European Polymer Journal Vol. 16, pp. 65 to 72
Pergamon Press Ltd 1980. Printed in Great Britain

DIFFUSION MECHANISM OF THE SYNERGISM OF u.v.-ABSORBERS AND ANTIOXIDANTS

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(*Received* 7 *May* 1979)

Abstract—The mechanism of synergism in mixtures of u.v.-absorbers with antioxidants is considered. The synergism is attributed to diffusion of the antioxidant from the deeper-lying layers of polymer film, protected from the action of light by a u.v.-absorber, towards surface layers where the photoreaction takes place. The effect of the antioxidant diffusion process on the duration of the induction period of the unbranched chain oxidation reaction of the polymer is analysed. The experimental investigation of the polybutadiene photo-oxidation process has verified the diffusion mechanism so allowing finding of the optimum relationship between the concentrations of u.v.-absorber and antioxidant and explanation of the observed enhancement of the effect of synergism in thicker polymeric films, for higher antioxidant diffusion coefficients and lower light intensities.

INTRODUCTION

The photostabilization of polyolefins, polydienes or their copolymers, polystyrene and other polymers is often achieved by stabilizing mixtures which exhibit synergism, i.e. the mutual enhancement of the protective effects of individual components of a mixture. The mixtures most commonly used consist of u.v.-absorbers and antioxidants (A) reacting with the free radicals and/or destroying peroxides without producing free radicals [1–4]. The mechanism of the synergistic effect of these mixtures has not yet been discovered despite its great importance. The present work is aimed at investigating such mechanism and a new diffusion mechanism is considered and substantiated.

Two hypotheses had been previously suggested to account for the synergism. In the first, the effect was attributed to the change of the kinetic law of termination of the oxidation chain in the presence of the antioxidant. This conclusion was based on analysis of the kinetic scheme of oxidation [5, 6]:

$$M + h\nu \xrightarrow[+ PH + O_2]{} P\dot{O}_2 \qquad (I)$$

$$P\dot{O}_2 + PH \xrightarrow[+ O_2]{k_2} POOH + P\dot{O}_2 \qquad (II)$$

$$P\dot{O}_2 + P\dot{O}_2 \xrightarrow{k_3} \text{chain termination} \qquad (III)$$

$$P\dot{O}_2 + A \xrightarrow{k_4} \text{chain termination} \qquad (IV)$$

where M is a chromophore which is part of the polymer (PH) or of an impurity. In the absence of an antioxidant, chain termination occurs via reaction (III), and the oxidation rate $w \sim I^{\frac{1}{2}}$, where I is light intensity. If A is present, chain termination follows reaction (IV), becoming linear and $w \sim I^1$. It follows that a u.v.-absorber which reduced light intensity n times will decrease the rate of uninhibited oxidation by a factor of $n^{\frac{1}{2}}$ and that of inhibited oxidation by a factor of n. It is seen that the presence of antioxidant enhances the effectiveness of the u.v.-absorber. According to this mechanism, which will be referred to as a chain mechanism, the effect of synergism is achieved in the absence of any interaction between u.v.-absorber and antioxidant. Within the framework of this mechanism, synergism relationships have been obtained for unbranched [7] and degenerately branched [8] chain reactions.

According to the second hypothesis, synergism is attributed to the u.v.-absorber quenching the excited electronic state of the antioxidant, suppressing or totally eliminating its photoinitiating effect, and so causing a relative enhancement of the protective function of the antioxidant.

DIFFUSION MECHANISM

(a) *The qualitative theory of the synergism*

While investigating the phenomenon of synergism, the authors considered that the diffusion of the antioxidant might have relevance and they suggested a diffusion mechanism [9] schematically illustrated in Fig. 1(b). In a polymer film of sufficient thickness l containing a u.v.-absorber and an antioxidant, the u.v.-absorber exhibits a very strong absorbing function. The intensity of the incident light therefore rapidly decreases with distance from the irradiated surface (Curve 1) and the photoreaction actually takes place only in the hatched narrow zone adjacent to the irradiated surface where most of the incident light is absorbed. In this zone both the polymer and the antioxidant which inhibits the oxidation undergo conversions. No reactions occur in the deeper polymer layers, where the antioxidant concentration remains at the original level. As a result, an antioxidant concentration gradient develops during the photoprocess causing diffusion of the antioxidant towards the photoreaction zone. The arrival of fresh antioxidant

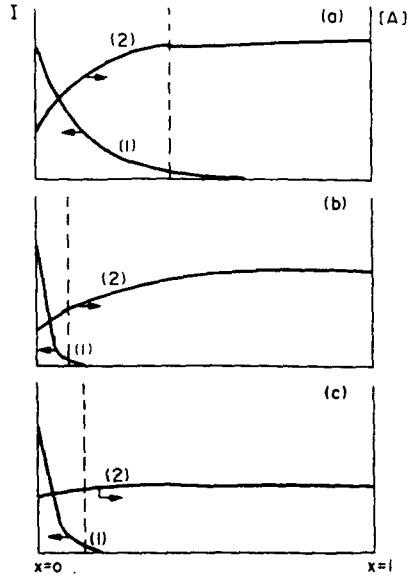


Fig. 1. Distribution of light intensity (1) and anti-oxidant concentration (2) across the polymer film thickness in photooxidation processes occurring in different modes: static (1a); diffusion-controlled (1b) and fast diffusion (1c). The hatched portion is the cross-section in which the reaction occurs at a twenty times lower rate than on the surface. The photoreaction zone is disposed between this line and the surface $x = 0$.

suppresses the reaction in the inhibited oxidation phase. This diffusion mechanism explains the effect of synergism. No interactions between the antioxidant and the u.v.-absorber are necessary.

In order that the diffusion mechanism should "work", the diffusion time (t_{D_A}) must be less than or comparable with the reaction time (t_{ox}). Only if this condition is satisfied will the time t_{ox} be enough for sufficient antioxidant for inhibition of the photoreaction to reach the reaction zone.

According to the Einstein–Smoluchowski formula, the diffusion time is:

$$t_{D_A} = x^2/4D_A \qquad (1)$$

where x is the path and D_A is the diffusion coefficient of the antioxidant. In Table 1 the values of t_{D_A} obtained according to (1) for film thickness (x) of 50 μm are compared with t_{ox}. The values of t_{ox} were estimated in accordance with destruction time tests of stabilized polymer film under natural conditions. The Table shows that the $t_{ox} \gg t_{D_A}$ condition is met by a number of common polymers. In these polymers, diffusion synergism is possible.

(b) *Quantitative treatment*

Provided that there is no interaction between the u.v.-absorber and the antioxidant, the rate of variation of radical R concentration at a point with coordinate x (in the polymer film section by a plane parallel to its surface) at moment t is:

$$\frac{\partial[R(x,t)]}{\partial t} = w_0 e^{-\alpha x} - k_3[R(x,t)]^2 - k_4[R(x,t)][A(x,t)] + D_R \frac{\partial^2[R(x,t)]}{\partial x^2} \qquad (2)$$

where $\alpha = c\epsilon$ is the extinction index of the u.v.-absorber (c is concentration and ϵ is coefficient of absorption); w_0 is the radical formation rate on the surface $x = 0$; D_R is the radical diffusion coefficient; $[A(x,t)]$ is antioxidant concentration at point x at time t.

The first term in the right-hand side of Eqn. (2) represents the radical generation rate under the action of light via reaction (**I**); the second term is the radical recombination rate via reaction (**III**); and the third term is the reaction rate between radicals and the antioxidant via reaction (**IV**); the fourth term represents the rate of the process of radical concentration equalization due diffusion.

The corresponding rate of variation of antioxidant concentration is:

$$\frac{\partial[A(x,t)]}{\partial t} = -k_4[R(x,t)][A(x,t)] + D_A \frac{\partial^2[A(x,t)]}{\partial x^2}. \qquad (3)$$

It will be assumed that the light source is turned on at $t = 0$. The initial radical concentration may then also be assumed to be zero and the corresponding antioxidant concentration to be constant:

$$[R(x,t)]_{t=0} = 0; \qquad [A(x,t)]_{t=0} = [A]_0 \qquad (4)$$

Due to the impenetrability of the film boundaries, the diffusion flow there may be taken to be zero:

$$\left.\frac{\partial[R(x,t)]}{\partial x}\right|_{\substack{x=0\\x=l}} = \left.\frac{\partial[A(x,t)]}{\partial x}\right|_{\substack{x=0\\x=l}} = 0. \qquad (5)$$

Thus, the kinetics of the unbranched oxidation process in the system in question are described by Eqns (2) and (3) with the initial conditions (4) and boundary conditions (5).

Throughout the induction period (T_{ind}), the radical recombination rate and oxidation rate proper are much smaller than the rate of reaction between the

Table 1. Comparison of t_{D_A} and t_{ox} values for various polymers

Polymer	D_A (cm^2/sec)	t_{D_A} (hr)	t_{ox} (hr)
Polydienes	10^{-7}–10^{-9} [10]	10^{-2}–1	10^3
Polypropylene	10^{-10}–10^{-12} [11, 12]	10–10^3	10^4
Polyisobutylene	10^{-10}–10^{-11} [10]	10–10^2	10^4–10^5
High-pressure polyethylene	10^{-10}–10^{-12} [13]	10–10^3	10^4–10^5

radicals and antioxidant:

$$k_2[PH] \ll k_4[A(x,t)];\quad k_3[R(x,t)] \ll k_4[A(x,t)] \quad (6)$$

whence the system of equations for diffusion kinetics describing the kinetics of the decay of antioxidant and the generation of the radicals in different polymer sections, may be written as follows:

$$\frac{\partial[R(x,t)]}{\partial t} = -k_4[A(x,t)][R(x,t)] + w_0 e^{-\alpha x} + D_R \frac{\partial^2[R(x,t)]}{\partial x^2} \quad (7)$$

$$\frac{\partial[A(x,t)]}{\partial t} = -k_4[A(x,t)][R(x,t)] + D_A \frac{\partial^2[A(x,t)]}{\partial x^2} \quad (3)$$

$$[R(x,t)]_{t=0} = 0;\quad [A(x,t)]_{t=0} = [A]_0 \quad (4)$$

$$\left.\frac{\partial[A(x,t)]}{\partial x}\right|_{x=0} = \left.\frac{\partial[R(x,t)]}{\partial x}\right|_{x=0} = 0 \quad (5a)$$

$$\left.\frac{\partial[A(x,t)]}{\partial x}\right|_{x=l} = \left.\frac{\partial[A(x,t)]}{\partial x}\right|_{x=l} = 0. \quad (5b)$$

Subtracting Eqn. (7) from Eqn. (3) in the case where the radical and the antioxidant have about the same diffusion coefficients $D = D_A = D_R$, we obtain:

$$\frac{\partial C(x,t)}{\partial t} = -w_0 e^{-\alpha x} + D\frac{\partial^2 C(x,t)}{\partial x^2},\quad 0 < x < l \quad (8)$$

where

$$C(x,t) = [A(x,t)] - [R(x,t)] \quad (8a)$$

Since

$$[R(x,t)] \ll [A(x,t)] \quad (9)$$

when $t < T_{ind}$, it may be assumed that $[C(x,t)] = [A(x,t)]$.

For polymer oxidation, another case of $D_R \ll D_A$ is much more common. Then, in view of conditions (8a) and (9), the kinetics of antioxidant decay are given by the following formula which is similar to Eqn. (8):

$$\frac{\partial[A(x,t)]}{\partial t} = -w_0 e^{-\alpha x} + D_A \frac{\partial^2[A(x,t)]}{\partial x^2};$$

$$0 < x < l,\quad 0 < t < T_{ind} \quad (8b)$$

with the boundary conditions given by (4, 5a and 5b).

The efficacy of a given pair of antioxidant and u.v.-absorber may be characterized by the observed period of oxidation induction (T_{ind}). It will be assumed that the induction period equals the time during which the relative antioxidant concentration variation at point $x = 0$:

$$Z(t) = \left.\frac{[A]_0 - [A(x,t)]}{[A]_0}\right|_{x=0} \quad (10)$$

attains certain level Z^* for which the inequalities (6) are no longer valid.

Solving Eqn. (8) with the boundary conditions (4, 5a and 5b), we have:

$$z(t) = \frac{t}{\rho\tau_2}(1 - e^{-\rho}) + \frac{2\rho\tau_1}{\tau_2}\sum_{k=1}^{\infty}\frac{1}{[\rho^2 + (\pi k)^2]k^2} \times [1 - (-1)^k e^{-\rho}][1 - e^{-k^2(t/\tau_1)}] \quad (11)$$

where $\tau_1 = l^2/\pi^2 D$ is the characteristic diffusion time in a film of thickness l; $\tau_2 = [A]_0/w_0$ is the characteristic time of variation of antioxidant concentration as a result of its reaction with the radicals under condition (8b); $\rho = \alpha l$ is the ratio of the film thickness to the characteristic light extinction path for a given sample.

We shall begin with a special case where the induction period is much smaller than the characteristic time τ_1. Expanding $e^{-k^2 t/\tau_1}$ in the expression for $Z(t)$ (Eqn. 11) into a series of parameter $k^2 t/\tau_1$, dealing with the first two terms of the series, and carrying out summation with respect to k via the following identities:

$$\sum_{k=1}^{\infty}\frac{1}{x^2 + k^2} = \frac{1}{2x}\left[\pi\frac{e^{\pi x} + e^{-\pi x}}{e^{\pi x} - e^{-\pi x}} - \frac{1}{x}\right];$$

$$\sum_{k=1}^{\infty}\frac{(-1)^k}{x^2 + k^2} = \frac{1}{2x}\left[\frac{2\pi}{e^{\pi x} - e^{-\pi x}} - \frac{1}{x}\right]$$

we obtain:

$$Z(t) = t/\tau_2 \quad \text{when} \quad 0 < t < T_{ind} \quad (12)$$

whence

$$T_{ind} = \tau_2 Z^* \quad (13)$$

The following relation between the problem parameters is necessary for the formulae (12) and (13) to be applicable:

$$\frac{Z^*\tau_2}{\tau_1} \ll 1. \quad (14)$$

The sufficient condition may be obtained by comparing the latter solution with the solution of Eqn. (8) for the boundary conditions (4, 5a and 5b) over an infinite interval $0 < x < \infty$ when condition (14) is *a priori* satisfied:

$$z(t) = \frac{w_0}{[A]_0\sqrt{\pi D}}\int_0^t d\tau\int_0^{\infty}\frac{e^{-(y^2/4D\tau)}e^{-\alpha y}}{\sqrt{\tau}}\,dy$$

$$= \frac{w_0}{[A]_0}\int_0^t e^{-\alpha^2 D\tau}[1 - \phi(\alpha\sqrt{D\tau})]\,d\tau. \quad (15)$$

For small t, the following expansion is valid:

$$z(t) = \frac{w_0}{[A]_0}\left[t - \frac{\alpha^2 D t^2}{2} - \frac{4}{3\sqrt{\pi}}\alpha\sqrt{Dt^3} + \ldots\right] \quad (16)$$

Therefore, the expression for the induction period is true when condition (14) and the following relationship:

$$\frac{Z^*\tau_2\rho^2}{\tau_1} \ll 1 \quad (17)$$

are satisified, or similarly, when the observed induction period is much smaller than the characteristic time of diffusion to a distance l and the characteristic time of diffusion to a distance α^{-1}. This case corresponds to "local" reaction conditions, the antioxidant (and radical) diffusion being insignificant.

The case of the induction period being much greater than the characteristic times of diffusfion to distance l and to distance α^{-1} may be analysed with the aid of the series (11) in which the exponential term $e^{-k^2\tau_1}$ is taken to be zero. Summation of this series yields:

$$Z(t) = \frac{t}{\rho\tau_2}(1 - e^{-\rho}) + \frac{2\pi^2\tau_1}{\rho\tau_2} \times \left\{\frac{1}{6} + \frac{e^{-\rho}}{12} - \frac{1}{2\rho}\left[1 - \frac{1}{\rho}(1 - e^{-\rho})\right]\right\}. \quad (18)$$

For small values of $\rho(\rho \ll 1)$, expression (15) coincides with an accuracy to small terms with respect to ρ and τ_1 with the "local" solution (12):

$$Z(t) = \frac{t}{8\tau_2} - \frac{t\rho}{2\tau_2} + \frac{\pi^2\tau_1\rho}{\tau_2} + \ldots \quad (19)$$

For large $\rho(\rho \gg 1)$ this expression for $Z(t)$ can be approximated by the following function

$$Z(t) = \frac{t}{\rho\tau_2} + \frac{\pi^2\tau_1}{2\tau_2\rho} + \ldots \quad (20)$$

The first term in (20) defines the antioxidant concentration as a function of time for large enough rates of the diffusion process and strong enough light absorption by the sample. The corresponding maximum value of the induction period:

$$T_{ind} = Z^*\tau_2\rho \quad (21)$$

characterizes the ultimate (for a given film thickness and light absorption level) efficacy of the antioxidant. The criterion for applicability of Eqn. (21) may be written as:

$$\frac{\tau_1}{\tau_2 Z^*\rho} \ll 1; \quad \rho \gg 1 \quad (22)$$

In the case described by relationship (21), the process involves rapid diffusion of the antioxidant towards the narrow reaction zone, the bulk of the polymer acting as a "passive" reservoir of antioxidant.

The diffusion dependence of the induction period, associated with the limited speed of antioxidant transport to the reaction zone, may be obtained in an explicit form if the following limiting case is considered. Suppose that a polymer sample absorbs light so strongly that radical generation takes place only in the narrow polymer zone adjacent to the surface $x = 0$. (This assumption is equivalent to supposing that the induction period is many times greater than the characteristic time of diffusion to distance α^{-1}). Then, the rate of variation of antioxidant concentration at any polymer point (except those on the boundaries) will be given by the following diffusion equation:

$$\frac{\partial[A(x,t)]}{\partial t} = D\frac{\partial^2[A(x,t)]}{\partial x^2}. \quad (23)$$

Apparently, the flow through the surface $x = 0$ must be assumed to be equal to the total antioxidant flow rate (instead of condition (5))

$$D\left.\frac{\partial[A(x,t)}{\partial x}\right|_{x=0} = w_0\int_0^t e^{-\alpha x}\,dx = \frac{w_0}{\alpha}(1 - e^{-\rho}) = \frac{w_0}{\alpha}. \quad (24)$$

The flow through the surface $x = l$ is zero as before.

Solving Eqn. (23) with the boundary conditions (24 and 4, 5b), we obtain:

$$Z(t) = \frac{2w_0 l}{D\alpha[A]_0}\left\{\sqrt{\frac{\tau}{\pi}} + 2\sum_{n=1}^{\infty} \times \left[\sqrt{\frac{\tau}{\pi}}e^{-(n^2/\tau)} + n\phi\left(\frac{n}{\sqrt{\tau}}\right)\right]\right\} \quad (25)$$

where

$$\tau = \frac{Dt}{l^2}; \quad \phi(Z) = \frac{2}{\pi}\int_0^Z e^{-z^2}\,dz.$$

For large l ($T_{ind} \ll \tau_1$), function (25) becomes the corresponding function obtained by solving Eqn. (23) with the boundary conditions (24 and 4) over the infinite interval $0 < x < \infty$:

$$Z(t) = \frac{2w_0}{\alpha[A]_0}\sqrt{\frac{t}{\pi D}} = \frac{2w_0 l}{\alpha D[A]_0}\cdot\frac{\tau}{\pi} \quad (26)$$

The corresponding induction period is:

$$T_{ind} = \frac{\pi D(Z^*\alpha[A]_0)^2}{4w_0^2} = \frac{\pi}{\tau_1}\left(\frac{Z^*\rho\tau_2}{2\pi}\right)^2 \quad (27)$$

The latter expression for the induction period is valid when the induction period is much greater than the time of diffusion to distance α^{-1} but at the same time much smaller than the time of diffusion to distance l, i.e. when $\rho \gg 1$ and the following relationships hold:

$$\frac{Z^*\tau_2\rho}{\tau_1} \ll 1 \quad (28)$$

$$\frac{Z^*\tau_2\rho^2}{\tau_1} \gg 1. \quad (29)$$

Thus three characteristic regions may be singled out of all the values of the parameters determining the process kinetics. The first region corresponds to the "local" reaction mode with $T_{ind} \ll \tau_1$ and $T_{ind} \ll \tau_1/\rho^2$, which is determined by inequalities (14) and (17). In this region, the antioxidant concentration at point $x = 0$ (12) varies in accordance with zero order kinetics, and $T_{ind} \sim [A]_0/I$ (I is light intensity) (13). This mode of reaction is illustrated in Fig. 1(a) in which the distribution of light intensity (Curve 1) and concentration A (Curve 2) across the film thickness are shown. In the "local" mode, the diffusion A during the period T_{ind} is too small and does not affect T_{ind}. In each film layer, the antioxidant is used only in reaction with the radicals generated in the layer. Therefore the antioxidant distribution across the film thickness at a certain moment t will be determined by light

intensity distribution. The diffusion exchange of the antioxidant between layers in negligible.

The second characteristic mode may be called a diffusion-controlled reaction. In this case $\tau_1/\rho^2 \ll T_{ind}$ when $\rho \gg 1$. Its region of existence is given by the inequalities (28, 29). In the diffusion-controlled mode, $Z \sim \sqrt{t}$ [see Eqns. (26, 27)] and $T_{ind} \sim [A]_0^2/I^2$.

Unlike the static mode, in the diffusion-controlled mode (Fig. 1b) an exchange of antioxidant between adjacent layers takes place. This results in a smoother pattern of antioxidant distribution across the film thickness than light intensity variation. Another characteristic feature of antioxidant distribution in this case is its constant concentration within the film thickness region $x \gg \alpha^{-1}$.

The third region is characterized by "fast diffusion" and $T_{ind} \gg \tau_1/\rho^2, \tau_1$. In the fast diffusion mode (Fig. 1c), the antioxidant concentration is practically the same throughout the film thickness. In this mode, as in the static one, the decrease of antioxidant concentration follows a zero order kinetic law and not depending on the diffusion parameters of the problem. However, the corresponding induction period in "thick" films ($\rho \gg 1$) [cf. Eqn. (21)] is αl times greater than the corresponding (for $\tau_2 = \text{const}$) induction period in the static mode.

In the general case, T_{ind} is found by solving the equation $Z(T_{ind}) = Z^*$, where the function $Z(t)$ is given by the series (11).

The object of this work has been qualitatively to verify the new diffusion mechanism. Polybutadiene (PB) was chosen as the polymeric model for the investigations because it is readily oxidized and allows rather fast diffusion in its bulk. The work on the quantitative verification of the mechanism is now in progress. Certain difficulties have arisen mainly because the experiments have to be carried out under conditions strictly conforming to the above-described kinetic mechanism, i.e. (a) it must be certain that the oxidation is unbranched and goes on at constant initiation rate; (b) the antioxidant and its conversion products do not directly participate in the photochemical reaction phases; (c) the antioxidant conversion products do not exhibit inhibiting activity.

The polymer used in the present study was SKD—LPR-grade polybutadiene (mol. wt about 250,000) purified of stabilizer and impurites by two-step precipitation from benzene solution, first with acetone and then with isopropanol. Thin films ($l \simeq 20\,\mu$m) were obtained on quartz supports by slowly drawing the polymer from its solution in chloroform. Thick films ($l \simeq 60\,\mu$m) were obtained by evaporating polymer solution from polypropylene supports. The necessary additives were added to the solution. The additives were previously purified by recrystallization from hexane or ethanol. Research grade chloroform was used without further purification. The films were irradiated by means of DB-60 bulbs ($\lambda = 254$ nm), except for cases specifically mentioned below where the full light of a DRSh-1000 bulb passed through a water thermal filter was used. The polymer oxidation kinetics were checked by observing variation of the hydroxy group absorption in the 3450 cm^{-1} band [14]. The efficacies of individual stabilizers and mixtures were estimated according to the duration of the induction period of polymer oxidation.

Experimental results

Figure 2 shows the kinetic curves of photooxidation of unstabilized polybutadiene as well as of polybutadiene constaining u.v.$_1$-absorber (2-hydroxy-4-heptoxybenzophenone) and phenol antioxidant additives in thin (about 20 μm) and thick (about 60 μm) films. The fact attracting attention is that in all cases the oxidation rate of thick films was smaller than that of thin ones during the initial reaction stages (Curves 4). The same effect was observed for u.v.-absorber mixtures with other antioxidants, such as diphenylamine (Fig. 3). The conclusion to be drawn is that the photooxidation of a thick film surface layer equal in thickness to the thin film occurs at a much lower rate than that of the thin film itself. This phenomenon can be attributed only to the effect on the oxidation rate of the surface layer due to the deeper lying layers in the thick film. In the static mode where the oxidation of each layer takes place independently of other layers, thick films are always oxidized much faster since they absorb more light. Consequently, the lower

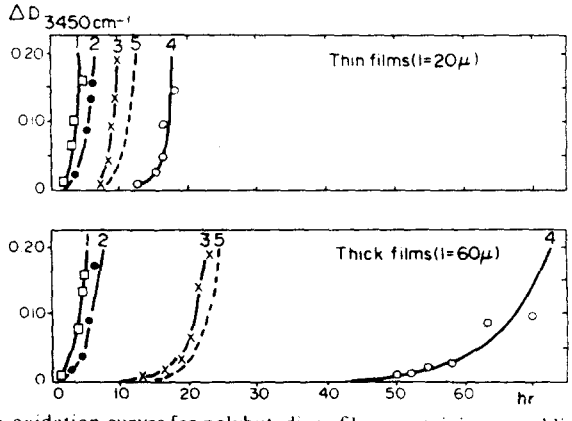


Fig. 2. Kinetic photo-oxidation curves for polybutadiene films containing no additives (1) and stabilized by u.v.$_1$-absorber (3.6×10^{-2} mol/l) (2), and by antioxidant-ionol (5×10^{-2} mol/l) (3) and their mixture with the same u.v.$_1$-absorber and antioxidant concentrations (4). Light wavelength—254 nm. (5) refers to the calculated curves for films containing mixed u.v.-absorber and antioxidant corresponding to their added effects.

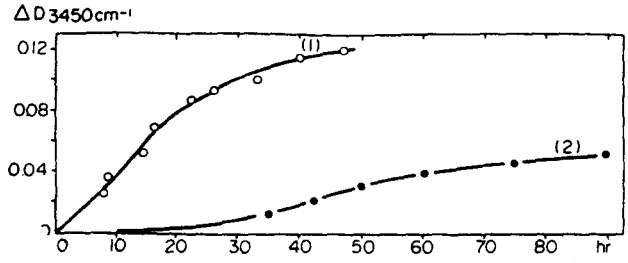


Fig. 3. Kinetic photo-oxidation curves of polybutadiene films stabilized with a mixture of diphenylamine (6.6×10^{-2} mol/l) and u.v.$_1$-absorber (3.6×10^{-2} mol/l). Film thickness—20 μm (1) and 60 μm (2). Light wavelength 254 nm.

oxidation rates of thick films may be regarded as ample evidence supporting the effect of the antioxidant diffusion processes on the light stability of polymer films.

In principle, nothing should be changed if the non-uniform light distribution across the film thickness were created by the light-absorbing polymer or the antioxidant rather than by a u.v.-absorber. In the latter case the stabilizing additives have to perform the functions of both components of a synergetic mixture, i.e. provide an effect which we propose to call a self-synergism effect. Figure 2 demonstrates that a thick film containing only a phenol antioxidant (Curves 3) is oxidized at a lower rate than the thin film. The same effect was obtained in experiments with diphenylamine and dibutyldithiocarbamate of nickel (Fig. 4). Thus the results provide clear proof of the considerable effect of antioxidant diffusion on the light-stability properties.

In order to obtain qualitative verification of the above relationships (21) and (27), the effects of polymer film thickness, light intensity and molecular weight of the antioxidant on the synergism were studied. The magnitude of the effect of synergism was determined by:

$$S = \frac{(T_{ind} - \tau_0) - (\tau_A + \tau_{u.v.} - 2\tau_0)}{\tau_A + \tau_{u.v.} - 2\tau_0} \qquad (30)$$

where τ_0, τ_A and $\tau_{u.v.}$ are photooxidation induction periods in an unstabilized sample and those containing A and a u.v.-absorber respectively.

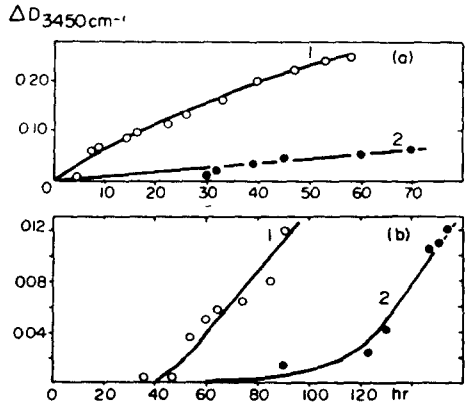
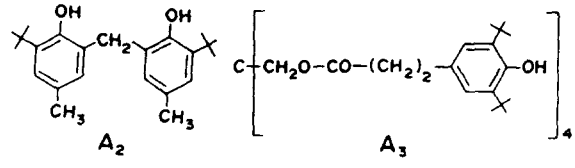


Fig. 4. Kinetic photo-oxidation curves for polybutadiene films, thickness 20 μm (1) and 60 μm (2) stabilized with: (a) diphenylamine (6.6×10^{-2} mol/l); (b) nickel dibutyl-dithiocarbamate (2.4×10^{-2} mol/l). Light wavelength $\lambda = 254$ nm.

As shown in Fig. 2, S = 0.9 for a thin film containing 3.6×10^{-2} mol/l of 2,6-di-tert-butyl-methylphenol (A_1) and 5×10^{-2} mol/l of u.v.$_1$, and S = 1.9 for the thick film. These results are not predicted by either the quenching or the chain mechanism, whereas such an increase of S with thickness is readily explained by the diffusion mechanism.

Varying the intensity of the incident light also affects the stabilizing efficacy of the mixtures. Thus, under the full light from a DRSh-1000 bulb, the induction period of 60 μm thick samples containing both A_1 and u.v.$_1$ was 2.6 times longer than that in the sample containing only A_1. A 4-fold decrease of light intensity enhances the effect of synergism and increases the ratio of the induction periods up to 5.8. Such effect of light intensity can be ascribed to the specific features of the diffusion-controlled photooxidation reaction, discussed earlier in the section where the diffusion problem was considered.

As shown above, in the same mode the induction period should decrease with decreasing diffusion coefficient of the antioxidant. To check this corollary, S values for A_1 were compared with the corresponding values for the antioxidants bis-(2-hydroxy-3-tert.butyl-5-methylphenyl)methane (A_2) and ether of 4-hydroxy-3,5-di-tert.butylphenylpropionic acid and pentaerythritol (A_3):



having reactivities close to that of A_1. The molecular weight ratio for $A_1:A_2:A_3$ is 1:1.5:5. The measured S values for mixtures of A_1, A_2 and A_3 with 2-hydroxy-4-heptoxybenzophenon (3:2, total stabilizer concentration 8.6×10^{-2} mol/l) are 1.9; 1.4 and 0.6, respectively. It is this progression that the molecular weight of A grows and the diffusion coefficients are decreased.

From Eqns. (21) and (27), it follows that T_{ind} depends on the composition of the stabilizer mixture in the following manner:
in the fast diffusion mode:

$$T_{ind} \sim C_\Sigma y(1 - y) \qquad (31)$$

in the diffusion-controlled mode:

$$T_{ind} \sim [C_\Sigma y(1 - y)]^2 \qquad (32)$$

where C_Σ is total concentration of u.v.-absorber + antioxidant, and y is the molar fraction of the antioxidant in the mixture.

Thus in both modes the $T_{ind}(y)$ function is parabolic: it is 2nd order in the fast diffusion mode and 4th order in the diffusion-controlled mode. In both modes the maximum value of T_{ind} is at $y = 0.5$, i.e. when the u.v.-absorber and antioxidant concentrations are the same. As demonstrated by Fig. 5, the relationships (31) and (32) give a qualitatively correct representation of T_{ind} as a function of the synergetic mixture composition.

The tests with films of different thicknesses and with varying light intensity and molecular weight of the antioxidant, as well as the measurements of T_{ind} as function of the stabilizing mixture composition, thus appear to support the diffusion mechanism of synergism. Neither the chain nor the quenching mechanism can account for all the experimental data obtained in this investigation.

It is now possible to explain the effects on the synergism of the stabilizing mixture composition, diffusion mobility of the antioxidant, polymer film thickness and light intensity. New light is also shed on the principles of selecting the synergistic mixtures for different polymeric materials and different service conditions, as well as on the requirements about sample thickness and about the conditions under which accelerated light stability tests of polymers stabilized with synergetic mixtures should be conducted. If the diffusion mechanism is accepted, the irradiation conditions may be expected to have a significant effect on the light stability characteristics. Pulsed irradiation enhances the synergistic effect compared to continuous exposure; for example, an overnight no-light period should contribute to the light stability, since in the dark period the diffusion would increase the antioxidant concentration in the surface zone of the polymer where it had been extensively consumed during the daytime. The diffusion mechanism is apparently able to account for the synergism between a u.v.-absorber and an antioxidant causing a non-radical decomposition of hydroperoxides.

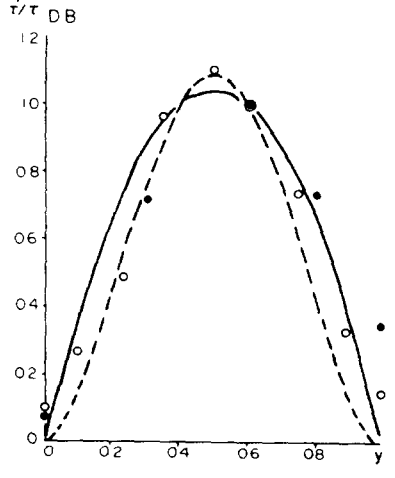


Fig. 5. The relationship between the oxidation induction period and the proportion of the inhibitor ●—in the mixture of A_1 + u.v.$_1$ under irradiation of polybutadiene films, 60 μm in thickness, by light with $\lambda = 254$ nm (total concentration of the stabilizers 8.6×10^{-2} mol/l); ○—in the mixture of A_2 and 2-hydroxy-4-octoxybenzophenone under irradiation of polychloroprene films [15]. The solid curve is calculated from Eqn. (31); the dashed line is calculated from Eqn. (32). The curves are normalized with respect to the experimental point $y = 0.6$.

The possibility of stabilization by the diffusion mechanism is limited by conditions (22), (28) and (29). Thus the effect cannot be produced with high-molecular stabilizers or with low-molecular ones having insufficient diffusion mobility. However, for low-molecular antioxidants a change in conditions, e.g. an increase of temperature of introduction of a plasticizer, may invalidate the limitations on the diffusion. Outside the effective range of the diffusion mechanism, the quenching mechanism will apparently come to the fore. It is particularly probable for antioxidants exhibiting a high photochemical activity, such as aromatic amines. The chain mechanism may not be expected to have a significant effect during the induction period in most polymers, since T_{ind} is usually proportional to the first power of light intensity even in the absence of an antioxidant.

Of course, not all the above conjectures are acceptable before further experimental study. The work of investigating the effect of synergism must no doubt go on as the problem is of paramount importance in the field of light stabilization of polymers.

CONCLUSIONS

The present investigation has provided ample evidence for the effect of antioxidant diffusion processes on the light stability of polymer films and has confirmed diffusion mechanism of synergism in mixtures of u.v.-absorbers with antioxidants. In this paper, the effect of antioxidant diffusion on the light stability of polymeric films is considered under the conditions of an unbranched chain reaction. The effect of diffusion on the degenerately branched reaction may be treated similary. Thus the new diffusion mechanism allows a quantitative evaluation of the synergism effect for different polymer matrices, u.v.-absorbers and antioxidants.

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