Electrical Properties of Polyaniline–Polystyrene Blends Above the Percolation Threshold

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ABSTRACT: Blends of conductive polymers with classical ones can exhibit good mechanical properties and good electrical conductivity and deserve great attention for application in electronic industrial technology. Conductive polyaniline solutions have been chemically prepared using bis(2-ethyl hexyl)hydrogen phosphate (DiOHP) as the dopant chemical species. The codissolution method leads to conductive polyaniline–polystyrene (PANI–PSt) composites with good mechanical properties. The dependence of electrical conductivity on the volume fraction of PANI in the blend is found to be characteristic of a percolation system. Electrical conductivity and thermoelectric power measurements are interpreted on the basis of hopping mechanisms between polaronic clusters. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1205–1208, 1998

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INTRODUCTION

Polyaniline is one of the most promising conducting polymers for electronic industrial applications (electronic devices,[1] lithography,[2] rechargeable cells[3]). It is an environmentally stable conducting polymer[4] which can exhibit high electrical conductivity.[5] A conducting blend with polyaniline and a classical polymer (polystyrene, PMMA, etc.) can exhibit good mechanical properties associated with interesting electrical properties.[6] Furthermore, it has been discovered that the protonation of polyaniline (PANI) carried out with an appropriate protonating agent can induce the solubility of the conducting form of PANI in common organic solvents such as toluene, chloroform, and *m*-cresol.[7]

In this article, the electrical characterization of polyaniline–polystyrene (PANI–PSt) blends synthesized by the codissolution method is described. At room temperature, the d.c. electrical conductivity variations with the volume fraction f of PANI in the blend are characteristic of a percolation system with a low percolation threshold ($f_c \sim 0.006$). The electrical conductivity variations with temperature between 77 and 300 K are explained by hopping mechanisms between polaronic clusters while thermoelectric power (TEP) variations show a quasi-linear dependence in the same temperature range.

EXPERIMENTAL

The polyemeraldine base (PANI) used in all experiments was prepared by oxidative polymerization of aniline in the presence of HCl. The resulting HCl
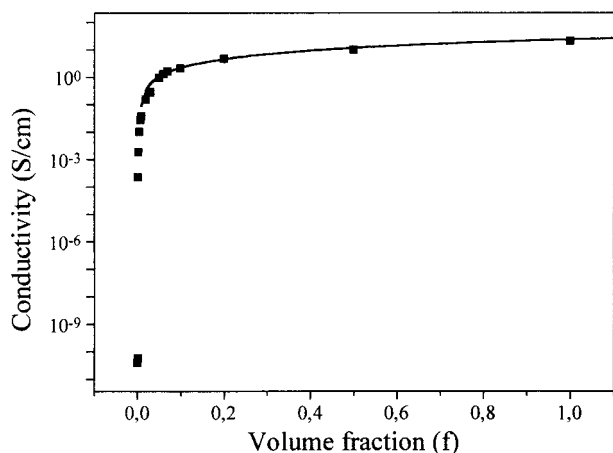

Figure 1 Electrical conductivity variations vs. volume fraction f of PANI in the blend. The percolation threshold is found to be equal to about 0.006. The theoretical variations are drawn as a full line.

partially protonated polymer was then deprotonated in a 3 wt % solution of ammonia.[8]

The protonation of PANI was achieved by treatment of PANI with bis(2-ethyl hexyl)hydrogen phosphate (DiOHP) in an m-cresol solution ($\frac{1}{2}$ molecule of DiOHP by the phenyl N repeat unit).

This solution was then mixed with an appropriate ratio with a solution of PSt in m-cresol. Films (thickness about 100 μm) were obtained by casting the blend solution onto a glass substrate before being dried at 60°C in a neutral atmosphere for 24 h. This method leads to free-standing films with good mechanical properties. Scanning electron microscope micrographs show a relatively smooth surface and a good homogeneity.

The experimental dependence of the electrical conductivity (σ) was measured in the temperature range 80–300 K using the four-probe method with special care to ensure good temperature stability for each experimental point. The thermoelectric power (TEP) was measured as a function of temperature in the range 80–300 K. The samples were placed between two microheaters made of constantan wire wrapped around an aluminum oxide tube (diameter $\sim$ 1 mm). The thermal emf's between the two copper and the two constantan wires were measured simultaneously using two digital nanovoltmeters. All measurements were computer-controlled.[9]

RESULTS AND DISCUSSION

The room-temperature electrical conductivity depends strongly on the fraction of PANI in the blend: σ decreases from 4.6 Ω^{-1} cm^{-1} ($f = 0.2$) to 2.10^{-4} Ω^{-1} cm^{-1} ($f = 0.002$). These experimental variations are correctly described by the scaling law of the percolation theory[10]: $\sigma = \sigma_T |f - f_C|^t$, in which σ_T is proportional to the conductance of the basis conducting unit and t is the critical exponent. The theoretical value is $t = 1$ in a two-dimensional system and $t = 2$ in three dimensions. The percolation threshold which is found to
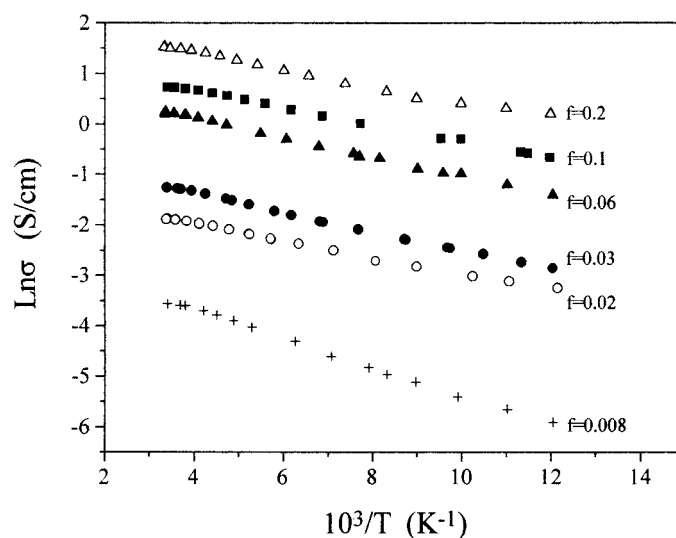

Figure 2 Electrical conductivity variations vs. $10^3/T$ of conducting PANI–PSt blends for different volume fractions of PANI.

Table I   Parameter Values Deduced by the Fit of the Electrical Conductivity Data of Conducting PANI–PSt Blends (T_m = 1400 K)

f	σ (300 K) (Ω^{-1} cm^{-1})	ρ_1 (Ω cm)	ρ_2 (Ω cm)	T_0 (K)
0.2	4.6	3.5	0.03	979
0.1	2.1	9.3	0.07	910
0.06	1.3	12.3	0.1	1132
0.03	0.28	53.5	0.44	1103
0.02	0.15	102	1.0	900
0.008	0.028	1070	1.3	2618

be nearly equal to $f_c \sim 0.006$ with a critical exponent $t = 1.2$ was deduced from the fit. The theoretical curve is drawn in a full line in figure 1. This small value of f_c can be attributed to the formation of a self-assembled interpenetrating fibrillar fractal network of PANI.[11] Furthermore, small values of the critical exponent t have been already reported for PANI–PMMA blends and attributed to a thermally induced hopping transport between disconnected or weakly connected parts of the fractal network.[12]

The experimental variations of ln σ vs. $10^3/T$ are shown in Figure 2 for samples with a volume fraction f of PANI in the blend above the percolation threshold. They are weakly thermally activated for all compounds. The activation energy is found to be less than 10 meV at room temperature.

At low temperatures, these variations are well fitted by a "$T^{-1/2}$" dependence:

$$\sigma = \sigma_0 \exp - (T_0/T)^{1/2}.$$

This is in good agreement with the model developed by Bussac and Zuppiroli[13] for which conduction results mainly from hoppings between conducting polaronic clusters. The counterions act as tunneling bridges between neighboring PANI chains and therefore create polaronic clusters in which the charge carrier motion is improved.

Above 250 K, the electrical conductivity variations deviate from the "$T^{-1/2}$" dependence for all the conducting blends (Fig. 2). This behavior was attributed by Kaiser et al. to the contribution of the intrinsic metallic conductivity of the conducting polymer.[14] Intrinsic electrical conductivity variations of conducting polymers given by $\sigma = \sigma_1 \exp(T_m/T)$ were first reported by Kivelson and Heeger in polyacetylene.[15]

In this work, deviations from the "$T^{-1/2}$" law are less pronounced than in the case of PANI protonated with camphor sulfonic acid (PANI–CSA) which shows a change to metallic behavior near room temperature.[5] The experimental variations of σ for the whole range of temperature investigated were correctly fitted by $\sigma^{-1} = \rho_1 \exp - (T_m/T) + \rho_2 \exp(T_0/T)^{1/2}$.

The resulting fit parameters are listed in Table I for each blend. The value of T_m represents the energy of phonons with the wave vector spanning the Fermi surface of the highly anisotropic "metallic polymer." For the fit, T_m was chosen to be equal to 1400 K as in the case of polyacetylene.[15] The thermoelectric power (S) shows low positive
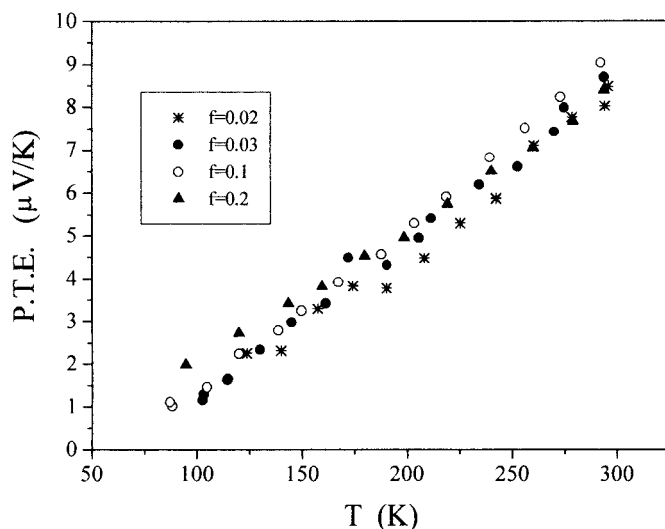

Figure 3   TEP S vs. T of conducting PANI–PSt blends for different volume fractions of polyaniline.

Table II Parameters Deduced by the Fit of the Thermoelectric Power Variations ($S = AT + B$)

f	A (μV K^{-2})	B (μV K^{-1})
0.2	0.032	−1.14
0.1	0.039	−2.53
0.03	0.038	−2.64
0.02	0.037	−2.74

values and exhibits a linear variation vs. temperature (Fig. 3). The experimental curves were fitted on the basis of a linear quasi-metallic model for which thermoelectric power is written as $AT + B$.[16] The resulting fit parameters are listed in Table II. The predominant AT term can be related to the "metallic" conduction within the conducting clusters while the B term can be associated to hopping mechanisms between the clusters.

Thermally activated variations of the electrical conductivity seems to be in contradiction to quasi-metallic variations of the TEP. This apparent conflict has also been reported in doped PANI,[16] doped polyacetylene,[17] and blends or composites with conducting polymers.[18] This conflict is based on the fact that the electrical conductivity is limited mainly by hopping between conducting clusters. On the contrary, the TEP, which is a nul-current coefficient, essentially reflects the intrinsic conduction mechanisms within the clusters in which the main temperature variations develop.

CONCLUSION

New PANI–DiOHP–PSt composites were chemically prepared by codissolution of conducting PANI–DiOHP with a solution of PSt in m-cresol. This method leads to free-standing films with good mechanical properties and a high electrical conductivity. At room temperature, electrical conductivity variations with the volume fraction of PANI in the blend are typical of a percolation system. The weak value ($f_c \sim 0.6\%$) of the percolation threshold is characteristic of the formation of a self-assembled interpenetrating fibrillar fractal network of PANI.

The electrical conductivity variations vs. temperature result mainly from hopping mechanisms between polaronic clusters in the PANI network. The TEP, similar to that in metals, essentially reflects the "metallic" conduction mechanisms within the clusters.

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