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Some aspects of structural electrophysics of irradiated polyethylenes

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Abstract

In the case of the insulation polymeric materials, such as polyethylenes, it is of essential interest to understand correlations between structural changes and (di)electric properties. The dielectric behavior of different polyethylenes, low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and high density polyethylene (HDPE), irradiated to different absorbed doses of gamma radiation, was studied through dielectric loss (tan δ) analysis. Dielectric relaxation behavior is related to the changes in the initial structure of different polyethylenes and to the radiation-induced processes of oxidative degradation and crosslinking. Differential scanning calorimetry (DSC), IC spectroscopy and gel measurements were used to determine the changes in the crystal fraction, oxidative degradation and degree of network formation, respectively.
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1. Introduction

Dielectric measurements can give valuable information about the structure of polymeric materials [1–3]. Also, for the application of polymers in insulation systems it is of essential interest to understand the dielectric phenomena in them [4]. On the other hand, the radiation processing of polymeric materials is the main step in certain modern technologies and has extensive application [5]. These facts explain the large interest in (di)electric study of the effects of radiation on polymers, especially on polyethylenes [6], because of their wide engineering application.

In dielectric relaxation studies, polyethylene displays three dielectric relaxations, designated as α, β, and γ, in the order of decreasing temperature, in addition to the melting point [7]. The origins of these three different relaxations were extensively studied in the past, mainly by mechanical and dielectric measurements [1–31]. Although some detailed molecular assignments are still open for debate, the reality of the basic relaxation processes is clear; these have been well summarized by Boyd [11,12]. The α and β

relaxations are commonly attributed to the relaxation mechanisms in the crystalline and amorphous phases [13–15], respectively; the γ relaxation, according to different authors, is due to the localized motions of either chain ends or branches associated with the amorphous phase [13,14,16], although originally it was proposed to arise also from the crystalline phase [17,18].

The effects of ionizing radiation on the molecular relaxation of polyethylene have been the subject of recent publications [3,6,10,19–23]. In the case of dielectric relaxation measurements, the polar groups that were introduced in apolar polyethylene were considered as tracer groups whose motion reflected the motion of the polymer chains. The amounts of polar groups and gel fraction increase with the increase of absorbed dose [22], causing modification of the dielectric properties, especially dielectric γ and β relaxations, with radiation. The reasons for this are found in the fact that these relaxations occur partially (as γ relaxation) or completely (as β relaxation) in the amorphous domains, and that the changes induced by radiation, such as oxidative degradation and crosslinking, occur primarily in this phase [23]. Radiation-induced crosslinking in the amorphous phase restricts the motion of macromolecules, changes their entropy and increases the activation energy of the molecular relaxation. On the other hand, the intensity of the relaxation, in the case of PEs, depends on the number of polar groups as well as on the molecules contributing to this relaxation.

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2. Experimental

We examined three types of polyethylenes: LDPE HIPTEN 22003A3 ($\rho = 0.922$ g cm^{-3}, $M_w = 110{,}000$), LLDPE ($\rho = 0.925$ g cm^{-3}, $M_w = 100{,}000$) and HDPE HIPLEX EHM ($\rho = 0.96$ g cm^{-3}, $M_w = 76{,}700$). Isotropic sheets, approximately 0.28 ± 0.02 mm thick, were prepared by compression molding, in 'Carver' laboratory press, at 150 °C and 1.75 MPa, followed by quenching in cold water. The samples were irradiated in a ^{60}Co radiation facility, in air, at room temperature, at a dose rate of 9 kGy h^{-1}, to absorbed doses of 100, 200, 300, 500 and 700 kGy.

The dielectric loss (tan δ) of the disc-shaped samples of 1.3 cm in diameter was measured on a Digital LCR Meter 4284A, in frequency (10^3–10^6 Hz) and in the temperature range (25–335 K) with convection heating of 1.7 K min^{-1}. A Carl–Zeiss Model 75IR Specord was used in recording infra-red spectra for the PEs films. The absorbance at 1720 cm^{-1} was determined from these spectra. For the DSC measurements, a Perkin–Elmer DSC-2 differential scanning calorimeter with nitrogen as the purge gas was used. Samples of 7–8 mg, cut from the neck, were analyzed by heating from 320 to 420 K at a rate of 10 K min^{-1}, and their heats of fusion (ΔH_f) and peak melting temperature (T_m) were derived. The degree of crystallinity, χ, was then calculated as $\chi = \Delta H_f / \Delta H_{f0}$, where ΔH_{f0} is the heat of fusion of a perfectly crystalline polyethylene ($\Delta H_{f0} = 289$ J g^{-1}). The amount of gel was determined by solvent extraction in boiling xylene for 17 h. The measurement of the weight loss was performed after drying the samples for 4 h in a vacuum oven at 60 °C.

3. Results and discussion

Fig. 1 depicts the dielectric relaxation, in LDPE, LLDPE and HDPE, of unirradiated samples (Fig. 1(a)) and samples irradiated to the absorbed dose $D = 300$ kGy (Fig. 1(b)). A transition observed at about 190 K (Fig. 1(a)) corresponds to the γ relaxation that occurs below the glass transition temperature [3,19]. The other peak observed at about 280 K corresponds to the β relaxation. Many studies point to the relationship between this relaxation and the amorphous content between the lamellae surfaces [24]. The inter-lamellar content increases with increasing degree of branching, due to which the β relaxation is more pronounced in branched polyethylenes, whereas in linear polyethylenes it may not occur [12,24]. The atomic force microscopy (AFM) and dynamic dielectric spectroscopy (DDS) measurements of Alon et al. corroborated the assumption that the source of this relaxation in HDPE is the interlamellar content [25]. Under the special conditions of ultra rapid quenching to produce amorphous samples, it can also be clearly observed in linear polyethylenes. Pegoretti et al. showed how transcrystallinity in HDPE, which increased greatly the lamellar interfacial region, also

generate a huge β transition—untypical of HDPE [26]. The amorphous nature of this relaxation was also determined by eliminating crystalline domains at an increased amount of co monomers in the process of copolymerization [27]. The molecular mechanisms involved can be fold-surface motion, chain-end motion, branch-point motion and chain rotation in the amorphous region. According to many authors, β relaxation is undoubtedly connected with the glass–rubber transitions, especially in the case of linear polyethylene. On the other hand, C^{13} NMR measurements have shown that there is no direct correlation between the temperatures of glass transition and β relaxation [28,29]. Nevertheless, significant differences between the reported activation energies of 59–65 kJ mol^{-1} [30,31] and 180–500 kJ mol^{-1} [6,13,26,32,33] suggest that in the former case the β relaxation in polyethylene should be treated as a motion in interfacial regions, and in the latter as a highly cooperative process such as glass transition. On the other hand, reported activation energies for γ relaxation are usually between 45–55 kJ mol^{-1} [1,3,7,34] but higher values (up to 120 kJ mol^{-1}) are also reported [26].

Differences in the structure will significantly influence the dielectric relaxation spectra of these polyethylenes, especially in the case of β relaxation. Contrary to LDPE whose dielectric β relaxation is of high intensity, in the case of LLDPE an evident decrease of intensity is noted. In the case of HDPE, even though the trace of this relaxation still exist (arrow at Fig. 1(a)), the relaxation cannot be clearly resolved and disappears in irradiated samples probable due to crosslinking (Fig. 1(b)). It was recently found by Ratner et al. that this transition in HDPE also disappeared upon peroxide generated crosslinking in interlamellar regions [32]. This should be expected taking into account the fact that this relaxation is connected entirely with the inter-lamellar content, which is low for unirradiated and especially irradiated HDPE samples (Fig. 2). Restricted chain mobility in interlamellar regions, as a consequence of radiation or peroxide generated crosslinking of HDPE, will lead to disappearance of β relaxation. This relaxation completely degenerate in more crystallized PEs as well. Our dielectric measurements indicate that the minimal inter-lamellar content needed for clear detection of dielectric β relaxation is higher than 35% which is in good agreement with some dynamic mechanical studies [33]. On the other hand, Raman spectroscopy correlated with dynamic mechanical measurements determines that the minimal interlamellar content needed for β relaxation registration is about 7%, while for an undoubtful insight it takes about 10–20% [24].

Fig. 3(a)–(c) show the temperature dependence of dielectric loss tangent for LDPE, LLDPE and HDPE samples irradiated in air to different absorbed doses. Two main effects result when polyethylene is subjected to ionizing radiation in the presence of air: crosslinking and oxidation. There is a competition between the oxidative degradation and crosslinking in the case of polyethylene. In
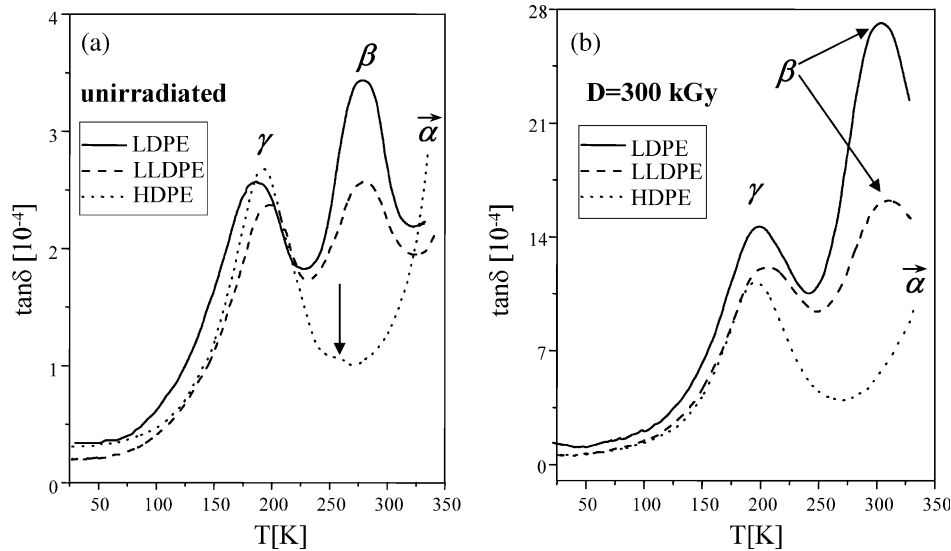
Fig. 1. (a) Dielectric loss tangent versus temperature, at $f = 10^5$ Hz, for various PE samples; (b) Dielectric loss tangent versus temperature, at $f = 10^5$ Hz, for various PE samples irradiated to absorbed dose of $D = 300$ kGy.

general, the domination of one or the other of these processes, under the same irradiation conditions (such as dose rate, temperature and oxygen pressure) is controlled by the structural peculiarities of the polymer. It is worth mentioning that in crystalline regions the macromolecules have very small mobility and the oxygen is almost unable to diffuse; diffusion constants for crystalline regions are small, 8–9 orders of magnitude smaller than in the amorphous region. For that reason, both these processes take place mostly in the amorphous region. The radiation-induced changes will also greatly influence the dielectric spectra; introducing the polar groups will intensify dielectric losses; crosslinking and the net structure formation, under

irradiation, will restrict the dipolar-segmental and dipolar-group motion of macromolecules, especially in the amorphous phase, causing a shift of the relaxation maxima and a increase in the activation energy of dielectric relaxations to which mentioned dipolar and molecular movement contributes.

Fig. 4(a) displays maximum intensities of the dielectric loss tangent of the relaxations as a function of absorbed dose for the various polyethylenes. On the other hand, our previous analysis of IR spectra indicates a significant growth in the absorption at about 1700 cm^{-1} with absorbed dose. The carbonyl groups are mainly ketone groups at 1718 cm^{-1} and aldehide groups at 1728 cm^{-1} and both are
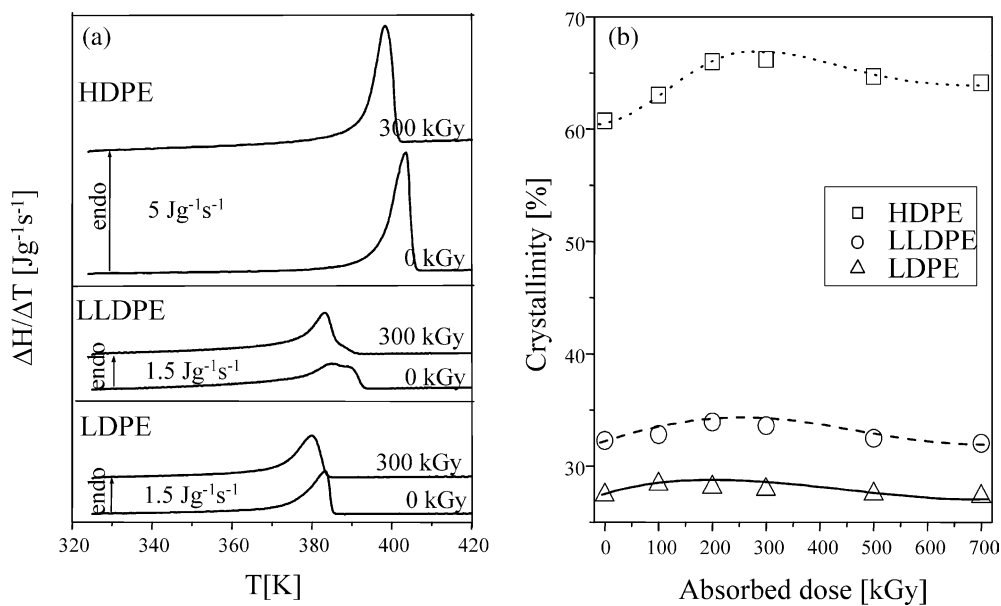

Fig. 2. (a) Melting endotherms of unirradiated and irradiated ($D = 300$ kGy) LDPE, LLDPE and HDPE samples; (b) Crystallinity as a function of radiation dose for various PE samples.
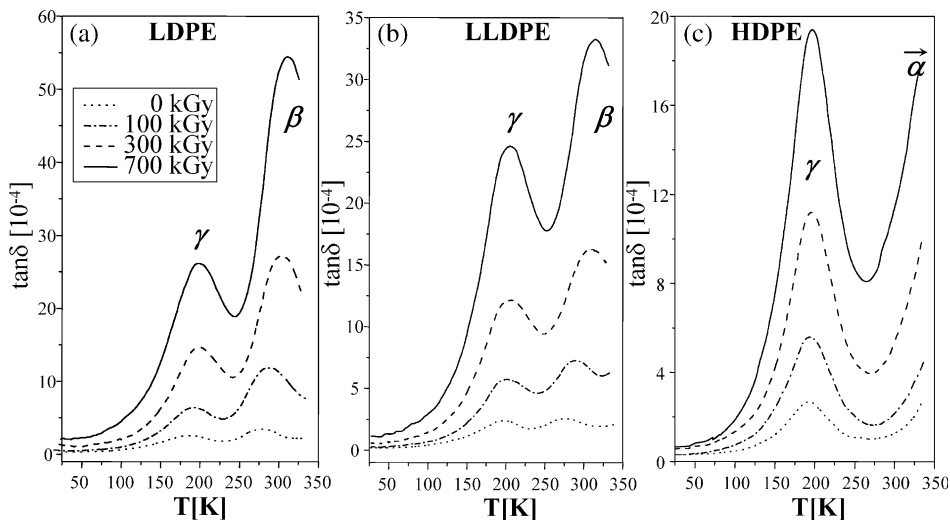
Fig. 3. Dielectric loss tangent versus temperature, at $f=10^5$ Hz, for PE samples; (a) LDPE; (b) LLDPE; (c) HDPE; irradiated to different absorbed doses.

formed in the amorphous region of the polymer. The relative contribution of aldehydes and ketones depends on the competition between the chain scission reactions and the reaction of decomposition of hydroperoxide in which the water is produced. The results of IC spectroscopic and dielectric measurements suggest a similarity, between the dependences of the concentration of carbonyl groups and the intensity of the relaxations, with the absorbed dose (Fig. 4(a) and (b)). For the β relaxation, which completely occurs in amorphous domains, the decrease in the amorphous fraction dramatically decreases the number of molecular motions contributing to this relaxation. Radiation-induced oxidation introduces carbonyl groups as statistically distributed tracer groups whose motion reflects the motion of the polymer chains. For that reason, the dielectric β relaxation monitors the changes in the carbonyl content caused by the radiation-induced oxidation, but it

only arises from the carbonyl groups which are in interlamellar region and are connected to molecules contributing to this relaxation. Since the γ relaxation (which corresponds not only to the amorphous phase but also to crystalline defects) is less sensitive to the content change of the amorphous/crystalline phase, the rise in the intensity of this relaxation with irradiation is in good agreement with the increase in the carbonyl content caused by the radiation-induced oxidation, and the correlation between the intensity of this relaxation and the carbonyl group concentration appears to be obvious for all polyethylenes.

From Fig. 5(a) it is also evident that gamma irradiation, besides the effects of increased relaxation intensities, causes shifting of the relaxation maxima. Radiation-induced crosslinks in the amorphous phase restrict the motion of polymer molecules, decrease their entropy and cause
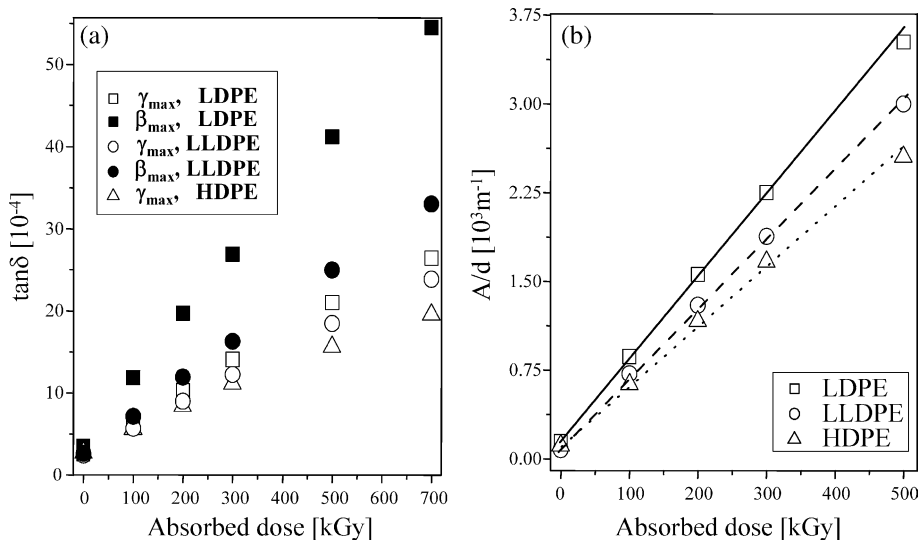

Fig. 4. (a) The maxima of the dielectric loss tangent for γ and β relaxation peaks, as a function of absorbed dose, for various PE samples; (b) IR absorbance (A/d values; A, absorbance; d, sample thickness) as a function of absorbed dose for various PE samples.
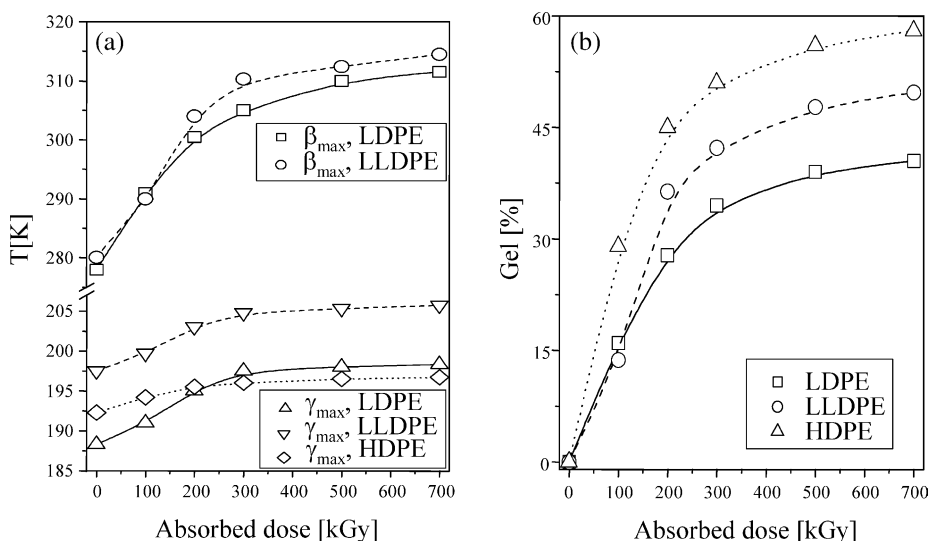
Fig. 5. (a) Temperature of dielectric γ and β relaxation loss tangent maxima as a function of absorbed dose for various PE samples; (b) Gel content as a function of radiation dose for various PE samples.

shifting of the relaxation maxima. With the increase of radiation dose there is a significant increase in the gel content for LDPE, LLDPE and HDPE samples, reaching saturation after 300 kGy (Fig. 5(b)). Also, with the absorbed dose, crosslinking causes a shifting of relaxation towards higher temperatures. In the case of LDPE and LLDPE, this effect is much more pronounced for the β than for the γ relaxation at the same gel content. This is a consequence of the fact that crosslinking induces greater restrictions in the motion of the side branches and side branch-points than in the local crankshaft-like motion related to the γ relaxation.

The complete isochronal loss scans for irradiated LDPE samples ($D = 300$ kGy), at several frequencies, are represented in Fig. 6(a). In accordance with earlier investigations, the results obtained show a slight increase in dielectric loss tangent and shift of $\tan \delta_{max}$ towards higher temperatures with increasing frequencies. Also, the loss factor curves for LDPE show that, while the temperature of the β relaxation has only a slight increase, the γ relaxation increases with the test frequency much more rapidly (suggesting a lower activation energy for this relaxation). Objective values for the temperatures of the relaxation peaks were obtained using curve fitting. The process is complicated for LLDPE, where the γ relaxation is closer to β relaxation, not only in the temperature at which it occurs, but also in intensity. Gaussian function was fitted to the relaxation peaks. In Fig. 6(b) the maps of $\log f_{max}$ versus $1000/T$ are shown for some gamma irradiated LDPE samples.

Changes in the activation energy of the relaxations with absorbed dose are represented in Fig. 7. The β relaxation for the initial samples of LDPE and LLDPE has high activation energies, of about 185 and 210 kJ mol^{-1} respectively, which are in conformity with other authors [34]; the high activation energies are consistent with the β relaxation

being associated with the (L)LDPE glass transition [33]. Furthermore, it can be observed that with irradiation the activation energies of relaxations increase, and also that the increase is much more pronounced for the β relaxation. Crosslinking produces a net structure in the material, which inhibits the motion of polymer chain and dipolar groups attached to the polymer chain, thus increasing the activation energy for molecular movement. The changes in the activation energy (Fig. 7), as well as the shifting of the relaxations towards higher temperatures (Fig. 5(a)), can be quantitatively correlated to the observed degree of crosslinking (Fig. 5(b)). The observed increase in the activation energy of the β relaxation for LDPE and LLDPE with radiation-induced crosslinking is much more pronounced than in the case of γ relaxation. The calculated values of activation energy for the dielectric γ relaxation were between 48 and 54 kJ mol^{-1} for all absorbed doses. This is a consequence of the fact that crosslinking leads to much greater restrictions in the motion of side branches and side branch-points than in the local crankshaft-like motion.

4. Conclusion

The presented results show that irradiation significantly affects the dielectric relaxation behavior of LDPE, LLDPE and HDPE. The mobility of the chain segments changes because of the effect of gamma irradiation, oxidized regions are redistributed and the amount of polar groups is increased by radiation oxidative degradation, causing the dielectric relaxation properties of polyethylenes to be modified. Changes in the intensity of the γ and β dielectric relaxations in LDPE, LLDPE and HDPE with gamma irradiation are mainly related with oxidation, but also with increasing/decreasing of the crystal fraction and the mobility of the chain
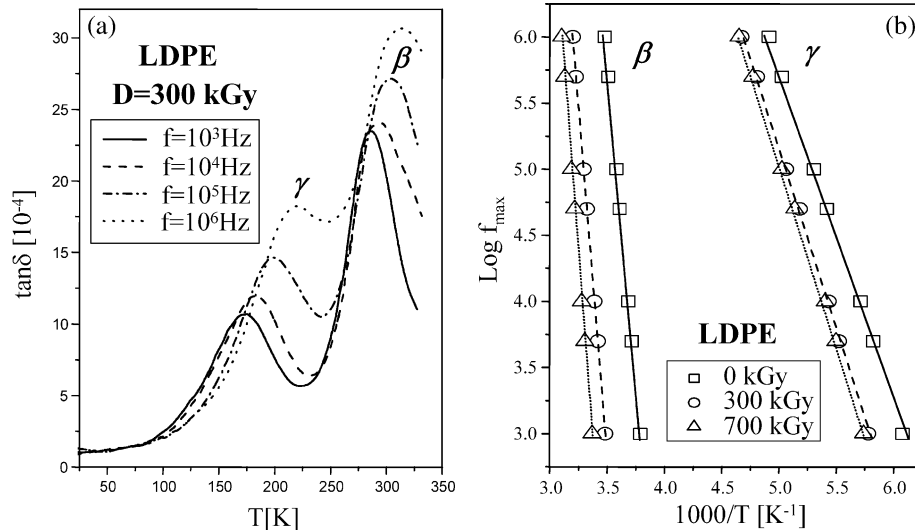
Fig. 6. (a) Dielectric loss tangent versus temperature for LDPE samples, irradiated to absorbed dose of $D=300$ kGy, at several frequencies; (b) Isochronal log f_{max} versus 1000/T map, for LDPE samples irradiated to different absorbed doses.

segments in the amorphous region. On the other hand, changes in the position and activation energy of these dielectric relaxations are mainly related to the changed chain mobility induced by crosslinking. Crosslinking produces a net structure in the material, which inhibits the motion of polymer chains and dipolar groups attached to the polymer chain and thus increases the activation energy for molecular and dipolar movements, especially for the dielectric β relaxation.
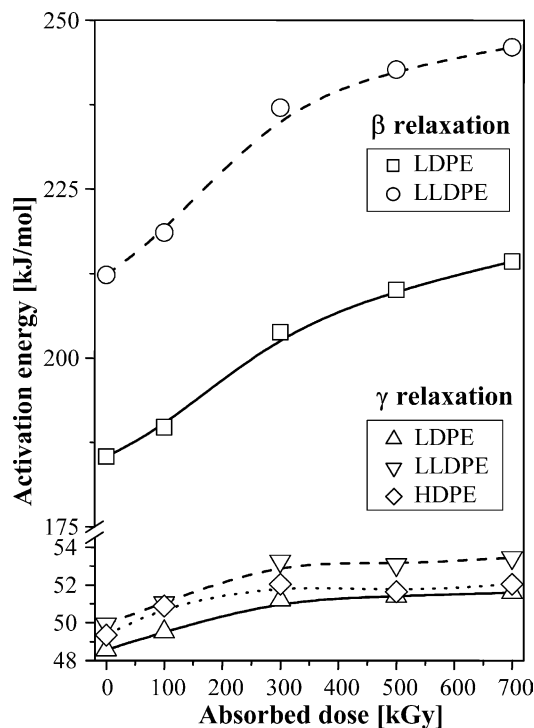

Fig. 7. Activation energies for the dielectric γ- and β-relaxations as functions of absorbed dose for LDPE, LLDPE and HDPE samples.

Acknowledgements

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