# Comprehensive Study of Metal on the Characteristic Properties of Epoxy Resins

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**ABSTRACT:** A series of different type of epoxy resins containing metal(s) have been prepared by the using cobalt acrylate ($CoA_2$), nickel acrylate($NiA_2$),bismuth acrylate ($BiA_3$) during resinification. The values of epoxide equivalent weight, chlorine content increases whereas hydroxyl content, refractive index decreases in the presence of metal acrylate(s). The influence of complex formation of metal acrylate with ether linkage of epoxy resins were investigated by spectroscopy. Epoxy resins containing cobalt acrylate which was cured by *p*-acetylbenzilidinetriphenylarsoniumylide (*p*-ABTAY) shows better conducting properties in comparison to $NiA_2$ and $BiA_3$ containing epoxy resins. The dispersion of metal(s) in epoxy resins matrix was confirmed by scanning electron microscope (SEM). The glass transition temperature of epoxy resins containing $CoA_2$ is lower than that of blank epoxy resins and epoxy resins containing bismuth and nickel acrylate.  J Appl Polym Sci 116: 3271–3277, 2010

**Key words:** nickel acrylate; bismuth acrylate; cobalt acrylate; DGEBA; *p*-ABTAY; PDMY

## INTRODUCTION

Epoxy resin is an example of step growth polymerization reaction. Controlling the initial state of its synthesis with the use of complexing agent is an important problem in the synthesis of epoxy resins based on diglycidyl ether of bisphenol-A (DGEBA). An enormous amount of work has been done during last four decades on the modification of epoxy resins by using different modifier such as use of trialkoxyboraxime/triaryloxy boroxime,[1] quinazolone ring,[2] thiocarbonohydrazone,[3] cyanurinc acid,[4] acids,[5] unsaturated acid.[6] Good mechanical and thermal resistant epoxy resins are prepared by aluminium borate whisper (treated) with λ-methoxy prophyl trimethoxy silane,[7] and polycarbonate and reactive polybutine.[8]

Recently the modification of epoxy resins by using different metal acrylate[9–11] on the properties of epoxy resins has been studied. The present system focuses the comprehensive study on the effect of metal acrylate on the characteristic properties of epoxy resins.

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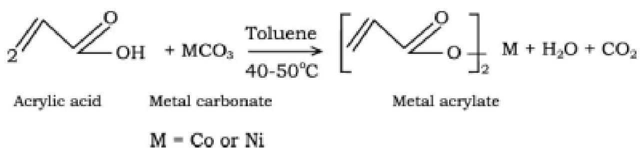
## EXPERIMENTAL

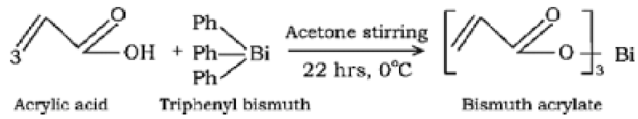
### Synthesis of metal acrylate

a. Nickel and cobalt acrylate were synthesized by Gronowski and Wojtczak,[12] (Scheme 1).




**Scheme 1** Synthesis of cobalt and nickel acrylate.

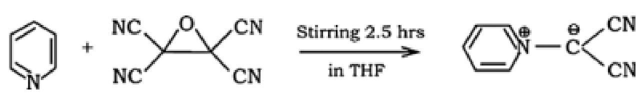
b. Bismuth acrylate was synthesized by Mohan and Srivastava[13] method (Scheme 2).




**Scheme 2** Synthesis of bismuth acrylate.

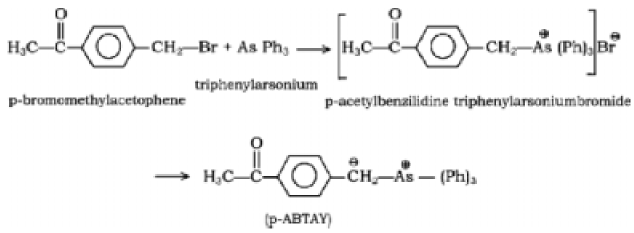
### Synthesis of ylide

a. Pyridiniumdicyanomethylide (PDMY) has been prepared by Linn et al.[14] method (Scheme 3).




**Scheme 3** Synthesis of pyridiniumdieyanomethylide (PDMY).

b. *p*-acetylbenzilidenetriphenylarsoniumylide (*p*-ABTAY) was prepared according to method reported by Tiwari,[15] (Scheme 4).



**Scheme 4** Synthesis of pacetylbenzilidenetriphenylarsoniumylide (*p*-ABTAY).

### Synthesis of epoxy resins

Epoxy resins were synthesized according to standard method[16] with following initial amount of the reactions: Epichlorodrin (0.18 mol), bisphenol-A (0.018 mol), Sodium hydroxide (0.15 mol) and cobalt acrylate/Nickel acrylate/bismuth acrylate ($1.49\times 10^{-3}$ molar equivalent).

## CHARACTERIZATION

### Epoxide equivalent weight (EEW)

Epoxide equivalent weight (EEW) of various resins was determined by pyridinium chloride method.[16]

$$\text{EEW} = \frac{16 \times \text{ sample weight}}{\text{gram of oxiran in sample}}$$

### Hydroxyl content

Hydroxyl content of various epoxy resins was calculated by using following formula.[17]

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

### Hydrolysable chlorine content

Chlorine content of various epoxy resins were obtained by using dehydrohalogenation method using following formula[16]:

$$\text{Chlorine content} = \frac{355 \times 10^{-4} \times N \text{ of KOH} \times \text{ volume of KOH neutralized by epoxy resins}}{\text{Weight of sample}}$$

### Molecular weight

Average molecular weight of various epoxy resins was determined by using gel permeation chromatography (GPC) model 440 (water associates, Milford, MA).

### Refractive Index

Refractive index was determined by using Abb Refract meter at 30°C.

### Specific viscosity

Specific viscosity of various epoxy resins was determined by using Ubbelohde viscometer at room temperature.

### Specific gravity

Specific gravity of various epoxy resins was calculated by using R.D. bottle at room temperature 30°C.

### $^1$H-NMR spectra

The $^1$H-NMR spectra of the epoxy resins were recorded on a Varian EM 390 spectrophotometer in $CDCl_3$ with TMS as the internal standard.

### Infrared spectra

Infrared spectra were recorded on a Perkin–Elmer 377 spectrophotometer.

### DSC techniques

Differential scanning calorimeter (DSC) was employed to investigate the thermal behavior of epoxy resins containing metal acrylate. DSC was recorded on V2-2A Dupont 9900 DSC (Std. error 0.0367 /sec) under a nitrogen atmosphere at a heating rate of 10°C/min. The sample weight was 3–5 g.

### Electrical conductivity

For the DC conductivity measurements the sample were mounted in the metallic sample holder and a vacuum of $\sim 10^{-3}$ Torr was maintained. A DC voltage was applied on the samples through the power supply and the resulting current was measured by a Digital Keithley Electrometer (Model-614).

### Scanning electron microscopy

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

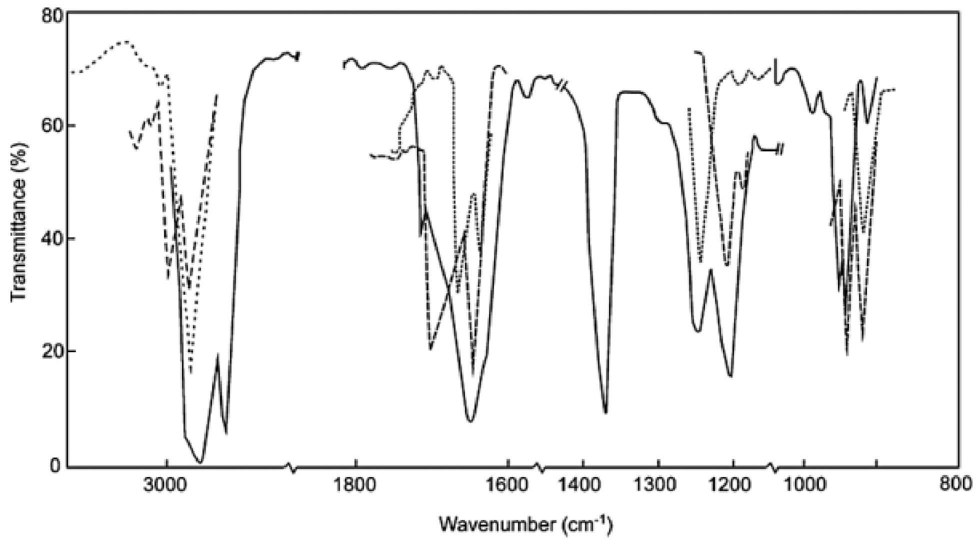
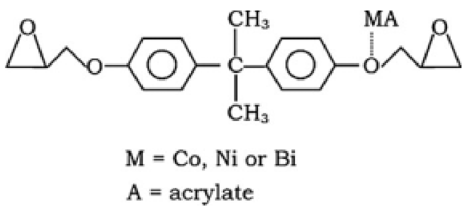



**Figure 1** IR spectrum of epoxy resins containing $CoA_2$($ER_1$——), $NiA_2$($ER_2$ ----), $BiA_3$ ($ER_3$. . .. . .).




**Scheme 5** Structure of epoxy resins and metal acrylate complex.

## Curing studies

PDMY, *p*-ABTAY and polyamide are used as curing agent for epoxy resins containing $NiA_2$, $CoA_2$ or $BiA_3$ respectively. The resins and calculated amount of curing agent (as required to EEW) were mixed in a beaker and applied on glass plate and kept at 120°C (24 h), 120°C (12 h), 180°C (2.5 h) for epoxy resins containing $NiA_2$, $CoA_2$, and $BiA_3$, respectively.

## RESULTS AND DISCUSSION

The effect of metals (Co, Ni, Bi) on the properties of epoxy resins, was based on the synthesis of epoxy resins in the presence of $NiA_2$, $CoA_2$, and $BiA_3$. The structural evidence of epoxy resins containing metal (Co, Ni, Bi) acrylate ($ER_1$, $ER_2$, $ER_3$) come from IR and $^1$H-NMR spectroscopy. Figure 1 indicates characteristic band of epoxy resins containing metal (Co, Ni, Bi) acrylate at 910–950 $cm^{-1}$ for phenyl ring, 2900–3000 $cm^{-1}$ for methyl and methylene groups. The presence of metal acrylate(s) in epoxy resins are confirmed by an additional band at 1700 $cm^{-1}$ of carboxylic group. The shifting of ether linkage from 1250 to 1200 $cm^{-1}$ in the case of metal acrylate containing epoxy resins and ratio of band depth due to ether linkage from IR spectra in $ER_0$ : $ER_1$ or $ER_0$ : $ER_2$ or $ER_0$ : $ER_3$ is 1.9 : 0.5 which is supported to earlear result.[7,13] It shows the

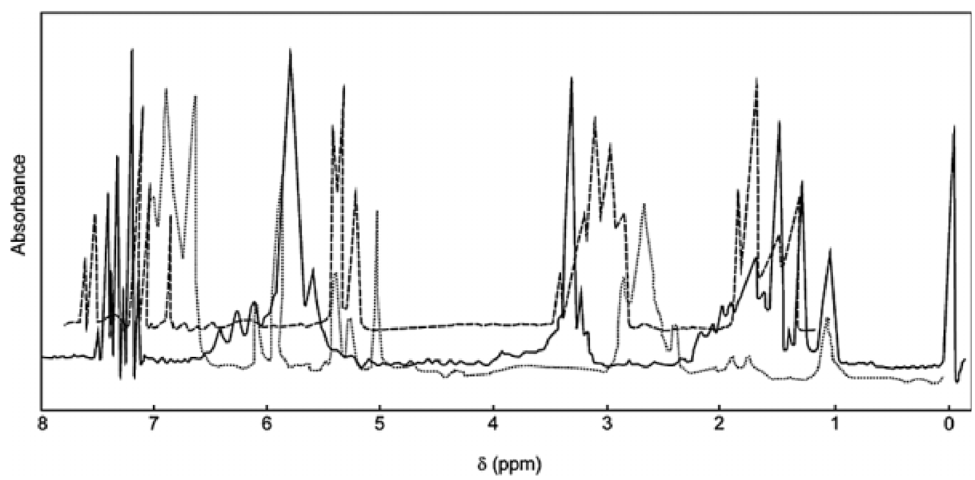



**Figure 2** $^1$H-NMR spectrum of epoxy resins containing $CoA_2$($ER_1$. . ...), $NiA_2$($ER_2$——), $BiA_3$ ($ER_3$-----).

possibility of complex formation between oxygen of ether linkage of epoxy resins and metal acrylate as reported earlier for other metal[19–11]. Based on the above discussion the complex may be assigned following structure (Scheme 5):

Figure 2 shows $^1$H-NMR spectrum of epoxy resins containing metal (Co, Ni, Bi) acrylates ($ER_1$, $ER_2$, $ER_3$): 1.0–2.0 δ (m, methyl protons); 2.5–3.0 δ (m, epoxy proton), 3.2–4.0 δ (m, methyl, methine, $CH{=}CH_2$ protons), 5.7–6.5 δ (m, OH protons), 6.8–7.6 δ (m, phenyl protons).

The peak areas ratio due to methylene and methine protons increases from 1.9[9] to 2.1($ER_1$), 3.8 ($ER_2$), 3.1 ($ER_3$) confirms the presence of metal acrylate in epoxy resins.

### Curing studies of IR spectroscopy

Figures 3–5 present the IR spectra of cured epoxy resins containing cobalt acrylate, nickel acrylate and bismuth acrylate, respectively.

After curing, the most obvious changes in the spectra are those due to the disappearance of the characteristic band for epoxy ring at 910–950 $cm^{-1.}$ The IR data has been concluded that thermosetting form of epoxy resins containing metal (Co, Ni, Bi) acrylates was carried out by using different curing agents.

### Effects of metal (Co, Ni, Bi) acrylate on the characteristic properties of epoxy resins

Refractive indices at 30 ± 2°C of epoxy resins containing different metal acrylate (Table I) is less than that of blank epoxy resins ($ER_0$). Study Table II reveals that the EEW of epoxy resins containing $CoA_2$ (325 eq/100 g), $NiA_2$ (247 eq/100 g) and $BiA_2$ (313 eq/100 g) is greater than that of blank epoxy resins and even epoxy resins containing $ZnA_2$,[18] $CuA_2$,[10] $CrA_3$.[11] Table II also reveals that molecular weight of epoxy resins is just double of EEW, thereby showing the presence of two epoxide groups per molecule. This data also explain the complex formation between metal and ether linkage of epoxy resins.

However, the hydroxyl content decreased in presence of metal acrylate. Specific viscosity of epoxy resins containing $NiA_2$ and $CoA_2$ is greater than that of blank epoxy resins but for epoxy resins containing $BiA_2$ is lower than that of blank epoxy resins. Specific gravity of resins containing $BiA_3$, $CoA_2$, and $NiA_2$ acrylate is greater than that of blank. Chlorine content of epoxy resins containing $NiA_2$ and $CoA_2$ is greater than that of blank but for $BiA_3$ it is lower than blank.

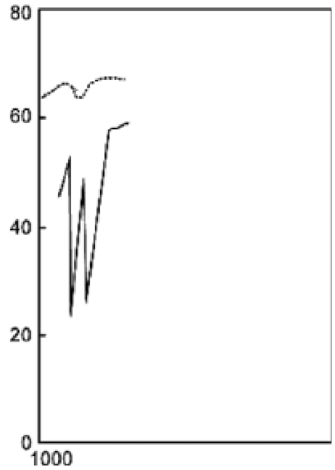



**Figure 4** IR spectrum of cured (--------) and uncured (——) epoxy resins containing $BiA_3$.

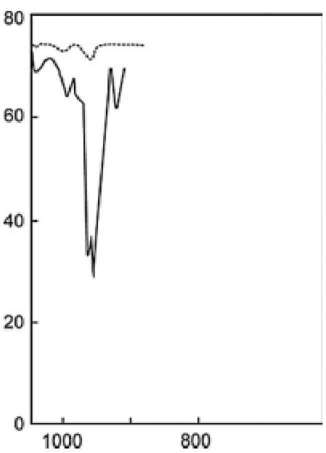



**Figure 3** IR spectrum of cured (--------) and uncured (——) epoxy resins containing $CoA_2$.

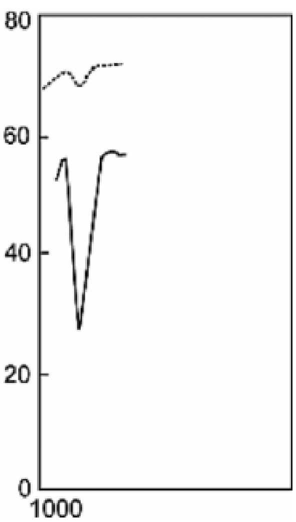



**Figure 5** IR spectrum of cured (--------) and uncured (——) epoxy resins containing $NiA_2$.

**TABLE I**
**Effect of Metal Acrylate(s) on the Physical Properties of Epoxy Resins**

| Resins | Metal acrylate | Molar equivalent of metal acrylate | Refractive index | Color | State |
|---|---|---|---|---|---|
| $ER_0$ | Blank | 0.00 | 1.5695 | Amber | Viscous |
| $ER_1$ | $CoA_2$ | $1.49 \times 10^{-3}$ | 1.552 | Light brown | Viscous |
| $ER_2$ | $NiA_2$ | $1.49 \times 10^{-3}$ | 1.547 | Light green | Viscous |
| $ER_3$ | $BiA_3$ | $1.49 \times 10^{-3}$ | 1.543 | White | Viscous |

**TABLE II**
**Effect of Metal Acrylate(s) on the Characteristic Properties of Epoxy Resins**

| Properties | $ER_0$ | $ER_1$ | $ER_2$ | $ER_3$ |
|---|---|---|---|---|
| Epoxide equivalent weight (EEW) (eq/100 g) | 194 | 325 | 247 | 313 |
| Hydroxyl equivalent (eq/100 g) | 0.12 | 0.054 | 0.036 | 0.049 |
| Chlorine content (%) | 0.5 | 1.0 | 1.008 | 0.23 |
| Specific viscosity (30°C) ($\eta_{sp}$) | 1.58 | 2.0 | 1.8 | 1.292 |
| Specific gravity | 1.1730 | 1.182 | 1.183 | 1.185 |
| Molecular weight | 380 | 650 | 485 | 626 |

**Figure 6** SEM secondary electron (SE) image of $ER_1$ at a magnification of 5000x. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

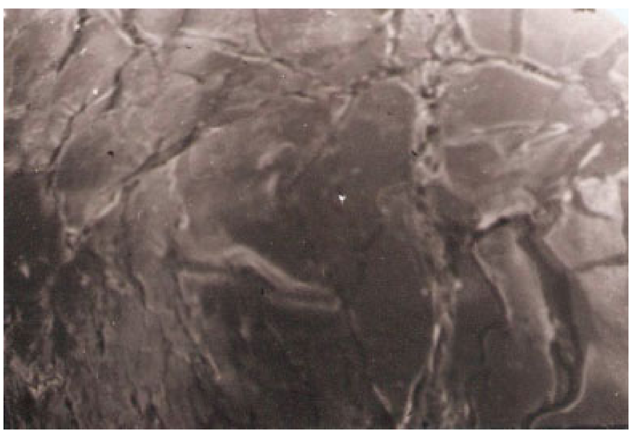


**Figure 7** SEM back scattered electron (BE) image of $ER_1$ at a magnification of 5000x. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

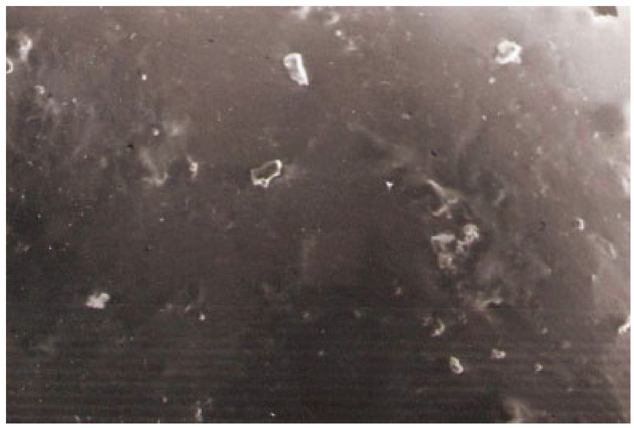


**Figure 8** SEM secondary electron (SE) image of $ER_2$ at a magnification of 5000x. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

**Figure 9** SEM back scattered electron (BE) image of $ER_2$ at a magnification of 5000x. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

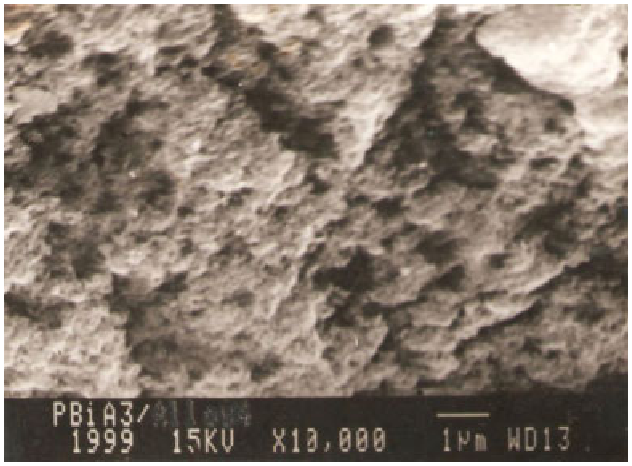



**Figure 10** SEM secondary electron (SE) image of $ER_3$ at a magnification of 5000x. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

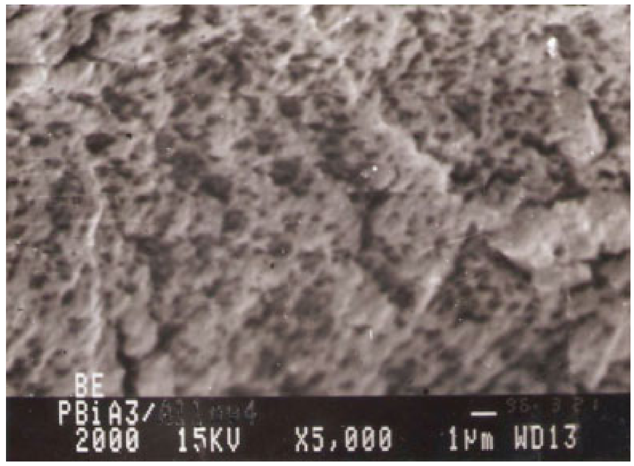



**Figure 11** SEM secondary electron (BE) image of $ER_3$ at a magnification of 5000x. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

**TABLE III**
**Effect of Metal Acrylate on the Electrical Conductivity and Flexibility of Cured Epoxy resins Films (0.2 min)**

| Properties | $ER_0$ | $ER_1$ | $ER_2$ | $ER_3$ |
|---|---|---|---|---|
| Electrical conductivity ($\Omega^{-1}$ cm$^{-1}$) | $1.3 \times 10^{-13}$ | $8.1 \times 10^{-3}$ | $5.3 \times 10^{-11}$ | $2.4 \times 10^{-12}$ |
| $T_g$ | 130°C | 0.75°C | 137°C | 149°C |

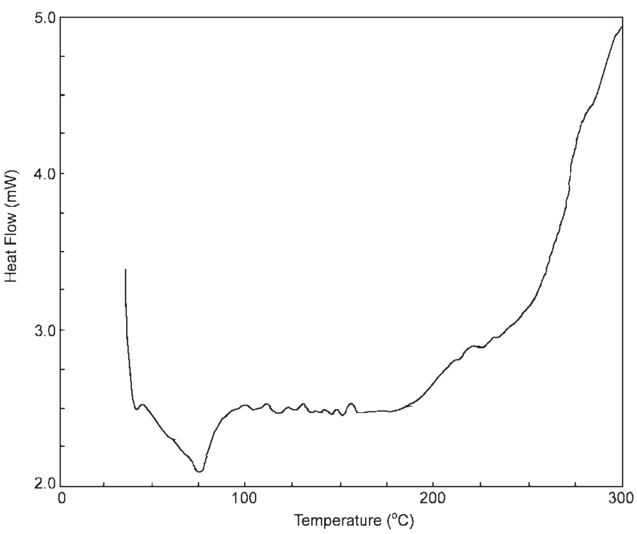



**Figure 12** DSC curve of epoxy resins containing cobalt acrylate ($ER_1$).

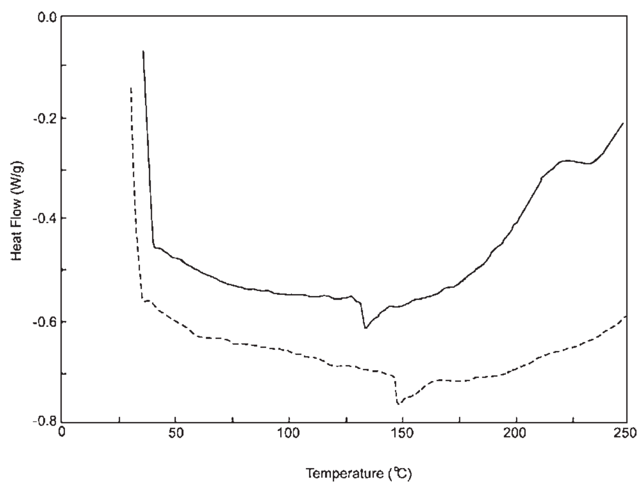



**Figure 13** DSC curve of epoxy resins containing nickel acrylate ($ER_2$——), $BiA_2$ ($ER_3$ -----).

## Morphology

The presence of metal (Co, Ni, Bi) in epoxy resins was confirmed by scanning electron micrographs of secondary electron beam (SE) and back scattered electron beam (BE). Figures 6–11 reveals that the distinct phase domains can be easily observed epoxy as a continuous phase and second component Co, Ni or Bi is in tangled in the matrix as white portions.

## Electrical conductivity

Electrical conducting property is the characteristic property of metal due to presence of partially filled bands of orbital. Bi has half filled p orbital electrons, whereas Co and Ni have partially filled d orbital and the interaction of d orbital give rise to the presence of electrons in a partially filled d band and metallic conductivity. Table III shows the electrical conductivity of cured epoxy resin film containing $CoA_2$ ($1.04 \times 10^{-8}$ $\Omega^{-1}$ cm$^{-1}$) which is greater than that of epoxy resins containing nickel acrylate ($5.3 \times 10^{-11}$ $\Omega^{-1}$ $cm^{-1}$) and $BiA_2$ ($2.4 \times 10^{-12}$ $\Omega^{-1}$ $cm^{-1}$). These data show that the electrical conductivity increases on increasing the number of unpaired electron in the d orbital of metals. These electrons are able to promote in their conduction band. And thus improve the electrical conductivity of epoxy resins.

### DSC studies

The glass transition of epoxy resins containing metal acrylates Figures 12 and 13 was calculated by DSC curve. The $T_g$ for epoxy resins containing $CoA_2$ is lower than that of blank epoxy resins although $T_g$ of epoxy resins containing $NiA_2$ (137°C) and $BiA_3$ (149°C) is greater than that of blank due to the more unpaired electron present in d orbital which shows batter conductivity.

## CONCLUSION

The epoxy resins containing cobalt acrylate ($CoA_2$) which has more unpaired electrons shows greater EEW, molecular weight, hydrolysable chlorine content and improve electrical conductive in comparison to those which has less no of unpaired electrons in d orbital ($NiA_2$) and half filled p orbital ($BiA_3$).

It can be concluded that conducting property is inversely proportional to the glass transition temperature.

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### References

1. Chen, C. S.; Bulkin, B. J.; Pearce, E. M. J Appl Polym Sci 1982, 27, 1177.
2. Fukami, A.; Mariwaki, T. J Macromol Sci Chem A 1989, 26, 877.
3. Thangamathesvaran, P. M.; Jain, S. P. J Polym Sci Part A: Polym Chem 1991, 29, 261.
4. Jain, R. K.; Chandra, R. S. Acta Polym 1991, 42, 668.
5. Mohan, P.; Srivastava, A. K. J Polym Mater 1997, 14, 277.
6. Mohan, P.; Srivastava, A. K. Ind J Chem Tech 1998, 5, 139.
7. Tang, Y.; Liang, G.; Zhang, Z.; Han, J. J Appl Polym Sci 2007, 106, 4137.
8. Bakar, M.; Kobusinska, J.; Szezerba, J. J Appl Polym Sci 2007, 106, 2892.
9. Mohan, P.; Srivastava, A. K. Macromol Rep 1995, 32, 1213.
10. Anand, M.; Srivastava, A. K. High Perf Polym 1992, 4, 97.
11. Anand, M.; Srivastava, A. K. Die Ang Makromol Chem 1994, 216, 1.
12. Gronowski, A.; Wojtczak, Z. J Therm Anal 1983, 26, 223.
13. Mohan, P.; Srivastava, A. K. J Appl Polym Sci 1997, 66, 1359.
14. Linn, W. J.; Webster, O.; Benson, B. E. J Am Chem Soc 1965, 87, 3615.
15. Tiwari, R. S.; Chaturvedi, S. S. Synthesis 1978, 611.
16. Lee, H.; Neville, K. Handbook of Epoxy Resins; McGraw Hill: New York, 1969.
17. Anand, M.; Srivastava, A. K. Polym. 1993, 34, 2860.
18. Anand, M.; Srivastava, A. K. J Appl Polym Sci 1992, 51, 203.