

# Curing Behavior and Properties of Epoxy Resins Cured with the Diamine Having the Quinoxaline or Triazine Structure

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**ABSTRACT:** 2,3-Bis(4-aminophenyl)quinoxaline (**1a**), 2,3-bis(4-aminophenyl)-6-methylquinoxaline (**1b**), and 5,6-bis(4-aminophenyl)-3-(2-pyridyl)-1,2,4-triazine (**2**) were studied as curing agents of epoxy resins. The exotherms on differential scanning calorimetry thermograms of the mixtures of diglycidyl ether of bisphenol A (DGEBA) with **1a**, **1b**, and **2** were observed at higher temperatures than that of the mixture of DGEBA with a commercially used diamine, for example, 4,4'-diaminodiphenylsulfone (DDS). However, the epoxy resin cured with **1a** (EP-**1a**) showed higher tensile strength to stainless steel at 20°C than that cured with DDS, and the high tensile strength of EP-**1a** was maintained even at 180°C. The epoxy resin cured with **1b** or **2** also possessed higher tensile strength at 20°C than that cured with DDS, but the high tensile strength lowered somewhat at 120°C. Using diamines **1a**, **1b**, and **2** as a curing agent improved heat distortion temperatures of the cured epoxy resins. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1737–1741, 1998

**Key words:** epoxy resins; aromatic diamines; curing agent; adhesive; thermal resistance

## INTRODUCTION

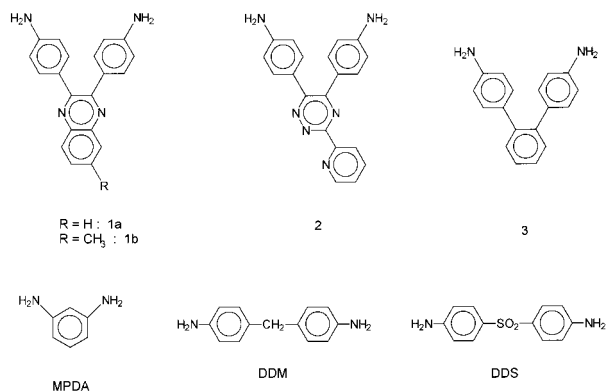
Epoxy resins have been known to possess good mechanical properties and excellent adhesive properties, and thus have been applied in various industries for coating, adhesive, flooring, and laminating.<sup>1,2</sup> However, one drawback in small numbers is low thermal resistance. In particular, when epoxy resins are used as adhesives, adhesive strength remarkably decreases as temperature heightens. Aromatic diamines are widely employed as curing agents of epoxy resins, but bonding strength of the epoxy resin cured with the aromatic diamine also lowers at high tempera-

tures. Although some modified aromatic diamines were investigated as curing agents to improve thermal resistance of epoxy resins,<sup>3–10</sup> their improvements have not been enough. In addition, curing with the aromatic diamine having a rigid structure is known to have an effect on improving the thermal resistance of epoxy resins, but using those diamines consequently accompanies lowering the processability because they have poor solubility in diglycidyl ether of bisphenol A (DGEBA). In many cases, the diamines were dissolved on heating or eutectic mixture was used.

It was previously found that the introduction of the heterocycle unit, such as the 2,3-quinoxalinediyl<sup>11–14</sup> or 1,2,4-triazine-5,6-diyl<sup>15,16</sup> structure, to the main chain of the aromatic polyamide heightened glass transition temperature as well as improved solubility in polar organic solvents,

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Scheme 1

attributed to the intermolecular dipole–dipole interaction between the heterocycle units in polymer chains or between a molecule of a polar solvent and the heterocycle unit in a polymer chain. In the present study, aromatic diamines having those heterocycles—such as 2,3-bis(4-aminophenyl)quinoxaline (**1a**), 2,3-bis(4-aminophenyl)-6-methylquinoxaline (**1b**), and 5,6-bis(4-aminophenyl)-3-(2-pyridyl)-1,2,4-triazine (**2**) as shown in Scheme 1—were studied as curing agents of epoxy resins. Curing behavior of DGEBA with the aromatic diamines and the properties of the cured epoxy resins were investigated. These properties were compared with those of an epoxy resin cured with 4,4'-diamino-*o*-terphenyl (**3**), of which the structure is similar to those of **1a**, **1b**, and **2** but having 1,2-phenylene unit instead of the heterocycles; or with those of epoxy resins cured with the diamines generally used, such as *m*-phenylenediamine (MPDA), 4,4'-diaminodiphenylmethane (DDM), and 4,4'-diaminodiphenylsulfone (DDS).

## EXPERIMENTAL

### Materials

The DGEBA used was EP-4100 (Asahi Denka Kogyo K. K., Tokyo, Japan; epoxy equivalent weight, 185;  $d$ , 1.16). MPDA, DDM, and DDS were commercially available (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), and used as received. Diamines **1a**,<sup>14</sup> **1b**,<sup>14</sup> and **3**<sup>17,18</sup> were prepared as reported previously. Diamine **2** was synthesized by the cyclocondensation of 4,4'-dinitrobenzil<sup>19</sup> with 2-picolinoamidrazone<sup>20</sup> forming a triazine ring,<sup>16,20</sup> followed by reduction using stannous chloride and hydrochloric acid.

### Tensile Test

A sample for tensile testing was prepared as follows. A surface of a test piece made of stainless steel ( $\phi$ , 1 cm<sup>2</sup>) was polished with alumina. DGEBA was mixed with a curing agent as a 1:2 molar ratio of an amino group/an epoxy group, degassed under reduced pressure, and applied to the polished test piece. Another test piece was bonded to the epoxy resin on the test piece and pressed under 7 kgf cm<sup>-2</sup> for 2 h at the fixed temperature (150–190°C) for curing. The bonded test pieces were cooled to room temperature, and tensile testing was carried out at 20, 120, and 180°C in a room held at the fixed temperature. After tensile testing, the fractured surface was examined by scanning electron microscopy (SEM).

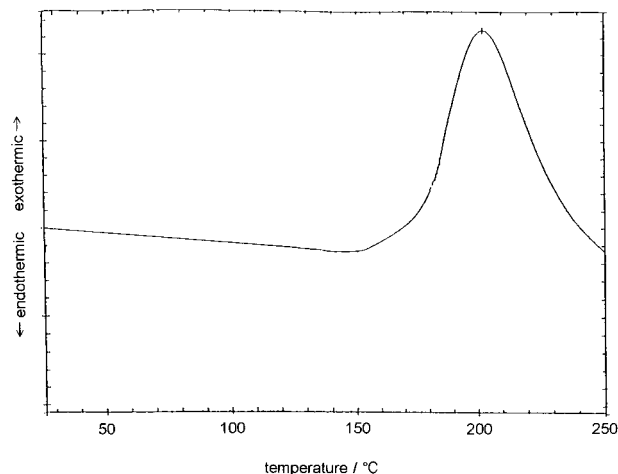
### Analysis

Thermoanalytical measurements by means of thermogravimetry (TG; MAC Science TG-DTA 2000) and differential scanning calorimetry (DSC; MAC Science DSC 3100S) were performed under a heating rate of 10 K min<sup>-1</sup> in a nitrogen atmosphere. Thermal mechanical analysis (TMA) by needle penetration method (MAC Science TMA 4000) was carried out according to the procedure of JIS K-7196 under the following conditions: heating rate, 5 K min<sup>-1</sup>;  $\phi$  of needle, 1 mm; load, 10 g. Tensile strength was measured with a universal testing machine (Shimadzu Autograph DSS-2000) at a cross-head speed of 1 mm min<sup>-1</sup>. SEM examination of the fractured surface was carried out using a Hitachi S-2100 SEM. The fractured surface was gold-sputtered prior to SEM examination.

## RESULTS AND DISCUSSION

### DSC Measurements of DGEBA–Diamines

Similar to primary and secondary amines, it is known that some tertiary amines also react with an epoxy group. DSC measurement of the mixture of DGEBA with 2,3-diphenylquinoxaline or with 4,5-diphenyl-3-(2-pyridyl)-1,2,4-triazine as a model compound, not having two amino groups, was carried out in order to investigate the reaction of the quinoxaline unit or the triazine unit with an epoxy group. On each DSC curve, no exothermic peak was observed up to 250°C. Accordingly, it was regarded that the quinoxaline structure in **1a** and **1b** or a triazine structure in **2**



**Figure 1** DSC thermogram of DGEBA-1a in a nitrogen atmosphere; heating rate: 10 K min<sup>-1</sup>.

does not react directly with an epoxy group. Thus, diamine content in DGEBA was calculated on the basis of epoxy equivalent weight as one amino group reacts with two epoxy groups.

To determine the curing temperature, DSC measurement of the mixture of DGEBA with the diamine was performed. Since diamines **1a**, **1b**, **2**, and **3** were soluble in DGEBA at room temperature, heating was not conducted and a solvent was not used. A typical DSC thermogram of the mixture of DGEBA with **1a** (DGEBA-1a) appears in Figure 1. On this DSC curve, a broad exothermic peak ranging from 130 to 230°C, of which the peak was at 202°C, was observed. Based on DSC curves,  $T_{\text{Bexo}}$  (the initial steep portion of the exotherm) and  $T_{\text{max}}$  (the peak) were determined; these results are tabulated in Table I. The exothermic transition of DGEBA-1a was found at a temperature higher not only than those of

**Table I** DSC Data for DGEBA-Diamine Systems

DGEBA-Diamine System	$T_{\text{Bexo}}$ (°C)	$T_{\text{max}}$ (°C)
DGEBA-1a	133	202
DGEBA-1b	122	190
DGEBA-2	121	179
DGEBA-3	57	137
DGEBA-MPDA	86	155
DGEBA-DDM	101	173
DGEBA-DDS	114	188

$T_{\text{Bexo}}$ , the initial steep portion of the exotherm;  $T_{\text{max}}$ , the exotherm peak.

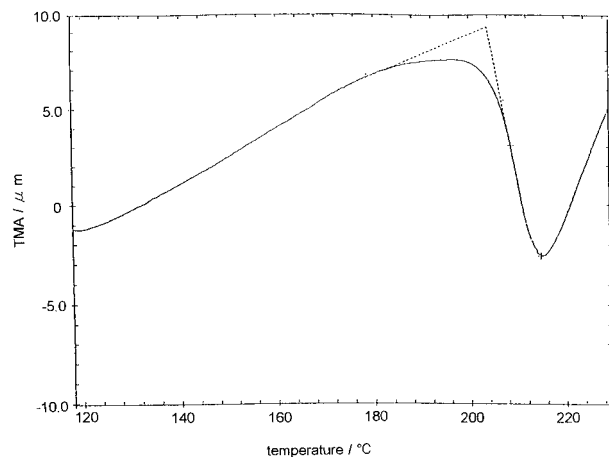
**Table II** Tensile Strength of Cured Epoxy Resins

Cured Epoxy Resin	Tensile Strength (kgf cm <sup>-2</sup> )		
	20°C	120°C	180°C
EP-1a	264	253	247
EP-1b	310	201	197
EP-2	283	229	189
EP-3	170	126	123
EP-MPDA	218	143	108
EP-DDM	208	172	139
EP-DDS	235	198	126

DGEBA with commercially employed diamines, such as MPDA, DDM, and DDS, but also than that of DGEBA-3. It is known that the polymerization of DGEBA with a diamine occurs via a nucleophilic attack of the amine nitrogen to the methylene carbon of the epoxy group, and that the exothermic transition strongly depends upon the nucleophilicity of an amino group. Because two aniline units in **1a** are not coplanar to the quinoxaline unit, a resonance effect does not have to be considered. The DSC thermogram of DGEBA-3 was observed as similar to that of DGEBA-MPDA, which suggests that the bulkiness of **1a** did not influence the reactivity of two amino groups as a steric effect. Therefore, the electron-attracting effect of the polar quinoxaline structure may make the nucleophilicity low. In the DSC thermograms of DGEBA-1b or DGEBA-2, similar broad exothermic peaks were observed; but these  $T_{\text{Bexo}}$ s or  $T_{\text{max}}$ s were somewhat lower than that of **1a**. The temperature for curing was fixed as that near the maximum slope of the exotherm on the DSC curve: i.e., DGEBA-1a, 190°C; DGEBA-1b, 180°C; DGEBA-2, 170°C; DGEBA-3, 150°C; DGEBA-MPDA, 150°C; DGEBA-DDM, 170°C; DGEBA-DDS, 180°C.

#### Adhesive Properties of Cured Epoxy Resins

A sample for tensile testing was prepared as follows. The mixture of DGEBA with the diamine was applied to a surface of a test piece made of stainless steel. Two bonded test pieces put together were pressed under 7 kgf cm<sup>-2</sup> at the curing temperature for 2 h. The tensile test was carried out at 20, 120, and 180°C, and results are summarized in Table II. The epoxy resin cured with **1a** (EP-1a) showed high tensile strength at 20°C as well as at 180°C. The value of the tensile



**Figure 2** TMA curve of EP-1a in a nitrogen atmosphere; heating rate: 5 K min<sup>-1</sup>.

strength was 264 kgf cm<sup>-2</sup> at 20°C, 253 at 120°C, and 247 at 180°C. Interestingly, high tensile strength of EP-1a to stainless steel was thus maintained even at 180°C. EP-1b indicated the highest tensile strength at 20°C in the used epoxy resin; the value was 310 kgf cm<sup>-2</sup>. But the tensile strength lowered at 120°C to a value of 201 kgf cm<sup>-2</sup>. At 180°C, the tensile strength was as high as that at 120°C. The relationship of tensile strength to temperature of EP-1a was obviously different from that of EP-1b, although the structure of 1a is similar to that of 1b. The reason is not clear. Tensile strength of EP-2 at 20°C also high (283 kgf cm<sup>-2</sup>), but the tensile strength decreased as temperature heightened. On the other hand, EP-MPDA, EP-DDM, and EP-DDS indicated lower tensile strengths at 20°C than those of EP-1a, EP-1b, and EP-2, and each tensile strength lowered remarkably as temperature heightened. In the typical case of EP-DDS, the value was 235 kgf cm<sup>-2</sup> at 20°C and that at 180°C was 126 kgf cm<sup>-2</sup>; i.e., the tensile strength at 180°C was half of that at 20°C. Thus, EP-1a, EP-1b, and EP-2 possessed excellent thermally stable adhesive properties to stainless steel.

The adhesive property of EP-3, having a 1,2-phenylene unit instead of the heterocycle units in 1a, 1b, and 2, was further investigated. Tensile strength of EP-3 at 20°C was the lowest of those of the epoxy resins used. Moreover, it decreased greatly at 180°C. This indicated that the excellent thermally stable adhesive properties of EP-1a, EP-1b, and EP-2 were not due to the characteristic zigzag and bulky structures of the diamines but due to the introduction of a heterocycle moi-

ety, such as the quinoxaline unit and triazine unit, to the structure of the curing agent. Thus, using 1a, 1b, and 2 as curing agents improved bonding strength of epoxy resins to stainless steel.

Fractured surfaces of test pieces after failure of the specimens under tensile loading were examined by SEM. Cohesive failure within the cured adhesive agent on all fractured surfaces of the bonded specimens was observed, and adhesive failure at the stainless-steel surface was not observed. This suggests that the adhesive properties depend primarily upon a cohesive power within cured epoxy resins because of the strong adhesion of epoxy resins to stainless steel at the interface.

### Thermal Properties of Cured Epoxy Resins

Heat distortion temperatures (HDTs) of the cured epoxy resins were determined by the needle penetration method of TMA. A typical TMA curve of EP-1a is illustrated in Figure 2, and HDTs are tabulated in Table III. The HDT of EP-1a was highest of those of the epoxy resins used; the value was 205°C. The HDTs of EP-1b and EP-2 were also high: 201 and 190°C, respectively. These HDTs were higher than those of EP-MPDA, EP-DDM, and EP-DDS as well as EP-3. These results suggest that the introduction of the quinoxaline unit or triazine unit to the structure of the curing agent has an effect on improving the HDT of an epoxy resin. This was attributed to the intermolecular dipole-dipole interaction between polar heterocycle segments of the polymer chains. The dipole-dipole interaction, presumably, may

**Table III** Thermal Properties of Cured Epoxy Resins

Epoxy Resin	HDT <sup>a</sup> (°C)	T <sub>d5</sub> <sup>b</sup> (°C)	Residual Weight at 600°C <sup>c</sup> (%)
EP-1a	205	359	34
EP-1b	201	358	32
EP-2	190	340	35
EP-3	167	366	29
EP-MPDA	135	354	20
EP-DDM	170	373	28
Ep-DDS	163	358	17

<sup>a</sup> Heat distortion temperature, determined by TMA. Scan rate: 5 K min<sup>-1</sup>, in a nitrogen atmosphere.

<sup>b</sup> Temperature at 5% weight loss, determined by TG. Scan rate: 10 K min<sup>-1</sup>, in a nitrogen atmosphere.

<sup>c</sup> Determined by TG.



improve a cohesive power within cured epoxy resins. The order of HDT of the epoxy resins roughly paralleled that of tensile strength at 180°C. The reason was considered to be that the adhesive properties depend mainly upon the cohesive power within the cured epoxy resins.

The thermal stability of the cured epoxy resins was investigated. The temperature at 5% weight loss ( $T_{d5}$ ) and residual weight at 600°C were determined by TG in a nitrogen atmosphere; these results are also shown in Table III. There was a slight difference in  $T_{d5}$ s of the epoxy resins used. On the other hand, residual weights at 600°C of EP-DDS and EP-MPDA were lower than those of the other epoxy resins. Considering that aromatic diamines **1a**, **1b**, and **2** do not have a thermally unstable linkage and are highly phenylated, the cured epoxy resins showed high thermal stability.

## CONCLUSION

It is concluded that the use of **1a**, **1b**, and **2** containing a heterocycle, such as the quinoxaline unit or triazine unit, as a curing agent of epoxy resins necessitated a higher curing temperature due to lower nucleophilicity, but had an effect on improving bonding strength to stainless steel as well as improving the HDT of the cured epoxy resins. In particular, the high tensile strength of EP-**1a** was retained even at 180°C.

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