Study of Electrical Properties for Albumin/Poly(vinyl alcohol) Blends

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ABSTRACT: Thermally stimulated depolarization current (TSDC), d.c. electrical conductivity (σ), and current–time characteristic techniques were used to study electrical polarization and conduction mechanisms for pure poly(vinyl alcohol) (PVA) and 2.5, 5, 10, 12, 15, and 20 wt % albumin content in PVA thin films. The TSDC spectrum for PVA revealed the existence of two broad peaks, while the blend samples show only one broad peak with a shoulder in the high-temperature side. The existence of this current maximum was analyzed and discussed in terms of dipole-orientation and space-charge phenomena. Quantitative analysis was carried out to determine the thermal activation energies of the conduction process, drift mobility, and carrier concentration. The crystallinty of the PVA matrix was enhanced by the addition of albumin, as indicated by X-ray diffraction and differential scanning calorimetry (DSC) measurements. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1748–1757, 2003

INTRODUCTION

Blending is an especially important process for developing industrial applications of polymeric materials. The importance of a polymeric blend is now well established[1–3] and both practical and fundamental studies have been conducted with a number of pairs of polymers. Blending natural polymer with synthetic polymer seems to be an interesting way of preparing polymeric composites.[4–7] Compatibility among components has a marked influence on the mechanical, thermal, and electrical properties of polymer blends.[8,9] Intermolecular interaction regulates the compatibility among the component polymer molecules.[8]

The thermally stimulated depolarization current (TSDC) technique provides vast information about transitions and relaxations in the material and their associated mechanisms.[10,11] The relaxation processes involved in most polymers are not elementary; they have to be described in terms of the distribution of relaxation times or of activation energies. Therefore, to elucidate the origin of a peak in the TSDC spectrum, various methods have been developed. They are related mainly to the behavior of the peak as a function of the polarization parameter[11] and the nature of the electrodes.[12]

Hydration in protein such as bovine serum albumin or hemoglobin is one of the more important factors controlling its electrical conductivity and elasticity and plays an important rule in maintaining the conformation of the material.[13,14] The optical, mechanical, and dielectric constant properties with different concentrations of albumin/poly(vinyl alcohol) (PVA) were investigated and the results were reported.[15] In this work, as continuation of these studies, TSDC, d.c. electrical conductivity, and current–time characteristics of albumin/PVA thin films were investigated as a function of the composition, field strength, and temperature.

EXPERIMENTAL

PVA granules (MW 125,000) and bovine serum albumin (MW 67,000) with high purity were obtained, respectively, from El-Nasr Co. (Cairo, Egypt) and Fluka Biochemica (Buchs, Switzerland). PVA material was dissolved in a mixture consisting of double-distilled water and ethanol in a ratio of 4:1. Albumin was dissolved in double-distilled water and added to a PVA solution in different percentages of albumin (2.5, 5, 10, 12, 15, and 20 wt %). The films of pure and albumin-content PVA were cast on to glass plates of double-distilled water and ethanol solutions and slowly dried in an air oven at 298 K for 72 h to minimize gelatin effects. Thin films of approximately 0.2 mm were cut into square pieces.

For ohmic contacts, the surfaces were coated with silver collidal paste. Before TSDC measurements, po-
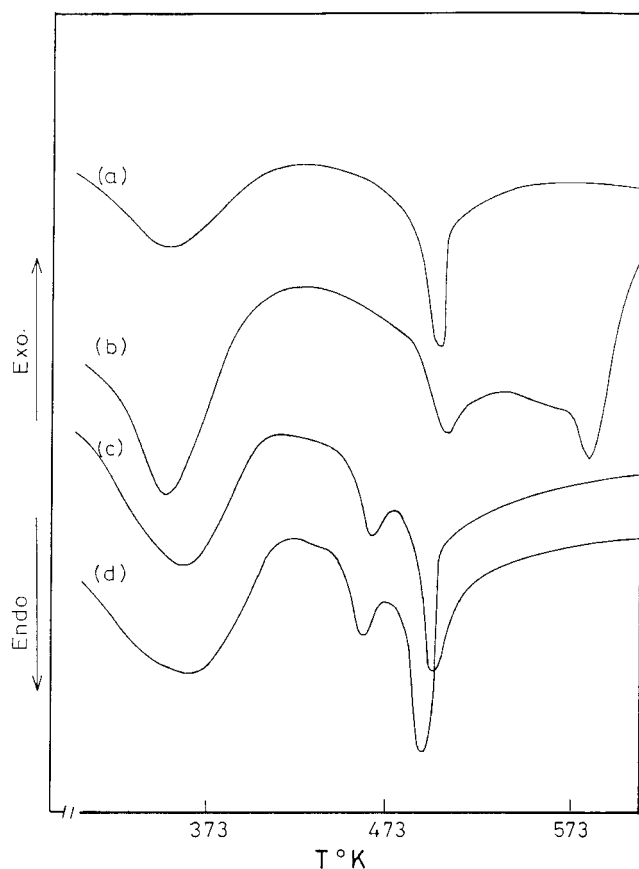
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Figure 1 DSC thermograms of (a) pure PVA, (b) pure albumin, (c) 2.5 wt % albumin, and (d) 10 wt % albumin content in PVA.

Figure 2 X-ray diffraction pattern for (a) pure PVA, (b) 2.5 wt % albumin, and (c) 10 wt % albumin content in PVA.

larization of the samples was carried out by first heating them to a specific polarization temperature, $T_p = 333$ K, and then applying an electric field, $Ep = 0.5$ kV/cm, for a polarizing time of 1 h. After polarization, the field was switched off at room temperature and the samples were shorted for about 15 min to remove frictional and stray charges[16] if any. Then, the depolarization current was recorded using a Keithley electrometer, Model 616. The d.c. electrical conductivity and current–time characteristics were measured by applying a constant field 1 kV/cm. All electrical measurements were made at a moderating heating rate of 1°C/min from room temperature to about 423 K.
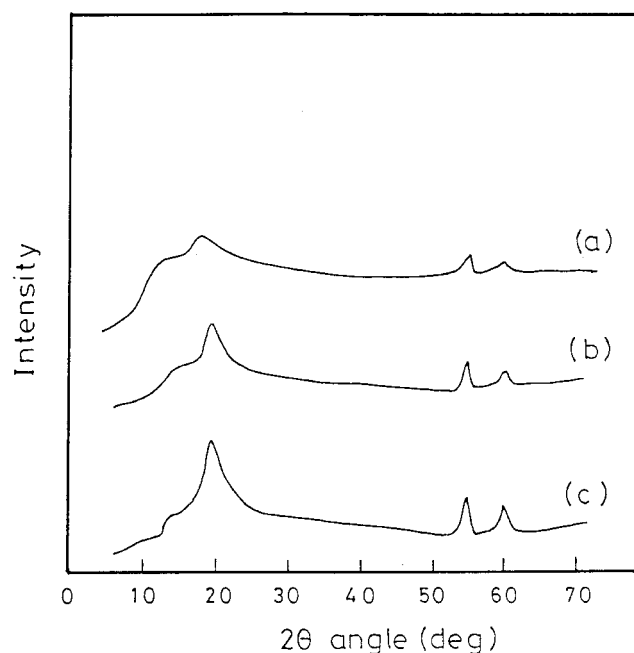
RESULTS AND DISCUSSION

Differential scanning calorimetry (DSC) thermograms

The thermal properties of pure PVA, pure albumin, and PVA with a 2.5 and 10 wt % albumin content were examined by DSC to estimate how the thermal transitions of PVA were affected by the concentrations of albumin. The pure PVA curve (a) in Figure 1 shows a broad glass transition (T_g) and a relatively large, sharp crystalline melting (T_m) peaks at 361 and 494 K, respectively.[5,6,17] For pure albumin, three endothermic phase transitions appeared, as in curve (b) of Figure 1. The first peak is broad and relatively intense at 358 K, while the other two peaks are minor at about 496 and 583 K. The melting point of albumin was measured using an electrothermal apparatus and it was found to be around 576 K. Therefore, it is suggested that the endotherms observed around 583 K can be attributed to the thermal decomposition of albumin. As PVA is blended with 2.5 and 10 wt % albumin, new endothermic peaks appeared

TABLE I
Glass Transition Temperature, T_g, Unknown Detected Phase Transition, T_{un}, Melting Temperature, T_m, and Heat of Enthalpy, ΔH kJ/g, for the Phase Transitions of Albumin Content in PVA Thin Films Measured by DSC

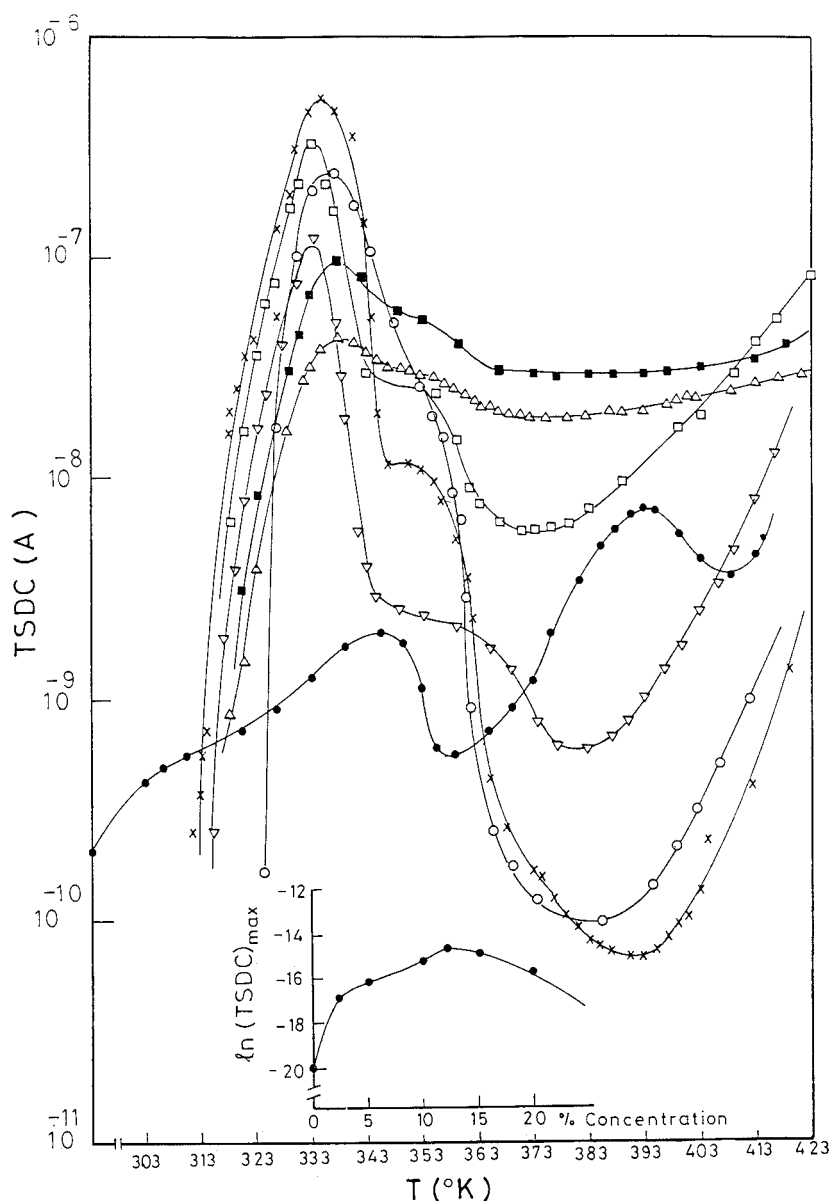| Albumin/PVA (%)	T_g (K)	ΔH_g (kJ/g)	T_{un} (K)	ΔH_c (kJ/g)	T_m (K)	ΔH_m (kJ/g)
100/0	357.6	0.32	496.04	0.049	583.32	0.085
0/100	361.02	0.35	—	—	493.56	0.814
2.5/97.5	366.12	0.41	466.66	0.042	491.20	0.10
10/90	369.8	0.62	465.02	0.060	489.31	0.11

Figure 3 TSDC for (●) pure PVA, (△) 2.5, (■) 5, (○) 10, (×) 12, (□) 15, and (▽) 20 wt % albumin content in PVA thin films.

at about 467 and 465 K, respectively, while the crystalline melting peak of albumin disappeared due to a low percentage of albumin material and/or the weakness of the transition. The values of the heat of reaction per gram of the sample and the enthalpy associated with these endotherms ΔH, thus analyzed, are listed together with T_g and T_m data in Table I. In the blend of the two polymers, as the composition increases from 0 to 10 wt % in albumin content, the T_g of PVA tends to shift to the higher-temperature region and there is a broadening of the width of the transition. This may allow one to consider the system to be more or less partially miscible in the amorphous region in the corresponding composition range. From Table I, it is observed that the enthalpy associated with these endotherms increases with an increasing albumin content. Also, the position of T_m shifts

to a lower temperature in comparison with pure PVA. The value of T_m depends on the degree of crystallinty and the size distribution of the crystallites. The sensitivity of ΔH and T_m to the blend composition indicated the presence of interaction between albumin and the PVA matrices. The tendency of an apparently disproportional increase in ΔH with an increase of albumin content implies a rapid increase of the degree of crystallinty of the PVA component due to blending with albumin, corresponding exactly to the observation in X-ray diffraction (XRD) profiles (see the next section).

X-ray diffraction

X-ray diffraction analysis[18] has yielded much valuable information on the configuration of macromolecules
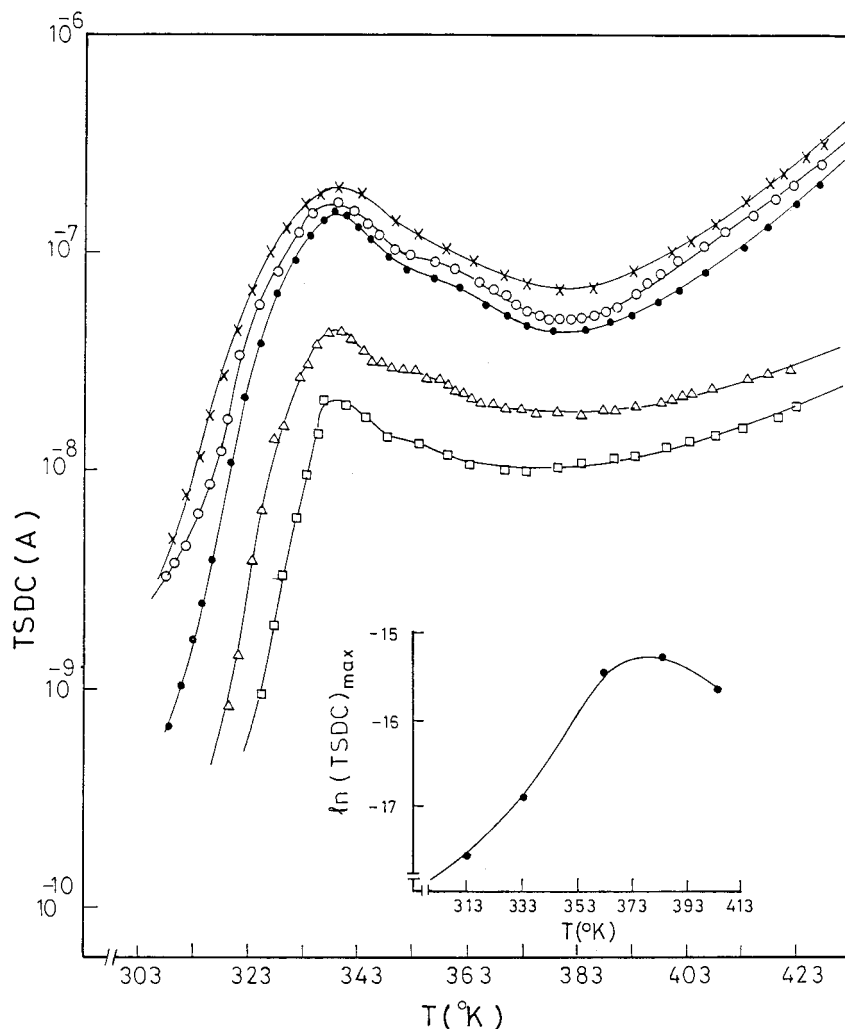
Figure 4 Effect of polarizing temperature T_p = ($\square$) 313, ($\triangle$) 333, ($\bigcirc$) 363, ($\times$) 383, and ($\bullet$) 403 K on TSDC for 2.5 wt % albumin content in PVA thin films at constant Ep = 0.5 kV/cm.

and on the structure, orientation, and size-ordered regions in the material. Pure PVA and blend samples with different concentrations of albumin are subjected to X-ray diffraction (XRD) analysis to check their crystalline formation and the compatibility of the blend system. The scanning of the samples was carried out by an X-ray diffractometer in a wide range of Bragg angles ($5 \leq 2\theta \leq 70°$) with monochromatized CuKα radiation (λ = 0.15418 nm) and a scanning speed of 2° min^{-1} at 303 K. The typical XRD patterns of pure PVA and 2.5 and 10 wt % albumin-content PVA are shown in Figure 2. The presence of sharp reflections and diffuse scattering in Figure 2 is characteristic of crystalline and amorphous phases, respectively, of the investigated blend polymers. The spectra show typical crystalline peaks for PVA that appear around 2θ = 20°, 54°, and 58°; the first one is due to the (101), (200) plane of the PVA crystal.[9,19] There is a noticeable change in the intensity of the XRD peaks of the samples, while there is no detectable change in the position of crystalline peaks and in the general shape of the position. The crystalline peaks' intensity increases with increasing albumin concentration, indicating an improvement of the crystallinty (see Fig. 2). The increase of crystallinty in the blend system may be due to the hydrogen bonding between —COOH and —NH$_2$ in albumin and —OH groups in PVA. These interactions prevent albumin from "crystallization," but does not significantly destroy the crystalline component of PVA.

Thermally stimulated depolarization currents

The charge produced during the polarization may be due to several microscope processes (induced dipolar polarization, alignment of permanent dipoles, drift of electrons or holes and their trapping, and charge injection from electrodes[20,21]). At the glass transition temperature, chain ends and a substantial number of chain segments acquire sufficient energy to overcome
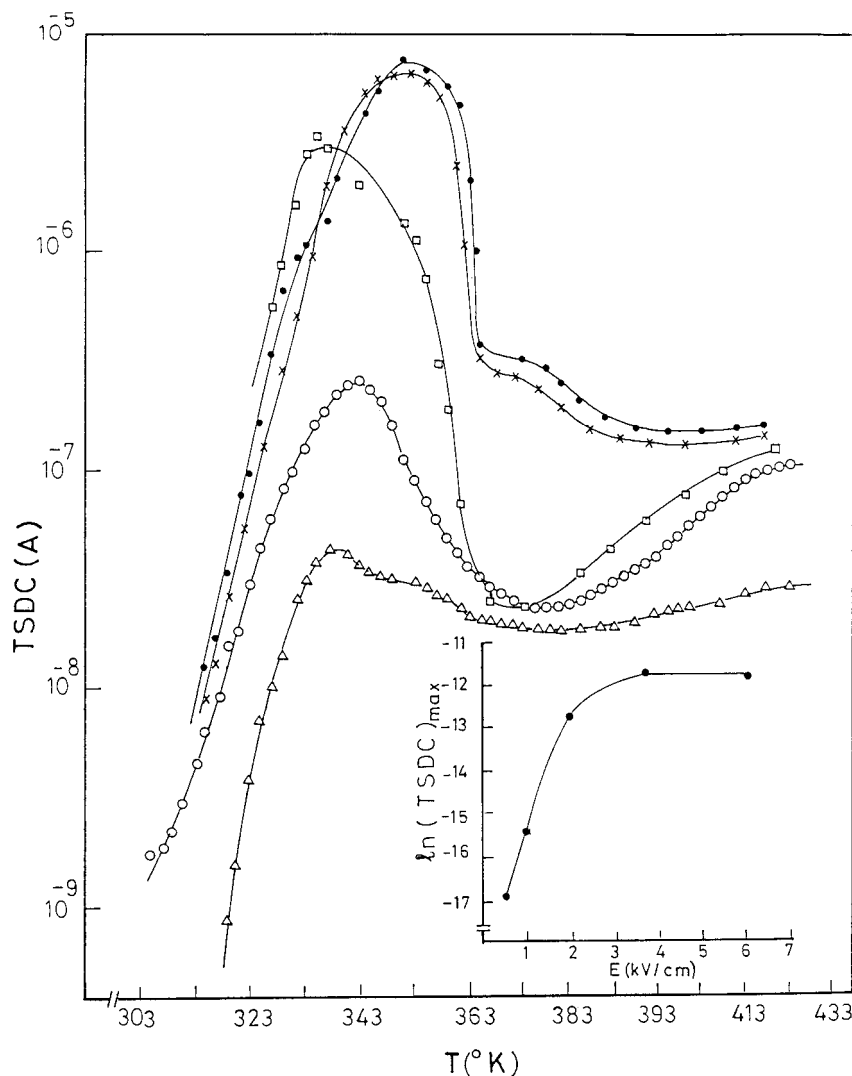
Figure 5 Effect of polarizing field Ep = (△) 0.5, (○) 1, (□) 2, (●) 4, and (×) 6 kV/cm on TSDC for 2.5 wt % albumin content in PVA thin films at constant temperature of 333 K.

intermolecular restraints and undergo rotational and translational motion. Below the T_g or in the glassy state, only atoms or small groups of atoms such as short sections of the main chain or pendent/side groups move against the local restraints of intermolecular interactions. However, above the T_g, or in the rubbery state, there is a sharp increase in the number of possible confirmations. The TSDC spectra of pure PVA and 2.5, 5, 10, 12, 15, and 20 wt % albumin content in PVA samples at a polarizing field of 0.5 kV/cm, polarizing temperature of 333 K, and polarizing time of 1 h are shown in Figure 3. Two separate broad current peaks are observed for the pure PVA sample, consistent with those reported in the literature.[22,23] The low-temperature peak which appears near the T_g of PVA can be attributed to the relaxation of permanent dipoles associated with the micro-Brownian motions of large chain segments. This micro-Brownian motion is a semicooperative action in-

volving tortional oscillation and/or rotation about the backbone bonds in a given chain as well as in neighboring chains.[23,24] The high-temperature peak observed at about 395 K may be the result of the diffusion of the space charge either at the electrode or due to thermal release of charges at high temperature from the increased chain mobility.[25,26]

In all the albumin/PVA blend samples, there is only one broad peak with a shoulder in the high-temperature side, which could be attributed to the relaxation of the poly-blend system. This resulted from the superposition of dipolar groups with a continuum distribution of the relaxation time.[27] The maximum temperature of the relaxation peak is nearly that of the glass transition of the blend system. The shoulder appearing at about 283 K on the higher-temperature side has been associated with an upper component of the glass transition involving the amorphous phase constrained by crystallites.[28]
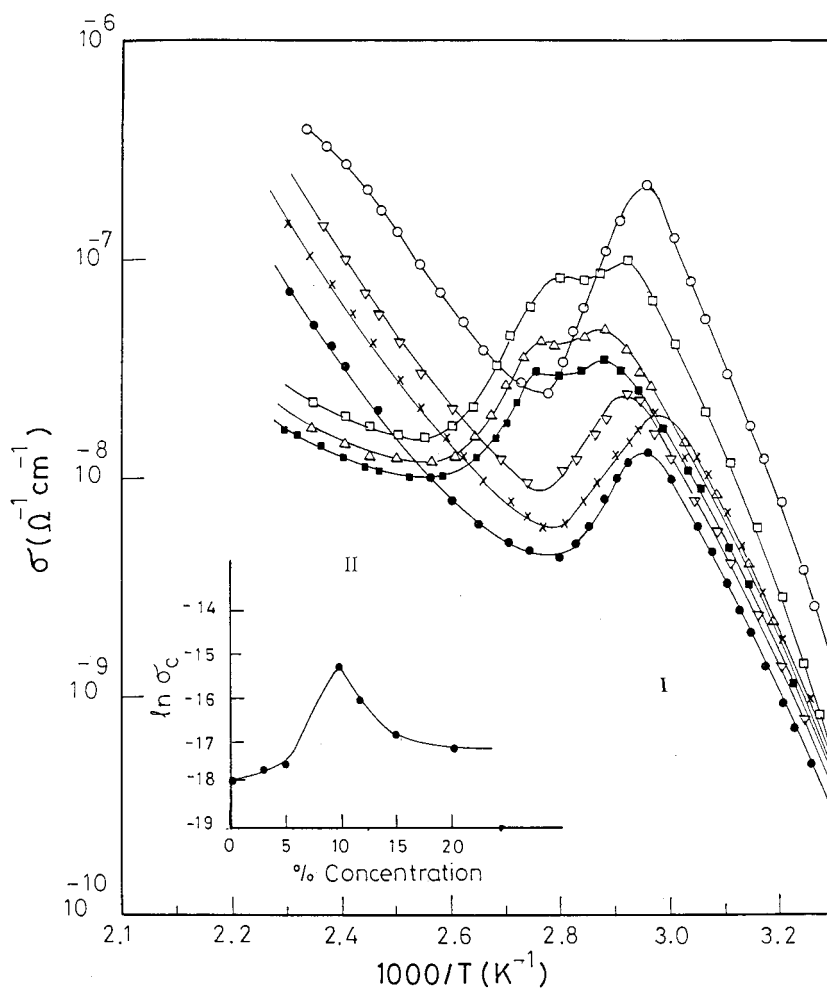
Figure 6 Variation of the electrical conductivity for (●) pure PVA, (×) 2.5, (▽) 5, (○) 10, (□) 12, (△) 1.5, and (■) 20 wt % albumin content in PVA thin films with reciprocal of temperature at 2 V.

It is observed that with an increase in the concentration of albumin in the PVA matrix the strength of the maximum TSDC increased up to the concentration of 12 wt % albumin and then decreased at higher albumin concentrations (see the inset of Fig. 3). The reduction of $(TSDC)_{max}$ is explained by the decrease in the mobility of the molecular chains, which is also related to the reduction of the free volume in the sample. The TSDC spectra obtained for a 2.5 wt % albumin content in PVA at different polarizing temperatures of 313, 333, 363, 373, and 393 K, while other polarizing parameters are kept constant, are shown in Figure 4. The magnitude of the relaxation peak increases with an increasing polarizing temperature, T_p, to 383 K, followed by a decrease at $T_p = 403$ K, while its position slightly shifts toward the higher-temperature side (see the inset of Fig. 4). The shift in the maximum temperature and the appearance of a maximum current as a function of T_p shows the effect of electrode polarization.[29] The intensity and position of the current peak depends on the polarization conditions and the crystallinty. The lowering of the peak

current at a higher polarizing temperature, 403 K, may be explained on the basis that, under this condition, more subpolarization of the inverse polarity is activated.[30] Saturation of the peak for $T_p > T_{peak}$ probably occurs because of the accumulation of carriers near the sample electrodes, which decreases the applied field. Thus, we can say that for a 2.5 wt % albumin content in the PVA sample the relaxation peak is due to the orientation of the molecular dipoles over which a free-charge contribution becomes increasingly important with the temperature, as a result of the increasing injection from electrodes and increasing conductivity.[31]

Figure 5 shows the effects of the polarizing fields of 0.5, 1, 2, 4, and 6 kV/cm on the TSDC spectrum for a 2.5 wt % albumin-content PVA samples while the other parameters are kept constant. The location of the peak temperature changes irregularly with an increasing field while the current peak reaches a constant value (saturation) at a field strength of 2 kV/cm. It should be noted that the current already saturates at relatively low fields of approximately 2 kV/cm, where

TABLE II
Values of the Activation Energy Calculated from D.C. Conductivity Measurements

Albumin/PVA (%)	Activation energy (eV)	
	Low-temperature region I	High-temperature region II
0/100	1.15	0.62
2.5/97.5	1.35	0.64
5/95	1.30	0.72
10/90	1.20	0.30
12/88	1.18	0.17
15/85	1.23	0.20
20/80	1.35	0.24

a dipolar current would usually saturate at much higher fields.[32] Therefore, the observations found in the insets of Figures 4 and 5 led us to believe that the TSDC peak does not correspond to a dipolar relaxation mechanism or, at least, that is masked by a superposed space charge-type mechanism.

D.C. conductivity

The temperature dependence of the d.c. electrical conductivity of pure PVA and blend samples of 2.5, 5, 10, 12, 15, and 20 wt % albumin-content PVA at a fixed applied field of 2 V is shown in Figure 6. It can be seen that the log σ versus $1/T$ plot in the temperature range of investigation can be divided into two straight regions obeying the normal Arrhenius equation. It is worthwhile to mentain that the plots of log σ versus $1/T$ at different fields show the same behavior. The appearance of an intermediate range within 25 K, deviating from the Arrhenius equation, may be due to a glass phase transition. The properties of the amorphous phase obviously play a major role in determining the overall response of the material.[33] It is to be noted that this observed transition was further elucidated in the previous sections concerning DSC and TSDC measurements.

The conductivity at the glass phase transition increases with increasing concentration of albumin up to 10 wt %, followed by a continuous decrease with an increasing albumin concentration (see the inset of Fig. 6). It is also observed that the conductivity in the blend samples is always more than that in the pure PVA sample, even at higher concentrations. The increase in albumin content up to 10 wt % increases the effective free volume in the PVA matrix and facilitates the mobility of ions or molecules. However, at a higher albumin concentration, the mobility of charge carriers decreases, due to their scattering resulting from the inhomogeneous distribution as well as the nonbonding parts of albumin in the PVA matrix.

The initial increase in conductivity with increase in temperature may be due to the formation of local

ordered regions in the otherwise disordered amorphous matrix of PVA. However, the increase in conductivity at higher temperature may be accounted for by the liberation of electrons or ions through the amorphous region of PVA and/or, probably, the interval stresses in the blend sample may also play a role in the motion of the charge carrier.[33,34] From the slopes of the plots in Figure 6 at below and above the glass phase transition, the activation energy values were calculated using the general Arrhenius relation

$$\sigma = \sigma_0 e^{-\Delta E/KT} \tag{1}$$

where σ_0 is constant; ΔE, the thermal activation energy; and K, the Boltzmann constant. The activation energies evaluated from Figure 6 are shown in Table II. In albumin/PVA blends, different processes contribute to the electrical conduction at different temperature ranges, leading to different values of activation energy. In the present study, the conduction mechanism was examined on the basis that the activation energy for electronic conductivity in the polymer is generally lower than that for ionic conduction. Therefore, the data in Table II indicate that the ionic conduction mechanism can be assumed to be effective in the low-temperature region I,
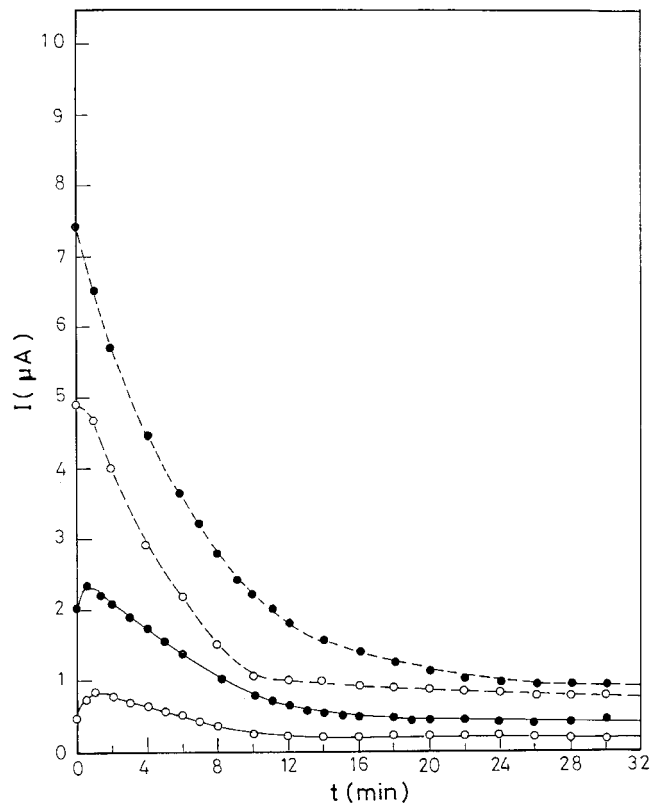

Figure 7 Current relaxation curves for 15 wt % albumin content in PVA thin films at field strength of 0.5 kV/cm with temperature of (–○–) 343 and (– –●– –) 373 K. Dotted lines refer to the first application of voltage, and solid lines, to the reverse polarity.
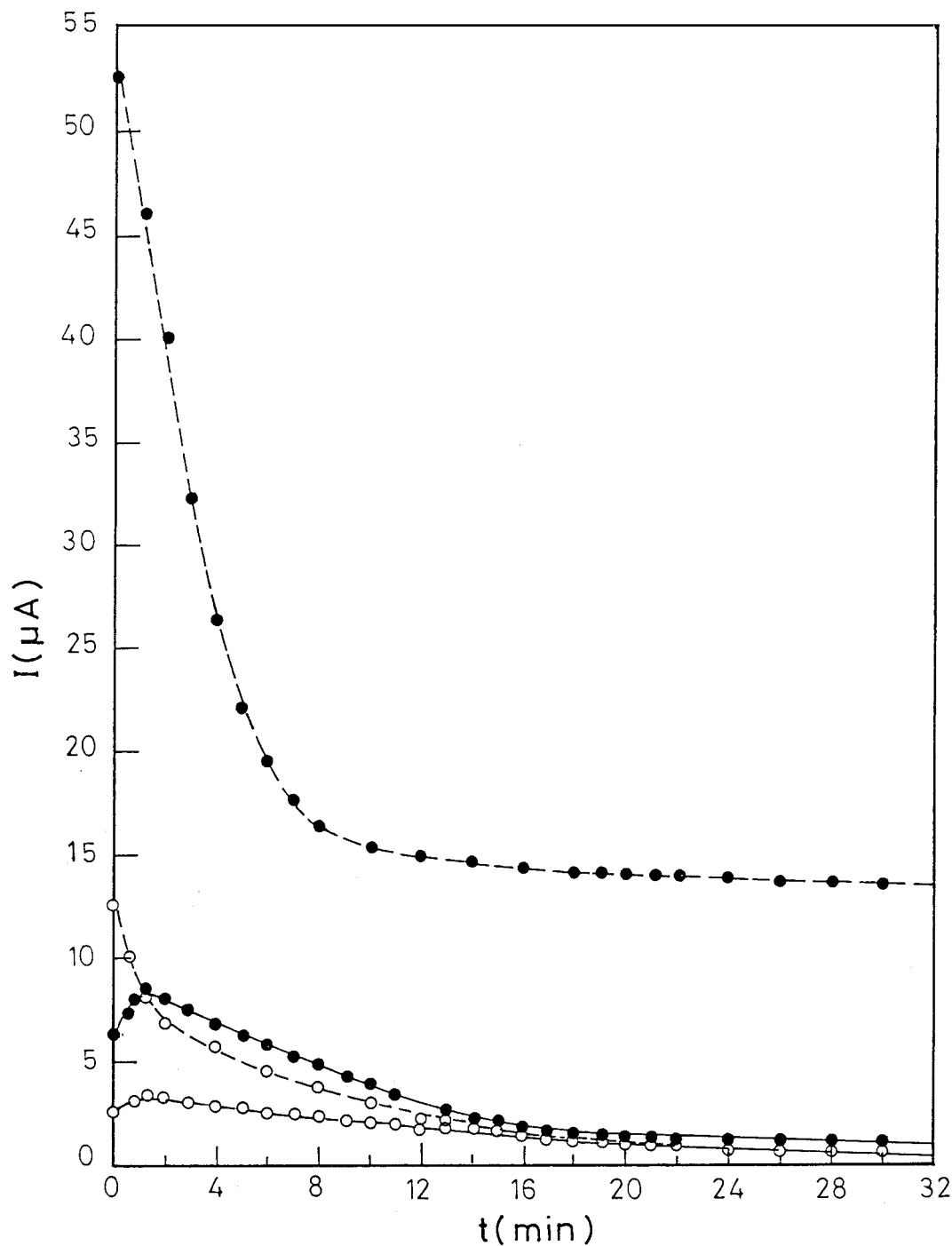
Figure 8 Current relaxation curves for 15 wt % albumin content in PVA thin films at field strength of 1 kV/cm with temperatures of (–O–) 343 and (– –●– –) 373 K. Dotted lines refer to the first application of voltage, and solid lines, to the reverse polarity.

while the electronic-conduction mechanism is effective in the high-temperature region II. These two activation energies for the two different temperature regions are associated with the intramolecular and intermolecular conducting processes. Specifically, the lower values of ΔE are associated with the intermolecular conduction process, while the higher are related to the intramolecular conduction process.[35] The fact that PVA and albumin

are considered as highly polar polymers suggests polarization conduction, which becomes predominant at the high-temperature region.

Current–time characteristics

Time-relaxation phenomena of the blend sample containing 15 wt % albumin at different field strengths

TABLE III
Values of μ (cm^2 V^{-1} S^{-1}) and n (cm^{-3}) for 15 wt % Albumin Content in PVA Thin Films at Temperatures of 343 and 373 K and Field Strengths of 0.5 and 1 kV/cm, Respectively

	Temperature = 343 K		Temperature = 373 K	
	E = 0.5 kV/cm	E = 1 kV/cm	E = 0.5 kV/cm	E = 1 kV/cm
μ (cm^2 V^{-1} S^{-1})	3.33×10^{-7}	1.11×10^{-7}	5×10^{-7}	1.43×10^{-7}
n (cm^{-3})	3.23×10^{16}	1.75×10^{17}	5.88×10^{16}	3.72×10^{17}

(0.5 and 1 kV/cm) and temperatures (343 and 373 K) were measured. When the blend sample is kept at a constant temperature and field, the electric current passing through the sample decreases with increase of the heating time. Initially, there is a linear but sharp decrease in the current flow, but with increase of the heating time, a gradual decrease is observed (Figs. 7 and 8). On reversing the polarity of the field, the time t_{max} required for the current to obtain its maximum value decreases greatly with increase of the temperature. On the other hand, t_{max} increases with an increase of the field. The observed relaxation phenomena can be analyzed using the equations.[36,37]

$$J = n\, q\, \mu\, E \qquad (2)$$

$$\tau \approx t_{max} = d^2/\mu V \qquad (3)$$

where J is the current density at a particular voltage V on a sample thickness d; E, the electric-field intensity ; q, the electronic charge ; μ, the drift mobility; n, the charge carrier density; and τ, the relaxation time.

The conduction parameters μ and n given in Table III were calculated using eqs. (2) and (3). That the value of the drift mobility is very low and increases with the temperature may indicate that the conductivity in the blend sample is approximate due to thermally activated mobility.[38] This provides further evidence to the above-mentioned data of electrical conductivity. Besides, it can deduced that conduction enhancement is due to the gradual increase of bulk-generated free-carrier density n. Therefore, the current may be at its maximum when the effective density of mobile ions in the bulk attains the highest value.

CONCLUSIONS

Blend films of albumin and PVA could be easily obtained over the whole composition range from solutions in doubled-distilled water by solution blending and casting onto a glass plate. By visual inspection, there was no evidence of phase separation in any of the blend compositions. The relatively good miscibility in this composition range may be due to the increased capability of albumin–PVA polymers, the former with abundant —NH$_2$ and —COOH groups and the latter with abundant —OH groups, to interact mutually through hydrogen bonding. The presence of such an interaction was supported by the melting-point depression of PVA observed in DSC characterization of the blends. The obtained results and the discussion in this work may allow one to conclude that the binary polymer forms a homogeneous dilute solution in double-distilled water, and on the removal of the solvent, a nonequilibrium, single-phase structure remains.

In view of the effect of the studied parameters in TSDC, it is concluded that the observed relaxation is of polar origin masked by space charge polarization, related to the amorphous regions of the blend system. The electrical conductivity and the drift mobility data indicate that the conduction is apparently due to the thermally activated mobility. Thus, the blend film is considered to be a promising candidate for new biomaterials having various functional properties of albumin coupled with the good electrical properties of PVA.

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