

MODELING OF THE LOCALIZED UV-DEGRADATION DAMAGE IN POLYMERS

I.D.Skrypnyk\*, H.D.Hoekstra†, J.L.Spoormaker†

The aim of the present work is to model UV-degradation localized on the micro scale. The system of evolution equations for the free radical chain mechanism for the oxidation of polyolefines, which accounts for branching, diffusion of polymer chains and stresses, is derived. Unlike the majority of the studies, the derived equations model the change of fractions caused not only by chemical reactions or oxygen diffusion, but also by the motions of polymer chains. It is shown, that this system has two threshold levels of controlling parameters. Under the lower level no deviations occur: every fluctuations of fractions from the uniform state diminish in time. Above the higher level the trivial distribution can not exist. At intermediate level localized peaks on top of the homogeneous distribution can occur.

INTRODUCTION

The long service time of polymers used outdoors result in its degradation. The auto-oxidation is considered as its leading mechanism (Bolland and Gee (1)). Three scales of localization of degradation are observed: a) the formation of oxidation products in surface layers; b) selective degradation of amorphous zone; c) damage of local sites of the amorphous phase.

The aim of the present paper is to construct the mathematical model of degradation localized on the micro level.

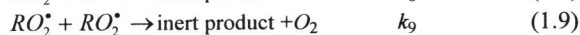
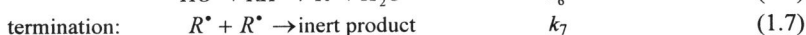
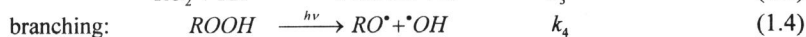
FORMULATION OF A PROBLEM

The following assumptions are accepted:

\* Faculty of Industrial Design Eng., TU Delft, The Netherlands  
on leave from: Karpenko Physico-Mechanical Institute, Lviv, Ukraine

† Faculty of Industrial Design Eng., TU Delft, The Netherlands

1. The amorphous phase of the polymer is an open thermodynamical system exposed to:
  - irradiation;
  - mechanical loading;
  - a constant transport of dissolved oxygen from the surface.
2. Following Bolland and Gee (1) and Vink (2) the mechanism of a chain auto-oxidation of free radicals is assumed:



3. The average mass fraction of reagents which take part in these reactions is very small. Therefore the amorphous zones can be considered as a weak solution.
4. Also, the concentration gradients of the reagents are small.
5. The system is isothermal and is under the condition of mechanical balance: there are no viscous flows.

Statements 3 and 4 imply the principle of local thermodynamic balance (Nicolis and Prigogine (3)). For a weak solution of reagents this leads to the assumption, that the rates of the reactions are proportional to the mass fractions of the reagents. An exception is the initiation of free radicals. The rate of initiation strongly depends on the applied stress (2). On other hand, the formation of free radicals due to link rupture causes a redistribution of stresses in the material. Other links can become overstressed. Therefore, non-linear positive feedback is supposed (Skrypnyk (4)):

$$\frac{\partial X}{\partial t} = k_1 \exp(\alpha X). \quad (2)$$

The evolution equations for the reagent mass fractions can be obtained from the principle of the mass balance (4). Since there are no viscous fluxes, the mass transfer can occur only by diffusion. Therefore, six "diffusion-reaction" equations (according to the number of reagents) can be formed.

However, certain simplification can be done. Since the oxidation reaction (1.2) runs considerably faster (Audouin et al (5)), than the dissociation reactions (1.3), (1.5), (1.6), it can be supposed, that the mass fraction of peroxy radical  $[RO_2]$  is always near its equilibrium value. Further, the equations (1.5) and (1.6) simulate a linear process with negative feedback (4). Therefore, these phenomena should not cause essential retardation effects at large time intervals. Thus, the mass fractions of  $[ROOH]$ ,  $[RO\cdot]$  and  $[OH\cdot]$  can be excluded from consideration by the assumption, that the concentration of above reagents is near its equilibrium value. As a result, following system of equations can be derived:

$$\frac{\partial X}{\partial t} = D_x \frac{\partial^2 X}{\partial x^2} + k_1 \exp(\alpha X) + 3 k_3 Z - k_2 XY - k_7 X^2 - k_8 XZ \quad ; \quad (3.1)$$

$$\frac{\partial Y}{\partial t} = D_y \frac{\partial^2 Y}{\partial x^2} + \frac{D_y}{\delta^2} (\bar{Y} - Y) - k_2 XY + k_9 Z^2; \quad (3.2)$$

$$k_2 XY - k_3 Z - k_8 XZ - k_9 Z^2 = 0. \quad (3.3)$$

#### ANALYSIS OF THE UNIFORM STATES

The trivial solutions to the system above are the solutions to the reduced system:

$$\begin{cases} f(X, Y, Z(X, Y), \dots) = 0; \\ F(X, Y, Z(X, Y), \dots) = 0, \end{cases} \quad \text{or} \quad \begin{cases} Y_1 = g(X, \dots); \\ Y_2 = G(X, \dots), \end{cases} \quad (4)$$

The solution exist, if the curves (4) are crossed. For the equations (3.1)-(3.3) of the auto-oxidation scheme these curves (4) are described by the formulae:

$$Y_1 = \frac{(k_8 X + k_3)(k_1 \exp(\alpha X) - k_7 X^2)}{2(k_8 X - k_3)k_2 X}; \quad (5.1)$$

$$Y_2 = \frac{D_y \bar{Y}}{D_y + \delta^2 k_2 X}. \quad (5.2)$$

Since constant  $k_9$  is as a rule much smaller than the others, the term  $k_9 Z^2$  is skipped in equations (5). Other parameters can be approximately evaluated as follows (4):

$$\begin{aligned} k_1 = 10^{-11} \text{ M}\cdot\text{s}^{-1}, \quad k_2 = 4.1 \cdot 10^9 \text{ (M}\cdot\text{s)}^{-1}, \quad k_3 = 72.73 \text{ s}^{-1}, \quad k_7 = 2.0 \cdot 10^9 \text{ (M}\cdot\text{s)}^{-1}, \\ k_8 = 10^9 \text{ (M}\cdot\text{s)}^{-1}, \quad D_y = 4.6 \cdot 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}, \quad \delta = 10^{-4} \text{ m}, \quad \bar{Y} = 8.4 \cdot 10^{-5} \text{ M}\cdot\text{s}^{-1}. \end{aligned} \quad (6)$$

If the value of the parameters change, the shape and the mutual location of the curves (4) can vary. Thus, it affects the trivial solutions to equations (3) too. Due to the characteristics of the function  $Y_1$ , the uniform states are addressed only for the range of the variable  $X$  values, where  $Z > 0$  (i.e., where the solutions to the system have physical sense). In the case that the polymer is not sensitive to the redistribution of stresses ( $\alpha \sim 0$ ), the curve  $Y_1$  varies:  $-\infty < Y_1(X) < \infty$  (Fig.1). Since curve  $Y_2$  is a descending hyperbola, the uniform state, corresponding to the thermodynamic branch, exists for a wide range of system parameters.

If the material is sensitive to stresses and under loading, the situation can change qualitatively (Fig.2). For  $\alpha \sim 2 \cdot 10^8$ , the  $Y_1$  curve changes its direction. An additional uniform state appears. An increase of the sensitivity to stresses leads to mutual approach of trivial solutions (Fig.2) and to their disappearance.

According to Kerner and Osipov (6), the unstable uniform state corresponds to the trivial solution (the crossing point) in the area, where

$$\text{sign}\left(\frac{\partial Y_1}{\partial X}\right) = \text{sign}\left(\frac{\partial Y_2}{\partial X}\right) \quad (7)$$

and visa verse. Thus, if there are no stresses in the system, in a wide range of parameters there is one stable uniform state. If the system is sensitive to stresses, then a pair of solutions can exist (stable and unstable uniform states) or there is no trivial solution at all.

Obviously, there are two thresholds of the system constitutive parameters. Below the first level only uniform distributions form. Above the second level the uniform state can not appear (there is no crossing point): more complex distribution (dissipative structure) will develop. If the constitutive parameters are between the two levels, both - uniform states and dissipative structures can form.

### DISSIPATIVE STRUCTURE OF DEGRADATION

In order to show the possibility of the stationary spatial distributions for the system (3), an area of amorphous zone of a length  $\sqrt{D_x/k_3} \ll l \ll \delta$ . is considered.

Then the distribution of solved oxygen is almost constant (6) and the system (4) for steady state case will be reduced to the form:

$$D_x \frac{\partial^2 X}{\partial x^2} + \frac{\partial U}{\partial X} = D_x \frac{\partial^2 X}{\partial x^2} + k_1 \exp(\alpha X) - k_7 X^2 + 2k_2 XY \frac{k_3 - k_8 X}{k_3 + k_8 X} = 0; \quad (8.1)$$

$$\int_{\Lambda} \left( -\frac{D_Y}{\delta^2} (\bar{Y} - Y) - k_2 X(x) Y \right) dx = 0; \quad (8.2)$$

The first equation formally describes the motion of a particle with coordinate  $X$  and time  $x$  in potential  $U$ . The trajectory of the particle depends on the oxygen mass fraction  $Y = \text{const}$ . The latter is determined from the condition of solvability of the system (3), i.e., equation (8.2). The potential  $U$  for various values of  $Y$  is illustrated in Fig.3. It represents a potential well. The only solution stable in time (6) is the singular one, with a trajectory passing through the maximum. By approaching the maximum the change in distribution vanish, therefore the solution to system (8) has the shape of a peak on a uniform distribution background (Fig.4).

USED SYMBOLS

- $k_{1...9}$  = constants describing reaction rate in chain auto-oxidation scheme;
- $\alpha$  = factor for the initiation stage dependence on alkylradical mass fraction;
- $X$  = mass fraction of free radicals [ $R^*$ ] per unit volume;
- $Y$  = mass fraction of oxygen solved in polymer [ $O_2$ ] per unit volume;
- $Z$  = mass fraction of peroxy radicals [ $RO_2^*$ ];
- $\bar{Y}$  = stable mass fraction of the solved oxygen at the material surface;
- $\delta$  = distance from the material surface to the amorphous layer (m);
- $D_X, D_Y$  = diffusion factors for free radicals and oxygen ( $m^2/s$ );
- $f(X, \dots), F(X, \dots)$  = functions of sources, which model internal irreversible processes (reactions); algebraic part of right side in equations (2.1) and (2.2)

REFERENCES

- (1) Bolland, J.L. and Gee, G., Trans. Faraday Soc., Vol.42., 1946, p.236.
- (2) Vink, P., "The photo-oxidations of polyolefins - structural and morphological aspects", Chapter 5, In: Degradation and stabilization of polyolefins. Edited by N.S. Allen, Appl.Sci.Publ., London, 1983, pp.213-246.
- (3) Nicolis, G., Prigogine, I., "Self-Organization in Non-Equilibrium Systems", Wiley, New York, 1977.
- (4) Skrypnyk, I.D. "Modeling of local degradation centers in polymers under stress", Report LMB, K343, Delft University of Technology, The Netherlands, 1995, 31 p.
- (5) Audouin L., Langlois V., Verdu J., de Bruijn J.C.M., J.Mat.Sci., Vol.29, 1994, p.569.
- (6) Kerner, B.S., Osipov, V.V., "Autosolitons: Localized strongly-unstable zones in homogeneous dissipative systems." Moscow, Nauka, 1991. p. 200. (In Russian).

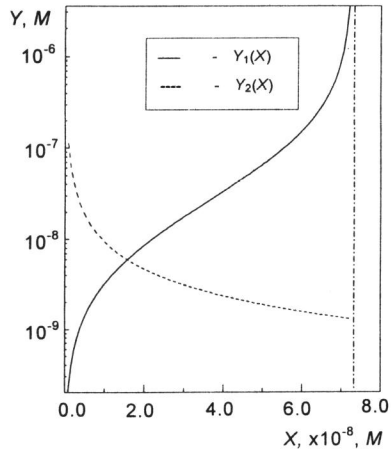


Fig. 1. The mutual location of curves  $Y_1$  and  $Y_2$  for parameter set (6).

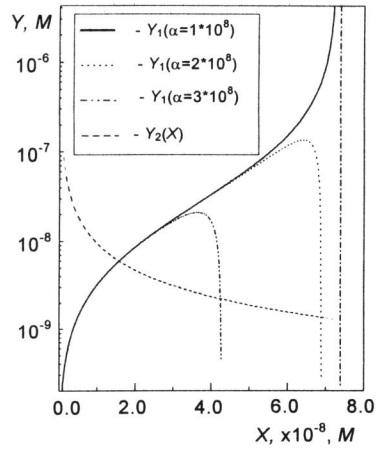


Fig. 2. The shape of curve  $Y_1$  for different values of the sensitivity factor.

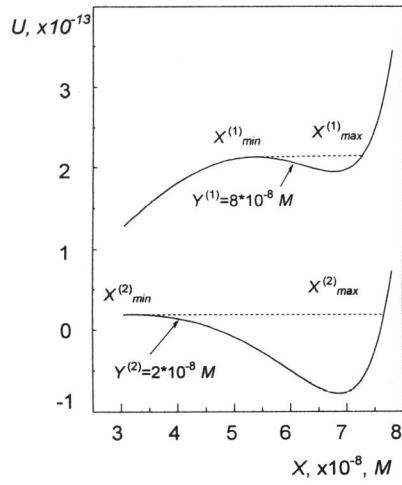


Fig. 3. The  $U$  potential for two different levels of oxygen mass fraction  $Y$ .

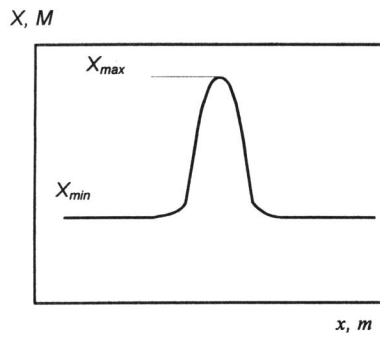


Fig. 4. Profile of stable steady state distribution of free radicals.