CURE MONITORING OF UV CHAIN CURING POLYMER BY FIBER OPTIC MEASUREMENT OF REFRACTIVE INDEX

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Abstract

Chain curing polymers (CCP) cured with ultraviolet rays have many advantages of the remarkable energy-saving feature over thermosetting polymers. In order to analyze the chain cure process, the fast and local monitoring method of the cure reaction of CCP has been desired due to the rapid and local reaction. In the present study, the refractive index measurement using optical fibers embedded in the polymers has been proposed for the cure monitoring of CCP. Three optical fibers were embedded in the polymer to investigate the behavior of the cure reaction at the different places. From the results, it was appeared that the cure reaction proceeded rapidly in a few second and the DOC was different in space. Therefore, it can be said that the refractive index measurements by embedded optical fibers were useful to evaluate the curing behavior of CCP at real time.

1 Introduction

From the viewpoint of energy saving, UV (ultraviolet) cured resin, which needs lower curing energy and shorter cycle time comparing to traditional thermosetting resin, has been developed as matrix of fiber reinforced polymers (FRP). However, there is a problem that UV light cannot propagate through thick and opaque materials such as carbon fiber/filler reinforced FRP. In order to solve the problem, UV chain curing polymers (CCP) have been developed [1]. Figure 1 illustrates initiation and proceeding of the cure reaction of CCP.

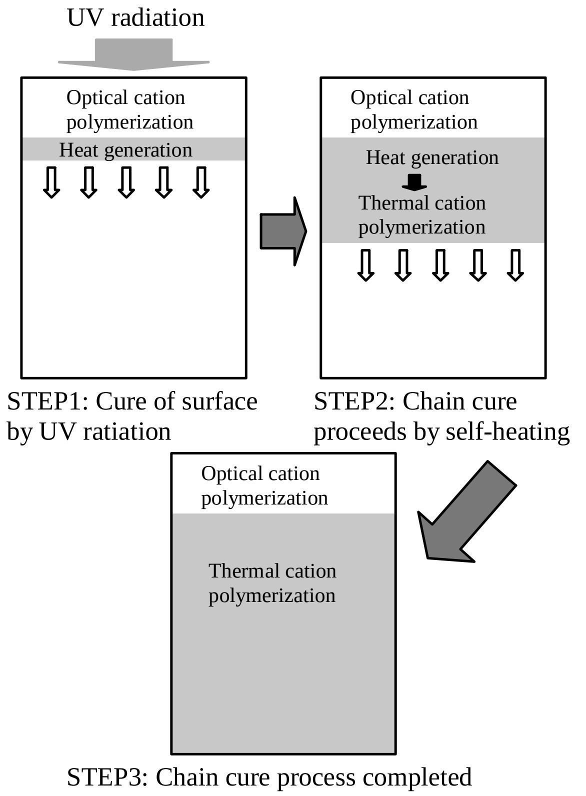

Fig.1 Chain cure reaction of CCP by UV radiation.

When a UV light radiates the surface of CCP, optical cation is generated and optical polymerization starts locally near the surface. Since the local cure reaction generates huge heat, temperature rises rapidly and thermal cation is generated in the neighborhood of the reacting place. Then, the thermal polymerization proceeds from the revealed surface to the depth without additional heating. This curing method of CCP can be applied to CFRP because the transparency of the materials to UV light does not affect the chain cure reaction.

Furthermore, the CCP can be used for closed moldings of FRP because only the partial revealed surface was necessary to start the reaction.

Although the CCP has high potential of low energy and low cost molding of FRP, the chain cure reaction of CCP has not been investigated well. This reason is that the cure reaction occurs very locally and progresses very rapidly. Therefore, the evaluation methods of the curing behavior at local and at high speed have been desired.

The common method to evaluate the degree of cure (DOC) of thermosetting resin is the thermal analysis by a differential scanning calorimeter (DSC). However, this method is not available to monitor the chain cure reaction of CCP since the method need uniform cure reaction in materials. In order to monitor the chain cure reaction, embeddable sensors for cure monitoring are essential. Another common cure monitoring method is a dielectric measurement by a dielectrometer. The embeddable dielectric sensors can be used for local cure monitoring. However, the general dielectric sensors have sensing length of several millimeters which is larger than the required sensing size to monitor the chain cure reaction. In addition, the former two methods have slow measurement speeds under 10 Hz typically. In order to evaluate the cure process of CCP, it is thought to be necessary that the monitoring sensor has small sensing region under one millimeter and high speed from hundred to thousand Hz.

In order to monitor the chain cure reaction, we have employed the refractive index measurement by embedded optical fibers [2-4]. Since the frequency of the light over hundred THz, the measurement of light power over kHz can be achieved easily. The sensing region, which is almost the same as the core diameter of the optical fibers, is about ten micron meters for single-mode fibers. Furthermore, embedded optical fibers can lead light easily in the resin. Thus, we have believed that the refractive index measurement by optical fibers is the only one to monitor the cure reaction of CCP.

At first, we have developed the cure monitoring method by embedding single-mode optical fibers into the thermosetting epoxy resin. In the experiments, the refractive index of the resin was measured and the idea to convert the measured value to the degree of cure was proposed. Then, the chain cure reactions of CCP at three different places were monitored simultaneously by this method using embedded three optical fibers. From the experimental results, the behavior of the chain cure reaction was discussed.

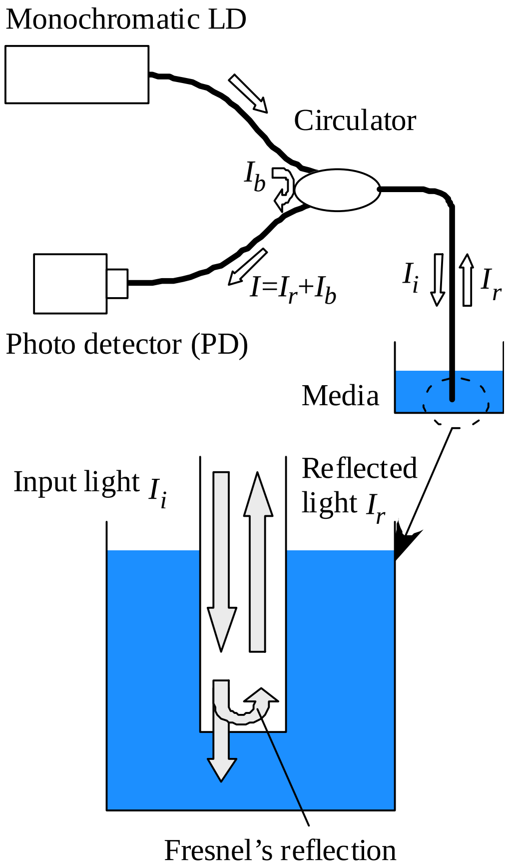

Fig.2 Optical system and Fresnel's reflection at the end of an optical fiber in media.

2 Evaluation of degree of cure (DOC) of resin during cure process

2.1 Absolute measurement of refractive index by embedded single-mode optical fibers

Figure 2 illustrates the optical system used to measure the optical power reflected at the flat end of the fiber. The optical light source was a laser diode (LD), whose wavelength was 1310 nm in the present study. The light propagates in an optical fiber through an optical circulator and reaches the end of the fiber. Fresnel's reflection occurs at the boundary between the end of the fiber and media as shown in Fig. 2. Since single-mode optical fibers and a monotonic light were used for the measurement, the reflection rate of light power R can be written as

$$R = \frac{I_r}{I_i} = \frac{\left(n_g - n\right)^2}{\left(n_g + n\right)^2}, \qquad (1)$$

where I_i is a power of the incident light to the end, I_r is a power of the reflected light from the end, n_g is a refractive index of the optical fiber (silica glass in the present study), and n is a refractive index of media. The backward light power I can be measured by a photo detector (PD) while the measured light power I includes a power of the backward lights I_b on the way to the end such as optical couplers, that is, $I = I_r + I_b$. It is noted that the only I is measurable by this system.

We measured the reflected power from the embedded optical fibers in epoxy resin during cure process. Bisphenol-A epoxy resin (Epikote 801N and Epicure 3080, Japan epoxy resin Co. Ltd.) was used as monitored media. The mixture ratio was 100:40 and curing temperature was 60 ºC after heating for 30 minutes. In the experiment, the flat end of the fiber was made by a fiber cutter and the degree of flatness was optically confirmed. Figure 3 illustrates the experimental setup. The silicon rectangular vessel of 2×2×3.5 cm was filled with epoxy resin and set in a small furnace. The temperature of epoxy was controlled by a thermo controller with the material temperature with the embedded thermocouples neighboring the tips of the optical fibers. Before embedding the optical fibers, optical powers reflected from the air were measured. Two optical fibers were used to confirm stability of the measurement.

Figure 4 shows the relationships between the reflected optical outputs from the two embedded optical fibers, temperature and time for the epoxy resin during cure process. From the figure, it appeared that the behaviors of the outputs of the two optical fibers were similar to each other while they have different absolute values from each other. The poor reproducibility of the absolute values of the reflected optical power is resulted from the negligible effects of I_b and I_i. Therefore, we have to eliminate the effects in order to obtain absolute values of the reflected power.

Because I_i does not have reproducibility and could not be measured, we have to measure the reference output I_{ref} corresponding to the known refractive index n_{ref}. When applying this method to the liquid moldings such as RTM (resin transfer molding), the air (n_{ref} =1) is the best materials for the reference due to the simple measurement. For the reference materials, the equation (1) becomes

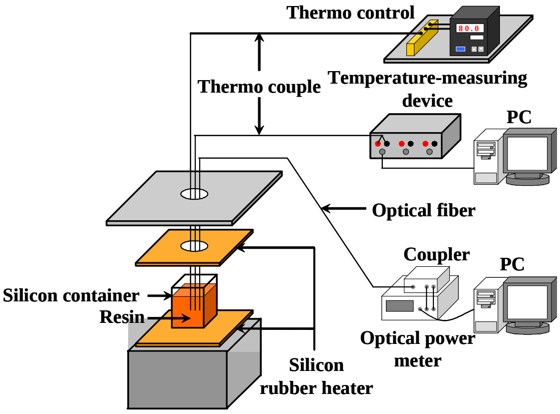

Fig.3 Experimental setup for measuring refractive index of epoxy resin during cure process.

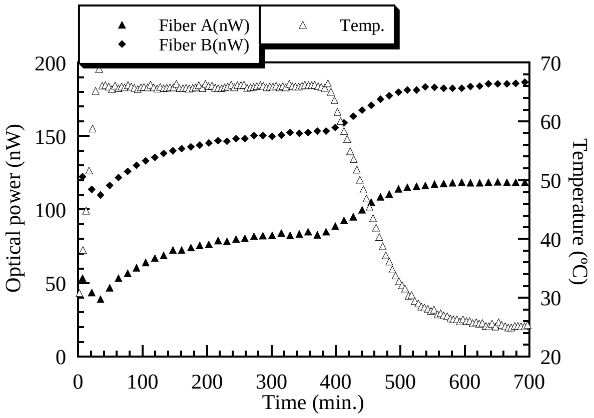

Fig.4 Relationships between the reflected optical outputs from optical fibers, temperature and time for epoxy resin during cure process.

$$\frac{I_{ref} - I_b}{I_i} = \frac{\left(n_g - n_{ref}\right)^2}{\left(n_g + n_{ref}\right)^2} \tag{2}$$

From the eqs. (1) and (2), the following relationship can be derived.

$$R = \frac{I - I_b}{I_{ref} - I_b} = \frac{\left(n_g - n\right)^2 \left(n_g + n_{ref}\right)^2}{\left(n_g + n\right)^2 \left(n_g - n_{ref}\right)^2} \tag{3}$$

Here, we have paid attention to the variation ΔI of I from the arbitrary standard output I_s. It is supposed that the standard refractive index ns of resin corresponding to I_s is already known. Then, it can be represented that

$$I = \Delta I + I_s \text{ when } n = \Delta n + n_s \tag{4}$$

where, Δn is the variation of refractive index from the standard refractive index. By substituting the eq.

(4) into the eq. (3) and solving the equation for *Δn*, the following relationships were obtained.

$$\Delta n = \frac{b_1\left(a_1^2 b_2\left(b_1+b_2\right)+a_2^2 b_1^2 \nu \pm a_1\left(b_1+b_2\right)\sqrt{a_1^2 b_2^2+a_2^2 b_1^2 \nu}\right)}{a_1^2\left(b_1^2-b_2^2\right)-a_2^2 b_1^2 \nu} \tag{5}$$

$$n_g+n_r=a_1,\ n_g-n_r=a_2, \tag{6}$$
$$n_g+n_s=b_1,\ n_g-n_s=b_2,\ \Delta I \big/ \left(I_{ref}-I_b\right)=\nu$$

When the reference material is the air, $\nu=\Delta I/I_{ref}$ because $I_{ref} >> I_b$. In this case, all necessary parameters to calculate the changes in refractive index *Δn* are known values, that is, real-time monitoring of refractive index can be accomplished easily.

In the present paper, the standard refractive index ns of uncured resin at room temperature (T_s = 25 °C) was 1.503. The refractive index of a silica optical fiber at Ts was 1.447 which was calculated by the Sellmeier's equation. The refractive index variation *Δn* was calculated by the equation (5) from the measured optical outputs. The Relationships between the refractive index variation, temperature and time for the epoxy during cure was shown in Fig. 5. At the heating stage, the refractive index becomes smaller when temperature increasing because the temperature dependency was negative and the changes of the refractive index by polymerization was smaller than that by increase of temperature. The behavior of the refractive index changed to monotonic increasing when the temperature became constant and converged to the constant value after about 400 minutes passed. Since the two curves from two sensors were almost the same as each other, it was found that the stability of this measurement method was very good.

2.2 Calculation of DOC

In this section, we have attempted to calculate DOC from the refractive index of the resin by eliminating the effect of temperature. The relationships between the refractive index variation and temperature for the epoxy before and after cure were shown in Fig.6 with linear regression curves. From the figure, it was confirmed that the refractive index of the epoxy resin used in this experiments varied with temperature linearly before and after cure. Therefore, the refractive index of uncured resin n_0 and that of cured resin n_1 at temperature T can be expressed as

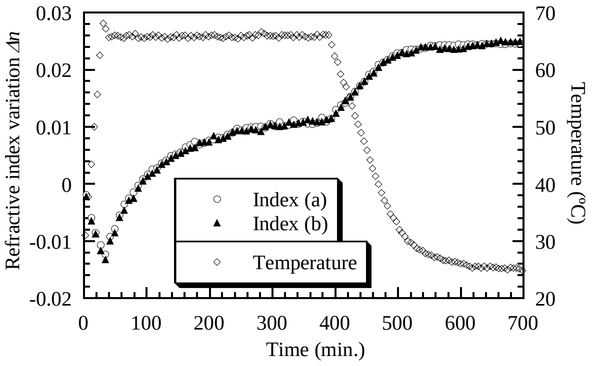

Fig.5 Relationships between the refractive index variation, temperature and time for bisphenol-A epoxy during cure.

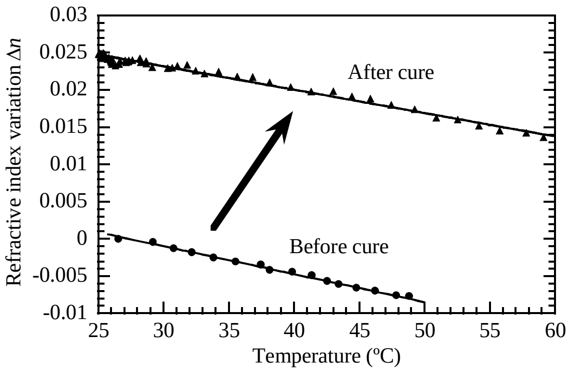

Fig.6 Relationships between the refractive index difference and temperature for bisphenol-A epoxy before and after cure.

$$n_0 = n_0\big|_{T=T_s} + \frac{dn_0}{dT}\left(T-T_s\right) \tag{7}$$
$$n_1 = n_1\big|_{T=T_e} + \frac{dn_1}{dT}\left(T_e-T\right)$$

where T_s is the standard temperature, T_e is the temperature at the end of the cure process and dn_0/dT and dn_1/dT are the temperature dependences of the refractive indices of the uncured and cured resins. Here, we defined the DOC α as a transition parameter from uncured resin to cure resin as follows:

$$n_\alpha = n_0\left(1-\alpha\right)+n_1\alpha \tag{8}$$

where n_α is the refractive index of resin of the DOC α. From the equations (7) and (8), the DOC can be calculated by

$$\alpha = \frac{\Delta n - \dfrac{dn_0}{dT}\left(T - T_0\right)}{\Delta n_1 + \dfrac{dn_1}{dT}\left(T - T_e\right) - \dfrac{dn_0}{dT}\left(T - T_0\right)} \qquad (9)$$

where

$$n_s = n_0\big|_{T=T_s},\ \Delta n_1 = n_1\big|_{T=T_e} - n_s \qquad (10)$$

Since Δn_1, dn_0/dT and dn_1/dT are specific properties of the resin, we can know these values before the measurement.

For the epoxy resin, Δn_1, dn_0/dT and dn_1/dT were 0.0137, -0.00037524 and -0.0003142, respectively. The DOC curves were calculated by the equation (9). Figure 7 shows the relationships between the DOC measured by the two sensors, temperature and time for the epoxy during cure. From the figure, it was shown that the temperature effect could be removed from the DOC curves successfully. The DOC grows gradually at the initial phase, increases rapidly at the middle phase and then converges gradually at the final phase. This behavior agreed qualitatively with behavior of a typical DOC curve obtained from thermal analysis. Since the DOC curves measured by two optical fibers agreed with each other, it appeared that the assumption that the parameters of Δn_1, dn_0/dT and dn_1/dT were specific properties of the resin was valid. Consequently, the DOC can be obtained from the variation of the refractive index Δn at real time.

3 Monitoring of cure process of chain cure polymer

3.1 Materials and experimental setup

In this section, the chain cure process of CCP was monitored by three embedded optical fibers. The CCP manufactured by Mitsubishi Heavy Industry Co. Ltd. was used for the present experiment. The schematic view of the mold was illustrated in Fig. 8. The mold was constructed of two duralumin plates and silicon spacers of 2 mm thickness. At first, the optical fibers and thermo couples were installed through the silicon side spacers. In order to place the sensors at the middle of thickness, the sensor part at a few mm from the tips were fixed by small silicon spacers of 1mm thickness.

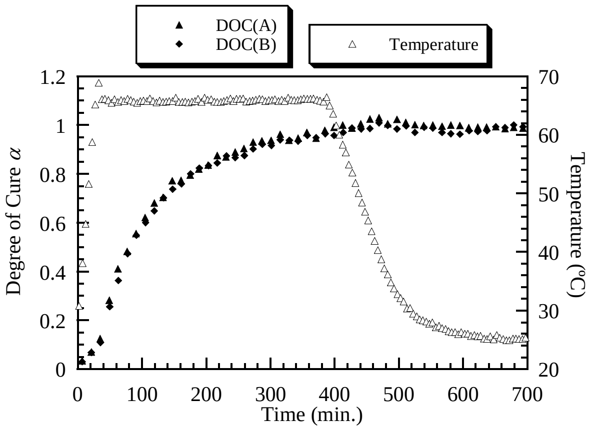

Fig.7 Relationships between the degree of cure measured by the two sensors, temperature and time for epoxy resin during cure process.

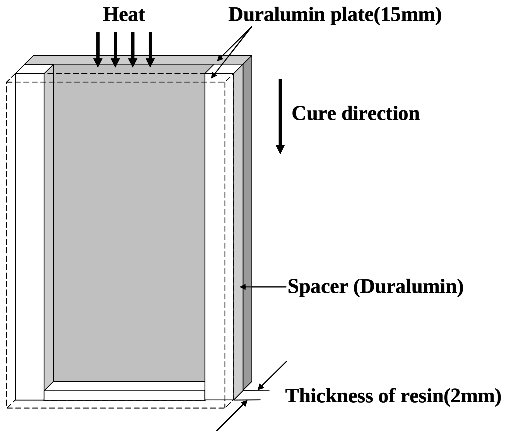

Fig.8 Schematics of the mold to manufacture CCP.

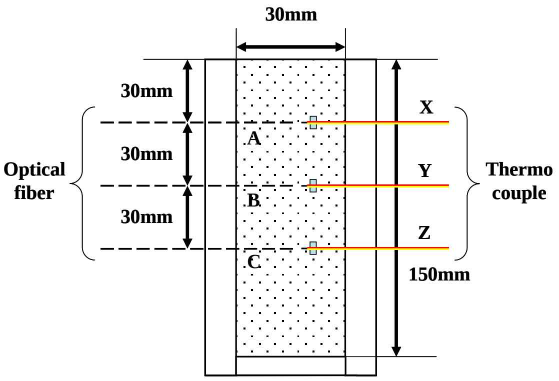

Fig. 9 Placements of the optical fibers and thermocouples in the mold.

The three optical fibers A, B and C were placed with intervals of 30 mm through the silicon spacer at one side as shown in Fig. 9. These sensors were also set at the middle in the thickness direction. Three thin thermocouples X, Y and Z were embedded very near to the optical fibers from another side. The diameters of the optical fibers and the thermocouples were 0.125 mm and 0.08 mm, respectively.

After installing the optical fibers, optical powers of Fresnel's reflection between glass and air were measured as the reference optical powers. After the reference measurement, the mold filled with the CCP. In this experiment, a peace of heated duralumin thin plate was used as a starter instead of UV radiation because the chain cure process can also start by local heating. Three optical powers from the three optical fibers were measured simultaneously by a multi-channel optical power meter (MT9812B, Anritsu Co. Ltd.). The monitoring of the optical powers was performed at one hundred Hz. After the chain cure reaction finished, the post-cure was conducted by heating up to 120 ºC.

3.2 Experimental results and discussions

At first, we measured relationships between the temperature and optical outputs of the optical fiber embedded in the CCP without hardner. The optical outputs were plotted against the temperature in Fig.10. It was appeared that the results showed the quadratic relationship which is predicted from the equation (5). The optical output became the minimum value at 120 ºC due to that $n = n_g$. The relationships between Δn obtained using the equation (5) and temperature were shown in Fig. 11. here, $n_s = n_g$ at T_s=120 ºC. From the figure it appeared that the refractive index of the CCP varies linearly with temperature as expected in the equations (7).

Next, we conducted the monitoring of chain cure process of the CCP. Figure 12 shows time histories of the refractive index variations (A, B and C) obtained from the optical outputs and temperatures (X, Y and Z) from thermocouples during chain cure process. In the calculation, only positive value of Δn shown in the equation (5) was used. From the results of temperatures, it was found that the CCP heated up explosively over 250 ºC within one second. After the temperature reached the maximum, it decreased gradually in about 30 seconds. The proceeding of the front of the chain cure reaction could be observed optically due to the change of color. The proceeding speed of the front was 2.5 mm/s. This fact means that the local gradient of temperature at the neighborhood of the front is very large and consequently the very local measurement is essential to monitor the chain cure reaction.

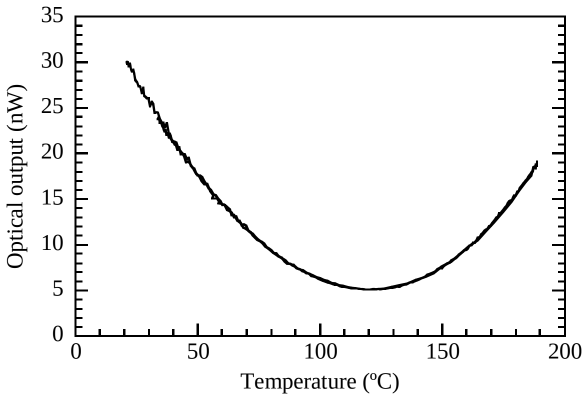

Fig.10 Relationships between optical outputs reflected from the CCP without hardner and temperature.

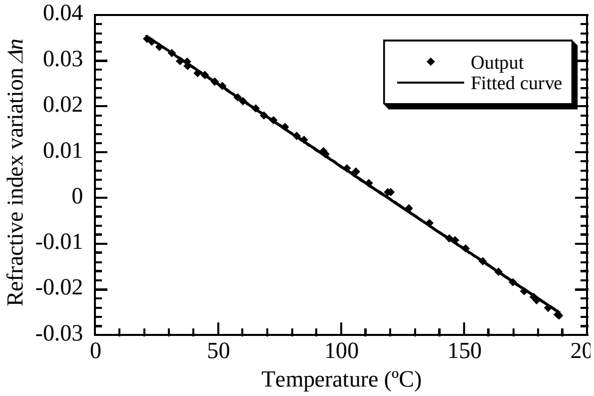

Fig.11 Relationships between refractive index variation of CCP and temperature.

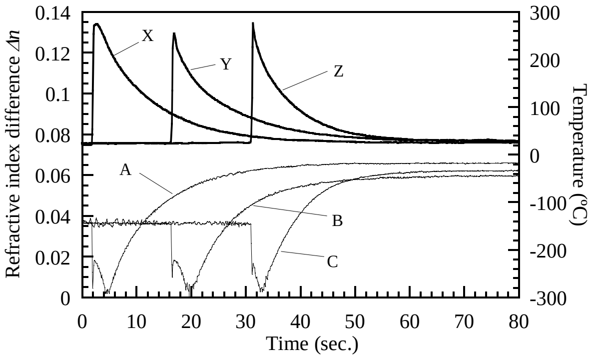

Fig. 12 Time histories of the refractive index variations and temperatures during chain cure process.

At the room temperature, the refractive indices showed the same as each other. The refractive indices change rapidly at the rise of temperature. The behaviors of the refractive indices were different from those of temperatures for a few seconds from the initiation of the local cure reaction. Then the refractive indices were converged to constant values when the temperatures became constant. In order to investigate the behaviors of the refractive indices in detail, the magnified view of the refractive index C was shown in Fig. 13. From the C-A to the C-B, the refractive index decreased linearly with the temperature rise. When the temperature reached 120 ºC at the C-B, the refractive index of resin became the same as that of the optical fiber. From the C-B to the C-C, the refractive index increased while the temperature grew because the refractive index was less than n_g at over 120 ºC. Thus the variation of the refractive index should be negative in the section from the C-B to the C-D when the temperature over 120 ºC, that is, the curve in the section from C-B to C-D should be inversed.

The calculated DOC curves were plotted against time with temperatures in Fig. 14. It was difficult to measure the accurate DOC in the sections in which the refractive indices were negative since the variation of temperature was too fast to measure precise temperature of the CCP at the tip of the optical fiber. Therefore, the expected DOC curves at the section were plotted using dotted lines. From the results, it was found that the behaviors of chain cure process were different from each other at different places. Table 1 lists behaviors of chain cure reaction of the CCP for the three sensors. The cure reaction at the position A progressed fastest. On the contrary, the speed of cure reaction at the position B was slowest among the three points. From the table, it was estimated that the speed of the cure reaction at the position B was double of that at the position A. Besides the fact of the cure reaction speed, the final DOC should be paid attention. It appeared that the final values of DOC at the three points were different from each other. The CCP was cured perfectly at the position A while the cure reaction cannot be wholly accomplished at the positions B and C. Thus it became obvious that the final cure state of the CCP was non-uniform. It should be noted that the DOC at these position became 1.0 during post-cure process.

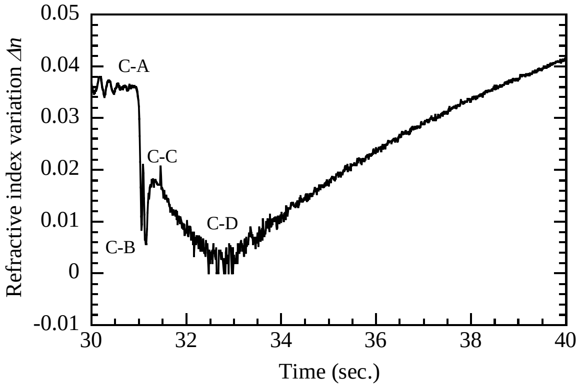

Fig. 13 Δn changing pattern of the sensor C during chain curing reaction

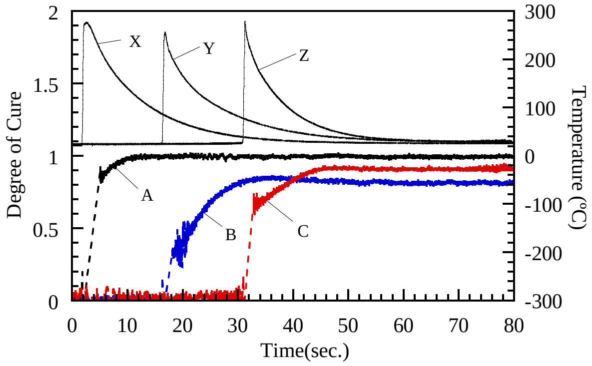

Fig. 14 Degree of cure for CCP during chain cure process.

Table 1. Behaviors of chain cure reaction of the CCP.

	Sensor A	Sensor B	Sensor C
Cure time (s)	9.4	20.4	14.6
DOC at 200 ºC	0.8	0.4	0.65
Final DOC	1.0	0.82	0.90

4 Conclusions

In this paper, we have developed the high-speed and local method to measure refractive index of resin during cure and to estimate degree of cure (DOC) by embedded optical fibers. From the experimental study, the proposed method is valid to monitor DOC of resin at real time. Then, this method was applied to monitor the behavior of cure chain reaction of cure chain polymers (CCP). It was shown that the DOC of the CCP could be monitored successfully at high speed. From the experimental result, it appeared that the behavior of the cure chain reaction is different in space. From these results, it is concluded that the proposed method in the present paper is very useful to investigate behavior of the cure chain reaction. In addition, we have emphasized that this method is available to monitor the cure state of CCP based FRP for large consumer products at real time.

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