TMPTA의 UV광중합 속도 측정

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Measurement of UV Photopolymerization Rate of Trimethylolpropane Triacrylate (TMPTA)

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1. Introduction

In various thin film applications UV photopolymerization is widely used due to its simplicity and wide applicability. However, monitoring the process is very difficult, because the photopolymerization is done in a range of seconds. Photorheometry has been used in monitoring the UV photopolymerization [1]. As the polymerization proceeds, the viscosity increase in the reactants is determined with the rheometer to calculate the polymerization degree. Spectroscopy has been widely employed in monitoring the reduction of carbon-carbon double bonds for the determination of polymerization degree. According to the wavelength of detecting light source, UV-VIS spectrometry, FT-IR, and NIR have been applied measuring the double bonds. The quartz crystal resonator has been used in various applications by monitoring mass changes in nano-gram scale and microrheological variation on its electrode surface. In a polymerization study, a stereo complex assembly of poly(methyl methacrylate) was developed on the resonator surface to investigate the assembling mechanism [2]. A thickness shear mode resonator was utilized in the characterization of an epoxy resin film [3]. While a contacting phase changes on the resonator surface, the resonant frequency and resistance of the resonator vary due to mass load change and rheological alteration on the surface.

In this study, the quartz crystal resonator is implemented in measuring the amount of acrylate monomer to examine the UV photopolymerization. A monomer of trimethylolpropane triacrylate is used in the monomer measurement. The resonant resistance of the resonator is used to determine the monomer amount. The relationship between the monomer amount and the resonant resistance is found from the experimental result, and the measuring technique is applied to a photopolymerization for the performance evaluation of the proposed measurement technique.

2. Experimental

2.1 Chemical, Resonator and UV source

A monomer of trimethylolpropane triacrylate (TMPTA, Sigma-Aldrich Co., U. S. A., Code No. 246808) was used as received. The quartz crystal resonator has a thin quartz plate of 9 mm in diameter, and either side of the quartz plate has a circular electrode of 5 mm in

diameter at the plate center. When the UV photopolymerization was performed, the resonator was placed at the distance of 6 mm from the tip of the optical fiber. The resonant frequency and resistance were measured using home-made devices, and an A/D converter was employed for signal processing. An AT-cut quartz crystal resonator having a base frequency of 8 MHz (Sunny Electronics Co., Korea) was utilized in this experiment. A spot UV light source (Lichtzen Co., Korea, Model Inno-Cure 100N) was used, and its light intensity is 3 W/cm^2 with UV wavelengths between 250 nm and 450 nm. Fig. 1 shows the experimental setup for the monomer measurement in the UV photopolymerization.

2.2 Experimental procedure

The monomer of TMPTA 0.1 g was dissolved in 10 g toluene, and various amount of sample was applied on the electrode surface of a quartz crystal resonator using a micro pipette. Without UV illumination the resonant resistance was measured for the different amounts of monomer, and the relationship between the monomer amount and resonant resistance of the quartz crystal resonator was obtained from the measured resistance and the known amount of monomer determined from the frequency change. For the evaluation of the relationship found from the experimental results, the proposed measuring technique was applied to the UV photopolymerization. A 1 g mixture of TMPTA and a photo initiator of 2-ethylanthraquinone at the weight ratio of 35 to 1 was dissolved in 10 g toluene, and a 0.8 μL of the solution was spread on the resonator surface. The variations of resonant frequency and resistance were measured with the irradiation of UV light for the specified time.

3. Results and Discussion

The measured resistances for known amounts of monomer are shown in circles in Fig. 2. A small amount of TMPTA dissolved in toluene was spread on the electrode surface as a thin film, and the solvent toluene was evaporated as soon as the sample applied. The resonant frequency drop in the bottom figure of Fig. 3. indicates the sample application, and no frequency increase after the sample dropping means that the vaporization of the solution is momentary. Though there is some scattering of the data from the fitted curve in Fig. 2., it is evident that the measured resistance using the quartz crystal resonator can be used for the determination of monomer amount. Fig. 3. shows the frequency drop due to the sample application and resistance decrease after the UV irradiation for one second. The moments of sample dropping and UV irradiation are indicated in the bottom figure. From the resistance measurement the calculated monomer amount is demonstrated in Fig. 4. The bottom figure of Fig. 3. demonstrates the variation of total amount of reactant on the resonator surface. No significant variation after a sudden drop for the sample dropping indicates that the total amount is not altered during the polymerization. Though the UV application was for one second only, the polymerization was continuous even after the UV was cut. The free radical generated by the UV irradiation has not been entirely consumed during the irradiation, and the remained radicals initiate the polymerization without the UV irradiation. Because the unreacted monomer was available, the continuous consumption of the monomer was observed in Fig. 4.

The on-line measurement of monomer amount in polymerization is difficult, though it is critically necessary for the process operation. The measurement in thin film processing, such as the UV photopolymerization, is even more difficult. The proposed measurement technique of this study is relatively simple and easy for the polymerization monitoring. The quartz crystal resonator has been used for many different applications, but its utilization in monomer measurement has not been attempted before. The usefulness of the resonator in polymerization is experimentally demonstrated here.

4. Conclusion

It is difficult to measure the monomer concentration in thin film polymerization, such as the UV photopolymerization of acrylates, though measuring the concentration is important for the control of polymerization. A quartz crystal resonator widely used in the determination of tiny amount of mass load and rheological variation has been applied to the measurement of monomer amount in the UV photopolymerization of trimethylolpropane triacrylate with an initiator of 2-ethylanthraquinone. The relationship between the resonant resistance and monomer amount obtained from the experimental results is used in the determination of monomer concentration in the UV photopolymerization. The measurement results of monomer concentration in the test applications indicate that the proposed measurement technique is effective to determine the concentration. The simplicity and usefulness of the proposed device have been demonstrated here.

References

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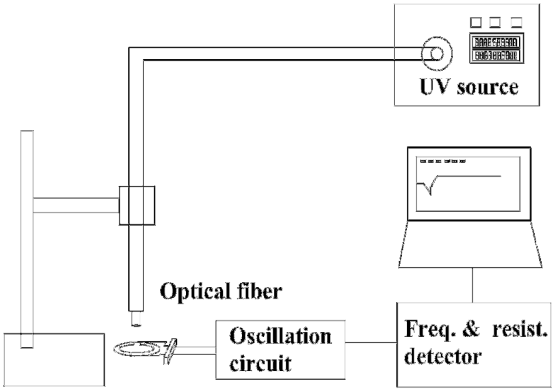

Fig. 1. A schematic diagram of experimental setup for UV irradiation.

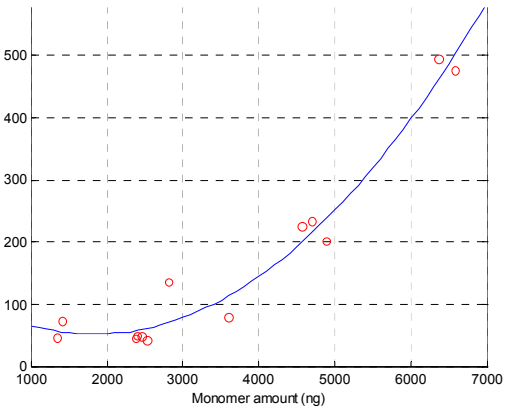

Fig. 2. Relationship between monomer amount and resonant resistance.

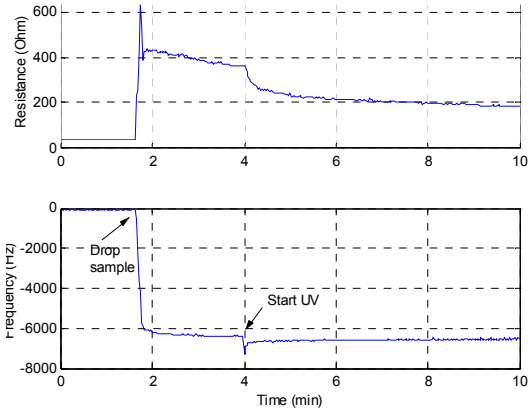

Fig. 3. Variations of resonant resistance and frequency in UV photopolymerization of trimethylolpropane triacrylate.

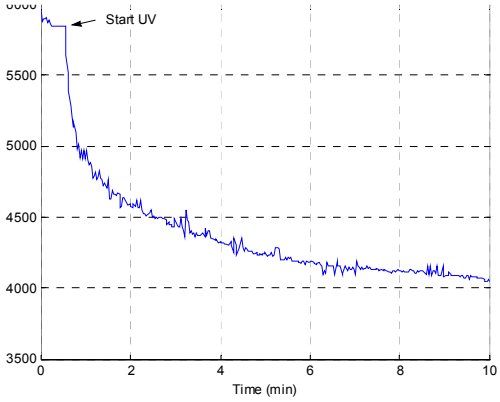

Fig. 4. Depletion of monomer after the UV irradiated for 1 second.