Effect of Cobalt on the Electrical Conductive Property of Epoxy Resins

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ABSTRACT: Cobalt acrylate (CoA_2) has been treated with bisphenol-A and epichlorohydrin to modify epoxy resins. It was cured with *p*-acetylbenzilidene triphenyl arsonium ylide. The properties such as epoxide equivalent weight (equiv/100 g), molecular weight, hydrolyzable chlorine content increases whereas hydroxyl content, refractive index decreases in the presence of CoA_2. The cured epoxy resins shows improve electrical conductivity due to the incorporation of CoA_2 with epoxy resins. The influence of complex formation of CoA_2 with either linkage of epoxy resins were investigated by spectroscopy. The decrease in T_g from differential scanning calorimetry support the improve in flexibility. The dispersion of cobalt in epoxy resins matrix was confirmed by scanning electron microscope. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1971–1975, 2009

Key words: cobalt acrylate; complex formation; *p*-acetyl benzilidine triphenyl arsonium ylide; conducting property

INTRODUCTION

Epoxy resins, a class of thermo set polymers, have been subjected to modification for various industrial applications. Such as the use of quanzolone ring,[1] thiocarbonohydrazone,[2] acids,[3] and unsaturated acids[4] on the properties of epoxy resins. Carbonate soybean oil was used for modification of bisphenol-A based epoxy resins.[5] Good mechanical and thermal resistant epoxy resins are prepared by aluminum borate whisker (treated) with λ-methoxy prophyl trimethoxy silane[6] and polycarbonate and reactive polybutine.[7] However, the search of literature reveals that the epoxy resins being an insulator hardly find any use in electrical field. The effect of incomplete d orbital electron on the property of epoxy resins[8] and acrylate(s) of metal (Cu, Zn, Cr)[9–11] have been reported to improve electrical conductive, but less satisfaction. Therefore, the present work was carried out and it is observed that the use of cobalt acrylate (Ar $3d^7$ $4s^2$) to improve the conductive property of epoxy resins which have been cured with *p*-acetylbenziliden triphenyl arsonium ylide.

EXPERIMENTAL

Synthesis of cobalt acrylate

CoA_2 (Scheme 1) was synthesized according to the method reported by Gronowaski.[12]

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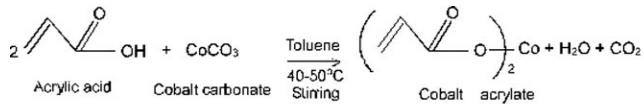


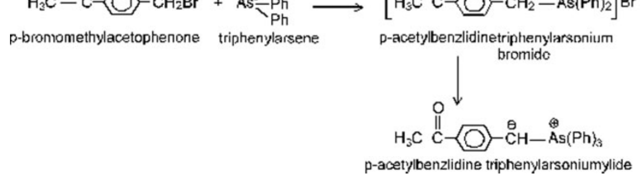
Scheme 1 Synthesis of cobalt acrylate.

Synthesis of epoxy resins

Epoxy resins were synthesized according to Lee and Neville[13] method, with following initial amount of the reactants: Epichlorohydrin (0.18 mole), bisphenol-A (0.018), sodium hydroxide (0.15 mole), and cobalt acrylate (1.49, 3.2, 4.57, 7.79× 10^{-3} molar equivalent).

Synthesis of ylide

p-Acetylbenziliden triphenyl arsonium ylide (*p*-ABTAY) was prepared according to the method reported by Tiwari[14]: The reaction (Scheme 2) is as follows.



Scheme 2 Synthesis of P-ABTAY.

CHARACTERIZATION

Epoxide equivalent weight

Epoxide equivalent weight (EEW) of various resins was obtained by pyridinium chloride method[15]

$$\text{Epoxide equivalent} = \frac{16 \times \text{sample weight}}{\text{grams of oxiran in sample}}$$

Hydroxyl content

Hydroxyl content of various epoxy resins were determined by acetyl chloride method using following method[16]:

$$\text{Hydroxyl content} = \frac{\text{Weight of sample}}{\text{Normality of NaOH} \times (v_1 - v_2) \times 170}$$

Hydrolyzable chlorine content

Chlorine content of various epoxy resins were obtained by using dehydrohalogenation method by using following formula[15]:

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

Molecular weight

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

Refractive index

Refractive index of various epoxy resins were determined by using Abb Refractometer.

Specific viscosity

Specific viscosity of of various epoxy resins (4.0% w/v) were determined by using Ubbelohde viscometer at (30°, 50°, 70°, 90°C) ± 2°C using dioxane as solvent.

Specific gravity

The specific gravity of of various epoxy resins were determined by using pyknometer at 30°C.

^{1}H-NMR spectra

The ^{1}H-NMR spectra of the epoxy resins were recorded on a Varian EM 390 spectrophotometer using tetramethylsilane as the internal standard.

Infrared spectra

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

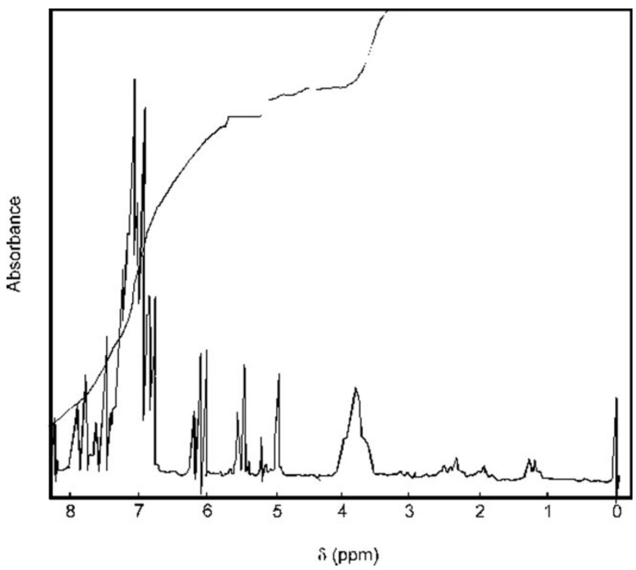


Figure 1 ^{1}H-NMR spectrum of epoxy resins containing 3.2×10^{-3} molar equivalent of cobalt acrylate (ER_2).

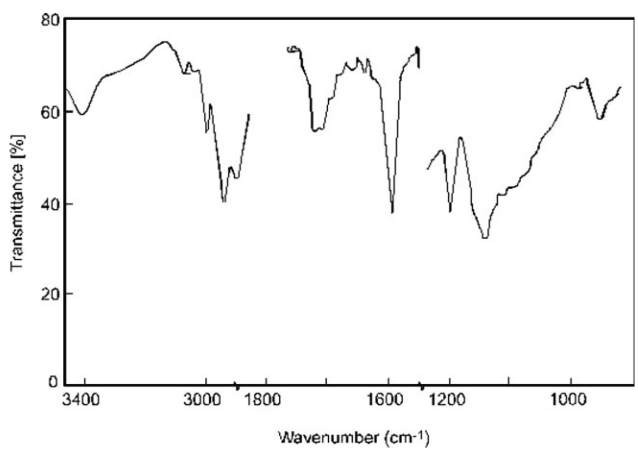


Figure 2 FTIR spectrum of epoxy resins containing 3.2×10^{-3} molar equivalent of cobalt acrylate (ER_2).

TABLE I
Effect of cobalt acrylate on the characteristic properties of epoxy resins.

Properties	ER_0	ER_1	ER_2	ER_3	ER_4
Molar equivalent of cobalt acrylate	0.0	1.49×10^{-3}	3.2×10^{-3}	4.57×10^{-3}	7.79×10^{-3}
Epoxide equivalent weight (equiv/100 g)	194	325	364	384	402
Hydroxyl content (equiv/100 g)	0.12	0.054	0.06	0.062	0.071
Chlorine content (%)	0.5	1.0	1.2	1.19	1.4
Molecular weight	380	650	725	770	790
Specific viscosity	1.58	2.0	2.5	3.6	1.58
Refractive index	1.5695	1.552	1.550	1.547	1.547
Specific gravity	1.173	1.182	1.184	1.184	1.192

DSC technique

Differential scanning calorimetry (DSC) was used to investigate the thermal behaviour of epoxy resins containing CoA_2. DSC was recorded on general V2-2A Dupont 9900 differential scanning calorimeter (Std. error 0.0367/s) 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 a 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 (SEM). The film was mounted vertically on a scanning electron microscopy (SAM) stub using silver adhesive paste.

Curing studies

p-Acetylbenzylidentriphenyl arsonium ylide was used as curative in an amount as required to Epoxide equivalent weight. The resins and the curing agent were mixed in a beaker, applied to glass plate and kept for 12 h.

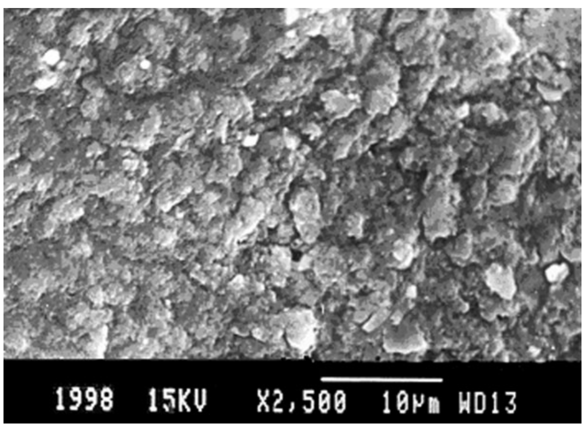


Figure 3 SEM secondary electron (SE) image of ER_4 at a modification of 5000×.

RESULTS AND DISCUSSION

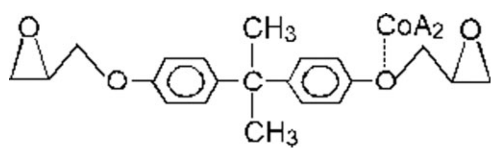
A theoretical generalization of experimental result, to investigate the structural evidence for epoxy resin containing cobalt acrylate comes from ^{1}H-NMR spectrum (Fig. 1) and IR (Fig. 2).

Figure 1 shows the ^{1}H-NMR spectrum of epoxy resins containing 3.2×10^{-3} molar equivalent of CoA_2 (ER_2), which shows following band position:

1.0–2.0 δ (m, methyl protons); 2.5–3.0 δ (m, epoxy protons); 3.8–4.0 δ (m, methylene and methine, $CH{=}CH_2$ protons); 5.7–6.5 δ (OH protons); 6.9–7.2 δ (m, phenyl protons).

The ratio of peak areas due to methylene and methine protons in ER_0[8] and ER_2 is 1.9 : 2.1, which indicate the presence of CoA_2 in epoxy resin (ER_2). However, the peak area ratio due to hydroxyl protons is lower than that of blank epoxy resins.[8]

Figure 2 indicate the characteristic band of epoxy resins (ER_2) at 910–950 cm^{-1} for epoxy ring, at 1650 cm^{-1} for phenyl ring, at 2900–3000 cm^{-1} for methyl group. The presence of an additional band due to carboxylic group at 1700 cm^{-1}, confirm the presence of CoA_2 in ER_2. The shift of ether group from 1250 cm^{-1} to 1200 cm^{-1} and ratio of bond depth due to ether linkage from IR spectra in ER_0[8] and ER_2 is 1.9 : 0.4. It shows the possibility of complex formation between O atom of ether linkage of epoxy resins and d-orbital of Co of cobalt acrylate as reported earlier for other metals,[9–11] which increases the EEW as well as molecular weight of epoxy resins. Therefore, the complex (Scheme 3) has been assigned following structure:



Scheme 3 Cobalt complex with epoxy resins.

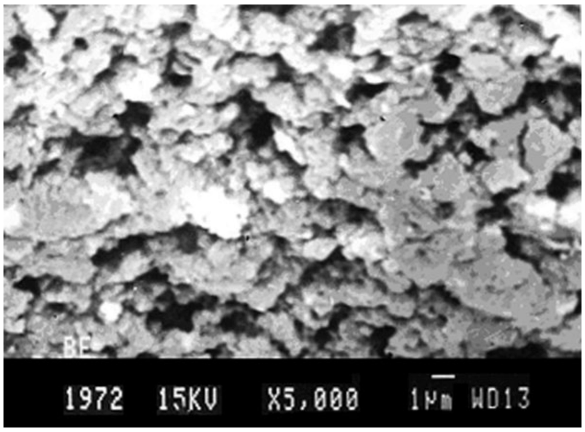


Figure 4 SEM beck scattered electron (BE) image of ER_4 at a modification of 5000X.

Effect of d-orbital electrons on the characteristic properties of epoxy resins

Table I shows the effect of unpaired d-orbital electrons on the characteristic properties of epoxy resins by using CoA_2 during resinification. The EEW of epoxy resins containing CoA_2 (325–395 equiv/100 g) is greater than that of blank epoxy resin (194 equiv/100 g) and even epoxy resin containing zinc acrylate (234 equiv/100 g),[10] copper acrylate (245 equiv/100 g),[9] chromium acrylate (270 equiv/100 g),[11] and nickel acrylate (238 equiv/100 g).[8] This is due to presence of unpaired electron in the d-orbital of metal. These data shows that the EEW increases on increasing the number of unpaired electrons in d-orbital except Cr(Ar $3d^5$,$4s^1$) which have half filled d-orbital. Table I further reveals that the molecular weight of epoxy resins is just double of EEW. Another important property of epoxy resins is hydroxyl content, which is lower than that of blank epoxy resin and increases on increasing the molar equivalent of CoA_2. However, the hydrolyzable chlorine content of modified epoxy resins is higher (1.0–1.4%) than that of blank epoxy resins. The greater value of percentage chlorine content of epoxy resin suggests that the Co act as catalyst for the side reaction and abnormal addition of epichorohydrin.

It also show that specific viscosity, specific gravity, and refrective index of epoxy resins is greater than that of blank, which is due to incorporation of cobalt acrylate in epoxy resins.

TABLE II
Effect of cobalt acrylate on the percentage of weight gain in cured epoxy resins films (100 mg wt)

Chemical	ER_0	ER_1	ER_2	ER_3	ER_4
Hydrochloric acid (1 *M*)	7.32	15.04	17.8	28.4	31.9
Toluene	10.4	12.2	15.0	20.4	22.8

Morphology

The presence of copper in epoxy resins (ER_4) was confirmed by scanning electron micrographs of secondary electron beam (SE) and back scattered electron beam (BE). Figure 3 reveals that the distinct phase domains can be easily observed epoxy as a continuous phase and second component cobalt is in tangled in the matrix as white portions. BE micrograph (Fig. 4) or epoxy resins (ER_4) shows molted texture and reveals internal appearance of the network.

Absorbance

The absorption (Table II) of epoxy resins was investigated by keeping film strips of cured epoxy resins (0.05 g weight) in toluene and hydrochloric acid (1*M*) at room temperature (30°C). After 7 days, weight of polymer increases due to absorption (Table II), which is maximum in hydrochloric acid. It may be due to increased flexibility of polymer chains (Table III).

Electrical conductivity

Electrical conductivity is a characteristic properties of partially filled bands of orbital. Transition metals have partially filled d-orbital and the interaction of d orbital can then 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 resins film containing CoA_2 greater ($8.1 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$) than that of blank ($1.3 \times 10^{-13}\Omega^{-1}\ cm^{-1}$) and even epoxy resins containing acrylate

TABLE III
Effect of cobalt acrylate on the electrical conductivity and flexibility in cured epoxy resins film (0.2 mm thick)

Properties	ER_0	ER_1	ER_2	ER_3	ER_4
Electrical conductivity ($\Omega^{-1}cm^{-1}$)	1.3×10^{-13}	8.1×10^{-13}	1.04×10^{-8}	0.6×10^{-8}	0.16×10^{-8}
Flexibility[a]	Passed	Passed	Passed	Passed	Passed

[a] Modulus (6.35 mm).

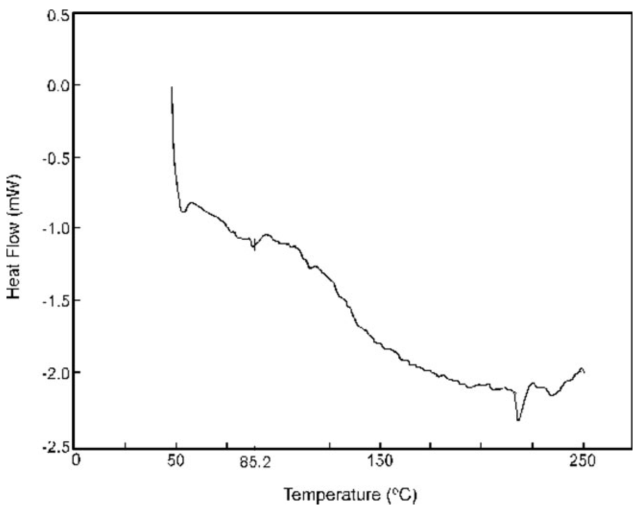


Figure 5 DSC curve of epoxy resins containing 1.5×10^{-3} molar equivalent of cobalt acrylate (ER_1).

of metal(s) of copper (8.7×10^{-13} Ω^{-1} cm^{-1})[9] and nickel acrylate (5.3×10^{-10} Ω^{-1} cm^{-1}).[8] These data show that the electrical conductivity increases on increasing the number of unpaired electrons in d orbital of metals. These electrons are able to promote in their conducting band. And thus improve the electrical conductivity of epoxy resins.

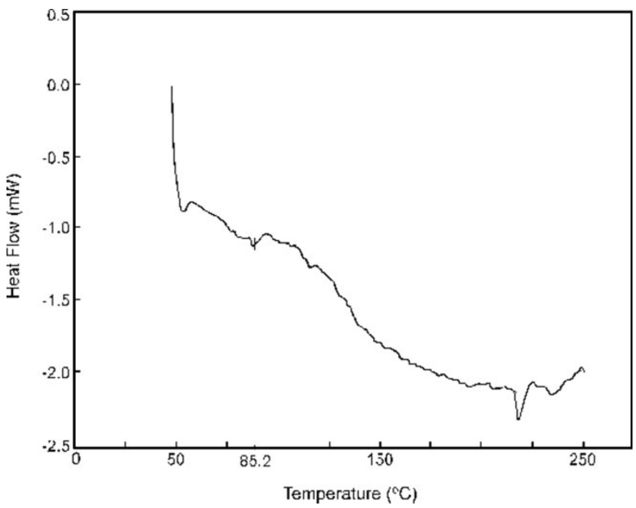


Figure 6 DSC curve of epoxy resins containing 3.2×10^{-3} molar equivalent of cobalt acrylate (ER_2).

DSC studies

The glass transition temperature of epoxy resins containing (1.5×10^{-3}) and (3.2×10^{-3}) molar equivalent of cobalt acrylate(ER_1 and ER_2) is calculated by DSC analysis (Figs. 5 and 6) are 75 and 85°C, respectively, which is lower than that of blank epoxy resins (130).[9]

CONCLUSION

The epoxide equivalent weight, molecular weight and hydrolyzable chlorine content are increased on increasing the unpaired electrons in d orbital. Chlorine content is increased because Co act as a catalyst for the abnormal addition of epichlorohydrin. It is concluded that electrical conductivity increases on increasing the number of unpaired electrons in d orbital of metals due to the passive promotion of electrons in conductive band.

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