A Scale Effect in the Durability of Oriented Thin-Wide Polypropylene Films during Oxidation under Load: Fracture Model of Stressed Polypropylene Films

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Studies have been made of the durability of oriented isotactic polypropylene (PP) films depending on their width during intensive oxidation ($T = 130°C$, $P_{O2} = 20$ kPa) under load. As the specimen width decreases under low stresses, mean durability is determined thermooxidative destruction rate at the nucleation sites the scale effect takes place. The durability values are found to be discrete multiples of integers for narrow specimens. The conclusion is drawn that the difference in polymeric specimen durability is determined by the concentration of defect zones, rather than by the versatility of their nature. The model of oriented PP films fracture under low-load oxidation conditions is proposed. This model is based on the dependence of durability on a number of oxidation destruction centers which are similar in nature (in the initiation rate) and cause specimen fracture while growing and joining together.

KEY WORDS Oxidation, polypropylene, films, load.

INTRODUCTION

The polymer fracture mechanism has been studied intensively so far, but nevertheless it still remains unclear. This is due to the complexity of the objects under investigation. The durability of materials depends on the size (a scale factor) and shape of the specimen, as well as on its chemical and physical properties. The complexity of testing techniques and materials studied corresponds to different theoretical approaches for studying fracture processes in solids.[1] The most significant advances have been made by the use of a kinetic strength theory,[2] but this does not take into account the influence of various random defects in real solids on their strength. In addition to the more or less regularly occurring structural defects (such as microfibrillar ends in the oriented polymer[3]), there are some statistically distributed random defects: inclusions of solid particles, voids, microcracks, and so forth. The influence of all these defects on material strength can be taken into consideration by using statistical methods.[1]

It is known that the properties at the surface of a solid differ from those in its

volume. So, the macromolecules have a higher orientation on the oriented polymer surface than in a block.[4] This may be responsible for the influence of a transverse dimension of a specimen on its strength.[5] The authors of Reference 6 however have supposed that the fracture mechanism changes in transition from large specimens to films. They have found, based on the statistical analysis of the durability of poly(ethylene)terephthalate films, that their durability has discrete values independent of stress. It is concluded that the most important process in the polymer film fracture is the formation of structure defects other than microcrack growth. The nature of these defects is not considered, although the possibility of their existence both in the volume and on the surface has been reported. As the specimen size decreases, the scale effect rises; this has been treated by other works.[7,8]

The conclusions above relate to mechanical fracture. The fracture mechanism of polymers in chemically aggressive atmospheres (in oxygen, for instance) is of special interest due to practical significance and the possibility of applying the local infrared-spectroscopy method. In References 9 and 10, where the durability of oriented PP films in the oxidizing medium at low stress is studied using this method, the local nature of fracture is found to be caused by nucleation-type polymer oxidation. It is shown[11] that potential fracture sites are not generated by stress, but already exist in a specimen during oxidation at low stresses. The stress only forms a site thus influencing the rate of propagation of oxidation reaction from the primary initiation center over the matrix. Thus, the local character of PP oxidation is a consequence of the microheterogeneity of the polypropylene structure and of the presence of statistically distributed primary initiation zones in it. Those include some foreign objects, such as transition metal compounds (polymerization catalyst residues, iron particles,[12-15]) which initiate the oxidation reaction. Such inclusions are localized in the least-ordered zones of the amorphous polymer phase, which have the highest reactivity.[15] This results in high initiation and oxidation rates at the nucleation sites. The confluence of suitably positioned sites leads to macroscopic sample fracture.

The random character of defects distribution manifests itself most clearly in a scale effect, which consists of an increase in the experimental data dispersion and in growth of the statistical mean strength of specimens with a decrease in their size. It arises, apparently, when two of three dimensions of a specimen (thickness and length or thickness and width) become comparable with the statistic mean distance between the defects. In this case the difference in concentration and the relative position of fracture sites in specimens results in a considerable disperse of durability. Let us consider this situation in more detail.

The isotropic film of small thickness (150 μm in our case) and of rather large length and width, as compared to the statistic mean distance between pointlike defects, can be considered as an infinite plane. Because of the random character of distribution of centers on the plane, their local concentration can be either higher, lower or equal to the statistical mean distribution. But if the specimen is large in size, the local deviations from the statistic mean distribution balance each other, so that their influence on the macroscopic properties of a body is not great.

Under orientation drawing of an isotropic film the defects are re-distributed as the distance between them grows in the film stretching direction and as the defects
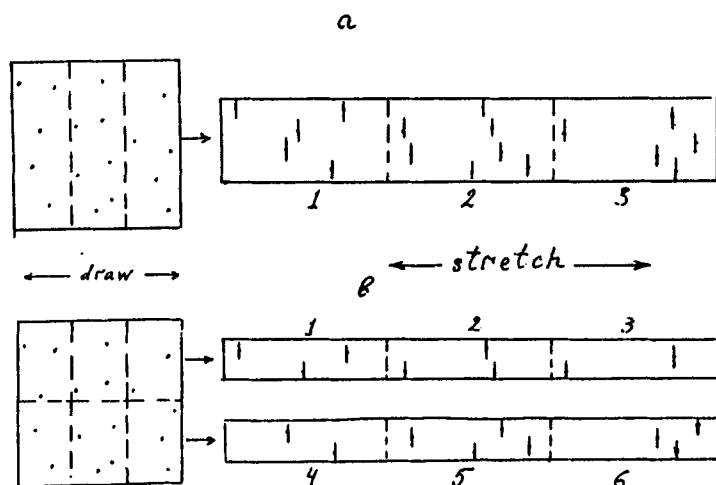
FIGURE 1   Distribution of primary initiation centers in isotropic and oriented specimens: (a) of standard size; (b) in narrow specimens. The vertical lines show the importance direction of the flows growth from primary initiation centers in the stressed films.

approach each other in the transverse direction (Figure 1). The character of distribution of sites changes and, apparently, some scale average distribution anisotropy should be observed, but the total number of sites remains the same.† And if the initial isotropic specimen is small in size and the concentration of sites in it differs from the statistic mean concentration, then the oriented film produced will conserve this difference (Figure 1b).

In the isotropic film of standard size (of width 10 mm) there exists a rather large number of sites, and in a standard oriented specimen 5 mm wide and 20 mm long (25 μm thick), obtained from this isotropic film, a group of sites is found with a rather high probability at the distance allowing the mergence of joining of sites along the interfibrillar layers during their growth (Figure 1a). The durability of such films is not high and varies within a rather narrow range.

If the specimen width (or length) becomes comparable with the distance between sites, then, as seen from Figure 1b, the number of sites and their relative position can differ considerably in neighboring specimens. This will result in the growth of the disperse of durabilities. The disperse of durability values takes place for standard samples as well; however, they can hardly achieve a high durability, which is possible for narrow films, because standard specimens include films with maximal density of sites.

Due to a higher maximum level of durability and to a denser population of high levels the statistic mean value of durability is higher for narrow then for standard films.

So, among six narrow films (Figure 1b) specimen 3 must probably have maximal durability, specimens 1 and 4 should have a slightly lower durability and then specimens 5, 6 and 2 should follow each other in order of decreasing durability.

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† An increase in the distance between sites during film drawing is, apparently, one of the reasons for a lower oxidation rate and for higher durability of oriented films as compared to isotropic ones.

This is a theoretical consideration. In reality, however, the durability of polymeric films depends not only on the number of fracture sites, but also on some structural factors. For this reason two similar samples—1 and 4—can obviously have different durabilities; at the same time we can expect with a rather high certainty that specimen 3 will have much higher durability than specimen 2.

In a previous paper[11] the authors did not consider the character of distribution of sites in a specimen in connection with its durability. The nature of centers was to be such that their primary initiation rates were to be different.

One of the most important problems is to find the relationship between the durability and the character of defects distribution in the sample as well as to determine their origin. This is necessary in forecasting the lifetime of polymeric products and in searching for effective ways of increasing their durability.

This paper analyzes in detail the scale effect with decreasing specimen width (the length is standard, the thickness is constant) and proposes the fracture model that relates durability with the number of defects of the same nature.

EXPERIMENTAL

The durability of the oriented IPP films (Moplen) with a density of 0.92 g/cm^3 and a draw ratio of $\lambda = 7$ and 9 at 130°C and $P_{O2} = 20$ and 80 kPa is measured as described elsewhere.[16] The content of carbonyl groups is determined by infrared spectroscopy on a sample area of 3.0 mm^2 with an infrared microscope on an UR-20 spectrophotometer and characterized by carbonyl index, i.e., the ratio between the optical densities of the 1710–1740 and 2720 cm^{-1} bands. The local values of the structural characteristics such as the crystallinity α are obtained from the 840 and 1170 cm^{-1} bands[17]; the ratio between the nonregular and regular conformers on the tie chains of the amorphous layers β is obtained from the ratio between the optical densities normal to the polarized 1155 and 810 cm^{-1} bands $(D^{\perp}_{1155}/D^{\circ}_{810})^{18}$; orientation of the crystal sites γ from the 840 cm^{-1} band[19] is determined by polarization infrared spectroscopy. The orientation drawing is performed by local heating at 130°C and annealing of the oriented films in the isometric conditions at 163°C in a vacuum.

RESULTS AND DISCUSSION

Figure 2 shows the dependence of the distribution of durability times for the oriented IPP films on the draw ratio and thermal treatment conditions and the width of a number of stresses. The durability levels are found to be independent on the draw ratio, thermal prehistory, oxygen pressure, i.e., on those factors which influence the oxidation rate. Since the rate of free radicals diffusion and mechanical initiation depend on the mechanical stress,[9] the durability levels are found to be affected by the load (Figures 2a,b and c). As the mechanical initiation contribution grows (Figure 2b), the data scatter for standard specimens increases. Because the growth of a single fracture site across a very narrow film requires less time than
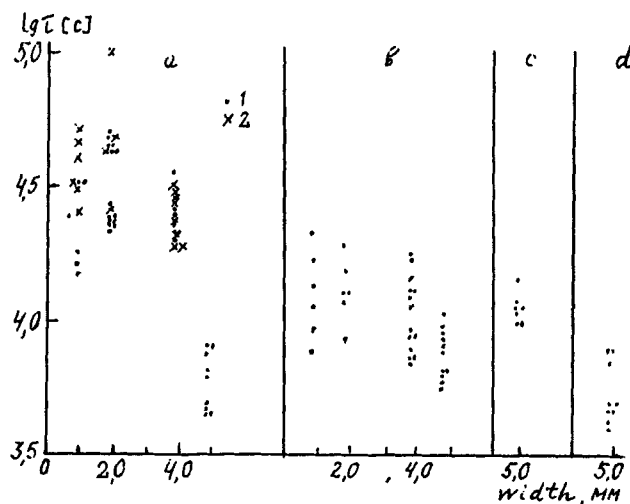
FIGURE 2 Range of durabilities for IPP films of various widths. λ = 7 (1) and 9 (2); σ = 5 (a), 26 (b) and 20 MPa (c), (d); 130°C; in experiments with 1.0–4.0-mm wide samples P_{02} = 20 kPa and with 5.0-mm wide samples P_{02} = 80 kPa; (d) annealed samples with λ = 7.

that across a wider specimen, we should expect the appearance of a maximum in the dependence of durability levels distribution on the width. Indeed, such a maximum is observed for a film 2.0 mm wide (Figure 2a). As in case of mechanical fracture,[6] the durability values are found to be discrete, which implies either the presence of defects of a different nature (the initiation rate and, hence, the oxidation intensity) in specimens, or a different number of defects. Table I presents the durability values for specimens of width 1.0 and 2.0 mm at stress of 5 MPa. These data clearly indicate the discrete character of durability values and, what is especially interesting, their multiplicity of integers.

For low stresses (5 MPa) the durability is determined by the time of oxidation growth of sites up to the size that make possible either their direct mergence or their joining along interfibrillar layers. The oxidation reaction propagates from primary initiation centers mainly due to physical diffusion of low molecular weight radicals-valency carriers, the diffusion rate being dependent on the structure at the center itself and in the adjacent area (at constant stress). In this case the topographic preconditions are necessary for the joining of centers, along with structural preconditions. In other words, the centers should not be situated at a large distance from each other. Thus, the durability should be determined by the size of defect zones and by their relative position, i.e., by the number of zones in some finite volume V.

Indeed, the data in Table 1 show the correlation between the durability, defect zone size and the depth of thermoxidation destruction in a zone before the fracture moment. These data do not explain, however, why the durability values are found to be multiples of integers. To explain this fact we have developed the following polymer fracture model.

Let us take the following assumptions: 1) The primary initiation centers are similar in nature (i.e., in the initiation rate) and have a submicronic size, so that

TABLE 1

Concentration of the oxidation products in the fracture and adjacent zones of the polymer and structural characteristics of these zones ($\lambda = 7$, $\sigma = 5$ MPa, 130°C, 20 kPa, sample width $= 2.0$ mm)

Sample Number	$\tau \cdot 10^{-3}$, s	D_{1710}/D_{2720}		D_{1740}/D_{2720}		D_{2720}		α		β		γ	
		Distance from the fracture point, mm											
		1	3	1	3	1	3	1	3	1	3	1	3
1	21.0	—	—	—	—	—	—	—	—	—	—	—	—
2	21.6	2.4	1.5	1.8	1.2	0.03	0.07	0.4	0.5	1.4	1.9	0.3	0.4
3	21.7	1.3	0.8	0.8	0.8	0.12	0.08	0.6	0.8	1.6	1.1	0.6	0.8
4	23.1	—	—	—	—	—	—	—	—	—	—	—	—
5	23.1	—	—	—	—	—	—	—	—	—	—	—	—
6	24.0	—	—	—	—	—	—	—	—	—	—	—	—
7	24.0	—	—	—	—	—	—	—	—	—	—	—	—
8	26.4	—	—	—	—	—	—	—	—	—	—	—	—
9	41.4	1.8	0.4	1.6	0.3	0.04	0.12	0.3	0.7	2.0	1.5	0.7	0.5
10	42.0	0.4	0.6	0.7	0.6	0.07	0.19	0.7	0.7	1.2	1.1	0.8	0.9
11	44.4	—	—	—	—	—	—	—	—	—	—	—	—
12	44.4	—	—	—	—	—	—	—	—	—	—	—	—
13	46.4	1.9	0.8	1.7	0.8	0.05	0.10	—	—	—	—	—	—
14	49.1	—	—	—	—	—	—	—	—	—	—	—	—
15	67.9	1.0	0.4	0.9	0.4	0.13	0.06	0.8	—	1.3	1.6	0.9	0.7
16*	—	—	—	—	—	—	—	0.6		1.0		0.8	

* Starting sample.

Note: The durability of 1.0-mm wide films ($\lambda = 8$) $\tau \cdot 10^{-3} = 15.9$; 24.8; 29.9; 30.7; 32.1; 39.7; 45.0; 50.4 s.
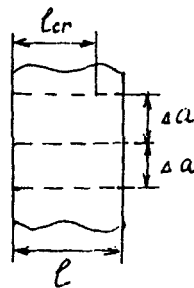

FIGURE 3   Illustration of the center-type fracture model. For explanations see the text.

their initial size can be neglected as compared to the final size of a center; the centers lie in less-ordered polymer zones. 2) The propagation rate of the oxidation reaction is the same for all centers, but differs in directions: the rate across the orientation is higher than that along the orientation.[20] 3) The specimen containing only one fracture center in volume V possesses maximal durability for the 1.0 mm width; the specimen of 2.0 mm width with a maximal durability fractures as a result of mergence of two centers in volume V. 4) The specimens with minimal durability are fractured by merging several centers which are situated in a polymer volume V at a distance of no more than Δa from some cross section (Figure 3); volume V $= 2\Delta \, a/T$, where T is the specimen thickness equal to 25 μm; 1 is the specimen

width; and Δa and T are constant for the given group of specimens (Δa depends on the specimen structure and on the stress). 5) The projection of final transverse dimension of centers on the cross section represents a continuous line whose length equals the critical length of a crack: 1. for 1-mm wide specimens $l_{cr} = 2/3$ 1 was determined spectroscopically from the dimensions of that 1-mm specimen part where the microcracks are not formed, thus indicating the absence of over-stresses; 2. for the 2.0-mm wide specimen $l_{cr} = 5/6$ 1. Thus, the durability is equal to the time of the oxidation reaction propagation from the primary initiation center to the distance, which is determined by the number of centers: $l_{cr}/n\omega$, where l_{cr}/n is the mean length of a defect zone near the primary center, and ω is the propagation rate of the reaction front. Therefore, the durability must be determined by finite dimensions of nucleation sites or by their number. For small width of a specimen, durability values τ should be multiples of integers.

Let us calculate the number of nucleation sites through which the catastrophic crack has propagated in specimens of 1.0 and 2.0 mm width, which possess different durabilities. Suppose that the specimen of 1.0 mm width, that has a maximal durability, is fractured as a result of growth of a single center and the 2-mm wide specimen due to the growth of two centers. We can then determine the rate of propagation of the oxidation reaction from the primary initiation center by known durability and critical size of a crack; $\omega = 2/3$ $1/\tau = 0.013$ μm/s (for width of 1.0 mm) and $\omega = 5/6$ $1/n\tau = 0.013$ μm/s (for width of 2.1 mm). Then the 1.0-mm wide films with durabilities of 15.9 10^3, 29.9 10^3, 39.7 10^3 s and critical crack size of 0.4, 0.75 and 0.5 mm, respectively, contain two centers in volume V and those with minimal durability contain six centers.

Thus, the calculation based on the assumption that the durability is determined by the number of defects of similar nature, yields quite reasonable results.

Various versions of relative position of centers along with the local features of structure yield experimentally observed values of durability for each group specimens (about ± 3.5 10^3 s; see Table I). This specific feature of each specimen manifests itself in the shape of a broken cross section (Figure 4). The complicated character of a fracture process, which results from the superposition and interaction of many factors (such as the strength and interaction of force fields against the background of local features of a structure at the supermolecular and molecular levels, the presence of random mechanical defects, etc.), makes it difficult, naturally, to determine the number of centers from the shape of a broken cross-section. But the extensive splitting of a specimen along fibrilles may be indicative of the joining of centers being at large distances from each other.

From this point of view the tabular data on the thermooxidation destruction depth and on structural characteristics of a fracture zone and adjacent area, as compared to the broken cross-section profile (Figure 4), can be explained as follows. The specimens possessing a great number of primary initiation centers have lowest durability. If these oxidation centers are close to each other (Figure 4, specimen 3), then the specimen fractures quickly with a relative small mean destruction depth in the catastrophic crack zone and in the adjacent area (see Table I). If this distance is large (Figure 4, specimen 2), then the mergence of centers with their partial joining along interfibrillar layers takes place at a higher degree of substance con-
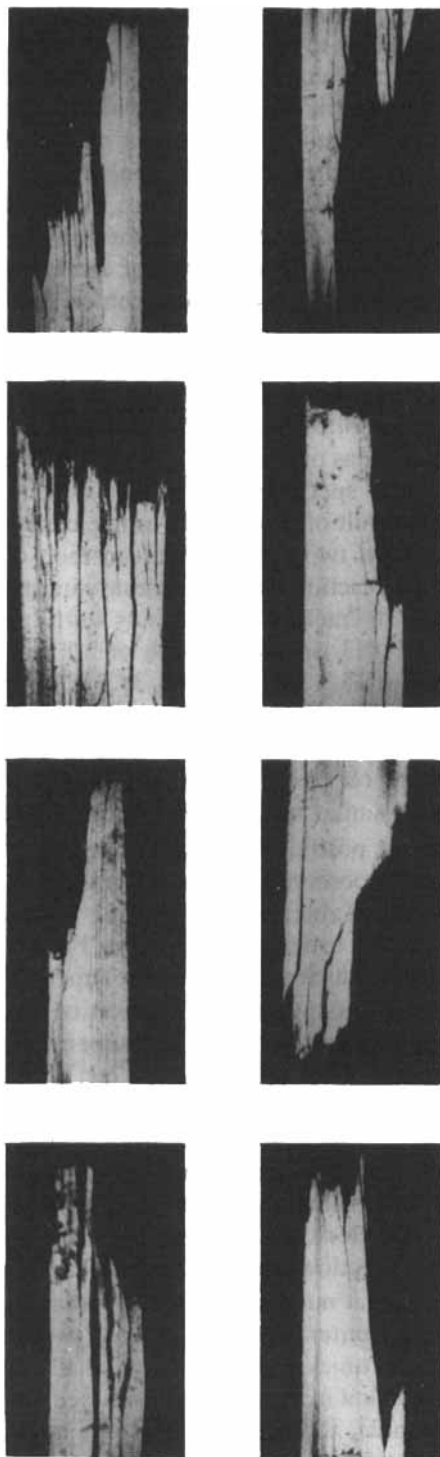
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FIGURE 4   Microphotographs of the IPP films fracture zones. Numbers correspond to the sample shown in Table I.

version in a broader zone than in the previous case. For a lower number of initiation centers (specimen 9) the expansion of centers up to their joining takes longer and occurs at a considerable oxidation depth. And, finally, if the number of centers is very small and the centers are at great distances from each other (specimen 15), the joining of centers occurs at a low degree of oxidation destruction in the fracture zone and in the adjacent area—by means of longitudinal crack growth along the nondurable interfibrillar layers.

Thus, this discrete character of durability values and their multiplicity of integers in a scale effect have allowed us to find a quantitative relationship between the durability and the number and position of statistically distributed primary initiation centers of similar nature, which originally existed in a specimen.

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