CHANGE IN THE PHYSICOMECHANICAL PROPERTIES OF POLYETHYLENE ON RADIATION AGEING*

YE. V. BYSTRITSKAYA, YE. V. BYKOV, A. L. POMERANTSEV, O. N. KARPUKHIN and YE. A. FEDOROVICH

Institute of Chemical Physics, U.S.S.R. Academy of Sciences

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The changes in the physicomechanical properties of LDPE are considered in the kinetic and diffusion regimes of radiation oxidation. In the kinetic regime fall in the instant modulus and strength at low doses is due to degradation of the macromolecules and at high doses to accumulation of oxygen-containing groups. In the diffusion regime strength is determined both by the size of the absorbed dose and depending on the dose rate by the ratio of the thicknesses of the internal crosslinked and external oxidized layers. In the heterogeneous sample the presence of a crosslinked layer does not lead to rise in the strength of the material as compared with that of the uniformly oxidized film.

RADIATION ageing of PE in air is accompanied by change in its physicomechanical properties. Depending on the relation between the geometric dimensions of the sample and the dose rate p two fundamentally different situations appear [1, 2]. For the flat sample of thickness h on fulfilment of the condition

$$\frac{h}{2} < \delta \approx \left(\frac{2Dc_0}{ap+b\sqrt{p}}\right)^{1/2} \tag{1}$$

(δ is the thickness of the oxidized layer; D is the oxygen diffusion coefficient; c_0 is the concentration of oxygen at the surface of the sample, a and b are coefficients determined through the kinetic parameters of the radiation oxidation process [3, 4]) oxidation accompanied by degradation proceeds uniformly over the entire thickness of the sample. In thick samples $h>2\delta$ oxidative degradation occurs only in the surface layers to a depth δ from each side and the internal layer to which oxygen does not penetrate because of diffusion hindrances is subject to radiation crosslinking. The present work considers the patterns of change in the physicomechanical properties of PE in these two different cases.

The experiment was conducted on LDPE of grade $107-01 \text{ K} (M_w \sim 2 \times 10^5)$, degree of crystallinity $\sim 50\%$) containing 0.1% stabilizer di- β -naphthyl-*p*-phenylene diamine. The samples in the form of films and plates 0.1 to 1.5 mm thick were pressed in air at 423 K and pressure 3.4×10^6 Pa and exposed to *y*-radiation from a ⁶⁰Co source in air and *in vacuo*. The dose rate was varied from 9 to 110 rad/sec. To measure the mechanical characteristics we cut out of the samples blades measuring 13×3.5 mm.

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The measurements were made on the Instron rupture machine at room temperature and strain rate 100 mm/min. Each value of strength and relative elongation at rupture was obtained as the mean of a series of five samples.

Let us first consider change in the mechanical properties in thin films $(h < 2\delta)$. Figure 1 shows the strain curves for the initial polymer and samples irradiated to a dose $\theta = 40$ Mrad in air and *in vacuo*. It will be seen that the character of the changes observed differs for high and low values of relative elongation ε . In the region of high strain ($\varepsilon > 1$) the slope of the curve characterized at each point by the instant modulus $E = d\sigma/d\varepsilon$ increases on irradiation *in vacuo* and drops in air in relation to the slope of the curve of the starting sample. This corresponds to the character of the processes occurring in the polymer. For high strains when a neck formed in the sample the polymer was in the strongly oriented state. Its mechanical properties are essentially determined by the number of extended communicating chains [5]. Oxidative degradation in air reduces this number while crosslinking *in vacuo* increases it with corresponding change in the instant modulus.



A different picture was observed in the region of low strains ($\varepsilon < 0.2$). Here irradiation *in vacuo* did not influence the strain curve but in air the instant modulus increased. It is known [5] that for low strains the physicomechanical properties chiefly depend on the conformational mobility of the polymer chains. Accumulation of the polar groups on oxidation reduces this mobility as a result of enhanced intermolecular interaction and, therefore, *E* rises. Thus, on radiation-oxidative degradation of LDPE change in the physicomechanical properties in the region of high strains is essentially determined by degradation and in the region of low ones by oxidation.

Similar patterns are also manifest in the dependence of the strength at rupture σ^* of a thin film on the radiation dose (Fig. 2). At comparatively low doses ($\theta < 60$ Mrad) rupture occurs for high strains and the strength drops with increase in dose because of degradation. At the same time on irradiation *in vacuo* crosslinking raises

strength. This agrees with the ideas developed in references [6–8]. At high doses elongation at rupture drops sharply and rupture occurs in the region of low strains where a decisive role is played by oxidation. Strength in this region rises with the absorbed dose.

According to the ideas outlined the dependence of change in strength on the dose rate must at low doses be determined by the corresponding dependence of the rate of degradation as was observed in reference [8] and at high ones on the rate of oxidation. According to the generally accepted mechanism of oxidative degradation [9] both these rates depend on the dose rate in line with the formula

$$W = ap + b\sqrt{p}, \qquad (2)$$

but the parameters a and b for oxidation and degradation may differ. For the polymer used in the present work the contribution to oxidation of the chain process determined by the parameter b is low [4]. Apparently this also applies to the rate of degradation since the dependences of σ^* on θ for different potencies practically match both for low and high θ values.

Now let us consider change in the physicomechanical properties of thick LDPE samples $(h>2\delta)$ which in the course of irradiation in air assume a trilayer structure [2] consisting of an internal crosslinked layer of thickness $h-2\delta$ and two outer oxidized layers each of thickness δ rigidly bound to the inner layer. Figure 2 shows that the strength at rupture of such samples depends not only on the absorbed dose θ but also on the dose rate p. However, this dependence is quite unusual. Firstly, the strength of the thick samples $\theta < 60$ Mrad is less than that for the thin film irradiated to the same dose with almost identical elongation at rupture (Fig. 3). Firstly (sic), the samples of different thickness irradiated with a dose of the same potency (curves 4 and 5) differ in strength. All this suggests that strength at a fixed dose depends on the ratio of the thicknesses $x=2\delta/h$ which is determined by the dose rate p from equation (1).

From Fig. 2 it will be seen that the strength σ^* as a function of x for a fixed dose $\theta > 60$ Mrad passes through a minimum. Let us see how this function may be described. For this we shall adopt the following simplifying assumptions: for sufficiently high radiation doses ($\theta > 60$ Mrad) the thick sample consitutes a three-layer system with a distinct boundary between layers; the strain curve and the rupture characteristics (σ_1^* , ε_1^* ,) of the inner layer are the same as in the thin film irradiated *in vacuo* and do not depend on the layer thickness; the strain curve and the rupture characteristics (σ_2^* , ε_2^*) of the outer layers are the same as in the thin film irradiated in air and also do not depend on the layer thickness.

Since as shown in Fig. 3, $\varepsilon_2^* < \varepsilon_1^*$, the first to rupture during strain is the outer layer and the stress σ in the whole sample will be

$$\sigma = \sigma_2^* x + \sigma_1(\varepsilon_2^*)(1 - x),$$
(3)

where $\sigma_1 \epsilon_2^*$ is the stress in the inner layer corresponding to the strain at rupture of the outer layer ϵ_2^* . After rupture of the outer layer the load is taken up by the inner

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layer rupturing when the stress in the whole sample is

$$\sigma = \sigma_1^* (1 - x) \tag{4}$$

If $\sigma_1^*(1-x) \leq \sigma_2^* x + \sigma_1(\varepsilon_2^*) (1-x)$ rupture of the inner layer occurs simultaneous with that of the outer one and for the opposite case additional strain of the sample is required to reach a critical stress in the inner layer. The equality of the two stresses mentioned determines the boundary point

$$x^{*} = \frac{\sigma_{1}^{*} - \sigma_{1}(\varepsilon_{2}^{*})}{\sigma_{2}^{*} + [\sigma_{1}^{*} - \sigma_{1}(\varepsilon_{2}^{*})]},$$
(5)

to the left of which $(x \le x^*)$ the first case is realized and to the right $(x > x^*)$ the second.

Thus, within this model the dependence of stress at rupture on the ratio of the layer thickness has the form of two straight lines intersecting at the point x^*

$$\sigma^{*}(x) = \begin{cases} \sigma_{1}^{*}(1-x), & 0 < x \le x^{*} \\ \sigma_{2}^{*}x + \sigma_{1}(\varepsilon_{2}^{*})(1-x), & x^{*} < x < 1, \end{cases}$$
(6)

which qualitatively truly reflects the nature of the dependence observed.

However, comparison of the dependence obtained for $\sigma_1^* \approx 25$ MPa, $\sigma_1(\varepsilon_2^*) \approx 10$ MPa, $\sigma_2^* \approx 13$ MPa with the experimental findings (Fig. 4) shows that the data presented for all the x values systematically lie below the calculated straight lines. This was



to be expected since the model considered does not allow for local overstresses appearing in the defects and at the apices of the cracks and leading to fracture of the samples for lower strains and also the end width of the zone of the transition between the inner and outer layers. In particular, for low thicknesses of the outer layer $(x < x^*)$ when rupture of the whole sample lags behind rupture of the outer layer and is determined by the strength of the inner layer, local overstresses may appear at the apices of the cracks of the outer layer. At $x > x^*$ the strength may be influenced by the overstresses which, as shown earlier [2], appear in the outer layer during irradiation. They are due to structural rearrangements accompanying oxidation and may lead to cracking of the outer layer of the samples even before the start of the mechanical tests. The last effect is a consequence of the heterogeneity of the structure of the sample and therefore, for $x \rightarrow 1$ the deviations of the experimental findings from the dependence (6) diminish. All this confirms the decisive role played by the magnitude x in change in the physicomechanical properties of thick samples.

Unfortunately, the experimental evidence available does not allow us to state categorically that the strength at rupture of the thick samples depends only on the absorbed dose θ and the magnitude x. It may be that a certain influence is also exerted by the absolute value of the thickness of the oxidized layer δ which increases with fall in p. Nevertheless, the formation in the thick sample in the course of irradiation of an internal crosslinked layer for x > 0.2 does not raise its strength as compared with the thin uniformly oxidized layer. On the other hand, at quite high radiation doses the strength of such a heterogeneous system is lower than that of the film irradiated to the same dose. An important practical conclusion follows from this. Where the service stability of LDPE is determined by its strength, odd as it may seem, less thick products may be preferable.

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