

Epoxy-Phenol-Cardanol-Formaldehyde Systems: Thermogravimetry Analysis and Their Carbon Fiber Composites

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SYNOPSIS

Systems consisting of epoxy resin and phenol-cardanol-formaldehyde (PCF) were prepared. The thermal characterization of the systems, investigated by thermogravimetry analysis, indicated that the increase of PCF content improves the thermal stability. Chemical resistance as well as mechanical properties of their carbon-fiber composites were also determined. The matrix-fiber interfacial study by scanning electron microscopy showed that the higher the PCF amounts in the system products, the better the interfacial bonding.

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INTRODUCTION

Epoxy resins are one of the most versatile materials used in industrial applications such as adhesives, coatings, and especially composites. Depending on the chemical structures of the resins and the curing agent, and the availability of numerous modifying reactants, epoxy resins can have a broad range of physical properties, mechanical capabilities, and processing conditions that make them invaluable compared to other thermosetting resins.¹⁻³

The broad interest in epoxy resins originated from the extremely wide variety of chemical reactions that can be used for curing and many different properties that follow. Therefore, the curing reactions of epoxy resins by various amines, anhydrides, and bismaleics with or without accelerator have received much attention during the last 6 years.⁴⁻¹¹

In recent years, there has been much interest in cardanol, a natural alkyl phenol with a C15 unsaturated chain extracted from Cashew nut shell liquid (CNSL), which can be polymerized through either reactions of the phenol group or double bonds.¹²⁻²³ The analysis of the characteristics of phenol-car-

danol-formaldehyde resins (PCF)²⁴⁻²⁶ indicates that the replacement of phenol by cardanol, with 15% phenolic resins, can improve the chemical resistance as well as most mechanical properties of the resins and, at the same time, the resins still have high thermal stability.²⁶

Phenolic resins with low molecular weight can be used as curing agents for epoxy resins in high chemical resistance applications. Phenolic resins can react with epoxy resins via the reactions of the hydroxyl groups of the phenolic resin with the epoxide groups of the epoxy resins.¹⁸ However, the characteristics of the combination of PCF and epoxy resin have not been researched.

This article reports the thermal stability of the epoxy-PCF systems and the characterization of their carbon-fiber composites.

EXPERIMENTAL

Materials

Epoxy resin (diglycidyl ether of bisphenol A) used in this study was EPOTUF 37140 (Reichhold Chemie GmbH, Austria) with an epoxide equivalent of 187 g/eq. Cardanol was distilled from CNSL at 2-4 mmHg at 225-235°C. Carbon fiber 98141 in the

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weave cloth and unidirectional form of CS-Interglas AG (Germany) was used for manufacturing the fiber-polymer composites. The unidirectional fiber was used in the investigation of the fiber-matrix interface, while the weave cloth form was used in the determination of the composite properties.

PCF was prepared using a 1-mol mixture of phenol (Fluka) and cardanol (with a cardanol/phenol ratio of 15/85 by weight) and 1.4 mol of 37% formaldehyde (Fluka) in the presence of 28% ammonia as a catalyst at 75–80°C for 3 h. The viscous resin was washed with water and then dried in a vacuum at 70–80°C for 1 h.

The PCF was mixed with epoxy resin using PCF/epoxy amounts of 10, 20, 30, 40, and 50% by weight (M1, M2, M3, M4, and M5), in the presence of 2-methyl imidazole as a catalyst for the curing reaction.

Thermogravimetric Analysis (TGA)

The resin systems were cured in a closed molding at 160°C for 1 h and postcured at 180°C for 2 h. TGA of the cured resins was performed on a TGA 7 thermogravimetric system (Perkin-Elmer, Norwalk, CT). The samples were heated from 40 to 550°C at a heating rate of 10°C/min under a dry nitrogen atmosphere (balance purge, 50 cm³/min; sample purge, 25 cm³/min).

Fabrication of Composites

The carbon fibers were immersed in the solutions of PCF-epoxy systems (in acetone) and then dried at 60°C in a vacuum. The composites were prepared by hot press molding, involving cure for 1 h at 160°C and postcured for 2 h at 180°C. The composites had resin contents of 38.5–40.5% by volume (or 31.6–33.1% by weight).

Measurements

Mechanical properties of the composites, such as tensile strength, flexural strength, and interlaminar shear strength (ILSS), were measured following ASTM D3039-76, D790-71, and D2344-84, respectively, at various temperatures between 20 and 300°C.

Resistance to chemical reagents (water, HCl 10%, NaOH 10%, and acetone) was estimated according to ASTM D543-87 at room temperature (~ 20°C).

RESULTS AND DISCUSSION

TGA

The thermograms of all the resins are given in Figure 1, and the selected weight loss and derivative thermogravimetric curve (DTG) of sample M4, representing all other samples, are illustrated in Figure 2. The general thermal degradation patterns of all the resins are very similar, exhibiting mainly four steps. The DTG curves reveal that these steps are composed reactions. An initial slight weight loss at about 230–250°C can be explained by the degradation started with olefin formation by loss of the secondary hydroxyl group of the propyl chain in epoxy resin.^{27,28} Then a sharp break occurs in each of the TGA curves at 360–380°C. Studies of Learmonth and Searle²⁹ on thermal stability of phenolic resins based on phenol and bisphenol A demonstrated that the isopropylidene linkage (in bisphenol A) is thermally less stable than the methylene linkage of the phenolic resin. The pyrolysis products of bisphenol A at 300–400°C by Kunnappallil et al.³⁰ were mainly identified as phenol and *p*-isopropenyl phenol. Therefore, the weight loss in this range of temperatures responds to the degradation of bisphenol A. The weight loss in the range of 440–500°C may be due to the breakdown of the methylene linkages in the alkyl chain of cardanol and also in the main PCF chain.^{24–26} The degradation takes place at temperatures above 500°C through thermooxidative reactions as reported by Mark and Rubin.³¹

The 5 and 10% decomposition temperatures (T_5 and T_{10}) and the weight loss at 500°C of all the resins are listed in Table I. The increase of PCF amount increases the T_5 and T_{10} and reduces the weight loss at 500°C. The general trend in thermal stability of the resins is clear because the PCF resin has a higher thermostability compared to the epoxy resin. Furthermore, the increase of PCF in the systems improved the crosslinking in the cured resins. There-

Table I Thermal Characterization of Cured Resins

Sample	T_5 (°C)	T_{10} (°C)	Weight Loss at 500°C (%)
M1	318.2	354.9	76.2
M2	350.4	381.2	72.3
M3	361.5	383.4	66.7
M4	362.2	384.2	57.1
M5	373.7	394.1	55.9

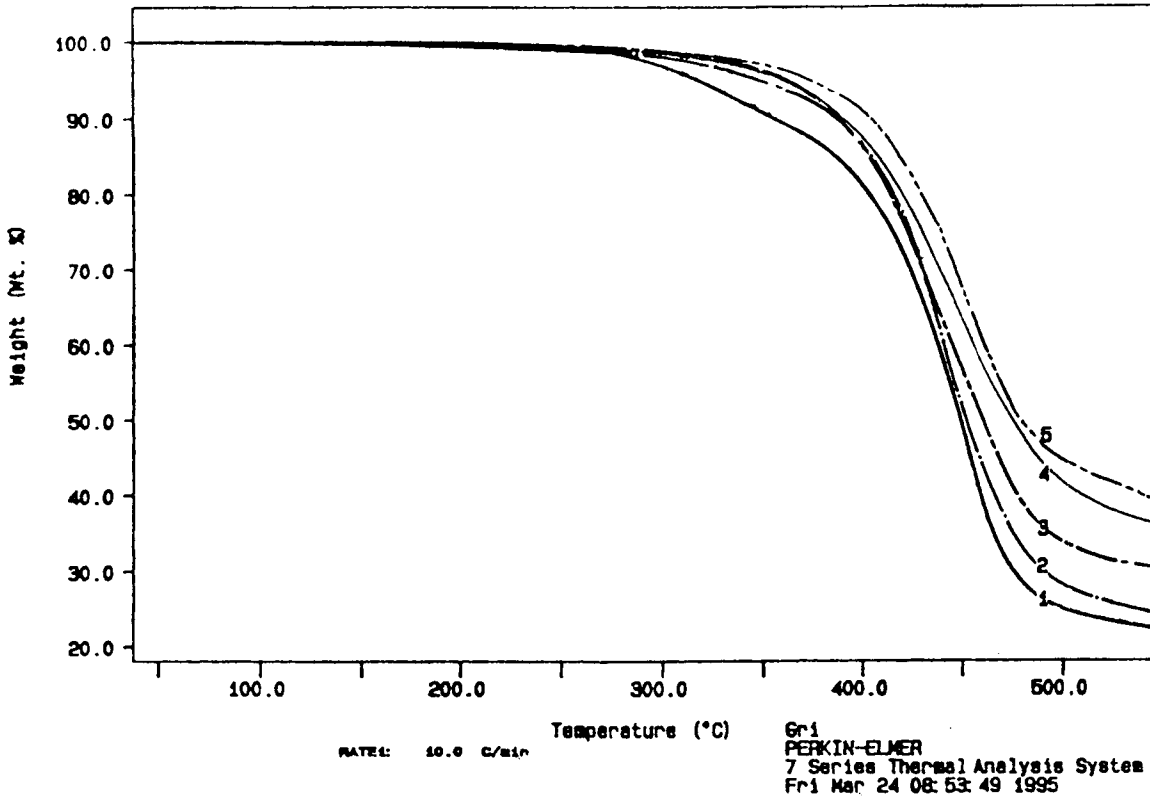


Figure 1 TGA cure of resins (1) M1, (2) M2, (3) M3, (4) M4, and (5) M5.

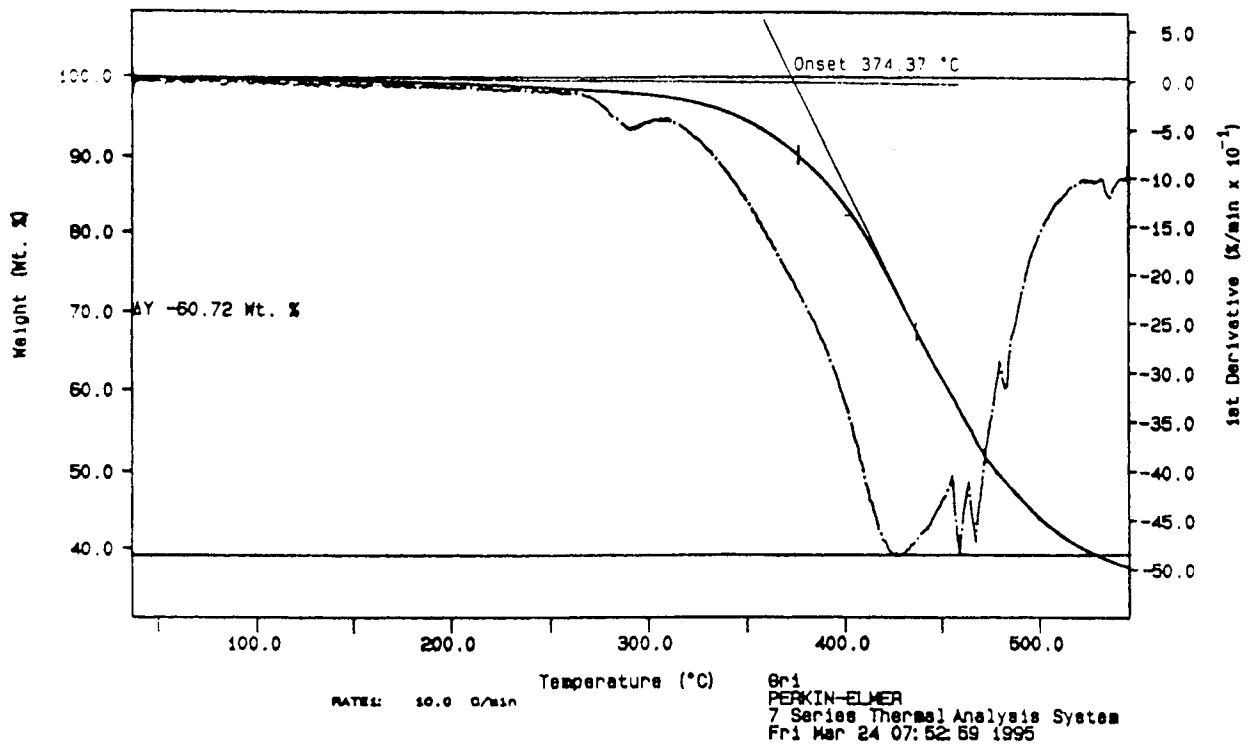


Figure 2 TGA curve and DTG curve of the selected resin M4.

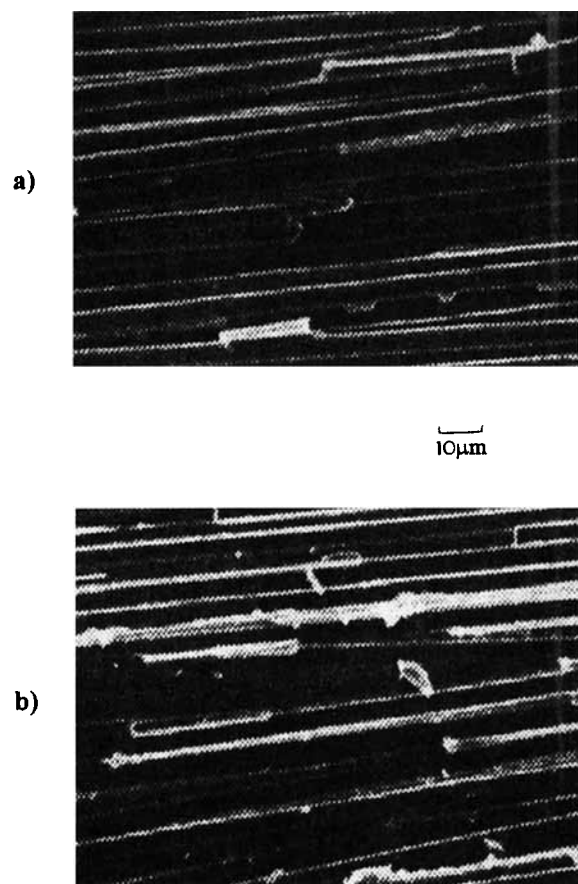


Figure 3 SEM photomicrographs of the fracture surface of the composites based on (a) M1 and (b) M5.

fore, a higher PCF amount in the system produces higher thermal stability.

Mechanical Properties of Composites

The fracture surface morphologies of all the composites under interlaminar shear were examined by scanning electron microscopy (SEM; performed on a JEOL JSM-5200, with an accelerating voltage of

25 kV). The selected micrographs of the composites M1 and M5 are shown in Figure 3. The fracture surface morphologies of all composites are very similar, exhibiting interface failure, matrix failure, fiber break, and fiber pull-out. However, the matrix failure is more dominant in the sample having high PCF (sample M5), as shown in Figure 3; this means that the increase of PCF improves the fiber–matrix interfacial bonding. This may be due to the high chemical reactivity of the methylol group contained in PCF.

The mechanical properties of the composites, such as tensile strength, tensile modulus, flexural strength, and ILSS are given in Table II. The tensile strength and tensile modulus increase in samples M1–M3 and decrease in M3–M5 while the flexural strength decreases and the ILSS increases continuously. This may be due to the fact that the increase of PCF amount improves the crosslinked density of the matrix and hence improves the tensile strength as well as the tensile modulus in samples M1–M3. On the other hand, PCF resin is brittle in nature and has low tensile strength and tensile modulus. The matrix with a high PCF amount should have more of the character of the PCF resin. Therefore, the tensile strength and the tensile modulus decrease in samples M3–M5. It is clear that the high PCF amount is related to a high aromatic density and crosslink density, which make the matrix more rigid, or in other words, it decreases the flexural strength. The increase of ILSS is explained by the improvement of PCF in fiber–matrix interfacial bonding as examined by SEM.

Sample M3 has properties more satisfactory than others; therefore, it was used to determine the influence of temperature on its mechanical properties. The results are shown in Table III. At temperatures below 100°C, the change in properties is not pronounced; however, at temperatures above 100°C, the properties were reduced dramatically. First, the fiber and the matrix may give off vapors due to the evaporation of absorbed water or other liquid. Further-

Table II Mechanical Properties of Composites

Sample	Tensile Strength (MPa)	Tensile Modulus (GPa)	Flexural Strength (MPa)	ILSS (MPa)
M1	428.9	44.7	688.3	52.6
M2	524.1	68.2	678.9	68.5
M3	592.5	72.8	672.6	75.4
M4	544.6	69.1	624.1	76.2
M5	465.4	58.6	583.5	81.7

Table III Influence of Temperature on Mechanical Properties of Composite M3

Temperature ($\pm 2^\circ\text{C}$)	Tensile Strength (MPa)	Modulus Strength (GPa)	ILSS (MPa)
20	592.5	72.8	75.4
50	564.7	70.5	72.4
100	494.2	66.4	63.2
200	365.1	54.7	44.6
300	214.3	38.9	28.2

more, at temperature above 200°C , the matrix may undergo some pyrolysis reactions that generate volatiles. These extend the damage in the composites and hence decrease all mechanical properties. A higher temperature is related to higher damage. Therefore, all the properties decrease at a faster rate at high temperature.

Chemical Resistance

After immersing the samples in various reagents for 14 days, there were not changes in color, surface appearance, or dimension, except for an increase in weight. The weight gain was measured and is reported in Table IV. The increase in weight can be explained by the fact that the matrix contains polar groups such as phenol and maybe also hydroxyl groups, which are hydrophilic in nature and can absorb water as well as aqueous solutions. The weight gains of all samples in water, HCl 10%, and acetone are not so much different from each other and are very small. In most cases, they slightly decrease with an increase of PCF amount. This can be easily understood because of the improvement in crosslinked density of the matrix as the PCF amount increases. However, the weight gain in NaOH 10% varies widely with the PCF amount used in the matrix. As discussed above, the high PCF amount relates to

the high crosslinked density, therefore, the weight gain in the NaOH solution decreases in samples M1–M2. However, the phenol group in PCF can react with the NaOH solution: the higher the PCF amount in the matrix, the higher the free phenol groups. This is the reason for the weight increase in samples M3–M5.

CONCLUSION

From this brief study of the TGA of the matrix, the mechanical properties, and the chemical resistances of their carbon-fiber composites, the following conclusions were made:

1. The thermal stability of the PCF-epoxy system depends on the PCF amount used. The increase of PCF amount in the matrix improves the thermal stability of the system.
2. The mechanical properties of the composites change with the quantity of PCF used. Sample M3 with 30% PCF in the matrix exhibits the most satisfactory mechanical properties. The mechanical properties of the composite are strongly affected by temperatures, especially at the range of temperatures above 100°C . It should also be mentioned that the

Table IV Weight Gain of Composites after Immersing in Chemical Reagents (14 Days)

Sample	Weight Gain (%)			
	Water	HCl 10%	NaOH 10%	Acetone
M1	0.21	0.23	0.28	0.26
M2	0.19	0.24	0.26	0.24
M3	0.18	0.22	0.29	0.25
M4	0.18	0.21	0.33	0.23
M5	0.17	0.23	0.39	0.26

increase of PCF amount improves the fiber-matrix interfacial bonding as determined by SEM.

- All composites have high chemical resistance in water, HCl 10%, and acetone; however, the presence of a high content of PCF in the resin reduces the resistance of the composites in NaOH solution.

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REFERENCES

- J. R. Theodore, Technical Chairman, *Engineered Materials Handbook*, Vol. 1, *Composites*, ASM International, New York, 1987.
- J. R. Theodore, Technical Chairman, *Engineered Materials Handbook*, Vol. 2, *Engineering Plastics*, ASM International, New York, 1987.
- M. M. Schwartz, *Composite Materials Handbook*, McGraw-Hill, New York, 1984.
- J. R. Thakkar, R. D. Patel, R. G. Patel, and V. S. Patel, *Angew. Makromol. Chem.*, **172**, 103 (1989).
- M. B. Patel, R. G. Patel, and V. S. Patel, *J. Therm. Anal.*, **35**, 47 (1989).
- I. K. Varma and R. Sharma, *Thermochim. Acta*, **160**, 209 (1990).
- R. H. Patel and R. G. Patel, *Thermochim. Acta*, **160**, 323 (1990).
- R. H. Patel and R. G. Patel, *Thermochim. Acta*, **173**, 95 (1990).
- S. R. Patel, V. S. Patel, and R. G. Patel, *Thermochim. Acta*, **182**, 319 (1991).
- H. K. Soni, V. S. Patel, and R. G. Patel, *Thermochim. Acta*, **191**, 307 (1991).
- S. R. Patel and R. G. Patel, *Thermochim. Acta*, **202**, 97 (1992).
- S. R. Patel and R. G. Patel, *Thermochim. Acta*, **202**, 97 (1992).
- J. R. Thakkar, R. D. Patel, R. G. Patel, and V. S. Patel, *Br. Polym. J.*, **21**, 243 (1989).
- J. H. P. Tyman and L. J. Moris, *J. Chromatogr.*, **27**, 287 (1967).
- J. H. P. Tyman and N. Jacobs, *J. Chromatogr.*, **54**, 83 (1971).
- R. S. Dracker and A. R. Siebert, *ACS Org. Coat. Appl. Polym. Sci. Proc. Prepr.*, **48**, 491 (1983).
- J. P. Agrawal and R. S. Satpute, *J. Macromol. Sci., Pure Appl. Chem.*, **A30**, 19 (1993).
- W. J. Roff and J. R. Scott, *Fibers, Films, Plastics and Rubbers: Handbook of Common Polymers*, Butterworth & Co., Ltd., London, 1971.
- J. H. P. Tyman, *Chem. Soc. Rev.*, **8**, 499 (1979).
- C. K. S. Pillai, V. S. Prasad, J. D. Sudha, S. C. Bera, and A. R. R. Menon, *J. Appl. Polym. Sci.*, **41**, 2478 (1990).
- R. S. Balakrishna, M. N. Sathyanaryana, B. B. Vishwanath, and M. M. Shirsalkar, *J. Appl. Polym. Sci.*, **41**, 1365 (1990).
- Rosy Antony and C. K. S. Pillai, *J. Appl. Polym. Sci.*, **33**, 1933 (1987).
- Rosy Antony, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 3187 (1993).
- D. O'Connor and F. D. Blum, *J. Appl. Polym. Sci.*, **33**, 1933 (1987).
- S. Manjula and C. K. S. Pillai, *Thermochim. Acta*, **159**, 255 (1990).
- T. T. M. Tan, N. H. Nieu, and U. Griesser, *Angew. Makromol. Chem.*, submitted.
- D. P. Bishop and D. A. Smith, *Ind. Eng. Chem.*, **59**, 32 (1967).
- E. C. Leisegang, A. M. Stephen, and J. C. Paterson-Jones, *J. Appl. Polym. Sci.*, **14**, 1961 (1970).
- G. S. Learmonth and D. P. Searle, *J. Appl. Polym. Sci.*, **13**, 437 (1969).
- S. Kunnappallil, S. Annakutty, and K. Kishore, *Makromol. Chem.*, **192**, 11 (1991).
- B. S. Mark and L. Rubin, *Org. Coat. Plast. Chem.*, **28**, 94 (1968).

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