Curing Study of Epoxy Resin of (2E, 6E)-Bis (4-hydroxybenzylidene)-4-methylcyclohexanone with Different Aromatic Diamines and Anhydrides Hardeners: Spectral and Thermal Analysis

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ABSTRACT

Conventional curing study of epoxy resin of (2E, 6E)-bis (4-hydroxybenzylidene)-4-methyl cyclohexanone (EMBHBC) was conducted at 140 ^{0}/150 ^{0}C by using 4,4'-diaminodiphenylmethane (DDM),4,4'-diaminodiphenylsulphone (DDS),4-4'-diaminodiphenyl ether (DDE), p-phenylenediamine (PDA), 1,2,3,6-tetrahydrophthalic anhydride(THPA), maleic anhydride (MAH) and pyromellitic dianhydride (PMDA). The gel time for DDS, THPA and DDM hardeners are found considerably longer than those of DDE, PDA, MAH and PMDA systems indicated different reactivity towards curing of EMBHBC. Sol–gel analysis of cured resins was carried out in DMF at room temperature. Diamines cured samples showed 76.3-97.5% gel fractions, while anhydrides cured samples showed 84.6-99.6% gel fractions. DDM, PDA and THPA are found suitable hardeners for curing of EMBHBC. Cured EMBHBC samples are characterized by FTIR, DSC and TGA techniques. DSC endothermic/exothermic transitions supported either physical or chemical change as supported by TGA. Diamines and anhydrides cured EMBHBC are thermally stable up to 224–315 ^{0}C and 237–300 ^{0}C, respectively and followed two step degradation reactions except EMBHBC-PDA and EMBHBC-MAH. Diamines and anhydrides cured EMBHBC showed respectively 30–52% and 32–41% residues at 700 ^{0}C. Use of selected hardeners affected curing and thermal behavior of the cured epoxy resins under selected experimental conditions.

KEYWORDS: *Epoxy resin, Curing, Sol-gel, Thermal stability, Kinetic parameters.*

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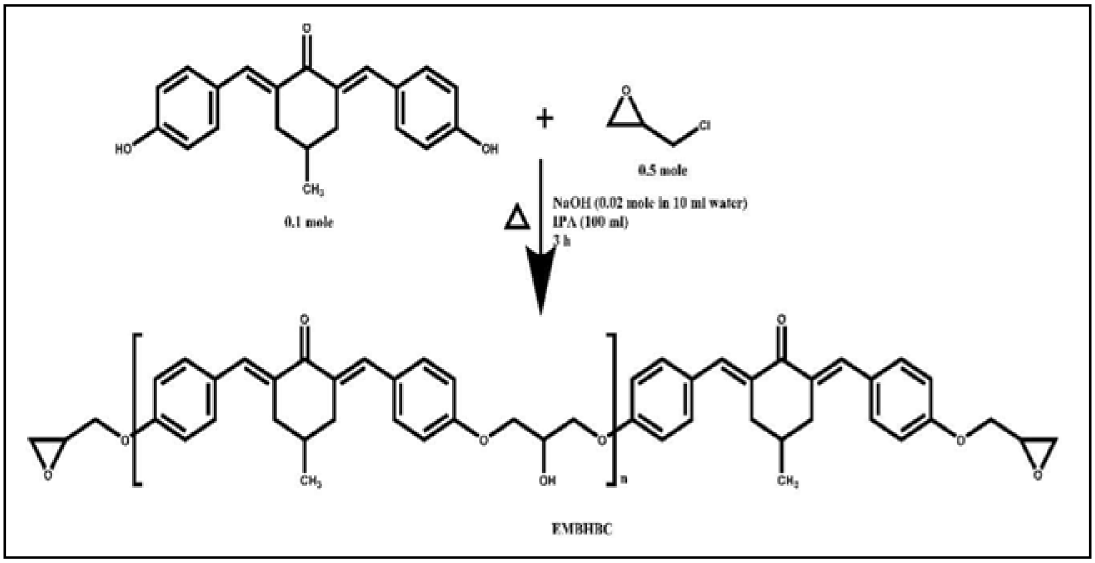
INTRODUCTION

Epoxy resins are well known as high performance thermosetting materials because of their outstanding thermo-mechanical and electrical insulating properties[1-6], mechanical stiffness and toughness[7,8], good heat, chemical and corrosion resistance[2-9], excellent adhesion and coating properties[10], good flame retardant property[11-13], outstanding dimensional stability and good durability. They find their broad range of industrial applications especially in coating[2], adhesives for aerospace[14] and automobile[15,16], electrical and advanced composites[17,18].

Uncured epoxy resins are linear molecules and exist in viscous liquid, semisolid or solid states depending on experimental conditions selected. The basic properties of epoxy resins can be modified by using suitable hardeners, modifiers, fillers and blending with different resins. For advanced microelectronic and packaging technology, epoxy resins must possess outstanding properties such as good thermal stability, low dielectric constant and dissipation factor, low water absorption, low coefficient of thermal expansion, low internal stress, high mechanical strength and low modulus, which are dependent on the chemical structure, curing agents and their functionalities, curing mechanism, curing conditions and ultimate network structure[19,20]. Low flame resistance and low thermal stability of epoxy resins restrict their applications in electronic and microelectronic industries[21,22], where a high flame resistance and a remarkable self-fire extinguishing properties are essential. Thermal properties of epoxy resins can be improved by using various methods. Flame retardants such as boron, phosphorous, and other inorganic materials can improve thermal properties of epoxy resins [23,24]. Curing of epoxy



Scheme I: Synthesis of epoxy resin of (2E, 6E)-bis (4-hydroxybenzylidene)-4-methyl cyclohexanone resins with other thermally stable resins[25,26] can also improve thermal properties. Epoxy resins have drawbacks such as intrinsic brittle nature and considerable moisture absorption tendency from environment, which adversely affect most physico-mechanical properties of the fabricated articles. Both these drawbacks increase by enhancing the cross-link density of the network. There are many reports found in literature on curing of the epoxy resins by using aliphatic and aromatic amines, anhydrides, bisamic acids, polyamines, polyamides, star polymers, etc. [19,20, 27,30]. The nature and structure of the curing agents affect ultimate thermal and mechanical properties of the cured products.

To the best of our knowledge, no work has been reported on diamines and anhydrides curing study of epoxy resins containing chalcone moiety except our recent work [31-34]. In present work we have carried out a comparative curing study of epoxy resin of (2E, 6E)-bis(4-hydroxybenzylidene)-4-methylcyclohexanone (Scheme I) by using various aromatic diamines, anhydrides and dianhydride. The cured products are characterized for their sol-gel, spectral and thermal studies.

EXPERIMENTAL

Materials

All the solvents and chemicals used in this study were of LR grade and were used as received or purified according to reported methods[35]. The epoxy resin of (2E,6E)-bis(4-hydroxybenzylidene)-4-methylcyclohexanone (EMBHBC, EEW 898) was synthesized and purified according to our recent communication[34]. 4,4'-Diaminodiphenyl methane (DDM) and 4,4'-diaminodiphenylsulphone (DDS) were supplied by National Chemicals Vadodara. p-Phenylenediamine (PDA), and 4-4'-diaminodiphenylether (DDE), and pyromellitic dianhydride (PMDA) were supplied by Spectrochem Pvt. Ltd, Mumbai, India. 1, 2, 3, 6-Tetrahydrophthalic anhydride (THPA) was supplied by Merck, Germany. All these hardeners were used as received.

Curing Study

Into seven different test tubes, 2 g EMBHBC and stoichiometric amounts of corresponding hardeners (Table 1) were dissolved in 5 mL chloroform in test tube at room temperature. The mixtures were stirred with glass rods. All these test tubes were placed in a water bath at 60°C to evaporate chloroform for 15 min. When chloroform was evaporated completely, the test tubes were transferred in an oil bath at 140°/150°C with

TABLE 1. Experimental details and sol-gel data of aromatic diamines and anhydrides cured EMBHBC.

Sample code	Hardener (g)	Temp. (°C)	Gel time (min)	Sol fraction (%)	Gel fraction (%)
EMBHBC-DDM	0.22	150	90	2.5	97.5
EMBHBC-DDS	0.28	150	150	23.4	76.6
EMBHBC-DDE	0.11	140	60	23.7	76.3
EMBHBC-PDA	0.06	140	60	4.3	95.7
EMBHBC-THPA	0.34	150	120	0.4	99.6
EMBHBC-MAH	0.12	140	65	13.4	86.6
EMBHBC-PMDA	0.12	140	50	15.4	84.6

TABLE 2. Characteristic FTIR spectral data of diamines and anhydrides cured EMBHBC.

Sample code	N-H/ O-H str.	C=Ostr.	Alkene C=C str.	N-H def.	O-H def.	C-O-H str.	C-O-C str.	S=O str.
EMBHBC- DDM	3222.57	1733.53	1669.47	1646.41	1262.08	1044.29	1256.96	-
EMBHBC- DDS	3410.26	1730.97	1660.23	1659.23	1265.35	1095.60	1259.52	1369.7
EMBHBC- DDE	3296.94	1746.34	1661.79	1600.29	1272.33	1044.29	1215.96	-
EMBHBC- PDA	3266.18	1741.22	1666.91	1646.43	1264.64	1036.61	1267.21	-
EMBHBC- THPA	3433.41	1728.28	1666.91	-	1257.63	1041.60	1264.64	-
EMBHBC- MAH	3343.07	1725.84	1664.35	-	1295.39	1039.17	1246.71	-
EMBHBC- PMDA	3255.93	1730.97	1659.23	-	1267.21	1041.73	1264.64	-

intermittent stirring. The viscosity of the reaction mixture was found to increase with the progress of the crosslinking reaction. The time at which reaction mixture was suddenly converted into infusible mass, known as gel point, and stirring was found difficult. The samples were further post cured at their respective curing temperatures for 30 min and cooled to room temperature. The gel points of diamines and anhydrides cured samples are presented in Table 2. Cured samples were collected carefully by breaking the test tubes and crushed into powder. The cured samples were found insoluble in common solvents like acetone, chloroform, tetrahydrofuran, 1,4-dioxane, 1,2-dichloroethane, dimethylformamide, dimethylsulfoxide, etc. Here after, the cured samples are designated as EMBHBC-DDM, EMBHBC-DDS, EMBHBC-DDE, EMBHBC-PDA, EMBHBC-THPA, EMBHBC-MAH and EMBHBC-PMDA. The gel time for DDS, THPA and DDM hardeners are found considerably longer than those of DDE, PDA, MAH and PMDA systems indicated different reactivity towards curing of EMBHBC. Thus, the nature and chemical structure of the hardeners have affected the crosslinking reactions.

Sol–gel Analysis

Sol–gel analysis of cured resins was carried out in DMF at room temperature. Into seven 100 mL stoppered conical flasks, 0.5 g corresponding cured resins and 25 mL DMF were transferred at room temperature and kept aside for 24 h with intermittent stirring. After 24 h, insoluble masses were filtered off and filtrates were collected into 100 mL conical flasks. The insoluble masses were dried in an oven at 70-75°C. The filtrates were evaporated to dryness. Dried insoluble (gel) and soluble (sol) masses were weighed and determined their % sol-gel fractions. Sol-gel fractions of diamines and anhydrides cured EMBHBC are reported in Table 1. From Table 1, it is observed that diamines and anhydrides cured EMBHBC showed 76.3-97.5% and 84.6-99.6% gel fractions, respectively indicating that the samples are not cured completely at their respective curing temperatures due to inherent nature and chemical structure of the hardeners. This might have been also due to either lower curing temperature or very high viscosity of the infusible mass, which practically restricted molecular motion resulting into incomplete curing. From the present curing study, it is concluded that DDM, PDA and THPA are suitable hardeners for curing of EMBHBC under selected experimental conditions.

Measurements

Fourier transform infrared (FTIR) spectra (KBr pellet) of cured EMBHBC were scanned on a Shimadzu FTIR-8400 spectrometer over the frequency range from 4000 to 400 cm^{-1}. Differential scanning calorimetric (DSC) measurements were carried out on a Shimadzu DSC60 at 10°C min^{-1} heating rate in nitrogen atmosphere (flow rate 100 mL min^{-1}) using standard aluminum pans. Known mass of the samples were taken in aluminum pans, covered by empty aluminum lids and sealed using a crimper. Thermogravimetric (TG) measurements were carried out on a Pyris-I Perkin Elmer TGA at 10°C cm^{-1} heating rate in nitrogen atmosphere (flow rate 100 mL min^{-1}). The DSC and TG thermograms were scanned over the temperature ranges from 40–400°C and 40–800°C, respectively.

RESULTS AND DISCUSSION

IR Spectral Analysis

Fourier transform infrared spectra of damines and anhydrides cured EMBHBC samples are presented in Figures. 1 and 2, respectively and characteristic IR absorption peaks are reported in Table 2 besides normal modes of vibrations and deformation of other functional groups. EMBHBC showed characteristic IR absorption peaks at 3456.55 cm^{-1} (O-H str. broad), 1660.71 cm^{-1} (C=O str.), 1246.02 cm^{-1} (C-O-C str.), 952.84 and 914.26 cm^{-1} (C-O str. epoxide).[34] Diamines cured EMBHBC showed absorption peaks at 3252–3410 cm^{-1} (N-H and O-H str., broad), 1731–1746 (C=O str.), 1600-1646 cm^{-1} (N-H def.), while anhydrides cured EMBHBC showed characteristic absorption peaks at 3256-3434 cm^{-1} (O-H str., broad) and 1726-1731 (C=O str.), From Figures. 1 and 2, it is observed that upon curing of EMBHBC, C-O str. peaks due to epoxide groups at 952.84 and 914.26 cm^{-1} are disappeared and new peaks at 3252–3410 cm^{-1} and 1600–1646 cm^{-1} are appeared due to N-H str. and N-H def. for diamines cured EMBHBC, while anhydrides cured EMBHBC showed absorption peaks at 3256–3434 cm^{-1} and 1726–1731 cm^{-1} due to C=O str. of ester groups. Uncured EMBHBC showed considerably strong O-H str. peak as compared to O-H and N-H str. (diamines cured) and O-H str. (anhydrides cured) of cured EMBHBC. The peaks due to O-H str., N-H str. (3256–3434 cm^{-1}) and C=O str. (1726–1731 cm^{-1}) are shifted towards lower range. Absorption peaks over the range 640–1519 cm^{-1} are masked due to strong absorption of amine and hydroxyl groups. Thus, IR spectral data supported the curing of EMBHBC.

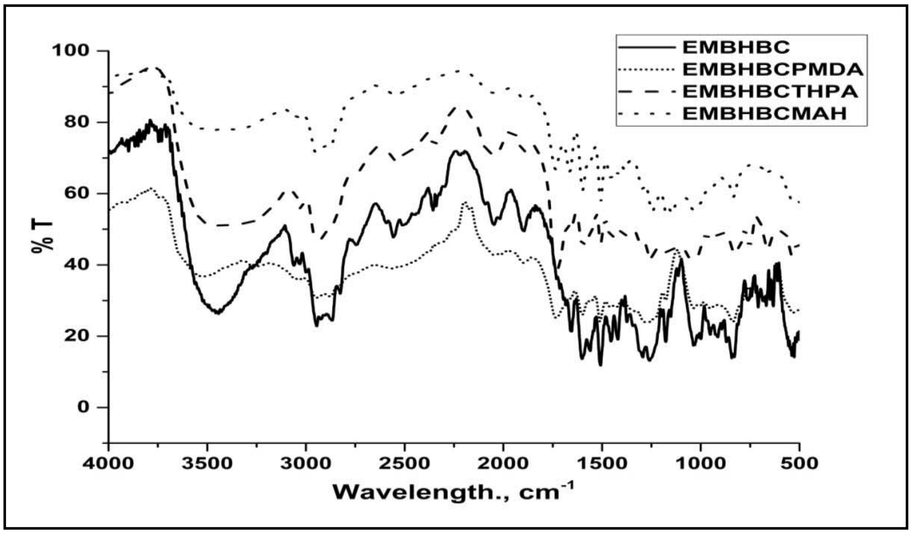


Figure 1. A comparative FT-IR spectra of EMBHBC, EMBHBC-DDS, EMBHBC-DDM, EMBHBC-DDE and EMBHBC-PDA.

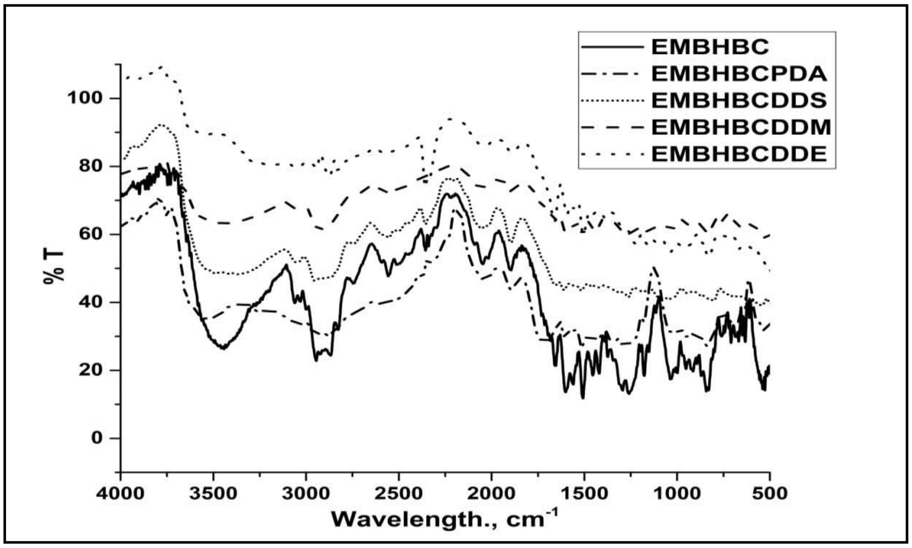


Figure 2. A comparative FT-IR spectra of EMBHBC, EMBHBC-MAH, EMBHBC-PMDA and EMBHBC-THPA.

Thermal Analysis

DSC thermograms of uncured, diamines and anhydrides cured EMBHBC at 10°C min^{-1} heating rate in nitrogen atmosphere are presented in Figures. 3 and 4, respectively. DSC endo-thermic/exothermic transitions of uncured, diamines and anhydrides cured EMBHBC are reported in Table 3. A small and broad endothermic transition centered at 71.76° (DDM), 82.27°(DDS), 57.52°(DDE), 100.82° (PDA) and 121.43°C (PMDA) is due to either melting of uncured EMBHBC or branched EMBHBC. An endothermic transition centered at 293.35°C (DDM), and 238.50°C (DDS) is due to some physical change, while an exothermic transition centered at 136.30°C (THPA), 232.81°C (MAH) and 237.30°C (PMDA) is probably due to residual curing reaction (chemical change) and further supported by no weight loss over those temperatures in corresponding TG thermograms (Figures. 5 and 6). An exothermic transition centered at 322.23°C (DDE), 318.72°C (PDA) and 399.99°C (THPA) is due to degradation reaction and it is supported by weight loss at those temperatures in their corresponding TG thermograms (Figures. 5 and 6).

TG thermograms of diamines and anhydrides cured EMBHBC at the heating rate of 10°C min^{-1} in nitrogen atmosphere are presented in Figures. 5 and 6, respectively from which it is clear that cured resins followed two step degradation reactions except EMBHBC-PDA and EMBHBC-MAH. Initial decmposition temperature (T_o), 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 3. The T_{max} values for each step were determined from corresponding DTG thermograms. DDE, PDA and MAH cured EMBHBC showed 4.6–5.9 % weight loss in the temperature range 143-

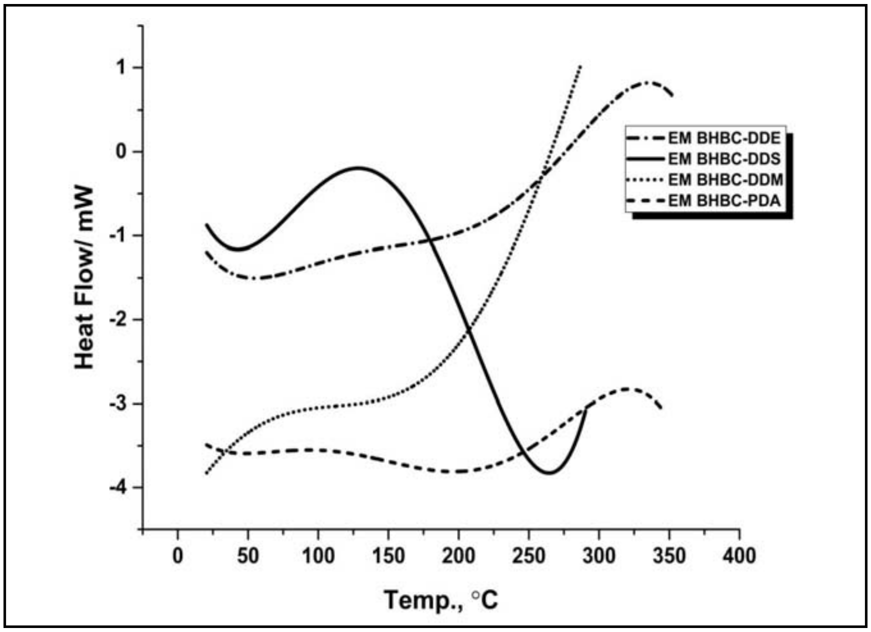


Figure 3. A comparative DSC thermograms of EMBHBC, EMBHBC-DDM, EMBHBC-DDE, EMBHBC-DDS, and EMBHBC-PDA at 10°C min^{-1} heating rate in nitrogen atmosphere.

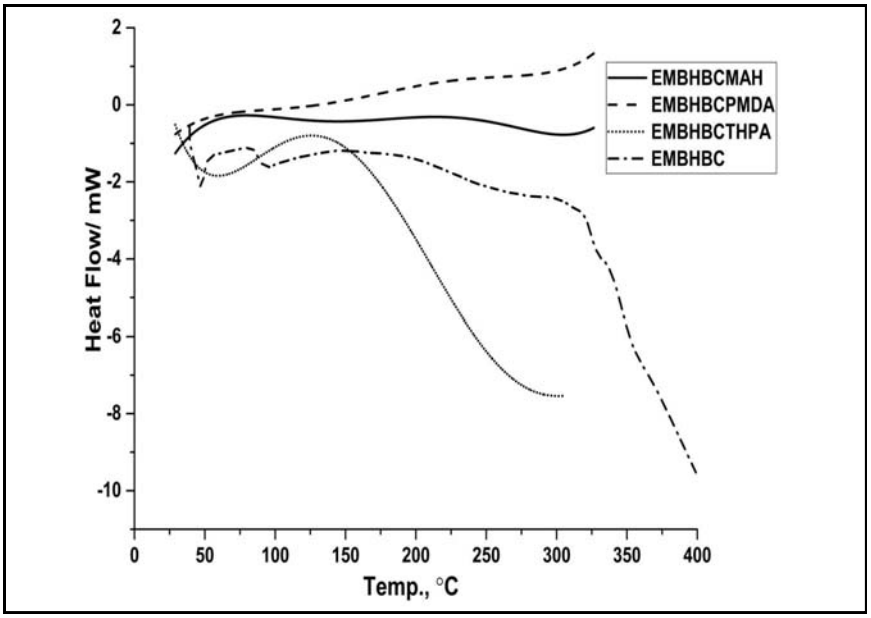


Figure 4. A comparative DSC thermograms of EMBHBC, EMBHBC-THPA, EMBHBC-MAH and EMBHBC-PMDA, and at 10°C min^{-1} heating rate in nitrogen atmosphere.

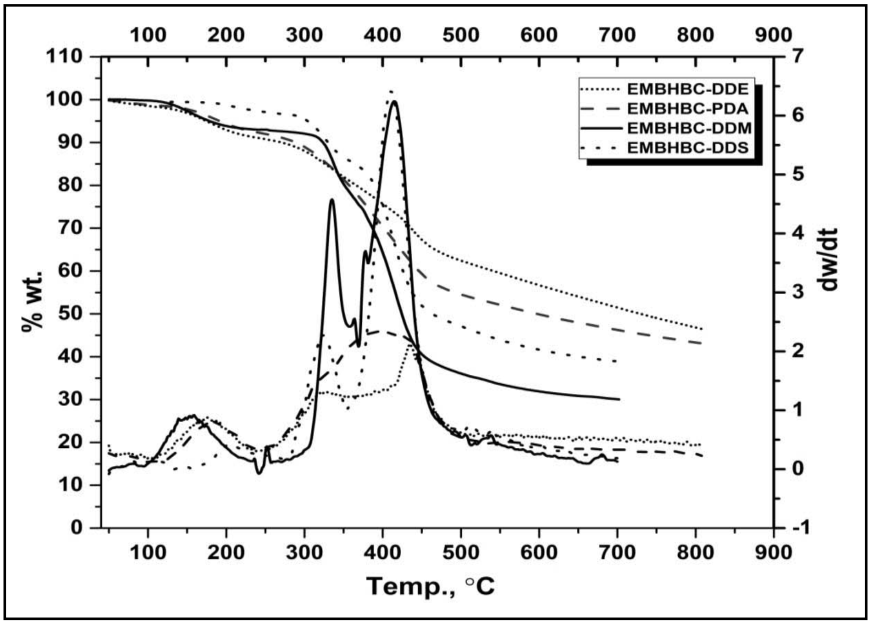


Figure 5. TG-DTG thermograms of EMBHBC-DDE, EMBHBC-PDA, EMBHBC-DDM, EMBHBC-DDS at 10°C min^{-1} heating rate in nitrogen atmosphere.

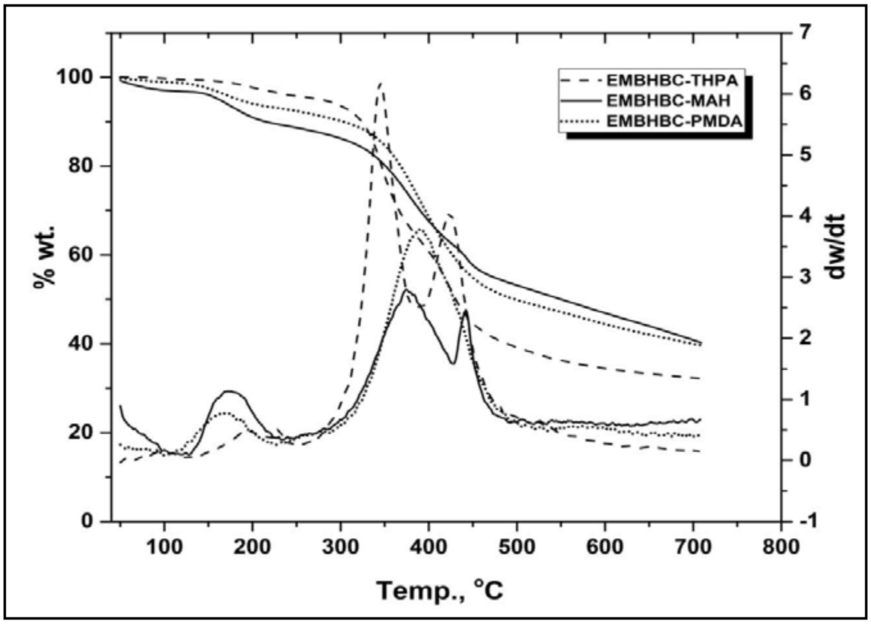


Figure 6. TG-DTG thermograms of EMBHBC-THPA, EMBHBC-MAH, and EMBHBC-PMDA at 10°C min^{-1} heating rate in nitrogen atmosphere.

TABLE 3. DSC and TGA data of aromatic diamines and anhydrides cured EMBHC.

Sample	**DSC transition**	**Transition temp., (°C)**	**T_0, (°C)**	**Decomp. range, (°C)**	**$T_{max,}$ (°C)**	**%Wt. loss**	**Residue at 700°C**
EMBHBC[34]	Endo Exo Exo	93.25 155.02 279.25	293 379	293-379 379-575	345.34 419.3	19.94 40.2	33.10
EMBHBC-DDM	Endo Endo	71.66 293.35	315 375	315-352 375-468	337 418	11.6 36.0	30
EMBHBC-DDS	Endo Endo	82.27 238.50	300 373	300-350 373-600	325 411	09.0 42.3	39
EMBHBC-DDE	Endo Exo Exo	57.52 236.02 322.23	143 224 402	143-224 224-394 402-546	181 329 438	5.6 15.2 15.7	52
EMBHBC-PDA	Exo Exo	100.82 318.72	146 280	146-215 280-511	185 425	4.6 36.7	46
EMBHBC-THPA	Exo Exo Exo	136.30 314.54 399.39	291 400	291-373 400-560	347 424	26.5 25.0	32
EMBHBC-MAH	Exo Exo	91.95 232.81	157 300 435	157-224 300-425 435-500	171 378 443	5.9 23.5 7.9	41
EMBHBC-PMDA	Endo Exo	121.43 237.30	145 320	145-190 320-586	165 393	3.17 43.6	40

224°C probably due to entrapped solvent and unconsumed hardeners. Diamines cured EMBHBC are thermally stable up to 224-315°C, while anhydrides cured EMBHBC are thermally stable up to 237-300°C. Observed thermal stability orders are EMBHBC-DDM (315°C) > EMBHBC-DDS (300°C) > EMBHBC-PDA (280°C) > EMBHBC-DDE (224°C) and EMBHBC-MAH (300°C) > EMBHBC-THPA (291°C) > EMBHBC-PMDA (237°C). DDM, DDS, and MAH cured EMBHBC showed somewhat higher thermal stability than thermally cured EMBHBC (293°C), while DDE, PDA and PMDA cured EMBHBC showed somewhat lower thermal stability than that of EMBHBC.[34] EMBHBC-THPA showed almost identical thermal stability with that of EMBHBC. Diamines (30-52%) and anhydrides (32-41%) cured EMBHBC showed considerably large residues at 700°C.

Kinetic parameters provide useful information about final characteristic properties of the cross-linked products. Associated kinetic parameters such as energy of activation (E_a), frequency factor (A), order of reaction (n) and entropy change (ΔS^*) are determined according to the Anderson-Freeman method[36]:

$$\Delta \ln dw/dt = n \, \Delta \ln W - (Ea/R) \, \Delta (1/T) \qquad (1)$$

$$A = Ea\beta / RT^2 \; e^{Ea/RT} \qquad (2)$$

$$\Delta S^* = R \ln (Ah/kT) \qquad (3)$$

TABLE 4. Kinetic parameters of aromatic diamines and anhydrides cured EMBHBC.

Sample	n	E_a, kJ mol^{-1}	A,s^{-1}	ΔS^*, JK^{-1} mol^{-1}	R^2
EMBHBC [34]	2.35 1.52	223.8 164.7	9.41×10^{16} 1.83×10^{10}	73.96 -55.45	0.9709 0.9956
EMBHBC-DDM	3.02 1.6	505.9 196.0	5.68×10^{41} 5.4×10^{12}	548.5 -8.2	0.9629 0.9844
EMBHBC-DDS	1.49 1.47	160.6 189.9	9.59×10^{11} 2.56×10^{12}	-21.3 -14.3	0.974 0.9774
EMBHBC-DDE	1.00 0.68 1.01	33.6 39.6 164.3	23.8 5.9 7.6	-222.0 -235.9 -63.0	0.9957 0.9885 0.9934
EMBHBC-PDA	1.13 0.63	47.6 39.9	1.20×10^{2} 1.6	-189.5 -248.1	0.9986 0.9903
EMBHBC-THPA	2.1 1.63	250.8 220.2	1.73×10^{19} 2.84×10^{14}	117.3 24.7	0.9846 0.9984
EMBHBC-MAH	1.51 0.73 0.47	66.5 62.9 310.6	4.49×10^{5} 3.28×10^{2} 5.5×10^{20}	-140.017 -203.3 144.9	0.997 0.9957 0.9318
EMBHBC-PMDA	1.20 1.49	46.2 91.1	1.57×10^{3} 5.75×10^{4}	-186.95 -160.5	0.9981 0.9771

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 namely n, E_a, and A are reported in Table 4 along with regression coefficients (R^2). The entropy change (ΔS^*) was determined at corresponding T_{max} and also included in Table 4, from which it is observed that cured resins followed either fractional or integral order degradation kinetics. First step degradation of DDM, PDA and THPA cured EMBHBC involved higher amount of energy of activation than that of second step degradation, while second step degradation of DDS, DDE, MAH and PMDA cured EMBHBC involved higher amount of energy of activation than that of first step degradation due to different nature and chemical structure of the hardeners used for curing purposes. In accordance with theory, it is observed that higher is the values of Ea higher is the values of A. Thermally cured EMBHBC[34] showed higher Ea than those of diamines and anhydrides cured EMBHBC except DDM and THPA cured EMBHBC. Large and negative values of ΔS^* of diamines and anhydrides cured EMBHBC showed that transition state is more in orderly state than individual resin molecules and vice versa[29-34]. Degradation of first step of the resin molecule proceeds with the dehydration of secondary hydroxyl groups with formation of allylic bonds[37,38] followed by either polymerization or homolytic cleavage of these bonds resulting into evolution of low molecular weight fragments.

Use of anhydrides as crosslinking agents result into formation of acids followed by crosslinking reactions and as a consequence formation of ester and ether bonds take place with the extent of the crosslinking reactions.[39] When dicarboxylic acids are used as crosslinking agents, they result into softening effect without affecting the thermal properties of the cross-linked products. Degradation products may be toxic to human beings and polluting the environment. The identification of the degradation products may be useful for the effective solutions to be taken[28, 40-42]. Ether and amine/ester linkages are thermally weak linkages in the cured EMBHBC molecules and therefore selective rupture takes place from such weak linkages on heating. The rupture of the resin molecules results into the formation of free radicals, which may further undergo a variety of secondary reactions such as recombination, branching, crosslinking, rearrangements, etc. and may further degrade at elevated temperatures. Thus, the degradation reactions are complex reactions and involve various toxic or nontoxic gases depending on constituent elements of the resin molecules. EMBHBC-DDM (30%), EMBHBC-DDS (38.9%), EMBHBC-DDE (51.5%), EMBHBC-PDA (46.3%), EMBHBC-THPA (32.4%), EMBHBC-MAH (40.8%) and EMBHBC-PMDA (39.9%) showed a considerable amount of residues at 700°C confirming the formation of highly thermally stable cross linked products. Thus, both nature and chemical structure of the hardeners affected the thermal behavior of the cured EMBHBC.

CONCLUSION

Epoxy resin of (2E, 6E)-bis (4-hydroxybenzylidene) -4-methylcyclohexanone (EMBHBC) was cured at 140°/150°C by using different aromatic diamines and anhydrides. Aromatic diamines and anhydrides cured EMBHBC revealed 76.3-97.5% and 84.6-99.6 % gel fractions, respectively. DDM, PDA and THPA are found suitable hardeners for curing of EMBHBC. DSC endothermic/exothermic transitions supported either physical or chemical change as supported by TGA. Diamines and anhydrides cured EMBHBC are thermally stable up to 224-315°C and 237-300°C, respectively and followed two step degradation reactions except EMBHBC-PDA and EMBHBC-MAH. Diamines and anhydrides cured EMBHBC showed respectively 30-52% and 32-41% residues at 700^{0}C due to further crosslinking. Cured resins followed either fractional or integral order degradation kinetics and showed different values of energy of activation, frequency factor and entropy change. Use of selected hardeners affected curing and thermal behavior of the cured epoxy resins under selected experimental conditions.

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