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Dielectric studies of molecular β-relaxation in low density polyethylene: the influence of drawing and ionizing radiation

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Abstract

The dielectric relaxation behavior of low density polyethylene, uniaxially oriented to different draw ratios (3, 7 and 10) and irradiated to different absorbed doses (100, 200, 300, 500 and 700 kGy) of gamma radiation was investigated. Molecular relaxation was studied through dielectric loss (tan δ) analysis, in the temperature range from 25 to 335 K, at several different frequencies ranging from 10^3 to 10^6 Hz. The β-relaxation was resolved from the γ by curve fitting and its parameters were determined. Its intensity, position and activation energy were found to be strongly dependent upon the changes in microstructure of the amorphous domain induced by orientation and irradiation. Since the dielectric relaxation processes are very sensitive to prior structure of the samples, we also used differential scanning calorimetry, IR spectroscopy and gel measurements to determine the changes in crystal fraction, oxidative degradation and degree of network formation, respectively. Conclusions derived according to these methods were compared with changes in intensity, position and activation energy of the molecular β-relaxation detected by dielectric relaxation measurements. © 2002 Published by Elsevier Science Ltd.

Keywords: Low density polyethylene; Dielectric relaxation; Activation energies

1. Introduction

Dielectric measurements can give valuable information about the structure and dynamics of polymeric dielectric materials [1–4]. Also, for the application of polymers in insulation systems it is of essential interest to understand the dielectric phenomena [5]. On the other hand, the orientation [6] and radiation processing [7] of polymeric materials are the main steps in certain modern technologies and have extensive application. These facts explain the high interest in the study of orientation and radiation effects on polymers, especially on polyethylene.

The molecular mechanisms responsible for the relaxations or transitions in polyethylene are still the subject of high interest [8,9]. From great number of studies it can be summarized that low density polyethylene (LDPE) shows three prominent dielectric relaxations designated as α, β, and γ in the order of decreasing temperature, in addition to the melting point [10]. The origins of these three different relaxations have been extensively studied in the past, mainly by mechanical and dielectric measurements [11–14]. Major contribution in analysis of the multiple dielectric relaxations are given together with theory for their mechanisms by Ashcraft [13] and (for the case of oxidized and chlorinated PE) by Hoffman [14]. Although some detailed molecular assignments are still open to debate, the reality of the basic relaxation processes is clear; experimental behavior and theoretical explanation of these dielectric relaxation in partially crystalline polymers, such as PE, have been well summarized by Boyd [15–17]. The α- and β-relaxations are commonly attributed to the relaxation mechanisms in the crystalline and amorphous phase [13,14,18], 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 [13,14,19], although originally it was proposed to arise also from the crystalline phase [8,13,14,20].

The β-relaxation, situated in the glass–rubber transition region, is attributed to the amorphous regions because its magnitude increases with decreasing crystalline fraction [13,14,17,21]. Many studies point to the relationship between this relaxation and the amorphous content between the lamellae surfaces [22]. The interlamellar content increases with increasing degree of branching [23], due to which the β-relaxation is more pronounced in branched

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polyethylene, whereas in linear polyethylene it may not occur. Under the special conditions of ultrarapid quenching to produce amorphous samples, it can also be clearly observed in linear polyethylene. Using Raman spectroscopy, the minimum interlamellar content necessary to record the molecular β-relaxation was found to be about 7%, and about 12% to clearly observe it. The amorphous nature of this relaxation was also determined by eliminating crystalline domains at an increased amount of comonomers in the process of copolymerization [24]. The molecular mechanism involved can be fold-surface motion, chain-end motion, branch-point motion and chain rotation in the amorphous region [2,13,14,25]. 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 (T_g) and β-relaxation [26, 27]. For LDPE (branched PE with small crystallinity) there are true amorphous regions, whereas LPE (linear PE with high crystallinity) may only consist of lamellae and severely constrained lamellar boundary regions [9]. Out of this reason LPE would not undergo a glass transition (and β-relaxation) in the same manner the amorphous regions of LDPE do. Changes of T_g with crystallinity (in the case of high crystalline PE) means changes in interlamellar content according to free-volume theory. As the crystallinity increases the free volume, as a whole, decreases and T_g changes as a consequence of increasing degree of strain in the intercrystalline links [14]. It has been also concluded, by Matthews [9], that the β-relaxation is often not observed in linear high crystalline PE because the interlamellar regions are too constrained to allow interlamellar shear without c-shear [9]. Nevertheless, significant differences between the reported activation energies of 60 to 65 kJ mol^{-1} [28, 29] and 200 [13] to 500 kJ mol^{-1} [9] suggest that in the former case the β-relaxation in polyethylene should be treated as a motion in interfacial regions [30], and in the latter as a highly cooperative process such as glass transition.

The effects of orientation and ionizing radiation on the molecular relaxation of polyethylene has been the subject of recent publications [31,32]. In the case of dielectric relaxation measurements, the polar groups that were introduced in apolar polyethylene [33] were considered as tracer groups whose motion reflected the motion of the polymer chains. It has been shown that the uniaxial orientation [21,34] and gamma irradiation change the mobility of the chain segments, leading to a shift in relaxation maxima and changes in activation energies of given relaxations. However, in semicrystalline polymers, such as the low-density polyethylene, the orientation process usually induces changes in the structure of the amorphous phase and lamellae distribution, introducing a preferential orientation of both regions. Dielectric and mechanical measurements performed on different types of polyethylene show clear anisotropy in the case of α-relaxation, but certain anisotropy has also been observed for the β- and γ-relaxations [31,35]. On the other hand, the amount of polar groups and gel fraction increases with increasing absorbed dose, causing modification of the dielectric properties, especially dielectric β-relaxation, with radiation [32]. Reasons for this are found in the fact that the β-relaxation occurs in the amorphous domains, and that the change in the mobility of the chain segments, oxidative degradation and crosslinking occur primarily in this phase [36]. Radiation-induced crosslinking in the amorphous phase restricts the motion of macromolecules, changes their entropy and decreases the activation energy of the molecular β-relaxation [37].

The aim of this work was to study the effects of orientation and ionizing radiation (on the dielectric β-relaxation) in LDPE. The reason for using differential scanning calorimetry (DSC) and gel measurements was to determine the changes in the crystal fraction and degree of network formation, respectively. The process of oxidative degradation was followed by infra-red spectroscopy. Conclusions and results obtained by these three methods are compared with the changes in intensity and position of the dielectric β-relaxation.

A further aim was to point out the changes in activation energy of the dielectric β-relaxation, induced by orientation and ionizing radiation. Therefore, it is also the purpose of this study to provide a better knowledge of the molecular β-relaxation, as well as of dielectric behavior of differently processed polyethylenes, because of their wide engineering application, especially as insulating materials.

2. Experimental

The polymer used for these studies was LDPE Union Carbide: $\rho = 0.922$ g cm^{-3} and $M_w = 110{,}000$. Isotropic sheets of different thickness, wrapped in thin aluminum containers, were obtained by compression molding at 150 °C and 1.75 MPa pressure for 5 min, followed by quenching in cold water. The aluminum container prevents water contact. The samples were drawn in air at 95 °C, using a Wick tensile testing machine, at a constant crosshead speed of 5 mm/min. The drawing times for various samples were varied to obtain draw ratios of 3, 7 and 10. The drawing was stopped after reaching the desired draw ratio λ, and then the samples were cooled to room temperature while being restrained in the grips. Samples were cut from the neck of the samples drawn to different ratios. The drawn and undrawn samples 0.28 ± 0.02 mm thick were wrapped in Al-foil and 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 samples in the form of discs 1.3 cm in diameter and approximately 0.28 mm thick was measured on a Digital LCR Meter 4284A as a function of temperature (25–335 K) with heating of 1.7 K min^{-1}, at several different frequencies ranging from 10^3 to 10^6 Hz. For oriented samples, dielectric measurements were performed in the direction perpendicular to the orientation. The β-relaxation was resolved from the γ-relaxation by curve fitting and its parameters were determined. A Carl-Zeiss Model 75IR Specord was used in recording infra-red spectra for the different LDPE samples. 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 were analyzed by heating from 320 to 430 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 $\chi = \Delta H_\text{f}/\Delta H_\text{f0}$, where ΔH_f0 is the heat of fusion of a perfectly crystalline polyethylene ($\Delta H_\text{f0} = 289\ \text{J g}^{-1}$) [38]. The amount of gel was (followed) determined by solvent extraction in boiling xylene for 48 h and the measurement of the weight loss after drying the samples for 10 h in a vacuum oven at 60 °C. For the same orientation and irradiation dose, measures were repeated three to five times.

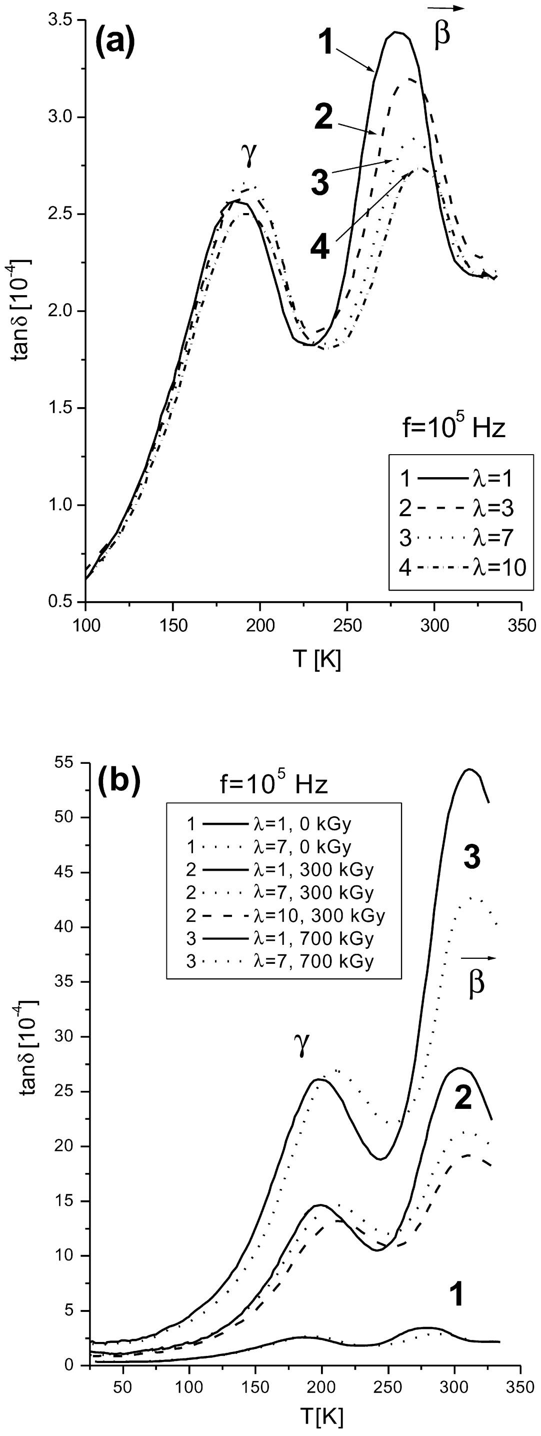

Fig. 1. (a) Dielectric loss tangent versus temperature, at $f = 10^5$ Hz, in the perpendicular direction for various oriented LDPE samples; (b) dielectric loss tangent versus temperature, at $f = 10^5$ Hz, for unoriented ($\lambda = 1$) and oriented ($\lambda = 7$, 10) LDPE samples irradiated to different absorbed doses.

3. Results and discussion

The uniaxial orientation changes the structure of the amorphous phase and lamellae distribution introducing a preferential orientation of both regions, more ordered noncrystalline region, high concentration of extremely strained molecules in the amorphous fraction, decreased mobility of the chain segments and decrease/increase of amorphous/crystalline fraction [39,40]. By comparing dielectric spectra, for unoriented and oriented samples, it can be concluded that the orientation process significantly decreases the relaxation strength of the β-process of LDPE, too (Fig. 1a). The results of dielectric measurements, in the direction perpendicular to the orientation, for samples of various draw ratios, are shown in Fig. 1a. A transition at about 185 K corresponds to the γ-relaxation that occurs below the glass transition temperature. The other peak observed at about 280 K corresponds to the β-relaxation. In contrast to the initial material, in the oriented samples a considerable decrease in the β-relaxation intensity with the degree of orientation is observed. Since the β-relaxation occurs in the amorphous domains, in the glass transition region (the molecular mechanism of the β-relaxation process results from the motion of side branches, as well as of the chain-end motion [13,14,19]), the decrease in the intensity with the orientation is a consequence of an amorphous fraction decrease and a decrease in the number of molecules contributing to this relaxation. On the other hand, in the case of γ-relaxation it is evident that the changes induced by orientation are much lesser than in the case of β-relaxation. Reasons for this behavior are the following: (1) according to different authors [8,13,14,20] this relaxation is attributed not only to the localized (crankshaft-like) motions in the amorphous phase but it also was originally proposed to arise from the crystalline phase, too; (2) because of this reason γ-relaxation is less sensitive in content change of amorphous phase; (3) small changes of γ-relaxation intensity occur as a consequence of

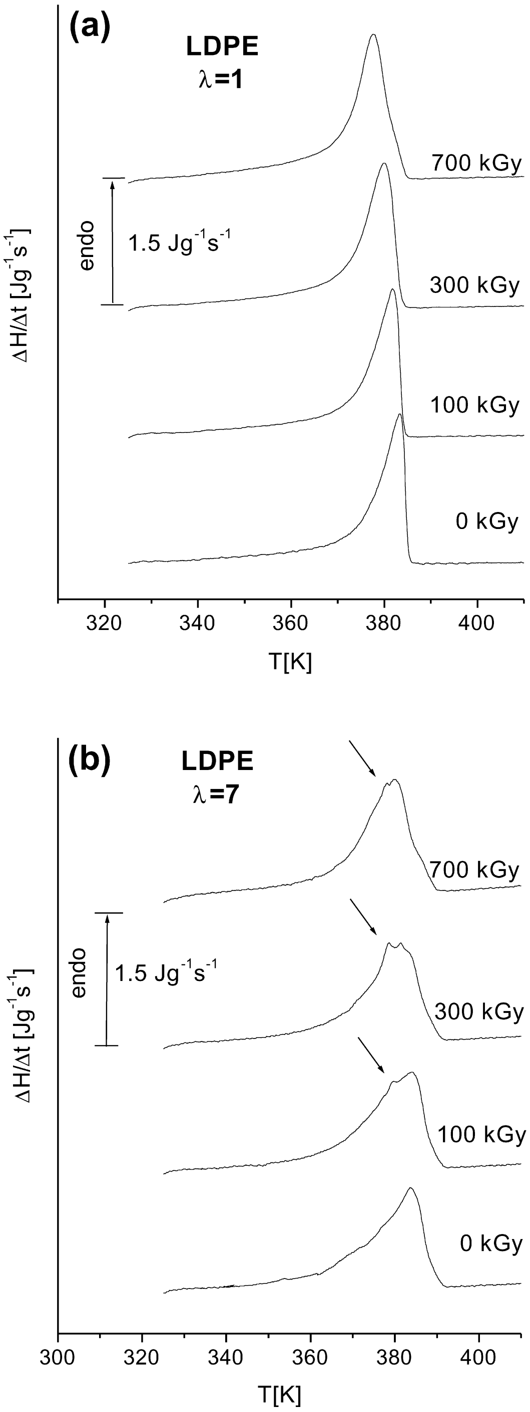

Fig. 2. Melting endotherms of (a) unoriented ($\lambda = 1$) and (b) oriented ($\lambda = 7$) LDPE samples for different absorbed doses.

chain and corresponding polar group redistribution caused by drawing (the consequence of which is a changed number of these groups in the field direction), and also from the altered mobility of segments that contribute to this relaxation. With the decrease in the degree of orientation there is also some shifting of the β-relaxation towards higher temperatures, which is most likely a consequence of reduced mobility of the chain and chain segments.

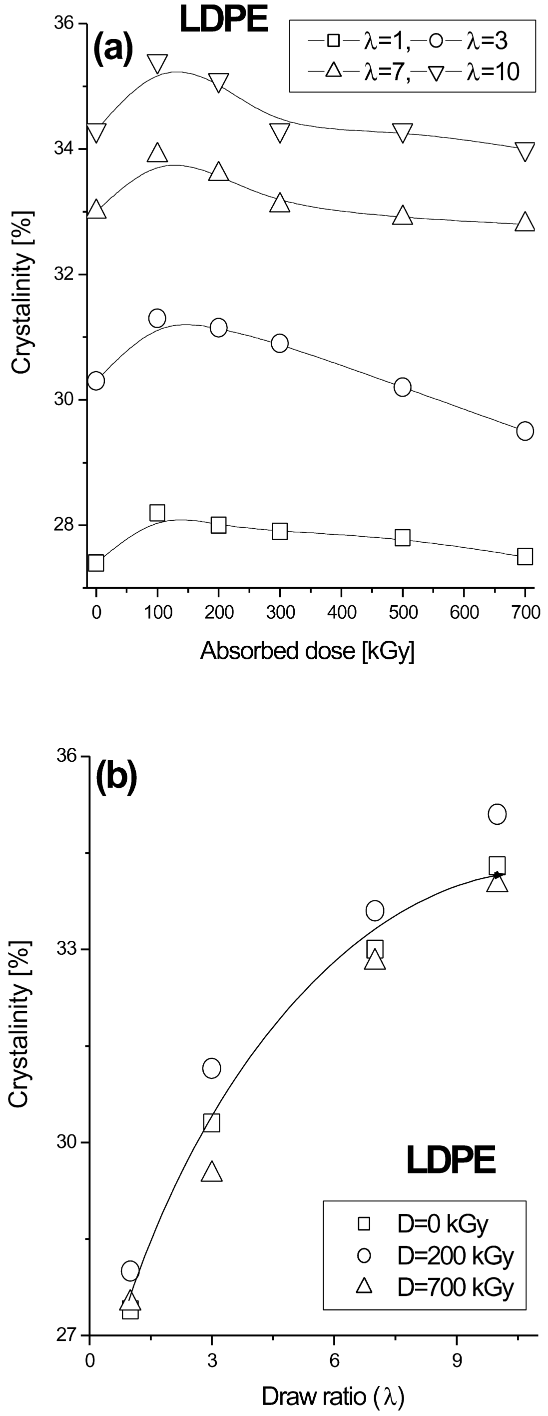

Fig. 3. (a) Crystallinity as a function of absorbed dose for unoriented (□ $\lambda = 1$) and oriented (○ $\lambda = 3$; △ $\lambda = 7$; ▽ $\lambda = 10$) LDPE samples; (b) crystallinity as a function of draw ratio for unirradiated samples (□) and for samples irradiated to different absorbed doses (○ $D = 200$ kGy, △ $D = 700$ kGy).

Two main effects result when polyethylene is subjected to ionizing radiation in the presence of air: crosslinking and oxidation [41]. 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

Table 1
Effects of irradiation dose on heats of fusion ΔH_f, melting temperatures T_m and crystallinity χ of unoriented and oriented LDPE samples

Draw ratio (λ)		Absorbed dose (kGy)					
		0	100	200	300	500	700
$\lambda = 1$	ΔH_f (J g^{-1})	79.2	81.4	81.0	80.5	80.4	79.5
	T_m (K)	382.4	382.7	381.6	380.2	379.1	377.7
	χ (%)	27.4	28.2	28.0	27.9	27.8	27.5
$\lambda = 3$	ΔH_f (J g^{-1})	87.5	90.5	90.0	89.3	87.3	85.6
	T_m (K)	384.2	384.6	382.9	380.4	379.5	378.8
	χ (%)	30.3	31.3	31.15	30.9	30.2	29.5
$\lambda = 7$	ΔH_f (J g^{-1})	95.3	97.8	97.1	95.8	95.2	94.7
	T_m (K)	385.2	386.0	384.3	381.2	380.9	379.8
	χ (%)	33.0	33.9	33.6	33.1	32.9	32.8
$\lambda = 10$	ΔH_f (J g^{-1})	99.2	102.2	101.4	99.6	99.1	98.3
	T_m (K)	386.6	387.1	386.0	384.9	384.3	383.8
	χ (%)	34.3	35.4	35.1	34.5	34.3	34.0

absorbed dose and structural peculiarities [42]. 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 amorphous region. For that reason, both these processes take place mostly in the amorphous region. The radiationally 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 motion of macromolecules, especially in the amorphous phase, causing shifting of the relaxation maxima, increase in the activation energy of molecular and dipolar movement and also molecular relaxation. Fig. 1b depicts the dielectric relaxation of unoriented ($\lambda = 1$) and oriented ($\lambda = 7$) samples irradiated in air to different absorbed dose. By comparing dielectric spectra for unirradiated and irradiated samples of LDPE it can be concluded that the irradiation significantly enhances the dielectric properties of polyethylene. An increase in the dielectric losses with the absorbed dose is noticed, which is a consequence of the radiation-induced formation of polar carbonyl groups in the nonpolar LDPE. The intensity of the β-relaxation decreases with orientation (Fig. 1a and b) for a given absorbed dose, which is related to the nature of this relaxation, decreased susceptibility of oriented samples to radiation-induced oxidation (Fig. 3b), reduced mobility of the chains in the amorphous phase, but also to an increase in the crystalline phase, i.e. crystallinity, in oriented samples (Fig. 2a and b).

Table 1 shows the heats of fusion, melting temperatures and crystallinity which are related to melting endotherms of unoriented (Fig. 2a) and oriented (un)irradiated samples (Fig. 2b). It can be noticed that with increase in the degree of orientation there is a decrease in the crystalline phase, i.e. in the degree of crystallinity, and in the melting temperature, but also that the changes in crystallinity are considerably greater than those caused by radiation (Table 1, Fig. 3a and b) [43]. Since sample orientation has been performed below the melting temperature, there is no possibility of nucleation and crystallization as is in the melt. The increase of crystallinity with draw ratio, to high degrees of sample orientation ($\lambda = 10$), is more than 20%, while it is less than 2% for annealed unoriented samples (for 60 min at 95 °C) under the same conditions. Therefore, the increase in the degree of crystallinity was assumed [44,45] to be a consequence of the flow of the amorphous phase. Using mechanical energy of drawing and increased temperature, macromolecules crystallize on the already existing lamellae. The rise in the melting temperature is a consequence of a better perfection of the crystalline phase after the transition from the spherulitic to the fibrillar structure [46]. With irradiation, independently of the degree of orientation, the melting temperature and crystallinity increase for low radiation doses (up to 100 kGy), and decrease for high doses (200, 300, 500 and 700 kGy) (Fig. 3b). Also, radiation-induced chain scission effects, due to a large number of taut-tie molecules, will indicate formation of new thin lamellae manifested as low temperature peak (marked by an arrow in Fig. 2b) on the melting endotherm of oriented samples. In the case of low radiation doses (up to 100 kGy) breaking of bonding molecules is a more dominant process than crosslinking [47]. It leads to an improved perfection of crystallites due to tension alleviation on the sites of lamellae surfaces where the molecules enter the lattice. Bhataja et al. have assumed that the radiation breaking of macromolecules gives rise to a summational effect; increased perfection of crystals and additional crystallization [48,49]. As a consequence of crosslinking on the lamellae surfaces at higher radiation doses, crystallinity and the melting temperature of the samples decrease. This is due to the fact that for high radiation doses the increase in the surface free energy is much more dominant than the increase in configurational entropy of chains [50].

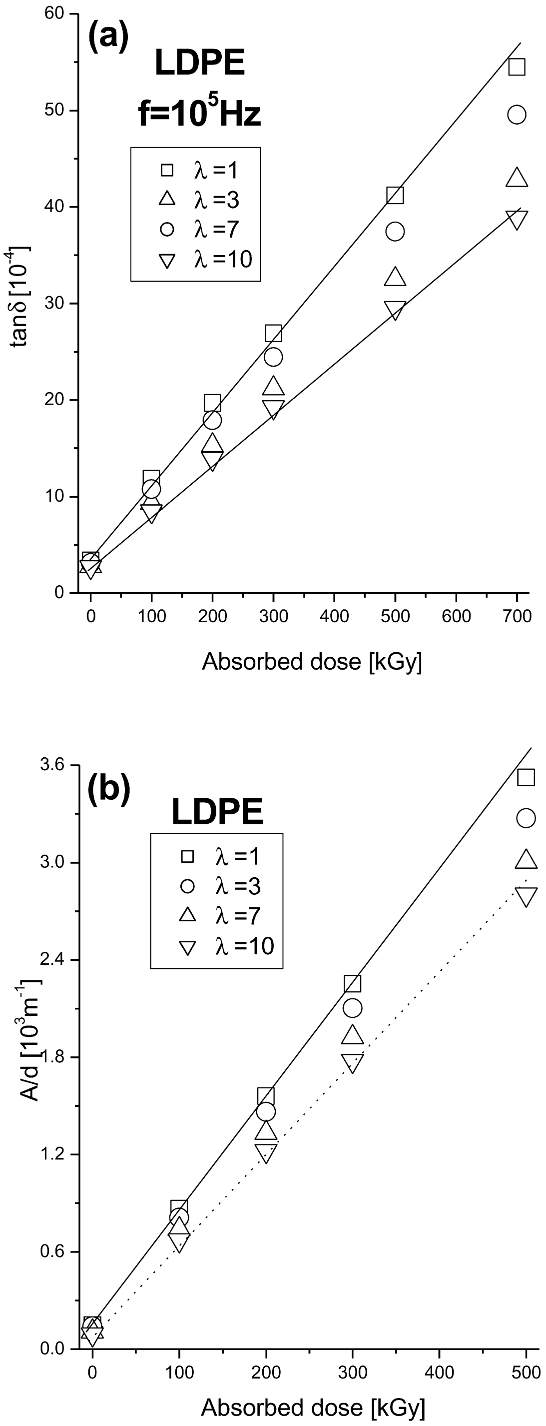

Fig. 4. (a) The maxima of the dielectric loss tangent for β-relaxation peaks (tan $\delta_{\beta\max}$) of LDPE as a function of absorbed dose for various oriented LDPE samples (□ $\lambda = 1$, ○ $\lambda = 3$, △ $\lambda = 7$, ▽ $\lambda = 10$); (b) IR absorbances (A/d values; A = absorbance; d = sample thickness) as a function of absorbed dose for various oriented LDPE samples (□ $\lambda = 1$, ○ $\lambda = 3$, △ $\lambda = 7$, ▽ $\lambda = 10$).

Fig. 4a displays maximum intensities of the dielectric loss tangent of the β-relaxation (tan $\delta_{\beta\max}$) as a function of absorbed dose for the samples oriented to different degrees of orientation and irradiated to different integral radiation doses. On the other hand, analysis of IR spectra indicates a significant growth in the absorption at about 1720 cm^{-1}, with absorbed dose (Fig. 4b). The carbonyl groups are mainly ketone groups at 1718 cm^{-1} and aldehyde groups at 1728 cm^{-1} [51,52] and both are formed in the amorphous region of the polymer [53,54]. Aldehyde-end groups are formed by the decomposition of peroxides and hydroperoxides formed in the polymer, or by a rearrangement of the peroxidic radical intermediate, causing chain scission [55,56]. 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 dependencies of the concentration of carbonyl groups and the intensity of the β-relaxation on the absorbed dose (Fig. 4a and b). A rise in the intensity of the β-relaxation with irradiation corresponds to the increase in the carbonyl content caused by the radiation-induced oxidation, and the correlation between the intensities of the β-relaxation and the carbonyl group concentration appears to be obvious and wholly justified. On the other hand, the absolute carbonyl group concentration values derived from the dielectric spectra are, according to Hedvig [3], much higher than those obtained by IR spectroscopy. The lower evolution of oxidized products in oriented samples (Fig. 4a and b), indicates the greater resistance of this polymeric material to the radiation-induced oxidation [57]. Although the oriented samples contain taut-tie molecules that have increased susceptibility to the chain scission reaction [58], the increased ordering of noncrystalline regions, density and crystallinity due to orientation, probably caused the lower carbonyl content. Confirmation for this can be found in the decrease of the transport properties obtained by measuring permeability of gases through oriented polymeric films. Some authors point to the fact that molecules of different gases are not only excluded from the crystalline regions of the polymer, but also from the more ordered noncrystalline regions [59].

From Figs. 1 and 5a it is evident that orientation/gamma irradiation, besides the effects of decrease/increased intensities of β-relaxation (Fig. 1), cause shifting of the relaxation maxima. According to the site model for mechanical relaxation [60], the variation in the temperature of tan $\delta_{\max}$ depends on the parameter that contains terms relating to the enthalpies and the entropies of chain segments and end groups as well as the number of chain segments involved in the relaxation. Radiation-induced crosslinks in the amorphous phase restrict the motion of polymer molecules, decrease their entropy and cause shifting of the relaxation maxima. Fig. 5b shows that the gel fraction varies with radiation dose for undrawn ($\lambda = 1$) and drawn samples ($\lambda = 3, 7, 10$). With increasing radiation dose there is a significant increase in the gel content of LDPE samples, reaching saturation after 200 kGy (Fig. 5b). This conclusion is also valid for the samples oriented to

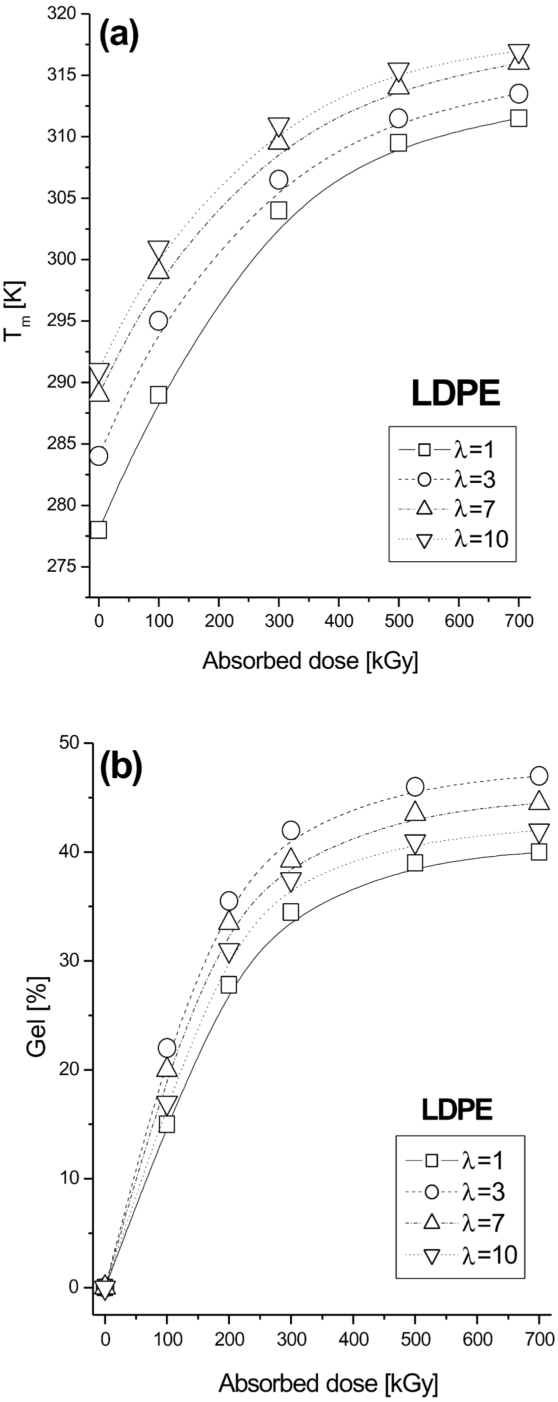

Fig. 5. (a) Temperature of dielectric β-relaxation loss tangent maxima as a function of absorbed dose for various oriented LDPE samples (□ $\lambda = 1$, ○ $\lambda = 3$, △ $\lambda = 7$, ▽ $\lambda = 10$); (b) gel content as a function of radiation dose for unirradiated (□) and oriented (○ $\lambda = 3$; △ $\lambda = 7$; ▽ $\lambda = 10$) LDPE samples.

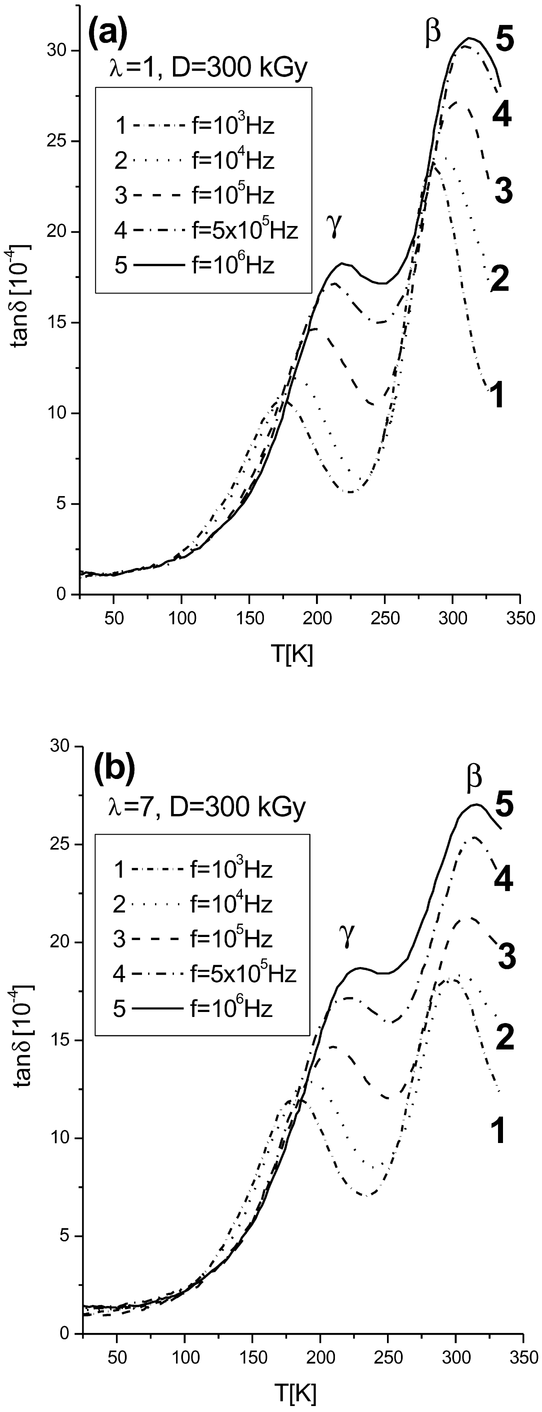

Fig. 6. Dielectric loss tangent versus temperature for (a) unoriented ($\lambda = 1$) and (b) oriented ($\lambda = 7$) LDPE samples, irradiated to the absorbed dose of $D = 300$ kGy, at several frequencies.

different degrees of orientation and is consistent with the results obtained so far for various types of polyethylenes [61,62]. As seen in Fig. 5b, the gel content rises with the degree of orientation to $\lambda = 3$, and then slowly decreases as the degree of orientation continues to increase. These results, in good agreement with Kostoski [43], can be interpreted in terms of structural differences between the unoriented samples and those oriented to different degrees of orientation as well as on the fact that crosslinks may occur only in the amorphous phase. The increase in the gel content with orientation is most likely a consequence of a smaller amount of oxygen present and a higher concentration of taut-tie molecules. These molecules are much more susceptible to breakage, due to which the number of free radicals, i.e. crosslinks, increases. However, as the greatest concentration of alkyl radicals is on the lamellae surfaces [63,64], the gel content is greatly influenced by interlamellar contact, too [65,66]. Disturbance in interlamellar contacts caused by orientation is sufficient reason for the occurrence of the gel content reduction. The gel content reduction may also occur due to increase/decrease of the crystalline/amorphous phase in the process of orientation (Fig. 3a). Since the crosslinking processes occur only in the amorphous phase, it is clear that its reduction may affect the gel content. It should also be emphasized that in the earlier studies it has been noticed that for high degrees of orientation the gel content much decreases below the values of unoriented samples. This is the consequence of reduced chain mobility in a strongly oriented structure, due to which the reaction of the obtained radicals with the neighboring molecules is reduced. However, crosslinking causes the shifting of relaxation towards higher temperatures, with the absorbed dose. In the case of LDPE, this effect is much more pronounced for the β than for the α and γ-relaxations, for the same gel content. This is a consequence of the fact that crosslinking gives rise to much greater restrictions in the motion of the side branches and side branch-points than in the case of the local three-bond crankshaft-like motion and the motions occurring in the crystalline phase, which are related to the α-relaxation.

The complete isochronal loss scans for unoriented (Fig. 6a) and oriented (Fig. 6b) irradiated samples ($D = 300$ kGy), at several frequencies, is represented in Fig. 6. In accordance with earlier investigations [37] the results obtained show a slight increase in dielectric loss tangent and shift of tan δ_{max} (for β-relaxation) 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 temperature of γ-relaxation increases with the test frequency much more rapidly (suggesting that the γ-relaxation has a low activation energy compared with the β-relaxation). The more intensive shift of γ-relaxation, towards higher temperatures with frequency increase, will have for a consequence a larger peak overlap of these two relaxations, whereby their intensities will apparently rise. Besides, in the case of γ-relaxation, rise in intensity is not just a consequence of overlap but partially for reasons discussed by Ashcraft [13]. Objective values for the temperatures of the relaxation peaks were obtained using curve fitting. The process is complicated at higher frequencies and for highly oriented samples, 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 γ- and β-peak. In Fig. 6 are shown log f_{max} versus $1000/T$ map for some oriented (Fig. 7a) and gamma-irradiated oriented samples (Fig. 7b). The dielectric β-relaxation for the initial sample of LDPE has a high activation energy of about 185 kJ mol^{-1}, which is in conformity with other authors [67]. The activation energy is consistent with the β-relaxation being associated with the glass transition of the amorphous portion in the polyethylene [9,13].

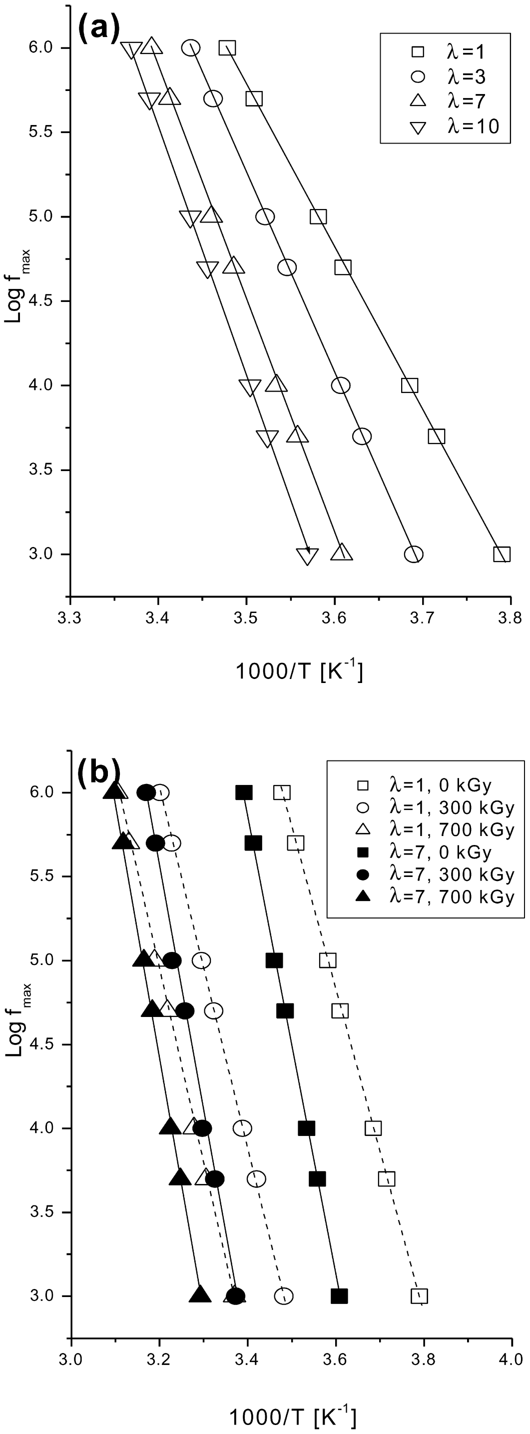

Fig. 7. Isochronal log f_{max} versus $1000/T$ map for (a) unoriented (□ $\lambda = 1$) and oriented (○ $\lambda = 3$; △ $\lambda = 7$; ▽ $\lambda = 10$) LDPE samples; (b) unoriented ($\lambda = 1$) and oriented ($\lambda = 7$) LDPE samples irradiated to different absorbed doses (□ $\lambda = 1$ $D = 0$ kGy; ○ $\lambda = 1$ $D = 300$ kGy; △ $\lambda = 1$ $D = 700$ × kGy; ■ $\lambda = 7$ $D = 0$ kGy; • $\lambda = 7$ $D = 300$ kGy; ▲ $\lambda = 1$ $D = 700$ kGy).

Changes in the activation energy of the β-relaxation with

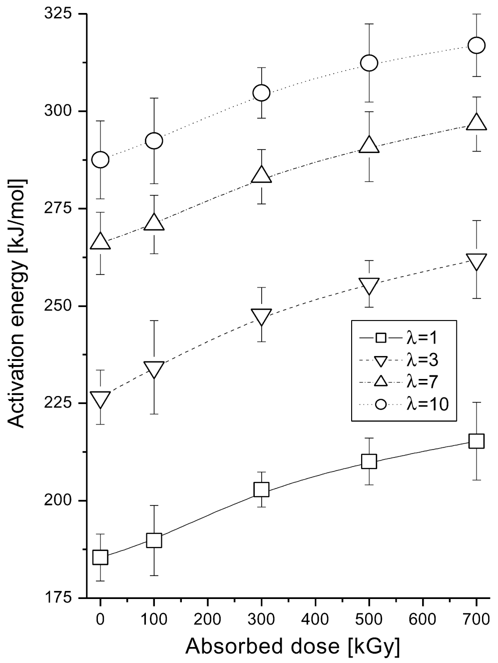

Fig. 8. Activation energy for dielectric β-relaxation as a function of absorbed dose for various oriented LDPE samples (□ $\lambda = 1$; ▽ $\lambda = 3$; △ $\lambda = 7$; ○ $\lambda = 10$).

orientation and absorbed dose are represented in Fig. 8. It can be observed that, with orientation and irradiation, activation energy of the β-relaxation increases, and also that this increase is much more pronounced with orientation. This suggests that the decrease with orientation in the mobility of the chain and chain segments participating in the β-relaxation is more intense than that caused by radiation-induced crosslinking. Uniaxial orientation introduces a preferential orientation, increasing ordering of noncrystalline regions and changing the mobility of the chain segments, which leads to shifting of the relaxation maxima (Figs. 1a and 5a) and to increasing activation energy of the dielectric β-relaxation (Fig. 8). Examination of the activation energy of the β-relaxation in oriented samples confirms that this relaxation has a higher activation energy that is consistent with the activating process being associated with a highly cooperative process, such as the glass transition. A considerable increase in activation energy of the β-relaxation with orientation, as well as its relation to the glass transition, has also been observed in the dynamical-mechanical measurements by Ward [9,31].

Crosslinking produces a net structure in the material, which inhibits the motion of polymer chain and dipolar groups attached to the polymer chain, thus increases the activation energy for molecular movement. The degree of crosslinking and shifting of the β-relaxation towards higher temperatures (Fig. 5b and a), as well as the changes in the activation energy will also be dose dependent (Figs. 8 and 5b). The observed increase in activation energy of the β-relaxation for LDPE with orientation and radiation-induced crosslinking is much more pronounced than in the γ-relaxation. The calculated values of activation for the dielectric γ-relaxation were between 48 and 54 kJ/mol for all degrees of orientation and 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 three-bond crankshaft-like motion.

4. Conclusion

The β-relaxation, in semicrystalline polymer such as polyethylene, is closely connected with structure and very sensitive for changes in amorphous phase (degree of branching, ordering of amorphous regions, glass transition and free volume, crosslinking, oxidative degradation, microbrownian motion of segments, tension of tie chains, etc.), crystalline phase content and molecular weight distribution.

Presented results show that changes with orientation and irradiation, as well as both together, significantly affect the dielectric β-relaxation behavior of LDPE. The mobility of the chain segments changes because of the effects of orientation and gamma irradiation, oxidized regions are redistributed and the amount of polar groups is increased by radiation oxidative degradation, causing the dielectric β-relaxation of LDPE to be modified. Changes in the intensity (of the dielectric β-relaxation) with orientation and gamma irradiation are mainly related with oxidation, but also with increasing/decreasing of the crystal fraction and the mobility of the chain segments in the amorphous region. On the other hand, changes in the position and activation energy of the β-relaxation are mainly related to the changed chain mobility induced by orientation and crosslinking.

The orientation of LDPE has considerably increased activation energies of the dielectric β-relaxation. Because of crosslinking and net structure, in the case of gamma irradiation, an increase in the activation energy, for molecular and dipolar movement in glass transition region, also occurs.

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