

Pressure Dependence of the Curing Behavior of Epoxy Resin

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ABSTRACT: Epoxy resin of bisphenol A type/aromatic diamine system was cured under high pressure up to 1,000 MPa. Pressure dependence of the mechanical and thermal properties of cured epoxy resin was investigated. Mechanical properties such as Young's modulus, tensile strength and elongation at break, and the glass transition temperature decreased with increasing curing pressure, though high pressure showed no effect on density. The swelling ratio of the cured resin with toluene increased with increasing curing pressure, and the IR absorption band assigned to epoxy group remained for the epoxy resin cured at high pressure. These results show that high curing pressure increases the glass transition temperature, restricts the diffusion and collision of molecules and the rate of curing reaction slow down. Poor mechanical and thermal properties for the epoxy resin cured under high pressure are considered to be due to insufficient curing of these resins.

KEY WORDS Ultrahigh Curing Pressure / Epoxy Resin / Thermal Property
/ Mechanical Property / Curing Behavior /

Epoxy resin is used in many important fields as an excellent thermosetting adhesive and protective for metals and semiconductors. A lot of studies on the curing mechanism of epoxy resin¹ and also on the residual stress² at the interface between metal and epoxy resin were reported, but little is known about the effects of pressure on curing behavior. It is well known that many reactions which could not be carried out under normal pressure, for example, polymerization of ethylene, can be carried out under high pressure.³ Pressure is considered to take part in various reactions for a many

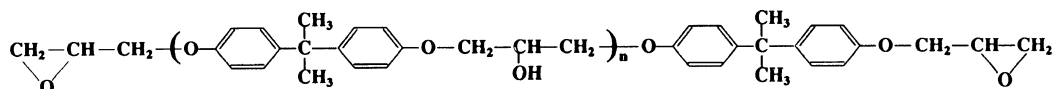
substances.

In this study, epoxy resin was cured under an ultrahigh pressure up to 1000 MPa, and the pressure dependence of the mechanical and thermal properties of cured epoxy resin was investigated.

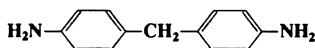
EXPERIMENTAL

Materials

A liquid diglycidyl ether of bisphenol A type epoxy resin (Epikote 828; Shell Chemical Co.; M_n 380, epoxy equivalent 190 ± 5 , $n=0.1$),



and 4,4'-diaminodiphenylmethane (DDM), an aromatic diamine curing agent,



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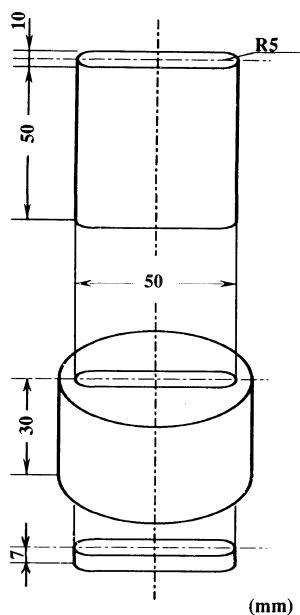


Figure 1. Schematic representation of the mold for curing at high pressure.

were used as the resin and curing agent in this study.

Preparation of Specimen

Epoxy resin was mixed with a stoichiometric amount (20.7 wt%) of DDM at 80°C, and the mixture was poured into a mold as shown in Figure 1. This mold could be pressed up to 1000 MPa and was heated with an electric heater up to 200°C through a volt slider, and the temperature was measured with a thermocouple inserted in the mold.

Figure 2 shows the typical curing process at high pressure (1000 MPa, 200°C, 1.5 h). The mixture was subjected to a pre-selected final pressure at room temperature followed by heating from room temperature to a curing temperature. It took 30 min to elevate the mold temperature to the required temperature, and after that the curing process was considered to start. After curing at 200°C for 1.5 h, the mixture was cooled down gradually while maintaining the pressure at 1000 MPa. When the temperature reached 120°C, which is below

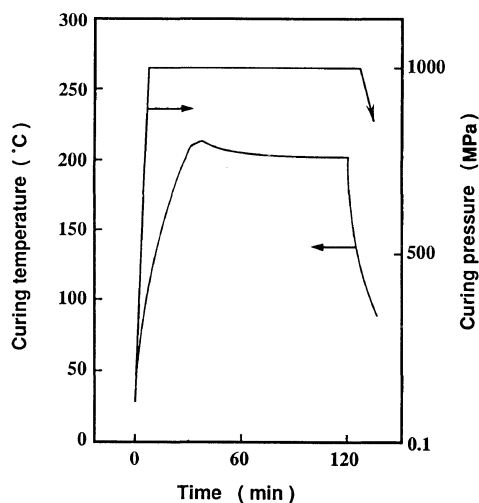


Figure 2. Relationships between curing temperature, curing pressure and time for a typical curing process.

the glass transition temperature, the pressure was released. The cured samples were 50 mm × 10 mm × thickness 1 mm. They were stored in a desiccator at room temperature.

Measurement

Mechanical properties of samples were measured by a tensile tester (Shimadzu, Autograph SD-100) at 25°C. The initial length of the specimen was 40 mm and the extension rate was 5 mm min⁻¹.

Thermal analysis was carried out on a differential scanning calorimeter (Daini Seikosha, SSC-560S) at a heating rate of 10°C min⁻¹ from room temperature to 200°C at ambient pressure. Sample weight was 10.0 mg. The system was calibrated with Indium. The glass transition temperature T_g and change in heat capacity ΔC_p were measured as described below.

The density of epoxy resin cured under various pressures was measured by a floating method using NaBr aqueous solution at 30°C.

The swelling ratio was evaluated by measuring the weight gain of a sample immersed in reflexing toluene for 4 h as follow:

$$\text{Swelling ratio} = (w - w_0) / w_0$$

where w , w_0 are the weight of swelled and original sample, respectively.

Infrared spectra were taken with FTIR (Shimadzu FTIR4200) spectrophotometer.

RESULTS AND DISCUSSION

Epoxy Resin Cured at 0.1 MPa

Figure 3 shows the relationship between the glass transition temperature T_g and curing time of epoxy resin cured under 0.1 MPa ambient pressure at 180°C and 200°C. T_g increased rapidly with curing time and reached a plateau at 167°C in both cases. Thus, it needs at least 1.5 h for sufficient curing at 200°C. In order to determine the best curing conditions at 0.1 MPa, the mechanical properties of epoxy resin cured at different temperature were investigated.

Figure 4 shows the relationship between Young's modulus, tensile strength, elongation at break of epoxy resin cured for 4 h and curing temperature. In all cases, the fracture processes were brittle type, and the stress-strain curves did not show clear yield points. Mechanical properties increased with increasing curing temperature followed by decrease at 220°C. The decrement at 220°C may be considered due

to thermal degradation. T_g of epoxy resin cured at 150°C for 4 h was about 145°C. Thus, the poor mechanical properties of epoxy resin cured at low temperature are considered due to insufficient curing. However, the density of the specimen was 1.197 g/cm³, which is just the same that at 200°C for 4 h. This indicates that density is not affected by curing degree, even though T_g and mechanical properties differed very much. In other words, T_g is a sensitive indicator whether curing is sufficient or not. As a result, epoxy resin cured at 200°C possessed both the highest T_g and best me-

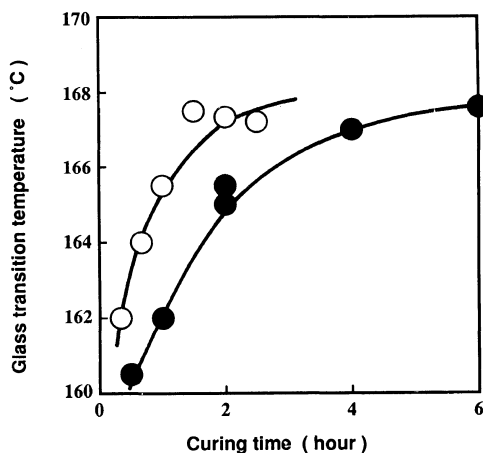


Figure 3. Relationship between glass transition temperature and curing time for epoxy resin cured under 0.1 MPa at (●) 180°C and (○) 200°C.

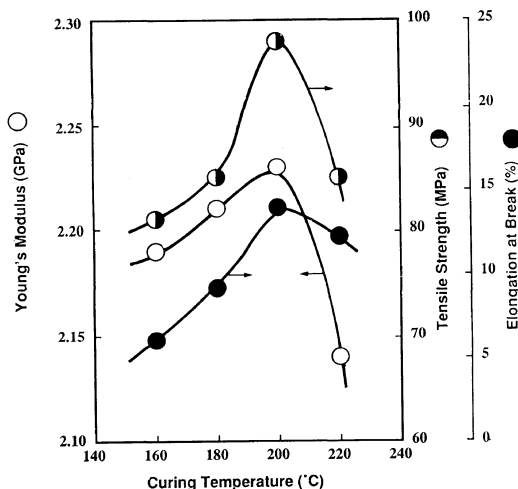


Figure 4. Relationship between (○) Young's modulus, (●) tensile strength, and (●) elongation at break and curing temperature for epoxy resin cured for 4 h.

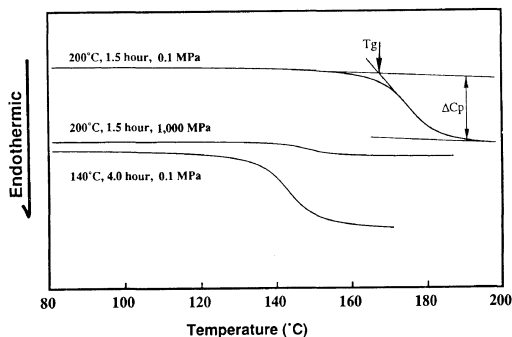


Figure 5. Thermograms of epoxy resins cured at 200°C for 1.5 h under 0.1 MPa, 1000 MPa, and at 140°C for 4 h under 0.1 MPa.

chanical properties in this system.

Epoxy Resin Cured at High Pressure

Figure 5 shows DSC thermograms of epoxy resin cured at 200°C for 1.5 h under 0.1 MPa and 1000 MPa, respectively. The thermogram for epoxy resin cured at 140°C for 4.0 h under 0.1 MPa is also shown in the figure. The arrow indicates T_g , and change ΔC_p in heat capacity with glass transition is defined as shown in figure. ΔC_p of the epoxy resin cured at 140°C,

0.1 MPa was almost as the same as that at 200°C, 0.1 MPa. However, epoxy resin cured at 1000 MPa showed both low T_g and low ΔC_p .

Figures 6 and 7 show the relationships between T_g , ΔC_p , and curing pressure for epoxy resin cured at 200°C for 1.5 h (filled circle) and 2.5 h (open circle). T_g decreased with curing pressure, and this tendency was more enhanced both for resins cured for 1.5 h and for those cured under a pressure of above 500 MPa. T_g and ΔC_p are affected both by the thermal history of the specimen and time of the experiment. Wunderlich *et al.* conducted the thermal analysis of glasses formed under elevated pressure.⁴ They reported that the lower temperature limit of the glass transition

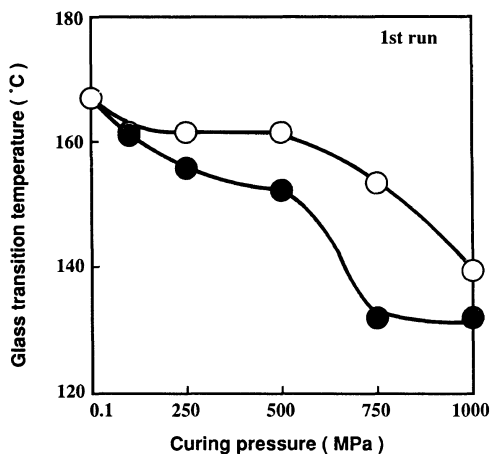


Figure 6. Relationship between glass transition temperature and curing pressure for epoxy resin cured at 200°C for (○) 2.5 h and (●) 1.5 h.

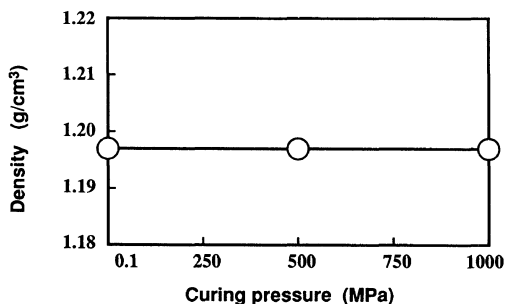


Figure 8. Relationship between density and curing pressure for epoxy resin cured at 200°C for 1.5 h.

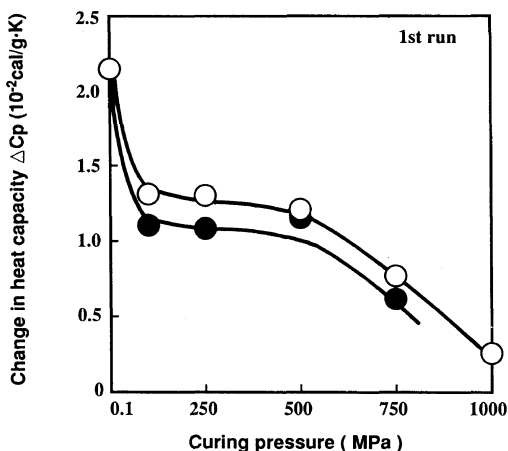


Figure 7. Relationship between change in heat capacity and curing pressure for epoxy resin cured at 200°C for (○) 2.5 h and (●) 1.5 h.

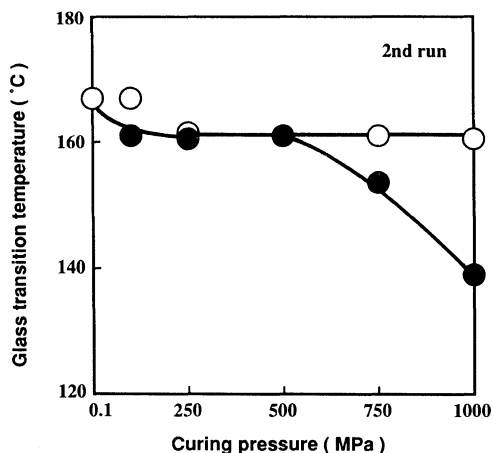


Figure 9. Relationship between glass transition temperature in the second run and curing pressure for epoxy resin cured at 200°C for (○) 2.5 h and (●) 1.5 h.

region shifted to lower temperature with increasing pressure, but the upper temperature limit of T_g was not significantly affected. This is in disagreement with the present data, in which both the lower and upper limits shifted to a lower temperature with increasing pressure.

Figure 8 shows the density of the epoxy resin cured at 200°C for 1.5 h under various pressures. While T_g and ΔC_p decreased with increasing pressure, density remained un-

changed. This indicates that the pressure induced densification did not occur for this system within experimental error.

Figures 9 and 10 show the relationships between T_g , ΔC_p , and the curing temperature of epoxy resin in the second run after heating to 200°C followed by slowly cooling to room temperature. T_g and ΔC_p became nearly the same as those under 0.1 MPa, except for T_g of epoxy resin cured for 1.5 h under a pressure higher than 500 MPa. To investigate these phenomena, a swelling test with toluene was carried out.

Figure 11 shows the relationship between curing pressure and swelling ratio for epoxy resin cured at 200°C for 1.5 h. The swelling ratio increased from 0.64% for 0.1 MPa to

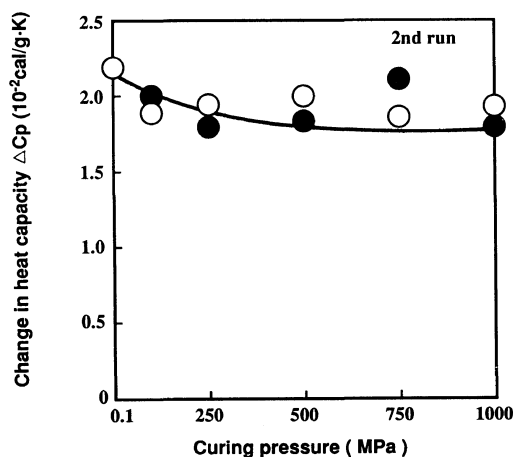


Figure 10. Relationship between change in heat capacity during the second run and curing pressure for epoxy resin cured at 200°C for (○) 2.5 h and (●) 1.5 h.

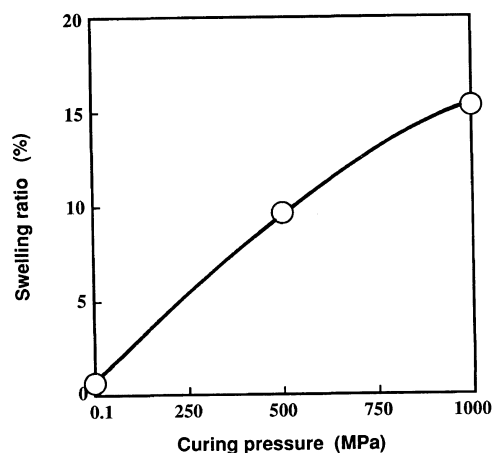


Figure 11. Relationship between swelling ratio with reflexing toluene and curing pressure for epoxy resin cured at 200°C for 1.5 h.

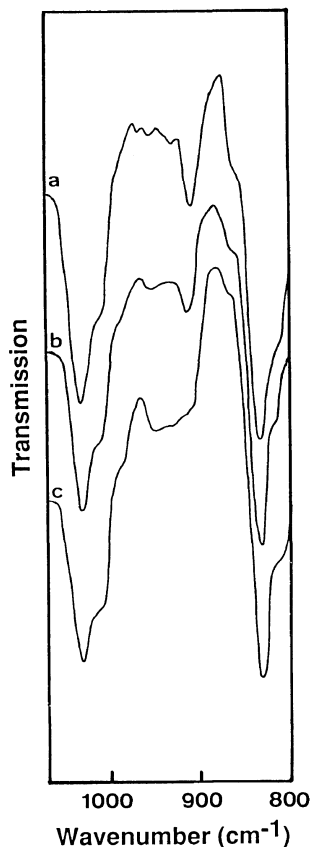


Figure 12. FT-IR spectra for epoxy resin cured under various conditions. a, 80°C, 1 h, 0.1 MPa; b, 200°C, 1.5 h, 1000 MPa; c, 200°C, 1.5 h, 0.1 MPa.

16.3% for 1000 MPa with increasing curing pressure. This indicates that crosslinking density decreased with increasing curing pressure. Thus, it is considered that high curing pressure would restrict the diffusion and collision of molecules, and accordingly, the rate of curing reaction would slow down. That is, it would take more time for epoxy resin to be cured completely at high pressure, and the glass transition temperature may increase. This is considered one reason for insufficient curing. The sample cured at high pressure may possess high T_g and sufficient cure, if cured at higher temperature and for a longer time provided thermal degradation does not occur. In order to clarify these points, the relationships between curing temperature/time/pressure should be examined. Hence, insufficient curing for the epoxy resin cured under high pressure is considered to be the cause of the decrement of T_g . This insufficiency was almost recovered after curing at 0.1 MPa as shown in Figures 9 and 10.

Figure 12 shows the FTIR spectra for epoxy resin cured under various conditions. The infrared band at 910 cm^{-1} may assigned to the epoxy group.⁵ This band was clearly observed for the resin cured at 80°C for 1 h. It disappeared for the epoxy resin cured under 0.1 MPa but it remained for that cured under 1000 MPa. This also supports insufficient curing for epoxy resin cured at high pressure.

Table I shows the mechanical properties of epoxy resin cured under various conditions. Because of the insufficient curing of epoxy resin under high pressure, properties were low compared with those cured at 200°C for 1.5 h under 0.1 MPa. Especially the tensile strength and elongation at break, in other words, mechanical properties at large deformation, depended strongly on curing conditions. This is considered due to mechanical properties in a small deformation region such as Young's modulus not being largely influenced by the

Table I. Mechanical properties of epoxy resin cured under various conditions

Curing condition	Young's modulus	Tensile strength	Elongation at break
	GPa	MPa	%
200°C , 1.5 h, 0.1 MPa	2.23	98.4	13.8
200°C , 3.0 h, 500 MPa	1.98	40.8	1.70
200°C , 5.0 h, 500 MPa	2.05	46.3	1.97
200°C , 1.5 h, 1000 MPa	1.39	18.5	1.45

number of crosslinkings in the glassy state.

CONCLUSIONS

Epoxy resin was cured under high pressure up to 1000 MPa. The glass transition temperature T_g , change ΔC_p in heat capacity and mechanical properties such as Young's modulus, tensile strength and elongation at break decreased with curing pressure. The high swelling ratio and residual IR band assigned to the epoxy group indicate that the cross linking density decreased with increasing curing pressure. It is considered that high pressure may restrict the diffusion and collision of molecules. Poor mechanical and thermal properties for epoxy resin cured under high pressure are considered due to the insufficient curing of the resin.

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