A lifetime prediction method for polymer geotextile oxidation

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ABSTRACT: The lifetime of hydrocarbon polymer geotextiles exposed in air near the ambient temperature can be predicted using a nonempirical model based on a mechanistic scheme of branched radical chain oxidation but free of usual simplifying hypotheses (oxygen in excess, stationary state, no substrate consumption). A chemical event of chain scission is added to this scheme. The endlife criterion is a critical value of the molar mass, corresponding to the transition from a ductile to a brittle tensile behaviour. Some important kinetic parameters are determined from experimental thermal ageing data, using the model though an inverse approach.

1 INTRODUCTION

Lifetime of polymer geotextile is limited by an oxidation process which normally occurs when polymer is exposed to oxygen. This oxidation process, which is accelerated by heat, leads to an embrittlement phenomenon. Since empirical laws (Arrhenius…) to extrapolate lifetime at ambient temperature from data obtained at temperatures typically greater than 100°C are questionable, a peculiar method is required to ensure a good prediction of lifetime of polymer geotextile.

2 STRATEGY FOR LIFETIME PREDICTION

According to Fig. 1, the first step is the elaboration of a kinetic scheme derived from mechanistic scheme (closed-loop in the case of oxidation).

The second step is the modelling of macromolecular changes in particular a reduction in molar mass which is induced by a chain scission process deduced from the previous kinetic scheme.

The last step is to put in evidence a physical criterion linking the reduction in molar mass to the embrittlement process.

3 KINETIC MODEL

3.1 *Kinetic scheme*

The proposed kinetic model is based on the fact that oxidation proceeds by a radical chain reaction initiated
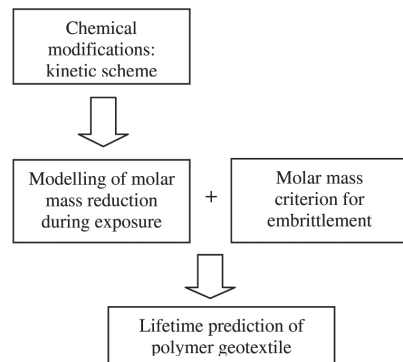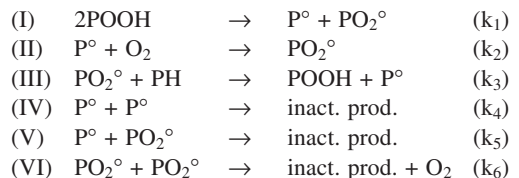

Figure 1. Methodology for lifetime prediction.

by hydroperoxide decomposition. In other words, the reaction generates its own initiator, which explains its strong autoaccelerated character. A similar kinetic model has been proposed by Tobolsky and co-workers in the early 50's and then, regularly used in the past half century. The "bimolecular closed loop scheme" (BCLS) is based on six "elementary" reactions:

(I)	$2POOH$	$\rightarrow$	$P° + PO_2°$	(k_1)
(II)	$P° + O_2$	$\rightarrow$	$PO_2°$	(k_2)
(III)	$PO_2° + PH$	$\rightarrow$	$POOH + P°$	(k_3)
(IV)	$P° + P°$	$\rightarrow$	inact. prod.	(k_4)
(V)	$P° + PO_2°$	$\rightarrow$	inact. prod.	(k_5)
(VI)	$PO_2° + PO_2°$	$\rightarrow$	inact. prod. $+ O_2$	(k_6)

The following set of (non linear) differential equations can be derived from this scheme:

$$\frac{d[P°]}{dt} = k_1[POOH]^2 - k_2C[P°] + k_3[PH][PO_2°]$$
$$- 2k_4[P°]^2 - k_5[P°][PO_2°]$$

$$\frac{d[PO_2°]}{dt} = k_1[POOH]^2 + k_2C[P°] - k_3[PH][PO_2°]$$
$$- k_5[P°][PO_2°] - 2k_6[PO_2°]^2$$

$$\frac{d[POOH]}{dt} = -2k_1[POOH]^2 + k_3[PH][PO_2°]$$

where C is the oxygen concentration into the polymer. r_{OX} is the oxygen consumption rate:

$$-\frac{d[PO_2]}{dt} = r_{OX} = -k_2C[P°]^2 - k_6[PO_2°]^2$$

This model contains eight parameters: k_1, k_2, k_3, k_4, k_5, k_6 plus the boundary values:

$[POOH] = [POOH]_0$ at $t = 0$;

$C = C_S$ at $t = 0$, C_S being the equilibrium concentration of O_2 into the polymer.

C_S can be obtained from independent physical measurements, generally from oxygen permeation measurements.

Analytical solutions have been proposed although they required three main assumptions (Audouin et al. 2000):

- The presence of oxygen in excess (hypothesis E)
- The existence of a stationary state for radical concentrations (hypothesis S)
- The fact that the onset of steady state can be observed in the domain of low conversions, where the substrate consumption can be neglected (hypothesis L).

Our purpose is to discuss the domain of validity of each assumption by solving numerically these schemes (Rincon-Rubio et al. 2001). Numerical simulations with no assumptions will enable us to check these assumptions (S, E and L) in the case of unstabilised polypropylene geotextile oxidation.

3.2 *The presence of oxygen in excess (hypothesis E)*

For every chain oxidation process, whatever its mechanism, the variation of the oxidation rate r_{ox} with the oxygen concentration C displays the shape of Fig. 2.

Above a critical concentration C_C, the oxidation rate tends to become independent of the oxygen concentration ($r_{OX} = r_S$). Since, in a thin sample, $C \approx C_S$ and $C_S = S p$, where S is the Henry's solubility coefficient and p the oxygen partial pressure. The curve $r_{ox} = f(p)$ would have exactly the same shape.

The domain of high oxygen concentrations ($C > C_C$) is the domain of oxygen excess, i.e. the domain of validity of hypothesis E. In this domain, since k_2
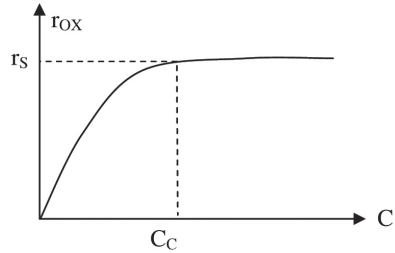

Figure 2. Universal shape of the variation of oxidation rate with oxygen concentration.

is very high ($k_2 \approx 10^8 - 10^9 \, l \, mol^{-1} \, s^{-1}$), each P° radical is rapidly transformed into a $PO_2°$ one, so that its probability to participate to a termination event (IV or V) is negligible. Then, both termination processes can be suppressed, which simplifies the kinetic scheme.

The hypothesis of oxygen in excess is valid only if the concentration of oxygen into the polymer is higher than a critical concentration C_C depending on the type of polymer.

3.3 *The existence of a stationary state for radical concentrations (hypothesis S)*

In the early 50's, Tobolsky and co-workers proposed to add the hypothesis of stationary state for radical concentrations (hypothesis S), but with an important (but questionable) peculiarity. As a matter of fact, the hypothesis S was applied to the whole radical concentration:

$$\frac{d[P°]}{dt} + \frac{d[PO_2°]}{dt} = 0 \qquad (1)$$

Indeed, normally, this equality tends to become valid in steady state and then:

$$d[P°]/dt = d[PO_2°]/dt = 0 \qquad (2)$$

But the authors considered that its domain of validity extended to short times, far before the true steady state is reached. The paradoxical character of this hypothesis is obvious: the fact that the radical concentration remains constant, whereas the initiation rate and the whole oxidation rate increase, is difficult to understand. Indeed, by solving kinetic equations numerically without steady state hypothesis, [P°] and $[PO_2°]$ as function of time of exposure as shown in Fig. 3 exhibit specific variations.

We can conclude that the steady state hypothesis is wrong during the early stage of the oxidation process.

3.4 *The substrate consumption can be neglected (hypothesis L)*

During oxidation, the polymer [PH] is consumed in propagation step (III). To take account this substrate
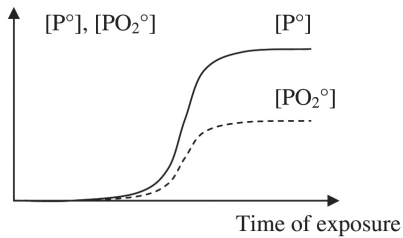
Figure 3. Shape of the variation of radical concentrations according to kinetic equations numerically solved without steady state hypothesis.

consumption, one can include the following equation in the differential equation system:

$$\frac{d[PH]}{dt} = -k_1[POOH]^2 - k_3[PH][PO_2°] \qquad (3)$$

By numerical way, one can distinguish the case where [PH] can considered constant or the case where [PH] decreases during oxidation process. In the first case POOH concentration reaches an asymptotic value [POOH](a) in Fig. 4. In the second case, [POOH](b) decreases because the polymer is consumed and [PH] decreases.

The fact that the substrate consumption can be neglected (i.e. [PH] = constant) depends on kinetic parameter values k_1, k_3 and k_6 and [PH] at initial state. In the case of polypropylene, this hypothesis is wrong.

To conclude, any simplification or assumption allowing simplifying the complex differential equation modelling the oxidation process of polypropylene is questionable: only a numerical way is possible to solve the differential equations. Let us now describe the methodology to determine kinetic parameters from experimental data.

4 RATE CONSTANT DETERMINATION BY INVERSE METHOD FOR PP OXIDATION

The "inverse kinetic problem" consisting to identify the kinetic parameters from the experimental kinetic
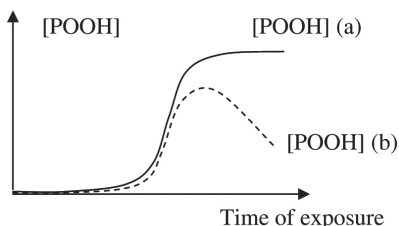

Figure 4. Shape of the variation of hydroperoxyde concentrations according to kinetic equations numerically solved without substrate consumption [POOH](a) and substrate consumption [POOH](b).

curves, for instance oxygen absorption ones C = f(t), is practically unsolvable without simplifications (Colin et al. 2004). Two of these simplifications can be obtained from a pertinent choice of exposure conditions:

- Using thin samples, to minimize oxidation gradients.
- Using high oxygen pressures, i.e. $C_S > C_C$ in order to suppress reactions IV and V and the associated kinetic constants.

With this exposure condition, the differential equation becomes:

$$\frac{d[P°]}{dt} = k_1[POOH]^2 - k_2C[P°] + k_3[PH][PO_2°]$$

$$\frac{d[PO_2°]}{dt} = k_1[POOH]^2 + k_2C[P°] - k_3[PH][PO_2°]$$
$$\qquad - 2k_6[PO_2°]^2$$

$$\frac{d[POOH]}{dt} = -2k_1[POOH]^2 + k_3[PH][PO_2°]$$

$$\frac{d[PH]}{dt} = -k_1[POOH]^2 - k_3[PH][PO_2°]$$

If k_2 and k_3 are known from literature data, k_1 and k_6 have to be determined by inverse method: Fig. 5 shows a typical oxygen absorption curve and which parts have to be used to evaluate both kinetic parameters.

In order to determine k_4 and k_5, we use variation of oxygen absorption with $C_S < C_C$, k_1 and k_6 being previously determined. In the case of polypropylene $C_C \sim 0.38$ mol l^{-1} at 80°C (Richaud et al. 2005). Table 1 shows the values of rate constants at 80°C.

Table 1. Rate constants (in l.mol^{-1}s^{-1}) for a polypropylene geotextile at 80°C (Richaud et al. 2005).

k_1	k_3	k_4	k_5	k_6
3×10^{-5}	2.5×10^{-2}	1×10^{12}	3.5×10^9	8×10^3

Since elementary rate constants obey the Arrhenius law, kinetic constants have determined at different temperatures of exposure in order to evaluate activation energies. With these activation energy values, extrapolation at 20°C is possible to simulate oxidation process at the temperature of use for geotextile fibre.

5 FROM CHEMICAL MODIFICATIONS TO EMBRITTLEMENT

To predict embrittlement of geotextile induced by oxidation (lifetime), we have to establish relationships between chemical modifications due to oxidation and the mechanical behaviour of geotextile fibre.
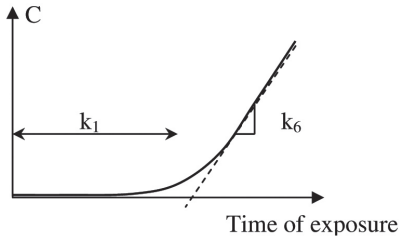
Figure 5. Shape of the variation of oxygen absorption and part of the curve used to determine k_1 and k_6 for $C_S > C_C$.

It's well known that in the case of polypropylene, oxidation leads to a chain scission process (i.e. molar mass decrease). To simulate this process, chain scissions concentration (s) is given by:

$$\frac{ds}{dt} = k_1 \,[POOH]^2 \qquad (4)$$

Knowing chain scissions concentration, molar mass value (M), at each time, is obtained by:

$$M = \left(s + \frac{1}{M_0} \right)^{-1} \qquad (5)$$

Where: M_0 is the initial molar mass of polymer.

The embrittlement of geotextile fibre occurs when the molar mass value becomes lower than a critical molar mass value M'_C as it is schematised in Fig. 6. In the case of isotropic polypropylene, M'_C is close to 200 kg mol^{-1} (Fayolle et al. 2004).
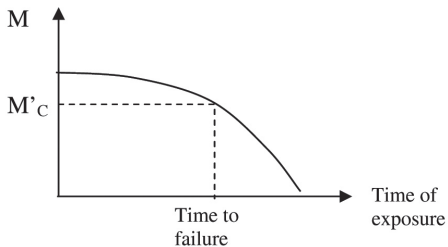

Figure 6. Shape of the variation of molar mass and the critical molar value M'_C governing failure of fibre.

6 CONCLUSIONS

We have proposed a method to predict lifetime of geotextile fibre in polypropylene. This method is based on the fact that classical extrapolation of the time to embrittlement obtained in accelerated test does not obey to classical Arrhenius law. For this reason, this methodology is linked to a kinetic modelling of the oxidation process responsible to embrittlement. Kinetic modelling involves each elementary reaction in a kinetic scheme. Differential equations allowing simulating oxidation are very complex and no simplifying assumption can be made: oxygen excess, existence of a stationary state for radical concentrations or constant substrate concentration. Determination of the kinetic parameters and the physical parameter governing the change of mechanical behaviour lead to a non empirical method of lifetime prediction for polymers. An application of this method in the case of geotextile fibre in polypropylene will be presented: a good agreement with experimental data is obtained.

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