

# Thermally Stimulated Depolarization Current Behavior of Polyethylene/Poly(vinyl acetate) Blends: Effect of Blending

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**ABSTRACT:** Thermally stimulated depolarization currents (TSDCs) were investigated in polyethylene/poly(vinyl acetate) blends as a function of the polarizing temperature, applied field, and poly(vinyl acetate) weight percentage in the blend. The magnitude of the TSDC peak current decreased and the peak current position shifted toward the lower temperature side as the poly(vinyl acetate) weight percentage in the blends was increased. The tendency of the current toward anomalous behavior (flowing in the same

direction as the charging current) also increased. It was concluded that blending with poly(vinyl acetate) modified the polyethylene morphology such that the amorphous part was increased. The carriers with mobility enhanced by hopping centers due to the C=O group in the amorphous part were localized largely in shallow traps. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3040–3045, 2006

**Key words:** orientation; activation energy; polyethylene

## INTRODUCTION

The organic polymeric material polyethylene (PE; low density) has been one of the most typical and suitable materials of the last several decades for electrical insulation in radio and TV engineering applications and for power cables and communication cables used in electrical transmission and distribution.<sup>1–6</sup> It possesses excellent dielectric properties such as low dielectric loss and small charging current. Because of its stability to light and heat and extremely high resistance to chemical agents, it has also been widely used as an anticorrosion coating on metals.

PE is a hydrophobic, nonpolar polymer, and it has been reported that in electrically irregular points of this polymer, such as voids and contaminants, the electrical condensation of water occurs easily.<sup>2–6</sup> A great amount of experimental evidence indicates that electrical and mechanical failure of the material initiates from such points. Furthermore, the weaker polarizability of the polymer main chain results in lower adhesion strength between the polymer and metal surface in applications involving anticorrosion coatings. Its potential use, however, has not yet been exhausted, and continuous attempts are being made to modify its physical and chemical properties to make it more useful for newer applications. Several approaches to suppressing the electrical/mechanical fail-

ure of PE have been suggested.<sup>2–6</sup> One way is grafting a polar group such as an maleic anhydride or acrylic acid onto PE as a side chain; however, a high percentage of grafting cannot be attained (normally <5 wt %). Another way is to copolymerize the polar groups into the main chain, in which the comonomer content can be varied as required. Alternatively, PE can be blended with a suitable polar polymer to give the desired properties. However, attention has to be paid to understanding the modification in properties thus brought about in molecular or morphological terms. Keeping this in mind, we carried out detailed investigations of the depolarization behavior of PE/poly(vinyl acetate) (PVAc) blends as a function of the polarizing field, polarizing temperature, and PVAc weight percentage by the thermally stimulated depolarization current (TSDC) technique. The results of these studies are reported here.

## EXPERIMENTAL

The PE and PVAc polymers used in this investigation were obtained from M/s Aldrich Chemical Co. Blend films about 70  $\mu\text{m}$  thick were prepared by the solution-casting method on plane glass substrates with chemically pure toluene (analytical-reagent-grade) as a common solvent. Blend films of different compositions were prepared with PE/PVAc weight percentage ratios of 80 : 20, 70 : 30, 60 : 40, and 50 : 50. The samples were outgassed in air for 24 h, and this was followed by room-temperature outgassing at a pressure of about  $10^{-4}$  Torr for a further period of 24 h. Both surfaces of these samples were then vacuum-

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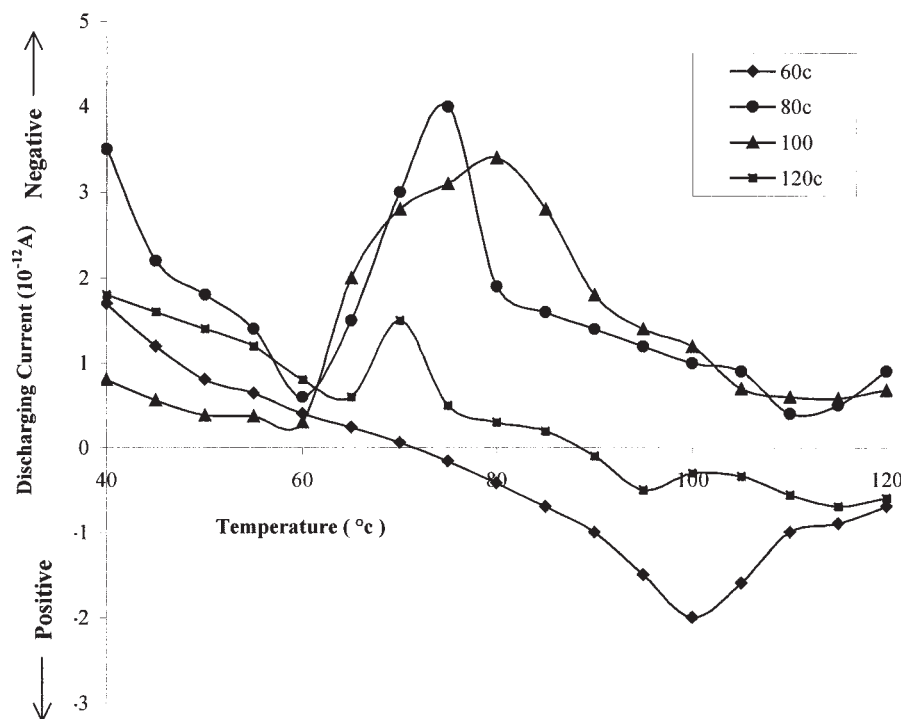


Figure 1 TSDC spectra for an 80:20 PE/PVAc blend polarized with a field of 60 kV/cm at 60, 80, 100, and 120°C.

aluminized over a central circular area 3.6 cm in diameter.

The samples were thermally polarized with fields of 20, 40, 60, and 80 kV/cm at 60, 80, 100, and 120°C. After polarizing for 3/4 h at the desired temperatures, the samples were cooled to room temperature (32°C) under the application of an applied step field. The total time of polarization was adjusted to 1.5 h in each case. The TSDCs of the electrets thus formed were obtained by reheating at a linear rate of 3°C/min, and the resultant current was monitored with a Keithley 610C electrometer (Cleveland, OH).

## RESULTS

### Temperature dependence

Figure 1 shows typical short-circuit TSDCs for 80 : 20 PE/PVAc thermoelectrets formed at various temperatures with a forming field of 60 kV/cm. A current flowing in the direction opposite to the charging current means a negative current and is called a normal current, whereas a current flowing in the same direction as the charging current is called a positive current and anomalous because its direction is opposite to the direction usually expected. From the various curves, it is clear that the thermograms are, in general, characterized by a low-temperature peak located between 50 and 60°C and a well-defined high-temperature peak around 75–85°C. In the case of the thermoelectrets obtained by polarization at the lowest temperature of

60°C, the current shows a reversal in polarity and during the high-temperature run of the TSDC cycle flows in the positive (anomalous) direction, exhibiting an anomalous current peak around 100°C. For thermoelectrets obtained at 80 and 100°C, the depolarization current flows in the normal sense throughout the TSDC cycle, and the thermograms are characterized by a well-defined peak around 75–85°C. For the electrets obtained by polarization at the highest temperature in this investigation, 120°C, a normal peak at 70°C can be observed. The current for the high-temperature part of the TSDC cycle for these electrets also shows a reversal in polarity at high temperatures around 90°C; thereafter, the current flows in the anomalous sense during the remaining part of the TSDC cycle. Similar behavior is shown by electrets of other PE/PVAc blend compositions.

The activation energy for the various peaks was evaluated with the initial rise method of Garlick and Gibson.<sup>7</sup> Semilogarithmic plots of (current versus reciprocal of temperature)  $\log I$  versus  $1/T$  (figure not given) yield a straight line whose slope gives the values of the activation energy. The activation energy value associated with the two peaks ranges from 0.3 to 1.75 eV.

### Field dependence

Typical TSDCs for thermoelectrets obtained by the polarization of 80 : 20 PE/PVAc blends at 80°C with

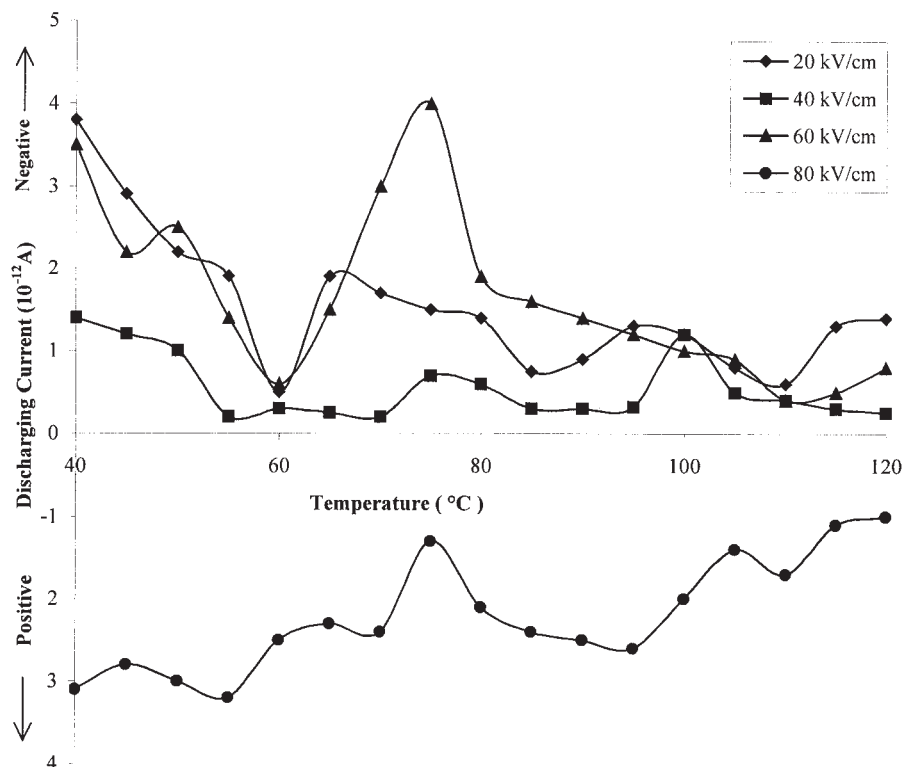


Figure 2 TSDC spectra for an 80:20 PE/PVAc blend polarized with fields of 20, 40, 60, and 80 kV/cm at 80°C.

various polarizing fields are shown in Figure 2. For electrets obtained with low fields, the depolarization current flows in the normal negative direction throughout the TSDC run. The thermograms are characterized by peaks: a hump or small peak in the low-temperature range of 45–55°C; a well-defined, broad peak in the temperature interval of 60–85°C; and sometimes a third small peak in the range of 95–110°C. The current initially decreases in magnitude with an increase in the polarizing field for low field values but then shows increase for large values of the step field. Astonishingly, for very large values of the step field (i.e., 80 kV/cm in this case), the depolarizing current flows in the anomalous positive direction for the entire TSDC cycle. Similar field dependence is exhibited by thermoelectrets prepared at other temperatures.

### Composition dependence

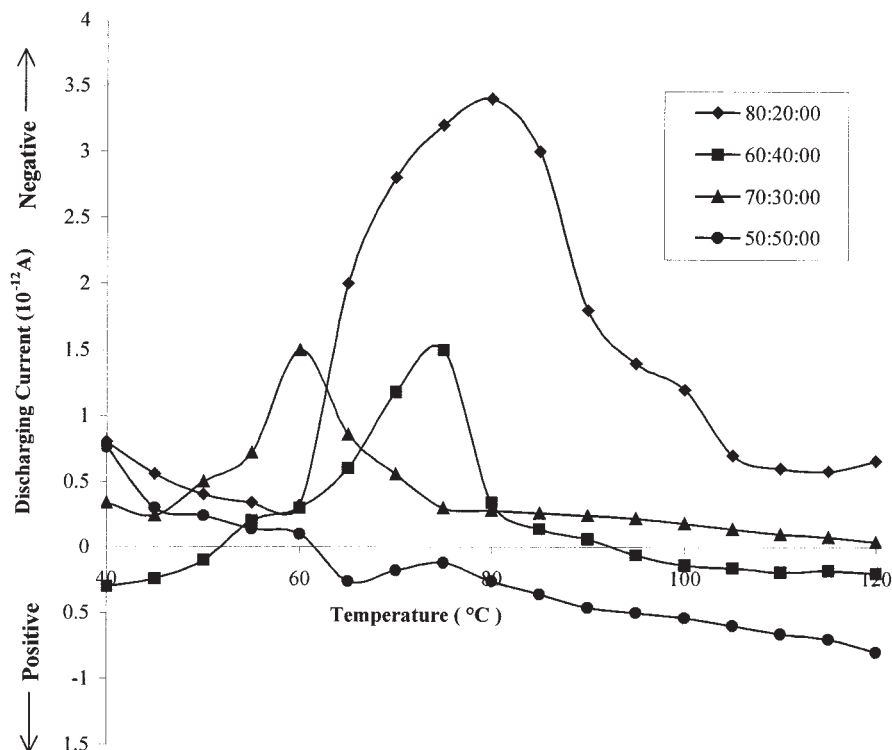
The dependence on the blend composition of the TSDCs is depicted in Figure 3. The figure shows TSDC spectra for 80 : 20, 70 : 30, 60 : 40, and 50 : 50 PE/PVAc blends polarized with a polarizing field of 60 kV/cm at 100°C. For blends containing a lower weight percentage of PVAc, the depolarization current, in general, flows in the normal negative direction for the entire TSDC cycle. However, as the PVAc content is increased, the current is reduced in magnitude and during the high-temperature part of the TSDC cycle in

certain cases flows in the anomalous direction. From the observed thermograms, it is not possible to draw any conclusion about the shift in the temperature scale of the current maxima with the blend composition; however, for a sample containing a higher weight percentage of PVAc, a reversal in polarity is attained at lower temperatures.

### DISCUSSION

Pure PE has been reported to show three dispersions:  $\alpha$ ,  $\beta$ , and  $\gamma$ .<sup>8–11</sup> With decreasing temperature, the strongest process ( $\alpha$  process), occurring between 20 and 80°C, has been attributed to longitudinal chain transport in the crystalline phase caused by 180° rotation.<sup>8</sup> The glass transition has been identified by Illers<sup>9</sup> as the  $\beta$  process occurring around  $-40^\circ\text{C}$ , which is commonly nearly invisible in linear, highly crystalline PE and is related to segmental motions in the amorphous phase.<sup>11</sup> The  $\gamma$  process (between  $-90$  and  $140^\circ\text{C}$ ) is composite in structure and can be attributed to kink inversion<sup>10</sup> or molecular motions in longer loops caused by local reorientations of short methylene units in crystalline phases, motions near crystalline defects.<sup>9</sup>

In pure, bulk PVAc, two relaxation processes,  $\alpha$  and  $\beta$ , have been reported by Yamafuji<sup>12</sup> and Ishida et al.<sup>13</sup> The  $\beta$  relaxation around  $\approx 50^\circ\text{C}$  is due either to the rotational motion of the flexible side groups or to the



**Figure 3** TSDC spectra for 80 : 20, 70 : 30, 60 : 40, and 50 : 50 PE/PVAc blends polarized with a field of 60 kV/cm at 100°C.

local twisting of the main chain around its equilibrium position. The  $\alpha$  relaxation at about 80°C can be attributed to the dipolar orientation due to the segmental rotation or translations of the main chain. In addition to these two relaxations, a third relaxation process, designated  $\alpha^1$ , has been observed in PVAc and is related to space-charge polarization.<sup>14</sup>

Many TSDC reports have been published for pure PE.<sup>15–17</sup> As discussed previously, the thermograms in this case are characterized by a small peak or hump around 50–60°C and a well-defined, broad peak around 80°C. Pure low-density PE is a nonpolar polymer and hardly contains any dipoles. The observed peaks, therefore, primarily cannot be assigned to dipoles. The location of the low-temperature peak almost coincides with the  $\beta$  process observed in PVAc. This peak can thus be assigned to the rotational motion of the flexible side groups or the local twisting of the PVAc main chain. However, the contribution of the  $\alpha$  process in PE to this peak cannot be excluded. Furthermore, as the observed characteristics (the magnitude of the current maxima and associated charge) do not exhibit a linear field dependence as in a dipolar process (curves not shown), the peak is composite in nature and involves dipolar and trapped space-charge contributions.

The high-temperature peak in this case is observed in the same temperature range as that of the  $\alpha$  process in PE. It can, therefore, be assigned to the  $\alpha$  process in PE attributed to longitudinal chain transport in the

crystalline regions. However, a contribution to this peak due to  $\alpha$  relaxations caused by dipolar orientations related to segmental rotation or translation of the PVAc main chain cannot be excluded. The peak exhibits thermal dependence. The  $\alpha$  process in PE has also been reported to be an activated Arrhenius process.<sup>9</sup> Again, the peak does not exhibit linear field and temperature dependence. It also cannot be identified completely as the manifestation of a dipolar process; rather, it probably is a complex peak arising because of both dipolar orientations and space-charge and trapping effects.

The existence of various kinds of traps in polymers is well established.<sup>18–20</sup> Ieda et al.<sup>21</sup> also reported the existence of a peak in the case of PE in this temperature interval and assigned it to the traps in the crystalline regions. Some trapping sites have also been reported to be located in the amorphous crystalline boundaries of PE as well.<sup>22,23</sup> The trapping sites in PE have been ascribed to carbonyl groups produced by oxidation,<sup>17,24</sup> physical defects such as cavities formed by a local arrangement of molecular chains,<sup>15,16</sup> and free radicals.<sup>25</sup> The traps can be volume traps or surface traps; their depth was estimated by Bauser.<sup>26</sup> Structural defects such as carbonyl groups or double bonds yield shallow or intermediate trapping levels of depths up to about 1.0 eV, whereas foreign molecules function as deeper traps. Experimental data on trapping have been obtained by a variety of methods based on thermoluminescence (TL), mobility, and

TSDC. The TL data uncovered a number of trap levels attributed to methylene groups<sup>27</sup> with depths of about 0.4 eV. However, mobility and TSDC data give trap levels, which are also attributed to structural features but show depths in excess of 1.0 eV.<sup>18,27,28</sup> These experiments clearly indicate that structural modifications, not impurities, are responsible for trapping sites for which activation energies of 1.2–1.7 eV have been derived. Davies and Lock<sup>28</sup> using mobility measurements reported an increase in the carrier mobility with the number of unsaturated terminal (vinyl) groups, indicating the contribution of these groups to carrier trapping in PE. The observed activation energy values are thus in agreement with the earlier reported values.

From the various curves, it is evident that the depolarization currents under certain conditions of the forming field, temperature, and sample weight percentage flow in the same direction as the charging current and thus exhibit anomalous behavior. Anomalous TSDCs in plastic insulators have been reported by a number of workers.<sup>18,29–31</sup> In a copolymer of vinylidene fluoride and trifluoroethylene, anomalous currents have been reported because of the diffusion of ionic charges bound with molecular dipoles in crystalline regions.<sup>29</sup> In high-density PE, anomalous currents are considered to originate from the injected space charges.<sup>30,31</sup> In the case of PE/PVAc blends, the anomalous currents can be considered to arise from injected charges trapped in various available sites forming space charges. Considering one type of carrier, we may have a distribution of injected space charges just after charging. The density of the space charges drops with increasing distance measured from the injecting electrode such that there exists a zero field plane inside the sample. The field acting on the injecting electrode side of the zero field point drives the carriers toward the injecting electrode, whereas that on the other side drives toward the other noninjecting electrode. The appearance of anomalous TSDCs requires the suppression of carrier flow to the injecting electrode, which results in a net carrier flow toward the other electrode and movement of the zero field plane away from the injecting electrode. As the carrier mobility increases with the temperature and as the density of the injected space charge increases with the applied step field, a high charging field and a high temperature may result in a high return rate of carriers to the injecting electrode. As a result, the high return rate of carriers may surpass the charge exchange rate of the electrode, causing partial blocking of the electrode and net flow of carriers toward the far electrode, resulting in an anomalous current.

The polarity reversal and occurrence of an anomalous peak for electrets obtained via charging at a lower temperature (i.e., 60°C) and the absence of this effect for high-temperature polarized specimens may be explained as follows: under the action of a high field, the

density of the injected charge is expected to be high. However, because of limited mobility at low temperatures, the carriers are localized in shallow traps only with short detrapping times. The release of charge carriers in very large numbers exceeding the charge exchange rate at the electrode during TSDC will result in a net carrier flow toward the far noninjecting electrode, resulting in an anomalous current. As the polarizing temperature is raised, the mobility of the carriers is increased. Charge carriers with high mobility under the action of a strong field are then localized in deep traps with long detrapping times. The slow release of carriers from such traps then does not result in the movement of carriers toward the injecting electrode in numbers large enough to cause partial blocking of the polymer electrode interface and hence anomalous currents. In the case of very high values of the polarizing temperature and in the presence of a strong field, the carriers with high mobility and high density occupy shallow traps as well as deep traps. The discharge current, therefore, exhibits anomalous behavior again during the high-temperature part of the TSDC run. For very strong fields under high-temperature conditions, the density of the charges localized in shallow traps as well as deep traps attains a such value that the release of carriers during discharge leads to a current that remains anomalous during the entire TSDC cycle.

The peak temperature and the magnitude of the peak current depend on the sample weight percentage and hence morphology (or the crystallinity) of the PE/PVAc blend. The peak current magnitude is maximum in the case of 80:20 samples, and the current maximum also occurs at the highest temperature, that is, 80°C. As the PVAc content in the blend is increased, the TSDC is reduced and the peak position, in general, is shifted toward the lower temperature side. The peak position of the  $\alpha$  process in PE has been reported to decrease with an increase in the vinyl acetate content.<sup>11</sup> This confirms our conclusion that the observed broad and well-defined high-temperature peak in this case is mainly the manifestation of the  $\alpha$  process observed in PE. Furthermore, for samples containing a higher weight percentage of PVAc, the current during the high-temperature part of the TSDC cycle becomes positive and anomalous in direction. The current inversion also occurs at a lower temperature. The reduction of TSDC and the shift in the current maximum toward a low temperature can be ascribed to an increase in the carrier mobility and/or an increase in the mobile carrier densities due to an increase in shallow traps. The blending with PVAc thus brings about a definite change in the morphology of PE. A qualitative explanation of these effects can be given under the assumption that carbonyl groups in the amorphous regions of PE act as trapping centers, whereas those in the crystalline surface regions become deep traps. It

appears that in 70:30 and 80:20 PE/PVAc blends, with a sufficient number of available deep surface traps, the injected charge is located in the C=O groups in the crystalline surface regions. The electrons have to move through the crystalline parts, and this effectively reduces the carrier mobility, giving a normal negative current. As the weight percentage of PVAc is increased, the amorphous part in the polymer blend is also increased. The carrier mobility is thus enhanced by the hopping centers due to C=O groups in the amorphous part, and more charge is localized in the shallow traps. The detrapping of a large number of charges from these traps results in partial blocking of the electrode polymer interface, thus leading to a positive anomalous current. Again, Ekstrom and Willard<sup>32</sup> explained the properties of organic glasses in terms of cavity traps formed by local arrangements of molecular chains. The depth of the cavity trap depends on the size of the cavity. If the C=O trap is ascribed to the cavity created by a C=O group in the PE chain, it is reasonable to assume that the C=O trap in the crystalline surface regions is deeper because the C=O cavity is smaller in the crystal surface region tightly bounded by crystallites than in the amorphous regions.

### CONCLUSIONS

Blending PVAc with PE modifies the morphology of PE, which influences remarkably the electrical behavior of the polymer. With increasing PVAc content, the net amorphous content in the polymer is increased. The trap structure of the polymer is, therefore, modified so that a large number of charge carriers are localized in shallow traps. The detrapping of carriers in large numbers from such sites results in a discharge current tending toward anomalous behavior with increasing PVAc content.

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