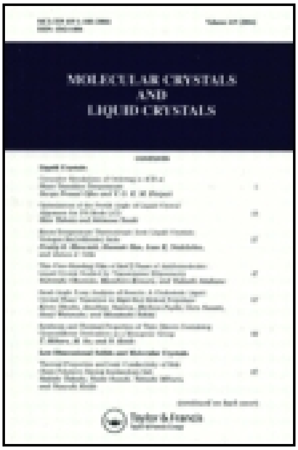

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Percolation Phenomena and Electron Spin Resonance in Nanoscale Polyaniline-Polymethylmethacrylate Blends

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The conductivity and electron spin resonance (ESR) of polyaniline (PANI) – polymethylmethacrylate (PMMA) nanoscale blends have been studied. It has been found that the dependence of the specific volume conductivity on the PANI content in PANI-PMMA blends can be described by a percolation model with extremely low percolation "threshold" in the range 0.8–2% (vol.). The temperature dependence of ESR for the higher percolation threshold of a PANI- PMMA blend has been studied in the temperature range 4.2–300 K. It has been shown that a g-value for unblended PANI and the PANI-PMMA composites is close to the free spin value and is constant at all temperatures, while the spin population is temperature-depended. Based on the temperature dependence of ESR, the existence of two types of spins (localized and delocalized) in the polymer blend is suggested.

Keywords: conductivity; ESR; PANI; percolation; PMMA; polymer blend

INTRODUCTION

Polyaniline (PANI) should be considered as a mesoscopic metal (a "nanometal") with the metallic core surrounded by a non-metallic (or semi-metallic) shell, having a primary particle diameter of 8–10 nm [1,2]. The electrical conductivities of PANI as an intrinsically conducting polymer range from values typical of insulators ($< 10^{-10}\,\Omega^{-1}\text{cm}^{-1}$) to

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those typical of semiconductors ($\sim 10^{-5}\,\Omega^{-1}\,\mathrm{cm}^{-1}$) and to those typical of metals (greater than $10^{2}\,\Omega^{-1}\,\mathrm{cm}^{-1}$). The conductivities are transformed from the former to the latter through the process of doping by a proton acid or electron acceptors. The temperature dependences of the conductivity and the thermo-power were dictated by two contributions: (a) a purely metallic one which is limited by the quantum size of the metallic core and (b) a temperature-activated tunneling process between the primary particles [3,4].

However, major problems related to the successful utilization of PANI are its poor mechanical property and a low solubility in common organic solvents. In addition, PANI cannot be processed in a melt, because it decomposes at temperatures below the melting point [5].

To improve the mechanical properties of PANI and its ability to thermo-procession, the polymer blends and compositions with elastic polymer matrixes have been used [1,5–8]. For these purposes, the electrochemical polymerization of aniline in a polymer film on the electrode surface [5] or blending of PANI with other polymers using a cosolvent can be employed. The method of template synthesis of PANI in polymer matrixes [7,8] gives the best results for obtaining PANI nanocomposites with polyvinyl alcohol (PVA) and polyacrylate matrixes.

It has been found that the blends of PANI doped by camphor sulphonic acid (CSA) with dielectric polymer matrices–polyvinyl chloride (PVC) and poly-methylmethacrylate (PMMA)-show the unexpected conductivity behavior [1,6]. The decrease of the conductivity as the temperature decreases is much smaller than that in unblended PANI. This leads to the conductivity in blends that is larger at low temperatures than that in unblended PANI. In addition, the PANI/PMMA blend with 40% PANI-CSA has a higher conductivity than unblended PANI even at room temperature [1,3].

To obtain the evidences for the mechanism of charge transport in the polymer blends, we will study the conductivity and the temperature dependence of the ESR spectrum of sulfuric acid (SA)–doped PANI/PMMA blends.

EXPERIMENTAL

SA-doped PANI was prepared by the oxidative polymerization of aniline with ammonium perchlorate in 0.5 M sulfuric acid according to [9]. Poly-methylmethacrylate with a molecular mass of 600000 and the temperature of destruction $T_D = 473\,\mathrm{K}$ was used as a dielectric polymer matrix. PANI/PMMA composites were obtained by the blending of PANI and PMMA in a mixed toluene-DMSO solution under ultra-sound treatment. The solvent was evaporated under dynamic vacuum conditions at $T = 323\,K$. The electrical conductivity of SA-PANI/PMMA blends was measured on pressed cylinder bulk samples ($d = 1.8\,mm$, $h = 2\,mm$) by the two-probe method described in [4] at room temperature in air.

The EPR spectra of the SA-PANI/PMMA blends in quartz cells were investigated by using a spectrometer with the microwave field frequency $\nu = 9.756 \pm 0.001\,GHz$ in the temperature interval $T = 4.2$–$300\,K$ [9].

RESULTS AND DISCUSSION

It has been found that the electrical conductivity of the obtained polymer blends can be controlled in a wide range (10–12 orders of magnitudes) by a small amount of a conducting polymer. The values of specific volume conductivity for SA-PANI/PMMA blends are typical of semiconductors and are in the range $10^{-7} - 10^{-5}\,\Omega^{-1}m^{-1}$ (or $10^{-4} - 10^{-3}\,\Omega^{-1}cm^{-1}$). Such polymer blends have conductivity suitable for the application as antistatic polymer materials [10]. At the SA-PANI content from 1 to 20 % (weight), the conductivity of the blends is higher than that for pure SA-PANI. The further increase of the PANI content leads to approaching the conductivity to that of the pure SA-PANI sample. Simultaneously, the deterioration of mechanical properties of the blends is observed.

To determine the “critical” concentration of the conductive polymer corresponding to the drastic increase of the conductivity, the semilogarithm dependence of the specific volume conductivity on the volume content of PANI has been plotted (Fig. 1).

As shown in Figure 1, the conductivity of (SA)-PANI/PMMA composites demonstrates a nonlinear dependence on the PANI volume concentration. The dependence of the conductivity on the PANI concentration can be described by the percolation model [8,11] with a “threshold” of percolation in the range 0.8–2% (vol.). Such low value of the percolation threshold is characteristic of composites with the conducting polymer phase [5–8]. The dependence of the specific conductivity (σ) on the volume content of a conductive component (P) in the range higher than the percolation threshold P_c, may be described by the relation

$$\sigma = |P - P_c|^t,$$

where t is the critical parameter which has average values from 1.6 to 1.9 for dispersed composites [8].

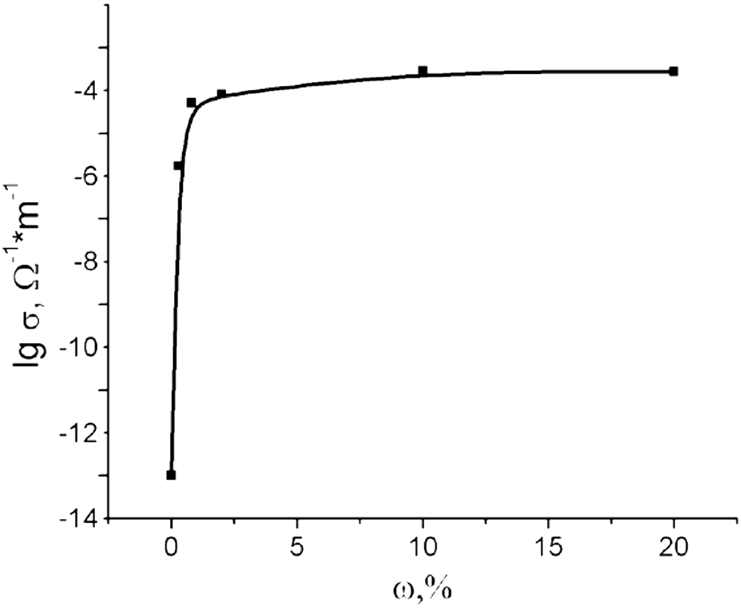

FIGURE 1 Semi-logarithmic dependence of the specific volume conductivity on the SA-PANI volume concentration in (SA) PANI/PMMA composites at T = 298 K.

The PANI/PMMA blend is a colloidal dispersion of polyaniline [12]. We have supposed that the extremely low threshold of percolation for the PANI/PMMA blend is due to the formation of a conducting network in the dielectric matrix inside the host polymer. From the other hand, the dielectric polymer matrix may affect the electron structure of the conjugated polymer and change the population of unpaired spins corresponding to the polaron carrier concentration [13].

The ESR study of the SA-PANI/PMMA blend has been carried out in the temperature interval 4.2–300 K. The ESR spectra of the polymer blend with a higher percolation threshold for 10% (SA) PANI-90% PMMA are shown in Figure 2.

With increase in the temperature, a g-value for unblended (SA) PANI and SA-PANI-PMMA composites is close to the free spin value and is constant at all temperatures (see Table 1).

It has been found that the line shape is close to symmetric at low temperatures. But when the temperature grows, the asymmetry ratio of peak altitudes (A/B) increases to 1.08 and demonstrates a minimum (A/B = 0.95) at the $T = 67\,\mathrm{K}$. This behavior is similar to that observed for the CSA-doped (40%) PANI-PMMA blend and can evidence for the

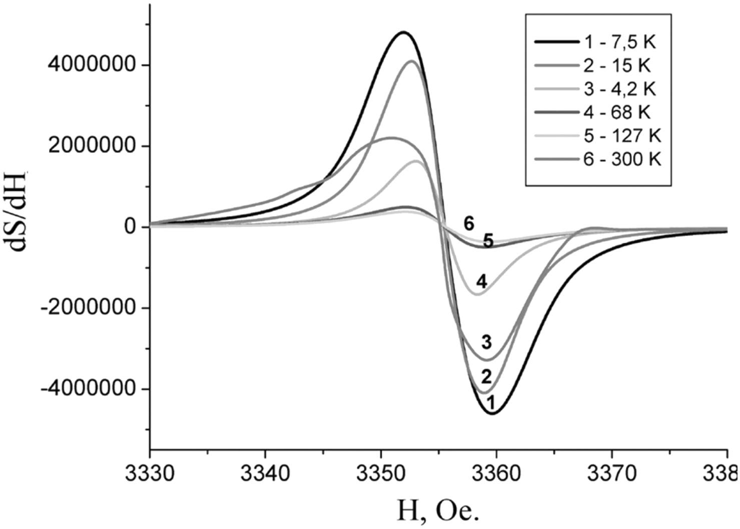

FIGURE 2 EPR spectra of the 10% SA-PANI-90%PMMA blend at different temperatures.

Dysonian line shapes [1,12]. The pure (SA) PAN is characterized by the line asymmetry near 1.5 [9].

For all temperatures, the *g*-values are similar to the free electron's value of 2.0023, which indicates that charge curriers in the PANI and PANI-PMMA samples exist primarily as polysemiquinone radical

TABLE 1 Parameters of EPR Spectra for the PANI-PMMA Blend at Different Temperatures

Temperature, T, K	$g \pm 0{,}0002$	Constant of spin-spin interaction, $T_2 * 10^8$, s	Peak-to-peak distance, ΔHpp, Oe	Degree of line asymmetry, A/B
4.2	2.0025	2.75	10.36	0.995
7.5	2.0025	2.18	8.21	1.001
15	2.0025	1.41	5.87	1.002
28	2.0025	1.37	5.15	1.003
68	2.0025	1.33	5.05	0.950
97	2.0025	1.81	6.81	1.050
127	2.0025	1.98	7.44	1.070
227	2.0025	2.06	7.76	1.075
245	2.0026	2.14	8.05	1.081
300	2.0027	2.20	8.29	1.080

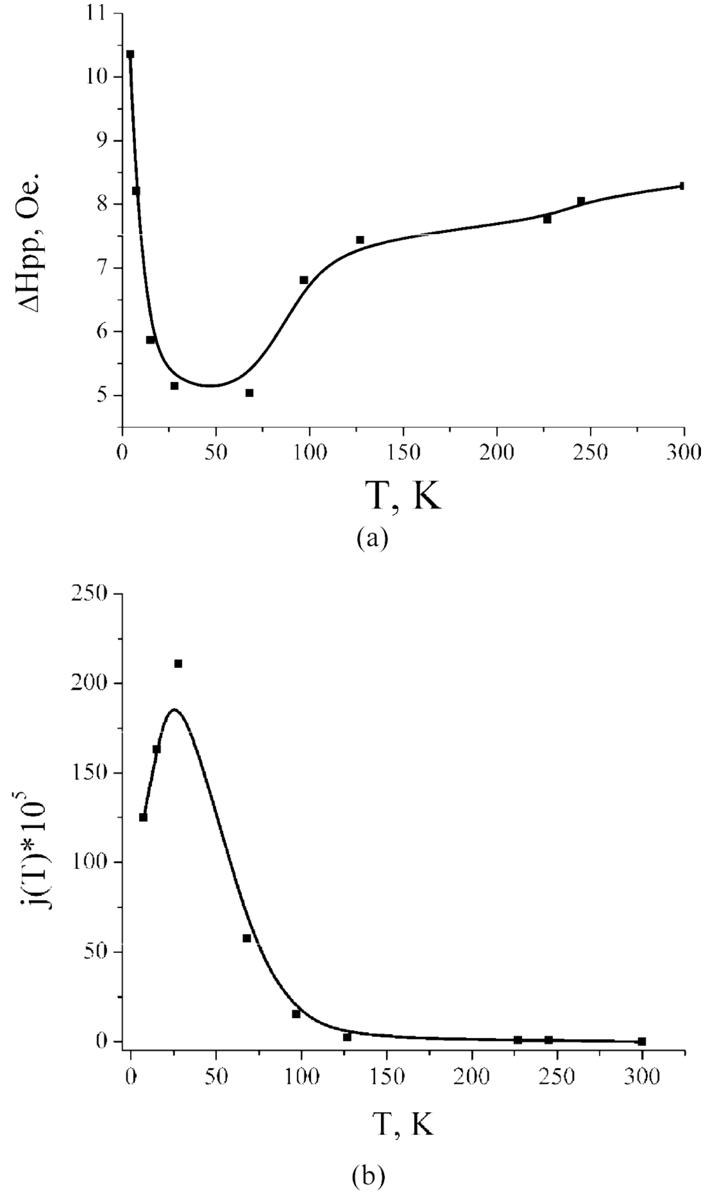

FIGURE 3 Temperature dependence (a) of the peak-to-peak EPR line width (ΔHpp) and (b) the differential distribution of the spin concentration of the PANI/PMMA blend.

cations – polaron carriers [3]. For the polymer blend (10% PANI), a value of ΔHpp is wider in comparison with that of PANI (3.1 Oe [9]) and increases from 3.5 to 8.3 Oe demonstrating a minimum near $T = 50\,\mathrm{K}$, as shown in Figure 3a. The time of the spin-spin relaxation (T_2) have a similar temperature behavior and achieves a value of $1.3{\cdot}10^{-8}$ s in the temperature interval 28–70 K (see Table). Further, a close correlation between the EPR parameters such as the line width ΔHpp and the peak ratio A/B demonstrates that both mobile and fixed spins are involved in the composites [3].

In the temperature region corresponding to the minimum of ΔHpp, a peak of the spin concentration is observed (Fig. 3b). These counter variations confirm the existence of highly localized charge carriers in the polymer blend at $T = 15$–$70\,\mathrm{K}$ and can be associated with the paramagnetic–anti-ferromagnetic transition about these temperatures [15].

CONCLUSION

The conductivity of PANI-PMMA blends can be described by the percolation model with extremely low percolation “threshold” in the range 0.8–2.6% (vol.). The EPR study of PANI/PMMA blends in the temperature range 4.2–300 K showed that a g-value for unblended PANI and PANI/PMMA composites is close to the free spin value and is constant at all temperatures, while the spin population is minimum near 50 K. Based on the temperature dependence of ESR, the existence of two types of spins (localized and delocalized) in polymer blend is suggested.

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