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EFFECT OF INCOMPLETE d ORBITAL ON THE EPOXY RESINS PROPERTIES: SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

The theoretical generalization of the experimental results, to investigate the effect of incomplete d orbital, using nickel acrylate (NiA_2) on the epoxy resins properties is repoted. The value(s) of epoxide equivalent, hydroxyl content, hydrolyzable chlorine content, specific gravity, refractive index of epoxy resins have been evaluated. DSC data have been used to determine the order of reaction, heat of reaction, activation energy & glass transition temperature (T_g). The epoxy resins, cured with pyridinium dicyano methylide (PDMY), as a new curing agent, showed improved chemical resistance, flexibility and electrical conductivity.

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INTRODUCTION

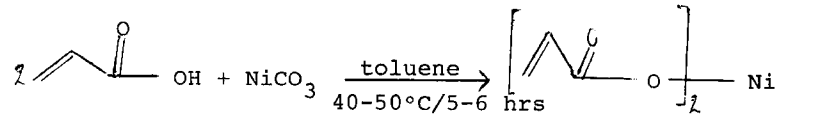
Epoxy resins by virtue of their extreme versality are extensively used in industrial applications and, therefore, have been subjected to various modifications. Amongst such are, use of quanazolone ring[1], thiocarbonohydrazone[2], trialkoxy boroxime/triaryloxy boroxime[3], and metal acrylates containing zinc[4] and copper[5] (transition metal containing complete d orbital). The values like epoxide equivalent, hydroxyl content, hydrolyzable chlorine content, viscosity, specific gravity increased in the presence of metal acrylate in comparison to blank epoxy resin. It was, therefore, of interest, to investigate the effect of transition metal containing incomplete d orbital, on the properties of epoxy resins. The present communication, using nickel acrylate (NiA_2), is an out come of such efforts.

MATERIAL

Epichlorohydrine, dioxane, methanol, acetone (Ranbaxy); toluene, acetyl chloride (Qualigens); bisphenol-A (Robert Johnson); pyridine were obtained from commercial sources and used as received.

METHOD

Synthesis of Nickel Acrylate: NiA_2 was prepared according to method reported by Gronowski.[6]



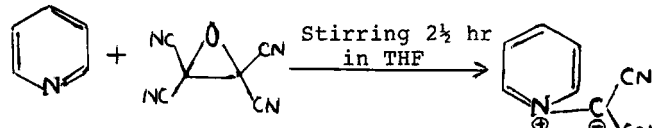
acrylic acid

Nickel acrylate

Yield = 82%
M.P. = 101°C

Synthesis of Epoxy resins: Epoxy resins were synthesised according to Lee & Neville[7] method, with the following initial amount of reactants: epichlorohydrin (0.18 mole), bisphenol-A (0.018 mole), sodium hydroxide (0.15 mole), nickel acrylate (1.49, 3.2, 4.57, 7.79×10^{-3} molar equivalent).

Synthesis of ylide: Pyridinium dicyano methylide (PDMY) has been prepared according to method reported by Linn et al[8]



Pyridine | Tetracyano ethylene oxide | PDMY

Yield = 80% M.P. = higher than 250°C

CHARACTERIZATION

Epoxy characterization: ^1H NMR (200 MHz) spectra were recorded on a varian EM 390 spectrophotometer in $CDCl_3$ with TMS as internal standard. A Perkin-Elmer Model 377 spectrophotometer was used to record infra-red spectrum of epoxy resin(s). Refractive index was obtained by using Abb Refractometer at 30°C. Viscosity of epoxy (4.0% w/v) resins was determined by using Ubbelhode viscometer at (30°C, 50°C, 70°C, 90°C) $\pm$ 0.2°C using dioxane as solvent.

Epoxide Equivalent: Epoxide equivalent of various resins was obtained by pyridinium chloride method[9] using following formula

$$\text{Epoxide Equivalent} = \frac{16 \times \text{sample weight}}{\text{gm of oxiran in sample}}$$

Hydroxyl content: Hydroxyl content was determined by acetyl chloride method using following formula[10]

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

V_1 = the volume of methanolic NaOH used for the blank.

V_2 = the volume of methanolic NaOH used for samples.

Hydrolyzable chlorine content: Chlorine content of various epoxy resins were obtained using dehydrohalogenation method using following formula[10]

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

DSC Technique: Differential scanning calorimetry (DSC) was employed to investigate the thermal behaviour of epoxy resins containing NiA_2. DSC was recorded on a general V2-2A Du-Pont 9900 differential scanning calorimeter (Std. error 0.0367/sec) under a nitrogen atmosphere at a heating rate of 10°C/min. The sample weight was 5.3 mg.

Electrical conductivity: For the DC conductivity measurements, the samples were mounted in a metalic 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).

Curing Studies: PDMY was used as curative in an amount as required to epoxy equivalent weight. The resin and the

curing agent were mixed in a beaker, applied to glass plate and kept at 120 ± 1°C for 240 hr.

RESULTS AND DISCUSSION

Structural evidence for the epoxy resin comes from IR (Figure I) and NMR spectrum (Figure II).

Fig. 1 indicates characteristic bands of blank epoxy resin[11] (ER_1) and that prepared in the presence of NiA_2 (ER_5) at 910-950 cm^{-1} for epoxy ring, at 2900-3000 cm^{-1} for methyl & methylene group and at 1650 cm^{-1} for aromatic ring. The presence of an additional band due to carboxylate group at 1700 cm^{-1} confirms presence of the NiA_2. The shifting of ether group from 1250 to 1200 cm^{-1} in the case of ER_5 and ratio of band depth due to ether linkage from IR spectra in ER_1 & ER_5 is 1.9:0.5. It shows the possibility of complex formation between oxygen of ether linkage[4] and incomplete d orbital of nickel. Based on above discussion, the complex may be assigned following structure:

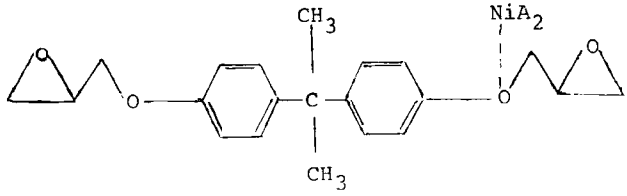


Figure II shows NMR spectra of blank epoxy resin[11] (ER_1) as well as that prepared in the presence of NiA_2 (ER_4)

2.5 - 3.0 δ (m, epoxy protons)

6.9 - 7.2 δ (m, aromatic protons)

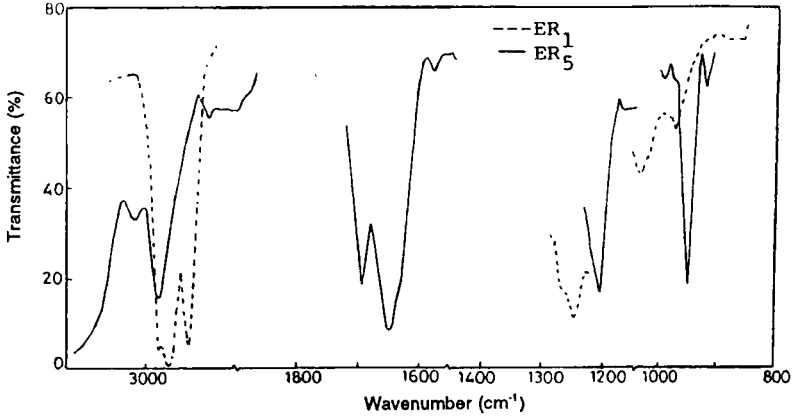


Fig.I: IR spectrum of epoxy resin (ER_5)

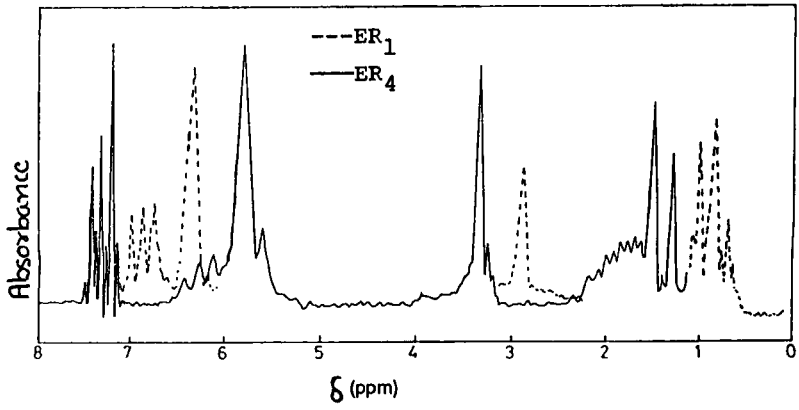


Fig.II: ^{1}H-NMR spectrum of epoxy resin (ER_4)

5.7 - 6.5 δ	(S, OH protons)
3.5 - 4.0 δ	(m, methylene methine protons $CH=CH_2$ conjugated protons also in ER_4)

The ratio of peak areas due to methylene and methine protons in ER_1 & ER_4 is 1.9:2.8 which confirm the presence of NiA_2 in ER_4. However, the peak area ratio due to hydroxyl proton for ER_1 & ER_2 is 6.1:4.1.

Refractive indices at 30°±2°C of modified epoxy resins (Table I) changes from 1.547 to 1.529 which is less than the observed value of ER_1.

Effect of incomplete d orbital on the characteristic propertis of epoxy resin

Study of Table-II reveals that the value of epoxide equivalent (343.9 for ER_4) is greater than that of blank epoxy resin (194 for ER_1), and even epoxy resins containing ZnA_2[4] (234) & CuA_2[5] (245). The complex formation with ether group increased epoxidation, hence the epoxide equivalent. This explains the greater value of chlorine content of ER_4 to ER_1. However, hydroxyl content decreases in the presence of NiA_2. The results obtained by using acetyl chloride method are also supported by the peak area ratio due to hydroxyl proton in the NMR spectrum of ER_4 (5.7 - 6.5 δ).

The viscosity of epoxy resins (Table-II) increases with an increase in concentration of NiA_2 in the epoxy resin. However, it decreases with temperature (Fig.III).

Solubility & Chemical resistance:

Chemical resistance of cured epoxy resins with PDMY is more than that of uncured epoxy resins (Table-III,IV).

Table-I: PHYSICAL PROPERTIES OF EPOXY RESINS

Resins	Metal acrylate	Molar Equivalent of metal acrylate	Refractive Index	Colour	State
ER_1	Blank	0.0	1.5695	Amber	Viscous
ER_2	NiA_2	1.49×10^{-3}	1.547	Light green	Viscous
ER_3	NiA_2	3.2×10^{-3}	1.544	Light green	Viscous
ER_4	NiA_2	4.57×10^{-3}	1.540	Light green	Viscous
ER_5	NiA_2	7.79×10^{-3}	1.529	Green	Highly viscous

Table-II: CHARACTERISTICS OF EPOXY RESINS

Properties	ER_1	ER_2	ER_3	ER_4	ER_5
Epoxide Equivalent (eq/100 g)	194	247	238	343.9	358
Hydroxyl Equivalent (eq/100 g)	0.12	0.036	0.040	0.052	0.056
Chlorine content	0.5	1.008	0.948	1.08	1.40
Specific viscosity (η_{sp}) (30°C)	1.58	1.8	2.6	3.4	3.9
Specific gravity (30°C)	1.1730	1.183	1.183	1.186	1.187
Molecular weight	380	485	467	679	695

However absorption (Table-V) was observed when samples were submerged in toluene, hydrochloric acid (1M), which may be due to increased flexibility of polymer chain (Table-VI).

Electrical Conductivity: Conductivity of cured epoxy resin containing NiA_2 is increased hundred times than that of blank epoxy resin (Table-VI).

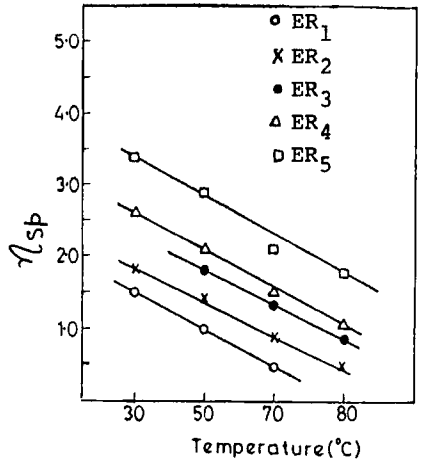


Fig.III: Relation between η_{sp} and temperature of various epoxy resins.

Table-III: Solubility[x] & Chemical Resistance of Uncured epoxy resins.

Chemical	ER_1	ER_2	ER_3	ER_4	ER_5
Toluene	+	+	+	+	+
Cyclohexane	-	-	-	-	-
Dioxane	+	+	+	+	+
DMSO	+	+	+	+	+
DMF	+	+	+	+	+
Methanol	-	-	-	-	-
Acetic Acid	±	±	±	±	±
Hydrochloric acid	-	-	-	-	-
Nitric acid	+	+	+	+	+
Sulphuric acid	+	+	+	+	+
Water	-	-	-	-	-
NaOH	-	-	-	-	-

x = +(soluble), -(insoluble), ±(Sparingly soluble)

Table-IV: Solubility[a] & Chemical Resistance of Cured epoxy resin films (0.2 mm thick)

Chemical	ER_1	ER_2	ER_3	ER_4	ER_5
Toluene	-	-	-	-	-
Dioxane	-	-	-	-	-
DMF	-	-	-	-	-
DMSO	-	-	-	-	-
Hydrochloric acid	-	-	-	-	-
Nitric acid	+	±	±	±	±
Sulphuric acid	+	+	+	+	+
Water	-	-	-	-	-
Acetic acid	-	-	-	-	-

a = + (soluble), - (insoluble), ± (Sparingly soluble)

Table-V: Weight gain (in %) for cured epoxy resin films when submerged in various solvents for seven days at room temperature.

Chemical	ER_1	ER_2	ER_3	ER_4	ER_5
Hydrochloric acid	7.32	12.03	16.02	18.04	25.10
Toluene	-	5.00	6.00	6.75	8.50

Table-VI: Flexibility & Conductivity of Cured epoxy resin film (0.2 mm thick)

Properties	E_1	E_2	E_3	E_4	E_5
Conductivity (Ω^{-1} cm^{-1})	1.5×10^{-13} (43°C)	5×10^{-11} (25°C)	5.3×10^{-11} (25°C)	5.5×10^{-11} (25°C)	5.5×10^{-11} (25°C)
Flexibility	Passed	Passed	Passed	Passed	Passed

Table-VII: Thermal Analysis - DSC

DuPont 9900 Thermal Analysis -- DSC
Size: 5.30 mg Kcell: 1.245

Temp. (°C)	Temp. (°K)	1000/Temp. 1/K)	k(T) (1/sec)	ln k(T) 1/sec)	1/2Life (min)
173.12	446.27	2.2408	0.00027	- 8.22	43.95
183.12	456.27	2.1917	0.00086	- 7.06	13.88
193.12	466.27	2.1447	0.00258	- 5.96	4.60
203.12	476.27	2.0997	0.00742	- 4.90	1.60
213.12	486.27	2.0565	0.02046	- 3.89	0.58
223.12	496.27	2.0151	0.05411	- 2.92	0.22

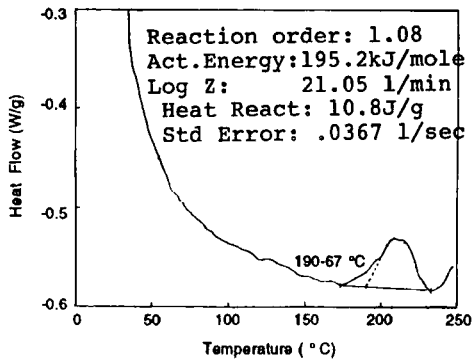


Fig. IV: T_g of epoxy resin ER_5 estimated by DSC curve.

Chemical Kinetics:

The value of the heat reaction, activation energy, order of reaction estimated by DSC studies (Table-VII) is 10.8J/g, 198KJ $mole^{-1}$, 1.08 respectively. The activation energy is higher than blank epoxy resin.[4] Glass transition temperature (T_g) (109.67°C) of ER_5 is calculated by DSC curve (Fig.IV).

CONCLUSION

(i) Novel epoxy resins containing Ni have been synthesized by reacting NiA_2 with bisphenol-A and epichlorohydrin.

(ii) Ni^{2+} plays the role of an activator by complexing with bisphenol-A.

(iii) The variation of epoxy properties due to presence of incomplete d orbital in NiA_2 are given below:-

Incomplete d orbital $\propto$ 1/hydroxyl equivalent
$\propto$ Chlorine content, Epoxide equivalent, viscosity, chemical resistance, refractive indices

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REFERENCES

1. A. Fukami & T. Moriwaki, J. Macromol. Sci., Chem. A., 26, 877 (1989).

2. P.M. Thangamathesvaran & S.R. Jain, J. Polym. Sci. Part A Polym. Chem., 29, 261 (1991).

3. C.S. Chen, B.J. Bulkin & E.M. Pearce, J. Appl. Polym. Sci., 27, 1177 (1982).

4. M. Anand & A.K. Srivastava, J. Appl. Polym. Sci., 51, 203 (1994).

5. M. Anand & A.K. Srivastava, High. Perf. Polym. 4, 97 (1992).

6. A. Gronowski & Z. Wojtczak, J. Therm. Anal. 26, 233 (1983).

7. H. Lee & K. Neville, Handbook of Epoxy Resin, Mc Graw Hill, New York, Chap 2-4 (1969).

8. W.J. Linn, O. Webster & R.E. Benson, J. Am. Chem. Soc., 87, 3651 (1965).

9. H. Lee & K. Neville, Handbook of Epoxy Resin, Mc Graw Hill, New York, Chap 4-7 (1967).

10. M. Anand & A.K. Srivastava, Polym. 34, 2860 (1993).

11. H. Lee & K. Neville, Handbook of Epoxy Resin, Mc Graw Hill, New York, Chap 4-3,4 (1969).