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

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ABSTRACT

The epoxymethcrylate resin (EMBHBCMA) of (2E, 6E)-bis(4-hydroxybenzylidene)-4-methylcyclohexanone(EMBHBC) was synthesized by condensing EMBHBC and methacrylic acid (1:2 mole ratio) by using 1,4-dioxane as a solvent and triethylamine as a catalyst at reflux temperature for 1-5 h to get acid value < 10. The structure of EMBHBCMA was supported by UV-Vis, FTIR, ^{1}HNMR and ^{13}CNMR spectroscopic techniques. Molecular weights and molecular weight distribution of EMBHBCMA were determined by gel permeation chromatography. EMBHBCMA is thermally stable up to about 300°C and followed two step degradation reactions. Kinetic parameters such as n, Ea, A and ΔS^* were determined according to Anderson-Freeman method and discussed.

KEYWORDS: *Epoxy methacrylate, Acid value, Hydroxyl value, Thermal stability, Kinetic parameters*

INTRODUCTION

Epoxy resins have been widely used in many fields such as aerospace and electronics industries in the form of surface coatings, structural adhesives and advanced composites because of their well-balanced physical properties[1]. Epoxy resins possess excellent adhesion property, good chemical and corrosion resistance, excellent electrical insulation, high tensile, flexural and compressive strength and thermal stability. The remarkable adhesion property is because of the existence of polar hydroxyl and ether groups in the epoxy resin molecules. Immense growth in the electronics market has markedly enlarge the demand for the epoxy materials for the manufacture of printed circuit boards and epoxy molding

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compounds for semiconductor encapsulation[2]. The existence of unsaturation at the end of the vinyl ester resins has shaped epoxy resins for the radiation curing industry. The Terminal unsaturated double bonds are the reactive sites for coatings and paints[3].

Epoxy acrylate resins are one class of the most important and extensively used reactive monomers that have excellent chemical and solvent resistance, good adhesion properties and so on. Epoxy acrylate oligomers are generally used in many polymer industries due to their magnificent adhesive and non-yellowing properties, flexibility, hardness and chemical resistance[4-7]. Epoxy acrylates can be used in a wide range of viscosities and formulations in the form of single- or two-part products[8,9]. The epoxy backbone imparts toughness to the cured films, while the carbon-carbon and ether bonds of the same improve the chemical resistance. Methacrylate resins furnish hardness, chemical resistance and other properties critical to coatings and adhesives. Their reaction with an acid produces hydroxyl groups, thereby introducing polarity, which can improve the wettability of adhesive[10].

Acrylic polymers that contain epoxy functional groups as pendant units have become increasingly capable of a rational designed formulation that provides good coating properties after curing[11]. There are many types of acrylated polymers with different structure such as epoxy acrylates, urethane acrylates, polyester acrylates, polyether acrylates and acrylated oils. The extensive use of epoxy acrylates based on bisphenoldiglycidyl ether and epoxy novolac is due to their adaptable chemistry to make products with good adhesion, hardness, and chemical resistance. Acrylic and methacrylic acids are used to make the acrylated products as per enduse requirements[12].

Recently we have reported physico-chemical properties of epoxy resin of (2E, 6E)-bis(4-hydroxybenzylidene)-4-methylcyclohexanone (EMBHBC)[13] but no work has been reported on synthesis and properties of epoxy methacrylate of (2E,6E)-bis(4-hydroxybenzylidene)-4-methylcyclohexanone (EMBHBCMA). In the present work we have reported synthesis, acid and hydroxyl values, spectral and thermal study of EMBHBCMA.

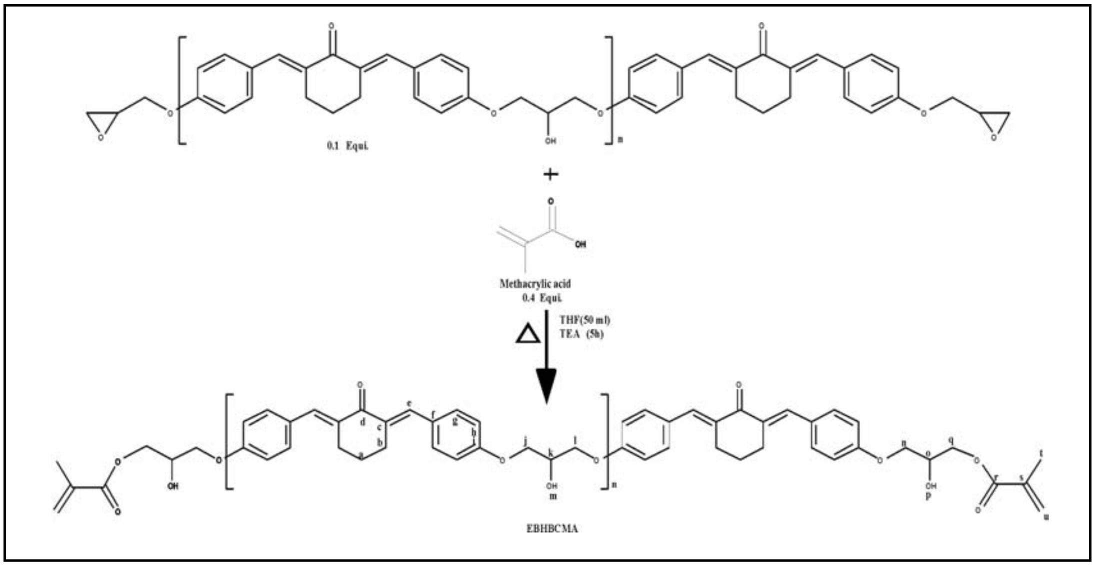
EXPERIMENTAL

Materials and Methods

Solvents and chemicals used in this study were of LR grade and were used as received or purified according to reported methods[14]. EMBHBC having EEW 898.3 was synthesized and purified according to our recent publication[13]. Chloroform, n-hexane and 1,4-dioxane were supplied by Allied Chemical Corporation, Vadodara. Triethylamine and methacrylic acid were supplied by Spectrochem, Mumbai and used as received.

Synthesis of Epoxy methacrylate

To a 100 mL three-neck round bottomed flask equipped with a condenser, mechanical stirrer, and thermometer was placed in an oil bath. To this flask 0.01equiv. EMBHBC, 0.02 equiv.methacrylic acid, 30 mL 1,4-dioxane and 0.2 mL triethylamine were charged and the temperature was raised to reflux with stirring for 1-5h. The reaction mixture was cooled to room temperature and the semisolid resin was isolated from hot water. 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-n-hexane system. The yield of the semisolid resin was 85% and melts over the temperature range from 68-72°C. The resin is soluble in common organic solvents like chloroform, DMSO, DMF,



Scheme-I Synthesis of epoxy methacrylate of (2E, 6E)-bis(4-hydroxybenzylidene)-4-methylcyclohexanone

THF, etc. Here after epoxy methacrylate resin is designated as EMBHBCMA.

Measurements

The acid and hydroxyl values of EMBHBCMA were determined according to reported standard test methods[15]. Molecular weights and molecular weight distribution of EMBHBCMA were determined by gel permeation chromatography by using Perkin Elmer GPC (Series 200) using THF as a solvent and standard polystyrene mixed beads at 30°C. UV-Visible spectrum of EMBHBCMA was scanned on a Shimadzu UV1700 over wavelength range from 250-700nm by using tetrahydrofuran as a solvent. The IR spectrum (pellet) of EMBHBCMA 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 EMBHBCMA were scanned on a Bruker AVANCE II (400 MHz) spectrometer by using DMSO-d6 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. A known amount of sample was taken in an aluminum pan and covered with an aluminum lid and sealed with the help of a crimper. 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 (20mL min^{-1} flow rate).

RESULTS AND DISCUSSION

Acid and Hydroxyl Values

Acid and hydroxyl values were determined at the interval of 1h and are reported in Table 1. It is observed that acid value decreased and hydroxyl value increased with the extent of reaction confirming practically completion of esterification reaction. For desired acid value 5h reaction time is the optimum time.

Molecular Weights and Molecular Weight Distribution

Observed weight average molecular weight ($\overline{M}_w$), number average molecular weight ($\overline{M}_n$)

TABLE 1. Acid and hydroxyl values of EBHBCMA.

Reaction time, h	1	2	3	4	5
Acid value, mg KOH/ g	63.4	58.6	19.5	14.6	9.8
Hydroxyl value, mg KOH /g	432.0	448.8	504.9	513.3	530.1

and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) are 1268, 584, and 2.17, respectively.

Spectral Analysis

UV-Visible spectrum of 10^{-3}% THF solution of EMBHBCMA is presented in Fig. 1. EMBHBCMA exhibited two absorption peaks (λmax) centered at 240 and 355 nm. These peaks are assigned as $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions due to presence of double bonds and lone pairs of electrons on oxygen atoms.

FTIR spectrum of EMBHBCMA is presented in Fig. 2. Characteristics IR absorption peaks (cm^{-1}) for EMBHBCMA are 3474.88 (O-H str.), 3046.1 (=C-H str.), 2947.33 (C-H asym. str.), 2883.68 (C-H sym. str.), 1715.74 (C=O str.), 1657.87 (C=C str. alkene), 1601.93, 1565.29 and 1508.38 (C=C str.), 1455.34 and 1419.66 (C-H def.), 1310.34 (C-OH def.), 1258.59 (C-O-C str.), 1294.28 (C-H ipd), 1030.99 (C-O str.), 952.18 (C-H def. alkene), 833.28 and 759.01 (C-H oopd.). The disappearance of peaks due to epoxide groups at 952.84 and 914.26 cm^{-1} and appearance of new ester peak at 1715.74 cm^{-1} confirmed the formation of methacrylate resin.

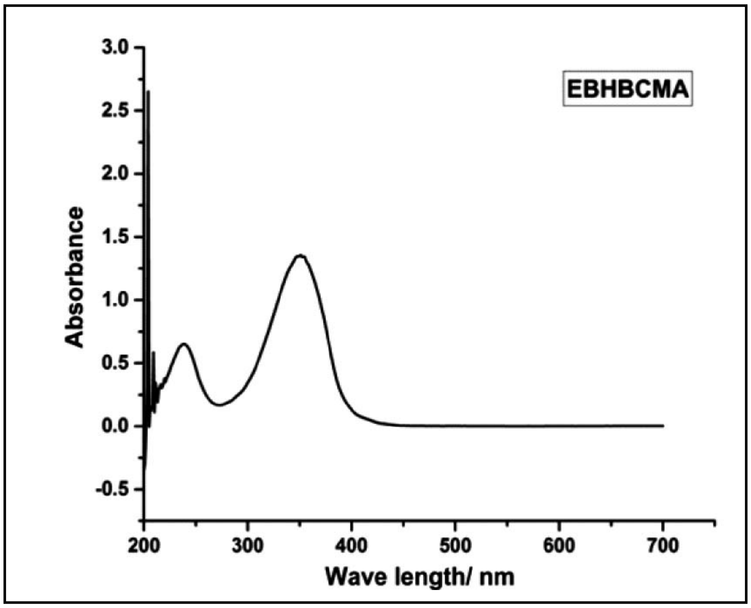


Fig. 1. UV-Visible spectrum of 10^{-3}% EBHBCMA in THF

^{1}HNMR (DMSO-d6) spectrum of EMBHBCMA is presented in Fig. 3. Different types of protons, their chemical shifts(ppm) and multiplicities are assigned as follows: 7.604 [s, H (h)], 7.509 [s, ArH (f)], 7.0057 [s, ArH (i)], 5.655 and 5.531 [s, 2H (v)], 5.041 and 4.749 [s, OH (n, q)], 4.409-4.383 [d, 2H(l,p)], 4.221-4.127[m, 1H(o)], 4.060-3.942[d, 4H(k, m)], 3.906-3.893[dd, 4H(r)], 2.973-2.936[d, 4H(u)], 1.786[s, H(b, c)], 1.038[s, 3H(a)].

^{13}CNMR spectrum of EMBHBCMA is presented in Fig. 4. Chemical shifts are assigned as follows: 21.35(u), 28.71(a), 35.78 and 43.7(b), 46.60 and 49.59 (c), 62.62(o), 66.32(r), 67.29(p), 68.52(l), 69.21 and 69.01(m), 69.85 and 69.67(k), 114.63(i), 128.21 and 127.78(h,g), 132.20 and 131.77(f), 133.44 and 133.21(t), 135.60(d), 159.27 and 158.64(s, j), 188.28(e).

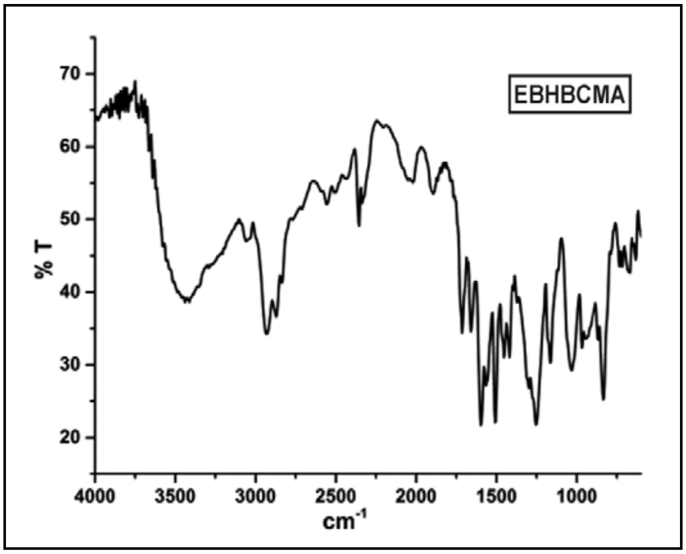


Fig. 2. FT-IR spectrum of EMBHBCMA.

Thermal Analysis

DSC thermogram of EMBHBCMA is presented in Fig. 5. Broad endothermic transitions centered at 58.06°C and 112.18°C are due to release of trapped solvent and melting of EMBHBCMA. A broad exothermic transition centered at 146.37 °C and an endothermic transition at about 292°C are probably due to thermal polymerization followed by decomposition of EMBHBCMA and further confirmed by onset of weight loss in its TG thermogram (Fig. 6). From Fig. 6, it is observed that EMBHBCMA is thermally stable up to about 300°C and followed two step degradation reactions. EMBHBCMA has shown slightly higher thermal stability than that of EMBHBC (293°C)[13]. First step involved 17% weight loss over 300-385°C with temperature of maximum weight loss at 347.5°C. Similarly second step involved 38% weight loss over 385-559°C with

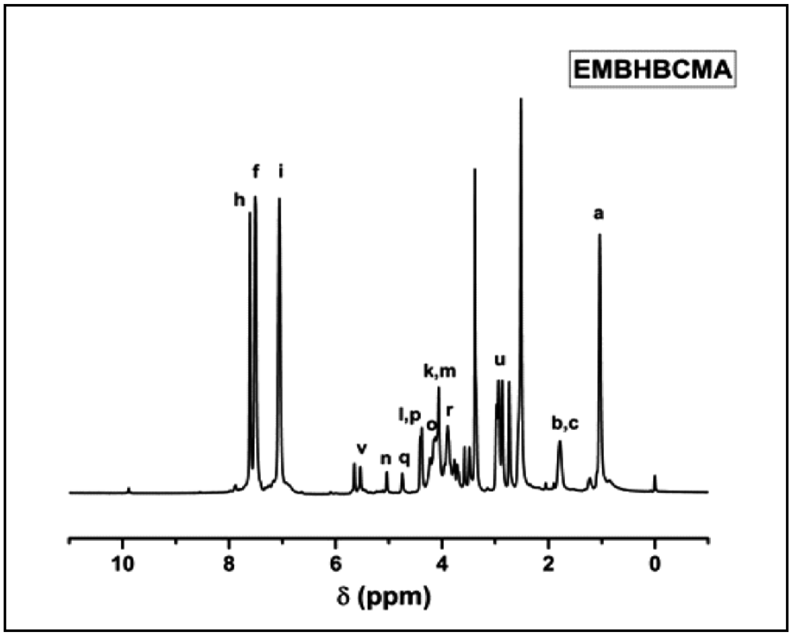


Fig. 3. ^{1}HNMR (400 MHz) spectrum of EMBHBCMA in DMSO-d6.

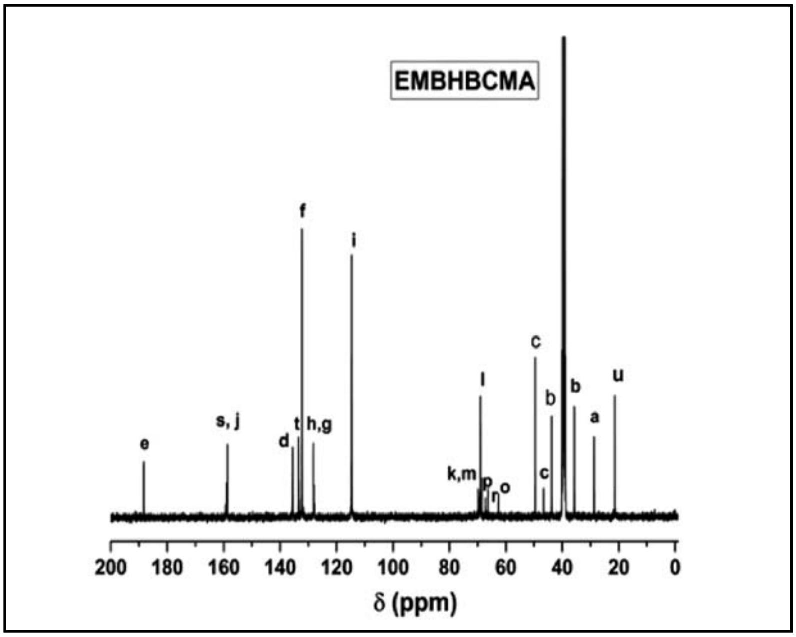


Fig. 4. ^{13}C NMR (400 MHz) spectrum of EMBHBCMA in DMSO-d6.

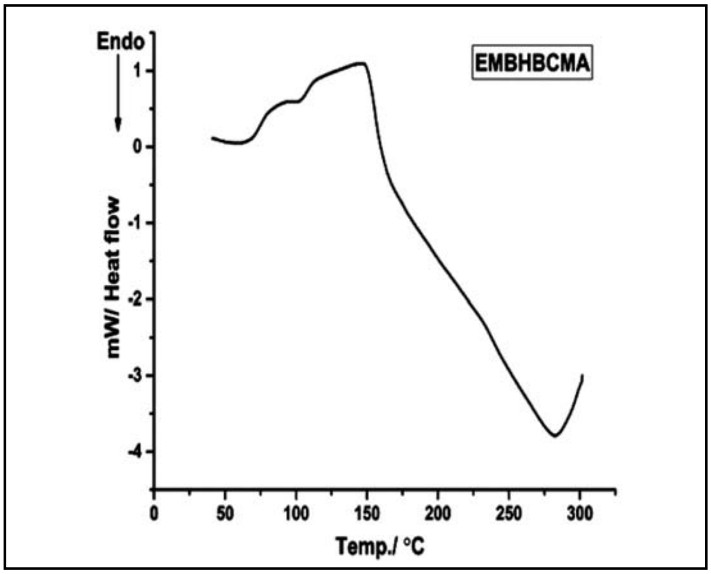


Fig. 5. DSC thermogram of EMBHBCMA at 10°C min^{-1} heating rate in nitrogen atmosphere.

temperature of maximum weight loss at 420 °C. EMBHBCMA showed 35.8 % residue at 700°C, which is slightly higher than that of EMBHBC (33.1%)[13].

Energy of activation (Ea), frequency factor (A), order of reaction (n), and entropy change (ΔH*) were determined according to Freeman Anderson[16] (Eqns. 1-3):

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

$$A = \left(\frac{Ea\beta}{RT^2}\right) e^{\frac{Ea}{RT}} \qquad (2)$$

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

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 observed least square values of n, E_a, A and regression coefficients R^2 for first and second steps are 0.53 and 1.18; 99.3 and 305.8 kJmol^{-1}; 1.18x10^{6} and 1.41 x 10^{21}s^{-1}; 0.980 and 0.988, respectively. The entropy change ΔS* was determined at corresponding temperature of maximum weight loss. Observed values of ΔS* for first and second steps are -134.7 and 153 JK^{-1}mol^{-1}, respectively. First degradation reaction proceed with a large and negative magnitude of ΔS*, which indicated that transition state is more in orderly state than that of individual resin molecules. Second step degradation reaction proceed with a large and positive magnitude of ΔS*, which indicated that transition state is less in orderly state[13,17-19].

Dehydration of secondary hydroxyl groups involved formation of allylic bonds[20, 21] followed by either homolytic bond cleavage or thermal crosslinking reaction with release of water and low molecular weight fragments. Thermal polymerization of allylic fragments lead to further crosslinking reaction and aromatization contribute to charring[20, 21]. Thus, dehydration step required comparatively low thermal energy than that of crosslinking followed by aromatization of allylic bonds. Ether, ester and pendant hydroxyl and methyl groups are weak linkages in the resin molecules and therefore selective degradation starts from such weak points on heating with the formation of free radicals. Formed free radicals further may undergo a variety of chemical reactions namely 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 700°C.

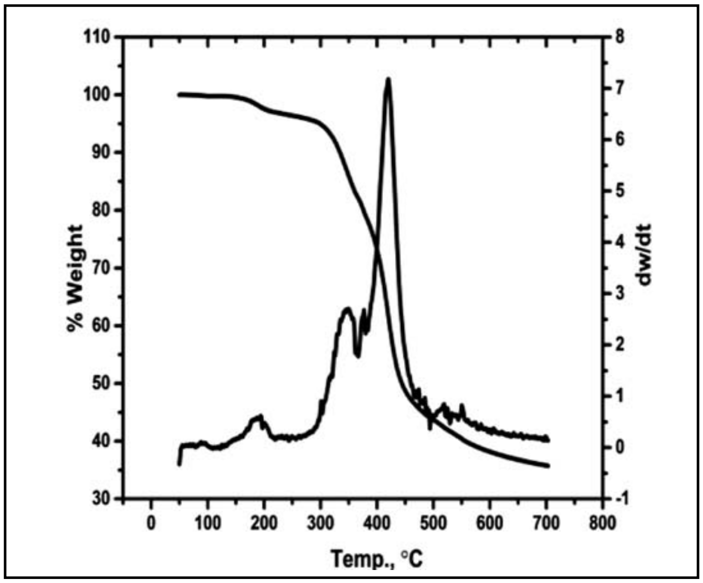


Fig. 6. TG and DTG thermograms of EMBHBCMA at heating rate 10°C min^{-1} under nitrogen atmosphere.

CONCLUSIONS

From experimental findings, it is concluded that EMBHBCMA is highly soluble in common solvents and its structure was confirmed by spectral techniques. EMBHBCMA possesses good thermal stability and followed two step thermal degradation kinetics. Degradation reactions followed fractional order kinetics with a considerably a large reside at 700°C.

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