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## Acrylic-based monocoat eco-friendly, anticorrosive coating for cathodic electrodeposition

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### ABSTRACT

In the present study, a grafted acrylic-epoxy polymer coating has been developed for cathodic electrodeposition. This is a mono-coat system where different colours (red, blue, black, grey, etc.) are developed in electrodeposition coatings. In this research, the mono-coat technology provides the dual coat (primer and overcoat). The mono-coat electrodeposition system has several advantages compared to conventional electrodeposition such as excellent durability, better UV resistance (500 h), lower cost in paint application and better metal protection against corrosion (500 h salt spray test as per ASTM B 117). The discussion would highlight the formulation concept and mechanism of electrodeposition coatings. The polymers of the grafted acrylic-epoxy system have been developed by varying the grafted acrylic/epoxy ratio. The grafted acrylic/epoxy composition of 80:20 has been found to have optimum anticorrosive and UV resistance properties.

### ARTICLE HISTORY

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### KEYWORDS

Electrodeposition; acrylic resins; emulsion polymerisation; anticorrosive coating; epoxy resin; UV resistance; Eco-friendly; Mono-coat coating

## Introduction

Corrosion is a big problem for metal. It is known to be a cancer of metal especially iron metal. Though corrosion cannot be eliminated but can be mitigated. Industrial coatings are formulated for interior and exterior applications [1,2]. The coating is affected by sunlight, heat, water, oxygen and gases when exposed to the external environment [3]. Electro-coat has a long history of use for corrosion prevention in both the automotive and appliance industries.

The paint industry is a developed industry that is continuously growing through nonstop challenges and acknowledges recent innovations. International and national legislation prospect of decreasing the volatile organic compounds (VOCs) has prompted significant modification in the design of anticorrosive coatings as conventional anticorrosive coatings are having a comparatively higher percentage of solvents. The current environmental pressure to decrease discharges of VOCs has encouraged the coating industry to promote and develop coatings with a low or nil percentage of organic solvent [4–6].

The grafting technique has been useful for effective and high-performance anticorrosive coating [7]. This strategy gives the benefits of each component used for grafting in the overall system. The present invention relates to acrylic graft copolymers modified with epoxy resin. This composition is designed for cathodic electrodeposition. Acrylic graft copolymer has excellent chemical resistance, high mechanical strength, high corrosion resistance, excellent weather resistance

and also other features of acrylic resin [8]. Acrylic resins are chosen in synthesis due to their wide range of applications and their spectrum of properties in automotive coatings. The epoxy resin is taken for better adhesion and better chemical resistance for modification. Epoxy resins are preferred in primer coatings while acrylic resins are popularly used in top-coats [9,10].

The synthesis and application of electrodepositable acrylic graft polymers are breakthrough technology in the paint industry as mono-coat coatings. The process advantages of this coating are automated properties, high level of paint utilisation, high throwing power and low level of contamination [11,12]. In view of national and international legislation, water is used as a thinner in coating design, to reduce the discharge of VOCs or to develop environmentally friendly coatings [13,14]. The coating is the most economical, convenient in application and highly dense on metal surfaces besides it is one of the effective ways of mitigating corrosion of metal. Acrylic-epoxy systems have improved features over individual acrylic or epoxy systems. Our research work describes the synthesis of acrylic-based anticorrosive mono-coat coatings for corrosion protection using various monomer contents and optimum levels of epoxy resin. The synthesis of coatings and the characterisation of their properties have been discussed with respect to their anticorrosive and eco-friendly characteristics.

## Materials and methods

### Raw materials: the materials/chemicals used in the preparation of acrylic resins and cathodic electrodeposition paints are

**Acrylic resin:** Acrylic resins were prepared in the laboratory. The monomers butyl acrylate (BA), methyl methacrylate (MMA), 2 hydroxy ethyl methacrylate, hydroxy propyl acrylate, styrene, and glacidyl methacrylate were purchased from Aldrich & Accord Chemical Corporation.

**Resins:** Epoxy resin, epoxy ESCN – bisphenol A and polyamide hardener were purchased from Allnex Chemical Industry. The diethyl amine was purchased from Balaji Amines Ltd.

**Pigments:** The TiO<sub>2</sub> (Rutile grade) pigment was obtained from M/s DuPont (India). Bismuth hydroxide was bought from Satyam Pharma-Chem Pvt. Ltd. The carbon black powder and carbon black R 5000 ultra were purchased from Connell Bros. Co. (India) Pvt. Ltd. The Paliotan red was purchased from BASF and electra kaolin clay was purchased from Kaomin Industries LLP.

**Chemicals and acids:** HDI (Hexamethylene Di-Isocyanate) polyisocyanate (Durante-TPA-100) was purchased from Asahi Kasei, and nonyl phenol was purchased from Alpha Chemika. Glycolic acid and acetic acid (glacial) were purchased from Multichem Specialities Pvt Ltd. The inhibitor, tertiary butyl catechol was procured from Sigma Aldrich Chemicals Pvt. Ltd.

**Solvent:** Methyl iso-butyl ketone (MIBK) and butyl cellosolve were purchased from Dow Chemicals Ltd., and deionised water was prepared in the laboratory.

### Preparation method of electrodepositable mono-coat coatings

The mono-coat coating was prepared with the following combinations:

1. Cationic acrylic resin dispersion along with cross linker.
2. Pigments (organic/inorganic pigments and extenders).
3. Cosolvents: suitable cosolvents are phenoxypropanol and propylene glycol mono-phenyl ether.
4. Additives: dispersing additive, edge protection additives, anti-cissing additive, anti-crater agents (incompatible with the E-coat), and pinhole additives (use of cosolvents is also possible).
5. Curing catalysts: curing catalysts are metal catalysts for the crosslinking and de-blocking of blocked aromatic isocyanates. DOTO and bismuth metallic compounds are used in coatings.
6. Deionised water: conductivity less than 2  $\mu\text{S}/\text{cm}$  and pH  $7 \pm 0.5$  at 28°C.

The synthesis of electrodepositable mono-coat coatings is shown via flowchart (Figure 1).

### Manufacturing process of pigment paste

A 2-L stainless steel vessel was used to make the pigment paste. To this is added deionised water, glacial acetic acid, emulsifier, wetting agent, epoxy resin, thickening agent and mixed homogeneously. The pigment material, extenders powder and bismuth hydroxide catalyst were added to the homogeneous mass under stirring at 1000 rpm (rotation per minute) for 30 min, maintaining the temperature below 35°C. The paste was checked for agglomeration. There should not be any beads or agglomerates. The slurry was then ground into 1.4 L laboratory scale dyno mill filled with zirconium silicate beads ( $\text{Ø}1.0\text{--}1.2$  mm). The fineness of the grind was kept to 5  $\mu\text{m}$  (maximum). Then flushed the material with water and the viscosity/solid contents of pigment paste were adjusted. The final physical parameters of the pigment paste are given in Table 2.

### Synthesis of acrylic resin

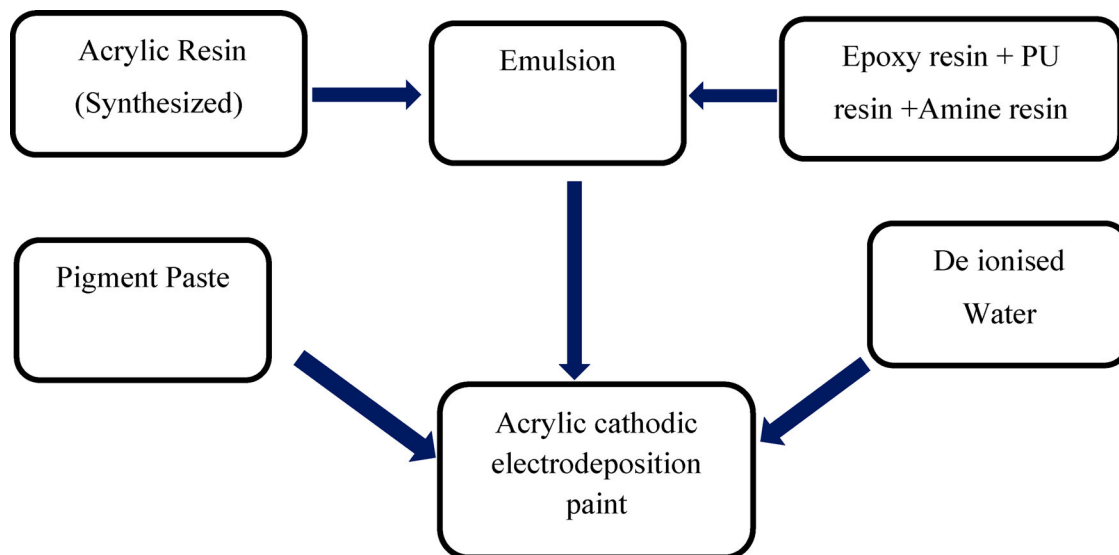
Synthesis of acrylic resins was performed in a four-necked flask equipped with a mechanical stirrer, water condenser, thermometer pocket, and a dropping funnel. The MIBK and butyl cellosolve solvents were taken in the flask and the purged materials were heated to a temperature of  $115 \pm 2^\circ\text{C}$ .

The designated amounts of monomers (BA, MMA, and 2 hydroxy ethyl methacrylate) were charged in a separate flask. In this flask, the initiator AIBN (Azo-Bis ISO-Butyronitrile) was added to the charge under stirring and further stirred for 15 min to dissolve. The prepared monomer mixture was added dropwise at a constant rate of flow to a four-necked flask over the period of 3 h at  $115 \pm 2^\circ\text{C}$  and the exothermic reaction was controlled for 1 h at  $115 \pm 2^\circ\text{C}$ .

The AIBN was added in four equal parts at 15 min intervals and kept at the temperature of  $115 \pm 2^\circ\text{C}$  for 1 h. The temperature of the flask was dropped to 65°C and diethyl amine was added. The material was heated to 100°C for about 90 min and kept at 100°C for 1 h. The temperature was gradually increased to 120°C for about 1 h and maintained until the required viscosity and epoxy values were obtained (approximately 120 min). The monomer/initiator addition time was 180 min and the processing temperature was  $115 \pm 2^\circ\text{C}$  [15,16]. The resin test results are shown in Table 3.

### Preparation of emulsion

The acrylic cathodic electrodeposition emulsion is prepared in the steps given below.



**Figure 1.** Flowchart of synthesis of electrodepositable mono-coat coatings.

**Table 1.** Characterisation of polymer emulsions.

Acrylic cathodic electrodeposition emulsion	% Acrylic resin (A) (% by weight)	% Epoxy resin (E) (% by weight)	% solid	Ratio (A:E)
PA	100.00	0.00	72	1:0
AE1	90.00	10.00	72.4	1:0.11
AE2	80.00	20.00	72.8	1:0.25
AE3	70.00	30.00	73.2	1:0.43

**Table 3.** Physical properties of acrylic resin.

Parameter	Theoretical value	Experimental results
Non-volatile (%) by weight (2 g sample/105°C/3 h in oven)	72	72.1
Appearance (visual)	Clear	Clear
Amine value (mg KOH/g)	26	26.1
Viscosity by Gardner bubble tube	J	K

### Neutralisation process

The above prepared acrylic resin was charged with epoxy resin and polyurethane oxime resin and catalyst in a 3-L stainless steel vessel. The charged material was stirred for 15 min at 43°C. The PU (Polyurethane) curing agent, cosolvents, phase dispersing agents, emulsifier, glycolic acid and acetic acid (glacial) were added to it under agitation for 30 min for complete neutralisation. The deionised water was then added to it at 31–33°C and particle size was maintained below 0.25 µm. It is called a pre-emulsion.

### Emulsification

A 5 L stainless steel vessel was taken and to this 28% deionised water and 72% pre-emulsion were charged for emulsification. This mass was stirred at 750 rpm for 30 min with a high-speed stirrer. In this process, an emulsion is formed. The temperature during the emulsion is maintained at  $20 \pm 2^\circ\text{C}$ . The emulsion was processed and the physical properties were tested as mentioned in Table 4.

### General cathodic electrodeposition chemistry

One of the popular polymeric materials used in cathodic electrodeposition is polyacrylate graft copolymer. The process of grafting is similar to that of chain transfer, where acrylic chains are attached by hydrogen abstraction. This graft copolymer is having polyamine/epoxy ester with acrylic polyamine backbone. This contains reactive groups of secondary amine and hydroxy functional groups in which some of the primary hydroxy groups are available at the terminal. The epoxy resin reacts with fatty acids to form a mono-epoxide ester that has a ratio of one or less epoxy groups per acid group. This ester is made to react with some portion of secondary amine available with acrylic backbone. This mechanism is designed for near-neutral pH. The cathodic dispersion thus formulated is having decent cure response at 160°C if conventional blocked aliphatic isocyanates cross-linkers are used.

**Table 2.** Physical properties of pigment paste.

Parameter	Theoretical value	Experimental results
Physical appearance (visual)	Homogeneous, free from bits	Homogeneous, free from bits
Non-volatile (%) by weight (2 g sample/120°C/1.5 h in oven)	40	39.8
Viscosity by Brookfield (cps)	85	80
pH value	5.5	5.6
Specific gravity ( $\text{g}/\text{m}^3$ )	1.20	1.19
Conductivity ( $\mu\text{S}/\text{cm}$ )	1400	1450

**Table 4.** Physical properties of prepared emulsion.

Test parameter	Theoretical value	Experimental results
Physical appearance (visual)	Homogenous and free from foreign matter	Homogenous and free from foreign matter
Non-volatile (%) by weight (2 g sample/120°C/2 h in oven)	34	33.8
Particle size (µm)	0.30	0.15
Viscosity (cps)	45	40
Specific gravity (g/m <sup>3</sup> )	1.06	1.05
pH value	5.50	5.90
Conductivity (µs/cm)	1050	1010
MEQ (milliequivalent)	28	28.5

### Modification of epoxidised acrylic resin to form adduct



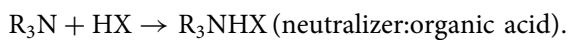
Epoxidized acrylic resin (water insoluble) + Secondary amine (water insoluble) → Modified epoxy acrylic resin or Adduct (water insoluble)

### Neutralisation



Modified epoxy resin or Adduct (Organic acid) (water insoluble) + RCOOH → Neutralized adduct (water soluble)

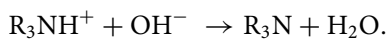
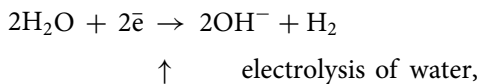
or



In this, water-dispersed positively charged resins and pigments are deposited on a conductive substrate.

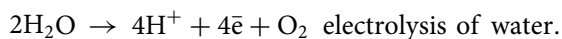
### Ionisation

At cathode (articles),

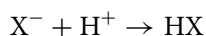


The positively charged resin  $\text{R}_3\text{NH}^+$  (water soluble) is deposited as  $\text{R}_3\text{N}$  (water insoluble deposit) on the substrate after an electrical discharge at the cathode as shown in Figure 2.

At anode (electrode),



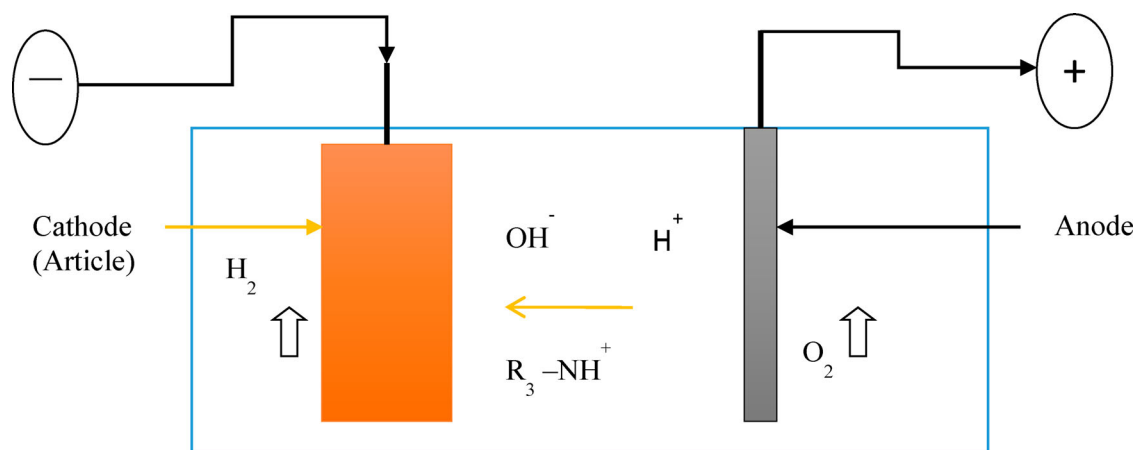
At the anode, the counter ions are neutralised by  $\text{H}^+$  ions and acid is produced.



drains the electrolyte to maintain pH.

### Preparation of panels

The test panels were made of mild steel material (iron 99.35%, carbon 0.16%, silicon 0.17%, copper 0.1%, manganese 0.15% and aluminium 0.07%). The standard dimensions (length × width × thickness) of mild steel panels for cathodic electrodeposition coatings are 150 mm × 50 mm × 0.25 mm. The panels are made in accordance with the standard procedures described in ASTM D 609. The panels were prepared according to the sequence described: the mechanical cleaning of the panel by using 400 # abrasive paper, degreasing process, rinsing process, pickling process with hydrochloric acid solution at 1:1 dilution ratio for 30 s, after rinsing with deionised water, these panels are phosphating for 3 min at 50–55°C as conversion coating based on zinc phosphate, passivation by chrome-free passivating agent and finally rinsing. The composition of phosphating chemicals consists of zinc phosphate, phosphoric acid, nickel nitrate, etc. which were



**Figure 2.** Acrylic cathodic electrodeposition process.

purchased under the brand name of Nipaphos 3020M, owned by M/s NIPA Chemicals Ltd., Chennai, India, and were dissolved in deionised water to form an aqueous solution of 20 g/L of zinc phosphate concentration. It was used for phosphate pre-treatment of mild steel panels [17].

### Coating formulation and film preparation

A homogenous mixture was prepared with 35% emulsion, 2.5% pigment paste and 62.5% deionised water in the bath for electrodeposition (Figure 1). The physical parameters of coating were solid content 12–16%, pH value 4–6, conductivity 600–1200  $\mu\text{S}/\text{cm}$ , MEQ-value 25–35 (milliequivalent acid/100 g solid resin) and low VOC content < 10 g/L.

Acrylic cathodic electrodeposition paint was applied to the pre-treated mild steel panels through an electrodeposition process, in which the pre-treated panels were placed at the cathode position and the bare panels at the anode position [12,13]. The ED rectifier 'Allied Electrodeposition Apparatus'/A.C. input voltage and D.C. output voltage power supply were used for electrodeposition. Its manufacturer is Allied Scientific Equipments, Mumbai. The D.C. (direct current) voltage (125–250 V) was applied for 1–3 min. The panels were then flushed and baked for 20 min at 160°C. The thickness of the coated film can be controlled by voltage and/or application time. A coating thickness of 25–28  $\mu\text{m}$  (microns) was maintained. After three days of maturation, the cured films were tested under ambient atmospheric conditions.

### Characterisation of physical parameter of pigment paste/resin/emulsion

#### Determination of viscosity

The viscosity of the pigment paste and the prepared emulsion was determined by a Brookfield viscometer at 28°C spindle no. 2 at 30 rpm, CAP 2000 (Sheen Instruments Limited, England). And the resin

viscosity was tested by a BYK Gardner bubble tube viscometer at 25°C with a sample/butyl cellosolve ratio of 16:7.

#### Determination of solid contents

The solid content was determined by placing 1–2 g of sample in a weighing dish and then drying until all volatiles were removed in the oven for the specified temperature and time.

The % non-volatiles are calculated as per the formula =  $\{(W3 - W1)/(W2 - W1)\} * 100$ , where  $W1$  is the weight of the empty disc,  $W2$  is the weight of empty disc + resin material and  $W3$  is the weight of empty disc + dried resin material.

#### Determination of epoxy and amine value

The epoxy value and amine values of the resins were determined by titration. The epoxy value is the number of moles of the epoxy group per 100 g of resin. The amine value is determined as the weight (in mg) of KOH required to neutralise 1 g of sample with protonated amine groups.

#### Determination of pH value

The pH value was determined by a digital pH meter (Komal Scientific Company India). It is used to test acidic and alkaline mediums.

#### Determination of particle size

The particle size of an emulsion is an important property that affects the viscosity of the emulsion, minimum film-forming temperature (MFFT) of the emulsion, the performance of the film and the stability of the emulsion against separation/settling. The particle size of the emulsion can be measured using a UV spectrophotometer, LASER (Light Amplification by Stimulated Emission of Radiation), diffraction spectroscopy.

### Determination of specific gravity

The weight per gallon cup (Komal Scientific Co. India) was used to determine the specific gravity of the pigment paste, emulsion and final application paint.

### Determination of conductivity

The conductivity of pigment paste, prepared emulsion and application paints was measured by a digital conductivity meter (Metler-Toledo Pvt Ltd, England).

### Determination of milliequivalent

The unit of measurement of the amount of chemical activity of an electrolyte is the milliequivalent. Automated potentiometric titrator (Spectra Lab Instruments Pvt Ltd, India) was used to test for milliequivalents. It was calculated as milliequivalent acid/100 g solid resin.

### Determination of Fourier transformed infrared

Fourier transformed infrared (FTIR) spectroscopy data of prepared resins were recorded using a NaCl cell on a Perkin Elmer 1750 FTIR spectrophotometer. The infrared spectra were studied for distinguishing bands of synthesised resins to check and confirm the uniqueness of experimental resins.

### Characterisation of prepared polymer emulsions

The prepared polymer emulsions were characterised for chemical and mechanical properties.

Coating samples as grafted poly acrylic resins were coded as PA and those grafted polymers with epoxy content of 10%, 20%, and 30% were coded as AE1, AE2, and AE3, respectively, as that is shown in Table 1.

### Characterisation of film properties

The paint coatings applied on panels as above were characterised for corrosion resistance properties such as salt spray test outcome (Table 5) and humidity test outcome (Table 6). The paint coated panels were also assessed for their chemical resistance properties like water resistance properties (Table 7), acid resistance properties (Table 8), alkali resistance properties (Table 9), and mechanical properties like adhesion,

**Table 6.** Humidity test results.

Parameter	Specification	Polymer	Results
Humidity	Humidity cabinet temperature: 50 ± 2°C, relative humidity: ≥95% for 500 h	PA	Inferior
		AE1	Slight inferior
		AE2	Passed
		AE3	Passed

**Table 7.** Water resistance of paint films.

Sample	Polymer	Deionised water	Sea water
Acrylic cathodic electrodeposited panel	PA	P	R
	AE1	P	Q
	AE2	P	P
	AE3	P	P

Note: P = unaffected, Q = slightly affected and R = affected.

**Table 8.** Acid resistance of paint films.

Sample	Polymer	Acetic acid		Hydrochloric acid	
		5% (v/v)	15% (v/v)	5% (v/v)	10% (v/v)
		Acrylic cathodic electrodeposited panel	PA	VG	G
	AE1	VG	G	G	S
	AE2	Ex	Ex	Ex	VG
	AE3	Ex	Ex	Ex	Ex

Note: Ex = excellent, VG = very good, G = good, S = satisfactory and P = poor.

hardness, flexibility, impact resistance and gloss (Table 10).

### Corrosion resistance properties

**Salt spray test.** The salt spray test was performed at 35 ± 1°C with 5% NaCl in distilled water. Panels were placed at 15–30° angle to vertical and fog collection was 1–2 mL/h. The tested samples were cleaned with deionised water, dried and tested within 1/2 h in accordance with ASTM-B117 and ASTM D1654. After the stipulated 500 h, the creep-age test was assessed with an X mark. There should not be any rust, blister and adhesion failure beyond 2 mm from the X mark (Table 5).

**Humidity test.** Humidity testing was performed in a humidity cabinet maintained at 98–100% relative humidity at a temperature cycle of 42–48–42°C/h. The distilled water was taken to maintain humidity

**Table 5.** Salt spray test (ASTM-B117) results.

Parameter	Specification	Polymer	Creep-age (mm)	Blister size (grade)	Blister density
Salt spray resistance	Crosscut mark on coated panel, 500 h exposure, creep-age width on either side of scribe line 2.0 mm max and blister size max 8F	PA	2.5	6	Medium dense
		AE1	2.1	4	Medium dense
		AE2	1.5	4	Medium
		AE3	1.2	2	Medium

**Table 9.** Alkali resistance of paint films.

Sample	Polymer	Sodium hydroxide		Ammonium hydroxide	
		5% (w/v)	15% (w/v)	5% (v/v)	10% (v/v)
Acrylic cathodic electrodeposited panel	PA	VG	G	VG	S
	AE1	VG	G	VG	G
	AE2	Ex	Ex	Ex	Ex
	AE3	Ex	Ex	Ex	Ex

Note: Ex = excellent, VG = very good, G = good, S = satisfactory and P = poor.

and the samples were examined in accordance with IS 101 (Part 6/Sec.1)1988 (Table 6).

### Chemical resistance properties

The chemical resistance properties of the cured films were assessed by immersion in a chemical method based on ASTM D 1308-02 and ASTM D 5402-19. Various immersion tests were performed to assess the water and different chemical resistance properties of the dried film. The exposure of the film to different chemicals can reduce the gloss, change the colour and produce a swelling or softening of the film. In the extreme case, the film can strip from the substrate or can be destroyed by solvent action.

The chemical resistance properties tests like water resistance test, acid resistance test and alkali resistance test were executed on the applied coating as mentioned earlier. Subjected tests were carried out after the maturation of all panels at ambient temperature [18]. The molten wax was used for sealing the three sides of the coated panel before immersing in different chemicals. The coated films were examined after the action of chemicals like water (Table 7), acids (Table 8) and alkalis (Table 9).

**Water resistance properties.** The water resistance results with respect to deionised water and seawater are shown in Table 7. The coated panels were half-immersed in a water bath at 40–50°C for 120 h and the exposed panels were assessed in deionised water and seawater.

**Acid resistance properties.** The acid solutions were prepared on a volume basis, by diluting the required quantity of acids with water to the preferred concentration. The subsequent concentrations of different acids were used, acetic acid (5% and 15%) and hydrochloric acid (5% and 10%). The coated glass panels were immersed in these chemicals for 24 h at ambient temperature. The acid resistance test of the films is shown in Table 8.

**Alkali resistance properties.** Alkali resistance was tested with sodium hydroxide and ammonium hydroxide chemicals. Five percent and 10% concentration of sodium hydroxide solution was prepared with dissolving in water on the basis of weight per volume. Ammonium hydroxide was diluted at 5% and 10% concentrations in water on the basis of volume. Coated panels were dipped in these freshly prepared chemicals at an ambient temperature for the duration of 24 h. The alkali resistance of the coating is given in Table 9.

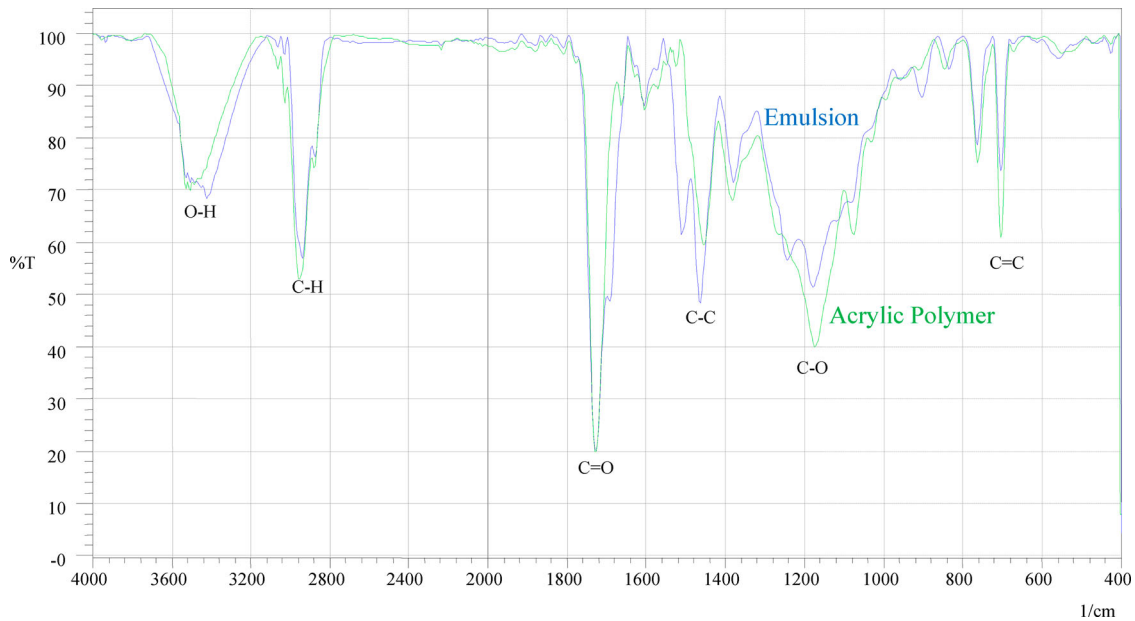
### Mechanical properties

**Determination of hardness.** The coating hardness was tested by the indent mark test which was measured by a scratch hardness tester (ASTM D 5178-16, Sheen Instruments Limited England). A panel was kept on the sliding base with the coated side upwards. Under

**Table 10.** Mechanical properties of paint films.

Sl. no.	Parameter	Specification	Polymer	Results
1	Hardness (scratch hardness tester)	Specific load 1800 g	PA	Inferior
			AE1	Passes
			AE2	Passes
			AE3	Passes
2	Adhesion crosshatch (1 × 1 mm) tape tester	The number of squares (coated film) is retained in mild steel	PA	Passes 100/100
			AE1	Passes 100/100
			AE2	Passes 100/100
			AE3	Passes 100/100
3	Flexibility (1/8 in. conical mandrel bend tester)	Coated panel was bent at 180° on mandrel having a conical rod of diameter 4–32 mm	PA	Passes
			AE1	Passes
			AE2	Passes
			AE3	Passes
4	Impact resistance (tubular impact tester)	Weight drop of 2 pounds at 50 cm height – no cracking or flaking observed on the impacted area	PA	Passes
			AE1	Passes
			AE2	Passes
			AE3	Passes
5	Gloss at 60° (tri-glossometer)	Minimum 85 unit	PA	90 unit
			AE1	88 unit
			AE2	87 unit
			AE3	85 unit





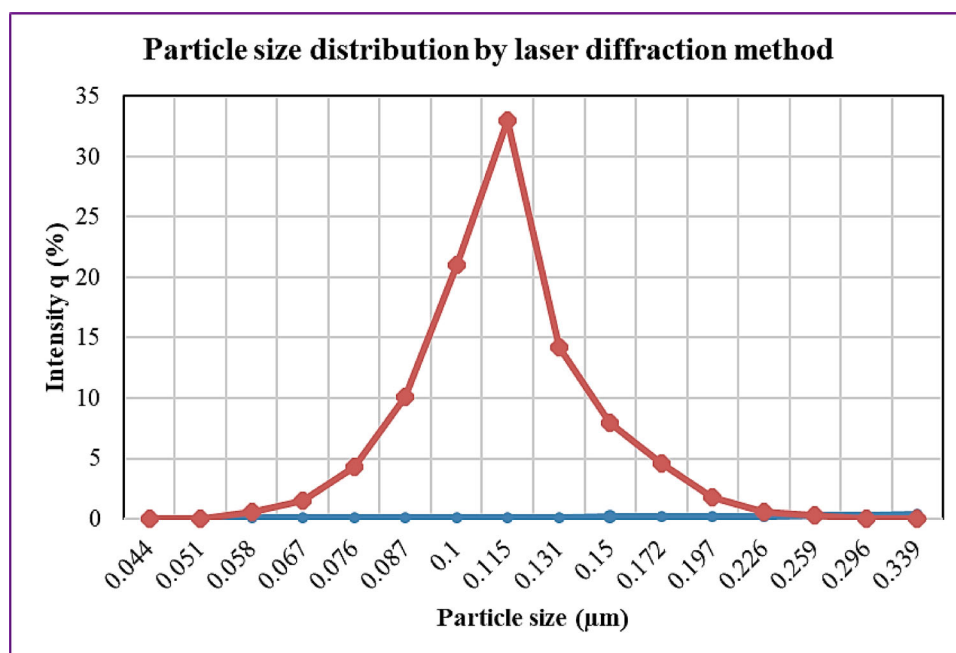
**Figure 3.** IR spectrum of emulsion overlapped with the spectrum of acrylic polymer.

a specific load, the needle was kept mounted on the panel and the panel was drawn under the needle. The test was repeated by increasing the load till a flawless scratch viewing the bare metal surface is observed. The results correspond to the maximum load the film takes before scratching shown in Table 10.

**Determination of adhesion.** The crosshatch adhesion tester (Sheen Instruments Ltd., England, as per ASTM D 3359-17) was used to test the adhesion of paint films. The testing equipment is made up of hardened carbon steel containing nine parallel blades 1/16 in. apart and 1 in. in length. The blades are having

tips with a radius of 0.003–0.004 in. with shoulders making the angle of 60° with one another. The test panel is subject to die under pressure where the die is moved in two directions at right angles to each other, superimposing the second move on the first, giving a square shape. A self-adhesive strip was stacked over the square pattern and left in contact for 10 s. The strip was pulled rapidly at an angle of ~120°. The adhesion properties were determined by the number of squares left on the panel and coating results are shown in Table 10.

**Determination of flexibility.** A 1/8 in. conical mandrel bend tester (Sheen Instruments Ltd, England, as per



**Figure 4.** Particle size distribution of acrylic graft polymer emulsion.

ASTM D 522-17) was used to determine the flexibility of paint films. The coated panel was bent at 180° on Mandrel having a conical rod of diameter 4–32 mm. A mild steel panel was inserted between the hinges and rod keeping the coated side outward from the direction of bending. The coated panel was bent through 180° in one second without giving any jerk. The coating was examined immediately after bending and before removing it from the hinge against loss of adhesion and cracking. The coating results are shown in Table 10.

**Determination of impact resistance.** The impact resistance test measures a combination of toughness and adhesion of coatings. Impact resistance was measured using a falling weight type tubular impact tester (Sheen Instruments Ltd, England, ASTM D 2794-93). This test was performed on cured film adhering over mild steel panels. In this, a weight of 2 pounds of a hemispherical shape was dropped at the base onto a specimen, and placed at the base of the instrument from a height of 50 cm. The test was carried out with the uncoated side facing the falling weight. The film was checked for any crack or detachment at the peak of the bulge as results shown in Table 10.

**Determination of gloss.** The glosso-meter directs a light at a specific angle to the test surface and simultaneously measures the amount of reflection. The coated panel was subjected to light and reflectance was quantified. The angle of light and the method by which reflectance is measured are determined by the surface. The tri-glosso-meter (20°, 45° and 60°) as per ASTM D 523-14 (BYK Gardner) was used to measure the gloss and the results are shown in Table 10.

**Gloss retention.** A QUV weatherometer was used to measure the gloss retention property of the coating. The paint films were subjected to alternate cycles of UVA-340 nm radiations for 4 h at 50°C and condensation for 4 h at 45°C with an irradiance of 0.67 W/m<sup>2</sup> using a UVB 313 lamp. This was followed by condensation at 50° cycle for 800 h test. The cycles were repeated and the coating was inspected for gloss retention as per ASTM D523 and colour as per ASTM D2244. The test results of gloss retention are shown in Figure 10.

## Results and discussion

### Physical parameter results of pigment paste/resin/emulsion

The physical parameters of the pigment paste, synthesis of acrylic resin and the prepared emulsion were characterised and evaluated with the results given in Tables 2–4, respectively.

### Spectral analysis

The polymer characterisation was performed by FTIR analysis. The FTIR analysis method uses infrared light to scan the prepared test samples and observe the chemical properties. The IR spectrum analysis was performed to confirm the presence of reactive functional groups in the monomers and to confirm that all groups reacted completely. Theoretically, all monomers should react and no unreacted monomer groups should be present in the final polymer. Acrylic monomers with reactive functional groups can be used to functionalise acrylic polymers to deliver properties such as grafting, crosslinking, self-crosslinking, improved adhesion or pigment wetting. The graphical peaks at 3560, 2959, 1734, 1440, 1146, and 720 cm<sup>-1</sup> result from O–H, C–H, C=O, C–C, C–O and C=C stretch vibrations, respectively. Acrylic resins functionalised with hydroxyl function were characterised as peaks at 3560 cm<sup>-1</sup> to confer grafting properties. The IR spectra of acrylic polymer and acrylic-epoxy emulsion are shown in Figure 3.

IR spectrum of emulsion and acrylic polymer are overlapping and showing the present groups in the spectrum in Figure 3, where it indicates monomers group existence in final emulsion products.

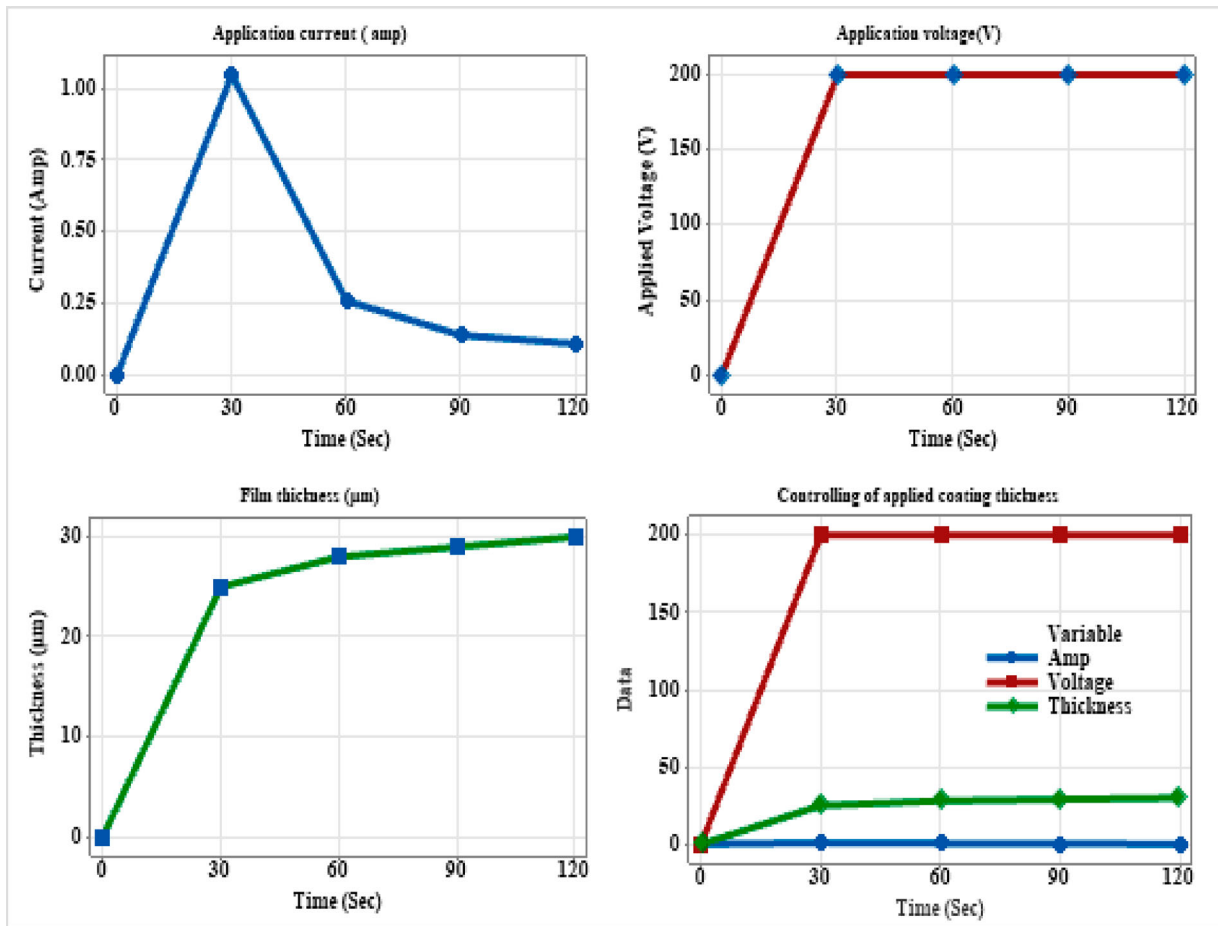
### Analysis of particle size distribution

The particle size graph (Figure 4) depicts the particle size and particle size distribution of acrylic graft polymer emulsion. The emulsion has a narrow range of particle size distribution, less than 0.30 μm. The particle size, distribution and concentration play important quality characteristics for the optimum functionality and workability of the emulsion. The film formation and pigment-binding ability are enhanced by fine particles. The finer particles of the synthesised emulsion provide superior film integrity and packing, resulting in excellent chemical and physical properties [19,20].

### Controlling applied coating thickness

In electrodeposition, the amount of deposition of coating material on the surface decreases with time. As the film begins to form, the conductivity of the coating layer decreases. The thickness of the film also depends on the softness of the electrodeposition – coat ( $T_g$  of the resin/polymer). The normal film thickness in electrodeposition is 20–30 μm which can go up to 50 μm in high film build. The basics of film thickness in electrodeposition are given here below:

- (1) The rate of deposition of paint/coating on the metal surface is a function of the local current density.



**Figure 5.** Paint film deposition thickness controlled by voltage and application time.

- (2) The local current density is maintained by electric potential and there is a linear relationship between surface potential and current density.
- (3) This relationship depends upon the existing paint film thickness and the properties of the paint [21–23].

Figure 5 shows coating thickness performance vs. time. Initially, the current density is increasing to the maximum level, then decreases after increasing time due to the insulation of the coating over a period at a constant voltage.

### Minimum coalescing temperature

The important variable of cathodic electrodeposition coating is the coalescence temperature. At constant application voltage and coating deposition time, minimum coalescing temperature (MCT) can be determined by plotting a graph between film build ( $\mu\text{m}$ ) vs. bath temperature ( $^{\circ}\text{C}$ ). At temperatures at and above MFFT of the polymer, the smooth film is formed. At temperatures below the coalescence temperature (MCT), the film growth behaviour led to the study and optimisation of the film thickness of the coatings (Figure 6).

At temperatures below the MFFT of the polymer, a continuous film is not formed as the polymer cannot

coalesce and thus causes an irregular deposition film with cracks. An accurate MFFT value indicates the completeness of product formulations that are properly cured under specified application conditions. As shown in Figure 6, the regular deposition of the coating started at  $28^{\circ}\text{C}$ .

### Corrosion resistance properties of acrylic cathodic electrodeposition films

Corrosion is the destruction of metal that can be detected by rust formation. Corrosion resistance properties results are given in Tables 5 and 6, and it can be observed that the incorporation of epoxy resin and acrylic grafting polymers helped to develop a coating with improved salt spray resistance and humidity. The corrosion resistance properties of the developed coating were optimised with the increase of epoxy content in the coatings [15,24–28].

### Salt spray test

The salt spray test was carried out as per the specification mentioned in section 'Salt spray test' and the results are shown in Table 5. The exposed electrodeposited films were evaluated by corrosion creep-age (in mm) by scribe, number (density) and size of

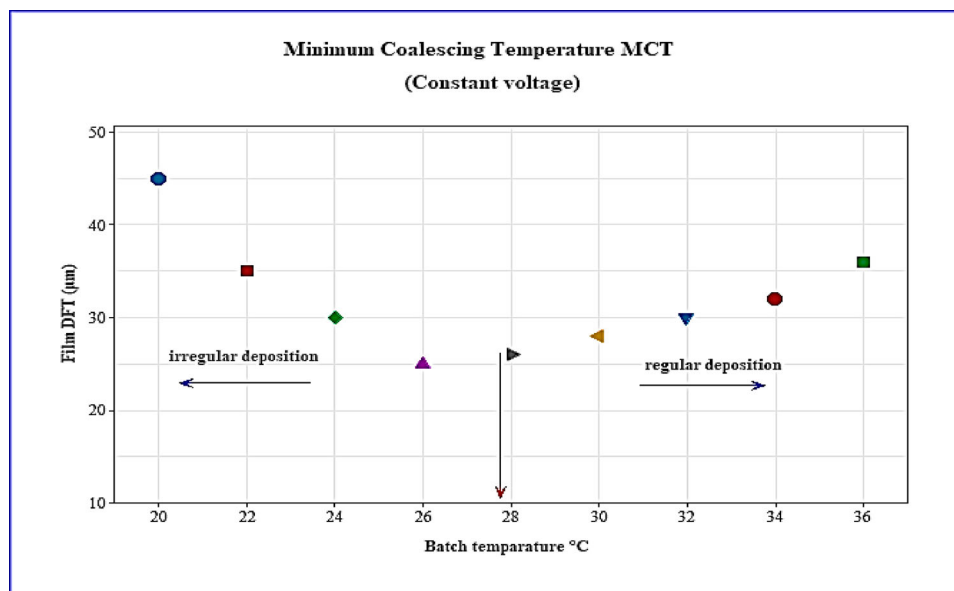


Figure 6. MCT and DFT ( $\mu\text{m}$ ).

developed blisters. The blisters were assessed as per ASTM B 117-94.

The corrosion creep-age in the scribes was very low, between 1.2 and 2.5 mm, with small blister sizes (2–6 grade) for all coated films after continuous exposure to the salt spray test.

Figure 8 illustrates the corrosion resistance test results of prepared samples. The creep-age analysis plots and blister analysis plots illustrate the reducing trend of creep-age (mm) and blister size (grade) from PA to AE3 polymer emulsions. The salt spray test results of polymers show the correlation between creep-age (mm) and blister size (grade).

The results of the analysis of samples exposed to salt spray tests are shown in Table 5, Figure 7 and Figure 8. It is observed that corrosion resistance of the film in AE3 and AE2 polymer emulsions was relatively better and within specification than that of AE1 and PA polymer emulsions after 500 h of uninterrupted exposure to a saline (salt spray) atmosphere.

### Humidity test

The humidity test was performed and the results are shown in Table 6.

There was found no rust formation, no blisters, no adhesion failure, no change in gloss and film appearance, after 500 h in AE2 and AE3 polymers film but inferior results were seen in PA and AE1 emulsion polymer. The adhesion tests are shown in Figure 9.

The corrosion resistance test results are depicted in Figure 7. The panels AE2 and AE3 do not show any rust or blister. The films of AE2 and AE3 are well intact and do not show any signs of adhesion failure in Figure 9. The panels of PA were significantly affected and showed blisters, rust in Figure 7, and loss of adhesion in Figure 9. The panels of AE1 were

less affected by corrosion, blistering and adhesion than panels of PA.

### Water resistance

The exposed panels were assessed as unaffected by deionised water and found that the seawater resistance of the film is unaffected in AE3 and AE2 against AE1 and PA emulsion polymers as shown in Table 7.

### Acid resistance

The functional group of epoxy resin, cured with a curing catalyst, builds the high dense chemical structure. Acid resistance increases with an increase in the epoxy resin content from AE1 to AE3 as shown in Table 8.

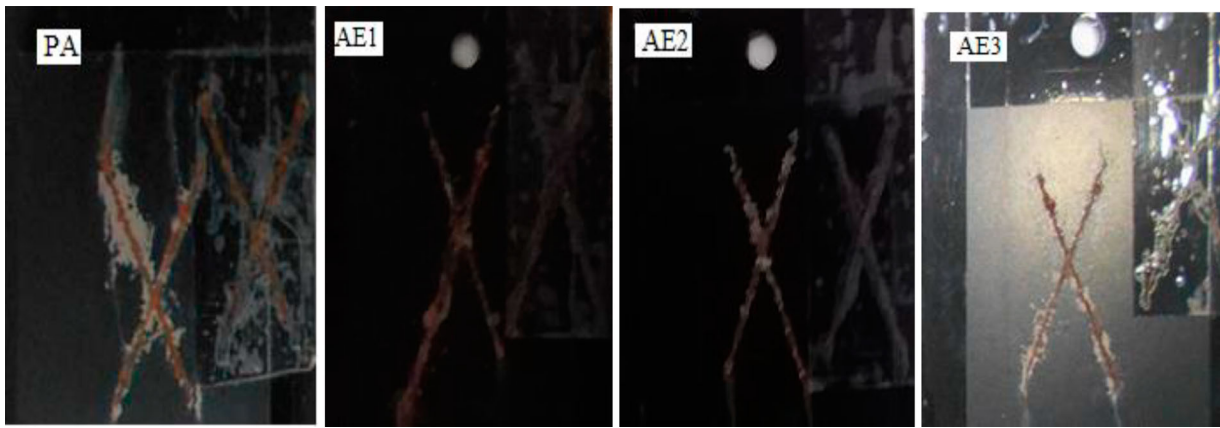
### Alkali resistance

The alkali resistance performance of all coatings, from acrylic resin to epoxy modified acrylic resin, was found to be satisfactory to excellent as shown in Table 9.

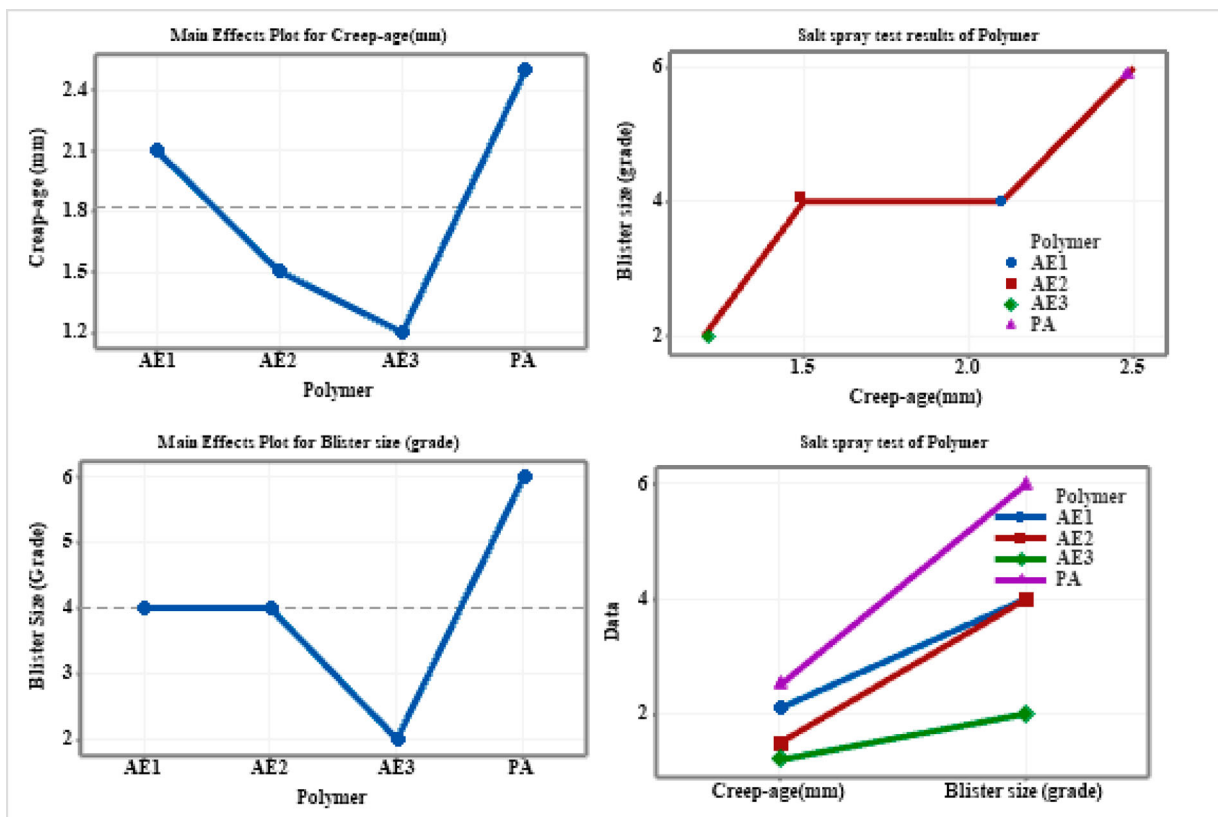
The assessment of immersed coated panel rated as no staining, dulling, peeling, blistering, softening or discoloration observed means excellent resistance. Poor means the coating is showing such abnormality as staining, dull, peeling, blistering, softening or discoloration.

### Mechanical properties of paint films

The mechanical properties are given in Table 10, and it can be seen from the data given in the table that the film hardness is better in AE3, AE2, and AE1 as compared to PA. This is due to the presence of high epoxy content. The adhesion test data show that all samples pass the adhesion test due to the hydroxyl group in epoxy resins. Flexibility test data also show



**Figure 7.** Corrosion resistance performance of electrodeposited polymer coatings after 500 h of exposure to salt spray.



**Figure 8.** Corrosion resistance performance analysis of prepared samples.

comparable results. The impact resistance is showing considerable improvement in the performance of polymer grafting in acrylic-epoxy emulsion systems. The gloss value is showing a decreasing trend from PA to AE3 polymer emulsion film. Thus it is seen that increase in optimum epoxy content gives better performance in terms of hardness and impact resistance. While the adhesion and flexibility of the system remain unchanged [29–32].

#### Gloss retention

The graph shows the gloss retention of different coatings as shown in Figure 10. The coatings AE2 have 80% gloss retention after 500 h of UV exposure

which is almost equal to 800 h of exposure to PA. The UV resistance of acrylic polymer (PA) is better than that of acrylic-epoxy polymers (AE1, AE2 and AE3). The UV radiation breaks the chemical bonds in the epoxy polymer. This process is called photodegradation. The photodegradation of various resins is related to the type of ester group and the presence of the  $\alpha$  methyl group in the main chain which has a low binding energy in the chain. The degradation of methyl group to main chain of epoxy produces carbonyl group. UV light absorbed by carbonyl groups can include bond scission by either Norrish type I or type II processes. In breaking the polymer chains, produces free radicals and reduces the

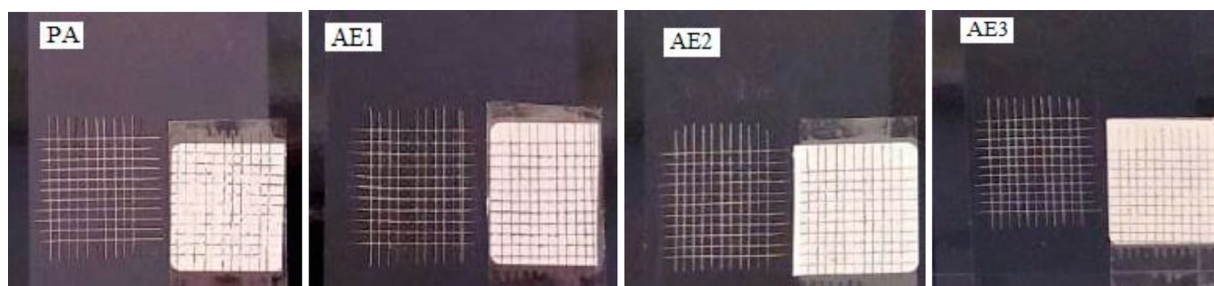


Figure 9. Adhesion test of polymer coated films.

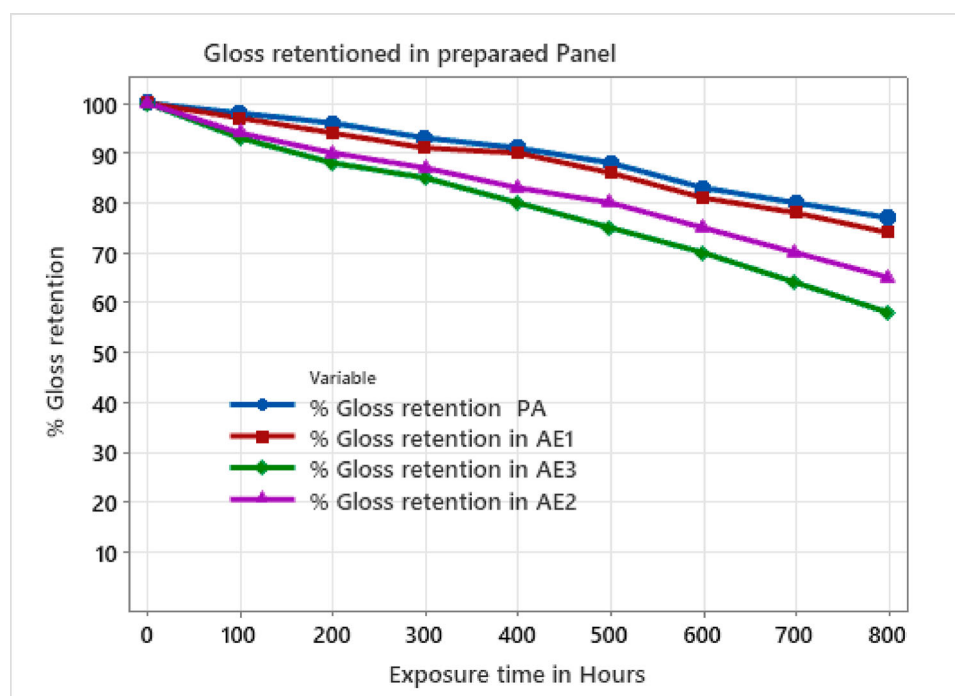


Figure 10. Gloss retention performance of the coatings.

molecular weight causing chalking, colour changes, cracking and loss of physical properties. In the photo-degradation of acrylic polymers, chain scission results in terminal carbon-carbon unsaturation. The concentration of unsaturated molecules increases as the fragmentation of the polymer chains increases. Acrylic grafted polymer protects the chemical bond to sustain the UV radiations. This was due to the presence of different functional groups (hydroxyl, carbonyl and amines) in the acrylic monomers and cross linker.

It is observed that the gloss retention decreases with an increase in the epoxy content, but at the same time, the corrosion resistance of the coating increases. Epoxy resins provided anticorrosive properties due to their extensive conjugation to polar functional groups such as  $-OH$ ,  $-CONH_2$ ,  $-NH_2$  and aromatic rings that can act as adsorption centres during their interactions with the metal surface. Epoxy resins adsorb at the interface of metal and environment (electrolyte) and form protective film. Therefore, the optimum ratio (80:20) of acrylic

resin and epoxy resin was selected in the developed coating.

## Conclusion

The grafted acrylic-epoxy system is synthesised by emulsion polymerisation in aqueous media. This polymer emulsion contains much lower VOCs than conventional systems, thus making the system eco-friendly. Following are the key features of the coating:

- The performance data depict that increasing the epoxy content improves the corrosion resistance and chemical resistance properties of the coating. The presence of an acrylic backbone improves the mechanical properties, e.g. adhesion, flexibility and toughness.
- The system can be used in the high-build mono-coat coating as it provides good corrosion resistance (500 h) and outstanding outdoor durability (500 h). For this system, an acrylic/epoxy ratio of

80/20 (AE2) has been found to be suitable compared to 90/10 (AE1) and 70/30 (AE3).

- Steps in application of the coating can be reduced to 3 (pre-treatment, single coat and baking) from 5 (pre-treatment, primer, baking, topcoat and baking) as used in the conventional process. Thus there are savings in painting cycle time and energy (since a baking step is eliminated) as well as savings in coating materials, which will reduce the process cost.
- Acrylic-epoxy system based coating has distinct advantages such as multi shades, mono-coat, good gloss retention, low solvent emission, low energy involvement, uniform coverage and better edge protection leading to better corrosion resistance and good UV protection.

This technology will have fast growth in application industries specially the automobile sector due to overall cost-cutting, economical use of materials, manpower, capital investment, energy, etc. which is claimed to be around 30–40% as compared to conventional coatings and application systems.

### Disclosure statement

No potential conflict of interest was reported by the author(s).

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