A mechanical investigation of reworkable resins was carried out using a reworkable monomer as an adhesive. 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.

**Keywords:** Reworkable resin, Photo-degradation, Mechanical property, Lap shear adhesion strength

1. Introduction

Reworkable resins [1-15], 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 point of view, we have developed a series of “reworkable” epoxy resins having tertiary ester linkages [5-11], sulfonate ester linkages [12], and hemiacetal ester linkages [13] as thermally-cleavable units. The reactivity, sensitivity, thermal or chemical stability, and re-dissolution property of the polymers must be improved in terms of their practical use. The mechanical properties of the reworkable resins after degradation are very important for practical use. Therefore, evaluation of the mechanical properties was very important in order to optimize the degradation conditions. However, there are few reports that focused on the mechanical properties of the degraded reworkable resins which are applicable as reworkable underfill materials in flip-chip technology [14] and the matrix of carbon fiber-reinforced plastics [15].

In this study, a mechanical investigation of reworkable resins was carried out using a reworkable monomer as an adhesive. A schematic

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**Fig. 1.** Schematic representation of reworkable resins investigated in this study.
representation of this study is shown in Fig. 1. At first, a methacrylate monomer which has both an epoxy moiety and a thermally cleavable tertiary ester moiety in a molecule (MOBH, Fig. 2) was polymerized on heating in a presence of a radical initiator. Homopolymer of the methacrylate was formed. On subsequent UV irradiation, the polymethacrylate containing photoacid generators became insoluble in organic solvents by crosslinking reaction of the epoxy moieties. When the crosslinked polymethacrylate were baked at elevated temperatures, they became soluble in solvents. The phenomenon is due to the degradation of the polymer networks, resulting in the formation of linear polymeric molecules and small molecules. We determined that the lap shear adhesion strength of the cured reworkable monomer decreased after decomposition by photo-irradiation followed by baking as shown in Fig. 1. The chemical structures of the degradation products were also followed by FT-IR measurements. The relationship between the chemical structures and mechanical properties of the cured or photo-degraded resins was also discussed.

Fig. 2. Chemical structures of MOBH, tBuTHITf, and AIBN.

2. Experimental

2.1. Materials

The chemicals used in this study are shown in Fig. 2. 1-Methyl-1-(6-methyl-7-oxabicyclo[4.1.0]hept-3-yl)ethyl methacrylate (MOBH) [5] and 7-(1,1-dimethylethyl)-1,3-dihydro-1,3-dioxo-2H[1,4]benzodithiino[2,3-f]isoindol-2-yl trifluoromethanesulfonate (tBuTHITf) were prepared as reported [16]. N-(Trifluoromethanesulfonyloxy)-1,8-naphthalimide (NITf) was obtained from Midori Kagaku. 2,2’-Azobisisobutyronitrile (AIBN) was purchased from Aldrich and purified by recrystallization from ethanol. All other solvents and reagents were purchased and used as received.

2.2. Measurements

The 1H NMR spectra were observed at 400 MHz using a JEOL JMN-ECS400 spectrometer. The UV-vis spectra were taken by a Shimadzu UV-2400 PC. The FT-IR measurements were carried out using a JASCO FT-IR-410. The intensity of the light was measured by an Orc Light Measure UV-M02 or Ushio USR-45VA. The thickness of films was measured by profilometry (Kosaka Surfcoeder ET-3000i). The lap shear adhesive strengths were measured using a tensile tester (Shimadzu Autograph AGS-X 1 kN).

2.3. Evaluation of lap shear adhesive strength

Test specimens for determining the lap shear adhesive strength of the samples were prepared using poly(ethylene terephthalate) (PET) films (Cosmoshine A4100, 125 μm, Toyobo, Japan). The PET films were used as received. The PET films were cut into small sheets with a length of 50 mm and width of 10 mm. A 1 μL aliquot of the sample liquid was placed on the PET film via a microsyringe and partially covered with another PET film. The lap joint was 10 mm square and the thickness of sample liquid was ca. 10 μm. The sample was cured by baking on a conventional hot plate at 100 °C for 10 min. Irradiation was performed in air using a xenon lamp (Asahi spectra MAX-301, 300 W) in combination with a bandpass filter of 365 nm (light intensity: 2.0 mW/cm²). The intensity of the light was measured by an Orc Light Measure UV-M02. After the irradiation, the cured sample was decomposed by baking on a conventional hot plate. The lap shear adhesive strengths of the cured and degraded samples were evaluated according to JIS K 6850 at a crosshead speed of 1 mm/min and temperature of 20 °C.

3. Results and discussion

3.1. Methodology

Generally, the mechanical properties of thermoplastics or thermosets can be easily estimated by a tensile measurement or dynamic mechanical analysis. These estimations require several grams of the cured samples with a high uniformity and relatively high thickness (> 100 μm). On the other hand, measurement of the lap shear adhesive strength is an easy, economical and versatile method to evaluate the mechanical properties of resins, especially weak and soft resins [17-19]. The drawbacks of the measurement of the lap shear adhesive strength are the strong dependence of the lapping materials and adhesion properties of the PET/resin interface. We chose PET films as the lapping material because of their
high transparency for incident light and relatively high modulus (~2.7 GPa) [20]. We believe that this method is applicable to evaluate the degradation properties of the samples in terms of their mechanical strength.

Photo-induced degradation is achieved by photoinduced acid-catalyzed decomposition which is obtained by the utilization of photoacid generators. Thus, selection of the photoacid generators is very important. Light absorption by the photoacid generators requires that the emission line from the light source overlaps with an absorption band of the photoacid generators. Thus, the absorption spectrum of the photoacid generators must be carefully selected. In this study, we used deep 365-nm light which is the strongest line spectrum of medium pressure mercury lamp, a conventional light source. The power spectra of the light sources used in this study are shown in Fig. 3. A xenon lamp was used to form the 365-nm light due to its easy access. The PET film was completely transparent against the 365-nm light as shown in Fig. 3. The optical properties of the matrices and photosensitive additives are very important when designing photosensitive materials. NITf and tBuTHITf are photoacid generators which generate triflic acid upon irradiation at 365 nm. Figure 4 shows the UV-vis spectra of the photoacid generators in acetonitrile. The molar absorption coefficient values of NITf and tBuTHITf are 330 and 1950 (M^{-1} cm^{-1}) at 365 nm, respectively [16].

Figure 5 shows the change in the lap shear strength of the cured MOBH film containing 1 wt% AIBN and 3 wt% tBuTHITf. Without irradiation, the cured MOBH film had the strongest adhesion.

![Figure 3](image-url)

Fig. 3. Power spectra of light sources. Solid line: Xenon lamp. Dashed line: Xenon lamp with a bandpass filter for 365 nm. For comparison, the UV-vis spectrum of the PET film used in this study (125 μm) is also shown.

![Figure 4](image-url)

Fig. 4. UV-vis spectra of tBuTHITf (solid line) and NITf (dashed line) in acetonitrile. Concentrations of the compounds were 1.0 ×10^{-4} M.

![Figure 5](image-url)

Fig. 5. Lap shear strength of cured MOBH film containing 1 wt% AIBN and 3 wt% tBuTHITf. Solid line: Cured by baking at 100 °C for 10 min. Dashed line: Irradiated at 365 nm with 200 mJ/cm² after curing. Dotted line: Subsequently baked at 100 °C for 10 min after irradiation of the cured sample. Bold line: Subsequently baked at 120 °C for 10 min after irradiation of the cured sample.
This strong adhesion may be due to thermally induced partial crosslinks of the poly(MOBH) produced by the radical polymerization of MOBH. The crosslinking easily occurs during the polymerization at 60 °C [5]. After irradiation, the adhesion strength did not changed in the range of experimental errors as mentioned below. After subsequent heatings, the strength decreased with the baking temperatures. Unfortunately, all of the failure modes in the experiments were interfacial, which indicates the strong effect on the interface between the PET films and MOBH film. However, we believe that the decrease is due to the mechanical decrease of the cured MOBH layers on the degradation conditions. The results of the lap shear strength of the cured MOBH films are summarized in Table 1. The values of adhesion strength in Table 1 ranged from 0.57 to 0.62 for unirradiated samples, which corresponds to the adhesion strength of lightly crosslinked poly(MOBH) (Table 1, columns 1, 8, and 12). On irradiation, the adhesion strength ranged from 0.34 to 0.73 regardless of irradiation dose and photoacid generators used (Table 1, columns 2, 9, 13, and 16). The photocrosslinking of epoxy slightly occur only irradiation. Thus, the author thinks that the adhesion strengths increased by only irradiation. The author considered that the deviation is the limitation of experimental conditions. Only irradiation, the degradation of tertiary ester linkages did not occur according to the FT-IR measurements in Fig. 6 as mentioned below. Thus, the values of adhesion strength did not decreased in the experimental conditions. In the previous paper [5], crosslinking occur on irradiation to the extent of insolubilization in solvents. The phenomenon is occurred by very low conversion of crosslinking reaction. Thus, we expect that adhesion strength

<table>
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increased on irradiation, the author cannot observe the phenomenon. The observation may be due to low conversion of epoxy units. By using NITf as a photoacid generator, no decrease in the adhesion strength was not observed due to low concentration of acid produced during the irradiation (Table 1, columns 1-11). We concluded that using tBuTHITf as a PAG and baking at 120 °C for 10 min after irradiation with a dose of 200 mJ/cm² at 365 nm is the optimal degradation condition for the experimental conditions (Table 1, column 15).

3.3. Reaction mechanism

The photo-thermal degradation process was monitored by FT-IR spectroscopy. Figure 6 shows the FT-IR spectral changes in the MOBH film containing 1 wt% AIBN and 3 wt% tBuTHITf upon irradiation at 365 nm with 200 mJ/cm² followed by baking at 120 °C for 10 min. The solid line shows the film before curing. After curing, the spectrum of the peak at 1636 cm⁻¹ ascribed to the C=C of MOBH almost completely disappeared. AIBN was decomposed to form radicals which initiated the polymerization of MOBH. Furthermore, tBuTHITf was photolyzed to produce an acid upon irradiation at 365 nm. Slight changes in the spectrum were observed only during the irradiation. When the irradiated film was heated at 120 °C for 10 min, the peak at 1720 cm⁻¹ due to the ester unit decreased and shifted to the peak at 1705 cm⁻¹ due to the carboxylic acid unit together with the decrease in the peak at 1130 cm⁻¹ due to the ester C-O-C stretching. The change strongly suggested the degradation of the tertiary ester linkages in the cured MOBH film. Unfortunately, the decreased peak at around 900 cm⁻¹ due to the epoxy C-O-C stretching was not clearly observed under these experimental conditions. A part of the epoxy moiety may react by heating, which may have the strongest adhesion of the cured samples. The proposed reaction mechanism is shown in Fig. 7.

4. Conclusion

We investigated the mechanical properties of the reworkable resins during decomposition. 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. The decrease was due to the acid catalyzed decomposition of the tertiary ester linkages in the cured reworkable monomer supported by FT-IR measurements.

Acknowledgement
This work was supported by JSPS KAKENHI Grant Numbers JP24550260 and JP16H02986.

References