Electrical Polarization Effects on LDPE Morphology

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ABSTRACT: The thermal and dynamic mechanical behavior of polarized low-density polyethylene (LDPE) was investigated, by applying electric fields in the range of 5.37 to 31.7 MV/m, for 2.75 to 43.5 h. The polarization strongly affected DSC and DMA spectra, indicating that a new and more ordered phase is formed, which disappears gradually after the removal of the electrical field. A shift of −21.3°C was found in the DMTA spectra for the T_g of the polarized material, and no changes could be found in comparing the results of WAXS analyses of the original and treated materials. Very similar effects were observed with mechanical loading of the materials, leading to the conclusion that the amorphous phase of LDPE might be orienting under high electric fields in a similar manner. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3107–3114, 2003

Key words: polyethylene; electrical polarization; morphology; mechanical properties; thermal properties

INTRODUCTION

Polyethylene has been widely employed as an insulating material because of its dielectric properties combined with long durability, low cost, easy manufacture, and good chemical resistance. Despite its widespread use in applications where high electric fields operate, a systematic study of the effect of these conditions on the polymer's properties is not found in the literature. In fact, to our knowledge, this is the first contribution approaching the subject, exploring the morphology alterations that take place after the polymer has been submitted to high electrical fields (about 5 to 31 MV/m). It is common practice in electrical engineering to perform a previous electrical conditioning of the material under study, through a previous polarization. In capacitors, cables, and transformers, the "aftereffect"[1,2] is often found, that is, the recovery tension and internal discharge varies according to the electrical treatment previously performed. Several effects related to melting and electrical treatment are known, such as electrofusion,[3] where the melting rate varies under the action of alternating or continuous electric fields, and the electro-thermoconductivity which occurs in the liquid phase, near the melting point, where the thermal conductivity changes with the imposition of an electric field.[4]

In this article, we report the variations detected in low-density polyethylene (LDPE) after polarization, using DSC, dynamic mechanical thermal analysis (DMTA), and WAXS techniques.

EXPERIMENTAL

Material and polarization procedure

LDPE, with no stabilizers, was supplied by Dow Brazil (São Paulo, Brazil) in film form, with an average thickness of (93 ± 3) μm.

The process of polarization consisted of placing the polymer film between two planar metallic electrodes, 50 mm diameter, as shown in Figure 1. The set was submitted to constant electric tension at room temperature during predetermined periods of time.

DSC

DSC scans were performed in Netzsch Thermische Analyze DSC200 equipment. The heating rate was 10°C/min in the temperature range 0–150°C, under a nitrogen flow of 15 mL/min. The samples (1 to 2 mg), collected from the polarized film and placed in aluminum pans, were submitted to only one heating step.

WAXS

The WAXS spectra were performed on polymer films by using CoKα radiation (λ = 1.79026 Å) in conven-

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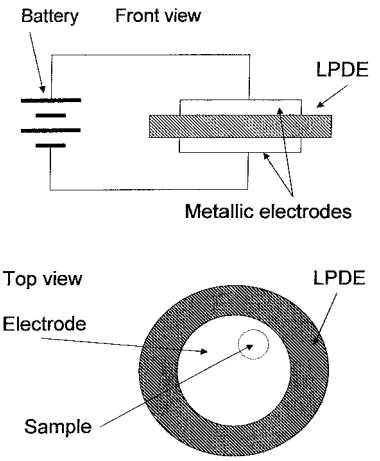

Figure 1 Experimental setup used for the electric polarization of LDPE.

tional horizontal axis Phillips X′ Pert equipment, with a scan rate of 1°/min between $2\theta = 5°$ and 90°.

DMTA

The mechanical dynamic characterization was performed in the tension mode, under a steady load of 1.78 MPa and a dynamic stress of 1.98 MPa, and under a nitrogen flow of 50 mL/min. The sweepings were made in the temperature interval of −150 to 100°C at a heating rate of 2°C/min at a frequency of 5 Hz. The dimensions of the samples were (4.8 × 10.0 × 0.093) mm.

Mechanical testing

Strips of 30 cm × 2.5 cm × 103 μm were submitted to mechanical loading, at 22°C and 44% relative humidity under the conditions shown in Table I.

RESULTS AND DISCUSSION

The effect of polarization on the thermal behavior was observed in maintaining constant either the time of polarization (5.77 h) or the electric field (5.37 MV/m). In Figure 2 the DSC thermograms of nonpolarized LDPE samples (curve a) are compared with those polarized with a field of 5.37 MV/m (curve b) and of 21.50 MV/m (curve c). Figure 3 shows the effect of applying a field of 5.37 MV/m during 2.75 h (curve a), 6.03 h (curve b), and 17.33 h (curve c). The main effects observed can be described as follows: (1) increases in the field intensity bring about a splitting in the melting peak; an additional lower temperature peak appears, which merges with the higher with further field increase. (2) The final melting endotherm is located at the same temperature of the nontreated sample, but is much sharper. (3) Time and field intensity operate in the same direction, that is, increases in field magnitude or in the duration of the treatment bring about similar effects. The effect of a long time–high field treatment is shown in Figure 4. All the tests were performed immediately after polarization, and the alterations were reversible, that is, the samples returned to their original state after a period of time, typically 48 h, and no memory effect was found.

To investigate whether the polarization could induce an increase in crystallinity, the nonpolarized and polarized samples were analyzed by WAXS immediately after polarization. No difference was detected, indicating that the morphology alterations occurred in the amorphous phase. Figure 5 shows the WAXS spectrum found for any sample. The location, the area, and the half-width of the orthorhombic crystalline peaks [(110), (200), and (020) shown in Fig. 5], as well as the amorphous halo, were essentially the same before and after polarization. The degree of crystallinity thus determined was (36 ± 1)%. An X-ray dose of 20 kV, 20 mA, for 5 min, did not alter the DSC results. The DSC scans of Figures 2 and 3 were performed just after the WAXS analyses.

Because no difference was detected in the diffraction patterns, the morphology effects should have taken place at the amorphous phase, as noted. It is known that above glass transition temperature (T_g) a variety of chain motions is permitted, although in the specific case of polyethylene a conclusive agreement in the literature data cannot be found regarding the assignment of the DMTA relaxations.[5,6] These relaxations have been attributed to the movements of ramifications and long range and localized chain motions. It has been argued that these microstructural relaxations, under the action of an electric field, play an important role in polymer's polarization, giving rise to the formation of regions with different electronic charge distributions than the rest of the bulk material. These regions, called clusters,[7,8] which are imperfectly ordered and spatially limited, cannot be detected by X-ray diffraction, but are detectable by electrical experiments. Electrical relaxation phenomena, for example, are attributed by inter- and intracluster interactions. When the polarizing electric field is removed, the clusters gradually disappear.

TABLE I

Sample	Nominal stress (MPa)	Time (h)	Permanent set (%)
a	2.37	40	3.03
b	5.89	29.34	3.33
c	11.78	19	Failure

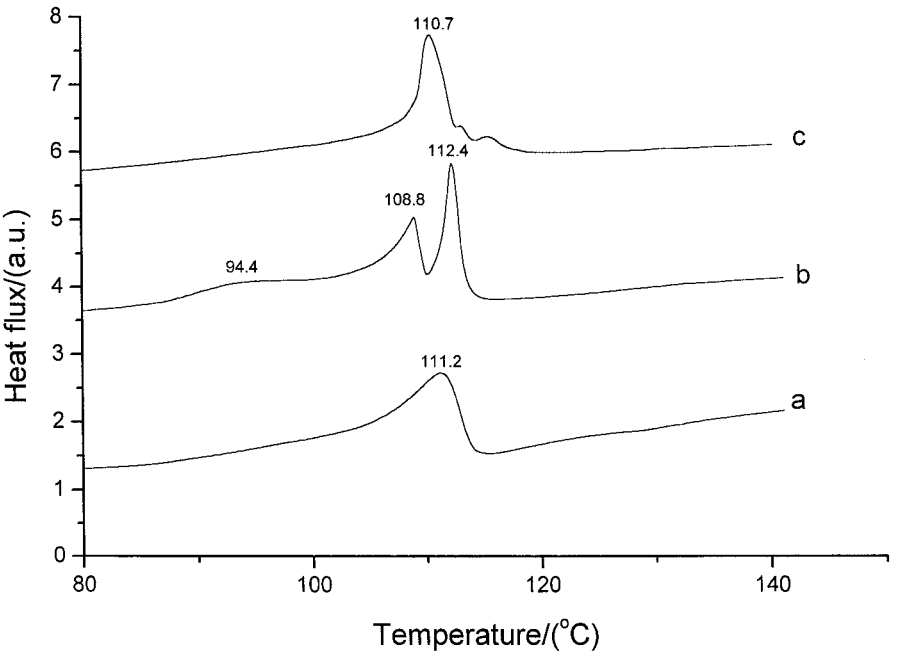

Figure 2 DSC thermograms of LDPE: nonpolarized (a); polarized with electric fields of 5.37 MV/m (b); and 21.50 MV/m (c). The time of polarization was held constant at 5.77 h.

One first hypothesis to explain the differences found in the melting behavior of the polarized samples would be the formation of ordered regions in the amorphous phase, similar to the electric clusters.[9] These regions would not possess the necessary long-range periodicity for X-ray diffraction, but the geometry alteration would be sufficient to modify phase transitions. The thermal motion after the removal of the electric field would be responsible for the gradual disappearance of the effect.

Another plausible explanation would be that the electrical field brings about an enhancement of orientation in the intraspherulitic amorphous phase, in a first stage. This material would be incorporated in the

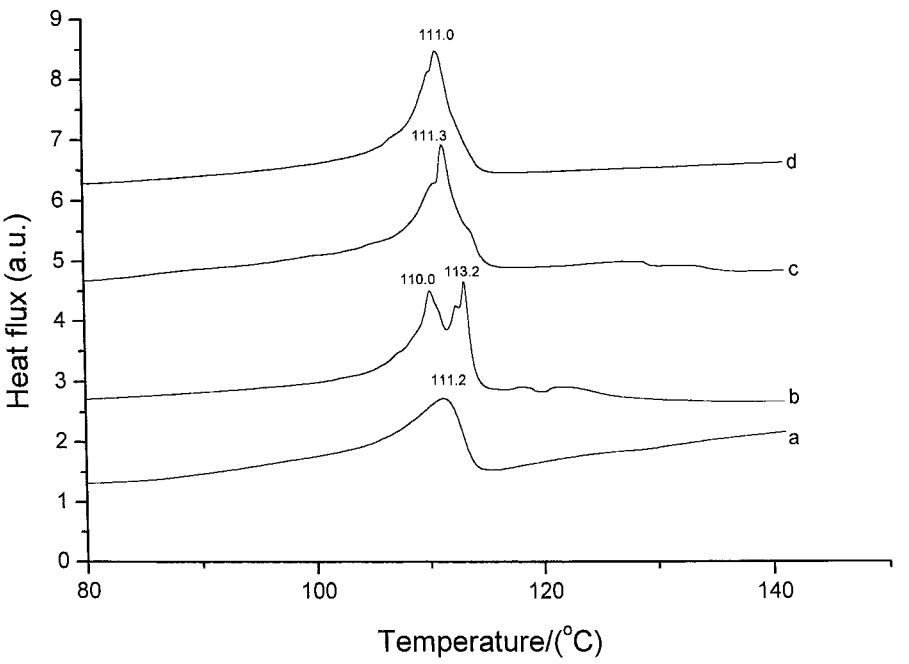

Figure 3 DSC thermograms of LDPE: nonpolarized (a); polarized for 2.75 h (b); 6.03 h (c); and 17.33 h (d). The electric field intensity was held constant at 5.37 MV/m.

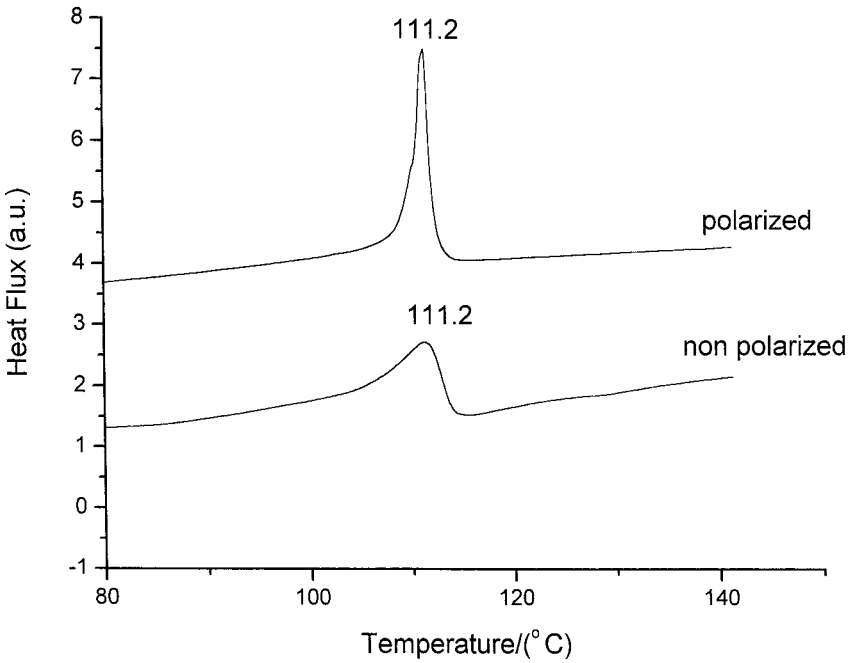

Figure 4 DSC thermograms of LDPE: nonpolarized (a); polarized for 31.7 h with electric field of 21.5 MV/m (b).

crystalline region subsequently as in secondary crystallization. That would explain the second melting endotherm seen in Figures 2 and 3, and the sharper melting endotherm seen in Figure 4, indicative of larger and more perfect crystalline regions of the polarized samples. These more perfect crystals would be unstable at ambient temperatures, after the removal of the electrical field.

The DMTA spectra shown in Figures 6 and 7 reveal that the glass transition temperature of the polarized samples was significantly shifted to lower temperatures as compared to the nonpolarized ones. The loss

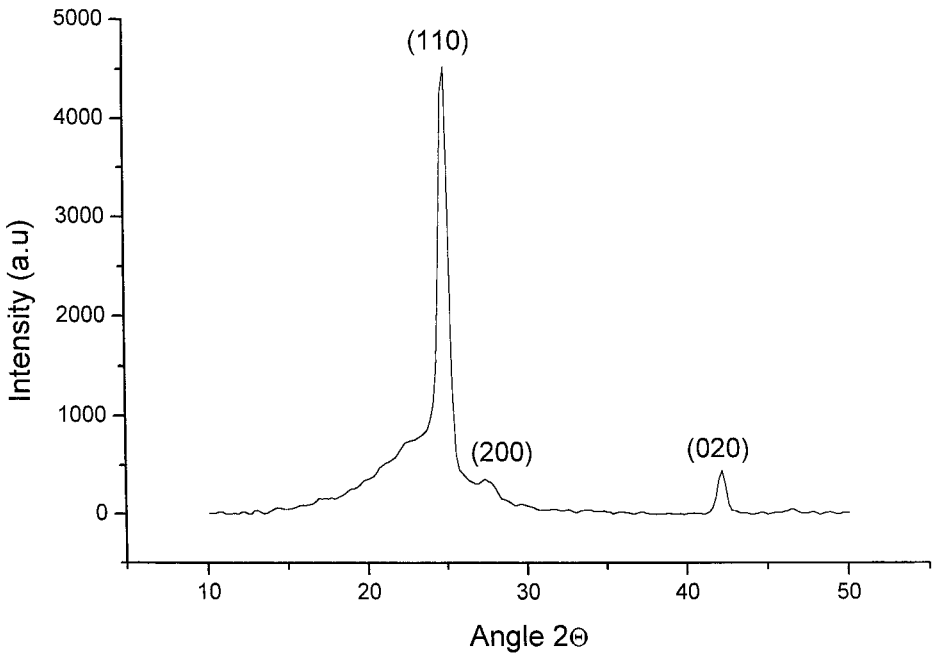

Figure 5 X-ray diffraction spectra of LDPE samples. Original and polarized materials afforded the same spectrum. The crystallographic planes are assigned.

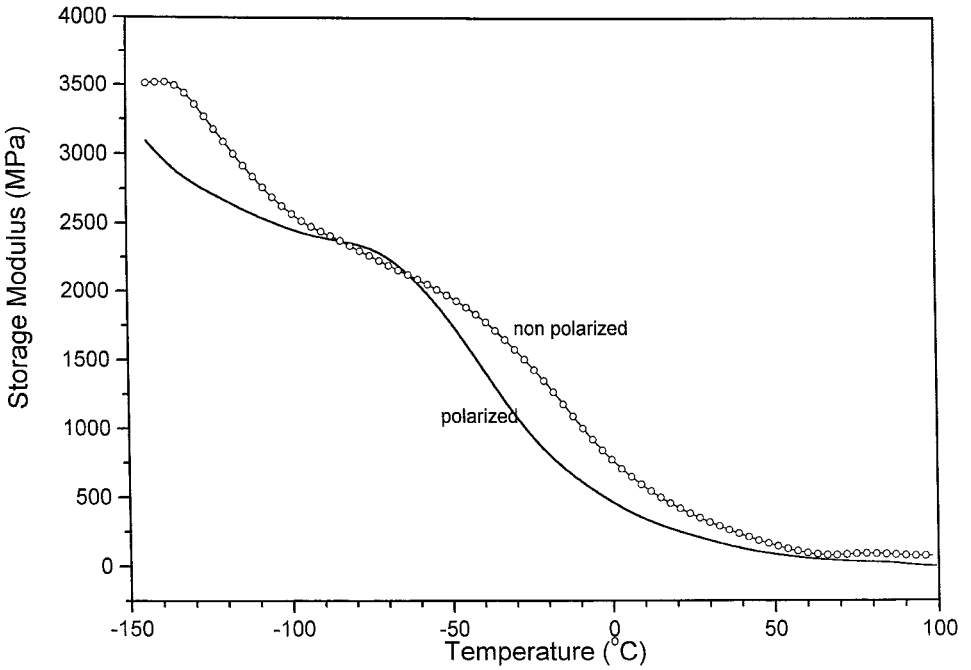

Figure 6 Storage modulus from DMTA of original and polarized LDPE. The polarization was performed by applying an electric field of 31.7 MV/m for 43.5 h.

modulus curves of Figure 7 show a significant shift of −21.3°C for T_g. These results indicate an enhancement in the chain mobility had occurred in polarized samples and are a strong argument in favor of the field-induced molecular alignment.

To gain further insight in the nature of the morphological changes that took place under the action of the electric field, mechanical tests were carried out by submitting strips of the material to a constant load for determined periods of time, as described in Experi-

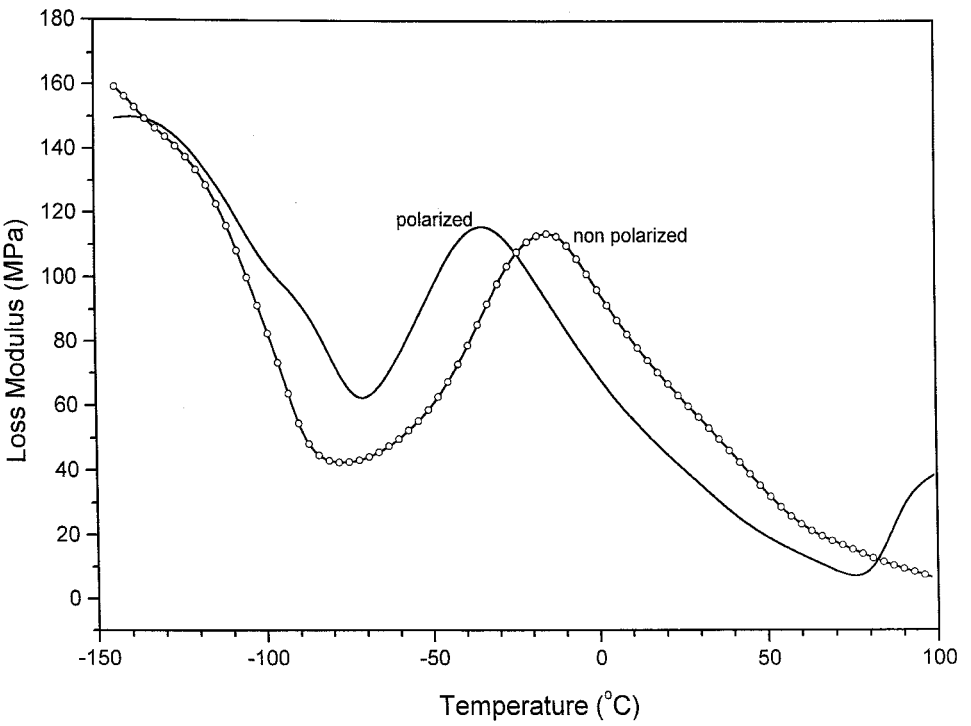

Figure 7 Loss modulus from DTMA of original and polarized LDPE. The polarization was performed by applying an electric field of 31.7 MV/m for 43.5 h.

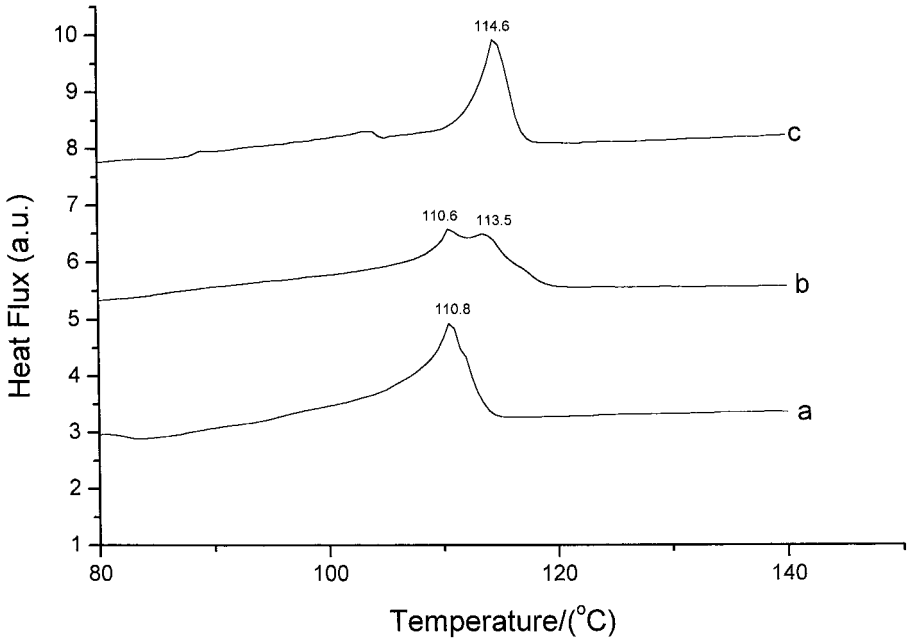

Figure 8 DSC thermograms of LDPE samples submitted to initial loads of 2.37 MPa (40 h) (a); 5.89 MPa (29.34 h) (b); and 5.89 MPa (19 h).

mental. The DSC and WAXS results of the mechanically treated samples were remarkably similar to those observed with the electrically treated ones, as clearly demonstrated by comparing the thermograms and WAXS spectra of Figures 8 and 9 (mechanically treated) with those of Figures 3 and 5 (electrically treated). The enhanced crystallinity (57%) found for sample c in Figure 9 was atypical, because this material was overstrained, resulting in mechanical breaking down.

DMTA spectra of the mechanically treated samples, presented in Figures 10 (E') and 11 (E''), show that the shape of the storage modulus (Fig. 10) of these follows the same pattern of the polarized ones, as compared with the nontreated materials. On the other hand, the shift observed for the loss modulus (Fig. 11) of the

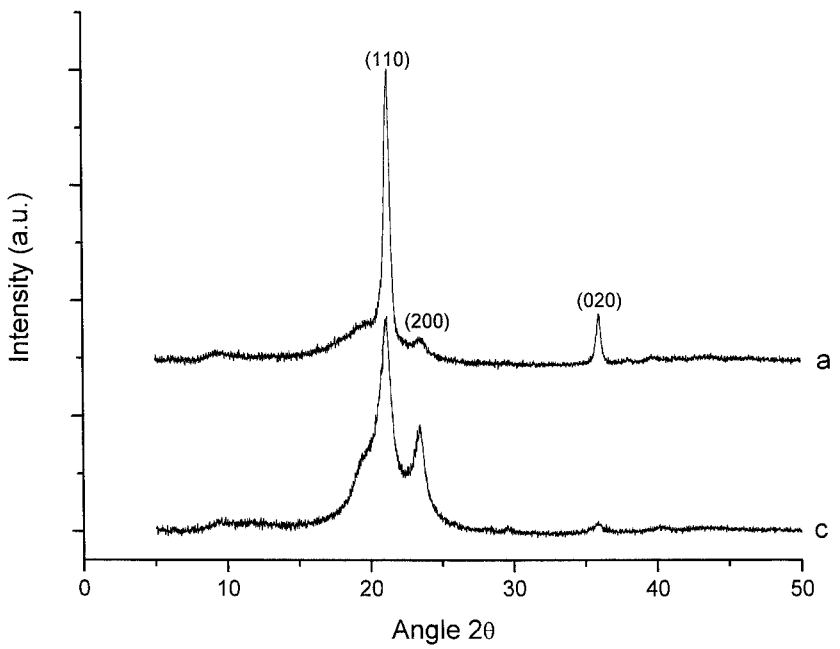

Figure 9 X-ray diffraction spectra of LDPE samples. Original and mechanically loaded materials afforded the same spectrum, except for sample (c). The crystallographic planes are assigned.

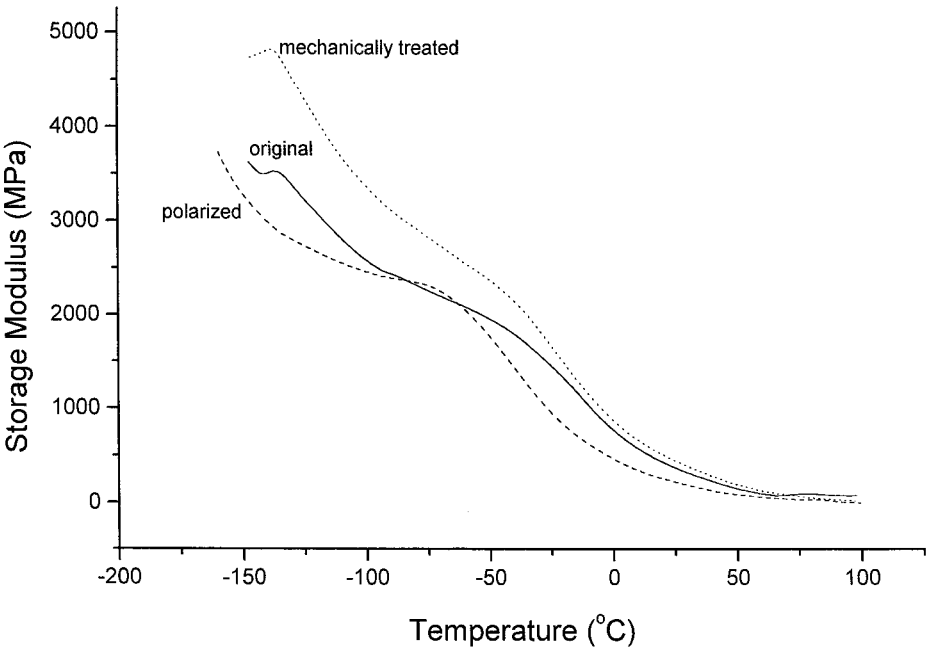

Figure 10 Storage modulus from DMTA of original, mechanically treated, and polarized LDPE. The nominal stress was 11.78 MPa (19 h). The polarization was performed by applying an electric field of 31.7 MV/m for 43.5 h.

mechanically treated samples is less pronounced (−5.5°C) than that of the polarized ones. Both moduli are substantially higher for mechanically treated than for the polarized LDPE.

CONCLUSION

In this work we have demonstrated for the first time that electric polarization exerts a strong effect on the thermal and dynamical mechanical behaviors of low-density polyethylene. Mechanical loading led to remarkably similar results as those seen after the electrical field was imposed, indicating that the amorphous region was mainly affected. Having in mind that the polymer is mainly used for electrical insulating cables, this result is of great technological significance. A conclusive and detailed scientific interpretation of the observed phenomenon was not possible at

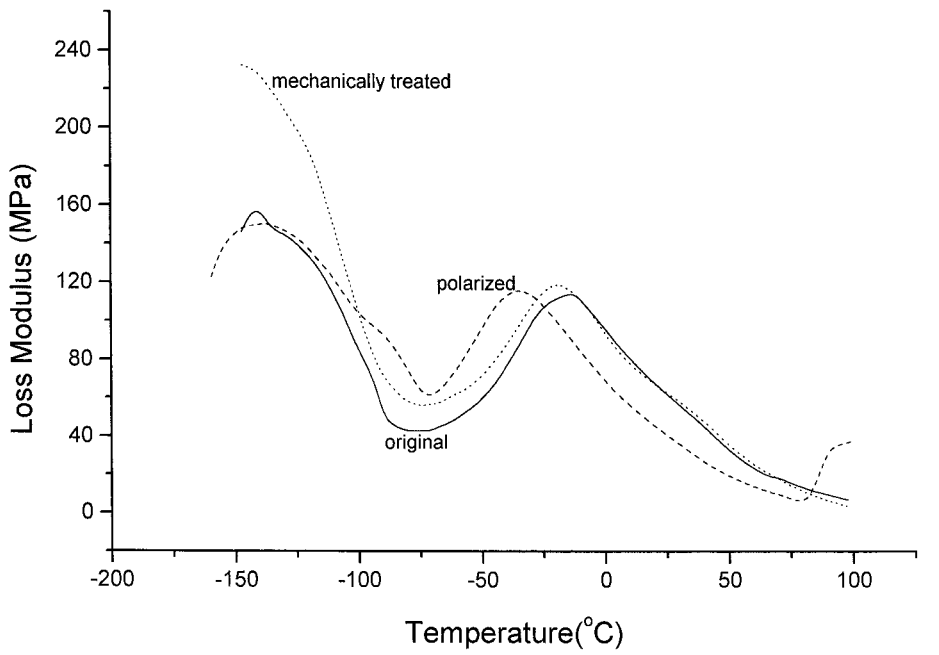

Figure 11 Loss modulus from DTMA of original, mechanically treated, and polarized LDPE. The nominal stress was 11.78 MPa (19 h). The polarization was performed by applying an electric field of 31.7 MV/m for 43.5 h.

the moment, but the WAXS results have shown that the alterations in morphology occurred in the amorphous phase. As it is temporary, it can be said that LDPE shows the phenomena of electrical aftereffect.

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