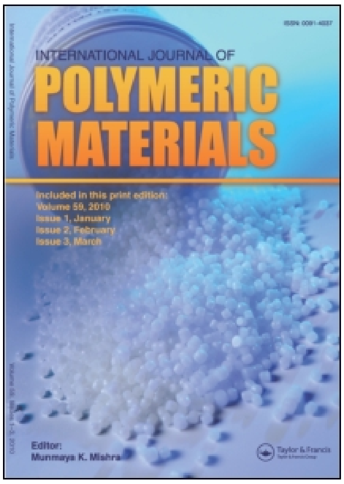

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Relationship Between Electrical Conductivity And Phase Morphology Of Polyaniline/polyacrylonitrile And Polyaniline/polystyrene Blends

Wei Pan[ab]; Shenglin Yang[a]; Guang Li[b]; Jianming Jiang[b]
[a] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai, P. R., China [b] Department of Material Science and Chemical Engineering, Zhongyvan Institute of Technology, Zhengzhou, P. R., China

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RELATIONSHIP BETWEEN ELECTRICAL CONDUCTIVITY AND PHASE MORPHOLOGY OF POLYANILINE/POLYACRYLONITRILE AND POLYANILINE/POLYSTYRENE BLENDS

Wei Pan
State Key Laboratory for Modification of Chemical Fibers
and Polymer Materials, Donghua University, Shanghai, P. R. China
Department of Material Science and Chemical Engineering,
Zhongyvan Institute of Technology, Zhengzhou, P. R. China

Shenglin Yang
Guang Li
Jianming Jiang
State Key Laboratory for Modification of Chemical Fibers
and Polymer Materials, Donghua University, Shanghai, P. R. China

Blends of dodecylbenzenesulfonic acid doped polyaniline (PANI-DBSA) with either polyacrylonitrile (PAN) in xylene/dimethylsulfoxide (DMSO) mixture or polystyrene (PS) in xylene were solution cast. The PANI-DBSA complex was obtained directly from emulsion polymerization, in which DBSA acted simultaneously as a surfactant and as a protonating agent. The morphologies of the blends were characterized by optical microscopy (OM), Scanning Electron Microscopy (SEM), wide angle X-ray diffraction (WAXD) and Dynamical Mechanical Analysis (DMA). Electrical conductivity was measured for various compositions. It was found that the formation of a continuous network was strongly associated with percolation and conductivity. The morphologies of the two blends were significantly different, which arose from the different compatibility between the components in the blends.

Keywords: polyaniline, polyacrylonitrile, polystyrene, morphology, conductivity

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Address correspondence to Dr. Guang Li, State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, 1882 West Yan'an Road, Shanghai 20051, China. E-mail: lig@dhu.edu.cn

INTRODUCTION

In recent years, intrinsic electrically conductive polymers (ICPs) have attracted considerable attention because of their potential application in light-emitting diodes, batteries, electromagnetic shielding, antistatic coating, gas sensors, and activators. Polyaniline (PANI) is one of the most intensively investigated ICPs due to its environmental stability, low cost of raw material, and ease of synthesis [1]. The great potential of PANI is, however, masked by its serious disadvantages such as insolubility, infusibility, and thus non-processability.

In order to improve the processability of PANI, a number of methods have been studied, of which the most widely adopted strategy is to dope PANI with organic acids containing long alkyl chain such as camphorsulfuric acid (CSA) or dodecylbenzenesulfonic acid (DBSA). Consequently, the bulk non-polar tail of the dopant renders the polyanilines in conducting form to be soluble in some ordinary organic solvent such as m-cresol, chloroform, and xylene [2,3]. Therefore, such doped PANI can be solution processed together with common insulating polymers in regular organic solvents. Generally, PANI-DBSA complex is prepared by dedoping and subsequent redoping with DBSA of the conventionally synthesized PANI. To ensure the dope level, excessive DBSA should be used, which may also affect other properties of matrix such as the mechanical strength. Recently, a straightforward method to synthesize PANI-DBSA complex has been explored by using the so-called emulsion polymerization, in which DBSA acted as a surfactant and as a dopant [4].

As a matter of fact, solution blendings of PANI doped by organic acids containing long alkyl chain with various polymer matrixes such as poly (methylmethacrylate) (PMMA) [5–7], polyethylene (PE) [8], polystyrene (PS) [9], polyvinylchloride (PVC) [10], and polyimide (PI) [11] have been investigated. It has been shown in these blends that the electrical properties were dependent on the morphologies, especially the formation of a conductive network structures of PANI. The morphologies were affected by several aspects such as the swellability of solvent and the compatibility between the components in the blends. It is reported that a lower percolation threshold come from a lower compatibility [11] or from a weaker swellability of the solvent [10], because in such systems PANI-DBSA phase dispersed as coarse aggregates and formed conductive paths at a relatively low content.

In this study, the emulsion polymerized PANI-DBSA was co-solved in xylene/DMSO with PAN and in xylene with PS. The solutions were cast into blend films. The relationship between the electrical conductivity and the morphologies was investigated and a comparison between PANI-DBSA/PAN and PANI-DBSA/PS was performed.

EXPERIMENTAL

Synthesis of PANI-DBSA

The emulsion polymerization of aniline was performed by a procedure described in the literature [3]. In a typical polymerization, a solution of 4.65 ml (0.05 mol) of aniline, 24.5 g (0.075 mol) of DBSA and chloroform was prepared in a 250 ml Erlenmeyer flask under stirring. The medium was kept at 0°C and an aqueous solution containing 4.68 g (0.02 mol) ammonium peroxide sulfate (APS) in 20 ml of water was slowly added. The total polymerization time was 24 h. The polymerization was terminated by pouring the emulsion into acetone. The precipitate dark green powder was filtered, washed with acetone, and dried under vacuum at room temperature.

Preparation of PANI-DBSA/PAN Blend

A 8 wt% dispersion of PANI-DBSA in xylene was prepared by mixing the conductive powder in xylene at 50°C for 2 h. Concomitantly, PAN was dissolved in DMSO at 60°C for 4 h. Then these two solutions were mixed together to obtain the desired composition, keeping the total polymer concentration at 18 wt%. Films were prepared by casting these blend solutions on glass plates. Solvent evaporation was done at room temperature for 48 h.

Preparation of PANI-DBSA/PS Blend

A 8 wt% dispersion of PANI-DBSA in xylene was prepared by mixing the conductive powder in xylene at 50°C for 2 h. A 17% solution of PS in xylene was prepared simultaneously by mixing at 60°C for 4 h. Then the PS solution was added to the conducting polymer solution at different amounts in order to obtain the desired compositions. The mixed solutions were stirred for 4 h at 60°C. Films were prepared by casting these blend solutions on glass plates. Solvent evaporation was done at room temperature for 48 h.

Characterization

Optical microscopy pictures were recorded using OLYMPUS BX51 microscopy. Scanning electron microscopy pictures were recorded using a Philips-CM120 scanning electron microscope. Wide angle X-ray diffraction was carried out using a BRUKER-AXC08 X-ray diffractmeter,. Dynamical mechanical analysis was carried out using TA 2980 DMA equipment. Electrical conductivity of the films was measured by the usual four-probe method using free-stand films.

RESULTS AND DISCUSSION

Phase Morphology Study

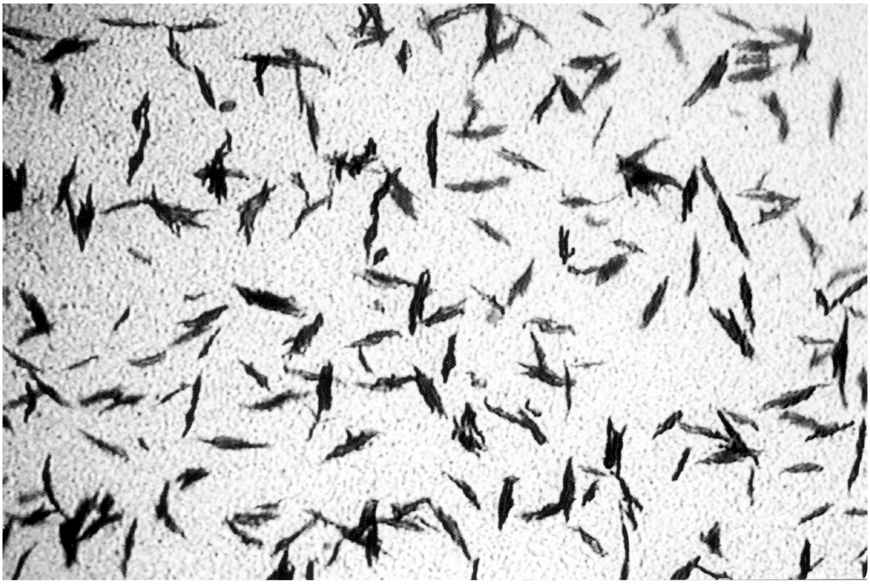
The optical micrographs of the PANI-DBSA/PS blend films are shown in Figure 1. The bright region is related to PS phase whereas the dark region is related to PANI-DBSA. It is clear that PS and PANI-DBSA phase are highly incompatible and thoroughly phase separated. At the low PANI-DBSA loading (2.5 wt%), PANI-DBSA dispersed as isolated clusters in the PS matrix. As the loading is increased to 5 wt%, the clusters appear to be interconnected. As the loading is increased further to more than 7.5 wt%, the fibrous structures are clearly found to form an interconnected network. Thus it can be concluded from the OM study that the percolation threshold of PANI-DBSA/PS blend lies in somewhere between the 5–7.5 wt%.

Comparatively, the optical micrographs of the PANI-DBSA/PAN blend films are shown in Figure 2. It is obvious that the PANI-DBSA phases are present in the form of agglomeration, touching each other while the PANI-DBSA loading was only at 2.5 wt%. At this low PANI-DBSA concentration, the conducting pathway has already been formed to some extent. Increasing the concentration, PANI-DBSA forms a denser conducting network that should be responsible for the higher conductivity.

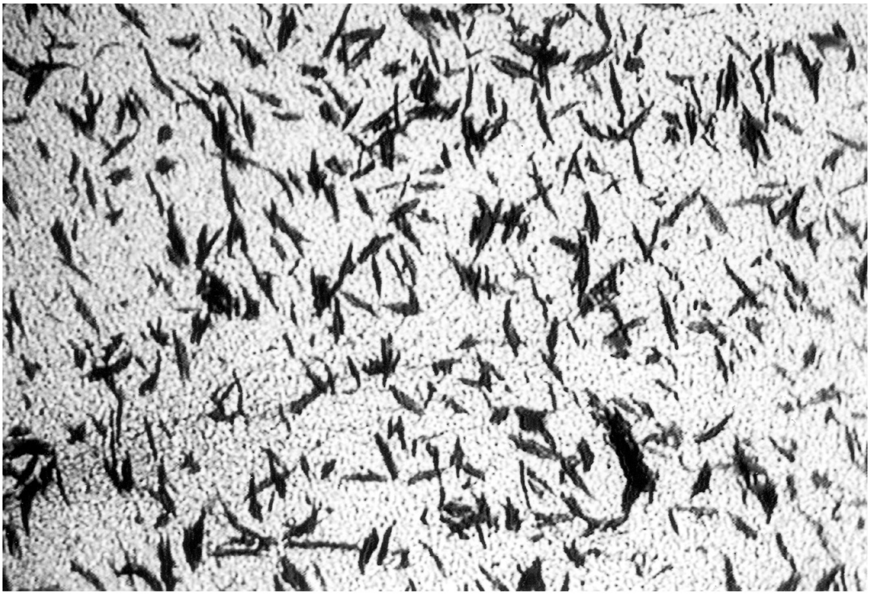
The distinction of the morphologies between PANI-DBSA/PS and PANI-DBSA/PAN is also confirmed by SEM analysis. Figure 3 shows the cross-section SEM micrographs of the PANI-DBSA/PS blend films containing 2.5 and 7.5 wt% PANI-DBSA, respectively (bright regions stand for PANI phase). At the low loading, PANI-DBSA disperses as tiny particles with size range of 50–100 nm. With the increased loading, the PANI-DBSA phase in the blend tend to coalesce into network. The cross-section SEM micrographs of the PANI-DBSA/PAN blend films containing 2.5 and 7.5 wt% PANI-DBSA are shown in Figure 4. Interestingly, those PANI-DBSA phases show a network structure at the lowest PANI-DBSA loading (2.5 wt%), that is, the conducting pathway has been formed at this point. As the loading of PANI-DBSA increased, the characteristic length of the PANI-DBSA phases remain unchanged whereas the network structure becomes denser.

Wide-Angle X-Ray Diffraction Study

The WAXD patterns of PANI-DBSA, PS, and PANI-DBSA/PS blends with different compositions are illustrated in Figure 5. PANI-DBSA shows a sharp scattering peak at $2\theta = 2.5^\circ$ together with a broad

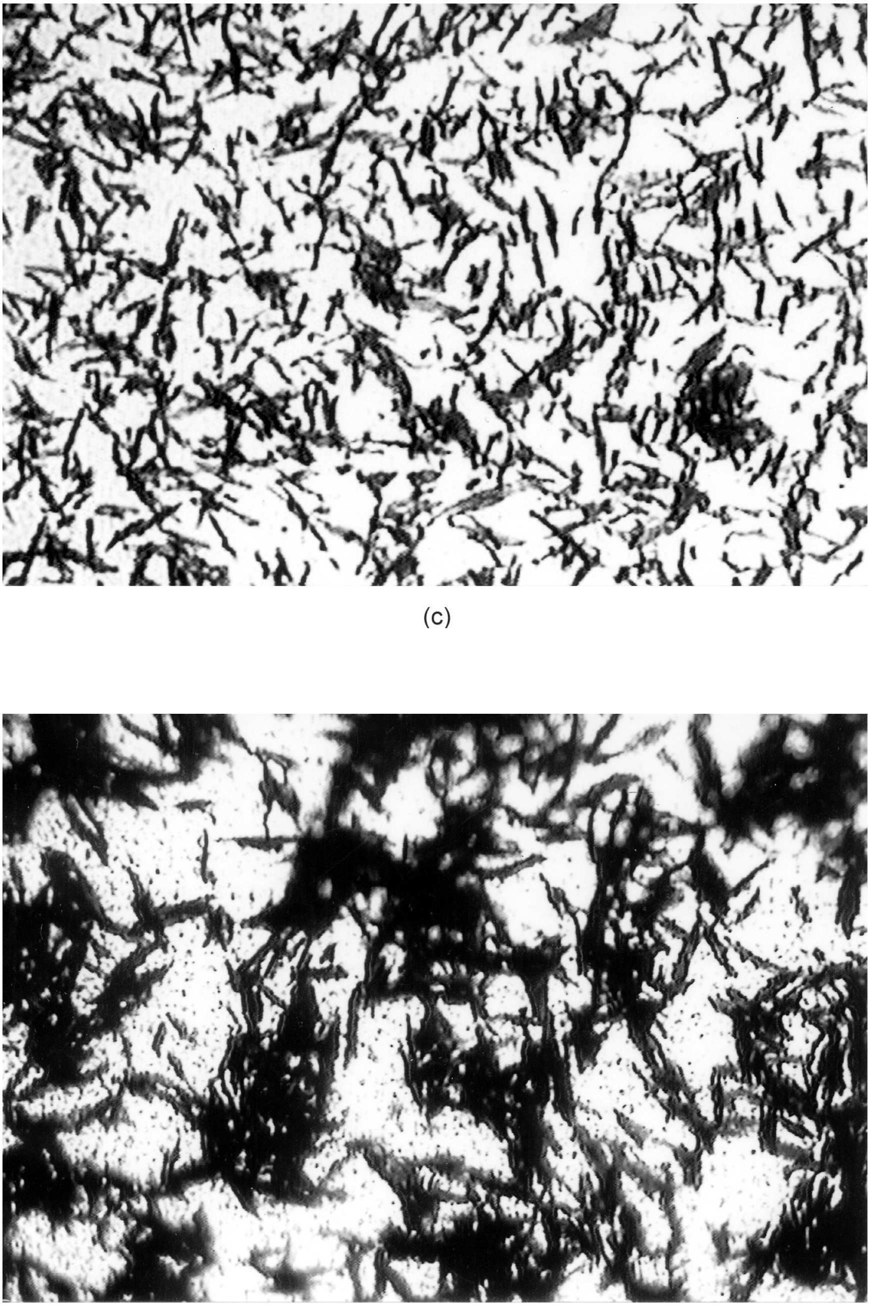


(a)



(b)

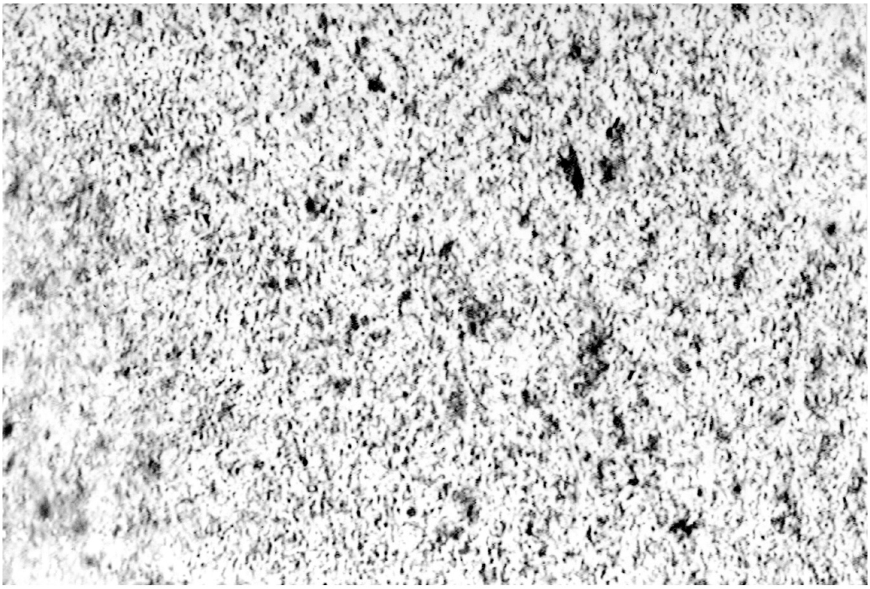
FIGURE 1 Optical micrographs of PANI-DBSA/PS blends including (a) 2.5 wt% PANI-DBSA, (b) 5 wt% PANI-DBSA, (c) 7.5 wt% PANI-DBSA, (d) 15 wt% PANI-DBSA (500 × magnification).



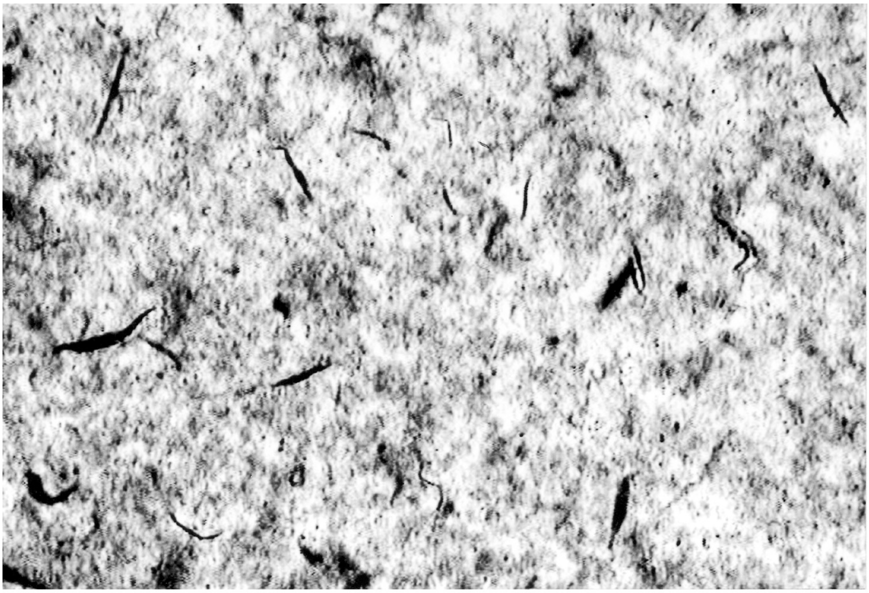
(c)

(d)

FIGURE 1 (Continued).

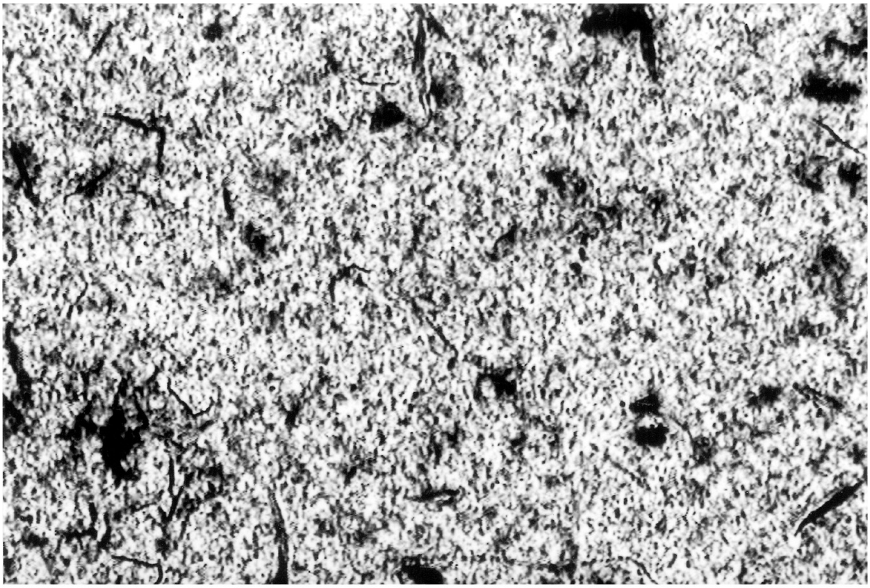


(a)

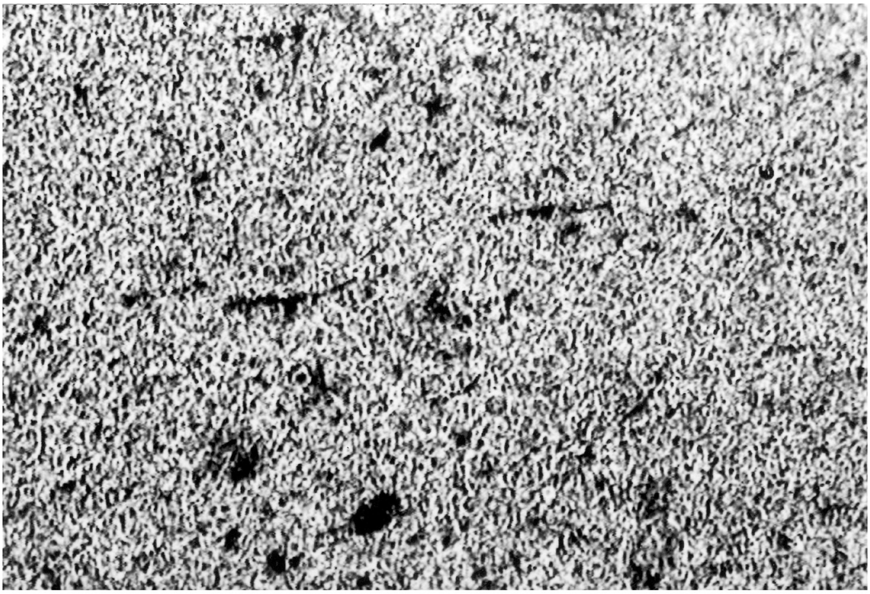


(b)

FIGURE 2 Optical micrographs of PANI-DBSA/PAN blends including (a) 2.5 wt% PANI-DBSA, (b) 5 wt% PANI-DBSA, (c) 7.5 wt% PANI-DBSA, (d) 15 wt% PANI-DBSA (500 × magnification).



(c)



(d)

FIGURE 2 (Continued).

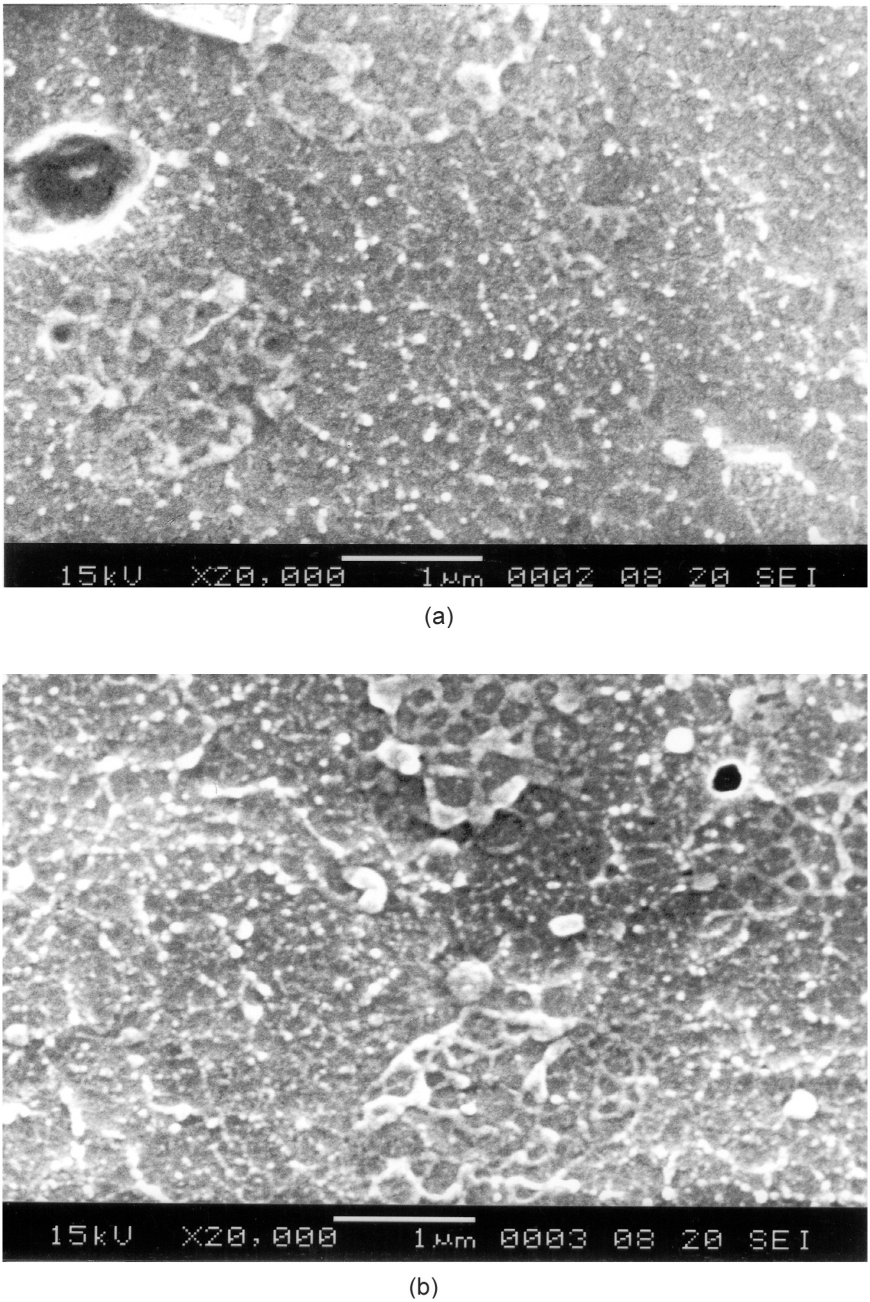


FIGURE 3 Cross section SEM micrographs of PANI-DBSA/PS blend films containing (a) 2.5 wt% and (b) 7.5 wt% of PANI-DBSA.

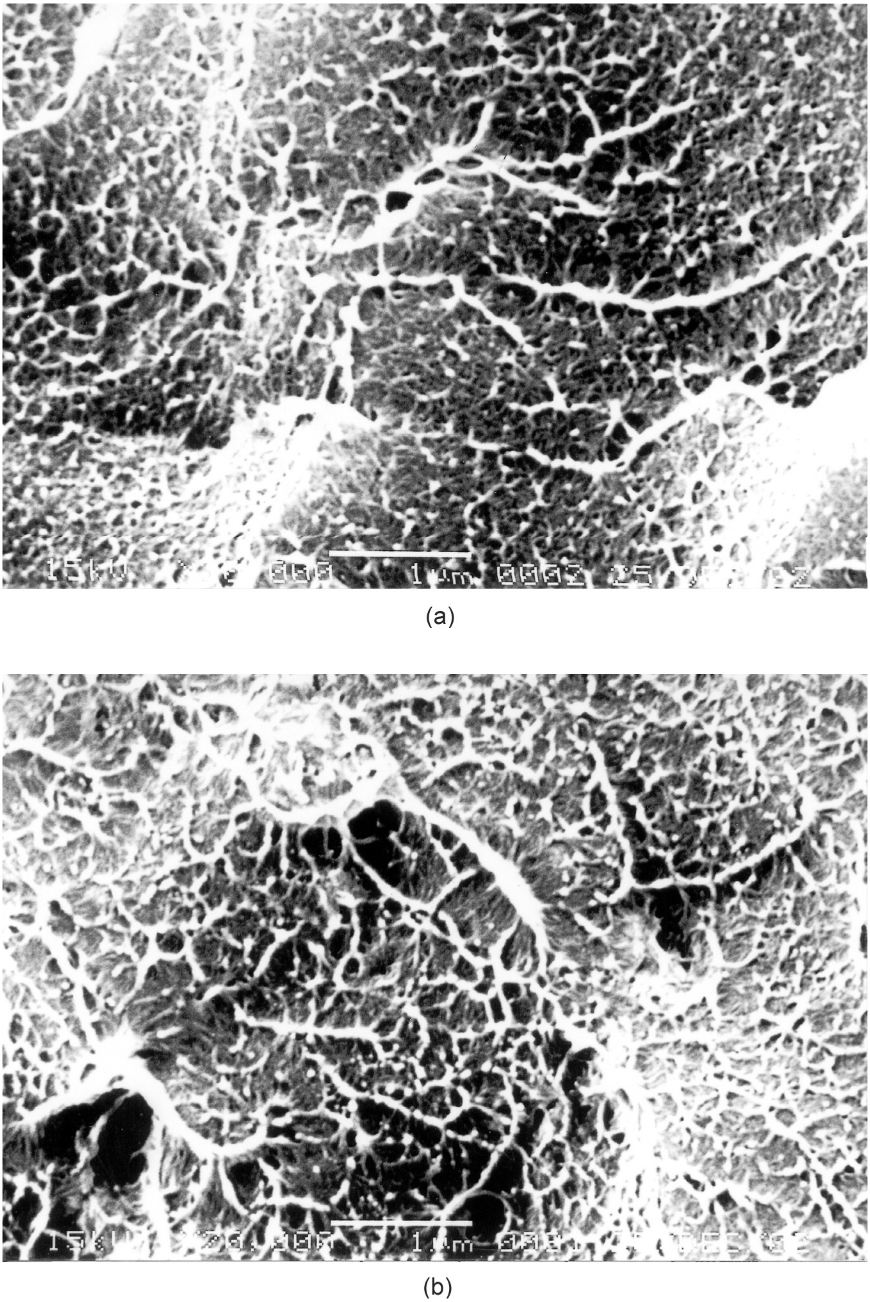


FIGURE 4 Cross section SEM micrographs of PANI-DBSA/PAN blend films containing (a) 2.5 wt% and (b) 7.5 wt% of PANI-DBSA.

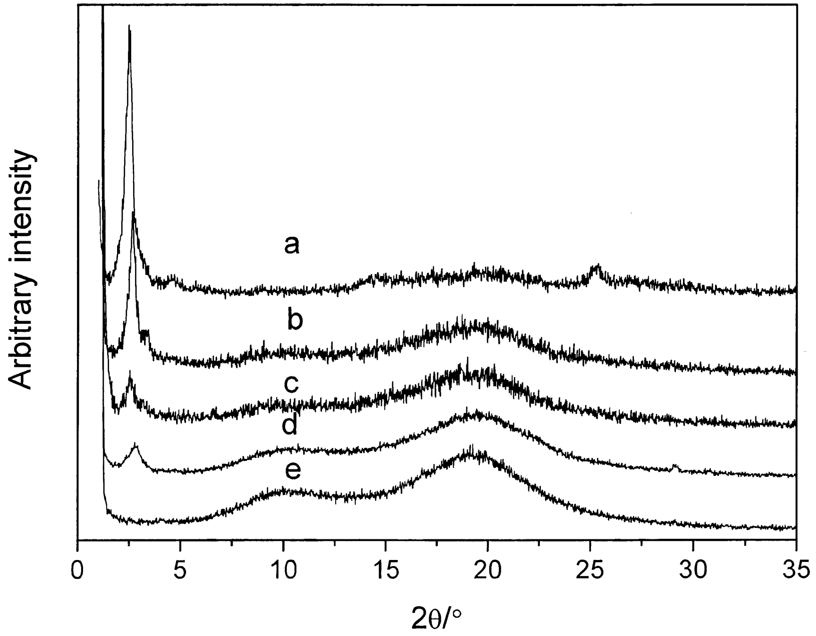


FIGURE 5 WAXD patterns of (a) PANI-DBSA, (b) 16 wt% PANI-DBSA content, (c) 7.5 wt% PANI-DBSA content, (d) 2.5 wt% PANI-DBSA content, and (e) PS.

amorphous scattering around $2\theta = 19^\circ$ and a scattering peak at $2\theta = 26^\circ$. The diffraction peak at low angle indicates the presence of layered structure of PANI-DBSA, that is, the rigid main chains (PANI backbones) are packed into platelike layers and they form a well-defined layered structure due to the alkyl side chains from the dopant arranged between the layers. Such a structure is well known for alkylated stiff polymers and has also been observed in polypyrrole-dodecylbenzene sulfonate salt by Neoh et al. [12], who showed that the presence of the alkyl groups prevents the close packing of the polymer chains increasing the entropy and at the same anisotropy. From Figure 5 it can also be observed that the intensity of the peak at $2\theta = 2.5^\circ$ is decreased with the decreasing of PANI-DBSA content. The WAXD patterns of PANI-DBSA, PAN, and PANI-DBSA/PAN blends with different weight fraction of PANI-DBSA are illustrated in Figure 6, which reconfirms the existence of low angle scattering. However, the scattering intensity is much weaker in PANI-DBSA/PAN than that in PANI-DBSA/PS at the same PANI-DBSA loading. The aforementioned results indicate that the PANI-DBSA/PS

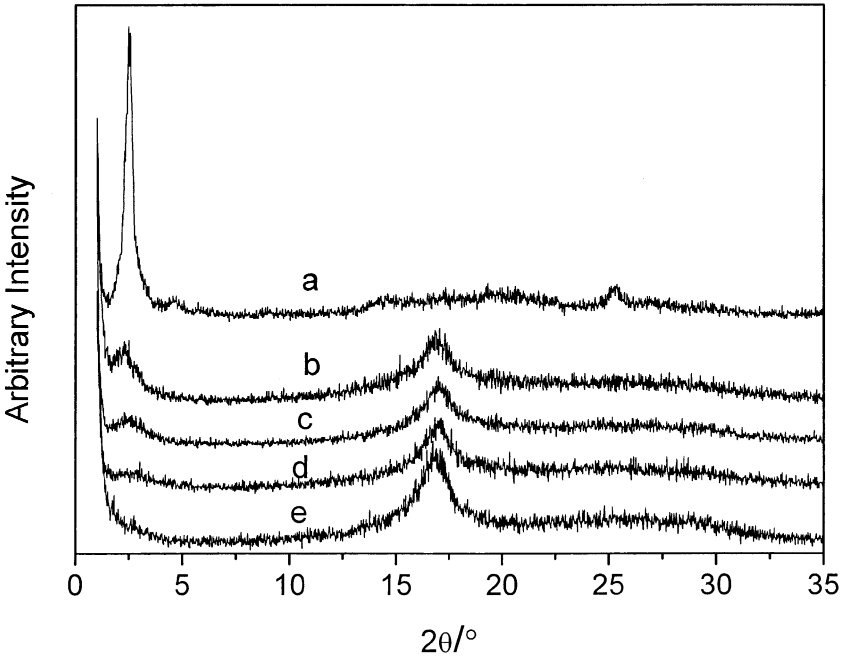


FIGURE 6 WAXD patterns of (a) PANI-DBSA, (b) 16 wt% PANI-DBSA content, (c) 7.5 wt% PANI-DBSA content, (d) 2.5 wt% PANI-DBSA content, and (e) PAN.

sample contains larger PANI-DBSA aggregates than the PANI-DBSA/PAN sample, which has been confirmed by OM study.

Dynamic Mechanical Thermal Analysis Study

Dynamic mechanical thermal Analysis (d.m.t.a) curves for PS and PANI-DBSA/PS (15 wt% PANI-DBSA content) are given in Figure 7, and those for PAN and PANI-DBSA/PAN are given in Figure 8. For PANI-DBSA/PS blend, the tanδ curve shows two T_g peaks, one at 72°C and the other at 105°C. The former responds for PANI-DBSA, which is higher than that D. Tsocheva et al. observed [13], 65°C. The latter is the T_g of PS, which is slightly lower than pure PS. This indicates that PANI-DBSA and PS are affecting each other. However, the presence of two T_gs means that PANI-DBSA and PS are highly incompatible and the PANI-DBSA phase aggregates coarsely in the blend. To the contrary, the tanδ curve f PANI-DBSA/PAN blend shows only one T_g peak, which means a partial compatibility between the PANI-DBSA and PAN.

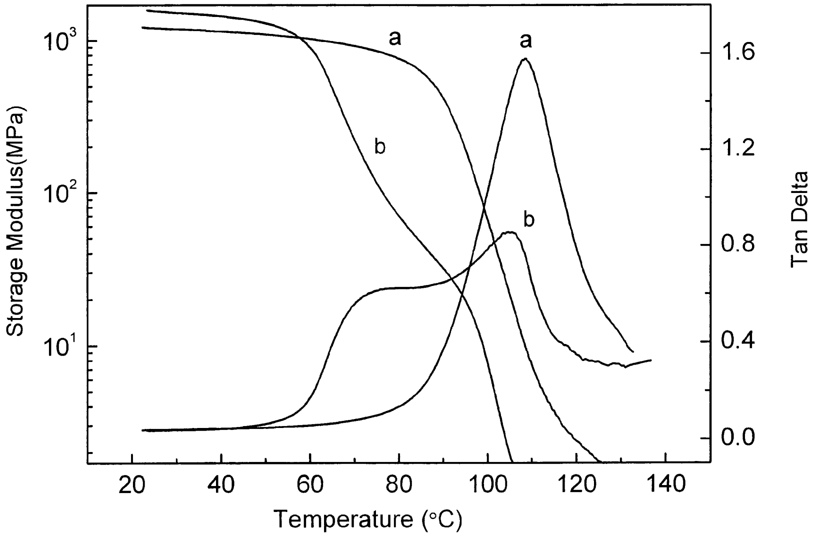


FIGURE 7 Tanδ and Dynamic storage modulus as a function of temperature for (a) PS and (b) PANI-DBSA/PS (15 wt% PANI-DBSA content).

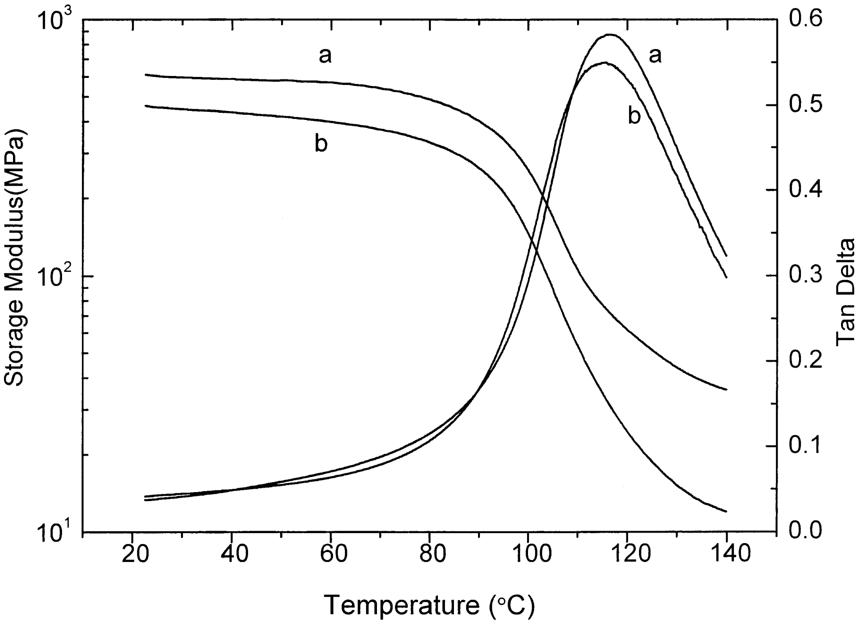


FIGURE 8 Tanδ and Dynamic storage modulus as a function of temperature for (a) PAN and (b) PANI-DBSA/PAN (15 wt% PANI-DBSA content).

Electrical Conductivity

The composite films prepared by casting blend solutions vary from light green to dark green with different weight fraction of PANI-DBSA in the polyblends. The effect of PANI-DBSA content on the electrical conductivity of the PANI-DBSA/PAN and PANI-DBSA/PS blend films is plotted in Figure 9. In both systems, the insulator-conductivity transition is very sharp. For PANI-DBSA/PAN, when the fraction of PANI-DBSA is 2.5%, conductivity increased from matrix polymer of 10^{-13} S/cm to the polyblend of 10^{-5} S/cm. When the PANI-DBSA is adding to 5 wt%, it is up to 10^{-3} S/cm. It is shown that the percolation threshold of the blend system is less than 5 wt%. For PANI-DBSA/PS, when the fraction of PANI-DBSA was 7.5%, conductivity increased from matrix polymer of 10^{-13} S/cm to the polyblend of 10^{-5} S/cm. It is shown that the percolation threshold of this blend system is around 7.5 wt%. This result is in good agreement with the conclusion of the morphology study, which showed that the conduction pathway formed in PAN matrix at lower PANI-DBSA loading.

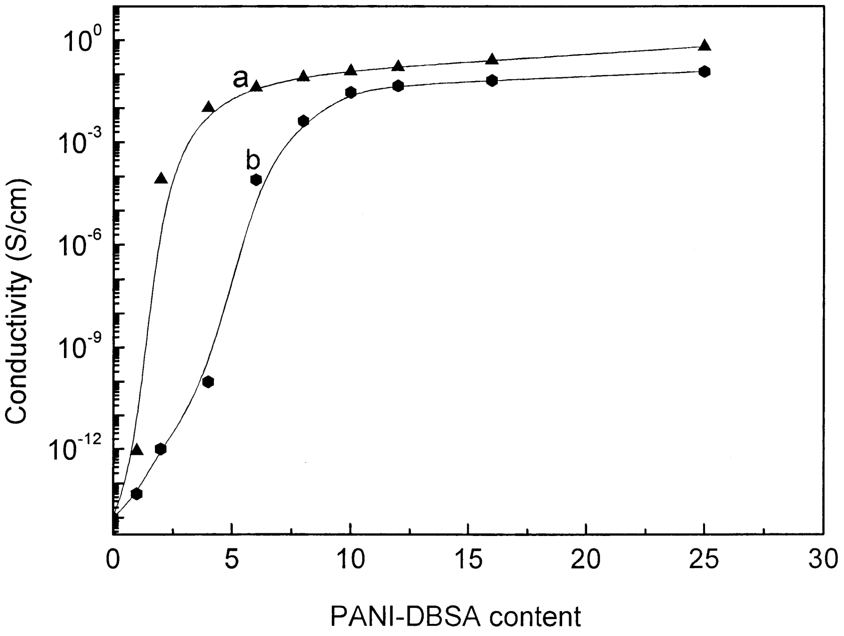


FIGURE 9 Electrical conductivity of PANI-DBSA/PS and PANI-DBSA/PAN as a function of PANI-DBSA content, (a) PANI-DBSA/PAN, (b) PANI-DBSA/PS.

CONCLUSION

Blends of PAN or PS with conductive PANI-DBSA were solution cast, and their electrical conductivity-morphology relationships were investigated. The two systems exhibited very different phase morphologies and percolation thresholds. The PANI-DBSA/PAN blend exhibits conductivity at lower (about 2.5%) PANI-DBSA contents than PANI-DBSA/PS blend (about 7.5% PANI-DBSA content). The difference is believed to come from their different phase morphology; that is, PANI-DBSA can form network structures at a lower content in PAN than in PS. It can also be concluded that the formation of conductive paths relates little with the dispersion size of PANI-DBSA but partially with the compatibility between the components in the blends.

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