

Water-Borne Melamine–Formaldehyde-Cured Epoxy–Acrylate Corrosion Resistant Coatings

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ABSTRACT: Organic protective coatings are widely used in corrosion control. However, environmental standards establish that the volatile organic compounds either must be removed or controlled at the lowest possible levels. The carcinogenic environmental impact of volatile organic compounds has led to the substitution of solvent-borne coatings by water-borne coating systems. Among recently developed water-borne coatings, epoxy- and acrylic-based coatings have a special significance over other reported water-borne systems. Keeping in mind, the importance of water-borne coatings in the present work, we report the synthesis of water-borne epoxy–acrylate (EpAc) and melamine–formaldehyde (MF) as well as formulation of their anticorrosive coatings. The structural elucidation of MF-cured EpAc was carried out by FTIR, ^1H NMR, and ^{13}C NMR spectroscopic techniques. The

coatings of EpAc-MF were applied on mild steel strips and were evaluated for physicochemical, physicomachanical characterization, and the anticorrosive performance under different environmental conditions. The present coating system EpAc coatings exhibited superior performance as compared to the reported water-borne epoxy–acrylate coatings. The presence of melamine–formaldehyde in the resin increases the scratch hardness, impact resistance, alkali resistance, and thermal stability of these coatings. EpAc-MF-1 was found to cure at ambient temperature and exhibit good physicomachanical properties. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 215–222, 2008

Key words: epoxy–acrylate; water-borne; melamine; anticorrosive; ambient-cured coatings

INTRODUCTION

Green Chemistry Revolution has provided an alternate mode for the chemists and industrialists to develop polymers via eco-friendly route, to minimize the utilization of toxic chemicals, particularly organic solvents, which are hazardous to health and environment.¹ These solvents act as vital constituents for paints and coatings industry. The Clean Air Act of 1972 of USA and its Amendment of 1990 ushered a new era in coatings and paints industry and has compelled the Scientists and technologists to innovate Green technologies like powder coatings, UV-cured coatings, solvent-less coatings, and water-borne coatings.²

Efforts are being made to develop industrially viable water-based coating systems.^{3,4} Several water-borne coatings have been developed, which are showing superior properties than those of solvent-based systems.⁵ Water-borne coatings exhibit water white color, good weather stability, better durability

as well as good physicomachanical properties.⁶ Lately, ambient-cured water-based polymer systems such as alkydes,⁷ polyepoxies,⁸ polyurethanes,^{9,10} and polystyrene¹¹ have been developed by the incorporation of acrylic derivatives. These systems were found to meet all the technical requirements required for long-term stability. Such coatings were found to exhibit higher polarity, better transparency, good dispensability, and excellent adhesion properties.^{12–14}

Generally, epoxy-based coating materials possess versatile properties such as good adhesion, high strength, and good corrosion resistance. However, they have poor or low fracture energy, high shrinkage, and show brittle behavior.¹⁵ Epoxy resins are being cured by a variety of curing agents¹⁶ to formulate a wide range of thermosetting plastics, protective coatings, and adhesives.^{17,18} In their virgin forms, epoxies are water insoluble. To develop epoxy-based water-borne coatings with improved performance of epoxy, some modifications in epoxy have been accomplished by previous workers either through chemical modification at the backbone of the virgin epoxy resin or by the use of water-soluble curing agents. Generally, solvent-borne curing agents are used for the curing of epoxy resin. To make them water-soluble, water-miscible solvents such as ethylene glycol is used to cure the water-soluble

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epoxy–acrylic resins at ambient temperatures.¹⁹ Furthermore, it is also observed that most of the reported water-borne coating systems are developed in solvent media.^{20,21}

Keeping these facts in mind, in this manuscript, we have attempted the modification of DGEBA epoxy resin via *in situ* grafting of acrylic acid in aqueous medium. For the first time, water-soluble melamine–formaldehyde resin (MF) was used^{22,23} to cure the water-borne EpAc resin, which led to the formation of water-borne anticorrosive coating material. The structural elucidation of the resin was carried out by spectral analysis (IR, ¹H NMR, and ¹³C NMR), while the thermal stability was investigated by the DTGA. The chemical resistance properties of water-borne MF-cured EpAc coatings in acid, alkaline as well as saline water environments have also been investigated.

EXPERIMENTAL

Diglycidyl ether of bisphenol A resin, LY 556 (epoxy equiv. 180–185, sp. gr. 1.2306, refractive index 1.5685, viscosity about 10,000 CP), was procured from Ciba Specialty Chemicals, New Delhi (India). Acrylic acid and melamine (Merck, India), and formaldehyde (Qualigens, India) were of analytical grade and were used as such. Ethanediol and sodium lauryl sulfate s.d. Fine-chem (India) were used as such.

SYNTHESIS

Water-soluble melamine–formaldehyde

Water-soluble melamine–formaldehyde was prepared by reacting melamine with formaldehyde in mol ratio of 1 : 8 (melamine:formaldehyde). Six hundred milliliters (8.0 moles) of 37% aqueous formaldehyde solution was taken in a four-necked round bottom flask and heated at 50°C for 10 min. Hundred and twenty-six grams (1.0 mole) of melamine was added to the aqueous solution of formaldehyde in the mol ratio 1 : 8 (melamine:formaldehyde), and the pH of the solution was adjusted to 9 by the addition of 1.5 mL 1N NaOH solution. The circulation of cold water surrounding the reaction kettle was continued for 6 h maintaining the temperature at 55–60°C. Finally, the product (MF) was thoroughly washed with water to remove the last traces of alkali; the removal of alkali was confirmed by litmus paper test.

Water-soluble epoxy–acrylic acid copolymer resin (EpAc)

Epoxy (0.01 mole) was dissolved in the solvent blend of ethylene glycol and demineralized water (DMW) (1 : 1 v/v ratio) along with sodium lauryl sulfate

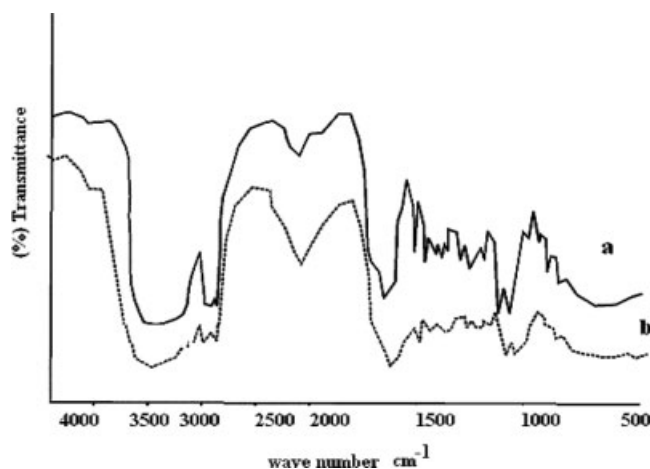


Figure 1 FTIR spectra of (a) EpAc and (b) EpAc-MF.

(0.3 g) was then placed in a four-necked round bottom flask, equipped with condenser, nitrogen inlet tube, thermometer, and magnetic stirrer heated at 100°C for 15 min. Ammonium per sulfate (1.38 g; 0.02 moles) and acrylic acid (0.1 g) were gradually added to the epoxy solution over a period of 1 h at 85°C. The reaction mixture was stirred further for 3 h and the progress of the reaction was monitored by acid value, epoxy equivalent, and TLC at regular intervals. The reaction was terminated on achieving the acid value 71 and epoxy equivalent 744. The purification of the EpAc resin obtained was carried out in a rotary vacuum evaporator to remove the unreacted impurities as well as excess of water.

Curing of EpAc-MF resin

The EpAc-MF resins were prepared by mixing EpAc and MF in solvent blend of water and ethylene glycol (50/50 v/v) under vigorous stirring at 80°C till the viscosity of the solution attained 1.18 CP. The curing of EpAc resin with MF was carried out using different weight percent of melamine as curing agent, i.e., 20, 30, and 40 wt %, and the resulting resins were designated as EpAc-MF-1, EpAc-MF-2, and EpAc-MF-3, respectively. It was observed that the coatings below 20 wt % melamine–formaldehyde (MF) failed to dry at ambient temperature due to incomplete curing of EpAc with MF, while the coatings with composition beyond 40 wt % MF were found to be brittle, which can be attributed to excessive crosslinking between EpAc and MF. Hence, the resins with optimum composition of EpAc-MF (20 wt % MF, 30 wt % MF, and 40 wt % MF) were chosen for the preparation of corrosion-resistant EpAc-MF coatings as they were found to cure at ambient temperature and form well adherent coatings on mild steel (MS).

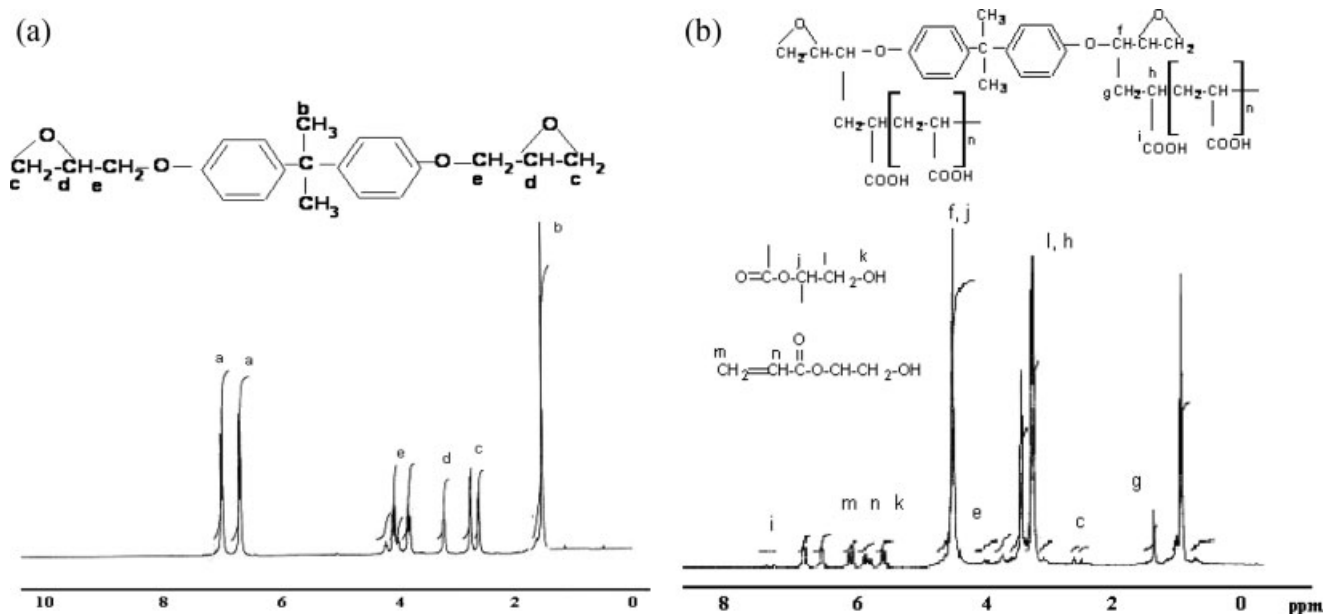


Figure 2 ^1H NMR of (a) Epoxy and (b) EpAc.

CHARACTERIZATION

Physicochemical characterization

Acid value, epoxy equivalent, hydroxyl value, specific gravity, and refractive index were determined by standard laboratory methods.²⁴ The inherent viscosity of EpAc and EpAc-MF (3% solution in ethylene glycol was used as a stock solution) were determined by Ubbelohde viscometer at 25°C.

Spectral analysis

FTIR spectra of the films of these polymers on a NaCl cell were recorded on a Perkin-Elmer (RX-1) spectrophotometer. ^1H NMR spectra of the polymer were taken on a Jeol (Peabody, MA) (JNM FX-1000) 300-MHz spectrometer with CDCl_3 as a solvent and tetramethylsilane was used as an internal standard.

Thermal analysis

DTGA (METTLER TA 4000 SYSTEM) was carried out in nitrogen atmosphere at a heating rate of 10°C/min to study the thermal stability of the cured films.

Morphological analysis

Scanning electron micrographs were taken on JEOL JSM840 scanning electron microscope under thin gold film.

Preparation and testing of coatings

The coatings of EpAc-MF resin were applied by brush on commercially available mild steel strips of $30 \times 10 \times 1 \text{ mm}^3$ size for chemical resistance and of $70 \times 25 \times 1 \text{ mm}^3$ size for physicomechanical properties. Specular gloss of these coatings was measured at 45° by Gloss meter Model RSPT 20 (Digital Instruments, Santa Barbara) scratch hardness (BS 3900), impact resistance (IS:101 part 5/sec 3, 1988), and bend test (ASTMD 3281-84) were carried out on these coatings. The coated samples were cured at room temperature. Dry-to-touch time and dry-to-hard times of EpAc-MF1 coatings were recorded as 60 min and 12 h, respectively. The thicknesses of these coatings were found to be in between 100 and

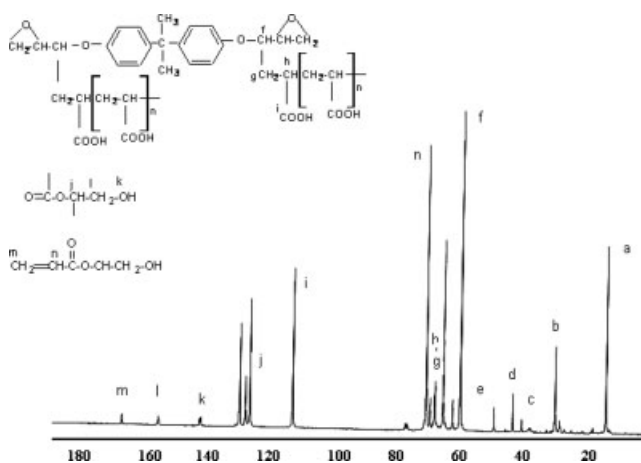
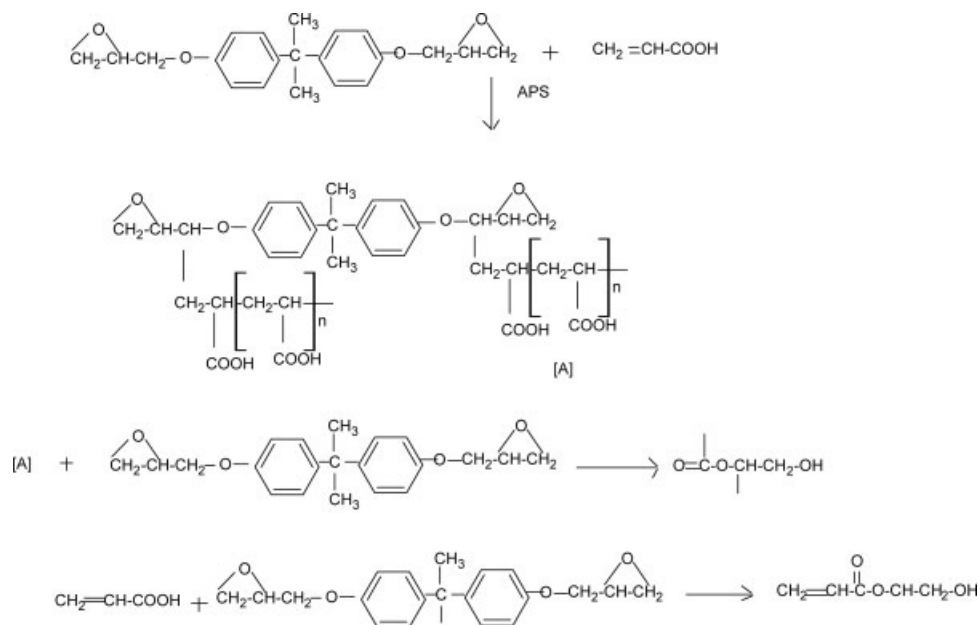


Figure 3 ^{13}C NMR of EpAc.



Scheme 1 Structure of EpAc.

115 μm as determined by Elcometer Model 345 (Elcometer Instrument, Manchester, UK). Corrosion tests were performed in acid (2 wt % HCl), alkali (2 wt % NaOH), and tap water by placing them in 3-inch diameter porcelain dishes in the aforementioned media. Periodic examination of these samples was conducted until the coatings showed evidence of softening or deterioration. Salt spray test (ASTM D 117-94) was also carried out for a period of 10 days in salt mist chamber.

RESULTS AND DISCUSSION

Spectral analysis

The structures of EpAc and EpAc-MF resins were confirmed on the basis of the FTIR and ^1H NMR spectral analysis.

FTIR

Pure epoxy (IR, cm^{-1}): 1297–1184 (C–O–C, aryl alkyl ether, asym str), 1087 (aryl alkyl ether, sym str), 2962 ($-\text{CH}_3$ of quaternary carbon), 3056.5, 1582, 787, 750 (aromatic rings, str), 2929 ($-\text{CH}_2$ sym str), 2872 ($-\text{CH}_2$ asym str), 972.4–915.8 (oxirane ring), 1381 (CH_3)²⁵.

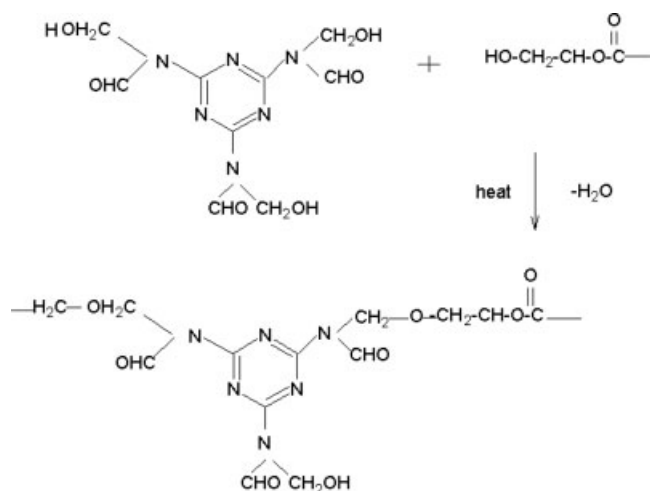
Epoxy-acrylic acid resin (EpAc) (IR, cm^{-1}): 3422 ($-\text{OH}$), 2935.5 ($-\text{CH}_2$, sym str), 2874.3 (asym str), 1298.9 (C–O–C, aryl alkyl ether, asym str), 1065.0 (aryl alkyl ether, sym str), 1639 ($-\text{COOH}$) [Fig. 1(a)].

EpAc-MF (IR, cm^{-1}): 1560 (s-triazine ring, in plane stretching), 1638 (CN), 1243–1111, 1062 (ethers linkages) [Fig. 1(b)].

The presence of a characteristic broad and pronounced band at 3422 cm^{-1} for hydroxyls and band at 1638 cm^{-1} for carboxylic group in EpAc [Fig. 1(a)] confirm the chemical reaction between epoxy and acrylic acid. The FTIR spectra of EpAc-MF [Fig. 1(b)] shows absorption peaks at $1243\text{--}1111\text{ cm}^{-1}$ and 1062 cm^{-1} for ether linkages formed by the reaction of EpAc and MF.

NMR

Pure epoxy (^1H NMR, CDCl_3) (δ ppm): 7.1–6.8 (aromatic ring protons), 4.19 ($-\text{CH}_2-\text{O}-\text{Ar}$), 3.31 ($-\text{CH}$ oxirane), 2.8–2.7 ($-\text{CH}_2$ oxirane), 1.8–1.6 ($-\text{CH}_3$) [Fig. 2(a)].



Scheme 2 Curing of EpAc with MF.

TABLE I
Physicochemical and Physicomechanical Characteristics of EpAc and EpAc-MF Resin

Characteristics	EpAc1	EpAc2	EpAc3	EpAc-MF-1	EpAc-MF-2	EpAc-MF-3
Dry-to-touch (h)	–	–	–	1	2.5	3.5
Dry-to-hard (h)	–	–	–	12	22	24
Acid value	71.4	56.24	28.88	–	–	–
Hydroxyl value	29.12	27.9	26.29	19.08	10.14	8.9
Epoxy equivalent	744	520	350	–	–	–
Specific gravity	1.09	1.08	.98	1.15	1.13	1.10
Refractive index	1.431	1.426	1.418	1.54	1.487	1.461
Scratch hardness (kg)	–	–	–	6	2	1.5
Impact resistance (150 lb/in.)	–	–	–	Pass	Pass	Fail
Bend test 1/8" in	–	–	–	Pass	Pass	Fail
Gloss at 45°	–	–	–	65	63	63

EpAc (^1H NMR, CDCl_3) (δ ppm): 6.3–6.8 (aromatic ring protons), 1.19–1.24 (protons of gem dimethyl grps), 4.3 ($-\text{CH}$ of oxirane of grafted epoxy), 3.32–3.31 ($-\text{CH}_2-\text{O}-\text{Ar}$), 5.4 (OH), 1.2 ($-\text{CH}_2$ of acrylic acid), 3.1 ($-\text{CH}$ of acrylic acid), 6.0–5.9 ($\text{CH}_2=\text{CH}-$), 3.3 ($-\text{CH}_2$ attached to OH), 6.7 (COOH) [Fig. 2(b)].

EpAc (^{13}C NMR, CDCl_3) (δ ppm): 49.3 ($-\text{CH}_2$ oxirane), 43.3 ($-\text{CH}$ oxirane), 69.4 ($\text{CH}_2-\text{O}-\text{Ar}$), 156, 142, 127.8, 113 (aromatic ring carbons), 40.5 ($-\text{C}(\text{CH}_3)_2$), 167 (carbonyl of acrylic acid), 128 and 127 ($\text{CH}_2=\text{CH}$ of acrylic acid), 68.1 ($\text{CH}-\text{OH}$), 62, 29 ($-\text{CH}$ and $-\text{CH}_2$ of acrylic acid) (Fig. 3).

In case of ^1H NMR spectra of EpAc [Fig. 2(b)], characteristic peaks of $-\text{OH}$ formed at $\delta = 5.4$, and $-\text{CH}$ and $-\text{CH}_2$ peaks of acrylic acid occurring at $\delta = 3.1$ and $\delta = 1.2$ further support the formation of EpAc by the chemical reaction of DGEBA epoxy and acrylic acid. The presence of characteristic peaks in ^{13}C NMR spectra [68.1 ppm ($\text{CH}-\text{OH}$), 167 ppm ($\text{CH}-\text{COOH}$), and 62 ppm, 29 ppm (CH and CH_2 of acrylic acid)] confirm the formation of EpAc (Fig. 3).

Physicochemical characteristics of EpAc and EpAc-MF resins

The reaction schemes for the synthesis of water-soluble epoxy-acrylic acid graft copolymer EpAc and its curing reaction with water-soluble melamine-formaldehyde EpAc-MF are given in Schemes 1 and 2,

respectively. The increase in the values of epoxy equivalent, specific gravity, refractive index, and acid value from pure epoxy to acrylic acid-modified epoxy system indicates chemical reaction of epoxy with acrylic acid leading to the formation of epoxy-acrylate copolymer (EpAc). The higher value of specific gravity and refractive index can be attributed to the dense structure of the copolymer. In case of EpAc, the presence of carboxyl group implies that the carboxyl formation occurs during the free radical addition reaction of aliphatic carbon of epoxy with acrylic acid²⁶ as shown in Schemes 1 and 2, which explains the reaction of EpAc with MF. In this case, curing occurs through the etherification reaction of EpAc and MF by SN^2 reaction mechanism along with the liberation of water. The dry-to-touch as well as dry-to-hard values were found to increase with the increase in the melamine content from 20 to 40 wt %. The gloss values were found to be comparable. It is observed that with the increase in the loading of MF in EpAc, a decrease in the hydroxyl value was recorded. This can be attributed to the reaction of hydroxyl group of EpAc with $-\text{OH}$ of MF. These coatings attained dry-to-touch and dry-to-hard conditions within 24 h. The room temperature-curing of EpAc-MF systems can be attributed to the etherification reaction, which occurs between hydroxyl groups of EpAc and MF through their terminal hydroxyl groups that causes an increase in crosslink density and molecular weight, and facilitates room temperature curing of coatings (Scheme 2).

TABLE II
Chemical Resistance Test

Resin code	H_2O (4 h)	NaOH (2%) (10 h)	HCl (2%) (12 h)	NaCl (3.5%) (240 h)
EpAc-MF-1 (unsealed)	c	c	c	c
EpAc-MF-1 (sealed)	a	a	b	a

a = no change but loss in gloss; b = films partially removed after 10 h; c = films completely removed within 6 h.

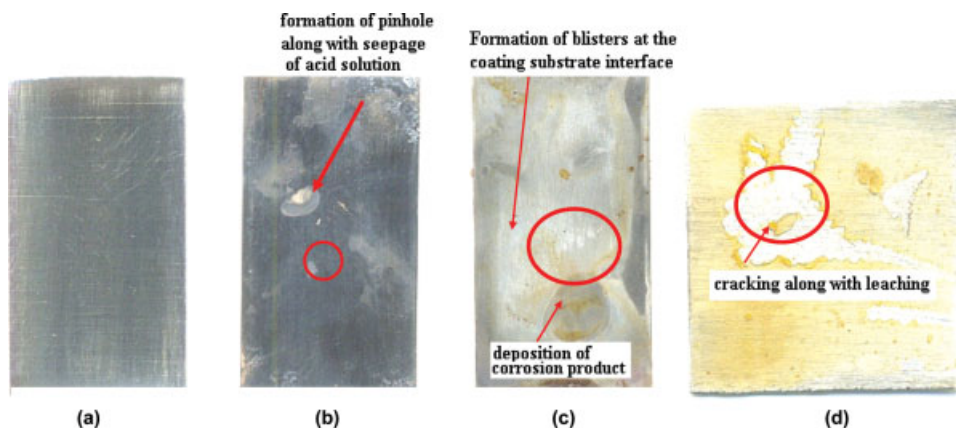


Figure 4 Photographs of (a) uncorroded EpAc-MF-1; (b) EpAc-MF-1 corroded in 2% HCl for 12 h; (c) EpAc-MF-1 corroded in 3.5% NaCl for 12 h; (d) EpAc-MF-1 corroded in 2% NaOH for 10 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Physicomechanical properties of EpAc-MF resins

The coatings of EpAc-MF were prepared on mild steel samples by using different amount of curing agent (MF), i.e. 20, 30, and 40 wt %. Table I gives the values for physicomechanical properties of different ratios of EpAc cured with MF. The scratch hardness was found to decrease appreciably with higher melamine-formaldehyde ratio in the resins, which can be attributed to the increase in the brittleness of the resins upon increasing the melamine content. The coatings were found to pass the impact strength as well as bend tests only up to 20 wt % MF in EpAc-MF-1 resin, which can be correlated to the increasing amount of polar groups, crosslink density, and dense structure of the coatings above 20 wt % MF.²⁷

The EpAc-MF-1 resin (20 wt % MF) coatings exhibited the best physicomechanical properties, comparable to some of the other water-borne epoxy systems reported in the literature and was chosen for investigating the corrosion resistance, morphological and thermal properties.^{28,29}

Corrosion resistance of EpAc-MF-1 coatings

The corrosion resistance of EpAc-MF-1 coatings (Table II) revealed that the sealed coatings exhibited better chemical resistance than those of unsealed coatings. When exposed to tap water, the sealed coatings remained unaffected for 36 h, while unsealed coatings were completely removed from the substrate within 10 h. The sealed coatings remained unaffected in 5% HCl and 5% NaCl up to 12 h, with only a slight loss in gloss after 12 h, while the unsealed coatings were completely removed in 6 h. The photographs of the sealed coatings in different corrosive media are shown in Figure 4. The coatings reveal the formation of slight blisters only after

12 h of exposure in 2% HCl [Fig. 4(a)], while exposure to 3.5% NaCl [Fig. 4(b)] for 12 h shows discoloration as well as deposition of corrosion products. The coatings in the former cases however are found to remain intact. In case of 2% NaOH [Fig. 4(c)], removal of the coating is observed after 10 h of exposure, indicative of the weak alkali resistance of the EpAc-MF-1 coatings. On exposure to sunlight for 1440 h, only a slight change in gloss was observed from 65° to 58° at 45°, which confirm the higher resistance of the EpAc-MF-1 coatings to UV rays (Fig. 5).

Thermal analysis

The TGA thermograms of EpAc and EpAc-MF-1 are given in Figure 6(a,b). The TGA thermogram of EpAc-MF resin shows an initial sluggish degradation

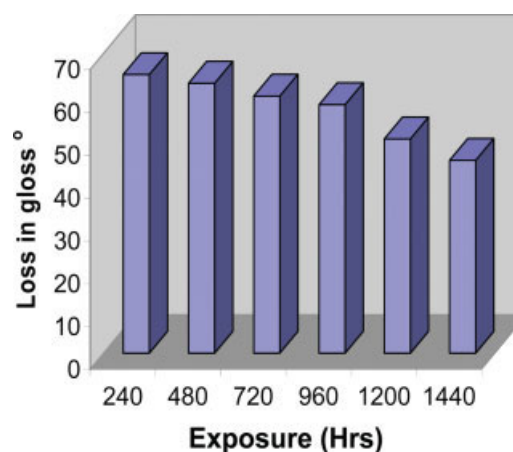


Figure 5 Effect of UV exposure on EpAc-MF coatings. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

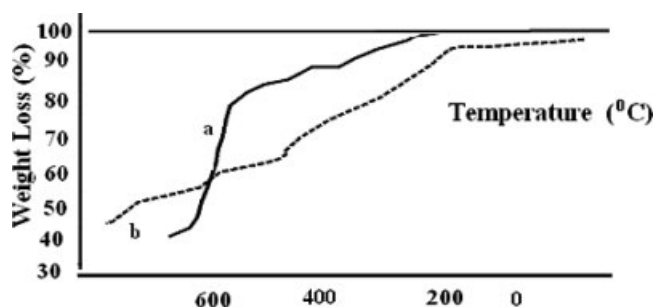


Figure 6 TGA of (a) EpAc and (b) EpAc-MF.

rate up to 241°C. Beyond this, a faster rate of degradation occurs, which extends up to 433°C. A 10 wt % loss is observed at 241°C and 50 wt % loss is observed at 637°C. The DTGA thermograms of EpAc show 10 wt % loss at 277°C and 50 wt % loss at 603°C. Finally, EpAc-MF decomposed at 637°C and EpAc at 603°C, which shows that EpAc-MF system possess higher thermal stability than EpAc system itself. Role of MF to determine thermal stability of resins becomes evident only at higher temperatures of degradation.³⁰

Melamine resin itself is thermally less stable, its progressive degradation at elevated temperatures leads to the loss of nitrogenous volatiles and the subsequent formation of N₂ polymeric products melam, melem, and melon by deamination.³¹ These nitrogenous degradation products of melamine are reportedly far more stable than melamine resin itself, thus improving the thermal stability of EpAc-MF resin at higher temperature of decomposition. It is also well known that an increase in crosslink density

increases the thermal stability of resin. The higher thermal stability of EpAc-MF at initial temperatures may be attributed to the presence of melamine moieties forming a highly crosslinked network.

Morphological analysis

The SEM micrographs of EpAc-MF-1 [Fig. 7(a,b)] reveals a two-phase system, where the acrylic particles (bright phase) appear to be embedded in the epoxy matrix (dark phase). The morphology of the film appears to be uniform, which can be correlated to the visual observation that the EpAc-MF-1 resin exhibited no phase separation even after 12 months. It was found that the epoxy system modified with acrylic particles shows higher fracture toughness, indicating that the modification has a significant effect on improving the material properties of the epoxy resin.

CONCLUSION

MF-cured EpAc water-soluble epoxy resins exhibit superior performance as compared to the reported water-borne epoxy resins. The presence of MF in the resin increases the scratch hardness, impact resistance, alkali resistance, and thermal stability of the coatings. EpAc-MF1 was found to cure at ambient temperature and showed good physicomechanical properties. However, these systems could not exhibit very good chemical resistance performance, which can presumably be attributed to excess of hydroxyl groups. Our future effort will be directed toward the improvement of these coating systems on these lines.

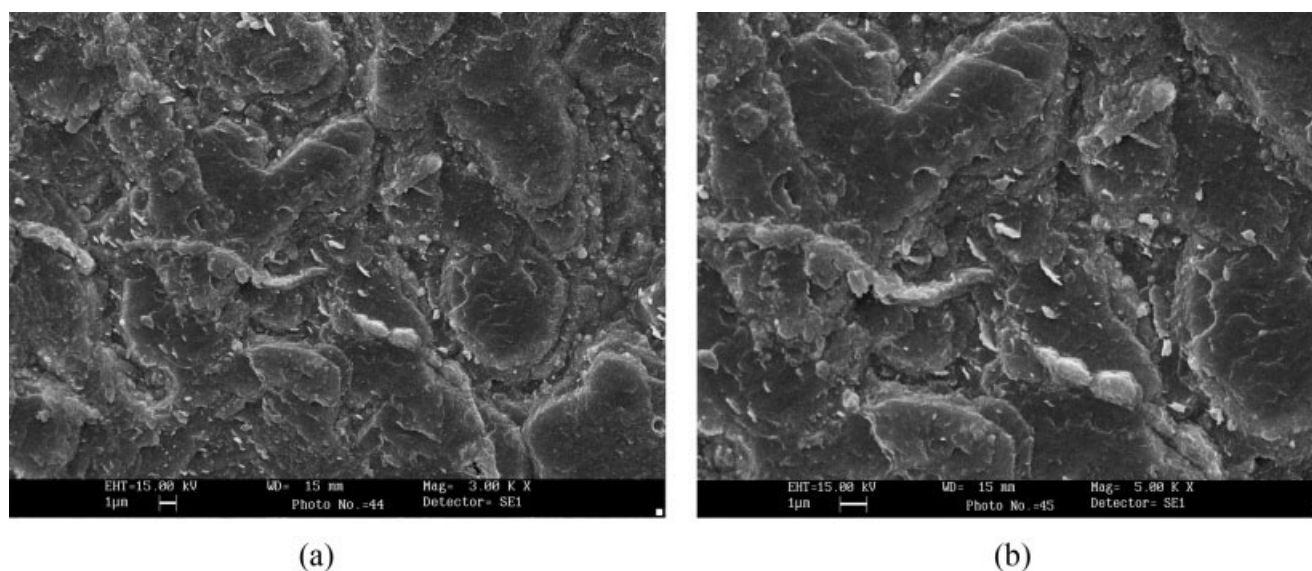


Figure 7 SEM micrograph of EpAc MF: (a) 3000×, (b) 5000×.

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