

CONFINING CONDUCTING POLYANILINE IN A STABLE INORGANIC NETWORK*

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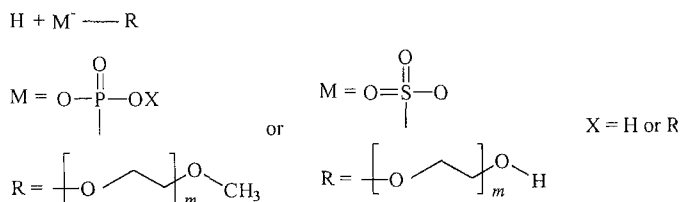
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Abstract Water soluble conducting polyaniline with electrical conductivity of 10^{-1} – 10^{-2} S/cm was prepared employing dopant induced water solubility technology. The water resistance of the conducting film was significantly improved employing sol-gel hybrids method, especially when the conductive polyaniline loading was below 30 wt%. The reason for the improvement is that the conducting polyaniline chains are confined in a stable inorganic network.

Keywords Conducting polyaniline, Sol-gel hybrids, Water resistance

INTRODUCTION

Conducting polyanilines have been regarded as tractable polymers suitable for melt processing and solution processing^[1, 2]. As far as solution processing is concerned, the counter-anion induced processability is a powerful aid. Conducting polyaniline has been made soluble or dispersible in many organic solvents of a wide range of polarity from *m*-cresol to xylene. However, with increasing environmental concern, water-borne conducting polyaniline is required. Early reports focus mainly on modification of parent polyaniline by sulfonic acid or acetic acid groups to obtain water soluble conducting polyaniline^[3]. In addition to being complicated, the preparation process is accompanied by loss of electrical conductivity of the final products. When dopants, like acidic phosphate esters, having many long hydrophilic ethylene oxide units were used (Scheme 1), conducting polyaniline could be made water soluble, but the water resistance of the electrical conductivity of the final film was not satisfactory^[4, 5].



Scheme 1 Hydrophilic acidic phosphate esters used as dopant of polyaniline

One way to improve the water resistance of the conducting film is to confine the conducting polymer chains in a stable network. Since the organic/inorganic hybrids have the processability of organic materials as well as the

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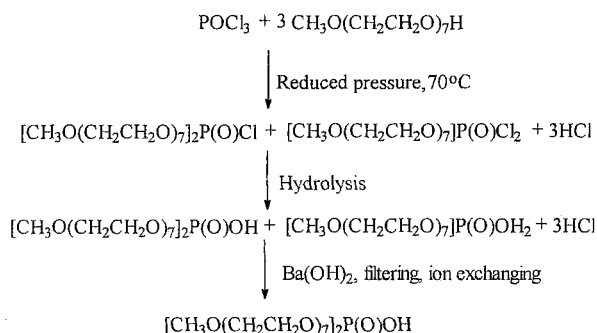
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abrasion-resistance and high adhesion properties of inorganic materials, conductive organic/inorganic hybrids should be a good solution^[6, 7]. In this work, by means of the organic-inorganic hybridization strategy, the conducting polyaniline chains were confined in an inorganic network to improve their water resistance.

EXPERIMENTAL

Polyaniline emeraldine base was prepared by chemical oxidation of aniline in aqueous HCl solution using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as oxidant, followed by treatment with ammonia^[8]. The acidic phosphate ester with long hydrophilic tail was prepared by esterification of poly(ethylene glycol) monomethyl ether (average molecular weight of 350) with POCl_3 according to Scheme 2^[9].



Scheme 2 Preparation and purification of phosphate ester (PA)

Polyaniline emeraldine base was doped with the acidic phosphate ester in a suitable doping ratio in distilled water. The conducting polyaniline film was prepared by casting the solution onto a glass plate and drying at 50°C .

The aqueous conducting polyaniline solution was used to make conductive organic-inorganic hybrids by reacting with organic silicates like tetraethyl orthosilicate (TEOS) in water/ethanol solution for a certain time. The choice of organic silicates is of key importance to assure high quality of conductive hybrids.

The electrical conductivity of the hybrid films was measured by the standard four-probe technique on a Keithley 6517A Electrometer/High Resistance Meter and a Keithley 2182 Nanovoltmeter. The FTIR spectra were recorded on a BIO-RAD FTS-7 spectrometer using KBr pellets. ^{29}S MAS NMR spectra were recorded at 7.4 MHz on a JEOL FX-200 spectrometer using tetramethylsilane as reference. The morphology of the conductive hybrid films was obtained by using transmission electron microscopy (TEM, JEOL JEM-2010).

RESULTS AND DISCUSSION

Phosphate mono-ester (PA) was used as dopant of polyaniline. The electrical conductivity of the conductive film depends on the ratio of PA to aniline units in polyaniline. When the ratio was below 0.2, the conductive polyaniline was neither soluble nor dispersible in water; its electrical conductivity was below 10^{-4} S/cm. When the ratio was between 0.2 and 0.45, the conductive polyaniline was dispersible in water, with an electrical conductivity of 10^{-3} – 10^{-2} S/cm. The conductive polyaniline became soluble in water when the ratio was over 0.5. The maximum electrical conductivity was obtained when the ratio was 1.5, and the conductive polyaniline film displayed an electrical conductivity of 8.2×10^{-1} S/cm. However, with the increase of the ratio of PA to polyaniline, the increase of electrical conductivity was accompanied by a decrease of water resistance. When the conductive polyaniline film with the ratio of 0.5 was soaked for one week and flushed with water, its mechanical properties quickly deteriorated until the whole film broke into pieces. Moreover, the electrical conductivity dropped sharply, it was only 10^{-5} S/cm when the film was soaked for one week, which was 3–4 orders of magnitude lower compared with the as-made film. Therefore, it is urgent that the water resistance of electrical

conductivity as well as the mechanical properties of the conductive film should be improved for further use.

The sol-gel process was carried out using conductive polyaniline and organic silicate. The gelation time of the silicate was an important parameter for the sol-gel process. As shown in Fig. 1, the gelation time was found to be dependent on the loading of conducting polyaniline (cPAn). It decreased significantly with increasing cPAn loading, from 35 days for pure TEOS to 7 days for 20 wt% cPAn loading, and to 2 days for 30 wt% cPAn loading. There was no significant change in gelation time when the cPAn loading varied from 30 wt% to 80 wt%; however, it started to increase when the cPAn loading was over 80 wt%.

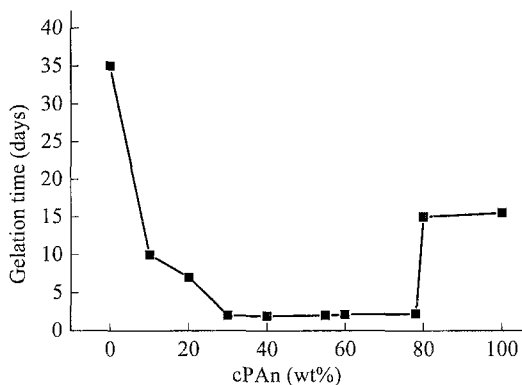


Fig. 1 Dependence of gelation time on cPAn loading

The acceleration of the gelation process may be due to the weak acidity of cPAn, which accelerated the hydrolysis and condensation of TEOS.

A broad valley of gelation time against cPAn loading was observed when the cPAn loading was in the range of 30 wt% to 80 wt%. One possible reason is that the maximum acid catalysis effect has been reached when the cPAn loading is 30 wt%. It should be noted that the aqueous cPAn solution undergoes a much slower gelation process than the TEOS solution, more cPAn loading may enhance the diluting effect on gelation of TEOS. It becomes more manifest when the cPAn loading is over 80 wt%, where the gelation time again increases.

It is quite important that the morphology of conductive domains in the hybrids changes significantly compared with that in pure conductive polyaniline samples. Figure 2 shows the TEM images of the pure conductive polyaniline film and hybrids with cPAn loading of 46 wt%. The conductive domain size of as-made pure conductive polyaniline films was around 300 nm, whereas that of cPAn/SiO₂ hybrids with 46 wt% of cPAn loading decreased to 20–200 nm. This may be caused by the hydrogen bonding between organic and inorganic moieties, which reduced the aggregation opportunity of conductive polyanilines. The hydrogen bonds among the silanol groups of the hydrolysate of TEOS and ether oligomers, —P=O groups of phosphate ester, or the amino group in conductive polyaniline, have been confirmed in the FTIR spectra of the hybrids^[6]. It is supposed that the hydrogen bonding should benefit the homogeneous formation of organic/inorganic hybrids. The decrease in conductive domain is also beneficial in reducing the electrical conductivity threshold percolation.

As can be seen from Fig. 2, the morphology of the cPAn/SiO₂ hybrids shows a star-like structure, which is quite different from the raspberry morphology well observed in PAN/SiO₂ from *in-situ* polymerization of aniline monomer in inorganic media^[10, 11]. The star-like morphology of the hybrids is also beneficial in reducing the electrical conductivity threshold percolation.

The interaction between organic and inorganic moieties was further supported by ²⁹Si MAS NMR spectra. As shown in Fig. 3, ²⁹Si MAS NMR spectra with various cPAn loadings showed three distinct peaks at $\delta = -90$, -101 , and -110 , corresponding to Si(OSi)_x(OH)_{4-x} framework units Q^x with $x = 2, 3$ and 4 , respectively^[6]. The chemical shifts of the Q^x are also listed in Table 1. The hydrolysis product of TEOS had a broad band around $\delta = -110$ characteristic of Q⁴ species, whereas the hybrids displayed peaks of Q², Q³ and Q⁴, respectively. The ratio

of peak intensity of Q^3 to Q^4 (Q^3/Q^4) increased with increasing cPAn loading. It was 0.84 for 20 wt% of cPAn loading, and 1.17 for 54 wt% of cPAn loading. The intensity of the Q^3 moiety exceeded that of Q^4 when the cPAn loading was 40 wt%; probably due to the strong hydrogen bonding between conductive polyaniline and inorganic moiety. Increasing cPAn loading in the hybrids may cause more incomplete condensation of silicate, resulting in more Q^3 moiety. As a reference, only a single broad peak at $\delta = -110$ existed in the pure TEOS system due to the complete cross-linking process. The change of Q^3/Q^4 ratio with cPAn loading reflected the good dispersion of cPAn in the inorganic network, otherwise the Q^3/Q^4 ratio should be constant once the two components aggregated with each other.

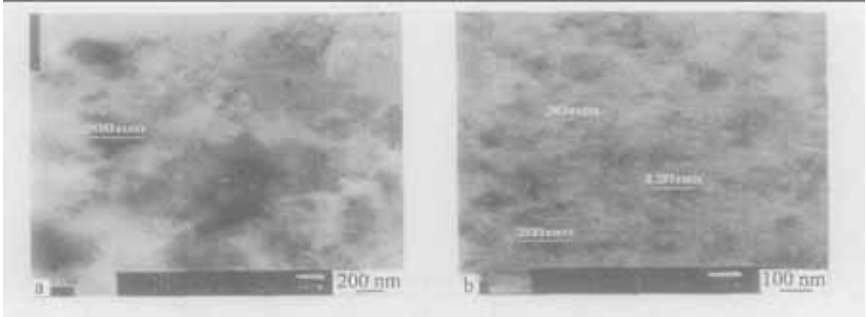


Fig. 2 TEM images of the pure conductive polyaniline film (a) and cPAn/SiO₂ hybrids with 46 wt% of cPAn loading (b)

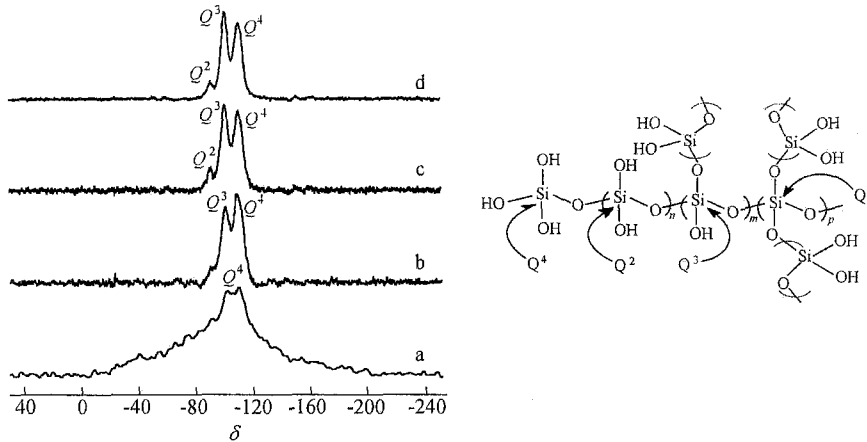


Fig. 3 ²⁹Si MAS NMR spectra of the hybrids with various cPAn loadings a) 0; b) 20 wt%; c) 40 wt%; d) 54 wt%

Table 1. ²⁹ Si MAS NMR data of cPAn/silica composites						
Sample	cPAn/SiO ₂	Q ⁴	Q ³	Q ²	Q ¹	Q ³ /Q ⁴
A	0/100	-110.41	—	—	—	—
B	20/80	-109.14	-101.44	-90.01	—	0.84
C	40/60	-110.35	-101.09	-91.07	—	1.10
D	54/46	-109.85	-100.67	-90.80	—	1.17

The electrical conductivity of the above cPAn/TEOS hybrids depends on the cPAn loading. As listed in Table 2, it is below 10^{-15} S/cm for pure silica, and increases to 2.2×10^{-8} S/cm for 10 wt% cPAn loading. It further increases to 1.6×10^{-4} S/cm for 20 wt% cPAn loading, and reaches a conductivity platform at a value of 4.6×10^{-2} S/cm when the cPAn loading is between 30 wt% and 80 wt%. The electrical conductivity percolation

threshold of the hybrids is at around 20 wt% cPAn loading, or 4.3 wt% polyaniline loading.

The above hybrid film was soaked in water. Its electrical conductivity was measured after one week, and the results are listed in Table 2. The electrical conductivity loss was less than 20% when the cPAn loading was below 20 wt%. As a reference, the pure conductive polyaniline showed a 3–4 order of magnitude loss of conductivity. However, when the cPAn loading was 30 wt%, the conductivity loss upon soaking was over 40%. As described earlier, the hybrids in this cPAn loading had more Q^3 structure, and cross-linking of the inorganic moiety was incomplete. Therefore, the conductive polyaniline chains failed to be completely confined in the inorganic network, leading to a significant conductivity loss.

Table 2. The change of the electrical conductivities of the hybrids before and after water soaking^a

Sample cPAn loading (wt%)	Electrical conductivity (S/cm) (Before soaking)	Electrical conductivity (S/cm) (After 7 days of soaking)
0	$< 10^{-15}$	$< 10^{-15}$
10	2.2×10^{-8}	2.2×10^{-8}
20	1.6×10^{-4}	1.4×10^{-4}
30	4.6×10^{-2}	2.5×10^{-2}
50	4.8×10^{-2}	6.1×10^{-3}
60	4.6×10^{-2}	3.1×10^{-4}
80	4.6×10^{-2}	1.3×10^{-4}
100	8.2×10^{-2}	2.2×10^{-5}

^a The molar ratio of phosphate ester to aniline unit in polyaniline was 0.5.

Though the organic-inorganic hybrids can improve the water resistance of the conducting polyaniline, this is limited only to the low cPAn loading hybrids. To further improve the water resistance of the hybrids, various precursors of inorganic moieties are chosen. The molar ratio of PA to aniline in polyaniline was 0.5; the results from corresponding sol-gel process are listed in Table 3. It can be seen from Table 3 that methyltriethoxysilane (MTES, $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$) showed good sol stability, and the film formed from cPAn/MTES was homogeneous, intact and tough.

Table 3. Sol-gel process of cPAn/organic silicates

Sol-gel precursor	Stability of sol	Film formation
$\text{Si}(\text{OC}_2\text{H}_5)_4$	Very stable	Brittle, but homogeneous
$\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$	Stable	Intact and tough, homogeneous
$\text{C}_2\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3$	Stable	Intact, but serious phase separation
$\text{C}_4\text{H}_9\text{Si}(\text{OC}_2\text{H}_5)_3$	Unstable	Difficult
$\text{C}_8\text{H}_{17}\text{Si}(\text{OC}_2\text{H}_5)_3$	Unstable	Difficult
$\text{HSC}_3\text{H}_6(\text{OCH}_3)_3$	Unstable	Difficult
$\text{C}_6\text{H}_5\text{Si}(\text{OCH}_3)_3$	Stable	Intact, serious phase separation

Table 4. Main properties of the cPAn/MTES hybrids

cPAn (wt%)	Electrical conductivity (S/cm)	Electrical conductivity (S/cm, upon 7 days soaking)	Film formation
10	1.3×10^{-5}	1.1×10^{-5}	Intact, transparent
20	9.0×10^{-4}	8.4×10^{-4}	Intact, transparent
40	6.8×10^{-2}	3.1×10^{-3}	Intact, opaque
60	6.6×10^{-2}	2.1×10^{-4}	Brittle upon soaking
80	6.6×10^{-2}	2.1×10^{-4}	Brittle upon soaking

Therefore, MTES was chosen to make hybrids with cPAn. Table 4 lists the main properties of the hybrids at various cPAn loadings. Combining the results from Table 4 and Table 2, it is concluded that the electrical conductivity of the cPAn/MTES hybrids is 1–2 orders of magnitude higher than that of the cPAn/TEOS hybrids. Moreover, the water soaking property of cPAn/MTES hybrids is much better than that of cPAn/TEOS hybrids.

Therefore, incorporation of hydrophobic methyl group in the organic silicate is beneficial in improving the film formation property, the conductivity as well as the water resistance property. It should be noted that larger hydrophobic groups like ethyl, butyl, octyl, and phenyl groups fail to give satisfactory results, probably because their hydrophobic properties are too strong.

CONCLUSIONS

Conducting polyaniline was made water soluble employing dopant induced water solubility technology. Water resistance of the conducting film was significantly improved by employing the sol-gel hybrid method, especially when the conductive polyaniline loading was below 30 wt%. Methyl triethoxy silane proved to be a better candidate than tetraethyl orthosilicate to confine the conducting polyaniline chains in the inorganic network.

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