Thermally Stimulated Depolarization Current and Space Charge Measurements on Low-Density Polyethylene: Influence of the Presence of Antioxidant

M. Tebani, L. Boudou, J. Guastavino

LAPLACE (UMR-CNRS 5213), 31062 Toulouse Cedex, France

ABSTRACT: The purpose of this study is an investigation upstream of polymer insulator ageing and rupture. We studied the electrical and physicochemical properties of a low-density polyethylene (LDPE) used in high-power insulated cables. Space charge measurements using pulsed electroacoustic method and thermally stimulated depolarization current (TSDC) were carried out on LDPE samples, with and without antioxidant, at different temperatures. TSDC peaks were observed only in the presence of an anti-oxidant. Furthermore, a TSDC anomalous peak was revealed for the sample containing an antioxidant and polarized at 50°C. All the TSDC peaks are interpreted as trapped charges and can be explained by measuring the space charge distribution within the sample bulk. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2768–2773, 2008

Key words: polyethylene; thermally stimulated depolarization current; space charge; antioxidant

INTRODUCTION

Numerous studies have dealt with the effects of additives and temperature in relation to the electrical properties and morphology of polyethylene.[1–3]

The additives have a direct influence on the crystallinity rate,[4,5] the spherulite diameter,[6] the density, and the nature of the traps.[3,7] In a recent work, we have shown[8] that the presence of antioxidant induces a morphological change and an increase in high-field conductivity. This has been explained by trap distribution and location changes.

Cartwright et al.[3] have noticed a conductivity increase due to a shallow trap density increase, which could be because of the structural defects caused by the presence of antioxidant.

The effect of temperature on the morphology of low-density polyethylene (LDPE) has also been extensively studied.[2,9,10] Polyethylene morphology, and, particularly, the percent crystallinity are mostly dependent on the cooling rate of the melt,[11] as well as the time and temperature of annealing.[2]

Thermally stimulated luminescence (TSL) and thermally stimulated depolarization current (TSDC) measurements have been recorded by several authors to correlate the influences of antioxidant and temperature on the electrical properties of LDPE; for example, Tu et al.[12] have shown a relationship between TSDC and TSL peaks. The C4 and α peak, both recorded at 50°C, have been attributed to the occurrence of structural defects in the crystalline phase, which act as traps.[13]

Furthermore, Yang et al.,[14] using dynamic mechanical analysis, have recorded a mechanical relaxation peak at 50°C which involves a complex process of molecular mobility within the crystalline phase.

In this article, we have used pulsed electroacoustic (PEA) and TSDC measurements to investigate the effects of antioxidant and temperature on LDPE charge trapping.

SAMPLES

LDPE is a semicrystalline polymer composed of lamellar crystals, which are typically arranged as spherulites when cooled from the melt. The polymer crystal formation and the spherulitic structure in bulk polymers have been extensively described in literature.[15–18] The macromolecular chains are arranged in a structure called lamellae. In polyethylene, the lamellae thickness is a few hundred angstroms, whereas the other dimensions are in the range of several micrometers. Furthermore, the lamellae thickness depends on the molecular weight of polymer, presence of antioxidant, thermal treatment, and crystallization conditions.[6,9]

We have focused on the melting temperature and strain rate during the cooling of films, to obtain a homogeneous reproducible structure and a well-defined thermal history for the samples.
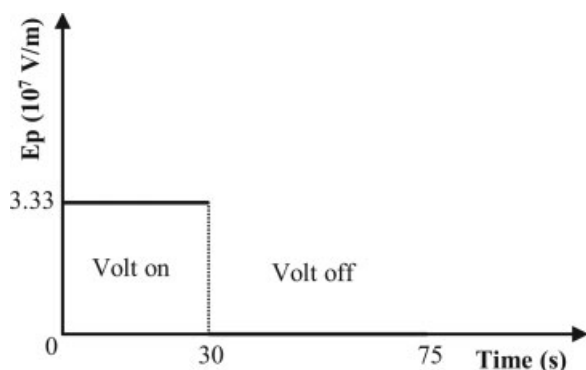
Figure 1 The electrical field protocol.

Test samples used for PEA measurements were films prepared from hot-pressed pellets. Two kinds of material have been studied: virgin LDPE and LDPE with Santonox-type antioxidant. The average thickness for both samples was 165 μm. For TSDC measurements, samples were prepared with the same procedure, using an average thickness of 75 μm. Furthermore, samples were gold coated on each face to obtain 30-nm-thick and 25-mm-diameter circular electrodes.
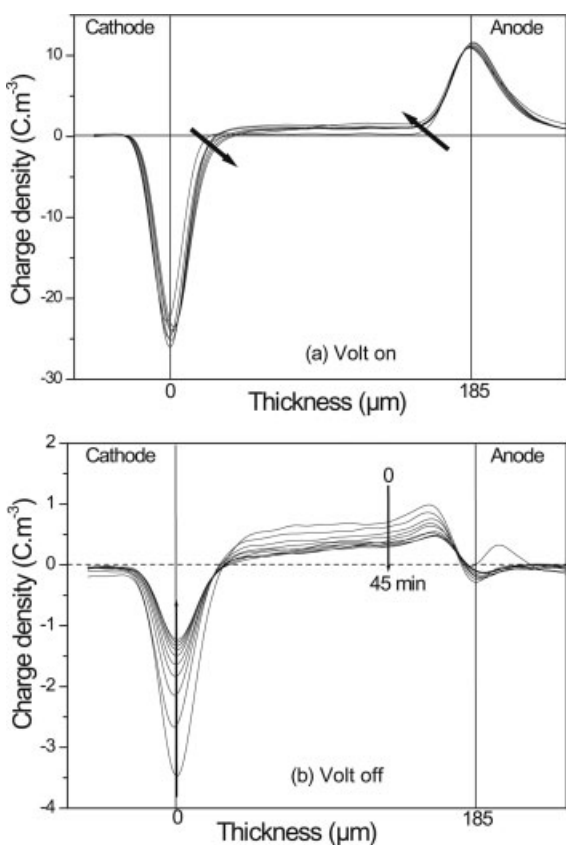
RESULTS

PEA measurements

The space charge distribution in samples was measured by PEA method at polarization temperatures (T_p) of 25°C and 50°C. The electric field protocol described in Figure 1 was applied. All the PEA measurements were done in atmospheric air.

Temperature effect

Figure 2(a) does not clearly show a charge injection during voltage application, but possibly an internal charge diffusion increasing with the time elapsed. When voltage is removed, positive charges are present in the bulk from anode to cathode, and the charge density decreases with elapsed time.

When the temperature is increased from 25 to 50°C, a small negative charge injection from the cathode is observed [Fig. 3(a)]. The voltage-off profiles [Fig. 3(b)] show a negative charge at cathode and a positive charge at the anode, their respective densities decreasing with time.

It seems that the temperature increases the charge mobility and injection.

Figure 2 The PEA profiles for virgin LDPE at T_p = 25°C. (a) Volt on; (b) Volt off.
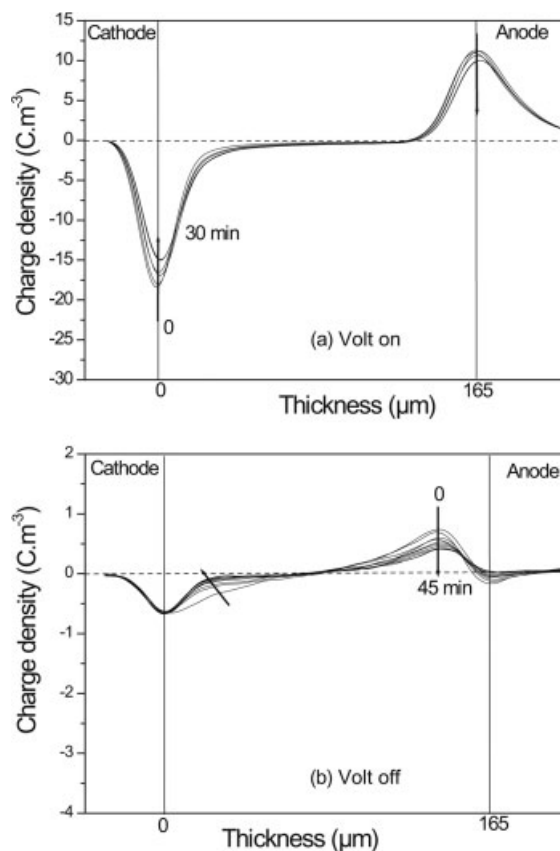
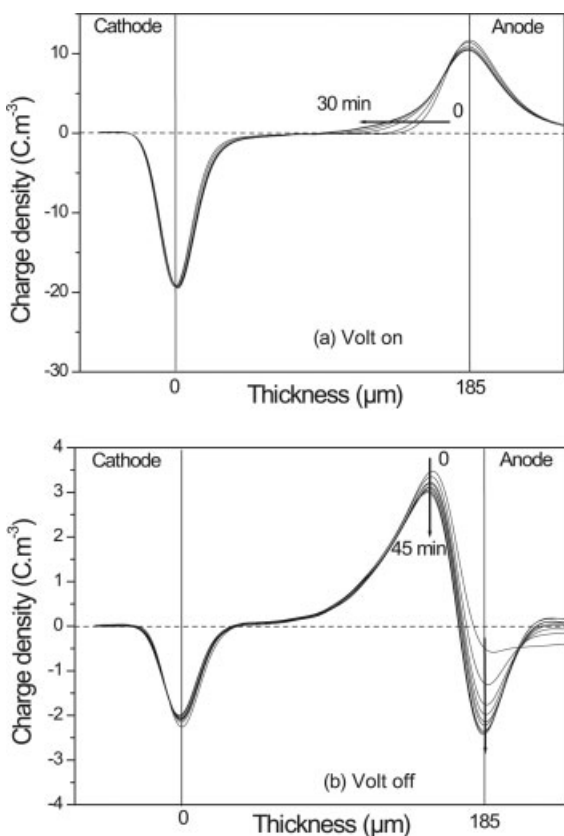**Figure 3** The PEA profiles for virgin LDPE at T_p = 50°C. (a) Volt on; (b) Volt off.

Figure 4 The PEA profiles for LDPE with antioxidant at $T_p = 25°C$. (a) Volt on; (b) Volt off.

Antioxidant effect

The PEA profiles obtained for LDPE with antioxidant are similar to those obtained for virgin LDPE and do not show any evidence of charge injection. However, voltage-off profiles show positive charges concentrated at the anode for LDPE-AO [Fig. 4(b)], whereas virgin LDPE measurements show positive charges within the whole sample bulk. A possible explanation is that negative charges are injected from cathode, inducing a negligible global charge density (positive and negative charges) near the cathode. We assume that the presence of antioxidant increases the negative charge injection. This result has been confirmed by several authors.[1–7]

Effect of both temperature and antioxidant presence

Figure 5(a) shows the negative charges at the anode. Figure 5(b) shows the negative charges at the cathode and anode. A temperature increase from 25 to 50°C, for LDPE-AO, leads to an increase in negative charge injection and propagation.

TSDC measurements

The TSDC is a well-known technique[19] based on the depolarization, or charge detrapping, of the sample by thermal activation.

Experiments were carried out in a thermally controlled chamber. Samples were first polarized with a dc voltage V_p at a polarization temperature T_p, for a fixed time (T_p = 30 min). After cooling at −70°C under applied voltage, the sample was reheated, using a constant heating rate β = 5°C/min, to 100°C under short circuit conditions. The corresponding discharge current was detected by a Keithley-617 electrometer and recorded by a computer. All the TSDC measurements were done under controlled helium atmosphere.

TSDC measurements done on virgin LDPE do not show any relaxation peaks over the temperature and the electrical field range explored (25°C < T_p < 50°C; 200 V < V_p < 2.5 kV). All the TSDC measurements presented have been recorded for LDPE with antioxidant.

Antioxidant effect

TSDC measurements show two relaxation peaks (Fig. 6). The first, called β, is located at −30°C. The second peak, named $α_1$, is located at 50°C and can be compared with the α peak revealed by mechanical spectroscopy.[14] One of the probable mechanisms
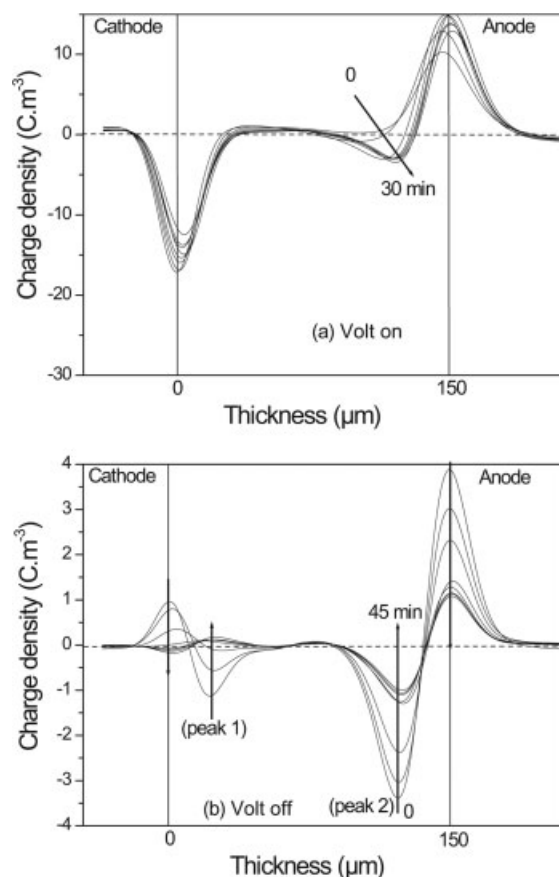
Figure 5 The PEA profiles for LDPE-AO with antioxidant at $T_p = 50°C$. (a) Volt on; (b) Volt off.
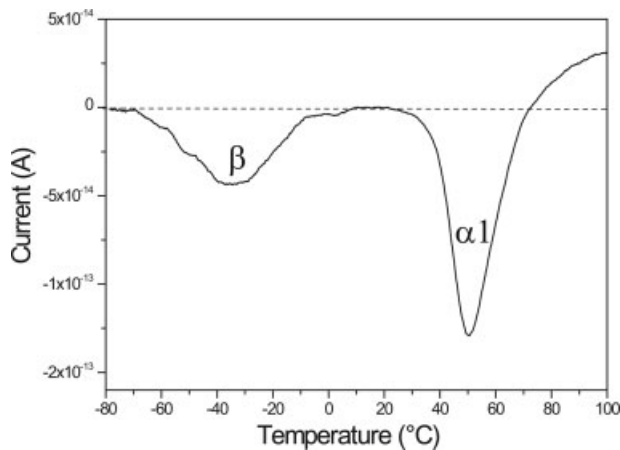
Figure 6 The TSDC curve for LDPE-AO at $T_p = 25°C$ and $V_p = 2.5$ kV.

responsible for the α peak is the slight movement of the polymer crystalline region. This will lead to the release of trapped charges within the interface between the crystalline region and the amorphous region.[20] Furthermore, the β and α_1 peaks are located at the same temperature as the C3 and C4 peaks shown by Tu et al.[12] or Mizutani et al.[21] These peaks are attributed to the presence of defects, which act as deep traps (0.8 at 1.4 eV) and are located in the amorphous-crystalline interface,[21] or in the crystalline region.[13]

Moreover, the β and α_1 relaxations are only observed in the case of LDPE with antioxidant, and so the antioxidant additive most probably acts as deep trap and is also responsible for the change in polymer morphology.

To obtain more information on the origin of the α_1 peak, the effect of the voltage (V_p) was studied. Figure 7(b) shows a linear increase of the α_1 peak area with the applied voltage, without any saturation in the field range explored. This suggests that the α_1 peak is most probably due to electric charges injected during the polarization timeframe under a relatively high field, more than a pure dipolar phenomenon.

Effect of both temperature and presence of antioxidant

Figure 8 shows a second peak of relaxation, α_2, at a higher temperature than α_1 and with an opposite sign, corresponding to an anomalous depolarization current. Usually, removing the applied voltage causes a discharge current of an opposite sign compared to the charging current.

Several articles concerning this anomalous depolarization current can be found in the literature. For example, Mizutani et al.[21–23] have shown that anomalous currents observed in polyethylene are the con-
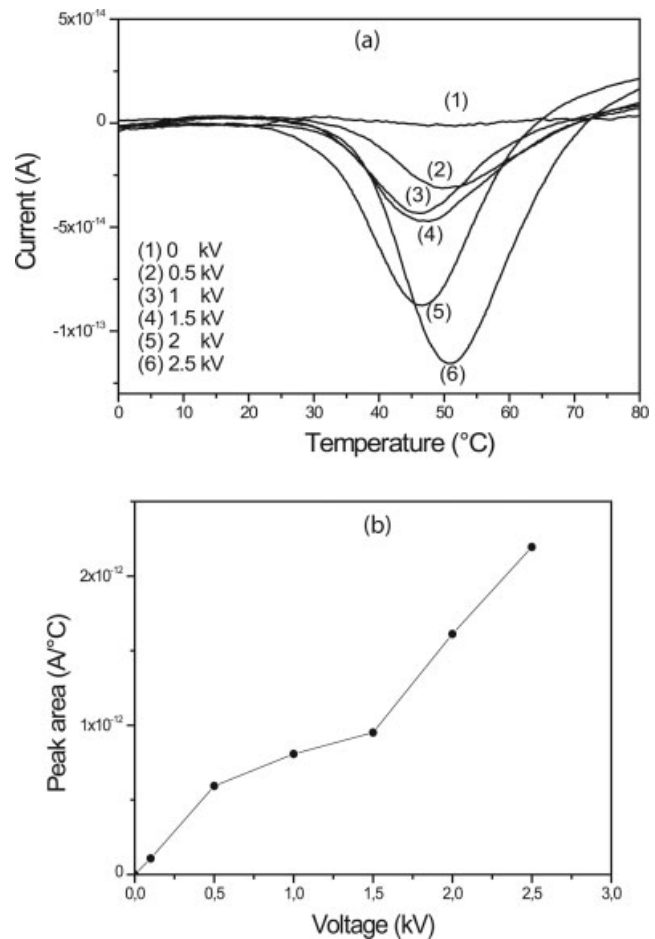
**Figure 7** (a) Evolution of the α_1 peak with the applied voltage V_p; (b) α_1 peak area vs. applied voltage V_p.

sequence of injected space charge and the blocking, or partial blocking, condition of the metal/polymer interface.

Kitani et al.,[24–26] using a numerical analysis, have concluded that the anomalous discharge current can
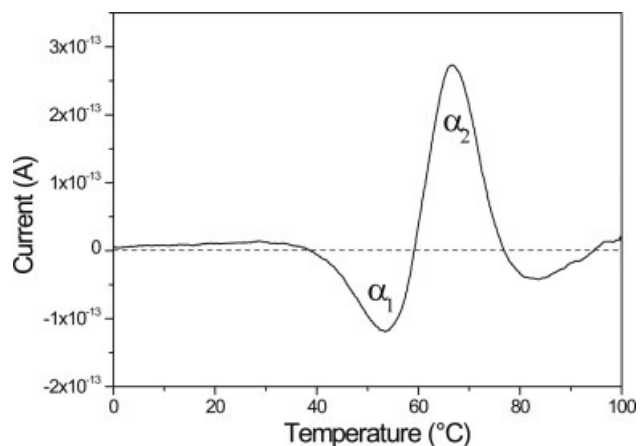
Figure 8 The TSDC curve for LDPE-AO at $T_p = 50°C$ and $V_p = 2.5$ kV.
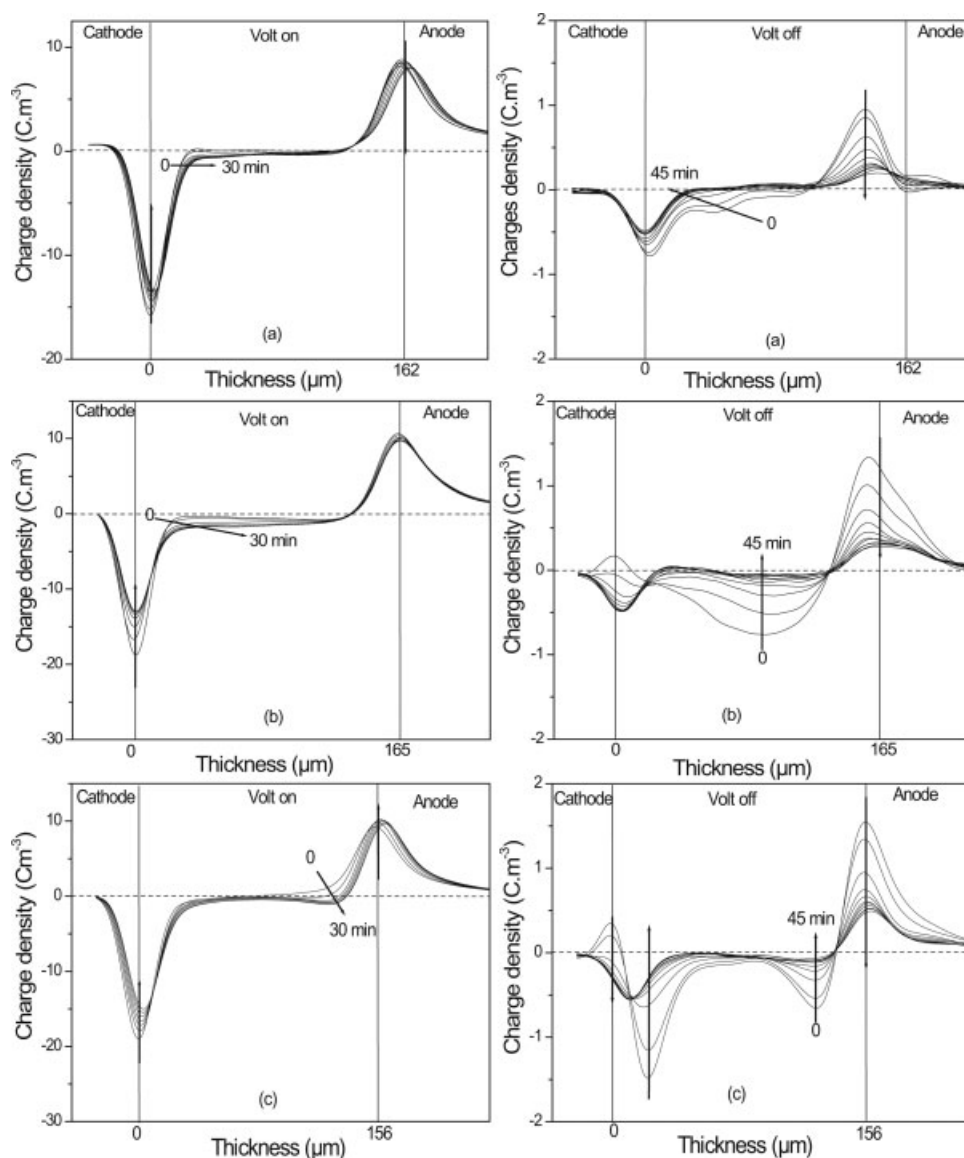
Figure 9 The PEA profiles for LDPE-AO with different antioxidant contents at $T_p = 50°C$: (a) 0.5 wt %, (b) 1 wt %, and (c) 1.5 wt %.

also be obtained with a bipolar injection (electrons and holes) and with a nonblocking interface.

In our case, the anomalous TSCD (peak α_2) appears only for the LDPE-AO sample and at $T_p = 50°C$. The temperature and the presence of antioxidant probably assist the trap diffusion from the crystalline part to the amorphous/crystalline interface, enhancing the charge injection and increasing the charge carrier mobility.

DISCUSSION

The results obtained from PEA measurements, for LDPE with antioxidant, are in good correlation with those obtained from TSDC.

When a sample is short circuited, negative charges accumulated near the cathode, linked to peak 1 on PEA profiles [Fig. 5(b)], are evacuated from the bulk to the cathode, inducing a normal discharge current, which corresponds to the α_1 observed in the TSDC curves (Fig. 8). In the same way, α_2 peak can be explained by the negative charges accumulated near the anode and evacuated from the bulk to the anode [peak 2 of the Fig. 5(b)], inducing an anomalous current in a short-circuit condition.

α_2 peak can therefore be observed only when negative charges are injected from cathode and accumulated in the nearby anode after crossing over the bulk. The combined effect of temperature and antioxidant facilitate this injection from the cathode, migration over the bulk, and accumulation in the

nearby anode. The effect of temperature most probably enhances the charge mobility and facilitates injection. The presence of antioxidant leads to the same consequences, but probably due to a change in the sample morphology.

To evaluate the antioxidant effect on injection, transport, and accumulation of negative charges, we prepared samples by mixing various proportions of pellets from virgin LDPE and LDPE-ox. We obtained samples with different antioxidant content (0.5, 1, and 1.5% by weight). The results obtained from PEA measurements at 50°C are shown in Figure 9.

The measurements have confirmed the results obtained for the LDPE with 2% weight content (Fig. 5). For the 0.5% weight content, we can observe a negative charge injection at the cathode as a positive anode charge. For the 1% content, negative charges are present in the entire bulk. For the 1.5% content, negative charges are accumulated at both the cathode and the anode. We can also conclude that the antioxidant enhances the negative charge injection and the transportation within the bulk. The exact mechanism is not well understood, but several studies show that the antioxidant decreases the spherulitic structure size.[3,6] It can also act as a trap and change the charge transportation within the bulk, inducing a conductivity increase at high fields.[27,28] Finally, injection is modified by a change in the polymer/metal interface properties.[29]

CONCLUSION

The analysis of LDPE characteristics, with or without antioxidant, by PEA and TSDC at various temperatures reveals that the temperature and the antioxidant content play an important role in electric charge injection, transportation, and accumulation.

Major results are summarized as follows:

1. Temperature increases the charge injection and mobility.
2. Presence of antioxidant enhances the negative charge injection and the transport within the bulk.
3. Charge distributions obtained from PEA measurements explain the anomalous TSDC observed for LDPE with antioxidant at 50°C temperature.

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