Synthesis and Characterization of Epoxy Resin of (2E, 6E) - Bis (4-hydroxybenzylidene) -4-methylcyclohexanone

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ABSTRACT

The epoxy resin (EMBHBC) of (2E,6E)-bis (4-hydroxybenzylidene)-4-methyl cyclohexanone (MBHBC) was synthesized by condensing 0.5 mol MBHBC and 2.5 mol epichlorohydrin in 500 mL isopropyl alcohol as a solvent and 1.0 mol NaOH in 50 mL water as a catalyst at 80°C for 3 h. The structure of EMBHBC was supported by UV-Vis, FTIR, ^{1}HNMR and ^{13}CNMR spectroscopic techniques. Molecular weights and molecular weight distribution of EMBHBC were determined by gel permeation chromatography. DSC thermogram of EMBHC showed one endothermic transition (95.9°C) and two exothermic transitions (317.7°C and 382.2°C) due to melting and decomposition transitions, respectively. EMBHBC is thermally stable up to about 293°C and followed two step degradation reactions.

KEYWORDS: *Photosensitive epoxy resin, Spectroscopic techniques, Thermal stability, Kinetic parameters*

1. INTRODUCTION

Epoxy resins represent an important class of polymers mainly due to their adaptability[1, 2]. They are well known for their characteristic excellent physico-chemical properties namely good to excellent thermal, mechanical and electrical properties, high strength and stiffness, good dielectric behavior, excellent resistance to chemicals, low shrinkage during cure, excellent hydrolytic stability, excellent adhesion, etc. make them suitable for increasing number of high performance engineering applications[3-9]. Because of these characteristic properties, epoxy resins are most widely used as high performance protective coatings, structural adhesives, low-stress IC. They are also used as matrices in advanced composites due to their good impregnation and

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adhesion to fiber reinforcement, resulting in excellent mechanical performance, electrical and chemical resistance and low shrinkage on cure.

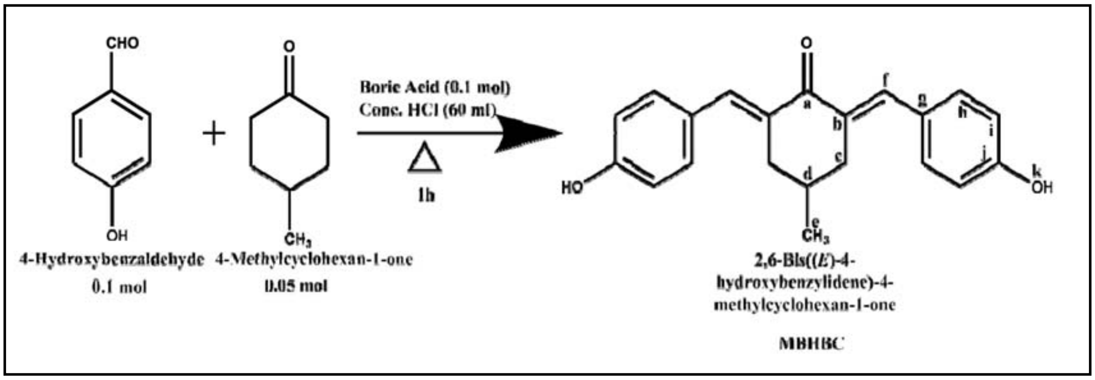
For advanced microelectronic and packaging technology, the epoxy resins must possess good thermal stability, low dielectric constant and dissipation factor, low water absorption, low coefficient of thermal expansion, low internal stress, high mechanical strength, and low modulus[10-13]. Polymers containing chalcone, cinnamate, dibenzalacetone, coumarine, and their derivatives in both main chain and side chain are used as photosensitive materials[14-16]. Such photo-sensitive materials are used in optical data storage devices, photo resists and photolithographic assemblies[17-19].

A few reports are available on the epoxy resins containing chalcone moieties[7, 20]. In this paper we have reported synthesis of epoxy resin of (2E, 6E)- bis(4-hydroxybenzylidene)-4-methylcyclohexanone.

EXPERIMENTAL

Materials and Methods

All the chemicals and solvents used were of LR grade and used as received or purified prior to their use[21]. 4-hydroxybenzaldehyde, 4-methylcyclohexanone and epichloro hydrin were supplied by Spectrochem Pvt. Ltd, Mumbai. Isopropyl alcohol, methanol, chloroform, n-hexane, dimethylsulphoxide (DMSO), N, N-dimethyl formamide (DMF), tetrahydrofuran (THF), sodium hydroxide, and boric acid were supplied by Allied Chemical Corporation, Vadodara. (2E,6E)-2,6-Bis (4-hydroxy benzylidene)-4-methylcyclohexanone (MBHBC) was synthesized and crystallized according to our recent publication[22] (Scheme-1).



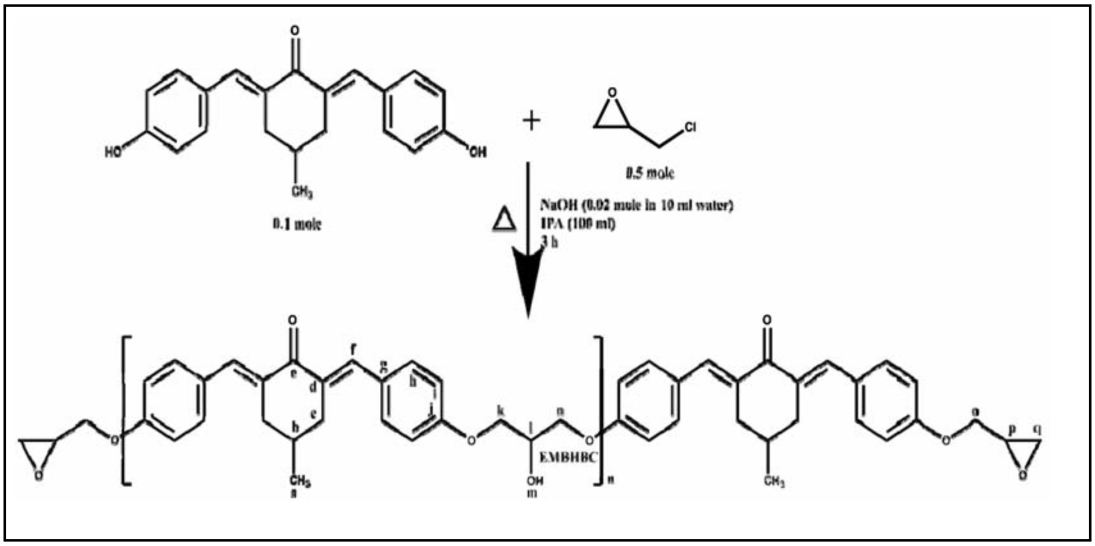
Scheme 1

Synthesis of Epoxy Resin of (2E,6E)-2,6-Bis(4-hydroxybenzylidene)-4-methylcyclohexanone.

Epoxy resin of (2E,6E)-2,6-bis(4-hydroxybenzylidene)-4-methylcyclohexanone was synthesized according to Scheme-2. The detail process is as follows. A 0.5 mol MBHBC, 2.5 mol epichlorohydrine (ECH), 500 mL isopropyl alcohol (IPA), 1mol NaOH in 50mL water as a catalyst were placed in a 2L round bottomed flask equipped with a condenser. The reaction mixture was refluxed for 3h and cooled to room temperature. The reaction mass was neutralized by using dilute hydrochloric acid and separated viscous semisolid resin was isolated, washed well with hot water and finally with methanol and dried at room temperature. The resin was dissolved in required quantity of chloroform, filtered through a cotton plug and precipitated by using n-hexane, filtered and dried at room temperature. The resin was purified three times from chloroform-hexane system. The yield of the semisolid resin was 70% and melts in the temperature range from 95° - 101°C. The resin is soluble in common organic solvents like chloroform, DMSO, DMF, THF, etc. Here after epoxy resin is designated as EMBHBC.

Measurements

Epoxy equivalent weight (EEW) of EMBHBC was determined by pyridine pyridinium chloride method[23]. Epoxy equivalent weight of EMBHBC is 898.3. Molecular weights and molecular weight distribution of EMBHBC 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, ($\bar{M}_n$) are 1092, 486 g/mol, respectively. UV-Visible spectrum of EMBHBC was scanned on a Shimadzu UV1700 over wavelength range from 250-700nm by using tetrahydrofuran as a solvent. The IR spectrum of EMBHBC 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 EMBHBC were scanned on a Bruker AVANCE III (400 MHz) spectrometer by using DMSOd6 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°C min^{-1} heating rate under a nitrogen atmosphere (20mL min^{-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°C min^{-1} heating rate under a nitrogen atmosphere (20mLmin^{-1} flow rate).



Scheme 2

RESULTS AND DISCUSSION

Spectral Analysis

UV-Visible spectrum of 10^{-4} % THF solution of EMBHBC is presented in Fig. 1. EMBHBC exhibited two absorption peaks (λ max) at 241 and 353.5nm. 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.

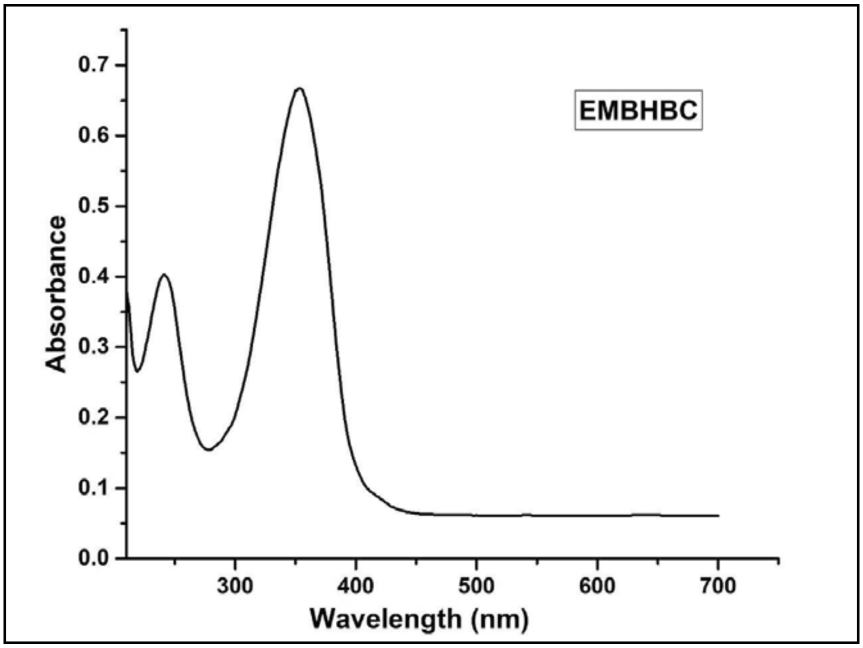


Fig. 1. UV-Visible spectrum of EMBHBC in THF (10^{-4}%).

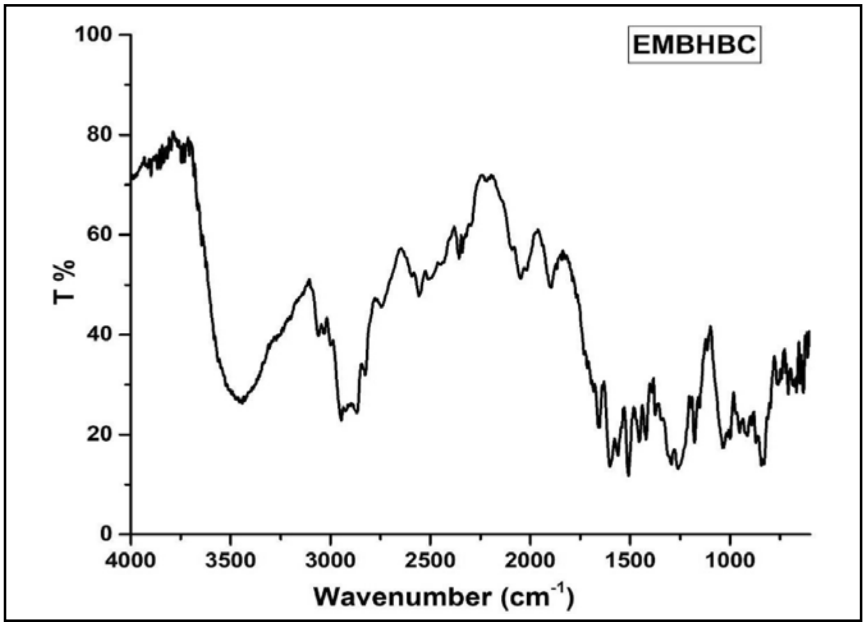


Fig. 2. FTIR spectrum of EMBHBC

FTIR spectrum of EMBHBC is presented in Fig.2. Characteristic IR absorption peaks (cm^{-1}) for EMBHBC are 3456.55 (O-Hstr.),3003.17(=C-Hstr.),2954.95 (C-H asym.str.), 2872.01 (C-H sym.str.), 1660.71 (C=O str.), 1595.13, 1564.27 and 1506.41 (C=C str.), 1454.33 and 1421.54 (C-H def.), 1294.24 (O-H def. CH-OH), 1246.02 (C-O-C str.), 1176.58 and 1143.79 (C-H ipd), 1029.99 and 1002.98 (C-Hstr. CH-OH), 952.84 and 914.26 (C-O str. epoxide), 831.32 and 752.24 (C-H oopd) and 665.44 (-C-H def. alkene). The absorption peaks at 1246.02, 952.84 and 914.26 confirmed the formation of the epoxy resin.

^{1}HNMR (DMSO d6) spectrum of EMBHBC is presented in Fig. 3. Different types of protons, their chemical shifts (ppm) and multiplicities are assigned as follows: 1.038-1.025 [d, H (a), J = 5.2)], 1.776 [s broad, H (b and c)], 2.524 (s, DMS Od6), 2.740 [s, H (q)], 2.869-2.859 [t, 3H (p), J=4], 2.996-2.930 [t, H (p)], 3.907-3.864 [m, (o)], 4.063 [t, H (k)], 4.224-4.135 [t,H (l)], 4.411-4.384 [d H(k and o)], 5.6 [s, H(m)], 7.062-7.044 [d, ArH(h), J=7.2], 7.511-7.492 [d, ArH (i), J=7.6], 7.601[s, H(f)], 8.351 [s, ArOH].

^{13}CNMR spectrum of EMBHBC is presented in Fig. 4. 21.33 (a), 28.69 (b), 35.76 (c), 40.05-38.79 (DMSO),43.74 (q), 49.60 (p), 69.00 (l),

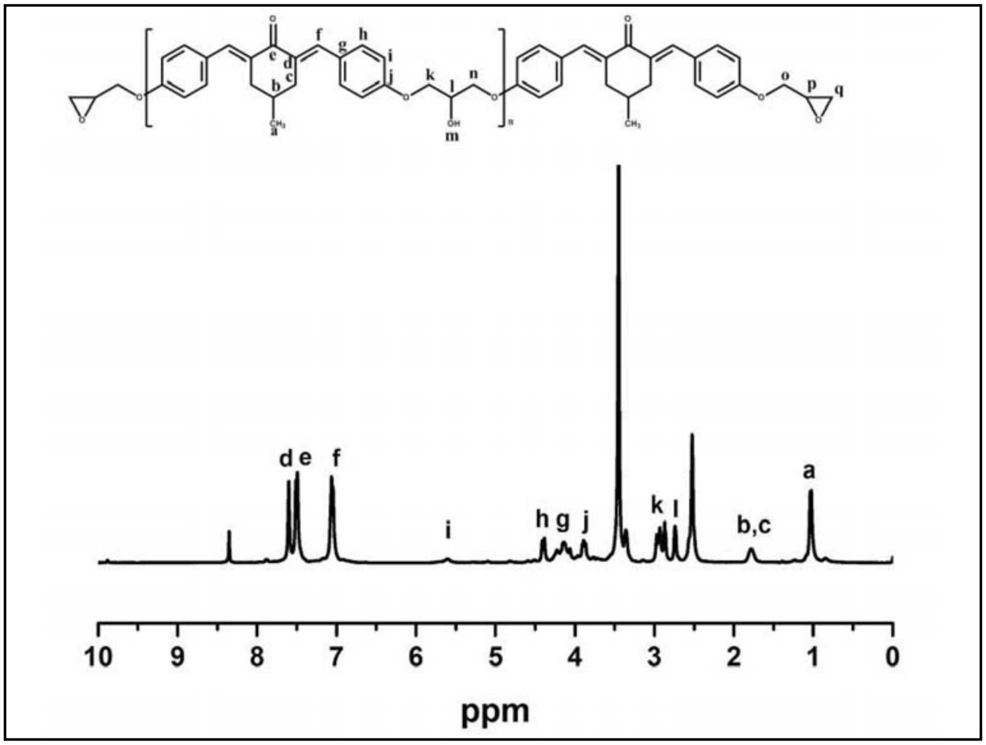


Fig. 3. ^{1}HNMR (400 Mz) spectrum of EMBHBC in DMSOd6.

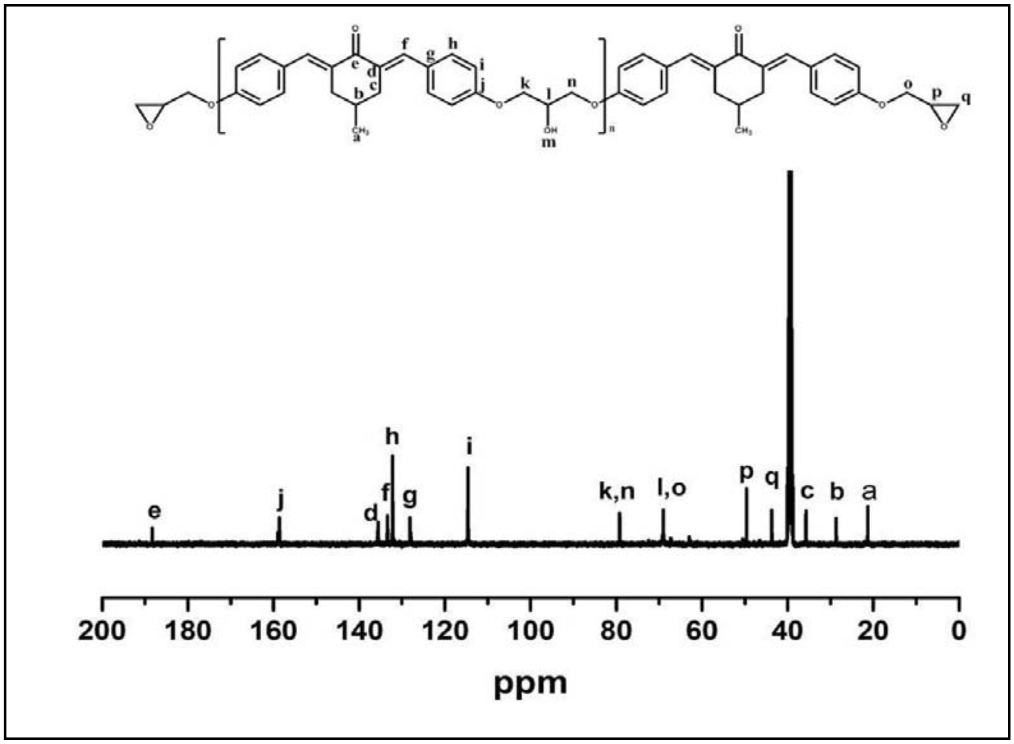


Fig.4 : ^{13}C NMR (400 MHz) spectrum of EMBHBC in DMSOd6.

69.16 (o), 79.19 (k, n), 114.62 (i),128.18 (g), 132.19 (h), 133.43 (f), 135.60 (d), 158.63 (j), and 188.30 (e).

Thermal Analysis

Kinetics of thermal degradation of thermosets is very important in understanding structure/property/processing relationships for manufacture and utilization of these polymeric materials. DSC thermogram of EMBHBC is presented in Fig. 5. A broad endothermic transition centered at 95.9° C is due to melting of EMBHBC and two broad exothermic transitions centered at 317.7° C and 382.2° C are due to decomposition of EMBHBC and further confirmed by weight losses at those temperatures in its TGA curve (Fig. 6). TGA thermogram of EMBHBC is presented in Fig.6 from which it is observed that it is thermally stable up to about 293° C and followed two step degradation reactions. First step involved 19.9% weight loss over 293-379° C with temperature of maximum weight loss at 345.3° C. Similarly second step involved 40.2% weight loss over 379-575° C with temperature of maximum weight loss at 419.3° C. EMBHBC has shown considerably higher thermal stability than epoxy resin of 1,3-bis(4-hydroxypphenyl)prop- 2-en-1–one ECH), 225° C)[7].

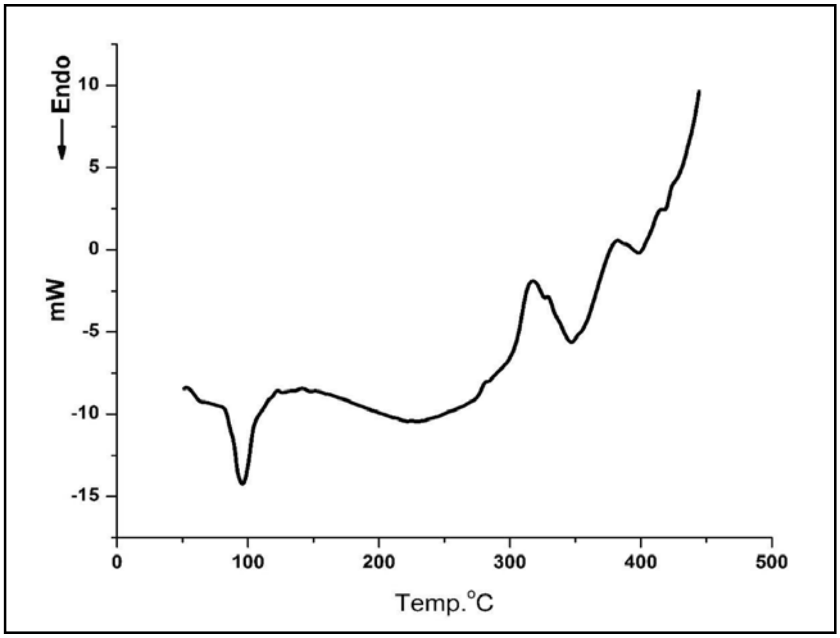


Fig. 5. DSC thermogram of EMBHBC at the heating rate of 10°Cmin^{-1} under nitrogen atmosphere.

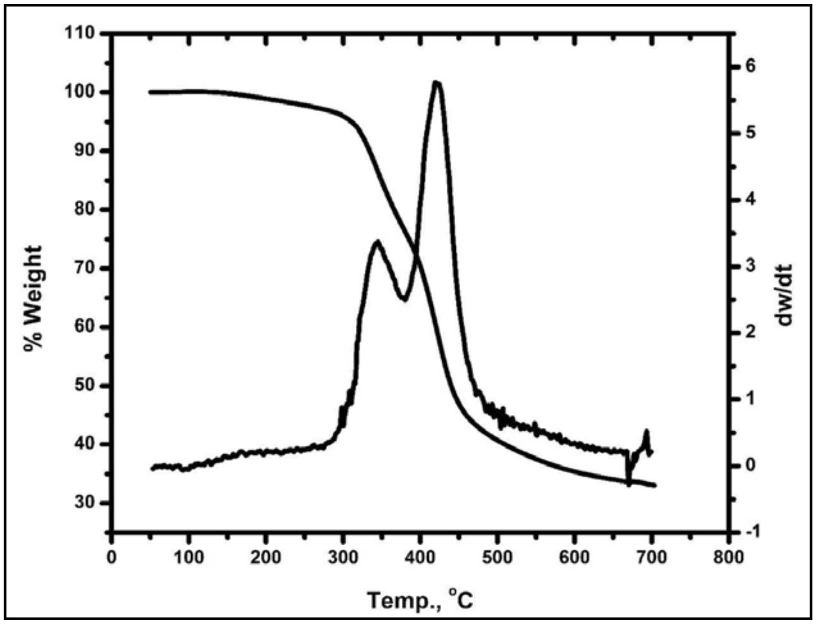


Fig. 6. TG-DTG thermograms of EMBHBC at the heating rate of 10°C min^{-1} under nitrogen atmosphere.

Associated kinetic parameters such as energy of activation (Ea), frequency factor (A), order of reaction (n) and entropy change (ΔS^*) are determined according to Anderson-Freeman method[24]:

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

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

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

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, Ea, A and regression coefficients R^2 for first and second steps are 2.35, 223.8 kJ mol^{-1}, $9.41x10^{16}$ s^{-1} and 0.971; and 1.52, 164.7 kJ mol^{-1}, $1.83x10^{10}$ s^{-1} and 0.996, respectively. The entropy change ΔS^* was determined at corresponding temperature of maximum weight loss and it is 73.96 and -55.45 JK^{-1} mol^{-1}, respectively for first and second steps. A 35.4% residue remained at 600°C. Comparatively EMBHBC has shown lower residue than that of ECH (47.2% at 600°C)[7]. High values of Ea and A of EMBHBC indicated rigid nature of the resin. Ea and A values for first step are higher than that of second step. Decomposition of first step of the cured resin involved dehydration of secondary hydroxyl groups with formation of allylic bonds[25, 26] followed by homolytic bond 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[25, 26]. Thus, dehydration step required high thermal energy than that of homolytic cleavage of allylic bonds. Ether and methyl 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 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 left at 600°C. A large and positive magnitudes of ΔS^* for step-1 indicated that transition state is in disordered state than that of individual in molecules, while a large and negative magnitudes of ΔS^* of the thermally cured resin indicated that transition state is more in orderly state than that of individual resin molecules[27-29].

CONCLUSIONS

Chalcone moiety containing epoxy resin has been synthesized. EMBHBC is highly soluble in common solvents and its structure was supported by spectral techniques. EMBHBC possesses good thermal stability and followed two step thermal degradation kinetics.

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