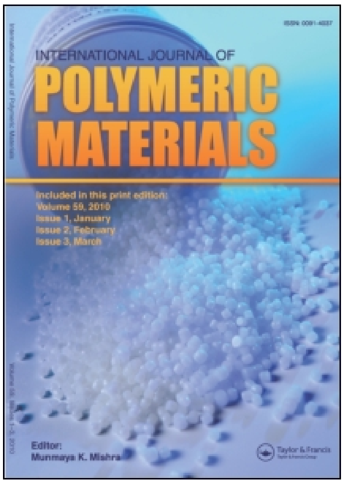

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Novel Metal Complex Based Epoxy Resin

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The novel metal complex synthesized by the condensation reaction of metal chloride ($NiCl_2$) with schiff base and hydroquinone (in 1:1:3 mole ratio) was epoxidized in presence of base catalyst to obtain metal complex based epoxy resin (i.e., Ni-epoxy).

An attempt has been made to carry out comparative curing study (by DSC) for Ni-epoxy, *di*glycidylether of *bis*phenol-A (DGEBA) and *tri*glycidylether of *p*-amino phenol (TGPAP) resin system using aliphatic and aromatic diamines as catalyst. On the basis of curing characteristics the mild steel panels were coated using all the three resins. The coated panels were tested for their flexibility, scratch hardness, impact strength and chemical resistancy.

Keywords: Epoxy resin; scratch hardness; flexibility; impact strength; chemical resistancy

INTRODUCTION

Epoxy resins form an important class within the family of thermoset materials. The processing and final physical properties of epoxy resin-curing agent systems applied in adhesives; sealants; coatings or laminates depend primarily on their chemical structure and degree of cure [1].

Epoxy resins are no longer a novelty to the coating industries also. Coatings based on epoxy resins are generally characterized by their excellent adhesion and overall chemical resistancy. They also exhibit a

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high degree of resistance to impact, abrasion and other types of physical abuse. It is therefore not at all surprising that epoxies have found utility in the end use areas like plant maintenance; automotive primers; can and drum coatings; pipe coatings; appliance coatings; adhesives for home and industry and millitary and aerospace usage etc. [2].

The mechanism and kinetics of epoxy-diamine reactions have been analyzed and reviewed by several authors [3–6], but Ni-epoxy complex system and their comparative coating properties has received no substantial attention inspite by ease of synthesis and its curing characteristics. Hence it was thought interesting to study the comparative curing and coating study of Ni-epoxy, DGEBA and TGPAP resin systems.

EXPERIMENTAL

Materials

DGEBA was procured from Synpol Chemicals Ltd; Ahmedabad, India having epoxy equivalent weight 190, viscosity 40–100 poise and density 1.16–1.17 gm/cm^3 at 25°C. The other chemicals used; salicylaldehyde; *m*-aminophenol, absolute alcohol, nickel chloride, hydroquinone, epichlorohydrin, sodium hydroxide, 1,2-ethylenediamine (EDA), 1,3-propylenediamine (PDA), 4,4′-diamino diphenyl methane (DDM), methanol and methyl cellosolve were of laboratory reagent grade.

Synthesis of Trifunctional Epoxy Resin (TGPAP)

TGPAP was synthesized by the method reported in literature [12–13].

Synthesis of Schiff Base

Schiff base was synthesized by the reaction of salicylaldehyde and *m*-aminophenol according to the method given in literature [7 8].

Synthesis of Metal Complex

Metal complex was prepared by the condensation reaction of nickel chloride with schiff base and hydroquinone in 1:1:3 molar ratio.

Synthesis of Resin (Ni-epoxy)

The metal complex based epoxy resin (i.e., Ni-epoxy) was synthesized according to method given in literature [12].

Coating on Mild Steel Panels

Coating compositions were prepared by combination of epoxy resin (Ni-epoxy, DGEBA and TGPAP) and two aliphatic and aromatic diamines stoichiometrically. The compositions were then thinned with methanol: methyl cellosolve mixture (1:3) to the required viscosity for application and were made free from coarse skin by passing through 150 μm sieve (IS:460 – 1960). All resin systems were then coated on the mild steel panel [confirming to deep drawing quality as per IS:513 – 1960; size 150×1.25 mm) using flat brush confirming to IS:384 – 1964. The coated mild steel panels were placed in vertical position for drying immediately; then examined after specific time intervals for the take free test and cured thermally.

Measurements

The films were applied on mild steel panels (6″×4″) and mechanical properties were studied as per Indian Standard specification [17]. The flexibility was measured using 1/4″ and 1/8″ conical mandrel. The scratch resistance and adhesion were determined as per IS methods [17]. Resistance towards water, acid, alkali and organic solvents were determined as per standard method described in the literature [18].

RESULTS AND DISCUSSION

The schiff base was synthesized according to the method reported in literature [7 – 8]. The metal complex was synthesized by the condensation reaction of metal chloride with schiff base and hydroquinone (in 1:1:3 mole ratio).

The resulting metal complex derivative was characterized by IR-spectroscopy. The IR spectrum of the ligand displays the bands reported by Ahmad and Ansari [9 – 10]. The C=N stretching frequency appears at 1630 cm^{-1}. This band appears in the complex at lower frequencies viz. 1600 cm^{-1} for the complex. The shift in C=N stretching in the spectra of the complex signifies the coordination of metal ions through the azomethine nitrogens of the ligand. The phenolic C—O vibration at 1300–1370 cm^{-1} in spectra of the ligands indicates a shift to lower energy of 3–33 cm^{-1} supporting the involvement of the deprotonated phenolic oxygen in coordination [11]. The presence of low frequency bands at 480 cm^{-1} in the spectra of complex are assigned to M—O stretching frequency.

The synthesis of metal complex based epoxy resin was carried out by the reaction of metal complex with epichlorohydrin according to method given in literature [12]. The resulting metal complex based epoxy resin (i.e., Ni-epoxy) was isolated as a viscous liquid. The examination of IR-spectra of this novel metal complex based epoxy resin revealed that they are identical almost in all aspects. They comprise most of features of metal complex derivative. The only discernible difference is that they comprise epoxy ring characteristic frequency at 840 cm^{-1} cofirming the formation of novel metal complex based epoxy resin.

The curing temperatures were decided from the evaluation of dynamic scans obtained from Differential Scanning Calorimetry (DSC) for Ni-epoxy, DGEBA and TGPAP resin systems using ethylenediamine, propylenediamine, diaminodiphenylmethane as catalysts are listed in Table I. On the basis of curing characteristics established by DSC, all the three resins were coated on mild steel panels and tested for the flexibility, scratch hardness, impact strength and chemical resistancy. The results are listed in Table II.

TABLE I Curing characteristics of Ni-epoxy by Differential Sacanning Calorimetry (DSC)

System resin: catalyst	*Kick-off temperature* $T_i(^\circ C)$	*Peak temperature* $T_p(^\circ C)$	*Final temperature* $T_f(^\circ C)$
Ni-Epoxy : DDM	116.6	128.0	152.0
Ni-Epoxy : EDA	84.46	88.29	94.4
Ni-Epoxy : PDA	70.0	76.0	89.0

DDM : 4,4′-diaminodiphenylmethane
EDA : Ethylenediamine.
PDA : Propylenediamine.

TABLE II Flexibility, impact strength and scratch hardness of the coated panels

System resin: catalyst	*Flexibility*	*Impact strength*	*Scratch hardness (gm)*
Ni-Epoxy : DDM	Pass	300	2000
Ni-Epoxy : EDA	Pass	240	1400
Ni-Epoxy : PDA	Pass	275	1600
DGEBA : DDM	Pass	200	1150
DGEBA : EDA	Pass	160	900
DGEBA : PDA	Pass	175	1000
TGPAP : DDM	Pass	250	1300
TGPAP : EDA	Pass	175	1100
TGPAP : PDA	Pass	200	1200

The values for Ni-epoxy system may be responsible for the aromatic rings and azomethine linkages present in the structure. The scratch hardness and impact strength properties reflect the thermally stable nature of azomethine linkage [14–16]. The data also reflect the role of catalyst used for the curing. Aliphatic amines have long aliphatic chain which is responsible for the flexibility of the coated film. While diaminodiphenylmethane (DDM) has aromatic ring structures, which play an important role in the scratch hardness of the coated films.

Data listed in Table II also indicate that TGPAP resin system show better coating properties than the system where DGEBA is used. This difference may be responsible for the higher functionality of the TGPAP resin. The higher functionality of this resin leads to higher crosslinking in the cured material. The TGPAP cured with DDM shows better results as aromatic rings of DDM play vital role in their scratch hardness and impact strength. It also improves the chemical resistancy of the coated panels. Aliphatic amines, used as catalyst, improve the flexibility and thereby improve the impact strength of the coated film.

The coating properties for DGEBA system are also listed in Table II. which indicate that EDA, PDA and DDM can be used as catalyst for the curing and coating application.

The flexibility test was carried out on 1/4″ and 1/8″ conical mandrel, which confirm the good flexibility of the coated films. All the panels passed stripping test for adhesion. These might be due to free hydroxyl groups present in the resin system which contribute to the strong metallic bond formation with the surface of the mild steel panels.

The coated films are tested for the water and solvent resistancy. In case of water resistance, coating based on all the resin systems show no colour change or blistering. The coated panels were immersed for 48 hours, in water and solvent but no cracking or loss in gloss were observed which indicate that all the systems have excellent solvent and water resistancy. Two % alkali solution test for 48 hours shows that all the panels were remained unaffected. The observation reveals that on exposing the coated panels to Two % H_2SO_4 for 48 hours no substantial loss in gloss or change in appearance were observed indicating excellent adhesion as well as good resistance to acid, alkali, water and organic solvents.

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