

Rheological Behavior of Epoxy Acrylate Prepolymer during UV Curing

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Synopsis

The effects of sample thickness and curing temperature on the dynamic viscoelastic behavior were investigated during UV curing of an epoxy acrylate prepolymer by the use of an oscillating plate rheometer which was devised in our laboratory. Independent of light intensity, the values of dynamic viscosity plotted against exposure energy lie on a single curve which is approximated by two straight lines. The minimum exposure energy, which corresponds to that at the intersection of two lines, increases with increasing sample thickness and then starts to increase abruptly at a certain thickness. The critical sample thickness is comparable to the penetration depth of a light having a wavelength of 365 nm. The spectral sensitivity shows that the $n-\pi^*$ absorption at 365 nm by the photoinitiator is of primary importance in polymerization.

INTRODUCTION

Many kinds of photosensitive polymers have been used in the field of image recording, one of which is UV-curable prepolymers. When such a liquid prepolymer is deposited on a substrate and exposed to UV irradiation, a solid film is formed almost immediately. Especially, due to the rapid cure rate and efficient utilization of energy many advances have been made on UV inks.

The determination of cure rate of photosensitive prepolymers is an important subject from a practical point of view. Generally, increasing amount of insoluble fraction gives a measure of the cure rate. Furthermore, several techniques have also been developed using a fact that the physical properties are remarkably affected by the degree of curing. McGinniss and his co-workers¹⁻³ have used dilatometry and electric resistance measurements to determine the rate of polymerization of ethylene glycol dimethacrylate. These techniques directly and continuously follow a progress of curing. The thickness of liquid which is coated or printed on a substrate is generally of the order of a few μm . For prediction of curing performance of pigment dispersions, study should be carried out using such a thin film. The UV-curable prepolymer can be applied to a flexible substrate, and the relative rate of cure can be determined by measuring dynamic viscoelastic properties as a function of exposure energy. A torsion pendulum was used for this purpose by McGinniss.⁴ He measured relative rigidity and logarithmic decrement under flash irradiation. However, the data are only qualitative because they are obtained as a combination of rigidity of substrate and viscoelasticity of sample coated. It is difficult to separate the contribution of viscoelasticity of sample liquid from the overall response.

We have constructed an oscillating plate rheometer for measuring the dynamic viscoelastic behavior of prepolymer during UV curing.^{5,6} The rheometer gives the cure rate of prepolymers even at a thickness less than 10 μm . In this study, the dynamic viscosity was measured during UV curing at various sample thicknesses and curing temperatures to examine the results in relation to spectral sensitivity.

EXPERIMENTAL

Samples

The prepolymer used was a solution of epoxy acrylate resin (Epicron 1050 from Dainippon Ink and Chemicals Inc.) in trimethylol propane triacrylate (TMPTA) at a concentration of 60% by weight. As a photoinitiator was used an alkyl ether of benzoin, whose concentration was 10% by weight. 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 aluminum 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. Since the light intensity varies depending on the wavelength, the peak height in the spectrum should be normalized by referring to the light intensity at the corresponding wavelength. However, the data were not normalized as the UV curing experiments were carried out with the UV sources having similar spectral energy distributions.

Apparatus

The apparatus used is an oscillating plate rheometer. The details of apparatus and the method of measurement have been reported elsewhere.^{5,6} The specimen is held in a gap between an oscillating plate and a fixed plate.

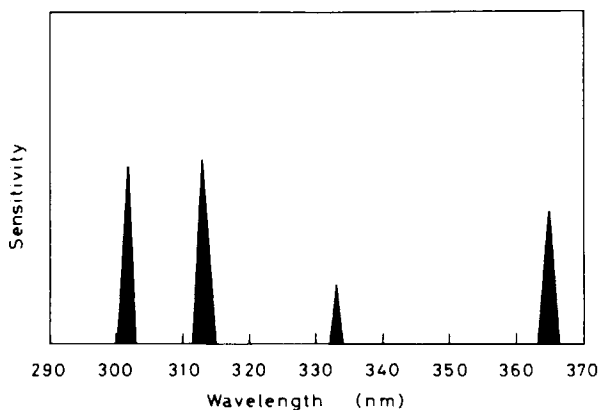


Fig. 1. Spectral sensitivity of prepolymer containing 10 wt % initiator.

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 formation; then the movement of the frame rapidly decreases. The time dependence of dynamic viscosity $\eta'(t)$ can be obtained by the following equation:

$$\eta'(t) = \frac{m(t)h \sin \delta(t)}{A \omega} \quad (1)$$

where $m(t)$ is the amplitude ratio of force-to-displacement, $\delta(t)$ is the phase angle between them, ω is the angular frequency, and h and A are the thickness and area of the sample, respectively.

The dynamic viscosity of the prepolymer (before UV irradiation) is independent of the sample thickness. However, for a thick sample, the degree of curing under irradiation may vary in the direction perpendicular to the shearing surface. To study the effect of sample thickness on the rheological properties, the sample thickness was adjusted in the range of 8–200 μm by the use of an optical interferometer and a thickness gauge.

The spectral output of the high pressure mercury lamp as a light source is shown in Figure 2. In the UV curing experiments, the total exposure intensity was varied from 20 to 70 mW cm^{-2} .

Procedure

Prior to a series of UV curing experiments, the dynamic viscosity of the prepolymer η'_0 was determined at different temperatures. The sample area was measured by a microscope. Figure 3 shows the dynamic viscosity η'_0 plotted against the reciprocal of the absolute temperature. A straight line is drawn, the slope of which gives the flow activation energy of 60.8 kJ mol^{-1} . Once η'_0 is determined, the time-dependent function of dynamic viscosity, $\eta'(t)$, during UV curing can be obtained by the following equation without measuring the sample area in each experiment:

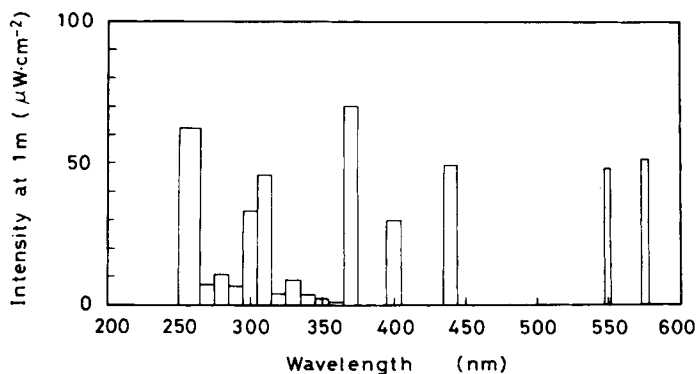


Fig. 2. Output energy distribution of UV lamp.

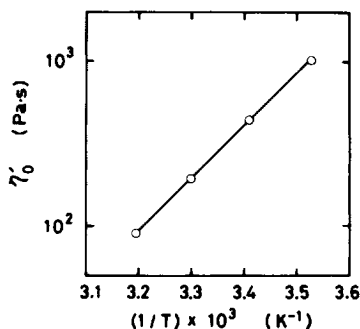


Fig. 3. Dynamic viscosity of prepolymer plotted against the reciprocal of the absolute temperature.

$$\eta'(t) = \frac{m(t) \sin \delta(t)}{m(0) \sin \delta(0)} \eta'_0 \quad (2)$$

where $m(0)$ and $\delta(0)$ are the initial values of amplitude ratio and phase angle, respectively.

In this study, all the experiments were carried out at an angular frequency of 503 s^{-1} (80 Hz).

RESULTS

Effect of Strain Amplitude

As previously pointed out,⁶ there is a serious limitation in this apparatus. Since only the amplitude of sinusoidal force applied to the moving component can be adjusted in the course of the experiment, both the stress and strain amplitudes change during UV curing. The experimental data are obtained under changing conditions. For the sample giving a nonlinear viscoelastic response, the analysis of rheological behavior during UV curing is very complicated. Therefore, the preliminary experiments were first carried out at various strain amplitudes. Figure 4(a) shows an example of the rheological change during UV curing. The dynamic viscosity increases rapidly with exposure time. During UV curing, the strain amplitude decreases linearly with increasing dynamic viscosity as shown in Figure 4(b). To test the linearity, the UV light source was turned off in the course of curing, and the dynamic viscosity was measured at different strain amplitudes. The strain dependence of dynamic viscosity at different stages of curing is shown by open circles in Figure 4(b). As the dynamic viscosity is independent of strain amplitude at any stages, viscoelastic responses are linear under strain amplitudes studied. Therefore, the change in dynamic viscosity directly reflects the structural change during UV curing.

Effect of Light Intensity

Figure 5 shows the effect of light intensity on the time dependence of dynamic viscosity at a sample thickness of $17 \mu\text{m}$. The dynamic viscosity rapidly increases after a certain period of irradiation, so that the UV curing

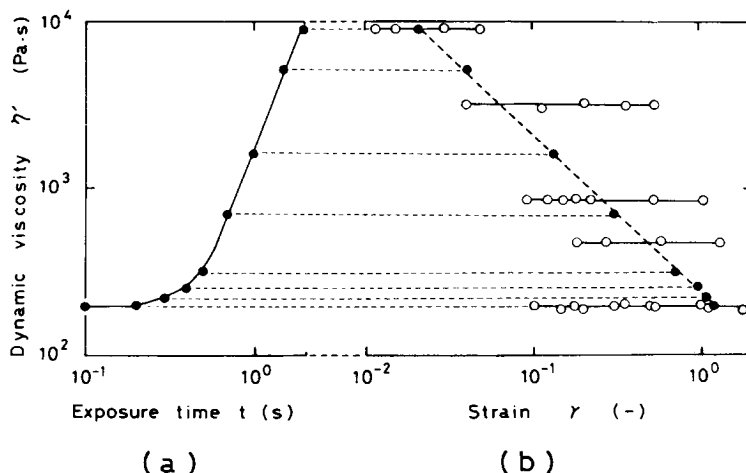


Fig. 4. (a) Time dependence of dynamic viscosity. (b) Strain dependence of dynamic viscosity: (○) dynamic viscosity measured at different stages of curing after UV light was turned off; (●) dynamic viscosity continuously measured in the course of UV curing. $T = 30^\circ\text{C}$; $h = 8.1 \mu\text{m}$.

process has an induction period for photopolymerization. Beyond the induction period, the plots for each light intensity are represented by a straight line. Since the slopes are almost the same irrespective of light intensity, the change in light intensity merely causes a horizontal shift of time-dependent curves.

The UV curing behavior can be related to the exposure energy. Figure 6 shows the dynamic viscosity plotted against exposure energy. All the plots lie on a single curve described by the following equation:

$$\eta'(t)/\eta'_0 = [1 + (E/E_m)^{2n}]^{1/2} \quad (3)$$

where n is the slope of asymptotic line and E_m is the minimum exposure energy required to initiate photopolymerization. The minimum exposure

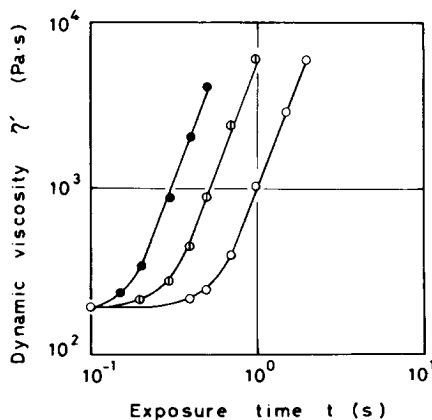


Fig. 5. Dependence of dynamic viscosity on exposure time at various light intensity: (○) 20 mW cm^{-2} ; (◊) 37 mW cm^{-2} ; (●) 70 mW cm^{-2} . $T = 30^\circ\text{C}$; $h = 17 \mu\text{m}$.

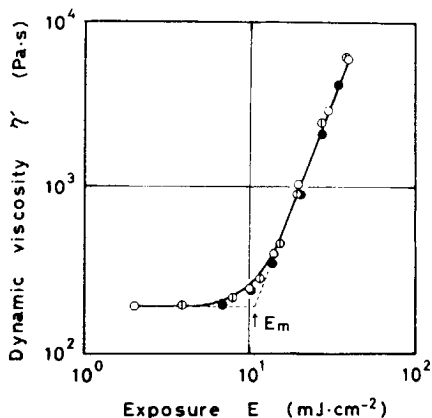


Fig. 6. Dependence of dynamic viscosity on exposure energy: (○) $20 \text{ mW} \cdot \text{cm}^{-2}$; (⊙) $37 \text{ mW} \cdot \text{cm}^{-2}$; (●) $70 \text{ mW} \cdot \text{cm}^{-2}$. $T = 30^\circ\text{C}$; $h = 17 \mu\text{m}$.

energy corresponds to that at the intersection of the base line and the asymptotic line. In image recording, the crosslinking reactions are used for efficient insolubilization of polymers. In this study, the crosslinking of polymers can be achieved by two major reactions: polymerization of multifunctional monomers (TMPTA) and self-crosslinking of polymers (Epicron). The reactive sites of prepolymer link together to form a network structure involving the ethylenic groups of TMPTA. Compared with polymerization without crosslinking, the theory of crosslinking and multicenter polymerization of monomers is more complicated. Therefore, it is difficult to derive an equation corresponding to eq. (3) from the change in chemical state of reactants. However, by applying the same procedure to the data obtained using different sample thicknesses and curing temperatures, the master curve for each can be determined in the form of $\eta'(t)$ vs. E . The curing behavior will be discussed in terms of E_m and n .

Effect of Sample Thickness and Curing Temperature

Figure 7 shows the effect of sample thickness on the UV curing behavior at 30°C . E_m increases with increasing thickness, but n is independent of

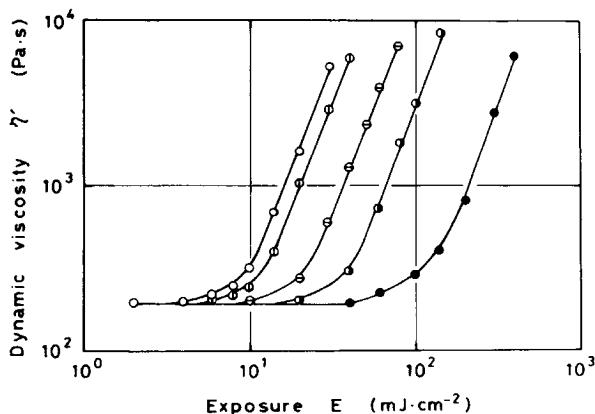


Fig. 7. Effect of sample thickness on the UV curing behavior at 30°C : (○) $8.1 \mu\text{m}$; (⊙) $17 \mu\text{m}$; (⊖) $35 \mu\text{m}$; (⊙) $100 \mu\text{m}$; (●) $200 \mu\text{m}$. $T = 30^\circ\text{C}$.

thickness. The dynamic viscosity shows about 2.6 power dependence on exposure energy. This implies that, once the crosslinking starts, the reaction kinetics is not affected by sample thickness. The results of experiments carried out at 10°C are shown in Figure 8. E_m varies also with sample thickness whereas n is constant.

Figure 9 shows the relative dynamic viscosity η'/η'_0 plotted against the exposure energy at a sample thickness of 17 μm . With increasing temperature, E_m decreases and n increases. Therefore, the cure rate increases with increasing temperature.

From the results given in Figures 7–9, two findings should be emphasized with regard to the UV curing behavior. First, n is affected by temperature, but not by sample thickness. The values of n are as follows: 1.7 at 10°C, 2.2 at 20°C, 2.6 at 30°C, and 3.1 at 40°C. Secondly, E_m varies depending on both the sample thickness and temperature. The logarithmic plots of E_m against the sample thickness are shown in Figure 10. At sample thickness less than 100 μm , E_m increases linearly with sample thickness and shows 0.7 power dependence irrespective of temperature. However, when the sample thickness exceeds 100 μm , E_m starts to increase remarkably and deviates from the straight line. More UV energy is required to cure such thick films completely. In addition, as almost no UV energy reaches the bottom of film, the degree of curing may be extremely inhomogeneous in the direction perpendicular to shearing surface. The sample thickness at which E_m abruptly increases is an important parameter to characterize the UV curability of prepolymers.

DISCUSSION

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 in the film. The rate of radical production at a depth x is written by the following equation:

$$\frac{d[R]}{dt} = \phi I_0 \epsilon [I_n] \exp(-\epsilon [I_n] x) \quad (4)$$

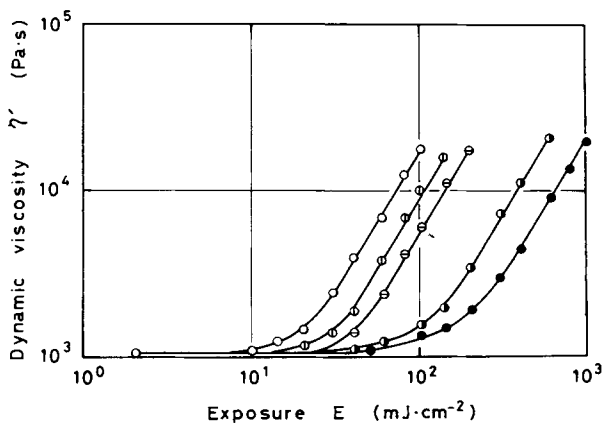


Fig. 8. Effect of sample thickness on the UV curing behavior at 10°C: (○) 8.5 μm ; (◻) 17 μm ; (◻) 30 μm ; (○) 100 μm ; (●) 200 μm . $T = 10^\circ\text{C}$.

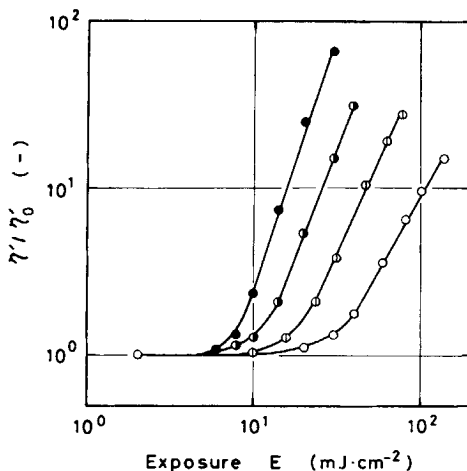


Fig. 9. Dependence of relative dynamic viscosity on exposure energy at different temperatures: (○) 10°C; (◻) 20°C; (◐) 30°C; (●) 40°C. $h = 17 \mu\text{m}$.

where I_0 is the initial light intensity at $x = 0$, ϕ is the quantum yield for radical production, and $[I_n]$ is the concentration of initiator with extinction coefficient ϵ . For the discussion of the rate of polymerization, an average of $d[R]/dt$ over x is often used. However, this procedure is not appropriate for the interpretation of the relation between E_m and h because the dynamic viscosity observed is not necessarily an arithmetic average over x . For instance, if a thin film layer still remains near the fixed plate of rheometer, a liquidlike response is observed even after UV irradiation. Therefore, we have examined the behavior at the bottom of film from a rheological point of view. Assuming that the abrupt increase in dynamic viscosity occurs when $[R]$ reaches a certain level $[R]_m$ at the bottom of film, we obtain

$$\begin{aligned} [R]_m &= \phi I_0 t \epsilon [I_n] \exp(-\epsilon [I_n] h) \\ &= \phi E_m \epsilon [I_n] \exp(-\epsilon [I_n] h) \end{aligned} \quad (5)$$

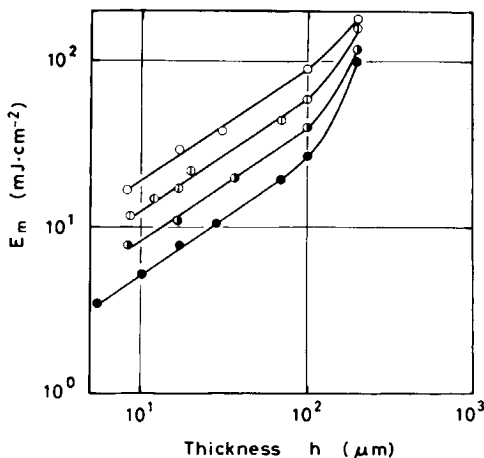


Fig. 10. Dependence of the minimum exposure energy on the sample thickness at different temperatures: (○) 10°C; (◻) 20°C; (◐) 30°C; (●) 40°C.

Equation (5) gives the relation between E_m and h . However, the results in Figure 10 cannot be explained by a single exponential decay with thickness.

The alkyl ethers of benzoin absorb UV energy at about 365 nm wavelength due to the $n-\pi^*$ transition; this results in direct photodecomposition to produce free radical species. If the sample is irradiated with monochromatic light of 365 nm, eq. (5) may be applicable. However, at wavelengths less than 365 nm, the initiator also has strong absorption which overlaps significant peaks of the UV output spectrum. We can see the major peaks at 302, 313, 334, and 365 nm (Fig. 1). The initiation of polymerization can be explained by a combination of energy absorption at different wavelengths. Then the relation between E_m and h is represented by the following equation:

$$E_m \propto \frac{1}{\sum_i A_i \exp(-\epsilon_i [I_n] h)} \quad (6)$$

where ϵ_i is the extinction coefficient at wavelength λ_i and A_i is the associated front factor. The evaluation of A_i is difficult because it consists of various factors such as the light intensity and quantum yield.

The extinction coefficient of benzoin alkyl ethers is about $280 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 365 nm.⁷ Among the wavelengths corresponding to the peaks in the spectrum, the light of 365 nm penetrates most deeply into the film. The density being taken as $1.05 \text{ g} \cdot \text{cm}^{-3}$, the penetration depth of light is estimated to be $86 \mu\text{m}$. This value is comparable to the sample thickness at which E_m starts to deviate from the straight line. At the bottom of film with this thickness, the light of 365 nm wavelength plays a predominant role in photopolymerization. Since the light intensity at the other wavelengths is already decreased to a considerable extent, E_m may exponentially increase with h at thicknesses larger than $100 \mu\text{m}$. In the case of thin film, the light of wavelengths other than 365 nm also contributes to radical production at the bottom of film. Therefore, E_m decreases with decreasing h . Presumably, E_m becomes constant when h is decreased to the order of $1 \mu\text{m}$. Therefore, the penetration depth of 365 nm light determines the maximum sample thickness to be cured.

CONCLUSIONS

The dynamic viscoelastic behavior during UV curing was investigated for epoxy acrylate prepolymer using an oscillating plate rheometer. Some of significant conclusions are as follows:

1. Independent of light intensity, the dynamic viscosity plotted against exposure energy lies on a single curve which is approximated by two straight lines.
2. The minimum exposure energy E_m decreases with increasing curing temperature and with decreasing sample thickness.
3. The slope n increases with increasing temperature, but it is independent of sample thickness. Therefore, once the crosslinking reaction starts, the reaction kinetics is not affected by sample thickness.
4. When the sample thickness exceeds $100 \mu\text{m}$, E_m starts to increase

abruptly and to deviate from the straight line. The critical sample thickness at which E_m abruptly increases is comparable to the penetration depth of 365 nm light. The $n-\pi^*$ absorption at 365 nm is of primary importance.

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