNTs/ILs disrupt the hydrogen bonds in TPU, thus increasing the dipolar polarizability of TPU. The increases in both dipolar polarizability and the interfacial polarizability are contributed in the

improvement of dielectric constant (ϵ') of TPU-CNTs/ILs composites. With the increasing dosage of CNTs/ILs (1:1) in TPU, the ϵ' of TPU composites at low frequencies increases by the simultaneous increase of both the dipolar polarizability and the interfacial polarizability. When the ratio of CNTs/ILs increases to 1:4, more ILs result in the increased ϵ' and the reduced modulus (Y), thus the electromechanical sensitivity of the TPU composites is significantly improved. As the content of CNTs/VHIMBr reaches 3/12, the electromechanical sensitivity of TPU composites increases to 23.6 at 200 Hz, which is 45 times to that of pure TPU.

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Appendix

Figure A1: Dielectric losses of TPU-CNTs/ILs composites.

Figure A2: The AC conductivity of TPU-CNTs/ILs composites.

Figure A3: The stress-strain curves of TPU-CNTs/ILs composites.