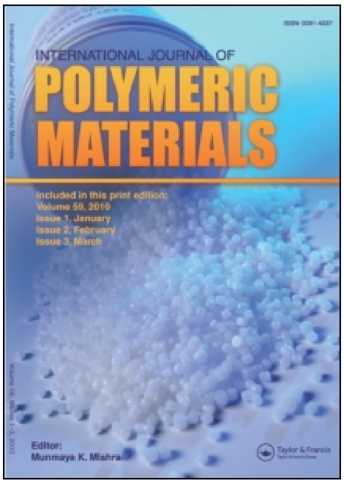

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The Depth of Penetration of Radiation Oxidation in the Presence of Stabilizers

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The disposable syringes manufactured from low pressure polyethylene (LPPE) and polypropylene (PP) are widely used in the USSR. Irradiation by ionizing radiation is one of the most prospective methods of sterilizing the disposable syringes. Problems in developing the polyethylene and polypropylene formulations that remain stable under the action of sterilizing doses of radiation and subsequent prolong storing are reviewed.

KEY WORDS Radiation, sterilizing, polyethylene, polypropylene.

DISCUSSION

To forecast the lifetime of the articles that are thick enough (more than 0.5 mm) after radiation action on air, it is necessary to know the so-called depth of penetration of the radiation oxidation reaction.[1–5]

Previously[5,6] we have considered the case of radiation oxidation of nonstabilized polyolefins which allows us to calculate the depth of penetration of the radiation oxidation reaction if nonstabilized samples are irradiated. An attempt to calculate theoretically and determine experimentally the depth of penetration of radiation oxidation reaction for stabilized low pressure polyethylene (LPPE) and polypropylene (PP) is undertaken in this work.

The samples of LPPE of 277-73 trademark and PP of 21060-16 trademark used in manufacturing syringes are used. The samples are investigated in the form of plates of various thickness that are manufactured at KAMIL combine (France) by the technique described earlier.[7] An ionol stabilizer is introduced into thin polymeric films (50 mcm) from a benzene solution. Thick films are prepared by melting thin ones. The stabilizer concentration is determined on the uv-spectrophotometer LAMBDA-6 Perkin-Elmer (USA) and after extracting with benzene from the film on the liquid-phase chromatograph with uv-detector LAMBDA 481 Millipore (USA), column NOVOPAC C-18, movable phase ACN- H_2O 80:20. Irradiation is carried out at different installations with the dose rate of from 0.022 to 2.8 Gy/sec in air atmosphere at room temperature.

Let us consider the scheme of radiation oxidation of polyolefins in presence of antioxidant:

$$\text{i) } RH \xrightarrow{Wi} R^{\cdot} + H^{\cdot}$$

$$\text{0) } RH + H^{\cdot} \xrightarrow{K_0} R^{\cdot} + H_2$$

$$\text{1) } R^{\cdot} + O_2 \xrightarrow{K_1} RO_2^{\cdot}$$

$$\text{2) } RO_2^{\cdot} + RH \xrightarrow{K_2} ROOH + R$$

$$\left.\begin{array}{l} \text{4) } RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{K_6} \\ \text{5) } R^{\cdot} + RO_2^{\cdot} \xrightarrow{K_5} \\ \text{6) } R^{\cdot} + R^{\cdot} \xrightarrow{K_4} \end{array}\right\} \text{molecular products}$$

$$\text{7) } RO_2^{\cdot} + InH \xrightarrow{K_7} In^{\cdot} + ROOH$$

$$\text{8) } RO_2^{\cdot} + In^{\cdot} \xrightarrow{K_8} InO_2R$$

$$\text{9) } InH + H^{\cdot} \xrightarrow{K_9} H_2 + In^{\cdot}$$

$$\text{10) } R^{\cdot} + In^{\cdot} \xrightarrow{K_{10}} InR$$

The solution of the i)–10) system using the Bodenstein–Semenov principle gives the expression

$$Wi = K_8RO_2^{\cdot}In^{\cdot} + K_{10}R^{\cdot}In^{\cdot} + 2K_6RO_2^{\cdot 2} + 2K_4R^{\cdot 2} + K_5R^{\cdot}RO_2^{\cdot}. \qquad (1)$$

The possibility of reaction 10) proceeding is shown in References 8–10. Let us simplify equation (1) for the case considered here. For the strong antioxidants to which hindered phenols of the type 2,6-di-*tert*-butyl-4-methylphenol (ionol) are regarded, the propagation reaction rate for the oxidation chain and the termination rate on RO_2 radicals is much less than the termination rate on inhibitor molecules at concentration 10^{-4}–10^{-2} mol/kg. As concerns reaction 6), special experiments are carried out to estimate the relationship between its rate and the rate of the reaction 10). The gel-point is determined upon irradiation of LPPE 277-73 (non-stabilized) and LPPE which contains $5 \cdot 10^{-3}$ mol/kg ional antioxidant using extraction sol-fraction of irradiated samples in Soxlet apparatus in nitrogen atmosphere for 48 h. The value of gel-formation dose in the presence of stabilizer increases from 2.6 kGy for nonstabilized LPPE to 60 kGy for the polymer containing $5 \cdot 10^{-3}$ mol/kg of ionol.

This fact is evidence that the stabilizer of the phenolic type can suppress the reaction the recombination of alkyl radicals in polyolefins. Therefore the two last terms in Equation (1) can be neglected. Thus we have

$$Wi = K_8[RO_2^\cdot][In^\cdot] + K_{10}[R^\cdot][In^\cdot]. \tag{1a}$$

The solution of the i)–10) system gives following expression for inhibitor radical concentration $[In^\cdot]$:

$$K_1[O_2]\left(\bar{W}i + \frac{K_8[In^\cdot]}{K_7[InH]}\,Wi\right) = \bar{W}i\,\frac{K_8}{K_7}\,\frac{K_{10}}{[InH]}\,[In^\cdot]^2 - K_{10}[In^\cdot]\bar{W}i,$$

$$Wi = K_0[RH][H^\cdot]. \tag{2}$$

Taking into account the values of rate constants of the reactions entering Equation (2) $K_1 = 10^6$ l/mol sec,[11] $K_{10} = 10^8$ l/mol sec,[10] $K_7 \simeq 10^4$ l/mol sec,[12] $K_8 = 10^8$ l/mol sec,[12] $Wi \simeq \bar{W}i$ (by physical sense) $= 10^{-6}$ mol/l sec for dose rate of 2.8 Gy/sec we can write

$$[In^\cdot] = \frac{K_1[O_2]}{2K_{10}}\left(\frac{Wi}{\bar{W}i} + I\right) + \frac{K_7}{2K_8}[InH]\left(I + \frac{3}{2}\,\frac{\bar{W}i}{Wi}\right) \tag{3}$$

or, taking into account, that $Wi \simeq \bar{W}i$ we have

$$[In^\cdot] = \frac{K_1[O_2]}{K_{10}} + 1.25\,\frac{K_7}{K_8}\,[InH]. \tag{4}$$

Then beginning from the i)–10) scheme, we can obtain the expression for quasistationary concentration of alkyl radicals $[R^\cdot]$:

$$\begin{aligned}[R^\cdot] &= \frac{2Wi}{K_1[O_2] + K_{10}[In^\cdot]} \\ &= \frac{2Wi}{2K_1[O_2] + 1.25\,\dfrac{K_7}{K_8}\,K_{10}[InH]}\end{aligned} \tag{5}$$

Taking into consideration Equation (5), we can write, for the polymer oxidation rate W_{0x},

$$W_{0x} = K_1[R^\cdot][O_2] = \frac{K_1[O_2]2Wi}{2K_1[O_2] + 1.25\,\dfrac{K_7}{K_8}\,K_{10}[InH]}. \tag{6}$$

The diffusion hindrances being in proceeding chemical reactions, we have for the case of stationary diffusion in film:

$$D\frac{d^2[O_2]}{dX^2} = \frac{A[O_2]}{C[O_2]+B}, \tag{7}$$

where

$$A = 2K_1\text{Wi}, \quad B = 1.25\frac{K_7}{K_8}K_{10}[\text{InH}], \quad C = 2K_1.$$

Equation (7) is easily reduced to the following form:

$$DPP' = \frac{A[O_2]}{C[O_2] + B}, \tag{7a}$$

where

$$P = \frac{d[O_2]}{dX}.$$

The expression for the polymer oxidation rate can be obtained easily as a flow through the film surface:

$$\begin{aligned} JO_{2}\big|_{x=0} &= \sqrt{2DA\frac{1}{C^2}(C[O_2] + B) - B\ln(C[O_2] + B)}, \\ [O_2] &= [O_2]_0. \end{aligned} \tag{8}$$

Taking into account all values of kinetic constants entering (8) and also the fact that oxygen solubility in polyolefins at the normal conditions is near 10^{-3} mol/kg,[11] Equation (8) is reduced to the following form:

$$JO_2 = \sqrt{2.5D\text{Wi}[O_2]_0}. \tag{8a}$$

The concentration profile of oxygen from the polymer surface is described by

$$\sqrt{[O_2]_0} - \sqrt{[O_2]} = \sqrt{\frac{\text{Wi}}{D}}\frac{X}{2}, \tag{9}$$

where X is the distance from the film surface.

Analogously to that proposed previously,[1,5] let us estimate the depth of penetration of the chemical reaction $l_{\text{ch.r.}}$ as X, at which $[O_2] = 0$. From this

$$l_{\text{ch.r.}} = 2\sqrt{\frac{D[O_2]_0}{\text{Wi}}}. \tag{10}$$

Let us compare $l_{ch.r.}$ values in the presence and the absence of antioxidant in the polymer. From References 1 and 5 it is known that $l_{ch.r.}$ is, in the case of nonstabilized polymer,

$$l^0_{ch.r.} = 2\sqrt{\frac{D[O_2]_0}{\frac{1}{2}\,Wi + \frac{K_2}{2K_6}\,[RH]\sqrt{Wi}}}. \tag{11}$$

Formulae (10) and (11) are similar except that the influence of the chain oxidation process on the depth of penetration due to the suppression thereof by antioxidant molecules is absent.

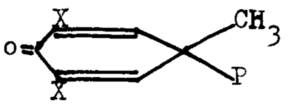
Let us estimate the antioxidant influence on $l_{ch.r.}$ from the expression

$$\frac{l_{ch.r.}}{l^0_{ch.r.}} = T = \sqrt{\frac{1}{2} + \frac{K_2}{2K_6}\,[RH]\,\frac{1}{\sqrt{Wi}}}. \tag{12}$$

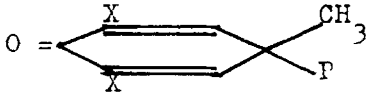
Analysis of the function $T = T(Wi)$ shows that at great Wi values (dose rates more than 280 Gy/sec) $T < 1$, i.e., introducing the antioxidant brings upon a decrease in the depth of penetration of the chemical reaction of radiation oxidation. At $Wi \rightarrow \infty$ $T \rightarrow \sqrt{1/2}$. At small values of initiation rates (dose rates less than 2.84 Gy/sec) introducing the inhibitor can increase the depth of penetration of oxidation reaction considerably. Let $Wi = 10^{-8}$ mol/l sec (dose rate about 0.03 Gy/sec); then the calculation of T for room temperature gives the values $T \simeq 35$ (K_2 and K_6 are values we have calculated from References 11 and 12 and substituted into (12); for polypropylene $[RH] = 24$ mol/l. Consequently, introducing the antioxidant increases the depth of penetration of chemical reaction of radiation oxidation considerably in this case.

To test the proposed relationships experimentally, the irradiation of thick polypropylene films (thickness 2 mm) is carried out with introduced stabilizer (ionol). The irradiation is carried out under the conditions mentioned above.

The products of chemical interaction of stabilizer with alkyl radicals forming in polypropylene at irradiation are analyzed. Before analysis by liquid chromatograph, thin-cut film pieces are placed into benzene, extraction is carried out for 150 h at 40°C. The peaks on the chromatogram using a uv-detector of wavelength 248 nm are detected in the product of extraction besides ionol after irradiating by a dose of 5 kGy. These peaks are inferred to chinoid structure compounds which are formed by the interaction of alkyl and phenyl radicals outside the oxidation zone.[8]



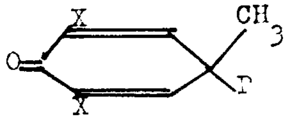
After benzene extraction the products of interaction of phenoxyl with relatively low molecular part of polymer are analyzed. Taking into account the fact that the mechanism of radiation action on polypropylene within the range of dose rates 0.3–3 Gy/sec does not change, and the quantity of the products of interaction of phenoxyl with low molecular part of polymer is proportional to the general content in polypropylene of the compounds of the type,



it can be assumed that

$$\frac{l - l^1_{\text{ch.r.}}}{l - l^2_{\text{ch.r.}}} = \frac{m^1}{m^2} = \frac{L_1}{L_2} \tag{13}$$

where l is a half of the thickness of polymer film, $l^1_{\text{ch.r.}}$ are the depths of penetration of chemical reaction of radiation oxidation at a dose rate of $p_1 = 0.28$ Gy/sec; $l^2_{\text{ch.r.}}$ is the same at $p_2 = 2.8$ Gy/sec; m^1 is the quantity of the products



for the case of dose rate p_1; m^2 is the same, but for dose rate p_2. L_1/L_2 is the value obtained using experimental data and is equal to 2.2. L_1/L_2 is the value obtained from theoretical calculations by formula (10) and is 1.7. The agreement is sufficiently good to support the results of the kinetic model proposed in this work.

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