Enhancement of Processability of Cyanate Ester Resin via Copolymerization with Epoxy Resin

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ABSTRACT: Two new matrices with enhanced processing characteristics, made from bisphenol A cyanate ester (BCE) and diglycidyl ether of bisphenol A epoxy resin or *o*-cresol formaldehyde novolac epoxy resin, were developed. Solubility, differential scanning calorimetry (DSC), gel time, and tack experiments were used to detect the processing characteristics of the two new systems and neat BCE. Results show that the two new systems have enhanced processability compared with neat BCE, especially improved tack and drape properties of prepregs, and faster thermal polymerization rate. In addition, the two new cured systems have more than two times improved impact strength without a great decrease in excellent dielectric properties or thermal and hot–wet resistance of neat BCE resin. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2377–2381, 2002

Keywords: cyanate ester; epoxy resin; processing characteristics; composites

INTRODUCTION

Over the last decade, cyanate ester (CE) has become established as a new and unique class of high-performance thermosetting resin for use as prepregs and matrices, in both the electronic and aerospace industries, because of their excellent elevated temperature and dielectric properties, low moisture absorption, and good flammability characteristics.[1–9] In addition, CEs can be processed by a wide range of methods, including prepreg technique, resin transfer moulding,[10,11] filament winding,[12] and as a sheet moulding compound (SMC).[13]

Despite possessing excellent physical properties, making them suitable for high-performance material applications, CEs have relatively high cost. In addition, prepregs based on CEs usually have poor tack and drape properties, so it is still necessary to broaden the application of CEs by further improvements in performance and costs.

The objective of this study was to develop new modified CE resins with good tack and drape properties and relatively low cost by co-curing with epoxy resins (EP). The effects of co-curing between bisphenol A CE and epoxy on the processing characteristics, such as tack and drape, solubility, reactivity, and viscosity characteristics, are investigated in detail. In addition, the thermal, mechanical, and hot–wet properties of cured resin are also discussed.

EXPERIMENTAL

Materials

The bisphenol A dicyanate resin (BCE) used in this study was synthesized by our group.[14] Epoxy resins were diglycidyl ether of bisphenol A (E-51; epoxy equivalent weight, 0.51), and *o*-cresol formaldehyde novolac epoxy (F-44; epoxy equivalent

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weight, 0.44), supplied by Wuxi Resins Company, China, and were used as the modifiers.

BCE (70 wt %) and E-51 epoxy resin (30 wt %) were put into a three-necked flask equipped with a thermometer and a stirrer, and heated to 110°C. After being maintained at that temperature for 15 min, the mixture was quenched to room temperature to obtain a modified CE resin, coded as #1 resin.

The #2 resin was also prepared using a similar procedure except the added epoxy resin was F-44 epoxy resin.

The #1 (or #2) resin was heated to 100 °C, and put into preheated clean molds. The resin was degassed at 110 °C in a vacuum oven, cured following the procedure: 130°C/2 h + 150°C/2 h + 180°C/2 h + 200°C/2 h, then slowly cooled to room temperature. The cured resin was demolded, and post cured at 220 °C for 10 h in an oven.

Prepregs were made by impregnating glass cloths with resin in acetone solution (resin:acetone = 1:1) following evaporation of the solvent.

Testing

The gel time of resins was determined with a standard hot-plate with a temperature controller. The resins were spread over hot plates heated to different temperatures. The time required for the resin to stop legging and become elastic is called the gel time.

Time–viscosity and temperature–viscosity curves for a resin were generated using a NDJ-79 viscometer with a temperature controller, and the heating rate was 10 °C/min.

Differential scanning calorimeter (DSC; Perkin-Elmer DSC-7) measurements were made at a scan rate of 10 °C/min with 4–6-mg samples in a nitrogen atmosphere.

Tensile, flexural, and impact strength data of cured resins were obtained according to GB1451-1483, GB3356-3382, and GB1843-1880, respectively. Heat deflection temperature (HDT) was obtained by GB1634-1679.

The thermal stability of cured resins was obtained with a Perkin-Elmer thermogravimetric analyzer (TGA) with a heating rate of 10 °C/min in a nitrogen atmosphere. Glass transition temperature (T_g) was obtained with a Perkin-Elmer DSC-7 in a nitrogen atmosphere at a heating rate of 10 °C/min.

The hot–wet resistance of cured resins was determined by placing samples into boiling distilled water for various lengths of time, removing and
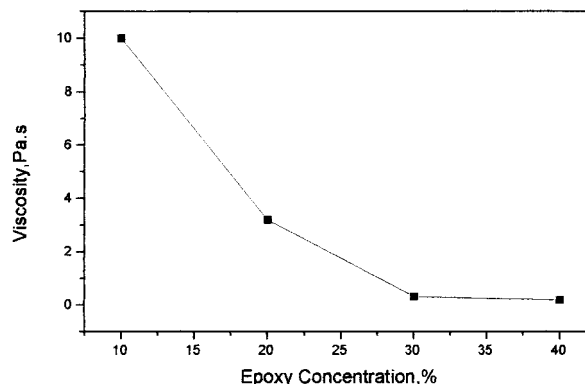
Figure 1   The influence of epoxy concentration on the viscosity of the #1 system.

wiping off the sample with a dry cloth, and weighing the sample to the nearest 0.001 g immediately. Then, the value of water absorption was calculated according to ASTM D 570-81, and the value of HDT was tested.

The dielectric properties were measured according to BG1409-78.

The tack and drape property of prepregs was tested by adhering a 1×3-in. prepreg specimen to a clean corrosion-resistant glass plate that was held in vertical position. Adherence of the specimen to the glass plate for 30 min indicated the prepreg passed the tack test, otherwise the prepreg failed.

RESULTS AND DISCUSSION

Processing Characteristics of CE Resins

BCE is a white or pale yellow crystal with a melting point (m.p) of 80 °C. At room temperature, E-51 and F-44 epoxy resins are viscous liquids. The #1 and #2 resins are pale brown transparent viscous liquids and can be dissolved into common solvents, such as acetone and ethanol. After storage at room temperature for 3 months, their color and solubility don't change, indicating that #1 and #2 systems have good storage stability.
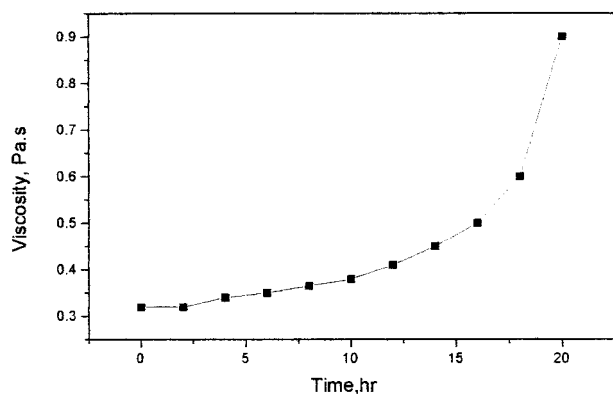
The influence of epoxy concentration on the viscosity of the #1 system is shown in Figure 1. When the epoxy concentration is 10 wt %, the system has a viscosity of 10 Pa.s at 50 °C. With increasing epoxy concentration, the viscosity of #1 resin decreases. When the epoxy concentration is >30 wt %, the viscosity of #1 resin decreases slightly.
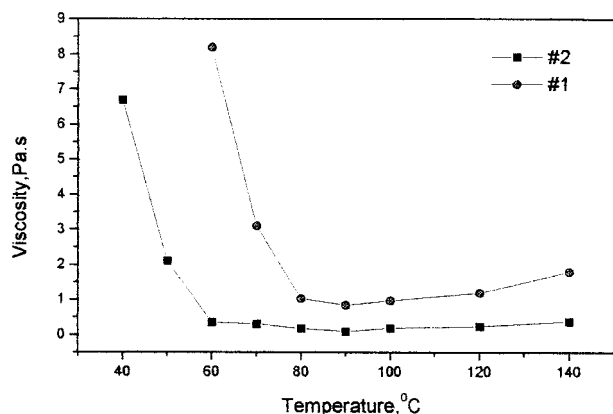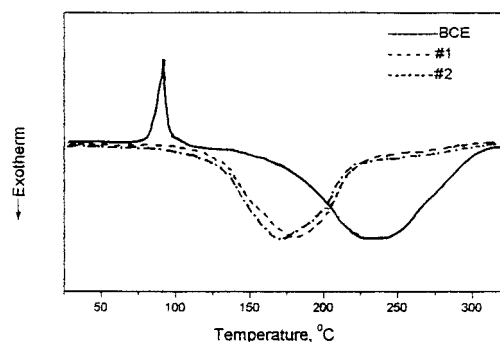
Figure 2 The influence of viscosity on temperature.

Figure 4 The thermal polymerization behavior of CE and the #1 and #2 systems.

The effect of resin viscosity on temperature is shown in Figure 2. When the temperature rises, the viscosity decreases, and the resin has its lowest viscosity at ≈90 °C. When the temperature is >90 °C, the viscosity slightly increases, which is mainly due to the curing reaction between components. The viscosity–time profile of #1 resin at 60 °C is depicted in Figure 3. After storage at 60 °C for 24 h, the viscosity of #1 resin is <1 Pa·s, indicating that #1 resin has low viscosity, good viscosity stability, and can be used to manufacture high-performance composites by resin transfer molding (RTM).

The thermal polymerization behavior of #1 and #2 systems at a scan rate of 10 °C/min was investigated, and the results are depicted in Figure 4. Neat BCE has a melting endotherm at 79.2 °C, and an onset of exothermic homopolymerization temperature at ~239 °C, with a processing window of 188–258 °C. The DSC scans of #1 and #2 do not show a melt endotherm because of the

prepolymerization between BCE and epoxy resin. Both of them exhibit an exothermic peak from ~122 to 200 °C, with each exothermic peak maximum shifting from ~239 to 170 °C, indicating that the thermal polymerization is faster than the thermal homopolymerization of neat BCE resin.

The "out-time" of prepregs is the time over which a prepreg maintains its tack, drape, and handleability. From Table I, it can be seen that the prepregs prepared from #1 and #2 resins have out-times in excess of three weeks, which exceeds the generally accepted out-time requirement of 10–14 days minimum.

The gelation time is also found to decrease with the addition of epoxy resin, and the reduction degree was associated with the type of added epoxy resin, as shown in Figure 5. A reduction in the gel times at 120 °C by ~60 and 55 min are observed for #1 and #2 resins, respectively.

Both processing characteristics and ultimate properties of a resin are very important for developing a new system. The former gives information on whether the resin can be processed via conventional industrial methods, and the latter determines whether the resin has the potential to be used widely. These investigations prove that the

Figure 3 The relationship between the viscosity of #1 and time at 60 °C.

Table I   Physical Properties of Prepregs

| Property	Value
Fiber area weight, g/cm^2	143 ± 3
Resin content, wt %	31
Volatile content, wt %	1
Flow, wt %	9.1
Gel time at 160 °C, min	8
Out-time at 23 °C, weeks	>3
Tack (self-adhesion)	good/pass
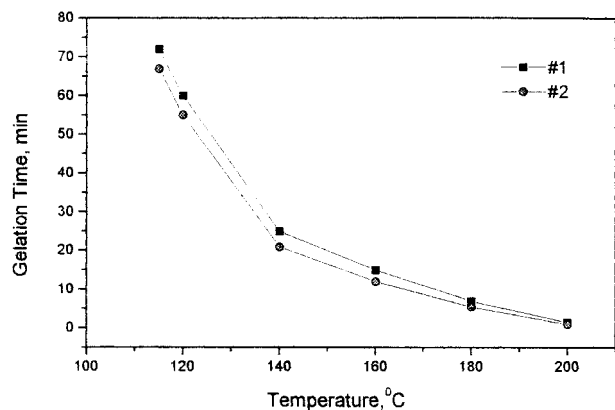
Figure 5 The relationship of gelation time versus temperature.

addition of epoxy resin in BCE can greatly enhance the processing characteristics, so it is necessary to study the ultimate properties of #1 and #2 systems and the effect of the addition of epoxy resin on the properties of neat BCE resin. The properties of BCE and #1 and #2 systems are listed in Table II. The #1 and #2 systems have good mechanical properties; in particular, their impact strengths are 2.4 and 1.9 times of that of BCE, respectively, which may be due to the existence of many soft linkages in their networks. This improvement may be also reflected by the increase of the tensile elongation with the addition of epoxy resin (#1 and #2 systems).

The thermal stability is defined by heat deflection temperature (HDT), glass transition temperature (T_g), and thermogravimetric analysis (TGA). Cured BCE resin has the best thermal stability, which may be attributed to its thermally resistant crosslinked cyanate structure. The ther-
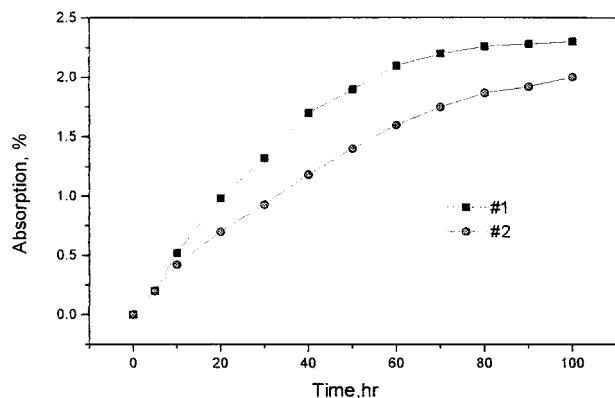
Figure 6 The relationship of water absorption versus aging time.
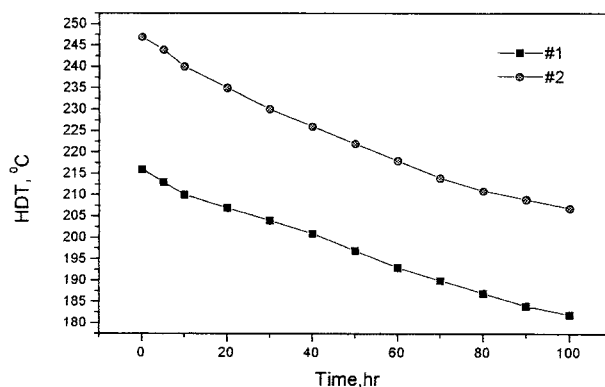
Figure 7 The relationship of HDT versus aging time.

mal stability of the #1 and #2 systems greatly depends on the type of epoxy resin used. The thermal stability of the #2 system is almost as good as that of neat BCE resin because F-44 has more functionalities than E-51, and hence the cured #2 system has a higher crosslinking density than the cured #1 system.

A resin with poor hot–wet resistance usually has high moisture absorption, causing a lowering of thermal stability and associated reliability problems. Therefore, hot–wet resistance is very important for developing a new resin. The relationships of moisture absorption versus aging time and HDT versus aging time, are shown in Figures 6 and 7, respectively. After aging for 100 h in boiling distilled water, #1 and #2 systems have water absorptions of 2.0 and 2.3%, respectively, their HDT values decrease from 216 to 182 °C and 247 to 207 °C, respectively. Both of these

Table II Properties of Neat Resins

Property	#1	#2	BCE
Tensile strength, MPa	87	83	71
Tensile modulus, GPa	3.3	3.6	3.7
Tensile elongation, %	3.4	2.9	3.7
Flexural strength, MPa	135	131	104
Impact strength, kJ/m^2	14.4	11.6	6.0
HDT, °C			
Dry	216	247	250
Wet (aged 100 h in			
boiling water)	182	207	215
T_g (DSC), °C	228	256	258
T_{di}, °C	440	440	445
T_{dp}, °C	456	457	461
tg δ (10 GHz)	0.0113	0.0109	0.007
ε' (10 GHz)	2.92	2.90	2.80

changes are ≈84% retention of their original values, indicating that #1 and #2 systems have good hot–wet resistance.

Having excellent dielectric properties is one of the most attractive features of CE resins, which indicates CEs have great potential to be used in microelectronic industries. Therefore, to develop a new modified CE system, it is necessary to retain the good dielectric property of the original CE resin. From the results in Table II, it can be seen that although the dielectric properties of #1 and #2 systems are not as good as that of BCE, the resins are better than conventional bismaleimide type resins, which are generally considered to be good dielectric materials.

CONCLUSIONS

To improve the tack and drape properties of prepregs based on BCE, two new systems, modified by two kinds of epoxy resins, have been developed. Investigations show that the properties of these modified CE resins are dependent on the type and the concentration of epoxy employed. Both of them have enhanced tack and drape feature, and good solubility, storage stability, and reactivity. In addition, the cured resins retain the positive characteristics of neat BCE, such as excellent dielectric properties, good thermal and hot-wet resistance properties, as well as improved impact strength.

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