

Properties of Networks Obtained by Internal Plasticization of Epoxy Resin with Aromatic and Aliphatic Glycidyl Compounds

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Synopsis

In order to improve the fracture properties of *p,p'*-diaminodiphenylmethane-cured epoxy resin, various kinds of aromatic and aliphatic glycidyl compounds were investigated as a modifier at an amount of 30 wt %. Several compounds promoted the fracture toughness. In any glycidyl compounds, however, heat resistance was decreased by the modification. The dynamic mechanical properties of the modified epoxy resins were measured. The crosslinking density ρ was calculated from the theory of rubber elasticity, and the mechanical properties of the resins were discussed in regard to the crosslinking density. Tensile strength was scarcely affected by the crosslinking density. Elongation at break and Izod impact strength increased remarkably with decrease in crosslinking density. The fracture toughness K_{Ic} increased with decrease in crosslinking density except at small ρ .

INTRODUCTION

Epoxy resins have many excellent properties such as high mechanical strength, good adhesion, and electrically superior insulation. These balanced good properties lead the resins to be used in the wide range of industrial materials. However, conventional liquid epoxy resins are relatively viscous. The high viscosity of the resins is considered to be the cause of occasional difficulty not only in the casting of liquid resin into the mold, but in the production of fiber-reinforced composite materials by the wet impregnation process usually by the hand layup technique.

Both in the casting parts with resin/filler system and in the fibrous composites, the failure usually begins at the interface between matrix resin and fiber reinforcement.¹ It is important to improve the resistance of the matrix to the crack fracture. In other words, the improvement of the fracture toughness of the resin is desirable. Recently much more interest is concerned with this improvement. In particular, carboxy-terminated copolymers of butadiene and acrylonitrile has been strongly investigated as liquid rubber modifier of epoxy resins.²⁻⁴

Glycidyl compounds have one or more epoxy functional groups. These epoxy groups of the glycidyl compounds can react with amino hydrogen as well as an epoxy group of the resin, and bond to polymer chain in the curing process of the liquid epoxy resin. Therefore, in the case of modification of

epoxy resin with glycidyl compounds, there seems to be no tendency for the bleeding of the modifiers. The cured resin is supposed to show any loss of transparency. These defects are usually observed in the polymer blend consisting of two phase system with domain structure. However, at present, the effect of glycidyl compounds on fracture toughness of the epoxy resin has scarcely been investigated.

Recently we have investigated five glycidyl compounds as a modifier of an epoxy resin, and it is found that a difunctional glycidyl compound, polypropylene glycol diglycidyl ether, was more effective for an improvement in the fracture toughness of the cured resin than monofunctional glycidyl ethers.⁵ In the present study, we have investigated the effect of 10 glycidyl compounds, mainly consisting of difunctional glycidyl compounds, on the strength and fracture properties of DGEBA type epoxy resin.

EXPERIMENTAL

The epoxy resin used was bisphenol A type, Epikote 828 (Yuka-shell Epoxy Co.). Table I shows the glycidyl compounds used. In this table glycidyl compounds of V, VI, and VIII were produced by Sakamoto Yakuhin Kogyo Co., Ltd., whereas the other glycidyl compounds were products of Nagase Chemicals Ltd. The glycidyl compounds from I to VIII are difunctional, and those of IX and X are trifunctional or more. In glycidyl ethers of polypropylene glycol and polytetramethylene glycol, the number of repeating unit of alkylene oxide in V, VI, VII, and VIII were calculated on the basis of a weight per epoxide equivalent (WPE) to be approximately 5, 8, 16, and 14, respectively.

Thirty weight percent of glycidyl compound was mixed with the epoxy resin. In all of the mixed liquid resins, any phase separation and any loss of transparency was not observed even after standing overnight. *p,p'*-Diaminodiphenylmethane (DDM) was used as a hardener. The amount of DDM was 1.1 times of the stoichiometric amount. In order to dissolve DDM, the liquid resin was heated with mixing at 120°C for 20 min. The mixture was degassed under reduced pressure and casted between two glass plates. The liquid resin was cured at 80°C for 3 h and postcured at 150°C for 2 h. In the cases of modification with VII and VIII, the resins were cured at 90°C for 3 h. The thickness of the cured epoxy plates were adjusted to 6 mm.

The deflection temperature under flexural load (DTUL) of the epoxy resins were measured according to ASTM D648 under maximum fiber stress of 1820 kPa.

Dogbone-shaped tensile specimens, ASTM D638 type I, 13 mm wide and 180 mm long, were prepared by cutting epoxy plates with a band saw and by abrading with a belt sander. The tensile strength of the resin specimens was measured with an Instron testing machine Model 1114 with a grip separation of 115 mm and at a crosshead speed of 5 mm/min at 23°C. The tensile modulus and elongation at break were measured by use of an extensometer at a distance between grips of 50 mm.

The Izod impact strength of the modified epoxides was determined according to ASTM D256.

TABLE I
Properties of Modified Epoxy Resins

| Glycidyl compound | WPE ^a | Viscosity at 25°C (MPa s) | Tensile strength (MPa) | Impact strength (J/m) | K_{Ic} (MPa m ^{1/2}) | DTUL ^b (°C) | T_g (°C) | Crosslinking density ($\times 10^3$ mol/m ³) |
|---|------------------|---------------------------|------------------------|-----------------------|----------------------------------|------------------------|------------|---|
| None | (0) | 14,000 | 79.3 | 28 | 1.12 | 161 | 173 | 4.49 |
| Resorcine diglycidyl ether | (I) | 2000 | 85.6 | 30 | 1.04 | 150 | 156 | 4.20 |
| Neopentyl glycol diglycidyl ether | (II) | 450 | 80.5 | 34 | 1.22 | 125 | 133 | 2.63 |
| 1,6-Hexane diol diglycidyl ether | (III) | 370 | 75.4 | 44 | 1.42 | 110 | 123 | 2.82 |
| <i>o</i> -Phthalic acid diglycidyl ester | (IV) | 10,000 | 92.6 | 33 | 1.09 | 139 | 148 | 2.90 |
| Polypropylene glycol diglycidyl ether | (V) | 810 | 74.3 | 44 | 1.92 | 101 | 114 | 2.28 |
| | (VI) | 1300 | 68.6 | 38 | 1.80 | 88 | 109 | 2.53 |
| | (VII) | 1500 | 60.0 | 65 | 1.16 | 56 | 80 | 1.31 |
| Polytetramethylene glycol diglycidyl ether | (VIII) | 1400 | 46.5 | 46 | 1.37 | 53 | 82 | 1.21 |
| Triglycidyl tris(2-hydroxyethyl) isocyanurate | (IX) | 16,000 | 81.8 | 35 | 1.40 | 131 | 143 | 3.49 |
| Pentaerythritol polyglycidyl ether | (X) | 4000 | 77.9 | 28 | 1.30 | 120 | 134 | 3.84 |

^aThe value indicates the weight per epoxy equivalent of glycidyl compound.

^bDeflection temperature under load.

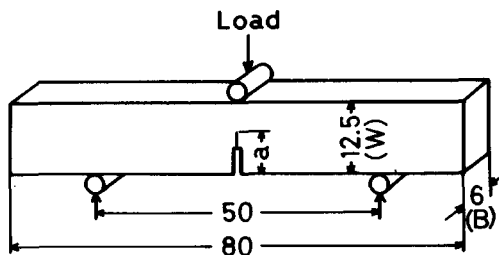


Fig. 1. Fracture test specimen (mm).

The plane-strain fracture toughness K_{Ic} of epoxy resins was measured according to ASTM E399-81 and Carisella's procedure with three-point bending test specimens.^{6,7} The dimensions of these specimens are shown in Figure 1. The specimens with dimensions of 6 mm (thick) \times 12.5 mm (high) \times 80 mm (long) had a 4.5 mm deep notch cut into them (by a band saw) followed by the introduction of sharp crack formed by tapping them with sharp razor blade at the base of the notch.^{5,7,8} The fracture toughness of the resins was measured with an Instron machine (using 50-mm span) at a crosshead speed of 1 mm/min at 23°C. The fracture toughness K_{Ic} of each specimen was calculated by

$$K_{Ic} = \frac{P_{\max} S}{BW^{3/2}} \cdot f\left(\frac{a}{W}\right) \quad (1)$$

where P_{\max} is the maximum load, a is the crack length, and $f(a/W)$ is a geometrical factor.⁶

Figure 2 shows the fracture surface of the fracture-toughness specimen of the unmodified epoxy resin. It is clear that beyond the notch an arrest line of precrack was formed. This initial crack then propagated by the application of the load. Most of the modified resin specimens showed similar fracture surface as that shown in Figure 2. However, on the basis of the results of both load-displacement curve and the fracture surface, the IV-modified resin specimen fractured somewhat "stick-slip" in nature.

The number of the specimens used for each measurement was 2 for DTUL test, 7 for the tensile test, 4-7 for the fracture toughness test, and 6 for the Izod impact test. Both the average and the range of these measurements will be presented in this article.

The dynamic mechanical properties of the epoxy resins were measured by a Dynamic Mechanical Spectrometer Model VES-N (Iwamoto Seisakusho Co., Ltd.) with specimen dimension of 2 \times 4 \times 40 mm, under an initial tensile force of 2.4N, at 10 Hz, at 2°C/min in air.

The overall features of the temperature dependence of the storage modulus E' in the cured modified resins were the same as those typically observed in conventional epoxy resins (see Fig. 3). As the vibration frequency was relatively small, the temperature at the peak of loss tangent ($\tan \delta$) was used as glass transition temperature T_g .

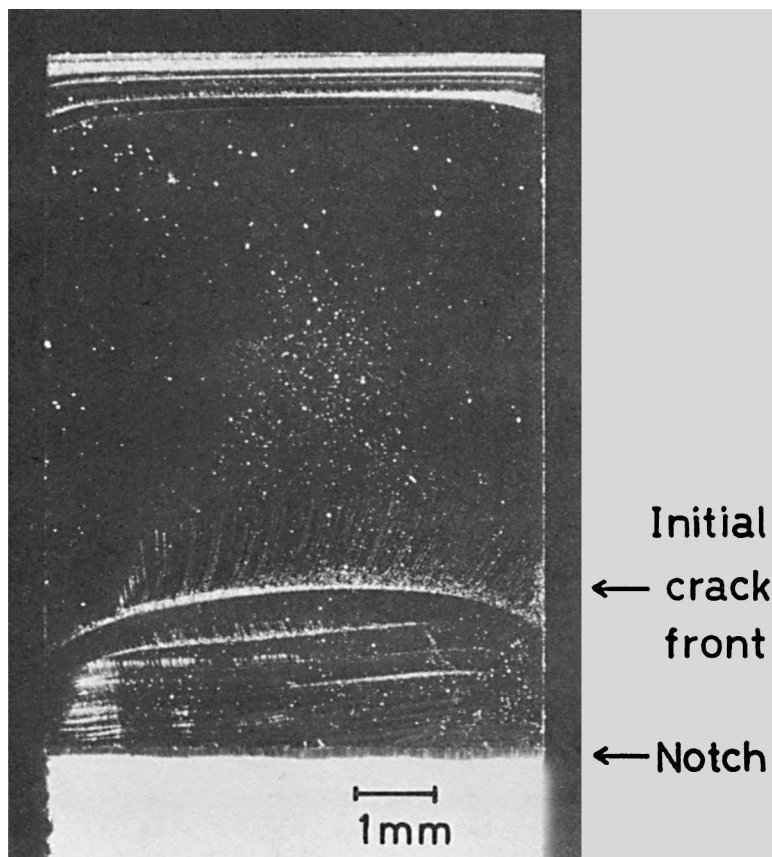


Fig. 2. Fracture surface of epoxy resin.

The crosslinking density ρ of a cured resin was calculated from the theory of rubber elasticity according to

$$E' = 3\phi\rho RT \quad (2)$$

where ϕ is front factor, E' is the modulus in rubbery plateau region at $T_g + 40^\circ\text{C}$, R is gas constant, and T is absolute temperature.^{9,10}

The front factor is a measure which represents a deviation from ideal rubber state, namely, for the ideal rubber ϕ , is unity. In an early work of an epoxy polymer, as the amount of amine hardener became stoichiometry, the value of ϕ was reported to be near 1.⁹ In the present study, in order to obtain cured resins with mechanically good properties, the amount of the hardener was chosen to be 1.1 times of stoichiometric amount. For the comparison purposes the front factor was assumed to be unity.

The crosslinking efficiency of the cured resin directly affects on the value of crosslinking density. In the curing reaction of difunctional epoxy resin with diamine, when only primary amine reacts, the value of crosslinking efficiency at the nitrogen become unity. As the relative crosslinking characteristic of

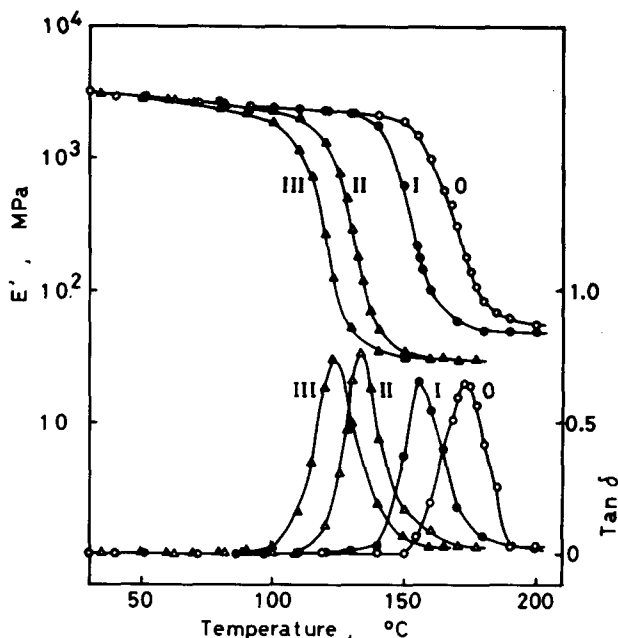


Fig. 3. Dynamic mechanical properties of modified epoxy resins; 0, I, II, and III indicate the resins in Table I.

modified resin will be discussed in the present study, the consideration of the crosslinking efficiency might be eliminated.

RESULTS AND DISCUSSION

Table I summarizes the properties of 30 wt % glycidyl-compound-modified epoxy resins. Generally the viscosity of the liquid epoxy resin was decreased by the modification. In the case of IV-modified resin, the tensile strength of the resin was largest. However, this strength decreased gradually with modification in the order of V > VI > VII > VIII. Izod impact strength of the resins modified by III, V, VII, and VIII was sufficiently larger than that of unmodified resin. V and VI were particularly effective for the improvement of the fracture toughness; however, VII was not. DTUL and T_g dropped largely by the modification with VI, VII, and VIII.

Figure 3 shows dynamic mechanical properties of unmodified and some modified epoxy resins. It is clear that in storage modulus E' -temperature curve, there are a glassy region, a glassy-rubbery transition region, and rubbery plateau region, as usually observed in typical epoxy resins.⁹ A modification with glycidyl compound caused a significant reduction in the temperature of the loss peak. The appearance of modified resin before and after curing was transparent, though colored to some extent, and any phase separation was not found with the naked eye. Both the appearance of the resins and the T_g reduction with addition of the modifier strongly indicated that the modified resin was homogeneous and that any phase separation did not occur.

In Table I the crosslinking density of the modified epoxy resins are shown. These values were calculated from the equation of rubber elasticity (2). The value of ρ was small in the cases of modification with V, VI, VII, and VIII. The crosslinking density is occasionally used in the consideration of thermal and mechanical properties of cured thermosetting resins with different chemical structure as a measure of structural characteristic of the polymer. In this report we will discuss the various properties of modified epoxy resins in regard to crosslinking density.

Figure 4 shows the relationship between tensile properties and crosslinking density. In small ρ , both strength and modulus increased with increase in ρ . However, beyond sufficiently larger ρ of ca. $2.5 \times 10^3 \text{ mol/m}^3$, the variation in the tensile values seems to become small with increase in ρ . The elongation at break was found to become small with increase in ρ . In DGEBA epoxy prepolymers of different molecular weight, cured with DDM, the tensile properties were reported to be basically unchanged with variation in the crosslink density, although there was a considerable scatter in the literature data.¹¹

The dependence of Izod impact strength on the crosslinking density shows that the smaller the crosslinking density was, the larger the impact strength became (Fig. 5). This result can be explained as follows: The larger crosslink-

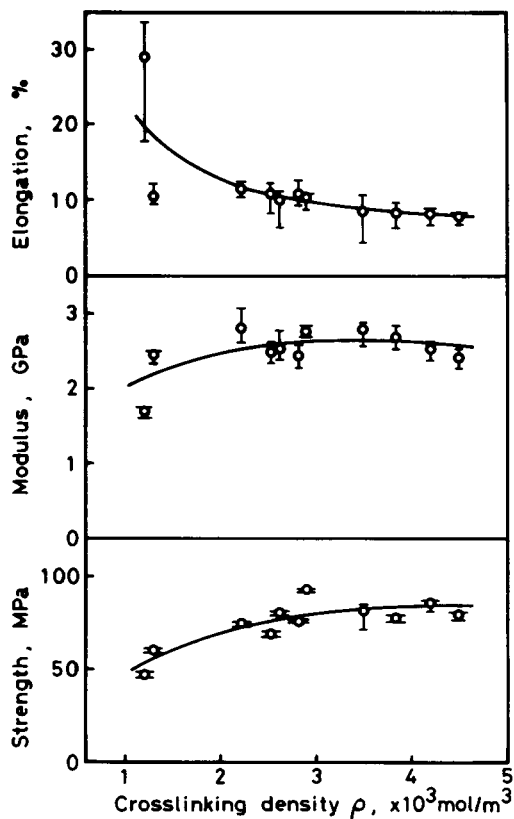


Fig. 4. Tensile properties vs. crosslinking density for glycidyl-compound-modified epoxy resins.

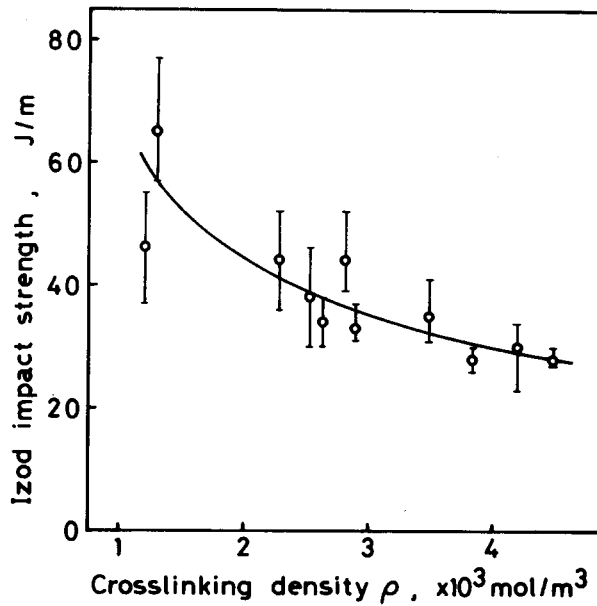


Fig. 5. Izod impact strength vs. crosslinking density for glycidyl-compound-modified epoxy resins.

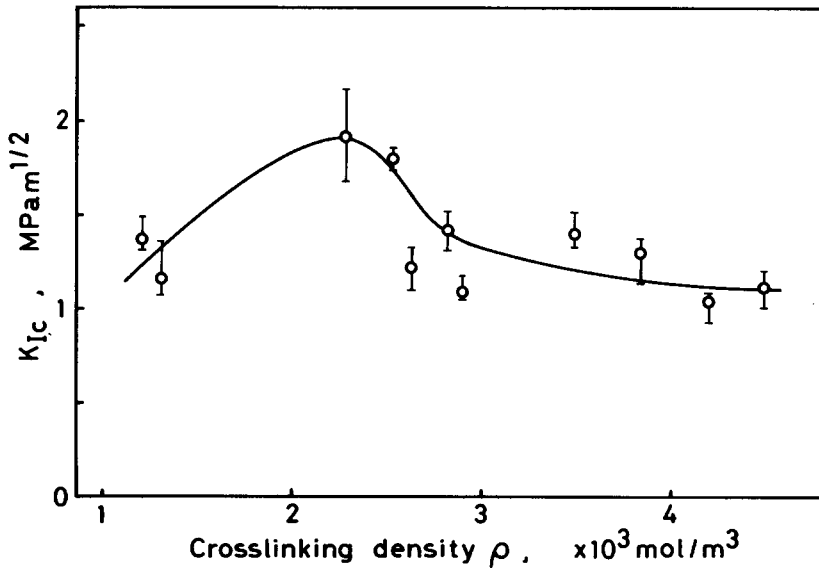


Fig. 6. Fracture toughness vs. crosslinking density for glycidyl-compound-modified epoxy resins.

ing density caused the polymer to be more rigid in structure and made them less resistible to the impact. A ductile or flexible material is favorable to fracture with crack branching and with more uneven fracture surface, requiring large energy to fracture.

The relationship between fracture toughness of modified resins and crosslinking density is shown in Figure 6. In the range of ρ larger than 2×10^3 mol/m³, the K_{Ic} of the resin decreased gradually with increase in the crosslinking density. However, when ρ was smaller than 2×10^3 mol/m³, the value of K_{Ic} was smaller than the value simply extrapolated by the $K_{Ic}-\rho$ relation obtained in ρ larger than 2×10^3 mol/m³.

In small ρ , the mobility of the polymer chains was supposed to become large. The plastic deformation in the small region of crack tip seemed to be large and larger energy was needed for the propagation of the crack, namely, the K_{Ic} was large.¹² However, the resistance to the crack propagation at the tip of a crack was supposed to be also governed by the easiness of the bond scission in the polymer chains. In the case of a very small value of crosslinking density, the number or the density of the polymer chains which aligned perpendicular to the plane of the crack propagation became insufficiently small. In such material, fewer polymer chains aligning vertically to the crack plane can be easily broken under small load; consequently, the crack propagation might be easy.

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Received October 14, 1987

Accepted May 18, 1988