Oxygen Consumption During Induction Period of a Photopolymerizing System

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Synopsis

Based on a simple, general kinetic scheme for the inhibition reactions of a photopolymerizing system, a solution is obtained for the differential equation which describes the oxygen concentration profile as a function of exposure time, light intensity, and absorption coefficient. The effect of the absorption coefficient on the oxygen concentration in a polymer slab is evaluated by numerical computation.

Introduction

Photochemical reaction conditioning requires removal of dissolved undesirable gases such as oxygen from a solid polymer system consisting of monomers and initiators dispersed in a binding polymer matrix. This is usually accomplished by purging the dissolved oxygen with inert gas. Since molecular diffusion is involved in purging, the process requires several hours or days depending on thickness of the polymer plate.
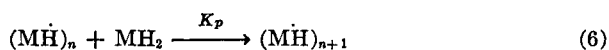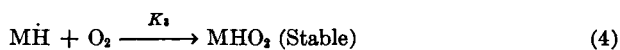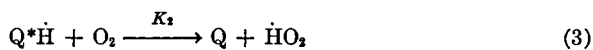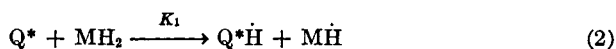
An alternate way to decrease the free oxygen concentration is to expose the polymer to light of suitable intensity and wave length so as to generate enough free radicals to react with oxygen without initiating polymerization. Oxygen is a well known inhibitor of free-radical polymerizations, yielding peroxide radicals of rather low activity.[1] The role of oxygen in photopolymerization of vinyl monomers in a polymeric binder was discussed in detail by McGraw.[2] If the inhibition is very fast, the free oxygen concentration in the polymer system will decrease rapidly.

In this work, we postulate a simple, general kinetic mechanism for the generation of free radicals and their termination by reaction with oxygen. We assume the intensity of the penetrating light follows Beer's law and calculate the time required for the oxygen concentration in the sample to reach a certain level as a function of thickness and absorption coefficient.

Reaction Kinetics

We shall consider an infinitesimally thin layer of the polymer slab consisting of monomer (MH_2) and initiator (Q) uniformly dispersed in a binding polymer matrix. In this thin layer the light intensity is assumed to be constant. The initiator absorbs monochromatic radiation from outside

and becomes activated. The activated initiator reacts with monomers, generating free radicals. These free radicals react with oxygen, thereby inhibiting the polymerization reaction. The details in kinetics of image-forming systems based on photopolymerization was discussed by Woodward et al.[3] For our purpose these reaction schemes may be represented by eqs. (1)–(6).

$$Q + h\nu \xrightarrow{\Phi I} [Q^*] \tag{1}$$

$$Q^* + MH_2 \xrightarrow{K_1} Q^*\dot{H} + M\dot{H} \tag{2}$$

$$Q^*\dot{H} + O_2 \xrightarrow{K_2} Q + \dot{H}O_2 \tag{3}$$

$$M\dot{H} + O_2 \xrightarrow{K_3} MHO_2 \text{ (Stable)} \tag{4}$$

$$2\dot{H}O_2 \xrightarrow{K_4} H_2O_2 + O_2 \tag{5}$$

$$(M\dot{H})_n + MH_2 \xrightarrow{K_p} (M\dot{H})_{n+1} \tag{6}$$

In the reaction, we assume the peroxide radicals generated by step (4) are low-activity products of the polymer containing oxygen. We assume further that the rate constant for the step is much larger than that of the polymerization, K_p.

The rate of formation of the activated initiator is[4,5]

$$d[Q^*]/dt = \Phi\gamma I_x - K_1[Q^*][MH_2] \tag{7}$$

where I_x is the light intensity at a distance x from the polymer slab surface, γ is the absorption or extinction coefficient, and Φ is the quantum efficiency which depends on wave length, concentration and light intensity.

The rate of consumption of oxygen is

$$- d[O_2]/dt = K_2[Q^*\dot{H}][O_2] + K_3[M\dot{H}][O_2] - K_4[\dot{H}O_2]^2 \tag{8}$$

We shall tacitly adopt the general assumption that the rate of generation of Q^* is equal to that of the disappearance so that a stationary state prevails. Furthermore the concentrations of free radicals, $[Q^*\dot{H}]$, $[\dot{H}O_2]$, and $[M\dot{H}O_2]$ are so small that their time derivatives are essentially equal to zero. Under these conditions we have

$$d[Q^*\dot{H}]/dt = K_1[Q^*][MH_2] - K_2[Q^*\dot{H}][O_2] \simeq 0 \tag{9}$$

$$d[M\dot{H}]/dt = K_1[Q^*][MH_2] - K_3[M\dot{H}][O_2] \simeq 0 \tag{10}$$

$$d[\dot{H}O_2]/dt = K_2[Q^*\dot{H}][O_2] - K_4[HO_2]^2 \simeq 0 \tag{11}$$

The three reaction rate constants in eqs. (9), (10), and (11) are

$$K_2 = K_1[Q^*][MH_2]/[Q^*\dot{H}][O_2]$$

$$K_4 = K_1[Q^*][MH_2]/[HO_2]^2$$

$$K_3 = K_1[Q^*][MH_2]/[M\dot{H}][O_2]$$

Substitution of these rate constants into eq. (8), the rate of oxygen consumption, yields

$$-d[O_2]/dt = K_3[M\dot{H}][O_2] = \Phi r I_x \tag{12}$$

The rate of monomer consumption due to polymerization at the conclusion of the inhibition reaction is

$$-d[MH_2)/dt = K_p[MH_2][M\dot{H}] \tag{13}$$

where K_p denotes the propagation rate constant and $[M\dot{H}]$ is a function of the light intensity.

From eqs. (12) and (13), we obtain an expression for the oxygen concentration (at the end of the inhibition reaction) as a function of monomer concentration and rate constants,

$$\ln[O_2]/[O_2]_0 = (K_3/K_p)\ln([MH_2]/[MH_2]_0) \tag{14}$$

where the zero subscript denotes initial concentration. If $K_3 \gg K_p$, eq. (14) suggests the oxygen concentration will be entirely exhausted before an appreciable amount of polymerization occurs.

Differential Equation for Oxygen Balance

Consider a large, thin polymer slab of thickness L with one side exposed to the surrounding air and the other side supported by a rigid plate. This is shown schematically in Figure 1. We shall assume that the oxygen concentration at the surface is always in equilibrium with the surroundings and the surface is exposed uniformly to light of intensity I_0 and known wavelength. The equilibrium oxygen concentration at the surface is equal to the initial concentration. The oxygen balance in a differential layer of thickness dx yields

$$\partial C/\partial t = D(\partial^2 C/\partial x^2) - \Phi r I_0 e^{-rx} \tag{15}$$

where C is the oxygen concentration and D is the diffusion constant. Since the amount of activated complex is assumed to be very small, the quantum efficiency Φ is assumed to be independent of the initiator concentration. Thus the computation of oxygen concentration in the slab requires a solution of the diffusion equation with a chemical reaction rate term which decreases exponentially in respect to light penetration distance.
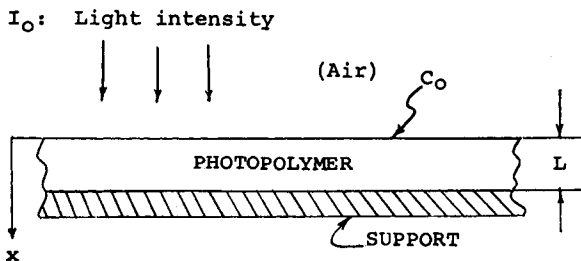

Fig. 1. A schematic diagram of photopolymerizing system.

Solution of the Equation

Equation (15) is to be solved subject to the following initial and boundary conditions:

Initial conditions:

$$C = C_0, \ (0 \le x \le L), \text{ for } t \le 0$$

Boundary conditions:

$$C = C_0, \ (x = 0), \text{ for } t \ge 0$$

$$\partial C/\partial x = 0, \ (x = L), \text{ for } t > 0$$

We take the Laplace transform of eq. (15) with respect to time and obtain

$$P\bar{C} - C_0 = D \frac{d^2\bar{C}}{dx^2} - \frac{KI_0}{P} e^{-\gamma x} \tag{16}$$

where

$$\bar{C} = \int_0^\infty e^{-Pt} C(x,t)dt$$

and

$$K = \Phi\gamma$$

A general solution of eq. (16) is

$$\bar{C} = A \sinh \sqrt{\frac{P}{D}} x + B \cosh \sqrt{\frac{P}{D}} x + \frac{KI_0 e^{-\gamma x}}{PD(D\gamma^2 - P)} + \frac{C_0}{P} \tag{17}$$

The constants A and B can be readily evaluated by applying the two boundary conditions to eq. (17). We find they are

$$A = \frac{KI_0\gamma e^{-\gamma L} + KI_0 \sqrt{P/D} \sinh \sqrt{P/D} \, L}{P(D\gamma^2 - P)\sqrt{P/D} \cosh \sqrt{P/D} \, L}$$

$$B = \frac{KI_0}{P(P - D\gamma^2)}$$

Substitution of these constants into eq. (17) and rearranging, yields

$$\bar{C} = \frac{KI_0 e^{-\gamma x}}{P(D\gamma^2 - P)} - \frac{\sqrt{D} \, KI_0\gamma e^{-\gamma L} \sinh \sqrt{P/D}x}{P^{3/2}(P - D\gamma^2)\cosh \sqrt{P/D} \, L}$$

$$- \frac{KI_0}{P(D\gamma^2 - P)} \frac{\cosh \sqrt{P/D} \, L(1 - x/L)}{\cosh \sqrt{P/D} \, L} + \frac{C_0}{P} \tag{18}$$

The inverse transformation of eq. (18) is

$$C(x,t) - C_0 = \frac{KI_0 e^{-\gamma x}}{D\gamma^2} (1 - e^{D\gamma^2 t})$$

$$-\sqrt{D}\ KI_0\gamma e^{-\gamma L}\mathcal{L}^{-1}\left[\frac{\sinh\sqrt{P/D}\ x}{P^{1/2}\cosh\sqrt{P/D}\ L}\frac{1}{(P-D\gamma^2)}\right]$$

$$+KI_0\mathcal{L}^{-1}\left[\frac{\cosh\sqrt{P/D}\ L(1-x/L)}{P\cosh\sqrt{P/D}\ L}\frac{1}{(P-D\gamma^2)}\right] \quad (19)$$

The evaluation of the inverse transform of the last two terms of eq. (19) involves some mathematical manipulation. This is done by splitting each function (as shown in the brackets) into two convenient parts and finding the inverse transform of each part. We obtain the final transformation by use of the convolution integral. We find the poles involved in the hyperbolic functions are all simple ones and the corresponding residues can be readily evaluated by using the theory of residue. The final results of the inverse transformations of these two terms are:

$$\mathcal{L}^{-1}\left[\frac{\sinh\sqrt{P/D}\ x}{P^{1/2}\cosh\sqrt{P/D}\ L}\frac{1}{(P-D\gamma^2)}\right]=\frac{x}{D^{1/2}\gamma^2}(e^{D\gamma^2 t}-1)$$

$$-\frac{2L}{D^{1/2}}\sum_{n=0}^{\infty}\frac{(-1)^n\sin B_n(x/L)\cdot[e^{D\gamma^2 t}-e^{-B_n^2 Dt/L^2}]}{B_n^2\ [(B_n/L)^2+\gamma^2]} \quad (20)$$

$$\mathcal{L}^{-1}\left\{\frac{\cosh\sqrt{P/D}\ L\ [1-(x/L)]}{P\cosh\sqrt{P/D}\ L}\frac{1}{(P-D\gamma^2)}\right\}=\frac{1}{D\gamma^2}(e^{D\gamma^2 t}-1)$$

$$-\frac{2}{D}\sum_{n=0}^{\infty}\frac{\sin B_n(x/L)\cdot[e^{D\gamma^2 t}-e^{-B_n^2 Dt/L^2}]}{B_n\ [(B_n/L)^2+\gamma^2]} \quad (21)$$

where

$$B_n=\pi[(2n+1)/2]$$

Substituting eqs. (20) and (21) into eq. (19) and rearranging, we obtain the solution for the oxygen concentration in a dimensionless form.

$$\frac{C(x,t)}{C_0}=1+\frac{A}{NC_0}(1-e^{D\gamma^2 t})(e^{-\gamma x}-1+\gamma x e^{-\gamma L})$$

$$+\frac{2A(L\gamma)^3}{NC_0}e^{-\gamma L}\sum_{n=0}^{\infty}\frac{(-1)^n\sin B_n(x/L)\cdot[e^{D\gamma^2 t}-e^{-B_n^2 Dt/L^2}]}{B_n^2\ [B_n^2+(\gamma L)^2]}$$

$$-\frac{2A}{NC_0}(\gamma L)^2\sum_{n=0}^{\infty}\frac{\sin B_n(x/L)\cdot[e^{D\gamma^2 t}-e^{-B_n^2 Dt/L^2}]}{B_n\ [B_n^2+(\gamma L)^2]} \quad (22)$$

where $A=(\Phi I_0/D\gamma)$, and N is the Avogadro number.

Computation of Oxygen Concentration

In order to compute the oxygen concentration as a function of exposure time and distance, the constants appearing in equation 22 must be known. All these constants can be determined experimentally. However, for the
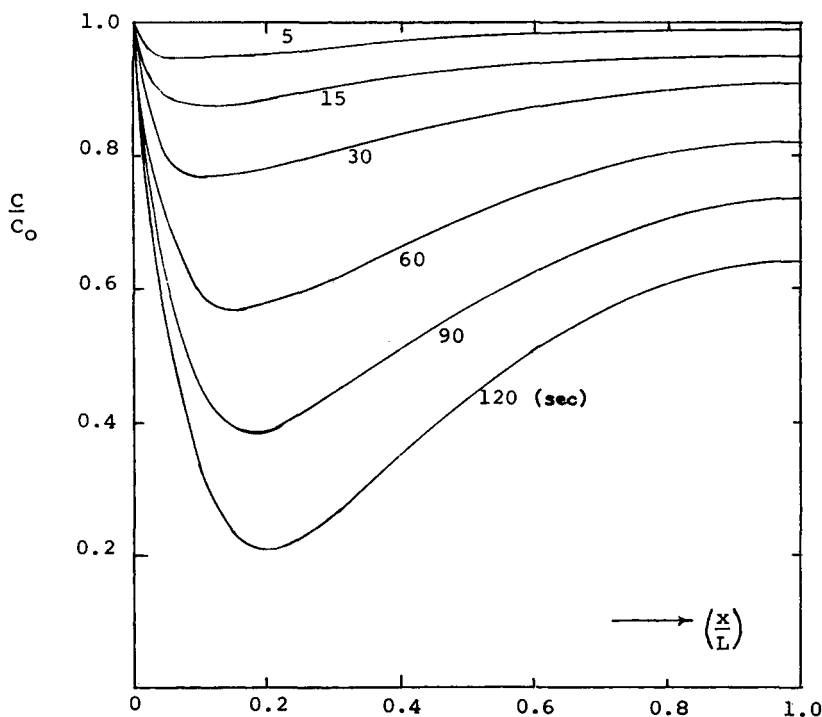
Fig. 2. Oxygen concentration as a function of thickness and time for $\gamma = 2.4$ cm^{-1}.

purpose of computation we assign suitable numerical values to each constant. These are:

$$D = 1.15 \times 10^{-7} \text{ cm}^2/\text{sec}$$
$$C_0 = 3.9 \times 10^{-7} \text{ g-mole/cm}^3$$
$$I_0 = 4.3 \times 10^{14} \text{ quanta/sec-cm}^2$$
$$\gamma = 2.4 \text{ and } 30 \text{ cm}^{-1}$$
$$L = 4.06 \times 10^{-2} \text{ cm}$$
$$\Phi = 1.0 \text{ mole/quantum}$$

Based on these values, the oxygen concentration was computed for two different values of the absorption coefficient.

The results are shown in Figures 2 and 3. These figures show that the absorption coefficient has a pronounced effect on the oxygen concentration profile. At a low absorption coefficient oxygen disappears relatively uniformly in the bulk of the slab and about 40% of the initial oxygen disappears within 2 minutes. However, at a higher absorption coefficient, practically all the oxygen below the surface, where the light intensity is high, is consumed within 10 sec, while at the bottom most of the oxygen remains practically unconsumed. This non-uniform oxygen concentration might cause the polymerization reaction to set in just below the surface layer.
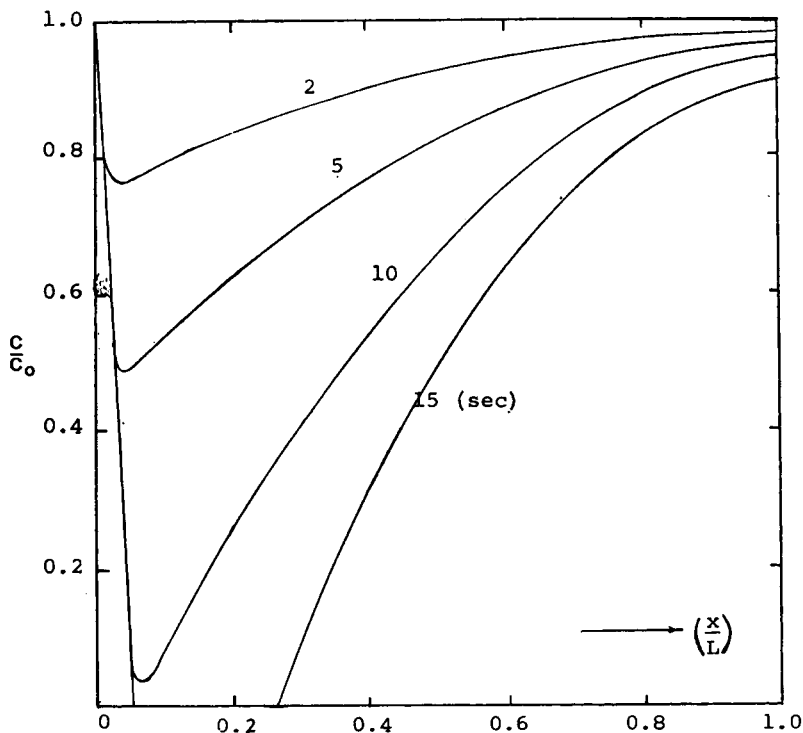
Fig. 3. Oxygen concentration as a function of thickness and time for $\gamma = 30$ cm^{-1}.

References

1. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953.

2. W. J. McGraw, *Proc. Tech. Assoc. Graphic Arts* 34 (1965).

3. D. W. Woodward, V. C. Chambers, and A. B. Cohen, *Photo. Sci. Eng.*, 7, No. 6, 360 (1963).

4. E. A. Moelwyn-Hughes, *Physical Chemistry*, 2nd Ed., Pergamon Press, New York-London, 1961.

5. A. E. Cassano, P. L. Silveston, and J. M. Smith, *Ind. Eng. Chem.*, 59, No. 1, 18, (1967).