

Novel Cycloaliphatic Epoxy Resins. II. Curing Reaction with BF_3MEA and Its Cured Properties

MAKOTO TOKIZAWA,* HIROYOSHI OKADA, and NOBUKATSU WAKABAYASHI

Research Center, Mitsubishi Kasei Corporation, Kamoshida-cho 1000, Midori-ku, Yokohama 227, Japan

SYNOPSIS

The BF_3MEA curing reaction and the cured properties of novel cycloaliphatic epoxy resins (CE-resins), which were derived from an octadienyl compound, were studied. Gelation time and the DSC scan of the CE resins, with BF_3MEA hardener, proved that the reactivity of the CE resins is intermediate among the reactivities of the conventional resins; it was found that the CE resins react faster than DGEBA, but slower than the conventional cycloaliphatic epoxy resins. The pot life of the CE-(III) resin with BF_3MEA hardener proved to be over 30 days at a temperature of 20°C. The thermal properties are affected by the amount of BF_3MEA used and the curing conditions. CE-(III) showed the highest HDT of over 200°C with 2–3 phr of BF_3MEA . The flexural properties of CE-(I) proved to be flexible and tough. CE-(II) exhibited the highest strength and elongation, while CE-(III) had the same flexural properties as DGEBA. Furthermore, the blending of CE-(II) with DGEBA produced greater flexural strength and greater elongation than each original resin had. The thermal stability at elevated temperature and the water resistance of the cured CE resins proved to be inferior to those of DGEBA and novolac epoxy resin, probably due to the use of BF_3MEA . These results suggest the CE resin will provide a new application for a one-component curing system for composites. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The cycloaliphatic epoxy resins have low viscosity and specific reactivity. Their cured resins are generally well characterized by high HDT and excellent electrical properties, but are poor in mechanical elongation and toughness because of their compact molecular structure and their high crosslinking density.¹

In a previous article, a new family of cycloaliphatic epoxy resins (CE resins), which were derived from 2,7-octadienol-1, was introduced. These resins were shown to have moderate reactivity with acid anhydrides in the presence of amines and to be well balanced in cured properties. In particular, this novel resin family exhibited good water resistance, thermal stability at elevated temperature, and thermal shock resistance.²

Thus, it is interesting to study this novel epoxy resin, cured with cationic hardeners, such as BF_3MEA latent hardener.

BF_3MEA has been widely used as a latent curing agent for *bis*-phenol A epoxy resins for coating, varnishes, electric insulation, and fiber reinforcing materials. The BF_3MEA cured epoxy resins have good mechanical strength.^{3,4} However, there are few articles in the literature on the cycloaliphatic epoxy resins cured with BF_3 -amine complexes, because they have high reactivity and their prepreps could not be obtained without specific modification, such as prepolymerization of the monomeric epoxy resin.

Another reason for the few number of studies is that the BF_3MEA -cured cycloaliphatic epoxy resins do not have thermal stability and electrical properties at highly elevated temperatures, which are required for composite materials.⁴

A new type of cationic hardener has been developed which contributes thermal stability and good electrical properties at highly elevated tempera-

* To whom correspondence should be addressed.

tures.⁵ Therefore, it will be valuable if a new type of cycloaliphatic epoxy resin, one part prepreg, which has thermal stability and good electrical properties could be obtained.

In this article, however, we would like to describe the curing behavior and the cured properties of this novel cycloaliphatic epoxy resin using the BF_3MEA that could be easily evaluated and compared with the known conventional epoxy resin.

EXPERIMENTAL

Materials

Bis-phenol A type epoxy resin, Epikote 828, and novolac epoxy resin, Epikote 154, were obtained from the Shell Chemical Company and were used without purification. Glycidyl ether of hydrogenated *bis*-phenol A type epoxy resin, EP-4080, was obtained from the Asahi Denka Kogyo Company.

Cycloaliphatic epoxy resin, Araldite CY-175, was obtained from Ciba Geigy, while ERL-4206 and 4221 were obtained from U.C.C. Glycidyl ester of hexahydrophthalate, Epikote 191, was obtained from the Shell Chemical Company.

BF_3MEA was obtained from the Hashimoto Kasei Company.

Preparation of the CE Resins from Di-(2,7-octadienyl) Hexahydrophthalate and from Di-(2,7-octadienyl) Tetrahydrophthalate

These CE-(I), (II), and (III) resins were obtained by the procedure described in the previous article.² The idealized chemical structures are shown in Figure 1.

Characterization

The epoxy value of the resin or the prepreg was measured by tetramethyl ammonium bromide-perchloric acid titration. Differential scanning calorimetry was performed on a Perkin-Elmer DSC-1B calorimeter.

Heat Distortion Temperature (HDT) and Vicat heat softening temperature (HDT_v) were determined on a Toyo Seiki heat distortion testing machine by the method of ASTM D648-56. Flexural properties (ASTM-D790-63T) were determined on a Shimadzu Auto-graph (Model DDS-5000). Testing of weight loss at a high temperature was done by using specimens ($50 \text{ mm} \times 50 \text{ mm} \times \frac{1}{8} \text{ in.}$).

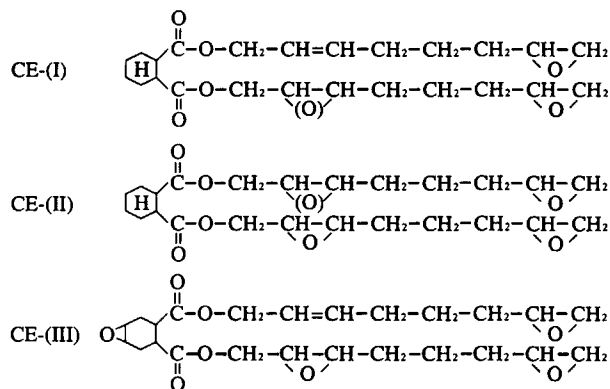


Figure 1 Idealized chemical structures of the CE resins.

Curing of the Epoxy Resin with BF_3MEA

One-hundred g of the CE-(III) resin was well mixed in various ratios with BF_3MEA and was heated to 80°C under reduced pressure until all the BF_3MEA was dissolved completely. The mixture was rapidly cooled to room temperature. The mixture was then poured into a preheated, Teflon-coated steel mold, was cured at 100°C for 4 h, and then was postcured under various conditions.

The commercial epoxy resins were also cured by the same procedure, but under the proper conditions for curing, because the cycloaliphatic epoxy resins were highly reactive and had to be cured under 90°C , followed by a postcure.

Determination of Gelation Time

A classical viscosimetric method was chosen. About 1 mL of the cooled mixture, which was obtained by the above curing procedure, was placed into a test tube (10 mm in diameter). The mixture was kept in an oil bath at a constant temperature. A glass bar (6 mm diameter) was dipped and rotated in the mixture by hand. The gelation time was determined at a time when the rotation of the bar could not be continued.

DSC Scan of the Model Reaction of the CE Resin with BF_3MEA

The mixture of 7,8-epoxy-2-octenyl acetate-1 (A), the terminal epoxide of 1-acetoxy 2,7-octadiene (1-AOD), with BF_3MEA (5 mol %), was obtained by the abovementioned procedure. Then 10 mg of the mixture was placed in an aluminum pan and was examined by DSC with a heating rate of $16^\circ\text{C}/\text{min}$.

from room temperature to 250°C in nitrogen atmosphere.

The reaction of 2,3-epoxy-7-octenyl acetate-1 (B), the inner epoxide of 1-AOD, with BF_3MEA and the reaction of dibutyl (4,5-epoxy)cyclohexyl-1,2-dicarboxylate (C) with BF_3MEA were also examined using the same method.

RESULTS AND DISCUSSION

Gelation Time of the CE Resins Cured with BF_3MEA

The cyclohexane epoxide-type epoxy resins are known to have higher reactivity with cationic hardeners than that of the glycidyl ether of *bis*-phenol A epoxy resins.^{4,6,7} Furthermore, the reactivity of the epoxide ring depends on its basicity.⁸ The gelation times of the CE resins, cured with BF_3MEA , are shown in Figure 2, in comparison with the typical commercial epoxy resins.

Because the gelation time of the epoxy resins, cured with BF_3MEA , is generally known to be affected by the number of functionalities (epoxide groups) in a molecule, by the concentration of BF_3MEA used, and by the purity of BF_3MEA because of its high hygroscopicity it is therefore difficult to evaluate quantitatively the reactivity of the

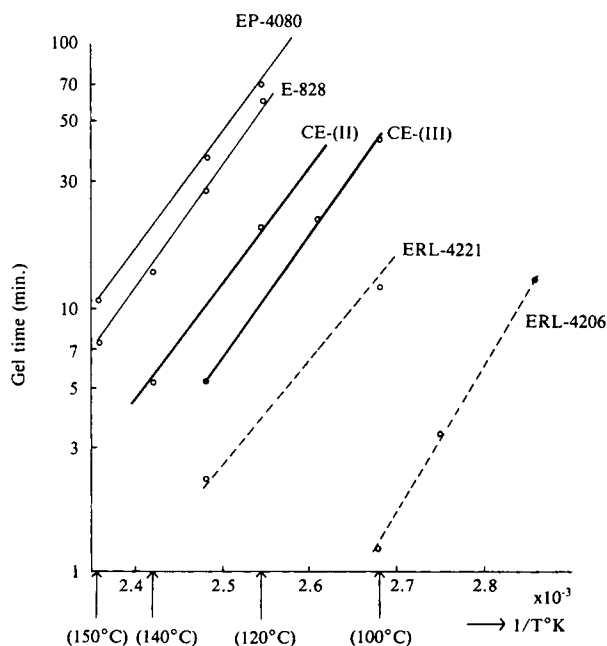


Figure 2 Gelation time of the BF_3MEA curing typical epoxy resins.

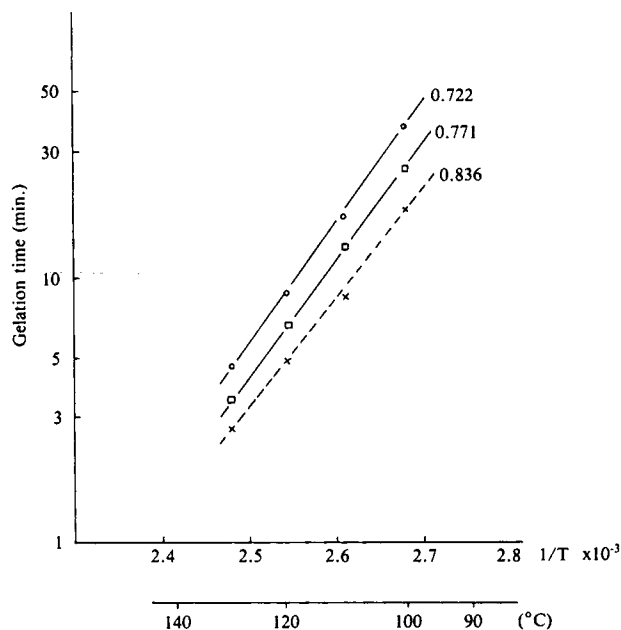


Figure 3 Gelation time of the BF_3MEA curing CE-(III): the effect of epoxy content.

epoxy resin from the gelation time. However, it is useful to understand the reactivity semiquantitatively, to determine the curing conditions, and also to evaluate the pot life of the resin mixture or the prepreg.

The results show that the gelation time of the CE resins is intermediate among those of commercial resins and is slower than those of the conventional cycloaliphatic epoxy resins, such as ERL-4206, 4221, and E-191.

Gelation of CE-(III), having one cyclohexane epoxide and at least one terminal and inner epoxide in the C_8 chain, is strongly affected by the epoxy content (Fig. 3) in comparison with the gelation time of the acid anhydride curing system.²

This result suggests that the reactivity of the terminal epoxide may be close to that of the inner epoxide, contrary to the case of the acid anhydride curing system. This functionality and the reactivity of each epoxide must also be considered when the prepreg is prepared under the conditions that are needed to give the proper flow characteristics.

DSC Scan of the BF_3MEA Curing of the CE Resins and of the Model Reaction

The DSC scan of the BF_3MEA -cured CE resins is shown in Figures 4 and 5, in comparison with the typical commercial resins.

As expected from the results of gelation time, the reactivity of the CE resins is intermediate among

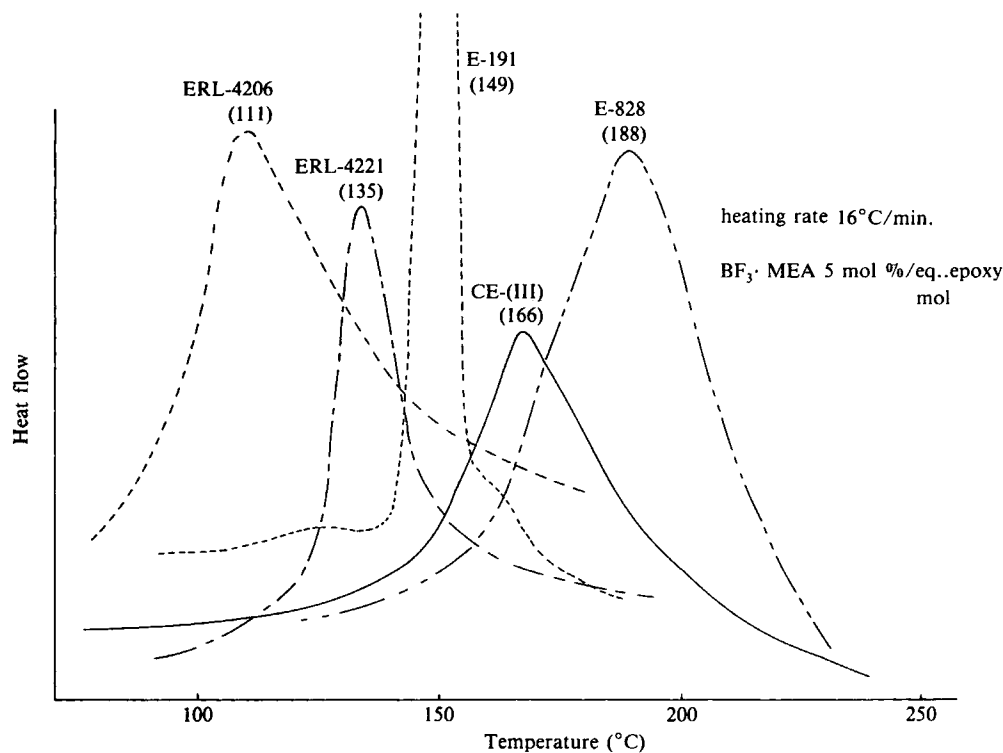


Figure 4 DSC thermograms of the BF₃MEA curing typical epoxy resins.

those of typical conventional resins, and the cycloaliphatic epoxy resins, such as ERL-4206 and 4221, are more reactive at lower temperatures than the CE-resins.

The order of the reactivity of resins is as follows:

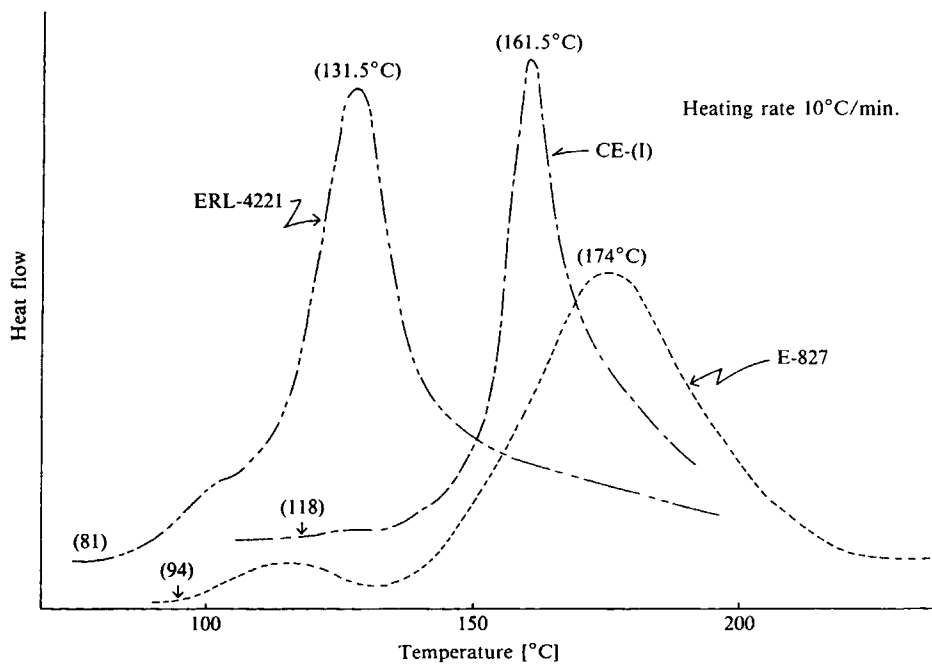
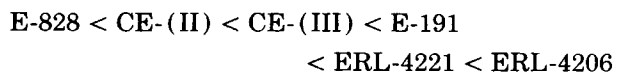


Figure 5 DSC thermograms of the BF₃MEA curing epoxy resins.

This order is explained by the result of the DSC scan of the model reaction using the terminal epoxide and inner epoxide of 1-acetoxy-2,7-octadiene (1-AOD), as shown in Figure 6.

The inner epoxide of 1-AOD (B), alkyl substituted glycidyl ester, proved to be more reactive at low temperature than the terminal epoxide of 1-AOD (A). Furthermore, the terminal epoxide proved to have a reactivity almost equivalent to that of phenyl glycidyl ether.

The above results of the gelation times and the DSC scan suggest that the prepreg of the CE resin-BF₃MEA system could be developed based on the stability of its shelf life and its retention of flow characteristics, provided that its temperature conditions are selected properly.

Pot Life of the CE Resin Containing BF₃MEA as Hardener

As shown in the introduction, the conventional cycloaliphatic epoxy resins have fast reactivity with BF₃MEA and a short pot life. Therefore, the prepreg of the cycloaliphatic epoxy resin, using BF₃MEA, could not usually be obtained without specific modifications, such as prepolymerization of the monomeric epoxy resin.

The reactivity of the CE resins on the curing with BF₃MEA is lower than those of conventional cycloaliphatic epoxy resins, which suggests the possibility of developing a prepreg of the CE resins.

The pot life of the CE-(III) resin, as shown in Figure 7, was 6 h at 60°C and 20 h at 50°C. The change in the epoxy content (84% of the original), under the same conditions, is also shown in Figure 7.

The shelf life of the prepreg, which was heat-treated for 10–12 min at 100–120°C after dipping into the MEK solution of CE-(III) resin, was over 30 days at 20°C. This value was consistent with the result of the pot life of the resin.

Thermal Properties of the Cured CE Resins

It is well recognized that the BF₃MEA curing of the epoxy resin proceeds through complex multiple steps of cationic character.^{9,10} Therefore, the thermal properties of the cured resin are expected to vary with the curing conditions and the amount of BF₃MEA used.^{3,4,11}

The thermal properties of the cured CE resins, under various conditions, are shown in Figures 8 and 9. The CE-(I) and (II) resins, which have at least one epoxide in the C₈ chain, could be cured with lower amounts of BF₃MEA as compared with E-828 and they showed lower HDT.

On the other hand, CE-(III), which has one additional cyclohexane epoxide, is strongly affected by the amount of BF₃MEA and showed a higher HDT over 200°C when 3 phr of BF₃MEA was used with a selected curing temperature of 175°C. When excess amounts of BF₃MEA were used, some decomposition

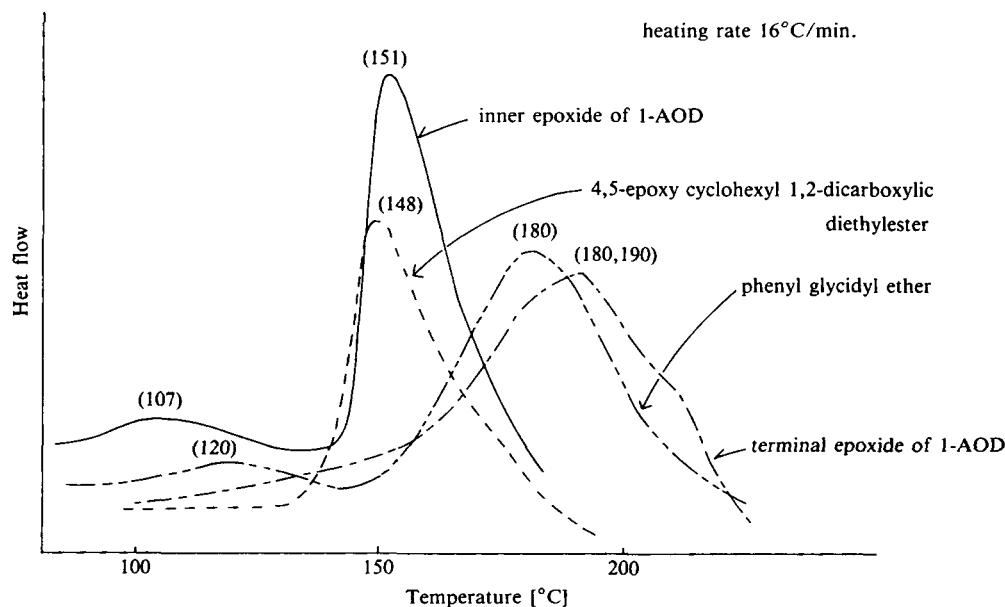


Figure 6 DSC thermograms of the model epoxy compounds, cured with BF₃MEA.

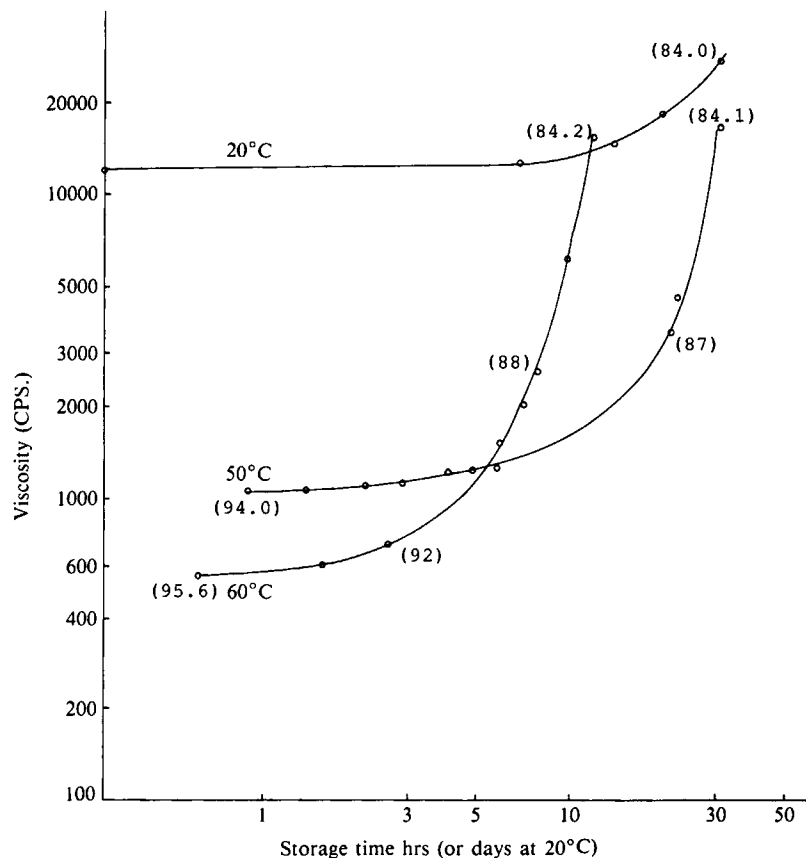


Figure 7 Viscosity change of the mixture of CE-(III) with BF_3MEA .

of the cured resin occurred and a lower HDT was observed, especially when it was postcured at highly elevated temperatures.¹²

Mechanical Properties

The mechanical properties of the cured epoxy resin are considered to be important, especially when used in composite materials. As reported in a previous article, the flexural properties of the HHPA-cured CE resins are nearly equivalent when compared to the commercial resins. However, the mechanical properties of the BF_3MEA -cured resin are supposed to vary, depending on the amount of BF_3MEA and the curing conditions based on the results of thermal properties.^{3,13,14}

Typical flexural properties of the BF_3MEA -cured CE resins are shown in Table I, which shows good mechanical strength and elongation.

The CE-(I) yielded a flexible and tough cured resin with almost the same properties using 1 phr and 3 phr of BF_3MEA , contrary to the behavior of the CE-(III) and E-828 resins.

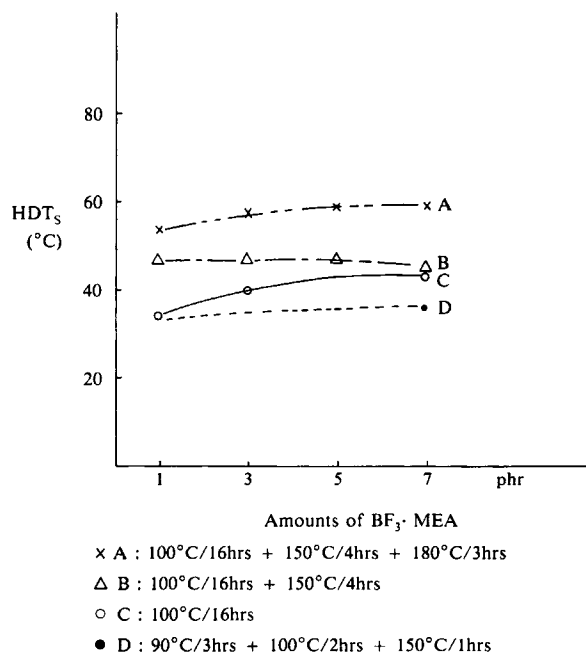


Figure 8 HDT_s changes of the BF_3MEA cured CE-(II) under the typical curing conditions.

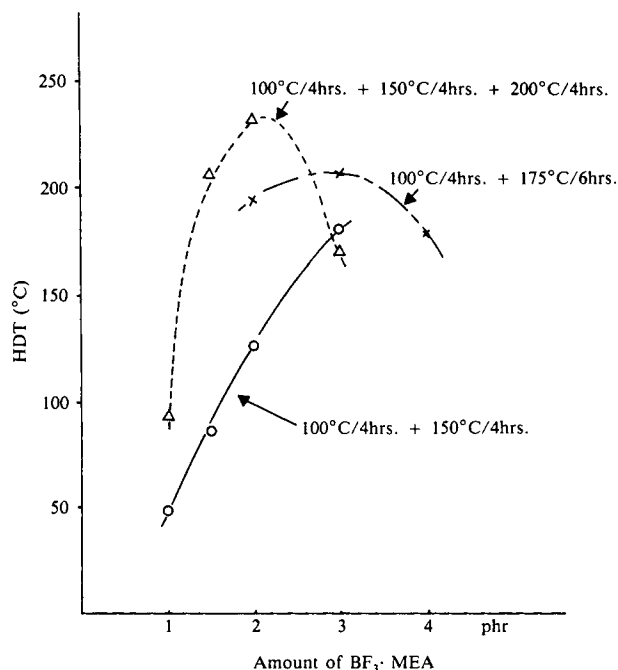


Figure 9 HDT changes of the BF₃MEA cured CE-(III) under the typical curing conditions.

The CE-(II) showed the highest strength among CE resins, and larger elongation than the CE-(III), which has almost the same properties as the E-828. This result suggests the need for further evaluation of the blending of the CE-(II) and E-828 resins. The flexural properties of the cured blending resin are shown in Table II. These results are interesting because the flexural strength of the cured blending resins are increasing without a sacrifice in elongation, as compared to those of the original CE-(II)- and E-828-cured resins.

Thermal Stability

The thermal stability of the BF₃MEA-cured epoxy resin is known to be affected by the amount of

BF₃MEA and to have a tendency to yield char at highly elevated temperatures.³ The cycloaliphatic epoxy resin, which has no aromatic nuclei, suggests the instability of the BF₃MEA-cured resin is due to the generation of acidic decomposition molecules or carbonium ion species.^{15,16}

The weight loss and the change in flexural strength of the BF₃MEA-cured CE-(III) are shown in Figures 10 and 11. The weight loss of the cured CE resin was larger than that of E-828 and proved to be proportional to the amount of BF₃MEA used, as expected.

In comparison with the studies of HHPA-cured resins,² the BF₃MEA cured CE-(III), having a high crosslinking density, had the same weight loss (4.5% weight loss, 100 h) as the HHPA cured ERL-4221-4090 (50/50) modified resin. Furthermore, the BF₃MEA cured E-154 (novolac type), showing the smallest weight loss in the BF₃MEA curing system, proved to have the same thermal stability as the HHPA cured CE-(I).

The initial drops in the flexural strength of the cured CE resin, as compared to that of E-828 and E-154, apparently strongly reflect the high temperature instability, due to the formation of pinholes or microcracks originating from the decomposition of the polymer.

Water Resistance

It is generally admitted that a cycloaliphatic epoxy resin has higher water absorption than the DGEBA resin, because of its poor rigidity and hydrophilic nature. The BF₃MEA hardener is also hygroscopic, suggesting that the BF₃MEA-cured CE resins have higher water absorption than the cured DGEBA, which creates a disadvantage in the application of lamination. The weight gains of the cured CE resins, immersed in water and in boiling water, are shown

Table I Typical Mechanical Properties of the BF₃MEA Cured CE Resins

Resin	Epoxy Value (eq. mol/100 g)	Amount of BF ₃ MEA (phr)	Flexural Properties (at 20°C)					HDT _s (°C)
			Yield Stress (Kg f/mm ²)	Yield Strain (%)	Break Stress (Kg f/mm ²)	Break Strain (%)	Young Modulus (Kg f/mm ²)	
CE-(I)	0.49	1	8.6	5.9	Not Break	—	230	43
CE-(II)	0.57	1	12.6	6.3	13.0	7.6	290	73
CE-(III)	0.76	3	—	—	11.9	4.8	300	200
E-828	0.53	3	—	—	11.1	4.2	300	155

Note: The curing conditions = 100°C/12 h + 150°C/4 h (CE resins); 120°C/4 h + 170°C/4 h (DGEBA).

Table II Mechanical Properties of the Blending Resin of CE-(II) and E-828

CE-(II)/E-828	Amount of BF ₃ MEA (phr)	Flexural Properties (20°C)					
		Yield Stress (Kg f/mm ²)	Yield Strain (%)	Break Stress (Kg f/mm ²)	Break Strain (%)	Young Modulus (Kg f/mm ²)	HDT ₁ (°C)
100/0	1	12.8	6.3	13.0	7.6	270	73
80/20	1	13.4	5.7	13.8	7.0	320	66
50/50	1	13.0	5.0	12.8	6.5	330	54
30/70	1	10.7	5.0	9.9	7.8	310	41
0/100	1	11.4	4.8	10.0	6.9	330	42
50/50	3	—	—	15.5	7.0	290	113
30/70	3	—	—	14.3	6.1	290	141
20/80	3	—	—	13.4	5.6	280	152
10/90	3	—	—	12.6	5.4	280	155
0/100	3	—	—	11.1	4.2	300	155

Curing conditions = 120°C/4 h + 170°C/4 h.

in Table III. The weight gains of the HHPA-cured resins are also shown in Table IV for comparison.

These results show that the water resistance of the BF₃MEA-cured resins is apparently lower than that of HHPA-cured resin.

The weight gains of the cured CE resins are proportional to the amount of BF₃MEA used. The CE-(II) has a slightly lower weight gain than the CE-(I) because of its crosslinking density, while the CE-

(III) has the highest water gain, despite its higher crosslinking density.

On the other hand, the weight gain on immersion in boiling water displayed the different behavior of the CE resin and showed the relation to the HDT of the cured resin.

Therefore, CE-(I) has the highest water gain, and CE-(III) and ERL-4221 have the lowest. In applying the BF₃MEA curing CE resin system to lamination,

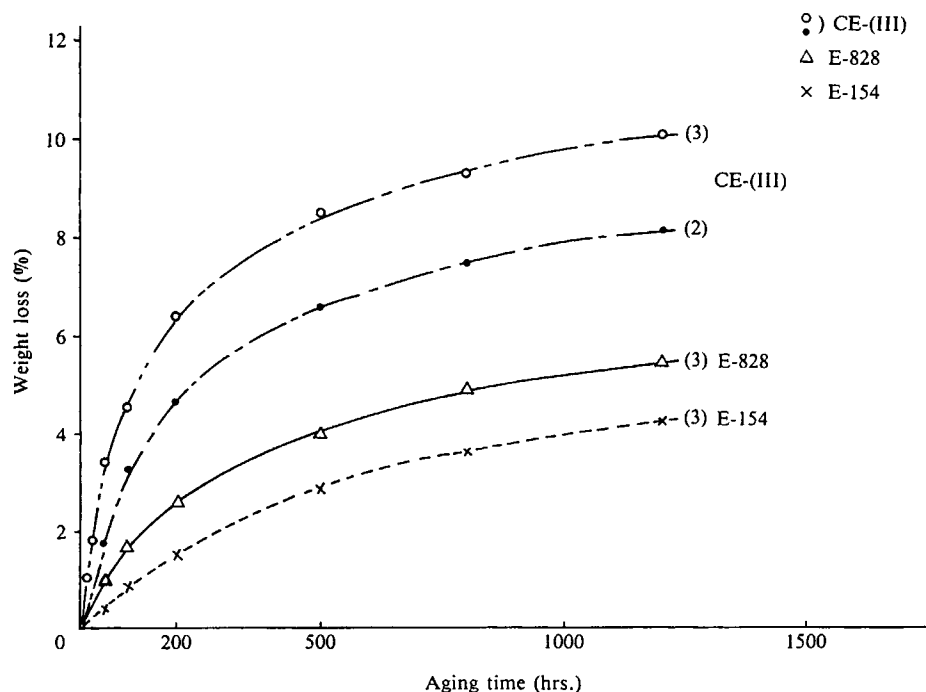


Figure 10 Thermal weight loss at 200°C.

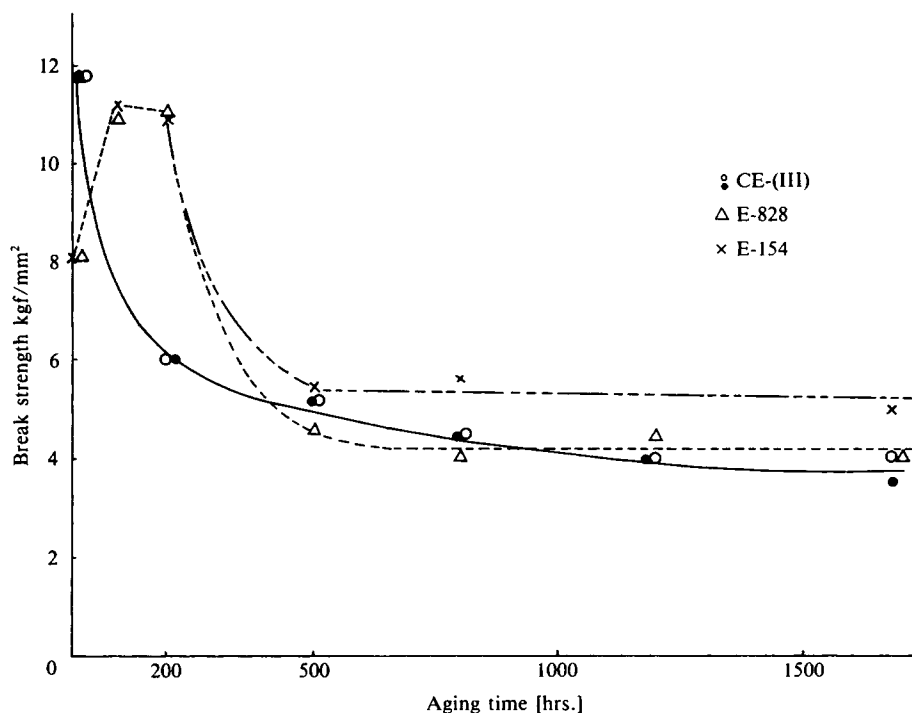


Figure 11 Thermal stabilities at 200°C.

some specific improvement will have to be considered for strong adhesion between the matrix resin and the fiber.

CONCLUSIONS

1. The BF_3MEA curing of the novel cycloaliphatic epoxy resins (CE resins), derived from 2,7-octadienol-1, was studied.
2. Based on the study using DSC and gelation

time, the BF_3MEA curing of this novel resin was found to show lower reactivity than the conventional cycloaliphatic epoxy resins and higher reactivity than DGEBA.

3. A mixture of the CE resins with BF_3MEA has a pot life of over 30 days at room temperature. In addition, the prepreg, created from a MEK solution at a temperature of 100–120°C, has a shelf life of over 30 days at room temperature.

Table III Water Resistance of the BF_3MEA Cured CE Resins

Resin	Amount of BF_3MEA (phr)	Percent Weight Gain			HDT ₅ (°C)
		Immersion in Water		Immersion in Boiling Water 1 h	
		1 Day	1 Week		
CE-(I)	1	0.24	0.62	1.14	42
	3	0.55	—	1.75	42
CE-(II)	1	0.20	0.53	0.84	60
	2	0.24	0.69	0.95	70
	3	0.47	—	1.2	110
CE-(III)	1	0.41	1.14	1.05	95
	1.5	0.54	1.51	0.92	207
	2	0.56	1.59	0.85	232
	3	0.57	—	0.95	—
ERL-4221	3	0.48	1.38	1.0	205
E-828	3	0.19	0.48	0.38	155

The curing conditions = 100°C/12 h + 150°C/4 h + 200°C/4 h.

Table IV Water Resistance of the HHPA Cured CE Resins

Resin	Percent Weight Gain			HDT, (°C)
	Immersion in Water		Immersion in Boiling Water 1 h	
	1 Day	1 Week		
CE-(I)	0.19	0.49	—	65
CE-(II)	0.11	0.32	0.35	95
CE-(III)	0.20	0.50	0.28	150
ERL-4221	0.36	0.88	0.65	200
E-828	0.13	0.37	0.22	125

The curing conditions = HHPA 0.85 eq. mol/epoxy, BDMA 1 phr, 100°C/3 h + 150°C/4 h.

- The thermal properties of the BF₃MEA-cured CE resins strongly depend on the amount of BF₃MEA used and the curing conditions. In the case of CE-(I) and (II) resins, 1 phr of BF₃MEA was the best amount; on the other hand, the use of 2–3 phr was proved to be the best for CE-(III) and yielded an HDT of over 200°C.
- The mechanical properties of the cured CE-(II) were greater than that of DGEBA, and CE-(III) was equivalent to DGEBA. Furthermore, the blending of CE-(II) with the DGEBA resulted in greater elongation and higher strength than when they are used separately.
- The water absorption and the thermal stability at elevated temperature of the BF₃MEA-cured CE resins were characterized by larger values and a larger weight loss than those of DGEBA, as was expected.
- Based on these results, it was concluded that the CE resins were expected to have new applications to one-component curing systems, such as fiber-reinforced matrix resin, if a good cationic, one-component hardener was utilized.

The authors express their sincere appreciation to Drs. S. Nishizaki and H. Teratani of Mitsubishi Electric Corpo-

ration, who have developed the manufacturing process for the casting and the lamination using our resins, and have given many suggestions throughout this work. The details on the casting and the lamination will be published by Drs. Nishizaki and Teratani in the future. The authors would also like to acknowledge Professor Takeshi Endo and Professor Emeritus Hiroshi Kakiuchi, who gave continuous encouragement.

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Received October 20, 1992

Accepted February 3, 1993