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EFFECTS OF VARIOUS PROCESS VARIABLES ON RESIN CHARACTERISTICS OF BROMINATED EPOXY POLYMERS*

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Abstract—Brominated epoxy polymers (BEPs) were prepared by condensing epichlorhydrin (ECH) with bisphenol-A (BPA) and tetrabromobisphenol-A (TBBPA). The effects of process variables such as mole ratio of ECH to the mixture of BPA and TBBPA, temperature, time of reaction and mole ratio of catalyst to the mixture of BPA and TBBPA were studied, considering the yield, epoxy content, hydrolysable chlorine content and oxirane oxygen of the BEP. Mathematical models have been derived to provide readily calculable parameters to obtain BEPs with optimum yield and low hydrolysable chlorine content. The calculated values derived from the model have been found to be close to the experimental results.

INTRODUCTION

Epoxy resins form an important class of thermosetting polymers and have such varied applications as adhesives and matrix resins for fibre compositions [1]. An important epoxy resin consists of diglycidyl ether (DGEBPA) formed by the reaction of bisphenol-A (BPA) and epichlorhydrin (ECH) [2, 3]. Another class of epoxies consists of brominated epoxy polymers (BEPs). They usually contain 10–50% bromine and are prepared by condensing tetrabromobisphenol-A (TBBPA) and ECH [4–6]. These resins possess flame retarding properties and are mostly used for making laminates for electronic applications (FR4 Grade NEMA specification) [7, 8]. In the case of a TBBPA epoxy polymer, the molecular species concerned is a linear polyether with terminal epoxide groups and secondary hydroxyl groups at regular intervals along the backbone, a large part of the chain consisting of aromatic rings each with four attached bromines (Fig. 1). The number of repeating groups (n) is dependent essentially on the molar ratio of TBBPA and ECH used during the resin synthesis. A series of resins can thus be obtained, each grade consisting of a mixture of molecules differing in chain length and molecular weight. Whereas bromine attached to the aromatic rings enhances the flame retardant properties, the hydrolysable chlorine present as 1,2-chlorhydrin as the result of incomplete dehydrohalogenation diminishes the purity of the product. Low hydrolysable chlorine content has been the main concern in synthesizing resin specially for electronic applications and its purification mainly involves removal of hydrolysable chlorine [9–12]. The other characteristics of the epoxy resins include epoxy content and oxirane oxygen both of which contribute to desired properties. Trivedi and Dedhia have studied the control of parameters for reaction of CNSL, BPA and ECH to obtain a resin with predetermined characteristics [13, 14]. The aim of the present study has been to prepare BEPs having minimum hydrolysable chlorine and optimum resin characteristics. Methods of factorial design were used to study the effects of process variables on the resin characteristics such as yield, epoxy content, oxirane oxygen and hydrolysable chlorine content of BEPs. Mathematical models have been derived and a comparative study made between the theoretically calculated and experimental results.

EXPERIMENTAL PROCEDURES

Materials

BPA (synthesis grade m.p. 160°) (Shah Research Lab. India), ECH (BDH LR Grade), NaOH (BDH) and Br_2 (Qualigens Fine Chemicals India) were used as received. Methanol and methyl cellosolve were distilled before use.

Preparation of TBBPA

TBBPA was prepared by bromination of BPA. BPA was dissolved in methanol and Br_2 in slight excess was added at 5–10° with constant stirring. The exothermic reaction was controlled by the rate of bromine addition over a period of 1 hr followed by refluxing of the system (65°) for $1\frac{1}{2}$ hr to allow the slower reaction between bisphenol-A and HBr. During this period, CH_3Br was vented through the overhead condenser system into a series of scrubbers and was collected in ether solution as a by-product; water was then added to precipitate TBBPA and the resulting slurry was cooled, filtered, washed and dried.

Preparation of BEP

For preparation of epoxy resins, a mixture of 29 g BPA and 34.4 g TBBPA was used. After adding ECH, the temperature was raised and maintained at a definite value; NaOH was used as a catalyst and stirring carried out for a particular period. The resin formed was filtered off, washed with distilled water and the unreacted ECH was removed by vacuum distillation.

Characterization

Infrared spectroscopy was carried out on NICOLET 5-MX model to characterize TBBPA and BEPs. Bromine contents in TBBPA and BEPs were determined by ASTM E-442, by the oxygen flask method. Epoxy contents of BEPs were determined by ASTM D-1652, by reaction of HBr with

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*To avoid further delay this paper has been published without the authors' corrections.

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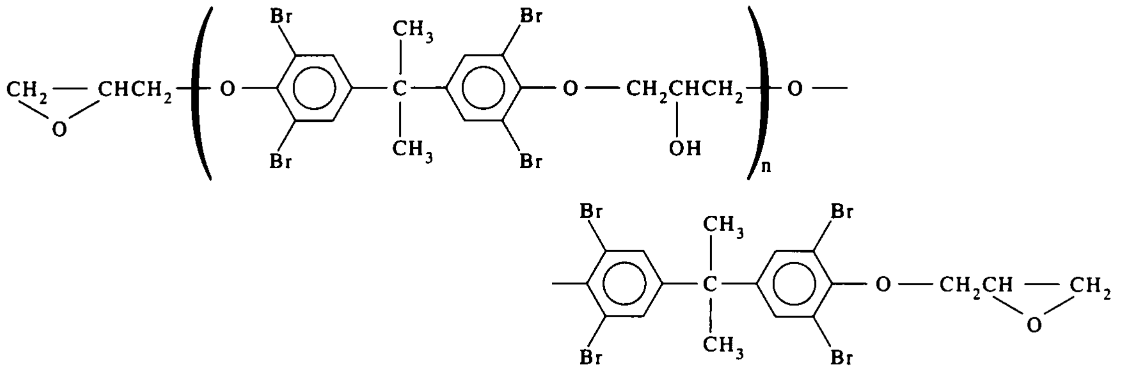

Fig. 1. Chemical structure of brominated epoxy resin.

epoxy groups to form bromohydrins. Hydrolysable chlorine contents were estimated by ASTM D-1726, by measuring the amount of standard alcoholic KOH consumed during titration. Oxirane oxygen was determined by ASTM D-1652.

RESULTS AND DISCUSSION

The structure of TBBPA has been confirmed by i.r. as shown in Fig. 2. Bromine content for TBBPA was found to be 54% i.e. close to the theoretical value of 58%. This value has been noted, while considering the quantities of BPA and TBBPA during synthesis of BEPs, to obtain the desired bromine content of about 20%. Similarly i.r. spectra also confirm the characteristics of BEPs as they match the standard products (Fig. 3).

Nine experiments for the preparation of BEPs were carried out according to Factorial design. The levels of process variables are given in Table 1 and the experimental plan for change of variables in these experiments are given in Table 2. The yields in the experiments and other resin characteristics of BEPs (i.e. epoxy content, hydrolysable chlorine content and oxirane oxygen of the products) are reported in Table 3. The effects of process variables on these characteristics have been represented as the differences between the averages of the responses at the higher limit of the variable and the averages of the responses at lower limit of that variable (see Table 4); a positive sign indicates that the value of a particular characteristic increases when the process variable increases from low to high level while a negative sign indicates the reverse. Thus the difference between the average of the yields of runs 1, 3, 5, 7 and the average of the yields of runs 2, 4, 6, 8 is +4.3, indicating that the yield increases when the mole ratio of ECH to (BPA + TBBPA) is increased from 6:1 to 12:1. The effects of various parameters are discussed subsequently.

Effect of mole ratio of ECH to (BPA + TBBPA)

When the mole ratio of ECH to (BPA + TBBPA) was increased from 6:1 to 12:1, the yield was increased by 4.3 g indicating that the excess of ECH

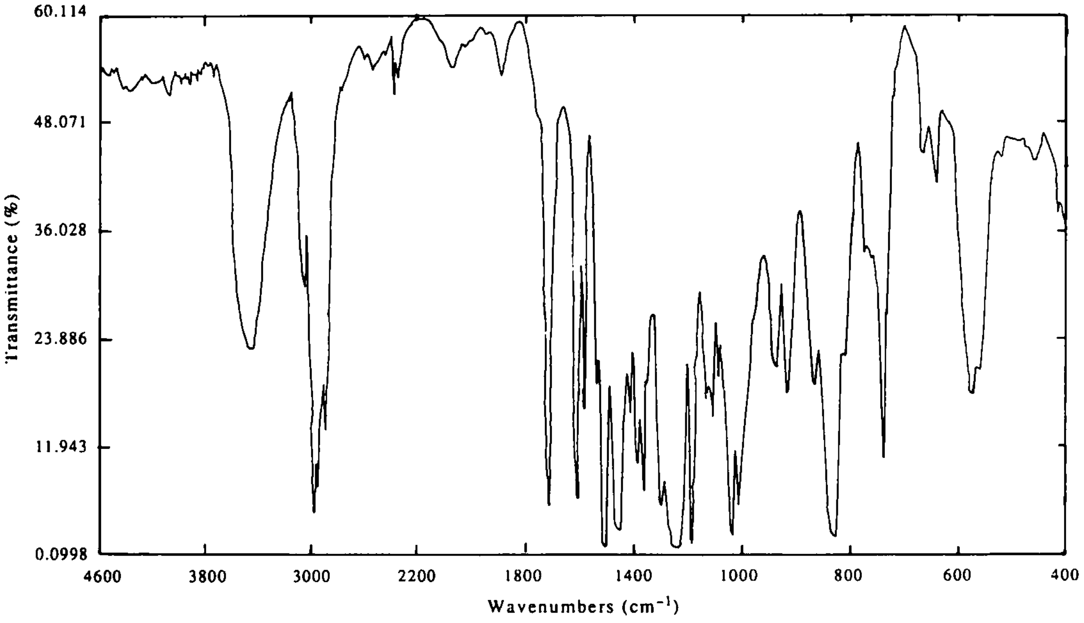

Fig. 2. Infrared spectrum of TBBPA.

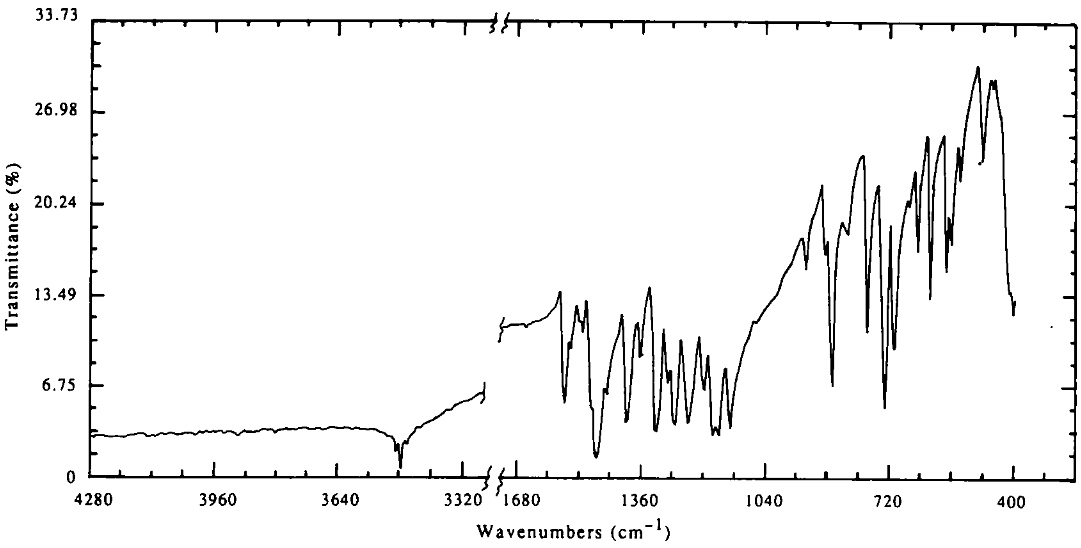

Fig. 3. Infrared spectrum of brominated epoxy resin.

Table 1. Levels of process variables in brominated epoxy polymers (BEPs)

Process variable		Low level (−)	Zero level mean	High level (+)
Mole ratio of epichlorhydrin to (BPA + TBBPA)	(X1)	6:1	9:1	12:1
Temperature (°C)	(X2)	65	72.5	80
Time (min)	(X3)	120	180	240
Mole ratio of catalyst to (BPA + TBBPA)	(X4)	1:1	1.5:1	2:1

facilitates the reaction of ECH with both hydroxyl groups of BPA and does not allow further extension of the chain length. This conclusion is confirmed by the increase in epoxy content by 0.020 g equivalent of epoxy groups per 100 g resin and oxirane oxygen by 0.35%. Due to the increase in mole ratio of ECH to (BPA + TBBPA) from 6:1 to 12:1, hydrolysable chlorine content increases by 0.35%.

Effect of temperature

Increase of temperature from 65 to 80° decreases the yield by 1 g but does not have any great effect on epoxy and hydrolysable chlorine contents. Slight increase in yield without noticeable effect on epoxy content has also been reported [13].

Table 2. Experimental plan for change of variables in the synthesis of BEPs

Run No.	X1	X2	X3	X4
1	12:1	80	240	2:1
2	6:1	80	120	2:1
3	12:1	65	120	2:1
4	6:1	65	240	2:1
5	12:1	80	120	1:1
6	6:1	80	240	1:1
7	12:1	65	240	1:1
8	6:1	65	120	1:1
9	9:1	72	180	1.5:1

Effect of time

Increasing the duration of reaction from 2 to 4 hr does not affect the yield but the epoxy content increased by 0.012 U. This result means the degree of polymerization decreases with an increase in time. Increase of hydrolysable chlorine content by 0.02% indicates the regeneration of halohydrin.

Effect of mole ratio of catalyst to (BPA + TBBPA)

Increase in mole ratio of catalyst NaOH to (BPA + TBBPA) from 1:1 to 2:1 has no remarkable effect on the yield but there are increases in epoxy content by 0.142 U and oxirane oxygen by 2.272%. The increase in mole ratio obviously promotes the addition of phenolic OH group to the epoxide ring and facilitates dehydrohalogenation of halohydrin to the epoxide group. This conclusion is confirmed by the observation that hydrolysable chlorine content decreases by 0.298%.

Experiments were also conducted under mean conditions. These values (Table 3, row 10) compare well with the calculated mean value with respect to yield, epoxy content and hydrolysable chlorine content of the resins (Table 3, row 9).

Mathematical models have been derived for calculating yield, epoxy content, hydrolysable chlorine and oxirane oxygen of the resins prepared using the

Table 3. Resin characteristics of brominated epoxy polymers

Run No.	Yield (g)	Epoxy* content	Hydrolysable chlorine (%)	Oxirane oxygen (%)
1	77.1	0.397	0.62	6.35
2	74.9	0.339	0.33	5.42
3	79.3	0.433	0.55	6.93
4	73.7	0.382	0.21	6.11
5	77.6	0.245	0.84	3.92
6	75.7	0.277	0.63	4.43
7	80.4	0.232	0.89	3.71
8	73.9	0.226	0.54	3.61
9 [Mean Exp.]	76.0	0.315	0.60	5.04
[Mean Cal.]	76.5	0.316	0.57	5.06

*g equivalent of epoxy groups per 100 g resin.

Table 4. Effect of process variables on yield and other properties of BEPs

Process variable	Yield	Epoxy content	Hydrolysable chlorine	Oxirane oxygen
X1	+4.3	+0.020	+0.300	+0.350
X2	−1.0	−0.004	+0.058	−0.060
X3	−0.3	+0.012	+0.020	+0.192
X4	−0.7	+0.142	−0.298	+2.272

process variables shown in Table 5. To illustrate, the yields of reactions under conditions X1, X2, X3 and X4 were calculated as following:

$$\text{Total Yield} = \text{Mean Yield} + \sum_{i=1}^{4} \frac{\text{Effect of } X_i}{\text{Difference of levels of } X_i} \times (X_i - \text{Mean of levels of } X_i).$$

A typical example can be illustrated thus:

Yield of Run No.1

$$= 76.0 + \frac{4.3}{6}(12.9) + \frac{-1}{15}(80\text{–}72.5) + \frac{-0.3}{120}(240\text{–}180) + \frac{-0.7}{1}(80\text{–}72.5)$$

The yield and resin characteristics of all the experiments were calculated (Table 6) and were compared with the experimental results. It can be seen from Table 6 that good agreement exists between the calculated and experimentally observed values.

Conclusions

1. The yield, epoxy content, oxirane oxygen and hydrolysable chlorine increase with increasing epichlorohydrin content during synthesis of BEP.
2. Temperature has practically no effect on the resin characteristics of BEPs, but increase in time slightly increases the hydrolysable chlorine because of regeneration of halohydrin.
3. Increase in the mole ratio of catalyst to (BPA + TBBPA) increases the epoxy content by promoting addition of phenolic OH to epoxide and facilitating dehydrohalogenation of the halohydrin to the epoxide group thereby decreasing the hydrolysable chlorine content.
4. Calculated resin characteristics derived from mathematical model are in close proximity with experimental results.

Table 5. Mathematical models for effect of process variables on resin characteristics

Total yield	$76.0 + 0.176(X1\text{–}9) - 0.066(X2\text{–}72.5) - 0.0025(X3\text{–}180) - 0.7(X4\text{–}1.5)$
Epoxy content	$0.315 + 0.33 \times 10^{-2}(X1\text{–}9) - 0.266 \times 10 (X2\text{–}72.5) + 0.1 \times 10^{-3}(X3\text{–}180) + 0.142(X4\text{–}1.5)$
Hydrolysable chlorine content	$0.60 + 0.05(X1\text{–}9) + 0.333 \times 10^{-2} (X2\text{–}72.5) + 0.1666 \times 10^{-3}(X3\text{–}180) - 0.298(X4\text{–}1.5)$
Oxirane oxygen	$5.04 + 0.058(X1\text{–}9) - 0.004 (X2\text{–}72.5) + 0.16 \times 10^{-2}(X3\text{–}180) + 2.272(X4\text{–}1.5)$

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Table 6. Comparison of experimental and calculated results of various resin product characteristics of brominated epoxy polymer

	Resin product characteristics							
	Yield (g)		Epoxy content*		Hydrolysable chlorine (%)		Oxirane oxygen (%)	
Run No.	Expt	Calc.	Expt	Calc.	Expt	Calc.	Expt	Calc.
1	77.1	77.1	0.397	0.399	0.62	0.63	6.35	6.41
2	74.9	73.2	0.339	0.368	0.33	0.32	5.42	5.88
3	79.3	77.5	0.433	0.392	0.55	0.56	6.93	6.27
4	73.7	73.8	0.382	0.384	0.21	0.28	6.11	6.14
5	77.6	78.1	0.245	0.246	0.84	0.91	3.92	3.92
6	75.7	73.6	0.277	0.238	0.63	0.63	4.43	3.81
7	80.4	78.8	0.232	0.261	0.89	0.88	3.71	4.17
8	73.9	74.8	0.226	0.229	0.54	0.56	3.61	3.66

*g equivalents of epoxy groups per 100 g resin.