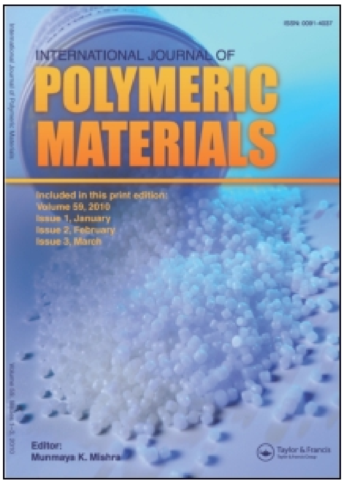

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

On the Nature of the Induction Stage in Polypropylene Oxidation

N. M. Livanova[a]; G. E. Zaikov[a]
[a] Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, ul., Moscow, Russia

To cite this Article Livanova, N. M. and Zaikov, G. E.(2000) 'On the Nature of the Induction Stage in Polypropylene Oxidation', International Journal of Polymeric Materials, 46: 3, 757 — 773
To link to this Article: DOI: 10.1080/00914030008033912
URL: http://dx.doi.org/10.1080/00914030008033912

Intern. J. Polymeric Mater., 2000, Vol. 46, pp. 757-773
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

On the Nature of the Induction Stage in Polypropylene Oxidation

N. M. LIVANOVA and G. E. ZAIKOV*

Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, ul. Kosygina 4, Moscow 117977, Russia

(Received 10 March 1999)

Propagation of fracture sites in stressed inhibitor containing polypropylene and the macrokinetics of oxidation of isotropic and oriented polypropylene films were studied. Localization of oxidation in the sites of primary initiation was considered. The induction period is given a new interpretation as the time of oxidation localized within the sites of primary high rate initiation at catalytic admixtures. The end of the induction stage is marked by the expansion of the oxidation reaction from the initiation sites and its propagation over the entire polymer. The mechanism of initiation of the kinetic chain process at this stage becomes controlled by the decomposition of hydroperoxides. An increase in induction period observed during orientation is explained by enhanced structure-related localization of the oxidation reaction within the initiation sites owing to morphological changes and by increased rigidity of the polymeric matrix.

Keywords: Polypropylene; oxidation; inhibition; macrokinetics; fracture sites

INTRODUCTION

Previously [1], in the course of studies of durability of oriented PP synthesized with various catalytic systems, the hypothesis was confirmed [2-4] that the initiation of polyolefin oxidation involves ions of transitional metals of the polymerization catalyst [5]. The complexones that form chelates with metal ions when used simultaneously with a chain-terminating inhibitor of radical reactions demonstrate a strong synergistic inhibiting effect on polymer oxidation [1]. This effect was

---

*Corresponding author.

attributed to a lower rate of primary initiation. Nevertheless, the calculations of the initiation rate at the catalytic centers in the primary deterioration sites (the number of these sites was accounted for) based on the data for durability under stress of both inhibitor- and complexone-containing polymers [6], disproved this hypothesis. It turned out that the rate of initiation of kinetic chains on the metal particles does not decrease, rather it is the total number of initiation sites that actually decreases. For such inhibitor- and complexone-containing polymers, durability under stress increases substantially and the macrokinetic parameters of polymer oxidation change dramatically.

The hypothesis put forward in [7] on the nature of the induction period assumed that the existence of the induction stage is due to changes in the initiation mechanism, and that primary initiation during the first stage of oxidation is further overshadowed by the hydroperoxide initiation during the autoacceleration stage. We suppose that the induction stage appears not only due to localization of primary initiation acts, but also due to structure-related and chemical (in the case of inhibited oxidation) localization of oxidation at the sites of primary initiation on the catalytic impurities. It is the degree of localization that governs the induction time. It is obvious that the induction stage depends also on the site concentration and their topology [6].

EXPERIMENTAL

Experiments were performed with isotropic and oriented films prepared from Russian polypropylene, Moplen (density of powder was 0.92 g/cm^3; melt index 2.2 g/min) and from Hungarian PP-2 produced in the Sumitomo gas-phase polymerization process. The latter polymer contained O.I wt% of Irganox-1010 inhibitor (ester of 3,5-di-tret-butyl-4-hydroxyphenyl propionic acid and pentaerythritol) with a synergistic agent [dilauryl ester of β,β^1-thiodipropionic acid (DLTDP)]. Isotropic films were obtained by molding on a laboratory press at 230°C with pressure of 150 atm. Orientational drawing was performed by local heating to 130°C [8]. The setup for durability tests was described in [8]. The kinetics of oxidation was studied with a static apparatus, incorporating a circular pump or water sorbate [9], using the method of oxygen consumption with a polymer sample having mass of 0.05 g. We defined the induction time as the time of consumption of 0.07 mol of oxygen per one kilogram of polymer. This oxygen consumption is marked on the kinetic curves (Fig. 2) with a horizontal dashed line. Oxidation of oriented films was performed at 150 and 163°C under isometric conditions. Orientation of the regular conformers of the molecular chains was evaluated by dichroism of the absorption band at 840 cm^{-1} (D_{11}/D_{1}) measured using polarization IR spectroscopy. The growth kinetics of the deterioration sites in inhibitor-containing oriented PP-2 was studied by optical transmission microscopy using a MIN-8 microscope (magnification of 6.3 × 16).

RESULTS AND DISCUSSION

Previously [10–12], inhomogeneity of oxidation in strained (both isotropic and oriented) PP films was discovered. This inhomogeneity revealed itself in local fractures of strained PP films. Topography of oxidation in [10–12] was studied by local IR spectroscopy with the spot area of 1 and 3 mm^2, obtained using either a microcondenser or an IR microscope. The sample was scanned with the IR beam. Local oxidation was characterized by the concentration of carbonyl groups accumulated by the time breakdown occurred. The lifetime of the films was close to the induction time, and the degree of oxidation of the film was on the average low (in the region of elastic deformations, *i.e.*, in region 1 of the durability isotherm [8]).

Results of these studies are presented in Figure 1 and demonstrate unambiguously that oxidation proceeded inhomogeneously. There are some sites of high rate of primary initiation. The degree of oxidation of the initiation sites and the bulk of the polymer varies substantially in both isotropic and oriented films of different structure (films drawn to different ratios and with different thermal histories were studied). In [11], similar results were obtained for samples the same draw ratio ($\lambda = 8.5$) as a function of the applied load.

Distribution of the reaction products along the film length (Fig. 1) indicates that for isotropic film, conversion in both initiation sites and the bulk of the polymer. Even at lower reaction times, is substantially higher than that in oriented film. Conversion decreases with the draw ratio of the film (Fig. 1) and with increased tensile stress (see [11],

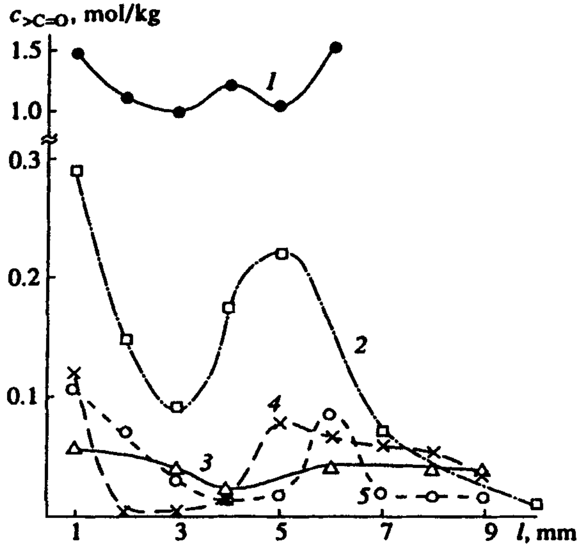

FIGURE 1 Distribution of carbonyl groups along the sample of Moplen PP film (for oriented films it is from failure cross-section): (1) isotropic, $T = 130°C$, $Po_2 = 150\,mmHg$, $\tau = 63\,min$; (2) oriented, $\lambda = 4-2$, $\sigma = 4.8\,MPa$, $\tau = 305\,min$; (3) drawn and annealed, $\lambda = 4$, $\sigma = 6.3\,MPa$, $\tau = 250\,min$; (4) oriented, $\lambda = 8$, $T = 120°C$, $\sigma = 17.0\,MPa$, $\tau = 223\,min$; (5) $\lambda = 8$, $T = 130°C$, $\sigma = 30.0\,MPa$, $\tau = 123\,min$.

Fig. 3). Obviously, with the similar nature of the initiation sites and, hence, the same initiation rates, the variation in the degree of oxidation of the bulk of the sample results from different structure-related localization of the reaction in initiation sites. The rate of reaction propagation over the bulk of the film depends on localization of oxidation. Because total volume of all initiation sites comprises a tiny fraction of the total polymer volume, the oxidation of polymer therein produces almost no effect on the overall consumption of oxygen measured manometrically with mercury-filled manometer. In Ref. [13] the oxygen consumption was measured by a high-sensitivity device (10^3 times more sensitive). It is obvious from these data that, during the induction period, the oxidation proceeds in the few nucleation sites around the particles of catalyst. The rate of oxygen consumption grows substantially when oxidation spreads from the initiation sites to the surrounding polymer matrix.

This explains the data on the changes in the relative share of the induction stage and the overall durability with variations in the mechanical stress (Fig. 2). As is seen, durability, which is governed by the rate of primary initiation at the sites where catalytic impurities are present, is almost constant, whereas the induction time varies substantially. Under low stress (lower than "frozen-in" residual stress) in conditions of partial relaxation of internal stress and enhanced mobility of molecular segments, the induction time is lower than durability. With growing stress, the rate of oxidation of the bulk of the polymer decreases and under sufficiently high stress, the induction time (τ_i) is higher than durability (τ_d) (at $T = 140°C$ and $Po_2 = 20\,kPa$ for Russian PP $\lambda = 7$ under $\sigma = 15\,MPa$, $\tau_l = 120\,min$ and $\tau_d = 68\,min$ and for inhibitor-containing PP $\tau_i = 560$ and $\tau_d = 440\,min$). This attests to oxidation being virtually locked within the initiation sites with the increase in mechanical stress. With an increase in rigidity of the polymeric matrix, a diminished segmental mobility, and an increased content of nonreactive regular conformers in the amorphous phase of the polymer, the rate of transfer of free valence (*via* transport of low-molecular-mass free radicals and relay transfers) diminishes, and the rate of transfer of kinetic chains decreases [7].

Thus, the end of the induction stage and the propagation to autoaccelerated oxidation means that the reaction spreads out of the primary initiation sites to the surrounding polymer. During the initial stage, the reaction is localized on relatively sparse (compared to the total

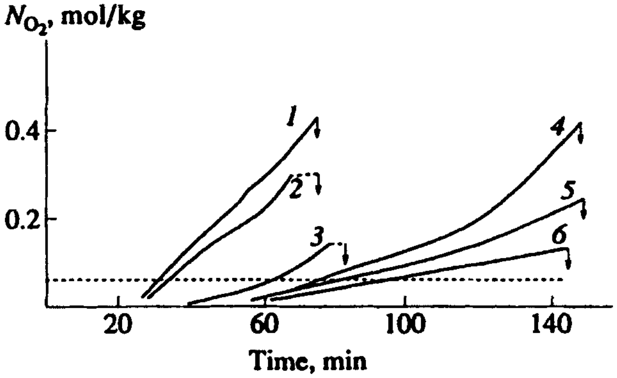

FIGURE 2 Kinetic curves of oxygen absorption by strained Moplen $\lambda = 8$ films. Failure of the film is indicated with an arrow. $T = 130°C$; $Po_2 = (1-3)$ 80 and (4-6) 40 kPa; $\sigma = (1, 4)$ 5.5, (2, 5) 7.3 and (3, 6) 10 MPa.

number of amorphous regions) initiation sites containing catalytic impurities and distributed over the bulk of the polymer randomly or according to some distribution law. Further, the reaction enters the stage where it is autoaccelerated in the bulk of the polymer due to decomposition of hydroperoxides produced by low-molecular-mass radicals that diffused from initiated sites. Previously [7], it was noticed that rate of primary initiation in oriented PP is high and virtually the same as that in isotropic polymer ($W_o = 10^{-8}$ mol/kg at 130°C).

This is readily explainable within the framework of the afore described picture of the process. In both cases, the mechanism of primary initiation is the same and involves the particles of a polymerization catalyst. In [5], it was shown that in the course of polymerization, the particles of a catalyst are dispersed to grains having the dimensions of hundreds of angstrom and enter the globules of the polymer, thus becoming randomly distributed in the isotropic polymeric matrix. In the course of orientational drawing of the polymer film the distribution of particles over polymer changes and middle-range anisotropy arises [14]: along the axis of the film site-to-site distances grow by a factor of L/L_0 (here L_0 and L are the lengths of the specimen before and after drawing); in the lateral direction, site-to-site distances diminish (approximately by two times at $L/L_o = 6-8$). As seen from Figure 1 the distance between maximum of carbonyl concentrations increase. The anisotropy is confirmed by the fact that the maximum dimensions of the sample, for which the scaling effects are still observable, are different; these dimensions are 14 mm along the film and 4 mm across [12, 14]. In the course of polymer crystallization and orientational drawing of the film, the particles of the catalyst are expelled to the least ordered and most reactive regions of amorphous phase. These regions constitute the cores of the initiation sites. Microheterogeneity of the polymer structure and hindered molecular mobility facilitate localization of the reaction within the initiation sites. The degree of localization depends on the morphology of the sample. It differs for isotropic and oriented films. Localization is higher in samples of greater orientation and it diminishes in an annealed sample (Figs. 3 and 4).

With higher orientation of taut tie molecules ((Fig. 3), lower mobility of segments (described by the correlation time of nitroxyl radical probe [15]) and stronger conformational restrictions [7], the reaction grows more localized within the initiation sites, permeabil-

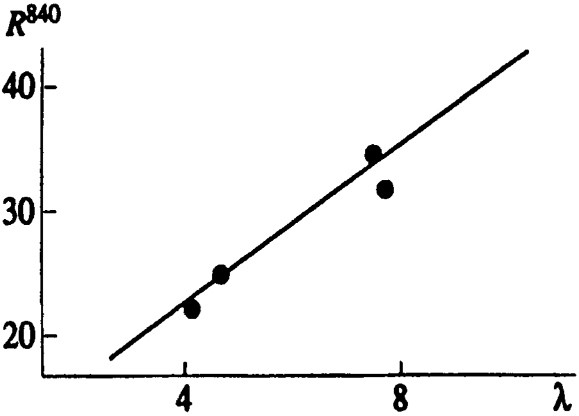

FIGURE 3 Dichroism of the 840 cm^{-1} absorption band of PP regular conformers *vs.* draw ratio.

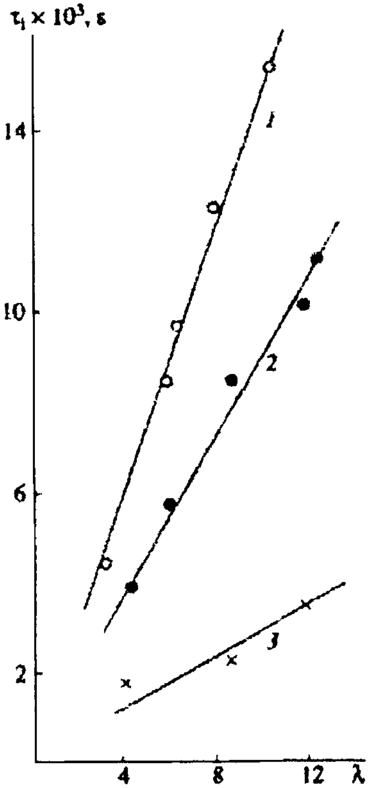

FIGURE 4 Induction time of oxidation in oriented PP films (Moplen) *vs.* draw ratio. $T = 130°C$, $P_{O_2} = 80$ kPa. 1 is dependence for as drawn films under isometric oxidation. 2 and 3 are dependences for drawn and annealed films. Annealing was performed at (2) 150 and (3) 163°C under isometric conditions.

ity of the polymer matrix to low-molecular-mass radicals diminishes, and the induction time increases (Fig. 4). Low-temperature annealing (150°C) virtually does not affect the long periodicity in the polymer [16], however, it facilitates relaxation of residual stress on taut tie molecules. This results in an increased transfer rate of the low-molecular-mass radicals in the matrix and growth of the induction time in annealed samples. Under high-temperature annealing (163°C), diffusion mobility of radicals is further promoted by emergent layered structures [16]. This results in a substantional decrease in induction time. All curves direct to coordinate origin. If we assume the sample with $\lambda = 0$ but possessing the structure of oriented one the induction stage of its oxidation must be zero. This shows that the value of τ_i is determined not only by structure but site-to-site distance, *i.e.*, their topographie.

Other kinetic characteristics of polymer oxidation, as well as the induction time, change due to orientational drawing (Fig. 5). At a higher draw ratio, the autoacceleration stage (the stage after the induction time and before a steady-state oxidation rate is established) also spans a longer time period.

The ratio of the volume of oxygen absorbed during the autoacceleration stage ΔN_{O_2} to the time-length of this state t_a, is virtually orientation-independent (see Tab. I), *i.e.*, the rate of reaction propagation from centres of primary initiation through the matrix are nearly the same for all λ. This is apparently due to the fact that diffusion of low-molecular-mass radicals and relay transfer of kinetic chains are possible within disordered amorphous regions. In this case,

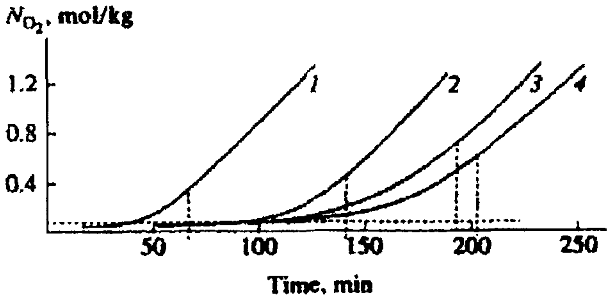

FIGURE 5 Kinetics of oxygen absorption by PP films. $T = 130$°C, $P_{O_2} = 20$ kPa, isometric oxidation. λ = (1) 0, (2) 4.5, (3) 7.0 and (4) 9.0.

TABLE I The macrokinetic characteristics of oxidation of PP films

λ	τ_l, *min*	t_a, *min*	ΔNo_2, *mol/kg*	$(\Delta No_2/t_a)\ 10^{-4}$, *mol/kg s*
0	33	29	0,26	1,5
4,5	70	74	0,50	1,1
7,0	90	110	0,85	1,3
9,0	110	105	0,78	1,2

the dependence of the length of the autoacceleration stage on draw ratio (see the table) may be caused by a changed spatial distribution of catalytic centers, namely, by increased site-to-site distances in the drawn polymer. The farther apart the induction sites are located, the more time it will take for the radical reaction to spread over the entire volume of the polymer. When equilibrium concentration of peroxy radicals is attained in the polymer matrix, the reaction enters the steady-state stage of oxidation. The maximum rate of oxidation is virtually the same for all samples, regardless of the draw ratio and polymer morphology. This could be explained by local fracture produced in isometrically-oxidized films by the internal stress and by the relaxation processes, which tend to level the kinetic dissimilarities of various samples.

Inhibitor-containing films demonsrate much higher localization of reaction within the initiation sites than the samples without the inhibitor. In [17], formation of through holes in stabilized films was observed in Hungarian PP-2 films produced in the Sumitomo process and oxidized to a complete failure. Thus, when complete burnout of polymer material is attained in the initiation site, no apparent oxidation is observed in the polymer bulk. This could be explained only due to high activity of catalytic system and by the high localization of reaction within the initiation sites in the presence of inhibitors (Irganox and DLTDP). In the inhibitor-free films oxidized to failure, through holes were never observed. In these films, localization of the reaction is low and the radical process soon spreads over the entire matrix well before complete degradation of the polymer occurs within the initiation sites.

The above consideration is confirmed by microscopic studies of time evolution of the sites in stabilized films of PP-2 until the failure of the sample (Fig. 6) these experiments also revealed some peculiarities of the deterioration mechanism in oriented polymers.

The deterioration of oxidized and strained PP films proceeds by coalescence of the sites with a high, rate of thermooxidative degradation of the polymer [14]. In [17], deterioration of the sample by direct merging of the sites *via* interfibrillar layers was modeled. Time of oxidation to failure depends on the rate of degradation within the sites (*i.e.*, the rate of primary initiation [1, 6, 14]), total number of the sites, and site-to-site distances [6, 14]. The time of merging of the sites *via* low-strength interfibrillar layers is short and for nonstabilized PP films it was 10 – 20 min [18]. In the case of oxidation of stabilized films, the time of merging of the sites is likely to be a small fraction of the total time required for the growing sites to attain the size when their projections onto the cross-section of the sample make a percolating cluster [17].

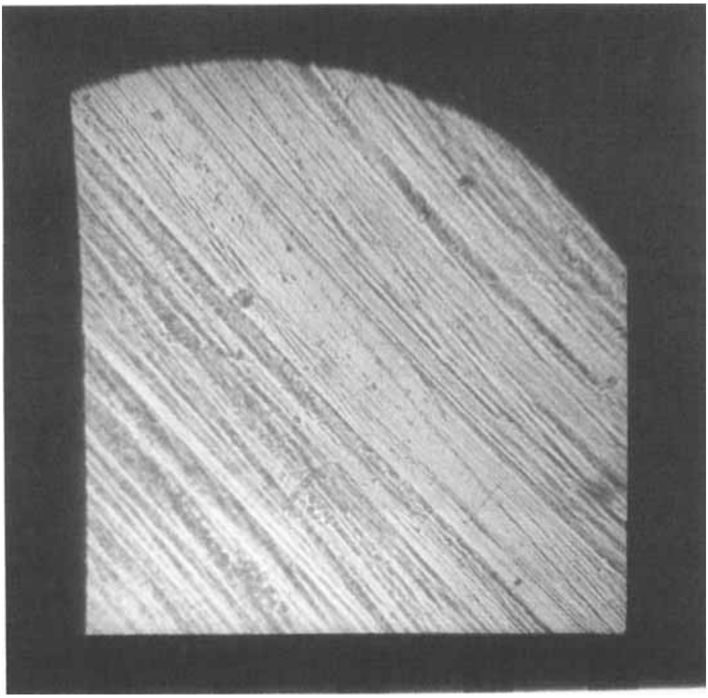

FIGURE 6 Microphotographs of loaded PP film containing inhibitor ($\lambda = 7.5$). Oxidation time is (1) 346, (2) 561, (3) 656, (4) 666, (5) 671, (6) 680 (the film is temporarily unloaded), (7) 690 and (8, failure) 710 min. $T = 120°C$, $PO_2 = 20\,kPa$, $\sigma = 15\,MPa$.

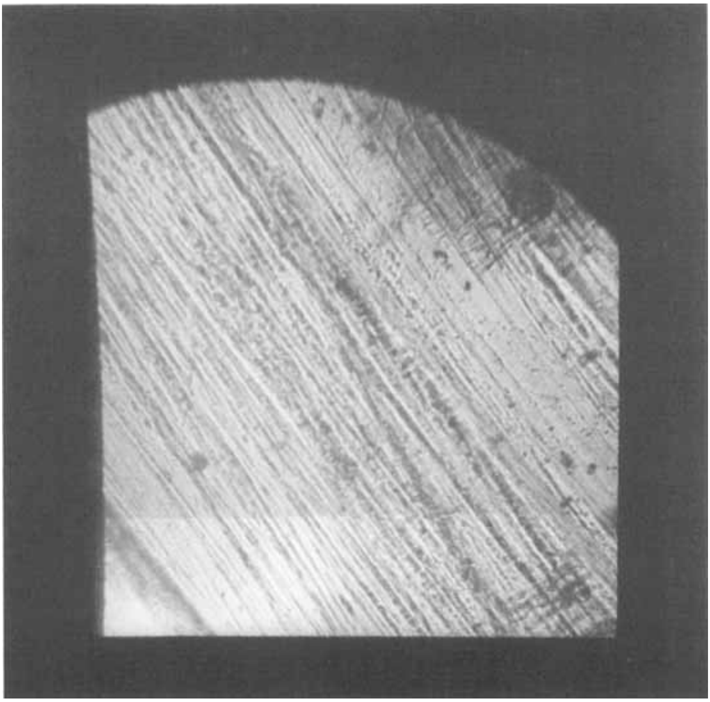

FIGURE 6 (Continued).

In oxidation of inhibitor-containing films, owing to the high rate of primary initiation, the inhibitor is consumed in initiation sites much faster than in the surrounding matrix. It was shown in [12, 19] that failure of the film occurs long before the inhibitor is consumed in the bulk of the polymer. Inhomogeneity of the inhibitor distribution in the polymer is likely to result in durability being governed by the rate of consumption of the inhibitor in stabilizer-deficient initiation sites. By the time the sample fails, the inhibitor in these sites has burned out completely and oxidation has reached deep stages (to complete the burnout of the polymer with the through holes being formed [17]). Figure 6 shows the stage-by-stage initiation, growth, and coalescence of the sites resulting in macroscopic failure of the sample.

The longest stage is the consumption of the inhibitor within the initiation site and development of the process to complete conversion

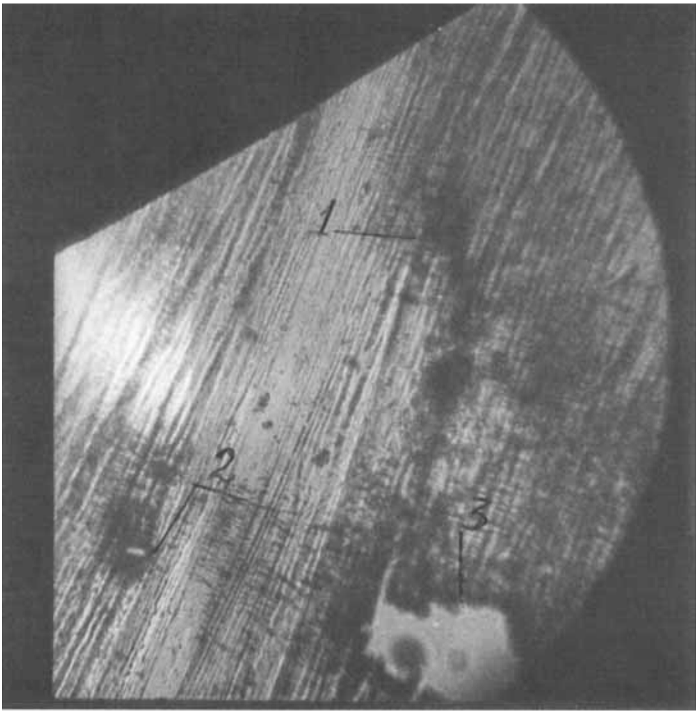

FIGURE 6 (Continued).

of the polymer therein (ca. 80% of durability). The sites differ in degree of oxidation (Fig. 6, image 3). Conversion within a site apparently depends on the concentration of the inhibitor, transport of inhibitor from the surrounding matrix to the site, and structure-related and chemical localization of oxidation in a particular site, *i.e.*, on supermolecular structure of the polymer, molecular-level structure of amorphous layers, and concentration of inhibitor in polymer matrix. At the same time there exist sites where the induction stage is already over, yet the oxidation did not developed to high conversion (Fig. 6, image 3, site 1) and sites where complete conversion of polymer occurred (sites 2 and 3) with various degrees of expansion of the process from the sites to surrounding material. Depending on chemical and structure-related containment of the process within the sites, the latter

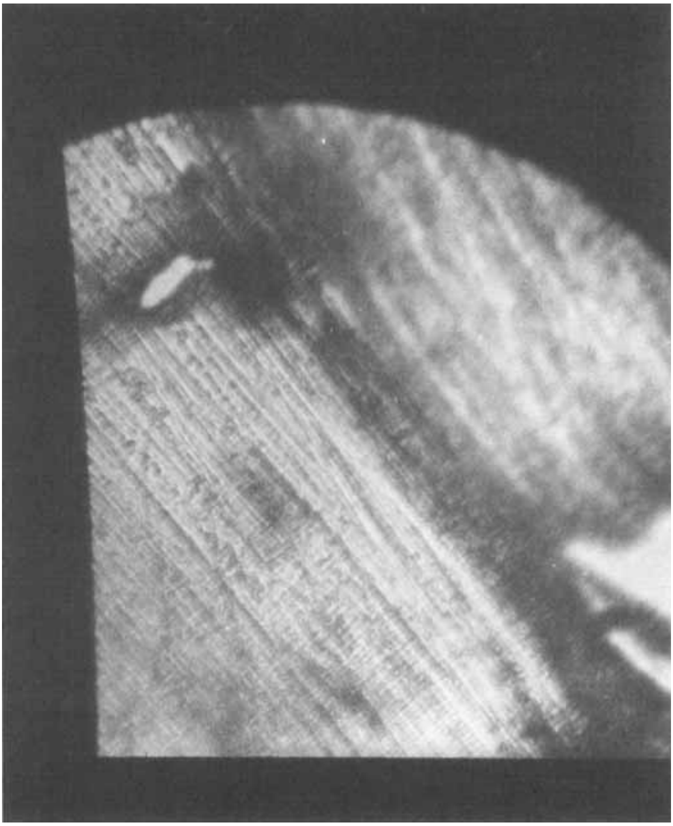

FIGURE 6 (Continued).

have various sizes. Apparently, the more isolated a site is, the smaller it is (site 2); the higher the concentration of the inhibitor within a site, the lower the rate of its growth (site 1).

Merging of the sites occurs predominantly by thermooxidative degradation and mechanical rupture of macromolecules in amorphous interfibrillar layers. Oxidation propagates primarily in a direction perpendicular to the orientation axis [20]. The sites that have grown over certain area diminish the "living" cross-section of the sample, the concentration of overstressed taut tie molecules in the cross-section increases, and this arrests propagation of the reaction front in the

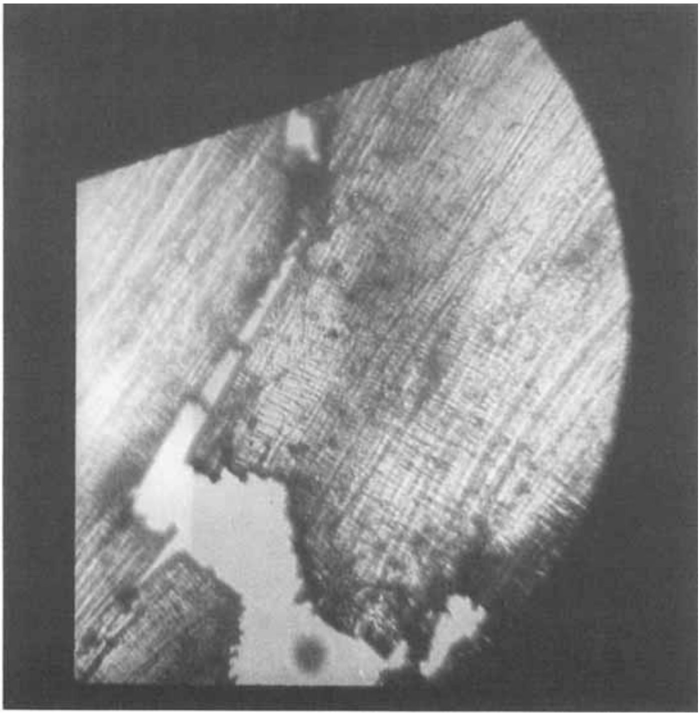

FIGURE 6 (Continued).

lateral direction; growth of the site ceases (Fig. 6, images 5 and 6, site 3). Thus, two adjacent sites in the same cross-section can not merge (image 3, sites 2 and 3). Merging of the sites located in different cross-sections is preferential *via* interfibrillar layers (sites 1 and 3), despite the fact that in one of them (site 1) developed with a substantial time lag (about 100 min). During the last 6% of durability ($\approx$ 45 min), the propagation of a major crack occurs across the initiation sites located in various cross-sections. This yields a characteristic step-shaped pattern of the fracture cross-section in oriented PP films [14].

In the micrographs (image 2) one can see that by the time the oxidative degradation of the polymer has developed to deep stages within initiation sites (80% of durability), the surrounding matrix

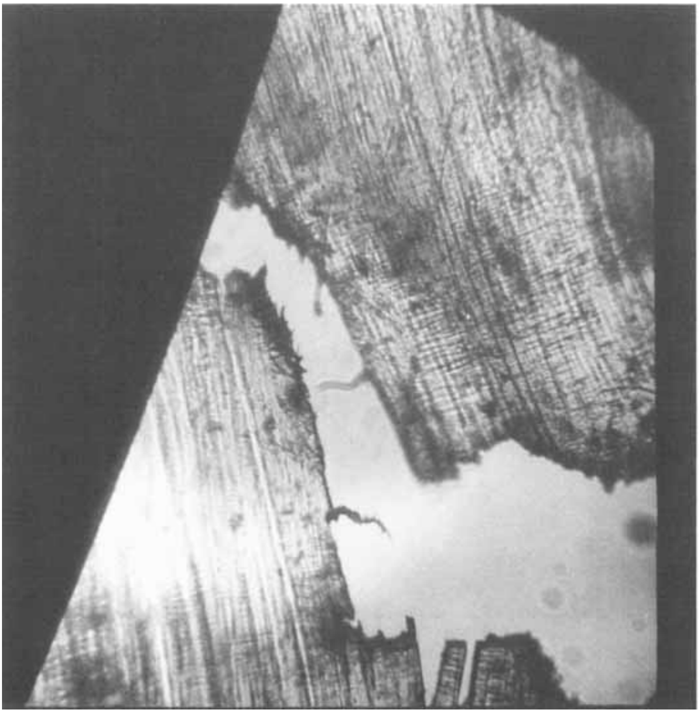

FIGURE 6 (Continued).

looks like it was not oxidized at all. Measurable oxidation of the matrix was not observed until 92% of durability, even in the domain of propagation of the fatal crack (image 4). Thus, localization of oxidation within initiation sites ii stabilized samples was high. This accounts for high induction times of inhibitor-containing polymer.

Chemical localization is most effective in diminishing the rate of polymer oxidation when it is complemented by structure-related localization. Microscopic studies of fractures in stabilized PP films provide an evident visual illustration for the afore described concept of the mechanisms responsible for the induction time in oxidation of the polymer, since these studies show localization of oxidative degradation at the sites of primary initiation on catalytic impurities.

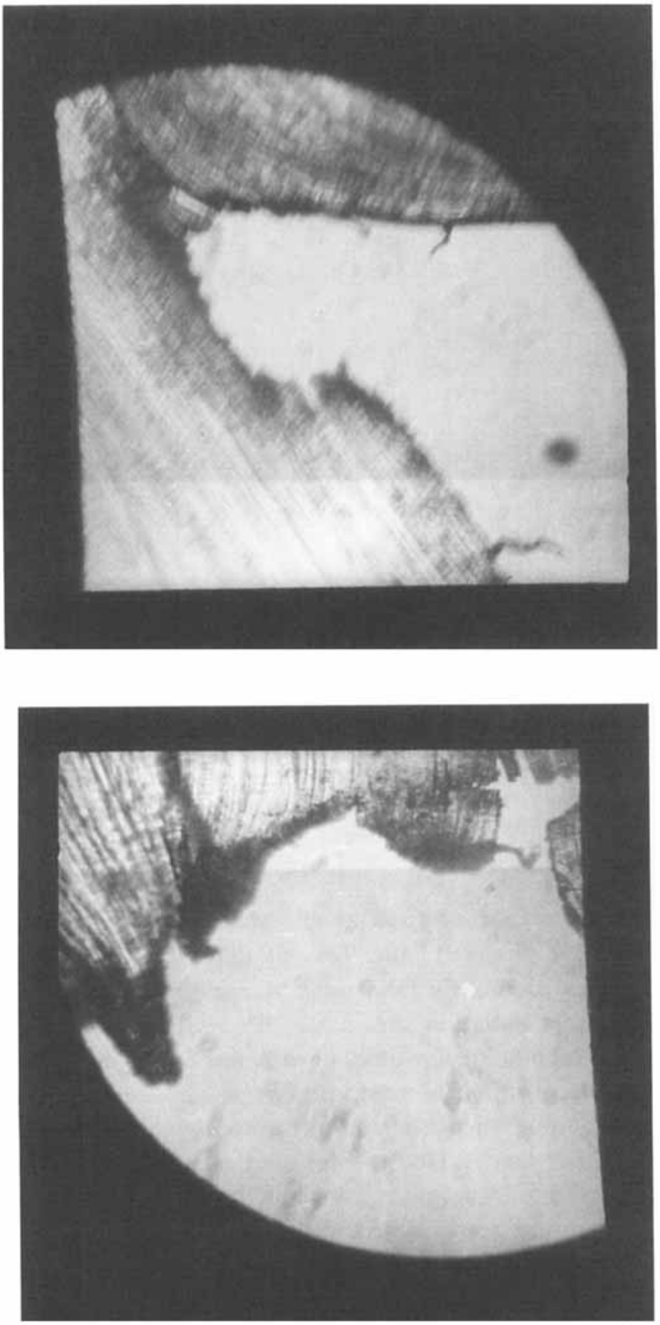

FIGURE 6 (Continued).

References

[1] Livanova, N. M., Nikolaeva, N. Yu., Gavrilov, Yu. A., Mukhina, O. V., Vol'eva, V. B., Kosikhina, S. A., Lebedeva, E. D. and Zaikov, G. E. (1993). *Plast Massy*, No. 2, p. 54.

[2] Richters, P. (1970). *Macromolecules*, **3**(2), 262.

[3] Van Sikie, D. E. (1972). *J. Polym. Sci.*, Part A-1. **10**(2), 355.

[4] Bilingham, N. C. (1985). *Polymer*, **86**(II), 1713.

[5] Bukatov, G. D., Zailkovskii, V. I., Zakharov, V. A., Kryukova, G. N., Fenelonov, V. B. and Zagrafskaya, R. V. (1982). *Vysokomol. Soedin. Ser. A*, **24**(3), 542.

[6] Livanova, N. M. and Zaikov, G. E. (1997). *Polymer Degradation and Stability*, **57**(1), 1.

[7] Rapoport, N. Ya. (1986). *Doctorate (Chem.). Dissertation*, Moscow: Inst. Chem. Phys. Acad. Sci. SSSR.

[8] Livanova, N. M., Rapoport, N. Ya., Miller, V. B. and Musaelyan, I. N. (1976). *Vysokomol. Soedin. Ser A*, **18**(10), 2260.

[9] Edemskaya, V. V., Miller, V. B. and Shiyapnikov, Yu. A. (1973). *Vysokomol. Soedin. Ser. A*, **15**(9), 1959.

[10] Livanova, N. M., Grigor'ev, A. G., Zaikov, G. E. and Rapoport, N. Ya. (1983). *Vysokomol. Soedin. Ser. A*, **25**(8), 1742.

[11] Rapoport, N. Ya., Livanova, N. M., Grigor'ev, A. G. and Zaikov, G. E. (1983). *Vysokomol. Soedin. A*, **25**(10), 2188.

[12] Livanova, N. M., Rapoport, N. Ya. and Zaikov, G. E. (1988). *Vysokomol. Soedin. Ser. A*, **30**(8), 1640.

[13] Shanina, E. L., Roginskii, V. A. and Miller, V. B. (1979). *Vysokomol. Soedin.* **21B12**, 892.

[14] Livanova, N. M. and Zaikov, G. E. (1992). *Polym. Degrad. Stab.*, **336**(2), 515.

[15] Rapoport, N. Ya., Berilava, S. I., Kovarskii, A. L., Musaelyan, I. N., Ershov, Yu. A. and Miller, V. B. (1975). *Vysokomol. Soedin. Ser. A*, **17**(11), 2521.

[16] Marikhin, V. A. and Myasnikova, L. P. (1977). Nadmolekulyarnaya Struktura Polimerov (Supermolecular Structure of Polymers), Leningrad: Khimiya.

[17] Rapoport, N., Livanova, N., Balogh, L. and Kelen, T. (1993). *Int. J. Polym. Mater.*, **19**(1/2), 93.

[18] Livanova, N. M., Rapoport, N. Ya. and Miller, V. B. (1978). *Vysokomol. Soedin. Ser. B*, **20**(7), 503.

[19] Livanova, N. M., Rapoport, N. Ya. and Zaikov, G. E. (1989). *Plast. Massy*, No. 7, p. 59.

[20] Regel, V. R., Slutsker, A. I. and Tomashevskii, E. E. (1974). Kineticheskaya Priroda Prochnosti Tverdykh Tel (The Kinetic Nature of Strength of Solids), Moskow: Nauka.