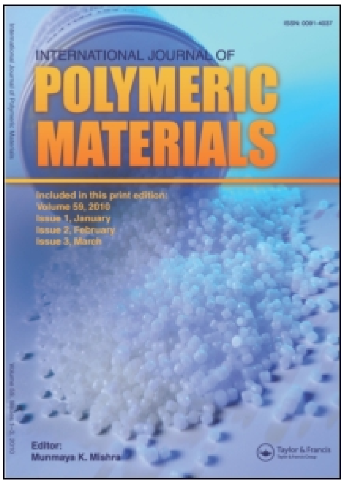
This article was downloaded by:
On: *19 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

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

Induction Period of Oxidation and Mechanism of Fracture of Polyolefins under Mechanical Stress

N. Rapoport[a]
[a] University of Utah, Salt Lake City, Utah

To cite this Article Rapoport, N.(1993) 'Induction Period of Oxidation and Mechanism of Fracture of Polyolefins under Mechanical Stress', International Journal of Polymeric Materials, 19: 1, 93 — 100
To link to this Article: DOI: 10.1080/00914039308012020
URL: http://dx.doi.org/10.1080/00914039308012020

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Intern. J. Polymeric Mater., 1993, Vol. 19, pp. 93–100
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in Malaysia

Induction Period of Oxidation and Mechanism of Fracture of Polyolefins under Mechanical Stress

N. RAPOPORT
University of Utah, Salt Lake City, Utah

(Received June 25, 1992)

Induction period of oxidation of solid polyolefins and mechanisms of fracture under mechanical stress are reviewed. It is proposed that the existence of a true induction period at the uninhibited oxidation of solid polyolefins should be attributed to uneven spatial distribution of oxidation sites and slow migration of radicals through the solid polymer matrix. The fracture of the stressed samples is the result of coalescing of damaged zones dispersed in the intact polymer matrix into clusters.

KEY WORDS Polyolefins, oxidation, induction period, mechanical stress, fracture mechanisms.

1. GENUINE INDUCTION PERIOD OF UNINHIBITED OXIDATION OF POLYOLEFINS

Autooxidation of solid polyolefins proceeds with a true induction period even when inhibitor is not added to a polymer[1]; the kinetic regularities of the initial stage of oxidation are quite different from that of the developed stage; the oxidation at the initial stage develops much slower than would correspond to the parabolic kinetic law characteristic of the developed stage (Figure 1c).[1] This initial stage (from the beginning of oxidation till the onset of parabolic law) was called the *genuine* (or true) induction period of oxidation (as distinct from the "instrumental" induction period, that depends on the sensitivity of the instrumental method of measuring oxygen consumption).

The duration of the induction period depends on polymer morphology: e.g. the induction period of oxidation of PP films with large spherulites is substantially longer than that of films with small spherulites.[2]

Polymer stretching also effects the induction period of oxidation: the higher the degree of stretching, the longer the induction period of oxidation of unannealed films (Figures 1a and 2).[1,3] The annealing of stretched polyolefin films close to the melting point in isometric conditions induces substantial decrease in the induction period (Figure 1b).[1,4]

The reason of the deviation of the kinetics of the initial stage of autooxidation

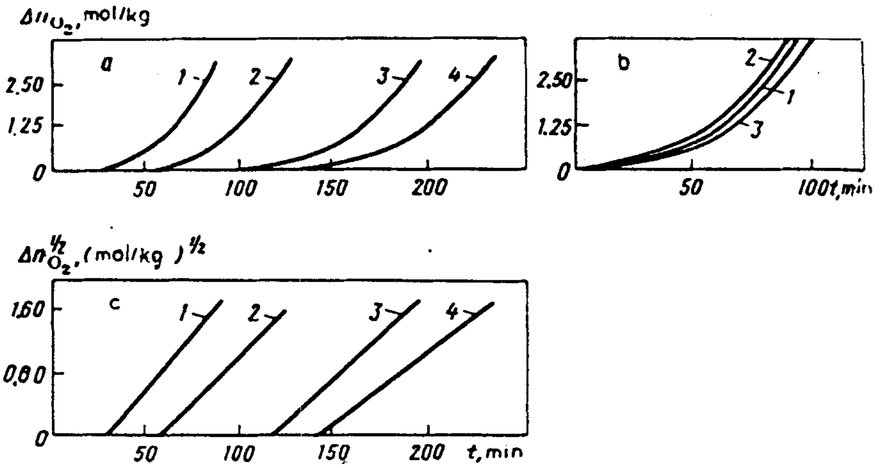


FIGURE 1 Kinetic curves of oxygen absorption in PP oxidation; 130°C, P_{O_2} = 600 mm Hg; degree of stretching λ = 1 (1), 5.5 (2), 10 (3) and 13 (4); (a)-unannealed samples, (b)-annealed samples; (c)-linear plot of kinetic curves in (a).

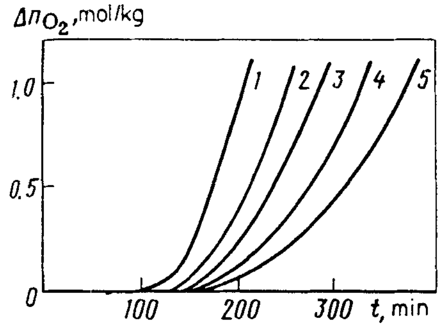


FIGURE 2 Kinetic curves of oxygen absorption in PMP oxidation; 130°C, P_{O_2} = 600 mm Hg; λ = 1 (1), 5 (2), 8 (3), 10 (4) and 13 (5).

from the regularities characteristic of the developed stage (and that of a liquid-phase oxidation) was not clear and stimulated a lot of discussions.[1,5–7]

Investigation of polypropylene oxidation under external stress revealed essentially uneven spatial distribution of the oxidation products (Reference 1, pp. 189–217) bound to *the heterogenous initiation of radicals, which apparently is the true cause of the differences in the kinetic regularities of the initial and developed stages of oxidation.*

The dependence of PP durability (time to break) on the value of applied stress, in oxygen at 130°C is given on Figure 3a. One can see, that in the region of low stresses the durability does not depend on stress and is many orders of magnitude lower, than that in an inert atmosphere. It is evident, that in this stress region polymer failure proceeds as a result of oxidative, and not mechanical degradation. In accordance with that, the durability in low stress region can be increased manyfold by the introduction of inhibitors (Figure 4).[8,9]

It was found, that *a substantial part of an initially introduced inhibitor was not*

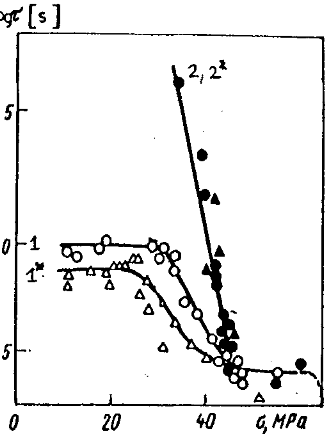


FIGURE 3 Durability isotherms of stretched PP: 1,1*—intense oxidation; 130°C, P_{O_2} = 600 mm Hg; 2, 2*—vacuum; 1, 2—unannealed samples, λ = 7; 1* and 2*-annealed samples.

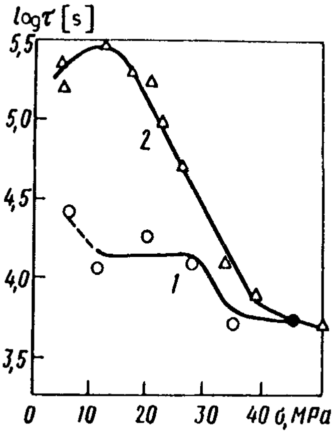


FIGURE 4 Durability isotherms of stretched PP (λ = 7) in the absence (1) and presence (2) of an inhibitor Nonox-WSP, 2.5 × 10^{-3} mol/kg; 130°C, air; ●—durability of an inhibited sample in vacuum.

consumed and stayed in the sample at the moment of fracture.[8] In accordance with that, the second durability *t* (2) of the parts of a broken sample was still much longer, than the durability of uninhibited samples; for example, the primary durability for inhibited samples, *t* (1) was 153,200 s, secondary durability, *t* (2) = 59,900 s whereas for uninhibited samples *t* (1) was more than twice lower and equaled to 22,000 s (PP, 130°C, σ = 5 MPa, air; inhibitor-Nonox-WSP, 2.0 × 10^{-3} mol/kg).

This implies, that *the oxidation of inhibited stretched PP proceeds unevenly in space*: in some zones of the sample inhibitor is quickly consumed, chain oxidation develops and leads to deep degradation, whereas in other zones of the sample there exist still a lot of an inhibitor and the polymer is not involved into the degradation process.

The combination of degraded zones into the percolation cluster leads to polymer fracture.

The investigation of the distribution of the oxidation products in the stretched PP films, oxidized up to the fracture under the external stress, confirmed this scenario. The distribution of the oxidation products in the stretched PP films is schematically represented on Figure 5: the degree of oxidation is approximately the same at different points along the fracture zone, but drops drastically with the increasing distance from the fracture zone. The higher the external stress, the more localized the oxidation reaction by the moment of fracture in the vicinity of the fracture zone (at the same oxidation time!).[9] One can anticipate, that PP oxidation starts at some special points and proceeds from those points throughout the sample at a rate that depends on stress value: the higher the stress, the lower the rate of reaction propagation along the stress direction. Hence the higher the stress, the lower the average degree of sample oxidation at the moment of fracture (at the same durability!). One could anticipate that the average rate of PP oxidation decreases with increasing stress. However it is much more likely that the reason of the phenomena is the decreasing rate of active center diffusion along the stress direction (the spreading of oxidation reaction throughout the solid polymer matrix

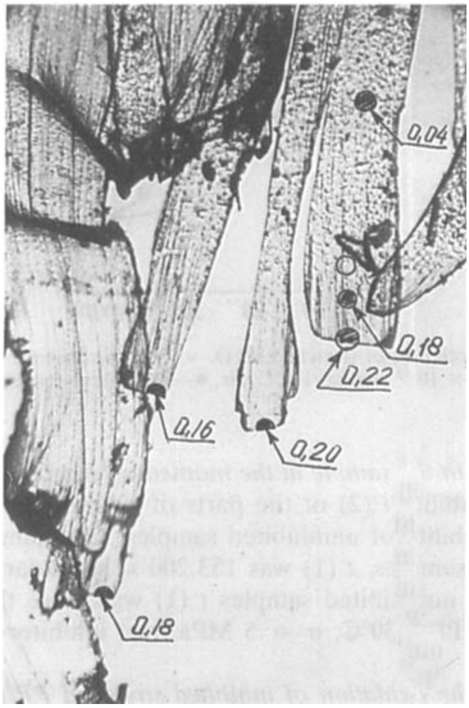


FIGURE 5 Schematic representation of the distribution of oxidation products in the fracture zone of stretched PP; numbers correspond to optical densities at the maximum of carbonyl absorption bands: along the fracture zone (perpendicular to the stress direction), and along the fibrils (e.g. along the stress direction).

proceeds by the way of migration of small "jogger"-radicals, born in the process of oxidative degradation).

As a result of a local initiation the real polymer volume, involved into the initial stage of oxidation, may be some orders of magnitude lower than the whole volume of the sample. *At the initial stage of oxidation two processes are proceeding simultaneously; the increasing degree of oxidation inside the regions involved in the chain process, and the spatial propagation of the reaction front.* We anticipate, that local initiation is the main reason of the deviation of the kinetics of the initial stage of oxidation from the regularities, characteristic for the developed stage. Shanina *et al.* observed very fast peroxide radical decay at the initial stage of polypropylene autooxidation and anticipated that rate constant of radical decay depends on hydroperoxide concentration.[6] Our data show, that the most probable reason for the phenomena, observed by Shanina *et al.*, was the drastic deviation of actual, local radical concentrations at the initial stage of oxidation from the average values, used in the calculations of rate constants. In fact measuring "rate constants" of peroxide radical decay at increasing degree of oxidation is the way to follow the space propagation of the reaction: *the onset of the constant value of the measured "rate constant" of peroxide radical decay may serve as a fingerprint of the moment when the whole volume of the polymer becomes involved into oxidation and the difference between the local and average radical concentrations is eliminated.*

FIGURE 6 Microphotograph of through holes formed in stretched inhibited PP at oxidation under stress; 140°C, air, σ = 15 MPa, durability τ = 198 min. Inhibitor—Irganox 1010.

Thus, we believe that the main reason for the existence of the true induction period at the uninhibited oxidation of solid polyolefins is a local initiation and slow migration of radicals through the solid polymer matrix. On this basis one can explain *morphological effects* in polyolefin autooxidation (e.g., the dependence of the induction period of oxidation on spherulite size, on the degree of stretching, polymer thermal history etc.): with local initiation the propagation of the reaction front at the initial stage of oxidation depends on radical migration rate and hence on polymer morphology.

In the case of inhibited oxidation the distribution of the initiation "points" in the samples was directly visible: inhibitor was quickly consumed at the initiation centers, after which chain autooxidation in these foci proceeded at a high rate until the substance was completely burned out (Figure 6). Meanwhile in the surrounding matrix the only source of radicals was their diffusion from the zones with high oxidation rate. On the way from initiation centers radicals were trapped by inhibitor molecules, and until the inhibitor was consumed in some volume, chain oxidation did not start there; thus the front of oxidation was slowly moving from the initiation points throughout the polymer matrix.

The distribution of initiation centers is highly uneven in space: in some cross-sections of the sample one can find numerous holes, in others there are none at all. In accordance with that, a pronounced scale effect was found in PP durability: the durability significantly increased with decreasing sample length below some limiting value, Figure 7.

Of primary importance was the revealing of the nature of the initiation centers. It was shown,[8] that they preexist in the polymer matrix rather than being created under the action of mechanical stress. Their separation in space and limited number in the sample implied that they were extraneous inclusions of microscopic size, catalyzing the primary radical initiation reactions: their most plausible origin, the residues of polymerization catalysts or of their transformation products.[10,11] It is well known, that transition metal ions catalyze hydroperoxide radical decomposition and activate molecular oxygen for direct interaction with hydrocarbons. Thus, traces of transition metal ions, being bound to chain ends and included into polymerizate particles stay in the polymer matrix after polymer purification and can catalyze the formation of radicals at the points of their localization. Then their

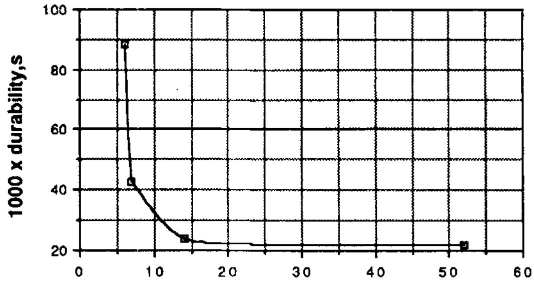


FIGURE 7 Durability vs. the sample length; uninhibited stretched PP, λ = 6.5; 130°C, air.

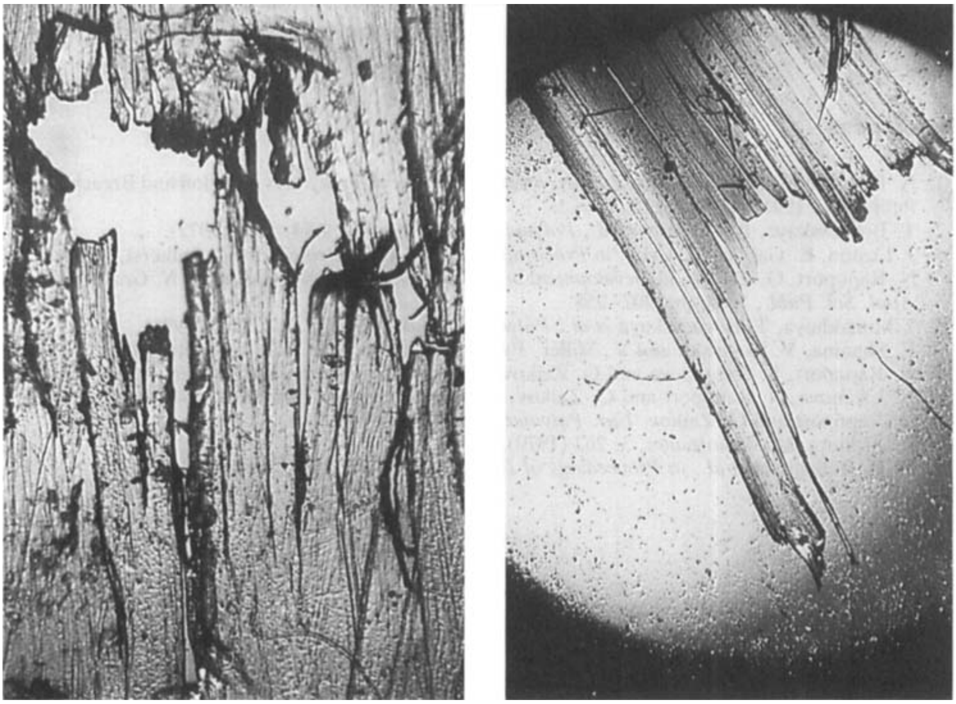


FIGURE 8 Microphotographs reflecting two different mechanisms of polymer fracture: (a)—coalescing of damaged zones into the percolation cluster (PP, inhibited oxidation, 140°C) and (b)—coupling of damaged zones by longitudinal cracks (PP, uninhibited oxidation, 130°C).

deactivation should increase polymer life time. Our attempts to use metal chelators as synergists for conventional oxidation inhibitors (sterically hindered phenols) gave indeed very promising results for PP stabilization. They are to be published in a following paper.

2. MECHANISM OF POLYMER FRACTURE AT LOCAL INITIATION

The fracture of the sample proceeds as a result of coalescing of damaged zones, dispersed in the intact polymer matrix, into the percolation cluster. Oxidation of stretched PP under external stress revealed two different ways of defect coalescence: the direct contact of damaged zone in some cross-section of the sample (microphotographs of Figure 8a, inhibited oxidation, 140°C) or the coupling of damaged zones, located at significant distances from each other, by the longitudinal interfibrillar cracks (Figure 8b, uninhibited oxidation, 130°C). The formation of these longitudinal cracks was stimulated by oxidative degradation (oxidative degradation being a limiting step); in this case the formation of the catastrophic crack proceeded without the direct contact of damaged zones. It is reasonable to anticipate, that the time to the formation of the catastrophic crack (durability) should depend on the concentration and distribution of initiation foci, on the rate of growth and mechanism of merging of damaged zones. Computer simulation of polymer failure for predicting polymer durability is described in the following paper.

References

1. A. Popov, N. Rapoport and G. Zaikov, *Oxidation of stressed polymers*, Gordon and Breach Science Publ., NY, 1991, pp. 124, 125.
2. T. Bogaevskaya, B. Gromov *et al.*, *Polymer Science (USSR)*, **A14**, 1552 (1972).
3. J. Luston, E. Gal and K. Cech, in *Proceedings of IUPAC Macro-82*, 1982, Amherst, #28, p. 308.
4. N. Rapoport, G. Zaikov, in *Development in Polymer Degradation-6, Edited by N. Grassie, Elsevier Appl. Sci. Publ.*, 1985, pp. 207–258.
5. T.Monakhova, T. Bogaevskaya *et al.*, *Polymer Science (USSR)*, **A17**, 1243 (1975).
6. E. Shanina, V. Roginskii and V. Miller, *Vysokomol. Soed*, **B21**, 892, 1979 (Russian).
7. N. Rapoport, L. Shibryaeva and G. Zaikov, *Polymer Degradation and Stability*, **12**, 191 (1985).
8. N. Livanova, N. Rapoport and G. Zaikov, *Polymer Science (USSR)*, **A30**, 1640 (1988).
9. N. Rapoport and G. Zaikov, *Eur. Polymer J.*, **20**, 409 (1984).
10. P. Richters, *Macromolecules*, 3, 262 (1970).
11. N. C. Billingham *et al., in Proceedings of IUPAC Macro-82*, 1982, Amherst, #28, 291.