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Conductive polyaniline/poly(vinylphosphonic acid) blends

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Summary

In-situ polymerization of aniline in poly(vinylphosphonic acid) (PVPA) resulted in conductive polyaniline/PVPA blends with conductivities in the order of 10^{-2} S/cm. The blends were characterized by FTIR and UV-vis spectroscopy. Thermogravimetric analysis showed that the blends have good thermal stability.

Introduction

Polyaniline (PANI) has received considerable attention due to its simple synthesis, good environmental stability and adequate level of electrical conductivity (1-3). The reversible control of its electrical properties by either changing the oxidation state of the backbone or via protonation of the imine nitrogen atoms makes PANI unique among the conducting polymers (4,5). In recent years, much effort has been made to improve the solubility and processability of PANI. These approaches include the polymerization of ring- or N-substituted aniline derivatives (6-8) and the use of functionalized protonic acids as dopants (9-11). Conventional PANI doped with HCl is susceptible to de-doping due to the small size of the dopant which can evaporate or sublime out of the polymer. The evolution of corrosive HCl can cause damage to equipment and pose a health hazard. The use of larger molecular size dopants, e.g. alkyl sulfonic acid, has been shown to be less prone towards de-doping. However, over time, the dopants may be phase segregated from the polymer, especially so when the temperature is high. This would inevitably lead to a decrease of conductivity. To circumvent this problem, polymeric-type protonating agents are used instead. The polyelectrolyte molecules are believed to form inter-twisted strand with PANI, improving the resistance towards de-doping. Aniline has been polymerized chemically or electrochemically in polyelectrolytes such as poly(acrylic acid) (PAA), poly(vinylsulfonic acid), poly(amic acid) and poly(styrenesulfonic acid) (12-19). Phosphonic acids which are thermally stable and non-volatile are good dopant candidates for PANI (20). Poly(alkylene phosphate)s have also been reported to be good dopants for PANI (21,22).

In this communication, we report the preparation and characterization of PANI/poly(vinylphosphonic acid) (PVPA) blends. PVPA was used in view of its good solubility in water, adequate acidity and thermal stability. PANI/PVPA blends were prepared by *in-situ* polymerization of aniline in PVPA. We have recently reported that similar to PAA, PVPA is also able to form interpolymer complexes with poly(vinylpyridine)s (23).

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Experimental

Materials

Aniline (from Aldrich) was double distilled and stored under a nitrogen atmosphere in the dark prior to polymerization. PVPA was obtained from Polysciences, Inc. The molecular weight information of PVPA is not available. Other reagents were used as received.

Preparation of blends

Aniline (43 mmol) was dissolved in 60 mL of 0.2 M aqueous PVPA solution and the aniline solution was cooled to 0-5°C in an ice bath. Ammonium persulfate (4.3 mmol) dissolved in 40 mL of 0.2 M aqueous PVPA solution was added dropwisely to the aniline solution. The reaction mixture was stirred continuously for 4 h before the precipitated PANI salt was filtered and washed repeatedly with cold 1:2 isopropanol/water solution. The molar ratio of PVPA to aniline in the feed corresponded to 1:2 and the resulting blend was designated as blend **I**. Blends **II** and **III** with PVPA:aniline ratios of 1:1 and 2:1 in the feed, respectively, were similarly prepared. All the blends were subsequently dried *in vacuo* at 30°C for at least 2 days. PANI-HCl was similarly prepared by polymerization of aniline in HCl solution. PANI-base was obtained by treating PANI-HCl with ammonia solution.

Characterization

The polymer samples were analyzed for their compositions using a Perkin-Elmer 2400 CHN analyzer and a Plasmascan 710 ICP for phosphorus content.

Thermogravimetric measurements were made on a TA Instruments 2100 system equipped with a TGA 2950 thermogravimetric analyzer. Samples were heated with a rate of 10°C/min under air purge at 50 mL/min.

Fourier-transform infrared (FTIR) spectra were obtained using a Perkin-Elmer 1600 FTIR spectrophotometer. Sixty-four scans were signal averaged at a resolution of 2 cm^{-1}. Samples were prepared by dispersing the polymer in KBr to form discs. To minimize the absorption of moisture, measurements were made at 80°C using a high-temperature cell.

UV-vis spectra of DMSO solutions of polymer blends were acquired on a Hewlett-Packard Model 8452A diode array spectrophotometer.

Conductivity measurements were carried out on a four-point probe connected to a Keithley voltmeter constant-current source system. The polymers were compacted into pellets for measurements. The reported conductivity values were the averages of at least ten pairs of reading at different parts on both sides of the pellets.

Results and Discussion

The various PANI/PVPA blends were greenish in color which is typical for doped PANI. Table 1 shows the compositions and electrical conductivity values of various blends. The conducting PANI emeraldine salt, in the idealized situation, would have all the imine nitrogen protonated. This implies that one out the two PANI repeating units will be protonated. Thus, two moles of N would require just one mole of P to achieve a fully doped state. This, however, is an ideal state where doping is not hampered by steric constraint or the dopants are not dissolved off during washing. On the other hand, inter-twisting between PANI and PVPA chains may results in higher than the ideal N/P ratio. As shown in Table 1, the P/N ratios in blends **I** and **II** are quite close to the ideal ratio of 0.5. For blend **III**, there could still be quite an excess of PVPA not acting as dopant for PANI, leading to a higher P/N ratio of 0.66. All the blends contained only trace amounts of sulfur.

Table 1. Characteristics of PANI/PVPA blends

	Composition	Conductivity (S/cm)
Blend I	$C_{7.08}H_{9.68}N_1P_{0.43}S_{0.058}$	2.1 x 10^{-2}
Blend II	$C_{7.15}H_{9.76}N_1P_{0.45}S_{0.055}$	2.3 x 10^{-2}
Blend III	$C_{7.47}H_{9.66}N_1P_{0.66}S_{0.058}$	5.3 x 10^{-2}

The FTIR spectra of PANI-base, PVPA, blend I and blend III are shown in Figure 1. The spectra of the blends, though dominated by the vibrational modes of the PANI backbone, are quite different from that of PANI-base. The quinoid absorption at 1570-1565 cm^{-1} is shifted downward by 10-20 cm^{-1} from 1585 cm^{-1} and is broadened. The benzenoid ring stretching mode at 1478 cm^{-1} is also shifted towards lower frequency by 10-20 cm^{-1} from 1496 cm^{-1}. Such low-frequency shifts are characteristics of protonated PANI (24). The aromatic hydrogen in-plane bending at 1165 cm^{-1} is masked by the more intense absorption of the phosphonate anion absorption at 1000-1200 cm^{-1}, which overlaps with P=O vibration mode at 917-1040 cm^{-1}. These peaks superimpose each others, giving rise to a strong absorption around 1100 cm^{-1} and a shoulder at 1000 cm^{-1}. The spectra indicate that with PVPA as counter-ion, the PANI vibration structure has not been significantly perturbed.

The UV-vis spectra of PANI-base, blend I and blend III are shown in Figure 2. PANI-base shows two transitions at 320 nm (π_B-π^* transition of the benzenoid ring) and 611 nm (π_B-π_Q exciton absorption of the quinoid ring). The spectra of the blends are distinctly different from that of PANI-base. First of all, the intensity of the π_B-π_Q exciton absorption is drastically reduced. When the imine nitrogens in PANI-base are fully protonated, the nitrogen and its neighboring quinoid ring become a semiquinoid radical cation and, therefore, the exciton absorption peak disappears (17). In contrast, the exciton absorption peak still appears in PANI/PAA blends (17). The results suggest that PVPA is a better dopant than PAA. The peaks at 274 and 376 nm for the PANI/PVPA blends are attributed to π_B-π^* and low-lying π_B-π_S transitions, respectively. The appearance of a well-defined peak of the π_B-π_S excitation to polaron band further confirms the presence of semiquinoid structures in the blends.

The TGA curves for PVPA, blend III and PANI-HCl are shown in Figure 3. In general, the thermal degradation of the blend can be divided into three main weight loss steps. The first weight loss from room temperature to about 140°C is due primarily to the expulsion of absorbed water. For PANI-HCl, the second weight loss step from 140°C to 350°C can be attributed to the loss of HCl dopant. However, for the blends, this cannot be explained by the expulsion of the polymeric dopant as in the case of PANI-HCl. It has been reported that in this temperature range, condensation of phosphonic groups is activated with a loss of 1 mole of water for every 2 moles of P in forming a dimeric P-O-P species (20). The weight loss for PVPA in this temperature range corresponds well with the occurrence of condensation involving the expulsion of water. The third weight loss step from 350°C is attributed to the thermal oxidative degradation of the polymer backbone. For PVPA,

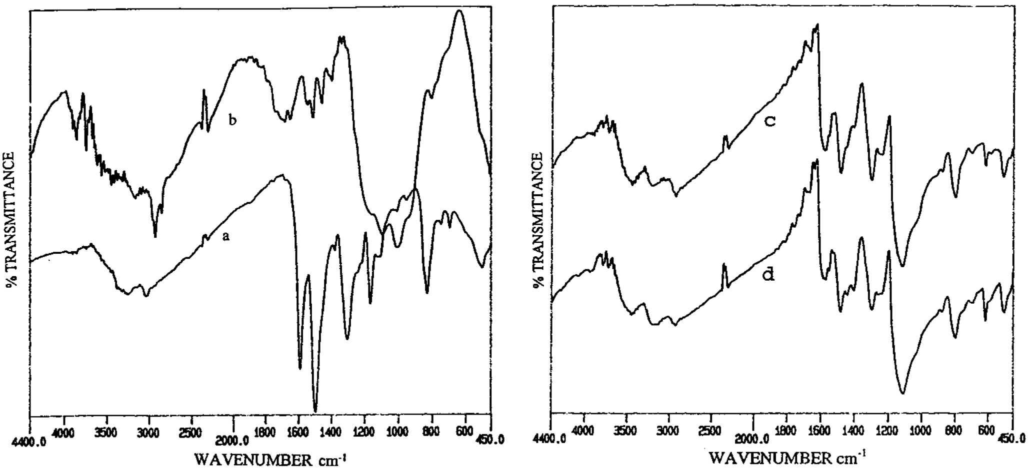

Figure 1. FTIR spectra of (a) PANI-base, (b) PVPA, (c) blend I and (d) blend III.

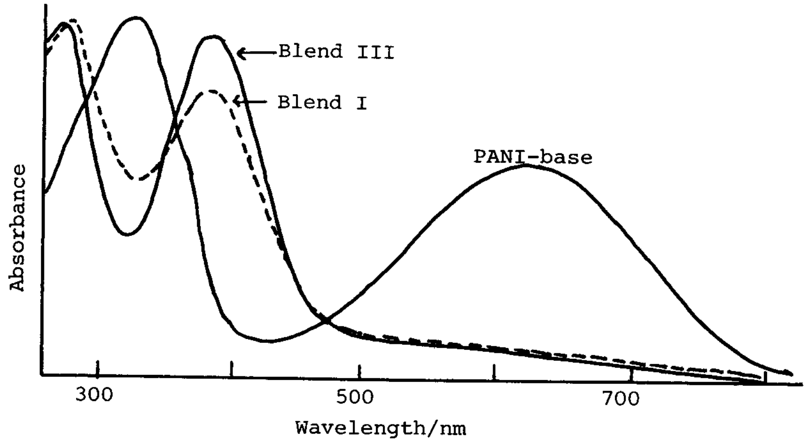

Figure 2. UV-vis spectra of PANI-base, blend I and blend III.

oxidation occurs at about 420°C, resulting in a slight increase in weight, and this is also observed for blend **III**. In the case of PANI-HCl, the third weight loss step occurs in a rather drastic manner, whereas the blends proceed in a more gentle mode of degradation. The enhanced thermal stability may be rationalized by the formation of cross-linkages when phosphonic acid undergoes condensation, which stabilizes the polymer against thermal decomposition.

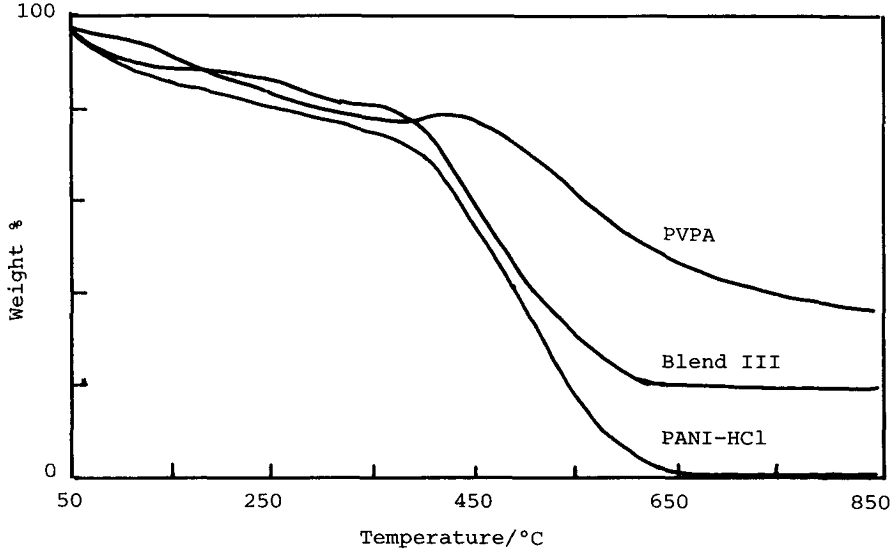

Figure 3. TGA curves of PVPA, PANI-HCl and blend **III**.

All the blends exhibit reasonably high conductivity values around 10^{-2} S/cm. The conductivities of these blends are 2 orders of magnitude larger than those of PANI/PAA blends (17). To study the possibility of de-doping of PANI through thermal elimination of dopant, the pelletized samples were subjected to isothermal heating at 120°C *in vacuo*. The conductivity of the sample was taken at various time interval and the results are tabulated in Table 2. A decrease of two orders of magnitude in conductivity for PANI-HCl after 2 h in air at 100°C was previously reported (25). Our study has shown that the conductivity of PANI-HCl subjected to isothermal heating *in vacuo* at 120°C also falls by two orders of magnitude. However, it is noted that although the conductivities of the blends are much lower than that of PANI-HCl prior to heating, the rate of decrease in conductivity is more gradual, falling by less than one order of magnitude. A more gradual decrease in conductivity for the blends is attributed to the non-volatility of PVPA. Nevertheless, the conductivities of PANI-HCl and the various PANI/PVPA blends are similar in magnitude after heating at 120°C for 4 hours.

Table 2. Effect of heating on conductivity

	PANI-HCl	Blend **I**	Blend **III**
Prior of heating	4.5×10^{0} S/cm	2.1×10^{-2} S/cm	5.3×10^{-2} S/cm
After 1 h at 120°C	6.4×10^{-1}	1.2×10^{-2}	1.8×10^{-2}
After 2 h at 120°C	3.2×10^{-2}	9.8×10^{-3}	9.7×10^{-3}
After 4 h at 120°C	8.8×10^{-3}	9.6×10^{-3}	9.7×10^{-3}

Conclusion

In-situ polymerization of aniline in aqueous PVPA solutions resulted in conductive blends with adequate conductivity in the order of 10^{-2} S/cm and good thermal stability.

Acknowledgment

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