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Conductive hybrid film from polyaniline and polyurethane–silica

Jing Luo, Xianhong Wang*, Ji Li, Xiaojiang Zhao, Fosong Wang

*State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry,
Graduate School of Chinese Academy of Sciences, Changchun 130022, PR China*

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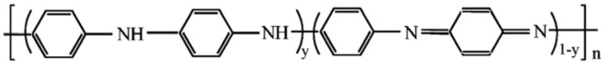
Abstract

In order to improve the mechanical performance and water resistance of water-borne conducting polyaniline film, conducting polyaniline/polyurethane–silica hybrid film was prepared in aqueous solution employing silanol-terminated polyurethane and methyltriethoxysilane as sol–gel precursors. The hybrid film showed surface resistivity of 10^8 Ω even though the conducting polyaniline loading was only 10 wt% (or 1.5 wt% of polyaniline), and the mechanical performance as well as water resistance was significantly improved, making it suitable for antistatic application. Therefore, a practical route to water-borne processing of conducting polyaniline is disclosed.

Keywords: Water-borne polyaniline; Polyurethane–silica; Hybrid film

1. Introduction

Polyaniline (PANI) is a kind of intrinsically conducting polymer consisting of phenylenediamine and quinonediimine structure as shown in Scheme 1 [1]. Like many other conducting polymers, polyaniline is not soluble in common organic solvents because of the stiffness of its backbone and hydrogen bonding interaction between adjacent chains. Dopant induced processability of polyaniline established since 1992 overcomes the difficulty in solution processing, which is successful especially in organic solvent system [2–4], and the improved processability of polyaniline has made it possible for many applications in anticorrosion, antifouling and antistatic coatings [5,6]. In contrast to the successful organic solvent processing, water-borne processing of polyaniline is far from satisfactory due to poor mechanical performance and electrical conductivity instability against water soaking [7,8].



Scheme 1. Structure of polyaniline, where *y* is between 0 and 1, *n* is integer.

Owing to restrictions on the commercial use of organic solvents from environmental issue, processing of polyaniline from aqueous system is an overwhelming trend. In fact, PANI has been made water-soluble or dispersible by various methods such as grafting sulfonic or phosphoric acid groups onto the benzene ring or nitrogen atom [9–11], synthesizing colloidal PANI particles in the presence of a water-soluble polymeric stabilizer [12,13] and doping PANI by water-soluble acid [14,15], etc. As one of the choices, water-soluble conducting polyaniline (cPANI) was obtained using a proton acid with a long hydrophilic tail as a dopant [14], but the comprehensive performances of the conductive film like water resistance and mechanical properties need further improvement. To enhance the water resistance, cPANI/silica hybrids have been prepared from water/ethanol solution where cPANI chains were confined into the inorganic network [16–18]. Although water stability was improved to some extent, high-quality cPANI hybrid films can hardly be made because of the inherent brittleness and severe shrinkage of the silica network due to the poor compatibility between cPANI and inorganic matrix. Therefore, it is suggested that a flexible polyurethane–silica hybrid matrix be designed as the host of the conductive PANI chains instead of pure silica

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* Corresponding author. Tel.: +86 431 85262250; fax: +86 431 85685653.
E-mail address: xhwang@ciac.jl.cn (X. Wang).

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network to enhance the compatibility between cPANI and silica, and improve the mechanical property of cPANI hybrids.

The reason why polyurethane (PU) is chosen is due to its balanced flexibility and hardness, good film-forming property and resistance to solvent [19]. Moreover, the interaction between −NH in polyaniline and −NHCOO in polyurethane may be a bonus to improve the compatibility of the system [20–24]. The strong tendency of PANI and PU to form hydrogen bonding has been verified by Rodrigues [20,21] through various spectroscopic techniques, which was believed to be responsible for a certain degree of phase mixing in PANI/PU blend. Ho and coworkers [22] also confirmed the hydrogen bonding between PANI and PU, and the stronger hydrogen bonding in the blend contributed to better miscibility, higher conductivity and tensile strength. In the characterization of PANI filled PU/PMMA interpenetrating network system, Siddaramaiah [23] mentioned that the hydrogen bonding formation between −NH of PANI and −NHCOO group of PU/PMMA polymer network had some effect on the physicomechanical, electrical as well as thermal properties of the conducting IPN. Yoshikawa et al. [24] also suggested that the interaction between the carboxyl groups in PU and imine groups in PANI could induce miscibility of PANI/PU blends.

In this report, silanol-terminated polyurethane was designed and used in combination with methyltriethoxysilane (MTES) as sol–gel precursors to prepare the cPANI/polyurethane–silica hybrids with the expectation to combine the electrical properties of cPANI with desired mechanical and water resistant properties of polyurethane–silica matrix.

2. Experimental section

2.1. Materials

Isophorone diisocyanate (IPDI, Aldrich), dibutyl tin dilaurate (DBTDL, Aldrich), dimethylol propionic acid (DMPA, Aldrich), aminopropyltriethoxysilane (APTES, Sigma), methyltriethoxysilane (MTES, Acros) were used as received. Polyethylene glycol 600 (PEG 600) was dried in vacuum for 5 h at 100 °C. Methyl ethyl ketone (MEK) was of analytical purity. Polyaniline emeraldine base was the product of Ben'an Co. licensed under this laboratory.

2.2. Preparation of the sol–gel precursor

A calculated amount of PEG 600, DMPA, DBTDL and freshly distilled MEK were charged into a three-necked flask equipped with a stirrer, a reflux condenser and a nitrogen purge and heated to 75 °C, IPDI was then slowly added to the flask, the reaction mixture was heated to 90 °C and stirred for 4 h to make the isocyanate-terminated prepolymer. The reaction mixture was then cooled to 60 °C and a solution of APTES in freshly distilled MEK was added and stirred for another 1 h. After MEK was distilled from the mixture under reduced pressure, water and ethanol (molar ratio of water/ethanol was 2/1) were added under vigorous stirring to produce a dispersion of silanol-terminated polyurethane. MTES was then added to the dispersion and stirred for 4 h at room temperature to give the silanol-terminated polyurethane/MTES precursor. The molar ratio of PEG 600/DMPA/IPDI/DBTDL/APTES/MTES was 1/1/4/0.01/4/6.

2.3. Preparation of conductive hybrids

The water-soluble conductive polyaniline was prepared according to earlier work in this lab [14]. Stoichiometric sol–gel precursor solution was added dropwise to the aqueous conductive polyaniline solution at room temperature under vigorous stirring. The mixture was stirred for another 4 h before film casting on substrate at room temperature. After gelation, the samples were transferred to oven at 50 °C for one day for thorough drying. The thickness of final film was around 40–80 μm. As a reference, cPANI/MTES hybrid was prepared employing MTES as the only precursor under the same conditions.

2.4. Measurements

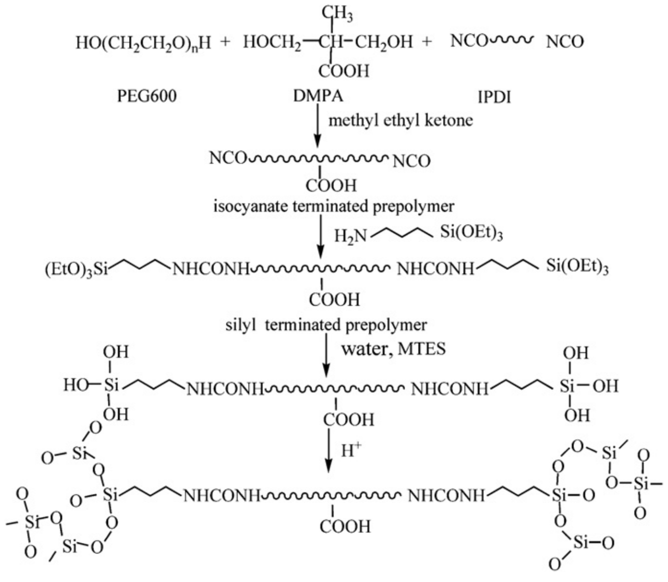
The electrical conductivity of the hybrid film was measured by standard four-probe method. The FTIR spectra were recorded on a BIO-RAD FTS-7 in KBr pellets. The morphologies of the conductive films were examined by a JEOL-JXA-840 scanning electron microscope (SEM). The solid-state ^{29}Si-MAS NMR spectra were recorded at 79.45 MHz on a Bruker AV-400 NMR spectrophotometer using tetramethylsilane (TMS) as internal standard. The tensile strength was measured in dumbbell specimens on Zwick/Roell 1010 Tester. The hardness, flexibility and impact strength of the coating were determined by pencil test, bending test and QCJ impact instrument according to China National Standard GB/T 1730-93, GB/T 1731-93, GB/T 1732-93, respectively. The surface resistivity was measured on Keithley 8009 resistivity test fixture.

3. Results and discussion

3.1. Preparation and electrical conductivity of the conductive hybrids

To prepare the water-borne cPANI/polyurethane–silica hybrids, the sol–gel precursors (silanol-terminated polyurethane and MTES) were added to the aqueous cPANI solution to afford a homogeneous solution. The hydrolysis and condensation of the trialkoxysilyl functional groups proceeded as depicted in Scheme 2. Upon gelation and drying, the polyurethane–silica network was obtained where the cPANI chains were trapped.

The dependence of the electrical conductivity of the hybrids on cPANI loading is shown in Fig. 1. The conductivity increased with increasing cPANI content, and a percolation threshold was found at around 10 wt% cPANI loading, where the actual polyaniline loading was only 1.5 wt%, since cPANI contained 15 wt% of polyaniline and 85 wt% of acidic



Scheme 2. Synthesis of the sol–gel precursor.

phosphate. In comparison, the conductivity percolation threshold of cPANI/MTES was 15 wt% cPANI.

In our work, the conductive PANI was prepared by directly doping PANI with acidic phosphoric ester containing hydrophilic chains. Because of the hydrophilic nature of the dopant, the doped PANI was soluble or dispersible in water. As discussed in our earlier publication [14], the conducting PANI became more hydrophilic with increasing length of hydrophilic chain in the dopant, leading to increase in its solubility in water. However, there exists paradox for the water-soluble conducting polyaniline: better the water solubility, more the difficulty for the film to resist water soaking. As a result, the pure cPANI film broke into pieces accompanied by sudden decline in electrical conductivity once it was soaked in water, whereas the cPANI/polyurethane–silica hybrid film still remained intact after soaking in water for three months. As shown in Fig. 1, enhancement of conductivity stability against water soaking was observed especially for the hybrid film with cPANI loading below 20 wt%, where the conductivity changed little after soaking in water, and the mass loss ratio was less than 8 wt%. As discussed in the following context, the improvement of water stability was attributed to the good dispersion and confinement of cPANI in the polyurethane–silica hybrid network.

3.2. Hydrogen bonding interaction in the conductive hybrids

Fig. 2 shows the FTIR spectra of isocyanate-terminated prepolymer as well as silanol-terminated prepolymer. The distinct absorption peak at 2272 cm^{-1} in Fig. 2a confirmed the existence of –NCO group. The characteristic peaks of urethane group were observed at 3326 cm^{-1} and 1716 cm^{-1}, corresponding to stretching vibrations of N–H and C=O groups, respectively. The peak at 1550 cm^{-1} was assigned to the stretching vibration of carboxyl group. The peak at 2272 cm^{-1} disappeared in Fig. 2b, while absorption peaks at 843 cm^{-1} and 770 cm^{-1} characteristic of Si–C bending vibration appeared, and the peak strength at 1080 cm^{-1} increased since the Si–O–C stretching vibration from ethoxysilane group located in this region and overlapped with C–O–C stretching vibration band. All these changes indicated that the –NCO group of the polyurethane prepolymer reacted with the $-NH_2$ group of APTES, and $-Si(OC_2H_5)_3$ group was incorporated with polyurethane covalently, generating the silanol-terminated polyurethane precursor.

Fig. 3 shows the FTIR spectra of the cPANI/polyurethane–silica hybrids with different cPANI loadings. Once cPANI was introduced into the hybrids, the absorption peak at 1716 cm^{-1} characteristic of C=O stretching vibration for polyurethane–silica hybrid red-shifted to 1701 cm^{-1}, indicating that the interaction between polyurethane–silica hybrids and cPANI presented in the hybrid, which was attributed to the hydrogen

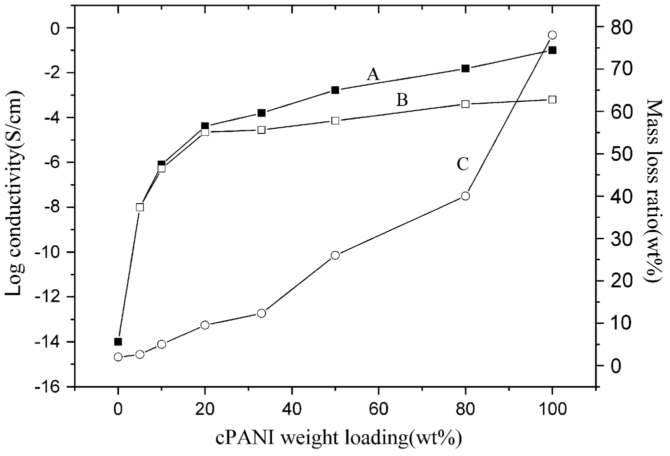


Fig. 1. Plots of logarithmic conductivity of the cPANI/polyurethane–silica hybrids against cPANI loading (A) before and (B) after water soaking. Plot of mass loss ratio of the extracted samples against the cPANI loading is shown in line C.

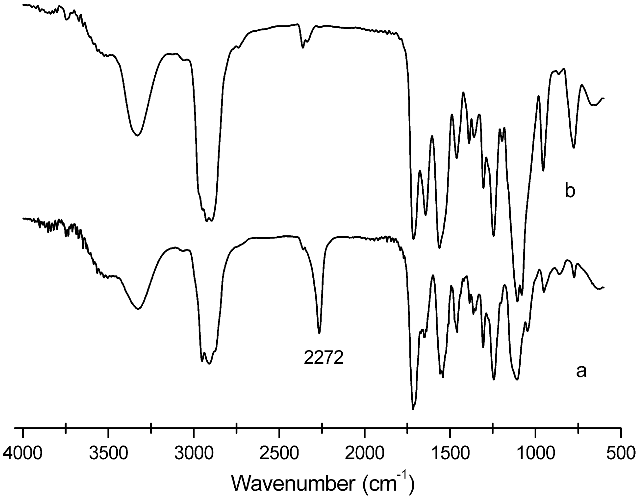


Fig. 2. FTIR spectra of (a) isocyanate-terminated prepolymer, (b) silanol-terminated prepolymer.

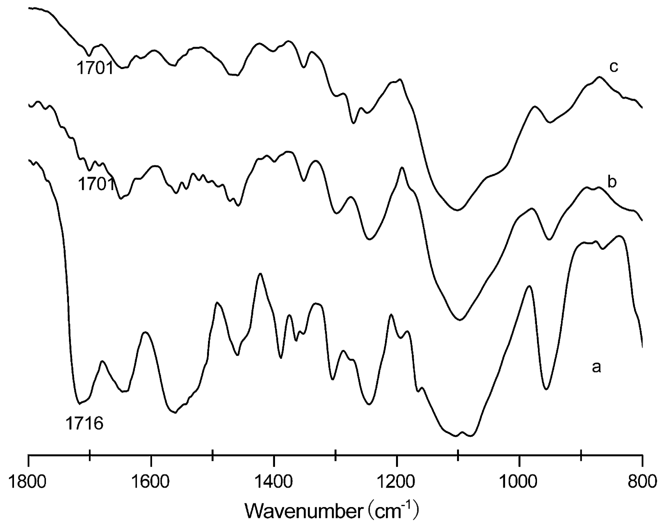
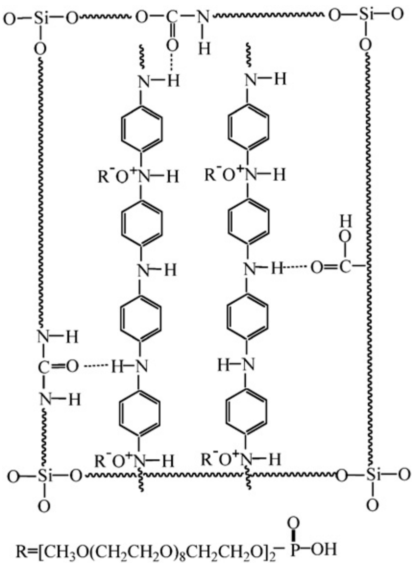


Fig. 3. FTIR spectra of cPANI/polyurethane–silica hybrids with different cPANI loadings of (a) 0 wt%, (b) 33 wt%, (c) 50 wt%.

bonding between –NH of cPANI and –C=O group of polyurethane–silica hybrid network. In addition, the –COOH group on the polyurethane chain may also have interaction with the amine group in the polyaniline backbone [24], though there was no significant change in FTIR spectra. Based on the chemical structure of polyurethane, the possible hydrogen bonding formed in cPANI/polyurethane–silica hybrids is drawn in Scheme 3.

The SEM images of cPANI/polyurethane–silica hybrid films are shown in Fig. 4. A smooth surface was observed for the polyurethane–silica hybrids (Fig. 4a), and a dispersed cPANI phase existed as isolated globule in the conductive cPANI/polyurethane–silica hybrids with low cPANI loading (Fig. 4b). When the cPANI loading increased to 10 wt%, cPANI was dispersed homogeneously and interconnected continuously in the insulating matrix (Fig. 4c). In other words, conductive pathway network in hybrid was formed at 10 wt% cPANI loading which was in agreement with the conductivity percolation threshold. Fibroid structure of the cPANI aggregation was observed when cPANI loading in the composite increased further (Fig. 4d), indicating that a more conductive pathway was formed, consistent with increase in electrical conductivity, whereas for cPANI/MTES hybrid with 20 wt% cPANI (Fig. 4e), distinct, large granular structure was observed. In addition, when the cPANI loading was below 20 wt% in the hybrid, the surface of cPANI/MTES hybrid film was coarse, and aggregation of the conducting polymer was apparent. In comparison, the cPANI/polyurethane–silica film was quite smooth and had a glossy surface, suggesting a more homogeneous dispersion of cPANI in hybrid. This great difference can be explained by the existence of hydrogen bonding as shown in Scheme 3. The hydrogen bonding interaction between cPANI and polyurethane–silica could enhance the compatibility between the cPANI and polyurethane–silica hybrid, leading cPANI to be homogeneously dispersed into the hybrid matrix to form conductive network during sol–gel process. The percolation threshold at low polyaniline loading (1.5 wt%) of cPANI/polyurethane–silica hybrids should also be attributed to the good dispersion of cPANI in hybrid matrix. In the case of cPANI/MTES hybrids, the lower hydrophilicity of MTES sol and poor interface interaction between cPANI and inorganic matrix resulted in phase separation between the two components, and consequently, higher conductivity percolation threshold was observed.



Scheme 3. Representation of hydrogen bonding formation.

The strong interaction between cPANI and polyurethane–silica can also find support from the solid-state ^{29}Si-MAS NMR spectra of the hybrids with different cPANI loadings. As shown in Fig. 5, the two peaks at −67.8 ppm and −58.3 ppm were assigned to T_3-type silicon and T_2-type silicon, respectively, where the subscript is the number of bridging oxygens surrounding the central silicon atom [25]. As shown in Fig. 5a and b, the relative ratio of peak intensity of T_2 to T_3 (T_2/T_3) was 0.2 for the pure polyurethane–silica hybrids, and it slightly increased to 0.23 in cPANI/polyurethane–silica hybrids with 7 wt% cPANI, indicating that incorporating low content cPANI did not significantly disturb the three-dimensional structure of polyurethane–silica hybrid network, and the conductive polyaniline chain was completely embedded in the hybrid network. This also gave reasonable explanation for the good water stability of cPANI/polyurethane–silica hybrids with low cPANI loading. The continued increase in cPANI loading led to the weakening of T_3 signal and strengthening of T_2 signal, correspondingly the T_2/T_3 ratio increased to 0.55 for 25 wt% of cPANI loading, and it reached 0.78 for 40 wt% of cPANI loading. Generally, the ratio of T_2/T_3 should remain constant regardless of cPANI loading if the two phases aggregated separately, the above T_2/T_3 changes again confirmed the existence of strong interaction between the constituent components via hydrogen bonding in the hybrids. The increase of T_2/T_3 with increasing cPANI loading was reasonable considering that the amount of hydrogen bonding between cPANI and polyurethane–silica matrix increased with increasing cPANI content, which could effectively

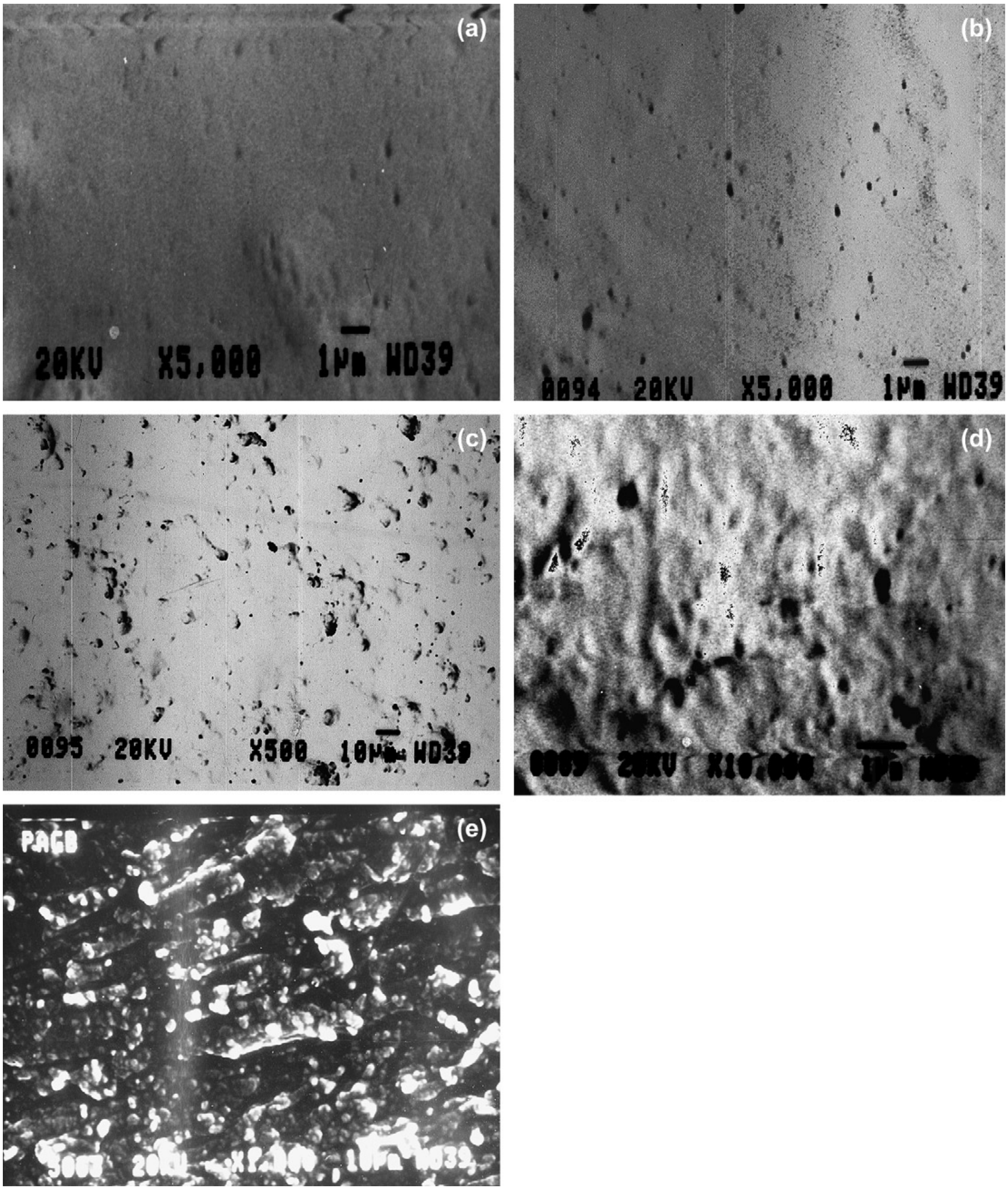


Fig. 4. SEM images of cPANI/polyurethane–silica hybrids with different cPANI loadings: (a) 0 wt%, (b) 5 wt%, (c) 10 wt%, and (d) 30 wt%, (e) cPANI/MTES hybrids with 20 wt% cPANI loading.

prevent the inorganic sols from aggregating for complete condensation, leading to decrease of three-dimensional network and increase of linear structure. Similar change in T_2/T_3 has been observed in cPANI/(3-glycidoxypropyl)trimethoxysilane hybrid [17] as well as electrostatic interaction cPANI/MTES hybrid [26]. The interaction between the organic and inorganic components became dominating once enough cPANI existed in the hybrid matrix, resulting in significant decrease of cross-linking degree of the hybrid and great increase of free cPANI chain, which would decrease the water resistance of the hybrid. Therefore, as can be seen in Fig. 1, the conductivity as well as mass loss upon soaking increased sharply when cPANI loading was beyond 20 wt%.

3.3. Mechanical property

The mechanical property of pure water-borne cPANI film is poor due to the large amount of poly(ethylene glycol) in the dopant. For the conductive hybrids, as shown in Table 1, the elongation at break, tensile modulus and strength for the cPANI/polyurethane–silica hybrids at 10 wt% cPANI loading reached 7.2%, 1451.69 MPa, 61.1 MPa, respectively, slightly higher than those of polyurethane–silica matrix.

The presence of second phase (disperse phase in the form of polymer or filler) in a matrix (disperse media) may affect the mechanical properties of the composites or blends, depending on the relative concentration of the two phases, nature

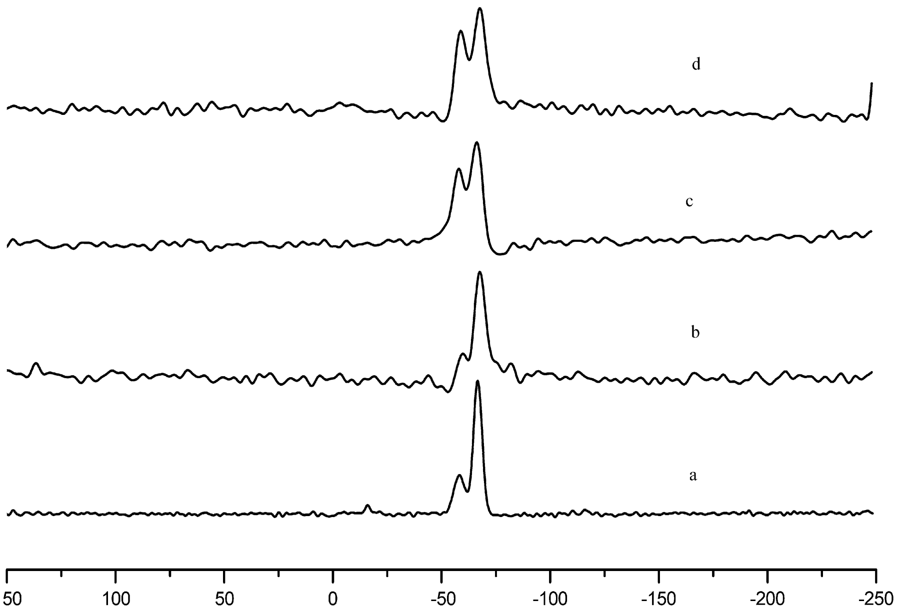


Fig. 5. ^{29}Si-MAS NMR spectra of cPANI/polyurethane–silica hybrids with different cPANI loadings: (a) 0 wt%, (b) 7 wt%, (c) 25 wt%, and (d) 40 wt%.

of the disperse phase, surface characteristics, distribution pattern, domain size and shape, in particular, the degree of compatibility. Siddaramaiah [23] showed that the original tensile strength of PU/PMMA did not change with incorporation up to 2.5 wt% PANI, but increased with increasing PANI content beyond 2.5 wt%. Ho and coworkers [22] presented interesting observations in two different kinds of PANI/PU blend with different degree of interfacial interaction, where the change of tensile strength on the conducting polymer loading in the blend followed opposite pattern: the tensile strength showed monotonical increase with increasing PANI loading for the blend with higher degree of hydrogen bonding, while a monotonical drop was observed for the blend with lower degree of hydrogen bonding.

Therefore, the improved mechanical performance of cPANI/polyurethane–silica hybrids at 10 wt% cPANI loading over the neat polyurethane–silica hybrid may be the result of good confinement of cPANI in the hybrid network and interaction between –NH groups in cPANI backbone and –C=O groups in polyurethane–silica matrix as shown in Scheme 3.

However, when cPANI content was beyond 20 wt%, the tensile strength as well as the modulus of the hybrids decreased, accompanied by increase of the elongation at break. With increasing cPANI loading, the polyurethane–silica network may be weakened due to the incomplete condensation of inorganic sols as discussed in ^{29}Si-MAS NMR spectra, therefore, the rigidity of the hybrids decreased, leading to decrease of tensile strength and modulus and increase of elongation at break for the hybrids. Since the cPANI/polyurethane–silica hybrid film containing 10 wt% cPANI also displayed good water resistance, it can be concluded that cPANI loading of 10 wt% may be optimal in balance of the cross-linking degree of hybrid network and hydrogen bonding interaction for better mechanical performance and water resistance ability.

As shown in Table 2, the neat polyurethane–silica matrix combined good hardness of silica component and flexibility of polyurethane component, and it experienced little change for the conductive hybrid film when cPANI loading was below 10 wt%. This was reasonable considering that the hardness of composite film was mainly determined by the cross-linking density of polyurethane–silica network, and it was nearly unaffected under low cPANI loading. High cPANI loading may reduce the cross-linking density leading to decrease in the rigidity of the hybrids, therefore, decrease in hardness with increasing cPANI loading was observed in Table 2. The result was consistent with its tensile performance and water resistance property. Generally, the comprehensive mechanical properties of the conductive hybrid film like hardness, impact

Table 1
Mechanical properties of cPANI/polyurethane–silica hybrid film

cPANI content (wt%)	Young's modulus (Mpa)	Tensile strength (Mpa)	Elongation at break (%)
0	1434.84	51.37	3.06
5	1074.94	53.17	17.12
10	1451.59	61.1	7.2
20	994.9	47.65	18.42
33	422.11	48.74	13.41

Table 2
Coating properties of cPANI/polyurethane–silica hybrid film

cPANI content (wt%)	Hardness (grade)	Impact resistance (kgf cm)	Flexibility (mm)
0	6H	40 cm	1
5	6H	50 cm	1
10	6H	50 cm	1
20	5H	50 cm	1
33	3H	50 cm	1

Table 3
Surface resistivity of cPANI/polyurethane–silica hybrid film

cPANI content (wt%)	PANI content (wt%)	Surface resistivity (Ω)
0	0	10^{14}
5	0.7	2.15×10^9
10	1.5	2.17×10^8
20	3	2.31×10^6

resistance as well as flexibility were satisfactory, especially when cPANI loading was below 10 wt%.

The surface resistivity of the hybrid coating is shown in Table 3. For the polyurethane–silica hybrid matrix alone, it was in the order of 10^{14} Ω, and it decreased to 10^9 Ω by addition of 5 wt% cPANI. Surface resistivity in the antistatic range (10^8 Ω) was achieved by incorporating only 10 wt% of cPANI (i.e., 1.5 wt% PANI). According to the above discussed results, the mechanical performance, water-soaking resistance of the conductive hybrid film reached a balance for practical application at this cPANI loading.

4. Conclusions

Conductive hybrids consisting of water-borne cPANI and polyurethane–silica hybrid sol–gel network were prepared, the mechanical strength and conductivity stability of the water-borne polyaniline film were simultaneously improved, making it suitable for antistatic applications.

Acknowledgement

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