

Synthesis and characterization of epoxy resins containing transition metals

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Novel epoxy resins containing zinc, chromium and copper have been synthesized by reacting acrylates of these metals with bisphenol-A and excess epichlorohydrin. Parameters, such as epoxide equivalent weight, hydroxyl content and viscosity, increase as a function of concentration of metals. The resins, characterized by i.r., SEM, n.m.r., ^{13}C n.m.r. and cured with polyamide at room temperature for 24 h and 80°C for 2 h, have improved thermal stability, chemical resistance and electrical conductivity as compared to unmodified epoxy resin. The results have been explained by the assumption that the metal(s) form a complex with bisphenol-A.

(Keywords: epoxy resin; zinc; chromium; copper; ^{13}C n.m.r.; t.g.a.; properties)

INTRODUCTION

The synthesis and polymerization of metal acrylates is a recent subject of study, probably because of difficulties associated with their synthesis. A search of the literature¹⁻⁴ reveals that most of the work has been devoted to chain growth polymerization; reports regarding applications in step growth polymerization are still scarce. It is therefore of interest to study the effect of transition metals, such as copper, chromium and zinc, on the properties of epoxy resins. The present paper details the results of such efforts.

EXPERIMENTAL

Materials

Epichlorohydrin (Ranbaxy), bisphenol-A (Robert-Johnson), toluene (Ranbaxy), pyridine (Ranbaxy) and methanol (Ranbaxy) were purified by standard methods.

Preparation of metal acrylates

Zinc acrylate⁵, copper acrylate⁵ and chromium acrylate⁶ were prepared by the procedures given in the literature.

Synthesis of epoxy resins

The epoxidation was carried out by refluxing bisphenol-A and epichlorohydrin, in 1:10 mole ratio, in a three-necked flask followed by gradual addition of sodium hydroxide over a period of 3.5 h. The content was 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 A) was stored in an air-tight container⁷. Epoxy resin B was prepared by reacting bisphenol-A and epichlorohydrin, in 1:10 mole

ratio, in the presence of 3.26×10^{-3} molar equivalent of chromium acrylate, 4.21×10^{-3} molar equivalent of copper acrylate and 4.17×10^{-3} molar equivalent of zinc acrylate, in a similar manner to epoxy resin A.

Characterization

Epoxide equivalent weight (EEW). The EEWs of resins were determined by the pyridinium chloride method⁷.

Hydroxyl content. This was determined by acetylation with acetyl chloride in pyridine. The excess of chloride was decomposed with water and the resulting acetic acid, formed both in hydrolysis and in the acetylation process, was titrated with standard alkali using the following formula:

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

where V_1 = volume of KOH used for blank and V_2 = volume of KOH used for sample.

Hydrolysable chlorine content. This was determined by treating the resin solution with alcoholic KOH and titrating it against standard HCl⁷:

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

Viscosity. Viscosity data of the synthesized resins were obtained using an Ubbelohde viscometer at various temperatures.

Infra-red spectrum. The infra-red spectrum was recorded on a Perkin Elmer spectrophotometer (model 377).

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N.m.r. spectrum. ^1H n.m.r. spectra were recorded on a Varian EM 390 spectrophotometer.

Electrical conductivity. For the d.c. conductivity measurement the samples were mounted on a metallic sample holder where a vacuum of about 0.133 Pa was maintained. A d.c. power supply and the resulting current were measured by a Digital Keithley electrometer (model 614).

Thermal analysis. Thermogravimetric analysis (t.g.a.) was carried out on a Stanton Redcroft at a heating rate of $15^\circ\text{C min}^{-1}$ under nitrogen atmosphere.

Scanning electron microscopy (SEM). Scanning electron micrographs were obtained from a Jeol JSM 840A

scanning electron microscope. The film was mounted vertically on an SEM stub using silver adhesive paste.

Curing studies

Polyamide was used as a curing agent. The resin and polyamide were mixed in a beaker, applied on glass and tin plates and kept for 24 h at 30°C , then post-cured for 2 h at 80°C .

Detection of metals

Metals were detected in the following ways.

The ash of epoxy resin B was prepared by heating resin at 400°C in a muffle furnace and dividing it into two parts. The first part was subjected to metal detection

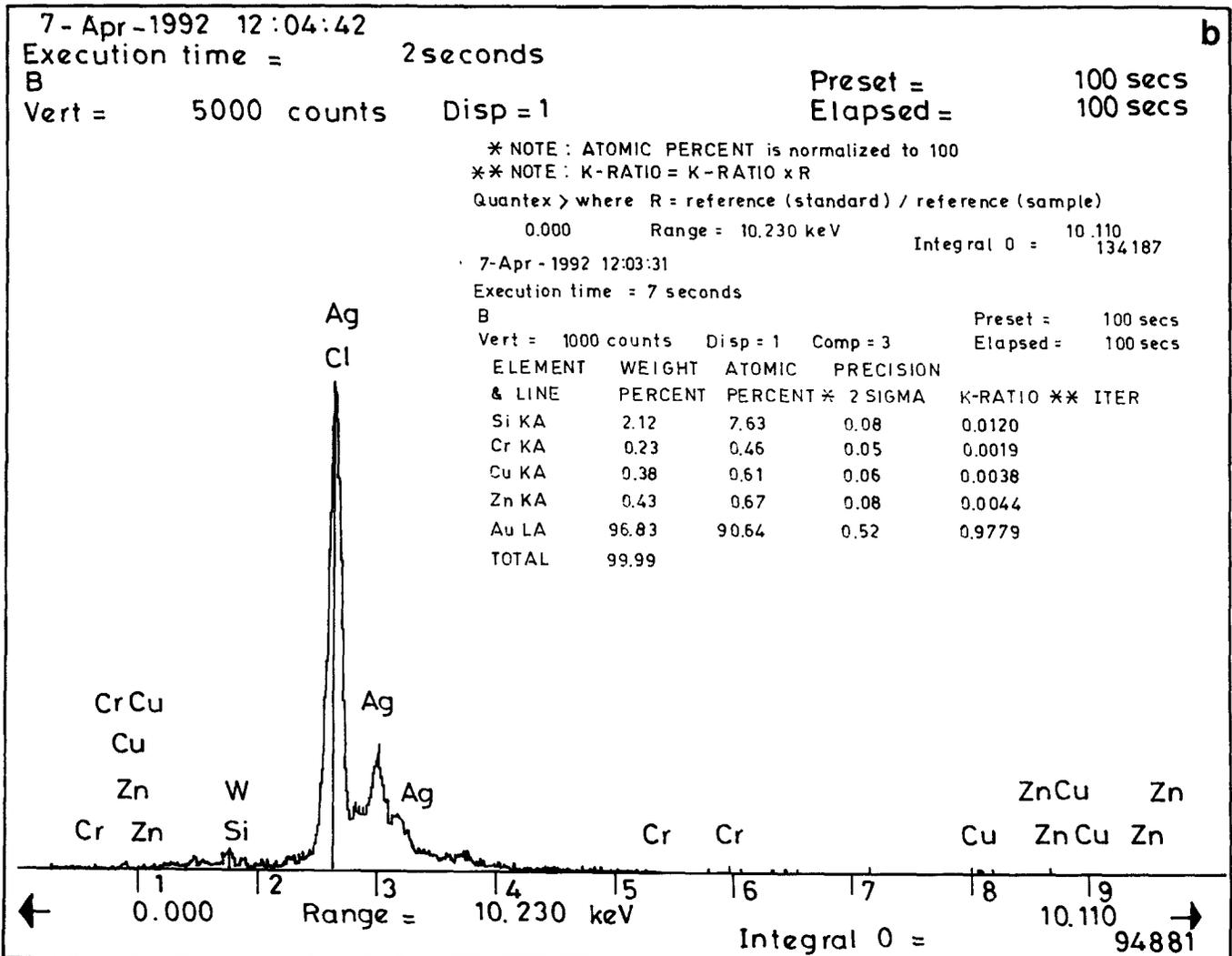
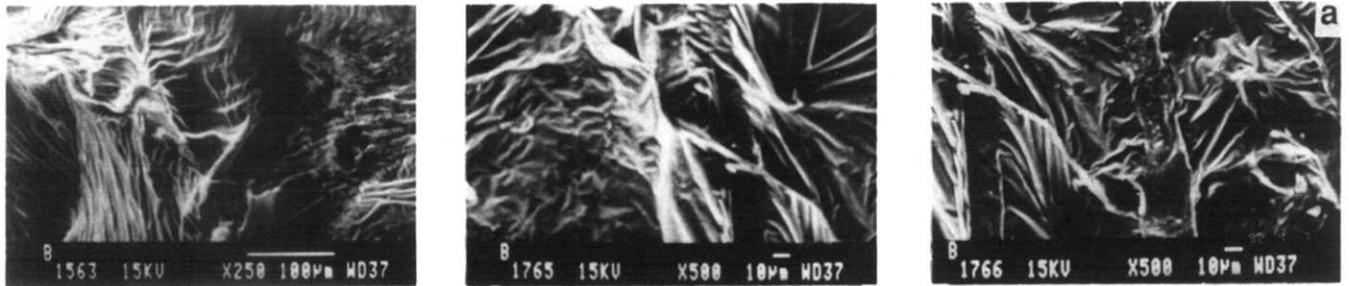


Figure 1 (a) Scanning electron micrographs and (b) spectra for modified epoxy resin containing transition metals

using Spectronic 20 by the method given in ref. 8. The second part was dissolved in concentrated sulfuric acid and divided into three parts:

part I + freshly prepared solution of diphenyl carbazide
→ violet colour

which confirms the presence of chromium.

part II + aq. sodium hydroxide → white precipitate
which confirms the presence of zinc.

part III + aq. ammonium hydroxide → blue colour
which confirms the presence of copper.

Table 1 Characterization of epoxy resins

Property	Epoxy resin A	Epoxy resin B
State	Viscous	Highly viscous
Colour	Light yellow	Light yellow
Refractive index (at 30°C)	1.5695	1.5350
Epoxide equivalent weight (eq./100 g)	194	280
Molecular weight	380	551
Hydroxyl content (eq./100 g)	0.12	0.15
Chlorine content (%)	0.5	0.6
Viscosity (η_{sp}) (at 30°C)	1.58	2.18
Specific gravity (at 30°C)	1.1730	1.1887

RESULTS AND DISCUSSION

Some physical properties of the epoxy resins are listed in *Table 1*. The reaction becomes highly exothermic. The resin was obtained as a highly viscous liquid. The value of the refractive index of modified epoxy resin B is 1.5350, which is less than the value obtained for epoxy resin A (1.5695).

Scanning electron micrographs (*Figures 1a and b*) show the presence and atomic percentage of metals (Zn, Cu and Cr) in the epoxy ring.

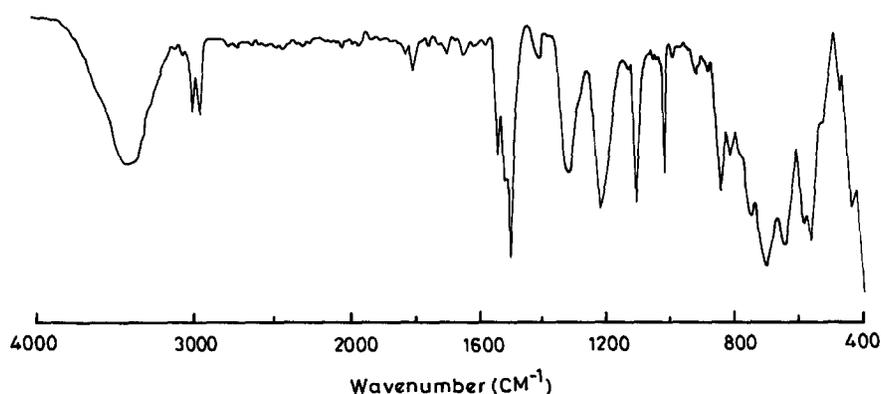


Figure 2 I.r. spectrum of epoxy resin B

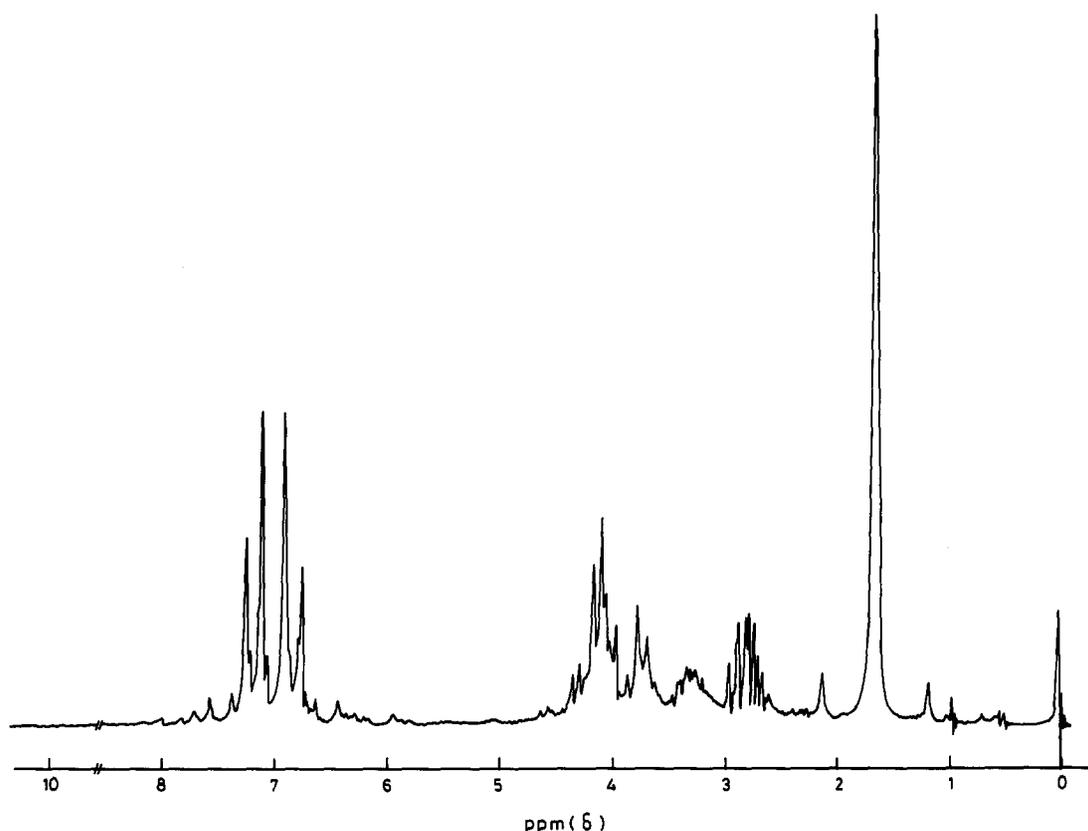


Figure 3 N.m.r. spectrum of epoxy resin B

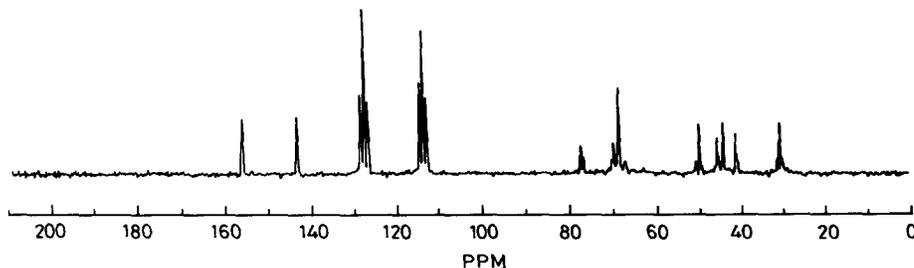
Figure 4 ^{13}C n.m.r. spectrum of epoxy resin B

Table 1 also shows the effect of transition metals on the value of EEW, hydroxyl content, hydrolysable chlorine content, specific gravity and viscosity. The EEW of modified epoxy resin B, containing transition metals, is much higher than that of epoxy resin A, showing that epoxy resin B has a higher molecular weight than epoxy resin A. The EEW values of various resins indicate that the EEW approximates to half of the average molecular weight, thereby indicating the presence of two epoxide groups per molecule. The hydroxyl content of modified epoxy resin B was higher than that of epoxy resin A, which may be due to the increase of EEW as reported.

The percentage of hydrolysable chlorine present, which may be due to many side reactions such as dehydrohalogenation, varied from 0.5 to 0.6. The change is not significant and this shows that side reactions are not greatly affected by the transition metals. Viscosity and specific gravity of modified epoxy resin B is higher than epoxy resin A, which may be due to the high molecular weight as well as the presence of transition metals.

The spectral analysis of epoxy resin B was as follows.

I.r. (DMF): 920 cm^{-1} (epoxy ring), 1760 cm^{-1} ($-\text{C}-$ group of acrylate), 3400 cm^{-1} ($-\text{OH}$ group), 2900 cm^{-1} (aromatic proton) (Figure 2).

N.m.r. (CDCl_3 , TMS; ppm): 2.7–3.0 δ (m, epoxy protons), 7–7.3 δ (m, aromatic protons), 1.6 δ (s, CH_3), 1–2 δ (m, methyl proton) (Figure 3).

^{13}C n.m.r. (CDCl_3 , TMS; ppm): $\delta = 30$ (t, $-\text{CH}_2$), $\delta = 40\text{--}60$ (s, $-\text{CH}$), $\delta = 118$ (t, aromatic), $\delta = 155$ (s, ester group) (Figure 4).

The presence of a band at 920 cm^{-1} in the i.r. spectrum confirms the presence of an epoxy ring. The presence of a band at 1760 cm^{-1} in the i.r. spectrum and the peak at $\delta = 155$ in ^{13}C n.m.r. confirms the presence of the acrylate group in epoxy resin B.

Table 2 shows the solubility and chemical resistance of the film (0.1 mm thick) of blank and modified epoxy resin, when submerged for 7 days in polar and non-polar solvents.

Epoxy resin B retains its initial state and flexibility. Therefore, it is clear that epoxy resin B has superior chemical resistance to epoxy resin A.

The thermal stability of the polymer was determined by weight loss measurement at 200°C for 5 h (Figure 5). Weight loss at 200°C in epoxy resin A is higher than in epoxy resin B, indicating that transition metals increase the thermal stability of the polymer chain.

The t.g.a. curve (Figure 6) shows the weight loss versus temperature of epoxy resin containing metal acrylates. The total weight loss at given stages are as follows: 25– 150°C , 4%; 200– 300°C , 11%; 300– 450°C , 60%.

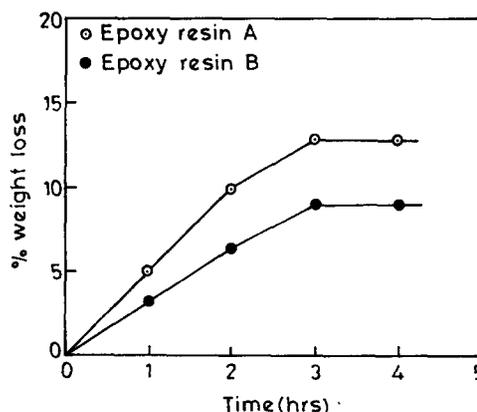
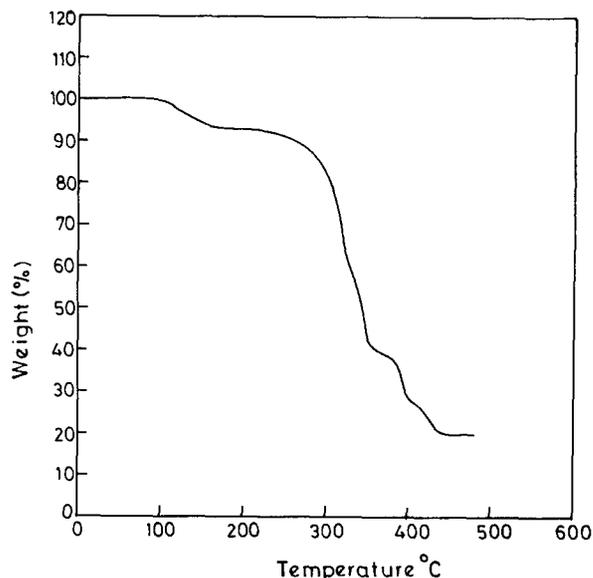
Figure 5 Weight loss of epoxy resin A and epoxy resin B at 200°C (sample size $0.1\text{ mm} \times 10\text{ mm} \times 10\text{ mm}$)

Figure 6 T.g.a. curve of epoxy resin B

Table 2 Solubility and chemical resistance of epoxy resin films cured with polyamide^a

Chemicals	Epoxy resin A	Epoxy resin B
Methanol	—	—
Benzene	—	—
Toluene	—	—
Dioxane	—	—
Carbon tetrachloride	—	—
Pyridine	—	—
Hydrochloric acid	—	—
Sulfuric acid	+	±
Nitric acid	+	±
Dimethyl formamide	—	—
Sodium hydroxide solution	—	—
Water	—	—

^a +, soluble; —, insoluble; ±, sparingly soluble

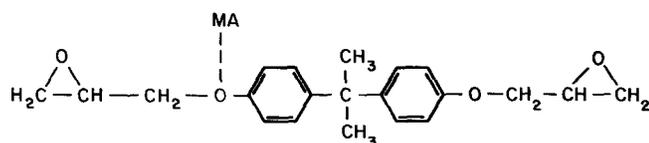
Table 3 Properties of epoxy resin films cured with polyamide

Properties	Epoxy resin A	Epoxy resin B
Conductivity ($\Omega^{-1} \text{ cm}^{-1}$)	1.5×10^{-13}	5.45×10^{-10}
Flexibility (6.4 mm mandrel)	Passed	Passed

This shows that maximum polymer degradation occurs between 300 and 450°C.

Table 3 shows that epoxy resin A is non-conductive ($1.5 \times 10^{-13} \Omega^{-1} \text{ cm}^{-1}$) at 43°C, whereas modified epoxy resin B has improved conductivity ($5.45 \times 10^{-10} \Omega^{-1} \text{ cm}^{-1}$) at room temperature, i.e. it acts as a semiconductor. The increase in conductivity in epoxy resin B is due to the presence of transition metals.

Although there is no real evidence as yet, the results can be explained by the assumption that the metal(s) (Zn, Cu, Cr) forms a complex with epoxy resin. Therefore the following structure may be proposed for epoxy resin containing metal acrylates:



MA = metal acrylates (Zn, Cr, Cu)

CONCLUSION

The modified epoxy resin B, containing transition metals, has higher values of epoxide equivalent weight and viscosity and superior properties of chemical resistance, thermal resistance and electrical conductivity than the unmodified epoxy resin A. The results can be explained by assuming a complex formation between bisphenol-A and the transition metal(s).

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