

Rapid Monitoring of Bisphenol-A Diglycidyl Ether Formation Through Byproduct Estimation: A Study by Fourier Transform Infra-Red Spectroscopy

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ABSTRACT: For identification and quantification of desired and undesired products during epoxy resin formation, polymerization of bisphenol-A with the stoichiometric excess of epichlorohydrin is carried out using catalytic excess of alkali. The reaction is monitored using Fourier transform infra-red (FT-IR) spectroscopy technique. Major undesired products are unreacted monomers (bisphenol-A and epichlorohydrin) and byproducts (chlorine and α -glycol substituted diglycidyl ether of bisphenol-A), whereas the desired product is only diglycidyl ether of bisphenol-A. Molar concentrations of epichlorohydrin, bisphenol-A, diglycidyl ether of bisphenol-A, chlorine substituted resin,

and α -glycol substituted resin in the polymerization mixture are analyzed and quantified using FT-IR characteristic frequency bands at 925, 3448, 1344, 773, and 3641 cm^{-1} , respectively. For optimal determination of process parameters on polymerization, effect of temperature and alkali loading on epoxy polymerization is carried to maximize the yield of diglycidyl ether of bisphenol-A with simultaneous minimizing the byproducts formation. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2894–2905, 2012

Key words: polycondensation; bisphenol-A diglycidyl ether; epoxy resin; reaction monitoring; FT-IR

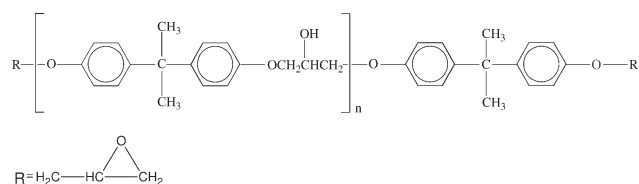
INTRODUCTION

Epoxy resin is a prepolymer of two or more reactive terminal oxirane groups, and finds useful application in bulk structural composite, thin specialty protective coating, electrical-electronic insulation, encapsulation, and stereolithographic rapid prototyping.^{1–3}

With wide formulation possibilities in presence of curing agent and processing versatilities, epoxy resin produces crosslinked or thermoset plastics, which have excellent strength, toughness, chemical resistance, adhesive, and electrical properties.^{1–3}

Epoxy resins are usually prepared from the materials having two or more reactive hydrogen atoms and epichlorohydrin. More than 75% of epoxy resin is derived from diglycidyl ether of bisphenol-A (DGEBA),¹ and prepared by the coupling of epichlorohydrin (EP) and bisphenol-A (BPA). The market dominance of epoxy resins is mainly due to its low cost and adequate-to-superior performance in

many applications.¹ The chief constituent of DGEBA resin is



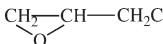
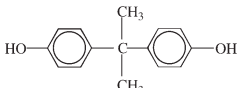
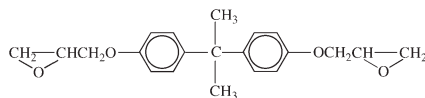
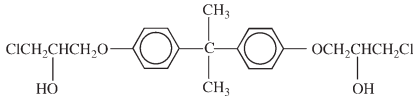
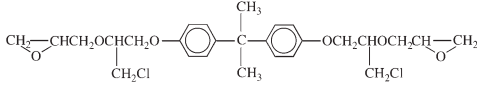
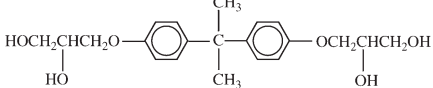
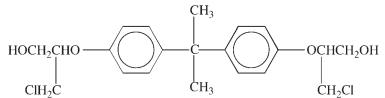
where $n = 0$ for pure monomeric DGEBA resin, and $n > 40$ for high molecular weight DGEBA resin.

A high molar ratio of EP to BPA (usually 10 : 1) is used to maximize the yield of monomeric DGEBA, whereas medium to high molecular mass of DGEBA resin is prepared using lower molar ratios of EP to BPA.³ A highly exothermic base catalyzed coupling of EP and BPA proceeds via mono- and dichlorohydrin intermediates, which further undergo dehydrochlorination to glycidyl ether with stoichiometric amount of base.^{2,3} Sodium hydroxide, lithium salts, and quaternary ammonium salts are the common base catalysts for coupling reaction.⁴ Two-stage reaction between EP and BPA usually occurred in the presence of alkali to produce monomeric DGEBA resin. The detailed description of monomers and polymerization products is summarized in Table I. Details of main reactions and side reactions are shown in Table II. Final resin properties are adversely affected by the purity of monomeric

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TABLE I
Details of Monomers and Polymerization Products

Name	Abbreviation	Formula
Epichlorohydrin	EP	
Bisphenol-A	BPA	
Diglycidyl ether of Bisphenol-A	DGEBPA	
Bis-chlorohydrin of DGEBPA	ClH-DGEBPA	
Bound chlorine of DGEBPA	bCl-DGEBPA	
Alpha glycol or bis-diol of Diglycidyl ether of Bisphenol-A (AG)	α -DGEBPA	
Abnormal chlorohydrin of DGEBPA	abClH-DGEBPA	

DGEBPA resin, which depends on undesirable side products, intermediates, and unreacted monomers content in monomeric DGEBPA resin. Common undesirable side products are α -glycol substituted DGEBPA resin (α -DGEBPA) and chlorine substituted DGEBPA resin (Cl-DGEBPA).^{3,5} Undesired side products in resin not only affect the processing characteristics and the resin purity but also reduce the

yield of monomeric DGEBPA resin, especially in large scale production. Details of byproducts formation are given in Table I. Dehydrochlorination of chlorohydrin intermediates produces water [Table II, eqs. (2) and (3)], which results unavoidable hydrolysis of epoxy ring producing hydrolyzed resin [i.e., α -DGEBPA: Table II, eq. (4)]. The α -DGEBPA content in resin increases the rate of curing with diamines,

TABLE II
Main and Side Reactions for DGEBPA Formation^{3,5}

Main reactions:

- (1) $\text{BPA} + 2\text{EP} + 2\text{NaOH} \rightarrow \text{ClH-DGEBPA} + 2\text{NaOH}$
- (2) $\text{ClH-DGEBPA} \rightarrow \text{DGEBPA} + 2\text{HCl}$
- (3) $2\text{HCl} + 2\text{NaOH} \rightarrow 2\text{NaCl} + 2\text{H}_2\text{O}$

Base catalyzed coupling
 Dehydrochlorination
 Water formation

Side reactions:

- (4) $\text{DGEBPA} + 2\text{H}_2\text{O} \rightarrow \alpha\text{-DGEBPA}$
- (5) $\text{ClH-DGEBPA} + 2\text{EP} + 2\text{NaOH} \rightarrow \text{bCl-DGEBPA} + 2\text{NaCl} + 2\text{H}_2\text{O}$
- (6) $\text{BPA} + 2\text{EP} \rightarrow \text{abClH-DGEBPA}$

α -Glycol formation
 Bound chlorine formation
 Abnormal addition to EP

and directly affects the mechanical properties of the cured resin.¹ Incomplete dehydrochlorination of mono- and dichlorohydrin intermediates results the formation of bischlorohydrins of DGEbPA resin [i.e., ClH-DGEbPA: Table II, eq. (2)]. Excess EP also reacts with ClH-DGEbPA resin giving bound chlorine in DGEbPA resin [i.e., bCl-DGEbPA: Table II, eq. (5)], which is responsible for chain branching in epoxy resin.^{3,5} Increased branching due to the formation of bCl-DGEbPA resin increases the viscosity of the reaction mixture and poses difficulties in handling of resin during reaction.⁵ Abnormal phenoxide attack on secondary carbon atom of EP results an end group, which is unable to undergo dehydrochlorination and produces abnormal chlorohydrins [i.e., abClH-DGEbPA: Table II, eq. (6)]. In the present study, *all* the chlorine substituted DGEbPA resins (i.e., ClH-DGEbPA, bCl-DGEbPA, and abClH-DGEbPA) are collectively termed as Cl-DGEbPA resin for simplification. These chlorine intermediates adversely affect the electrical properties of resin.^{3,5} For microelectronic applications, the increased level of total-, ionic-, and/or saponifiable-chlorine also affects the dielectric properties of the resin.⁵ Presence of chlorine in epoxy resin also produces corrosive and obscuring smoke while burning, and gives supertoxic halogenated dibenzodioxines and dibenzofurans, which has deleterious effects on environmental impact and human health.⁶ Unreacted BPA in epoxy resin is also toxic and migrates from can-coating into food on prolonged storage that affects adversely human estrogenic activity.⁷ It has also been reported that α -DGEbPA resin and Cl-DGEbPA resin can attack and bind covalently DNA molecules causing mutagenic events.^{8,9} Thus, the presence of undesirable products in DGEbPA resin (i.e., α -DGEbPA, Cl-DGEbPA, and unreacted BPA) not only reduces the yield of resin but also affects adversely the resin properties in the large extent. To improve the yield and quality of DGEbPA resin, it is necessary to identify and quantify *all* the undesirable products during DGEbPA resin formation under varying process conditions. Quantitative estimation of the byproducts is usually carried out by the chemical methods of analysis which requires several hours to quantify, and difficult to apply for reaction monitoring of DGEbPA resin formation. Details of the chemical method of analysis are reported by Lapkin and Weir,¹⁰ and Stenmark and Weiss.¹¹

Reaction monitoring of epoxy resin formation was carried out by several investigators through the quantification of desired product only, and the quantification is *mostly* based on molecular weight determination using gel permeation chromatography.^{12–15} Moreover, above studies did not account (i) the variation of process conditions (e.g., polymerization temperature, alkali concentration, and molar ra-

tio of EP to BPA), and (ii) the estimation of the side products during polymerization. Till date, detection and quantitative estimation of undesired products during polymerization of EP and BPA with varying process conditions is not available in the open literature. Due to rapid development of reliable instrumentation technique and computerized data processing facilities, now-a-days, Fourier transform infrared spectroscopy (FT-IR) is becoming a very powerful tool for detection and quantitative estimation of compounds,^{16,17} and this technique is applied for quantitative estimation of epoxy resin curing frequently.^{10,18,19} Due to the well-defined characteristic FT-IR transmittance peaks of EP and BPA polymerizing mixture^{10,20–24} [i.e., epoxy ring (EP), glycidyl group (mono- and diglycidyl ether), hydroxyl group (BPA and α -glycol), and chlorine group (Cl-DGEbPA)], FT-IR technique can be used for rapid reaction monitoring through identification and quantification during epoxy resin formation.

In the present study, monomeric DGEbPA resin is synthesized using BPA and controlled molar excess of EP with catalytic excess of sodium hydroxide. Polymerization reaction is monitored through detection and quantification of desired product (i.e., DGEbPA resin), undesired byproducts (i.e., α -DGEbPA resin and Cl-DGEbPA resin), and unreacted monomers (i.e., EP and BPA) using the characteristic FT-IR transmittance peaks. Effect of temperature and alkali loading on polymerization is also studied for finding the optimal process parameters such that the yield of desired product is maximized with simultaneous minimization of the undesired products during monomeric DGEbPA resin formation.

EXPERIMENTAL

Materials

Bisphenol-A, epichlorohydrin, and sodium hydroxide were purified for molecular weight control of monomeric DGEbPA resin. Bisphenol-A (CDH, New Delhi) was purified by recrystallization from toluene.²⁵ Epichlorohydrin with 98% assay (CDH, New Delhi) was purified by distillation under vacuum.²⁵ Sodium and potassium hydroxide pellets (Sd Fine Chem Ltd, Mumbai) were dried in silica gel filled vacuum desiccators before use. Pyridine (Aldrich) was purified after total refluxing using dry sodium hydroxide pellets for 6.0 h followed by distillation.²⁵ Reagent grade benzene, toluene, isopropanol, chloroform, methanol, glacial acetic acid, hydrochloric acid (AR), oxalic acid, cetyltrimethyl ammonium bromide, quaternary ammonium periodate, potassium iodide, silver nitrate, sulfuric acid, sodium thiosulphate, phenolphthalein, potassium chromate were used directly for analysis without purification.

Synthesis of DGEBA resin and byproducts for standardization

Diglycidyl ether of bisphenol-A, DGEBA resin

Epoxy resin (average molecular weight: 370 i.e., monomeric DGEBA) was synthesized using 10 : 1M ratio of EP and BPA with catalytic excess of sodium hydroxide at 333 K in a 1.0 L semibatch SS 316 autoclave [Table II, eqs. (1)–(3)].²⁶ The autoclave (Amar Equipments Pvt. Ltd., Mumbai) was equipped with automatic temperature controller (split range type with simultaneous heating and cooling arrangement) and overhead chilled water circulated reflux condenser. Autoclave was fitted with a six-blade turbine and connected through a magnetic coupling for zero leakage. Chilled water at 283 K was circulated through cooling coil inside the reactor to remove high exothermic heat of polymerization. After the completion of reaction, excess EP in the reaction mixture was removed through the overhead condenser under vacuum. Residual EP in resin was removed under vacuum drying at 313 K for 24.0 h. Epoxy equivalent of DGEBA resin was determined using pyridinium chloride-pyridine method.¹⁰ The weight per epoxy equivalent (WPE) was found to be 184.8 g of epoxy resin per gram equivalent of epoxy group, which confirms the purity of monomeric DGEBA resin (i.e., average molecular weight of resin = 370).

α -Glycol of DGEBA, α -DGEBA resin

α -DGEBA was synthesized after hydrolysis of monomeric DGEBA resin [Table II, eq. (4)].²⁷ Hydrolysis of DGEBA was also carried out in 1.0 L automatic temperature control semibatch SS 316 autoclave (Amar Equipments Pvt. Ltd., Mumbai). The resin was mixed with molar excess of distilled water and refluxed at 373 K in the autoclave. Hydrolysis was continued till the exothermic reaction subsides. Time required to complete the polymerization was almost 4.0 h. Excess of water in the reaction mixture was removed through overhead condenser under vacuum. Residual moisture was removed by drying under vacuum at 313 K for 24.0 h. Dried mixture was analyzed for α -glycol content in the resin by Stenmark and Weiss method,¹¹ which was found to be 0.825 mol/100 g of resin.

Bis-chlorohydrin of DGEBA,
ClH-DGEBA resin

To synthesize ClH-DGEBA resin, monomeric DGEBA resin was dissolved in tetrahydrofuran and allowed to react with concentrated hydrochloric acid (35% wt/wt) maintaining at 253 K using cryostat (refrigerant: glycol and water) for 6.0 h in 1.0 L

SS 316 autoclave (Amar Equipments Pvt. Ltd., Mumbai).²⁸ Excess of tetrahydrofuran was removed though the chilled water circulated overhead condenser under vacuum and residual tetrahydrofuran was removed after drying under vacuum at 313 K for 24.0 h. Hydrolysable chlorine in the resin (i.e., an incomplete dehydrochlorination intermediate readily undergoes epoxy ring formation) was determined using potassium hydroxide solution and liberated chlorine was titrated with silver nitrate solution using potassium chromate indicator.¹⁰ Total chlorine content in resin i.e., sum of hydrolysable chlorine [Table II, eq. (2)], bound chlorine [Table II, eq. (5)], and abnormal chlorohydrin [Table II, eq. (6)] of DGEBA resin was determined by Parr bomb procedure.¹⁰ In the present study, the estimated hydrolysable chlorine and the total chlorine were found to be *almost* identical. Therefore, it is assumed that total chlorine is *mostly* due to the hydrolysable chlorine *only*, which was found to be 12.5% (wt/wt).

FT-IR characterization of monomers, DGEBA resin, and byproducts

In the present study, coupling between EP and BPA in presence of catalytic excess of alkali was monitored using FT-IR technique. FT-IR spectrums were obtained using IR Prestige 21, Shimadzu Corp., Japan. Scanning conditions during spectral analysis were maintained at (i) wave number: 4000 to 400 cm^{-1} , (ii) resolution: 4 cm^{-1} , (iii) number of scans: 64, (iv) scan speed: 0.63, and (v) detector: Ge coated KBr pellet. The sample chamber was purged with dry nitrogen at 120 cm^3/s flow rates before analysis. Benzene was found to be suitable solvent for standardization of EP, BPA, DGEBA, Cl-DGEBA, and α -DGEBA in infra-red region.¹⁰ Following characteristic infrared transmittance frequency bands of EP, BPA, DGEBA, Cl-DGEBA, and α -DGEBA were considered for the calibration^{10,20–24}:

EP: 925 cm^{-1} (in phase stretching frequency due to ring breathing vibration in EP of C–C, C–O, and C–O bonds),

BPA: 3448 cm^{-1} (asymmetric stretching vibration of OH group),

DGEBA: 1344 cm^{-1} (in phase stretching frequency due to the ring breathing vibration of C–C, C–O, and C–O bonds in DGEBA),

Cl-DGEBA: 773 cm^{-1} (symmetric stretching of C–Cl bond), and

α -DGEBA: 3641 cm^{-1} (OH stretching deformation in the nonbonded primary alcohol).

Above characteristic infrared absorption frequency bands are used for detection and quantitative estimation of the above components present in the

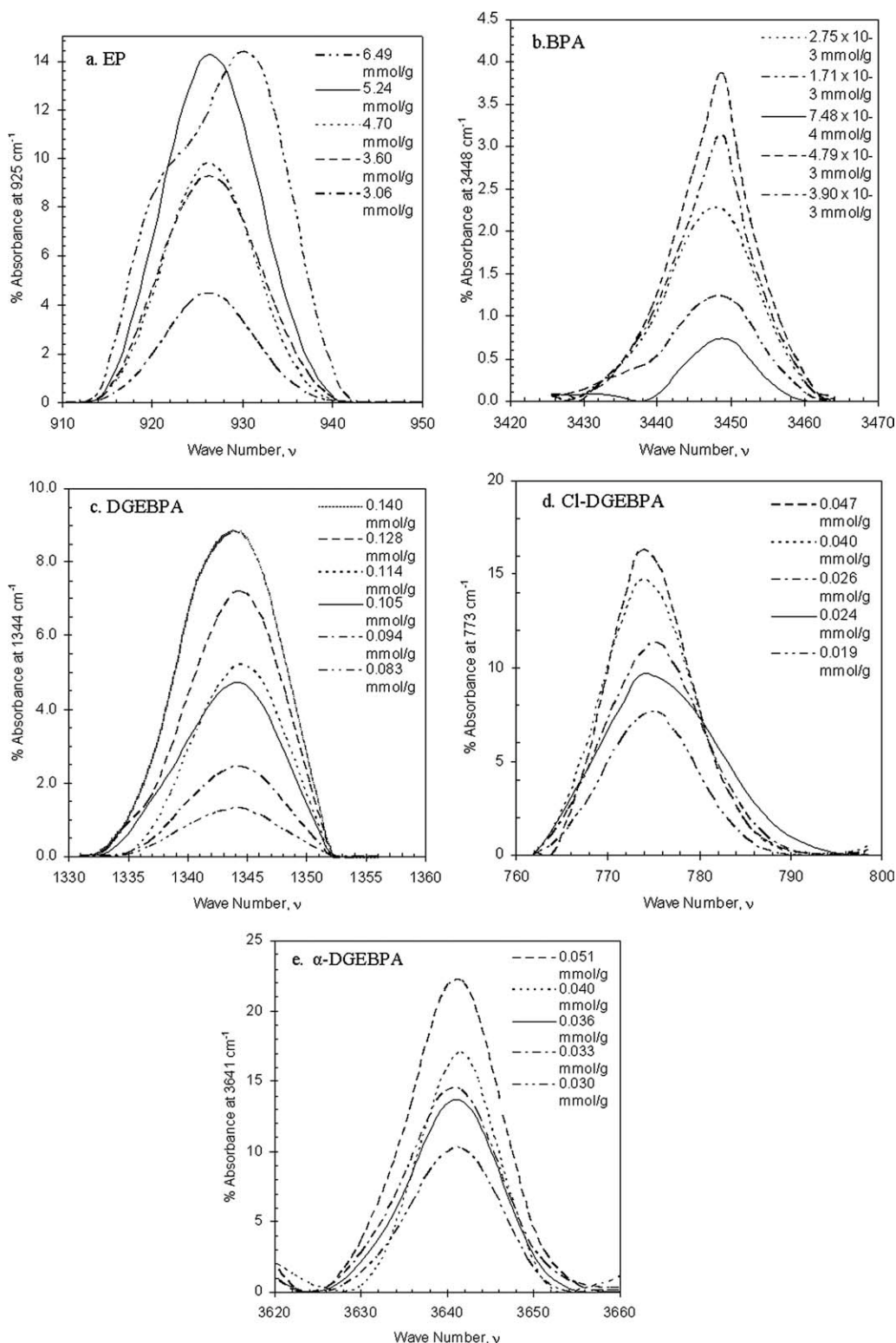


Figure 1 FT-IR spectra (percent absorbance versus wave number) for (a) epichlorohydrin, (b) bisphenol-A, (c) diglycidyl ether of bisphenol-A, (d) chlorine substituted diglycidyl ether of bisphenol-A (chlorohydrins), and (e) diol substituted diglycidyl ether of bisphenol-A (alpha glycol, AG) using standard solutions.

polymerizing mixture. It is also noted that the symmetric stretching of C—Cl bond in EP appears at 735 cm^{-1} due to its stable conformer,²⁴ whereas symmetric stretching of C—Cl bond in Cl-DGE BPA appears

at 773 cm^{-1} .²³ Though, these frequencies are close to each other, but the transmittance peak at 773 cm^{-1} is sufficient for identification of C—Cl bond in Cl-DGE BPA resin.

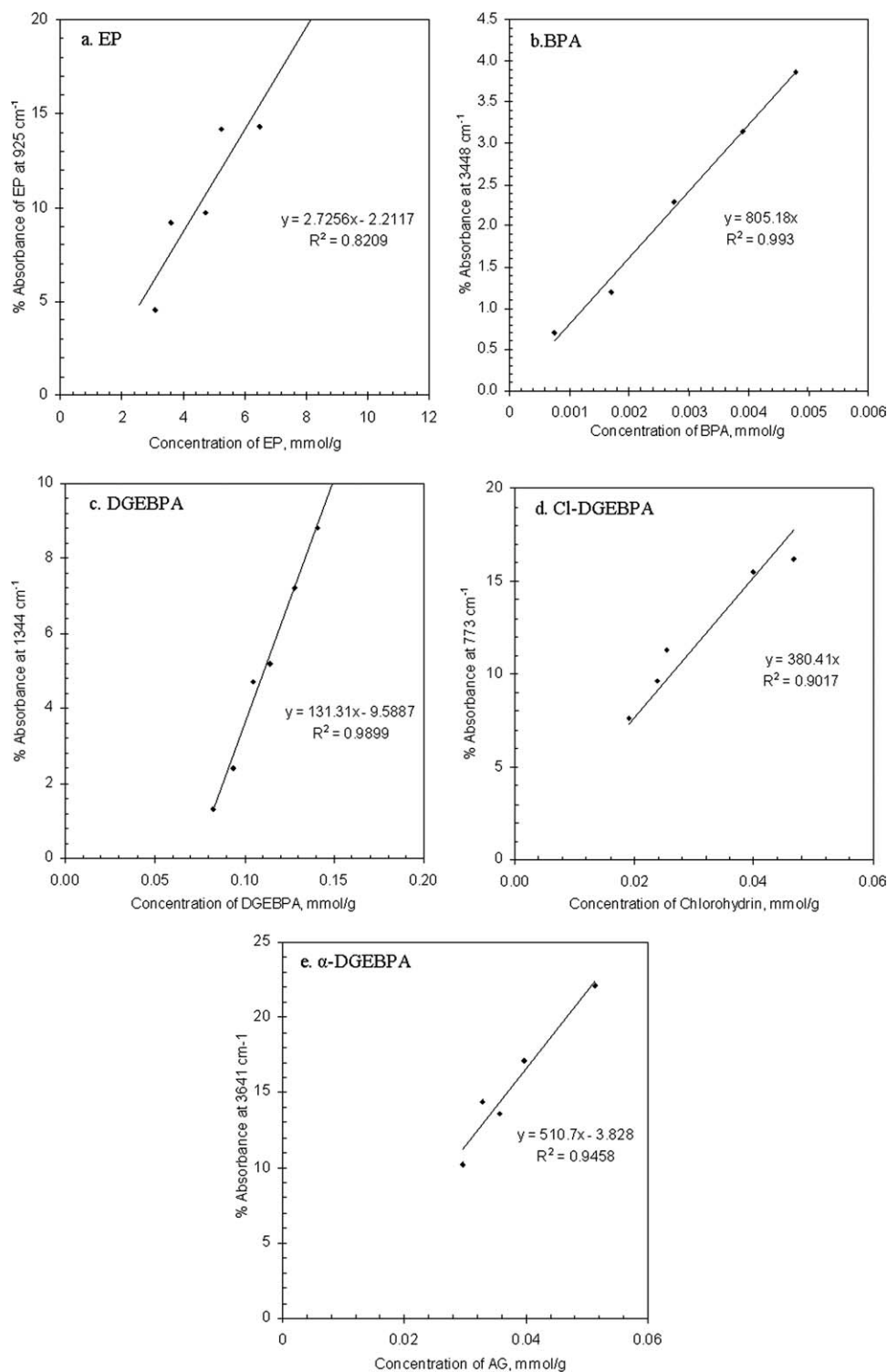


Figure 2 Calibration plots (percent absorbance vs. molar concentration) for (a) epichlorohydrin, (b) bisphenol-A, (c) diglycidyl ether of bisphenol-A, (d) chlorine substituted diglycidyl ether of bisphenol-A (chlorohydrins), and (e) diol substituted diglycidyl ether of bisphenol-A (alpha glycol, AG).

Calibration of monomers, DGEBPA resin, and byproducts

Standard liquid samples with varying molar concentration (i.e., mmol/g of benzene) of EP, BPA, DGEBPA, Cl-DGEBPA, and α -DGEBPA were prepared

using cold benzene solvent. Here, molar concentrations were reported in weight basis instead of volume basis to ensure the accuracy of the calibration plots. First, standard FT-IR plots (i.e., percent transmittance vs. wave number) for *all* the standard

TABLE III
Details of the Polymerization Experiments

Experiment no	Temperature (K)	EP, g (mol)	BPA, g (mol)	NaOH, g (mol)
1	333	231.25 (2.5)	57 (0.25)	20.5 (0.5125)
2	353	231.25 (2.5)	57 (0.25)	20.5 (0.5125)
3	363	231.25 (2.5)	57 (0.25)	20.5 (0.5125)
4	373	231.25 (2.5)	57 (0.25)	20.5 (0.5125)
5	383	231.25 (2.5)	57 (0.25)	20.5 (0.5125)
6	363	231.25 (2.5)	57 (0.25)	21.0 (0.5250)
7	363	231.25 (2.5)	57 (0.25)	22.0 (0.5500)
8	363	231.25 (2.5)	57 (0.25)	25.0 (0.6250)

samples of EP, BPA, DGEbPA, Cl-DGEbPA, and α -DGEbPA were generated using IR Prestige 21, Shimadzu Corp., Japan. A multipoint base line corrections were made for *all* the desired transmittance peaks and shifted to 100% transmittance line to avoid instrumental errors.¹⁸ Now, the absorbance peaks for each corrected transmittance peaks were calculated and percent absorbance versus wave number plots were generated for *all* the standard samples of EP, BPA, DGEbPA, Cl-DGEbPA, and α -DGEbPA. The calibration results for EP, BPA, DGEbPA, Cl-DGEbPA, and α -DGEbPA are shown in Figure 1(a–e), respectively. Corresponding to the Figure 1(a–e), calibration plots (i.e., percent absorbance vs. molar concentration in mmol/g) for EP, BPA, DGEbPA, Cl-DGEbPA, and α -DGEbPA are shown in Figure 2(a–e), respectively. Linear relationship between percent absorbance versus molar concentration (mmol/g) for *all* the calibration plots are obtained with high correlation coefficients and shown in Figure 2(a–e). Corresponding to each best fit calibration plots, best fit equations are also shown in Figure 2(a–e) for *all* the standard samples. Now, these best fit equations are used for the determination of unknown molar concentrations of EP, BPA, DGEbPA, Cl-DGEbPA, and α -DGEbPA in the polymerizing mixture.

Procedures for temperature and catalyst loading study

Polymerization of EP and BPA in presence of catalytic excess of NaOH was carried out with varying reaction temperature and catalyst loading for given molar ratio of EP and BPA. For reaction monitoring, polymerization was carried in a smaller capacity semibatch 400 mL SS 316 autoclave (Amar Equipments Pvt. Ltd., Mumbai) with automatic temperature controller to remove exothermic heat of polymerization efficiently. In this autoclave, a six-blade turbine was also fitted with the stirrer through a magnetic coupling for zero leakage. Chilled water at 283 K was used to circulate through cooling coil

inside the reactor to remove high exothermic heat of reaction during epoxy resin formation. For uniform mixing, stirrer rotation was kept at 1000 rpm, which also helps to maintain uniform polymerization temperature. A typical reactor charge consisting of 231.25 g (2.50 mol) EP, 57.00 g (0.25 mol) BPA, and 20.50 g (0.5125 mol) NaOH was taken into the autoclave and allowed for the complete dissolution. Then, reaction temperature was raised to the desired temperature. Molar ratio of EP and BPA for resin formation was fixed at 10 : 1 to produce monomeric DGEbPA. Details of the polymerization temperature, EP, BPA, and alkali loadings in the present study are reported in Table III. Initial sample was collected after attaining the desired polymerization temperature and thereafter samples were collected at the regular interval of time. Collected samples were weighted and quenched with known amount of cold benzene at 283 K to precipitate sodium chloride [Table II and eq. (3)]. Sodium chloride was removed after centrifugation and filtrate was analyzed for FT-IR analysis. Spectral analysis of the polymerizing samples containing BPA, DGEbPA, Cl-DGEbPA, and α -DGEbPA were made and the characteristic transmittance peaks were found to be identical with the reference transmittance peaks. In the case of EP, characteristic transmittance peak is shifted from 925 cm^{-1} to 912 cm^{-1} , and the shifting of this peak is mainly due to hydrogen bonding between oxirane ring oxygen with hydroxyl compounds in BPA and/or α -glycol, which are present in the polymerizing mixture. Shifting of this transmittance peak was also confirmed by analyzing FT-IR spectrum for the mixture of EP and isopropyl alcohol in benzene. Therefore, the molar concentrations of *all* the components in the polymerizing mixture are directly obtained from the calibration plots at 925 cm^{-1} , 3448 cm^{-1} , 1344 cm^{-1} , 773 cm^{-1} , and 3641 cm^{-1} FT-IR peaks for EP, BPA, DGEbPA, Cl-DGEbPA, and α -DGEbPA respectively. Usually, molar concentration of the component present in the reaction mixture is expressed in terms of mmol/L or mol/L of reaction mixture volume. In the present study, molar

concentration of the reaction mixture is reported in mmol/L of reaction mixture. Following procedure was followed to convert mmol/g of benzene (calibration plot) to mmol/L of polymerizing mixture:

- i. mmol/g of benzene was calculated from the calibration plot [Fig. 2(a–e)] based on the actual absorbance value of the withdrawn sample, which was mixed with cold benzene.
- ii. Based on the amount of benzene added (in grams) for quenching, mmol of component in the polymerizing mixture was calculated.
- iii. Volume of withdrawn sample (excluding benzene) was calculated based on the weight of sample collected and the average density of the polymerizing mixture. The average density of the polymerizing mixture in the present study was measured and found to be 1.2473 g/cm³.
- iv. Finally, mmol/L of polymerizing mixture was obtained from the number of mmol calculated and the volume of polymerizing mixture withdrawn from the autoclave.

The quantitative analysis by FT-IR technique in the present study was also confirmed by the chemical method of analysis for the estimation of resin byproducts, mainly, DGEBPA, CI-DGEBPA, and α -DGEBPA. For this, final polymerization sample at 240 min was analyzed for DGEBPA, CI-DGEBPA, and α -DGEBPA content using pyridinium chloride-pyridine method,¹⁰ Stenmark and Weiss method,¹¹ and Parr bomb procedure,¹⁰ respectively, and the results were compared with the results obtained from FT-IR analysis. It was found that the analytical results were *almost* identical with FT-IR results. Therefore, FT-IR technique can be used for the quantification of EP, BPA, DGEBPA, CI-DGEBPA, and α -DGEBPA accurately during epoxy resin formation. In the present study, monomeric DGEBPA (i.e., $n = 0$) is obtained and weight per epoxy equivalent is 184.8 g epoxy/g equiv epoxy group with average molecular weight of resin is 370. Therefore, the effect of chain length on FT-IR results will be *almost* identical for all the analysis.

RESULTS AND DISCUSSION

Effect of temperature on DGEBPA resin and byproducts formation

Effect of polymerization temperature on the product distribution including main product and undesired products was studied, keeping constant molar ratio of EP to BPA and alkali loading (Table III). Polymerization temperatures were fixed at 333 K, 353 K, 363 K, 373 K, and 383 K. Though the reaction is highly

exothermic, it is possible to maintain the desired temperature within $\pm 1.0^\circ\text{C}$ using chilled water at 283 K with high recirculation rate, and keeping the stirrer rotation at 1000 rpm. Samples were collected at the regular interval of time and analyzed using previously mentioned conditions of FT-IR. Molar concentrations of EP, BPA, DGEBPA, CI-DGEBPA, and α -DGEBPA (mmol/L) were measured using the respective calibration plots [i.e., Fig. 2(a–e)]. Variation of molar concentration in mmol/L of EP, BPA, DGEBPA, CI-DGEBPA, and α -DGEBPA with polymerization time at different temperatures are shown in Figure 3(a–e) respectively.

Figure 3(a) shows the variation of EP concentration (mmol/L) with polymerization temperature. It is found that the molar concentration of EP gradually decreases with polymerization time and conversion of EP is enhanced with the increase in polymerization temperature. Enhancement of EP conversion at higher temperature is an indication of the strong temperature dependent polymerization reaction. However, the depletion of BPA is different from EP. At lower polymerization temperature (i.e., 333 K, 353 K, and 363 K), molar concentration of BPA decreases rapidly to zero concentration level and overlaps with the X-axis [Fig. 3(b)]. Similarly, molar concentration of BPA remains nonzero at higher temperature especially at 373 K and 383 K [Fig. 3(b)]. Usually, phenol compounds are acidic in nature and results the corresponding phenoxide ions in presence of strong alkali e.g., NaOH.²⁹ Therefore, the vanishing molar concentration of BPA at low temperature is mainly due to formation of the corresponding phenoxide ion and results the disappearance of OH group due to asymmetric stretching vibration at 3448 cm⁻¹. It is also noted that the molar concentration of BPA remains unchanged at 383 K, when polymerization is carried out for the longer period of time [Fig. 3(b)]. Usually, in aqueous solutions phenol exists in equilibrium with phenoxide ion²⁹ and reversible reaction (i.e., sodium phenoxide to BPA) predominates at higher temperature, which controls the disappearance of BPA during polymerization [Fig. 3(b)]. Therefore, it is desirable to keep low polymerization temperature to maintain minimum molar concentration of BPA in the resin. It is also mentioned that the initial molar concentration of EP and BPA (i.e., after attaining the desired polymerization temperature) is lower than that the starting individual molar concentration of EP and BPA. The depleted initial molar concentration of BPA and EP is mainly due to the prepolymerization of EP and BPA before attainment of the desired polymerization temperature.

Formation of DGEBPA resin during polymerization is shown in Figure 3(c) with varying polymerization temperature. Here, molar concentration of

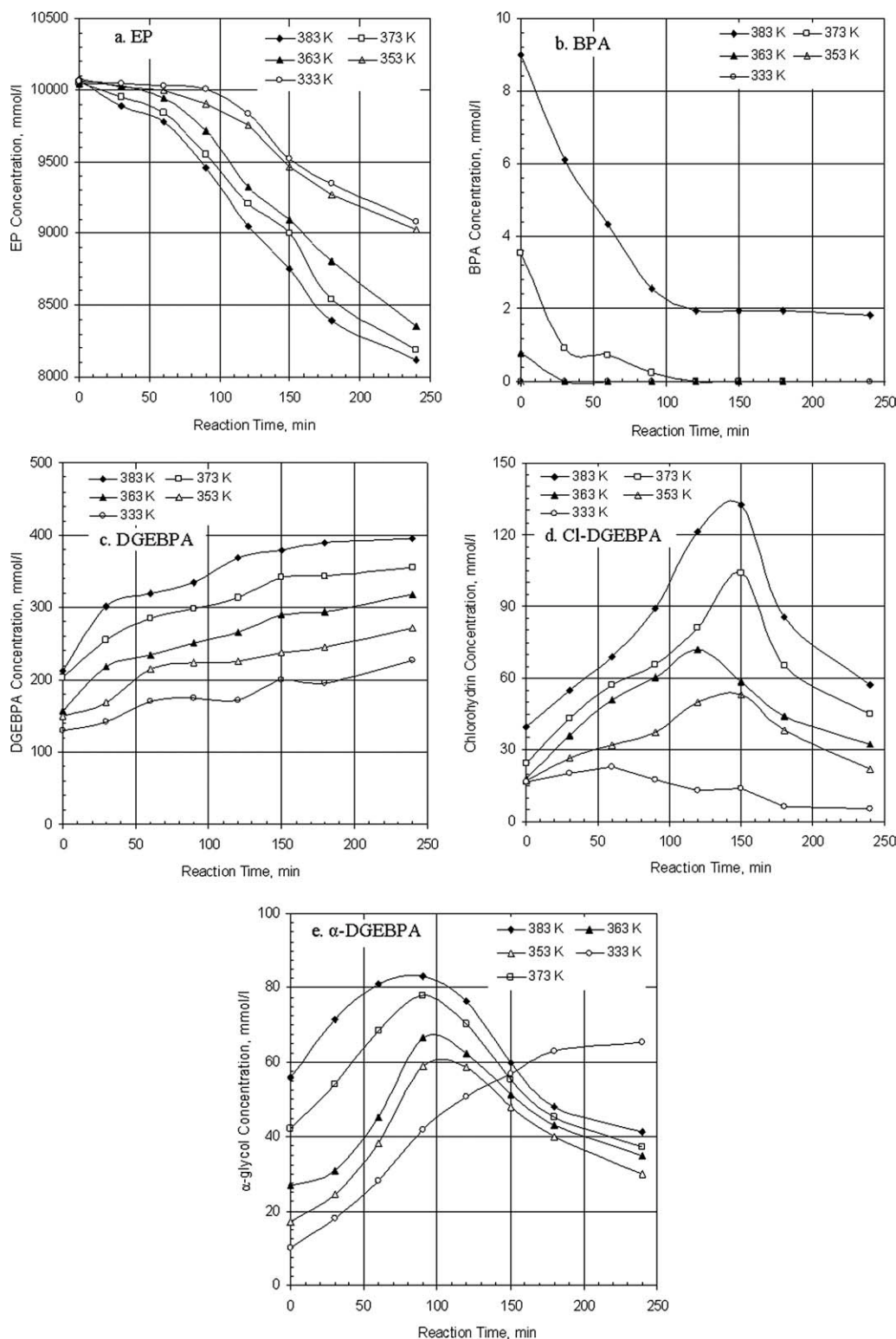


Figure 3 Variation in molar concentration with time under varying polymerizing temperature for (a) epichlorohydrin, (b) bisphenol-A, (c) diglycidyl ether of bisphenol-A, (d) chlorine substituted diglycidyl ether of bisphenol-A (chlorohydrins), and (e) diol substituted diglycidyl ether of bisphenol-A.

DGEBA resin steadily rises with time and attains *almost* a steady value after allowing sufficient polymerization time. As expected, molar concentration of DGEBA resin increases with the increase in po-

lymerization temperature. It is also noted that the initial molar concentration of DGEBA resin for *all* temperature studied takes positive value and this is mainly due to the formation of DGEBA

resin takes place before attending specified reaction temperature.

The variation in molar concentration of Cl-DGEBA resin with polymerization temperature is shown in Figure 3(d). It is observed that molar concentration of Cl-DGEBA resin increases at the beginning of polymerization and falls to a minimum value at the end of polymerization after attaining the maximum peak. The typical concentration profile of Cl-DGEBA resin confirms that the formation of DGEBA resin proceeds via formation of chlorohydrin intermediates. With the increase in polymerization temperature, formation of chlorohydrins is also increased, and favors the formation of DGEBA resin.

The variation in molar concentration of α -DGEBA resin with polymerization temperature is shown in Figure 3(e). The formation α -DGEBA resin steadily increases at lower temperature (i.e., 333 K) and attains a steady value at the end of polymerization. Attainment of steady concentration profile in reaction kinetics is an indication of equilibrium followed by the equal rates of formation and disappearance of the component.³⁰ Here, reaction between DGEBA resin and water results α -DGEBA resin [Table II; eq. (4)], and the steady molar concentrations of α -DGEBA resin in the polymerizing mixture with reaction time at lower temperature are the indication of *mild* reversible reaction between DGEBA resin and α -glycol. It is interesting to note that the formation of α -DGEBA resin attains a maximum value at higher temperature and thereafter molar concentration starts declining at the end of polymerization. It is also noted that molar concentrations of DGEBA resin *almost* remain unchanged at the end of polymerization [Fig. 3(c)], and corresponding molar concentration of EP [Fig. 3(a)] and α -DGEBA resin [Figs. 3(e)] falls rapidly with polymerization time. This suggests the possibility of forming α -DGEBA resin substituted product and formed due to the combination of α -DGEBA resin and EP. Therefore, the decrease in molar concentration of α -DGEBA resin is mainly due to formation of α -DGEBA resin substituted product with EP at higher temperature [Fig. 3(e)]. Maximum molar concentration of α -DGEBA resin also increases with increase in temperature, which indicates the formation of α -DGEBA resin substituted product and favors at the higher temperature. It is also mentioned that the inter conversion of DGEBA resin to α -DGEBA resin is much more easier due to rapid epoxy ring opening as compared with the reversed reaction and favors the coupling between α -DGEBA resin and EP. In other words, depletion of α -DGEBA resin favors the formation of α -DGEBA resin substituted EP rather than DGEBA resin at the higher temperature. Therefore, the higher temperature enhances the conversion of EP and

increases the yield of DGEBA resin, Cl-DGEBA resin, and α -DGEBA resin (except α -DGEBA resin formation at 333 K), whereas conversion BPA is reduced with the increase in temperature for given alkali loading.

Effect of alkali concentration on DGEBA resin and byproducts formation

Effect of catalytic excess of sodium hydroxide loading on the formation of DGEBA resin and undesired byproducts was also studied at constant temperature. Various amounts of NaOH [e.g., 2.5% (wt/wt), 5.0% (wt/wt), 10.0% (wt/wt), and 25.0% (wt/wt)] were considered for polymerization keeping reaction temperature at 363 K. Details of the polymerization experiments are given in Table III. Variation of molar concentration of EP, BPA, DGEBA, Cl-DGEBA, and α -DGEBA with polymerization time are shown in Figure 4(a–e) respectively. It is found that molar concentration of EP falls rapidly with decrease in alkali loading [Fig. 4(a)]. Similarly, molar concentration of BPA falls rapidly with the decrease in alkali loading [Fig. 4(b)]. It is also found that molar concentration of BPA becomes nonzero above 10% (wt/wt) alkali loading after allowing sufficient polymerization time. The decrease in conversion of EP and BPA at higher alkali loading is an indication of the inhibition of EP and BPA dissociation at higher alkali concentration. Therefore, it is desirable to keep little catalytic excess of alkali concentration to maintain minimum molar concentration of EP and BPA in the polymerizing mixture.

Molar concentration of DGEBA resin increases with alkali loading and results are shown in Figure 3(c). It is noted that molar concentration of Cl-DGEBA resin vanishes quickly at higher alkali loading (i.e., 25.0, 10.0, and 5.0% at 363 K) and results are shown in Figure 4(d). Here, the rapid depletion of Cl-DGEBA resin [mainly, chlorohydrin intermediates: Table II, eq. (1)] favors the formation DGEBA resin [Fig. 4(c)]. Though the conversion of EP and BPA reduces with the increase in alkali loading [Fig. 4(a,b)], but the interconversion of chlorohydrins to DGEBA resin favors at higher alkali loading [Fig. 4(d)]. Therefore, overall DGEBA formation is enhanced with increase in alkali loading keeping minimum molar concentration of chlorohydrins [Fig. 4(c)]. With the increase in alkali loading, molar concentration of α -DGEBA resin attains a maximum value and thereafter it decreases to a minimum value [Fig. 4(e)]. As explained earlier, the formation of α -DGEBA resin substituted EP formation during polymerization favors at higher alkali loading. Therefore, higher alkali loading helps to increase the yield of DGEBA resin keeping minimum concentration of chlorohydrins intermediate, whereas

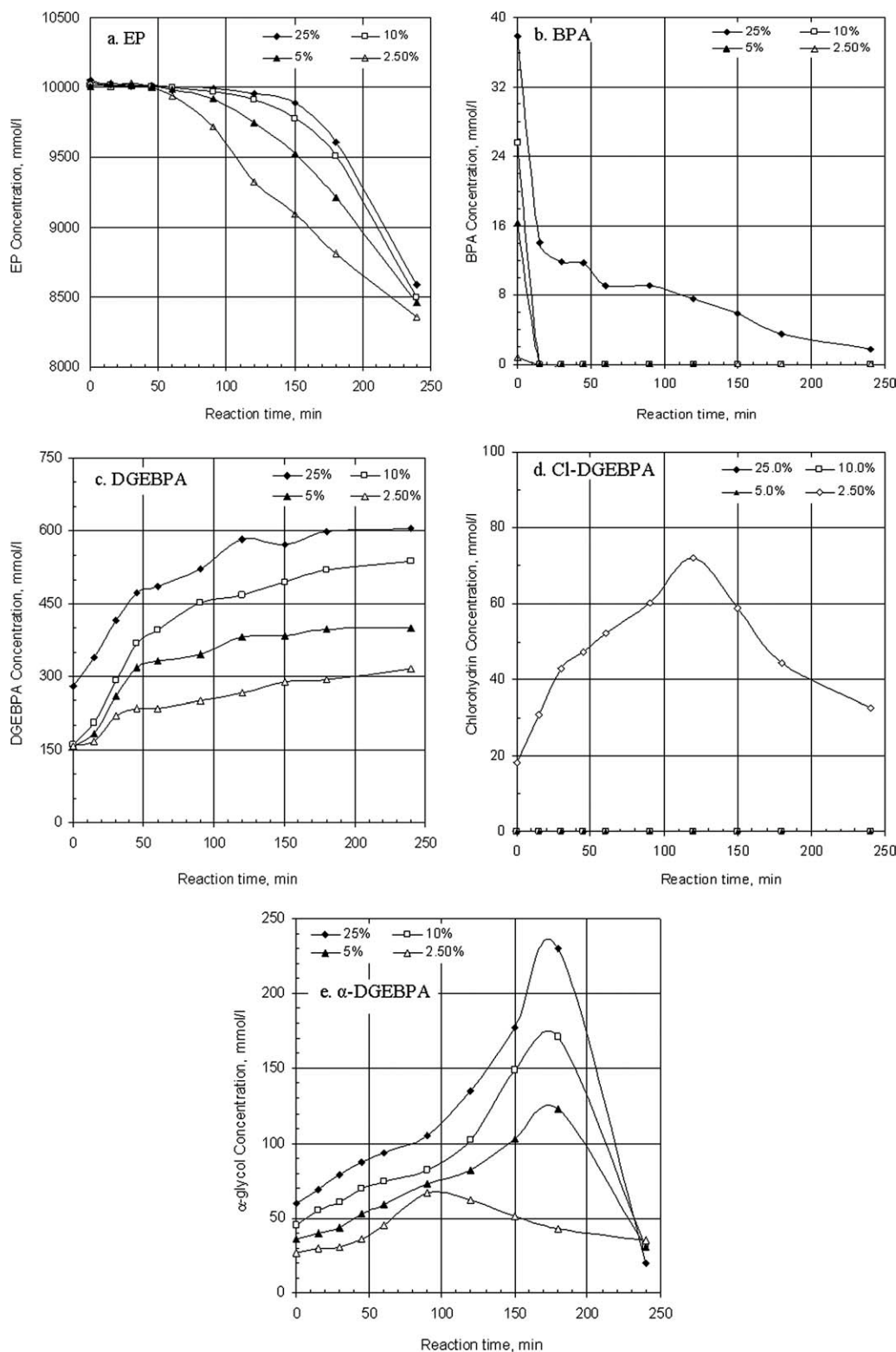


Figure 4 Variation in molar concentration with time under varying alkali loading for (a) epichlorohydrin, (b) bisphenol-A, (c) diglycidyl ether of bisphenol-A, (d) chlorine substituted diglycidyl ether of bisphenol-A (chlorohydrins), and (e) diol substituted diglycidyl ether of bisphenol-A.

conversion of EP and BPA is reduced with enhanced formation of α -DGEBPA resin with the increase in alkali loading at a given temperature.

CONCLUSIONS

Polymerization of EP and BPA with 10 : 1M ratio is carried out in presence of catalytic excess of alkali.

Formation of monomeric DGEbPA is monitored using FT-IR technique through rapid identification and quantification of desired product (DGEbPA), unreacted monomers (EP and BPA), and byproducts (Cl-DGEbPA resin and α -DGEbPA resin). Several calibration plots (percent absorbance vs. molar concentration) of EP, BPA, DGEbPA, Cl-DGEbPA, and α -DGEbPA are presented for the standard samples at their characteristic transmittance peaks. Effects of polymerization temperature and catalytic excess of alkali loading on the desired product, and byproducts are studied in an automatic temperature controlled autoclave. Temperature and catalytic excess of alkali have a marked effect on DGEbPA resin formation, byproducts formation, and unreacted monomers. Because of the presence of conflicting objectives i.e., maximizing the yield of DGEbPA resin and minimizing the yield of byproducts, it is very difficult to select unique combination of the process parameters (i.e., temperature and alkali loading) for which both objectives will be satisfied. Low temperature and low catalytic excess of alkali helps to maintain low molar concentration of BPA in polymerizing mixture. Conversion of EP is favored at higher temperature and lower catalytic excess of alkali. Higher temperature and increased catalytic excess of alkali favors the formation DGEbPA resin. High catalytic excess of alkali and low temperature helps to keep Cl-DGEbPA resin concentration as low as possible in the polymerization mixture. Molar concentration of α -DGEbPA resin attains a maximum for all the polymerizing mixtures except at the lowest polymerization temperature studied for epoxy polymerization.

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