



# CURE MONITORING OF UV POLYMERS BY RAMAN SPECTROSCOPY

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## *Abstract*

In the present study, cure monitoring by Raman Spectroscopy was conducted for ultraviolet(UV)-curable polymers under UV radiation. An UV lamp and an UV LED were used in the experiments as the radiation apparatus. Raman spectra of the polymers were measured at the radiation power of 64.3 mJ/cm<sup>2</sup> for the UV LED and at three kinds of the power for the UV lamp. In some experiments, Raman spectra were measured controlling the UV radiation and the temperature of the polymers. From the obtained results, it was found that DOC (Degree Of Cure) was decided by the total radiation energy provided to the polymers. In addition, it was shown that the total UV doses needed for complete curing by using the two kinds of UV radiation apparatus were different. It was also found that the temperature of the polymer affected the curing behavior even in the consolidation under the UV radiation.

## **1 Introduction**

FRP consisting of ultraviolet(UV)-curable polymers and reinforcing fibers collects much attention from the viewpoint of energy saving in its molding[1,2]. In addition, it can be molded with less residual stresses induced by heat shrinkage during molding because the UV polymers are cured without heating. Molding under the optimum condition is very important for the FRP consisting of the UV polymers as well as for that of the thermoset polymers. But its quantitative determination method has not been established. The monitoring method with sensors detecting curing states of the matrix resins is one of the most promising techniques for determination of the optimum condition. Degree of cure (DOC) is used as the index of curing states in the matrix polymers. Several methods have been proposed to measure the DOC. Among them, Raman spectroscopy has been

reported as one of the most promising methods[3,4]. It can measure transition of molecule structures due to development of curing, so obtained DOC should have higher validity than other monitoring methods. An Automated Fiber Placement (AFP) molding method is suitable for the UV-curing FRP because its consolidation needs no heating. The common UV radiation apparatus is an UV lamp. But it is too large and heavy in order to be attached to AFP molding machine. Recently, an UV LED has been developed which is enough to be small and light for the AFP machine. It can, therefore, realize the molding of the UV-curing FRP by the AFP machine. UV lights of the UV lamp and the LED have different wavelengths. It is important to investigate the curing behavior of the UV polymers using the UV lamp and the LED as the radiation apparatus.

In the present study, a monitoring technique of the DOC by the Raman spectroscopy has been investigated for UV polymers as the first step to that of UV-curing FRP. The spectra of the Raman scattering were obtained for the polymers curing under the radiation of the UV lights. In the monitoring experiments, the UV lamp and the LED were used for the consolidation. A Raman peak associated with the carbon-carbon double bonds was used to determine the DOC. The DOC curves were obtained and the relation between the cure development and the UV radiation was examined. The cure development behaviors were also measured under the radiation by the UV lamp and the LED.

## **2 Monitoring for Epoxy Resins**

The DOC of epoxy resins was measured with the monitoring method by the Raman spectroscopy and other commonly used methods to make clear difference between their evaluation characteristics of the cure. The adopted conventional methods were based on the thermochemical properties measured by DSC (Differential Scanning Calorimeter) and the dielectric properties by the dielectric sensor[5,6].

## 2.1 Cure Monitoring Methods

### 2.1.1 Raman Spectroscopy

When a monochromatic light is incident, light scattering can be observed. While most of the scattered light has the same frequency as the incident light, some has the shifted frequency. The latter effect is called Raman scattering. The frequency shift of Raman scattering is strongly affected by the vibration of molecules in the materials. Therefore, the spectrum of frequency shift of the scattered light (Raman spectrum) provides us important information on the molecular composition of the materials. During the polymerization of epoxy resin, an epoxy ring is opened by the reaction with curing agent and disappears at the end of the cure process. Therefore, it can be considered that the Raman band of an epoxy ring indicates the degree of the cure process. The experiment set-up for acquisition of Raman spectra is shown in Fig. 1. In this experiment, the epoxy resins were in a laboratory dish and a probe of the Raman measurement equipment was used to deliver light to the resins and retrieve the Raman scattering. The example of the obtained Raman spectrum before the cure process is shown in Fig. 2. The strong Raman peak of an epoxy ring can be observed at  $1250\text{ cm}^{-1}$ . Fig. 3 shows an enlarged view of the Raman spectrum near  $1250\text{ cm}^{-1}$  at the start and end of the cure process. It was found that the peak intensity decreased at the end of the cure process. Then, the DOC  $\alpha_R$  could be defined as

$$\alpha_R = \frac{R_t - R_0}{R_e - R_0} \quad (1)$$

where  $R_t$  is the peak intensity at time  $t$  and  $R_0$  and  $R_e$  are the beginning and the ending values.

### 2.1.2 Thermo-chemical Method

The DSC is the industry-standard device to measure heat flow  $\dot{q}$  generated by the cure reaction of resins. Using the heat flow data, the DOC is defined simply by dividing the reaction heat at time  $t$  by the total heat. The DOC at temperature  $T$  under the condition of constant heating rate can be written as

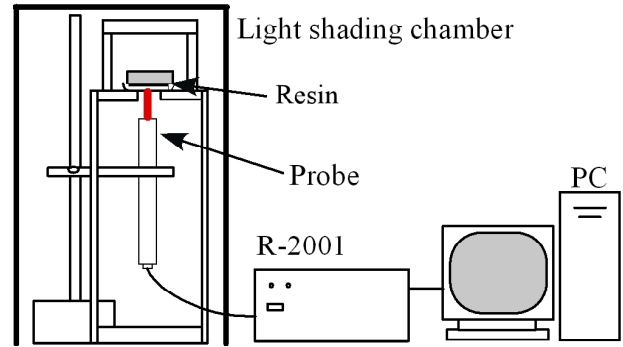


Fig.1 Experimental set-up for measurement of Raman shift spectra during cure of the epoxy resins.

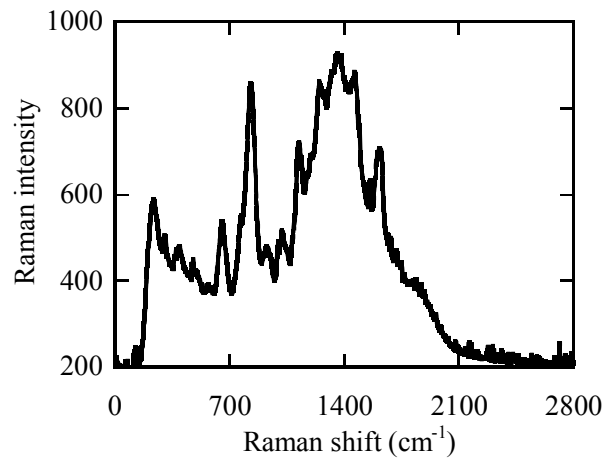


Fig.2 A measured Raman shift spectrum of the epoxy resin.

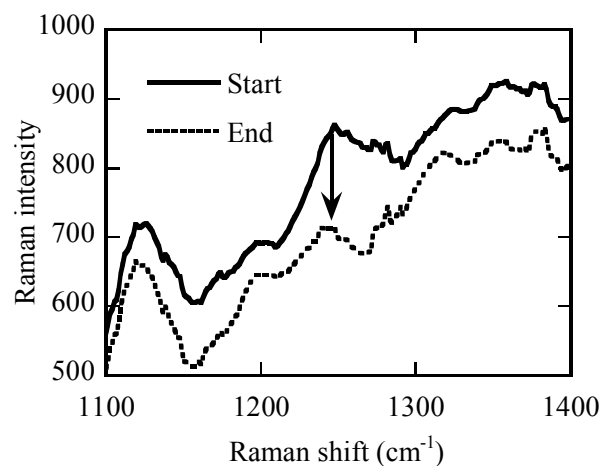


Fig.3 Enlarged view of Fig.2 at the range of  $1250\text{ cm}^{-1}$  Raman shift.

$$\alpha_{DOC}(t) = \frac{\int_{t_0}^t \dot{q} dt}{\int_{t_0}^{t_e} \dot{q} dt} = \frac{\int_{T_0}^T \dot{q} dT}{\int_{T_0}^{T_e} \dot{q} dT} \quad (2)$$

where  $t_0$  and  $t_e$  are the start and end times and  $T_0$  and  $T_e$  are the start and end temperatures during the cure process. The rate of DOC can also be obtained as

$$\frac{d\alpha_{DOC}}{dt} = \frac{\dot{q}}{\int_{t_0}^{t_e} \dot{q} dt} = \frac{dT}{dt} \frac{\dot{q}}{\int_{T_0}^{T_e} \dot{q} dT} \quad (3)$$

Thus, we can obtain relationships among the DOC, the rate of DOC and the temperature by measuring the DOC curves at various constant-heating rates. The model of the relationship has been proposed as

$$\frac{d\alpha_{DOC}}{dt} = (k_1 + k_2 \alpha_t^m)(1 - \alpha_t)^m \quad (4)$$

$$k_1 = A_1 \exp\left(-\frac{E_1}{RT}\right), k_2 = A_2 \exp\left(-\frac{E_2}{RT}\right) \quad (5)$$

where  $R$  is gas constant and  $n, m, A, E$  are constant parameters.

In order to determine the parameters, the heat flows during cure of the epoxy were measured at the five different constant heating rates (2.5, 5, 10, 15, 20 K/min.) with a DSC (Pyris 1 DSC, Perkin Elmer Inc.). From the experiments, relationships between the DOC, curing rate and temperature were obtained. Fig. 4 shows relationships between the curing rate and temperature of the epoxy resins. From the measurement results, the constant parameters were determined as  $m=0.166709$ ,  $n=1.75949$ ,  $A_1=226417$ ,  $A_2=18418.4$ ,  $E_1=74823.1$ ,  $E_2=46784.0$  by a nonlinear fitting method. The relationships between thermo-chemical DOC calculated from the eqs (4) and (5) and temperature were shown in Fig 5.

### 2.1.3 Dielectric Method

The measurement of the dielectric properties of resins is another commonly used method of cure monitoring. A dielectrometer (Eumetric 100A, Micromet instruments, Inc.) was employed to measure the dielectric properties of the epoxy resins. In this study, log ion viscosity, which is a logarithmic reciprocal value of an imaginary part of

a complex dielectric constant, was used to evaluate the DOC because its value is the most sensitive to proceeding of the cure reaction. A dielectric sensor and a thermocouple were embedded into the epoxy resin in a plat-plate mold.

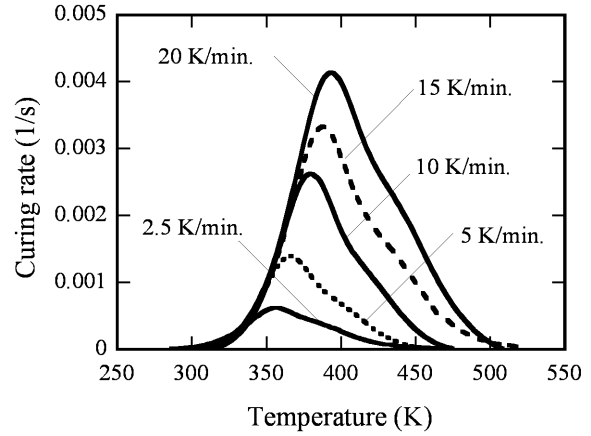


Fig.4 Curing rate obtained by DSC at various constant heating rates.

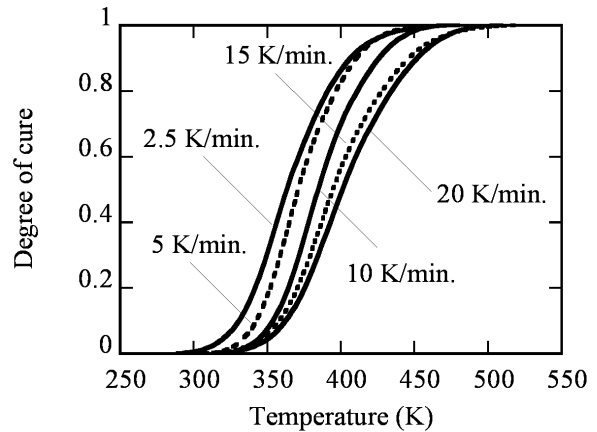


Fig.5 Relationships between DOC and temperature at various constant heating rates.

Fig. 6 shows relationships between the log ion viscosity, temperature and time during cure. From the figure, it was found that the log ion viscosity decreased in the first 25 minutes due to decrease of the viscosity and then increased monotonically until the value converged at the end of cure. The monotonically increasing part was used to determine the dielectric DOC as follows;

$$\alpha_{LIV} = (I_t - I_{\min}) / (I_{\max} - I_{\min}) \quad (6)$$

where  $I_t$  is the log ion viscosity at time  $t$  and  $I_{min}$  and  $I_{max}$  are the minimum and the maximum values.

### 2.2 Comparison between DOC by Three Monitoring Methods

Fig. 7 shows the DOC curves of the epoxy resins obtained with the three kinds of the DOC evaluation methods. The curve by the dielectric properties has the lower value in the initial curing stage than that by the DSC because the ion viscosity shows the lowest value at the initial curing. The DOC value by the dielectric properties earliest reaches the value of 1.0 designating the complete cure. On the other hand, the DOC curve by the Raman spectroscopy increases slower than that by the DSC and then shows almost the same value at about 120-minute curing time. These DOC curves have a little different increasing rate but they show the same value beyond 120-minute curing time. They were derived from the different properties of the epoxy resins so it is reasonable for them not to show the same DOC curve. From the above-mentioned results, it can be said that the DOC evaluation by the Raman spectroscopy can be used for evaluation of the cure development as well as other commonly used evaluation methods by the DSC and the dielectric properties.

### 3. Cure Monitoring for UV Polymers

#### 3.1 Experiment

The UV polymers used in the present study were provided by Mitsubishi Rayon Co.Ltd.. An experimental set-up used for the Raman spectrum measurement is shown in Fig. 8. As shown in the figure, the polymers were placed into the petri dish and a monochromatic laser light from the probe was radiated to their surface. The Raman shift spectra of the polymers were measured using a Raman spectroscope (R-2001 Raman System, Ocean Optics, Inc.). After applying radiation for several seconds, the UV light was cut off using a shutter and then Raman spectrum was obtained. This procedure was repeated until the polymer cured completely. In the experiments, the UV lamp and the LED were used as radiation apparatus. The measurements with the UV lamp were performed at three intensity levels of the UV light radiation of 3.4, 4.5 and 11.4 mW/cm<sup>2</sup>. The radiation intensity of the UV LED was set at 64.3 mW/cm<sup>2</sup>.

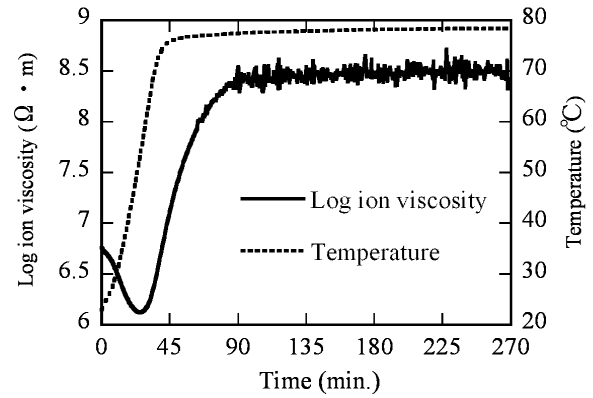


Fig.6 Relationships between log ion viscosity, temperature and time during cure.

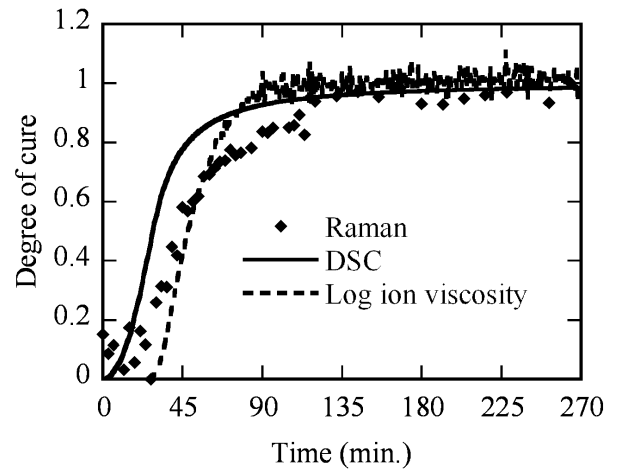


Fig.7 Three kinds of DOC obtained by Raman spectroscopy, thermo-chemical and dielectric methods for the epoxy resins.

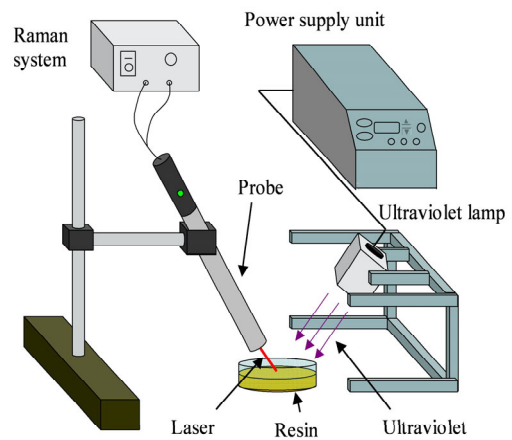


Fig.8 Experimental set-up for measurement of Raman shift spectra during cure of the UV polymers.

### 3.2 Cure Evaluation Method

The evaluation of the UV polymers was performed in the same manner as that of the epoxies. But the different Raman spectrum peak was used to determine the DOC of the UV polymers because they include methacrylate and acrylate groups. Radical groups were generated by the radiation of UV light during the cure reaction. Then carbon-carbon double bonds (C=C) react with the radical and disappear during the radical polymeric reaction. A measured Raman shift spectrum is shown in Fig. 9. The Raman shift peak concerned with vibration of C=C is found at  $1627\text{ cm}^{-1}$  as shown in the figure. In the experimental approaches, we had to pay attention to Rayleigh scattering because the variation of the scattering was very large with increase of the DOC. The Rayleigh scattering was subtracted from the measured Raman spectrum. Since the C=C peak was superposed by one of the main chain peaks ( $1600\text{ cm}^{-1}$ ), the peak separation method was employed to obtain the C=C peak. The concentration of the C=C group was decided from the normalized C=C peak by one of the main chain peaks ( $820\text{ cm}^{-1}$ ). The DOC of the UV polymer was defined by the concentration.

### 3.3 Results and Discussions

#### 3.3.1 DOC under Radiation by UV Lamp

Fig. 10 shows the obtained DOC curves under the three kinds of radiation intensity of the UV light. The curves increase rapidly in a few hundred seconds and then their increasing rates gradually decrease. In the end, they converge to the value of 1.0 designating the complete cure. In these curves, the larger the UV radiation intensity is, the faster the cure development rates become. The relations between the DOC and the integrated radiation dose are shown in Fig. 11. In this figure, the curve of  $11.4\text{ mW/cm}^2$  shows the lower value than the other two curves in  $2,000\text{--}6,000\text{ mJ/cm}^2$ . Excluding this discrepancy, these three DOC curves overlap each other. From these results, it could be anticipated that the DOC of the UV polymers could be controlled by the total radiation energy.

#### 3.3.2 DOC under Radiation by UV LED

The DOC of the polymers cured by the UV LED was obtained in the same way of the measurement under the radiation by the UV lamp. The relationship between the measured DOC and the

integrated radiation dose is shown in Fig. 12. The gradient of the curve is steep below the UV dose of  $10\text{ J/cm}^2$  and then it changes gentle. The curve converges to the complete cure of DOC 1.0 above the UV dose of  $100\text{ J/cm}^2$ . This DOC changing pattern is similar to that of the UV lamp.

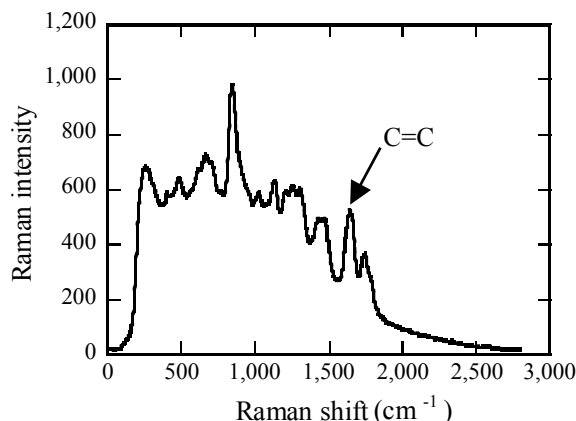


Fig.9 A measured Raman shift spectrum of UV polymers.

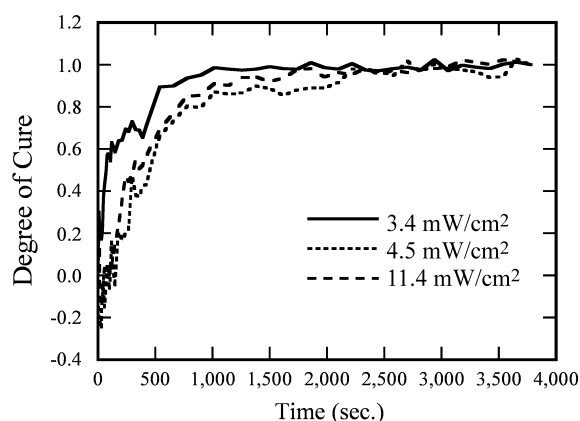


Fig.10 Relations between DOC and curing time for the UV polymers.

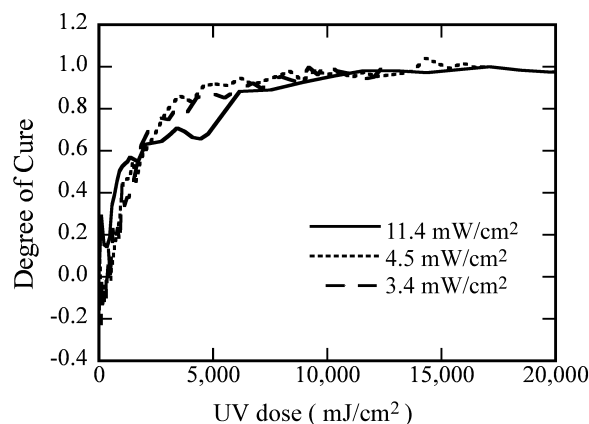


Fig.11 Relations between DOC and UV dose for the UV polymers.

Comparison of the DOC curves in Figs.11 and 12 shows a significant difference of the UV radiation dose needed for the complete curing of the polymers using the UV lamp and the LED. In the Fig.11, the DOC reaches to 0.6 at the UV dose of 1.0 J/cm<sup>2</sup>. On the other hand, the radiation dose for the UV LED is 10 J/cm<sup>2</sup> as shown in the Fig.12. The doses for the UV polymer cured by the UV lamp and the LED differ by an order of magnitude. A possible cause is that the UV lamp radiates lights containing many wavelengths, on the other hand the UV light contains the narrow range of the wavelength. In relation to it, it is possible that the temperature of the polymers cured by the UV lamp, whose lights include infrared rays, is higher than that by the UV LED. In order to make clear the cause of the difference in the radiation dose for complete cure, the temperature effects of the polymer was examined. The results are shown in the following section.

### 3.3.3 Effects of Temperature on DOC

In the previous experiments in this study, the time of UV radiation onto the polymers was different in each curing stage. The radiation time was short in the early stage to collect Raman spectrum in short intervals and it was a little longer in the last stage. In these measurements, the effects of the radiation time on the temperature of the curing polymer had not been taken into account. In the following experiment to cure the polymer completely, the temperature of the polymers was examined under the continuous UV radiation. The pattern of the radiation exposure time was the combination of 300 seconds of radiation and nonradiation. The obtained temperature results are shown in Fig.13. During the first 300 minutes of the radiation, the temperature increases sharply to 59 C° at 90 seconds and then decreases to 50 C°. After stopping of the radiation, the temperature falls to 30 C°. After that, the temperature repeated the same changing pattern between 30 C° and 45 C°. These temperature-changing patterns in which the chemical reaction heat was not observed seems to show that the cross-linking reaction did not occur after 600 seconds. The DOC curve shown in Fig.12 designates 0.5 at 5.8 J/cm<sup>2</sup> that is the radiation dose at 300 seconds in the Fig.13. This result shows that the radiation time and the temperature can affect the cure progress significantly.

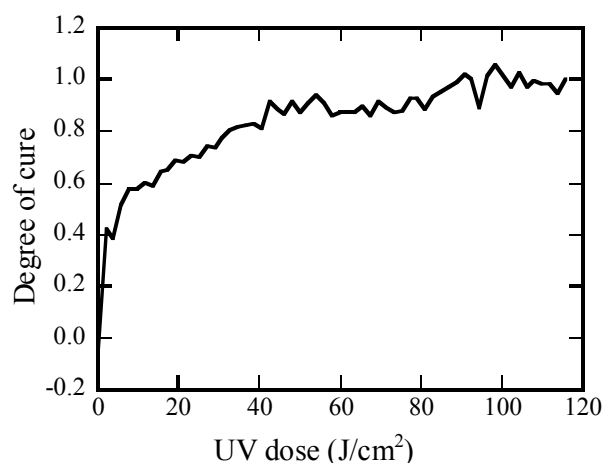


Fig.12 Relation between DOC and UV dose for the polymers cured by the UV LED.

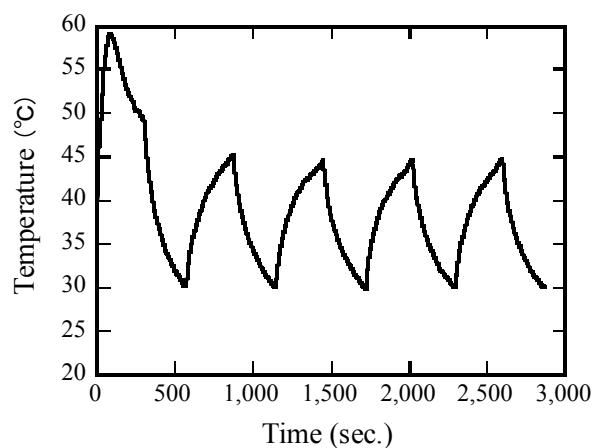


Fig.13 Temperature of the polymers under 300 second UV radiation by the UV LED.

### 3.3.4 DOC without Temperature Effects

The DOC monitoring experiments were performed, taking the temperature effects into account. First, the DOC progress was measured at 40 C° during 24 hours for the UV polymers held in the constant temperature furnace. The results showed that the cross-linking reaction did not proceed at 40 C°. Secondly, the Raman spectrum measurements were performed during cure in the condition of the temperature which did not exceed 40 C° under the UV radiation. The temperature of the curing polymer was measured by the thermocouple embedded in the polymer. Fig.14 shows the results during cure and assures that the temperature does not affect cure behaviors of the polymers under the UV radiation. The DOC obtained under the temperature condition in the figure is shown in Fig.15. It includes the result in

Fig12 designated as the broken line. These two DOC curves show almost the same curing progress. From these results, it was found that both DOC curves in the figure were obtained without the effects of the temperature on the cure progress.

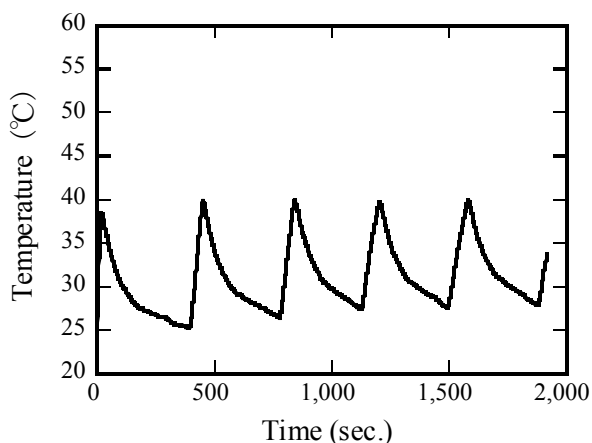


Fig.14 Temperature of the polymers under UV radiation by the UV LED in the experiments to obtain the cure development without the temperature effects.

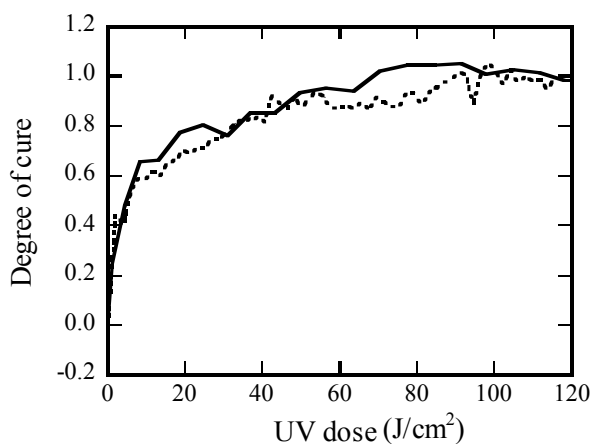


Fig.15 Relation between DOC and UV dose for the polymers cured by the UV LED, obtained without effects of the polymer temperature (shown with the solid line). The dashed line shows the relation in Fig.12.

#### 4 Conclusions

In the present study, a monitoring technique of the DOC by Raman spectroscopy has been investigated for the UV polymers. The DOC was evaluated at three intensity levels of the UV lights by using the UV lamp. The monitoring experiments were also performed by using the UV

LED to cure the UV polymers. The obtained DOC curves were compared and the relations between the DOC and the total UV dose were then examined. From the results, it was ascertained that the larger the UV radiation is, the faster the cure development speed is. In addition, it was found that the three kinds of DOC-UV dose curves overlapped each other. It could therefore be anticipated that the DOC of UV polymers could be controlled by the total radiation energy. Comparison between results using the UV lamp and the LED revealed that the doses for the UV polymer curing under the radiation by them could differ by an order of magnitude. It was also made sure that the temperature of the polymer affected the curing behavior even in the consolidation under the UV radiation.

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