Visible-Light Sensitive Reworkable Resins: A Rheological Study

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A rheological study of visible-light sensitive reworkable photocuring resins was carried out using reworkable monomers. A dimethacrylate monomer containing tertiary ester units in a molecule and a methacrylate monomer, which has both an epoxy moiety and a thermally-cleavable tertiary ester moiety in a molecule, were employed as the reworkable monomers. The reworkable monomers were successfully cured by green light irradiation (530-nm light) using a visible-light sensitive photoradical initiator. When the cured reworkable resins were baked after UV light irradiation (365-nm light) in the presence of a photoacid generator, the storage moduli of the cured resin decreased at elevated temperatures. The decreased storage moduli revealed by rheological studies were due to the acid-catalyzed decomposition of the tertiary ester linkages in the cured reworkable monomers. The effect of the chemical structure on the rheological properties was discussed.

Keywords: Reworkable resin, Photocuring, Photo-degradation, Visible light, Rheological study

1. Introduction

Visible-light sensitive curable resins are widely studied not only in terms of environmental perspective such as utilization of sunlight but also medical applications because visible light is harmless to the human body compared to UV light [1]. Visible-light sensitive curable resins are widely used as base resins of additive manufacturing to fabricate 3D structures [2]. Thus, reworkable resins [3-12], which are thermosets thermally or chemically degradable under a given condition, have been extensively studied as environmentally-friendly materials without damaging the underlying materials. Based on this information, we have developed a series of “reworkable” resins which are applicable to functional materials [8-12]. Especially, a mechanical investigation of reworkable resins was very important in terms of the practical use such as an adhesive. In a previous study, a rheological investigation of reworkable resins was carried out [12]. Two reworkable monomers, 2,5-dimethyl-2,5-hexanediol dimethacrylate (DHDMA) [6-8,12,13] and 1-methyl-1-(6-methyl-7-oxabicyclo[4.1.0]-hept-3-yl)ethyl methacrylate (MOBH) [9-12] were employed as the reworkable monomers. DHDMA is a dimethacrylate having two tertiary ester linkages. On the other hand, MOBH is a methacrylate monomer which has both an epoxy moiety and a thermally-cleavable tertiary ester moiety in a molecule. The reworkable monomers were cured upon irradiation by near UV light (365 nm) to form reworkable resins. After irradiation by deep UV light (254 nm), the reworkable resins were heated. We evaluated the reworkable properties of the cured reworkable resins using the values $G'_{\text{max}}$ and $G'_{\text{min}}$ which are the maximum and minimum $G'$ values between 100 and 150 °C, respectively. We found that the $G'_{\text{max}}/G'_{\text{min}}$ values of the cured reworkable resins strongly depended on the experimental conditions. The photocured reworkable resins showed high $G'_{\text{max}}/G'_{\text{min}}$ values during heating after irradiation.

In this communication, we extend the previous study to investigate the visible-light sensitive reworkable resins. Rheological studies of the
Reworkable photocuring resins are a straightforward way to realize the mechanical properties of the reworkable resins under a certain heated or irradiated condition. We believe that the knowledge obtained in this study is useful for practical applications such as degradable adhesives for medical and 3D photopatternable materials.

The reaction mechanisms of DHDMA, a dimethacrylate monomer, 3-methyl-1,3-butanediyl dimethacrylate (MBDMA) [17], and MOBH upon heating and irradiation are shown in Schemes 1-3, respectively. The monomers, DHDMA, MBDMA, and MOBH, were polymerized upon irradiation by 530-nm light in the presence of the photoradical initiator, bis(η⁵-2,4-cyclopentadien-1-yl)bis[2,6-difluoro-3-(1H-pyrrol-1-yl)phenyl]titanium (I784) [14] (Scheme 1). The crosslinked DHDMA, MBDMA, or poly(MOBH) was formed. Upon subsequent UV irradiation at 365 nm in the presence of the photoacid generator 7-(1,1-dimethylethyl)-1,3-dihydro-1,3-dioxo-2H[1,4]benzodithiino[2,3-f]isoindol-2-yl trifluoromethanesulfonate (tBuTHITf) [15] (Scheme 1), the crosslinked DHDMA degraded to form

![Scheme 1. Reaction mechanism using DHDMA.](image1)

![Scheme 2. Reaction mechanism using MBDMA.](image2)
poly(methacrylic acid) after heating (Scheme 1). MBDMA was investigated to determine the role of the degradation of the tertiary ester linkages in Schemes 1 and 2. On the other hand, the crosslinked poly(MOBH) may form networks after UV irradiation in the presence of the photoacid generator (Scheme 3). After subsequent heating, poly(methacrylic acid), polyepoxide from poly(MOBH), and limonene [16] may be formed (Scheme 3). The effect of the chemical structures or the reaction conditions on the rheological properties of the cured or photo-degraded resins is also discussed.

2. Experimental

2.1. Materials

DHDMA [6], MOBH [10], and tBuTHITf [15] were prepared as reported. MBDMA was kindly donated from Kuraray (Japan) and used as received. I784 was purchased from Angene (China) and used without further purification.

2.2. Measurements

The intensity of the light was measured by an Orc Light Measure UV-M02 or Ushio USR-45VA. The UV-vis spectra were obtained by a Shimadzu UV-2450. The thickness of the films was measured by profilometry (Kosaka Surfcoorder ET-3000i). Rheological experiments were performed by a Thermo Scientific HAAKE MARS III rotational rheometer. For the rheological measurements, the sample films (discs) were placed between parallel plates and an oscillation applied at the constant frequency of 1 Hz under a 1% strain (γ = 0.01) in the rheometer. During the measurement, the films were in-situ heated or illuminated at 25 °C with 530-nm light which was introduced through a quartz bottom plate. The irradiations at 365 nm or 530 nm were performed in air using a xenon lamp (Asahi spectra MAX-301, 300 W) in combination with a band path filter of 365 nm or 530 nm, respectively.

3. Results and discussion

3.1. Reaction conditions

In a recent study by Liska et al. [18], a comprehensive understanding of the rheological properties of the photocurable resins was found still challenging even if multiple analytical techniques were used in the measurements. Thus, we focused on the increase and decrease in the moduli of the reworkable monomers which were affected by the reaction conditions. The main topic of this study is to clarify the effect of the wavelength dependence on the previously studied rheological properties [12]. Thus, a commercially-available green-light (530-nm light) sensitive photoradical initiator I784 was chosen as the Type I photoradical initiator. On the other hand, an i-line (365-nm light) sensitive photoradical generator, tBuTHITf, was used due to complete light penetration to the bottom part of the samples. In this study, photocrosslinking was carried out by irradiation of the 530-nm light. The photodegradation was performed using the 365-nm light.

Figure 1 shows the power spectra of the 365-nm and 530-nm light and UV-vis spectrum of the MOBH film (thickness: 100 µm) containing 1 wt% I784 and 1 wt% tBuTHITf. The intensities of the 530-nm and 365-nm lights were 1.34 and 2.4 mW/cm², respectively. The absorbance of the MOBH film was less than 1 above 350 nm, which
indicated that both the 530-nm and 365-nm lights had completely penetrated based on the experimental conditions.

3.2. Rheological properties
3.2.1. Photocuring
At first, the visible-light sensitivities of DHDMA, MOBH, and MBDMA were checked using a rheometer [12,19,20]. Figure 2 shows the changes in the viscoelastic parameters of DHDMA, MOBH, and MBDMA containing 1 wt% I784 and 1 wt% tBuTHITf during the irradiation at 530 nm. The storage ($G'$) and loss ($G''$) moduli rapidly increased during irradiation after 1 min. The $G'$ values of DHDMA and MOBH reached plateaus after 3 min and 2 min, respectively. On the other hand, the $G'$ value of MBDMA did not reach a plateau during the irradiation before 6 min. Thus, we concluded that the sensitivities of the monomers were in the order of MOBH > DHDMA > MBDMA.

3.2.2. Photo-thermal degradation
When the photocured DHDMA, MOBH, and MBDMA previously irradiated at 530 nm were irradiated at 365 nm, tBuTHITf photolyzed to generate trifluoromethanesulfonic acid as shown in Schemes 1-3. The generated trifluoromethanesulfonic acid catalyzed the decomposition of the tertiary ester or ether linkages in the cured DHDMA, MOBH, and MBDMA. Figure 3 shows the changes in the cured and irradiated DHDMA, MOBH, and MBDMA viscoelastic parameters during heating. The low $G'$ values of the cured and irradiated DHDMA, MOBH, and MBDMA before heating were due to the difficulty in preparing the completely cured samples. Thus, the $G'$ values of MOBH and MBDMA increased below 80 °C due to thermal curing of the MOBH and MBDMA. No viscoelastic changes were observed after irradiation at 365 nm without heating for all samples. In the case of MOBH, the $G'$ value reached a maximum value, decreased, and increased again upon heating. We consider that the decrease is due to the decomposition of the crosslinking structures of MOBH. The decrease was also clearly observed in the cured and irradiated MOBH as shown in Fig. 3 (b). The decrease in the $G'$ values was due to the acid-catalyzed decomposition of the crosslinking structures of MOBH.
DHDMA and MOBH. In order to evaluate the decreased $G'$ values, we defined the values $G'_{\text{max}}$ and $G'_{\text{min}}$, which are the maximum and minimum $G'$ values between 80 and 120 °C, respectively. The ratios of $G'_{\text{max}}$ and $G'_{\text{min}}$ ($G'_{\text{max}}/G'_{\text{min}}$) strongly depend on the experimental conditions. We consider that the $G'_{\text{max}}/G'_{\text{min}}$ value is important for practical applications, such as removable sealants or adhesives, after use. Table 1 summarizes the obtained $G'_{\text{max}}/G'_{\text{min}}$ values. The obtained $G'_{\text{max}}/G'_{\text{min}}$ values of DHDMA and MOBH were 2.9 and $1.3 \times 10^5$, respectively. On the other hand, the $G'_{\text{max}}/G'_{\text{min}}$ value of MBDMA was not obtained. After decomposition, the cured and irradiated DHDMA and MOBH generated low-molecular-weight fragments, such as 2,5-dimethyl-2,4-hexadiene [8] and limonene [16] (Schemes 1 and 3). On the other hand, the cured and irradiated MBDMA may form poly(methacrylic acid) and poly(3-methyl-3-butene methacrylate) (Scheme 2), and no low-molecular-weight fragments may be generated. We consider that the generation of the low-molecular-weight fragments have a very important effect on the rheological changes after degradation.

4. Conclusion

Rheological studies of visible-light sensitive reworkable photocuring resins were carried out using the monomers DHDMA, MOBH, and MBDMA. We evaluated the reworkable properties of the cured DHDMA and MOBH using the values $G'_{\text{max}}$ and $G'_{\text{min}}$ which are the maximum and minimum $G'$ values between 80 and 120 °C, respectively. The obtained $G'_{\text{max}}/G'_{\text{min}}$ values of DHDMA and MOBH were 2.9 and $1.3 \times 10^5$, respectively. On the other hand, for the cured MBDMA, the $G'_{\text{max}}/G'_{\text{min}}$ value was not obtained. The findings suggest that the generation of the low-molecular-weight fragments plays a very important role in the rheological changes after degradation.

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