Rheological Studies of Reworkable Photocuring Resins

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Rheological studies of reworkable photocuring resins were 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. When the cured reworkable monomers were irradiated and baked in the presence of a photoacid generator, the storage moduli of the cured resin decreased at elevated temperatures. The decreased storage moduli revealed by the rheological studies were due to the acid-catalyzed decomposition of the tertiary ester linkages in the cured reworkable monomers.

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

1. Introduction

Photocurable resins are widely used as adhesives, coatings, etc., due to their toughness and wide availability. On the other hand, reworkable resins [1-9], 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 [6-9]. Especially, a mechanical investigation of reworkable resins was very important in terms of practical use such as an adhesive. In a previous study, a mechanical investigation of reworkable resins was carried out [7]. A methacrylate monomer, which has both an epoxy moiety and a thermally-cleavable tertiary ester moiety in a molecule, was employed as the reworkable monomer. The lap shear adhesion strength of the cured reworkable monomer decreased after decomposition by photo-irradiation followed by baking. The decrease revealed by FT-IR measurements was due to the acid-catalyzed decomposition of the tertiary ester linkages in the cured reworkable monomer.

In this study, we extend the previous study to investigate the rheological properties [10-20] of the reworkable resins. Rheological studies of reworkable photocuring resins are a straightforward way to realize the mechanical properties of the reworkable resins under a certain heated or irradiated conditions. We believe that the knowledge obtained in this study is useful for practical applications such as degradable adhesives and photopatternable materials.

Two reworkable monomers, 2,5-dimethyl-2,5-hexanediol dimethacrylate (DHDMA) [4-6,21-24] and 1-methyl-1-(6-methyl-7-oxabicyclo[4.1.0]-hept-3-yl)ethyl methacrylate (MOBH) [7-9], were selected in this study. 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 reaction mechanisms of DHDMA and MOBH upon heating and irradiation are shown in Schemes 1 and 2, respectively. The reworkable monomers, DHDMA and MOBH, were polymerized upon heating in the presence of the radical initiator AIBN (Scheme 1) or upon...
irradiation in the presence of the photoradical initiator 2,2-dimethoxy-1,2-diphenylethanone (DMPA) (Scheme 1). The crosslinked DHDMA or poly(MOBH) was formed. Upon subsequent UV irradiation at 254 nm in the presence of the photoacid generator bis[4-(1,1-dimethylethyl)phenyl]iodonium trifluoromethanesulfonate (DITf) (Scheme 1) or 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) [25] (Scheme 1), the crosslinked DHDMA degraded to form poly(methacrylic acid) after heating (Scheme 1). On the other hand, poly(MOBH) may form networks after UV irradiation in the presence of the photoacid generators (Scheme 2). After subsequent heating, poly(methacrylic acid) and polymers generated from the cationic ring opening.
polymerization of the epoxy moiety in MOBH are formed (Scheme 2). For comparison, a dimethacrylate monomer, ethylene glycol dimethacrylate (EGDMA) and glycidyl methacrylate (GMA) were chosen to investigate the role of the degradation of tertiary ester linkages in Schemes 1 and 2. The effect of the chemical structures or the reaction conditions on the rheological properties of the cured or photodegraded resins is also discussed.

2. Experimental

2.1. Materials

DHDMA, MOBH, and tBuTHITf were prepared as reported. DITf was obtained from Midori Kagaku. N,N’-Azobis(isobutyronitrile) (AIBN) was purchased from Aldrich and purified by recrystallization from ethanol. EGDMA and GMA were obtained from the Tokyo Chemical Industry and distilled before use.

2.2. Measurements

The intensity of the light was measured by an Orc Light Measure UV-M02 or Ushio USR-45VA. The thickness of the films was measured by profilometry (Kosaka SurfCorder ET-3000i). Rheological experiments were performed by a Thermo Scientific HAAKE MARS III rotational rheometer. For rheological measurements, sample films (discs) were placed between parallel plates and an oscillation applied at a constant frequency of 1 Hz under a 1% strain (γ = 0.01) in the rheometer. During the measurement, films were in-situ heated or illuminated at 25 °C with 365 nm LED light which was introduced through a quartz bottom plate. Irradiation at 254 nm was performed in air using a xenon lamp (Asahi spectra MAX-301, 300 W) in combination with a band path filter of 254 nm.

3. Results and discussion

3.1. Choice of monomers and reaction conditions

The main topic of this study is to clarify the effect of tertiary ester linkages incorporated in the networks of the cured resins upon degradation. Thus, we chose DHDMA having two tertiary ester linkages and compared it to the result using EGDMA with no tertiary ester linkages. When using MOBH as a reworkable monomer, GMA was used for comparison. We were also interested in the relationship between the adhesion properties of the MOBH-based resins [7] and the rheological properties obtained in this study. We found that the lap shear adhesion strength of the cured MOBH film containing 1 wt% AIBN and 3 wt% tBuTHITf decreased after irradiation at 365 nm with 200 mJ/cm² followed by baking at 120 °C for 10 min [7]. The decrease was due to the acid-catalyzed decomposition of the tertiary ester linkages in the cured reworkable monomer supported by FT-IR measurements. In this study, direct information about the mechanical properties of the cured and degraded MOBH can be obtained. The relationship between the adhesion properties obtained in a previous study and the mechanical properties are also discussed.

In a recent study by Liska et al. [11], a
comprehensive understanding of the rheological properties of the photocurable resins is 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.

3.2. DHDMA and EGDMA

We selected DHDMA, a reworkable monomer having two methacryl units connected together with two tertiary ester linkages. On the other hand, EGDMA has two primary ester linkages in a molecule instead of tertiary ester linkages. The thermal curing of DHDMA and EGDMA was accomplished in the presence of a thermal radical initiator such as AIBN or benzoyl peroxide. We selected AIBN as the thermal radical initiator. Figure 1 shows the rheological properties of DHDMA containing 1 wt% of AIBN and 1 wt% DITf, a photoacid generator. Table 1 summarizes the experimental conditions for the viscoelastic measurements of DHDMA and EGDMA during heating. The storage ($G'$) and loss ($G''$) moduli rapidly increased during heating at around 80 °C (Fig. 1 (a), DHDMA-H in Table 1), which correspond to the formation of crosslinked DHDMA by thermal radical polymerization. After heating at 100 °C for 10 min, the $G'$ value reached 1.7 MPa. In Fig. 1 (b), the rheological properties of cured DHDMA (DHDMA-H-H in Table 1) are shown. Due to the experimental settings, the $G'$ value (1.7 MPa) of DHDMA-H in Table 1 was not reproduced upon heating at 100 °C in the measurement. The phenomenon was also observed in the experiment using the irradiated sample (DHDMA-H-P254-H in Table 1) shown in Fig. 1 (c). The improved sample setting to decrease the deviation is now in progress. However, we consider that the deviation does not affect the conclusion of this study regarding the limitation of the change in the $G'$ value within the range of the same experimental conditions.

In Fig. 1 (b), the $G'$ value of DHDMA-H-H in Table 1 increased, reached a maximum value, and decreased upon heating. We consider that the decrease is due to the decomposition of the crosslinking structures of DHDMA. The decrease was clearly observed in the cured DHDMA after irradiation (DHDMA-H-P254-H in Table 1) as shown in Fig. 1 (c). The decrease in the $G'$ value was due to acid-catalyzed decomposition of the crosslinking structures of DHDMA. 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 100 and 150 °C, respectively. The $G'$ values of the thermal- or photo-cured DHDMA and EGDMA were about 1 MPa, which are consistent with the previously reported values [11].

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. Figure 2 shows the changes in the viscoelastic parameters of the cured DHDMA after heating at 100 °C for 10 min followed by irradiation at 365 nm for 1000 mJ/cm² during heating (DHDMA-H-P365-H in Table 1). The \( G'_\text{max}/G'_\text{min} \) value is 19, which showed the highest value obtained among the experiments in Table 1. We concluded that the DHDMA-H-P365-H sample showed an effective degradation of the networks formed by the radical polymerization of DHDMA due to the high acid concentration generated from tBuTHITf after irradiation at 365 nm.

In terms of the photocured DHDMA (DHDMA-P365, DHDMA-P365-H and DHDMA-P365-P254-H in Table 1), changes in the viscoelastic parameters during heating were similar to the thermally-cured DHDMA as shown in Figs. 1 and 2. The \( G'_\text{max}/G'_\text{min} \) value of DHDMA-P365-P254-H is 14, which was slightly lower than that of the thermally-cured DHDMA (DHDMA-H-P365-H). We concluded that the photocured DHDMA also degraded by subsequent irradiation by tuning the formulation and the employed experimental conditions.

Compared to DHDMA, the samples containing EGDMA (EGDMA-H, EGDMA-H-H, EGDMA-P365, and EGDMA-P365-H in Table 1) showed no \( G'_\text{min} \) values after heating below 150 °C, suggesting that the degradation of the networks in the cured EGDMA did not occur based on the experimental conditions in this study. Thus, the incorporation of tertiary ester linkages is very important to control the rheological properties of the cured samples.

3.3. MOBH and GMA

As already mentioned, we are also interested in

| Table 2. Experimental conditions for viscoelastic measurements of MOBH and GMA during heating. |
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| code | monomer | sequence of experiment | \( G'_\text{max} \) (MPa) | heating temp. for \( G'_\text{max} \) (°C) | \( G'_\text{min} \) (MPa) | heating temp. for \( G'_\text{min} \) (°C) |
| MOBH-H | MOBH | r.t.-100° | 2.8 | 100 | - | - |
| MOBH-H2 | MOBH | r.t.-100° | 2.6 | 100 | - | - |
| MOBH-H1-H | MOBH | 100° | r.t.-150° | 3.6 | 150 | - | - |
| MOBH-H2-H | MOBH | 100° | r.t.-150° | 4.3 | 150 | - | - |
| MOBH-H-P254-H | MOBH | 100° | 254° | 2.6 | 150 | - | - |
| MOBH-H-P365-H | MOBH | 100° | 365° | 3.3 | 121 | 0.15 | 150 |
| MOBH-P365 | MOBH | 365° | 1.4 | 15 | - | - |
| MOBH-P365-H | MOBH | 365° | r.t.-150° | 0.10 | 49 | 8.4 x 10⁻³ | 150 |
| MOBH-P365-P254-H | MOBH | 365° | 254° | r.t.-150° | 1.3 | 141 | 5.5 x 10⁻³ | 150 |
| GMA-H | GMA | r.t.-100° | 1.2 | 100 | - | - |
| GMA-H-H | GMA | 100° | r.t.-150° | 5.1 | 68 | 0.19 | 150 |
| GMA-P365 | GMA | 365° | 0.44 | 15 | - | - |
| GMA-P365-H | GMA | 365° | r.t.-150° | 2.9 | 150 | - | - |

\( ^a \) Contained 1 wt% AIBN and 1 wt% DITf. \( b \) Contained 1 wt% AIBN and 3 wt% tBuTHITf. \( c \) Contained 1 wt% DMPA and 1 wt% DITf. \( d \) Heating rate: 5 °C/min. \( e \) Heating time: 10 min. \( f \) Irradiation dose: 924 mJ/cm². Irradiation intensity: 1.54 mW/cm². \( g \) Irradiation dose: 1000 mJ/cm². Irradiation intensity: 9.3 mW/cm². \( h \) Irradiation dose: 48600 mJ/cm². Irradiation intensity: 81 mW/cm². \( i \) Irradiation dose: 2748 mJ/cm². Irradiation intensity: 5.48 mW/cm². \( j \) Additional heating at 150 °C for 10 min was carried out. \( k \) Not observed.
the relationship between the adhesion properties of the MOBH-based resins [7] and the rheological properties obtained in this study.

Table 2 summarizes the experimental conditions for the viscoelastic measurements of MOBH and GMA, a monomer having both a methacryl unit and an epoxy unit during heating. Figure 3 shows the changes in the viscoelastic parameters of MOBH containing 1 wt% AIBN and 3 wt% tBuTHITf during heating (MOBH-H2, MOBH-H2-H, and MOBH-H-P365-H in Table 2). It is known that the thermally-cured MOBH showed a drastic decrease in the lap shear adhesion strength of the cured MOBH film after irradiation at 365 nm in a previous study [7], which corresponds to the MOBH-H-P365-H sample in Table 2.

The $G'_\text{max}/G'_\text{min}$ value of MOBH-H-P365-H in Fig. 3(c) is 22, which is coincident with the decrease in the lap shear adhesion strength of the cured MOBH (from 0.57 MPa with no irradiation to 0.15 MPa after irradiation) [7]. Thus, we concluded that the MOBH-H-P365-H sample showed the effective degradation of the networks formed by the radical polymerization of MOBH due to high acid concentration generated from tBuTHITf after irradiation at 365 nm.

In terms of the photocured MOBH (MOBH-P365, MOBH-P365-H and MOBH-P365-P254-H in Table 2), the changes in the viscoelastic parameters during heating were similar to those of the thermally-cured MOBH as shown in Fig. 3. The $G'_\text{max}/G'_\text{min}$ value of MOBH-P365-P254-H is 24, which was slightly higher than that of the thermally-cured MOBH (MOBH-H-P365-H in Table 2). We concluded that the photocured MOBH also degraded by the subsequent irradiation by tuning the employed formulation and experimental conditions.

Compared to MOBH, the samples containing GMA (GMA-H, GMA-H-H, GMA-P365, and GMA-P365-H in Table 2) showed no $G'_\text{min}$ values after heating below 150 °C except for the thermally-cured GMA sample after heating below 150 °C (GMA-H-H in Table 2). The decrease in $G'$ started at around 100 °C and continued during elevated temperatures till 150 °C. The decrease in $G'$ was accompanied with the increase in $G''$ and reached a maximum value at around 120 °C, then decreased again. We concluded that the decrease in $G'$ is due to the glass transition of poly(GMA) formed by the thermal radical polymerization. In addition, we consider that the degradation of the networks in the cured GMA did not occur under the experimental conditions used in this study. Thus, incorporation of tertiary ester linkages is very important to control the rheological properties of the cured samples.

4. Conclusion

Rheological studies of reworkable photocuring
resins were carried out using the reworkable monomers DHDMA and MOBH. 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 100 and 150 °C, respectively. The $G'_{\text{max}}/G'_{\text{min}}$ values of the cured DHDMA and MOBH strongly depended on the experimental conditions. The thermally and photo-cured DHDMA and MOBH showed high $G'_{\text{max}}/G'_{\text{min}}$ values during heating after irradiation. As a photoacid generator, tBuTHITf, is more effective compared to DITf due to high acid generation upon irradiation.

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