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Polymer 40 (1999) 2631–2637

polymer

Influence of orientation and irradiation on stress relaxation of linear low-density polyethylene (LLDPE): a two-process model

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Received 2 March 1998; revised 27 May 1998; accepted 16 June 1998

Abstract

Change in the stress relaxation behavior of linear low-density polyethylene (LLDPE) with drawing and irradiation has been investigated. Samples of isotropic LLDPE were oriented to draw ratios $\lambda = 6,9,11$ and irradiated to integral doses between 35 and 500 kGy. Stress relaxation was interpreted in terms of a two-process model, first associated with the crystal and second with the amorphous fraction. Analyses of viscoelastic properties of these two fractions have revealed their different behavior upon drawing and irradiation. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Viscoelastic; Amorphous fraction; Crystal fraction

1. Introduction

Oriented polyethylene fiber and sheets produced by different techniques possess favorable properties, such as high Young moduli, toughness, strength, chemical resistance, etc. [1,2]. On the other hand, during orientation, considerable structural changes in a polyethylene sample occur, e.g. transformation from the spherulitic into the fiber structure [3]. This transformation leads to different viscoelastic properties of polyethylene with respect to the initial material [4,5]. Treatment of polyethylene with high energy radiation also induces changes in viscoelastic behavior [5–11], as a consequence of crosslinking and main-chain scission in the polyethylene sample during irradiation.

Stress relaxation associated with creep is one of the basic methods for investigations of viscoelastic properties of polymers. Bhataya and Andrews [10] have used stress relaxation in order to investigate changes in mechanical behavior with irradiation of unoriented ultra-high-molecular-weight polyethylene (UHMWPE). They have shown that residual stress (after 48 h) increases with increasing irradiation dose, providing better mechanical properties of UHMWPE. In our previous paper [11] we obtained a similar trend for oriented and unoriented linear low-density polyethylene (LLDPE). Boiko and co-workers [12,13] have shown, using the time–temperature superposition principle, that an increase in draw ratio (λ) increases the relative intensity of stress relaxation.

Besides the basic Maxwellian, there are two theoretical models that interpret the stress relaxation in polymers. One of them, the spectral theory (the theory of relaxation times), describes the decaying stress as

$$\sigma(t) = \varepsilon_0 \int H(\tau) \exp\left(- \frac{t}{\tau} \right) \mathrm{d}(\ln(\tau))$$

where ε_0 is the constant strain and $H(\tau)$ the distribution of relaxation times τ [14]. $H(\tau)$ is usually taken as a box-shape. The other one (cooperative model) interprets the stress relaxation as a two-level system where stimulated emissions of phonons may occur. The ‘phonons’, in fact, are clusters of varying size that can be assumed to obey Bose–Einstein statistics [15,16].

In this paper we interpret the influence of drawing and irradiation on stress relaxation in terms of a two-process model. Polyethylene is a semicrystalline material and it can be reasonably assumed that application of stress produces different reactions in amorphous and crystalline fractions. Bearing that in mind, we separated the influence of those two fractions using stress relaxation as the superposition of the two activated processes acting in parallel, similar to the method proposed by Wilding and Ward [17] for high-density polyethylene (HDPE). The results obtained are also in agreement with previous papers [4,5,7,17], where the two-process model has been used in order to interpret the tensile creep behavior of highly drawn polyethylene fibers.

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PII: S0032-3861(98)00510-2

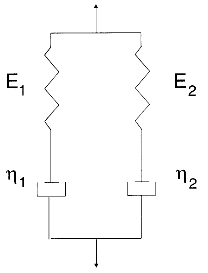

Fig. 1. Maxwell–Wiechert model.

2. The two-process model

Stress relaxation is described in terms of a model that consists of a combination of two dissipative viscous elements (dashpots) and two elastic elements (springs), connected as in Fig. 1. Thus, the two-process model is a continuum–mechanical model. The molecular structure of the crystalline and amorphous fractions is not considered or taken into account. This multielement combination is called the Maxwell–Wiechert model [14]. In an approximation of linear viscoelastic behavior each Maxwell element will show the response of one fraction (crystalline or amorphous) when the loading is applied to the sample.

The differential equation for this system is

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}t^2}+\frac{\dfrac{\eta_1}{E_1}+\dfrac{\eta_2}{E_2}}{\dfrac{\eta_1\eta_2}{E_1E_2}}\frac{\mathrm{d}\sigma}{\mathrm{d}t}+\frac{E_1E_2}{\eta_1\eta_2}\sigma = (E_1+E_2)\frac{\mathrm{d}^{\varepsilon}\varepsilon}{\mathrm{d}t^2}+\frac{\eta_1+\eta_2}{\eta_1\eta_2}E_1E_2\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} \qquad (1)$$

where η_1, η_2 and E_1, E_2 are coefficients of viscosity and elasticity respectively, σ is the applied stress and ε is the strain. Assuming strain as an impulse described by $\varepsilon(t) = \varepsilon\delta(t)$, where $\delta(t)$ represents the Dirac function, the following solution of Eq. (1) is obtained [14]

$$\sigma(t) = \varepsilon E_1 \exp\left(-\frac{E_1}{\eta_1}t\right) + \varepsilon E_2 \exp\left(-\frac{E_2}{\eta_2}t\right) \qquad (2)$$

by using the Green function method.

Polymer molecules, of course, are not ideal springs and it can be reasonably assumed that cold flow increases with prolonged times until total permanent deformation. Also, multiple stress relaxation measurements on the same specimen have revealed the existence of structural changes [18]. That is the reason why we introduced the time dependence of characteristic coefficients η_1 and η_2, given by

$$\eta_1 = \eta_1^0(1+t) \qquad (3a)$$

$$\eta_2 = \eta_2^0(1+t) \qquad (3b)$$

where η_1^0 and η_2^0 are the values of the viscosity coefficients at $t = 0$. In the first approximation it is assumed that the responses of crystalline and amorphous fractions are independent and solutions for each Maxwellian element were found. The modified differential equation for one Maxwell element is given by

$$\frac{\mathrm{d}\sigma_1}{\mathrm{d}t}+\frac{1}{1+t}\frac{E_1^0}{\eta_1^0}\sigma_1 = 0 \qquad (4)$$

where $\mathrm{d}\varepsilon/\mathrm{d}t = 0$ due to $\varepsilon = \text{const}$. Using boundary condition $\sigma = \sigma^0$ at $t = 0$, the following solution of Eq. (4) is obtained

$$\sigma_1(t) = \sigma_1^0(1+t)^{-E_1^0/\eta_1^0} \qquad (5)$$

and similarly for $\sigma_2(t)$. The response of the whole system is now given as a linear combination of $\sigma_1(t)$ and $\sigma_2(t)$

$$\sigma(t) = \sigma_1(t)+\sigma_2(t) = \sigma_1^0(1+t)^{-E_1^0/\eta_1^0}+\sigma_2^0(1+t)^{-E_2^0/\eta_2^0} \qquad (6)$$

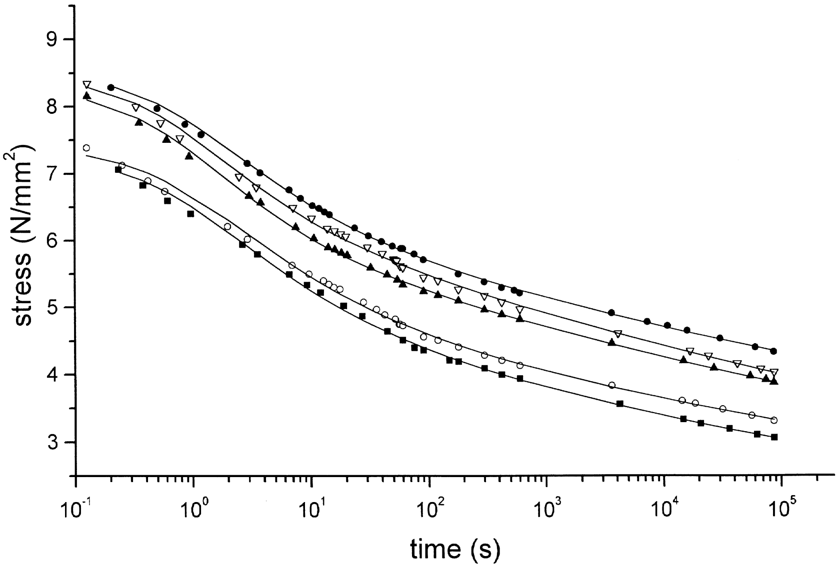

Fig. 2. Stress versus log time for oriented (λ = 1) samples, unirradiated (■) and irradiated with 35 (○), 100 (▲), 300 (▽) and 500 (●) kGy in air. Solid line is fit to Eq. (6).

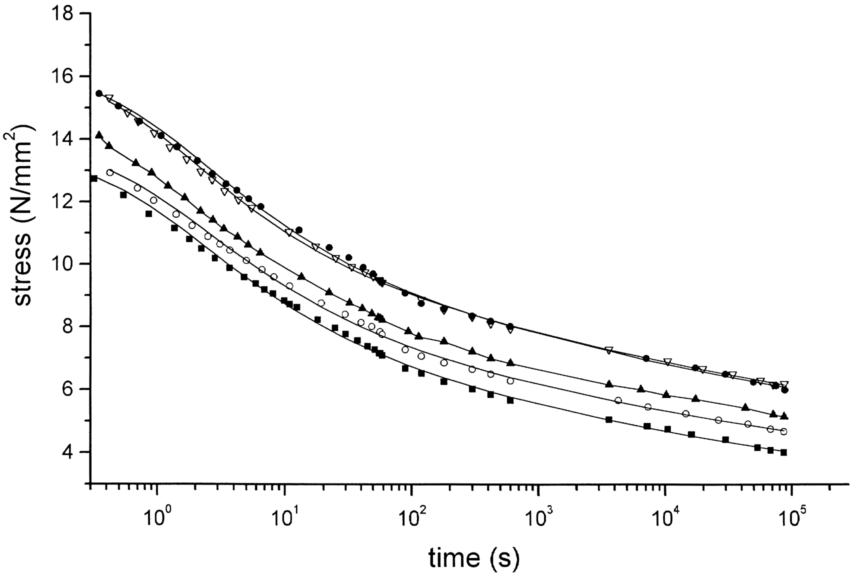

Fig. 3. Stress versus log time for oriented (λ = 6) samples, unirradiated (■) and irradiated with 35 (○), 100 (▲), 300 (▽) and 500 (●) kGy in air. Solid line is fit to Eq. (6).

When t tends to zero, Eq. (6) equals Eq. (2) because $(1+t)e^{t}$ and σ_1^0, σ_2^0 are then equal to εE_1^0 and εE_2^0 respectively.

3. Experimental

Isotropic sheets of LLDPE (Union Carbide, $M_w = 110\,000$ and $\rho = 0.92$ g cm^{-3}) were prepared by compression molding at 150°C and 1.75 MPa for 5 min, followed by quenching into water at 20°C. Samples (55 × 18 × 2 mm) were kept in air for 60 min at 100°C and then oriented at the same temperature. The drawing was carried out using a Zwick tensile machine at a rate of 5 mm min^{-1}. After reaching the desired draw ratio (λ = 6,9,11), drawing was stopped and the sample was cooled down to room temperature while still being loaded. Samples varying in thickness from 0.7 to 1.2 mm were cut in the neck and irradiated together with the unoriented sample at room temperature in the air using a ^{60}Co γ-source. Absorbed doses of 0, 35, 100, 300 and 500 kGy were employed, the dose rate was 8 kGy h^{-1}.

For the stress relaxation measurement, samples were preconditioned for 2 h at 23°C and then loaded to 4% strain at a rate of 200 mm min^{-1}. Decaying of stress was monitored over a period of 24 h.

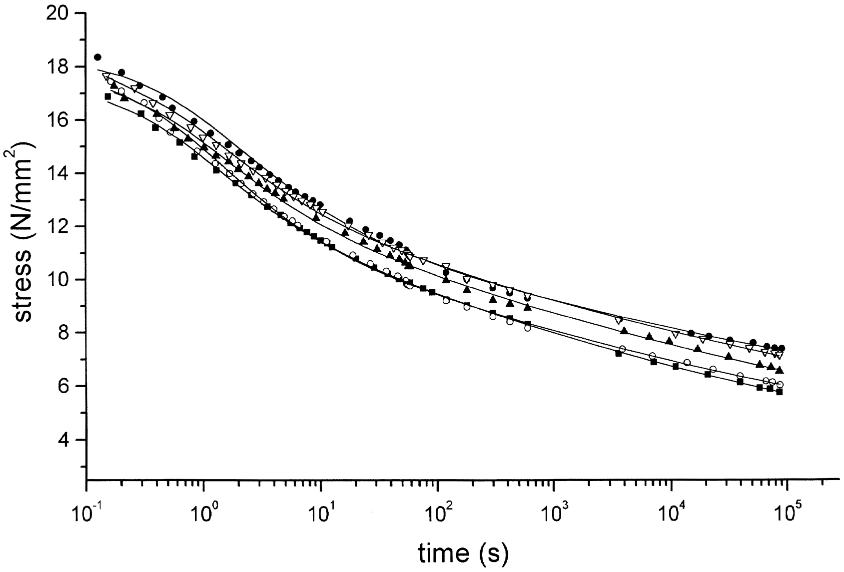

Fig. 4. Stress versus log time for oriented (λ = 9) samples, unirradiated (■) and irradiated with 35 (○), 100 (▲), 300 (▽) and 500 (●) kGy in air. Solid line is fit to Eq. (6).

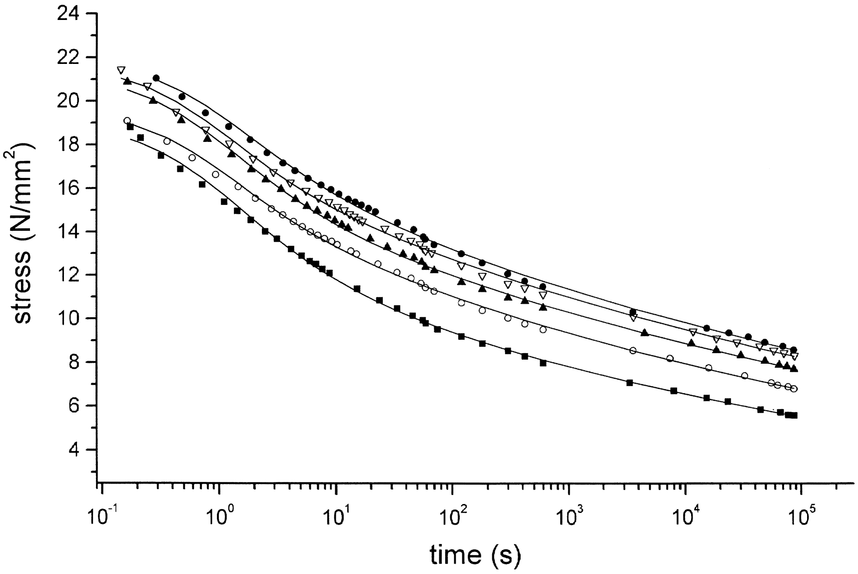

Fig. 5. Stress versus log time for oriented (λ = 11) samples, unirradiated (■) and irradiated with 35 (○), 100 (▲), 300 (▽) and 500 (●) kGy in air. Solid line is fit to Eq. (6).

4. Results and discussion

Stress relaxation data of unoriented (λ = 1) and oriented samples (λ = 6,9,11) of LLDPE for various irradiation doses are shown in Figs 2–5. Stress decays with time, showing two trends, exponential and a power-law [15]. In the beginning, decaying is very fast, but gradually slows down with time. One of the possible explanations for such behavior is associated with the *c*-axis slip in crystal lamellae of a loaded specimen [10]. Namely, during fast loading, short and taut tie molecules in the specimen are pulled out from crystal lamellae because they impose large local stresses. After that, due to the increase in distance between the lamellae, stress is distributed on a larger number of stretched tie molecules and passes into a slow decay.

It has already been shown that stress relaxation is highly influenced by drawing and irradiation [10–13]. In our previous paper [11] we found that decrease of stress is much higher in unoriented than in the oriented samples. Higher values of stress changes obtained by orientation show a decrease in viscoelastic properties. This corresponds to a higher level of creep in oriented samples [4,5]. From Figs 2–5 it can be seen that for all samples the initial stress as well as the residual stress increases with increasing irradiation dose. Thus, the increase in the residual stress due to irradiation exhibits an improvement in the mechanical properties of polyethylene.

In order to investigate the influence of drawing and irradiation on the viscoelastic properties of crystal and amorphous fractions, experimental data were fitted to

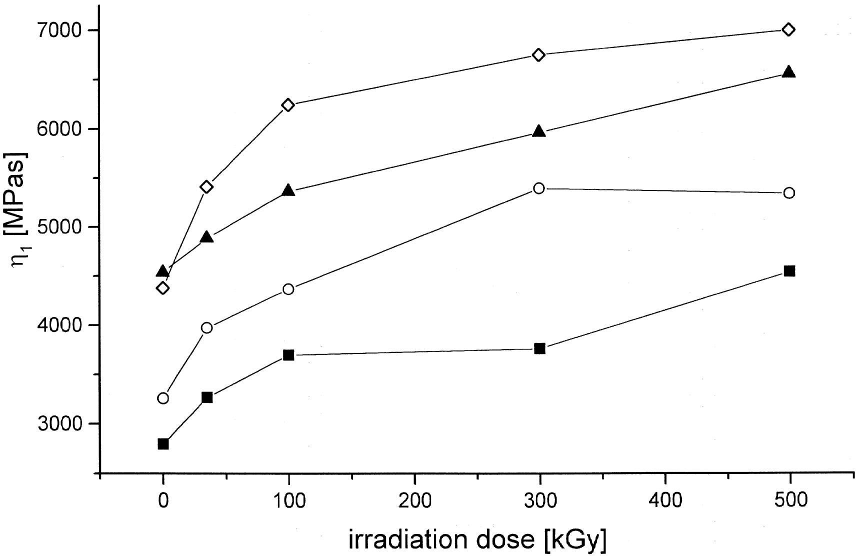

Fig. 6. Coefficient of viscosity η_1 versus irradiation dose, for unoriented λ = 1 (■) and oriented λ = 6 (○), λ = 9 (▲) and λ = 11 (◇) LLDPE samples.

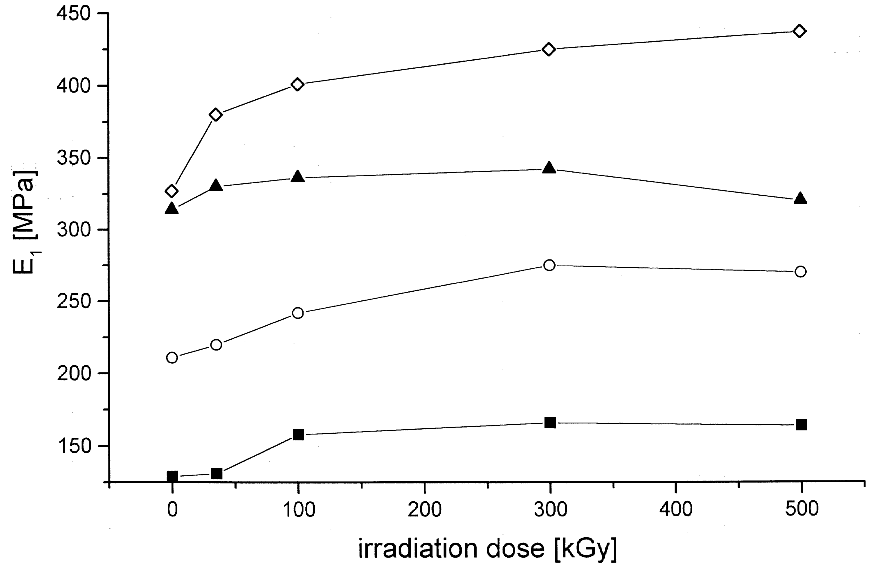

Fig. 7. Modulus E_1 versus irradiation dose, for unoriented λ = 1 (■) and oriented λ = 6 (○), λ = 9 (▲) and λ = 11 (◇) LLDPE samples.

Eq. (6). In the fitting procedure the Hook–Jewes non-linear estimation method was used and the fit is given as a solid line in Figs 2–5. Standard deviations for all the fits were between 0.001 and 0.004, which shows good agreement between experimental curves and Eq. (6). Variation of four parameters, σ_1^0, σ_2^0, E_1^0/η_1^0 and E_2^0/η_2^0 allows estimation of viscosities η_1^0, η_2^0 and moduli E_1^0, E_2^0 of crystal and amorphous fractions. Viscosities and moduli for various λ were plotted versus irradiation dose (Figs 6–9).

Coefficients η_1^0, η_2^0 were analyzed in terms of the Doolittle equation given by [19]

$$\ln \eta = \ln A + B\frac{v^*}{v} \tag{7}$$

where A and B are constants characteristic of the given material, v^* is the hard core (incompressible) volume and v is the free volume. From Figs 6, and 8 it can be seen that the coefficient of viscosity η_1^0 (from now on η_1), which is related to process 1, has a value one order of magnitude larger than η_2^0 (η_2), for one specific irradiation dose and one specific λ. Since Eq. (7) predicts inverse dependence between η and v, process 1 is characterized by a relatively small free volume and corresponds to the crystal fraction. Process 2 is characterized by a high activation volume and it can be associated with the amorphous fraction. This is in agreement with results of the two-process model for creep [4,5,7,17].

4.1. Influence of drawing

Fig. 6 shows an increase in crystal viscosity η_1 and consequent decreasing of the free volume v_1 as λ increases. The

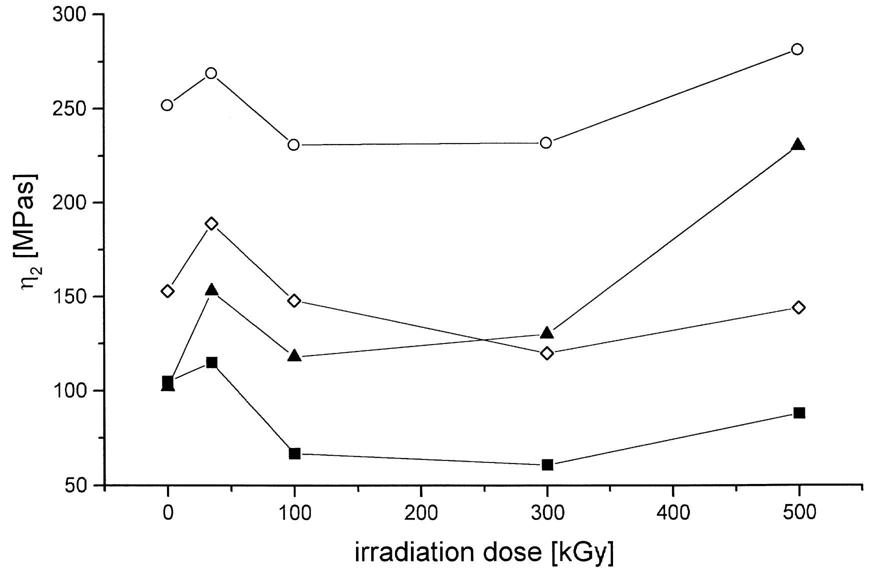

Fig. 8. Coefficient of viscosity η_2 versus irradiation dose, for unoriented λ = 1 (■) and oriented λ = 6 (○), λ = 9 (▲) and λ = 11 (◇) LLDPE samples.

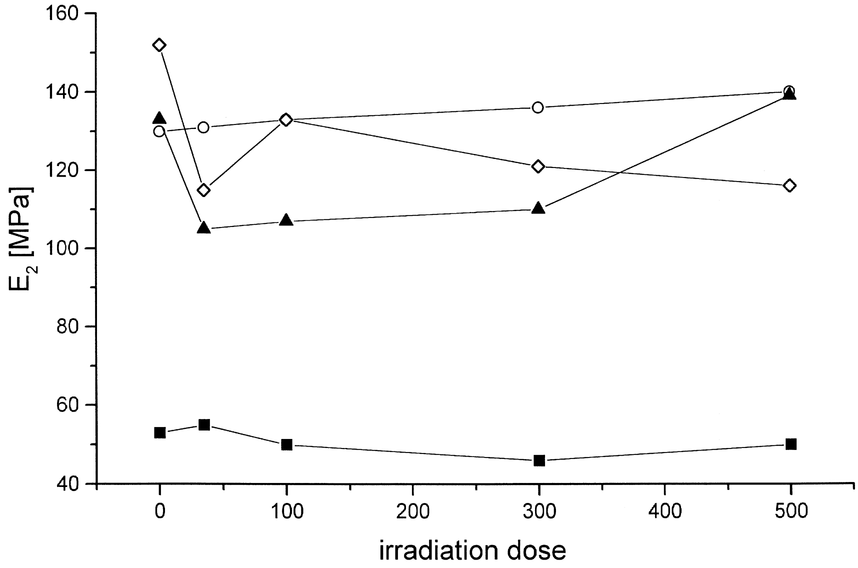

Fig. 9. Modulus E_2 versus irradiation dose, for unoriented $\lambda = 1$ (■) and oriented $\lambda = 6$ (○), $\lambda = 9$ (▲) and $\lambda = 11$ (◇) LLDPE samples.

process occurring in the crystal is a consequence of an intermolecular shear due to propagation of defects through the lattice [4,5,7,17] and corresponds to the assumption of the *c*-axis slip [10]. Thus, decreasing of v_1 as λ increases shows a better perfection and alignment of lamellae structure, which is in agreement with a previous paper [8]. Crystal moduli E_1^0 (from now on E_1) are larger for a higher draw ratio due to increasing of crystallinity with orientation [11] (Fig. 7).

The uniaxial drawing of isotropic polyethylene produces a fibrous material with a high concentration of taut tie molecules in amorphous regions connecting the lamellae they are anchored in [20]. The concentration of taut tie molecules increases with orientation, leading to larger values of modulus E_2^0 (E_2) along the draw direction (Fig. 8). However, highly stretched tie molecules show a reduced conformational mobility. Thus, in oriented samples loading produces an increase in mutual slippage of tie molecules, hence an increase in viscosity η_2 (Fig. 9). The coefficient η_2, obviously a non-linear function of the draw ratio, has the largest value for $\lambda = 6$ because transformations from the spherulitic into the fiber structure are not complete. Such a structure is less stable on loading, therefore the effect of the cold flow is more pronounced. In our previous study [11] we found that the residual stress, for relaxation curves normalized with respect to the initial stress, exhibited the same dependence versus draw ratio as η_2. Since the residual stress shows the extent of permanent deformation (which is a consequence of the cold flow) it can be concluded that process 2 becomes dominant in a power-law region.

4.2. Influence of irradiation

Irradiation leads to the higher viscosity coefficients η_1 of crystal fraction for one specific λ (Fig. 6). An increase in η_1 for low doses (less than 200 kGy) can be attributed to the increase in crystallinity due to the effects of chain scission [21–23]. Broken tie molecules are then incorporated into the crystal lamellae [22]. This effect induces better perfection of crystalline regions and consequent decreasing of free volume v_1. At higher doses (300 and 500 kGy) crosslinking takes place in the amorphous fraction and on the surface of lamellae [24,25]. Crystallinity slightly decreases also [11], due to the high concentration of defects in the lattice. In spite of the large number of defects, η_1 slowly increases because the crosslinked network makes a larger contribution to the stress relaxation. Andrews [26] has shown that irradiation of single crystals of polyethylene suppresses the *c*-axis slip. Thus, the amorphous network on the lamellae surface inhibits intermolecular shear and larger values of η_1 are obtained. The crystal modulus E_1 also increases for low doses (35 and 100 kGy) due to the increase in crystallinity (Fig. 7). E_1 is only slightly changed at high doses because crystallinity reaches a maximum at 200 kGy and after that begins to decrease, as has already been mentioned [11,21–23].

Fig. 8 shows an apparent jump in η_2 for the 35 kGy dose as the consequence of scission effects which for low doses override the effects of crosslinking. Due to the effects of chain scission, the amorphous fraction becomes less stable on loading and gives rise in the cold flow. Thus, overall, η_2 increases although the chain mobility is higher than in the unirradiated sample. At 100 kGy crosslinking begins [11], the network suppresses the cold flow and η_2 drops below the value for the pure sample. After that, η_2 slightly decreases (300 kGy) due to a high gel content [11] and then again increases because of degradation of the network at a higher dose (500 kGy). The coefficient of elasticity of the amorphous fraction E_2 versus the irradiation dose shows different behavior for unoriented ($\lambda = 1$) and lower oriented ($\lambda = 6$) samples compared to those highly oriented (λ = 9,11). For λ = 1 and λ = 6 modulus E_2 changes slowly with increasing irradiation dose due to high conformational mobility of the chains. Since for λ = 9 and λ = 11 the samples have a high concentration of taut tie molecules, scission in those samples is more pronounced and elasticity of the amorphous fraction decreases with irradiation. Unfortunately, some scattering in experimental data for λ = 9 made it impossible for us to state the dependence of E_2 on the irradiation dose.

It should be noted that the coefficients E_1 and E_2 are smaller than those obtained from X-ray measurements [27,28]. The main reason for these low values is incapability of the structure to adjust because of a very high rate of loading (20 cm min^{-1}). This corresponds to extremely small values for E' that are obtained by using high stress amplitudes in dynamical measurements [29]. The other reason is the difference between the theoretical and the actual stress (obtained in measurements) due to the influence of stress concentration [30]. It has been shown that the theoretical strength of polymers σ_{th} depends on the maximum strength σ_{m} as

$$\sigma_{\mathrm{th}} = q\sigma_{\mathrm{m}} \tag{8}$$

where $q = v/v_{\mathrm{d}}$ is the stress concentration factor. Factor q is a measure of changing the activation volume without considering stress concentration v_{d} and actual activation volume and shows the influence of thermal fluctuations [30]. Applying a similar method to our σ_1^0 parameter, using $q = 470$ for polyethylene [30], led us to values between 60 and 260 GPa for E_1, close to the value of 255 GPa obtained by Clements et al. [28]. Despite the low values we obtained in these estimations, the functional dependence of the characteristic coefficients with respect to the draw ratio and irradiation shows exactly the behavior that could be expected on the basis of phenomenological discussions.

5. Conclusion

Stress relaxation behavior of drawn and irradiated LLDPE can be described well by an established two-process model. In this model the first process is characterized by a relatively small free volume and corresponds to the polymer crystal fraction. The second process, characterized by a high free volume, corresponds to the amorphous fraction. Estimations of coefficients of viscosities η_1, η_2 and moduli E_1, E_2 of these two fractions showed that their behavior depends on the draw ratio following the main changes induced by orientation, tautening of tie molecules and increase in crystallinity. Coefficients and moduli also showed the influence of crosslinking and main-chain scission effects, which are the consequence of irradiation, on viscoelastic properties.

The present model does not give such a good picture of the origin of flow processes as the cooperative model [15,16]. However, this approach gives a very good insight into the nature of changes in the crystal and amorphous fractions with drawing and irradiation.

Acknowledgements

The authors wish to thank M. Tomašević for helpful discussions.

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