1. Introduction

Reworkable and dismantlable polymer materials are used as smart adhesives, printing, coatings, and composite materials in various application fields. Recently, we reported a new type of readily curable and degradable thermosetting resin, which was synthesized by radical alternating copolymerization of maleic anhydride (MAn) and diene monomers and subsequent epoxy curing as post-polymerization reaction. In order to obtain a copolymer of MAn with diene monomers, we proposed the use of diene monomers with a twisted conformation, such as 2,4-dimethyl-1,3-pentadiene (DMPD) and several other methyl-substituted dienes, as the comonomers. For a long time, it has been accepted that 1,3-diene compounds, such as butadiene, isoprene, cyclopentadiene, and furan, react with MAn to yield Diels-Alder adducts in a high yield, rather than alternating copolymers. In fact, there are very few reports on the radical copolymerization of 1,3-diene monomers with MAn in the literature. In order to obtain a copolymer of MAn with diene monomers, we proposed the use of diene monomers with a twisted conformation, such as 2,4-dimethyl-1,3-pentadiene (DMPD) and several other methyl-substituted dienes, as the comonomers (Scheme 1). The obtained copolymers containing a carbon-to-carbon double bond in the polymer main chain were characterized by oxidative ozonolysis accompanying a decrease in the molecular weight and the introduction of polar and functional groups. In this paper, we report the synthesis of a readily curable and degradable resin by the radical alternating copolymerization

\[
\text{MAn} + \text{DMPD} \rightarrow \text{Copolymer}
\]

Scheme 1
of MAn and DMPD and the post-polymerization reactions using various difunctional compounds as the crosslinkers to produce network polymers by thermal curing (Scheme 2). The ozone degradation of the thermosetting resins induced the cleavage of a carbon-to-carbon double bond in the polymer main chains. The resolubilization and surface modification of the polymers were also investigated.

2. Experimental

2.1 Materials

Commercially available MAn (Kishida Chemicals Co., Ltd.) was used after sublimation under reduced pressure. DMPD was purchased from Tokyo Chemical Industry Co., Ltd., Tokyo and used as received. 2,2’-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMVN) was purchased from Wako Pure Chemicals Co., Ltd. and recrystallized from methanol. Bisphenol A diglycidyl ether (BADGE), difunctional alcohols and amines as the crosslinkers and N,N’-dimethylbenzylamine (DBA) were used as received (Wako Pure Chemicals Co., Ltd. or Tokyo Chemical Industry Co., Ltd.). The solvents were distilled before use.

2.2 General Procedures

The NMR and IR spectra were recorded using JEOL ECS-400 and ECX-400 FT NMR spectrometers and JASCO FT-IR410 spectrometer, respectively. The thermogravimetric and differential thermal analyses (TG/DTA) were carried out using Shimadzu TGA-50 in nitrogen at the heating rate of 10°C/min. The decomposition temperatures, \( T_{ds} \) and \( T_{d50} \) values, were determined as the 5 and 50% weight-loss temperatures in the TG curves, respectively. The maximum decomposition temperature \( (T_{max}) \) was determined from the differential TG curves. The differential scanning calorimetry (DSC) was carried out using Shimadzu DSC-60 in nitrogen at the heating rate of 10°C/min to determine the glass transition temperature \( (T_g) \). Spin-coated films were prepared using a Mikasa 1H-D7 spin coater. Film thickness was determined by interferometric measurement using a Nanometrics Nanospec AFT M-3000 series. Water contact angles were determined using a DMs-400 contact angle meter (Kyowa Interface Science Co., Ltd.). Ozone gas was generated using Ozone Mart O3 Clear (Earth Walker Trading Co., Ltd.).

2.3 Curing Procedures

The copolymerization of MAn with DMPD was carried out in chloroform in the presence of AMVN \(^\text{[33]}\). The reaction mixture was poured into a large amount of diethyl ether/n-hexane mixture to precipitate the copolymers, then the isolated copolymers were dried in vacuo at 110°C. The copolymers were purified by a repeated precipitation procedure using acetone and a diethyl ether/n-hexane mixture. A mixture of the copolymer, BADGE \([\text{anhydride}] / [\text{epoxy}] = 1/1\) molar ratio) and DBA (3 wt% to BADGE) in cyclohexanone (10 wt% to the polymer) was spin-coated on a Si plate at 1000 rpm for 30 sec, then prebaked at 60°C for 5 min, followed by curing at a determined temperature for 1 h in air. The insoluble fraction was determined based on
a change in the film thickness after dipping in acetone for 5 min. For diol curing, a mixture of the copolymer, a diol ([anhydride]/[hydroxy] = 1/1 molar ratio), and cyclohexanone was put in an aluminum pan, then prebaked, followed by curing at a determined temperature. The insoluble fraction was determined after removing a soluble fraction by immersing the samples in a pan into acetone for 15 min. The reaction of the copolymer with diamines was carried out in tetrahydrofuran (THF) at room temperature. The precipitated amic acid polymers were isolated and dried. The imidization was carried out in an oven at 200-240°C for 0.5 h.

2.4 Ozonolysis

The ozonolysis of the cured copolymers was carried out in acetone by bubbling ozone-containing air at room temperature or 0°C. After ozone bubbling for a determined time, nitrogen gas was bubbled, followed by the reduction of the produced ozonides with 5 wt% triphenylphosphine in acetone at room temperature for 10 min.

3. Results and Discussion

3.1 Epoxy Curing

The crosslinking of the copolymer of MAN and DMPD (\(M_n = 1.4 \times 10^4\)) was carried out using BADGE as the diepox compound in the presence of DBA as the base catalyst at various temperatures for 1 h. The thermal curing rapidly proceeded at a high temperature, as shown in a change in the IR spectrum (Fig. 1) and an increase in the insoluble fraction after curing (Fig. 2). The epoxy curing were confirmed to proceed in a high temperature range over 80°C, based on the IR spectral change of the reaction mixture accompanying a decrease in the peak intensity of the dissymmetric and symmetric C=O stretching of the anhydride ring at 1855 and 1778 cm\(^{-1}\), respectively, and the dissymmetric C-O stretching of the epoxy group at 864 cm\(^{-1}\) as well as an increase in the peak intensity of the C=O stretching of the produced ester moiety at 1738 cm\(^{-1}\). The insoluble fraction value rapidly increased around the \(T_g\) value of the copolymer (\(T_g = 95^\circ\)C), as shown in Fig. 2. This was because the crosslinking reaction was accelerated when the polymer chain mobility was high enough to change its conformation during the epoxy curing. Fig. 3 shows the comparison of TG

![Fig. 1](image1.png)

IR spectra of the copolymer of MAN and DMPD (a) before curing and after epoxy curing at (b) 80°C, (c) 85°C, and (d) 180°C. Curing conditions: [anhydride]/[epoxy] = 1/1 in mol/mol, DBA 3 wt%, for 1 h.

![Fig. 2](image2.png)

Temperature dependence of the insoluble fraction of the copolymer of MAN and DMPD during the epoxy curing. Curing conditions: [anhydride]/[epoxy] = 1/1 in mol/mol, DBA 3 wt%, for 1 h. Dissolution in acetone for 5 min after curing.

![Fig. 3](image3.png)

TG curves of the copolymer of MAN and DMPD (a) before and (b) after epoxy curing. Curing conditions: [anhydride]/[epoxy] = 1/1, DBA 3 wt%, 120°C, 1 h. TG measurement was carried out in a nitrogen stream at a heating rate of 10°C/min.
Table 1  Thermal stability of the copolymers of MAn and DMPD after curing with BADGE, diols, and diamines as crosslinkers

<table>
<thead>
<tr>
<th>Crosslinker</th>
<th>Curing conditions</th>
<th>$T_d$ (°C)</th>
<th>$T_d50$ (°C)</th>
<th>$T_{max}$ (°C)</th>
<th>Residual weight at 500°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before crosslinking</td>
<td>-</td>
<td>280</td>
<td>354</td>
<td>354</td>
<td>2.2</td>
</tr>
<tr>
<td>BADGE (3 wt% DBA)</td>
<td>180 1.0</td>
<td>301</td>
<td>378</td>
<td>360</td>
<td>24.5</td>
</tr>
<tr>
<td>HO(CH$_2$)$_3$OH</td>
<td>180 0.5</td>
<td>228</td>
<td>349</td>
<td>341</td>
<td>4.7</td>
</tr>
<tr>
<td>HO(CH$_2$)$_2$OH</td>
<td>180 0.5</td>
<td>280</td>
<td>349</td>
<td>351</td>
<td>7.7</td>
</tr>
<tr>
<td>Glycerin</td>
<td>180 0.5</td>
<td>271</td>
<td>348</td>
<td>355</td>
<td>2.0</td>
</tr>
<tr>
<td>H$_2$N(CH$_2$)$_2$NH$_2$</td>
<td>240 0.5</td>
<td>326</td>
<td>404</td>
<td>395</td>
<td>24.7</td>
</tr>
<tr>
<td>H$_2$N(CH$_2$)$_2$NH$_2$</td>
<td>240 0.5</td>
<td>317</td>
<td>425</td>
<td>462</td>
<td>24.6</td>
</tr>
<tr>
<td>H$_2$N(CH$_2$)$_2$NH$_2$</td>
<td>200 0.5</td>
<td>255</td>
<td>411</td>
<td>425</td>
<td>15.3</td>
</tr>
<tr>
<td>H$_2$N(CH$_2$)$_2$NH$_2$</td>
<td>220 0.5</td>
<td>357</td>
<td>397</td>
<td>437</td>
<td>7.9</td>
</tr>
<tr>
<td>H$_2$N(CH$_2$)$_2$NH$_2$</td>
<td>240 0.5</td>
<td>364</td>
<td>399</td>
<td>438</td>
<td>8.6</td>
</tr>
</tbody>
</table>

Curing conditions: [anhydride]/[functional group]= 1/1 in mol/mol. TG measurement was carried out in a nitrogen stream at the heating rate of 10°C/min.

3.2 Curing Using Difunctional Alcohols

The thermal curing using several difunctional alcohols, i.e., diethylene glycol, 1,4-butanediol, and 1,8-octanediol, was carried out. Fig. 4 shows the results for the curing of the copolymer by the diols for 0.5 or 1 h at different temperatures. As the curing temperature increased, the insoluble fraction values increased. The temperature required for the formation of a spread network structure, i.e., the rising point of the curves, was in the order of 1,4-butanediol < ethylene glycol < 1,8-octanediol. This result suggested an intermediate alkylene length was favorable for the occurrence of an effective crosslinking reaction in this thermosetting system. It was assumed that too short spacer of ethylene glycol was disadvantage for the complete reactions of the both hydroxy groups of the crosslinkers and that too long and flexible alkylene spacer of 1,8-octanediol was not suited to produce insoluble and rigid network polymers.

The thermal stability of these cured copolymers was similar to that for the linear polymer before crosslinking, as seen in the decomposition temperature values in Table 1. The reaction of the anhydride and alcohols slowly proceeded, while the epoxy curing led to the rapid formation of a crosslinked polymer in a quantitative yield under similar temperature conditions. In fact, the incomplete ring-opening of the anhydride moiety of the copolymers as the repeating units was confirmed during the reaction of the copolymer with methanol under reflux conditions for several hours. As a result, the crosslinking density was low for the alcohol-curing systems. The slow reaction between the anhydride and alcohols was confirmed by the change in the IR spectrum during the curing at different temperatures. The absorption due to the anhydride moiety...
remained after the reaction with 1,8-octanediol even at 180°C for 1 h (Fig.5). The use of glycerin as the trifunctional alcohol was also attempted to improve the process of curing reaction. As a result, a high insoluble fraction was obtained during the reaction with glycerin compared to the case with ethylene glycol and the other difunctional alcohols, as shown in Fig. 4. The detailed results for the thermal curing behavior using polyfunctional alcohols including glycerin will be reported elsewhere in near future.

3.3 Crosslinking Using Diamines and Postcuring

The reaction of the anhydride moiety of the copolymer with an amine immediately proceeded in a solution and quantitatively yielded an insoluble product at room temperature. In this study, we carried out the crosslinking reaction of the copolymer in THF by the dropwise addition of a dilute THF solution of the corresponding amines with stirring. The produced precipitant was filtered, dried, then characterized by IR spectroscopy. The isolated crosslinked polymers were further provided for the thermal curing to obtain the copolymers containing the maleimide repeating structure in the main chain (Fig. 5). The IR spectrum confirmed the formation of the maleamic acid polymers during the reaction of the anhydride with amines at room temperature (Fig. 6). It was also revealed that the heating at a high temperature range over 220°C was necessary for the process of quantitative transformation from the amide acid copolymer to the corresponding maleimide copolymer. The TG data also supported this conclusion (Table 1). The decomposition temperatures and the residue at 500°C were constant after the thermal curing at a temperature higher than 220°C. The endothermic dehydration reaction accompanying a weight loss was observed during the thermal analysis of the copolymer samples which were preheated at a temperature below 220°C for the imidization by thermal curing. These copolymers consisting of the maleimide and diene alternating repeating units in the main chain and the crosslinking structures formed between the intermolecular maleimide repeating units exhibited excellent thermal stability; the \( T_{d,5} \) and \( T_{d,50} \) values higher than 350 and 400°C, respectively, when the 1,6-hexanediamine was used as the crosslinker.

3.4 Ozone Degradation

The unsaturated carbon-to-carbon bond included in the main chain of the copolymers rapidly reacted with ozone and subsequently the scission of the polymer chains occurred by the reaction with triphenylphosphine as the reducing agent. This suggested the application of the quick degradation of the copolymer for the re-solubilization of the cured resins by ozonolysis. Actually, the cured copolymer was decomposed by ozonolysis, resulting in the re-solubilization of the cross-linked polymers. The insoluble fraction value of the copolymer decreased during the ozonolysis for several minutes. The re-solubilization rate of the diol-cured polymers was much higher than that of the epoxy-cured one (Fig. 7). This was due to the low crosslinking density of the diol-cured polymers, leading to the re-solubilization by less-frequent chain scission during the ozonolysis. The ozonolysis was also valid for modifi-
The slow curing process using polyfunctional alcohols significantly depended on the curing conditions, such as the structure of the alcohols and the curing temperature. The reaction of the copolymer with diamines immediately proceeded even at room temperature and the obtained amic acid copolymers were further converted to the crosslinked maleimide copolymers by thermal curing at a high temperature. It was also found that ozone degradation induced the cleavage of a carbon-to-carbon double bond in the polymer chains, leading to the re-solubilization of the crosslinked copolymers and their surface modification, i.e., the increasing hydrophilicity of the polymers.

References