In Situ Study of Photopolymerization by Fourier Transform Infrared Spectroscopy

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SYNOPSIS

The Fourier transform infrared (FTIR) *in situ* method was developed for the investigation of photopolymerization. Ultraviolet (UV) cure of a mixture of a cycloaliphatic epoxide, a 2-ethylhexyl acrylate, and photoinitiators, which forms simultaneous interpenetrating polymer network (IPN), was monitored while the sample was irradiated with UV light. Triphenylsulfonium salt and benzoin ether were used as photoinitiators. For the sake of comparison, similar experiments were performed for the epoxide with the triphenylsulfonium salt photoinitiator and the acrylate with the benzoin ether photoinitiator. The epoxy photopolymerization was monitored using an epoxy CH stretching band at 3005 cm^{-1} and a ring vibration band at 790 cm^{-1}. The acrylic photopolymerization was monitored using a C=C stretching band at 1637 cm^{-1}. The epoxy conversion was less than 60% when the acrylic polymerization was completed in the IPN.

INTRODUCTION

Photocurable polymer materials such as UV curable coatings, printing inks, adhesives, and photoresists have been widely utilized in various industries.[1,2] The kinetic analysis of reactions is one of the most significant themes in studies of photopolymerization. Ultraviolet (UV) curing parameters such as the type and concentration of a photoinitiator, curing temperature, and UV light source have considerable effects on the cure rate and the properties of the UV-cured polymers. Thus, it is very important to study the effects of such curing parameters on the cure rate and to determine the optimum condition. The *in situ* analysis of photopolymerization is highly desirable. However, there exist only a few good techniques due to the inherent difficulties such as insolubilization by network forming and the high rate of reactions.

In the past several years, a modified differential scanning calorimetry (DSC) has been used to monitor reactions of photopolymerization.[3-8] Ultraviolet light is introduced to the sample and reference hold-

ers of a differential scanning calorimeter, and the enthalpy of photopolymerization of UV-irradiated sample is measured directly and continuously. The cure rate and the conversion are calculated from the enthalpy data thus obtained by the DSC analysis. The modified DSC technique is a powerful tool for the *in situ* study of photopolymerization, but there are some disadvantages; e.g., this technique cannot yield information on the structural change during the polymerization reaction.

Infrared (IR) spectroscopy has been used to study photopolymerization.[9-13] For example, the cure rate and conversion are determined from the structural information, such as the intensity change of an acrylic C=C vibrational band.[9,10] The change in chemical structure during UV exposure can be observed directly by IR spectroscopy. The IR analysis has been usually performed in a discontinuous mode; i.e., samples are exposed to light for varying times, and subsequently they are subjected to the analysis. The discontinuous IR measurements are generally laborious and time consuming.

The *in situ* analysis of photopolymerization with Fourier transform infrared (FTIR) spectroscopy is discussed in this article. In FTIR spectroscopy, a spectrum is obtained in a few seconds, so it is effective to monitor a rapid photoinitiated polymeriza-

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tion. The term *FTIR in situ analysis* used in this article means that spectra are simultaneously measured while UV-curable samples are irradiated with UV light introduced to the sample chamber of an FTIR spectrometer through an optical guide.

Two typical types of photopolymerization, photoinitiated cationic[14-16] and radical[17] polymerizations, were investigated by the FTIR *in situ* analysis. First, the photoinitiated cationic polymerization was investigated for a cycloaliphatic epoxide with a triphenylsulfonium salt photoinitiator. This reaction, which was well studied by Crivello et al.,[18-22] is a living polymerization, and the epoxide is postcurable after UV exposure. Second, the photoinitiated radical polymerization was investigated for a 2-ethylhexyl acrylate with a benzoin ether photoinitiator. Since the reaction is performed in a few seconds, the conventional discontinuous IR method is inapplicable to monitor this reaction. The FTIR *in situ* method is appropriate in this case.

Finally, a UV-curable epoxy–acrylic simultaneous interpenetrating polymer network (IPN) was investigated. An IPN is defined as a combination of two polymers in network form, at least one of which is synthesized and/or crosslinked in the immediate presence of the other.[23] The UV-curable IPN consisted of a mixture of the cycloaliphatic epoxide, the 2-ethyl hexyl acrylate, and the photoinitiators for both cationic and radical polymerizations. The epoxide and the acrylate in the mixture are polymerized simultaneously by noninterfering polymerization modes when the mixture is irradiated by UV light. The acrylate was chosen as the acrylic component in the IPN in order to improve the brittleness of the cycloaliphatic epoxide.

It is important to know respective cure rates of the epoxide and the acrylate in the IPN because they affect the final properties.[23] However, the modified DSC analysis is impossible to separate the respective rates in this case because its information is only about the sum of enthalpy from the two reactions. To the contrary, each reaction of the two components in the IPN is successfully monitored by the FTIR *in situ* analysis.

EXPERIMENTAL

All spectra were obtained with a Perkin-Elmer 1720 FTIR spectrometer with a deuterated triglycine sulfate detector (pyroelectric detector) at 4 cm^{-1} resolution. The mirror speed of the interferometer was 0.5 cm/s. The *in situ* spectra were obtained with one scan and smoothed with the FTIR computer. Figure

1 shows the schematic illustration of optics in the FTIR sample chamber for the FTIR *in situ* analysis. A Macam Photometrics Flexicure model UVLS102 UV light source (Philips HPA400 metal halide lamp) was used and UV light was introduced to the FTIR sample chamber through a flexible light guide. Spectra were obtained while a sample was being exposed to UV light introduced by a light guide. The distance between the sample and the exit of the light guide was 5 mm. The UV light guide was positioned at an angle of 45° to the KBr tablet in order not to block the IR beam path of FTIR spectrometer. The UV light intensity on the surface of the KBr tablet was approximately 1 mW/cm^{-2} at 250 nm in this geometry. The sample was exposed for 25 min. In the case of the epoxy sample, thermal cure was performed at 60°C for 20 min.

Cycloaliphatic epoxide was 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate, ERL4221, purchased from Union Carbide, and 2-ethylhexyl acrylate was purchased from Mitsubishi Yuka. Triphenylsulfonium hexafluoroantimonate obtained from 3M was used as a photoinitiator for epoxy cationic polymerization, and benzoin isobutyl ether obtained from Krogane Kasei was used as a photoinitiator for acrylic radical polymerization.

Three kinds of liquid samples were prepared. An epoxy sample consisted of 100 parts of the epoxide and 2 parts of the cationic initiator. An acrylic sample consisted of 100 parts of the acrylate and 2 parts of the radical initiator. An IPN sample consisted of 75 parts of the epoxide, 25 parts of the acrylate, 1.5 parts of the cationic initiator, and 0.5 parts of the radical initiator.

A pair of KBr plates are often used to sandwich a liquid sample for IR measurements. But the KBr plates cannot be used in the FTIR *in situ* measurement because of network forming and adhesion of the sample after UV exposure of the sample. Pure and disposable KBr tablets made in house were therefore used instead of expensive KBr plates in
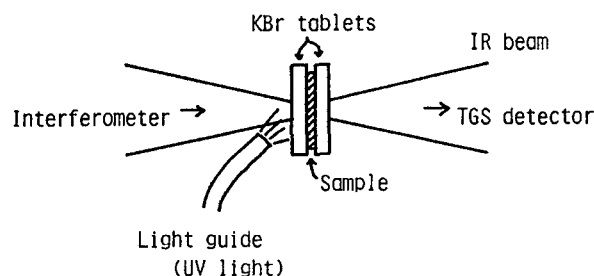
Figure 1 Schematic illustration of optics in an FTIR sample chamber for the FTIR *in situ* analysis.

this research. The tablet had no UV absorption bands at wavelengths larger than 200 nm. One drop of a sample whose weight was approximately 1 mg was sandwiched between a pair of KBr tablets.

RESULTS AND DISCUSSION

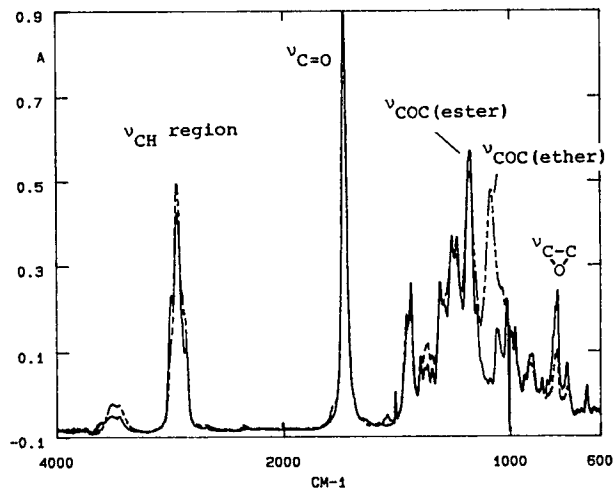### Effect of UV Exposure on FTIR Spectra

The effect of UV exposure in the FTIR sample chamber on FTIR spectra was investigated at first. A sample sandwiched between a pair of KBr tablets is measured with FTIR *in situ* during UV exposure. Although the detector is insensitive in the UV region, there is a possibility of weak visible and IR light irradiated by UV light affecting FTIR spectra.

The effect of UV exposure on an FTIR interferogram and the spectrum was investigated when a pair of KBr tablets without a sample were set in the sample chamber. It was found that in the interferogram, during UV exposure, a kind of periodic noise overlapped onto the ordinary interferogram. This result suggests that light irradiated by the UV light source entering into the interferometer was modulated there, passed through the sample chamber, and finally reached the detector.

Figure 2 shows the FTIR spectrum of a 100% line during UV exposure. A reference spectrum was measured without UV exposure. There are two different periodic noises in the spectrum: the sharp and strong noises appearing at intervals of about 500 cm^{-1} and the weak sinusoidal noises appearing in the whole IR region. The noises appearing in Fig-
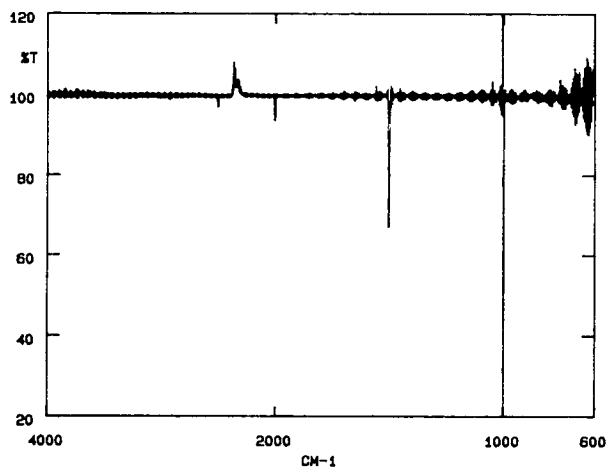
Figure 3 FTIR spectra of 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate with a triphenylsulfonium salt photoinitiator. The assignment is indicated in the figure. The solid line is the spectrum without UV exposure, and the dotted line is the spectrum after 25 min UV exposure.

ure 2 are the result of the Fourier transform of the noise in the interferogram during UV exposure. Careful attention should be paid in interpreting the spectra obtained by the FTIR *in situ* analysis in order to remove the effect of such noises. The spectra obtained by the FTIR *in situ* analysis were dealt with the smoothening process in the FTIR computer to take away the weak noises.
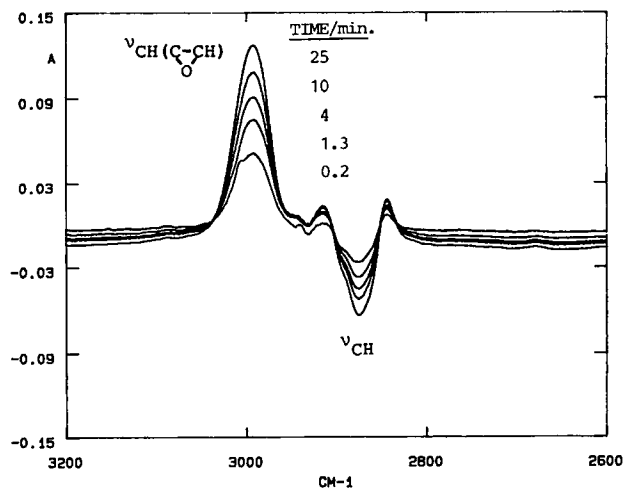
Photopolymerization of Epoxide

Photoinitiated cationic polymerization of an epoxy homopolymer was investigated by the FTIR *in situ* analysis. Figure 3 shows the FTIR spectra of the epoxy sample. The solid line indicates the spectrum without UV exposure, and the dotted line indicates the spectrum after 25 min UV exposure. The assignment of several bands is indicated in the figure. The CH stretching band of epoxy ring at 3005 cm^{-1} disappeared and the ordinary CH stretching band at 2874 cm^{-1} appeared after UV irradiation due to a ring-opening polymerization of the epoxide. In addition, the strong COC stretching band of ether around 1100 cm^{-1} appeared and the epoxy ring vibration band at 790 cm^{-1} disappeared.

To clarify the spectral change, a difference spectrum was processed as a subtraction of the spectrum without UV irradiation from that during UV curing. The peak intensities were normalized by the intensity of a CH$_2$ antisymmetric stretching band at 2937 cm^{-1}. Upward bands correspond to the decrease of

Figure 2 FTIR spectrum of 100% line during UV exposure to a pair of KBr tablets. The reference was measured without UV exposure. Periodic noises appeared in the spectrum.
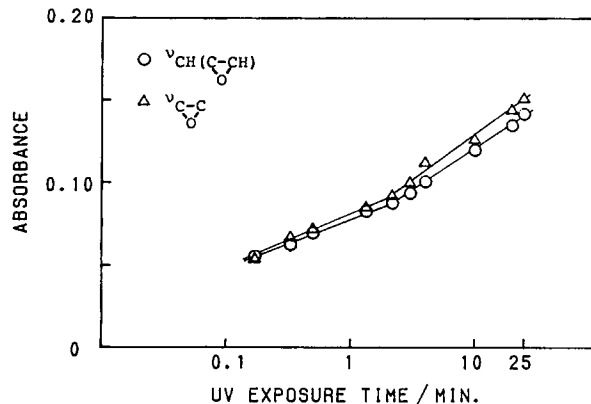
the intensity during UV exposure in the original spectra; downward bands do the opposite. That is, the intensities of those peaks in the difference spectrum are proportional to the epoxy conversion.

The effect of UV exposure time on the epoxy photopolymerization was investigated on the basis of the interpretation of the FTIR spectra described in the preceding. Figure 4 shows the difference spectra in the CH stretching region obtained by the FTIR *in situ* analysis. The UV exposure time is indicated in the figure. The upward bands are assigned to the CH stretching of the epoxy ring, which disappears during UV exposure, and the downward bands are assigned to ordinary CH stretching. Although epoxy ring vibration bands have been studied by IR spectroscopy,[11-13] there have been few studies concerning epoxy CH stretching bands due to the complexity of the CH stretching region of IR spectra. The difference spectra clarified the IR spectral change of the CH stretching bands during UV exposure. The FTIR *in situ* analysis is useful in monitoring epoxy photopolymerization.

Then difference spectra obtained from the FTIR *in situ* analysis was investigated quantitatively. Figure 5 shows the dependence of peak intensities of the epoxy CH stretching and epoxy ring vibration bands on UV exposure time. The scale of the abscissa is in logarithms. Both data behave similarly in the figure and can be fit by two straight lines whose slopes are different before and after $\sim$3 min UV exposure. The slope change is attributable to gelation of the sample.[24]

Figure 5 Dependence of intensities of the epoxy CH stretching band at 3005 cm^{-1} and the epoxy ring vibration band at 2874 cm^{-1} on UV exposure time.

As was mentioned, the band intensity of the difference spectra is proportional to the epoxy conversion. The solid line in Figure 6 indicates the dependence of relative photoinduced epoxy conversion on UV exposure time when the photoinduced conversion at 25 min UV exposure is defined as 100%. The conversion in Figure 6 is calculated from the intensity of the epoxy CH stretching band. The result using the data of the epoxy ring vibration band is almost identical with Figure 6. The photoinduced conversion is approximately 50% at 1 min UV exposure. After UV exposure, this cationic polymerization, which is a living polymerization, is postcurable and is accelerated at higher temperatures. The dotted line in Figure 6 indicates the time dependence of relative overall epoxy conversion when the overall conversion after 20 min postcure at 60°C is defined as 100%. The relative overall conversion was less
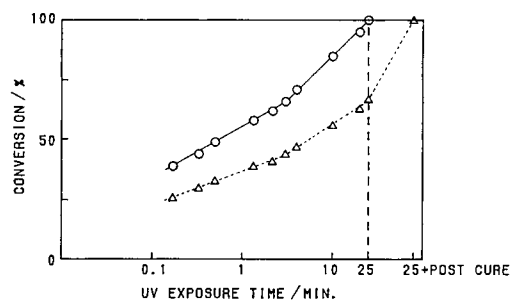

Figure 4 Difference spectra of 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate with a triphenylsulfonium salt photoinitiator in the CH stretching region obtained by the FTIR *in situ* analysis. The UV exposure time is indicated in the figure.

Figure 6 Dependence of the epoxy conversion on UV exposure time. The conversion was calculated from the intensities of the epoxy CH stretching band. In the case of the solid line, the conversion at 25 min UV exposure is defined as 100%, and in the case of the dotted line, the conversion at 20 min postcuring at 60°C is defined as 100%.
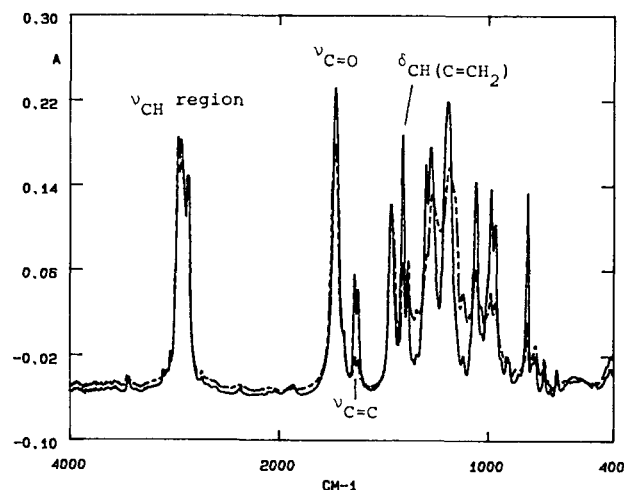
than 60% when UV exposure ceased. This result clearly indicates the acceleration of the epoxy polymerization by postcure.
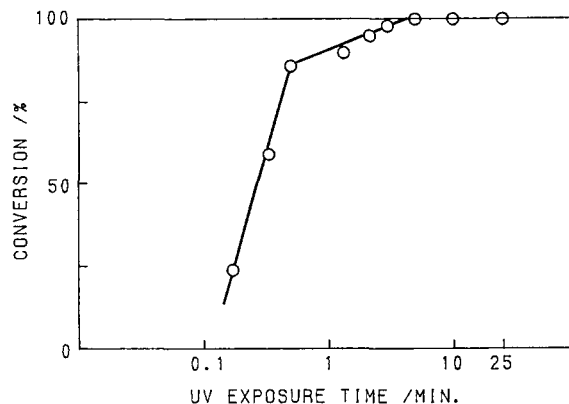
Photopolymerization of Acrylate

Photoinitiated radical polymerization of an acrylic homopolymer was investigated in the same way as the case of the epoxide. Figure 7 shows FTIR spectra of the acrylic sample. The solid line is the spectrum without UV exposure, and the dotted line is that after 25 min UV exposure. The assignment of several bands is indicated in the figure. The $C=C$ stretching bands at 1637 and 1620 cm^{-1} and the $C=CH_2$ in-plane bending band at 1407 cm^{-1}, which are the characteristic ones of acrylates, disappeared by UV exposure. This indicates that almost all $C=C$ groups have reacted during 25 min UV exposure. The $C=C$ groups resonate with bonding $C=O$ groups in acrylates. So the $C=O$ stretching band at 1728 cm^{-1} was shifted to 1740 cm^{-1} when the $C=C$ double bonds were opened and the resonance disappeared by UV exposure.

Then a difference spectrum was processed between the spectrum without UV exposure and that during UV curing. Intensities were normalized by a CH_3 antisymmetric stretching band at 2961 cm^{-1}.

Figure 8 shows the dependence of the relative acrylic conversion calculated from the intensities of the acrylic $C=C$ stretching band on UV exposure time when the conversion at 25 min UV exposure

Figure 8 Dependence of the acrylic conversion on UV exposure time. The conversion was calculated from the intensities of the $C=C$ stretching band. The conversion at 25 min UV exposure is defined as 100%.

is defined as 100%. The data are also fitted by two straight lines in this case, and the slope changes around 20 s of UV exposure. Comparing Figure 9 with the solid line of Figure 6, we recognized that the acrylate reacts much faster than the epoxide. Photopolymerization of the acrylate is almost completed within only 20 s UV exposure. Postcuring is not done because radical polymerization is not a living one.

Photopolymerization of Epoxy–Acrylic Simultaneous IPN

The photopolymerization of an epoxy–acrylic simultaneous IPN was investigated based on the in-

Figure 7 FTIR spectra of a 2-ethylhexyl acrylate with a benzoin ether photoinitiator. The assignment is shown in the figure. The solid line is the spectrum without UV exposure, and the dotted line is the spectrum after 25 min UV exposure.
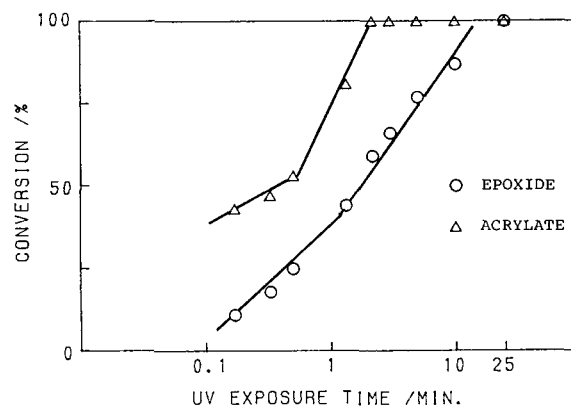

Figure 9 Dependence of the epoxy and acrylic conversions of the IPN, consisting of 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate, 2-ethylhexyl acrylate, and photoinitiators, on UV exposure time. The conversion at 25 min UV exposure is defined as 100%.

terpretation of the photopolymerization of the epoxide and the acrylate described in the preceding. The epoxide and the acrylate are simultaneously polymerized by UV irradiation with the combination of the photoinitiators for cationic and radical polymerizations in the epoxy–acrylic IPN. The properties and morphology of the IPN depend on the relative rate of each reaction in the IPN. Nevertheless, each reaction rate cannot be obtained by the modified DSC technique. However, each reaction can be selectively monitored by the FTIR *in situ* method because of the additivity property of intensity in IR spectroscopy.

Both epoxy and acrylic characteristic bands distinctly appeared in the difference spectrum of the epoxy–acrylic simultaneous IPN calculated by the subtraction of the spectrum during UV exposure from that without UV exposure. The epoxy reaction can be monitored using the epoxy ring vibration band, and the acrylic reaction can be monitored using the C=C stretching band in the same way as described in the preceding.

Then the difference spectra obtained by the FTIR *in situ* analysis were investigated quantitatively. The solid lines in Figure 9 indicate the dependence of relative epoxy and acrylic conversions in the IPN on UV exposure time when each conversion at 25 min UV exposure is defined as 100%. Both epoxy and acrylic conversions of the initial three points, which are UV exposed within 1 min, are smaller than the respective homopolymer initial conversions shown in Figures 6 and 8. However, after 1 min exposure, both conversions in Figure 9 show almost the same tendency as those in Figure 6 and 8. These results reveal that the phase separation of the epoxy and acrylic components took place within 1 min UV exposure; then each component reacted independently and noninterferingly to form two-phase polymeric domains. The acrylate reacted much faster than the epoxide in the IPN. The photoinduced epoxy conversion is less than 60% when the acrylic polymerization is completed. Thus the FTIR *in situ* analysis was successfully used to monitor respective reactions of two species of monomer components in the IPN consisting of an epoxide and an acrylate.

CONCLUSIONS

The FTIR *in situ* method was developed for the investigation of polymerization. The UV cure of a cycloaliphatic epoxide, 3,4-epoxycyclohexylmethyl-

3',4'-epoxycyclohexane carboxylate, and 2-ethylhexyl acrylate were monitored by FTIR. Difference spectra were processed to analyze IR spectra obtained by the FTIR *in situ* analysis.

The epoxy photopolymerization was monitored using the epoxy CH stretching band at 3005 cm^{-1} and the epoxy ring vibration band at 790 cm^{-1}. The effect of postcure was also confirmed. The acrylic photopolymerization was monitored using the C=C stretching band at 1637 cm^{-1}. This polymerization was almost completed during 20 s UV exposure.

Then photopolymerization of an epoxy–acrylic simultaneous IPN was investigated based on the interpretation of each epoxy and acrylic polymerization. The acrylate reacts much faster than the epoxide in the IPN. The epoxy conversion was less than 60% when the acrylic polymerization was almost completed.

The FTIR *in situ* analysis developed here was found to be a useful and convenient technique that is complementary to the modified DSC technique in the study of photopolymerization.

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