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Internal stresses in cold-drawn and irradiated polyethylene

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The influence of high-energy radiation on the internal stress level in cold-drawn, high- and low-density polyethylene, with and without subsequent annealing, has been determined using a stress relaxation method described earlier. The internal stress level (σ_i) is found to increase substantially with the radiation dose for doses below 40 Mrad, while the increase at higher doses is only moderate. It is suggested that the initial increase is due to a preferred cross-linking of the amorphous phase or the fold surface of the lamellae. An exception to this behaviour was observed for cold-drawn low-density polyethylene, where the internal stress decreased as the radiation dose was raised.

1. Introduction

In a previous paper the authors reported on measurements of internal stresses in polyethylene as related to its structure [1, 2]. The samples used were primarily cold-drawn specimens of both low (LDPE) and high (HDPE) density polyethylene. One of the results of that investigation was a strong indication that, in cold-drawn specimens, the internal stress level appears to be associated with the tie molecules connecting the crystalline lamellae. The present paper is a short account of measurements of internal stresses in cold-drawn and irradiated samples of LDPE and HDPE. The results support the view presented earlier, that the internal stresses, according to the present method, are associated with changes in the state of the amorphous parts of the semicrystalline structure. For the sake of completeness the results presented below also comprise data obtained with isotropic, compression moulded samples.

It is known that low irradiation doses at room temperature bring about a preferential cross-linking in the amorphous part of PE [3–7] or in the fold surface of the lamellae [8–10]; the crystalline phase is affected at substantially higher doses. When correlating results of internal stress (σ_i) determinations with the dose, one should be able to find a pronounced influence of low doses on the σ_i level, whilst an increase in the dose should result in minor σ_i changes only. The experiments reported below support such a hypothesis for cold-drawn polyethylene with and without subsequent annealing. An exception was cold-drawn, unannealed LDPE, where an increasing dose resulted in a lower σ_i level.

It may be added that the determination of the internal stress level of the samples was based on an analysis of stress relaxation kinetics. The results obtained have been shown to correlate with other methods for determining internal stresses [1, 11, 12].

2. Experimental

2.1. Determination of internal stress

The method used to determine the σ_i level was based on an analysis of the kinetics of stress relaxation in the sample under study. The method, originally used for metals [13], has been applied by the authors to polyethylene [1, 2]; it utilizes the applicability of the power law for stress relaxation at sufficiently long periods of time [13–15]. The power law can be written as

$$\sigma - \sigma_i = K(t+a)^{-n} \qquad (1)$$

where σ and σ_i denote the stress and the internal stress, respectively, t the time and a, n and K constants. Plotting $(-d\sigma/d\log t)$ versus σ, a straight line is obtained, having a slope of $2.3n$, and inter-

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cepting the σ-axis at σ_i. Using this method, σ_i values between 10 and 20 MPa, independent of the initial stress σ_0 were recorded for cold-drawn LDPE and HDPE [1, 2].

2.2. Samples

The materials used were as follows; LDPE: Lupolen 1810H (BASF), density 0.917 to 0.918 g cm^{-3}, melt index 1.2 to 1.7 g/10 min, MFI 190/2, (ASTM D 1238-57T). HDPE: Lupolen 6011L (BASF), density 0.960 to 0.963 g cm^{-3}, melt index 4.0 to 6.0 g/10 min, MFI 190/2, (ASTM D 1238-57T).

The compression moulded samples (170° C, 2 MPa, dimensions; 50 x 5 x 1 mm) were cold-drawn at room temperature to an orientation degree of $\lambda = 6$. Some of the drawn samples were subsequently annealed; LDPE at 70° C and HDPE at 124° C, both for 12 h. The samples were then subjected to irradiation with 2 MeV electrons in a nitrogen atmosphere at room temperature. The dose was varied between 1 and 400 Mrad.

The relaxation measurements were carried out using a conventional tensile testing machine (L & W Alwetron TCS 250) in a testing room where the temperature was kept at 22 ± 0.5° C and the humidity at 65 ± 4% r.h. The initial deformation in the relaxation experiments was for all samples lower than 1%, i.e. approximately within the linear range of the stress–strain curves.

3. Results

Examples of stress relaxation curves used for the determination of the internal stress value are given in Fig. 1. These curves relate to cold-drawn HDPE-samples irradiated with 10 and 400 Mrad, respectively. The initial stress in the two experiments was practically equal (106 and 100 MPa). It can be seen that the stress decay is slower in the sample which received the highest radiation dose. This is in accordance with earlier experiments [7].

As discussed in our previous paper, the relaxation curves can be divided into two parts. In the first part, corresponding to short periods of time, the curves are normally linear in the $\sigma(\log t)$ plot. At longer periods of time a marked curvature can be seen. This latter part fits normally well into the description provided by Equation 1, that is to say the power law, and can be used to determine the σ_i level according to the procedure outlined above (see also [1, 2]). Fig. 2 shows the result of such an evaluation when applied to one of the curves reproduced in Fig. 1 (10 Mrad irradiation). The intercept of $(-d\sigma/d \log t)$, when plotted versus σ, with the stress axis gives in this case a σ_i value of 32 MPa.

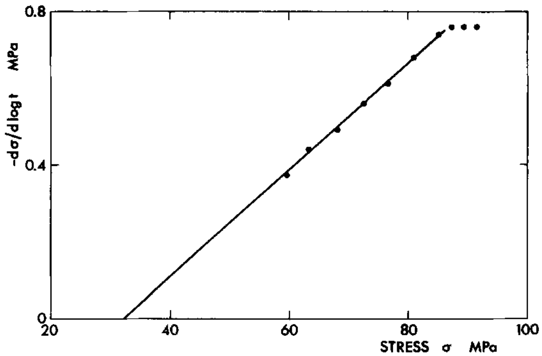

Figure 2 Determination of the internal stress value from the relaxation curve shown in Fig. 1 (radiation dose: 10 Mrad).

The influence of the radiation dose on the σ_i value of HDPE samples is shown in Fig. 3. The different curves in this diagram relate to cold-drawn samples with and without annealing prior to irradiation, and to compression moulded samples. The common feature of these results is the pronounced tendency of the σ_i level to show the largest increase at small doses, up to ~ 40 Mrad. When increasing the irradiation dose further, the increase in the σ_i level is moderate only.

The largest σ_i value is recorded for the unannealed, cold-drawn samples; the opposite applies to samples prepared by compression moulding. For the investigated samples, this value is with good accuracy independent of the initial stress σ_0 of the

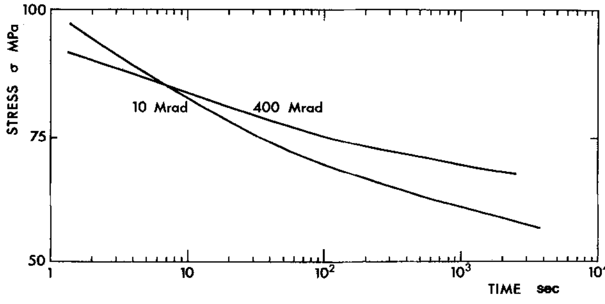

Figure 1 Stress relaxation of cold-drawn HDPE, irradiated with 10 and 400 Mrad. The initial stress values (σ_0) were 106 and 100 MPa, respectively, and the strain-rate $\dot{\epsilon} = 2.5 \times 10^{-3}$ sec^{-1}.

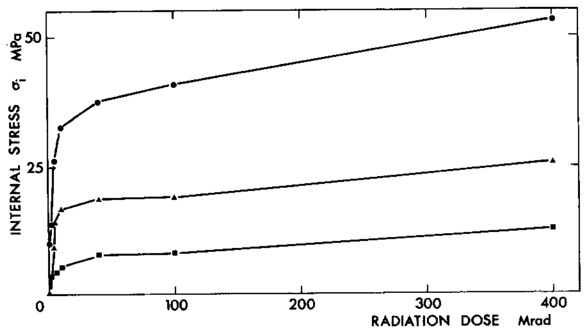

Figure 3 The internal stress value versus the radiation dose for HDPE. Upper curve, cold-drawn samples; middle, cold-drawn and annealed; lower, compression moulded.

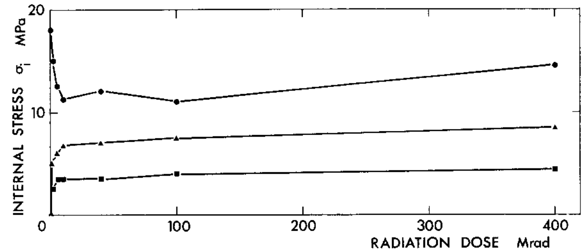

Figure 4 The internal stress value versus the radiation dose for LDPE. Upper curve, cold-drawn samples; middle, cold-drawn and annealed; lower, compression moulded.

stress relaxation experiments.

Corresponding results for LDPE are reproduced in Fig. 4. The highest internal stresses are also in this case found in the cold-drawn samples. As expected, the compression moulded samples are comparatively stress-free. On the other hand, the overall σ_i level is lower than observed on HDPE. Another difference is a remarkable decrease of the σ_i value for low radiation doses for cold-drawn LDPE. However, the results obtained with the cold-drawn and subsequently annealed LDPE samples and the compression moulded samples support the assumption that the σ_i value should increase substantially at low radiation doses.

4. Discussion

The idea of relating internal stresses in cold-drawn polyethylene to the state of the amorphous part of this semicrystalline polymer appears to have gained additional support in the results presented above. These results show that low radiation doses, representing a specific means to change the structure of the amorphous portion of the polymer, are especially effective in influencing the σ_i level. With the exception of unannealed LDPE, this is true of all the samples investigated, that is annealed, cold-drawn LDPE, cold-drawn HDPE with and without subsequent annealing, and moulded LDPE and HDPE samples.

In this context it would have been desirable to correlate the results reported above with the actual number of cross-links induced in the amorphous regions by different radiation doses. For various reasons, measurements of this type could not be included within the scope of the present work. It may suffice here to mention that the number of cross-links in the amorphous phase increases monotonously with the dose within the irradiation range used here.

As is evident from Fig. 4, cold-drawn LDPE shows a behaviour which differs from the general pattern exhibited by all the other samples. In this case, the σ_i level decreases upon increasing the radiation dose. No satisfactory explanation of this behaviour could be found. In order to further analyse the peculiar behaviour of LDPE, some experiments were carried out on samples cold-drawn after irradiation (orientation degree $\lambda = 4.5$). The doses used were 1, 5 and 10 Mrad. For samples prepared in this way, a monotonous increase in the σ_i level with the dose was found.

Although measurements of internal stresses perpendicular to the draw direction could yield useful information, such measurements have not been performed, mainly due to experimental difficulties involved in applying the relaxation method in that direction. In a future paper, we intend to report on the angular dependence of the internal stress.

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