

Irradiation of Oriented LDPE Films

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SYNOPSIS

Low-density polyethylene (LDPE) films deformed uniaxially at 70°C and to low draw ratios have been irradiated on a ⁶⁰Co source with a dose rate of 0.33 Mrad/h in air. Their elastic modulus has been determined at room temperature and at 145°C, and their crystallinity has been studied by wide-angle X-ray scattering (WAXS). A two-stage process has been proposed for the influence of irradiation on the structure and properties of the films. The first stage is characterized by enhanced chain scission in the strained regions, as a result of which structural reorganization takes place there and the crystallinity increases. This increase is greater for higher draw ratios and higher doses. The second stage is characterized by no structural changes in the material. The value of *D*, which separates the two stages, shifts toward higher doses for higher draw ratios. Under the conditions of the present experiment, the orientation of the films decreases the efficiency of network formation by the irradiation.

INTRODUCTION

It has been pointed out in a number of papers¹⁻⁴ that the efficiency of network formation in irradiated polymers depends on the degree of interlamellar contact. Cross-linking has been shown to predominate in isotropic polyethylene,^{5,6} but chain scission becomes important in highly drawn fibers,^{4,7} films,^{8,9} etc.

Some of the authors indicate a decrease in the cross-linking efficiency in drawn high-density polyethylene (HDPE) exposed to γ radiation,¹⁰ compared with the isotropic material obtained by melting and crystallization of the drawn polymer. Others note that the transfer from an initial isotropic structure to a fully oriented fibrillar one in HDPE films results in an increase of the cross-linking efficiency at relatively low irradiation doses.⁹ A model has been proposed⁷ where the tensile creep behavior of irradiated HDPE fibers is explained by two parallel thermally activated processes—a low-stress one

related to the amorphous fraction and a high-stress one related to the continuous crystal fraction.

The aim of the present paper is to investigate the changes in the elastic modulus of low-density polyethylene (LDPE) films, subjected to small degrees of orientation at 70°C and irradiated to comparatively low doses.

EXPERIMENTAL

Films 350 μ m thick produced from LDPE-type Rotopoten, a Bulgarian product, have been studied. The density of the polymer is 0.92 g/cm³, and the melt index is 3.2 g/10 min. The films have been extruded at 145–170°C. Samples with lengths *l*₀ have been cut out, and their drawing has been accomplished on a Zwick dynamometer (FRG) at 70°C and with a rate of 6.5 mm/min. The samples have been kept strained on the dynamometer for about 40 min at the temperature of drawing and then have been cooled down to room temperature with a rate of 1.5°C/min by blowing air into the camera. The samples have been further kept strained at room temperature for 1 h and then have been removed from the dynamometer and their length *l* has been

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measured. The orientation of the samples is characterized by the parameter $\lambda = l/l_0$.

Irradiation of the samples has been done on a ^{60}Co source with a dose rate of 0.33 Mrad/h in air and at 35°C. The Young's modulus E has been determined from the stress-strain curves, obtained on a Zwick dynamometer at room temperature and at 145°C, at a rate of 1.5 mm/s. The crystallinity of the films has been determined by wide-angle X-ray scattering (WAXS) on a USSR apparatus URS-50 IM by the Hermans-Weidinger method.¹¹

RESULTS

Figure 1 represents the dependence of $E(D)/E(0)$ on the irradiation dose D . $E(D)$ is the Young's modulus measured at room temperature for a dose D , and $E(0)$ is the modulus of the nonirradiated sample, both determined from the stress-strain curves for several λ . The nonoriented sample ($\lambda = 1$) exhibits only a slight increase of $E(D)/E(0)$ with the increase of D —the corresponding curve is almost coinciding with the abscissa. On the other hand, even a small orientation of the samples results in a growth of $E(D)/E(0)$ with D . The increase of λ leads to an increase of $E(D)/E(0)$ for a fixed D .

Figure 2 represents the behavior of the elastic modulus E measured at 145°C, with the irradiation dose. It exhibits a linear growth with the growth of D for all values of λ , and the increase of λ results in a decrease of E for a fixed value of D .

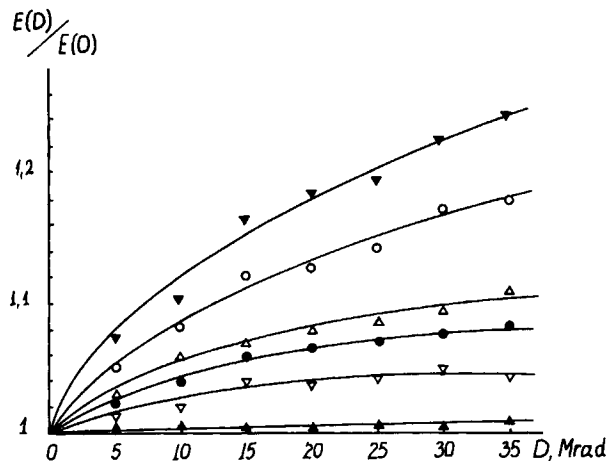


Figure 1 The ratio of the elastic modulus at a dose D and the modulus of the nonirradiated sample, measured at ambient temperature, vs. irradiation dose. (\blacktriangle) Non-oriented sample; (∇) $\lambda = 1.1$; (\bullet) $\lambda = 1.3$; (\triangle) $\lambda = 1.5$; (\circ) $\lambda = 1.8$; (∇) $\lambda = 2.1$.

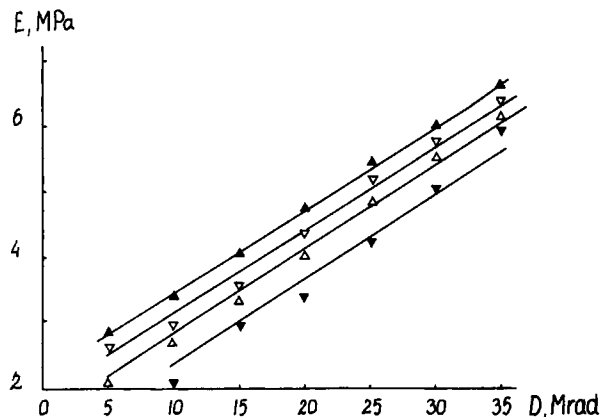


Figure 2 Elastic modulus at 145°C vs. irradiation dose. (\blacktriangle) Nonoriented sample; (∇) $\lambda = 1.1$; (\triangle) $\lambda = 1.5$; (\blacktriangledown) $\lambda = 2.1$.

Figure 3 shows the results of the crystallographic measurements. The changes of $\alpha(D)/\alpha(0)$ with the irradiation dose are presented for the nonoriented and some oriented samples. $\alpha(D)$ is the degree of crystallinity for a dose D , and $\alpha(0)$ is that for the nonirradiated samples. The data are a little bit scattered, but the values for the films with higher orientation are higher than those for the less oriented samples. For each λ , $\alpha(D)/\alpha(0)$ increases to a maximum and then remains almost the same with the increase of D . The position of the maximum is shifted toward higher doses with the increase of λ . For the film with the highest orientation, the maximum is not established within the interval of doses considered in the present investigation.

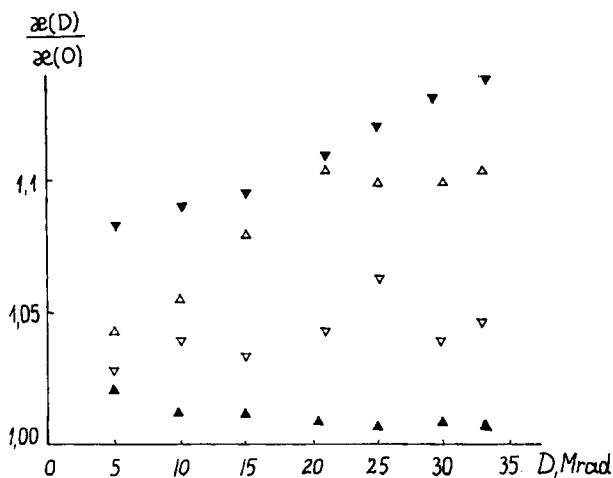


Figure 3 The ratio of the crystallinity at a dose D and the crystallinity of the nonirradiated sample vs. irradiation dose. (\blacktriangle) Nonoriented sample; (∇) $\lambda = 1.1$; (\triangle) $\lambda = 1.5$; (\blacktriangledown) $\lambda = 2.1$.

DISCUSSION

The Young's modulus at room temperature depends on the degree of crystallinity, the structure or the topology of the noncrystalline region, the crystallite thickness, the relative amount of the interfacial region, etc.¹² The stress-strain curves in the dry state of a cross-linked polymer are influenced not only by the average molecular weight between cross-links M_c , but also by the unrelaxed entanglements and the supermolecular structure with all the factors mentioned above. Only measurements above the melting point T_m in the rubbery state of the polymer (or in the swollen state) make possible the determination of the concentration of the elastically active chains in the network, formed as a result of irradiation. In this case, the contribution of the structure on the elastic behavior of the polymer may be excluded and some conclusions can be drawn on the efficiency of network formation. Except for very low degrees of cross-linking, the following relation between E and M_c is valid¹²:

$$E = k\delta RT/M_c$$

where k is a numerical coefficient, δ is the density of the polymer, R is the gas constant, and T is the absolute temperature.

The drawing of the samples in our experiments was accomplished below the melting temperature of the crystallites and the stress is low—the maximum λ is only 2.1. It could be expected that the deformation would result in straining of macromolecular chains and entanglements mostly from the amorphous and the interfacial regions, leaving intact the crystalline phase. Curved chains and knots from the amorphous region would be straightforward, and the strain would be concentrated predominantly in the interfacial region.

Cross-linking and chain scission of the macromolecules take place simultaneously in the irradiated polymers, their relative ratio depending on the structure and the morphology. Oxidative degradation plays an important role in the case of low irradiation doses and in the presence of oxygen. It has been reported¹³ that orientation results in a decrease of the γ -radiation-induced oxidative degradation mainly as a consequence of the drop in the transport properties, measured by sorption, diffusion, and permeability. This should be taken into account when comparing the results of our investigation and those obtained in Refs. 9 and 14, etc. There, an increase of the cross-linking efficiency is reported for low degrees of orientation—up to $\lambda = 5$ –9. Besides,

the temperature of drawing also influences the structures obtained as a result of orientation—in Ref. 14, this temperature is about 120°C, and in Ref. 9, is 60–80°C.

In the present study, E (Fig. 2) decreases with the increase of λ for a fixed D value; that is, the increase in orientation even to a very small degree results in an increase of M_c and a decrease in the efficiency in network formation. Those results are contradictory to Refs. 9 and 14 but support Ref. 15, etc.

The increase of E with D is the same for the different λ . This probably means that the higher orientation results in a definite change of the ratio cross-linking/chain scission. In the amorphous region, the eventual acts of chain scission most probably lead to an immediate recombination of the radicals, due to the so-called cell-effect.¹⁶ The regions that are strained (the interfacial, for instance) are affected by chain scission more intensively—due to the reduced probability of this effect.

A definite D means a definite number of elementary acts, leading to different results due to structural and other factors. The increase of orientation leading to more intensive chain scission in the interfacial region will cause certain structural changes in it. At a certain D , different for each λ , the mechanical strain will be taken off as a result of the structural reorganization and the ratio of the cross-linking and the chain scission will be influenced by the new relative amounts of the crystalline and the noncrystalline regions. That is why E (Fig. 2) increases with D for each λ almost in the same way.

The behavior of $\alpha(D)/\alpha(0)$ with the dose justifies a similar model of the processes taking place in the irradiated oriented samples (Fig. 3). For the nonoriented films, the increase of D leads to no changes in the crystallinity, that is, the crystalline region remains unaffected by the irradiation within the interval of doses up to 35 Mrad. The increase of λ leads to an increase of the crystallinity, but what is more important, to an increase of the $\alpha(D)/\alpha(0)$ with D for each λ . This increase reaches a certain maximum that shifts to higher D for the higher λ , and after that, the crystallinity stays almost constant. So an increase of the relative amount with λ and with D should be expected as a result of the structural reorganization of the strained regions. As a result of the relaxation processes, the strained macromolecules that have undergone chain scission form new crystallites by aligning the segments and thus joining the crystalline phase at the expense of the amorphous and the interfacial regions. The greater the orientation, that is, the greater the me-

chanical strain, the more intensive the chain scission and the bigger the probability of the formation of new crystallites as a result of stress relaxation.

After the organization of the additional crystalline structures, the irradiation, that is, the further growth of D , leads to no changes in the crystalline region but results in the formation of cross-links in the amorphous phase. So after the maximum of the crystallinity is reached, it changes no further.

On the basis of this concept for the structural changes in the irradiated oriented films, the behavior of $E(D)/E(0)$ (Fig. 1) could be explained. The increase of λ leads to an increase in the crystallinity—this results in an increase in the Young's modulus.¹² The process of crystallite formation is predominating at the beginning of the irradiation procedure and is responsible for the increase of $E(D)/E(0)$ at the lower doses. After a certain D , determined for each λ by the crystallinity maximum, the increasing network formation in the amorphous and the interfacial regions (both reduced in amount) lead to a further growth of $E(D)/E(0)$ with D .

It should also be pointed out that, altogether, the cross-linking formation is not a very intensive process, judging by the behavior of the value of $E(D)/E(0)$ with D for the nonoriented sample. This is probably due to the intensive oxidative destruction at the comparatively low-dose rate of the experiments described.

CONCLUSIONS

The processes taking place in oriented LDPE films, irradiated to technological doses, could be explained by a two-stage model of the influence of irradiation on the structure and the dynamic mechanical characteristics of the films. The first stage is characterized by cross-linking in the amorphous and chain-scission in the interfacial strained region; as a result, crystallinity increases with the increase of the orientation and the dose. This is responsible for the growth of the elastic modulus at room temperature with λ and with D . The value of D that marks the end of the first stage is higher for higher orientations.

The second stage is characterized mainly by cross-linking in the noncrystalline regions of the structurally reorganized material, and that is the reason for the continuing increase of the elastic modulus (both at ambient and at 145°C temperatures) with the increase of D . No further structural changes take place at this stage.

Under the conditions of the experiments described in the present article, the efficiency of network formation is reduced by the orientation of the films, due to the structural changes in the material.

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