

Ultraviolet-Curing Behavior of an Epoxy Acrylate Resin System

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ABSTRACT: Ultraviolet (UV)-curing behavior of an epoxy acrylate resin system comprising an epoxy acrylate oligomer, a reactive diluent, and a photoinitiator was investigated by Fourier transform infrared (FTIR) spectroscopy. The conversion changes of the resin system containing 20 phr of 1,6-hexanediol diacrylate as a reactive diluent and 2-hydroxy-2-methyl-1-phenyl-propan-1-one as a photoinitiator were measured under different UV-curing conditions. The fractional conversion was calculated from the area of the absorption peak for the vinyl group vibration occurring at 810 cm^{-1} . The effects of photoinitiator concentration, total

UV dosage, one-step or stepwise UV irradiation, UV intensity, atmosphere, and temperature on the curing behavior of the resin system were investigated. The conversion of the resin system increased rapidly at the initial stage of the UV-curing process but increased very slowly after that. The final conversion of the resin system was mainly affected by total UV dosage. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1180–1185, 2005

Key words: UV-curing; epoxy acrylate; photopolymerization; curing of polymers

INTRODUCTION

The ultraviolet (UV)-curing process is highly adaptable to surface protection coatings of all kinds of materials (plastic, metal, glass, paper, wood, fabrics, etc.), adhesives, printing inks, varnishes, special paints, and even dentistry.^{1–5} It is a solventless process—it avoids the use of solvents, so volatile organic compound emissions are eliminated; a room temperature process—it has lower energy consumption, because substrates and components are generally not heated; and a high-speed process—occasionally within the subsecond range.

In general, conventional thermally dried coatings are composed of a resinous binder, pigments and fillers, and solvents. After application to the substrate, heat is applied to dry the film by driving off the solvents. However, the evaporated solvents are usually flammable and toxic and can be serious airborne pollutants. But in UV-curing, the oligomers essentially take the place of the resinous binder, and monomers function as reactive diluents, substituting for solvents.⁶ Usually, UV-curable coating resins consist of three major components, a reactive oligomer end-capped with acrylic functional groups, a mono- or multifunctional reactive diluent, and a photoinitiator. Additionally, nonreactive additives such as pigments,

adhesion promoters, and surface active agents are also introduced into formulations depending on the specific application.^{7–12}

The oligomers impart properties associated with their basic structure. Typical commercial oligomers are urethane acrylate, polyester acrylate, silicone acrylate, and epoxy acrylate.^{13–18} Generally, the rate of polymerization depends first on the reactivity of the functional groups, on their concentration, and on the viscosity of the resin, whereas the chemical structure and the functionality of both the oligomer and the monomer determine the final degree of polymerization. For a given formulation, the polymerization kinetics depend on reaction conditions such as atmosphere, temperature, light intensity, and photoinitiator concentration.^{19–28} Thus, to obtain the best physical properties of the polymerization product one must consider not only the materials used but also the UV-curing conditions under which the polymer was formed. These reaction conditions, along with the type of reactant system chosen, will completely control the polymerization rate and conversion of the resin system.

Understanding the curing behavior of the epoxy acrylate resin system is important in optimizing polymer processing conditions and in producing UV-cured polymer products comprising the resin with excellent quality. So, the epoxy acrylate resin systems with different compositions were formulated, and the effects of photoinitiator concentration, total UV dosage, one-step or stepwise UV irradiation, UV intensity, atmosphere, and temperature on the curing behavior

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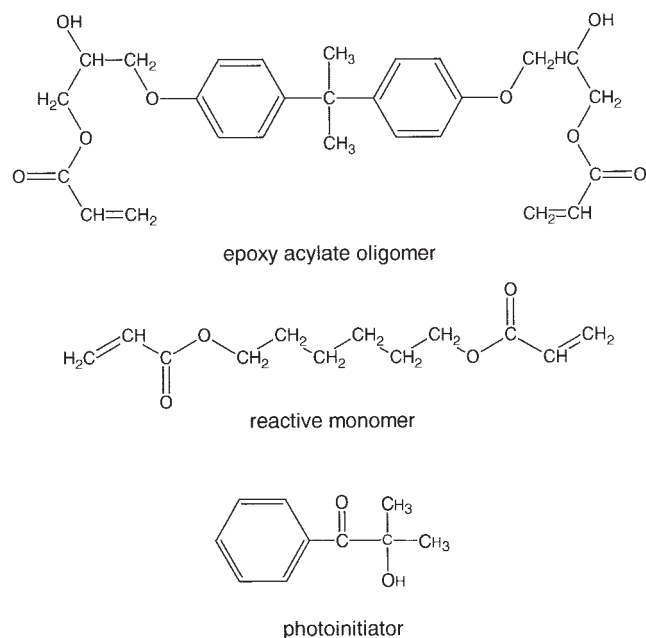


Figure 1 Chemical structures of the epoxy acrylate oligomer, reactive diluent, and photoinitiator used in this work.

of the resin system were investigated by Fourier transform infrared spectroscopy (FTIR).

EXPERIMENTAL

Materials

The epoxy acrylate resin used in this study was a bisphenol-A-epoxy diacrylate oligomer ($M_w = 500$ g/mol, viscosity = 3000 cP at 60 °C, SK-UCB Co., Ulsan, Korea). 1,6-Hexanediol diacrylate (HDDA, $M_w = 226.3$ g/mol, viscosity = 10 cP at RT, SK-UCB) was used as a reactive monomer. The content of HDDA in the epoxy acrylate resin system was fixed to 20 phr (parts per hundred of epoxy acrylate resin). The photoinitiator used was 2-hydroxy-2-methyl-1-phenylpropan-1-one ($M_w = 164.2$, evaporation temperature = 80 °C, liquid at RT, from SK-UCB). The content of the photoinitiator in the resin system was changed to 3 phr. The chemical structures of the epoxy acrylate oligomer, reactive diluent, and photoinitiator are shown in Figure 1.

UV-curing process

UV-curing of the epoxy acrylate resin system was carried out using a UV-curing apparatus (JU-101 table type UV cure system, Jeil UV Co., Korea). The instrument could be equipped with a high-pressure mercury lamp (80 W/cm, length = 15 cm, diameter = 2.54 cm, Jeil UV). The high-pressure mercury lamp released UV light in the wavelength range of 250–450 nm with

an intensity maximum at about 365 nm. The UV radiation spectra of the high-pressure mercury lamp were given by the supplier and are shown in Figure 2. To investigate the effects of nitrogen atmosphere on UV-curing of the epoxy acrylate resin system nitrogen gas was flown on the position where UV-curing was occurring. To measure UV intensity and UV dosage irradiated by the UV-curing instruments, an UV intensity tester (UVICURE Plus, EIT) was employed. The UV intensity at the position where UV-curing occurred was changed by changing the distance between the lamp and the resin coatings. The thickness of the resin coatings was controlled to be 15 μm .

Curing analyses by FTIR

FTIR spectroscopy gives information on the chemical structure change of a reacting system by monitoring the IR absorption spectra change during reaction. Infrared spectra of the epoxy acrylate resin system were measured during UV-curing using an FTIR spectrophotometer (Bomem MB100, Bomem, Inc., Quebec, Canada) in the wavenumber range of 4000–400 cm^{-1} . An epoxy acrylate resin system was coated (thickness = 15 μm) on a NaCl plate and cured with a certain UV dosage, and then it was analyzed by the FTIR immediately. During the UV-curing process, the chemical structure of the epoxy acrylate resin system changes and so does the IR spectra. By monitoring the disappearance of the specific IR absorption band at 810 cm^{-1} for the acrylate functional group, the chemical conversion of the epoxy acrylate resin system could be determined.

RESULTS AND DISCUSSION

Effect of photoinitiator concentration

The concentration of a photoinitiator in a UV-curable acrylate resin system influences substantially not only

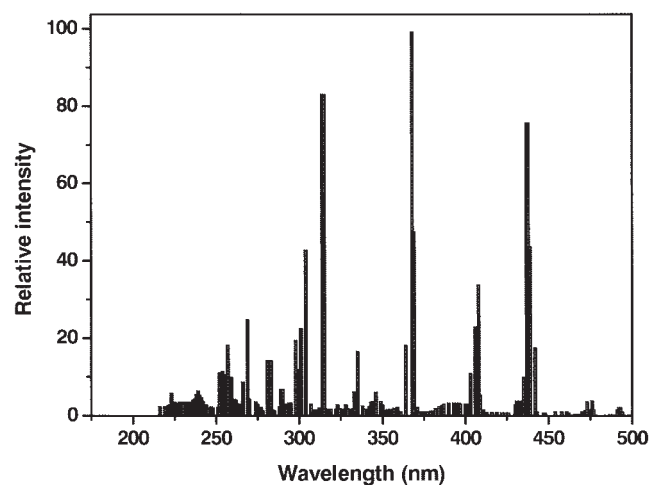


Figure 2 UV radiation spectra of the high-pressure mercury lamp.

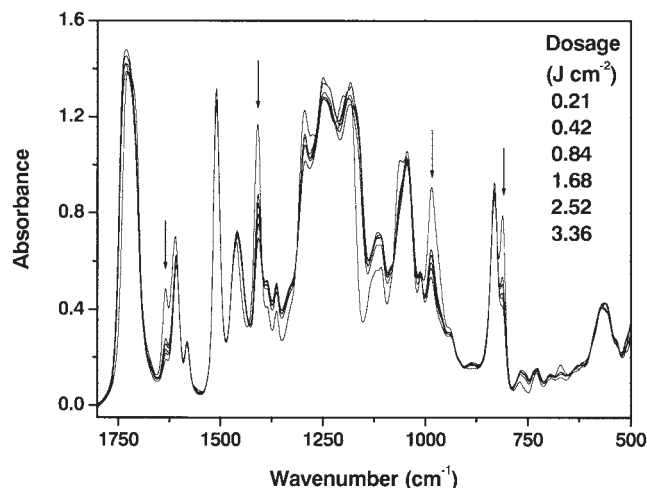


Figure 3 FTIR spectra of the epoxy acrylate resin system obtained after repeated exposure to UV radiation (resin thickness = 15 μm).

the maximum polymerization rate and the final conversion of acrylate but also the properties of the final product.²⁹ Consequently, it is necessary to determine an optimum photoinitiator concentration for each specific application.

Several NaCl plates coated with an epoxy acrylate resin system containing HDDA 20 phr and the photoinitiator 3 phr were prepared and UV-cured with various UV dosages for FTIR analyses. Some selected FTIR spectra of the epoxy acrylate resin system for various UV irradiation dosages are shown in Figure 3. The assignments of each characteristic peak in Figure 3 are listed in Table I. The spectra exhibited several invariant peaks in the vicinity of the assigned peaks. This feature is required for the strict control of experimental procedures for spectrometric measurements. It also shows that a single type of chemical event takes place at this stage of the UV-induced polymerization. Because of the alkoxy-aromatic structure of the oligomers, the acrylate deformation band centered at 810 cm^{-1} was mixed with the tailing of another band exhibiting a maximum at 830 cm^{-1} (A_D^{830}). The apparent changes of the absorbance measured at 810 cm^{-1} (A_D^{810}) needed to be corrected to permit a quantitative

TABLE I
The Peaks in the FTIR Spectra of the Epoxy Acrylate Resin System

Wavenumber (cm^{-1})	Assignment
810	Out of plane bending of C—H on $\text{RCH}=\text{CH}_2$
984	Stretching vibration of the $\text{C}=\text{C}-\text{C}=\text{O}$
1409	Scissor deformation of the $=\text{CH}_2$
1635	Stretching vibration of the $\text{CH}=\text{CH}_2$

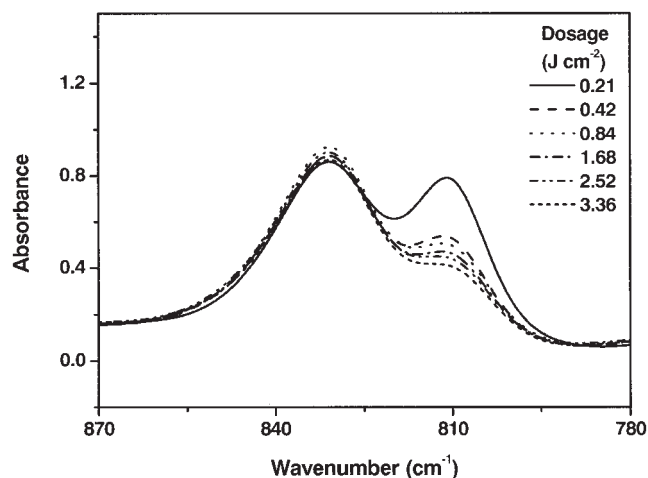


Figure 4 Expanded part of the FTIR spectra showing the peak centered at 810 cm^{-1} used to analyze polymerization kinetics (resin thickness = 15 μm).

measurement of monomer conversion after application of the UV radiation.

The expanded part of the spectra displayed in Figure 4 shows that the peak at 830 cm^{-1} on the left side of the decreasing absorption maximum at 810 cm^{-1} is almost unaffected by the UV treatment. A careful investigation of the infrared absorption characteristics of this type of acrylate systems, in the form of thin films, has allowed us to determine the value A_{tail}^{810} representing the unwanted contribution of this tailing of the peak at 830 cm^{-1} .³⁰ The measured value of each peak was corrected from the quantity $A_{tail}^{810} = 0.15 A_D^{830}$ and normalized to the absorbance measured at 830 cm^{-1} . The fractional conversion of acrylate functional groups, α , after exposure to a given dosage D , was thus calculated from the following equation.

$$\alpha = 1 - \frac{[\text{Acrylate}]_D}{[\text{Acrylate}]_0} = 1 - \frac{(A_D^{810} - 0.15 A_D^{830}) / (A_0^{810} - 0.15 A_0^{830})}{A_D^{830} / A_0^{830}} \quad (1)$$

Some other acrylate peaks centered at 984, 1409, and 1635 cm^{-1} have their intensity decreasing with UV dosage but they do not offer the same accuracy over the whole conversion range. This is due to the presence of other peaks in their vicinity that are not strictly invariant upon the UV treatment. The conversion changes of the epoxy acrylate resin system containing 3 phr of the photoinitiator for various UV dosages were calculated from the above equation using the peaks at 810 cm^{-1} and are plotted in Figure 5.

Figure 5 shows the effect of photoinitiator concentration on the UV-curing behavior of the epoxy acrylate resin system. High photoinitiator content leads to

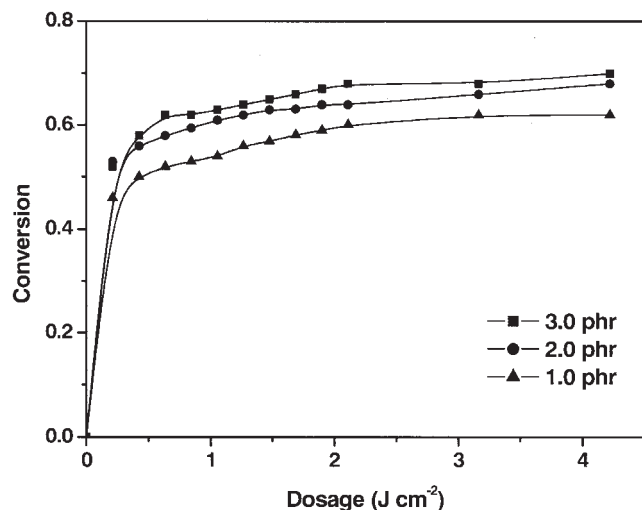


Figure 5 Conversions of the epoxy acrylate resin systems with various photoinitiator contents (resin thickness = 15 μm).

both a high polymerization rate and a high degree of conversion. Upon increasing the concentration of the photoinitiator from 1 to 3 phr, the conversion increased about 10%. The conversion difference between the system containing 2 phr and the system containing 3 phr was considerably smaller than that between the system containing 1 phr and the system containing 2 phr. This result shows that 3 phr was enough for an effective initiation of the reaction and, over 3 phr, further addition of the photoinitiator would affect very slightly the polymerization rate and final conversion. It is important to control the concentration of a photoinitiator within a limited concentration range because even though the polymerization rate increases with increasing concentration of the photoinitiator, the chain length of polymer matrix formed during curing decreases with increasing concentration of the photoinitiator. Therefore, the content of the photoinitiator in the resin system was fixed to 3 phr for the current work.

Effect of irradiation method

The effect of one-step or stepwise UV irradiation on the conversion of acrylate groups was investigated. In the case of stepwise irradiation, infrared spectra of the resin system were obtained between each exposure. The conversion of each sample prepared by stepwise curing is plotted in Figure 6 as symbols as a function of dosage. All the experimental points for stepwise curing are very close to the conversion curve obtained for one-step curing. The extremely high reactivity of the acrylate resin system was confirmed by the steep initial slope of the conversion curve. The cumulation of a small stepwise dosage gave almost the same final

conversion as like as a one-step dosage when total dosage of each radiation method was the same. The amount of dosage increment per step hardly affected the final conversion of the epoxy acrylate resin system.

Effect of atmosphere

UV-curing polymerization under inert gas has attracted considerable attention because oxygen in the air may interact with free radicals in the reacting system to inhibit polymerization.³¹⁻³³ A lot of information is already available on the positive effects of UV-curing at relatively low intensity under completely oxygen-free conditions, but only a few data are available on UV-curing at high intensity under oxygen-free conditions. The final conversions of both samples cured under either nitrogen or air atmosphere were almost the same: 0.68 for nitrogen atmosphere and 0.67 for air atmosphere. The effect of atmosphere change on the curing behavior of the epoxy acrylate resin system was negligible. Because the high-intensity UV light resulted in a drastic conversion increase on the resin surface, the diffusion of oxygen into the resin through the coating surface was quite difficult.

Effect of UV light intensity

The influence of UV light intensity on the polymerization kinetics of the epoxy acrylate resin system was investigated. The conversion changes for two UV intensities are shown as a function of dosage in Figure 7. The dependence of the initial polymerization rate on UV intensity can be deduced from these plots. The polymerization rate increased with UV intensity. Chemical conversion at an equal dosage increased also

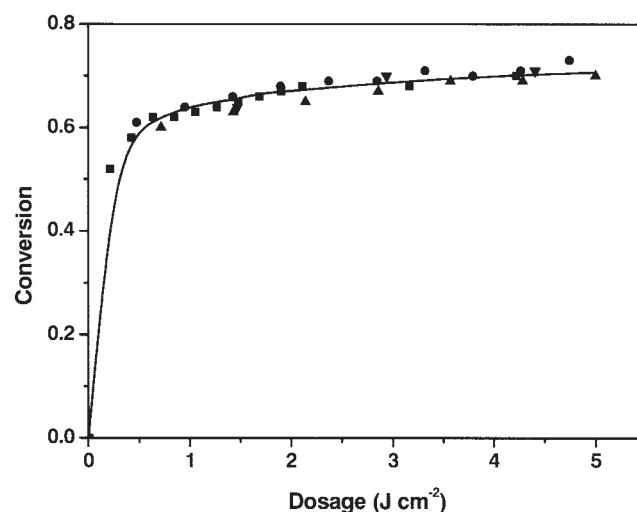


Figure 6 Conversions of the epoxy acrylate resin system for one-step (curve) and stepwise (symbols) curing (resin thickness = 15 μm).

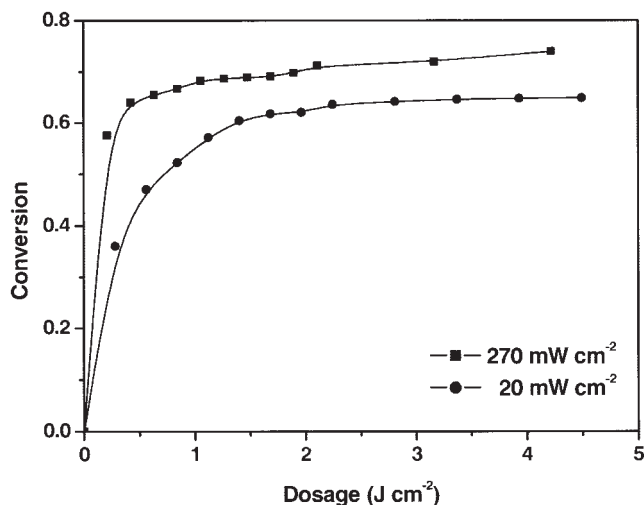


Figure 7 Conversion changes of the epoxy acrylate resin system UV-cured at different intensities (resin thickness = 15 μm).

with UV intensity. Lecamp et al.³⁴ reported that in the case of photoinitiated polymerization, the initiation rate is very high. Thus, crosslinking systems cannot be in voluminal equilibrium because volume shrinkage rate is much slower than chemical reaction rate. This difference generates a temporary excess of free volume that increases the mobility of the residual functional groups and allows the reacting system to reach higher conversion than for systems in voluminal equilibrium. So, the higher the light intensity, the higher the polymerization rate and the more the free volume excess, which leads to higher conversions. The experimental data points plotted in Figure 8 are in good agreement with the line predicted from the general

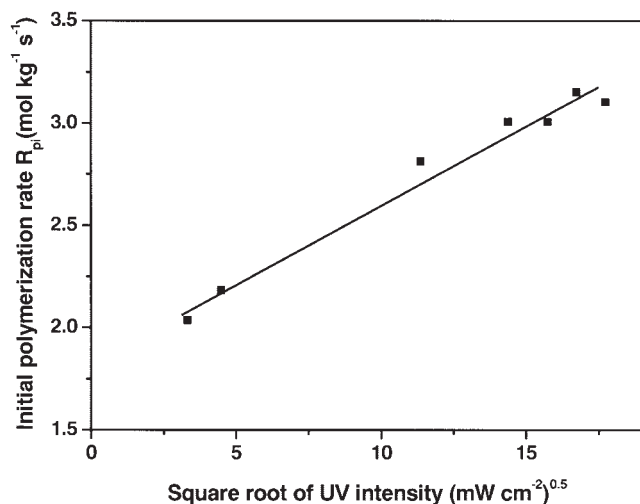


Figure 8 Initial polymerization rate of the epoxy acrylate resin system versus square root of the UV intensity (resin thickness = 15 μm).

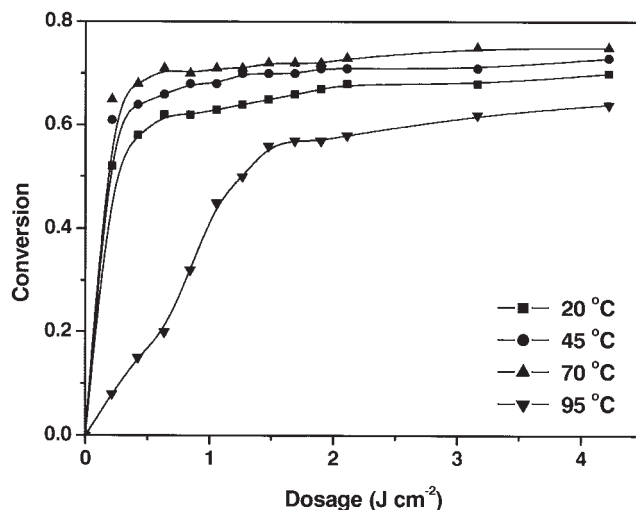


Figure 9 Conversion changes of the epoxy acrylate resin system for various curing temperatures (resin thickness = 15 μm).

kinetic model for a photoinitiated free radical polymerization.

Effect of temperature

To investigate the effect of temperature on the curing reaction of the epoxy acrylate resin system, the resin sample was coated on a NaCl plate, and then it was placed in a convection oven that was being controlled to a constant temperature for 5 min. The temperature dependence of the photoinitiated polymerization is shown in Figure 9. The initial polymerization rate of the epoxy acrylate resin system increased with increasing reaction temperature up to 70 $^{\circ}\text{C}$ but decreased at 95 $^{\circ}\text{C}$ because the photoinitiator evaporates over 80 $^{\circ}\text{C}$. Increasing the reaction temperature also raised the final conversion of the epoxy acrylate resin system since more residual acrylate groups become accessible for polymerization by enhancing chain segmental mobility in the resin system.

CONCLUSIONS

The effects of photoinitiator concentration, total UV dosage, one-step or stepwise UV irradiation, UV intensity, atmosphere, and temperature on the curing behavior of the epoxy acrylate resin system were investigated. The conversion of the epoxy acrylate resin system increased rapidly at the initial stage of UV-curing process but increased very slowly after that. The conversion of the epoxy acrylate resin system was mainly affected by total UV dosage. The final conversion was not affected very much by atmosphere. The initial polymerization rate of the epoxy acrylate resin system increased linearly with the square root value of

UV intensity. The polymerization rate and final conversion of the epoxy acrylate resin system increased with increasing photoinitiator content. The initial polymerization rate and final conversion of the epoxy acrylate resin system increased with increasing reaction temperature up to 70 °C, but decreased at 95 °C because the photoinitiator evaporates over 80 °C.

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