

Rheological Measurements of Cure Rate of UV Inks

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Synopsis

The dynamic viscosity of UV inks during curing was measured at various film thicknesses using an oscillating plate rheometer. Logarithmic plots of the dynamic viscosity versus exposure energy are closely related by two straight lines. A useful concept in discussing the curability is the minimum exposure energy defined as the exposure energy at the intersection of two lines. On exposure to a monochromatic light of 365 nm, the minimum exposure energy increases exponentially with film thickness; this resulting from an exponential decay of the light intensity with depth in the film. Magenta ink shows the fastest cure rate at a given thickness, followed by yellow, cyan, and black inks in that order. The difference in cure rate is attributed to different absorbances of pigments. The UV curability on direct exposure to UV lamp is predicted from the spectral sensitivity of the photoinitiator and the viscosity data obtained during curing under 365 nm light. The model calculation shows good agreement with the experimental results.

INTRODUCTION

An ultraviolet-curable ink (UV ink) consists of a pigment dispersed in a UV-curable vehicle. The principal ingredients of the vehicle are reactive monomers, prepolymers, and photoinitiators. In general, polyfunctional monomers such as trimethylol propane triacrylate (TMPTA) and pentaerythritol triacrylate (PETA) are used to ensure the high rate of crosslinking. The prepolymers contribute to the viscosity, tack, and gloss of the printed film. The photoinitiators undergo direct photodecomposition on exposure to UV irradiation and yield free radicals that initiate a cross-linking reaction to form three-dimensional networks. The most important advantage of UV inks is that they are very rapidly cured without evaporation of solvent. Moreover, the UV curing may require less energy than thermally induced processes. However, one of the problems is the absorption of UV irradiation by the dispersed pigment. Since the pigment reduces the penetration depth of UV irradiation, the cure rate and the thickness of film that can be cured, are greatly reduced. To cure the film completely, UV irradiation must reach the bottom of the film and free radicals must be generated at an adequate rate throughout the film. The attenuation of UV irradiation varies with type, particle size and concentration of pigment, and wavelength of the light used to cure the film. It is essential to know the degree of absorption of irradiation and its effect on the UV curability.

Although the cure rate of UV-curable polymers has been determined in several studies,¹⁻³ the conventional techniques are not directly applicable to curing of very thin film. In practice, the thickness of printed ink film is of the order of μm , so the UV curability should be measured for such a thin film. For this purpose, we have developed an oscillating plate

rheometer^{4,5} capable of directly and continuously following the progress of curing. In this study, the dynamic viscosity of UV inks was measured during curing at different sample thicknesses. The rheologically determined cure rate was examined in relation to the absorption of UV irradiation by the photoinitiator.

EXPERIMENTAL

Samples

TMPTA was used as the reactive monomer. A commercial epoxy acrylate resin (Epicron 1050 from Dainippon Ink & Chemicals Corp.) and 2,2-dimethoxy-2-phenylacetophenone were used as the prepolymer and the photoinitiator, respectively. The vehicle was formulated using 54 wt% prepolymer, 36 wt% TMPTA, and 10 wt% photoinitiator. Figure 1 shows the spectral sensitivity of the vehicle. The spectrogram was taken in a nitrogen atmosphere under UV irradiation from a high pressure mercury lamp. The vehicle is sensitive to lights of 297, 302, 313, 334, and 365 nm wavelengths. However, the peak height does not give the absolute sensitivity as the light intensity varies with wavelength.

The pigments used were phthalocyanine blue (cyan), brilliant carmine (magenta), diazo yellow (yellow), and carbon black (black). Four color inks were prepared at a pigment concentration of 5% by weight.

Apparatus

The apparatus used was an oscillating plate rheometer in which the sample was sheared between a fixed plate and an oscillating plate made of a quartz glass. The details of apparatus and the method of measurement have been reported elsewhere.⁴ To clarify the effect of sample thickness on the curing behavior, the dynamic viscosity was measured at various

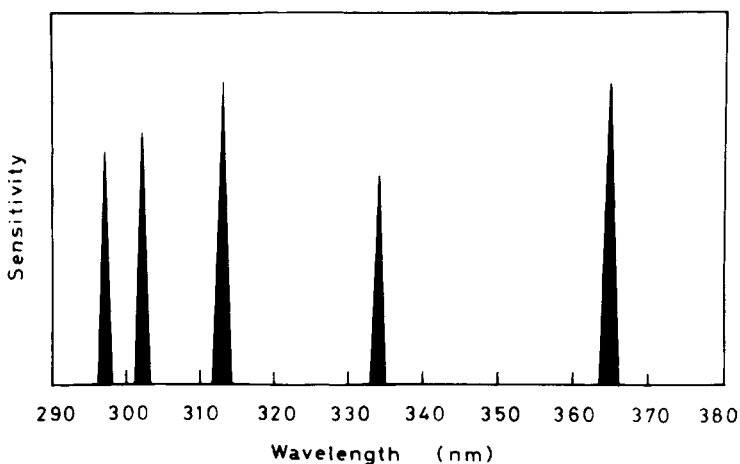


Fig. 1. Spectral sensitivity of vehicle.

sample thicknesses in the range of 4–35 μm . For all runs, the frequency was held at 80 Hz and the temperature at 30°C.

The UV source was a high pressure mercury lamp, the spectral output of which was a continuum with superimposed sharp peaks at various wavelengths. The vehicle had strong absorption which overlapped five 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. The light intensity was 27 $\text{mW}\cdot\text{cm}^{-2}$ at the surface of filter or at the surface of oscillating glass without the filter.

RESULTS

Curing under a Monochromatic Light of 365 nm

The initial dynamic viscosity η'_0 (before UV irradiation) was first measured. Once η'_0 is determined, the dynamic viscosity during UV curing can be obtained without measuring the sample dimension in each experiment. The results were as follows: vehicle; 20 Pa·s, magenta; 24 Pa·s, yellow; 21 Pa·s, cyan; 22 Pa·s, black; 24 Pa·s.

Figure 2 shows the effect of sample thickness on the rheological behavior of magenta ink during UV curing under a monochromatic light of 365 nm. The abscissa does not mean the exposure energy of 365 nm light but the total exposure energy. To compare with the curing on direct exposure to the UV lamp, the total exposure energy defined as the product of exposure time and the light intensity at the upper surface of the UV filter was used. This corresponds to the UV energy applied to the sample surface without the UV filter. The relative viscosity η'/η'_0 abruptly begins to increase beyond a certain exposure energy depending on the sample thickness and then linearly increases with exposure energy. In the beginning of curing, the

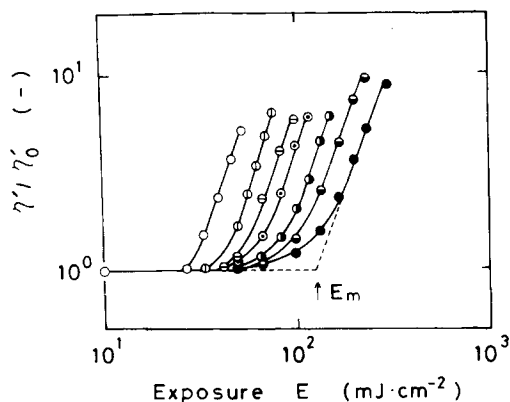


Fig. 2. Dependence of relative viscosity on the exposure energy at different sample thicknesses for magenta ink during curing under 365 nm light: (○) 4; (◐) 10; (⊖) 15; (⊙) 20; (●) 25; (◑) 30; (●) 35 μm .

thinner the sample, the more rapidly the curve approaches a straight line. The slope of asymptotic line is about 3.0 irrespective of thickness. Since the data can be approximated by two straight lines, the exposure energy at the intersection between two lines gives a measure for UV curability. We refer to it as the minimum exposure energy E_m . The minimum exposure energy increased with sample thickness.

Figure 3 shows the effect of sample thickness on the rheological behavior of black ink. Similarly, the relative viscosity begins to increase beyond a certain exposure energy and linearly increases. The slope of the line decreases with increasing sample thickness in contrast to the constant slope for magenta ink. In the previous paper,⁶ we have reported that the cure rate of UV-curable polymer is markedly reduced when the sample thickness exceeds the penetration depth of light. The film thickness to be effectively cured was about 5 μm for black ink. Carbon blacks have been reported to cause curing problems in UV application because they absorb so much of UV energy.⁷

The experiments were repeated for vehicle, yellow ink, and cyan inks. Figure 4 shows the rheological behavior at a film thickness of 10 μm . The fastest cure rate, of course, was observed with the vehicle, and the addition of pigments reduced the cure rate. Among the four inks, magenta ink gave the fastest cure rate, followed by the yellow, cyan, and black inks in that order. The difference in cure rate observed with these inks is attributed to different absorbances of pigments over the wavelength range 290–370 nm. Although the transmission of light varies with wavelength, that for magenta ink generally gives the highest transmission in the UV region.⁸

Figure 5 shows the thickness dependence of the minimum exposure energy for all samples studied during curing under 365 nm light. The increase of logarithmic plots of the minimum exposure energy with thickness is linear; this occurs because the light intensity in the film shows an exponential decay with depth. The influence of thickness dependence of the minimum exposure energy is caused by the inconsistency of degree of curing in the direction perpendicular to the shearing surface.

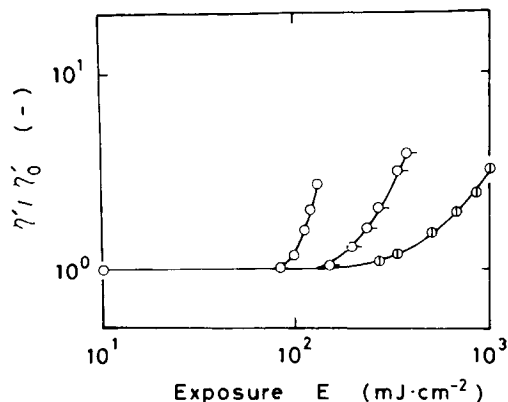


Fig. 3. Dependence of relative viscosity on the exposure energy at different sample thicknesses for black ink during curing under 365 nm light: (○) 4; (○—) 7; (⊖) 10 μm .

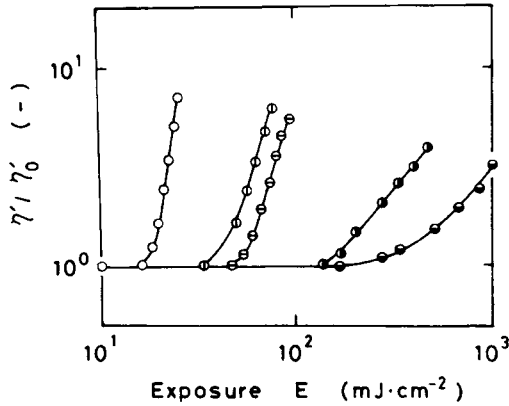


Fig. 4. Dependence of relative viscosity on the exposure energy at a sample thickness of $10\ \mu\text{m}$ for vehicle and inks during curing under $365\ \text{nm}$ light: (○) vehicle; (⊕) magenta; (⊖) yellow; (⊙) cyan; (⊗) black.

Curing on Direct Exposure to UV Lamp

Figure 6 shows the effect of sample thickness on the rheological behavior of magenta ink during UV curing on direct exposure to the light emitted from the mercury lamp. Each curve seems to be satisfactorily superimposed by a horizontal shift along the abscissa. Probably, the sample thickness affects only the minimum exposure energy for thin films. The minimum exposure energy decreases more rapidly with decreasing thickness than that observed in the curing under $365\ \text{nm}$ light. For example, the cure rates are almost the same at $35\ \mu\text{m}$, while at $4\ \mu\text{m}$ the minimum exposure energy for curing under $365\ \text{nm}$ light is about 7 times that for curing on direct exposure to the UV lamp. The contribution of lights with shorter wavelengths to radical production becomes predominant in ink films with thicknesses of a few microns.

Figure 7 shows the effect of sample thickness on the rheological behavior of black ink. With increasing sample thickness, the minimum exposure

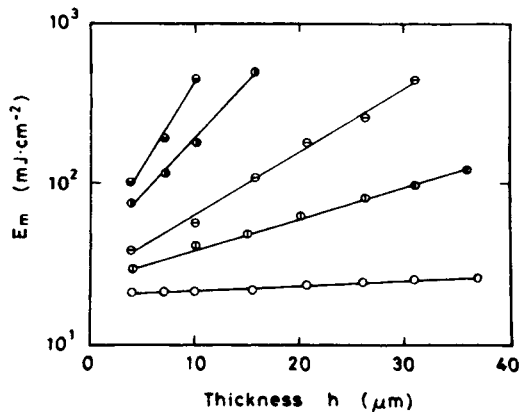


Fig. 5. Thickness dependence of the minimum exposure energy during curing under $365\ \text{nm}$ light: (○) vehicle; (⊕) magenta; (⊖) yellow; (⊙) cyan; (⊗) black.

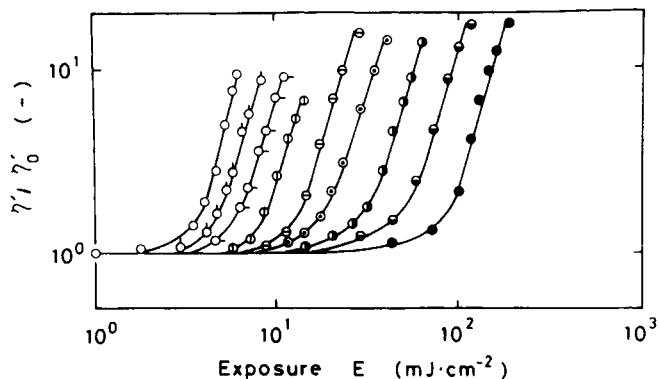


Fig. 6. Dependence of relative viscosity on the exposure energy at different sample thicknesses for magenta ink during curing on direct exposure to UV lamp: (○) 4; (◐) 5; (◑) 7; (⊕) 10; (⊖) 15; (⊙) 20; (●) 25; (◉) 30; (◊) 35 μm .

energy increases but the slope of line decreases, that is, the cure rate remarkably decreases. As expected, the slope begins to decrease when the thickness is increased and becomes equal to the penetration depth of light. More UV energy is required to cure such thick films completely. Otherwise a thin liquid layer remains at the bottom of the ink film even after UV irradiation. Therefore, in multicolor printing, the fact that black UV inks are the most difficult to cure necessitates these applications early in the process sequence.

Figure 8 shows the results at a film thickness of 10 μm for vehicle and four inks. The minimum exposure energy increases in the same order as in Figure 4: vehicle, magenta, yellow, cyan, and black. It is interesting to note that except for black ink, the relative viscosity shows about 3.0 power dependence on the exposure energy beyond the minimum exposure energy.

Figure 9 shows the logarithmic plots of the minimum exposure energy against the sample thickness during curing on direct exposure to the UV lamp. In the case of direct exposure, the data for each sample are also correlated by a straight line. Compared with the curing under a mono-

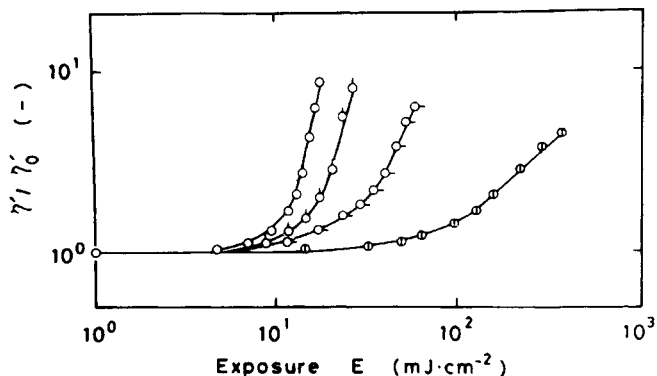


Fig. 7. Dependence of relative viscosity on the exposure energy at different sample thicknesses for black ink during curing on direct exposure to UV lamp: (○) 4; (◐) 5; (◑) 7; (⊕) 10 μm .

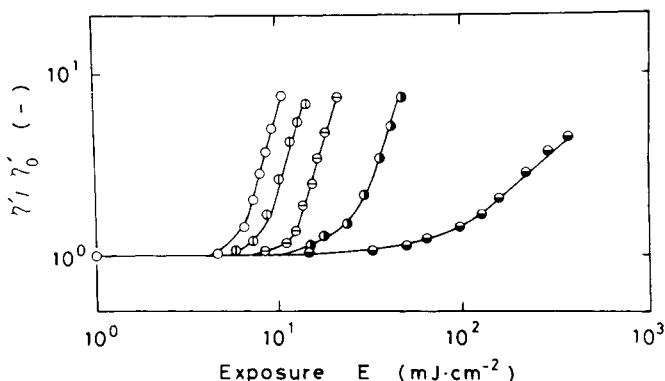


Fig. 8. Dependence of relative viscosity on the exposure energy at a sample thickness of $10 \mu\text{m}$ for vehicle and inks during curing on direct exposure to UV lamp: (○) vehicle; (◻) magenta; (◻) yellow; (●) cyan; (●) black.

chromatic light, the slope is steeper, and hence, the minimum exposure energy is markedly reduced especially at a few microns for all inks. From these slopes, we can calculate the absorption of UV energy by the photoinitiator in the pigmented films.

DISCUSSION

In the earlier paper,⁶ we have discussed the rheological behavior of photopolymer containing a photoinitiator during UV curing induced by a monochromatic light. The minimum exposure energy rheologically determined

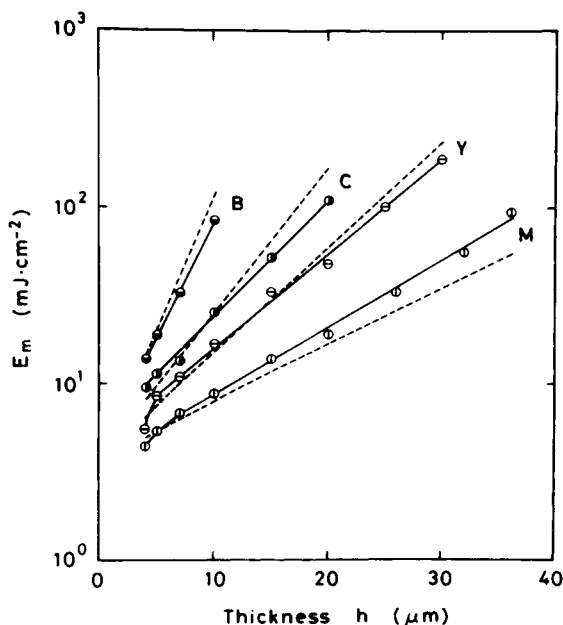


Fig. 9. Comparison of the theoretical prediction (---) with the experimental results (—) for the thickness dependence of the minimum exposure energy on direct exposure to UV lamp: (B) black; (C) cyan; (M) magenta; (Y) yellow.

by the oscillating plate rheometer is given as follows:

$$E_m = E_o \exp(0.72\alpha h) \quad (1)$$

where h is the sample thickness, E_o is the minimum exposure energy at $h = 0$, giving the value for a thin film in which the degree of curing is considered to be homogeneous in the direction perpendicular to the shearing surface, and α is the absorption coefficient defined as $2.303\epsilon[I_n]$, where $[I_n]$ is the concentration of photoinitiator with molar extinction coefficient ϵ . Combining Eq. (1) and the linear relation for the vehicle in Figure 5, the molar extinction coefficient of 2,2-dimethoxy-2-phenylacetophenone was estimated to be $96 \ell \cdot \text{mol}^{-1} \text{cm}^{-1}$ at 365 nm. According to the manufacturer's data obtained with a solution in chloroform, it is $90 \ell \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. A good agreement can be seen between the rheological experiments and the absorption spectrum.

In the vehicle film, UV irradiation is absorbed mainly by the photoinitiator. Although the epoxy acrylate prepolymer is sensitive to UV, the fraction of irradiation absorbed by the prepolymer is negligibly small. Therefore, the absorbed irradiation effectively contributes to radical production. On the other hand, in the ink films, absorption and scattering by the pigments are also responsible for the attenuation of UV irradiation in addition to the absorption by the photoinitiator. The absorption by the pigments are very large and is not involved in photochemical reaction. Wicks and Kuhhirt⁹ have theoretically investigated the absorption of UV irradiation by photoinitiators in pigmented coatings on the basis of Kubelka-Munk equations.¹⁰ Their model calculations indicate that in thin films with a high scattering coefficient even more irradiation is absorbed by a photoinitiator than in the absence of pigment, because of the increase in optical length of irradiation passing through the film. Moreover, the presence of a highly absorbing pigment will drastically reduce the irradiation absorption by the photoinitiator, especially at the bottom of film. In the UV inks used in this study, the absorption by pigment is an important factor affecting the UV curability. Applying Eq. (1) to the data in Figure 5, the absorption coefficient α_t for the ink film can be determined which includes the absorption due to the photoinitiator (α) and the pigment (α_p). The results are shown in Table I. Here the reciprocal absorption coefficient, $1/\alpha_t$ is the penetration depth of 365 nm light in the ink film. Since the absorption coefficient for the photoinitiator alone is about 90 cm^{-1} , more than 85% of the total absorbed energy is due to the pigment even in the magenta ink which gives the fastest cure rate. In the black ink, it increases to about

TABLE I
Absorption Coefficient for Four Pigments and Penetration Depth of 365 nm Light for Their Ink Films

	Magenta	Yellow	Cyan	Black
α_p (cm^{-1})	554	1200	1730	3300
$1/\alpha_t$ (μm)	15.5	7.8	5.5	2.9

97%. Fundamental requirements for curing UV inks which contain a highly absorbing pigment are an efficient photoinitiator and a high-intensity UV source. However, it is still difficult to avoid the inconsistency of degree of curing in the film.

In the case of direct exposure to UV irradiation without a UV filter, the total absorption at various wavelengths is responsible for radical production. The minimum exposure energy decreases more rapidly with decreasing sample thickness than under 365 nm light because the extinction coefficient of the photoinitiator increases for light shorter than 365 nm. The minimum exposure energy is written as a function of energy absorption at different wavelengths as follows:

$$\left(\frac{E_m}{E_o}\right)^{-1} = \sum_i A_i \exp\{- (\alpha_i + \alpha_{p,i})h\} \quad (2)$$

where α_i and $\alpha_{p,i}$ are, respectively, the absorption coefficients for the photoinitiator and for the pigment at wavelength λ_i , and A_i is the associated front factor. The absorption coefficient for the photoinitiator is defined as $\alpha_i = 2.303 \epsilon_i [I_n]$, where ϵ_i is the molar extinction coefficient at the corresponding wavelength. Although the absorption by pigment varies with wavelength, especially in visible range, the wavelength dependence is not so strong in the range of 290–370 nm. Therefore, $\alpha_{p,i}$ for each ink is assumed to be constant as a first approximation (Table I). The front factor A_i consists of various factors such as light intensity and quantum yield, and hence its evaluation is generally difficult. Fortunately, the mercury lamps used in the sensitivity measurement and curing experiments have a similar output spectrum. The relative estimation is possible from the spectral sensitivity. In this study, A_i was determined as the ratio of peak height at wavelength λ_i to that at 365 nm. Table II shows the molar extinction coefficient of the photoinitiator, ϵ_i , and the front factor A_i at different wavelengths.

The minimum exposure energy for a very thin film is $E_o = 20 \text{ mJ}\cdot\text{cm}^{-2}$ from Figure 5. However, this value should be corrected because the UV filter used decreases the 365 nm light by 20%. The corrected value ($16 \text{ mJ}\cdot\text{cm}^{-2}$) is then adopted for the prediction of thickness dependence of the minimum exposure energy in the case of direct exposure. The results of calculation are shown by broken lines in Figure 9. The theoretical prediction shows a good agreement with the experimental results. The lights other than 365 nm contribute to radical production at the bottom of a thin film, while they are already reduced to a considerable extent in a thick film.

TABLE II
Molar Extinction Coefficient of the Photoinitiator (2,2-dimethoxy-2-phenylacetophenone)
and Front Factor at Various Wavelengths

Wavelength (nm)	297	302	313	334	365
ϵ_i ($\text{l}\cdot\text{mol}^{-1} \cdot \text{cm}^{-1}$)	500	270	120	190	90
A_i (-)	0.78	0.85	1.0	0.70	1.0

Therefore, the minimum exposure energy on direct exposure to UV lamp decreases more rapidly with decreasing thickness than under irradiation through the UV filter. Although the minimum exposure energy for the film with comparable thickness to the penetration depth of 365 nm did not depend on whether the UV filter was used or not, the degree of curing was more inconsistent in the latter case. In conclusion, an important factor controlling the UV curability is the irradiation absorption by the photoinitiator at the bottom of the film.

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