Carbon Fiber Cardanol-Epoxy Composites

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SYNOPSIS

Carbon fiber composites based on tetrafunctional epoxy resin N,N,N',N'-tetraglycidyl-2,2-bis[4-(4-aminophenoxy)phenyl]propane modified with cardanol were investigated. The differential scanning calorimetric technique was used to study the curing reaction of the neat resins. The dielectric properties of the composites were compared. The use of cardanol in epoxy resins at cardanol/epoxy molar ratios less than 0.3/1 improved the chemical resistance as well as the mechanical properties of the composites, such as the flexural strength and modulus, tensile strength and modulus, and interlaminar shear strength. Higher cardanol contents decreased such properties. The highest properties of the composites were observed with the epoxy–cardanol resin having a cardanol/epoxy molar ratio of 0.3/1. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Properties of unidirectional carbon fiber composites are greatly affected by the nature of the resins.[1] The mechanical properties of the composites based on epoxy resins can be improved by increasing the epoxide functionality because the resins can participate better in crosslinking.[1-3] Therefore, many tetrafunctional epoxy resins have been developed for high performance composites, such as tetraglycidylmethylenedianiline (TGMDA), tetraglycidyl-4,4'-(4-aminophenyl)p-disopropyl benzene (TGADB),[1,2] and recently N,N,N',N'-tetraglycidyl-1,1'-bis[4-[4-aminophenoxy)phenyl]cyclohexane (TGBAPC) and N,N,N',N'-tetraglycidyl-2,2-bis[4-(4-aminophenoxy)phenyl]propane (TGBAPP).[3]

In addition, the incorporation of additives in epoxy resin systems may be used to achieve some specific properties. In recent years, much attention has been paid to the additives based on cardanol. Cardanol extracted from cashew nut shell liquid (CSNL) is a natural alkyl phenol with a C_{15} unsaturated side chain at the meta position.[4,5] Cardanol can take part either in reactions of the phenol group or those of double bonds.[6] Epoxidized cardanol[7] has been used as a reactive diluent for epoxy resins,

which improved the flexural strength as well as tensile strength[8,9] but decreased the curing rate.[10] Epoxy flexibilizers/plasticizers based on cardanol can be used with epoxy resins in the inhibition of composite rocket propellants, which demands large elongation and moderate tensile strength.[11]

On the other hand, cardanol can react with epoxy resin through the reaction between the OH group of cardanol and the epoxide groups of epoxy resins at a suitable temperature with or without a catalyst.[12] The presence of cardanol with the long alkyl chain in the cardanol-epoxy products can give the brittle matrix some specific characteristics, such as more elasticity, flexibility, hydrophobic properties, etc., thereby improving some properties of the materials. However, these effects have not been fully researched until now.

This article reports on the curing behavior of the cardanol-epoxy resins based on epoxy resin TGBAPP measured by DSC and some properties of their carbon fiber composites, such as dielectric properties, mechanical properties, and chemical resistance.

EXPERIMENTAL

Materials

The epoxy resin TGBAPP, which was prepared according to the procedure reported elsewhere,[13-15] has

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an epoxy equivalent weight of 188 g/eq (determined by the hydrochloride method[12]). The chemicals used were laboratory grade reagents. Cardanol, obtained by vacuum distillation of CNSL at 2–4 mmHg and 225–235°C, has a refractive index of 1.5094 and a Broofield viscosity of 485 cps at 20°C.

Cardanol-epoxy resins were prepared using cardanol/epoxy molar ratios 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 (corresponding to CE1, CE2, CE3, CE4, CE5, and CE6, respectively) in the presence of 2-methyl imidazole as a catalyst at 150 ± 5°C. The reaction was carried out until the epoxy equivalent stopped changing. Bis(p-aminocyclohexyl)methane (PACM-20) was used as a curing agent.

The carbon fiber used in this study was Tenax HTA 200 tex f3000 (Tenax Fibers GmbH & Co. KG, Germany). According to manufacturer's data, the properties of the fiber are twist 0/Z15 t/m, filament diameter 7 μm, density 1.77 g/cm^3, tensile strength 3,950 MPa, tensile modulus 238 GPa, and elongation at break 1.55 %.

DSC

DSC measurements of the neat resins were performed on a Perkin-Elmer differential scanning calorimeter (Norwalk, CT). The system was calibrated with a sample that had a known heat of function. The resins were mixed with a curing agent at an epoxide/amine equivalent ratio of 1/1 for 5 min before carrying out the measurement. The specimens (~10 mg) were scanned at a scanning rate of 10°C/
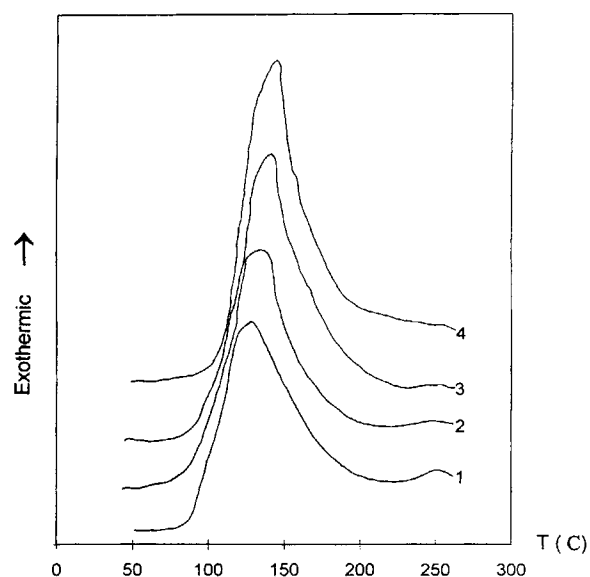
Table I   Curing Characteristics of Neat Resins

System	T_i (°C)	T_p (°C)	T_f (°C)	E_a (kJ/mol)	n
Epoxy	78	136	192	84.2	1.10
CE1	79	138	196	86.0	1.08
CE2	81	139	198	88.8	1.04
CE3	82	141	204	92.5	0.99
CE4	84	143	210	95.9	0.92
CE5	86	145	218	101.3	0.85
CE6	92	146	232	109.7	0.80

min in the temperature range of 20–240°C under dry nitrogen gas.

The exothermic peak obtained from the DSC scan was analyzed to get heat flow as a function of temperature and time. From the heat flow, the activation energy (E_a) and the order of the curing reaction (n) were calculated according to the Freeman–Carroll method.[16]

Composite Fabrication

Unidirectional carbon fiber epoxy-cardanol composite was used for this study. The composite plate was made of prepreg consisting of a fiber content of 60% by volume. The prepreg was laminated unidirectionally and cured in a hot press at 160°C for 1 h. Postcuring of the composite was done at 180°C for 2 h.

Measurements

All measurements for evaluating laminates were carried out at room temperature (~20°C). The measurement of the dielectric properties was performed using an electronic bridge as described in the literature.[17] The impedance, dielectric constant, and dielectric loss factor (tan δ) were measured at a frequency of 1 kHz. The electrical fields were applied perpendicular to the unidirectional carbon fiber layers.

Mechanical properties, such as tensile, flexural, and interlaminar shear strengths, were determined using the ASTM D3039-76, D790-71, and D2344-84, respectively.

Chemical resistance was evaluated according to ASTM D543-87. The specimen was dipped in water and different solutions, such as 20% NaOH, 20% HCl, 10% HNO$_3$, and acetone for 30 days.

Figure 1   DSC curve of the neat epoxy and cardanol-epoxy resins: (1) epoxy, (2) CE2, (3) CE4, and (4) CE6.

Table II   Dielectric Properties of Composites

System	Z (MΩ/cm)	ε	tan δ
Epoxy	0.94	4.12	0.065
CE1	0.93	4.18	0.067
CE2	0.90	4.27	0.071
CE3	0.88	4.41	0.074
CE4	0.82	4.67	0.082
CE5	0.76	4.95	0.090
CE6	0.67	5.21	0.096

RESULTS AND DISCUSSION

DSC

Some selected scans are illustrated in Figure 1.Curing characteristics obtained directly from the DSC scans, such as the temperature of initial curing (T_i), peak exotherm (T_p), and completion of curing (T_f), activation energy (E_a), and order of curing reaction calculated according to the Freeman–Carroll method are presented in Table I.

It can be seen that the epoxy system began to crosslink at 78°C and formed a peak at 136°C, indicating a sharp reaction, while CE systems needed higher temperatures. The effect of cardanol in the CE systems is obvious because their T_i as well as T_p and T_f increased as the amount of cardanol increased. This means that the increase of cardanol increased the activation energy (from 86.0 to 109.7 kJ/mol, as shown in Table I) and lowered the curing rate and the finally attainable degree of reaction of the epoxy group. This may be due to the increase of molecular weight and spatial effect of the long hydrocarbon of cardanol and the decrease of epoxide functionality as the cardanol content increases.

Dielectric Properties

The measurement of the dielectric properties such as impedance (Z), dielectric constant (ε), and di-

electric loss factor (tan δ) of the composites (in Table II) showed that the presence of cardanol in the matrix decreased the dielectric properties of the composites. The increase in the amount of cardanol decreased the polarity of the matrix because of the weak or nonpolarity in the nature of the long hydrocarbon chain of cardanol, thereby improving the insulating properties. On the other hand, the increase of cardanol content decreased the epoxide functionality and hence decreased the crosslinked density, which has a strong influence on the dielectricity of thermoset resins. However, the second effect has a greater influence on the dielectricity than the first one; and therefore, the dielectric properties decreased with the increase in the amount of cardanol. It is also obvious that with the low cardanol content (from CE1 to CE3) the values of Z, ε, and tan δ varied slowly whereas with the high content (from CE4 to CE6) they varied at a faster rate.

Mechanical Properties

Some mechanical properties such as tensile strength and modulus, flexural strength and modulus, and interlaminar shear strength (ILSS) of the laminated composites are given in Table III.

Mechanical properties of the composites were greatly affected by nature of the resin. The mechanical properties increased with the addition of cardanol from CE1 to CE3. This may be due to the fact that the presence of the long alkyl chain of cardanol improved the flexibility as well as the elongation and the fracture toughness of the rigid epoxy matrix; therefore, the tensile strength, flexural strength, and modulus, and ILSS increased.[8] Furthermore, the fracture surface morphologies of the epoxy and CE3 composites were also examined with scanning electron microscopy (SEM) as illustrated in Figure 2. For both cases, there is evidence of interfacial and matrix failure, fiber break, and fiber pull-out; however, the matrix deformation is more dominant in the CE3 than in the epoxy specimen,

Table III   Mechanical Properties of Composites

System	Tensile Strength (MPa)	Tensile Modulus (GPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)	ILSS Strength (MPa)
Epoxy	1933	142	1866	172	82
CE1	2136	149	1974	181	91
CE2	2253	153	2263	187	99
CE3	2341	157	2496	192	104
CE4	2398	150	2552	184	101
CE5	2316	139	2415	172	93
CE6	2152	121	2199	157	79

showing that the fiber–matrix interfacial adhesion was improved by the presence of cardanol in the matrix. This leads to an increase of the tensile modulus as well as ILSS and the other mechanical properties.

On the contrary, the increase of cardanol decreased the epoxide functionality and hence decreased the crosslinking of the matrix (as discussed with reference to the dielectric properties), thus greatly affecting the mechanical properties. Therefore, at higher cardanol amounts (>0.4) in the CE matrices, the mechanical properties decreased with the increase of cardanol.

Chemical Resistance

After immersing the specimens in water and chemicals for 30 days, there was neither a change in di-

Table IV   Chemical Resistance of Composites

System	Weight Gain after 30 Days (%)				
	Water	20% NaOH	20% HCl	10% HNO_3	Acetone
Epoxy	0.42	1.28	0.87	1.68	1.45
CE1	0.25	0.62	0.41	1.12	0.98
CE2	0.14	0.57	0.35	0.86	0.82
CE3	0.14	0.51	0.38	0.94	0.86
CE4	0.20	0.74	0.52	1.24	1.07
CE5	0.27	0.88	0.71	1.55	1.31
CE6	0.32	1.12	0.93	1.96	1.59

mension nor in color; however, changes in weight were determined and the results are given in Table IV.

It is obvious that most CE composites had a weight gain lower than the epoxy composite, and the reagent absorption lowered considerably with the increase of cardanol content from CE1 to CE3 whereas it increased from CE4 to CE6. The improvement of the reagent absorption can be explained by the hydrophobic nature of the long alkyl chain in cardanol.[8] The decrease of crosslinked density in the matrix may be responsible for the increase in weight gain of the specimens having a high cardanol content. The weight gains in HNO_3 solution and acetone are higher than in water and the other solutions because HNO_3 is an oxidative reagent that can react not only with the matrix but also with the carbon fiber,[1] and acetone is a good solvent for the resins before curing. The weight loss in HNO_3 solution and acetone was also concerned; however, there was no loss in weight observed.
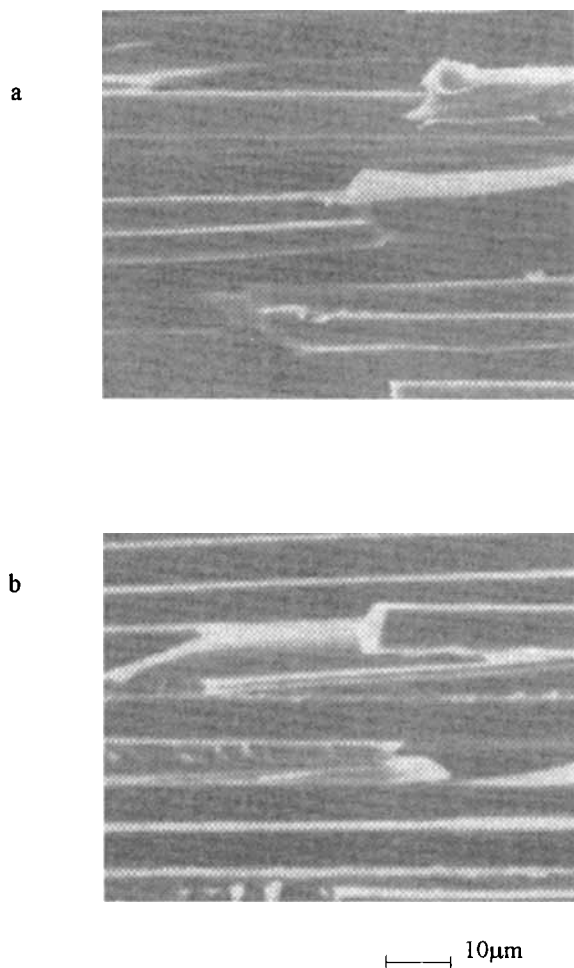

a

b

⊢——⊣ 10μm

Figure 2   SEM photomicrographs of the fracture surface of the composites based on (a) epoxy and (b) CE3 matrix. Performed on a JEOL JSM-5200, accelerating voltage of 20 kV.

CONCLUSION

The activation energies of curing reactions of epoxy and cardanol epoxy resins were found to be in the range 84.2–109.7 kJ/mol. Epoxy resin modified with cardanol at the cardanol/epoxy molar ratio less than 0.3 improved the chemical resistance as well as the mechanical properties, such as the flexural strength and modulus, tensile strength and modulus, and interlaminar shear strength; however it decreased the dielectric properties of their carbon fiber composites. On the other hand, the high contents of cardanol decreased the crosslinking of the matrix, which had a negative affect on many properties of the composites.

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