

Application of 1,2-Dipolar Compound as a Modifier for Polyaddition of Bisphenol-A Diglycidyl Ether with Epichlorohydrin

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α -Picolinium-*p*-bromophenacylide (α -PBPY) was prepared by the reaction of *p*-bromophenacyl bromide with α -picoline followed by proton abstraction with a base and applied as novel modifier in the polyaddition of bisphenol-A diglycidyl ether with epichlorohydrin as a model system of epoxy novolac resins. The nitrogen ylide has decreased values of epoxide equivalent weight, hydroxyl content, viscosity and specific gravity. The cured epoxy resins (with polyamide, molecular weight 3000, make Hindustan Ciba-Geigy Ltd, at room temperature for 24 h, at $80 \pm 1^\circ\text{C}$ for 2 h) have been characterized by IR, $^1\text{H-NMR}$, DSC and TGA. On the basis of FTIR., it is concluded that a complex between —OH group of bisphenol-A and α -PBPY is formed and it decreases epoxydation.

Key words: 1,2-Dipolar compound, modifier, polyaddition, bisphenol-A diglycidyl ether, epichlorohydrin

INTRODUCTION

Polymer-ylide chemistry is a novel branch of polymer science having a recent history of about 20 years¹⁻⁵. Epoxy resins are one of the most important classes of thermosetting polymer⁶ and have many desirable properties, including excellent thermal resistance, chemical resistance and processability⁷. To date, there have been a few communications reporting the modification of epoxy resins^{8,9} with quinazolone rings¹⁰, acrylate groups¹¹, thiocarbonohydrazones¹² and vinyl groups¹³. However, there is no information regarding applications of ylides

(1,2-dipolar compounds having the general formula $\text{>}\overset{-}{\text{C}}-\overset{+}{\text{X}}$ where X may be N, P, As, S, Bi, Sb, Ti, etc.) in the modification of epoxy resins. This N_2 ylide has been successfully used in polymerization reactions¹⁴ but not used as epoxy modifier. In the present article α -picolinium-*p*-bromophenacylide (α -PBPY) has been used as a new modifier for [DGEBA] epoxy resins. The effect of nitrogen-ylide on properties such as chemical resistance, thermal resistance, glass transition temperature and electrical conductivity has been studied.

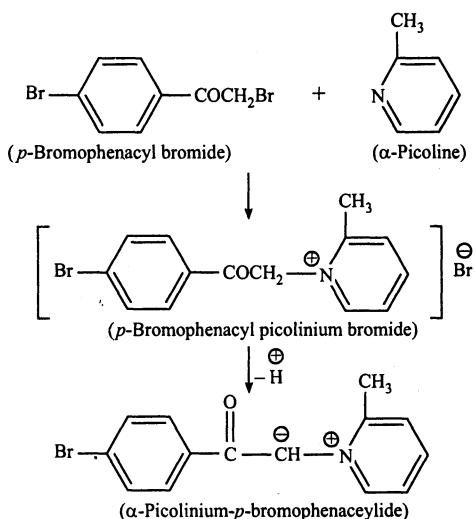
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EXPERIMENTAL

Epichlorohydrin (Ranbaxy), bisphenol-A (Robert Johnson), toluene, pyridine and methanol (all Ranbaxy), polyamide (Hindustan Ciba-Geigy Ltd.) and acetyl chloride (Ranbaxy) were purified by standard methods¹⁵.

Preparation of α -picolinium *p*-bromophenacylide [α -PBPY]

α -Picolinium-*p*-bromophenacylide (α -PBPY) has been synthesized¹⁶ by the reaction of *p*-bromophenacyl bromide with α -picoline followed by proton abstraction with a base. The scheme is given below:



Yield 85%, m.p. 240°C

Synthesis of epoxy resins

The syntheses of epoxy resins were carried out by reacting bisphenol-A and epichlorohydrin in 1 : 10 molar ratio, in a three-necked flask followed by gradual addition of sodium hydroxide (3 moles) over a period of 3.5 h. Heating was continued for an additional 15 min and the contents were dissolved in toluene and the solution was filtered to remove the salt. The excess epichlorohydrin and toluene were removed by distillation under reduced pressure. The resulting viscous product (epoxy resin-ER₁) was stored in an air-tight container. The modified epoxy resins (ER₂, ER₃ and ER₄) were synthesized by refluxing bisphenol-A and epichlorohydrin in 1 : 10 molar ratio in the presence of the requisite concentration of α -picolinium-*p*-bromophenacylide (α -PBPY) respectively.

Epoxide equivalent: The epoxide equivalents of various resins were obtained using the pyridinium chloride method¹⁷.

Hydroxyl equivalent: The hydroxyl content was determined by acetylation with acetyl chloride in pyridine. The excess chloride was decomposed with water and the resulting acetic acid was titrated with standard alkali solution using the following formula¹⁷.

$$\text{Hydroxyl content} = \frac{\text{Weight of sample}}{\text{Normality of KOH} \times (V_1 - V_2) \times 170}$$

where, V_1 = volume of KOH used for blank, V_2 = volume of KOH used for modified.

Hydrolyzable chlorine content: This content was determined by heating the resin solution with alcoholic KOH and titration against standard HCl¹⁷.

$$\% \text{ Cl} = \frac{355 \times 10^{-4} \text{ normality of KOH} \times \text{volume of KOH neutralized by epoxy resin}}{\text{Weight of sample}}$$

Viscosity: Specific viscosity (η_{sp}) was determined in toluene at various temperatures (30 to 90°C) using Ubbelohde viscometer.

IR Spectra: The IR spectrum was recorded on a Perkin-Elmer-1320 spectrophotometer. The sample was presented as KBr disk.

¹H-NMR spectra: The ¹H-NMR spectra of the epoxy resins were recorded on a Jeol JNK-PMX-60 spectrometer (at 298 K, operating frequency 60 MHz) in CDCl₃ using tetramethylsilane (TMS) as an internal standard.

Electrical conductivity: The electrical conductivities of all DGEBA resins (ER₂ to ER₄) were measured on an electrometer (model 715) under a vacuum of 10⁻³ torr. The conductivity was unchanged in the presence of the ylide (1.5 × 10⁻¹ Ω⁻¹/cm).

Thermogravimetric Analysis (TGA): Thermogravimetric analysis (TGA) was carried out on a Stanton Red Croft thermal analyzer (UK) at a heating rate of 15K/min under nitrogen atmosphere, flow rate 20 mL/min.

Differential Scanning Calorimetry (DSC): The differential scanning calorimetric analysis was carried out on Dupont-910200 at a heating rate of 10 K/min using 3–5 mg of sample.

Curing Studies: Polyamide (3000 mol wt.) was used as the curing agent. The resins and polyamide were mixed in a beaker, applied on glass plates and kept for 24 h at 30°C, then post-cured for 2 h at 80 ± 0.1°C.

RESULTS AND DISCUSSION

Physical properties of the resins have been listed in Table-1. When the epoxidation was carried out, the reaction became highly exothermic and the product was a highly viscous liquid. The refractive indices of the modified epoxy resins range from 1.395 to 1.385, which is less than that observed for the unmodified resin (ER₁). The epoxy resin (ER₁) was pale yellow and the modified epoxy resins (ER₂, ER₃ and ER₄) were dark brown in colour.

Data show (Table-2) the effect of α-PBPY on the values of the epoxy equivalence, hydroxyl content, hydrolyzable chloride content and viscosity of epoxy resins; all decrease as function of molar equivalent of nitrogen ylide (α-PBPY). The decrease in epoxide equivalent in the presence of α-PBPY may be attributed to the fact that the ylide may react with bisphenol-A/epichlorohydrin, or both, and thereby increase the concentration of reactant undergoing epoxidation.

TABLE-1
PHYSICAL PROPERTIES OF EPOXY RESINS

S.No.	Property	ER ₁	ER ₂	ER ₃	ER ₄
1.	Colour	Pale yellow	Dark brown	Dark brown	Dark brown
2.	State	Highly viscous liquid	Viscous liquid	Viscous liquid	Viscous liquid
3.	Refractive index (at 30°C)	1.571	1.395	1.388	1.385
4.	Corrosion	Passed	Passed	Passed	Passed
5.	Scratch hardness* (g) ³	1000	1100	1250	1300
6.	Flexibility†	Passed	Passed	Passed	Passed

*Mechanically operated scratch hardness tester.

†Mandrell (6.35 mm).

TABLE-2
VARIOUS PROPERTIES OF EPOXY RESINS

S.No.	Property	ER ₁	ER ₂	ER ₃	ER ₄
1.	Epoxide equivalent weight (Eq./100 g)	196	170	157	148
2.	Molecular weight	392	340	314	296
3.	Hydroxyl content (Eq./100 g)	0.14	0.10	0.086	0.074
4.	Chlorine content (%)	0.5	0.8	0.7	0.6
5.	Specific gravity (25°C)	1.1765	1.1177	1.1017	1.0902
6.	Viscosity (η_{sp}) (at 50°C)	1.24	1.15	1.08	1.02

$[\alpha\text{-PBPY}] \times 10^{-4}$: ER₁ = Zero, ER₂ = 8.56, ER₃ = 17.12, ER₄ = 25.68

TABLE 3
SOLUBILITY AND CHEMICAL RESISTANCE OF EPOXY FILM

Sr.No.	Chemicals	ER ₁	ER ₂	ER ₃	ER ₄
1.	Hydrochloric acid (N) → (1N)	--	+-	+-	+-
2.	Sulfuric acid (N) → (1N)	++	+-	+-	+-
3.	Nitric Acid (N) → (1N)	++	+-	+-	+-
4.	30%	--	--	--	--
5.	Carbon tetrachloride	--	--	--	--
6.	Benzene	--	--	--	--

++ Non soluble, -- Soluble

In order to confirm this, the ylide was stirred and refluxed with bisphenol-A for 3.5 h and then this bisphenol-A was used to prepare epoxy resin (ER_5) with epichlorohydrin. The epoxide equivalent wt. of this ER_5 was 168, which is similar to that of ER_2 (170). On the other hand, when the epichlorohydrin was used to prepare epoxy resin (ER_6) with bisphenol-A, the epoxide equivalent wt. was 190, which is near about that of ER_1 (196).

Therefore, it can be concluded that the reaction of α -PBPY with bisphenol-A results in a decrease of epoxidation and hence epoxide equivalent wt. decreases.

The value of viscosity (η_{sp}) (Table-2) decreases with an increase in (α -PBPY) the epoxy resin and Fig. 1 gives the variation of viscosity (η_{sp}) with temperature for various epoxy resins. No significant difference in viscosity was observed for the epoxy resins (ER_2 , ER_3 and ER_4) with an increase in molar equivalent of α -PBPY.

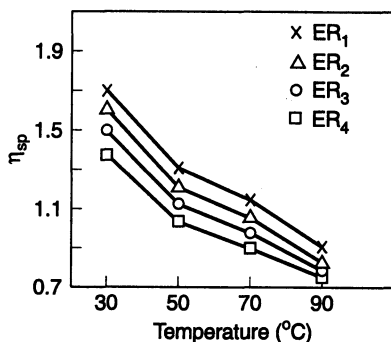


Fig. 1. Relationship between η_{sp} and temperature of various epoxy resins

IR Spectrum: cm^{-1} (KBr) (Fig. 2): 3400 ν (—OH stretch), 2900 ν (— C_6H_5 — aromatic), 1760 ν (>C=O stretch, group of acrylate), 920 cm^{-1} (epoxy ring breathing).

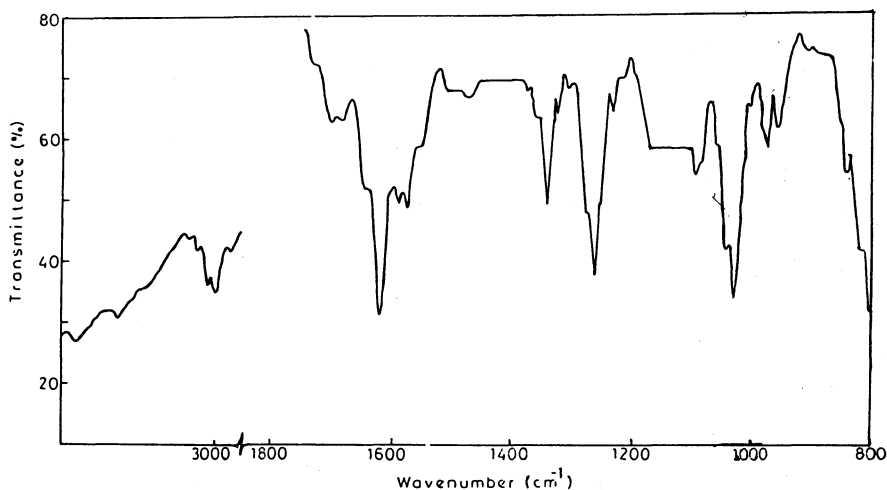


Fig. 2. IR Spectrum of epoxy resin ER_4

$^1\text{H-NMR}$ Spectrum: CdCl_2 , TMS, $\delta = \text{ppm}$ (Fig. 3): 1.0–2.0 (m, methoxy protons), 2.7–3.0 (m, epoxy protons), 7.0–7.8 (m, aromatic protons).

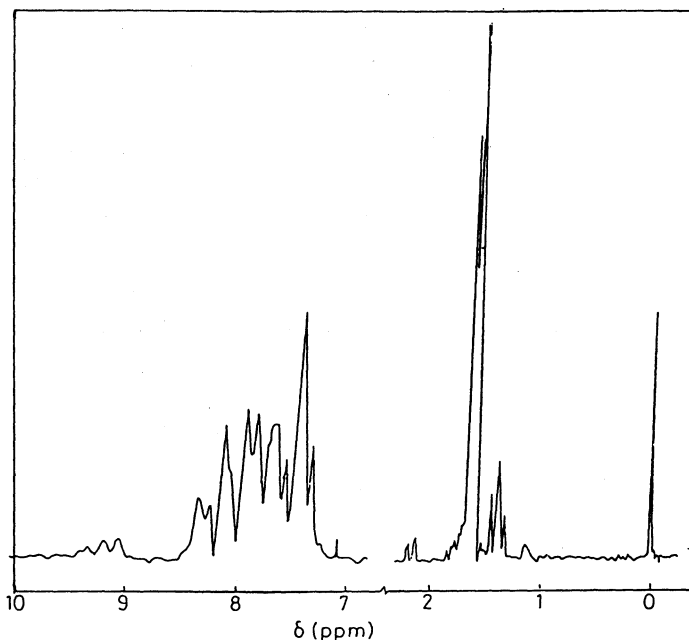


Fig. 3. $^1\text{H-NMR}$ spectrum of epoxy resin ER_4

Table-3 shows the solubility and chemical resistance of the film (0.1 mm thick) of blank (ER_1) and modified epoxy resins (ER_2 to ER_4), when submerged for 7 days in polar and non-polar solvents. It is clear that the modified epoxy resins retain flexibility and appearance. However, absorption was observed when they were submerged in acids, which may be due to the increase in flexibility of the polymer chain (Table-1). The scratch hardness increases as the molar equivalent of ylide [α -PBPY] in the epoxy resin increases. The films of modified resins were more resistant to scratch hardness as the molar equivalent of ylide in epoxy resin increased. The thermal stability of epoxy resins was determined by weight loss measurement at $200 \pm 1^\circ\text{C}$ for a period of 5 h. The weight loss at $200 \pm 1^\circ\text{C}$ in epoxy resin ER_1 is higher than the modified epoxy resin (ER_2 – ER_4), including that the ylide decreases the thermal stability of the polymer chain.

The TGA curves (Fig. 4) of modified resins are stable up to 90°C and start losing weight above this temperature. The modified epoxy resins, containing α -PBPY, undergo rapid decomposition between 350 to 400°C . The almost total volatilization of polymer occurred around 600°C . However, an initial weight loss about 8–15% was observed around 200°C . This shows that maximum polymer degradation occurs between 300 and 400°C .

The glass transition temperature (T_g) for epoxy resin ER_4 was 95°C , *i.e.*, lower than for epoxy resin ER_1 (130°C). The value of T_g increases as the concentration of ylide increases in the resin (Fig. 5).

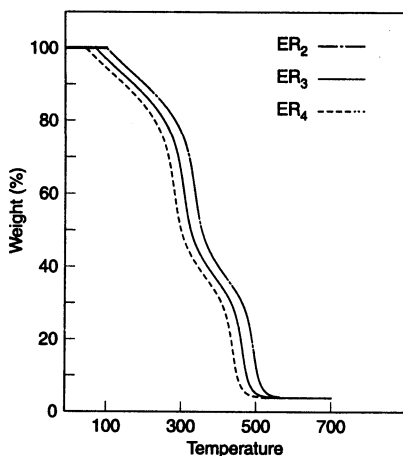


Fig. 4. Thermogravimetric curve of modified epoxy resins

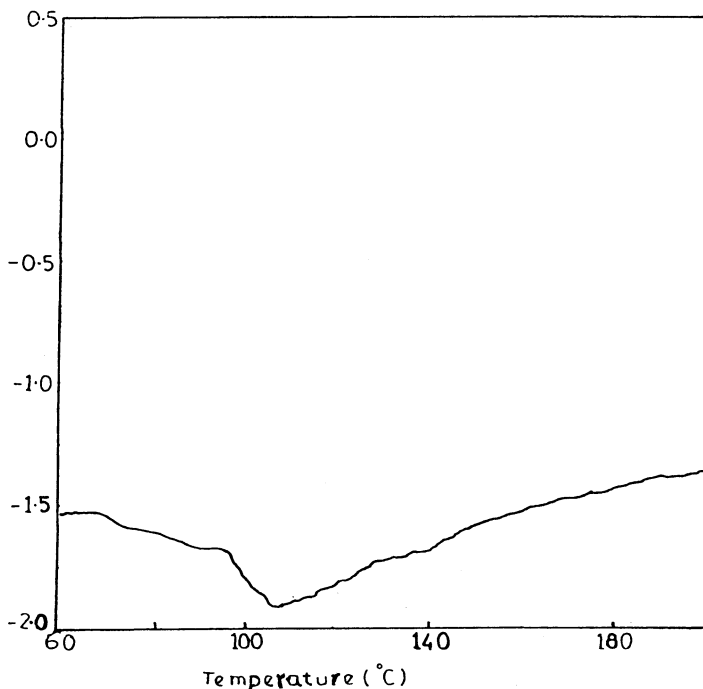


Fig. 5. Glass transition temperature (T_g) of epoxy resin (ER_4) by the DSC method.

Mechanism

The possible point of attachment of α -PBPY in the epoxy ring is either epichlorohydrin or bisphenol-A. The comparison of the IR spectrum of pure epichlorohydrin with that containing α -PBPY showed no shift in the position of the band¹⁸. On the contrary, a shift in a band position due to the —OH group of bisphenol-A was noted in bisphenol-A containing α -PBPY. This shows (Fig. 6)

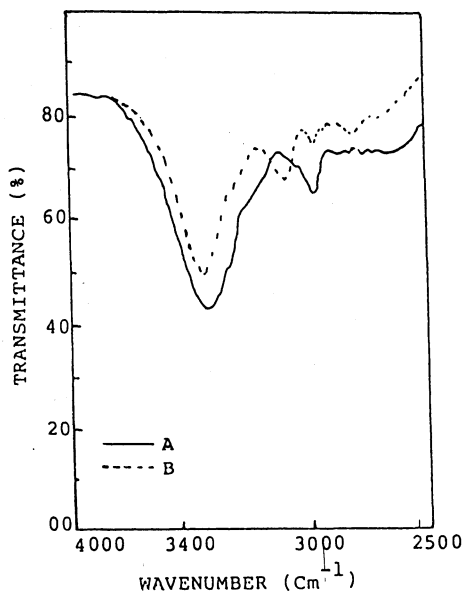


Fig. 6. IR spectrum of bisphenol-A (A) and bisphenol-A containing α -PBPY (B)

the probability of complex formation between —OH group of bisphenol-A and α -PBPY, which decreases epoxidation and hence molecular weight⁹. Therefore, the following structure may be proposed for the modified epoxy resin containing α -PBPY (Fig. 7).

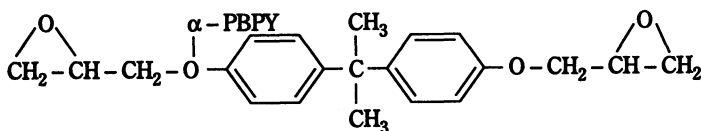


Fig. 7

Conclusion

Ylide (α -PBPY) reacts with bisphenol-A, thereby decreasing the concentration of bisphenol-A; as a result, epoxide equivalent wt., molecular wt., hydroxyl content and chloride content decrease and the cured epoxy resins showed acid resistance.

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REFERENCES

1. M. Kaur and A.K. Srivastava, *Macromol. Rapid Comm.*, **21**, 291 (2000).
2. G.S. Mishra and A.K. Srivastava, *Polym. Intl.*, **42**, 281 (1997).
3. M.A. Marx, A.L. Grillot, C.T. Louer, K.A. Beaver and P.A. Bartlett, *J. Am. Chem. Soc.*, **119**, 6153 (1997).
4. S. Pandey and A.K. Srivastava, *Desg. Mono. Polym.*, **3**, 123 (2000).
5. M. Kaur and A.K. Srivastava, *J. Photo. Chem. Photo. Bio.*, **1191A**, 67 (1998).
6. C. Carfagna, L. Nicolais, E. Amendola, C. Carfagna and A.C. Fillippov, *J. Appl. Polym. Sci.*, **44**, 1465 (1992).
7. W.G. Potter, *Epoxy Resin*, Springer, New York (1970).
8. M. Kobayashi, F. Sanda and T. Endo, *Macromol.*, **32**, 4751 (1999).
9. M. Anand and A.K. Srivastava, *High Perf. Polym. J.*, **4**, 97 (1992).
10. A. Fukami and T. Moriwaki, *J. Macromol. Sci. Chem.*, **26A**, 877 (1989).
11. T. Nishikubo, M. Impura, T. Muzuko and T. Takaoka, *J. Appl. Polym. Sci.*, **13**, 3445 (1974).
12. P.M. Thanagamathesvarna, S.R. Jain, *J. Polym. Sci. & Polym. Chem.*, **29**, 261 (1974).
13. M. Anand and, A.K. Srivastava, *J. Appl. Polym. Sci.*, **51**, 203 (1994).
14. R. Vasishta, A.K. Srivastava, *J. Macromol. Sci. Reve. Macromol. Chem. Phy.*, **29C**, 39 (1989).
15. B.S. Furniss, A.J. Hannaford, V. Ragers, P.W.G. Smith and A.R. Tatchell, *Vogel's Textbook of Practical Org. Chem.*, ELBS Publication, Great Britain (1984).
16. G.S. Mishra, A.K. Srivastava, International Conference "Polymer-94", IPCL, Vadodara, India, *Poly. Sci. Rec. Adv.*, **2**, 45 (1994).
17. H. Lee and K. Neville, *Handbook of Epoxy Resin*, McGraw-Hill, New York (1967).
18. M. Anand and A.K. Srivastava, *Macromolecular Reports*, **30A** (Suppl. 5), 435 (1993).

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