Comparison of Cure Conditions for Rigid Rod Epoxy and Bisphenol A Epoxy Using Thermomechanical Analysis

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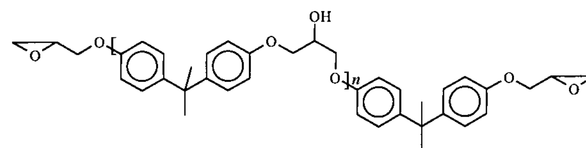
ABSTRACT: Thermomechanical analysis was used to compare cure conditions of a bisphenol A epoxy resin composition and the same composition prepared with a rigid rod biphenol epoxy resin. The rigid rod system exhibited a lower curing rate and lower thermal expansion than did the bisphenol A system. The glass transition and thermal expansion of the rigid rod system can be varied by manipulation of the ratio of curing agent to epoxy. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2163–2167, 1998

Key words: epoxy; rigid rod; biphenol; bisphenol A; thermomechanical analysis

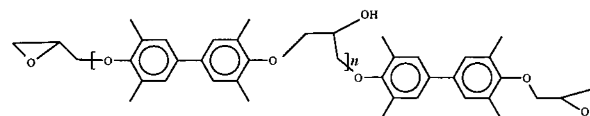
INTRODUCTION

Interest in rigid rod thermosets has increased in recent years because of their good thermal stability and unique physical properties. Previous work at Westinghouse[1] and elsewhere[2] showed that rigid rod epoxy resins in particular offer potentially enhanced thermal stability and dielectric properties over conventional epoxy resins. In fact, one rigid rod epoxy resin recently became commercially available from Shell Chemical Co.

A rigid rod material typically has a rigid rod segment in the polymer chain either on the polymer backbone or on side chains. Under certain conditions, these rigid rod segments may form highly crystalline domains, which are responsible for the enhanced properties of these materials over conventional polymers. Because of the different morphology of these materials, the optimum cure conditions for a rigid rod epoxy are expected to be rather different from those for conventional epoxies, which are essentially amorphous materials. This report compares the cure conditions of a typical insulation formulation prepared with either a bisphenol A type resin or a commercial rigid rod biphenol resin. The structures of the repeat units in the two systems are given below for comparison. Their properties are listed in Table I. Compositions having various curing agent/epoxy ratios were prepared.



bisphenol A



biphenol

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Table I Properties of Bisphenol A Epoxy and Biphenol Epoxy

	Biphenol Epoxy (Shell RSS-1407)	Biphenol A Epoxy (Dow DER 332)
Epoxide equivalent weight	180–190	172–176
Melting point (°C)	104–110	—
Viscosity (cps @25°C)	—	4000–6000

EXPERIMENTAL

Sample Preparation

An epoxy resin formulation used in high voltage insulation[3] was prepared by mixing the components at room temperature. Resins used were either DER 332 bisphenol A epoxy resin or Shell RSS-1407 biphenol epoxy resin. A reactive diluent is also used in this formulation to reduce viscosity: diglycidyl ether of neopentylglycol (DGENPG, Shell Heloxy 68). The curing agent was 1-methyl tetrahydrophthalic anhydride (ECA-100, Dixie Chemicals). A small amount of an amine catalyst (Super Van Go SD, Vanderbilt Chemical Co.) was also added. Various stoichiometries containing the biphenol epoxy were investigated and are listed in Table II. Comparison was made to the bisphenol A epoxy resin composition having 24.2 parts DER 332, 24.2 parts DGENPG, 51.6 parts ECA-100, and 0.086 parts Super Van Go SD. Resin cakes (10 g) were cured under the conditions listed in the tables and were submitted for thermal analysis.

Thermal Analysis

Thermomechanical analysis (TMA) was carried out on cured samples between room temperature and 150°C at 1°C/min using a Perkin–Elmer TMA-7 thermomechanical analyzer. A flat quartz probe was used to monitor the dimensional change of the cured resin versus temperature. The glass transition temperature (T_g) was determined from the temperature of the largest sample dimension change while the sample was heating. The percent thermal expansion data were reported in the temperature range from room temperature to 150°C.

RESULTS AND DISCUSSION

TMA monitors the thermal expansion of a thermosetting resin while it is heating. At the glass transition temperature, the sample undergoes thermal expansion during the transition from a crystalline state to a rubbery state. If the resin has a low degree of crosslinking (i.e., low cure), the resin melts upon heating and a negative thermal expansion results. With an increasing degree of cure, the T_g and the thermal expansion will increase. Therefore, the extent of cure can be determined from TMA results.

Bisphenol A Epoxy

The TMA results for the bisphenol A epoxy are summarized in Table III. Even after 20 h, the composition was not significantly cured at 80°C. Beginning at 100°C (for 4.5 h), however, there was increasing evidence of cure of the formulation shown by expansion. The T_g and z-axis expansion increased with cure temperature up to approximately 130°C (Fig. 1). From the T_g results we conclude that this particular formulation reached full cure after 2 h at 140°C. A higher temperature

Table II Rigid Rod Epoxy Formulations (Parts by Weight)

Formulation	Anhydride/Epoxy Ratio	Biphenol Epoxy	Diluent	Anhydride	Accelerator
A	0	100	0	0	0
B–G	1.41	19.8	19.8	60.3	0.1
H	0.95	24.7	24.7	50.6	0.05
I–L	0.71	28.4	28.4	43.1	0.14

Table III TMA Results for Bisphenol A Epoxy Resin Under Various Curing Conditions

Sample	Cure Conditions			Z-Axis Expansion (%)
	Time (h)	Temp (°C)	T_g (°C)	
O	20	80	52.81	−26.68
N	4.5	100	62.05	−0.407
P	2	110	72.76	2.633
Q	2	120	82.15	3.289
R	2	130	87.35	3.669
M	2	135	84.85	3.529
U	3	135	86.82	2.058
S	2	140	88.64	3.863
T	2	150	84.83	4.095

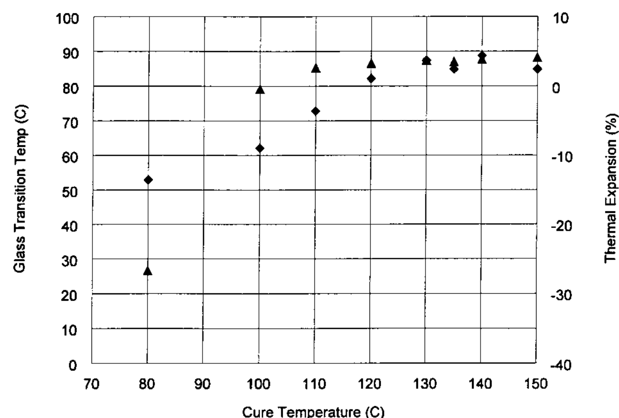

Figure 1 Glass transition temperature (◆) and z-axis expansion (▲) of bisphenol A epoxy resin formulation cured for 2 h at various temperatures.

caused degradation of the sample, as indicated by the lower T_g of the sample cured for 2 h at 150°C.

Biphenol Epoxy

The TMA results for rigid rod epoxy formulations at three different stoichiometries are summarized in Table IV. At 135°C the rigid rod formulation was clearly not cured, even after 18.5 h and with an excess of anhydride. There was less shrinkage, however, in the sample cured at 18.5 h than in the sample cured for 2 h. Presumably with additional time at 135°C, the sample would eventually reach full cure.

At 150°C the T_g continued to increase with cure time at anhydride/epoxy ratios of 1.41 and 0.71 (Fig. 2). At the stoichiometric ratio of anhydride/epoxy (0.95), the T_g decreased with curing time up to 6 h, then it started to increase with cure time. This behavior may be a manifestation of two phenomena occurring in this system. There is a mixing of the three components, which dilutes the rigid material. Because the cure reaction is slow, at short cure times the T_g of the system decreases because the components are more intimately mixed but not cured. At times longer than 6 h, the curing reaction has time to occur, resulting in increased T_g from that point.

Table IV TMA Results for Rigid Rod Epoxy Formulations

Sample	Molar Ratio Anhydride/ Epoxy	Time (h)	Temp (°C)	T_g (°C)	Z-Axis Expansion (%)
A	0.0			112 (m.p.)	
B	1.41	2	135	70.59	−6.111
C	1.41	18.5	135	74.3	−1.831
D	1.41	2	150	72.47	−0.046
E	1.41	3	150	72.51	−0.046
F	1.41	4	150	79.96	1.328
G	1.41	5	150	90.32	1.441
H1	0.95	4	150	91.585	3.60
H2	0.95	5	150	83.48	3.87
H3	0.95	6	150	77.8	4.00
H4	0.95	12	150	87.5	0.43
H5	0.95	23	150	88.65	1.5
I	0.71	3	150	66.74	5.752
J1	0.71	4	150	69.18	4.68
J2	0.71	5	150	73.49	4.528

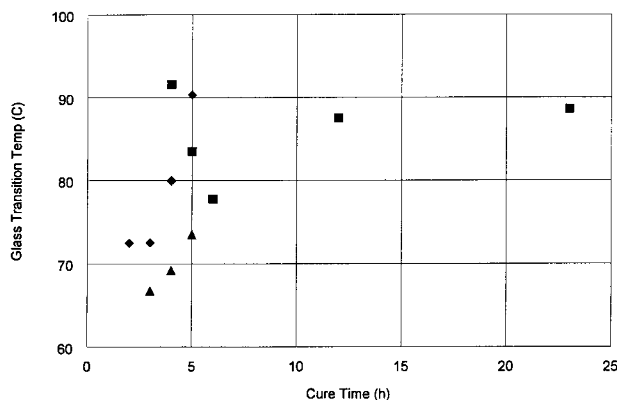

Figure 2 Glass transition temperature of rigid rod epoxy resins cured at 150°C for various times. Anhydride/epoxy ratio: (◆) 1.41, (■) 0.95, (▲) 0.71.

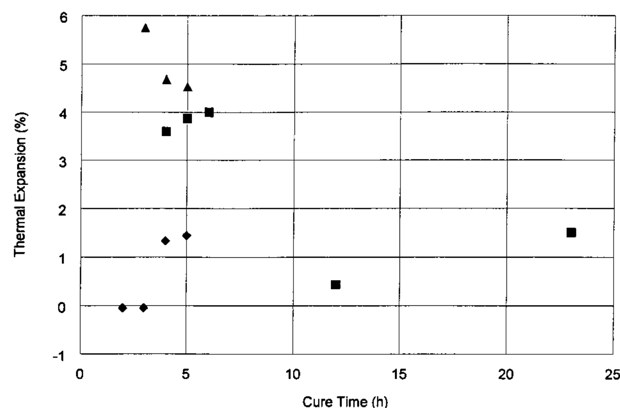

Figure 3 Thermal expansion of rigid rod epoxy resins cured at 150°C for various times. Anhydride/epoxy ratio: (◆) 1.41, (■) 0.95, (▲) 0.71.

The biphenol epoxy sample H5, which was cured at 150°C for 23 h, had a comparable T_g (88.65°C) to that of the fully cured bisphenol A epoxy sample S (88.64°C). However, sample S reach full cure in less time (2 h) and at a lower temperature (140°C). This result indicates that the curing rate of rigid rod biphenol epoxy is much slower than that of bisphenol A epoxy. A curing process is predominately kinetically controlled. With the rigid rod structure of biphenol epoxy, the probability of effective chemical orientation collisions between the epoxy and curing agent is less than in the bisphenol A epoxy system. This effect was observed by varying the concentration of biphenol epoxy in the formulations. At the same curing condition (150°C and 5 h), the highest concentration of biphenol epoxy in the formulations (anhydride/epoxy ration of 0.71, sample J2) exhibited the lowest T_g (73.49°C) compared to that of samples H2 (ratio, 0.95; T_g, 83.62°C) and G (ratio, 1.41; T_g, 90.32°C), The excess anhydride (mp < 25°C) increased the rate of curing by providing better flow during cure than that of rigid rod epoxy (mp 112°C).

The thermal expansion of rigid rod epoxy with the anhydride/epoxy ratio of 1.41 increased with cure time because of the low concentration of rigid rod material in the formulation. On the other hand, the thermal expansion of samples with ratios of 0.71 and 0.97 decreased with cure time (Fig. 3), presumably because of the rigid rod structure of biphenol epoxy. With a greater degree of cure, the rigid rod segments are aligned and packed better. Thus, reduced thermal expansion is expected. As shown in the Table IV, the well-cured biphenol epoxy samples had a lower thermal expansion (sample H6, 1.5%; sample G, 1.4%) compared to that of biphenol A epoxy (sample S, 4.1%).

It is also noteworthy that several samples having a large excess of anhydride showed a temperature regime in which there was essentially no change in sample dimensions (Fig. 4). Such behavior could be important in certain applications of these materials in which it is necessary to match thermal expansion characteristics of the resin with those of other materials, such as composites, adhesives, and so forth.

CONCLUSIONS

The rigid rod biphenol epoxy exhibits a lower curing rate and a lower thermal expansion than does the bisphenol A epoxy. By manipulation of

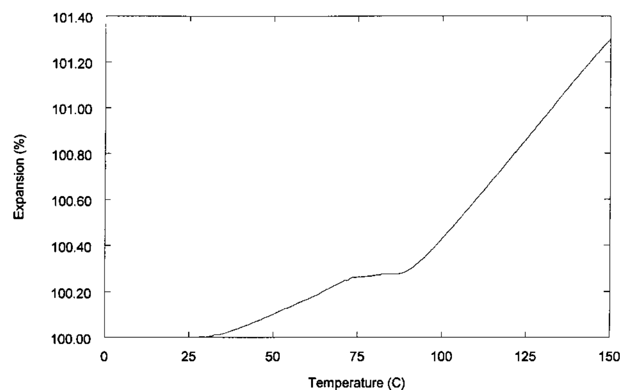

Figure 4 Thermal expansion of a rigid rod epoxy formulation having an anhydride/epoxy ratio of 1.41 and cured for 4 h at 150°C.

the ratio of curing agent to epoxy, it is possible to vary the T_g and thermal expansion of the rigid rod system. Use of a rigid rod curing agent and/or a rigid rod diluent would be expected to increase the thermal expansion and raise the T_g of the cured material because of the increased crystallinity of this material compared to the system described in this work.

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