Non-Stoichiometric Curing Effect on Dynamic Mechanical Properties of Bisphenol A-Type Epoxy Resins

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Abstract
The effects of non-stoichiometric curing on the dynamic compressive properties of bisphenol A-type epoxy resins were investigated experimentally to take into consideration the relation between mechanical properties and network structures in the epoxy resin. The yield stresses were found to be approximately linear to the strain rate regardless of crosslinking densities. Stress after yielding was clarified to rapidly reduce in epoxy resins with lower crosslinking densities and for higher strain rates.

Key words
Epoxy Resin, Non-stoichiometric Curing, Dynamic Compression, Mechanical Properties, Crosslinking Density, Strain Rate

1. Introduction
Epoxy resins are currently being widely applied to various fields of engineering, because they have excellent mechanical and insulation properties. Epoxy resins have also been used as matrix resins in composite materials. Therefore, the properties of the epoxy resins need to be improved to use them in the manufacture of advanced composite materials.

The mechanical properties of thermosetting resins are known to be governed by network structures in the resins. Resins with different network structures can be manufactured by incompletely curing them with non-stoichiometric mixtures of co-polymers and curing agents. The relations between the properties of epoxy resins and network structures have been discussed in several papers. Wingard and Beatty [1] reported that the glass transition temperature and secondary glass transition temperature of epoxy resins identified from thermo-viscoelastic properties were varied by non-stoichiometrically cured epoxy resins. Palmese and McCullough [2] found that the elastic modulus and glass transition temperature of epoxy resin were significantly affected by relatively small variations in stoichiometry. d’Almedia and Monteiro [3] showed that composites consisting of glass microspheres in epoxy resins fabricated with hardener-rich formulations had the best deformation capacity. Vanlandingham et al. [4] denoted the relation between microstructures in the epoxy resins and their properties as a function of epoxy-amine stoichiometry. Calvenus et al. [5] found that the glass transition temperatures of cured epoxy resins reduced their highest during stoichiometric curing. Fang et al. [6] improved the fracture toughness and flexural strength of nano-composites filled grapheme sheets into epoxy resin by modulating the stoichiometric ratio around grapheme sheets to construct a hierarchical structure that could dissipate more strain energy during fractures. Bignotti et al. [7] reported that epoxy-clay nano-composites and neat epoxy with the same stoichiometric ratio had basically the same crosslinking density. García et al. [8] studied the influence of stoichiometry on the curing of epoxy-clay nano-composites and their viscoelastic properties. The relation between network structures in epoxy resins and dynamic mechanical properties have not been considered. Therefore, the relation must be clarified to apply epoxy resins to advanced composite materials used in several industrial fields.

We experimentally clarified non-stoichiometric curing effects on the mechanical properties of bisphenol A-type epoxy resins. The epoxy resins were prepared by curing an excessive mixture of epoxide resin relative to the curing agent. The crosslinking densities and glass transition temperatures of the epoxy resins were identified from thermo-viscoelastic properties measured with dynamic mechanical analysis. Static and dynamic compression tests were conducted to measure the dynamic behavior of resins by using a universal material testing machine and a split Hopkinson pressure bar (SHPB) testing machine. Finally, the relations between crosslinking density and dynamic mechanical properties were found on the basis of static and dynamic compressive stress-strain curves.

2. Specimens
2.1 Materials
The materials for the specimens used in the study were bisphenol A-type epoxy resins. The epoxy resins were a blend of bisphenol A-type epoxide resin (Asahi Kasei E-Materials, AER 2603) with methyl-tetrahydro-phthalic anhydride (New Japan Chemical, RIKACID MH-700) as the curing agent and 2,4,6-tris (dimethyl aminomethyl) phenol (Mitsubishi Chemical, jER BM12) as the accelerator. The average molar weight of the epoxide resin was 380 moles and its epoxy-equivalent-weight was 188 grams/equivalent. The molar of the curing agent was 168 moles and its acid anhydride equivalent weight was 162 grams/equivalent. The stoichiometric mixture weight ratio of the epoxide resin, the curing agent, and the accelerator was 100: 86: 1.

The mixture ratios of the epoxide resin to the curing agent were changed to take into consideration the interaction between dynamic deformation and network structures in the resins. The changed mixture ratio will be expressed after this as the epoxy-equivalent-weight ratio (EEWR) defined by the epoxide resin weight over the stoichiometric epoxide resin weight. The EEWRs in the experiment ranged from 1.0 to 3.2, and the amounts of accelerator were kept constant at one. Therefore, for the case of EEWR = 1.0, i.e., in stoichiometric condition, complete network structures were formed in the cured resins and for EEWR > 1, network structures were formed incompletely due to the excessive

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mixture of epoxide resin. Epoxy resins having the EEWRs of over 3.2 were too weak to enable viscoelastic properties to be measured. We did not select EEWRs below 1.0 because unreacted curing agents might be transferred from the resins. The epoxy resins used in the experiment are listed in Table 1.

After the mixture of bisphenol A-type epoxide resin, the curing agent, and the accelerator was stirred, it was stored in a vacuum vessel to remove voids from the mixture and was poured into an aluminum mold coated with a Teflon sheet. The mold was 260 mm long, 5 mm wide and 120 mm deep. The mixture in the mold was heated for curing in an oven. The curing procedure was carried out in two steps. First, the mixture was kept at 373 K for 2 h to gel the matrix resin (pre-curing). Then, post-curing, which greatly affects the cross-linking reaction of the resin, was done at 403 K for 15 h. The heating rate from pre-curing to post-curing was constant at 72 K/h.

The densities of the cured materials were measured according to ASTM standard 792-08. The results are listed in Table 1. The densities of the epoxy resins were confirmed to be independent of the EEWRs.

2.2 Characterization

The dynamic mechanical properties of the epoxy resins were measured by using a dynamic viscoelastometer (Rheogel-E4000, UBM) with a non-resonance tensile method to identify crosslinking densities. The specimens were 40 mm long, 5 mm wide and 2 mm thick. The dynamic complex moduli of the specimens for tensile oscillation with a frequency of 10 Hz were measured each 1 K that ranged from 223 to 493K. The heating rate was 1 K/min.

Figure 1 plots the dependencies of the storage moduli, $E'$, and loss moduli, $E''$, of the epoxy resins on temperature with different EEWRs. The storage moduli of the resins decreased gradually as temperature increased in glassy states, and reduced rapidly; viz., glass transition occurred. After that, the moduli increased gradually in rubbery states. The storage moduli in the glassy and rubbery states, and the glass transition temperatures were clarified to be strongly dependent on the EEWRs.

The network structure can be expressed by the degree of cross-linking reactions. In terms of rubber elasticity theory for incompressible material, the crosslinking density, $n$, can be determined from the dynamic storage moduli, $E'$, in the rubbery state according to [7],

$$E' = 3nRT,$$  

where $T$ and $R$ are the absolute temperature and the gas constant (= 8.3145 J/(mol·K)). The glass transition temperature, $T_g$, was defined as the temperature at the maximum loss tangent, tan δ peaks.

The crosslinking densities were calculated from the storage moduli between $T_g + 30$ K and $T_g + 50$ K in Fig. 1(a) by using Eq. (1). Figure 2 shows the relation between the glass transition temperature and crosslinking density of epoxy resins.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>EEWR</th>
<th>Relative weight</th>
<th>Density $\times 10^3$ kg/m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP-10</td>
<td>1.0</td>
<td>100 86 1</td>
<td>1.20</td>
</tr>
<tr>
<td>EP-16</td>
<td>1.6</td>
<td>160 86 1</td>
<td>1.20</td>
</tr>
<tr>
<td>EP-20</td>
<td>2.0</td>
<td>200 86 1</td>
<td>1.20</td>
</tr>
<tr>
<td>EP-24</td>
<td>2.4</td>
<td>240 86 1</td>
<td>1.20</td>
</tr>
<tr>
<td>EP-28</td>
<td>2.8</td>
<td>280 86 1</td>
<td>1.20</td>
</tr>
<tr>
<td>EP-32</td>
<td>3.2</td>
<td>320 86 1</td>
<td>1.20</td>
</tr>
</tbody>
</table>

**Table 1** Epoxy resins in experiment
crosslinking densities and the glass transition temperatures with EEWRs. The crosslinking densities and the glass transition temperatures were found to have a linear relation. The crosslinking densities and the glass transition temperatures were inversely correlated with EEWRs. The epoxy resins with high EEWRs were confirmed to have low crosslinking densities. Therefore, the epoxy resin with higher EEWR > 1 had rougher network structures and lower entanglements between molecules.

3. Compression Tests

Static compression tests for epoxy resins were conducted to obtain stress-strain curves. The specimens were 10 mm long, 10 mm wide and 5 mm high. A specimen between two steel platens was compressed by using a universal material testing machine (Shimadzu, DCS-25T) with a displacement rate of 1 mm/min. The strain rate for the tests was approximate $3.3 \times 10^{-3}$ 1/s.

Dynamic compression tests for all epoxy resins were conducted to obtain stress-strain curves by using SHPB equipment (Fig. 3) [9]. The striker bar was 750 mm long and 20 mm in diameter. The input and output bars were 2 m long and 20 mm in diameter. Every bar was made of aluminum alloy (JIS A7075-T6). The specimens were 5 mm high, 10 mm wide and 10 mm long. The incident strain wave, $\varepsilon_I(t)$, the reflecting one, $\varepsilon_R(t)$, and transmitting one, $\varepsilon_T(t)$, to the specimens were evaluated from the strain histories, $\varepsilon_1(t)$ measured at the middle point of the input bar and $\varepsilon_2(t)$ measured at 500 mm from the tip of the output bar with strain gages (Kyowa, KFG-5-120-C1). The histories of stress, $\sigma(t)$, strain rate, $\dot{\varepsilon}(t)$ and strain, $\varepsilon(t)$ in the specimens were evaluated from the strains according to

$$\sigma(t) = \frac{AE}{A_s} [\varepsilon_I(t) + \varepsilon_R(t)] = \frac{AE}{A_s} \varepsilon_T(t), \quad (2)$$

$$\varepsilon(t) = -\frac{2C}{L_s} \int \varepsilon_a(\tau) d\tau, \quad (3)$$

$$\dot{\varepsilon}(t) = \frac{2C}{L_s} \varepsilon_a(t), \quad (4)$$

where $C$ is the velocity of the longitudinal stress wave in the bars and $A$ is the sectional area of the bars. $L_s$ and $A_s$ correspond to the thickness and sectional area of the specimens. The middle and right hand sides of Eq. (2) express stresses applied to the front and back faces of the specimens. The stress-strain curves of the specimens were calculated from the histories of stress and strain. The strain rates were evaluated by averaging the numerical results calculated from Eq. (4). The strain rates in the dynamic tests were ranged from 600 to 1500 1/s.

Figure 4 plots the strain histories, $\varepsilon_1(t)$ and $\varepsilon_2(t)$, in the input and output bars for a specimen, EP-16, as an example. The stress histories on the front and back faces of the specimens were evaluated from both strain histories in Fig. 4, as shown in Fig. 5. The stress histories on the front and back
Fig. 6 Stress-strain curves of epoxy resin

(a) Epoxy resin with crosslinking density of specimen: EP-10

(b) Epoxy resin with crosslinking density of specimen: EP-16

(c) Epoxy resin with crosslinking density of specimen: EP-20

(d) Epoxy resin with crosslinking density of specimen: EP-24

(e) Epoxy resin with crosslinking density of specimen: EP-28

(f) Epoxy resin with crosslinking density of specimen: EP-32
sides of the specimens were confirmed to coincide. Therefore, dynamic equilibrium in the SPBH test was found to be satisfied. The validities of the other SHPB tests were also confirmed.

4. Experimental Results

Figure 6 shows the compressive stress-strain curves of the epoxy resins listed in Table 1. No epoxy resin was broken within the stress-strain curves in Fig. 6. The interruptions in the stress-strain curves mean that stress and strain could not be measured until fracture occurred in the SHPB tests.

The compressive stress-strain curves for the stoichiometrically cured epoxy resin with EEWR = 1.0 are plotted for various strain rates in Fig. 6(a). After linearly elastic deformation, yielding occurred. The compressive stress varied rapidly after the region of constant stress. The compressive stress-strain curves were confirmed to be general.

As the strain rates increased, Young’s modulus increased due to the viscoelastic properties shown in Fig. 1 and the yield stress also increased. The non-stoichiometrically cured epoxy resin with EEWR = 1.6 and 2.4 in Figs. 6(b) to (d) had similar curves to those in Fig. 6(a). The yield stresses were approximately the same as those of the stoichiometrically cured resins under the same strain rates. However, the stresses in the regions of constant stress after yielding reduced.

Epoxy resins with lower crosslinking densities (larger EERW than 2.8) are shown in Figs. 6(e) and (f). Young’s moduli could be explained by viscoelastic properties. The yield stresses increased as the strain rate increased. The stresses rapidly and distinctly reduced after yielding. Softening after yielding was found in epoxy resins with low crosslinking densities.

5. Discussion

Figure 7 plots Young’s moduli measured with static compression tests at a strain rate of approximate $3.3 \times 10^{-3}$ 1/s. As the crosslinking density decreased, Young’s modulus decreased. Young’s moduli in Fig. 7 were confirmed to coincide with the relaxation modulus evaluated from the complex modulus in Fig. 1.

The yield stresses were determined as the peak values after the elastic regions in the stress-strain curves (Fig. 6). Figure 8 shows the strain rate dependence of yield stress. The yield stresses were found to increase for higher strain rates. The yield stresses were independent of the crosslinking densities and approximately linear to the strain rates. The strains at the yielding points were larger for higher crosslinking densities, because Young’s moduli were dependent on the crosslinking densities (Fig. 7). Therefore, the yield stresses would be insensitive to network structures and/or the entanglements between molecules in epoxy resins.

Figure 9 plots the ratio of minimum stress after yielding to yield stress in order to clarify softening after yielding. The results for the strain rate of approximate 600 1/s were eliminated because the compressive deformations at this strain rate were insufficient to measure the stress-strain curves after yielding by using SHPB tests. The ratio of stoichiometrically cured epoxy resin was approximately constant and independent of the strain rate. The ratio largely reduced as the crosslinking density decreased and the strain
rate increased. The ratio of epoxy resins having lower crosslinking density was sensitive to the strain rate. It seems that the entanglement of molecules in the resins was easily released after yielding due to low crosslinking density and high strain rate deformation.

In summary, Young’s moduli in epoxy resins for static and dynamic deformations reduced slightly due to non-stoichiometric curing, viz., lower crosslinking density in the epoxy resins. The yield stress was dependent on the strain rate regardless of non-stoichiometric curing. Softening after yielding increased as the crosslinking density reduced and the strain rate increased. Non-stoichiometric curing was clarified to affect dynamic compressive deformation in epoxy resins.

6. Conclusion
Non-stoichiometric curing effects on the mechanical properties of bisphenol A-type epoxy resin was experimentally clarified to take into consideration the relation between compressive behavior and network structures in the resin. The epoxy resins were prepared by curing an excessive mixture of epoxide resin relative to the curing agent. The crosslinking densities and the glass transition temperatures decreased for larger EEWRs. The crosslinking densities of the cured epoxy resins ranged from 490 to 2740 mol/m$^3$. Static and dynamic compression tests were conducted by using a universal material testing machine and a split Hopkinson pressure bar testing machine with the strain rates of $3.3 \times 10^{-3}$ to 1500 1/s.

Young’s moduli in epoxy resins for static and dynamic deformations reduced slightly due to non-stoichiometric curing, viz., lower crosslinking density in the epoxy resins. The yield stress was dependent on the strain rate regardless of non-stoichiometric curing. Softening after yielding increased as the crosslinking density reduced and strain rate increased. Non-stoichiometric curing was clarified to affect the dynamic compressive deformation of epoxy resins.

References