

Research Article

Thermal Study of Anhydrides Cured Tetrafunctional Cardo Epoxy Resin

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Tetrafunctional cardo epoxy resin (EBCF) was cured by using 10 wt% maleic anhydride (MA), pyromellitic dianhydride (PMDA), phthalic anhydride (PA), tetrahydrophthalic anhydride (THPA), tetrabromophthalic anhydride (TBPA), and tetrachlorophthalic anhydride (TCPA) as hardeners at 120°C for 40–105 min (gel time) and then postcured 1 h at 130°C. Gel time is found to depend on the structure of the anhydrides used. Cured samples were found insoluble in common solvents. Cured and uncured EBCF were characterized by FTIR, DSC, and TGA techniques. Cured and uncured resins followed multistep degradation reactions. Kinetic parameters, namely, order of degradation, energy of activation, frequency factor, and entropy change, were determined according to the Anderson-Freeman method and interpreted in light of the nature of hardeners used for curing purpose. The resins followed integral or fractional order degradation kinetics. Complex degradation reactions are due to different types of linkages in cured resins. Both nature and structure of resin and hardeners affected the curing behavior and the resultant thermal properties of the cured resins.

1. Introduction

Epoxy resins are well known for their outstanding processing behavior and physicochemical properties such as mechanical stiffness and toughness; chemical, moisture, and corrosion resistance. They are most widely used in advanced technologies, aerospace, electronics, communication, adhesives, primers, coatings, and semiconductor encapsulation industries. They are also used for storage and management of nuclear waste as matrices for advanced fiber-reinforced composites [1–6]. The basic properties of epoxy resins can be modified by blending different resins, by selection of curing agents, and by the use of modifiers and fillers.

Multifunctional epoxy resins are well known for their high glass transition temperatures, high decomposition temperatures, long term high temperature performance, and good wet strength performance [7–11]. These materials suffer two important limitations because of their intrinsic brittle nature and considerable moisture absorption tendency from environment, which adversely affect most physicomechanical

properties of the fabricated articles. Both these drawbacks increase by enhancing the crosslink density of the network.

To the best of our knowledge, no work has been reported on anhydrides cured multifunctional epoxy resin containing cyclohexyl as a cardo (Latin meaning a loop) group, which encouraged us to investigate the present work. In this paper, we have reported curing study of cardo group containing tetrafunctional epoxy resin (Scheme 1) by using 10 wt% of various anhydrides. The cured resins are characterized by IR, DSC, and TGA techniques. Our future objective is to prepare and characterize fiber reinforced composites of this resin and hardeners used.

2. Experimental

2.1. Materials. Solvents and chemicals used were of laboratory grade and purified prior to their use [12]. Tetrafunctional cardo epoxy resin (EE 800) was synthesized according to our recent work [13]. Maleic anhydride (MA)

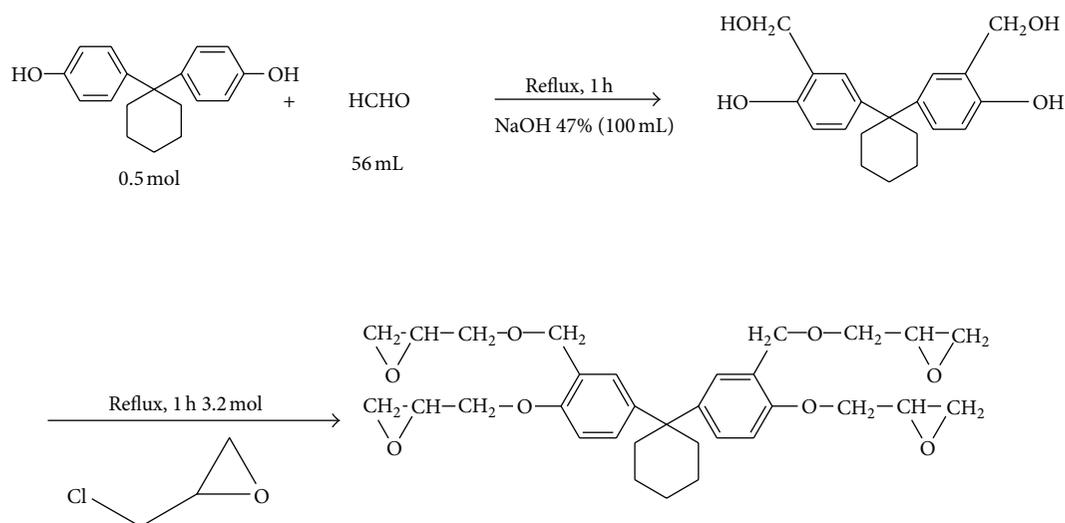


TABLE 1: Gel time of EBCF cured by various anhydrides at 120°C.

Sample	Gel time (min)
EBCF-PA	105
EBCF-MA	80
EBCF-THPA	70
EBCF-TBPA	40
EBCF-TCPA	75
EBCF-PMDA	45

(Sisco-Chem, Mumbai), phthalic anhydride (PA) (Sisco-Chem, Mumbai), tetrahydrophthalic anhydride (THPA) (Merck, Germany), tetrachlorophthalic anhydride (TCPA) (National Chemicals Vadodara), tetrabromophthalic anhydride (TBPA) (Lancaster, England), and pyromellitic dianhydride (PMDA) (Spectrochem, Mumbai) were used as hardeners and received.

2.2. Curing Study. In the present investigation, curing study of EBCF was carried out by using 10 wt% of PA, MA, THPA, TBPA, TCPA, and PMDA as hardeners at 120°C. Into six different test tubes, 2 g EBCF and 0.2 g hardener were dissolved in 5 mL acetone and were placed in a water bath at about 70°C. Acetone was allowed to evaporate slowly with stirring. Then the test tubes were placed in an oil bath at 120°C. With the progress of the curing reaction, viscosity of the resin was found to increase, and stirring was also found difficult. The time at which viscous resin was set into infusible mass was considered as gel time. The gel times of different hardeners cured EBCF are reported in Table 1. The samples were further postcured at 130°C for 1 h. Cured samples are insoluble in common solvents. Hereafter, the cured samples are designated as EBCF-MA, EBCF-PA, EBCF-THPA, EBCF-TCPA, EBCF-TBPA, and EBCF-PMDA.

2.3. Measurements. Fourier transform infrared FTIR spectra (KBr pellets) of EBCF and anhydrides cured EBCF samples were scanned on a Shimadzu FTIR-8400 spectrometer over the frequency range from 4000 to 400 cm⁻¹. Differential scanning calorimetric (DSC) and thermogravimetric analyses (TGA) were carried out on a Shimadzu DSC60 and Pyris-I Perkin Elmer TGA at 10°C min⁻¹ heating rate in nitrogen atmosphere.

3. Results and Discussion

3.1. IR Spectral Analysis. IR spectra of EBCF and anhydrides cured EBCF are presented in Figures 1 and 2. EBCF showed characteristic IR absorption peaks (cm⁻¹) at 3339 (OH str.), 1244 (Aryl-O-Alkyl str.), 1119 (Alkyl-O-Alkyl str.), and 876 and 816 (C-O str. of epoxide). Cured EBCF showed absorption peaks at 3651–3524 (broad O-H str.), 1740–1722 (ester str.), 1265–1217 (Aryl-O-alkyl str.) and 1167–1071 (Alkyl-O-alkyl str.), 1121–1109 (C-OH str.), and 1354–1310 (O-H def.), beside the normal modes of aromatic and aliphatic groups. Upon curing, peaks due to epoxide C-O str. disappeared, and new C=O str. peak appeared. Aryl-O-alkyl str. and alkyl-O-alkyl str. peaks also shifted from 1244 to 1265–1217 and from 1119 to 1167–1071 cm⁻¹, which are due to the different structure and nature of the hardeners used. In case of cured resins, absorption peaks over the range 1500–650 cm⁻¹ are masked by ester and hydroxyl groups. Thus, IR spectral data confirmed transformation of epoxy groups into network structure. Both nature and structure of the resin and hardeners affected curing behavior of the resin.

3.2. Thermal Analysis. DSC curves of cured and uncured EBCF are presented in Figures 3 and 4. Endothermic/exothermic transitions are reported in Table 2. A broad

TABLE 2: DSC and TGA data of anhydrides cured and uncured EBCF.

Sample	DSC transition (°C)	T_0 (°C)	Decomposition range (°C)	T_{max} (°C)	% wt loss	Residue at 700°C
EBCF	68.3 (Endo)	120	120–210	187.9	10.2	—
	188 (Endo)		340–400	369.9	11.3	
	259.8 (Endo)		455–515	505.1	28.9	
	354.5 (Exo)		515–550	548.2	20.6	
EBCF-MA	244.9 (Endo)	230	230–370	338.6	16.8	36.9 (600)
			415–510	433.6	30.5	
EBCF-PMDA	258.0 (Endo)	170	170–250	—	11.7	33.5
			250–280	267.5	4.3	
			280–390	329.3	20.6	
EBCF-PA	168.5 (Endo) 266.6 (Endo)	135	390–500	456.8	25	26.4
			135–270	—	12.7	
			270–380	322.1	20.6	
EBCF-THPA	133.9 (Endo) 289.8 (Endo)	255	390–500	446.3	31	20.7
			255–360	340	16.1	
			360–520	421.3	57.2	
EBCF-TBPA	232.5 (Endo) 313.4 (Exo)	170	170–255	256	8.1	29.5
			260–315	285.5	14.3	
EBCF-TCPA	212.8 (Endo) 253.2 (Exo)	150	375–485	407.1	20.9	52.6
			150–270	219.5	12.9	
			270–350	288.6	11.5	

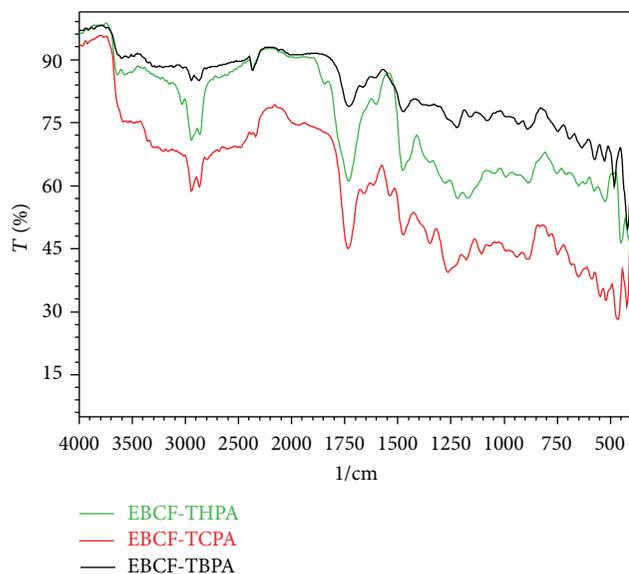


FIGURE 1: IR spectra of EBCF-THPA, EBCF-TCPA, and EBCF-TBPA.

endothemic transition at 68.3°C is assigned as melting transition of EBCF. Two broad endothermic transitions (188°C and 259.8°C) and one broad exothermic transition (354.5°C) are due to some chemical change (probably condensation of unreacted methylol groups with elimination of formaldehyde and water), which are further confirmed by weight losses over those temperatures in its TGA curve (Figure 5). Endothermic

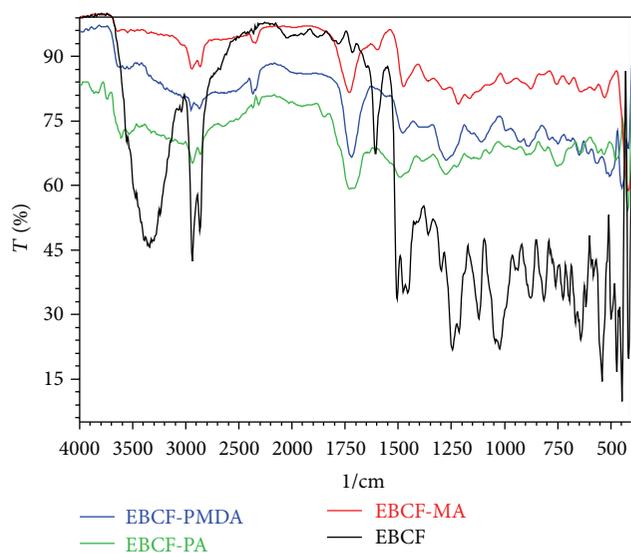


FIGURE 2: IR spectra of EBCF, EBCF-MA, EBCF-PA, and EBCF-PMDA.

transitions in cured resins at 244.9°C (EBCF-MA); 258°C (EBCF-PMDA); 168.5°C and 266.6°C (EBCF-PA); 232.5°C and 313.4°C (EBCF-TBPA); and 212.8°C and 253.2°C (EBCF-TCPA) is/are assigned as decomposition reaction and further confirmed by weight loss in corresponding TG curve (Figures 5 and 6). Endothermic transitions of EBCF-THPA at 133.9°C and 289.8°C are assigned as physical and chemical change, respectively, and further confirmed by no weight loss and

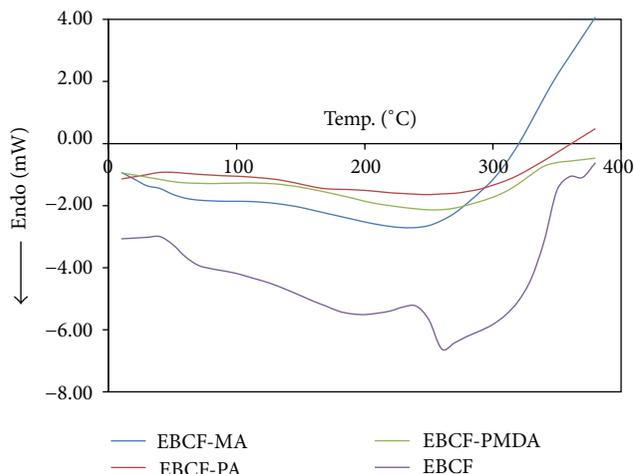


FIGURE 3: DSC thermograms of EBCF, EBCF-MA, EBCF-PA, and EBCF-PMDA at $10^{\circ}\text{C min}^{-1}$ heating rate in nitrogen atmosphere.

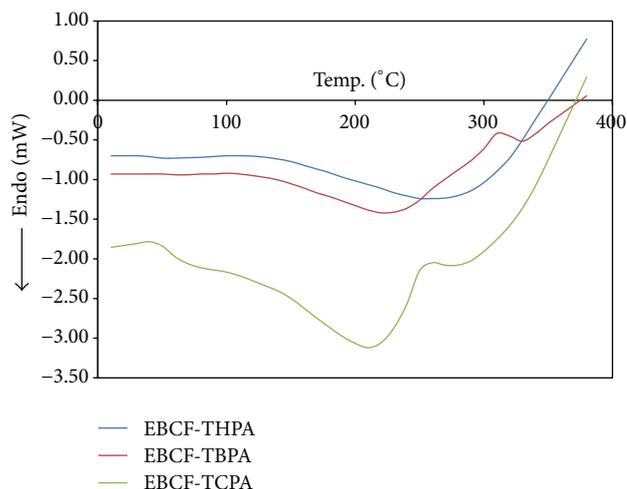


FIGURE 4: DSC thermograms of EBCF-THPA, EBCF-TCPA, and EBCF-TBPA at $10^{\circ}\text{C min}^{-1}$ heating rate in nitrogen atmosphere.

weight loss over those temperatures in its TG curve (Figure 6).

TG curves of cured and uncured EBCF are presented in Figures 5 and 6, from which it is clear that decomposition reactions are very complex and followed multistep degradation reactions. Initial decomposition temperature (T_0), decomposition range, temperature of maximum weight loss (T_{max}), % weight loss involved in each step, and % residue remained at 700°C are reported in Table 2. Decomposition of epoxy resin begins with dehydration of secondary hydroxyl groups followed by homolytic cleavage of the formed allylic bond [14, 15]. Repetition of bond cleavage of the epoxy network leads to the evaporation of the low molecular weight fragments, whereas polymerization of unsaturated

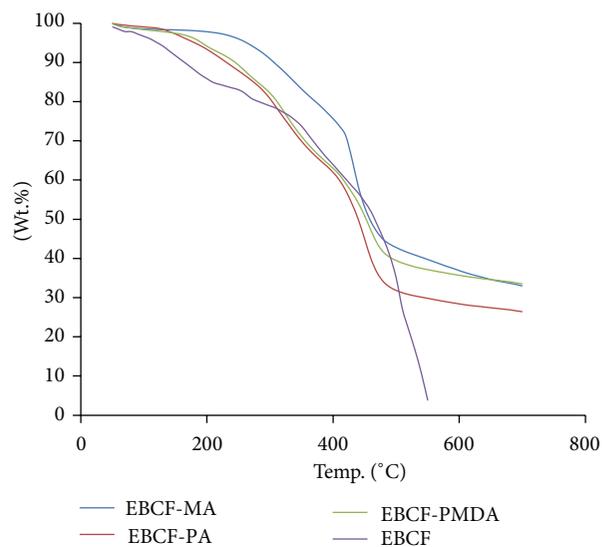


FIGURE 5: TGA thermograms of EBCF, EBCF-MA, EBCF-PA, and EBCF-PMDA at $10^{\circ}\text{C min}^{-1}$ heating rate in nitrogen atmosphere.

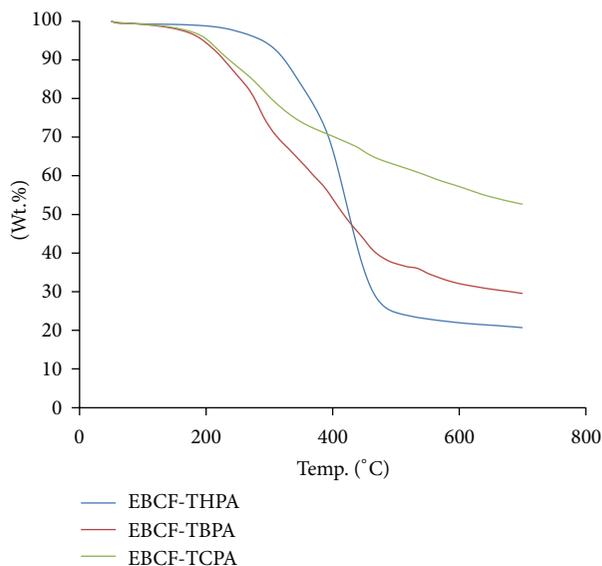


FIGURE 6: TGA thermograms of EBCF-THPA, EBCF-TCPA, and EBCF-TBPA at $10^{\circ}\text{C min}^{-1}$ heating rate in nitrogen atmosphere.

fragments results from dehydration and subsequent aromatization contributing into charring. Crosslinking density depends on the chemical structure of the resin, curing agent, and their functionalities, also on the curing mechanism and conditions selected. Thermal stability order is $\text{EBCF-THPA} > \text{EBCF-MA} > \text{EBCF-PMDA} = \text{EBCF-TBPA} > \text{EBCF-PA} > \text{EBCF}$. The use of MA and THPA as hardeners for EBCF resulted in improvements in good thermal stability, while other hardeners improved it to some extent.

Associated kinetic parameters such as energy of activation (E_a), frequency factor (A), order of reaction (n),

TABLE 3: Kinetic parameters of anhydrides cured and uncured EBCF.

Sample	E_a (kJ mol ⁻¹)	n	A (s ⁻¹)	ΔS^* (JK ⁻¹ mol ⁻¹)	R^2
EBCF	43.90	0.69	4.80×10^2	-197.1	0.986
	29.93	0.26	0.39	-259.1	0.973
	309.61	0.78	6.21×10^{18}	106.9	0.983
	155.97	0.19	3.85×10^7	-108.1	0.992
EBCF-MA	28.27	0.27	0.39	-258.6	0.961
	543.74	2.18	3.38×10^{38}	485.5	0.962
EBCF-PMDA	—	—	—	—	—
	43.15	0.24	43.8	-218.4	0.978
	97.11	1.53	1.41×10^6	-133.2	0.982
	171.94	1.05	1.30×10^{10}	-58.7	0.981
EBCF-PA	—	—	—	—	—
	73.5	1.2	1.17×10^4	-172.8	0.979
	90.37	0.70	1.28×10^4	-173.6	0.978
EBCF-THPA	—	—	—	—	—
	136.18	1.40	9.93×10^6	-98.3	0.973
EBCF-TBPA	48.14	0.39	1.95×10^2	-205.8	0.962
	126.95	1.11	1.27×10^5	-62.9	0.972
	164.62	2.59	1.65×10^5	-50.9	0.992
EBCF-TCPA	110.91	2.63	5.28×10^5	-62.95	0.985
	102.81	2.05	3.63×10^9	-109	0.972

and entropy change (ΔS^*) are determined according to the Anderson-Freeman method [16]:

$$\Delta \ln \left(\frac{dW}{dt} \right) = n \Delta \ln W - \left(\frac{E_a}{R} \right) \Delta \left(\frac{1}{T} \right)$$

$$A = \left(\frac{E_a \beta}{RT^2} \right) e^{E/RT} \quad (1)$$

$$\Delta S^* = R \ln \left(\frac{Ah}{kT} \right),$$

where dW/dt is the weight loss with time, W is the active weight of the substance, β is the heating rate, R is the gas constant, h is the Planck's constant, T is the temperature, and k is the Boltzmann constant. The least square kinetic parameters n , E_a , and A are reported in (Table 3) along with regression coefficients (R^2). The entropy change (ΔS^*) was determined at corresponding T_{\max} and also included in Table 3, from which it is clear that both cured and uncured resins followed either fractional or integral order decomposition kinetics. Ether and ester linkages are thermally weak points in the polymer chain, and hence, selective degradation occurs from those points on heating. The degradation may result in the formation of free radicals, which may further undergo recombination and degrade at high temperatures. The degradation process is a complex process, which involves a variety of reactions such as crosslinking, branching, recombination, and rearrangement. EBCF decomposed completely into low molecular mass substances, while EBCF-MA (37%),

EBCF-PMDA (34%), EBCF-PA (26%), EBCF-THPA (21%), EBCF-TBPA (30%), and EBCF-TCPA (53%) showed a considerable amount of residue at 700°C confirming the formation of highly thermally stable crosslinked product, which may further degrade at elevated temperatures. Large and negative magnitudes of ΔS^* indicated that transition state is more in orderly state than individual resin molecules and vice versa [13, 17–22]. Thus, both nature and structure of the hardeners affected the thermal behavior of the cured resins.

4. Conclusions

Anhydrides cured EBCF is found insoluble in common solvents. IR spectral data supported curing of EBCF. DSC endo/exothermic transition(s) supplemented chemical or physical change when cured and uncured resins were heated under nitrogen atmosphere. Cured and uncured EBCF followed complex and multistep degradation kinetics. Thermal stability order of the cured resins is EBCF-THPA > EBCF-MA > EBCF-PMDA = EBCF-TBPA > EBCF-PA > EBCF. The use of MA and THPA, EBCF-MA (37%), EBCF-PMDA (34%), EBCF-PA (26%), EBCF-THPA (21%), EBCF-TBPA (30%), and EBCF-TCPA (53%) showed a considerable amount of residue at 700°C confirming the formation of highly thermally stable crosslinked product. Curing behavior is also found dependent on both nature and structure of EBCF and hardeners used. MA and THPA hardeners proved to be the best hardeners for EBCF.

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