A Study on the Laser Curing of Acrylic Resin for the Application in Screen Printing

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ABSTRACT: For the development of an economic, automated, and computer-aided manufacturing process of screen for textile printing, photocuring of acrylic resin by an argon ion laser was studied. A commercially available polyurethane–acrylate resin was selected as a test resin for the representative study on laser curing behavior. The photoreaction by laser was observed by infrared spectroscopic analysis of vinyl group. With 1-W input power, the degree of curing increased linearly with exposure time, which reached, however, a plateau with exposure time of more than 4 μs. The curing reaction could be characterized in an S-shaped curve due to the combined effect of oxygen inhibition at lower power and photon saturation at higher power. The viscosity of acrylic resin could be controlled by addition of water as diluent without any significant drawback in curing speed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 515–520, 1999

Key words: laser curing; acrylate; printing screen; vinyl group; viscosity

INTRODUCTION

Photopolymerization and photocrosslinking are widely applied in industry.[1] The coating industry is a representative field, which includes coatings of wood, plastic, metal, and paper. Another important application field is graphic art, such as offset, silk-screen, and overprinting varnish (OPV). In addition, laminating adhesives, printed circuit board (PCB), and dry film photoresist cannot be processed without the aid of this technique.

Screen printing of textiles is a technology in which dyes or pigments mixed with binder are transferred onto textiles through a patterned screen. The patterning of the screen is usually performed by photocuring of the polymer and subsequent wash-out of the uncured part.

Multifunctional acrylic monomers and oligomers are most popularly used systems in the industrial application of photopolymerization and photocrosslinking.[2] In such a system, a multifunctional acrylic group is a functional moiety for photoreaction, while the other structural parts are related to apparency and mechanical properties. Polyurethane, polyester, epoxy, and polysiloxane are commonly adapted structural parts containing multifunctional acrylic groups.

Several light sources can be used for photopolymerization. Reaction with infrared (IR) is used more as a heating source. Visible light can initiate polymerization when using the right photoinitiator system and is used mainly for safety reasons, for example, in dental fillings. Ultravio-

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let (UV) light is the light most commonly used, and many photoinitiators are commercially available for that. Accelerated electron beam, X-rays, and γ-rays are powerful enough to initiate polymerization but are usually used in limited areas.

Laser-induced photopolymerization is a new technology linking computer graphics and a rapid solid-shaped object, whose typical example is stereolithography.[3] In the field of textile screen printing, the application of this technology is an emerging process because a tedious and laborous manufacturing step of mask can be skipped out by direct scanning of image from computer onto photoresponsible screen.[4,5] For the patterning of the image, two different methods are generally available. One is the patterning by laser ablation of cured resin and the other is by laser curing and the subsequent wash-out of the uncured part. Our study is related to the latter, and then the water solubility of acryl resin has an important role for industrial application.

We have reported in a previous article that poly(vinyl alcohol) is crosslinked with diazonium photosensitizer by laser, and it is also applicable as a new technology in textile screen printing.[6] In this study, we are interested in photocurable resin with multifunctional acrylic moieties, which is more widely used in industry.

In the conventional manufacturing process of printing screen, it is necessary to prepare masks before photocuring. The development of a laser-curing system for printing screen can lead us to more economic and automated process for printing screen due to skipping-out of the mask.

EXPERIMENTAL

Materials

Three types of acrylic resin were supplied from Sunkyung-UCB. The first was IRR-159 that was 50% aqueous emulsion of acrylic resin used for sprayable wood coating. The second was IRR-160 that was a trifunctional urethane acrylate diluted with 30% hexanediol diacrylate. The third was a trifunctional acrylate polyester graded as IRR 210, which was water-soluble and had a maximum water uptake of 45%.

OTA 480 was used as a diluting monomers and oligomers and D 184 was used as a photoinitiator; both were supplied from Sunkyung-UCB.

Light Source and Setup of Laser

In the preliminary experiments, photocurings of several samples by UV lamp were investigated.

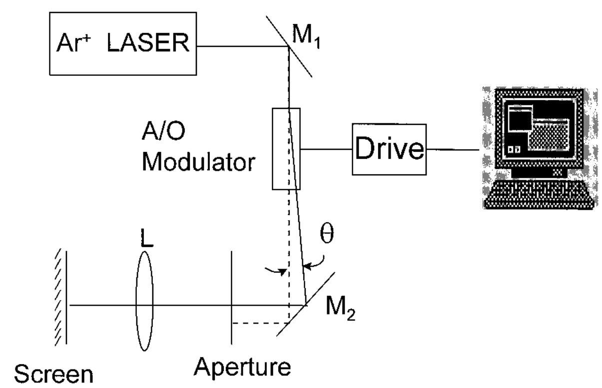

Figure 1 Schematic diagram of the experimental setup.

As an UV source, B-100A UV lamp of Black-Ray was used, which irradiated output power of 7 mW/cm^2 with λ_{max} = 365 nm at distance of 30 cm.

The laser used in these experiments was a Coherent Innova 328 CW argon ion laser, which had 1-W output power and radiated multiline UV (333.6–363.8 nm). As a beam on/off system, an A/O modulator ASM-702-8 of Intra Action Co. was used, which was operated with modulation frequency of 70 MHz, TTL level on/off, and a rise time of 55 ns. The spot size could be controlled through the lens, and the scan of laser was controlled by a scan mirror. The equipment arrangement for laser curing is shown in Figure 1.

Measurements

The samples in preliminary experiments were prepared by coating of resin on slide glass or oriented polypropylene film. The degree of reaction were observed after irradiation by washing the samples with hot distilled water and weighing the photocured residue.

The reaction degree of radiation curing by laser was investigated with analysis of infrared (IR) spectra. Pure KBr discs are clearly prepared with a typical pressor for that. On the KBr disc, formulated acrylic resin was coated with RDS bar coater No. 34 and irradiated with laser. From the IR spectra of the acrylate photoresponsible group, the twisting vibration absorption band of a double bond at 810.4 cm^{-1} can be analyzed relative to the stretching vibration absorption band of carbonyl at 1721 cm^{-1}.

RESULTS AND DISCUSSION

Laser-Curable Polymer System

Two types of screen printing for textiles are used commercially. One is rotary screen that is made of

Table I Materials, Formulations, and Apparent Shapes of Cured Films Used in Preliminary Test with UV Lamp

Test No.	Formulations (Wt %)			Exposure Time (s)	Appearance
	Polymer	Photosensitizer	Additives		
1	PVA[a] (90)	diazo photosensitizer[b] (0.8)	DW[d] (9.2)	4	resistant to washing
2	IRR 160 (78)	D 184 (2)	OTA 480 (20)	30	resistant to washing
3	IRR 210 (78)	D 184 (2)	OTA 480 (20)	60	tacky and resistant to washing
4	IRR 159 (90)	D 184 (10)	OTA 480 (20)	>120	not resistant to washing
5	Gelatin (8.5)	APC[c] (3)	DW (87.5) glycerine (1)	>300	slow, curable, not resistant to washing

[a] PVA emulsion of SCR 102 from Stork Co.
[b] Diazo photosensitizer from Kurita Chemical Co.
[c] Abbreviation for ammonium dichromate.
[d] Abbreviation for distilled water.

nickel drum, and the other is flat screen made of polyester, in which we are interested. For the flat screen printing, photocurable resin that is coated on it should have enough flexibility and toughness to tolerate with repeated blading of dye paste and tension from rectangular frame. For the photocuring with laser, the resin should have, in addition, a very fast photopolymerization rate because reaction proceeds with the scanning of the laser in a few microseconds. This process is different from conventional one, in which the whole surface of the screen is irradiated with UV light for minutes.

As preliminary experiments, we have irradiated UV light on several formulated polymeric materials and observed the apparent change of films. Table I shows the summarized results.

It is well known that natural polymer, such as gelatin and casein, can be photocured by UV light with photosensitizer ammonium dichromate.[7] In the preliminary test of photocuring using gelatin and casein, it is observed that the curing rate is too slow to be applied in this laser curing.

The emulsion of poly(vinyl alcohol) with photosensitizers containing the diazonium group is commonly used in textile screen printing.[8] We observed that this system can be cured enough fast to be applied to laser curing.[6] But this system is unconvenient in the screen manufacturing process since it needs more drying processes and seldom gives the chance for the modification in physical properties through chemical structures and formulations.

In comparison with the poly(vinyl alcohol) system, photocurable acrylic resins are very diverse in chemical structures and formulations, which leads to many kind of films and bulk compounds of wide physical properties from rubber to hard plastics. In selecting a proper acrylic resin for screen manufacturing process, it is a requisite for resin to have water solubility since unirradiated image of film should be removed by washing with water.

For the preliminary experiments, three acrylic resins were selected. Excess amount of photoinitiator was added to the resin for the test by a UV lamp. Although a photocurable acrylic resin of emulsion type, that is, IRR 159 was a good candidate for industrial application, it was found that its photocuring rate is too slow to be applied in laser curing. Another clear acrylic resin IRR 210 showed a fast photocuring response, but photocured films were so brittle that it should not be recommended for the application to the manufacture of flat screen. We have found that IRR 160 had a fast rate of UV curing and water dilutability, and the cured IRR 160 had further proper flexibility, heat resistance, and water resistance. It was the reason for that more detailed and precise study was only limited to IRR 160, which was urethane acrylate resin diluted with hexanediol diacrylate.

Laser-Curing Behavior of Acrylic Resin

The degree of curing in laser scanning was observed by IR spectroscopy, in which characteristic

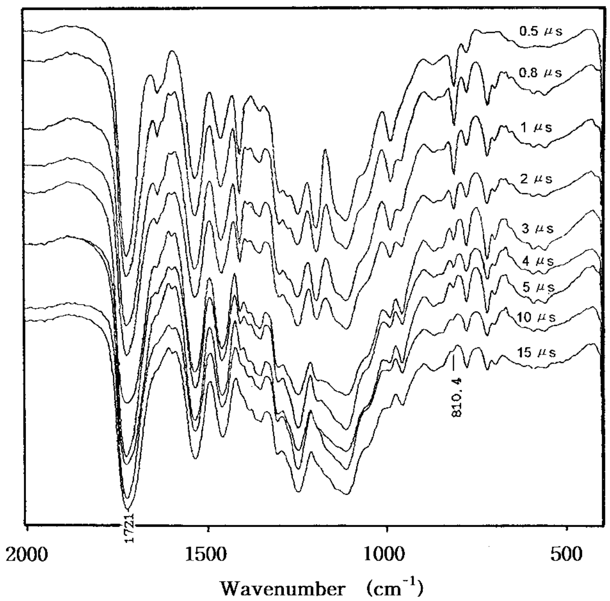

Figure 2 The changes in IR spectra of photocurable acrylic resin with the exposure of argon ion laser.

absorption peak due to twisting vibration of vinyl groups decreased with an increase of laser exposure time.[9] In Figure 2, the decrease of absorption bands at 810.4 cm^{-1} results from chain reaction of vinyl group to crosslinked polymer with photocuring, the strength of which could be relatively calculated in calibration with a constant absorption strength of C═O stretching vibration at 1721 cm^{-1} of ester groups. The change of IR spectra supports also that the curing reaction proceeds almost with radical polymerization of vinyl groups initiated by radical fragments of photoinitiator.

Figure 3 shows the curing degree of acrylic films with argon ion laser calculated from the decrease of the absorption at 810.4 cm^{-1}. From Figure 3, it is observed that the degree of photocuring increases with irradiation time of laser and then comes to a plateau with more than 4 μs exposure. It is known that induction period is caused by the presence of oxygen in photopolymerization.[10] The induction period due to oxygen inhibition were also reported in laser-induced photopolymerization.[11,12] The cure kinetics have been shown as a characteristic S-shaped curve due first to the inhibition effect of oxygen and then to the gellation of the resin.[13–15] From a practical point of view, it is not necessary to cure resin to the extent of plateau that can is achieved by more than 4 μs exposure because the longer exposure relates to the decrease of screen productivity. The relation of exposure time t (μs) to scanning speed ν (m/s) is as follows for the laser used in this experiments.

$$t = 100/2\nu$$

In industrial production, the short exposure time relates directly to production speed. The exposure time can be shorter with the decrease of spot size and the increase of scanning speed, but too fast of scanning causes the speckle effect in screen preparation due to laser interferences as in microlithography technology. Then, too fast of scanning by the increase of power density means that the decrease of spot size is not recommendable for the sharp image formation in screen. For the washing-out of the uncured part in practical manufacturing process, we have found that about 50% degree of curing showed enough strong adhesion to polyester screen mesh resistant to the following washing-out step.

Another important factor for industrial applications is the amount of photoinitiator since it is very expensive than acrylic photocurable resin. The curing speed of resin linearly relates to the amount of photoinitiator.

With a constant exposure time of 4 μs, the degree of curing as a function of input power was plotted in Figure 4. The dependence of curing degree on input power shows a typical S-shaped curve. The induction effect by oxygen is appeared relatively strong in lower input power, which re-

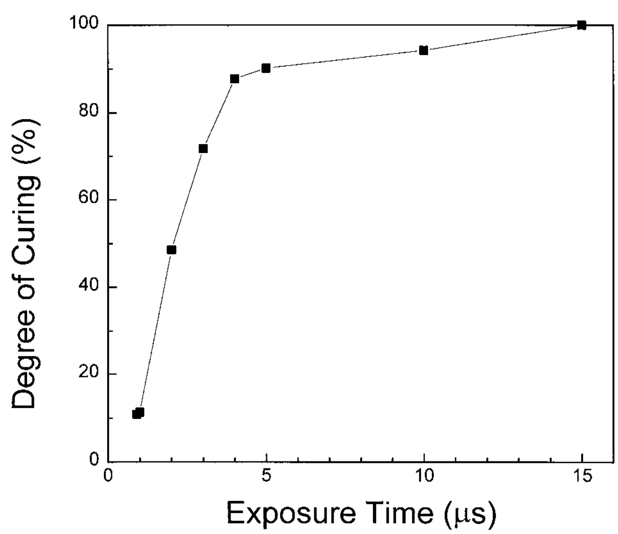

Figure 3 Dependence of the laser-curing degree on exposure time: laser power (1 W), IRR 160 (90%), and D 184 (10%).

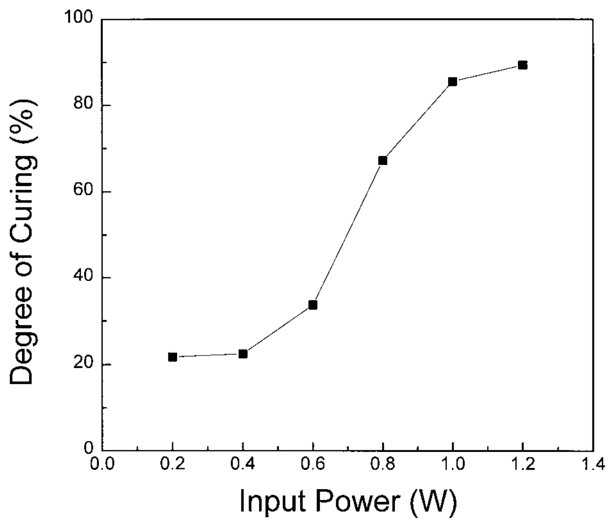

Figure 4 Dependence of the laser-curing degree on the input power of the laser: exposure time (4 μs), IRR 160 (93 wt %), and D 184 (7 wt %).

sults in a lower degree of curing in vicinity of low input power. The plateau in curve that is shown with input power of larger than 1 W is caused by the excess of photons in comparison with the amount of photoinitiator. S-shaped kinetic curve in Figure 4 results from the combined effect of the presence of air and the saturation of photons.

The viscosity of resin in the coating process could be regulated through addition of a small amount of water, which gave a convenient clue in practical doctor-blading. In the manufacturing of printing screen, it is not suggested to excessively add multifunctional acrylic monomer more than the formulated amount to reduce the processing viscosity since it causes the change of physical properties and curing behavior of films. Figure 5 shows the effect of water content on curing speed of resin. The reported viscosity of IRR 160 at 25°C is about 17,000 cps. With addition of 5 and 10% water to it, the viscosities drop to 6000 and 3000 cps, respectively. From Figure 5, it can be observed that the addition of water causes a little decrease of curing velocity, but the decrease of curing velocity is small in comparison with that of viscosity and then not significant to affect laser curing system itself.

In the aspect of industrial application, it takes about 15 min to cure flat screen of the size of 1 × 2 m with a 1-W argon ion laser. This curing time is competible with conventional curing by UV lamp. This study is performed with a representative acrylic resin. We believe that principles and basic properties obtained in this study can be expanded to other kind of photocurable acrylic resins.

CONCLUSIONS

In the manufacturing of printing screen, photocurable acrylic resin can be applied to the automated and simplified process through adapting argon ion laser as light source, in which a multifunctional acrylic resin based on a polyurethane backbone is suggested as a good candidate.

The degree of laser curing in acrylic resin can be determined by IR spectroscopic analysis of a characteristic twisting absorption band of vinyl group. Water-soluble acrylic resin can be cured to insoluble state through the irradiation of 1-W argon ion laser with exposure time of a few microseconds. The degree of curing was shown in a S-shaped curve to exposure time and input power of laser, which results from the combined effect of oxygen inhibition at lower power and gellation or photon saturation at higher power.

The water added for the viscosity regulation of acrylic resin causes no significant decrease of curing speed.

From the results, it is suggested to replace the conventional UV curing system by a laser-curing system, which leads to more economic and automated process for printing screen and basic prop-

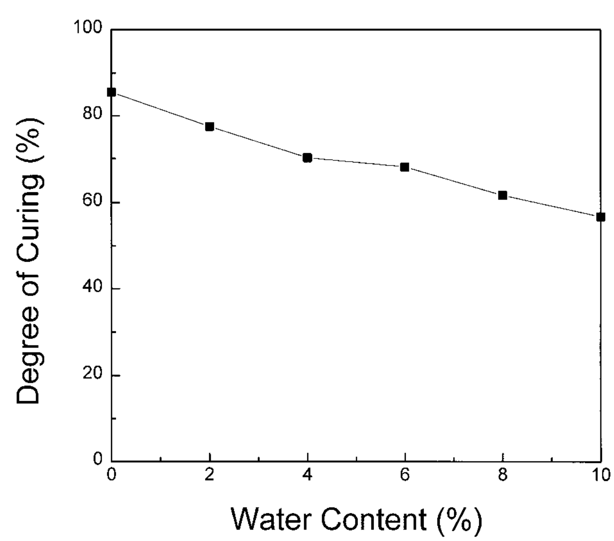

Figure 5 The effect of water as a viscosity reducer on the curing velocity of resin: laser power (1 W), exposure time (4 μs), IRR 160 (93 wt %), and D 184 (7 wt %).

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