

# Electrical Studies on PVA–PE Copolymer

A. S. IBRAHIM, G. ATTIA,\* M. S. ABO-ELLIL, and F. H. ABD EL-KADER†

Department of Physics, Faculty of Science, Cairo University, Giza, Egypt

## SYNOPSIS

The electrical transport properties including electrical conductivity ( $\sigma$ ), dielectrical constant ( $\epsilon'$ ), thermally stimulated depolarization current (TSDC), and pyroelectric coefficient ( $P$ ) of a poly(vinyl alcohol)–polyethylene (PVA–PE) copolymer were studied in the temperature range 296–433K. Two stages of behavior have been observed with activation energies 1.49 and 0.05 eV. Discussion of conduction mechanism was carried out in terms of relevant theories. The existence of a relaxation peak in  $\epsilon'$  versus  $T$  relation has been analyzed taking into consideration space charge effects and dipole orientation phenomena. The TSDC spectra showed two peaks with differing intensity and position independent of field intensity. Pyroelectric current data provide further support to space charge effects. © 1997 John Wiley & Sons, Inc.

## INTRODUCTION

In recent years copolymers have attracted the attention of material researchers, with increasing interest for obtaining intermediate properties with respect to the homopolymers. Various types of molecular relaxations are possible in both polymers and copolymers.<sup>1–8</sup> Most of the interesting properties of polymers are attributable to molecular motions allowed in their amorphous phases. In blends and copolymers, the interphase regions are important.

It is known that the pyroelectric properties depend not only on externally controllable factors such as temperature, but also on intrinsic properties of the pyroelectric material, such as the dielectric constant. Therefore, in order to obtain information about carrier traps in the poly(vinyl alcohol)–polyethylene (PVA–PE) copolymer, experiments were carried out on d.c. conduction, dielectric constant, thermally stimulated depolarization current, and pyroelectric current. Furthermore, ultraviolet and infrared spectra were also studied.

## EXPERIMENTAL

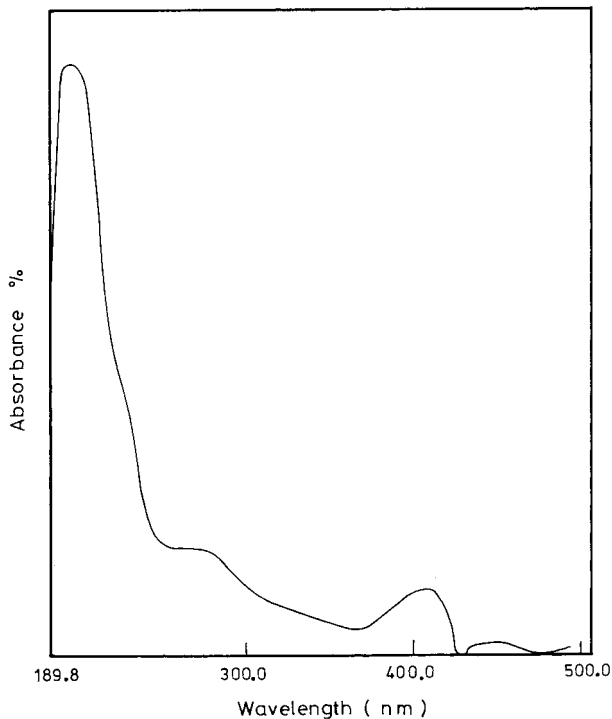
The (PVA–PE) copolymer (65% PVA and 35% PE) commercial sample from Kunststoffe Hoechst was dissolved in *N,N*-dimethyl formamide (DMF), maintained at 363 K. Then, the solution was left at room temperature 296-K for 30 days until the solvent was completely evaporated. Thin films of approximately 0.015 nm were cut into square pieces and coated with silver paste to achieve ohmic contacts.

Optical absorption measurement was carried out on PVA–PE copolymer sample in the wavelength range 200–900 nm using a Perkin–Elmer 4B spectrophotometer. Figure 1 shows remarkable absorption bands in the ultraviolet region around 284 and 411 nm, and an intense band at 195 nm, showing resemblance to that reported before for the PVA.<sup>9</sup> An additional band at 450 nm is observed, which may be due to electronic transitions in PE.

The infrared spectral analysis of the sample was performed using PYE Unicam-spectrophotometer over the range 400–4000  $\text{cm}^{-1}$ . Figure 2 shows the absorption spectrum and assignment of the bands for PVA–PE copolymer. A slight variation has been observed in the absorption bands of PVA–PE copolymer when compared with that

\* Present address: Department of Physics, Faculty of Science, Cairo University, Fayoum, Egypt.

† To whom correspondence should be addressed.



**Figure 1** The optical absorption of PVA-PE copolymer thin film.

previously reported for PVA thin film.<sup>10</sup> A new absorption band is observed at  $1660\text{ cm}^{-1}$  which is attributed to absorbed  $\text{H}_2\text{O}$ .<sup>11</sup> On the other hand, the absorption bands at  $1560$  and  $1710\text{ cm}^{-1}$  assigned for  $\text{C}=\text{O}$  group in PVA thin film, which are likely due to the absorption of the residual acetate group,<sup>12</sup> are not observed in the PVA-PE copolymer thin film.

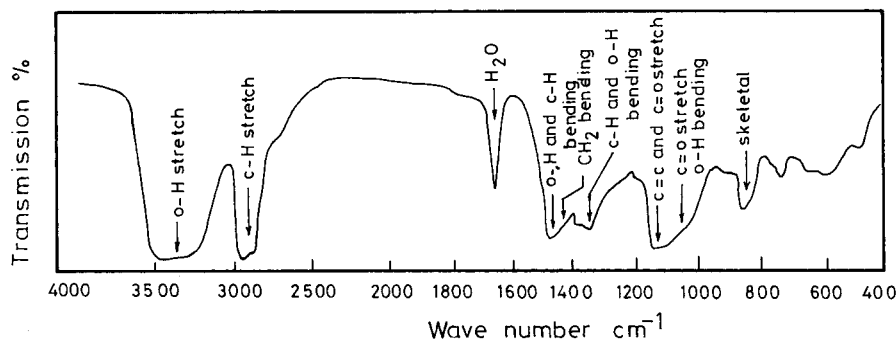
Correlation of the spectral data may allow one to suggest that minor spectral changes result from incorporation of PE into PVA. This may be attributed either to the lower percentage of PE added to PVA or to the occurrence of  $\text{CH}_2$  group in the structure of PVA, or to both factors.

D.C. electrical conductivity was measured by applying a constant voltage of 5 V and the conduction current was measured using a Keithley electrometer model 616. Thermally stimulated depolarization current TSDC studies were done in sandwich configuration with an effective area of  $1\text{ cm}^2$ . Before TSDC measurements, polarization of samples was carried out by first heating them to a specific polarizing temperature  $T_p = 348\text{ K}$  and then applying an electric polarizing field  $E_p = 334, 667, 4000, 6000,$  and  $8000\text{ V cm}^{-1}$  for a polarizing time ( $t_p$ ) = 2 h. After polarization, the samples were cooled to room temperatures with the field on. Then, the field was switched off at room temperature and the samples were shorted for about 30 min to remove frictional and stray charges,<sup>13</sup> if any. The pyroelectric currents were measured after 24 h from first heating run (TSDC). The dielectric constant  $\epsilon'$  was measured using a capacitance bridge type WEYNE KERR B 900 working at 1 kHz with a least count of 1 PF. All electrical measurements were made at a moderate heating rate of 1 K/min from 298 to 423 K.

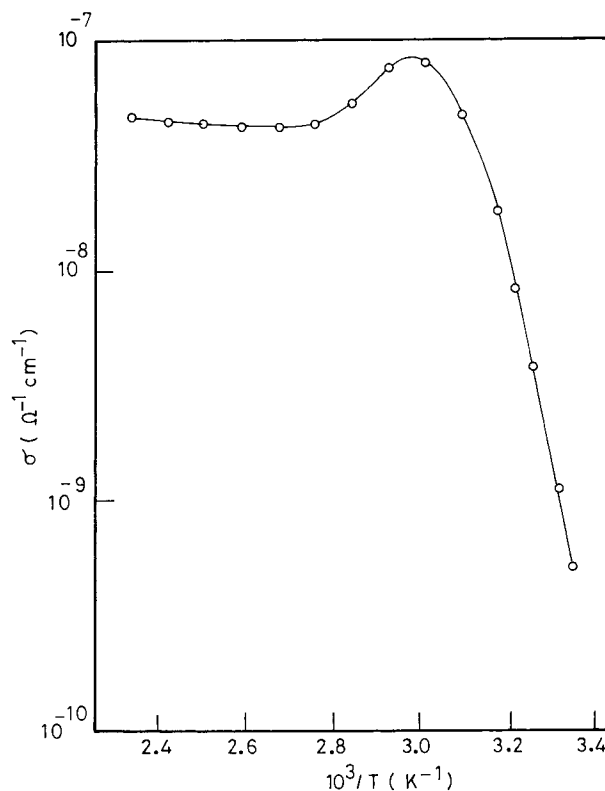
## RESULTS AND DISCUSSION

### Electrical Conductivity

The temperature dependence of d.c. electrical conductivity of PVA-PE copolymer sample at a fixed applied field of 5 V is shown in Fig. 3. It can be seen that the  $\log \sigma$  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 mention that the plots of  $\log \sigma$  versus  $1/T$  at different fields show the same behavior. The increase of conductivity with increasing temperature may be attributed to



**Figure 2** Infrared absorption spectrum of PVA-PE copolymer thin film.



**Figure 3** Variation of electrical conductivity of PVA-PE copolymer with the reciprocal of temperature at 5 V.

the liberation of more charge carriers from traps or to the greater mobility through the amorphous region of PVA-PE copolymer.

The variation of conductivity  $\sigma$  with temperature  $T$  can be represented by the general relation

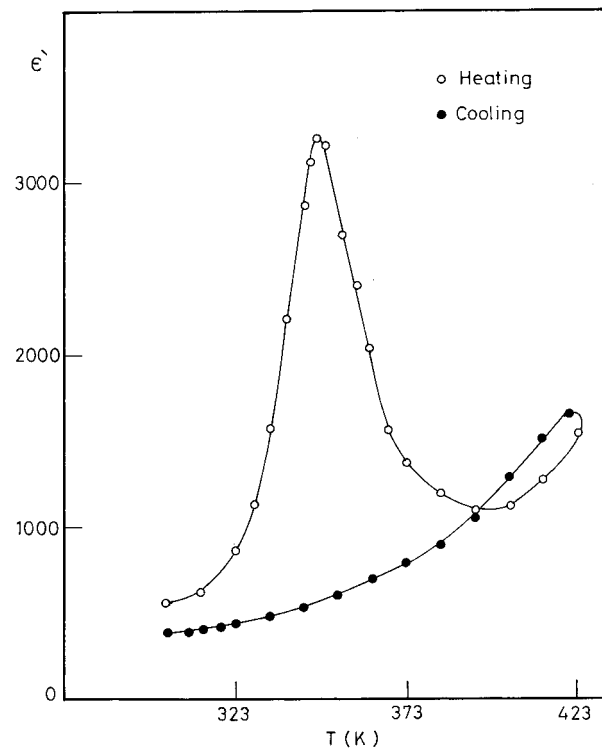
$$\sigma = \sigma_0 \exp^{-\Delta E/KT} \quad (1)$$

where  $\sigma_0$  is constant,  $\Delta E$  is thermal activation energy, and  $K$  is the Boltzmann constant. The activation energy for conduction can be estimated from the slope of  $\log \sigma$  versus  $1/T$  plot. The change in the slope for the low and high temperature regions indicates two conduction mechanisms. The appearance of an intermediate range within 30 K, deviating from the Arrhenius equation, may be due to molecular or crystallographic rearrangement. Activation energies of 1.49 and 0.05 eV are found to be characteristic of the regions of behavior. These values of activation energies indicate that the ionic conduction mechanism can be assumed to be effective in the low-temperature region while the electronic conduction mechanism is effective in the high-temperature region. It is usually accepted for polymeric material that dif-

ferent conduction mechanisms are possible.<sup>14,15</sup> Almost all mechanisms are related to different types of polarization taking place in such systems. Each of these mechanisms predominates in a given temperature range and certain applied field. The fact that PVA and PE are considered as highly polar polymers suggests polarization conduction which becomes predominant at a high-temperature region.

### Dielectric Constant

Figure 4 shows the temperature dependence of the dielectric constant  $\epsilon'$  through heating and cooling processes. Over the range of temperature investigated one relaxation peak is found to appear for heating process and disappears through cooling. This may be ascribed to space charge polarization of the thermally generated charge carrier. On cooling,  $\epsilon'$  monotonically decreases to less than the room temperature value. This may be related, at least in part, to a gradual decrease of adsorbed water molecules inside the sample.<sup>16</sup> On heating,  $\epsilon'$  increases with temperature and reaches a maximum at about 347 K, then begins to fall at relatively high temperature. The in-



**Figure 4** The temperature dependence of  $\epsilon'$  for PVA-PE copolymer at heating and cooling processes.

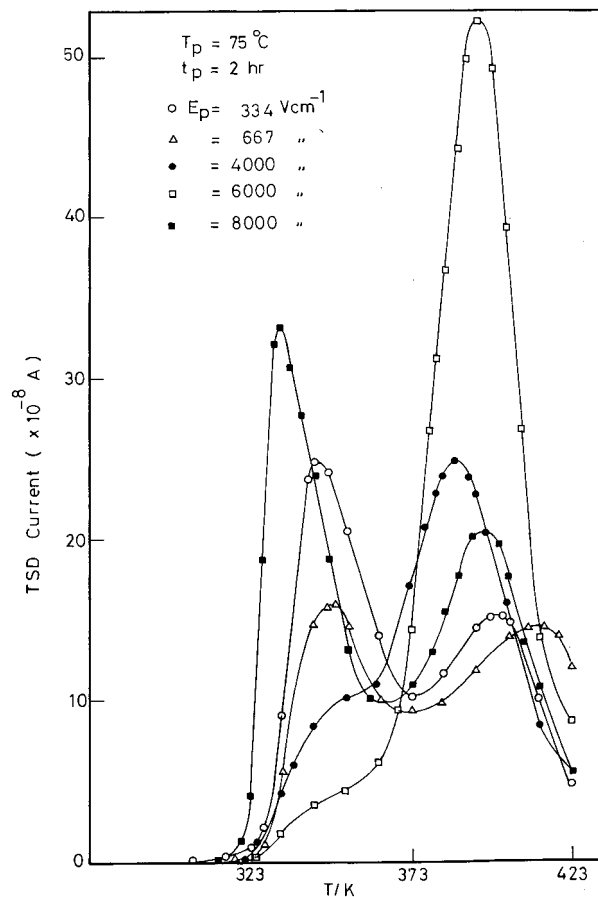
crease of  $\epsilon'$  with temperature for PVA-PE copolymer, being a polar polymer, indicates that the dependence is mainly owing to change in the intra- and intermolecular interactions.<sup>17</sup> These interactions may involve the alignment or rotation of the dipoles present in the copolymer with temperature. Trapped charge carriers are also expected to take part in the total polarization as the copolymer systems normally contain large numbers of trapping sites.<sup>18</sup> Polarization of trapped charge carriers is more significant at relatively high temperatures and at low frequencies.<sup>19</sup> A copolymer of two materials with different conductivities and permittivities may exhibit an additional dielectric polarization mechanism due to bonding heterogeneity. The decrease of  $\epsilon'$  with temperature is due to the increase in the chaotic thermal oscillations of the molecules and the diminishing degree of order of the orientation of the dipoles.<sup>20</sup>

### Thermally Stimulated Depolarization Currents

The TSDC method is known to be inherently sensitive in comparison to a dielectric loss measurement, and owing to its low equivalent frequency ( $10^{-2}$ – $10^{-4}$  Hz), the resolution is usually much better. It is a powerful tool for understanding the charging and discharging behavior of polymers. As a matter of fact, dipolar and space charge polarization coexist in thermo-electrets formed at high temperatures.<sup>21</sup>

Figure 5 shows the effect of electric field strengths from 334 to 8000  $\text{V cm}^{-1}$  on the TSDC spectra of PVA-PE copolymer while the other polarizing conditions of temperature and time are kept unchanged at 348 K and 2 h, respectively. TSDC spectra contain two peaks, except that at field strengths of 4000 and 6000  $\text{V cm}^{-1}$ , which show a composite peak. It may result from a variation in the distribution function of the associated relaxation times. The magnitude of the current peaks and their positions change irregularly with electric field strength. The total charge stored should increase linearly with the applied field for uniform polarization and nonlinearly for space charge. The positions and magnitudes are markedly different from those observed in the homogeneous polymers.<sup>22-24</sup> Thus, one can expect that the two peaks in the copolymer appear as a result of some sort of solidarity polarization due to the previously mentioned "bond heterogeneity."

The current released during a TSDC run is a measure of the degree of polarization of the sample which in turn is conditioned by the degree



**Figure 5** Effect of polarizing field ( $E_p$ ) on TSD current for PVA-PE copolymer films.

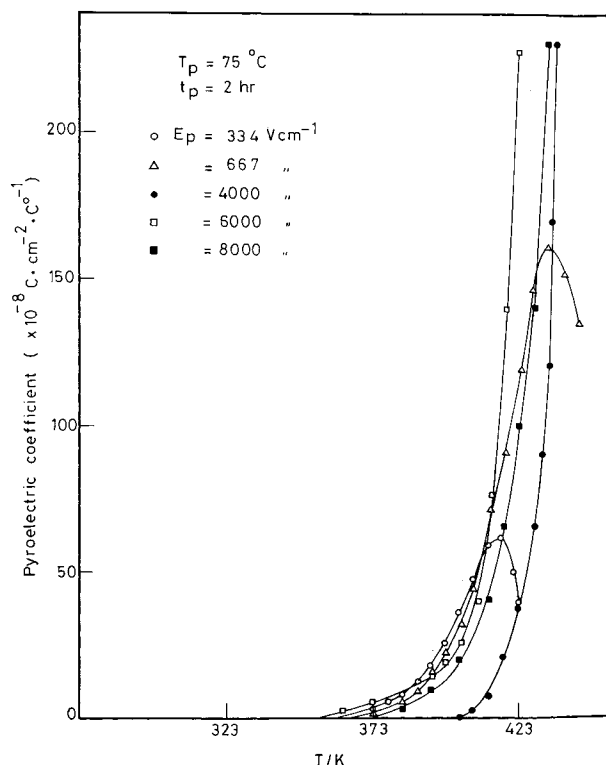
of molecular mobility. Under the influence of an electric field the irregularly distributed dipoles of side chains are mobilized/oriented in a certain direction. Thermal activation at a constant rate causes the release of charges due to their mobilization giving a peak at the site of maximum release of charge.<sup>25</sup> It is to be mentioned that electrodes play a dominant role in either carrier injection or diffusion of carriers on them.<sup>26</sup>

### Pyroelectric Current

The behavior of the pyroelectric coefficient has become a valuable tool in the study of the mechanism of polarization in polymers.<sup>27-29</sup>

The pyroelectric coefficient ( $P$ ) was computed from the measured pyroelectric current using the formula

$$P = -I/AB \quad (2)$$



**Figure 6** Temperature dependence of pyroelectric coefficient of PVA-PE copolymer films polarized at 75°C for different polarizing fields.

where  $I$  is the pyroelectric current,  $A$  is the area of the electrode, and  $B$  is the heating rate. The sign of  $P$  was taken as positive for the pyroelectric currents with the same polarity as the first depolarization currents. Figure 6 shows the variation of the pyroelectric coefficient for PVA-PE copolymer films at different polarizing fields  $E_p$  from 334 to 8000  $\text{V cm}^{-1}$  and fixed polarizing temperature and period, 348 K and 2 h, respectively.

Films polarized at  $E_p = 334$  and  $667 \text{ V cm}^{-1}$  showed a peak in the pyroelectric coefficient at about 418 and 433 K, respectively. With increasing polarization field the peak disappeared within the range of temperature investigated. However, the magnitudes of the pyroelectric coefficient are large in the sense that they reached their maximum value at a much lower temperature. The pyroelectric coefficient may be due to space charge polarization. The increase of pyroelectric activity with increasing field and temperature supports this view. Moreover, the pyroelectric properties of the copolymer films will result from nonuniform temperature dependence or electrical permittivity or thermal expansion coefficient.<sup>23</sup>

The obtained results and discussion in this

work may allow to conclude that the binary polymer forms homogeneous dilute solution in DMF, and on the removal of the solvent, a nonequilibrium, single-phase structure remains. The dielectric relaxation is invariably attributed to dipolar and space charge polarization. Bond heterogeneity polarization, detrapping of charge carriers from trapping sites of various types, and conductive network in the copolymer matrix are among the important factors to be considered in accounting for the proposed mechanisms responsible for TSDC in PVA-PE copolymer. The preparation condition (especially solvent removal, drying, and annealing temperature) play an important role in determining the properties of the solvent-cast films. These factors must be taken into account in future processing protocols.

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