



Development of anti-corrosive paint with improved toughness using carboxyl terminated modified epoxy resin

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ABSTRACT

Epoxy resins despite having excellent adhesion to various substrates, good corrosion and chemical resistance are less suitable for high-performance applications, as they are poor in ductility. In the present study, carboxyl terminated polyethylene glycol adipate (CTPA) and carboxyl terminated polyethylene glycol succinate (CTPS) modifiers were synthesised and then used to modify bisphenol-A epoxy resin to raise the latter's toughness. The study showed that in both the cases, 5 wt.% addition gave rise to the highest toughness as well as corrosion protection against salt fog and synthetic sea water exposure. However, between the two modifications the epoxy resin modified with 5 wt.% CTPS gave a better performance and so was pigmented with a mixture of zinc phosphate and red iron oxide to obtain the paint. The study showed that the epoxy resin modified with 5 wt.% CTPS + 30 vol.% pigments gave rise to the highest toughness (flexibility), adhesion and corrosion resistance when applied on to mild steel panels.

1. Introduction

Epoxy resin, with its excellent resistance to moisture, various solvents and chemical species along with good adhesion, has been a popular candidate for development of corrosion resistant coating systems for marine applications [1–3]. However, unmodified epoxies are relatively brittle, have low impact strength and toughness, which restrict their widespread applications in the field of coatings [4–6]. Therefore, modification of epoxy to improve its toughness and other functional properties like corrosion resistance is essential [7–10].

Physical blending of epoxy with other systems such as a carboxyl-terminated copolymers of butadiene and acrylonitrile (CTBN) to modify its properties has been used by various researchers [11–14]. Also blending of cardanol-based epoxy novolac resin with carboxyl-terminated polybutadiene (CTPB) [15], and addition of telechelic acrylate copolymers and terpolymers, amine terminated polysiloxane [16] have also been done for toughness enhancement of epoxy. Epoxy resins have also been modified chemically using modifiers such as carboxyl-terminated butadiene-co-acrylonitrile, isocyanate-terminated oligomers and hyperbranched polyesters that improved their toughness [17–19]. Thus, Ratna et al. have demonstrated that use of carboxyl-terminated polyethylene glycol adipate as a modifier results in the incorporation of carboxyl terminated component into an epoxy resin in turn enhanced

the epoxy resins' toughness [20]. However, these studies were focused on merely modifying epoxy systems for structural applications such as composites; and development of corrosion resistant coatings has not been their objective. So, there is a need to explore these techniques to develop epoxy resins that provide not only very high toughness, but also corrosion resistance.

In this regards, in the present work, an epoxy resin (bisphenol-A) was modified with in-house synthesised carboxyl terminated polyethylene glycol adipate (CTPA) and carboxyl terminated polyethylene glycol succinate (CTPS) to improve formers' toughness. The epoxy resin so-formulated was then pigmented with mixture of zinc phosphate, red iron oxide and barium sulphate. Zinc phosphate is one of the most popular pigments owing to its morphology that influences the barrier action, corrosion inhibiting effect and eco-friendly character [21–27]. Red iron oxide gave high tinting strength as well as good dispersion, and barium sulphate served as an extender [28,29].

2. Experimental

2.1. Materials

Polyethylene glycol PEG-400 (Glaxo Laboratory, India), adipic acid, succinic acid, (M/s S. D. Fine Chemicals, India) and *p*-toluene sulfonic

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acid (PTSA) (M/s Sisco Laboratories, India) were used for the synthesis of CTPA and CTPS modifiers. Diglycidyl ether of bisphenol-A (DGEBA) epoxy resin LAPOX P-101 (epoxide equivalent weight: 465) was used for coating. The curing agent was polyamide LAPOX K-29 (amine hydrogen equivalent weight: 140) procured from M/s Atul Limited, India. Red iron oxide (ISO: 1248:1974) and zinc phosphate (ISO: 6745:1990) were used as pigments and barium sulphate (ISO: 3262:2:1998) as an extender. Analytical grade chemicals and reagents were used, in the as-received condition.

2.2. Synthesis of CTPA and CTPS

CTPA and CTPS have been synthesised by the reaction of polyethylene glycol and adipic/succinic acid in a mole ratio of 1:1.5 respectively. 150 g of polyethylene glycol (PEG-400) was transferred to a three-necked flask and heated up to 80 °C and charged with the appropriate amount of adipic/succinic acid in the presence of *p*-TSA catalyst in toluene under a nitrogen atmosphere. The reaction mixture was maintained at 110 °C for 4 h to obtain the modifiers.

2.3. Modification of epoxy resin by CTPA and CTPS

Epoxy and CTPA/CTPS (3, 5, 8 and 10 wt.%) were taken in a three-necked flask and xylene (20 wt.%) was used as a solvent. The above reaction mixture was heated and maintained at 110 °C under an inert nitrogen atmosphere with continuous stirring for 4 h to form CTPA modified epoxy and 5 h for CTPS modified epoxy resins.

2.4. Pigmentation of paint formulations

The optimised resin (CPSE5-epoxy with 5 wt.% CTPS) was used as a film-forming material, whereas pigments were incorporated in the resin to enhance the barrier effect of coatings. Zinc phosphate acted as an inhibitive pigment, red iron oxide gave high tinting strength as well as good dispersion, and barium sulphate served as an extender [27–29].

Required quantities of the pigment-mixture containing 70 wt.% Zinc phosphate (ZP), 25 wt.% red iron oxide (RIO) and 5 wt.% barium sulphate (BS) were added to the optimised resin (CPSE5) to obtain desired pigment volume concentrations (PVC) of 25, 30, 35 and 40%. Subsequently, the pigment + resin mixtures were charged in an attritor; the viscosity was adjusted by using a solvent mixture [xylene: diacetone alcohol (DAA) = 25:75] and were grounded until the pigment dispersion of 6+ on Hegman gauge was obtained. The mill base was discharged, and the viscosity of the so prepared paint was adjusted using xylene and DAA for application and further studies.

3. Characterization

3.1. Determination of acid value and epoxide equivalent weight

Acid value (*z*) of CTPA/CTPS and CTPA/CTPS modified epoxy resin was determined by volumetric titration method as per the procedure described in IS:354 (part 5)-1986. A known amount of reaction product was dissolved in 10 ml (1:1, v/v) mixture of benzene and methanol solution and titrated against 0.1 N ethanolic KOH with phenolphthalein as an indicator. The acid value was calculated using the following equation:

$$z = \frac{56.1 \times v \times 0.1}{m} \times 100 \quad (1)$$

where, '*v*' is the volume of KOH consumed in ml, and '*m*' is the mass of the product used in g.

The epoxide equivalent weight (EEW) is an important parameter for determination of the amount of curing agent required for coating application. EEW of epoxy and CTPA/CTPS modified epoxy resins were determined by volumetric titration method as per the procedure in

IS:354 (part 4) – 1986. A known quantity of reaction product was dissolved in 10 ml (1:1, v/v) mixture of chlorobenzene and chloroform, then titrated against 0.1 N hydrogen bromide (HBr) in glacial acetic acid with crystal violet as an indicator. HBr solution was standardised with potassium hydrogen phthalate before titration. EEW was calculated using the following formula:

$$EEW = \frac{m \times 1000}{v \times N} \quad (2)$$

where, '*m*' is the mass of product used in g, '*v*' is the volume of HBr consumed in ml, and '*N*' is the normality of HBr solution.

3.2. Fourier transformed infrared spectroscopy

Epoxy resins and KBr salt powder were mixed thoroughly in the ratio 1:1 (w/w) using a pestle and mortar to get a homogenised mixture which were then compacted into pellets using an appropriate press for FTIR studies. FTIR spectra of these pellets mounted on a sample holder were recorded using FT/IR-610 type-A instrument. For each spectrum 16 scans were recorded in the range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹.

3.3. Thermal analysis

Thermal decomposition of PEG-400, the synthesised CTPA and CTPS were studied using thermo-gravimetry analyser (TGA/SDT Q600 V8.3 analyser, TA Instruments). Samples were heated from ambient temperature to 600 °C at a rate of 10 °C/min under an inert nitrogen atmosphere.

3.4. Thin layer chromatography

The crude reaction mixture of CTPA/CTPS-modifiers was run in silica gel thin layer chromatography (TLC) using ethyl acetate and hexane (30:70, v/v) as eluent. The TLC plate was prepared by coating the silica gel slurry over a smooth aluminium plate.

3.5. Preparation of free films

Unmodified epoxy and CTPA/CTPS modified epoxy resins were coated on pre-coated methyl cellulose glass plates using a motorised film applicator (Model No. 335/1 Erickson) containing 400 μm clearance blade. The unmodified and modified epoxy coated glass plates were kept in a dust free chamber for drying in order to form films. After 7 days, the films were peeled off from plates, washed thoroughly under running water to remove the methyl cellulose layer and dried at room temperature.

3.6. Determination of tensile strength and elongation at break

Tensile strength and elongation at break of the epoxy and CTPA/CTPS modified epoxy films were determined using Universal Testing Machine (Model LR30 K plus, Lloyd Instruments, UK) as per the procedure described in ASTM-D882. The test specimens were prepared using a film applicator (Model 335/1, Erichsen). The dry film of size 100 mm × 15 mm and thickness 200 μm, were strained at a rate of 20 mm min⁻¹. The tests were repeated ten times to check for reproducibility.

3.7. Scanning electron microscopy (SEM)

The dispersion of pigments in paint systems was examined using a scanning electron microscope (Hitachi S-3400N). For this, the cross-sections of the free-standing films were examined. All the specimens were gold coated prior to examination in a SEM.

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