

Effects of Chemical Structure Changes on Curing Reactions and Thermal Properties of Cyanate Ester-Cured Rigid-Rod Epoxy Resins

W-F. A. SU, CHIH-MIN CHUANG

Department of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan, Republic of China

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ABSTRACT: How chemical structure changes affect the curing reactions and thermal properties of 2,2'-bis(4-cyanatophenyl) propane (cyanate ester) cured rigid-rod epoxy resins has been studied for biphenol and tetramethyl biphenol epoxies. The formation of an oxazolidinone ring is the dominant curing reaction for biphenol epoxy, whereas the formation of a cyanurate ring is the dominant curing reaction for tetramethyl biphenol epoxy, due to the bulky methyl substitutions on the biphenol chain. The crosslinkable cyanurate structure has a higher thermal stability than that of the linear oxazolidinone structure, giving the cyanate ester cured tetramethyl biphenol epoxy resin (molar equivalent) a higher glass transition temperature (260 vs. 218°C) and thermal decomposition temperature (366 vs. 312°C) than that of cyanate ester cured biphenol epoxy resin. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2419–2422, 2002

Key words: cyanate ester; epoxy; rigid rod; biphenol; liquid crystalline

INTRODUCTION

Recently, rigid-rod epoxy resins have been synthesized as a new class of high-performance polymers for electronic and aerospace applications.

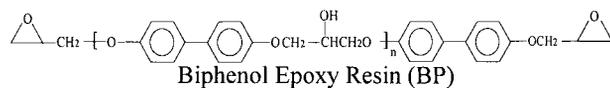
The amine, anhydride, or phenolic cured rigid-rod epoxies show improved thermal, mechanical, and electrical properties compared to those of flexible bisphenol A epoxies cured by the same type of curing agents. For instance, Ochi et al.¹ showed that biphenol epoxy cured with phenol novolak and aromatic diamine exhibit increased lap shear strength, adhesive strength, tensile strength, and fracture toughness. We² cured biphenol epoxies with trimellitic anhydride and diamino diphenylsulfone, respectively. The cured resins exhibited improved thermal and electrical

properties. Sue et al.³ obtained high fracture toughness ($G_{IC} = 580 \text{ JM}^{-2}$ compared with $G_{IC} = 180 \text{ JM}^{-2}$ for bisphenol A system) and high tensile modulus when α -methyl stilbene epoxy was cured with sulfanilamide. Muller et al.⁴ reported an increased tensile modulus (3070 MPa vs. 2346 MPa for bisphenol A epoxy) when dihydroxy phenyl benzoate epoxy was cured with a hexahydrophthalic anhydride. We⁵ have found that sulfanilamide cured biphenol epoxies exhibited a liquid crystalline network with a low coefficient of thermal expansion (CTE) of $20.8 \mu\text{m}/\text{m}^\circ\text{C}$ and a high glass transition temperature (T_g) of 219°C; sulfanilamide-cured azomethine epoxy has a low weight loss (39%) at high temperature (450°C). Their outstanding thermal properties are suitable for flame-resistant high-performance composites.

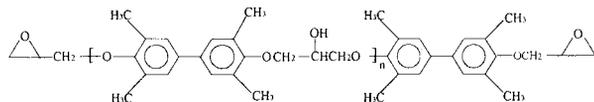
Cyanate resins have many excellent properties, such as good thermal stability, high glass transition temperature, and low dielectric constant, but they are very expensive, and have to be

Correspondence to: W.-F. A. Su (suwf@coms.ntu.edu.tw).
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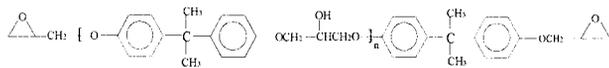
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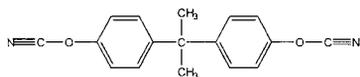
Biphenol Epoxy Resin (BP)



Tetramethyl Biphenyl Epoxy Resin (TMBP)



Diglycidyl Ether of Bisphenol A (DGEBA)



2,2'-bis(4-cyanatophenyl)propane (B10)

Figure 1 Chemical structures of epoxy resins and cyanate ester.

processed at high temperature.⁶ Thus, we have cured rigid-rod epoxies by cyanate ester to minimize costs of an easily processed high-performance resin. Figure 1 shows the chemical structures of the investigated epoxy resins and cyanate ester. Effects of chemical structure changes on the curing reactions and thermal properties of cyanate ester cured rigid-rod epoxy resins have been investigated in detail, and are reported in the following sections.

EXPERIMENTAL

Biphenol epoxy [4,4'-bis(2,3-epoxypropoxy) biphenyl] (BP) was synthesized according to our previously reported procedure.⁷ Tetramethyl biphenol epoxy (trade name RSS1407), with an epoxy equivalent of 185, was supplied by Shell Chemical. Bisphenol A epoxy (trade name DER 331), with an equivalent epoxy weight of 186, was supplied by Dow Chemical Company. Cyanate ester (AroCy B-10), with cyanate equivalent weight 139, was supplied by Ciba-Geigy Company. Cop-

per acetoacetate was purchased from the Aldrich Chemical Company.

The epoxy resins were melt mixed with the appropriate amounts of cyanate ester. Copper acetoacetate catalyst (0.1% of total weight of epoxy resin and cyanate ester) was used in preparing all the samples. The curing schedule and the degree of curing of each sample were determined by DSC and DMA. Table I lists the curing schedule of each sample.

DuPont 9900 Series, Model 954 TGA (at 10°C/min in N₂), Model 910 DSC (in N₂ at 10°C/min), Model 983 DMA (in N₂ at 2°C/min, at 1 Hz frequency and 0.2 mm magnitude of vibration), and Model 943 TMA were used to evaluate the thermal properties of the epoxy resins. TMA T_g of the samples was determined using the tangent of the slope change (plot of dimension vs. temperature) upon heating. DMA T_g of the samples was determined by the tan δ max (ratio of loss modulus over storage modulus) of DMA thermograms.

MAGNA-IR 550 Fourier Transform Infrared Spectrometer was used to determine the amount of cyanurate and oxazolidinone structures in the cured samples.

RESULTS AND DISCUSSION

The curing reactions between cyanate esters and epoxy resin have been proposed by Bauer pathways^{7,8} that involve: (1) cyanurate formation through trimerization of cyanate ester, (2) insertion of glycidyl ether epoxide into aryl cyanurate, (3) rearrangement of aryl cyanurate into alkyl isocyanurate, (4) oxazolidinone formation through the reaction of epoxy and cyanate ester. To determine which is the dominant reaction—cyanurate formation or oxazolidinone formation during the curing of rigid epoxy resin with cyanate ester—we have prepared samples using three molar ratios of epoxy to cyanate ester. The cured samples were monitored using FTIR. The structures of cyanu-

Table I Curing Conditions of Different Epoxy Resins

Epoxy Resin	Curing temperature and curing time
DGEBA	130°C/6 h + 175°C/6 h + 200°C/6 h
TMBP	130°C/6 h + 200°C/6 h + 230°C/6 h
BP	130°C/6 h + 150°C/6 h + 175°C/6 h + 200°C/6 h

Table II IR Transmittance Peak Area and Ratio of Cyanurate to Oxazolidinone of Epoxy Resins Cured by Cyanate Ratio in Three Molar Ratios

Epoxy : Cyanate ester	Epoxy Resin	Cyanurate at 1564 cm ⁻¹	Oxazolidinone at 1750 cm ⁻¹	Ratio of Cyanurate to Oxazolidinone
1 : 0.5	DGEBA	74.98	828.38	0.090
	TMBP	27.31	410.80	0.066
	BP	5.24	380.94	0.013
1 : 1	DGEBA	114.29	307.55	0.371
	TMBP	247.01	214.44	1.151
	BP	113.40	318.26	0.356
1 : 2	DGEBA	450.63	329.71	1.366
	TMBP	409.64	114.42	3.580
	BP	411.52	416.67	0.987

rate and oxazolidinone have IR absorption peaks at 1564 cm⁻¹ and 1750 cm⁻¹, respectively. The flexible bisphenol A epoxy was included in the study for the purpose of comparison. The results are summarized in Table II.

When the sample contains excess epoxy resin (molar ratio of epoxy to cyanate ester = 1 : 0.5), the peak ratio of cyanurate to oxazolidinone is less than 0.10. Therefore, the oxazolidinone formation is the dominant curing reaction for samples containing excess epoxy resin. On the other hand, when the samples contain excess cyanate ester (molar ratio of epoxy to cyanate ester = 1 : 2), the peak ratio of cyanurate to oxazolidinone is greater than 0.99. The formation of cyanurate is clearly the dominant curing reaction in this case. However, chemical structure changes in the epoxy resin have the largest effect on the curing reactions. Regardless of the molar ratio of epoxy to cyanate ester, tetramethyl biphenol epoxy has the highest rate of cyanurate formation among all

three epoxies. The bulky tetramethyl group retarded the reaction rate greatly between the epoxy and cyanate ester, as shown in the samples with an equivalent ratio and excess ratio of cyanate ester to epoxy. When we compared the same molar ratio samples with different type of epoxies, biphenol epoxy had the lowest cyanurate-to-oxazolidinone peak ratio. The flexible bisphenol A epoxy has its peak ratio in the middle range, and tetramethyl biphenol epoxy has the highest ratio. Therefore, comparing the reaction rate between epoxy and cyanate ester, biphenyl epoxy is the highest, bisphenol A epoxy next, and tetramethyl biphenol epoxy is the lowest. The biphenol epoxy has a higher reaction rate than that of bisphenol A epoxy, which may be due to the ordered structure of rigid rod biphenol epoxy with a high kinetic reaction rate.

The cyanurate structure has a crosslinking capability to form three-dimensional networks,

Table III Glass Transition Temperatures of Cyanate Ester Cured Epoxy Resins in Three Molar Ratios

Epoxy : Cyanate Ester	Epoxy Resin	DMA T _g (°C)	
		DMA T _g (°C)	TMA T _g (°C)
1 : 0.5	DGEBA	187	100
	TMBP	234	168
	BP	184	164
1 : 1	DGEBA	237	200
	TMBP	260	219
	BP	218	199
1 : 2	DGEBA	257	205
	TMBP	270	235
	BP	240	207

Table IV Coefficients of Thermal Expansion (CTE) of Cyanate Ester-Cured Epoxy Resins in Three Molar Ratios

Epoxy : Cyanate Ester	Epoxy Resin	CTE (μm/m°C)	
		α ₁ , Below T _g	α, Above T _g
1 : 0.5	DGEBA	97.4	1350
	TMBP	67.1	128
	BP	63.3	264
1 : 1	DGEBA	71.6	297
	TMBP	64.9	141
	BP	63.1	194
1 : 2	DGEBA	68.0	262
	TMBP	64.4	198
	BP	63.7	213

Table V 5% Weight Loss Temperatures and Residual Weights of Cyanate Ester-Cured Epoxy Resins in Three Molar Ratios

Epoxy : Cyanate Ester	Epoxy Resin	5% Weight Loss at T ($^{\circ}\text{C}$)	Residual Weight at 450°C (%)
1 : 0.5	DGEBA	344.3	16.80
	TMBP	361.4	19.39
	BP	309.9	27.00
1 : 1	DGEBA	344.7	23.80
	TMBP	366.2	26.26
	BP	312.4	28.81
1 : 2	DGEBA	345.4	35.40
	TMBP	366.3	37.57
	BP	320.5	34.95

whereas the oxazolidinone structure forms polymer chains in a linear fashion; samples with a high concentration of cyanurate structure are expected to have a better thermal stability than those samples with high concentration of oxazolidinone structure. In Tables III, IV, and V, it is shown that, for the same type epoxy, the thermal stability of cured samples increases with increasing cyanate ester concentration (i.e., increasing cyanurate concentration). For different epoxies with the same cyanate ester concentration, tetramethyl biphenol epoxy has the highest concentration of cyanurate concentration and exhibited the highest T_g (260°C) and thermal decomposition temperature (366°C).

The TMA T_g of rigid-rod biphenol epoxy is higher than that of flexible bisphenol A epoxy (Table III). The coefficient of thermal expansion of rigid rod biphenol epoxy is the lowest ($63 \mu\text{m}/\text{m}^{\circ}\text{C}$) among the test samples before T_g , and is also lower than that of the flexible bisphenol A epoxy after T_g (Table IV). When the molar ratio of epoxy to cyanate ester is less than or equal to 1 : 1, the rigid-rod biphenol epoxy has the highest residual weight (29%) at 450°C (Table V). Unusual thermal properties of rigid-rod biphenol epoxy may be explained by its highly ordered liquid crystalline structure. The cured biphenol epoxy has a more densely packed structure and less free volume than other epoxies that results in less intermolecular motions. The balance of intramolecular and intermolecular motions determines thermal properties of polymers. The cyanurate structure restricts the intramolecular motions, and the rigid-rod biphenol structure restricts the

intermolecular motions. Therefore, the overall thermal properties of cyanate ester-cured epoxies are dependent on the chemical structures of the epoxies. Thermal instability of the oxazolidinone structure in the rigid-rod biphenol epoxy can be compensated by using highly ordered rigid-rod structures that are more thermally stable, especially in samples cured with less than a molar equivalent of cyanate ester.

In summary, the ranking of thermal stability of cyanate ester-cured epoxies in decreasing order is: tetramethyl biphenol epoxy > biphenol epoxy > bisphenol A epoxy.

CONCLUSIONS

The competition between cyanurate formation and oxazolidinone formation during the curing process of epoxy resin and cyanate ester is dependent on the chemical structure of the epoxy resin. The rate of cyanurate formation is the highest for bulky substituted tetramethyl and is the lowest for biphenol epoxy. The thermal stability of cured samples is dependent on the amount of crosslinkable cyanurate structure in the samples, so tetramethyl biphenol epoxy is the most stable and the biphenol epoxy is the least stable. The highly ordered structure of rigid rod biphenol epoxy has been shown by the properties of low coefficient of thermal expansion and high residual weight.

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