

Electrical, Physicomechanical, and X-Ray Studies on Ethylene-Vinyl Acetate Copolymer/Polyaniline Blends

T. JEEVANANDA,¹ SIDDARAMAIAH,¹ H. SOMASHEKARAPPA,² R. SOMASHEKAR²

¹ Department of Polymer Science and Technology, S. J. College of Engineering, Mysore 570 006, India

² Department of Studies in Physics, University of Mysore, Mysore 570 006, India

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ABSTRACT: The conductive blend consisting of ethylene-vinyl acetate (EVA) and a polyaniline/*p*-toluene sulfonic acid (PAn/TSA) complex were prepared by a thermal doping process using a Brabender plasticorder at 150°C. The conductivity, dielectric constant, dissipation factor, mechanical behavior, and structural aspects of these blends were investigated. A higher percentage of the PAn/TSA complex in the EVA matrix resulted in an increase in the electrical properties and a decrease in the mechanical properties like the tensile strength and percentage of elongation. These results were compared with the microcrystalline parameters of the blend obtained from X-ray profile analysis. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1730–1735, 2002

Key words: polyaniline; ethylene-vinyl acetate; thermal doping; electrical properties; wide-angle X-ray scattering

INTRODUCTION

Polyaniline (PAn) is an environmentally stable conducting polymer with excellent electrical, magnetic, and optical properties. Because of this, it has many potential applications in secondary batteries, electromagnetic interference shielding, molecular sensors, nonlinear optical devices, electrochromic displays, and microelectronic devices.^{1–6} However, PAn is insoluble in common solvents in its conductive form and begins to degrade before melting. The poor processability of PAn by methods used in the plastics industry and its inadequate mechanical properties limit its commercial applications. Methods were recently de-

veloped to overcome these problems. Using functionalized acids, such as *p*-toluene sulfonic acid (TSA),⁷ dodecylbenzene sulfonic acid, and camphor sulfonic acid,^{8,9} improves the solubility of the polymeric complex in common solvents. Besides, these dopants increase the thermal stability of the conducting polymers, enabling melt blending with conventional polymers on a large scale.^{10,11} Currently conductive polymer blends and composites are receiving increased attention because they offer a convenient and economic way of producing materials with desired electrical and mechanical properties for end use applications. Recently, a “thermal doping” process was developed in which a dedoped form of PAn referred to as emeraldine base (EB) and a functionalized protonic acid mixed with an insulating polymer matrix is blended at a higher temperature using a plasticorder to form a conductive PAn blend. This method enables the doping of PAn without using an auxiliary solvent. Only a few studies dealing with the blending of PAn with an insulating ma-

Correspondence to: Siddaramaiah (siddaramaiah@yahoo.com).

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trix by melt processing were reported.^{12–16} These investigations mainly focused on the electrical, mechanical, morphological, and thermal studies of PAn blends with an insulating polymer matrix using a thermal doping process.

In the present study ethylene-vinyl acetate (EVA) and a conductive PAn-TSA complex were blended by the thermal doping process using a Brabender plasticorder to form a conductive EVA-PAn blend. The EVA was selected as a matrix polymer because it offers excellent ozone and weather resistance and good mechanical properties. The electrical and mechanical properties of these blends were determined experimentally. The structural investigation of a thermally processed conducting EVA-PAn blend was carried out using a wide-angle X-ray scattering (WAXS) study. We recently reported the thermal behavior and surface morphology of these blends.¹⁷

EXPERIMENTAL

Materials

Aniline (E. Merck) was distilled under nitrogen and stored at low temperature prior to use. Reagent grade ammonium persulfate, hydrochloric acid, TSA, and sodium hydroxide (SD Fine Chemicals) were used as received. An EVA copolymer (M/S Polyolefins Industries Ltd.) was obtained that had a density of 0.93 g/mL, a melt flow index of 2 g/10 min, a VA content of 12%, and a softening point of 74°C.

Synthesis of PAn

The PAn was chemically synthesized by oxidation of aniline with ammonium persulfate in hydrochloric acid in large scale according to the literature procedure.¹⁸ The PAn-HCl complex obtained was dedoped by stirring in 1% NaOH solution for 24 h and dried in a vacuum oven at 50°C for 24 h. The obtained dedoped PAn is referred to as EB. The EB was mechanically mixed with TSA using an agate mortar and pestle for about 10–15 min with a weight ratio of 1:3 EB:TSA.

Thermal Processing of EVA-PAn Blend

The conductive blend of the EVA and PAn/TSA complex was melt blended in a Brabender plasticorder. The following sequence was adopted to blend EVA with the conductive PAn: first the temperature of the plasticorder was set to 150°C.

After attaining the temperature the EVA was loaded and melt mixed at 60 rpm for 5 min. The mechanically mixed PAn-TSA complex was then loaded in varying contents (10–30%) to the plasticorder at 40 rpm and thoroughly blended with EVA for another 5 min. The obtained mass was made into sheets using a compression mold at 150°C with a pressure of 1 MPa for 1 min and cooled to room temperature by water circulation.

Characterization

The obtained blends were characterized for volume resistivity (ρ_v) using a Dr. Thidigg instrument (MILLI-T02) according to ASTM D257 at the applied dc voltage of 500 ± 5 V under a laboratory atmosphere. Conductive rubber was used as an electrode (20 cm²). The instrument gives the direct volume resistance (R_v , ohms) at the applied voltage. The volume resistivity (ohm cm) was calculated using the relation

$$\rho_v = AR_v/t \quad (1)$$

where A is the area of the measuring electrode (cm²) and t is the average thickness of the specimen (cm).

From the volume resistivity we can calculate the volume conductivity (σ_v , S/cm) using the relation

$$\sigma_v = 1/\rho_v \quad (2)$$

The dielectric constant and dissipation factor ($\tan \delta$) were measured with a HP LCR meter according to ASTM D150. The dielectric constant and $\tan \delta$ were both measured at varying frequencies from 100 to 30,000 kHz. Physical properties like the density and surface hardness (Shore A and Shore D) were measured according to ASTM 792-86 and ASTM D785, respectively. The mechanical properties such as the tensile strength and percentage of elongation at break (ASTM D638) were measured using a Hounsfield 4302 universal testing machine. A minimum of six samples were tested at room temperature for each composition and the average value was reported.

X-Ray Recording and Profile Analysis

The X-ray diffraction data on the EVA-PAn samples were collected on a Shimadzu XD-D1 X-ray powder diffractometer with germanium monochromated CuK α ($\lambda = 1.5406$ Å) radiation in

Table I Conductivity, Dielectric Constant, and $\tan \delta$ Values of EVA-PAn Blends

EVA/PAn Composition (%, w/w)	Conductivity (S/cm) (± 4)	Dielectric Constant at 100 kHz (± 0.05)	Dissipation Factor ($\tan \delta$) at 100 kHz (± 0.005)
100/0 (pure EVA)	2.27×10^{-15}	1.715	0.023
90/10	5.37×10^{-11}	2.295	0.094
85/15	3.00×10^{-10}	2.543	0.204
80/20	6.00×10^{-9}	2.819	0.586
75/25	1.20×10^{-8}	6.364	0.877
70/30	4.37×10^{-8}	11.380	1.660
0/100 (pure PAn)	2×10^{-1}	—	—

transmission mode; a curved position sensitive detector was used in the 2θ range from 5 to 30° at a scan rate of $4^\circ/\text{min}$.

We estimated the parameters such as the crystal size ($\langle N \rangle$) and lattice strain (g , %) by simulating the profile employing the procedure described earlier^{19–22} and using Bragg reflection at $2\theta \approx 21.1^\circ$.

Using eqs. (13) and (14) of Somashekar and Somashekarappa²³ we simulated the X-ray reflection profile by inputting $\langle N \rangle$ and g values. This process is continued for varying input values of $\langle N \rangle$ and g till one gets a good match between an experimental and simulated profile. To carry out such a computation we wrote a program using a multidimensional minimization simplex algorithm. This program gives the best values of $\langle N \rangle$ and g .

RESULTS AND DISCUSSION

Electrical Properties

The electrical properties such as the conductivity, dielectric constant, and $\tan \delta$ of EVA-PAn blends with varying compositions (10–30%) of PAn were measured at room temperature and are tabulated in Table I. The PAn and EVA had average conductivities of 2×10^{-1} and 2.27×10^{-15} S/cm, respectively. Observe from the Table I that all the electrical properties increase with an increase in the PAn content and lie in the range of 5.37×10^{-11} to 4.37×10^{-8} S/cm and 2.295–11.380 and 0.094–1.660 for the conductivity, dielectric constant, and $\tan \delta$, respectively. The increase in the electrical properties is due to the increase in the delocalization of π electrons. This material can be used for dissipation of electrostatic charges.

We also measured the dielectric constant and $\tan \delta$ values at different frequencies (100–30,000 kHz). The effect of the frequency on the electrical properties like the dielectric constant and $\tan \delta$ for EVA-PAn blends are graphically represented in Figure 1(a and b), respectively. Figure 1 shows that the electrical properties decrease with an increase in the frequency. This may be due to delocalization of charge carriers at higher frequency.²⁴

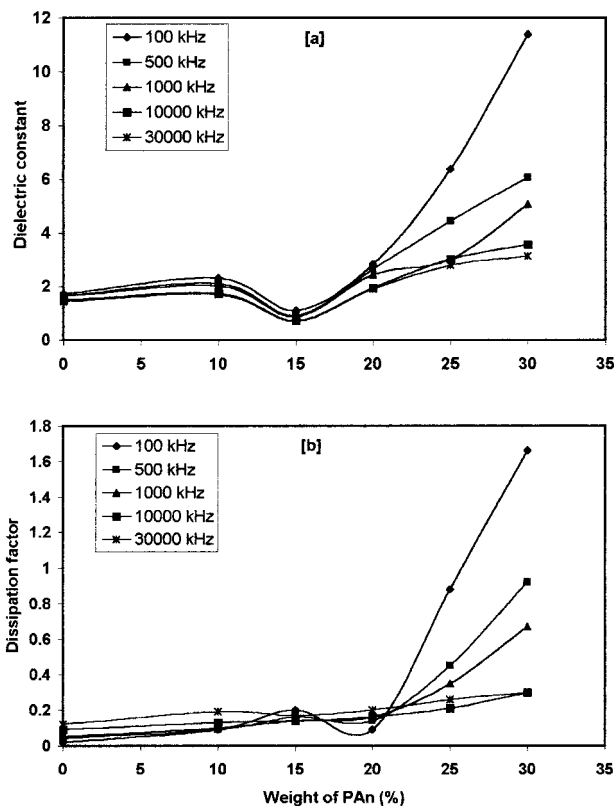


Figure 1 The effect of the frequency on the (a) dielectric constant and (b) dissipation factor for different percentages of PAn in the EVA matrix.

Table II Physicomechanical Properties of EVA-PAn Blends

EVA/PAn Composition (%, w/w)	Density (g/mL)		Tensile Strength (MPa) (± 2)	Elongation at Break (%) (± 3)	Surface Hardness	
	Theor.	Expt.			Shore A (± 2)	Shore D (± 2)
100/0 (pure EVA)	—	0.930	22.1	445	90	37
90/10	0.959	1.018	9.0	182	95	45
85/15	0.973	1.051	6.7	103	97	47
80/20	0.988	1.103	5.4	41	93	44
75/25	1.002	1.111	4.5	22	95	60
70/30	1.017	1.160	4.1	18	92	57
0/100 (pure PAn)	—	1.220	—	—	—	—

Physicomechanical Properties

The physicomechanical properties such as the density, surface hardness (Shore A and Shore D), tensile strength, and percentage of elongation at break for EVA and EVA-PAn blends are tabulated in Table II. PAn and EVA had an average density of 1.22 and 0.93 g/mL, respectively. It can be observed from the Table II that the density value increases with the increase in the PAn content in the blend because the PAn density is higher than that of EVA. All EVA-PAn blend density values lie between the densities of their homopolymers and are 1.018–1.160 g/mL. We also calculated the densities by the volume additive principle, which states that $[d = w_1d_1 + w_2d_2]$, where d is the density of the blend, w_1 and w_2 are the weight fractions of the constituents, and d_1 and d_2 are the corresponding densities. The Table II shows that the experimental density values are higher than the calculated ones. These higher density values that were observed may be due to a chemical interaction between the —NH of PAn and the —C=O of EVA or the presence of excess unbounded dopant (TSA). However, in the present case it is due to the presence of excess unbounded dopant. The excess unbounded dopant was extracted with water and the density was recorded again. A reduction in the density values was observed after extraction of the dopant. This result clearly reveals that the higher density value observed is due to excess unbounded dopant, even though some amount of chemical interaction between EVA and PAn cannot be completely ruled out. The surface hardness values fall in the range of 90–97 Shore A and 37–60 Shore D. The decrease in the hardness value (Table II) above a 15% addition of PAn is again attributable to the presence of excess unbounded dopant. This

excess dopant is acting as a nonreinforcing filler in the resulting blend.

Table II reflects a drastic reduction in the tensile strength from 9.0 to 4.1 MPa with the increase in the PAn-TSA complex from 10 to 30% in the EVA matrix. This reduction is due to the following reasons: PAn possesses a very stiff polymer backbone from the presence of the aromatic rings, and the double bonds that form usually result in an extremely brittle polymer^{13,25}; and the presence of excess unbounded dopant in the blend, which acts as a nonreinforcing filler that weakens the interaction (secondary interaction) between the PAn and EVA. Table II also reveals the drastic reduction in the percentage of elongation from 182 to 18 as expected.

X-Ray Profile Analysis

An X-ray diffractogram of EVA and all EVA-PAn blends is given in Figure 2. It is evident from the figure that there is one intense broad reflection at 21.1° (2θ), which suggests that the diffraction also contributed to an amorphous polymer region and was almost equivalent to an insulating EB state observed in PAn.^{26–28} In those articles the values of the crystal size in PAn were estimated using the Scherrer equation without considering the effect of strain broadening, and these values lie between 30 and 70 Å. In the present case the crystal size was estimated by including the lattice distortion of the second kind on the basis of Hosemann's paracrystalline model,²⁹ and the values lie between 75 and 90 Å. Table III gives the various microcrystalline parameters like the crystal size ($\langle N \rangle$), smallest crystal unit (p), crystal size distribution width (α), lattice strain (g , %), enthalpy (α^*), and the surface weighted (D_S) and volume weighted (D_V) crystal size values and

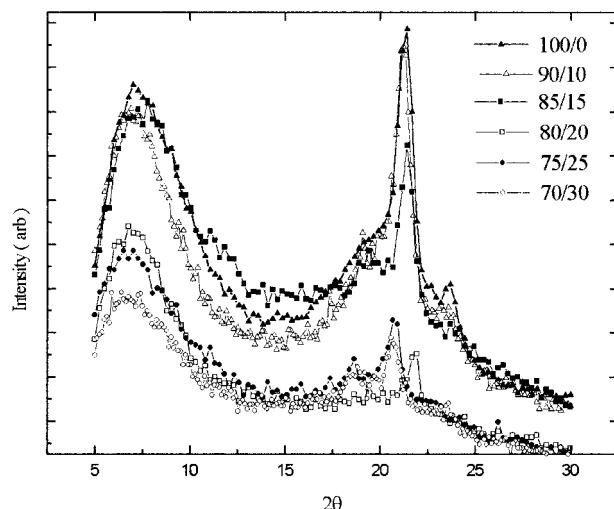


Figure 2 Wide angle X-ray scattering for EVA and EVA-PAN blends.

their ratio. From Tables I and III it is observed that these microstructural parameters change with the PAN concentration and hence the conductivity.

Also observe from Tables I and III that there is relatively high conductivity for the blends having less crystal size and lattice strain values. This is consistent with an earlier observation by us in sodium lauryl sulfate doped PAN and its blend with polycarbonate³⁰ and it is due to the fact that PAN has an intrinsic in-chain conductivity. The lower conductivity value reflects the presence of increased localization of charges and hence leads to changes in the crystal size values. In fact the variation of the crystallinity parallel and perpendicular to the polymer chain direction leads to delocalization of charges and hence affects the conductivity values. With an increase in the disorder of the polymer network, the conductivity associated with a free ion increases because of a lower potential barrier. The α^* calculated using

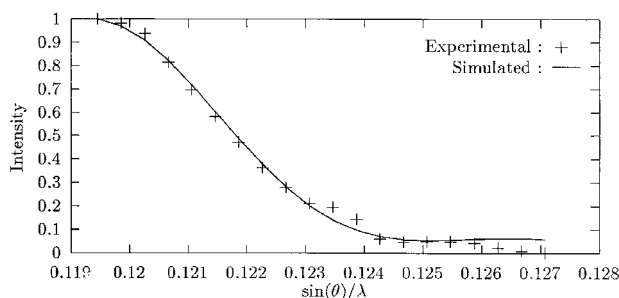


Figure 3 Experimental and simulated X-ray profiles for the 75/25 EVA/PAN blend.

Hosemann's paracrystalline disorder²⁹ decreases with the percentage of PAN in the EVA matrix. Here α^* physically means that the growth of paracrystals in a particular material is appreciably controlled by the level of strain (g) in the net plane structure. The minimum value of α^* indicates the phase stabilization of EVA-PAN blends. A rapid loss in the crystal size value occurs for the 85/15 EVA/PAN blend composition onward because of excess unbounded dopant (TSA), which in turn leads to structural rearrangement and hence influences the conductivity values.¹⁴ A slight increase in the crystal size is observed for the 70/30 EVA/PAN blend and this may be due to the organizational changes in the polymer network.

For the sake of completeness we reproduced the simulated and experimental profile for the 75/25 EVA/PAN blend in Figure 3. In fact, the goodness of the fit was less than 2% in all the samples.

From these studies we can conclude that the EVA-PAN blends that have a small crystal size consume less energy in order to build up the crystal network compared to pure EVA copolymer. It may also be noted from Table III that the D_v/D_s ratio is less than 1.3, which is in good agreement with earlier observations using the integral

Table III Microcrystalline Parameters for EVA-PAN Blends Obtained by WAXS Studies

EVA/PAN Composition (%, w/w)	$\langle N \rangle$	g (%)	p	α	α^*	D_s (Å)	D_v (Å)	Ratio
100/0 (pure EVA)	21.42 ± 0.14	3.15 ± 0.02	15.34	0.165	0.146	90.41	96.73	1.07
90/10	21.24 ± 0.17	1.77 ± 0.02	13.32	0.126	0.082	87.72	96.35	1.10
85/15	16.96 ± 0.35	1.31 ± 0.03	8.68	0.128	0.054	68.70	82.09	1.19
80/20	15.82 ± 0.27	2.38 ± 0.04	8.14	0.130	0.009	66.43	80.94	1.22
75/25	12.38 ± 0.28	1.53 ± 0.03	5.16	0.138	0.005	53.43	69.15	1.29
70/30	17.80 ± 0.15	3.84 ± 0.03	17.19	1.634	0.006	74.54	74.55	1.00

breadth method for both man-made and natural polymers and most of the experiment gives a ratio of 1–2.³¹

CONCLUSIONS

The following conclusions can be drawn from the present investigation:

1. the increase of the electrical properties with the increase in the PAn content in the blend is due to the increase in delocalization of π electrons;
2. PAn acts as a nonreinforcing filler in the EVA matrix;
3. the mechanical properties of the resulting blend decrease with an increase in the PAn content, which is due to the stiff backbone aromatic rings and double bond in the structure of PAn and the presence of excess dopant in the resulting blend; and
4. the microcrystalline parameters decrease with an increase in the PAn content.

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