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CURING BEHAVIOR AND PROPERTIES OF EPOXY RESINS CURED WITH THE DIAMINE HAVING HETEROCYCLIC RING

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ABSTRACT

Diamines having heterocyclic ring, 4,5-bis (4-aminophenyl)-2-phenylimidazole (BAPI), 4,5-bis(4-aminophenyl)-2-methyloxazole (BAPO) and novel diamine, 2,3-bis(4-aminophenyl)benzo[*g*]quinoxaline (BABQ) were prepared as curing agents for epoxy resin. Epoxy resins were obtained by curing diglycidyl ether of bisphenol A (DGEBA) with the above diamines. Properties of these DGEBA-diamine systems were studied and compared to that of DGEBA cured with commercially available diamine, 4,4′-diaminodiphenyl sulfone (DDS). On differential scanning calorimetry (DSC), the peaks of exotherms of the mixtures of DGEBA with these diamines having heterocyclic rings were observed at lower temperature and these reactions were completed in shorter time than that of DGEBA with DDS. The epoxy resins cured with these diamines containing heterocyclic ring showed excellent bonding strength even at high temperature and thermal resistance, e.g., DGEBA-BABQ gives greater bonding strengths as 35.1, 30.0, and 26.2 MPa when tested at 20, 120, and 180°C, respectively and residual weight at 600°C was 44% after being cured at 160°C for 2 hours. In the curing of DEGBA-BAPI, the reaction

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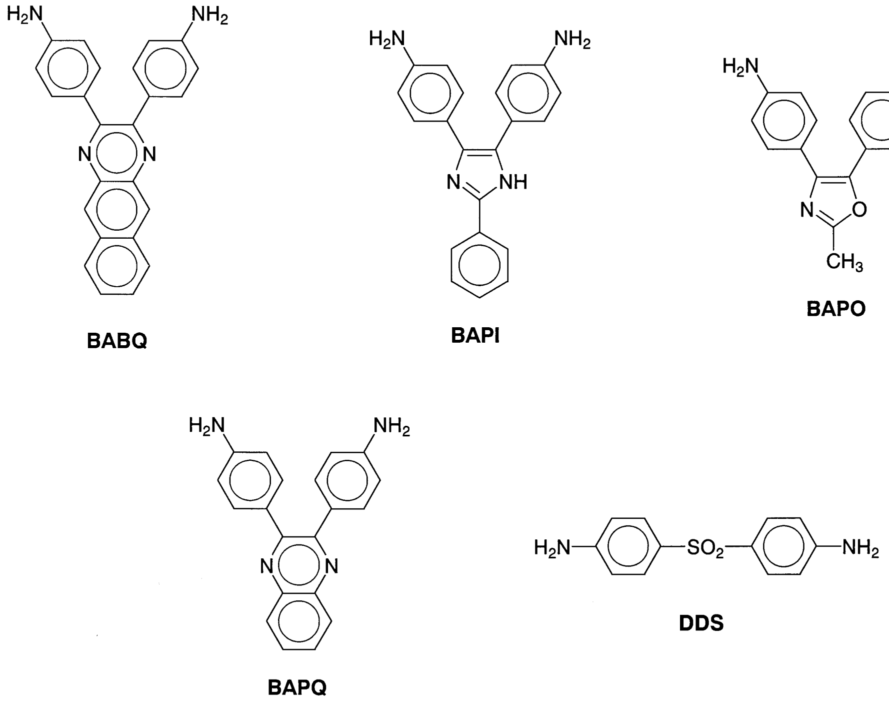
was accelerated and completed in a shorter time, but the bonding strength lowered somewhat, since the tertiary amine in the imidazole ring acts as catalytic curing agent which leads to epoxy homopolymerization.

Key Words: Epoxy resin; Structural adhesive; Bonding strength; Thermal resistance

INTRODUCTION

Structural adhesives based on epoxy resins are widely used in various industries because of their major advantage of processing without the use of diluents and evolution of volatiles during cure, along with their weight reduction. Despite the increased demand for the adhesives for high temperature resistance in aerospace and automobile field, epoxy resin's thermal stabilities are limited for their structure, even though they are highly crosslinked.

In our previous report [1], epoxy resins cured with aromatic diamines having heterocyclic ring, especially 2,3-bis(4-diaminophenyl)quinoxaline (BAPQ), displayed both excellent bonding strength and thermal stabilities. Although commercially available diamines, such as DDS, 4,4′-diaminodiphenylmethane or *m*-phenylenediamine have high bonding strength at lower



Scheme 1.

temperatures, they fall off markedly at elevating temperatures, while the epoxy resin cured with BAPQ's high bonding strength maintained even at 180°C.

In the present paper, we prepare other diamines containing heterocyclic ring, such as BABQ, BAPI, and BAPO as shown in Sch. 1 for the curing agent and study their adhesive strengths and thermal stabilities. The properties of BABQ were compared with those of BAPQ, for BABQ has another benzene ring attached to BAPQ.

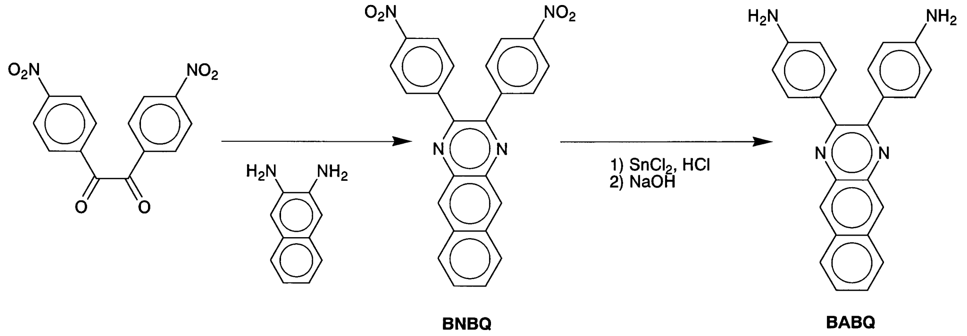
EXPERIMENTAL

Materials

The DGEBA used was EP-4100 (Asahi Denka Kogyo K.K., epoxy equivalent weight, 190). BABQ was prepared from 4,4′-dinitrobenzil followed by reduction of 2,3-bis(4-nitorophenyl)benzo[*g*]quinoxaline (BNBQ) as in Sch. 2.

BNBQ: 4,4′-Dinitrobenzil [2] 1.9 g (12.0 mmol) and 2,3-diaminonaphthalene 1.0 g (9.0 mmol) were refluxed in acetic acid (175 mL) for 6 hours and the mixture was cooled to room temperature [3, 4]. The precipitate was filtered and dried, then purified by recrystallization from methanol and dried in vacuo at 60°C for 24 hours. Yield: 2.3 g (85%). m.p. 260.1°C (DTA). I.R. (KBr: cm^{-1}) 1518 (NO_2), 836 (C-N), while 1672 (C=O) disappeared. E.A. calculated for ($C_{24}H_{14}O_4N_4$ 422.10): C, 68.23%; H, 3.34%; N, 13.26%. Found: C, 68.19%; H, 3.10%; N, 13.14%.

BABQ: BABQ was obtained by the reduction of BNBQ using stannous chloride and hydrochloric acid according to the method previously reported [5]. Results were as follows. Yield: 90%. m.p. 289.0°C. I.R. (KBr: cm^{-1}) 3440, 3340, 1606 (NH_2), 1344 (C-N, aromatic nitro). E.A. calculated for ($C_{24}H_{18}N_4$ 362.15): C, 79.54%; H, 5.01%; N, 15.46%. Found: C, 78.30%; H, 5.08%; N, 15.12%.



Scheme 2.

BAPI [6, 7], BAPO [8, 9], and BAPQ [1] were prepared according to the method previously reported. DDS was used as received from Tokyo Chemical Industry Co., Ltd. 2,4,5-Triphenylimidazole was prepared from benzil, benzaldehyde, and ammonium acetate similar to the method reported by Van Es and Backberg [8].

Measurements

DSC measurements were carried out on a MAC Science DSC 3100. Thermal mechanical analyses (TMA) were performed by means of the penetrometer on a MAC Science TMA 4000 under the following conditions: heating rate, 5°C min^{-1}; φ of needle, 1 mm; load, 10 gf. Thermoanalytical measurements were obtained by thermogravimetry (TG) on a MAC Science TG-DTA 2000 at a heating rate of 10°C min^{-1}. All the above measurements were carried out in a nitrogen atmosphere. I.R. spectra were recorded on a Hitachi 270-30 spectrophotometer. Molecular weight were measured by gel-permeation chromatography (GPC) with a TOYO SODA HCL-802UR type high speed liquid chromatograph equipped with a TOYO SODA G2500HXL type polystyrene gel columns at 40°C. THF was used as an eluent.

Tensile Tests

DGEBA and diamine were well mixed in an agate mortar for half an hour, applied on surfaces of polished stainless-steel test pieces (φ, 1 cm^2) and bound together under 0.7 MPa at fixed temperature for 2 hours to be cured. Then the test pieces were cooled to room temperature and kept at 20, 120, and 180°C for 15 min in the thermostat, respectively. Bonding strengths were measured at each temperature with a universal-testing machine (Shimadzu Autograph AG-10TB) at a crosshead speed of 1 mm min^{-1}.

RESULTS AND DISCUSSION

Reactivity of DGEBA-Diamines

All diamines used were solid at room temperature, but neither extra diluent nor being melted at elevated temperature was required, since they were miscible with DGEBA. Dynamic DSC measurements in raising the temperature by 5°C min^{-1} were carried out to determine the curing temperatures of DGEBA with diamines. Figure 1 shows the DSC curves of DGEBA-BABQ and DGEBA-BAPI, and the initial steep portion of the exotherm (T_i) and the exothermic peak (T_p) of mixture of the DGEBA with BABQ, BAPI or BAPO are listed in Table 1. Those of DGEBA-DDS and

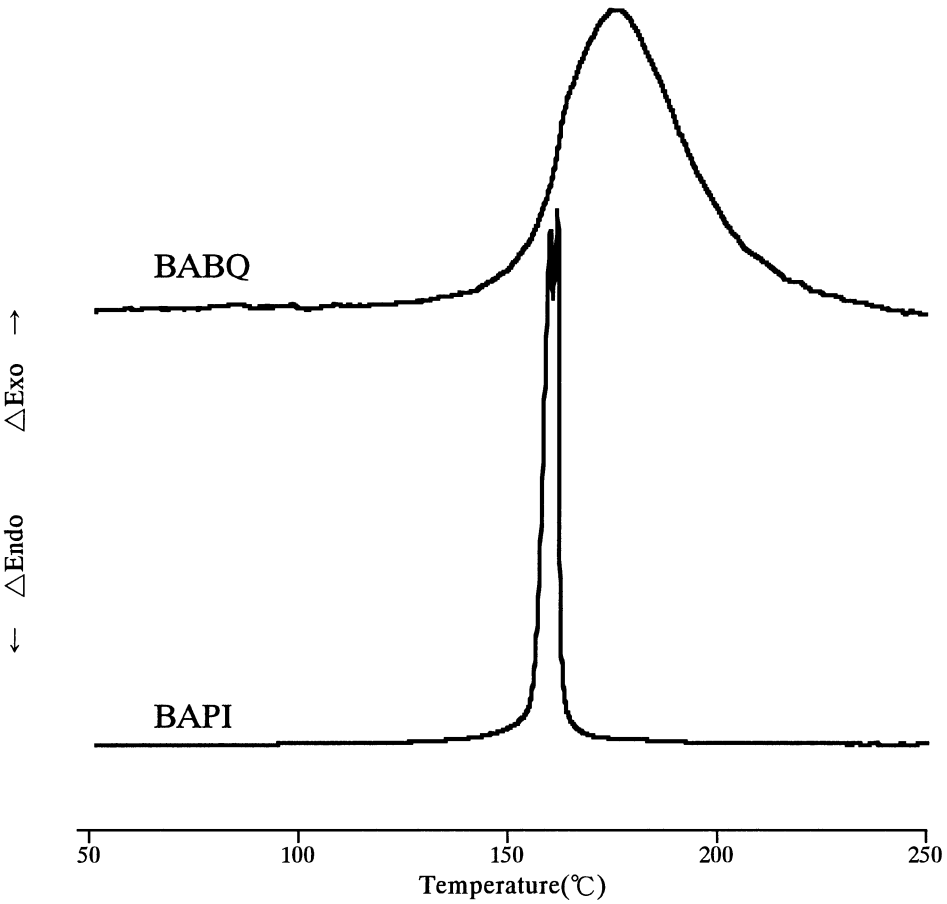


Figure 1. DSC thermograms of DEGEBA-diamine in a nitrogen atmosphere with heating rate of 5°C min^{-1}.

DGEBA-BAPQ are on Table 1 for the comparison. The exothermic peak of DGEBA-BABQ was broad and ranging from 123 to 222°C, which peak top was 176°C. Comparing the peak of DGEBA-BABQ to that of DGEBA-BAPQ, the peak of the former shifted to a lower temperature and also the T_p was 27°C lower than that of the latter. In our previous paper [1], we showed that bulkiness of BAPQ did not influence the reactivity of two amino groups as a steric effect, it is also proved by the fact that bulkier BABQ is more reactive than BAPQ with the epoxy group. This broad DSC curve DGEBA-BABQ is the typical of DGEBA-diamine systems except for DGEBA-BAPI.

As is different from DGEBA-BABQ type curve, that of DGEBA-BAPI was sharp and split at the peak top, which were 159 and 162°C. The split peak top suggested that the diamine reaction with epoxy groups was not only the reaction which occurred. It is known that a tertiary amine at position 3 of imidazole ring initiates epoxy homopolymerization and acts as a catalyst to

Table 1. DSC Data for DGEBA-Diamine Systems

DGEBA-Diamine	T_i (°C)[1]	T_p (°C)[2]
DGEBA-BABQ	123	175
DGEBA-BAPI	135	159, 162
DGEBA-BAPO	91	164
DGEBA-BAPQ	133	202
DGEBA-DDS	114	188

[1] The initial steep portion of the exotherm.

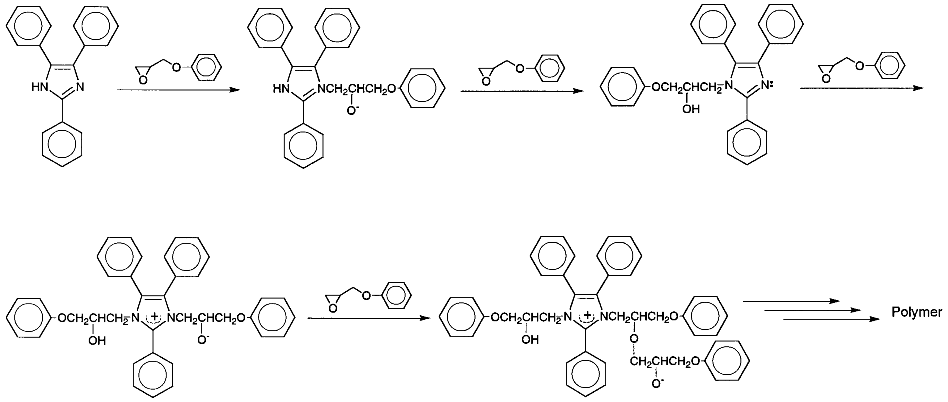
[2] The exotherm peak.

Measured in a nitrogen atmosphere with heating rate of 10°C min^{-1} on a MAC Science DSC3100.

accelerate epoxy reaction [10, 11], nitrogen in the imidazole ring of BAPI was also considered to react with DGEBA. As a model reaction, 2,4,5-triphenylimidazole, having no amino group, with 5 times molar weights of phenyl glycidyl ether, were mixed at 140°C for 2 hours, the polymeric material was obtained. Measurement with GPC indicated that the number-average molecular weight of the product was 6,000. Unsubstituted, mono- or di-substituted imidazoles were reported to initiate polymerization [12], also the 2,4,5-triphenylimidazole presumably initiates the polymerization as shown in Sch. 3.

As the ratio of diamine to DGEBA was calculated basically as one amino group reacts with two epoxy groups, that of BABQ and BAPO were calculated as one diamine monomer reacts with four epoxy groups, whereas the DGEBA-BAPI ratio was determined on the basis that one BAPI had six reactive functions.

The curing temperatures were fixed for the temperature near each epoxy resin's peak top on DSC curves. The curing temperatures for DGEBA-



Scheme 3.

diamine were fixed as follows: DGEBA-BABQ; 160°C, DGEBA-BAPI; 170°C, DGEBA-BAPO; 160°C. The isothermal DSC measurement of DGEBA-BABQ at 160°C showed that the exothermic reaction was completed in 30 minutes, and that of DGEBA-BAPI at 170°C, the exothermic reaction was completed in 17 minutes.

Tensile Tests

Tensile tests were carried out nine times at each temperature. Fractured surfaces of epoxy resins cured with BABQ, BAPO or BAPI were all attributable to cohesive failure. Table 2 shows the results of tensile testings. Bonding strengths of DGEBA-BAPO were 23.3, 17.0, and 15.4 Mpa at 20, 120, and 180°C, respectively and the results showed that the strength at 180°C was superior to that of DDS. Those of DGEBA-BAPI were 18.4, 17.3, and 13.6 MPa at 20, 120, and 180°C. These values were relatively low. As pointed out before, the reaction of DGEBA-BAPI is rather different from other DGEBA-diamine systems since the imidazole ring is considered to act as a catalyst to homopolymerize DGEBA. Generally, when the epoxy resin is cured with primary or secondary amines, the hydroxyl groups generated in the reaction are capable of reacting with other epoxide groups, thus increase the crosslink density. In contrast, DGEBA-BAPI system has higher epoxide content and presumably react as shown in Sch. 3. Thus hydroxyl groups are decreased relatively and yield the cured epoxy resin with lower crosslink densities, which reduced the bonding strength, while the catalytic curing agent greatly accelerated the cure. However, the advantage of epoxy resin cured with BAPI or BAPO was that the resin was clear, although that cured with BAPQ or BABQ was yellow.

Table 2. Bonding Strengths of Cured Epoxy Resins

		Bonding Strength[2] (Mpa)		
Epoxy Resin	Bonding Temperature (°C)[1]	20°C	120°C	180°C
DGEBA-BABQ	160	35.1	30.0	26.2
DGEBA-BAPI	170	18.4	17.3	13.6
DGEBA-BAPO	160	23.3	17.0	15.4
DGEBA-BAPQ	190	25.9	24.8	24.2
DGEBA-DDS	180	23.3	19.4	12.4

[1] The temperature at which stainless-steel test pieces were bounded under pressure of 0.7 Mpa for 2 h.

[2] Measured with a universal testing machine (Shimadzu Autograph AG-10TB) at a crosshead speed of 1 mm min^{-1}.

The DGEBA-diamine having benzo[*g*]quinoxaline for the curing agent provide maximum bonding strength as 35.1 MPa at 20°C, but it fell to 30.0 MPa at 120°C and to 26.2 MPa at 180°C. However, even at 180°C, DGEBA-BABQ gave 75% retention of bonding strength at 20°C. Previously, we reported that the DGEBA cured with BAPQ having quinoxaline unit showed high bonding strength at 20°C and the retention of 94% of that strength maintained even at 180°C [1]. Although the retention of the bonding strengths were not so high as DGEBA-BAPQ, strengths of DGEBA-BABQ having benzo[*g*]quinoxaline unit were greatest of all the diamines used at 20, 120, and 180°C.

Thermal Properties of Cured Epoxy Resins

TGAs were carried out at heating rate of 10°C min^{-1} in nitrogen atmosphere and results are shown in Fig. 2. T_{d5} (Temperature at 5%

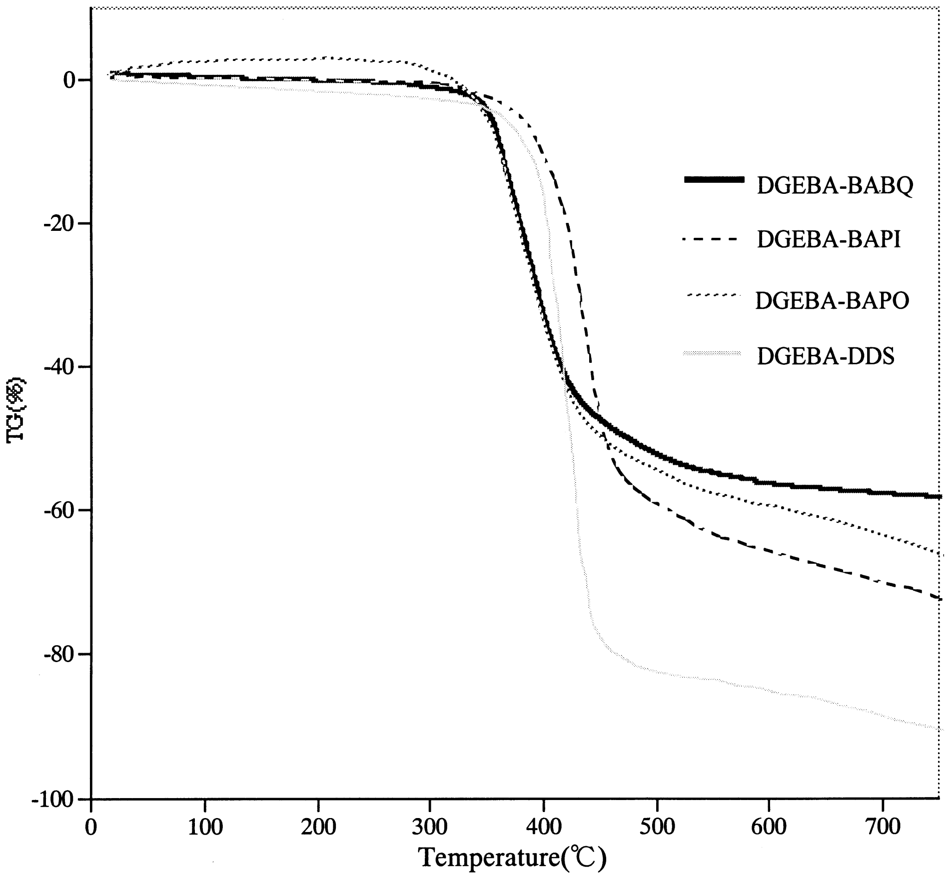


Figure 2. TG curves of cured epoxy resins.

Table 3. Thermal Properties of Cured Epoxy Resins

Epoxy Resins	T_{d5} (°C)[1]	Residual Weight at 600°C (%)[2]	HDT (°C)[3]
DGEBA-BABQ	354	44	186
DGEBA-BAPI	376	34	189
DGEBA-BAPO	346	40	177
DGEBA-BAPQ	359	34	205
DGEBA-DDS	358	17	163

[1] Temperature at which 5% weight loss was observed by TG with heating rate of 10°C min^{-1}.
[2] Determined by TG.
[3] Heat distortion temperature, measured by TMA, with heating rate of 5°C min^{-1}.
All measurements were carried in a nitrogen atmosphere.

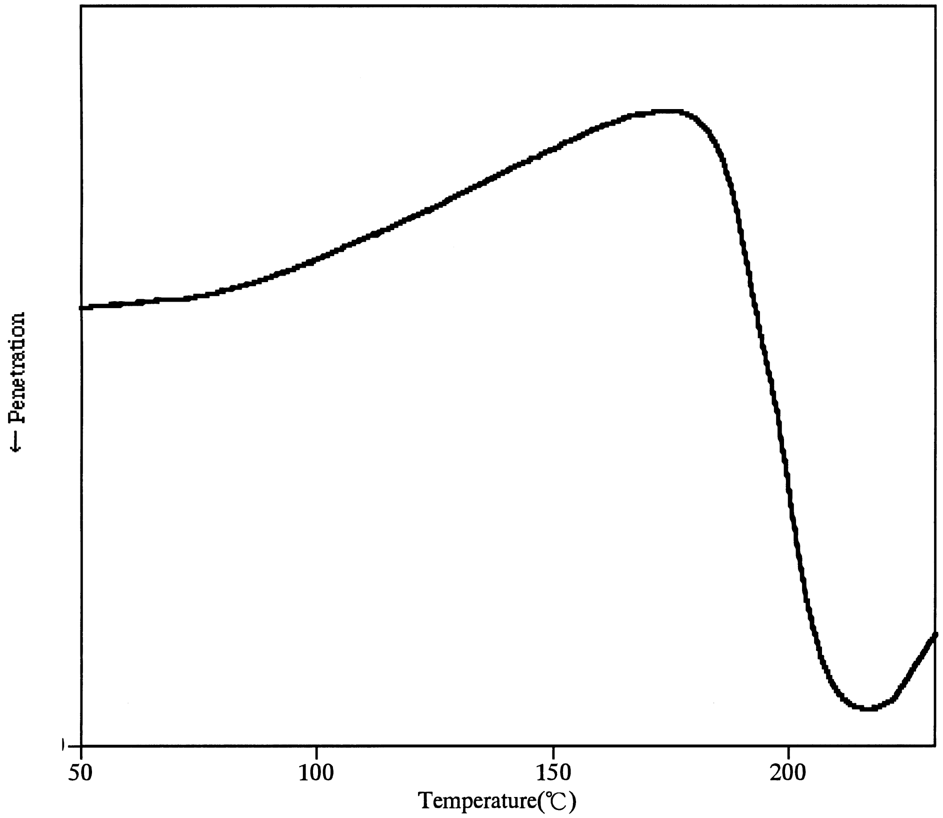


Figure 3. TMA curve of DGEBA-BABQ.

Table 4. HDTs[1] of DGEBA-BABQ

Curing Temperature (°C)	160	170	180	190
HDT (°C)	186	203	210	220

[1] Heat distortion temperature, measured by TMA with heating rate of 5°C min^{-1}.

weight loss was observed)s and residual weights at 600°C are summarized in Table 3. Figure 2 shows that T_{d5}s are ranging from 346 to 359°C and there's little difference in the T_{d5}s of epoxy resins cured with diamines. The degradation of the cured epoxy resin may occurred initially in the formation of an alkene derivative by volatilization of H_2O and the further degradation may take place at the N-C rather than C-C bonds [13, 14], indicating that heat resistance is not affected by the substitution of diamine.

Residual weights at 600°C of DGEBA-diamine systems in the present work were ranging from 34 to 44%. Using BABQ for the curing agent led to the 44% of the highest residual weight at 600°C. In addition to BABQ's high aromatic content, DGEBA is reactive with BABQ and the increase in the crosslink density due to its good reactivity improve the bonding strength and thermal property.

HDTs were measured with TMA by the needle penetration method. A typical TMA curve of DGEBA-BABQ is shown in Fig. 3. The results of epoxy resins cured by other diamines are listed also in Table 3. HDT of DGEBA-BABQ, DGEBA-BAPI and DGEBA-BAPO were 186, 189 and 177°C, respectively. These values were 14–27 degrees higher than that of DGEBA-DDS. In addition, HDTs of DGEBA-BABQ on different curing temperatures are shown in Table 4. The HDT of DGEBA-BABQ rose in according to the rising of curing temperature. When cured at 190°C, it showed as high as 220°C.

CONCLUSION

Three diamines, BABQ, BAPI and BAOP, containing heterocyclic ring were prepared as curing agent for epoxy resin. Epoxy resins cured with these diamines possessed high adhesive bonding strength and thermal resistance. Especially, the epoxy resin cured with BABQ showed excellent bonding strength and its high bonding strength at room temperature was almost retained even at 180°C. These results show that introduction of benzo[*g*]quinoxaline unit for a curing agent improves adhesive strength as well as high temperature resistance.

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