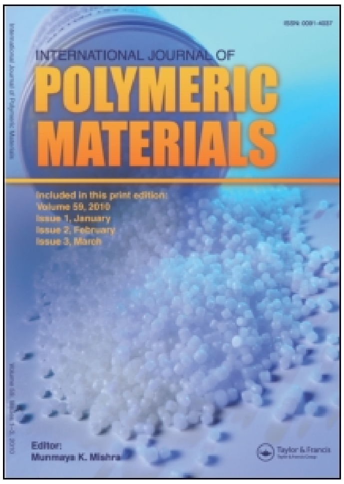

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Simulation of the Durability and Approach to the Stabilization of Polyolefins Undergoing Oxidative Degradation under Mechanical Stress

N. Rapoport[a]; N. Livanova[b]; L. Balogh[c]; T. Kelen[c]
[a] University of Utah, Salt Lake City, Utah [b] Institute of Chemical Physics, Moscow, Russia [c] Koshut Lajosh University, Debrecen, Hungary

To cite this Article Rapoport, N. , Livanova, N. , Balogh, L. and Kelen, T.(1993) 'Simulation of the Durability and Approach to the Stabilization of Polyolefins Undergoing Oxidative Degradation under Mechanical Stress', International Journal of Polymeric Materials, 19: 1, 101 — 108

To link to this Article: DOI: 10.1080/00914039308012021

URL: http://dx.doi.org/10.1080/00914039308012021

Intern. J. Polymeric Mater., 1993, Vol. 19, pp. 101–108
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in Malaysia

Simulation of the Durability and Approach to the Stabilization of Polyolefins Undergoing Oxidative Degradation under Mechanical Stress

N. RAPOPORT†
University of Utah, 304 EMRO Bldg., Salt Lake City, Utah 84112

and

N. LIVANOVA
Institute of Chemical Physics, Moscow, Russia

and

L. BALOGH and T. KELEN
Koshut Lajosh University, Debrecen, Hungary

(Received June 25, 1992)

This study concerns two problems; the simulation of durability and stabilization of polypropylene undergoing oxidative degradation under mechanical stress. The simulation assumes that the time to the formation of the catastrophic crack and hence the durability depends on the concentration and distribution of radical initiation centers, their rate of growth and mechanisms of merging into clusters. With regard to the oxidative stabilization of propylene under mechanical stress it is shown that the deactivation of catalytic impurities that promote the initiation of oxidation, is under specific conditions, an effective way to increase the life time of solid polymer under stress.

KEY WORDS Oxidative degradation, mechanical stress, polyolefins, polypropylene, simulation, stabilization.

The fracture of polypropylene (PP) samples oxidized under relatively low mechanical stress proceeds as a result of merging of deeply oxidized zones, dispersed in the intact polymer matrix.[1]

Oxidation of stretched PP under external stress revealed two different ways of defect merging: the direct contact of damaged zones in some cross-section of the sample (Figure 8a of Reference 1 and upper scheme, Figure 1 of this paper) or

---

†To whom correspondence should be directed.

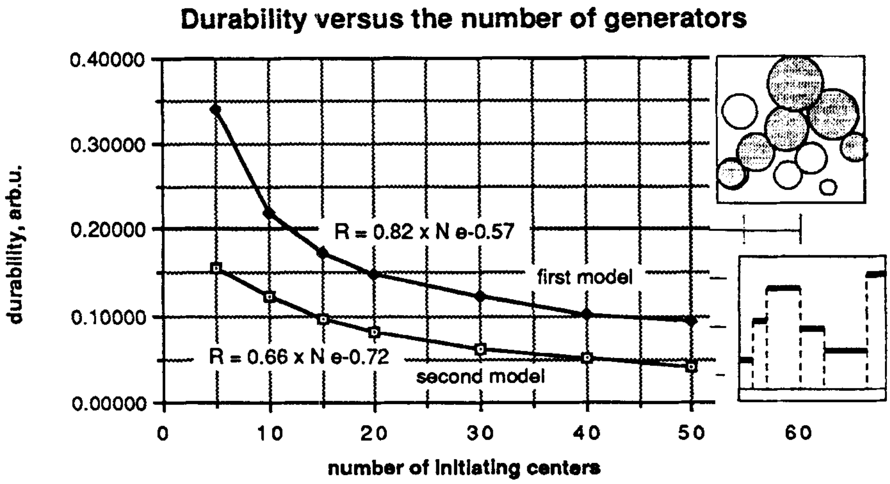

FIGURE 1 Polymer durability vs. the number of radical initiation centers: results of computer simulation of the first (upper) model and the second (lower) model.

the combination of damaged zones, located at significant distance from each other, by the longitudinal interfibrillar cracks, the formation of which is stimulated by oxidative degradation (Figure 8b of Reference 1 and lower scheme, Figure 1 of this paper); in this case the formation of the catastrophic crack proceeded without the direct contact of deeply degraded 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 radical initiation centers, their rate of growth and mechanism of merging into the percolation cluster. Here we describe the results of a computer simulation of the formation of percolation cluster for two different mechanisms of fracture, mentioned above.

The models used in computer simulation were as follows:

1. The oxidative degradation starts at randomly distributed centers and propagates from these centers by way of radical translational diffusion. All centers are activated simultaneously at $t = 0$. The growth rate W of all centers is the same: $W \sim \sqrt{kD_{tr}}$, where k is rate constant of kinetic chain branching and D_{tr} is translational diffusion coefficient of small radicals that are responsible for the space propagation of the oxidative degradation.
2. Two types of cracks are involved into the failure process: primary transverse microcracks induced by oxidative degradation and secondary longitudinal microcracks, induced by mechanical stress around primary microcracks (Figure 2). The growth of those secondary cracks is much faster, than that of primary ones, due to the anisotropy of strength of a stretched polymer (chemical C—C bonds are acting along fibrils whereas in the perpendicular direction much weaker Van-der-Waals forces are keeping fibrils together).

The limiting step of the fracture is the growth of transverse microcracks due to the chemical degradation (microcracks are formed at some degree of oxidative degradation of the stressed polymer).

3. The catastrophic crack is either formed when *transverse microcracks come to*

FIGURE 2 Microphotographs of transverse and longitudinal microcracks in PP, oxidized under stretching stress; PP-1, uninhibited sample; 130°C, air, $\sigma = 10$ MPa, $\tau = 100$ min.

direct contact (first model) or transverse microcracks located in different cross-sections merge into the catastrophic crack being *connected by longitudinal cracks (second model)*.

THE SCHEME OF THE COMPUTER SIMULATION

First Model

Various numbers of initiation points (from 5 to 1,000) with random coordinates were generated inside the square of unit area. The centers were growing isotropically as circles, with constant rate. The Y-axis was regarded to be stress direction. The end of computer experiment corresponded to the moment of the formation of the percolation cluster (catastrophic crack) through the X-axis, when degraded zones "touched" each other throughout the whole cross-section from $X = 0$ to $X = 1$ (the third dimension was neglected in the modeling due to the minimal film thicknesses). The time to the formation of percolation was characterized by radii of circles corresponding to degraded zones at the moment of fracture (the higher the radius, the longer time to break or durability). We were also interested in the fraction of initiation centers used in the formation of percolation cluster in respect to their total number in the sample.

Second Model

In this case the direct contact of degraded zones is not necessary because of their merging into the percolation cluster by longitudinal microcracks. The moment of fracture in this case corresponds to the situation when *the projections* of degraded zones on X-axis cover the whole distance from $X = 0$ to $X = 1$. It happens when the longest crack is formed between primary centers, the most separated in X-direction. In this case it is sufficient just to find the maximum value of distance between the neighboring centers in X-direction (the problem can be handled as being one-dimensional). At a given rate of oxidative degradation the maximum separation of the neighboring centers is proportional to the durability.

For each given number of centers 50 realizations were fulfilled.

The simulation program was run on IBM AT-286 computer equipped with mathematical coprocessor.

RESULTS OF SIMULATION

The results of the simulations are presented as a dependence of a radius of a damaged zone (which is proportional to the corresponding durability) on the number of initiation centers.

The results are shown in Figure 1; they demonstrate *the substantial increase of polymer life time with decreasing concentration of the initiation centers*. They also show, that at the same number of initiation centers, the average durability is much longer in the case, when the formation of a catastrophic crack demands for the direct contact of damaged zones (first model).

The dependence of the durability on the number of initiating centers may be presented in an analytical form as:

$$R = 0.82 \times N^{-0.57} \text{ (first model)}$$

and

$$R = 0.66 \times N^{-0.72} \text{ (second model).}$$

One can see, that in the second case the dependence of durability on the number of initiation centers is more powerful.

The number of centers, involved into the formation of a catastrophic crack may be much lower than the whole number of centers in the sample. The number of

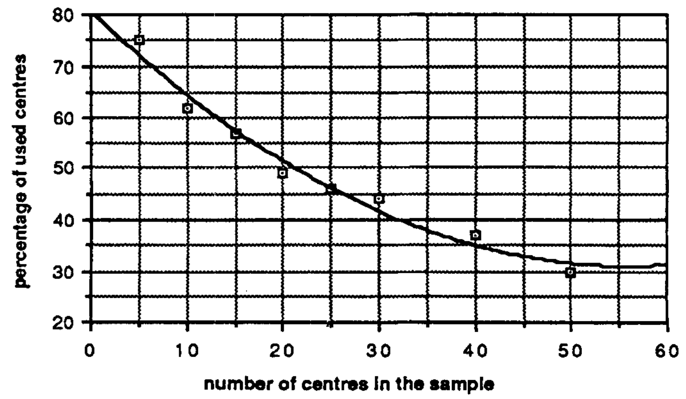

FIGURE 3 Percentage of used centers vs. their number in the sample.

the used centers depends on their total number and spacial distribution (Figure 3). The fraction P of used centers for the first model of fracture can be presented by

$$P = 1.33 \times N^{0.7}$$

At low numbers of centers there is a substantial scatter in the durability values depending on centers spacial distribution; with the increasing number of centers both the durability and the scatter in the durability values drop drastically: there always exist some combination of centers that gives a particular low durability. It should be also mentioned, that the scatter in durability is much lower for the second model of fracture than for the first one: when the direct contact of degraded zones is not a must there exist much more ways for the propagation of the catastrophic crack.

DURABILITY AND FRACTURE PATTERNS OF PP, POLYMERIZED WITH DIFFERENT CATALYTIC SYSTEMS (EXPERIMENT)

We showed elsewhere,[2] that initiation centers were preexisting in the initial unstressed PP samples rather than formed under the action of mechanical stress. We have anticipated that the centers of oxidation initiation were catalytic impurities of submicron size, namely transition metal ions from the polymerization catalyst residues. It is well known, that transition metal ions catalyze the hydroperoxide decomposition into radicals and may also activate oxygen and catalyze its direct reaction with polyolefin macromolecules. Thus, the most plausible source of radical initiation are metal ion-catalyzed reactions of radical formation.

It was interesting to compare the durability and fracture patterns for different brands of PP. In this investigation we used two types of Hungarian PP (TVK products): PP-1 was polymerized *in solution* according to the Hercules technology, while PP-2 was polymerized *in the gas phase* according to the Sumitomo technology at which a very active catalytic system is used. The concentration of catalyst residue, characterized by ash-number, was higher in PP-I than in PP-2 (300 vs. 80 ppm). The composition of the catalyst residue was also different: PP-1 contained less Ti and more Al, than PP-2. In other respects the two brands of PP were very similar (e.g. MMR, stereoregularity, degree of crystallinity, MFI etc.). Both kinds were stabilized by Irganox 1010 (0.1% weight) with DLTP used as synergist for hydroperoxide decomposition.

We found a big scatter in the durability of stabilized PP-1 (70; 127; 389 and 420 min at 140°C and $\sigma = 5$ MPa); much lower scatter of the durability was found for PP-2 (327; 401; 405; 480; 494 and 520 min). Standard deviation in the first case was 180 min, in the second one −60 min. It implies that though the *weight* concentration of the catalytic residue was much higher in PP-1, the distribution of initiative *particles* in PP-1 was less uniform than in PP-2; apparently, the *number of initiating particles* was lower in PP-1, than in PP-2, i.e. catalytic particles in PP-1 were agglomerated to higher degree, than in PP-2. The microscopic investigation of fractured films seems to confirm this assumption: whereas numerous small holes, scattered in polymer matrix, were found in PP-2 (Figure 4a), the formation of big

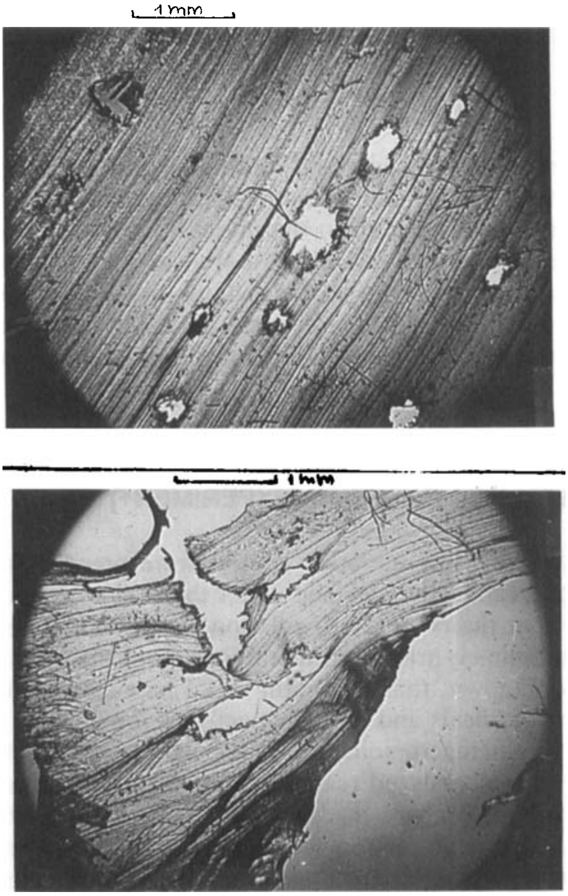

FIGURE 4 Microphotographs of defect distribution in the oxidized inhibited samples of PP-2 (a) and PP-1 (b); 140°C, air, $\sigma = 15$ MPa; $\tau = 198$ min (PP-2) and 226 min (PP-1).

holes, apparently initiated by conglomerates of initiating centers, was characteristic of PP-1 oxidation (Figure 4b). It is interesting, that the scatter of durability of uninhibited samples of PP-1 and PP-2 is much lower than that of inhibited samples, and practically the same for both types of polymer: $\tau = 87 \pm 26$ min (PP-1) and 94 ± 19 min (PP-2) (mean values from 5 measurements): in this case fast diffusion of active radicals, which are not being trapped by inhibitor, in combination with branching of kinetic chains leads to the quick elimination of differences between the samples with different concentration/space distribution of *initial* initiation centers.

We have tried to deactivate catalytic residues in PP samples by complexation with various chelating agents. We used metal chelators as synergistic additives to the conventional inhibitors of phenolic type (Irganox 1076 for Russian PP or Irganox 1010 in combination with DLTP (hydroperoxide decomposer) for Hungarian PP-2. In the latter case sterically hindered oxiquinon was used as a second synergist.

TABLE I

Polypropylene durability, min. (Russian polypropylene, product of MNPZ). Inhibitor: Irganox 1076, 0.1% weight; Temp = 140°C. λ = 5; σ = 15 MPa

	DURABILITY, min			
	without inhibitor		with inhibitor	
Control	55		750	
	Synergist Concentration, mole/kg			
	0.01	0.05	0.01	0.05
Synergist				
1*	55	125	1800	3600
2*	390	530	1100	1900
3*	270	730	2000	6800

* Synergist 1 is sterically unhindered dioxiquinon, whereas synergists 2 and 3 belong to the class of sterically hindered catechols.

TABLE II

Polypropylene durability, min. (Hungarian PP-2). Inhibitor—Irganox 1010, 0.1% weight; Temp = 140°C; λ = 6; σ = 15 MPa

	DURABILITY*, min	
	without inhibitor	with inhibitor
Control	80	250
Synergist	72	610

* each durability is mean value from 10 measurements.

The results are given in Tables I and II. One can see, oxiquinons on themselves are not inhibitors of PP oxidation, but they demonstrate rather effective synergism with inhibitors of phenolic type. We do not claim, that the deactivation of initiation centers is the only mechanism of oxiquinons action (e.g. the regeneration of an inhibitor may be also involved), but the change of the fracture pattern in the presence of a synergist (long separation of degraded zones) implies, that catalyst deactivation is definitely involved in the stabilization mechanism.

Sterically hindered catechols show a weak PP stabilizing effect without Irganox; effect is substantially increased in the presence of phenolic inhibitor. Again, catalyst deactivation may be not the only mechanism of synergist action, but definitely one of its components.

Our results demonstrate, that the deactivation of catalytic impurities that catalyze the initiation of oxidation may be a very effective way of increasing solid polymer life time. This is a new type of synergism, based on the combination of suppression of oxidation initiation with radical trapping. This type of synergism can be active only in solid systems with heterogeneous initiation and *low rate of active centers migration*, that is low rate of spatial propagation of oxidative degradation.

References

1. N. Rapoport, International Journal of Polymeric Materials, 1992, in press.
2. N. Livanova, N. Rapoport and G. Zaikov, *Polymer Science (USSR)*, **A30**, 1640 (1988).