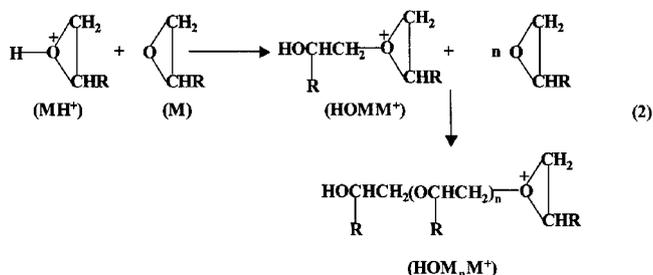


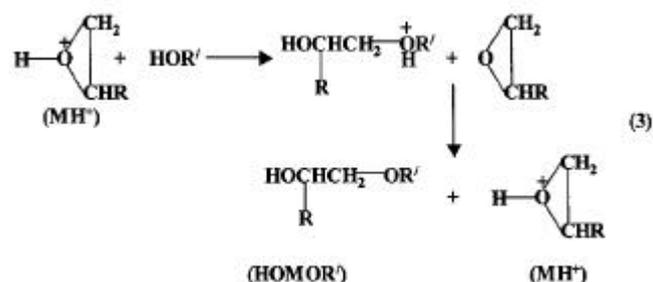


The propagation in such cationic polymerization proceeds via two competing mechanisms known as the activated chain end (ACE) and activated monomer (AM) given in (2) and (3) below:

*ACE mechanism:*

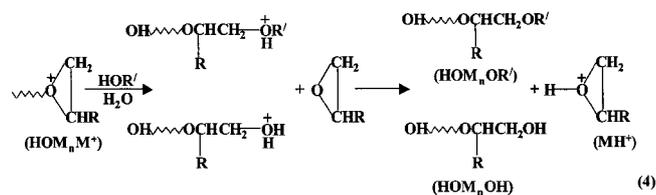


*AM mechanism:*



In ACE, growing chain cyclic tertiary oxonium ions ( $\text{OHMM}^+$ ) are formed, and polymerization proceeds by chain addition of monomer. On the other hand, the AM mechanism proceeds via the addition of molecules containing hydroxyl groups to the activated monomer. This is accompanied by a transfer of charge to regenerate  $\text{MH}^+$ . During the initial stages of reaction and in systems with low initial concentration of hydroxyl groups, ACE mechanism is predominant. However, the presence of hydroxyl groups, i.e. water, alcohol, polymer chain ends, and comonomer, can favour the AM mechanism.

Other reactions include the chain transfer reactions as shown below in which an activated chain end reacts with hydroxyl moiety, water or alcohol. The transfer reaction via OH group containing compound results in an inactive oligomer, as shown in (4) below.



Despite good thermal properties and significant processing advantages, composites manufactured using e-beam-curable resin systems suffer from low compressive strength, poor interlaminar shear strength, and low fracture toughness. The reaction mechanisms of e-beam induced cationic polymerization of epoxides and the influence of hydroxyl group containing species (e.g. absorbed water in resin system, intermediates formed during reactions, monomers and comonomers) on the kinetics of reaction and polymer network formation must be well understood to properly address the resin dominated shortcomings associated with the e-beam-curable systems. Commercially available epoxy resins absorb a significant amount of water from the air, and water is often found on the surfaces of reinforcements. Such absorbed water plays an important role in the polymerization reaction.

In this work, we investigate the effect of presence of water and alcohols on the e-beam induced polymerization of epoxides. This is motivated by the understanding that OH group containing intermediates, generated during the cure reactions by the creation of growing chains, or the reaction of absorbed water with active centres as well as hydroxyl containing comonomers, and modifiers, can significantly influence the reaction pathways in these systems.

In this communication, we report the effect of primary aliphatic alcohol, phenol and water on the e-beam induced cationic polymerization of a model epoxy system, phenyl glycidyl ether (PGE). PGE was used as a model epoxy because it contains only one epoxy group per molecule; consequently, it polymerizes to linear soluble products, which are easily analysed by size exclusion chromatography (SEC) to provide insight concerning reaction pathways.

## 2. Experimental

The materials used were (i) phenyl glycidyl ether (PGE) (Aldrich Chemical Company Inc. USA), (ii) 2-cyclohexyl ethyl alcohol (CHEA) (Aldrich Chemical Company Inc. USA), (iii) phenol (Aldrich Chemical Company Inc. USA) and (iv) double distilled water. The photoinitiator diphenyl iodonium hexafluoroantimonate (DPI-1) was obtained from Applied Polymeric Inc., USA. All the chemicals except water and DPI-1 were dried using 4 Å molecular sieves obtained from Aldrich Chemical Company Inc. USA. The sieves were activated at 175°C for 24 h prior to use. Such drying limits water concentration below 0.1% in the reactants.

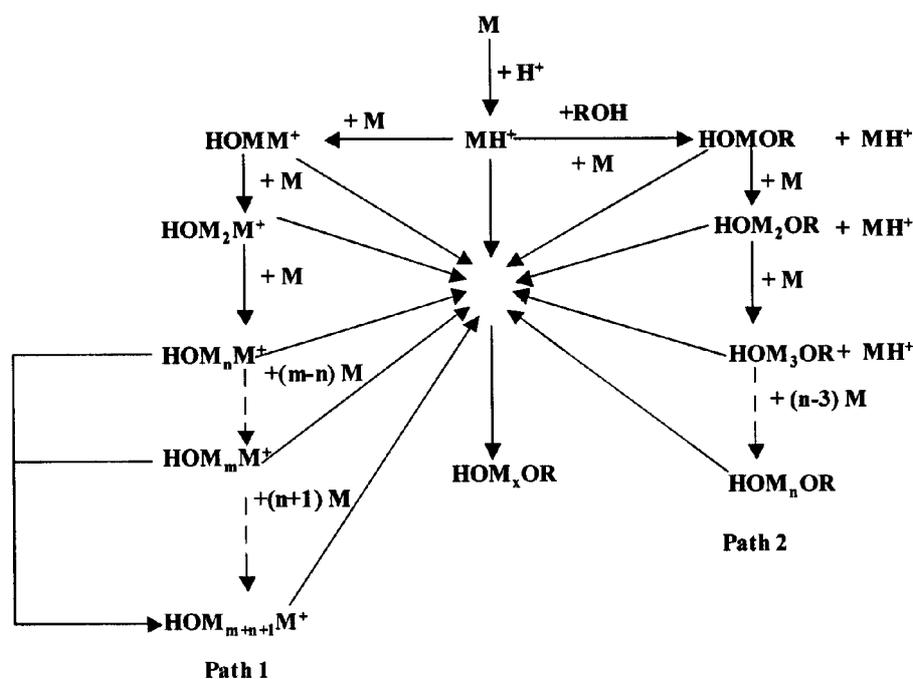
3 wt% DPI-1 was mixed with PGE, and two types of samples were prepared by adding CHEA and phenol to this mixture while keeping PGE : alcohol molar ratio 1 : 1. All the samples were sealed in polypropylene bottles containing additional molecular sieves. Another sample was prepared by mixing 2 wt% water with PGE and DPI-1 mixture and sealed in a polypropylene bottle. The samples were irradiated by e-beam at 20 MRad using

5-MeV accelerator. 0.1 g samples of initial reaction mixture and samples after e-beam irradiation were dissolved in 10 ml tetrahydrofuran (THF) (chromatographic grade, from Aldrich Chemical Company Inc. USA) for size exclusion chromatography (SEC) analysis using Perkin Elmer HPLC, model 200, equipped with refractive index detector. The column used is 5-micrometer PL gel-mixed C column (packed by highly cross linked spherical polystyrene-divinyl benzene matrix). The standardization of SEC was performed by using polystyrene standards having molecular weight 2930, 10850, 59500, 148000, 320000 and 841700. THF was used as the mobile phase, and elution was carried out at 1 ml/min flow rate. SEC was employed to measure the depletion of reactants and the formation of products resulting from e-beam induced cationic polymerization products.

### 3. Results and discussion

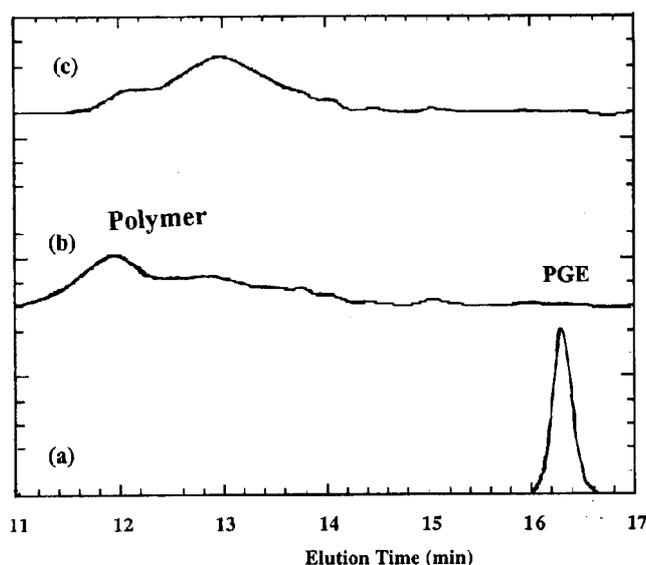
Diphenyl iodonium hexafluoroantimonate undergoes photolysis during e-beam irradiation and releases a powerful Bronsted acid (Crivello and Lam 1977; Fouassir *et al* 1994). In subsequent steps, this strong protonic acid ( $H^+$ ) initiates the polymerization of epoxy group containing monomer (M). The  $H^+$  ion, produced during e-beam photo-initiation, reacts with the epoxy group of the monomer and produces an active species  $MH^+$ .

The experiments conducted using PGE and alcohols were designed to gain some understanding concerning the relative rates of reaction of the oxonium ion with epoxy group versus that of the oxonium ion with an organic hydroxyl group. The reaction scheme shown in figure 1 summarizes the complex reaction pathways for a cationically cured mixture of epoxy monomer (M) and with an alcohol (ROH). The nomenclature used here follows the convention adopted in (1) to (4), where the mechanism of cationic polymerization has been described. The left branch, denoted as path 1, represents polymerization by the ACE mechanism, and the branch to the right, denoted as path 2, represents polymerization via the AM mechanism. The chain transfer reactions are represented by the cross-arrows of the diagram. The molecular weight of the products is greatest when the overall reactivity favours path 1. This will happen in the absence of alcohol or when the intrinsic reactivity of the hydroxyl group of an alcohol with an active centre is much less than that of an epoxy moiety with the same centre. In fact, in case of an equimolar mixture of monoepoxy monomer and alcohol, two limiting cases are apparent. First, if the alcohol-active centre reactivity is much less than the epoxy-active centre reactivity, the polymer of the highest molecular weight should form. Second, if the alcohol-active centre reactivity is much greater than the epoxy-active centre reactivity, then only oligomeric products will form and a significant fraction of the alcohols will be consumed.

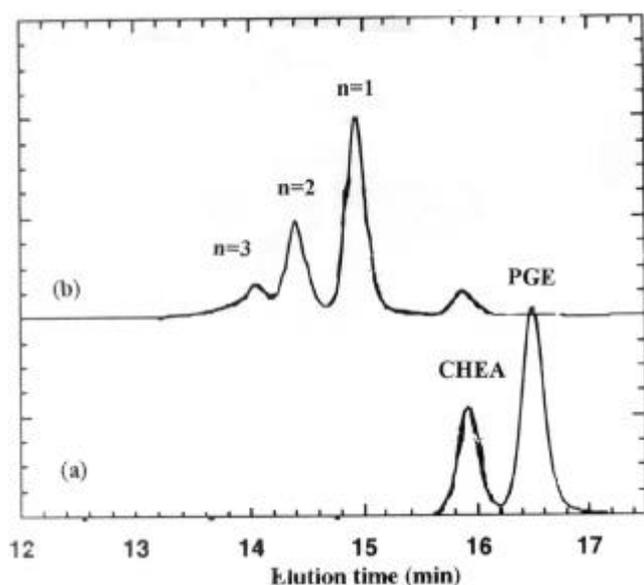


**Figure 1.** Scheme showing reaction pathways of cationic polymerization of epoxies in the presence of alcohol. Path 1 represents ACE mechanism, yielding the highest molecular polymers. Path 2 represents polymerization by the AM mechanism and leads to lower molecular weight products. Chain transfer reactions are indicated by the cross-arrows.

Figure 2 shows the SEC chromatogram of pure PGE and the products, formed due to the e-beam irradiation of dry PGE and PGE mixed with 2 wt% water. SEC separates mixtures by size, with molecules possessing higher molecular weight eluting first. The broad peaks appearing in the chromatogram represent the polymeric products



**Figure 2.** SEC of (a) PGE, and e-beam induced polymerization products of (b) dry PGE and (c) PGE and 2 wt% water. Note that higher molecular weight materials elute at shorter times.

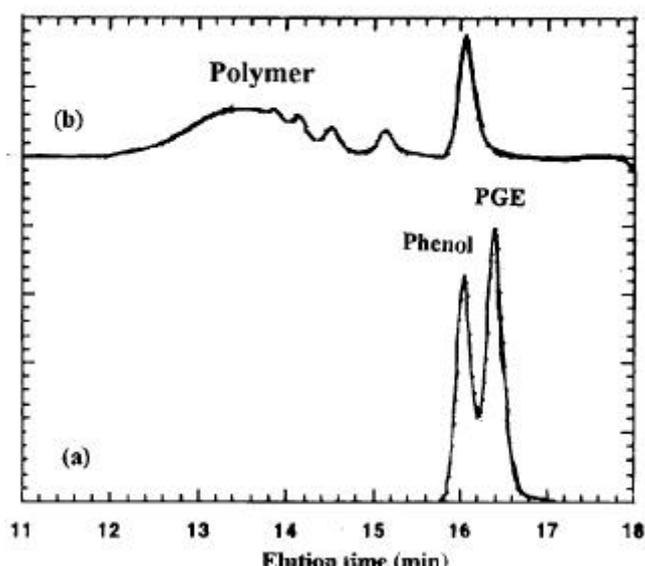


**Figure 3.** SEC of (a) initial reactants and (b) final products of e-beam induced cationic polymerization of an equimolar mixture of PGE and CHEA showing the formation of oligomeric products.

having high molecular weight. In case of the product of dry PGE irradiated by e-beam, a broad peak is observed from 11–14 min, having highest peak height at ~12 min. But in case of the reaction mixture where dry PGE is mixed with 2 wt% water, a broad peak is observed from 11.5–14.5 min, having highest peak height at ~13 min after e-beam irradiation. It is clear from these results that water, at a concentration comparable to that found in epoxy resin exposed to typical ambient conditions, reduces the molecular weight of the resulting polymeric product.

Results of SEC analysis for the e-beam irradiation products of PGE and CHEA (1 : 1 molar ratio) and PGE and phenol (1 : 1 molar ratio) are shown in figures 3 and 4, respectively. Each plot contains chromatograms of the starting mixtures and final products after e-beam irradiation. In figure 3, peaks appearing at 15.9 and 16.5 min have been assigned to CHEA and PGE, respectively. After e-beam irradiation, all PGE is consumed and ~70% of CHEA is reacted. It is clear that this combination of the reactants does not generate polymeric products having high molecular weight. The peaks at 14.9, 14.4 and 14.1 min correspond to the oligomeric products of CHEA and PGE as described in figure 1 by reaction path 2 (i.e. HOMOR, HOM<sub>2</sub>OR, HOM<sub>3</sub>OR, respectively).

Figure 4 shows the SEC chromatogram for the initial reaction mixture and irradiation products of PGE and phenol system. In contrast to the PGE-CHEA reaction, a broad peak is observed from 12–15 min that corresponds to the polymeric product. Moreover, ~50% of the phenol remains unreacted. Thus it can be concluded that compared to the CHEA the OH group of phenol is less reac-



**Figure 4.** SEC of (a) initial reactants and (b) final products of e-beam induced cationic polymerization of an equimolar mixture of PGE and phenol showing the formation of polymeric products.

tive with the oxonium active centre allowing a significant portion of the reaction to follow reaction path 1 in figure 1.

#### 4. Conclusions

From the results of the experiments described, it has been found that the presence of materials having hydroxyl groups, whether derived from impurities in the system or as part of the monomer system play an important role in the e-beam induced cationic polymerization of epoxy resins. The aliphatic hydroxyl group was found more reactive with the oxonium active centre than that of phenolic OH group. These findings have significant implications regarding the formation of networks in cationically cured multifunctional epoxides. In addition, the results indicate that potential exists to tailor the network structure of such systems based on intrinsic differences in hydroxyl group reactivity. Current work is directed towards the investigation of network formation by e-beam curing of diepoxy based systems (e.g. diglycidyl ether of bisphenol A) and the effect of presence of different OH containing species on the structural as well as mechanical properties of the e-beam cured materials.

#### References

- Bednarek M, Kubisa P and Penczek S 1989 *Macromol. Chem. Chem. Suppl.* **15** 49
- Bednarek M, Biedron T, Szymanski R, Kubisa P and Penczek S 1991 *Macromol. Chem.* **42/43** 475
- Benziers D and Capdepuy B 1990 *Proceedings of SAMPE international symposium* (USA: SAMPE) **35** p. 1220
- Bouillon N, Pascault J P and Tighzert L 1990 *Macromol. Chem.* **191** 1403, 1435
- Chabanne P, Tighzert L and Pascault J P 1994 *J. Appl. Polym. Sci.* **53** 769, 787
- Crivello C J and Lam J H W 1977 *Macromolecules* **10** 1307
- Fouassir J P, Burr D and Crivello J V 1994 *JMS-Pure Appl. Chem.* **A31** 677
- Goodman D L, Bix D L, Palmese G R and Chen A 1996 *Proceedings of 41st SAMPE international symposium* (USA: SAMPE) **41** p. 207
- Janke C J, Havens S J, Dorsay G F and Lopata V J 1996 *Proceedings of 41st international SAMPE symposium* (USA: SAMPE) **41** p. 196
- Janke C J, Norris R E, Yarborough K, Havens S J and Lopata V J 1997 *Proceedings of 42nd international SAMPE symposium* (USA: SAMPE) **42** p. 477
- Lopata V J, Chung M, Janke C J and Havens S J 1996 *Proceedings of 28th international SAMPE technical conference* (USA: SAMPE) **28** p. 901
- Matejka L, Chabanne P, Tighzert L and Pascault J P 1994 *J. Polym. Chem. Chem. Ed.* **32** 1447
- Matejka L, Chabanne P, Tighzert L and Pascault J P 1997 *J. Polym. Chem. Chem. Ed.* **35** 651, 665
- Saunders C B, Lopata V J, Kremers W, McDougall T E, Tateishi M and Sing A 1993 *Proceedings of 38th international SAMPE symposium* (USA: SAMPE) **38** p. 1681
- Saunders C B, Lopata V J, Kremers W, Chung M and Barnard J W 1995 *Proceedings of 40th SAMPE international symposium* (USA: SAMPE) **40** p. 112