Direct Evaluation Method of UV Curing Process on the Basis of Conductivity Change of Photopolymerization Materials

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Abstract

A novel evaluation method is proposed for UV curing of photopolymerization materials. The method is based on the measurement of photodecrease of the conductivity, which is caused by the photopolymerization of acrylate monomer during the curing process of the ink film. The current changing rate by UV irradiation is in proportion to relative hardness of ink layer in the surface type cell. The evaluation of sensitivity and curing mechanism of UV curable materials is possible by the measurement of photochange of sample current in either surface or sandwich type cell. The information for non-cured ink layer thickness in the surface type cell can be get from the relationship between the initial thickness and the resistivity of ink layer before UV irradiation. In the case of the sandwich type cell, the curing rate of UV curable resin is in proportion to square root of UV intensity and photoinitiator concentration, respectively. These results satisfy the theoretical equation of the photopolymerization.

Introduction

Now, radiation cured products by UV/EB polymerization process are comprised of coatings, electronics, inks, adhesives and others. The benefits of UV curing are comprised of no solvent emission, low energy requirement, high productivity, product quality and low VOC gener-ation.[1)] The UV and EB radiation curing market for inks and coatings now are growing. [2),3)] UV curing of inks and coating is composed of radical photopolymerization which involves initiation, propagation and termination process. Many kinds of ink and coating which have different curing speeds are used in practical production process. UV curing speed or sensitivity has been practically evaluated by the measurements for NMR, IR and / or gelling rate of cured materials. These measurement techniques are very complicated and the measurement process takes a long time. In order to design the most suitable curing system by using UV curing materials and UV light source, it may be required that we have the exact information for UV curing speed of photosensitive materials and spectral and energy data of UV source. Our goal is to develop the simple evaluation method for UV curing speed or sensitivity of photopolymer and to apply the method to a practical UV curing system. In this study, we focused on the conductivity change (negative photo-conductivity) of UV curing materials caused by photo-polymerization which involves a highly crosslinked system.

Experimentals

Conductivity Measurement System

Figure 1 shows the experimental set-up for the measurement of the conductivity change of UV curable ink layer. Hg short arc lamp (180W) was used. The light was guided by quartz optical fiber and the UV ink sample was illuminated by the guided light through the interference filter (λ = 365nm).

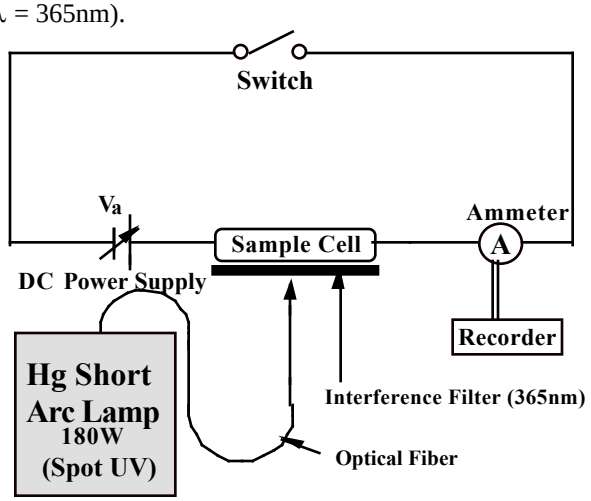

Figure 1. Experimental setup for measurement of conduction current in UV curable ink.

We used two kinds of cell for the conductivity measurement, that is, surface type cell and sandwich type cell as shown in Figure 2. The surface type cell had Al electrodes spaced of 2mm on slide glass as shown in Figure 2-(a) and UV curable ink was coated at about 9μm thickness on the cell electrodes. The sandwich type cell was composed of two slide glasses having Al electrode deposited on its surface, which were faced each other and was spaced by 9μm polymer film as shown in Figure 2-(b). The transmittance of Al electrodes was about 50%. The cell space of 9μm was filled

with UV curable ink. The applied voltage to both cells was D.C 100V, and the circuit current changes caused by UV irradiation were measured.

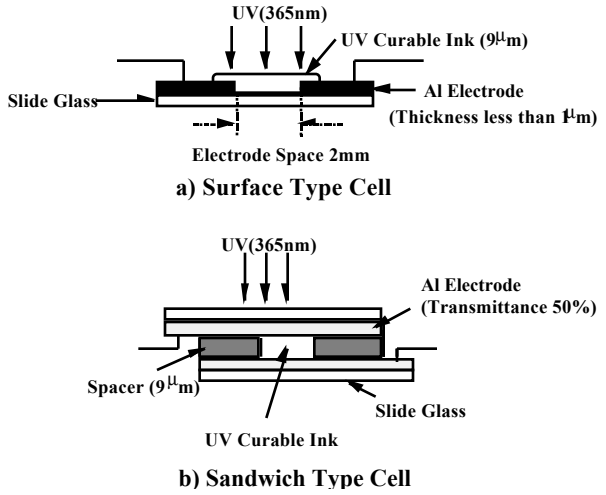

Figure 2. Cell configurations.

Table 1. Tested UV ink

Maker	Types of UV Ink	Ink Color
Dainippon Ink Chem. (DIC)	DC-Clear 109 L (Offset)	Clear
	RT-7 (Offset)	Yellow Magenta Cyan Black
	SEPTER (Offset)	Yellow Magenta Cyan Black
Sakata Ink (SKT)	ACRASET (Offset)	Magenta Cyan Black
Teikoku Ink	SERICOL UV FIL (Screen)	Yellow Magenta Cyan Black
Hand Made	Bisphenol A- diacrylate Benzoin	

Samples

Table 1 shows the list of UV inks used in this study, which mainly involve the process color ink. The chemical composition of DC-Clear 109 L is composed of acrylate monomer, acrylate origomer, photoinitiator (BenzilDimethylketal) and others. The monochrome light of 365nm, was irradiated to samples, because the absorbance of the wavelength range from 320nm to 380nm is caused by the photoinitiator.

Results and Discussion

Photochange of conductivity of clear UV ink[4)]

Figure 3 shows the time dependence of the photochanges of sample current in surface type cell at various UV intensities. The sample currents rapidly decrease within 5 sec after UV light-on, and after that, gradually decrease. At any UV intensity, sample current reaches its equilibrium value (Is) after about 30 sec of UV light-on. The value of Is is dependent on UV intensity. In the case of sandwich type cell, the photochange of sample currents decreases more rapidly than that of surface type cell as shown in Figure 4.

After about 10 sec from UV light-on, the current decay curves reach all same level in equilibrium value (Is) and Is shows no dependence on UV intensity. It is thought that the difference of UV intensity dependence of Is value between both cells may suggest the existence of difference of information in photopolymerization process obtained by conductivity measurement.

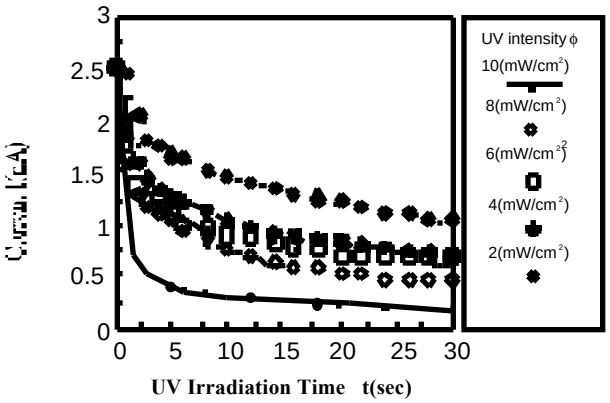

Figure 3. Photochange of sample current in surface type cell by UV irradiation. Parameter is UV intensity (DIC DC-Clear 109L).

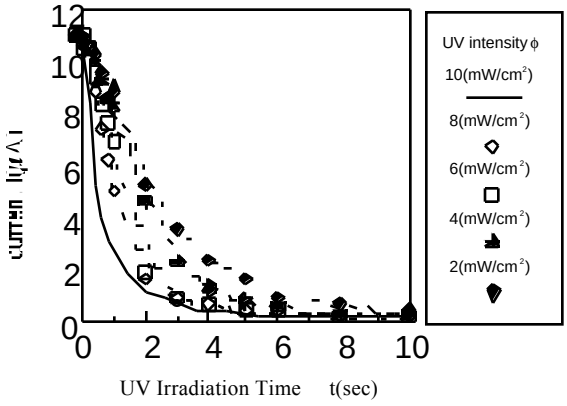

Figure 4. Photochanges of sample current in sandwich type cell by UV irradiation. Parameter is UV intensity(DIC DC-Clear 109L).

Photochange model of UV ink conductivity

It is mentioned in previous section that the curing information contained in conductivity change of curable ink in surface type cell is different from that in using sandwich type cell. The physical meaning of this difference may be explained by the proposed model as follows.

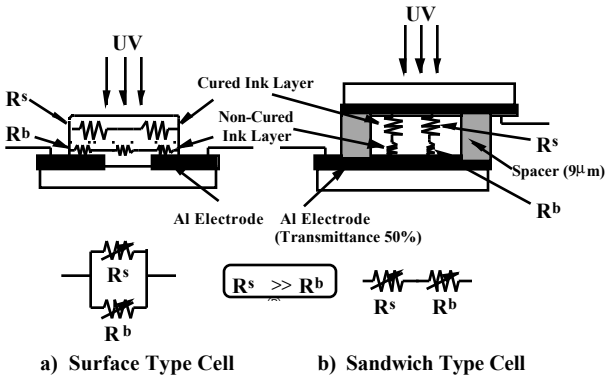

Figure 5. Model of photochange of the sample current in surface and sandwich type cells.

In surface type cell, the resistances in the ink layer are in parallel with the ink surface. Figure 5-(a) explains the state of some degree of UV curing of ink layer. Some portion of the upper side of ink layer is cured by UV irradiation. The cured ink layer is photopolymerized and have some thickness and the increased resistance R_s. On the hand, the inner side of the ink layer is not cured, because sufficient UV light flux to initiate the curing does not reach that portion. The non-cured inner layer have low resistance R_b in surface type cell. The resistance R_s and R_b from parallel circuit as shown in Figure 5-(a). In this case, it may be thought that the cured layer resistance R_s is much larger than non-cured portion resistance R_b and the conductivity change data contain only the information of non-cured portion in UV ink layer(R_s>>R_b).

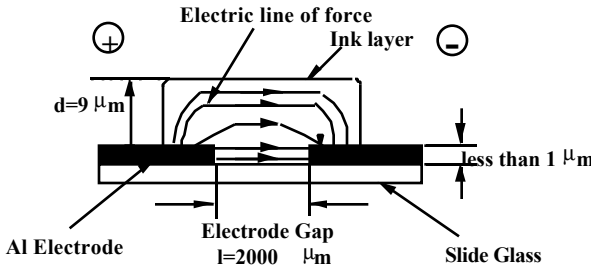

Figure 6. The model of current flow in the ink layer of surface cell.

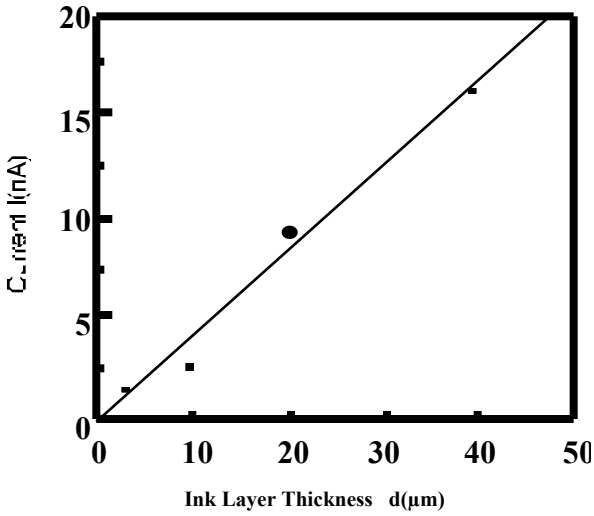

Figure 7. Ink layer thickness vs. current in clear UV ink.

Now, we have to discuss the physical meaning of current flow of ink layer in surface type cell. Figure 6 shows the model of electric line of force and current flow in ink layer of surface type cell. At an applied voltage V, total current I is give by

$$I = \frac{V}{R} = \left(\frac{r\,V}{l}\right)\bullet\frac{d}{\rho} = \left(\frac{V}{l}\right)\bullet\frac{S_c}{\rho}, \qquad (1)$$

where R is the layer resistance, r is the width of electrode, l is the gap length between electrodes, d is the ink layer thickness, ρ is the specific resistance of UV ink and S_c is the cross section of ink layer (S_c=r_~d). Equation (1) shows that I is in proportion to the ink layer thickness d or the cross section Sc. Figure 7 shows experimental data for the dependence of current I on ink layer thickness d (μm) in UV clear ink and the linear relationship between I and d as indicated by equation (1).

In the case of surface type cell, the photodecay current I_b is governed by non-cured ink layer resistance R_b because of R_s>>R_b as shown in Figure 5-(a). I_b is given by

$$I_b = \frac{V}{R} = \left(\frac{r\,V}{l}\right)\bullet\frac{d_b}{\rho} \qquad (2)$$

where d_b is the non-cured ink layer thickness under some UV intensity. We can get the value of the non-cured ink layer thickness d_b from equation (2), because the values of r, V, l and ρ are known. But d_b is the average thickness, because the incident light intensity may not be uniform distribution to the thickness direction. Assuming that d_b and d are the cured and initial ink layer thickness, respectively, d is given by

$$d = d_s + d_b\ . \qquad (3)$$

Table 2. UV intensity dependency of cured and non-cured ink layer thickness of clear UV ink layer

UV Intensity (mW/cm^2)	Cure Layer Thicknes ds (μm)	Non-Cured Layer Thickness db (μm)
10.0	8.1	0.9
8.0	6.9	2.1
6.0	6.7	2.3
4.0	6.4	2.6
2.0	5.0	4.0

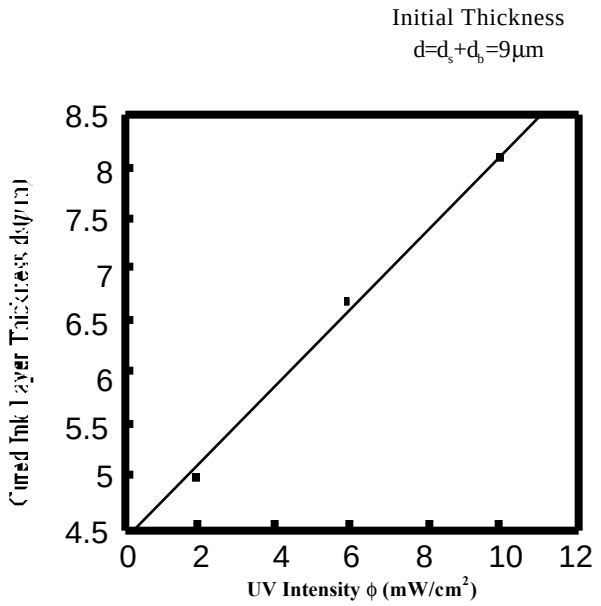

Figure 8. Cured ink layer thickness vs. UV intensity

Table 2 and Figure 8 shows UV intensity dependence of cured and non-cured ink layer thickness in clear UV ink (d=9μm). It is indicated by these analysis that the photopolymerized layer thickness in UV curable ink is given by the measurement of conduction currents and layer thickness in surface type cell. In sandwich cell as shown in Figure 5-(b), the resistance R_s of upper UV cured ink layer is connected in series to the resistance R_b of low non-cured ink layer. R_s always is much larger than R_b (R_s>>R_b).

It can be seen by comparing Figure 3 and Figure 4 that total currents of the sandwich layer will be controlled by the series resistance R_s of cured ink layer in some thickness. This is reason why the equilibrium current Is does not depend on UV intensity and shows the constant value at some lapse of time. It is suggested that the time dependent change of series resistance of sandwich type cell will be strongly related to the mean curing rate of UV photopolymerization.

Dependence of mean curing velocity on UV intensity[5)]

It has been reported that the mean curing velocity Vt of UV curable resin is generally in proportion to a square root of UV intensity and initiator concentration as indicated in equation (4)[6)].

$$Vt = \frac{k\rho}{kt^{1/2}}[M]\left(\Phi\eta f \times 2.303\varepsilon_\lambda[P]d\right)^{1/2} = \Lambda\Phi^{1/2}[P]^{1/2}, \qquad (4)$$

where ϕ is the UV intensity, η is the radical generation quantum efficiency by light, f is initiation efficiency of polymerization, ε_λ is the spectral absorption coefficient of monomer, d is the thickness, [M] is monomer concentration and [P] is the initiator concentration.

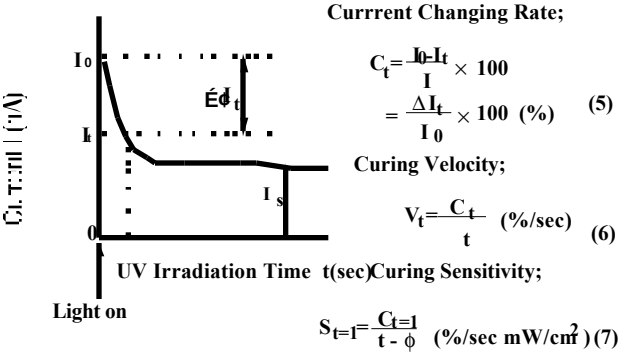

Figure 9. The definitions of current changing rate, curing velocity and cure sensitivity.

Figure 9 shows the definitions of current changing rate, curing velocity and cure sensitivity by using a time dependent curve in photochange of current. Figure 10 shows the relationship between UV intensity ϕ and curing velocity Vt in surface and sandwitch type cells. It can been seen in the Figure that Vt is in proportion to $\phi^{0.3}$ for surface type cell and $\phi^{1/2}$ for sandwich type cell, respectively.

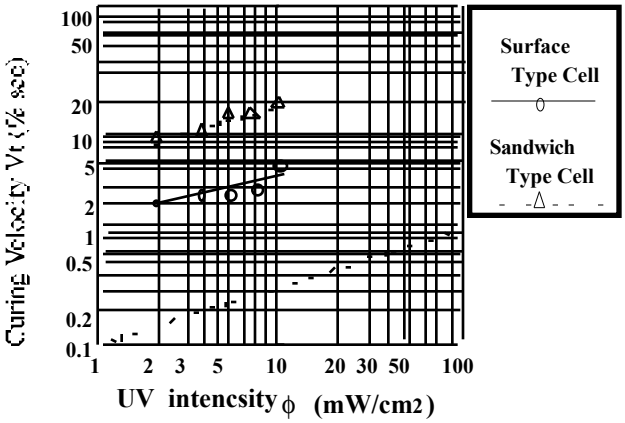

Figure 10. Relationship between UV intensity f and curing velocity V_t

Figure 11 shows the relationship between photoinitiator concentration [P] and curing velocity Vt in sandwich type cell. It can been seen in the Figure that Vt is in proportion to $[P]^{1/2}$. In the case of sandwich type cell, the curing

velocity obtained from photodecay curve satisfies the theoretical equation (4) in ideal case of photopolymerization.

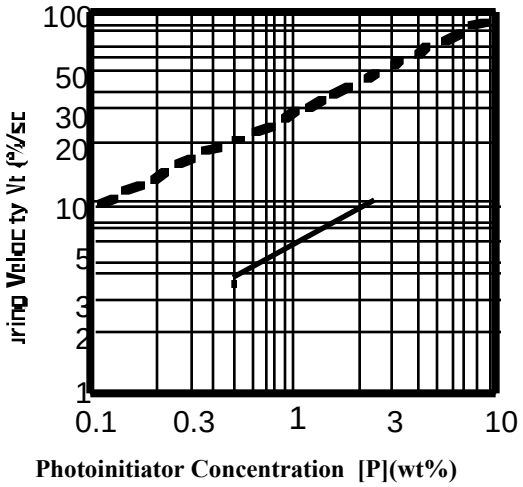

Figure 11. Relationship between photoinitiator concen-tration [P] and curing velocity V_t

Table 3 Cure sensitivity of tested UV ink

Maker	Types of UV Ink	Ink Color	Cure Sensitivity $S_{t=1}$ (%/sec mW/cm^2)	
			Surface	Sandwich
Dinippon Ink Chem (DIC)	DC-Clear 109L	Clear	6.68	7.55
	RT-7 (Offset)	Yellow	2.55	5.76
		Magenta	2.40	5.24
		Cyan	2.50	5.59
		Black	0.60	1.72
	SEPTER (Offset)	Yellow	1.85	4.56
		Magenta	2.27	3.81
		Cyan	1.64	3.13
		Black	0.90	0.83
Sakata Ink (SKT)	ACRASET (Offset)	Magenta	3.50	5.58
		Cyan	1.82	3.57
		Black	0.67	0.80
Teikoku Ink	SERICOL UV FIL (Screen)	Yellow	2.67	6.00
		Magenta	3.19	5.88
		Cyan	2.50	5.55
		Black	1.82	3.33
Hand Made	Bisphenol A -diacrylate Benzoin			5.33

*[I]=2.5wt%

Cure sensitivity of UV curable clear and color inks

The photochanges of sample current in surface and sandwich type cells were measured for color process UV inks listed in Table 1. The cure sensitivity $S_{t=1}$ is defined as the current changing rate Ct during 1 sec after UV light-on per 1mW/sec cm^2 of UV intensity(%/sec mW/cm^2). The cure sensitivities of all tested UV inks are listed in Table 3.

Conclusion

This paper has presented a novel direct evalution method of sensitivity and curing process of UV curable materials based on conductivity change.

(1) The amount of photochange of sample current is related to the amount of photopolymerization of curable molecule.

(2) The measured photochange data of sample current contain the information of both cured and non-cured portions of UV curable material layer in surface type cell.

(3) The evaluation of curing sensitivity and mechanism of photocurable materials is possible by measurement of photochange of sample current in either surface or sandwich type cell.

(4) In practical measurement of negative photocurrent of photocurable materials, the use of surface type cell is desirable, because the preparation of sample and electroded cell are simple and easy.

References

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