

A Novel Ternary Composite of Polyurethane/Polyaniline/Nanosilica with Antistatic Property and Excellent Mechanical Strength: Preparation and Mechanism

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Electronic Supplementary Information

Abstract Antistatic and strength properties are of vital importance for polyurethane rubber used in moving parts of many industrial instruments. Herein, polyurethane was composited with polyaniline and nanosilica based on *in situ* synthesis of polymer and physical mixing of these fillers to reach desired antistatic and mechanical properties. Chemical, morphological and thermal properties of the polyurethane/polyaniline/nanosilica composites were studied. The electrical resistivity of the composite decreased from 1.1×10^6 MΩ to 7.6×10^4 MΩ as a result of the addition of 4% polyaniline. The tensile strength and elongation at break of the polyurethane composites improved by nearly 300% and 100%, respectively, when compared with those of the neat polyurethane. The electronic resistance of PU/PANI/NS ternary is low enough for its antistatic property and decreases with the increase of the added nanosilica, which is unexpectedly and rather significant. Our results would shed light on the development of antistatic PU with excellent mechanical performance.

Keywords Polyurethane/polyaniline/nanosilica composites; Antistatic property; Mechanical property; Molecular simulation

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INTRODUCTION

Industrial rubber has a broad range of applications in various fields, including multiple rollers on machinery, transportations and aerospace. Polyurethane (PU) has been widely used for these applications due to its excellent mechanical properties. Unfortunately, PU is a typical insulation material,^[1,2] with poor antistatic properties limiting its applicability in some instances. For example, rubber rollers used in textile machinery must have good antistatic properties to function properly. In fact, the electrostatic forces developed on these rubber rollers led to many machinery accidents every year.^[3] However, the service life of these rubber rollers could be expanded by at least 30% if the electrostatic effect is resolved.^[3] Therefore, PU modification is required to achieve the desired electro-conductivity for these applications.

For several decades, researchers have been investigating different PU modification methods. The chemical modification

involves using additives in the PU polymerization process to obtain covalent bonds with polyurethane.^[4,5] Following the chemical modification, the degree of crosslinking in polyurethane increases, thereby enhancing its breaking strength, while decreasing the elongation at break. The physical modification of PU can resolve the contradiction of the strength-elongation issue and impart additional functionalities to the PU materials.^[6] Numerous publications have been reported on polyurethane chemistry, such as changing the cross-linking between isocyanate groups (—NCO) and hydroxyl groups (—OH) and increasing the degree of cross-linking.^[7] However, most of the chemical modifications do not change the antistatic property of PU.

Furthermore, the use of functional fillers to prepare PU composites with some unique properties has been well reported.^[8–10] For this purpose, various nanomaterials such as nanosilica (NS),^[11,12] nano-titanium dioxide,^[13] nanocrystalline cellulose (NCC),^[14] organic clay,^[15,16] carbon nanotubes (CNTs),^[17] graphene oxide (GO),^[18] carbon dots (CDs)^[19] were investigated. Among them, CNTs or GO are electro-conductive. Thus, adding a suitable quantity of these conductive fillers can impart the antistatic property to the PU matrix. However, the

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use of antistatic fillers may negatively affect the mechanical properties of PU.^[20,21] As CNTs and GO are comparatively expensive materials,^[22–25] the ultimate challenge is to explore cost-effective antistatic agents that are effective in the PU matrix while simultaneously improving its mechanical properties.

Conductive polymers, such as polypyrrole and polyaniline, have paved the way for the development of conductive PU.^[26] Conductive polymers are cheaper and easier to obtain, compared with other expensive conductive fillers such as graphene.^[27,28] The use of polypyrrole-polyurethane composites in medical devices was investigated by Li *et al.*, and the conductive polypyrrole was found being effectively compounded on the surface of PU and being changed with the stretching of elastomer.^[29] Therefore, multi-component polyurethane composites could be utilized to improve the properties of conductive PU. Liow *et al.* reported the introduction of polypyrrole- and polyaniline-surface modified nanosilica into polyurethane composites for dye-sensitized solar cells. The electric properties of the composites were excellent, but the mechanical properties were not examined in the study.^[30,31]

In the present work, polyurethane/polyaniline/nanosilica (PU/PANI/NS) composites were prepared to improve the mechanical strength and antistatic property of PU elastomer. The idea is shown in Scheme 1. Actually, Luo *et al.* and Liu *et al.* studied the composites of PU, PANI and silica respectively.^[32,33] However, Luo adopted PU and silica (not nanosilica) to improve the strength and water-resistance of the polyaniline,^[32] while Liu attempted to prepare conductive PU by the way of compositing with silica-polyaniline core-shell nanoparticles.^[33] The current study is different from those published works. Nanosilica was adopted and the surface of NS was organically modified. Further, PANI was doped with sulfonic acid aiming at improving their dispersion in the PU reaction system and PU matrix. Conductive polymer PANI and inorganic particle NS played their roles as conduction enhancers and reinforcing filler, respectively. In addition, the effect of PANI and NS on the mechanical and antistatic properties of

PU/PANI/NS composite was evaluated. Interestingly, the electro-resistance of the polyurethane composite decreased by increasing the nanosilica content. Furthermore, the molecular simulation of PU/PANI binary and PU/PANI/NS ternary composite has been employed to elucidate the mechanism of the decrease in electrical resistance.

MATERIALS AND METHODS

Materials

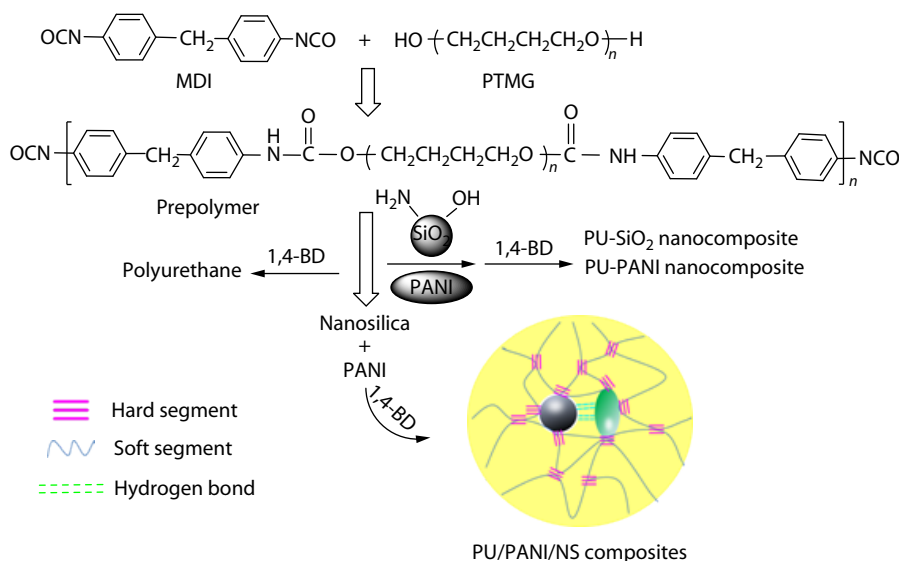
4,4'-Diphenylmethane diisocyanate (MDI, 98%), poly(tetramethylene glycol) (PTMG, the average M_n is 1000 g/mol), nanosilica (NS) (diameter: 4–70 nm), 3-aminopropyltriethoxysilane (KH-550), dodecylbenzenesulfonic acid (DBSA) and dibutyltin dilaurate were purchased from Aladdin (Shanghai, China). 1,4-Butanediol (1,4-BD), dimethylformamide (DMF, 99.8%), ammonium persulfate (APS), aniline and methyl ethyl ketone (MEK) were acquired from Sinopharm Chemical Reagent Co., Ltd. (SCRC). DMF and 1,4-BD were dehydrated with the molecular sieves for 24 h and redistilled under vacuum, and PTMG was used after drying under vacuum at 110 °C for 2 h. Aniline was used after vacuum distillation.

Synthesis of Sulfonic Acid-doped Polyaniline

Sulfonic acid-doped polyaniline was prepared with ammonium persulfate initiated oxidative polymerization method. Aniline and dodecyl benzenesulfonic were dispersed in a 1:4 in volume ratio of acetone-water mixture. Oxidative titration was carried out for 1 h with 0.8 mol/L of aqueous ammonium persulfate. The molar ratio of APS to aniline was 1:1, the reaction temperature was 0–5 °C, and the mixture of the reaction was mechanical stirred for 12 h to obtain a dark green polyaniline cloudy solution. After that, the resulted solution was filtered, washed and dried in a vacuum oven at 30 °C for 24 h.

Surface Modification of Nanosilica

The nanosilica was dispersed in methyl ethyl ketone while stirring, adding 3% of 3-aminopropyl triethoxysilane until the turbidity became stable and uniform.



Scheme 1 Synthetic procedure of PU, PU/NS, PU/PANI, and PU/PANI/NS composites.

Synthesis of Polyurethane and Its Composites

The neat PU, PU/NS, PU/PANI and PU/PANI/NS were prepared for this work. Synthesis was carried in two steps. Firstly, PU prepolymer was prepared *via* the reaction of MDI and PTMG in DMF solvent. The reaction took place at a temperature of 65 °C and under dry N₂ for 2 h with mechanically stirring. Subsequently, the surface modified nanosilica was added to the prepolymer and the mixture was kept stirring at the speed of 500 r/min for 0.5 h. The predetermined loading of PANI dispersed in DMF solvent was incorporated with continuous stirring for another 1 h at high speed. Then, an appropriate amount of 1,4-BD was added, and the reaction was stirred for 40 min to obtain a stable viscous polymer solution. The prepared polymer solution was cast on a custom-made glass plate coated with a release agent, cured in an oven at 80 °C for 2 h, followed by 90 °C for 10 h and finally post-cured at 60 °C for 12 h.

Characterizations

Structural analysis of the composites was performed on a Fourier transform infrared spectrometer equipped with attenuated total reflection (ATR, Nicolet IS 10), with structural records in the range of 600–4000 cm⁻¹ and resolution of 4 cm⁻¹. Another structural analysis method, namely wide-angle X-ray diffraction, was also employed to record the crystal structure of PU, PU/NS and PU/PANI using a D8 X-ray diffractometer (German Bruker AXS Co., Ltd.). To record the data, copper target Cu K α (λ =0.154 nm) with power of 1600 W (40 kV $\times$ 40 mA) was used, and NaI crystal scintillation counter was adopted to measure the X-ray intensity with the scan range of 5°–40°, scan speed of 4 (°)·min⁻¹ and step size of 0.02°.

Differential scanning calorimetry (DSC 200) (TA Instruments, USA) was utilized to observe the glass transition temperatures of the hard and soft segments of the composites (T_{gHS} and T_{gSS} , respectively) of the samples. An empty aluminum crucible was used as reference. Prior to analysis, the sample was heated in a N₂ atmosphere at a rate of 10 °C·min⁻¹ in the range of –70 °C to 200 °C.

The mechanical properties of the composites were tested on a universal material prototype machine. The samples were made into a shape of 25 mm $\times$ 6 mm $\times$ 2 mm and subjected to a tensile test at a tensile speed of 50 mm·min⁻¹.

The storage modulus of the samples at temperatures ranging from –80 °C to 100 °C was examined using dynamic mechanical analysis (TA Instruments Q800 DMA) to investigate the properties of composites during the dynamic process and the $\tan\delta$ of the samples was measured as well.

The fracture surfaces of the composites were observed with a scanning electron microscope (SEM Hitachi S4800), and the distribution of nanoparticles in the composites was observed with a transmission electron microscope (Tecnai G2 Spirit).

PU composites were tested to determine the change in electrical resistance of the composites, as well as the effect of polyaniline and nanosilica on the electrical conductivity.

Calculation Interfacial Energy with Molecular Simulation

The molecular simulation was carried out in Materials Studio (MS version 2017). The MS software was used to construct MDI, PTMG (the average M_n is 1000 g/mol) and their polymer polyurethane (PU), polyaniline (PANI) and nanosilica (NS) aniline.

The crystals of PU, PANI and NS, were simulated, and the crystal planes were cleaved, and then the layers of the PU, PANI and NS were constructed to calculate the interface energy by Forcite function modules, with the mole ratio of urethane/aniline/SiO₂ as 8/4/3 and 8/4/6, respectively. We selected COMPASS force field and the Ewald and atom-based summation methods were used for electrostatic and the van der Waals interactions, respectively. Finally, the energy of the interface action in the ternary composite was calculated.

RESULTS AND DISCUSSION

Structures of PU and Its Composites

There are probable chemical reactions between PU matrix and the modified NS or PANI, so that there should be several chemical characters in PU/NS, PU/PANI and PU/PANI/NS composites that are different from neat PU. The chemical structures of PU, PU/NS, PU/PANI and PU/PANI/NS composites were studied with FTIR spectra, as shown in Fig. 1. New bands at 1646 and 1510 cm⁻¹ appear in FTIR spectra of PU composites, which are attributed to the absorption of carbonyl groups (C=O) and N–H bending deformation combined with C–N asymmetric stretching, respectively.^[34,35] These results indicate the –NH₂ and –NCO react on nanosilica after surface modification. A very small absorption band at 1646 cm⁻¹ is observed for neat PU, which may be owing to the small proportion of the reaction of the urethane and the –NCO groups due to the high temperature of the reaction system. The absorption bands can be observed at 3300 cm⁻¹ in all spectra of PU and its composites are attributed to N–H stretching vibrations. Moreover, the absorption bands at 1708 and 1730 cm⁻¹ are attributed to the hydrogen bonded and free carbonyl group, respectively.^[35] The intensity ratio of these adsorption bands is defined as the hydrogen bonded carbonyl index (R). The intensity ratio decreases with the addition of NS, which could be explained that the addition of nanoparticles inhibited the formation of hydrogen bonds between the hard segments. The magnitude of R reflects the phase separation of the material.^[36] However, the absorption band of hydrogen bonded carbonyl group at 1708 cm⁻¹ in the FTIR spectrum of PU/PANI/NS composite increases. It is probable that, formation of the hydrogen bond is originated from PANI. This supplementation of hydrogen bonds demonstrate that NS and PANI play a synergistic role in improving the mechanical properties of PU composites.

The PU elastomer film, polyurethane/nanosilica composite (PU/NS) elastomer film, and polyurethane-polyaniline composite (PU/PANI) elastomer film were analyzed by X-ray diffraction as shown in Fig. 2. It is well known that the soft segment of PU, which is PTMG in our study, can crystallize in a monoclinic system.^[37] The characteristic diffractions of PTMG with molecular weight above 2000 (PTMG2000 or PTMG3000 or above) are located at which 2θ values are about 20° and 25°, respectively.^[38] However, in case of PTMG1000 used in this study, the two diffraction peaks connected each other and generated a wide diffusion peak, which was formed due to the weak crystallization of the short PTMG chains.^[38] As PU is concerned, a hard unit that was MDI had been introduced, and the crystallization was expected to be weaker, apparently. It shows a broad diffusion peak, and no sharp diffrac-

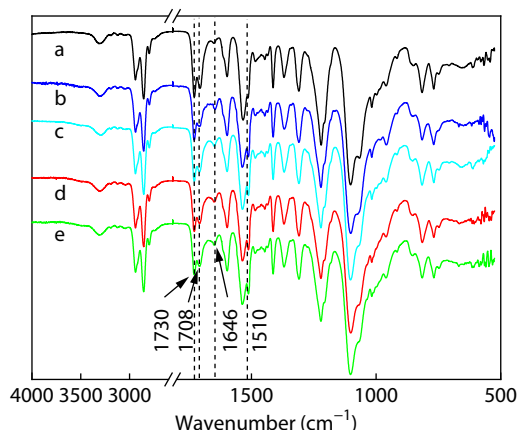


Fig. 1 FTIR spectra of (a) PU, (b) PU/NS, (c) PU/PANI, (d) PU/PANI/NS-1 and (e) PU/PANI/NS-2 composites.

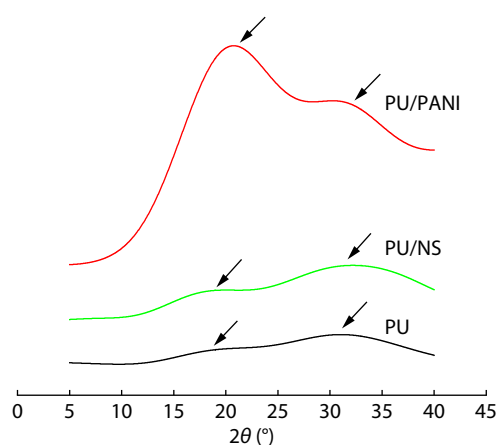


Fig. 2 X-ray diffraction patterns of PU, PU/NS and PU/PANI composites.

tion peaks can be observed, indicating the amorphous structure in PU. Thus, the addition of hard segment monomers reduced the mobility of PU molecular chains and limited their crystallization. Despite that, two broad peaks can be distinguished in all the three diffraction spectra in Fig. 2 that are characteristic of amorphous PU. The diffraction spectrum of PU/NS is similar to that of PU, whereas the diffraction peaks of PU/PANI are more potent than those of PU and PU/NS, as shown in Fig. 2 (red curves). The probable mechanism will be discussed based on the results of the molecular simulations.

Mechanical Properties and Its Composites

The mechanical properties of polyurethane composites including PU/NS, PU/PANI and PU/PANI/NS were studied with a universal material prototype machine. The stress-strain curves are shown in Fig. 3, and the data of tensile strength and the elongation at break are shown in Table 1. The tensile strength, elongation at break, and modulus of the as-prepared neat PU are 5.6 ± 1.5 MPa, $800\% \pm 50\%$ and 6.3 ± 0.6 MPa, respectively, as shown in Table 1. The stress of PU/NS composite with 2 wt% NS is 7.9 ± 1.0 MPa, which shows a slight increase from that of neat PU. The modulus of PU/NS also increased apparently, which was 14.2 MPa. However, the elongation at break of PU/NS is $344\% \pm 40\%$, less than half of PU. This result differs from the previous study,^[11] and most likely, the NS that was blended with

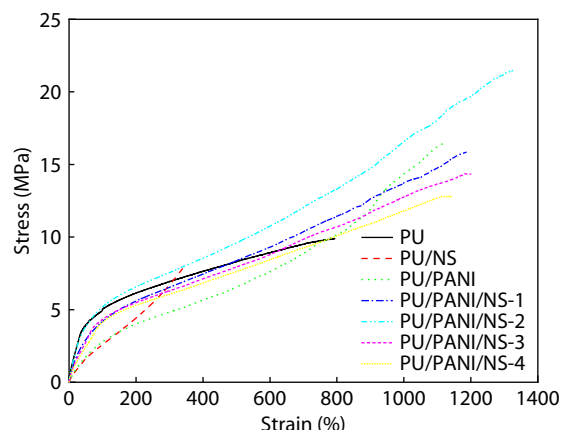


Fig. 3 Tensile testing curves of PU, PU/NS, PU/PANI and PU/PANI/NS composites.

Table 1 Mechanical properties of PU, PU/NS, PU/PANI and PU/PANI/NS including tensile strength, elongation-at-break and Young's modulus.

Samples	Stress (MPa)	Strain (%)	Modulus (MPa)
PU	5.6 ± 1.5	800 ± 50	6.3 ± 0.6
PU/NS	7.9 ± 1.0	344 ± 40	10.4 ± 1.4
PU/PANI	16.5 ± 1.0	1132 ± 30	14.2 ± 1.2
PU/PANI/NS-1	15.5 ± 2.0	1185 ± 45	13.6 ± 1.2
PU/PANI/NS-2	22.0 ± 2.0	1380 ± 50	17.6 ± 1.6
PU/PANI/NS-3	14.3 ± 2.7	1200 ± 45	13.2 ± 1.3
PU/PANI/NS-4	12.8 ± 2.5	1141 ± 35	11.5 ± 1.5

PU directly was not compatible with PU. On the other hand, PU/PANI composite with 4 wt% of PANI shows a surprising increase in strength and elongation with a stress of 16.5 ± 1.0 MPa, elongation at break of $1132\% \pm 30\%$ and modulus of 14.2 ± 1.2 MPa, respectively.

Comparing the mechanical properties of PU/PANI/NS composite to PU/NS and PU/PANI, the results show a significant difference. The tensile strength and modulus of all PU/PANI/NS composites are higher than those of PU and PU/NS, which suggests that the addition of PANI reinforce the composite, as shown in Fig. 3 and Table 1. All PU/PANI/NS composites show high elongation at break values than those of PU, PU/NS and PU/PANI. The most exciting results are obtained from PU/PANI/NS-2 with 2 wt% of NS and 4 wt% of PANI. The tensile strength, the elongation at break, and the modulus of the composite are 22 ± 2 MPa, $1380\% \pm 50\%$ and 17.6 ± 1.6 MPa, respectively, which are far higher than those of neat PU, PU/NS and PU/PANI. However, as shown in Fig. 3, the mechanical properties of the PU/PANI/NS composites initially increase and subsequently decrease as the amount of NS increases. This is probably due to the degree of crosslinking of the fillers and PU decrease with higher addition of NS. It can be concluded that PU/PANI/NS composite get a best mechanical property with 4 wt% of PANI and 2 wt% of NS, which is denoted as PU/PANI/NS-2. As a result, both PANI as a conductive polymer and NS as a nanofiller play strengtheners' role in improving PU mechanical properties. The strengthening effect could be explained by the formation of interaction forces between nano SiO_2 particles and polyaniline chains and the stress transferring between the PU matrix and fillers during the stretching process.

Thermal Properties of PU and Its Composites

The thermal properties of PU and its composites were measured. PU and most PU composites exhibit two glass transition temperatures except for the composite PU/NS as shown in Fig. 4. The two glass transition temperatures are for the soft segment (T_{gSS}) and the hard segment (T_{gHS}). T_{gSS} and T_{gHS} of PU in this study are -28 and 99 °C, respectively. The melting temperature of the soft segment (T_1) of PU is recorded as 14.3 °C. The composites PU/PANI and PU/PANI/NS give a lower T_{gSS} and T_1 as plotted in Fig. 4 and detailed in Table 2. The T_{gSS} of PU/PANI/NS composite is -38 °C as the content of NS was 2 wt%, which is the lowest. The T_{gSS} of the composites reduces to about -34 °C as the amount of NS reached 4 wt%. Generally, T_g depends on the flexibility of the PU chain.^[39] The distribution of hard segments in the soft zone of PU became denser with the increase of NS and PANI, resulting in a reduction in the free volume of the chain segment. In the meantime, the decrease of T_{gSS} and T_1 demonstrated that the addition of nanofiller induced the microphase separation of PU,^[40,41] and the strength of PU was improved, which were confirmed by mechanical properties analysis. Simultaneously, the T_{gHS} of PU composites increased very little with the addition of nano-fillers, rising from 99 °C to 101 °C. It also indicated that PANI and SiO_2 entered the hard segment of the PU and cross-linked with it. In conclusion, the micro-phase separation of PU was induced by the increase of nano-fillers, and the T_{gSS} and T_1 of composites were reduced. In addition, the hard segments were difficult to cleave, likely due to the crosslinking of nano-particles and hard segments, thus increasing the T_{gHS} slightly.

Dispersion Property of PANI and NS in PU Matrix and Morphology of PU Composites

The dispersion of PANI and NS in the PU matrix was studied in

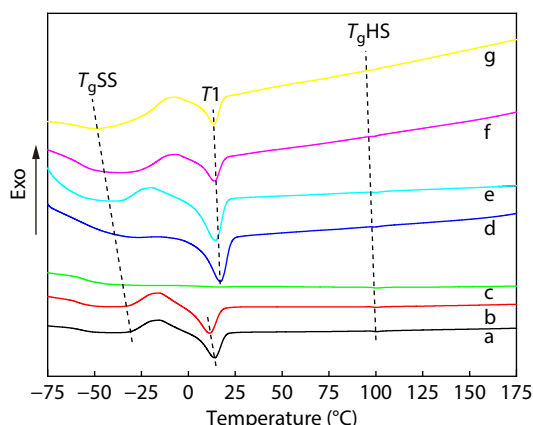


Fig. 4 DSC curves of (a) PU, (b) PU/NS, (c) PU/PANI; (d) PU/PANI/NS-1, (e) PU/PANI/NS-2, (f) PU/PANI/NS-1 and (g) PU/PANI/NS-1.

Table 2 Thermal properties of PU, PU/NS, PU/PANI and PU/PANI/NS.

Sample	T_{gSS} (°C)	T_1 (°C)	T_{gHS} (°C)
PU	-28	14.3	99
PU/NS	—	—	—
PU/PANI	-31	11.5	100
PU/PANI/NS-1	-33	18.3	101
PU/PANI/NS-2	-38	13.5	101
PU/PANI/NS-3	-25	13.8	101
PU/PANI/NS-4	-34	13.9	101

detail through the TEM observation. TEM images of PU/NS, PU/PANI, and PU/PANI/NS at different magnifications are shown in Fig. 5. As can be seen from the image of PU/NS, the SiO_2 nanoparticle was dispersed uniformly in the PU matrix with very few aggregations. Instead, PANI in the PU/PANI composite showed a small, short tubules and flaky structure with a particle size of about 100 nm, which could be dispersed in the PU matrix uniformly. The flake-shaped tubules were connected to each other so that a certain number of conductive pathways formed. The surface of polyaniline was covered with nanosilica, with the formation of a micro-phase structure of NS-PANI, as shown in Fig. 5(e). More importantly, uniform distribution of the micro-phase structure in PU matrix can be clearly seen in Figs. 5(f) and 5(g). The uniform distribution of the micro-phase structure promoted the micro-phase separation of the PU material and improved the mechanical properties of the composites, which is consistent with the result of the mechanical performance analysis. However, the addition of NS would hinder the formation of polyaniline conductive pathways, which was confirmed from the antistatic properties.

Moreover, the morphology of PU composite was studied (Fig. 6). The SEM image of the fracture surface of PU shows a continuous and near-smooth surface (Fig. 6a). The SEM image of the PU/NS samples shows many bumps on the ruptured surface, as shown in Fig. 6(b). The probable reason was that the distribution of SiO_2 nanoparticles led to more cross-linking in some areas of the composites, which had stronger tensile strength and lower toughness than other parts. Moreover, the fracture surface of the PU/PANI sample is rougher and more entanglement than that of neat PU, according to Fig. 6(c). Furthermore, most deformation of the substrate can be observed in the fracture surface PU/PANI/NS composite material, where the rough multilayer structure and entangled fracture appear (Figs. 6d–6g). Interestingly, a clear "claw structure" is evident in the fracture surface of the sample of PU/PANI/NS-2, which is rare in other PU composites. The "claw structure" indicated that polyaniline chains and nanosilica particles interacted to promote the micro-phase separation of the materials. Meanwhile, there was some internal force between them, which increased the cohesion of hard segments of the PU composite. The diffusion of the cracks became difficult when the sample was stretched, so the fracture took place at higher stress and elongation. As a result, PANI and NS reinforced the PU composite. The fracture surface structure of the composite also validated the analysis of the mechanical test result.

Dynamic Mechanical Properties of PU and PU Composites

The dynamic mechanical properties of PU/PANI/NS composites were studied, while PU and PU/PANI composite was adopted as control. As demonstrated in Fig. 7(a), the storage modulus of the composites increases about 400% over that of at -80 °C. This can be explained by the fact that the storage modulus of the composites strongly depends on the movement of the soft segment when frozen or almost frozen at low temperature. Further, the hydrogen bond between nanofiller and polyurethane would slow down the movement of the soft segment at low temperatures. Therefore, the storage modulus of PU/PANI/NS composites also increased by about 400% while

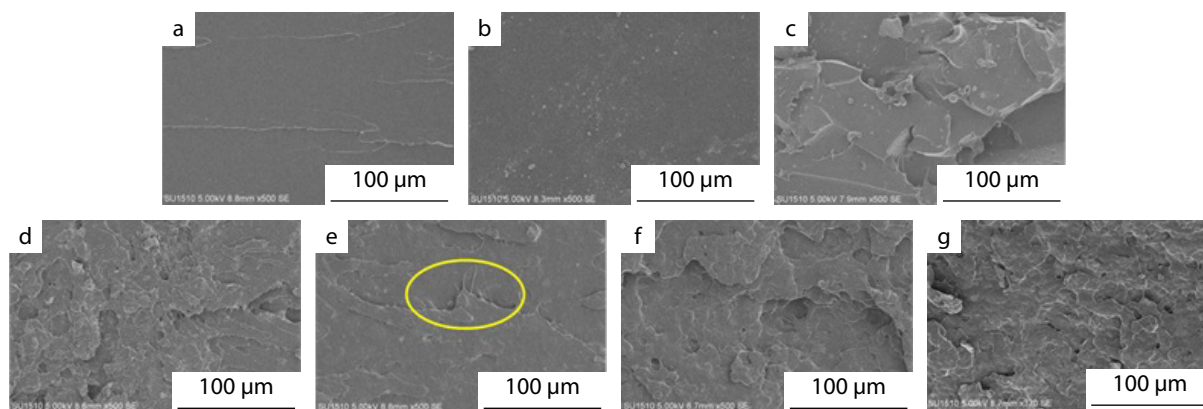


Fig. 5 The SEM images showing fracture surfaces of PU, PU/NS, PU/PANI and PU/PANI/NS. The images marked as (a)–(g) is PU (a), PU/NS (b), PU/PANI (c), PU/PANI/NS-1 (d), PU/PANI/NS-2 (e), PU/PANI/NS-3 (f) and PU/PANI/NS-4 (g) respectively.

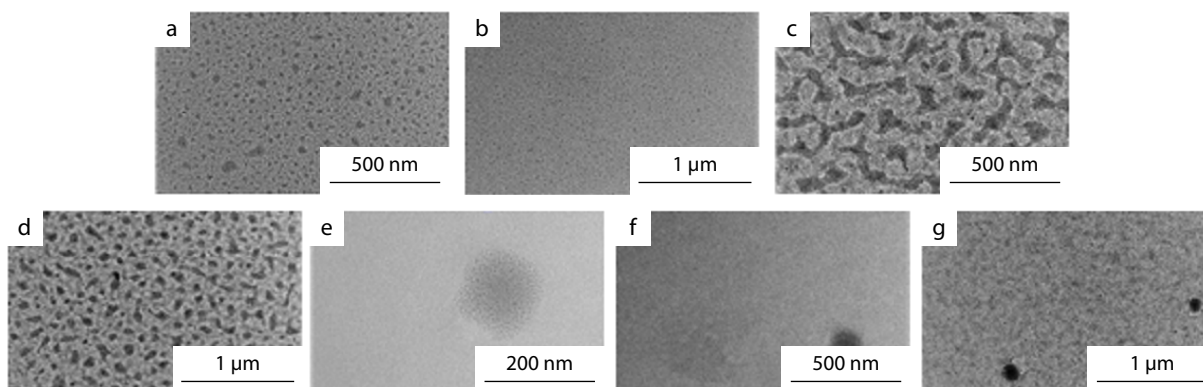


Fig. 6 TEM images of polyaniline (PANI) and nanosilica (NS) in polyurethane (PU) matrix. (a, b) PU/NS; (c, d) PU/PANI; (e, f, g) PU/PANI/NS nano-composites with different magnifications.

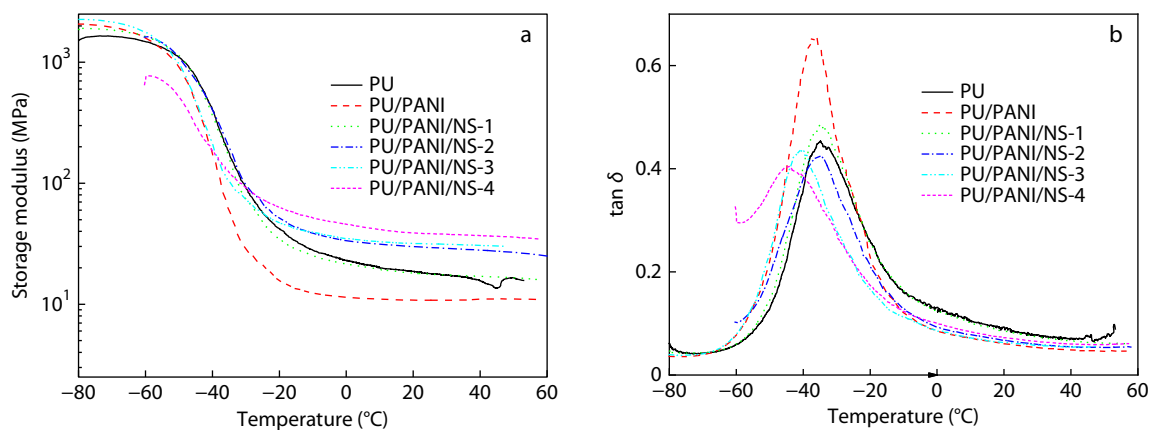


Fig. 7 Dynamic mechanical properties of polyurethane/polyaniline (PU/PANI) and polyurethane/polyaniline/nanosilica (PU/PANI/NS), which is marked as PU/PANI/NS-1, PU/PANI/NS-2, PU/PANI/NS-3 and PU/PANI/NS-4, respectively. (a) Storage modulus and (b) $\tan \delta$.

the temperature was as low as -80 °C. However, as seen in Fig. 7(a), the storage modulus of PU/PANI/NS-4 decreased, suggesting that adding additional nanosilica would make it difficult to sustain the storage modulus. The excessive amount of nanofillers resulted in a significant phase separation, which adversely affected the mechanical properties of the composite. These results are accordance with the prior mechanical properties test.

The storage modulus of the composites depends on the

crystallization of the hard segment of the composites at high temperatures.^[42] The storage modulus of PU composites increases nearly 500% at 40 °C, compared with neat PU. Meanwhile, the crystallinity of the hard segment increases as the amount of NS and PANI increases, leading to improved rigidity and mechanical properties of the composite.

The loss factor graphs of PU composites are plotted in Fig. 7(b). The T_{gSS} of the composite decreases further with the increasing content of the nanofiller, indicating that the

nanofiller promotes the micro-phase separation of the polyurethane, consistent with the results from DSC. The improvement in microphase separation reduced the mechanical loss of the composites, which enhanced the elasticity of rubber. The peak of $\tan\delta$ depended on the compatibility between the filler and the matrix. The untreated $-\text{OH}$ on the surface of the nanosilica affected the compatibility with the PU. Therefore, the peak of $\tan\delta$ decreased when the amount of nanosilica increased.

Conductive Property

The conductive properties of PU, PU/NS, PU/PANI and PU/PANI/NS were studied as illustrated in Fig. 8. The resistance value of the PU/SiO₂ sample keeps substantially unchanged from that of neat PU, because the SiO₂ particles were conductive inert matter. As a conductive polymer, the addition of PANI reduced the resistance of the PU by 2 to 3 orders of magnitude, which largely improves the conductive property of PU and makes PU an antistatic material. This result is in accordance with the previous study.^[43] However, the conductive performance of the ternary composite of PU/PANI/NS composites is less optimistic than that of PU/PANI, based on Fig. 8. With the same dosage of PANI, the electrical resistance of PU/PANI/NS decreases by only 1 to 2 orders of magnitude compared with that of PU or PU/NS. The resistance of PU/PANI/NS is higher than that of PU/PANI, which may be attributed to the link between SiO₂ and PANI that hindered the interactions of PANI particles. Besides, the conductive component PANI was unable to function fully as a conductive polymer. Although, the conductivity of PU/PANI/NS was not as high as PU/PANI, the conductivity inertness was improved compared with the original PU, and PU/PANI/NS could be used as an antistatic rubber. Furthermore, the resistance decreases with the rise of the content of NS, which was very interesting and has not been anticipated before. The probable mechanism is discussed in next section.

On the other hand, the mechanical properties of PU/PANI/NS were optimized based on the discussion of mechanical

properties, especially PU/PANI/NS-2, the mechanical properties of which were better than those of PU, PU/PANI and PU/NS. It could be concluded that the resistance of PU is more than $10^{12} \Omega$, which can be defined as an insulator and possesses no antistatic ability. The electric resistance of the PU/PANI/NS composites was approximately 10% that of the original PU, indicating that the material could be defined as antistatic material. Therefore, the ternary composite of PU/PANI/NS is a potential candidate for antistatic rubber. It could be used in any rubber rotating parts subjected to continuous friction such as textile rolls, to provide a longer service life due to its better antistatic and mechanical properties.

Mechanism of the Conductivity's Rising with the Content of NS

The electric resistance of the PU/PANI/NS composite decreases with the increasing content of NS, as the electrical resistance test results shown in Fig. 7. Theoretically, the electric resistance of the composites with a higher content of NS must be higher because that NS is an inorganic non-conducting particle. However, the electrical resistance of the PU/PANI/NS decreased, implying that the conductivity of the composites increased as the content of NS increased from 1% to 4%.

The molecular simulation was adopted in the current study to understand the variation of the electric resistance with the NS's content in the PU/PANI/NS composites. In addition, the interactive energy of the compositions of PU/PANI/NS composites was calculated to explain the influence of NS on the conductivity of the composites. Fig. 9 depicts the simulated composite structure, and Table 3 summarizes the energy calculation results. More molecular simulation results are given in Figs. S1–S6 in the electronic supplementary information (ESI). The non-bond energy of the PU/PANI/NS ternary composite was far higher than that of PU/PANI systems, which might be a probable reason for the conductivity of the PU/PANI/NS increasing with the rising of the NS content. Moreover, the blend energy of PU/PANI/NS ternary composite was also calculated, as shown in Fig. 10 and Fig. S7 (in ESI), the related structures are shown in Fig. S8 (in ESI). The blends were constructed with PU as base compound and polyaniline and/or nanosilica as screen compounds. E_{bb} is the blend energy of PU, E_{bs} is the blend energy of PU and PANI or NS, and

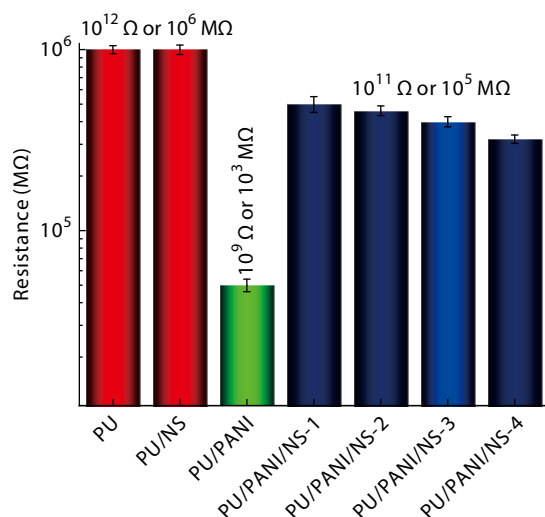


Fig. 8 Resistance value of each sample (specification: 3 cm × 1 cm) measured by a high resistance meter, the samples are PU, PU/PANI/NS-1, PU/PANI/NS-2, PU/PANI/NS-3 and PU/PANI/NS-4 respectively.

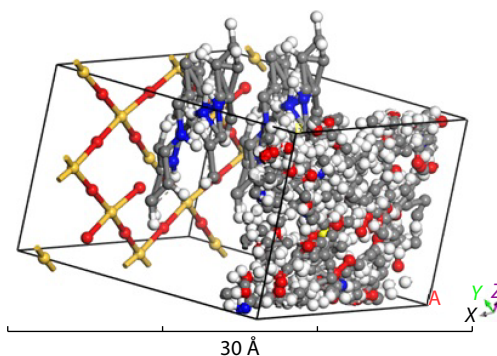


Fig. 9 The simulation structure of polyurethane-polyaniline-nanosilica with the mole ratio of urethane unit/aniline unit/NS is 8/4/3. The model is shown as ball-stick style, the element was distinguished with the color of balls, which was defined as, white=hydrogen, black=carbon, red=oxygen, blue=nitrogen, yellow=silicon, respectively.

Table 3 The calculated results of the energy of PU/PANI binary composite that the mole ratio of urethane unit and aniline unit was 8/4 and two kinds of PU/PANI/NS that the mole ratio of urethane unit, aniline and nanosilica was 8/4/3 and 8/4/6, as shown as PU/PANI/NS-2 and PU/PANI/NS-4 respectively.

Models	Valence energy ^a		Non-bond energy ^a			Total ^a
	Diag. ^b	Cross ^c	Van ^d	Lc ^e	E ^f	
PU/PANI	53.78	0.194	846.9	−0.022	0.814	901.7
PU/PANI/NS-2	716.6	2.316	6885	−0.029	1.226	7605
PU/PANI/NS-4	238.0	2.322	6369	−0.011	−0.049	6609

^a The unit of energy is 10³ kcal/mol; ^b Diag. terms of valence energy; ^c Cross terms of valence energy; ^d van der Waals energy; ^e Long range correction energy; ^f Electrostatic energy.

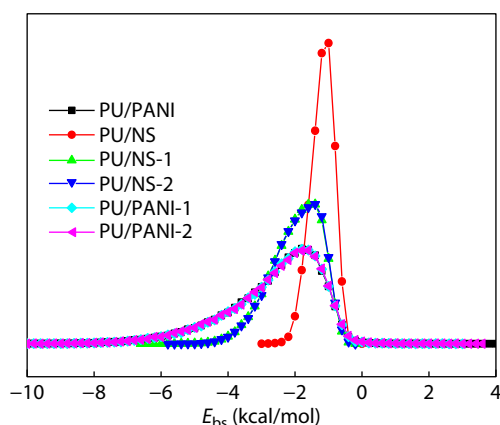


Fig. 10 Blend energies (E_{bs}) of PU, PANI and NS in their binary or ternary composites. PU/PANI, the E_{bs} between PU and PANI in PU/PANI binary composite; PU/NS, the E_{bs} between PU and NS in PU/NS binary composite; PU/NS-1, the E_{bs} between PU and NS in PU/PANI/NS ternary composite with 2% of NS; PU/NS-2, the E_{bs} between PU and NS in PU/PANI/NS ternary composite with 4% of NS; PU/PANI-1, the E_{bs} between PU and PANI in PU/PANI/NS ternary composite with 2% of NS; PU/PANI-2, the E_{bs} between PU and PANI in PU/PANI/NS ternary composite with 4% of NS. The content of PANI in all composite is 4%, all of the percentage is mass percentage based on PU.

E_{ss} is the blend energy of PANI or NS themselves. It can be concluded that E_{ss} of NS was far higher than that of PU and PANI. The blend energy of PU/PANI/NS ternary blends was affected by NS largely. It was accordant with the calculated results of the non-bond energy. The mechanism of the variation of the conductivity of PU/PANI/NS ternary composites could be explained.

CONCLUSIONS

PU/PANI/NS ternary composites with high strength, toughness, and desired antistatic properties were prepared with the addition of a small amount of polyaniline (PANI) and modified nanosilica (NS). The tensile strength of the PU/NS composite increased but the toughness decreased with the addition of NS as the only reinforcing filler. The mechanical properties and conductivity of the PU/PANI composite were improved when PANI was also added as the conductive polymer. The tensile strength of PU/PANI/NS composites increased to 22 MPa, the

elongation at break increased to 1380%, and the resistivity decreased by 1 to 2 magnitudes (from X to 7.6×10^4 M Ω) with the addition of 4 wt% of PANI and 2 wt% of NS. The reactive groups such as $-\text{OH}$, $-\text{NH}_2$ of PANI and NS reacted with the isocyanate groups of PU prepolymer so that PANI and NS were well dispersed in matrix based on the analysis of FTIR, DSC, DMA, TEM and SEM. The resistivity of the ternary composites decreased unexpectedly with the increase content of NS. Molecular simulation results of the interactive energy in the simulated crystals and the blends energy in the simulated blends gave further explanation on the interactions of the composites material. In one word, PANI is propitious to both mechanical and conducting properties of PU, while NS is in favor of strength but makes against conductivity. Fortunately, the resistance of the PU/PANI/NS ternary is low enough for its antistatic property and decreases with the rising of the amount of NS. This study presents a new polyurethane composite material with antistatic property and high strength, which can have application in many rubber rotating parts, such as textile rolls, industrial transfer motion, medical devices and aerospace.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2703-7>.

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