Electrical and Structural Analysis of Conductive Polyaniline/Polyimide Blends

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ABSTRACT: Conducting films of dodecylbenzenesulfonic (DBSA)-doped polyaniline/ polyimide (PANI/PI) blends with various compositions were prepared by solvent casting followed by a thermal imidization process. Electrical and physical properties of the blends were characterized by infrared spectroscopy, an X-ray diffraction technique, thermal analysis, a UV-vis spectrophotometer, a dielectrometer, and conductivity measurements. The blends exhibited a relatively low percolation threshold of electrical conductivity at 5 wt % PANI content and showed higher conductivity than that of pure DBSA-doped PANI when the PANI content exceeded 20 wt %. A lower percolation threshold and a lower compatibility was shown between the two components in the blends than those of PANI–camphorsulfonic acid/polyamic acid (PANI–CSA/PAA). A well-defined layered structure due to the alignment of the long alkyl chain dopant perpendicular to the PANI main chain was evidenced by WAXD spectra. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2169–2178, 1999

Key words: polyaniline; polyimide; percolation threshold; blends; conductivity

INTRODUCTION

Polyaniline (PANI) is superior to other conducting polymers in that it is soluble and therefore processable in the conducting form, and it is both environmentally and thermally stable^{1,2} together with a high conductivity when it is doped by functionalized protonic acids like camphorsulfonic acid (CSA) and dodecylbenzenesulfonic acid (DBSA).³ The charged (SO₃⁻) head group of these dopants easily associates with the positively charged polymer backbone through Coulomb attraction, providing side-chain compatibility with organic solvents such as xylene, *m*-cresol, dimethyl sulfoxide, toluene, and chloroform in addition to *N*-methyl-2-pyrrolidone⁴ (NMP) (counterion-induced processability). Thus, conduct-

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ing polyblends can be made by codissolving the conducting PANI complex and a suitable matrix polymer in a common solvent and processing the conducting blend directly from a solution.

The fundamental requirement for creating these conducting polyblends is the need for a solvent in which both the conducting PANI complex and the desired bulk polymers are cosoluble. Given such a solvent, conducting polyblends can be made by codissolving the PANI complex and the bulk polymer at concentrations such that when cast from solution the resulting blends will have the desired ratio of the conducting PANI complex to the bulk polymer. That PANI doped by functionalized protonic acids like CSA and DBSA have a higher solubility together with much room for choosing of the solvent is also advantageous in making conducting polyblends. Thus, PANI-D-BSA or PANI-CSA can easily be blended with other bulk polymers by solvent blending or thermal processing.

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We already showed that PANI–CSA complexes could be well blended with polyamic acid (PAA) in the solution phase and prepared with films by solvent casting.⁵ Also, these PANI–CSA/PAA films were converted to PANI–CSA/PI films by a thermal imidization process. Likewise, PANI– DBSA/PAA films could also be prepared. DBSA was the more favorable dopant to the PANI complex in a NMP solvent.⁶ Also, it is thought that the long alkyl tail of DBSA is able to endow flexibility in the polymer chain. A structural change derived from the long alkyl tail of the dopant DBSA was also anticipated.

So, here, we report our observation of the electrical properties and structural analysis of PANI– DBSA/PAA films using pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) as a PAA matrix material and PANI–DBSA as a conducting material made by solution blending using NMP as a cosolvent. Also, PANI–CSA/PAA films were used for a comparison study.

EXPERIMENTAL

Chemicals

Aniline (Aldrich) was purified by distillation in a vacuum before use and ammonium peroxydisulfate $[(NH_4)_2S_2O_8]$, HCl, NH_4OH , and DBSA (Kando Chemical) were used as received. ODA (TCI) and PMDA (TCI) were recrystallized. NMP was used as received.

Preparation of PANI-DBSA/PI Blend Films

PANI powder was prepared by a conventional chemical method.⁷ A PANI–DBSA solution was obtained by mixing an emeraldine base powder with DBSA and dissolving it in NMP (1% w/w). The PANI : DBSA mixture molar ratio was 1 : 0.5 (H⁺/PhN = 0.5).⁶ After sonicating, the resulting solution was filtered to remove any undissolved particles. The weight of the undissolved particles of PANI was measured after being dried in a vacuum oven at 120°C for 1 day. The actual weight of the PANI in solution could be calculated by compensating for the weight of the undissolved particles.

PAA was synthesized by the following method: First, ODA (7.5 g) was dissolved in NMP (12.7 g) under N_2 purging at room temperature with stirring by a mechanical stirrer in a three-neck flask. PMDA (8.175 g) was dissolved in NMP (50 g) in another flask with minor heating. This was also added to the three-neck flask in which ODA was dissolved. After 12 h of stirring under N_2 purging, PAA, which is a precursor of polyimide (PI), was prepared.

Then, PANI–DBSA/PAA blend solutions were prepared by blending the PANI–DBSA solution with the PAA solution with proper weight ratios (PANI content 1, 2, 5, 10, 15, 20, 30, 50 wt %) which was determined by the volume ratio of an individual solution with the respective concentrations. PANI–DBSA/PAA films were prepared by solvent casting at 50°C under a vacuum. These PANI–DBSA/PAA films and pure PAA film were converted to the PI state by a thermal imidization process. PANI–DBSA film was prepared by solvent casting the PANI–DBSA solution in the same way as with PANI–DBSA/PAA.

Measurements

The electrical conductivity of the blend films was measured using the standard four-probe method, and for measuring the conductivity variation with temperature, a four-probe cell was inserted into a glass tube. Wide-angle X-ray diffraction patterns were taken with Ni-filtered CuK α radiation using a Rigaku Denki instrument. The scanning range was from 2 $\theta = 0.2^{\circ} - 40^{\circ}$. FTIR analysis was done using a Prospect-IR (MIDAC) using a NaCl cell. Thermal gravimetric analysis (TGA) was done with a Perkin-Elmer TGA 7 up to 800°C. UV-vis absorption spectra of the blends were recorded with a UNICAM 8700 series UV-vis spectrophotometer. Dielectric properties were measured with an Eumetric System microdielectrometer at a frequency of 100 Hz, and the temperature range was 35-350°C.

RESULTS AND DISCUSSION

Conductivity Study and Morphology

The effect of PANI content on the electrical conductivity of the PANI–DBSA/PAA blend films is plotted in Figure 1. The conductivity of the blend rapidly increases with PANI content below 5 wt %, then gradually increases until the PANI content reaches 20 wt %. It keeps an almost constant value with slight increases, which is higher than that of the pure PANI–DBSA film prepared from the NMP solvent. From these results, it is confirmed that the percolation threshold is around 5





Figure 1 Log conductivity of $(\bigcirc$ PANI–DBSA/PAA blends as the PANI content and (\blacksquare) pure PANI–DBSA.

wt % PANI content. The observed percolation threshold concentration of 5 wt % is comparable with Cooper and Vincent's results for their PANI composites and is appreciably lower than that of polypyrrole composites (20-30 wt %).⁸ Also, it can be compared with our previous results of the percolation threshold of PANI–CSA/PAA,⁵ which shows a lower percolation threshold (20 wt %).

Heeger⁹ reported that in all his polyblends which utilized the counterion-induced processability of PANI the percolation threshold turns on at a lower concentration, at least one order of magnitude than that predicted ($f \approx 0.16$)¹⁰ and observed by others¹¹ in the insulating matrix. The percolation threshold of PANI–DBSA/PAA also shows a similar result to Heeger's.

Figure 2 shows the conductivity variation of the blend films with different PANI contents as a function of the imidization temperature. Temperatures on the *x*-axis are the final temperatures of the imidization proceeded by the steps 100, 120, 150, 180, 210, and 250°C, respectively, for 30 min. With increasing temperatures, the conductivity variations of all the samples show a similar tendency regardless of PANI content. In all the samples, the conductivity rapidly decreases after 180°C, and the decreasing scale seems to be dependent on the PANI content. The sudden decreasing of the conductivity is thought to be caused by the volatilization of the dopant DBSA from the PANI-DBSA complex. This assumption will be discussed from the TGA results in Figure 7. The dependence of the decrement of the conductivity on the PANI content at high temperature could be attributed to the good thermal stability of the PI matrix. Slight increases of conductivity with increasing temperature are observed below 120°C for the samples with 20 and 50 wt %PANI content. The samples with 5 wt % PANI content also show recovery of the conductivity above 100°C. In contradiction to the general thought of the decreasing of the conductivity due to the evaporation of small water molecules, the reversed phenomenon was observed at around 100–150°C, which seems to be caused by the annealing effect of the PANI chain¹² which is the result of hydrogen bonding between the amine and imine sites of PANI.¹³

Scanning electron micrographs of the surface of PANI–DBSA/PAA blend films are shown in Figure 3. At the low PANI loading [Fig. 3(d)], the dispersed PANI phase appears to exist in isolated globules. The sample with 5 wt % PANI content represents a relatively even surface morphology even though PANI has a globular and particulatelike structure in the PAA matrix [Fig. 3(a)]. The conductive PANI was dispersed and interconnected homogeneously and continuously in the insulator PAA matrix without cutting of the connectivity. Thus, it can be suggested that the blends at this composition have reached the per-



Figure 2 Conductivity versus imidization temperature at different PANI contents.



Figure 3 SEM photographs of (a) PANI–DBSA/PAA (5 wt %), (b) 20 wt %, (c) 50 wt %, and (d) 1 wt % (below the percolation threshold).

colation threshold. A relatively low percolation threshold of our blends could be attributed to the network morphology because in order to obtain a low percolation threshold special morphology of the self-assembled network type must be created.¹⁴ But it has a higher percolation threshold than that of Heeger⁹ and some other results^{15,16} because the PANI-DBSA in NMP could not form a needle-shaped morphology which has an aspect ratio greater than unity. The size of these particles is around 1.0 μ m. Also, as the PANI content increases, the interconnected network becomes denser although the PANI remains organized and aggregated into a fibrillar morphology indicative of connected pathways, probably because of increase in the interaction between PANI and PAA [Fig. 3(b,c)], that is, interaction like hydrogen

bonding can be increased as the PANI content increases to 50 wt % of PANI because the N—H group in PANI and the C=O group in PAA can be the hydrogen-bonding moiety.

Wide-angle X-ray Diffraction Study

The WAXD patterns of PAA and PANI–DBSA are illustrated in Figure 4(A). For comparison purposes, that of PANI–CSA is shown by the b curve in Fig 4(A).⁵ PAA shows only a broad amorphous scattering around 2 θ = 19.5°. In PANI–CSA, another peak at 2 θ = 14.4, 25.2° is revealed. PANI–DBSA shows a sharp scattering peak at 2 θ = 2.5° together with amorphous scattering at 19°. Thus, it is concluded that the chain structure of PANI is dependent on the dopant. These differ-



Figure 4 (A) WAXD patterns of (a) PANI–DBSA, (b) PANI–CSA, and (c) PAA. (B) WAXD patterns of PANI–DBSA/PAA: (a) 5 wt % PANI content; (b) 50 wt % PANI content.

ences in chain structure together with the surface morphology seemed to lead to the variance of the percolation threshold of the conductivity between CSA-doped and DBSA-doped PAA blends. The pattern of PANI–DBSA/PAA is like that of PANI– DBSA blends. The intensity of the peak at a low angle is increased with the PANI content in Figure 4(B). It was confirmed that the peak at the low angle is due to the layered structure of PANI– DBSA,¹⁷ that is, the rigid main chains (PANI backbones) are packed into the platelike layers and they form a well-defined layered structure due to the alkyl side chains from the dopant arranged between the layers.¹⁸ The scattering peak of PAA is likely to be invisible. The (002) reflection of PAA at 2 θ = 19.5 may be overlapped with a broad amorphous scattering of PANI-DBSA. For a detailed study, the *d*-spacing obtained from the X-ray diffraction spectra for various blends are listed in Table I. The *d*-spacing of the peak in the small-angle range of pure PANI-DBSA was 33.95 Å. The sharp peak shown in the small-angle range shifts to a somewhat higher angle as the PAA content increases. Hence, the *d*-spacing between the polymer chains are increased as the PANI content increases. But the small magnitude of the variation of the *d*-spacing suggests that the PAA chains exist in a similar molecular packing with PI and lie in parallel with that. It, therefore, can be explained that the chain structure of these blends is only the function of the PANI content if the dopant is fixed.

Figure 5 shows wide-angle X-ray diffraction patterns with the imidization steps. As the imidization proceeds, the intensity of the low-angle peak at 2 θ = 2.5° increases, except that the temperature reaches 250°C. From this result, it can be concluded that as the blends are converted from PAA to PI a well-packed layered structure becomes a more ordered structure. But the extreme curing that led to the destruction of the layered structure resulted from the volatilization of the dopant DBSA with a long alkyl chain.

FTIR Analysis Related to Imidization Studies

The FTIR spectra of PANI–DBSA/PI (20 wt % PANI content) with the imidization are shown in Figure 6. In this case, imidization proceeded to 120, 180, and 250°C, respectively. The temperature indicates the last temperature of the imidization process. The assignments of the main peaks in the IR spectra are listed in Table II. They exhibit numerous characteristic bands of PAA

Table 3	I d -S	pacing	of the	e Blends	Calcu	lated
from V	VAXD	Pattern	ns			

Materials	d-Spacing (Å)	
PANI-DBSA	33.95	
PANI-DBSA/PAA (50 wt %)	33.44	
PANI-DBSA/PAA (30 wt %)	33.19	
PANI-DBSA/PAA (20 wt %)	32.87	
PANI-DBSA/PAA (15 wt %)	32.46	
PANI-DBSA/PAA (10 wt %)	32.22	
PANI–DBSA/PAA (5 wt %)	29.82	



Figure 5 WAXD patterns of PANI–DBSA/PAA as the immunization process: (a) PANI–DBSA/PAA (5 wt %); (b) PANI–DBSA/PI (imidized up to 150°C); (c) PANI–DBSA/PI (imidized up to 210°C).

and PI. The C=O in-phase peak which can be an indication of the PI state is revealed at 1776.5 cm^{-1} . The intensity of the band increases as the curing temperature increases. Amide II, the C=O out of phase, and C-N stretching in CN(OC)₂NC of PI are shown at 1664.6, 1726.4, and 1373.4 cm⁻¹, respectively. With the imidization proceeding, the intensities of these peaks also grow sharply. This means that the conversion of the blends from PAA to PI is promoted as the curing temperature increases. The aliphatic C-H bands of the dopant DBSA located at 3068 and 2926.2 cm^{-1} are also seen. The intensities of these peaks are diminished in the case of films cured at 250°C, which can be due to the volatilization of the dopant DBSA during the samples that are exposed at high temperature. C=C stretching in the benzenoid and quinoid rings, which are attributed to PANI, is seen at 1500.7 and 1597.2 cm⁻¹. Anyway, from the above-mentioned results, imidization of PANI-DBSA/PAA can be thought to be successfully fulfilled.

The degree of imidization calculated from the FTIR results is presented in Table III. The C—C band of *para*-substituted benzene at around 1494.9 cm⁻¹ can be a good internal reference for calculating the degree of imidization because of its unchangeability and nonshifting regardless of the degree of imidization. Also, the $CN(OC)_2NC$ peak shown at about 1373.4 cm⁻¹ can be the characteristic peak of the PI ring which linearly



Figure 6 FTIR spectra of PANI–DBSA/PI blends (20 wt % PANI content) as the imidization process.

grows in the imidization process. The degree of imidization, therefore, could be calculated with the peak area ratio¹⁹:

Degree of imidization = $(A_{1373.4}/A_{1494.9})_{\text{sample}}/(A_{1373.4}/A_{1494.9})_{\text{completely imidized sample}} \times 100$

Table II FTIR Assignment of PANI-DBSA/PI Blend

$\begin{array}{c} Frequency \\ (cm^{-1}) \end{array}$	Assignment
1776.5	C=O in phase of PI
1726.4	C=O out of phase of PI
1664.6	Amide of PI
1597.2	C=C stretching in quinoid ring of PANI
1500.7	C=C stretching in benzeneoid ring of
	PANI and C—C band of para-
	substituted benzene
1373.4	C—N stretching in CN(OC) ₂ CN of PI
1116.9	SO_3^- of dopant DBSA

Materials						
Temperature	PANI–DBSA/PAA (20 wt %)	PANI–DBSA/PAA (50 wt %)				
120	35.8	29.1				
150	52.7	41.4				
180	79.8	69.8				
210	87.3	82.6				
250	94.3	88.3				

Table IIIDegree of Imidization at DifferentImidization Steps

where A is the peak area.

A completely imidized sample was obtained by curing PANI–DBSA/PAA up to 300°C. In both samples, the degree of imidization increased as the curing temperature increased. The higher degree of imidization in the 20 wt % blend is ascribed to the higher content of PAA in the blends. The degree of imidization of about 80% cured up to 180°C indicates that this temperature is the optimal imidization circumstance of the PANI– DBSA/PAA system without a definite loss of the electrical conductivity.

Compatibility Study from Thermal Analysis and Dielectric Responses

Figure 7(A,B) shows the results of the TGA measurement of the blends as the imidization process to compare the effect of the dopant on the thermal property and blend behavior. In Figure 7(A,B), the weight loss up to 260°C is probably attributed to the loss of NMP together with the degradation of the dopant which cannot dope PANI. In this region, the steepness of degradation is changed around 185 and 160°C, respectively, for the DBSA-doped blend and the CSA-doped blend. These points can be related to the T_g of PANI in the blends.²⁰ It is well in accord with the dielectric measurement in Figure 8. Another change in weight is visible up to 370°C in both samples, which may be due to the degradation of dopants or PANI low molecular weight PANI. The weight loss from 370°C to about 520°C is probably due to the degradation of the PANI chain. Their degradation tendencies are also changed at around 400 and 440°C, respectively, for PANI-DBSA/PAA and PANI-CSA/PAA probably because of different interactions, that is, hydrogen bonding in the latter case of the degradation rate, between PANI

and PAA. The degradation rates before and after these temperatures are different for the different blends. The decomposition of the PI chain occurs over this temperature. With the imidization proceeded, the weight loss of NMP and the dopant seems to disappear. This may be due to the decomplexation of NMP and a small amount of the dopant as the imidization proceeded. The weight loss over 520°C is the decomposition of the PI chain. The thermal stability of the blends was superior in proportion to the degree of imidization. But the CSA-doped PANI blends have a higher content of the remaining undecomposed



Figure 7 (A) TGA thermograms of PANI–DBSA/PAA blends with different imidization histories: (a) controlled; (b) cured up to 120°C; (c) cured up to 150°C; (d) cured up to 210°C; (e) cured up to 250°C. (B) TGA thermograms of PANI–CSA/PAA blends with different imidization histories: (a) controlled; (b) cured up to 120°C; (c) cured up to 150°C; (d) cured up to 210°C; (e) cured up to 250°C.



Figure 8 Dielectric responses of (a) PANI–CSA/PAA (5 wt %), (b) PANI–DBSA/PAA (5 wt %), (c) PAA, and (d) PANI–HCl.

polymer. Thus, we can suggest that the dopant in the blends affects the thermal property and the blend behaviors.

The spectrum of the dielectric response of (a) PANI–CSA/PAA, (b) PANI–DBSA/PAA 5 wt % blends, (c) PAA, and (d) PANI–HCl films are shown in Figure 8 against the temperature at a constant frequency (100 Hz). In Figure 8(c), the tan δ curve shows two maxima. The first maximum at 80°C is probably attributed to the evap-

oration of water or the NMP molecule and the second maximum at 245°C is due to the T_g . The T_g of the PANI–HCl film occurs at 175°C. The spectra of the tan δ curves of the blends were affected by the dopants in the blends, that is, the T_g , the peak temperature with the highest tan δ value, showed dependency on the dopant. PANI–DBSA/PAA shows two tan δ maximum (T_g) at 170 and 250°C, which are attributed to PANI and PAA, respectively. But PANI–CSA/PAA shows only one T_g , which is ascribed to the PAA. This indicates that the compatibility between PAA and the PANI–dopant of PANI–CSA/PAA is higher than that of PANI–DBSA/PAA.

UV-vis Spectra

UV-vis spectra of PANI-DBSA/PAA and PANI-CSA/PAA are shown in Figure 9(A,B). Both samples show three distinctive absorption peaks at about 650 and over 860 nm, which are attributed to the exciton band of the quinoid ring and the localized polaron band, respectively, together with a shoulderlike peak at around 440 nm. In contrast to the general spectra of PANI-DBSA and PANI-CSA, the exciton band of the quinoid ring, which can be seen in the PANI emeraldine base, still remains, meaning that the PANI is partially dedoped. This dedoping effect can be explained as follows²¹: NMP is a polar, basic solvent and has a strong interaction with acids, so that there exists a competition between PANI + H^+ (doped PANI) and NMP · H^+ (hydrogen bonding). Anyway, the absorption spectra of PANI-DBSA and PANI-CSA are resemble each other. But compared with the spectra of PANI-DBSA/PAA, the polaronic band of above 860 nm of PANI-CSA/PAA is revealed at a higher wave number [Fig. 9(A,a), 869 nm, Fig. 9(B,a), 874.5 nm], indicative of a higher conjugation length. When the PANI-dopants are blended with PAA in proper ratios, the two spectra are slightly different without changing the tendency, that is, when the PANI content of the blends is 2 wt %, the polaronic band at a high wave number (above 860 nm) is likely to disappear in both samples. But in 5 wt %-content blends, PANI-DBSA/PAA almost recovers the polaronic absorption contrast to PANI-CSA/PAA. This is well in accord with the difference of the percolation threshold in both blends that contain different dopants (CSA and DBSA). In the CSA-doped blends which contain a high content of PANI [Fig. 9(B,d,e)], the band appears at a higher wave number [870 and 871



Figure 9 (A) UV-vis spectra of (a) PANI–DBSA, (b) PANI–DBSA/PAA (2 wt %), (c) the same blends (5 wt %), (d) 20 wt %, and (e) 50 wt %. (B) UV-vis spectra of (a) PANI–CSA, (b) PANI–CSA/PAA (2 wt %), (c) the same blends (5 wt %), (d) 20 wt %, and (e) 50 wt %.

nm, respectively, for (d) and (e)], while it appears at a lower wave number [864, 867, and 869 nm, respectively, for (c), (d), and (e)] in DBSA-doped blends. So, we can conclude that the dopants affect the chain structure and the blend behavior in the PANI-dopant/PAA system.

CONCLUSIONS

It was shown that PANI/PAA blend films could be prepared with a DBSA-doped PANI solution and a PAA solution by solvent casting using NMP as a cosolvent. The morphology of the surfaces of the resulting blends show a continuously connected self-assembled network structure above the percolation threshold. The electrical conductivity of the blends was increased as the PANI content increased and showed a higher conductivity than that of pure PANI-DBSA. The percolation threshold of the blends was around 5 wt %. As the thermal imidization proceeded, the blends are converted from PAA to PI. After being converted to the imide state, the blends showed a more stable thermal behavior. The well-defined layered structures were observed in the blends, which may be due to the PANI-DBSA. These blends have a lower compatibility than that of the PANI-CSA/PAA blends verified from TGA and dielectric analysis. But they have a somewhat higher conductivity than that of PANI-CSA/PAA. Thus, the dopants in the PANI affect the chain structure and the blend behavior of the blends.

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