

Rheological Studies of Ultraviolet Curing with an Oscillating Plate Rheometer

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SYNOPSIS

The dynamic viscoelastic behavior during UV curing was studied for thin liquid films of epoxy acrylate prepolymer by the use of an oscillating plate rheometer. The dynamic viscosity rapidly increases after a certain period of irradiation, so that the UV curing process has the minimum exposure energy required to start polymerization. The minimum exposure energy markedly increases with increasing sample thickness; this results from the inconsistency of degree of curing in the direction perpendicular to the shearing surface. Since free radicals which initiate polymerization are formed by photochemical decomposition of initiator, the ability to cure a film depends on the light intensity at a given depth of the film. The attenuation of light in the film is primarily responsible for this inconsistency. When UV light is applied through a UV filter, the curing behavior is analyzed by a single exponential decay of light with depth because the curing is induced by absorption of a monochromatic light of 365 nm. On the other hand, when UV light from a UV lamp whose output spectrum is a continuum is directly applied, the curing behavior is explained by a combination of energy absorption at different wavelengths. In both cases, the theoretical curves of dynamic viscosity predicted in relation to spectral sensitivity show a good agreement with the experimental results.

INTRODUCTION

Ultraviolet (UV) curing offers a solvent-free process for coating and printing applications which may consume less energy than conventional heating processes. Practically the thickness of layer which is printed on a substrate is a few μm and the curing is completed within a second, so that the systematic studies on photochemistry related directly to image recording are very difficult. For the prediction of curing performance of such UV curable systems, we have developed an oscillating plate rheometer which can directly and continuously follow a progress of curing.^{1,2} The rheometer gives the cure rate for a liquid film with a thickness less than 10 μm .

In the previous paper,³ the dynamic viscoelastic behavior during UV curing was measured for an epoxy acrylate prepolymer containing photoinitiators. Some of the conclusions are as follows. First, independent of light intensity, the dynamic viscosity plotted against the exposure energy lies on a single curve which is approximated by two straight lines. Secondly, the minimum exposure energy defined as the exposure energy at the intersection of two lines decreases with decreasing sample thickness, whereas the slope of line is constant. The thickness dependence of the minimum exposure energy is attributed to the attenuation of light in the direction perpendicular to the shearing surface. In general, the attenuation of a monochromatic light follows an exponential decay with depth in the film.

However, a high pressure mercury lamp whose spectral output is a continuum is frequently used in the UV curing industry. Since light absorption at various wavelengths contributes to radical production, the curing behavior is complicated. In this study, the dynamic viscosity of epoxy acrylate prepolymer during UV curing is measured at various sample thicknesses and the results are compared with the theoretical prediction in relation to spectral sensitivity.

EXPERIMENTAL

Samples

The epoxy acrylate prepolymer used was a 60 wt % solution of a commercial resin (Epicron 1050 from Dainippon Ink and Chemicals Inc.) in trimethylol propane triacrylate (TMPTA). As a photoinitiator was used an alkyl ether of benzoin, whose concentration was 10 wt %. It has been a common practice in the UV curing industry to employ a high concentration of photoinitiator to ensure efficient absorption of light.

Figure 1 shows the spectral sensitivity of the prepolymer containing the initiator. A 30 wt % solution of prepolymer in acetone was applied to an aluminium plate in a whirler which spread the solution over a whirling plate by centrifugal force. After dried at room temperature, the plate was set to a spectrograph in a nitrogen atmosphere and exposed to UV light from a high pressure mercury lamp. The major peaks appear at 302, 313, 334, and 365 nm wavelengths. The peak height does not necessarily give the absolute sensitivity as the light intensity varies depending on the wavelength.

Apparatus

The apparatus used was an oscillating plate rheometer. The details of apparatus and the method of measurement have been reported elsewhere.² A small amount (about 10 μg) of sample is held in a gap between an os-

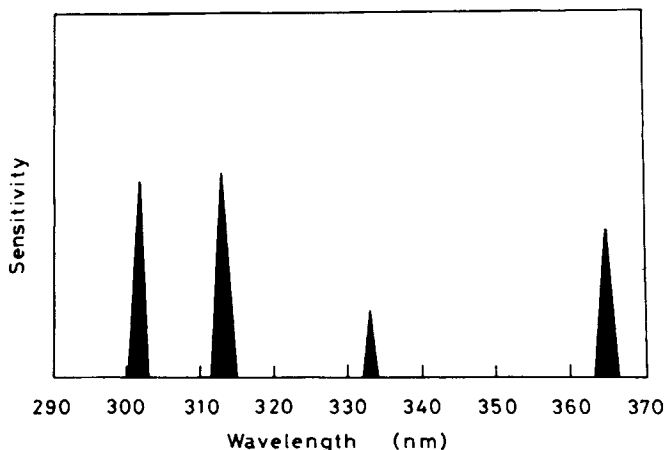


Fig. 1. Spectral sensitivity of prepolymer containing 10 wt % initiator.

cillating plate and a fixed plate. The oscillating plate is made of a quartz glass and attached to a duralumin frame. A forced oscillation is applied electromagnetically by passing an alternating current through a coil in a constant magnetic field. The resultant displacement of the frame is detected as a change in capacity of a small condenser. When the UV light is applied to the UV curable prepolymer, the dynamic viscosity rapidly increases due to network polymerization; then the movement of frame rapidly decreases. The time dependence of dynamic viscosity η' can be obtained by measuring the amplitude ratio of force-to-displacement and the phase angle. In this study, the frequency was held at 80 Hz and the temperature at 30°C.

Since the ability to cure a liquid film of prepolymer depends on the light intensity at a given depth in the film, the degree of curing under irradiation is inconsistent in the direction perpendicular to the shearing surface. Hence, the time-dependent function of dynamic viscosity varies with sample thickness. To study the effect of sample thickness on the curing behavior, the dynamic viscosity was measured at various thicknesses in the range of 4–200 μm . The thickness was adjusted by the use of an optical interferometer⁴ and a thickness gauge.

The UV light source was a high pressure mercury lamp, the spectral output of which was a continuum with superimposed sharp peaks at various wavelengths. Figure 1 shows that the prepolymer has strong absorption which overlaps four significant peaks of the UV output spectrum. In the UV curing, the 365 nm absorption is of primary importance. Therefore, a UV filter which cut off the light below 350 nm was used to examine the rheological behavior during UV curing induced by a monochromatic light of 365 nm. Table I shows the exposure intensity at the surface of prepolymer film for light of different wavelengths.

RESULTS

Figure 2 shows the effect of sample thickness on the rheological behavior during UV curing induced by direct application of light emitted from the mercury lamp. The dynamic viscosity abruptly begins to increase beyond a certain exposure energy depending on the sample thickness and then linearly increases with exposure energy. The slope of line is about 2.6 irrespective of sample thickness. It seems likely that the change in sample

TABLE I
Exposure Intensity for Light of Different Wavelengths

Wavelength (nm)	Exposure Intensity (mW cm^{-2})	
	Without filter	With filter
302	1.7	0
313	3.7	0
334	0.7	0
365	5.6	4.5
Total	11.7	4.5

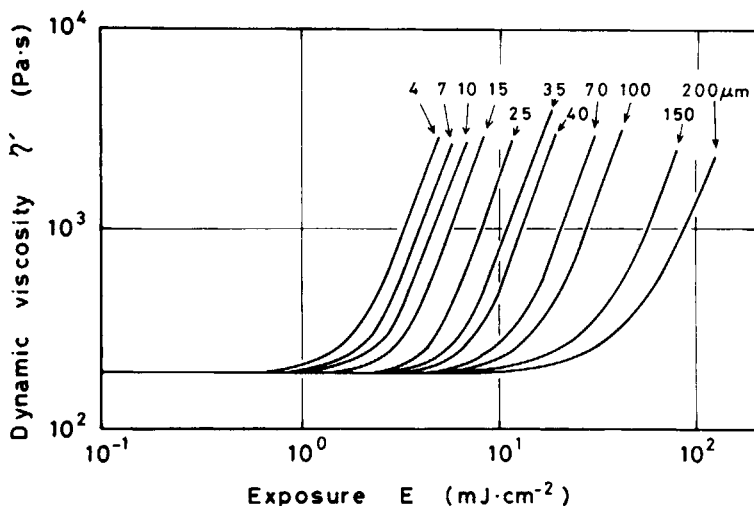


Fig. 2. Dependence of dynamic viscosity on exposure energy during UV curing induced by direct application of UV light emitted from the high pressure mercury lamp.

thickness merely causes a horizontal shift of curves. Each curve can be represented by the following equation^{3,5}:

$$\eta'/\eta'_0 = [1 + (E/E_m)^{2n}]^{1/2} \quad (1)$$

where η'_0 is the initial dynamic viscosity of prepolymer (before UV irradiation), n is the slope of line, and E_m is the minimum exposure energy required to initiate photopolymerization. Since the curve can be approximated by two straight lines, the minimum exposure energy is defined as the exposure energy of intersection between the base line and the asymptotic line. In image recording, the crosslinking reactions are used for efficient insolubilization of polymers. Compared with linear polymerization, the theory of crosslinking and multicenter polymerization with monomers is more complicated.⁶⁻⁸ It is difficult to derive an equation corresponding to eq. (1) from the change in chemical state of reactants. Therefore, the curing behavior will be discussed in terms of the minimum exposure energy.

Figure 3 shows the effect of sample thickness on the rheological behavior during UV curing induced by a monochromatic light of 365 nm. The dynamic viscosity abruptly increases when the exposure energy exceeds 4.2 mJ cm⁻² irrespective of sample thickness. At the beginning of curing, the thicker the sample, the more slowly the dynamic viscosity increases to the point where the data are approximated by a straight line. The slope of asymptotic line is also about 2.6 at sample thicknesses less than 150 μm .

Figure 4 shows the minimum exposure energy plotted against the sample thickness. In the case of direct application of UV light from the mercury lamp, the minimum exposure energy markedly decreases with decreasing sample thickness. However, when the prepolymer is irradiated with 365 nm light, the minimum exposure energy seems to approach an equilibrium value at thicknesses less than 10 μm . At these sample thicknesses, the

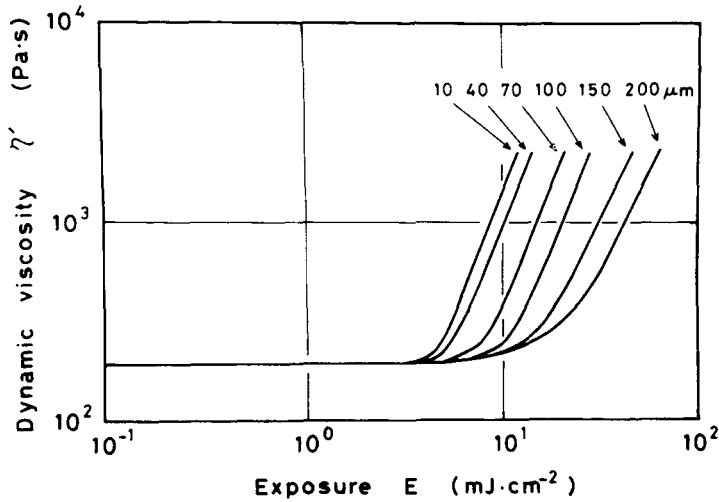


Fig. 3. Dependence of dynamic viscosity on exposure energy during UV curing induced by a monochromatic light of 365 nm.

degree of curing may be homogeneous in the film. The data obtained with the UV filter are represented by an exponential function of sample thickness as follows:

$$E_m = (4.2 \text{ mJ cm}^{-2}) \exp[h/(120 \mu\text{m})] \tag{2}$$

where h is the sample thickness. It is of interest to note that the front factor (4.2 mJ cm⁻²) coincides with the exposure energy at which the dynamic viscosity begins to increase. In any case, the appearance of thickness dependence of the minimum exposure energy is caused by the inconsistency

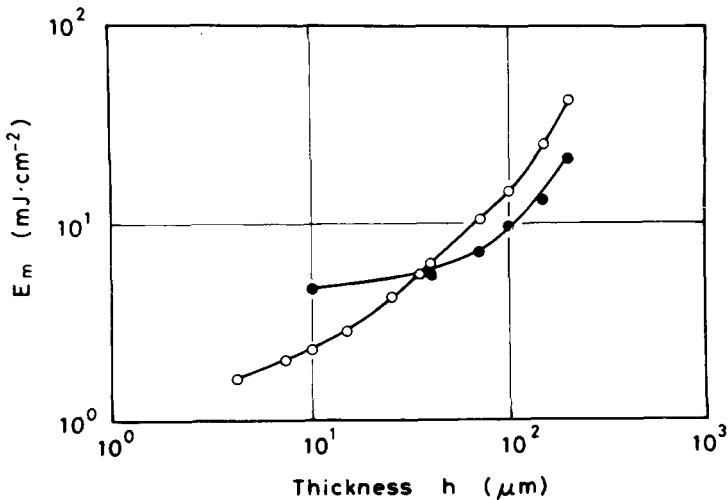


Fig. 4. The minimum exposure energy plotted against the sample thickness: (●) with UV filter; (○) without UV filter.

of degree of curing, which in turn is related to the decreasing UV energy with depth in the film.

DISCUSSION

First of all, the UV curing induced by a monochromatic light will be discussed. In general, the light intensity I at a given depth x in the film is written as

$$I = I_0 \exp(-\alpha x) \quad (3)$$

where I_0 is the incident light intensity at $x = 0$ and α is the attenuation constant defined as $2.303\epsilon [I_n]$, where $[I_n]$ is the concentration of initiator with molar extinction coefficient ϵ . The reciprocal attenuation constant, $1/\alpha$, means the penetration depth of light.

In Figure 4, the exposure energy becomes constant when the sample thickness is decreased to the order of μm . For such a thin film in which the degree of curing is considered to be homogeneous, eq. (1) may also be acceptable. Thus,

$$\eta'/\eta'_0 = [1 + (E/E_0)^{2n}]^{1/2} \quad (4)$$

where E_0 is the equilibrium value of the minimum exposure energy. Accordingly, the dynamic viscosity $\eta'(x)$ of very thin layer at a depth x in the film is given by

$$\begin{aligned} \eta'(x)/\eta'_0 &= [1 + (I_0 t/E_0)^{2n} \exp(-2n\alpha x)]^{1/2} \\ &= [1 + (E/E_0)^{2n} \exp(-2n\alpha x)]^{1/2} \end{aligned} \quad (5)$$

where t is the exposure time.

The purpose of this study is to analyze the rheological behavior in the early stage of curing. The storage modulus G' is negligibly small compared with the loss modulus $G'' (= \eta'\omega)$ in this stage studied. In addition, the shear stress is independent of the depth in the oscillating plate rheometer, whereas it increases in the course of curing. Therefore, the dynamic viscosity observed using this rheometer is written as

$$\eta' = \frac{h}{\int_0^h \frac{dx}{\eta'(x)}} \quad (6)$$

Substituting Eq. (5) into Eq. (6) gives

$$\eta'/\eta'_0 = \frac{2n\alpha h}{\ln\left(\frac{\eta'_1 - \eta'_0}{\eta'_1 + \eta'_0} \cdot \frac{\eta'_2 + \eta'_0}{\eta'_2 - \eta'_0}\right)} \quad (7)$$

where η'_1 and η'_2 are the dynamic viscosities at $x = 0$ and $x = h$, respectively, and are given by

$$\eta'_1/\eta'_0 = [1 + (E/E_0)^{2n}]^{1/2} \quad (8)$$

$$\eta'_2/\eta'_0 = [1 + (E/E_0)^{2n} \exp(-2n\alpha h)]^{1/2} \quad (9)$$

The alkyl ethers of benzoin absorb UV energy at about 365 nm wavelengths due to the $n-\pi^*$ transition; this results in direct photodecomposition to produce free radical species. The molar extinction coefficient is about $120 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 365 nm.⁹ The density of the sample being taken as 1.05 g cm^{-3} , the attenuation constant is estimated to be 114 cm^{-1} . The penetration depth of 365 nm light is $88 \mu\text{m}$, and this value is comparable to that determined by eq. (2) through the rheological measurements. The values of η'_0 , E_0 , and n are determined from Figures 3 and 4 as follows: $\eta'_0 = 1.98 \times 10^2 \text{ Pa s}$, $E_0 = 4.2 \text{ mJ cm}^{-2}$, and $n = 2.6$. Therefore, the dependence of dynamic viscosity on the exposure energy can be calculated. Figure 5 shows the comparison of experimental data with the theoretical prediction. Although slight discrepancy can be seen at the beginning of curing, the theory may show a good agreement with experimental results. It is concluded that the relation between the minimum exposure energy and the sample thickness can be explained by a single exponential decay of light intensity with depth in the film.

Next, we shall consider the rheological behavior during UV curing induced by direct application of light emitted from the mercury lamp. If the molar extinction coefficient of initiator is constant in the wavelength range studied, the dependence of dynamic viscosity on the exposure energy is given by the similar equation to eq. (7). However, the extinction coefficient

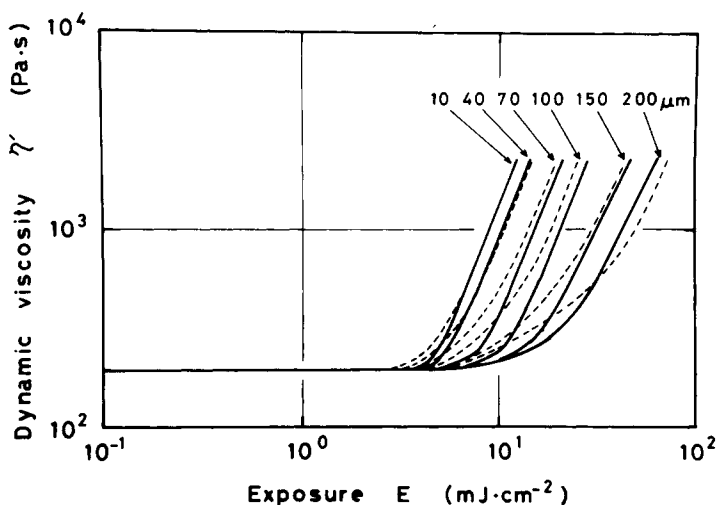


Fig. 5. Comparison of the theoretical prediction (---) with the experimental results (---) for UV curing induced by a monochromatic light of 365 nm.

of benzoin alkyl ethers increases for light of wavelengths less than 365 nm. Among the wavelengths corresponding to the peaks in the spectrum, the light of 365 nm penetrates most deeply into the film. The initiation of polymerization can be explained by a combination of energy absorption at different wavelengths. Then the dynamic viscosity $\eta'(x)$ of thin layer at a depth x is written as

$$\eta'(x)/\eta'_0 = \left\{ 1 + \left[\sum_i (E_i/E_{0,i}) \exp(-\alpha_i x) \right]^{2n} \right\}^{1/2} \quad (10)$$

where E_i , $E_{0,i}$, and α_i are, respectively, the exposure energy, the equilibrium value of the minimum exposure energy, and the attenuation constant at wavelength λ_i . The attenuation constant is defined as $\alpha_i = 2.303\epsilon_i[I_n]$, where ϵ_i is the molar extinction coefficient at the corresponding wavelength. Figure 1 shows that the light of 302, 313, and 365 nm plays an important role in photopolymerization, and so we have focused the attention on the energy absorption at these wavelengths. From Table I, the light intensity is given as follows: $E_{302} = 0.15E$, $E_{313} = 0.32E$, and $E_{365} = 0.48E$, where E is the total exposure energy. Combining Figure 1 and Table I, the equilibrium values of the minimum exposure energy for each light are determined as follows: $E_{0,302} = 0.21E_{0,365}$, and $E_{0,313} = 0.44E_{0,365}$, because the 3:3:2 ratio can be seen for the peak heights at 302, 313, and 365 nm in the spectrum. Furthermore, the molar extinction coefficient at 310 nm is about 6 times that at 365 nm, i.e., $\alpha_{302} = \alpha_{313} = 6\alpha_{365}$. Thus, Eq. (10) results in

$$\begin{aligned} \frac{\eta'(x)}{\eta'_0} &= \left\{ 1 + \left[\left(\frac{0.15E}{0.21E_{0,365}} + \frac{0.32E}{0.44E_{0,365}} \right) \exp(-6\alpha_{365}x) \right. \right. \\ &\quad \left. \left. + \left(\frac{0.48E}{E_{0,365}} \right) \exp(-\alpha_{365}x) \right]^{2n} \right\}^{1/2} \\ &= \left\{ 1 + \left(\frac{E}{E_{0,365}} \right)^{2n} \left[1.44 \exp(-6\alpha_{365}x) + 0.48 \exp(-\alpha_{365}x) \right]^{2n} \right\}^{1/2} \quad (11) \end{aligned}$$

Here, $E_{0,365}$ is 4.2 mJ cm^{-2} from the results obtained using the UV filter and α_{365} is 114 cm^{-1} . Now then, the dynamic viscosity as a function of exposure energy can be determined by numerically integrating eq. (6). Figure 6 shows the calculated (broken lines) and experimental (solid lines) results at various sample thicknesses. It can be seen that the behavior is closely correlated by eq. (11). At the bottom of film with thicknesses larger than $100 \mu\text{m}$, the light of 365 nm wavelength plays a predominant role in radical production because the light intensity at the other wavelengths is already decreased to a considerable extent. If the sample thickness exceeds $100 \mu\text{m}$, the minimum exposure energy may exponentially increase with sample thickness. In the case of thin film, the light of wavelengths of 302 and 313 nm also contributes to radical production at the bottom of film.

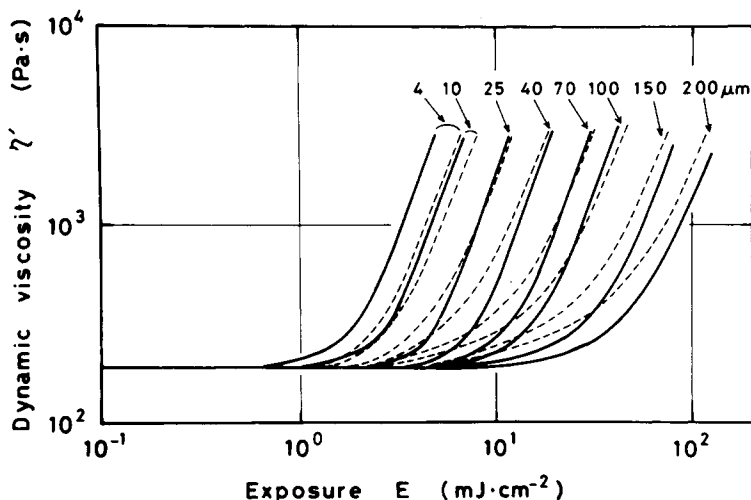


Fig. 6. Comparison of the theoretical prediction (---) with the experimental results (---) for UV curing induced by direct application of UV light emitted from the high pressure mercury lamp.

The minimum exposure energy markedly decreases with decreasing sample thickness. Presumably, the minimum exposure energy becomes constant when the sample thickness is decreased to about $1 \mu\text{m}$.

For further discussion, we have examined the curing behavior at the bottom of film. The rate of radical production at the bottom of film, R_h , may be written as

$$R_h = C_1 \left[3 \exp(-6\alpha_{365}h) + \exp(-\alpha_{365}h) \right] \quad (12)$$

where C_1 is a constant relating to various factors such as the light intensity and quantum yield. Generally, the evaluation of C_1 is very complicated. Assuming that the minimum exposure energy is inversely proportional to the rate of radical production at the bottom of film, that is, $E_m = C_1 C_2 / R_h$, the thickness dependence of the minimum exposure energy is obtained as shown in Figure 7. Here, C_1 is 5.2 mJ cm^{-2} , thus determining that the curve fits the experimental results shown by open circles. The agreement of calculated and experimental results shows that the overall response is very sensitive to the behavior of very thin layer near the bottom. For instance, if a thin liquid layer still remains near the fixed plate of rheometer, a liquidlike response is observed even after UV irradiation. Therefore, it is concluded that the degree of curing at the bottom of film governs the rheological response measured by the oscillating plate rheometer.

CONCLUSIONS

The dynamic viscoelastic behavior during UV curing was investigated for epoxy acrylate prepolymer using an oscillating plate rheometer. The dependence of dynamic viscosity on exposure energy can be theoretically

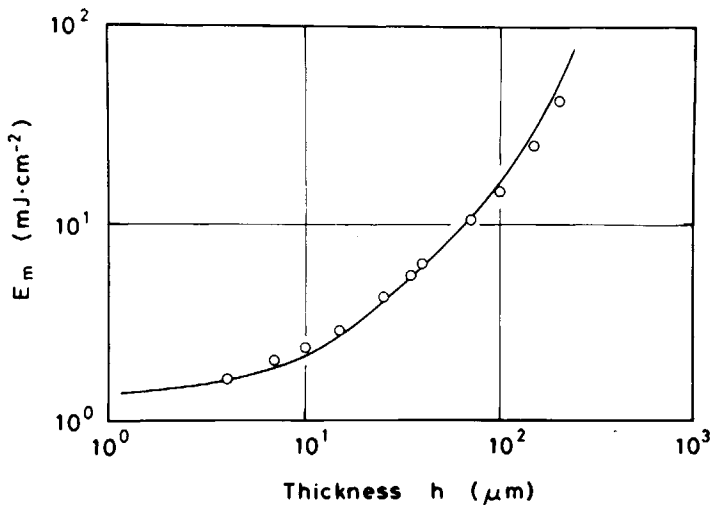


Fig. 7. Thickness dependence of the minimum exposure energy: (---) predicted from the rate of radical production at the bottom of film; (○) experimental data.

predicted in relation to spectral sensitivity and the calculated results show a good agreement with the experimental results. When the UV light is applied through a UV filter, the minimum exposure energy is represented by a single exponential function of sample thickness because the polymerization is induced by absorption of a monochromatic light of 365 nm. When the UV light from the UV lamp is directly applied to the sample, the initiation of polymerization can be explained by a combination of energy absorption at different wavelengths.

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