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Relaxation Behavior of Polyethylene Oriented by Various Techniques

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Stress relaxation of high-density polyethylene extrudates and those crystallized from highly deformed melt (PE-1) have been investigated in a wide range of temperatures (-50 to $+120^{\circ}\text{C}$) and draw ratios from 5.5 up to 12.2 at the different constant tensile strains from 1 up to 20%. The experimental data obtained have been summarized by the time-temperature superposition principle. Relative intensity of stress relaxation (the stress drop in 10^3 s divided by the initial stress) has been observed to increase together with the growth of draw ratio despite the enhancement of the short-term properties. The radiation cross-linking of the PE-1 samples may only decrease the stress relaxation intensity by 30%. The relaxation properties of a number of oriented polyethylene samples produced by various techniques were compared. It has been established that all the investigated materials are characterized by similar values and high relative drops in stress, whereas the short-term properties are essentially different. It points out to the relaxation processes being intensive both in the oriented and unoriented PE.

KEY WORDS Polyethylene, orientation, stress relaxation.

INTRODUCTION

Over the last few years many different methods for producing flexible polymer films, fibers and articles with enhanced mechanical properties have been developed.^{1–10} Some of them are a modification of conventional drawing widely used in industry.^{1,3,4,6,7} Others are a combination of a drawing technique with various methods of induced crystallization.^{2,5,8–10} In all cases polymers with a high degree of molecular orientation are obtained. They demonstrate high short-time mechanical characteristics in orientation direction when high draw ratios λ are achieved. Essential dependence of mechanical properties versus the strain rate is noted for some oriented materials,^{11,12} in particular, for high-density polyethylene (HDPE) crystallized from highly deformed melt.¹¹ This testifies to the resistance effectiveness of these materials under fast loading on the one hand and points out the intensity of relaxation processes on the other hand. Therefore, these materials require a detailed

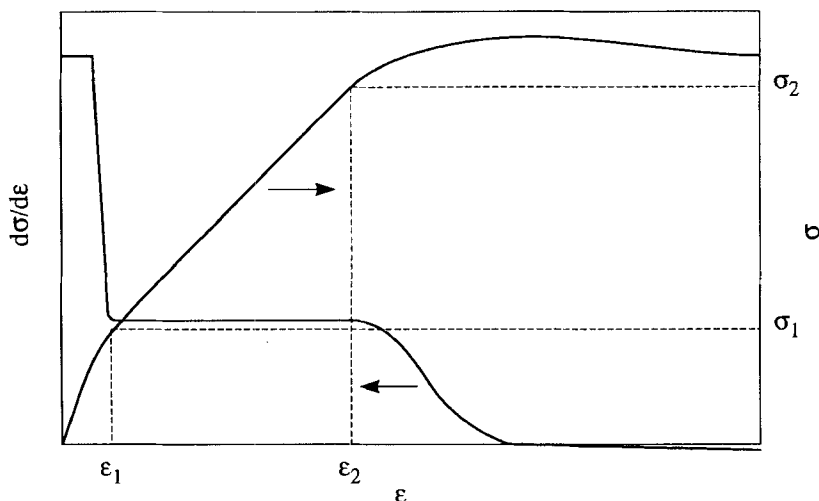


FIGURE 1 A typical stress-strain curve of PE-1 samples and scheme for determination of specific points on it.

description of their behavior under short-time loading, as well as a thorough analysis of their long-time relaxation properties to enable prediction and choice of optimal exploitation conditions (temperature, strain, draw ratio).

EXPERIMENTAL

Materials

The materials used for investigation have been based on HDPE and produced by extrusion (PE-1) with subsequent crystallization of extruded highly deformed melt² with draw ratios 5.5, 7.5, 9.1, 10.9, and 12.2 isotropic HDPE with $\lambda = 1$ (initial extruded material before high-deformation induced crystallization) having been also investigated. The samples of oriented HDPE produced by multi-stage zone-drawing³ (PE-2), hydrostatic extrusion⁴ (PE-3) and injection molding⁵ (PE-4) along with those of oriented UHMWPE produced by cold rolling⁶ (PE-5) and gel-spinning/hot-drawing^{8,9} (PE-6) have been studied too, the investigation objects including both bulk materials, films and fibers.

Radiation cross-linking of samples

The PE-1 samples were irradiated by electrons in the air with radiation absorption doses of 1, 3, 5, 10, 50, and 100 Mrad. The dose rate was 1 Mrad/min. Maximum warming-up on surface of the samples was 30°C.

Measurements

Stress relaxation experiments for original HDPE and PE-1 were carried out in a wide temperature range ($-50^\circ < T < 120^\circ\text{C}$) and fixed tensile strains $1\% < \epsilon_0 < 20\%$ on a test machine Zwick. Stress relaxation for the all oriented PE samples produced by the above mentioned techniques^{3-6,8,9} was investigated at room temperature and at different fixed ϵ_0

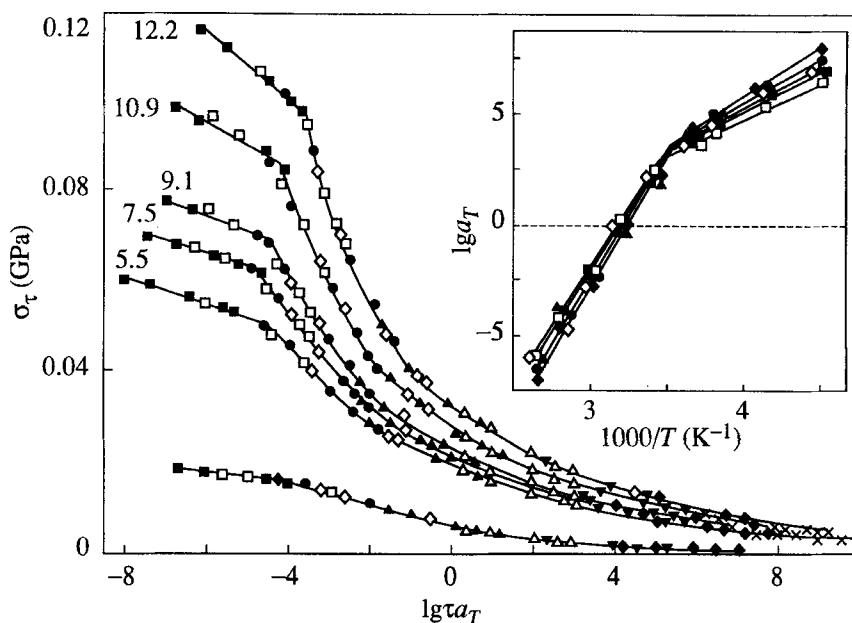


FIGURE 2 Master curves of stress relaxation at ϵ_0 for the PE samples drawn up to different λ (the values of λ are shown near the each curve). The measurements were carried out at $T = -50^\circ\text{C}$ (■), -30°C (□), -10°C (●), 0°C (◇), 20°C (▲), 40°C (△), 60°C (▼), 80°C (◆), 100°C (×). τ is measured in sec. The inset represents the dependences of the horizontal shift factor a_T on reciprocal temperature at $\epsilon_0 = 1\%$ for PE samples of various λ : $\lambda = 1$ (■), 5.5 (◆), 7.5 (●), 9.1 (▲), 10.9 (◇), and 12.2 (□).

($1\% < \epsilon_0 < 5\%$). The experiment time τ was 10^3 s. The specimen extension rate up to given tensile strain was 20 mm/min. Values of ϵ_0 were measured in extension experiment using the electron extensometer. It is very important because of essential pulling out of the oriented samples from the clamps when extended. The distance between clamps in the test machine was 50 mm.

RESULTS

Stress-strain curve

The typical shape of the stress-strain curve for PE-1 is shown in Figure 1. Of special interest is the linear part at high levels of the strain. The left and right boundaries of this part are marked on the plot by ϵ_1 and ϵ_2 , respectively. An essential change of stiffness during the extension was observed at these points. Variation ranges of the strain at specific points of the stress-strain curve for PE-1 were $1.2\% < \epsilon_1 < 4.7\%$ and $8\% < \epsilon_2 < 20\%$. The temperature range of the specific points on the stress-strain curves was found to be wider for greater values of draw ratio. Due to the observed peculiarities of deformation process for PE-1 the stress relaxation has been investigated not only for the specimens deformed up to voluntary chosen strain levels ($\epsilon_0 = 1, 2.5, 5, 7, 10, 15$, and 20%) but also for samples deformed to the levels where the change in a shape of stress-strain curves were found (ϵ_1, ϵ_2). (The latter, however depend on temperature and draw ratios.) It allows to compare the relaxation properties of the investigated samples more adequately because in

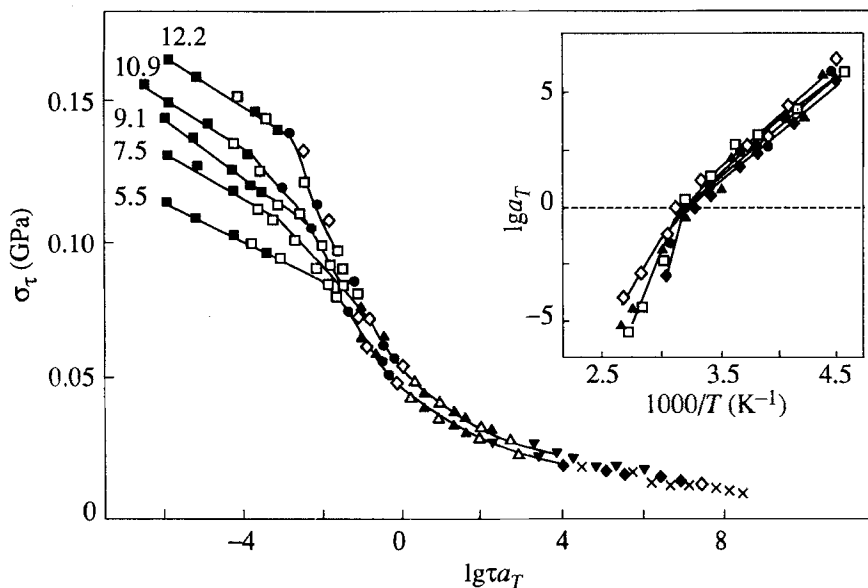


FIGURE 3 Master curves of stress relaxation for PE-1 samples deformed up to ϵ_1 which is the first specific point on the stress-strain curve. τ is measured in sec. The inset gives the dependences of the horizontal shift factor a_T on reciprocal temperature. The symbols for the values of λ and T are the same as in Figure 2.

these specific points the mechanism of deformation is believed to be identical.

Stress relaxation

Generalization of deformation properties was made using the principle of time-temperature superposition¹³ by means of the horizontal shift of isotherms of stress relaxation. Master curves of stress relaxation at fixed tensile strain (Figure 2) and at specific points ϵ_2 and ϵ_2 of the stress-strain curve (Figure 3 and 4) show essential decrease of stress σ_τ (more than in decimal order) versus increase reduced time $\lg(\tau a_T)$. It testifies to intensive relaxation in PE-1. It is noteworthy that the values of σ_τ for various λ on the master curves at point ϵ_1 (Figure 3) were more close to each other in contrast to those of other families of master curves (Figures 2, 4). It testified to the expedience of the long-term relaxation properties analysis at specific points of the stress-strain curve (which were determined by short-term loading), because the similarity of mechanical characteristics for the PE samples of different λ enables one to assume the identity of deformation mechanism. Linear approximation of temperature dependences of the shift factor in certain temperature ranges allowed to use the Arrhenius equation to calculate the effective activation energy of deformation process ΔH : $\Delta H = (2.3R \lg a_T) / (1/T - 1/T_0)$ where T_0 was the reference temperature, T was the current temperature. Figure 4 shows the correspondence of the main levels of ΔH for PE-1 to the main levels of ΔH which are characteristic of β -, α_1 -, and α_2 -relaxation processes in PE.¹⁴ In this case the main levels of ΔH were the same for isotropic and oriented materials. The data obtained in References 14–17 also confirm the closeness of the values ΔH of the α -relaxation process for oriented^{15,16} and isotropic^{14,17} HDPE.

In the range of small strains ($\epsilon = 1\%$) and negative temperatures the level of ΔH was practically characteristic of all λ values and was approximately 60–65 kJ/mol, which

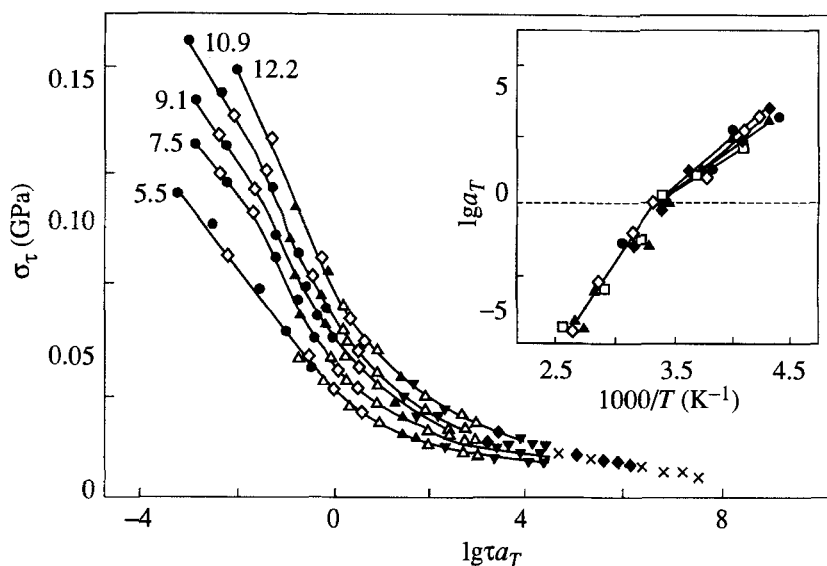


FIGURE 4 The same as in Figure 3 for a specific point ϵ_2 .

corresponds to β -relaxation. As the strain in this temperature range increases, the rise of ΔH for all values of λ was observed with transition to higher level of ΔH , which corresponds to α_1 -relaxation. This level of ΔH of α_1 -relaxation at $\epsilon_0 > 2.5\%$ was characteristic in the temperature range -50 to $+40^\circ\text{C}$. At $T = 0$ – 40°C ($\epsilon_0 = 1, 2.5\%$) and $T = 40$ – 100°C ($\epsilon_0 \leq 5$ – 7%) the ΔH values correspond to α_2 -relaxation. Higher values of ΔH at $T = 40$ – 100°C were characteristic of smaller values of λ (1 and 5.5). The strain increase at $T \geq 40^\circ\text{C}$ and $\epsilon_0 \geq 5\%$ led to the decrease of ΔH values for oriented specimens and at $\epsilon_0 > 5\%$ this regularity extended to all the range of investigated $\lambda = 1$ – 12.2 . The decrease of ΔH with the increase of λ may be explained in the following way: the more the material was subjected to preliminary stretching (during crystallization of highly deformed melt), the weaker was the temperature dependence of the subsequent stretching (in extension experiment). Identical values of the effective activation energy were calculated as well from the results of generalization of the deformation properties at specific points of stress-strain curve. The increase of ΔH value (from 81 to 117 kJ/mol) with decrease of λ (from 12.2 to 5.5, respectively) was observed for strain ϵ_2 at $T = 0$ – 40°C . At $T \geq 40^\circ\text{C}$ (for ϵ_2) values of ΔH were practically identical for various draw ratios (165–175 kJ/mol). It is indicative of the equivalence of deformation state in this temperature range at the specific point ϵ_2 on the stress-strain curve for materials with various values of λ . This analysis of the ΔH values of deformation process in PE-1 samples and isotropic HDPE revealed that they fit the levels of ΔH for the main relaxation processes in HDPE (determined by other methods).^{14–17} In addition, the action of tensile strain can act like the temperature rise and at low temperatures the mechanism of deformation typical of higher temperature region can occur. However, there are certain ranges of temperature and strain where the reverse phenomenon is observed: the deformation mechanism typical of lower temperature can be realized in the range of higher temperature.

TABLE I
Values of Young's modulus and $1/\beta$ for a number of oriented PE materials (at room temperature)

Preparation technique	Polymer	Draw ratio	Young's modulus (GPa)	$1/\beta = \sigma_0/(\sigma_0 - \sigma_e)$ at fixed tensile strain		
				1%	2.5%	5%
Extrusion and crystallization of extruded highly deformed melt ²	HDPE	5.5	3.6	2.000	1.892	1.841
		12.2	7.1	1.750	1.550	1.454
Multi-stage zone-drawing ³	HDPE	15.7	10	1.549	1.423	1.427
		28	25	1.664	1.462	—
Hydroextrusion ⁴	HDPE	11.2	12	1.795	1.758	—
Injection molding crystallization ⁵	HDPE	—	3.4	1.631	—	—
Cold rolling ⁶	UHMWPE	—	1.1	1.610	—	1.766
Gel-spinning/hot-drawing ^{8,9}	UHMWPE	60†	50	1.870	1.862	1.694
		80†	183	1.520	—	—
		60‡	30	1.610	1.872	2.008
Isotropic sample	HDPE	1	1.1	1.642	1.666	1.788

† Using paraffin as solvent.

‡ Using paraffinic oil as solvent.

For comparison of relaxation properties of materials with various values of λ it is expedient to present the experimental data on stress relaxation expressed in normalized units: $\sigma_0/(\sigma_0 - \sigma_e) = 1/\beta$ (see Reference 18) where σ_0 is the stress at $\tau = 0$, σ_e is the stress at $\tau = 10^3$ s. Table I shows values of $1/\beta$ calculated from the experimental data on stress relaxation at a fixed extension both for PE-1 and for all other PE samples investigated. Relaxation properties of these materials are compared in temperature range of intensive stress relaxation for PE-1 at room temperature.¹⁹ Increase of relative intensity of stress relaxation (decrease of $1/\beta$) with the increase of λ was observed for PE-1 (it occurred in the case of all ranges of fixed tensile strain and temperature).¹⁹ This testifies to specific reaction of these materials to mechanical load which is manifested in the effective resistance to fast loads¹¹ (increase of Young's modulus and tensile strength with the increase of λ) and in the insignificant resistance to low loads¹⁹ (the decrease of $1/\beta$ with the increase of λ). The same ranges of $1/\beta$ variation for isotropic HDPE and PE-1 in spite of the essential increase of short-term properties for oriented samples (Table I) allow to assume that the rate of relaxation processes depends on the nature of the molecular chain. Table I shows that together with some peculiarities of $1/\beta$ dependence versus the fixed tensile strain, the draw ratio and influence on $1/\beta$ the technique of producing the samples all the materials under study have close values of $1/\beta$, which testifies to the intensity of relaxation processes in spite of the essential differences in the short-term mechanical properties (values for Young's modulus in Table I).

High values of Young's modulus (183 GPa) and tensile strength (3 GPa) for fibers produced by gel-technology (at $\lambda = 80$) do not decrease the intensity of the stress relaxation either.

The similarity of $1/\beta$ values for the PE-1 and isotropic HDPE samples is observed together with the similarity of $1/\beta$ values for materials which essentially differ in molecular

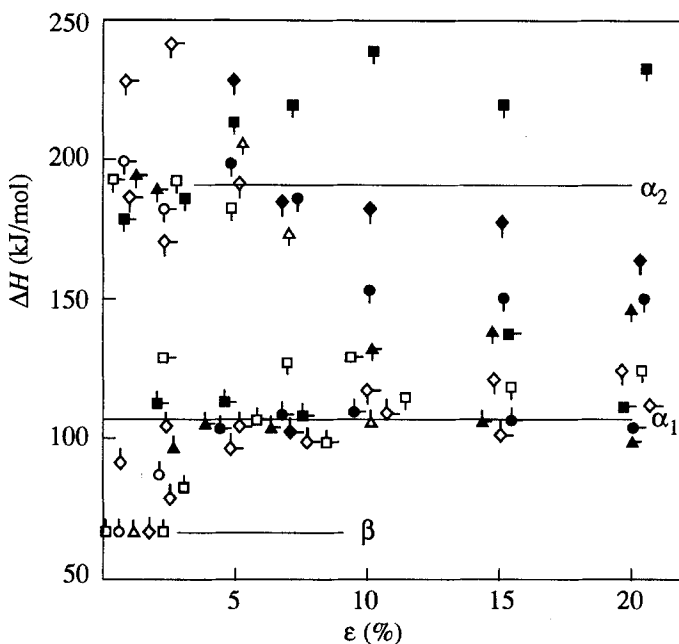


FIGURE 5 The dependences of the effective activation energy of PE-1 deformation process on strain. The bars added above, beneath or horizontally to the symbols corresponding to different λ (see inset in Figure 2) show the temperature range of deformation: (-50°C to 0°C), (0°C to 40°C), and (40°C to 100°C), respectively. Solid lines stand for ΔH values given in Reference 14.

weights (HDPE and UHMWPE), which enables one to assume that the relaxation behavior of the PE materials under study depends on the nature of the molecular chain.

Along with the analysis of the relaxation properties in normalized units ($1/\beta$), that was also made for absolute relaxation drop of stress $\Delta\sigma = \sigma_0 - \sigma_e$ in time 10^3 s. Figure 6 shows the results of the experiments on stress relaxation for three values of ϵ_0 and various values of the draw ratio for all investigated materials. A linear dependence of $\Delta\sigma$ versus σ_0 was found. It signified that $\Delta\sigma$ depends on the initial stress value and not on ϵ_0 and λ for all the investigated oriented PE materials. The experiments aimed at determining $\Delta\sigma$ for some values of the draw ratio and the fixed tensile strain enable the prediction of $\Delta\sigma$ value, provided σ_0 value is known (from the extension experiment, for example). It opens up new opportunities for developing express methods to determine $\Delta\sigma$ values.

Stress relaxation in electron irradiated samples

The PE-1 samples were cross-linked by electron irradiation in the air to decrease intensive stress relaxation, three years later they were investigated in the temperature range of intensive relaxation at room temperature. Dependences of $1/\beta$ on the absorbed dose of radiation ν (Figure 7) confirm that radiation cross-linking of PE-1 samples by electron irradiation in the air with an absorption of maximal the radiation dose 100 Mrad can decrease the intensity of the stress relaxation by about 30%.

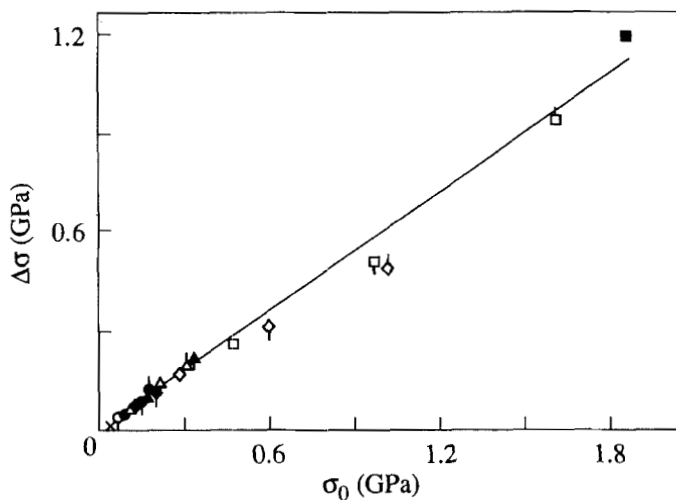


FIGURE 6 Dependences of a stress drop $\Delta\beta$ in 10^3 s after loading on the initial stress σ_0 for the strained up to $\epsilon_0 = 1\%$ PE samples: PE-1 (Δ , $\lambda = 5.5$; \bullet , $\lambda = 12.2$),² PE-2 (Δ , $\lambda = 15.7$; \blacktriangle , $\lambda = 28$),³ PE-3 (\blacklozenge , extrusion draw ratio 11.2),⁴ PE-4 (\times , λ is unknown),⁵ PE-6 (\square , $\lambda = 60$; \blacksquare , $\lambda = 80$),^{8,9} PE-6 (\diamond , $\lambda = 60$, other conditions of production),^{8,9} The vertical bars added beneath or above the initial symbols indicate the level of ϵ_0 (2.5 or 5%), respectively, at which stress relaxation was also studied.

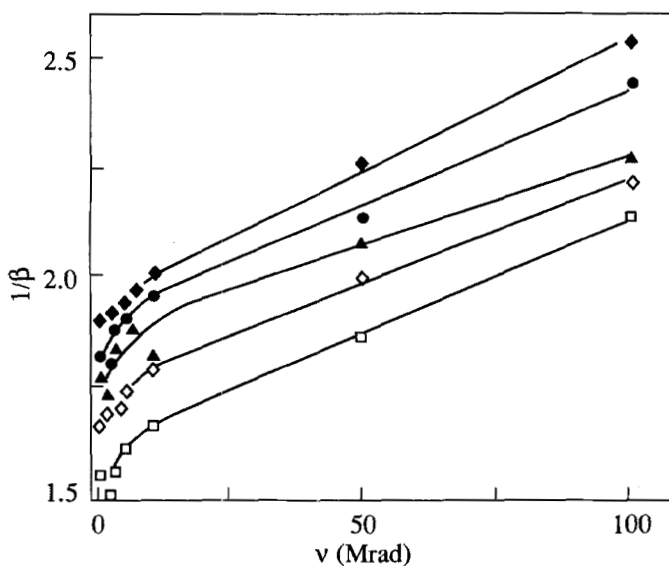


FIGURE 7 Dependences of stress relaxation in normalized units on absorbed radiation dose ν for PE-1 samples at $\epsilon_0 = 2.5\%$ and at room temperature.

CONCLUSION

It was found that despite various techniques used to produce the oriented polyethylene samples, all the samples investigated in this work had close values of $1/\beta$ (in spite of the significant difference in the values of Young's modulus) which testify to the intensity

of stress relaxation. Of special interest is the closeness of $1/\beta$ values for isotropic and oriented samples on the one hand, and for samples which essentially differ in molecular weights (HDPE and UHMWPE), on the other hand. It enabled us to draw a conclusion that relaxation behavior of materials based on polyethylene depends on the nature of the molecular chain.

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