Conductive Hybrids from Water-Borne Conductive Polyaniline and (3-Glycidoxypropyl)trimethoxysilane

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ABSTRACT: Free-standing conductive films of organic−inorganic hybrids were prepared employing the sol−gel process of (3-glycidoxypropyl)trimethoxysilane (GPTMS) and water-borne conductive polyaniline (cPANI) in water/ethanol solution. The hybrids displayed a percolation threshold for electrical conductivity at a volume fraction of 2.1% polyaniline (PANI); the maximum conductivity of the hybrids reached 0.6 S/cm. GPTMS showed good compatibility with water-borne cPANI during the sol−gel process, and free-standing conductive films were obtained at room temperature. Transmission electron microscopy images of the hybrids indicated that the cPANI was dispersed in the inorganic phase in nanoscale. Because of good confinement of cPANI chains in the inorganic network, water resistance of the hybrid films was significantly improved compared with that of pure cPANI; the electrical conductivity of the films kept stable for 6−7 days soaking in water, whereas it decreased sharply for 1 day soaking for the pure cPANI.

Introduction

The conducting polyanilines have found many applications in corrosion-prevention coatings, light-emitting devices, antifouling coatings, and antistatic materials due to their good environmental stability and special chemical and electrochemical properties.[1−3] They have been regarded as processable polymers thanks to the ongoing efforts in the past decades.[4−8] However, organic solvents such as *m*-cresol, chloroform, and xylene are generally necessary for their solution processing. With the increasing environmental concern, an environment-benign process becomes an inevitable tendency.[9,10] In fact, conducting polyaniline has been made water-soluble by various approaches. The first water-soluble conducting polyaniline was prepared by incorporation of hydrophilic units to aromatic rings or on the nitrogen sites.[11−16] Blending or doping of parent polyaniline by water-soluble polymeric acid was another route to water-soluble polyaniline.[17,18] Recent development on water-soluble conducting polyaniline was employing protonic acid carrying long hydrophilic tail as dopant, and free-standing conducting polyaniline film with high electrical conductivity was available.[17] However, the water resistance of the electrical conductivity of the film was far from satisfactory. When the film was soaked in water, it rapidly broke into pieces, accompanied by sudden decline in the electrical conductivity. A chain confinement strategy was thus proposed where the conducting polyaniline chains were confined within networks of organic polymers or inorganic media; a film with improved water resistance and good electrical conductivity was prepared.[19]

Sol−gel organic−inorganic hybrids offer an unique opportunity not only to combine the advantages of both components but also to create novel composites of unique property.[20−27] In fact, the sol−gel technique has been used to make conducting polyaniline/silica hybrids with good electrical conductivity as well as improved adhesion.[28,29] However, all these hybrids were prepared in high boiling point or toxic solvents like *N*-methylpyrrolidone and *m*-cresol. Recently, in our group, to enhance water resistance of the water-borne conducting polyaniline, cPANI/silica hybrids were successfully prepared in water/ethanol solution where cPANI chains were confined into the inorganic network.[30] Owing to the lower hydrophilicity of the inorganic precursor like tetraethyl orthosilicate (TEOS), there existed phase separation between inorganic sol and water-borne cPANI emulsion, accompanied by severe shrinkage during condensation process, which made it difficult to obtain robust and intact films.

To further improve the mechanical property of the organic−inorganic hybrids, appropriate selection of precursor with sufficient hydrophilicity is important. GPTMS is a modified sol−gel precursor containing an epoxide ring, and GPTMS-based hybrids are among the most successful organic−inorganic materials.[31,32] Under acidic conditions, the hydroxyl group directly linked with a silicon atom in TEOS hydrolysate is unstable due to its self-condensation, endowing the inorganic sols with less hydrophilicity. However, the opening of epoxy ring in GPTMS allows the formation of hydroxyl group linked with silicon atom by inert Si−C chemical bond compared with Si−OH bond, endowing the inorganic sols with good hydrophilicity. If this sol is blended with water-borne cPANI in water/ethanol solution, the GPTMS sol should show good compatibility with the organic polymer. On the basis of this consideration, GPTMS is chosen as the inorganic precursor herein to form free-standing, robust, and intact conductive films with water-borne cPANI.

Results and Discussion

Electrical Conductivity of the cPANI/GPTMS Hybrids. Figure 1 shows the dependence of the electrical conductivity of cPANI/GPTMS hybrid films on cPANI volume fraction. The electrical conductivity displayed a sharp increase with the increasing cPANI loading up to 33 v/v %. When cPANI loading was 12 v/v

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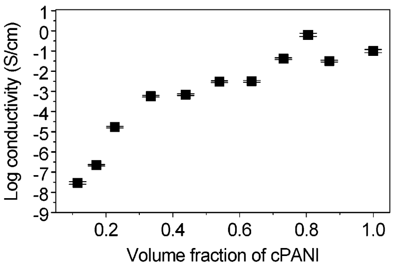
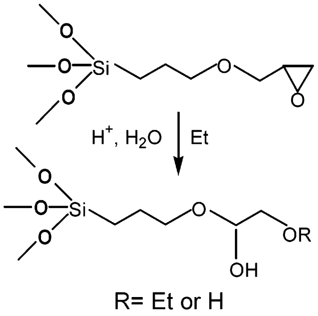


Figure 1. Dependence of logarithmic conductivity of the hybrid films on cPANI volume fraction.

Scheme 1



%, it was only 2.9×10^{-8} S/cm, and it showed a 3 orders of magnitude increase to 1.7×10^{-5} S/cm when cPANI loading was 23 v/v %. It should be noted that the actual polyaniline loading was only 2.1 v/v % since the cPANI consisted of polyaniline in 9 v/v % and high bulk acidic phosphate in 91 v/v %. As a comparison, the electrical conductivity percolation threshold in cPANI/silica hybrids is 6.5 v/v % polyaniline loading,[30] where the cPANI loading is 32 v/v %. Moreover, the electrical conductivity at percolation threshold is 3×10^{-8} S/cm for cPANI/silica hybrids, which is 3 orders of magnitude lower than that for cPANI/GPTMS hybrids (1.7×10^{-5} S/cm). In addition, the hybrid films made from cPANI/GPTMS were more intact and robust than those from cPANI/silica hybrids.

Interaction between cPANI and GPTMS. As shown in Scheme 1, the epoxy ring of GPTMS can react with water or alcohol in acidic condition to form a hydroxyl group.[33] The terminal hydroxyl groups may enhance the hydrophilicity of the inorganic sols, which make themselves well compatible with water-borne conductive polyaniline. Moreover, the ether groups and $-P{=}O$ groups in dopant as well as amine groups in the polyaniline backbone tend to form hydrogen bonding with the terminal hydroxyl groups in GPTMS sols. These hydrogen bonds may be beneficial for cPANI to be well dispersed into GPTMS and form the conductive network during the sol–gel process, leading to lower electrical conductivity percolation threshold for polyaniline loading. In the meantime, thanks to these hydrogen bonds, the organic and inorganic components can form intact films with less internal stress during the sol–gel process. As a comparison, in the cPANI/TEOS hybrids, though the hydrogen bonds between the silanol groups of the hydrolysate of TEOS and cPANI have been confirmed,[30] the silanol groups are more prone to self-condense to form Si–O–Si units than form hydrogen bonds with the organic polymer during the sol–gel process, leading to the phase separation between TEOS sols and water-borne cPANI, and aggregates of the two components in addition to interpenetrating networks are formed. Therefore, the electrical conductivity percolation threshold for polyaniline loading in cPANI/TEOS hybrids is higher than that in cPANI/GPTMS hybrids.

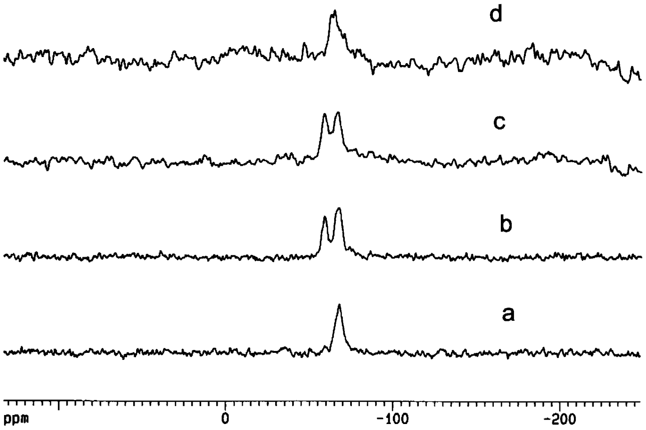


Figure 2. ^{29}Si-MAS NMR of cPANI/GPTMS hybrids with different cPANI loading: (a) 0, (b) 17, (c) 28, and (d) 54 v/v %.

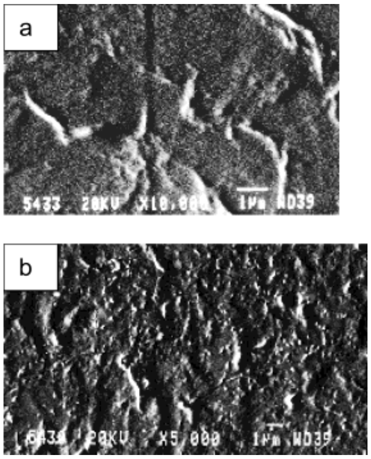


Figure 3. SEM images of pure cPANI (a) and cPANI/GPTMS hybrids (b, volume ratio: 44:56).

Figure 2 is the solid-state ^{29}Si-MAS NMR for the hybrids with different cPANI loading. For the pure GPTMS, as shown in Figure 2a, there is only one peak assigned to T_3-type silicon at −67.8 ppm, where the subscript denotes the number of bridging oxygens surrounding the central silicon atom. For the cPANI/GPTMS hybrids, as shown in Figure 2b–d, additional peaks located at −58.3 ppm in addition to −67.8 ppm were observed, which were assigned to linear T_2-type silicon.[34] The relative ratio of peak intensity of T_2 to T_3 (T_2/T_3) increased with increasing cPANI loading. It was 0.6 for 17 v/v % of cPANI (Figure 2b) and became 0.9 for 28 v/v % of cPANI (Figure 2c). When cPANI loading in hybrids was 54 v/v % (Figure 2d), accompanying the weakening of T_3 signal and strengthening of T_2 signal, there was an overlap between T_2 and T_3 signals in the spectrum, and the T_2/T_3 value approached 1.0. These changes were quite reasonable considering that hydrogen bonds between the conductive polyaniline and inorganic component existed in the whole sol–gel process. The strong hydrogen bonding between organic particles and inorganic sols effectively prevented GPTMS sols from aggregating to completely condense, leading to decrease of three-dimensional network and increase of linear structure. Introducing more conductive polymers into the hybrids resulted in more incomplete condensation of GPTMS sols, which raised the content

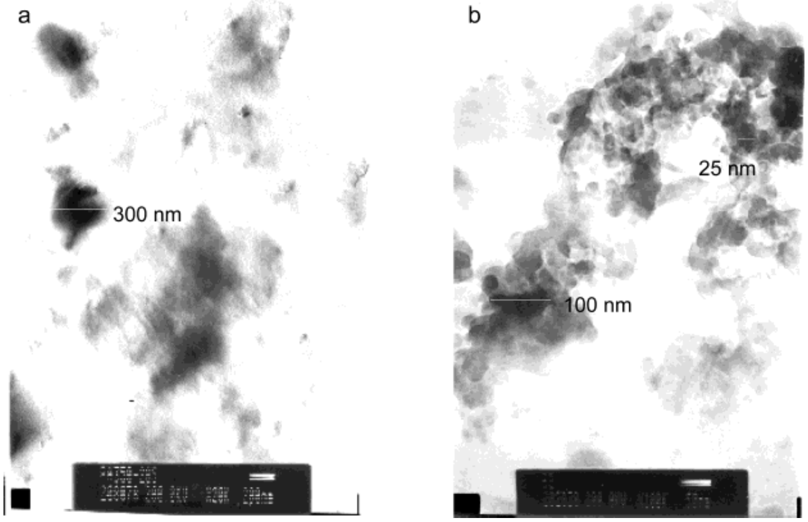


Figure 4. TEM images of pure cPANI (a) and cPANI/GPTMS hybrids (b, volume ratio: 44:56).

of T_2 species. These changes of T_2/T_3 value with different cPANI loading also indicated the fine dispersion of cPANI in the inorganic network. It is noteworthy that the ratio of T_2/T_3 should remain constant regardless of cPANI loading, if the two phases aggregated separately.

The interaction between organic and inorganic components also resulted in the changes of the morphology of cPANI in the hybrids. The SEM images of cross sections of cPANI/GPTMS hybrids are shown in Figure 3. There exist fiberlike domains in pure cPANI (Figure 3a); they become smaller and are more homogeneously dispersed in the matrix when the GPTMS content was 56 v/v % in the hybrids (Figure 3b). It is reasonable considering that the strong hydrogen bonds between organic and inorganic components may help cPANI to be well dispersed in the inorganic networks during the sol−gel process.

The above morphology is further studied by TEM images. As shown in Figure 4, the domain size in the pure cPANI (Figure 4a) was larger than 300 nm, while that in the cPANI/GPTMS hybrids (Figure 4b, volume ratio: 44/56) was within the range of 25−100 nm. The morphology is consistent with the existence of strong hydrogen bonds between cPANI and GPTMS. It was noteworthy that the raspberry domain in Figure 4b was composed of GPTMS surrounded by cPANI, the cPANI chains knotted together to form the conducting pathways, analogous to a conductive network.[35] This morphology gives a reasonable explanation on the smooth onset of electrical conductivity shown in Figure 1.

It is interesting to notice that the electrical conductivity of pure cPANI was only 0.1 S/cm, but it increased to 0.6 S/cm for the hybrids with 19 v/v % of GPTMS gel. This phenomenon was also observed by Wessling in cPANI/PMMA blends and in our earlier work.[30,36] This is attributed to the good dispersion and self-assembly of the conductive polyaniline networks in the inorganic entity,[37] as shown from SEM and TEM images.

Electrical Conductivity Stability of the cPANI/GPTMS Hybrids. Pure cPANI film is poor in water resistance, since its film is easy to be broken upon 1 day of water soaking. To evaluate the electrical conductivity stability of the hybrids, the hybrid films were soaked in water for 14 days, where the water was refreshed every 24 h. Two hybrids films with cPANI loading of 33 and 44 v/v %, respectively, were chosen for this experiment. As shown in Figure 5, each sample has a platform at the first stage of soaking, indicating good resistance to water soaking. For the hybrids with cPANI loading of 33 v/v %, the electrical conductivity kept almost constant until 7 days, while it started to decrease after 6 days of soaking for the hybrids containing 44 v/v % cPANI. The reason probably lies in the degree of cross-linking of the inorganic network, which decreases with increasing cPANI loading, as described earlier from ^{29}Si-MAS NMR spectra. Therefore, the hybrids containing 33 v/v % cPANI showed better confinement to cPANI chains than those containing 44 v/v % cPANI.

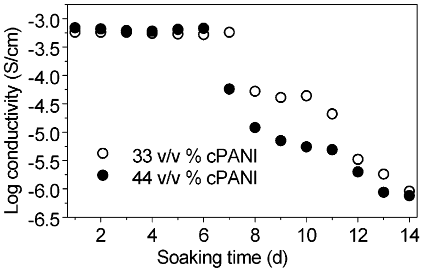


Figure 5. Plots of logarithmic conductivity of the hybrid films against soaking time in water. cPANI loading is 33 v/v % (open circle) and 44 v/v % (solid circle).

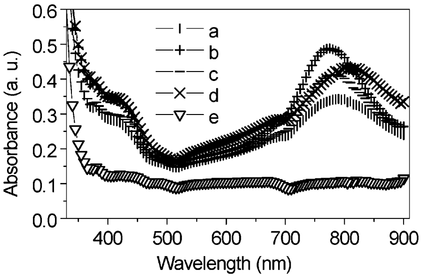


Figure 6. UV−vis spectra of cPANI/GPTMS solutions with different cPANI loading: (a) 100, (b) 23, (c) 44, (d) 64, and (e) 0 v/v %.

It is encouraging that the solutions containing waterborne cPANI and GPTMS sol were very stable. No precipitation was observed in the solution after 4 months. As shown in their UV−vis spectra (Figure 6b−d), which were quite similar to that of freshly prepared cPANI solution (Figure 6a), where intensive absorption bands at 420 and 780 nm characteristic of cationic radical in the conductive polyaniline were observed,[38,39] indicating that the interaction between dopant and polyaniline was hardly changed before sol−gel process despite the addition of GPTMS sol. This solution stability was very important for many practical applications.

Concluding Remarks

A facile route has been developed to prepare free-standing conductive hybrid films using GPTMS as inorganic precursor and cPANI as functional organic polymer via in-situ hydrolysis and condensation. The hybrid films showed much improvement in the electrical conductivity stability against water soaking. Moreover, unlike conventional methods, the cPANI/GPTMS hybrids were prepared from the water/ethanol system, which was an environment-benign approach. In comparison with cPANI/silica hybrids, it was easy to obtain intact films using GPTMS as inorganic precursor since GPTMS can form strong hydrogen bonds with cPANI during the sol−gel process, and the conductivity percolation threshold was as low as 2.1% of polyaniline volume loading. ^{29}Si-MAS NMR spectra and SEM and TEM images demonstrated that it was easy to manipulate the level of the dispersion of the two components and the size of conductive domains by this approach.

Experimental Section

Materials. (3-Glycidoxypropyl)trimethoxysilane (GPTMS) and poly(ethylene glycol monomethyl ether)-350 (PEGME-350, where 350 is the average molecular weight of the ether oligomer) were of analytical purity purchased from Acros Co. $POCl_3$ was used after distillation. Polyaniline emeraldine base was the product of Zhengji Tech. Co. licensed under this laboratory. Ethanol and formic acid were of analytical purity and used without further treatment; distilled water was used in all the experiments.

Preparation of Water-Borne cPANI. The acidic phosphate (PA-350) was synthesized according to Imokwa method from the reaction of $POCl_3$ and PEGME-350.[40] The acidity value of PA-350 determined by potentiometric titration was 1.8×10^{-3} mol/mL. The cPANI solution was obtained by adding distilled water to PANI/PA-350 complex at 50 °C under vigorous stirring for 2 h.[41] The resultant solution was filtered through a glass funnel with apertures of 30−50 μm before it was blended with GPTMS sol.

Preparation of GPTMS Sol−Gel Precursor. The hydrolysis−condensation of GPTMS was catalyzed by formic acid in ethanol (Et)/water solution. The molar ratio of GPTMS/Et/H_2O/HCOOH was 1:5:4:0.1. The sol−gel solution was stirred vigorously at 60 °C for another 2 h before it was blended with water-borne conductive polyaniline.

Preparation of Conductive Hybrids. Stoichiometric sol−gel solution was added dropwise to the aqueous conductive polyaniline solution at 50 °C under vigorous stirring. The mixture was stirred for another 24 h before film casting on polyester substrate at room temperature. After gelation, the samples were then transferred to a vacuum oven at 50 °C for 7 days for thorough drying. The thickness of final films was 0.1−0.2 mm.

Measurements. Electrical conductivity of the hybrid films was measured by standard four-probe method. The solid-state ^{29}Si-MAS NMR spectra were recorded at 79.45 MHz on a Bruker AV-400 NMR spectrometer using tetramethylsilane (TMS) as the internal standard. UV−vis spectra were recorded by a Cary 50 Bio UV−vis spectrophotometer. The morphologies of the conductive films were examined by a JEOL-JXA-840 scanning electron microscope (SEM) and a JEOL JEM-2010 transmission electron microscope (TEM). Samples for SEM were cryofractured in liquid nitrogen, and the fracture surfaces were sputter-coated with gold to create better contrast. Samples for TEM were prepared by drop-casting of diluted hybrid solutions on carbon-coated copper grids and allowing them to dry freely.

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(41) Notes: Generally, the molar ratio of H^+ in PA-350 to phN- in PANI was only 0.5 in pure cPANI solution. However, precipitation was observed when GPTMS sol was added, especially when cPANI loading was below 23 v/v %. The final film became blue, indicating that dedoping has happened. This is probably caused by the strong hydrogen bonds between the dopant and GPTMS sol. Therefore, the molar ratio of H^+ in PA-350 to phN- in PANI was raised from 0.5 to 0.75 to avoid the dedoping when cPANI loading was above 54 v/v %, where the PANI loading in the complex was 14 v/v %. It became 1.25 when cPANI loading was lower than 54 v/v %, and PANI loading in the complex was 9 v/v %.

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