Synthesis and Characterization of Epoxy Resins Containing Bismuth

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ABSTRACT: The synthesis of epoxy resins in the presence of Bi as bismuth acrylate (BiA_3) showed that the properties such as epoxide equivalent weight (eq/100 g), molecular weight, and viscosity (η_{sp}) increased; whereas hydrolyzable chlorine content, hydroxyl content, and refractive index decreased in the presence of BiA_3. The metal forms a complex with ether linkage of epoxy resins, as evidenced from infrared spectroscopy. The presence of Bi in epoxy resins has been confirmed by scanning electron microscopy (SEM) and qualitative analysis. The glass transition temperature (T_g) of epoxy resins containing 1.18×10^{-5} and 2.8×10^{-5} molar equivalent of BiA_3 is 131.58 and 190°C, respectively, and is greater than that of blank (130°C). The heat of reactions for epoxy resins containing 1.18×10^{-5} molar equivalent of BiA_3, calculated by differential scanning calorimetry, is 4.75 J g. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1359–1365, 1997

INTRODUCTION

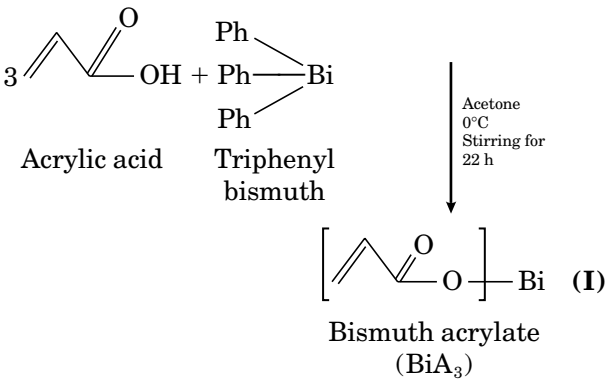
Epoxy resins, a class of speciality polymers, due to their versatile properties for the various endless applications, are receiving a lot of attention among polymer chemists. They have been subjected, therefore, to a number of modifications, such as the use of quinazolone ring,[1] thiocarbonohydrazole,[2] and acrylate.[3] Recently, the effect of the oxidation state and incomplete d-orbital of metals in the form of metal acrylate, such as Zn,[4] Cu,[5] Cr,[6] and Ni,[7] on the properties of epoxy resin (DGEBA) has been reported from our laboratory. Therefore, it is worthwhile to study the effect of half-filled p-orbitals on the properties of epoxy resins by using Bi in the form of bismuth acrylate (BiA_3), which has been prepared for the first time by us.

EXPERIMENTAL

Synthesis and Characterization of Bismuth Acrylate

Synthesis

BiA_3 was prepared by the the reaction of triphenyl bismuth (Merck No. 40612205) with acrylic acid (30 wt % stoichemetric excess) and a solution in acetone; and the reaction was carried out with constant stirring in an ice bath for 22 h. The evaporation of excess solvent yielded the BiA_3. The reaction scheme is as follows.



Characterization

BiA_3 was soluble in acetone and benzene and insoluble in polar solvent (DMSO, DMF, dioxane). It decolorized Bayer reagent. Bi in acrylate was

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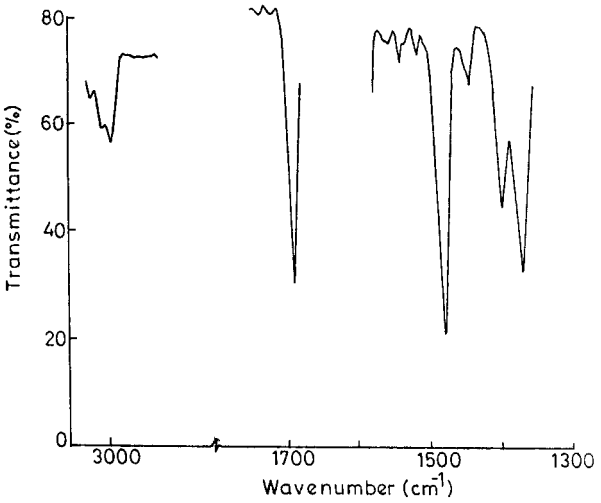


Figure 1 IR spectrum of bismuth acrylate.

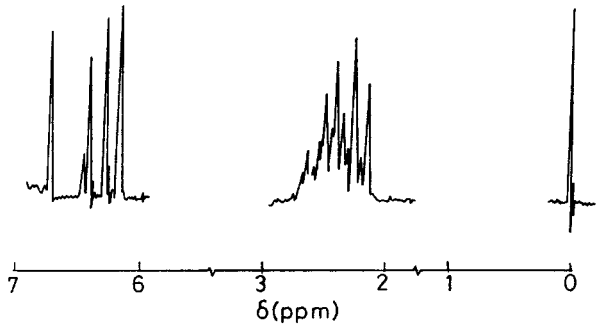


Figure 2 ^{1}H-NMR spectrum of bismuth acrylate.

tested qualitatively.[8] Experimental conditions are as follows. Yield is 70%. M.P. is 76°C.

The infrared spectrum (IR cm^{-1}; Fig. 1) was recorded on a Perkin Elmer spectrophotometer: 2990–3000 cm^{-1} (C—H, alkene stretching); 900 cm^{-1} (alkene bending); 1680 cm^{-1} (carboxylic group).

The ^{1}H-NMR (200 MHz) spectrum (^{1}H-NMR TMS, δ; Fig. 2) was recorded on a Varian EM 390 spectrophotometer: 2–3 δ (m, CH_2); 6–7 δ (m, conjugated CH_2=CH).

Synthesis of Epoxy Resins

Epoxy resins were synthesized according to the method of Lee and Neville[9] with the following initial amount of reactants: epichlorohydrin (0.18 mol), bisphenol A (0.018 mol), sodium hydroxide (0.15 mol), bismuth acrylate (1.18×10^{-5}, 2.8×10^{-5}, 6.0×10^{-5}, and 1.2×10^{-4} molar equivalent).

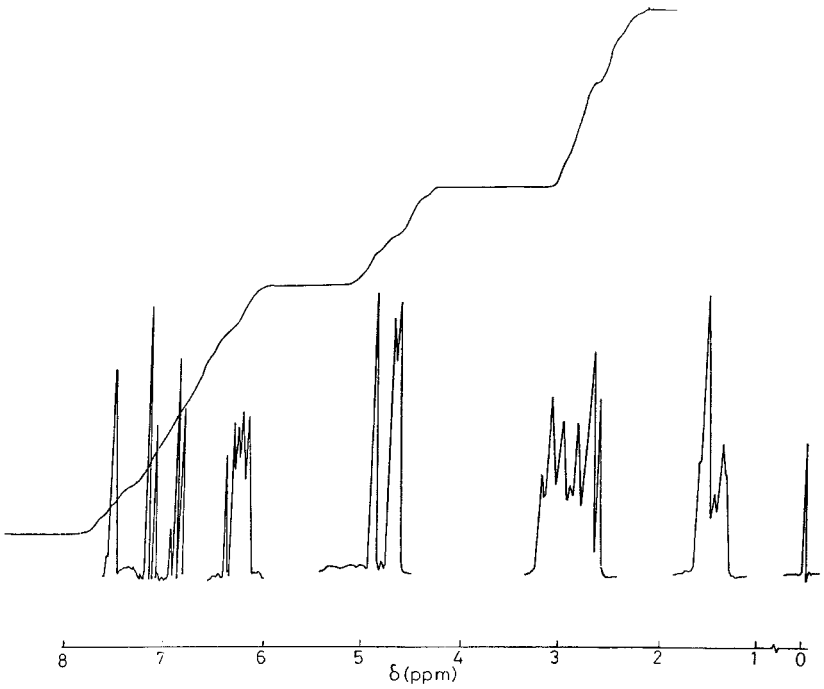
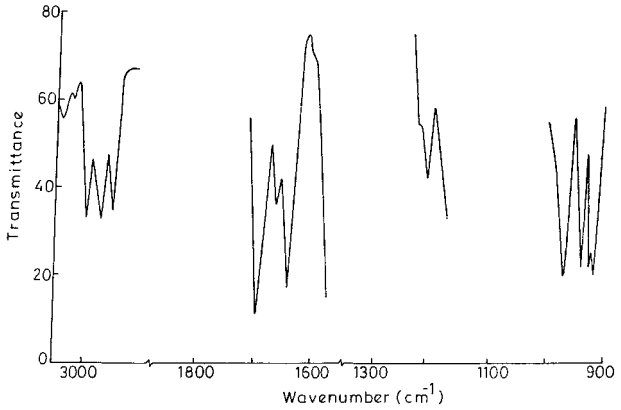
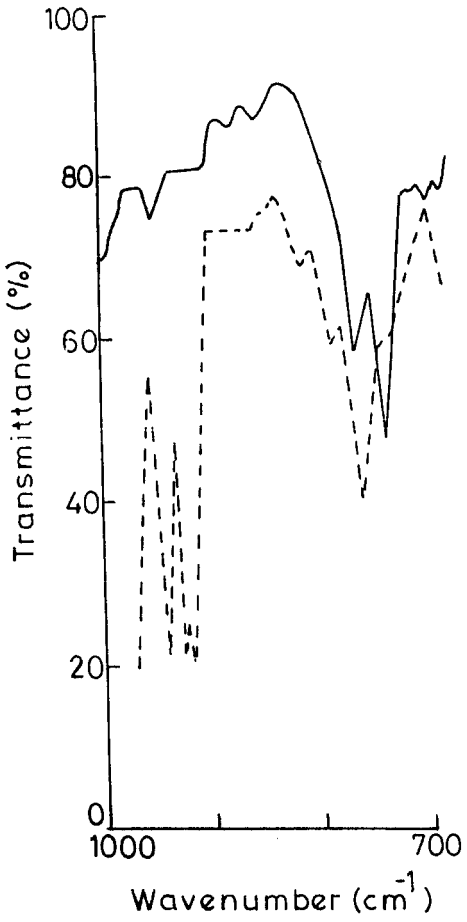


Figure 3 ^{1}H NMR spectrum of epoxy resins containing 6×10^{-5} molar equivalent of bismuth acrylate (ER_3).



(a)



(b)

Figure 4 (a) IR spectrum of epoxy resins containing 6×10^{-5} molar equivalent of bismuth acrylate (R_3). (b) IR spectrum of cured and uncured epoxy resins containing 6.0×10^{-5} molar equivalent of BiA_3 (ER_3).

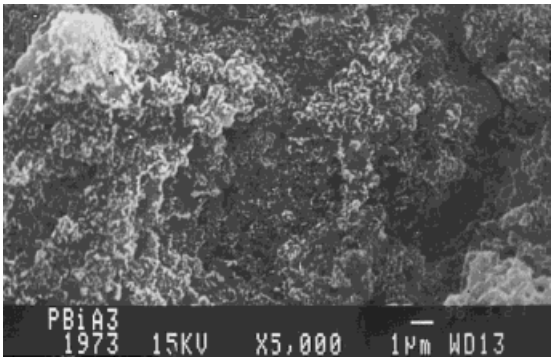


Figure 5 SEM secondary electron (SE) image of ER_1 at a magnification of 5000×.

Characterization

Viscosity

A Ubbelohde viscometer and Abb Refractometer were used to determine the viscosity (in dioxane 40% w/v) and refractive index, respectively.

Epoxide Equivalent Weight

The epoxide equivalent weight (EEW) of various resins was determined by pyridinium chloride method[10] using following formula:

$$\underset{(\text{eq/100 g})}{\text{EEW}} = \frac{16 \times \text{sample weight}}{\text{weight of oxirans in sample}}$$

Hydrolyzable Chlorine Content

Hydrolyzable chlorine content of resins was determined using following formula[11]:

$$\text{Hydrolyzable chlorine content (\%)} = \frac{355 \times 10^{-4} \times \text{normality of KOH} \times \text{volume of KOH neutralized by epoxy resins}}{\text{weight of sample}}$$

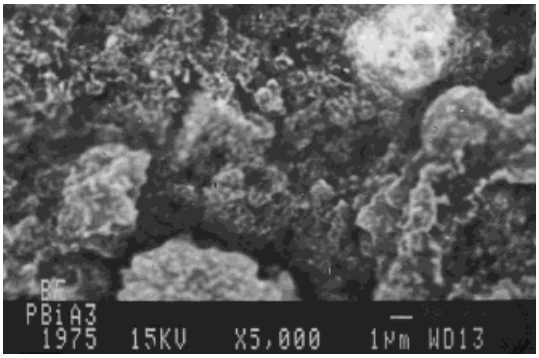


Figure 6 SEM back-scattered electron (BE) image of ER_1 at a magnification of 5000×.

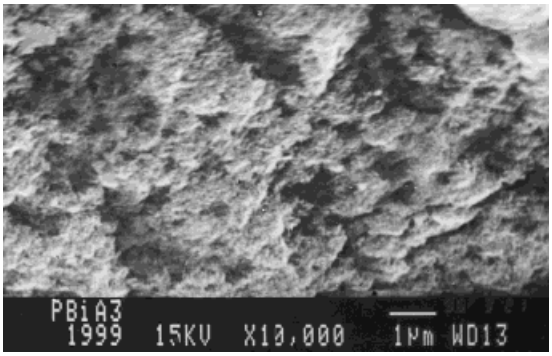


Figure 7 SEM secondary electron (SE) image of ER_4 at a magnification of 5000×.

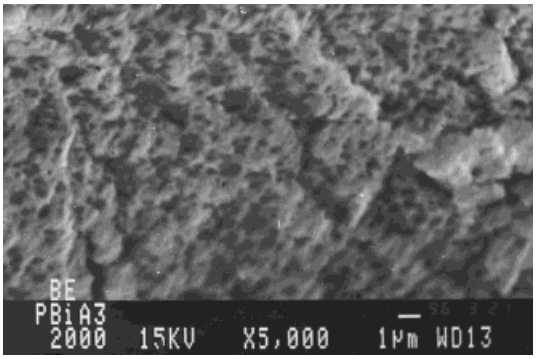


Figure 8 SEM back-scattered electron (BE) image at a magnification of ER_4 of 5000×.

Hydroxyl Content

Hydroxyl content of various resins was calculated by acetyl chloride method using following formula[11]:

$$\text{Hydroxyl content (eq/100 g)} = \frac{\text{weight of sample}}{\text{normality of NaOH} \times (v_1 - v_2) \times 170}$$

where v_1 is the volume of methanolic NaOH for blank, and v_2 is the volume of methanolic NaOH for sample.

DSC Technique

Differential scanning calorimetry (DSC) was employed to investigate the thermal behavior of epoxy resins containing BiA_3. DSC was recorded on a general V2-2A Du-Pont 9900 differential scanning calorimeter under a nitrogen atmosphere at a heating rate of 10°C min. The sample weight was 3.5–5.0 mg.

Curing Studies

Polyamide was used as a curative in an amount as required to epoxide equivalent weight. The resins and the curing agent were mixed in a beaker and applied on glass plate and kept at 180 ± 1°C for 2.5 h.

Scanning Electron Microscopy

Scanning electron micrographs were obtained from Jeol JSM 840A scanning electron microscope. The film was mounted vertically on an scanning electron microscopy (SEM) stub using silver adhesive paste.

Detection of Metals

The ash of epoxy resins was prepared by heating resins at 400°C in a muffle furnace. The ash was dissolved in dilute HNO_3 and then added thio-

Table I Properties of Epoxy Resins

Properties	ER	ER_1	ER_2	ER_3	ER_4
Molar equivalent of BiA_3	00	1.18×10^{-5}	2.8×10^{-5}	6×10^{-5}	1.2×10^{-4}
Color	amber	whitish	whitish	whitish	pale yellowish
Epoxide equivalent weight (eq/100 g)	194	443	382	268	400
Hydrolyzable chlorine content (%)	0.5	0.15	0.18	0.20	0.17
Hydroxyl content (eq/100 g)	0.12	0.007	0.052	0.014	0.009
Specific gravity (30°C)	1.173	1.297	1.190	1.296	1.292
Specific viscosity	1.58	1.84	1.89	1.96	1.94
Refractive index (30°C)	1.5695	1.553	1.549	1.547	1.546
Molecular weight	380	880	694	525	800

Table II Effect of BiA_3 on the Solubility and Chemical Resistance of Uncured Epoxy Resins

Chemicals	ER	ER_1	ER_2	ER_3	ER_4
Toluene	+	+	+	+	+
DMF	+	+	+	+	+
Dioxane	+	+	+	+	+
DMSO	+	+	+	+	+
Nitric acid	+	+	+	+	+
Sulphuric acid	+	+	+	+	+
Acetic acid	+	+	+	+	+
Water	−	−	−	−	−
Methanol	−	−	−	−	−
Cyclohexane	−	−	−	−	−
Acetone	−	−	−	−	−

+ Soluble, − insoluble.

urea. A yellow coloration confirmed the presence of bismuth in epoxy resins.

RESULTS AND DISCUSSION

Structure evidences for epoxy resins containing BiA_3 come from ^{1}H-NMR (Fig. 3) and IR spectroscopy.

Figure 3 shows ^{1}H-NMR spectrum of epoxy resins containing 6×10^{-5} molar equivalent of BiA_3 (ER_3): 2.5–3.0 δ (m, epoxy protons); 6.8–7.6 δ (m, phenyl protons); 5.0 δ (S, OH proton); 1.0–2.0 δ (m, aliphatic protons); and 3.2 δ (m, methylene, methine, $CH{=}CH_2$ protons).

The ratio of peak areas due to methylene and methine protons ER^7 & ER_3 is 1.8 : 3.1, which confirms the presence of BiA_3 in epoxy resins.

Figure 4(a) indicates characteristic bands of ER_3 at 910–950 cm^{-1} for epoxy group, at 2900–3000 cm^{-1} for the methyl and methylene group, and at 1650 cm^{-1} for phenyl group. The presence of an additional band due to the carboxylate group at 1700 cm^{-1} confirms the presence of BiA_3 in epoxy resins. The shifting (1250 to 1210 cm^{-1}) and low bond depth area (1.9^7 to 0.5 cm) of the ether group shows the formation of a complex between the oxygen of ether linkage and Bi, as reported earlier for other metals.[4–7] Therefore, the complex has been assigned following structure.

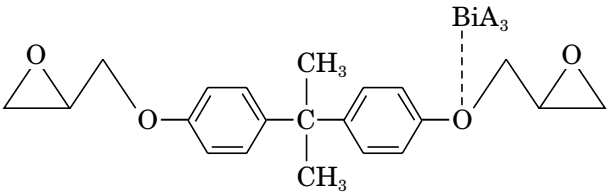


Table III Effect of BiA_3 on the Solubility and Chemical Resistance of Cured Epoxy Resin Film (0.8 mm thick)

Chemicals	ER	ER_1	ER_2	ER_3	ER_4
Toluene	−	−	−	−	−
Dioxane	−	−	−	−	−
DMSO	−	−	−	−	−
DMF	−	−	−	−	−
Nitric acid	+	+	+	+	+
Sulphuric acid	±	±	±	±	±
Acetic acid	−	−	−	−	−

+ Soluble, ± sparingly soluble, − insoluble.

Curing Studies by IR Spectroscopy

Figure 4(b) presents the IR spectra of uncured and cured epoxy resins, respectively; both in the frequency range of 700–1000 cm^{-1} were the main modifications of the epoxy resin spectrum that took place during curing.[12]

After curing, the most obvious changes in the spectra are those due to the disappearance of the characteristic band for the epoxy ring at 910–950, 870, and 760 cm^{-1} and the decrease in the band depth ratio from 0.6 to 0.3 cm at 760 cm^{-1}. The IR data permit the conclusion that epoxy reins are cured with polyamide.

Morphology

The presence of bismuth in epoxy resins was confirmed by SEM of the secondary electron beam and back-scattered electron beam. Figures 5–8 reveal that following two distinct phase domains can be easily observed, with the epoxy as a continuous phase, in which the second component Bi is intangled in the matrix as a white portion. Back-scattered electron micrographs of epoxy resins show a mottled texture and reveal the internal

Table IV Effect of BiA_3 on the Percentage of Weight Gain in Epoxy Resins Films (100 mg wt)

Chemicals	ER	ER_1	ER_2	ER_3	ER_4
Hydrochloric acid	7.32	15.3	18.5	—	21.4
Toluene	10.4	20.3	25.0	27.0	33.4
Dioxane	—	10.4	14.3	15.2	14.9

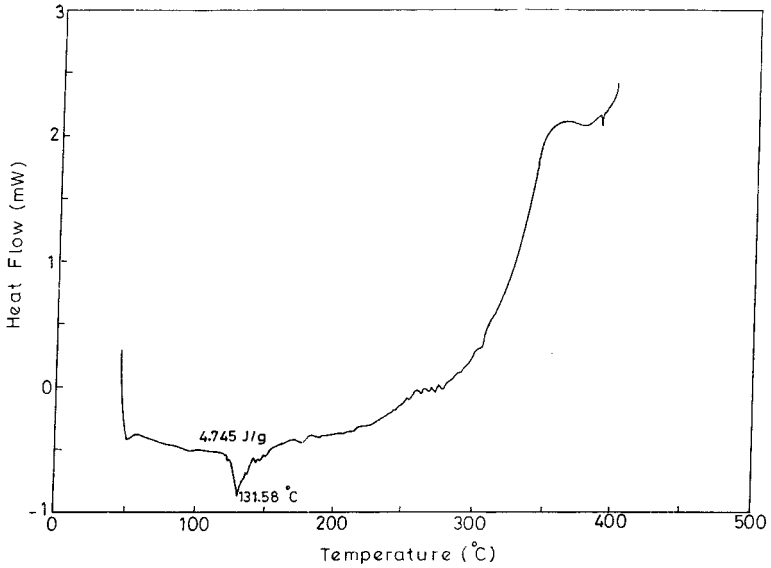


Figure 9 DSC curve of epoxy resins containing 1.18×10^{-5} molar equivalent of BiA_3 (ER_1).

appearance of network. It is clear for Figures 6 and 8 that the dispersion of Bi in the constant volume of epoxy resins increases on increasing the molar concentration of BiA_3 in epoxy resins.

Table I shows that the epoxide equivalent weight (EEW) of ER_4 (400 eq/100 g) is greater than that of the blank epoxy resin (194 eq/100 g) and even the epoxy resin containing ZnA_2^4 (234 eq/100 g), CuA_2^5 (245 eq/100 g), CrA_3^6 (586 eq/100 gm) and NiA_2^7 (343.9 eq/100 g). Table I also reveals that the molecular weight of epoxy resins is approximately double that of EEW, thereby showing the presence of two epoxide groups per molecule. The complex formation between bismuth and the ether group increased epoxide equivalently, as well as the molecular weight. However, the hydroxyl content decreased in the presence of BiA_3. The results, obtained by using the acetyl chloride method, were also supported by the low peak area ratio (6.1 : 3) due to hydroxy protons in the ^{1}H-NMR of ER^7 and ER_3. Similarly, the low value of the hydrolyzable chlorine content indicates less possibility of side re-

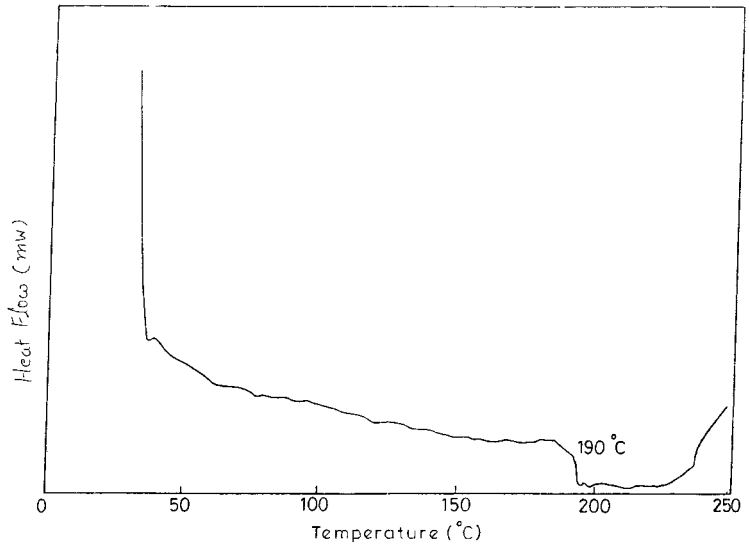


Figure 10 DSC curve of epoxy resins containing 2.8×10^{-5} molar equivalent of BiA_3 (ER_2).

actions, such as partial dehydrohalogenation and abnormal addition of epichlorohydrin.

The viscosity of epoxy resins (Table I) increases with BiA_3 concentration in the epoxy resins. The refractive index of modified epoxy resins at 30°C changes from 1.553 to 1.546, which is less than that of blank due to the density difference. However, the specific gravity of the modified epoxy resin is greater than that of the blank epoxy resin.

Solubility and Chemical Resistance

Chemical resistance of cured epoxy resins is more than that of uncured epoxy resins (Table II and III). However, the absorption (Table IV) was observed when the samples were submerged in toluene and hydrochloric acid ($1M$), which may be due to increased flexibility of the polymer chains.[5–7]

DSC Studies

The glass transition temperature (T_g) of epoxy resins containing 1.18×10^{-5} molar equivalent of BiA_3 (ER_1) and 2.8×10^{-5} molar equivalent of BiA_3 (ER_2), calculated by DSC analysis (Figs. 9 and 10, respectively), is 132 and 190°C, which is greater than that of the blank epoxy resins[5] (130°C). The heat of reaction calculated by DSC for epoxy resin containing 1.18×10^{-5} molar equivalent of BiA_3 is 4.75 J g.

CONCLUSION

Epoxide equivalent weight, viscosity (η_{sp}), and molecular weight are increased in presence of the half-filled p orbital element. However, the hydroxyl content, hydrolyzable chlorine content, and specific gravity decreased in the incorporation of half-filled p-block element with epoxy resins.

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REFERENCES

1. A. Fukami and T. Moriwaki, *J. Macromol. Sci. Chem.,* **26,** 877 (1989).
2. P. M. Thangamathesvaran and S. R. Jain, *J. Polym. Sci., Poly. Chem.,* **29,** 261 (1991).
3. T. Nishikubo, M. Imaura, T. Muzuko, and T. Takaoka, *J. Appl. Polym. Sci.,* **13,** 3445 (1974).
4. M. Anand and A. K. Srivastava, *J. Appl. Polym. Sci.,* **51,** 203 (1992).
5. M. Anand and A. K. Srivastava, *High Perf. Polym.,* **4,** 97 (1992).
6. M. Anand and A. K. Srivastava, *Die Ang. Makromol. Chem.,* **216,** 1 (1994).
7. P. Mohan and A. K. Srivastava, *Macrom. Rep.,* **32,** 1213 (1995).
8. A. I. Vogel, *A Text Book of Practical Inorganic Chemistry,* Longman, London, 1969.
9. H. Lee and K. Neville, *Hand Book of Epoxy Resin,* McGraw Hill, New York, 1969, Chap. 24.
10. H. Lee and K. Neville, *Hand Book of Epoxy Resin,* McGraw Hill, New York, 1969, Chap. 4–7.
11. M. Anand and A. K. Srivastava, *Polym.,* **34,** 2860 (1993).
12. D. Feldman, D. Banu, and M. Khoury, *J. Appl. Polym. Sci.,* **37,** 887 (1989).