Synthesis and Physico-chemical Studies on Chalcone Based Epoxy Resin of (2E, 6E)-Bis (4-hydroxybenzylidene) cyclohexanone

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ABSTRACT

Chalcone based epoxy resin (EBHBC) of (2E, 6E)- bis(4-hydroxybenzylidene) cyclohexanone (BHBC) was synthesized by condensing 0.5 mol BHBC and 2.5 mol epichlorohydrin in 500 mL isopropanol as a solvent and 1.0 mol NaOH in 50 mL water as a catalyst at 80°C. The structure of EBHBC is supported by spectral techniques. Molecular weights and molecular weight distribution of EBHBC were determined by gel permeation chromatography. DSC thermogram of EBHC showed one endothermic transition (146.1°C) and two endothermic transitions (253.52°C and 397.34°C) due to melting, some physical change and decomposition transitions, respectively. EBHBC is thermally stable up to about 300°C and followed two step degradation reactions. First step involved 21.2% weight loss over 300-390°C with temperature of maximum weight loss at 382°C. Similarly second step involved 39% weight loss over 390-555°C with temperature of maximum weight loss at 418°C.

KEYWORDS : *Photosensitive epoxy resin, Epoxy equivalent weight, Thermal stability, Kinetic parameters.*

1. INTRODUCTION

Chalcones are the compounds containing α, β- unsaturated carbonyl groups and possess a variety of biological activities such as anti-inflammatory, anti-oncogenic, anti-microbial, anti-viral and anti-oxidant[1,2]. Polymers containing chalcone, cinnamate, dibenzalacetone, coumarine, and their derivatives in both main chain and side chain are used as photosensitive materials[3-5]. Such photosensitive materials are used in optical data storage devices, photo resists and photolithographic assemblies [6-8].

Epoxy resins are all-round thermosetting polymers and are used in diverse fields such as in advanced composites for engineering and

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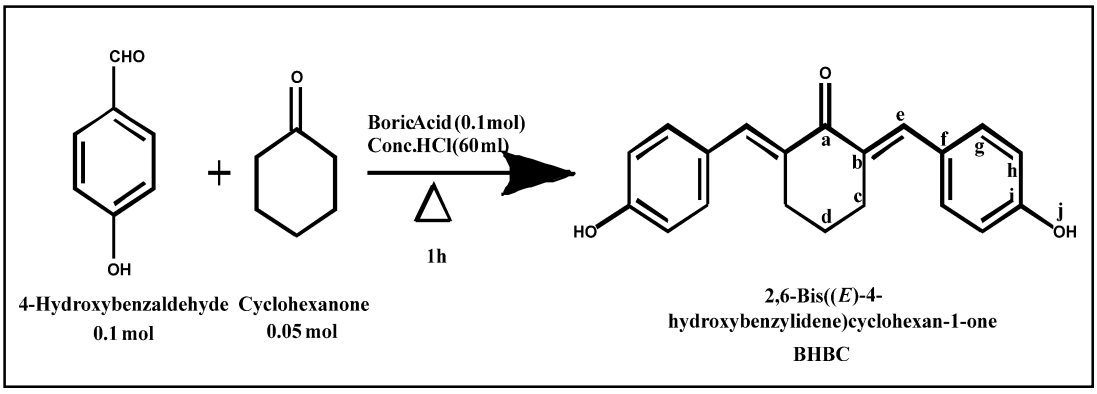
aerospace applications, coatings, nanocomposites, structural adhesives, matrices for fiber-reinforced composites and lithographic inks, microelectronics, protective coatings, low stress IC encapsulates, excellent mechanical and electrical properties, excellent adherence to many substrates, etc. because of their high strength, high stiffness, dimensional stability and good chemical resistance[9-17].

A few reports are available on the epoxy resins containing chalcone moieties[15, 18]. In this paper we have reported synthesis of photosensitive epoxy resin of (2E, 6E)-bis (4-hydroxybenzylidene) cyclohexanone.

EXPERIMENTAL

Materials and Methods

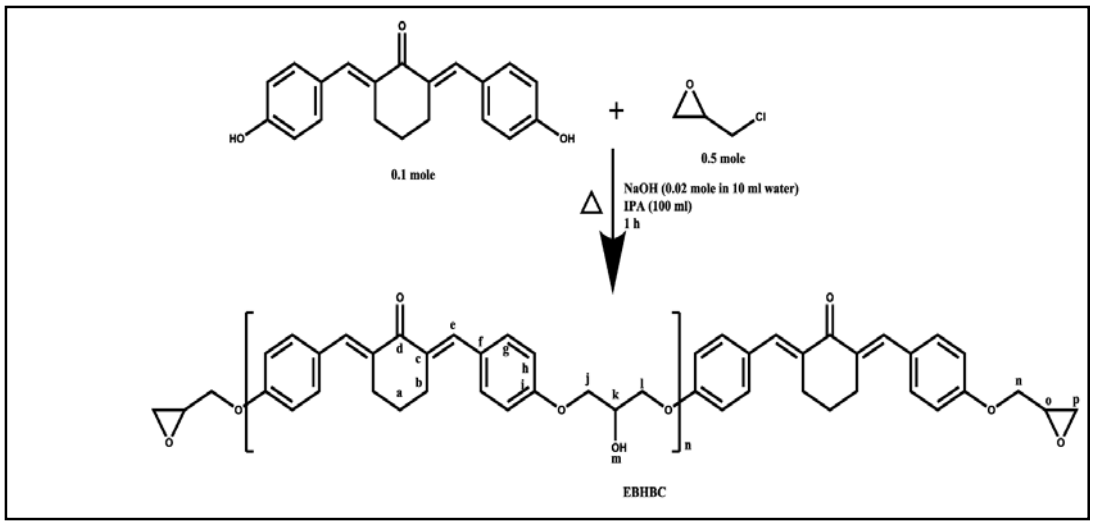
All the chemicals and solvents used were of LR grade and used as received or purified prior to their use [19]. 4-Hydroxybenzaldehyde and epichlorohydrin were supplied by Spectrochem Pvt. Ltd, Mumbai. Isopropyl alcohol, methanol, chloroform, n-hexane, dimethyl-sulphoxide (DMSO), N, N'-dimethylformamide (DMF), tetrahydrofuran (THF), 1,4-dioxane, methyl-ethylketone (MEK), 1,2-dichloromethane, sodium hydroxide and boric acid were supplied by Allied Chemical Corporation, Vadodara. Cyclohexanone was supplied by Sisco Chem., Mumbai. (2E,6E)-2,6-Bis (4-hydroxybenzylidene) cyclohexanone (BHBC) was synthesized and crystallized according to our recent publication[20] (Scheme-1).



Scheme 1.

Synthesis of Chalcone based Epoxy Resin of (2E,6E)-2,6-Bis(4-hydroxybenzylidene) cyclohexanone

Epoxy resin of (2E,6E)-2,6-bis(4-hydroxybenzylidene) cyclohexanone was synthesized according to Scheme-2. The detail process is as follows. A 0.5 mol BHBC, 2.5 mol epichlorohydrin (ECH) and 500 mL isopropyl alcohol (IPA) were placed in a 2L two necked round bottomed flask equipped with a mechanical stirrer and a condenser and the mixture was brought to reflux with stirring and 1.0 mol NaOH in 50 mL water was added drop wise and refluxed for 1.0 h. The reaction mass was cooled to room temperature and neutralized by using dilute hydrochloric acid and yellow colored resin was isolated from cold water, filtered, washed well with water and dried at 50°C. The resin was purified three times from chloroform-hexane system to get shining yellow colored powder. The resin is soluble in chloroform, tetrahydrofuran, 1, 4-dioxane, dimethyl formamide, 1,2-dichloromethane and N,N′-dimethyl formamide. The yield and melting point of the resin are 83 % and 98-105°C, respectively. The epoxy resin here after designated as EBHBC.



Scheme 2

Measurements

The epoxy equivalent weight (EEW) of EBHBC was determined by pyridine pyridiniumchloride method [21]. and it is found to be 341.4. Molecular weights and molecular weight distribution of EBHBC were determined by gel permeation chromatography using Perkin Elmer GPC (Series 200) using THF as a solvent and standard polystyrene mixed beads at 30°C. Observed weight average molecular weight ($\bar{M}_w$), number average molecular weight, ($\bar{M}_n$) and molecular weight distribution ($\frac{\bar{M}_w}{\bar{M}_n}$) are 1015, 547 and 1.86, respectively. The UV-Visible spectrum of EBHBC (10^{-3} %) was scanned on a Shimadzu UV1700 over wavelength range from 200-700nm by using tetrahydrofuran as a solvent. The IR spectrum of EBHBC was scanned on a Shimadzu 1S-IR affinity FTIR spectrometer over the frequency range from 4000-600 cm^{-1}. ^{1}HNMR and ^{13}CNMR spectra of EBHBC were scanned on a Bruker AVANCE III (400 MHz) spectrometer by using CDCl3 as a solvent and TMS as an internal standard. Differential scanning calorimetric (DSC) measurements were carried out on a Shimadzu DSC60 (Kyoto, Japan) at 10°Cmin^{-1} heating rate under a nitrogen atmosphere (20mLmin^{-1} flow rate) with standard aluminum pans. Thermogravimetric analysis (TGA) was carried out on a Pyris-I Perkin Elmer TGA (Massachusetts, USA) at a 10°Cmin^{-1} heating rate under a nitrogen atmosphere (20mLmin^{-1} flow rate).

RESULTS AND DISCUSSION

Spectral Analysis

UV-Visible spectrum of 10^{-3} % THF solution of EBHBC is presented in Fig. 1. EBHBC exhibited two absorption peaks (λ_{max}) at 238 and 349 nm. These peaks are assigned as π-π^* and n-π^* transitions due to presence of double bonds and lone pairs of electrons on oxygen atoms, respectively.

FTIR spectrum of EBHBC is shown in Fig. 2. The characteristic absorption peaks (cm^{-1}) are assigned as follows: 3481.51 (O-H str.), 3068.75 (=C-H str.), 1660.71 (C=O str. and C=C str. alkene), 1597.06, 1562.34, 1508.33 and 1456.26 (C=C str.), 1425.40 and 1382.96 (C-H def.), 1348.24 O-H def. C-OH, 1249.87 (C-O

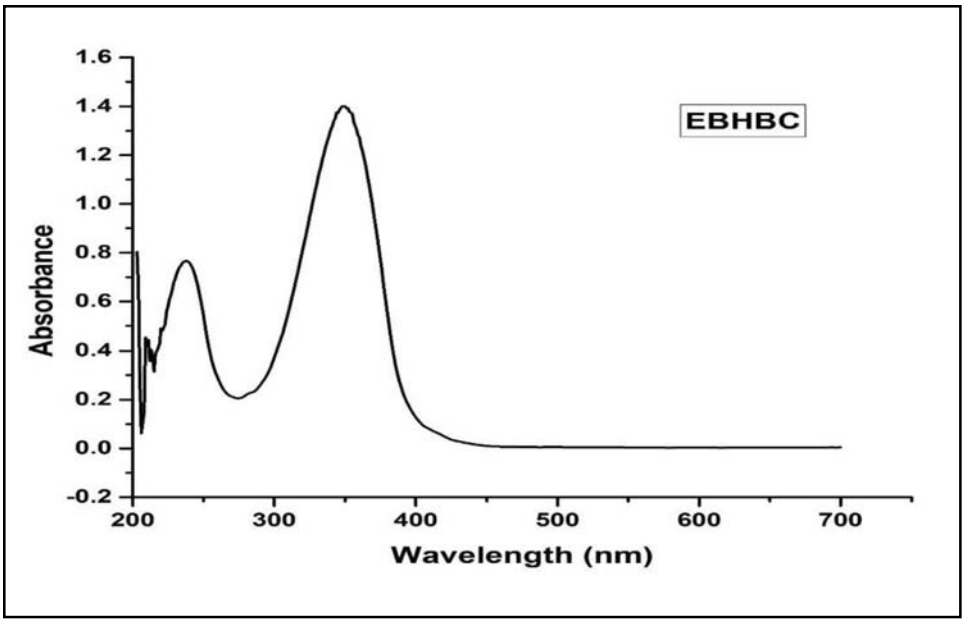


Fig. 1. UV-Visible spectrum of EBHBC (10^{-3}%) in THF.

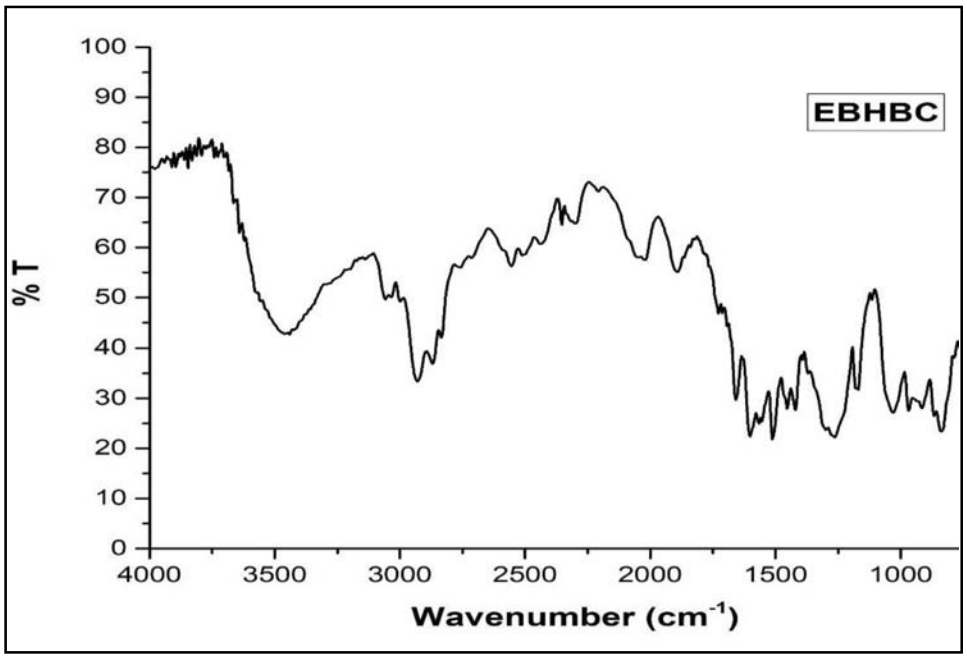


Fig. 2. FTIR (KBr) spectrum of EBHBC.

str.), 1161.75 and1139.93 (C-H ipd), 1028.06 (C-O str. C-OH), 970.19 and 914.26 (C-O str. epoxide), 862.18, 833.25 and 734.88 (C-H oopd). The absorption peaks at 1249.87, 970.19 and 914.26 confirmed the formation of the epoxy resin.

^{1}HNMR spectrum of EBHBC is shown in Fig. 3 from which it is observed that the spectrum is

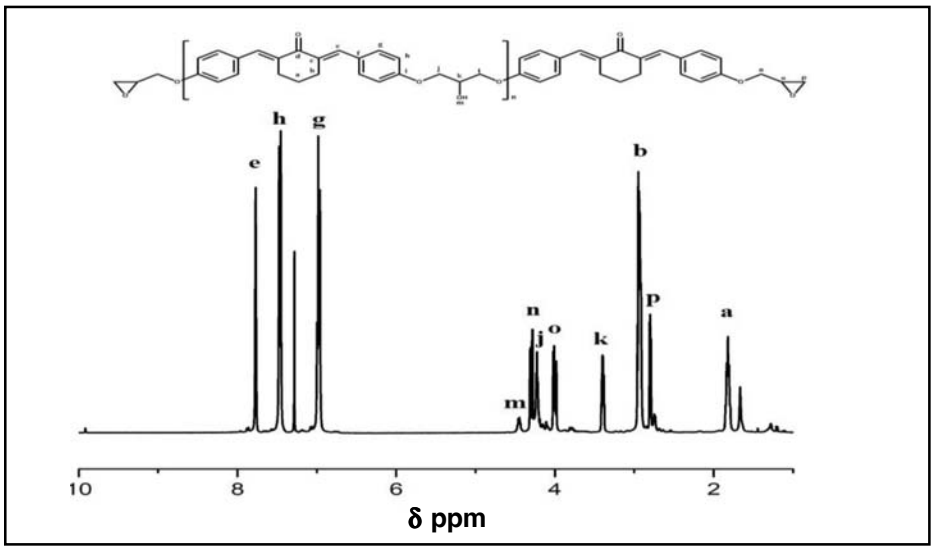


Fig. 3. ^{1}HNMR (400 MHz) spectrum of EBHBC in CDCl3.

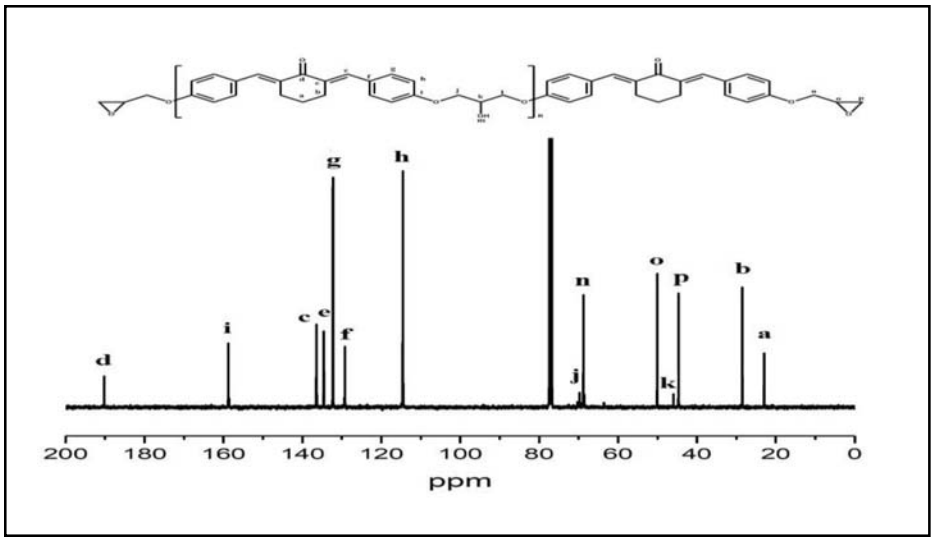


Fig. 4. ^{13}CNMR (400 MHz) spectrum of EBHBC in CDCl3.

complex due to $–OCH_2CHOHCH_2$- and epoxide residues in the resin. The chemical shift and type of protons are as follows: 1.851-1.791 [m, H(a)] 2.808-2.789 [m, H(p)], 2.961-2.981 [m, H(b)], 3.416-3.378 [m, H(k)], 4.024-3.982[m, H(o)], 4.261-4.213[m, H(j)], 4.315-4.287 [m, H(n)], 4.45[broad s, OH(m)], 6.998-6.961[dd, ArH(g), J=8.4], 7.284[s $CDCl_3$], 7.475-7.454 [dd, ArH(h), J=8.4] and 7.771 [s, H(e)].

^{13}CNMR spectrum of EBHBC is shown in Fig. 4. The chemical shifts of different carbon atoms are assigned as follows: 22.99(a), 28.50(b), 44.67(p), 45.96(k), 50.06 (o), 68.77 (n), 69.77 (j), 70.32 (l), 77.4.-76.66 ($CDCl_3$), 114.55(h), 129.22(f), 132.26(g), 134.55(e), 136.43(c), 158.77 (i) and 190.21(d).

Thermal Analysis

Thermal analysis of thermosetting materials are very useful in understanding structure/property/processing relationships for manufacture and utilization of such materials. DSC thermogram of EBHBC is presented in Fig. 5. A broad endothermic transition centered at 146.1°C is due to melting of EBHBC and two broad endohermic transitions centered at 253.52°C and 397.34°C are due to some physical change

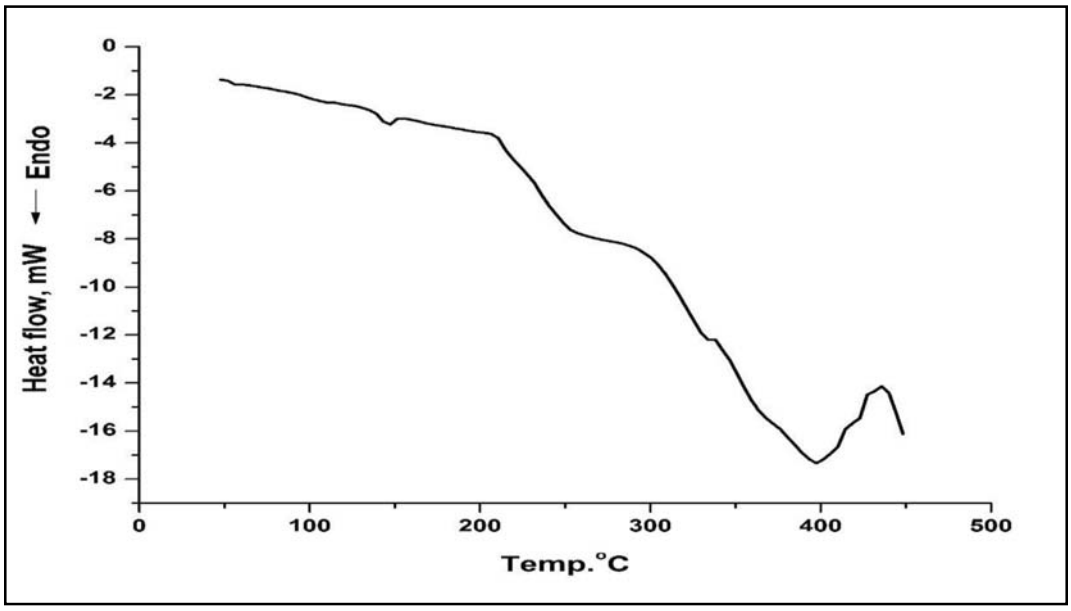


Fig. 5. DSC thermogram of EBHBC at the heating rate of 10°Cmin^{-1} under nitrogen atmosphere.

and decomposition of EBHBC, respectively and it is further confirmed by no weight loss and weight loss at those respective temperatures in its TG curve (Fig. 6). TG thermogram of EBHBC is presented in Fig. 6 from which it is observed that it is thermally stable up to about 300°C and followed two step degradation reactions. First step involved 21.2% weight loss over 300-390°C with temperature of maximum weight loss at 382°C. Similarly second step

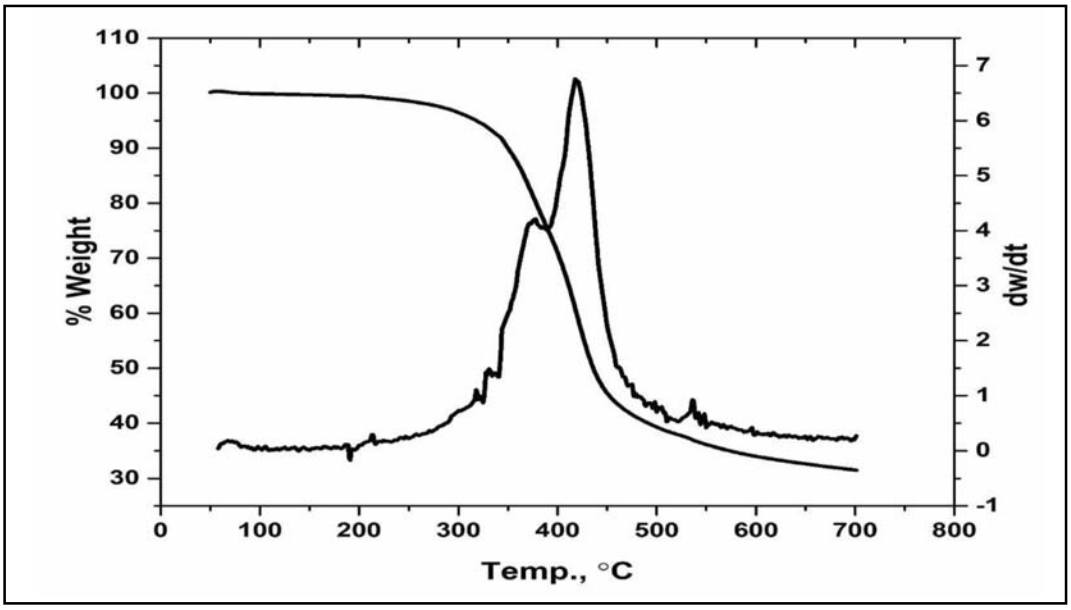


Fig. 6. TG-DTG curves of EBHBC at the heating rate of 10°Cmin^{-1} under nitrogen atmosphere.

involved 39% weight loss over 390-555°C with temperature of maximum weight loss at 418°C. A 34% residue was observed at 600°C. EBHBC has shown considerably higher thermal stability than epoxy resin of 1,3-bis(4-hydroxypphenyl) prop- 2-en-1–one (ECH), 225°C)[15].

Kinetic parameters such as energy of activation (E_a), frequency factor (A), order of reaction (n) and entropy change (ΔS^*) were determined according to Anderson-Freeman method[22]:

$$\Delta \ln dW/dt = n \Delta \ln W - (Ea/R) \Delta (1/T) \quad (1)$$

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

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

Where dW/dt is the weight loss with time, W is the active weight of the substance, β is the heating rate, R (8.314 JK^{-1}mole^{-1}) is the gas constant, h(6.626 x 10^{-34} Js^{-1}) is the Planck's constant, T is the temperature and k(1.380 x 10^{-23} JK^{-1}mol^{-1}) is the Boltzmann constant. The derived least squares values of n, E_a, A and regression coefficients R^2 for first and second steps are 0.02, 39.91 kJmol^{-1}, 2.83s^{-1} and 0.974; and 1.55, 206.19 kJmol^{-1}, 3.32x10^{13} s^{-1} and 0.998, respectively. The entropy change ΔS^* was determined at corresponding temperature of maximum weight loss and it is -242.8 and 6.93 JK^{-1}mol^{-1}, respectively for first and second steps. Comparatively EBHBC has shown low residue than that of ECH (47.2 % at 600°C)[15]. Ea and A values for first step are smaller than that of second step indicated that dehydration step requires lower thermal energy than thermal polymerization followed by degradation of cross-linked resin. Decomposition of first step of the resin involved dehydration of secondary hydroxyl groups with formation of allylic bonds [23,24] followed by

homolytic cleavage of these bonds. Repetition of the bond cleavage of the epoxy network led to evolution of low molecular weight fragments. Polymerization of allylic fragments led to further crosslinking reaction and aromatization contributing charring[23, 24]. Thus, homolytic cleavage of allylic bonds required high thermal energy than that of dehydration step. Ether and hydroxyl linkages are weak points in the polymer chain. Selective cleavage occurs from such weak points on heating with the formation of free radicals, which may further undergo various reactions such as recombination, crosslinking, branching, rearrangement, etc. Recombination of free radicals resulted into highly thermally stable cross-linked product as evident from the large residue (34 %) left at 600°C. A large and negative magnitude of ΔS^* for step-1 indicated that the transition state is in highly ordered state than that of individual resin molecules, while small and positive magnitude of ΔS^* of the thermally cured resin indicated that transition state is disorderly state than that of individual resin molecules[25-27].

CONCLUSIONS

Epoxy resin containing chalcone moiety was synthesized and characterized by spectral and thermal techniques and also by molecular weights and molecular weight distribution. EBHBC is highly soluble in common solvents. EBHBC possesses good thermal stability and followed two step thermal degradation kinetics.

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