

Synthesis, Characterization, and Anticorrosive Coating Properties of Waterborne Interpenetrating Polymer Network Based on Epoxy-Acrylic-Oleic Acid with Butylated Melamine Formaldehyde

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ABSTRACT: The present study reports the synthesis and characterization of waterborne interpenetrating network (IPN) of epoxy-acrylic-oleic acid (EpAcO) with butylated melamine formaldehyde (BMF). The effect of BMF on the formation of IPN was investigated in terms of physico-chemical, spectral, morphological, and thermal analyses. The coating properties of the IPN were investigated for their physicochemical, corrosion resistance, and antimicrobial activity. The formation of the IPN was confirmed by FTIR and ^1H NMR analyses as well as physicochemical properties. The EpAcO-BMF IPN coatings were found to

exhibit far superior corrosion resistance performance and good thermal stability when compared with the reported waterborne epoxy acrylic-melamine formaldehyde systems [EpAc-MF]. The preliminary antimicrobial investigations of the IPNs were carried out by agar diffusion method against some bacteria and fungi. The results revealed that antimicrobial activities were enhanced upon the formation of IPN. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 827–838, 2009

Key words: coatings; interpenetrating network; renewable resources; crosslinking

INTRODUCTION

Waterborne epoxy systems (WBES) have recently gained much popularity for the most important benefit of reduced emissions of volatile organic compounds (VOCs).^{1,2} WBES were commercially introduced about 40 years ago, mainly as an environment friendly system to replace the solvent borne epoxies in countries dealing with strong environmental and work safety regulations.^{3,4} WBE formulations exhibit a wide range of uses and properties that can frequently match and even exceed the conventional solvent borne polymers.^{5–7} They have been commercially utilized in a wide variety of applications for civil engineering, adhesives, structural end-uses, fiber sizing, glass, synthetic and carbon fibers, tie-coats, primers and laminates, textiles, sealants, insulating materials, electronic photo imaging, and coatings; floor, corrosion, and microbial resistant.^{8–10}

Although the WBES represent significant improvements over solvent borne system, they still have limited applications owing to poor corrosion and chemical resistance. To improve these characteristics, the systems have been developed based on a medium molecular weight, polyfunctional epoxy resin dispersion, and modified curing agents.^{11,12} Recently, the present authors reported first time, the waterborne diglycidyl ether of bisphenol A [Ep]-acrylic acid copolymer [Ac], developed by grafting of acrylic acid at aliphatic carbon of Ep.^{13,14} EpAc cured with water soluble melamine formaldehyde [MF] shows ambient temperature cured eco-friendly coatings that exhibited good thermal stability (safely used up to 241°C) and excellent physicochemical properties, but exhibited poor chemical resistance performance and poor compatibility at higher loadings of EpAc.¹⁴ Therefore, there is need to improve their performance for their commercialization in the field of eco-friendly heavy duty coatings.

Interpenetrating polymerization represents an innovative approach to solve the problem of polymer incompatibility. Interpenetrating polymer networks (IPNs), (composed of two or more different crosslinked polymers), are relatively an emerging class of engineering materials. They have been among the fastest growing areas in the field of blends during the past twenty years. IPNs are defined as blends of two or more polymer networks

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where at least one polymer component is prepared or crosslinked in the immediate presence of others.¹⁵ Besides ideal or full IPNs, in which both components are crosslinked independently of each other, there are also other types of IPNs such as semi IPNs or grafted IPNs. Semi IPNs have only one component crosslinked, whereas grafted IPNs have covalent crosslinks between both networks. There are a variety of combinations possible with these materials resulting in a broad range of properties.¹⁶ IPNs with special characteristics have found many interesting applications, such as impact strength modification,¹⁷ pH-sensitive hydrogels,¹⁸ and biocompatibility materials.¹⁹

The performance of IPNs is determined by the physical and chemical nature of the constitutive networks, the relative proportion of components, the physical interactions between constitutive networks, the IPN preparation procedure, and so on. When IPNs are used as materials for coating applications, they cannot be prepared by conventional routes (sequential and simultaneous interpenetrating polymerization) due to the presence of volatile monomers. To avoid this problem, IPNs are prepared from preformed prepolymers containing complementary functional groups that enhance their miscibility. The maneuverability of the IPNs allow the formulator to manipulate the composition and other factors of the constituent polymers to arrive at tailor made products to suit a specific requirement, which can be considered as a major advantage in the field of coatings.^{20–22} The main advantages of IPNs are that they are relatively not easily affected by external stresses (which happen to polymer blends where the component polymers are not compatibilized due to simple physical mixing). IPNs also possess improved properties than two chemically dissimilar homo/neat polymers.^{23,24}

The use of epoxy coatings for high-performance applications is restricted mainly because of their low impact strength and high rigidity. Numerous investigations have been conducted over many years in an attempt to develop a process and procedure that would allow significant improvements in toughness achieved at minimum expense of mechanical properties.^{24,25} The demand for high performance polymeric coatings having superior properties such as impact strength, toughness, flexibility, dielectric behavior, high-temperature applications, low coefficient of thermal expansion, and easy processability¹⁷ has led to the development of water-borne copolymer (epoxy-acrylic-oleic) polymeric coatings by the interpenetrating polymer network (IPN) mechanism.

The present article reports synthesis, characterization, and corrosion protective performance of EpAcO [semi IPNs] and EpAcO-BMF [IPNs]. The properties

of the synthesized IPNs were compared with those of previously reported WBES [EpAc-MF].

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A resin (Ep, LY 556, epoxy equivalent: 180–185, specific gravity: 1.2306, refractive index: 1.5685, viscosity \sim 10,000 CP) was procured from Ciba Speciality Chemicals, New Delhi. Acrylic acid (Ac, molecular weight: 72.06, specific gravity: 1.050) and oleic acid (OA, molecular weight: 282.47, specific gravity: 0.889–0.895) from Merck, India. 2-ethoxy ethanol (molecular weight: 90.12, specific gravity: 0.929–0.93, s.d. fine-chem, India), ammonium persulfate (APS, molecular weight: 228.20 Qualigens, India), butylated melamine formaldehyde (BMF, Synthetic and Polymer Industries, Gujarat, India), and demineralized water (DMW) were used as such. Water-borne EpAc was synthesized and characterized as per reported method mentioned in our earlier studies.¹⁴

Synthesis of water borne semi IPNs

EpAcO were synthesized by the reaction of EpAc (10 g), and different weight loadings of oleic acid (OA) [4.0 g (0.14 mol), 5.0 g (0.18 mol), and 6.0 g (0.2 mol)] using APS (0.1 g, 0.0004 mol) as initiator. The EpAc was placed in a four-necked round-bottomed flask, equipped with condenser, nitrogen inlet tube, thermometer, and magnetic stirrer and add 50-mL aqueous blend (2-ethoxy ethanol and DMW 1 : 1) along with the APS. The contents were heated at $85 \pm 5^\circ\text{C}$ with continuous stirring at the same temperature in N_2 atmosphere. The TLC and acid value determination was used to monitor the progress of the reaction. The reaction was allowed to continue till the desired acid value was obtained. The reaction was stopped by attaining desired acid value and cooled. Aqueous blend was removed by rotary vacuum evaporator under reduced pressure to obtain pure EpAcO. The EpAcO semi IPNs were designated as EpAcO-4, EpAcO-5, EpAcO-6 depending upon the amount of oleic acid used. It was observed that EpAcO-5, EpAcO-6 semi-IPNs failed to crosslink with BMF and form coatings. Owing to higher loading of OA, they exhibited gelation upon crosslinking with BMF (even below 2 wt %), whereas with EpAcO-4, ambient cured coatings were obtained upon crosslinking with BMF above 30 wt % loading of the later. Hence, EpAcO-4 was chosen for the formulation of EpAcO-BMF IPNs.

Synthesis of EpAcO-BMF IPNs

EpAcO-BMF was developed by mixing of EpAcO-4 with 40–60 wt % of BMF in aqueous blend under vigorous stirring at $75 \pm 5^\circ\text{C}$ using different weight percent of BMF: 40, 50, and 60 wt %, respectively. The resulting IPNs were designated as EpAcO-BMF-40, EpAcO-BMF-50, and EpAcO-BMF-60, respectively. The reaction was continued till the desired acid and hydroxyl value obtained. Finally, aqueous blend was removed from the reaction mixture by vacuum rotary apparatus under reduced pressure to obtain EpAcO-BMF. It was observed that the EpAcO-BMF coatings below 40 wt % BMF failed to dry at ambient temperature due to incomplete curing of EpAcO with BMF, whereas the coatings with composition beyond 60 wt % BMF were found to be brittle, which can be attributed to excessive cross-linking between EpAcO and BMF. Hence, the IPNs with optimum composition of EpAcO-BMF (40, 50, and 60 wt % BMF) were chosen for the preparation of corrosion-resistant EpAcO-BMF coatings as they were found to cure at ambient temperature and form a transparent and well adherent coatings on mild steel (MS).

CHARACTERIZATION

Spectral analysis

FTIR spectra was taken on Perkin-Elmer 1750 FTIR spectrophotometer [Perkin-Elmer Instruments, Norwalk, (CT)] using a NaCl cell. ^1H NMR spectra was recorded on JEOL GSX 300 MHZ FX-100 spectrometer using deuterated chloroform as a solvent, and tetramethylsilane (TMS) as an internal standard.

Physicochemical analysis

Acid value (ASTM D5555-61), epoxy equivalent (ASTM D 1652), hydroxyl value (ASTM D1957-86), specific gravity (ASTM D792), and refractive index (ASTM D 1747) were determined by standard ASTM methods.²⁶ The inherent viscosity of EpAcO (3% solution in 2-ethoxy ethanol was used as a stock solution) was determined by Ubbelohde viscometer at 25°C .

Thermal analysis

Thermal analysis was carried out on TG thermo gravimetric analyzer Dupont USA in nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ to study the thermal stability of the cured films.

Morphological analysis

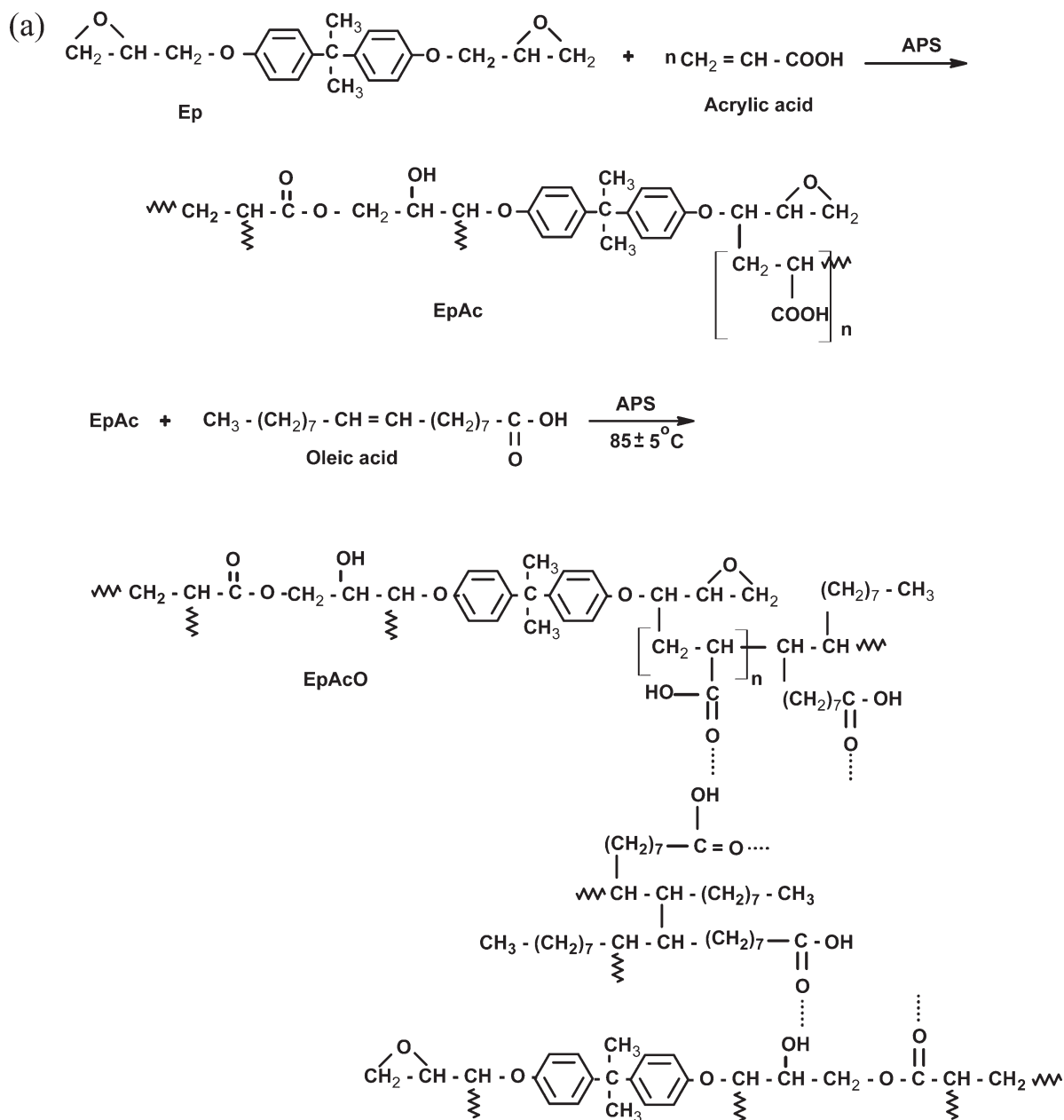
Scanning electron micrographs were taken on Jeol JSM840 scanning electron microscope under thin gold film.

Preparation and testing of coatings

The coatings of EpAcO-BMF-40 was applied by brush on commercially available mild steel strips of $30 \times 10 \times 1$ mm size for chemical resistance and of $70 \times 25 \times 1$ mm size for physicomechanical properties. Specular gloss at 45° by Gloss meter Model RSPT 20 (Digital Instrument, Santa Barbara), scratch hardness (BS 3900), impact resistance (IS: 101 part 5/s 3, 1988), and bend test (ASTMD 3281-84) were carried out on the coatings. The coated samples were cured at room temperature. The standard deviation was calculated by taking the mean of five readings. The thickness of these coatings was found to be in between 100 and 115 μm as determined by Elcometer Model 345 (Elcometer Instrument, Manchester, UK). Corrosion tests were performed in acid (4 wt % HCl), alkali (5 wt % NaOH), salt (3.5 wt % NaCl), and water by placing them in 3 inch diameter porcelain dishes in the aforementioned media. Actual weathering process of exterior exposure under UV radiation (sunlight) was simulated in this testing for 768 h. The protective behavior of the coatings against the dissolution of MS was evaluated by calculating the corrosion rate (V_c) for each one of the samples.³²

Antibacterial activity tests

OA, Ep, EpAc, EpAcO, and EpAcO-BMF-40 were screened for their antibacterial activity against *Bacillus*, *S.aureus*, *E.coli*, and *Salmonella* bacteria. The antibacterial activity was evaluated with respect to *Amekasin* (aminoglycoside) as standard controlled drug in the nutrient agar diffusion method.²⁷ One loopful of bacteria was inoculated in 10 mL of nutrient broth (peptone 5 g/L, pH 6.8) and incubated at 37°C for 28–30 h in a test tube shaker at 100 rpm. The actively growing bacterial cells were used for inhibition studies. The nutrient agar (20 mL) was poured into sterile Petri dishes and allowed to solidify at room temperature. After solidification, 0.1 mL of the bacterial culture was spread on the nutrient agar. A circular well (9 mm, diameter) was made with a sterilized steel borer, 0.1 mL of each test solutions were added into the well and incubated at 37°C for 24 h. Although antifungal activity was studied on *Candida*, *Fusarium*, and *Aspergillus*, *Candida* is a dimorphic fungus, which is regarded as a harmful opportunistic pathogen. It is responsible for many diseases especially in the oral and vaginal regions.



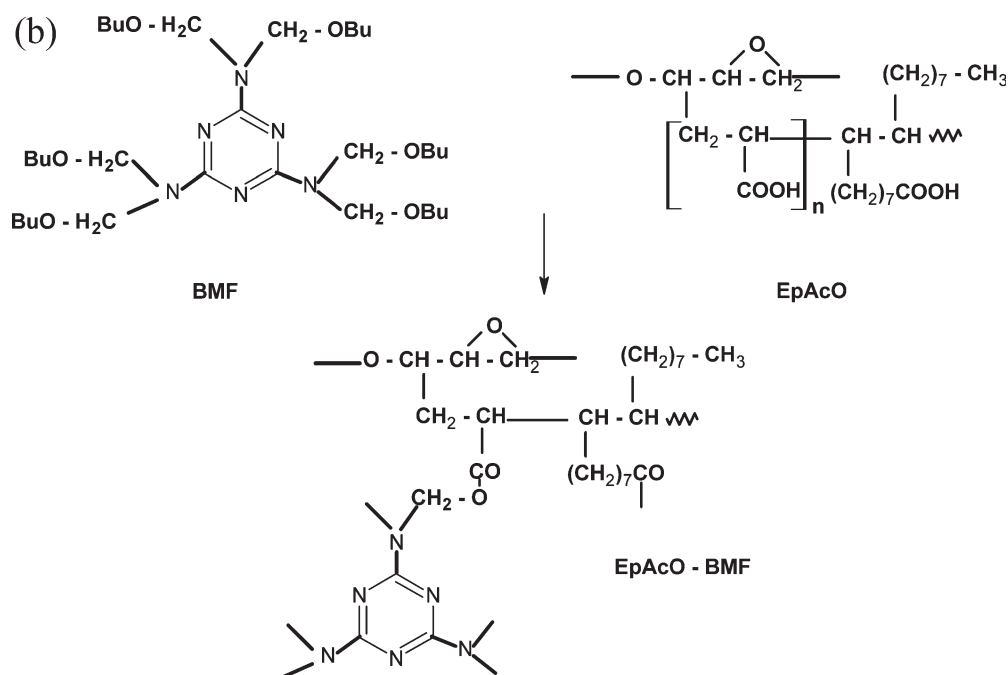
Scheme 1 (a) Synthesis of EpAcO and (b) curing reaction of EpAcO with BMF.

They can infect human beings through contaminated water containing *Candida* cells. The stock cultures of *C. albicans* and *Fusarium* were maintained on nutrient agar slant at 4°C.²⁸ To initiate growth for experimental purposes, cells from agar cultures were inoculated into a nutrient medium YEPD (yeast extract 1%, peptone 2% and D-glucose) and were grown at 30°C for 24 h, that is, up to stationary phase (primary culture). The YEPD medium containing 2% agar was poured into sterile Petri dishes and allowed to solidify at room temperature. After the solidification, 0.1 mL each of the primary cultures of *Candida*, *Fusarium*, and *Aspergillus* was spread on the

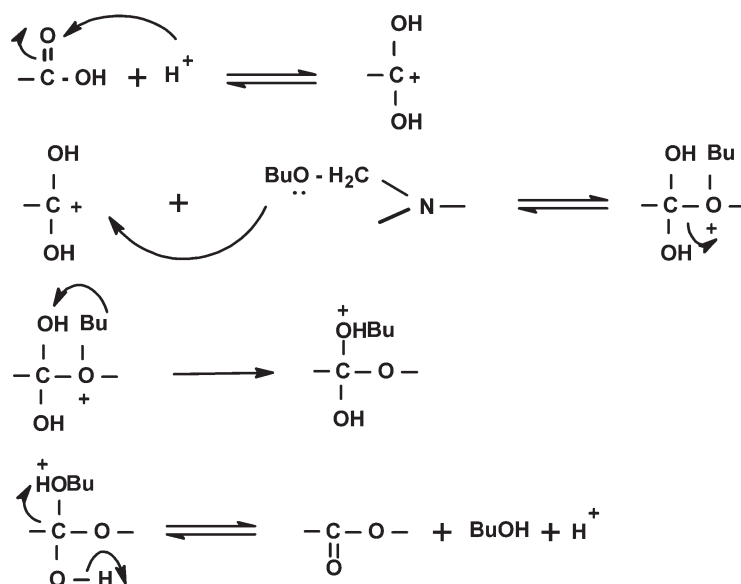
Petridishes containing the media. A circular well (9 mm in diameter) was made at the center of each one of the Petridishes with a sterilized borer. Test samples (0.1 mL) were added to the well and incubated at 37°C for 48 h. After incubation the antimicrobial activity determined by the diameter and clarity of inhibited zone that were measured in millimetres (mm).

RESULTS AND DISCUSSION

The IPN morphology may be controlled by either the kinetics of phase separation or the kinetics of



The mechanism of esterification involves the following steps



Scheme 1 (Continued)

gelation. Starting with a miscible blend of monomers in a simultaneous IPN synthesis, as polymerization of both components proceeds, the mixture eventually phase separates if the polymers are immiscible while if phase separation occurs more rapidly than gelation, the two components will separate into rather large phase domains. However, if the two components in the mixture polymerize rapidly and/or are able to crosslink before they can phase sepa-

rate, the phase separation will be constrained to occur only at the microscopic level, creating a micro heterogeneous system. In our case as epoxy-acrylic monomer and oleic acid were miscible, they were polymerized by the simultaneous method. Similar studies have been extensively reported in literature on the synthesis of IPNs.^{15,16} The EpAcO was synthesized in the aqueous blend (DMW and 2-ethoxy ethanol, 1 : 1) using EpAc and Oleic acid in the

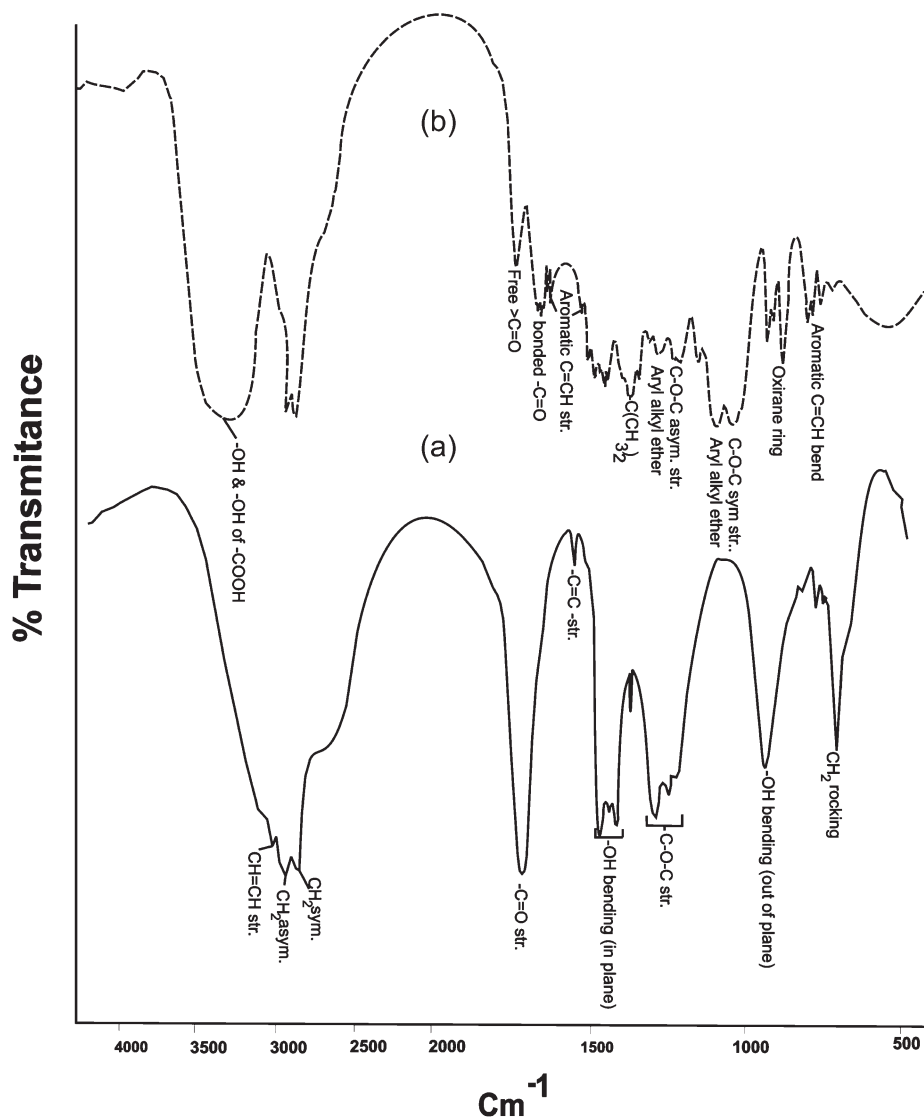


Figure 1 FTIR of (a) OA and (b) EpAcO.

presence of an initiator [APS]. The miscibility of the IPN with the aqueous blend can be attributed to the formation of hydrogen bonds between free carboxyl groups of acids and water, resulting in good solubility. The compatibility of EpAcO with water was found to be dependent upon the acid value. The IPNs EpAcO-4 and EpAcO-5 with desire acid value exhibited the formation of transparent solution of the IPNs in aqueous blend, which can be attributed to grafting of acids on the active sites of the epoxy. Hence, the grafted semi IPNs exhibit good solubility and higher clarity in aqueous blend, whereas EpAcO-6 reveals poor solubility, this is due to the presence of higher ratio of acid monomers than epoxy, leads to insufficient active sites in the epoxy backbone, which causes opacity and slight gelation in the EpAcO6. The increase in the carboxyl functionality of the semi IPNs led to enhanced interaction with hydroxyl group of the

BMF, resulting in the formation of highly cross-linked IPN of EpAcO BMF. During the synthesis of IPNs of EpAcO-BMF with 20–60 wt % of BMF, gelation was not observed, whereas in case of EpAcO-5 and EpAcO-6, gelation took place upon 40 wt % loading with BMF, due to the formation of a highly crosslinked structure. Scheme 1(a) shows the synthesis of EpAcO. In the formation of semi IPNs, crosslinking takes place through the physical interaction of oleic acid with EpAc. The crosslinking as well as free radical polymerization occur simultaneously.¹⁵ Scheme 1(a) also shows the esterification between carboxyl functionality of acrylic acid and oxirane ring of epoxy that produces free hydroxyl groups. The crosslinked structure of EpAcO-BMF was formed by the esterification reaction between $-\text{COOH}$ group of EpAcO and $-\text{OH}$ functionality of BMF as shown in Scheme 1(b). The curing reaction mechanism is

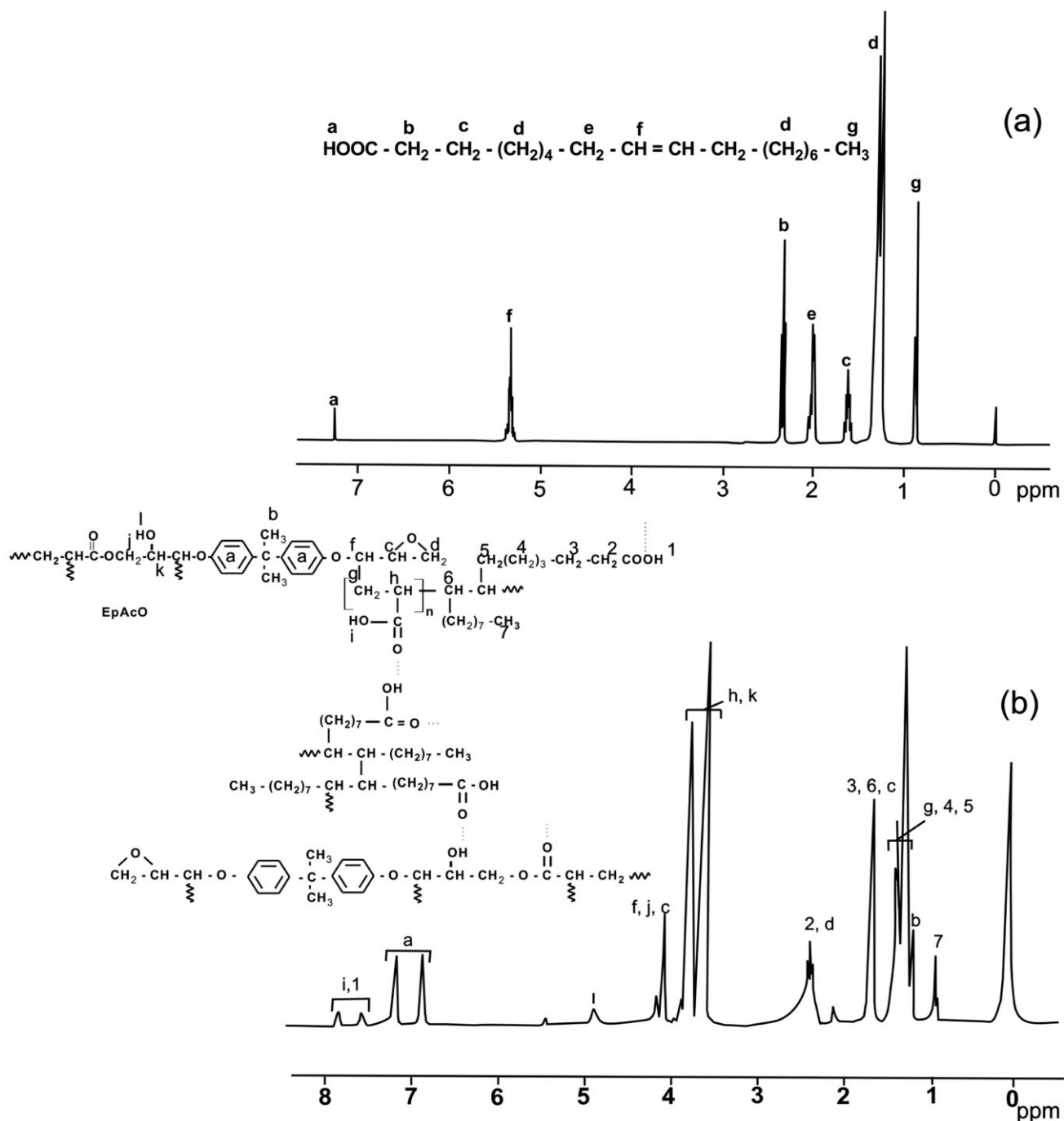


Figure 2 ^1H NMR of (a) OA and (b) EpAcO.

governed by bimolecular nucleophilic substitution [$\text{S}_{\text{N}}2$] (addition-elimination).²⁹

Spectral analysis

Figure 1 shows FTIR spectra of oleic acid and EpAcO. The spectra of EpAcO showed all the characteristic absorption band of EpAc along with the additional band of oleic acid.¹⁴ Upon close examination, the disappearance of the absorption band at 3009 cm^{-1} ($\text{C}=\text{C}-\text{H}$ stretching) and 1548 cm^{-1}

($\text{C}=\text{C}$ stretching) were observed in the spectra of oleic acid [Fig. 1(a)]. Shifting was also observed in the absorption frequency of carbonyl ($>\text{C}=\text{O}$, oleic, 59 cm^{-1}) and hydroxyl ($-\text{OH}$, $-\text{COOH}$, 34 cm^{-1}). The disappearance and shifting of aforementioned frequency bands in EpAcO [Fig. 1(b)] spectra can be attributed to the addition polymerization through double bond of oleic acid as well as hydrogen bonding between the polymeric chains forming the cross-link IPN structure.²³ The ^1H NMR spectra of EpAcO, Figure 2(b), exhibited all the characteristic

TABLE I
Physicochemical and Physicomechanical Properties of EpAcO and EpAcO-BMF IPNs

Characteristics	EpAcO-4	EpAcO-5	EpAcO-6	EpAcO-BMF-40	EpAcO-BMF-50	EpAcO-BMF-60
Physicochemical						
Acid value	75.00	78.21	84.05	23.91	18.20	15.00
Hydroxyl value	27.9	26.29	20.01	12.10	10.00	11.14
Epoxy equivalent	745	749	750	–	–	–
Specific gravity	1.04	1.05	1.06	1.09	1.11	1.14
Refractive index	1.431	1.456	1.480	1.516	1.523	1.533
Intrinsic viscosity (gm/mL)	0.13	0.15	0.18	0.35	0.45	0.52
Physicomechanical						
Dry to touch (h)	–	–	–	1.5	2	2.5
Dry to hard (h)	–	–	–	34	30	24
Scratch hardness (kg)	–	–	–	4.0	4.5	5.0
Impact resistance (150 lb/inch)	–	–	–	Pass	Pass	Pass
Bend test 1/8" inch	–	–	–	Pass	Pass	Pass
Gloss at 45°	55	58	60	62	64	67

peaks of EpAc¹⁴ along with the additional sharp peaks at $\delta = 1.3$ ppm and $\delta = 1.1$ ppm that can be correlated to the methene and methylene protons of oleic acid. The formation of IPN was also confirmed by the disappearance of peaks at $\delta = 5.34$ ppm (CH=CH) and $\delta = 2.05$ ppm (CH₂-C=C-) of oleic acid in EpAcO spectra. The shifting of the peaks was also observed in the region between $\delta = 3.5$ – 3.98 ppm (CH₂OH and CH-COOH) of EpAcO that was observed between 3.1–3.34 ppm in EpAc and can be correlated to the hydrogen bonding as well as IPN formation.^{14,23}

Physicochemical and physicomechanical characteristics of EpAcO and EpAcO-BMF IPNs

The epoxy equivalent, specific gravity, refractive index, and inherent viscosity, Table I, was found to increase from EpAc¹⁴ to EpAcO-6 which can be attributed to the dense and crosslinked structure of the semi-IPN. The presence of hydroxyl value implies that the hydroxyl formation occurs during the ring opening addition reaction of epoxy with acrylic acid. The values for hydroxyl as well as the trend for other physicochemical properties suggest the formation of EpAcO. It is also observed that the acid value and hydroxyl value decreases while specific gravity, index refractive, and inherent viscosity increases from EpAcO to EpAcO-BMF which further confirmed the crosslinked structure (Table I). The higher value of specific gravity and refractive index can be attributed to the dense structure of the IPN. Table I shows the physicomechanical properties of EpAcO-BMF IPNs. The dry to touch as well as dry to hard times were found to decrease with the increase in the melamine content from 40 to 60 wt %. The gloss values were also found to increase. The room temperature curing of EpAcO-BMF IPN systems can be attributed to the formation of interpenetrating network via esterification reaction, which occurs between carboxyl groups of EpAcO and BMF through their terminal hydroxyl groups that causes an increase in crosslink density and molecular weight, and facilitates room temperature curing of coatings. This effect can be explained considering that with a particular amount of loading of BMF, the polymer attains a reasonable longer chain length, along with desired crosslink density, resulting in a fine and crosslinked dense structure. The scratch hardness was found to decrease appreciably with higher BMF ratio in the IPNs, which can be attributed to the increase in the hardness of the coatings upon increasing the crosslinking agent. The coatings were found to pass the impact strength as well as bend tests only up to 60 wt % BMF in EpAcO-BMF IPN. Gloss values were, however, found to be comparable among IPNs. This indicates that the dense structure formed in all the coatings contributes to the good gloss of the IPNs. Based upon the physicomechanical properties, the coated test panels of the IPNs EpAcO-BMF-40, EpAcO-BMF-50, and EpAcO-BMF-60 were chosen for the analysis of the corrosion resistant properties discussed in the proceeding section.

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Salt spray test and weather resistance test

The UV tests were monitored by the determination of variation of the loss in gloss of the samples on exposure to sunlight for 768 h, Figure 3(a). A slight change in gloss was observed from 60 to 55° in case of EpAcO-BMF-40, which confirms the higher UV resistance of the EpAcO-BMF-40 coatings, Figure 3(a). This property is due to the high interpenetration and high crosslink density that resist the UV radiation. The loss of gloss in the EpAcO-BMF-60 was found to be higher than EpAcO-BMF-40 and EpAcO-BMF-50, that is, from 60 to 45° The salt spray

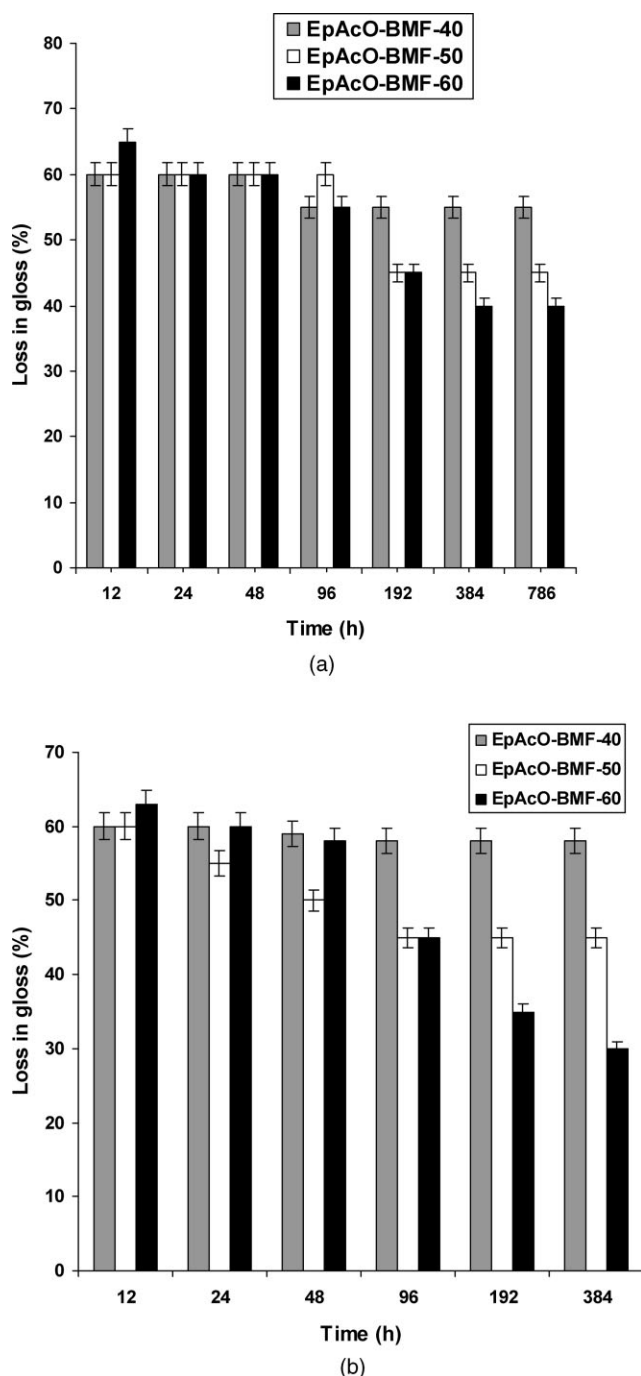


Figure 3 (a) Variation of gloss with time of exposure to UV test (768 h) and (b) variation of gloss with time of exposure to salt mist test (384 h).

exposure to 384 h, Figure 3(b), revealed only a slight change in gloss in the EpAcO-BMF-40 test panels, while considerable loss in gloss was observed in case of EpAcO-BMF-50 and EpAcO-BMF-60 test panels from 60 to 45° and 62 to 30°, respectively. The UV resistance of EpAcO-BMF IPNs was found to be higher than EpAc resins.¹⁴The relationship between the loss in the gloss on exposure to salt spray test and weathering tests with the increase in the wt %

loading of BMF is shown in Figure 4. An increase in the BMF content in EpAcO semi-IPNs is subsequently accompanied by an increase in ester linkages and presumably a greater number of crosslinks per unit chain length. A higher number of ester linkages enhance the flexibility to polymeric coatings which makes them prone to deterioration due to the formation of excessive free radicals by the unzipping process of acrylic polymer upon UV exposure.

Corrosion resistance of EpAcO-BMF IPN coatings

To evaluate the corrosion resistance of the coating, all the coating systems under study were immersed in selected chemical solutions at ambient aerated conditions for 400 h. In this study, the prepared specimens were immersed in the following: (i) distilled water (free from ions); (ii) sodium chloride, 3.5% w/v aq. solution; (iii) hydrochloric acid, 4% w/v aq. solution; (iv) sodium hydroxide, 5% w/v aq. solution. The chemical resistance tests, Table II, revealed that EpAcO-BMF-40 showed better performance than EpAcO-BMF-50 and EpAcO-BMF-60 under all corrosive media, in particular, against an alkaline environment. The coatings of composition EpAcO-BMF-40, EpAcO-BMF-50, and EpAcO-BMF-60 in water render good resistance and remains unaffected for 400 h with slight loss in gloss observed for EpAcO-BMF-60. When immersed in 4% HCl and 3.5% NaCl, the coatings of EpAcO-BMF-40 and EpAcO-BMF-50 exhibited slight loss in gloss after 300 h but remain intact while those of EpAcO-BMF-60 are completely removed after 192 h. The EpAcO-BMF-50 and EpAcO-BMF-60 also showed poor alkaline resistance when compared with EpAcO-BMF-40 coating which remained unaffected

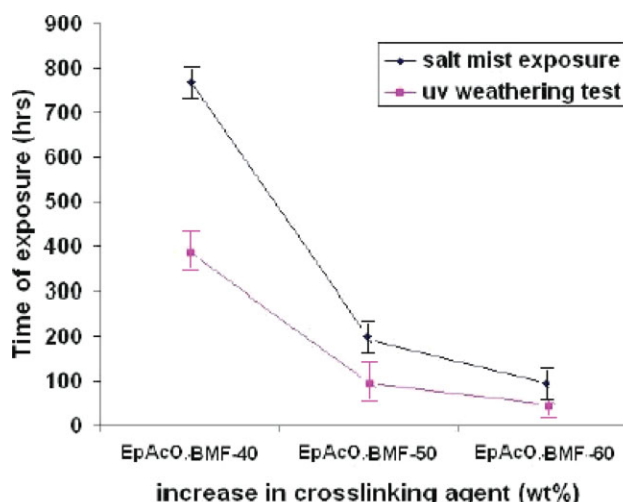


Figure 4 Effect of BMF loading on the properties of the IPN. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Corrosion Resistance Test of EpAcO-BMF IPNs (400h)

Resin Code	H ₂ O	NaOH (5 wt %)	HCl (4 wt %)	NaCl (3.5 wt %)
EpAcO-BMF-40	a	b	a	b
EpAcO-BMF-50	a	d	c	c
EpAcO-BMF-60	c	d	d	d

^a Unaffected films.

^b Unaffected films but slight loss in gloss.

^c Unaffected films but loss in gloss.

^d Films removed from the substrate.

up to 360 h. The corrosion rate of the EpAcO-BMF coatings revealed that EpAcO-BMF-40 and EpAcO-BMF-50 exhibited comparative corrosion rate in water media, Figure 5, being 5.5 mpy (EpAcO-BMF-40, EpAcO-BMF-50) and saline media, Figure 5, 4.75, 4.8 mpy respectively, whereas EpAcO-BMF-60 showed higher rate of corrosion in the same media being 5.8 mpy in water and 5.5 mpy in saline media. In case of acid medium, Figure 5, the EpAcO-BMF-40 exhibited the lowest corrosion rate 4.5 mpy, when compared with EpAcO-BMF-50 6.8 mpy and EpAcO-BMF-60 8.5 mpy, whereas in alkaline medium, Figure 5, the EpAcO-BMF-40 exhibited corrosion rate of 5 mpy, EpAcO-BMF-50 7.8 mpy, and EpAcO-BMF-60 8.8 mpy, respectively. The superior performance of EpAcO-BMF-40 IPN can be correlated to the formation of IPN that prevents the entrance of corrosive ions. Beyond 40 wt % loading of BMF, the melamine segments increase the crosslink density of the coatings that become highly strained, brittle, and lose their adhesion. This provides an easy passage for corrosive ions to penetrate through the coatings, causing damage to the coating framework. It was observed in our previous work that 40 wt % loading of MF in EpAc¹⁴ showed very poor film performance while the presence of 20 wt % of MF shows best result in EpAc-MF systems. However, in the present study up to 40 wt % loading of BMF in EpAcO shows excellent film performance. This can be attributed to the formation of IPNs in which the presence of oleic acid imparts flexibility at higher loading of BMF.

Morphological analysis

The SEM micrograph of IPN of EpAcO-BMF-40, Figure 6(a) revealed the formation of a closely packed, continuous, dense uniform, and fine crosslinked structure. The micrograph reveals a well knit and homogeneous dispersion indicating intimate mixing between EpAcO and BMF. The SEM micrograph of EpAcO-BMF-40 specimen corroded in 4% HCl medium for 400 h, Figure 6(b), shows shrinkage and the onset of formation of blisters. The SEM micro-

graph of same specimen corroded in 5% NaOH medium, Figure 6(c), shows slight crazing, whereas in 3.5% NaCl, Figure 6(d), the coating reveals onset of formation of cracks and fissures. However, the overall coating remains intact revealing higher adhesion and dense structure of the IPN.

Thermal analysis

The Figure 7 depicts that EpAcO-BMF-40 decomposes 5–10 wt % in the temperature range 0–250°C which can be attributed to the evaporation of entrapped moisture. About 40 wt % loss is observed at 430°C followed by substantial loss in weight at around 450–600°C (50–90 wt %). The former weight loss is due to the decrosslinking of the network of the EpAcO-BMF while the latter can be correlated to the decomposition of IPN structure.¹⁴

Antimicrobial assessment

The Table III depicts the antimicrobial activity of OA, Ep and EpAc, and EpAcO-BMF-40. It was observed that OA, Ep, and EpAc exhibited no activity against any bacteria, while EpAcO rendered

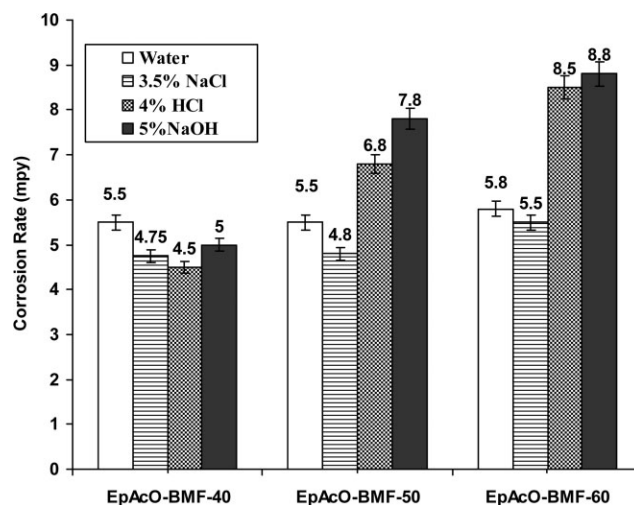


Figure 5 Corrosion rate of EpAcO-BMF IPNs in different media.

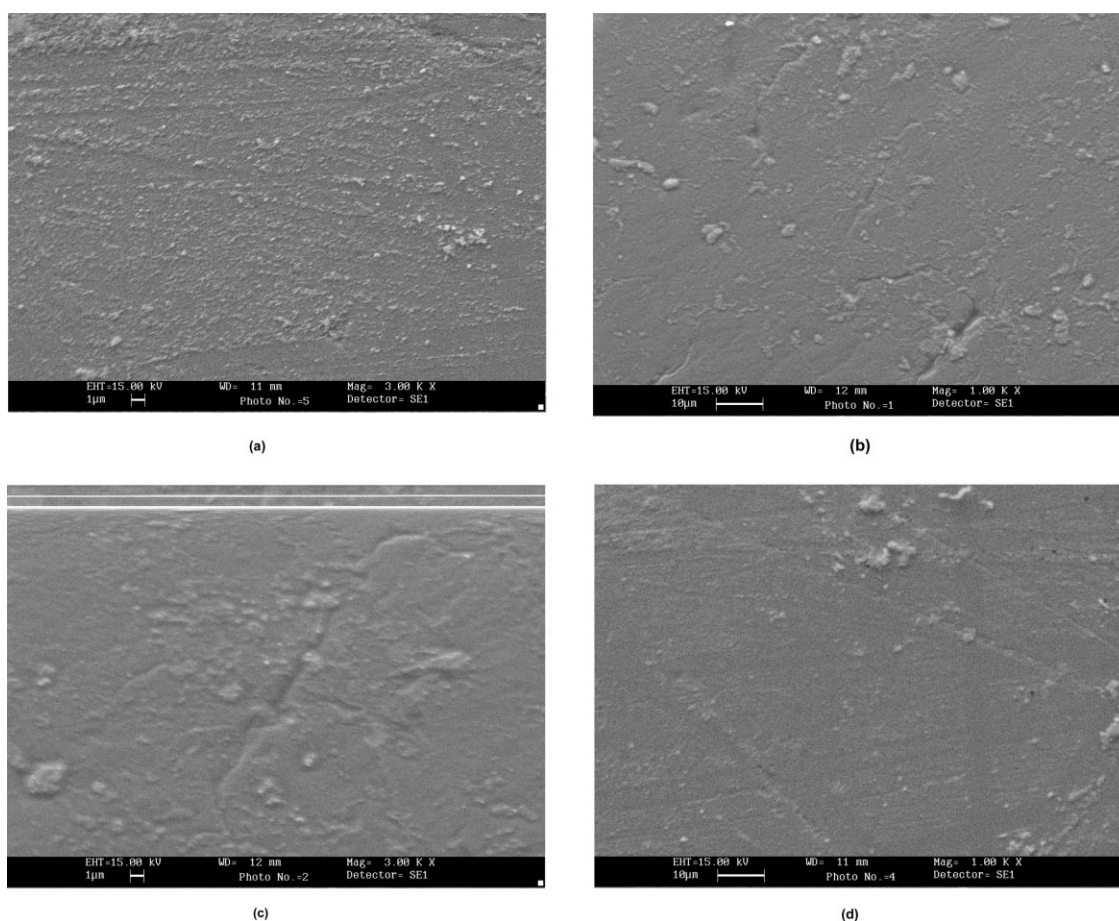


Figure 6 SEM micrographs of (a) EpAcO-BMF-40 IPN, (b) EpAcO-BMF-40 corroded in 4% HCl (400 h), (c) EpAcO-BMF-40 corroded in 5% NaOH (400 h), and (d) EpAcO-BMF-40 corroded in 3.5% NaCl (400 h).

good activity against *S. aureus* (12 mm), *E. coli* (15 mm), and *Bacillus* (17 mm), whereas EpAcO-BMF was found to be highly active against *Candida*, *S. aureus*, *E. coli*, and *Bacillus* exhibiting a higher inhibition zone of 25, 15, 22, and 20 mm, respectively, than the standard drug as well as EpAcO semi-IPN. The variations in the bacterial activity can be correlated to the structure of the IPNs. Hydroxyls as well as carboxyl groups of OA and EpAc are bonded through hydrogen bonding (both intermolecular and intermolecular) which prevent the interaction of polymer with bacteria, resulting in poor antibacterial activity.³⁰ In case of EpAcO, some carboxyl groups remains free; which are confirmed by FTIR spectra of EpAcO (band at 1725 cm^{-1} for $-\text{COOH}$), that chemically and physically interact with the microbes, and cause the inhibition in the bacterial growth. While in EpAcO-BMF-40, the presence of BMF was found to drastically enhance the antibacterial activity owing to its IPN structure. The gram cell wall of bacteria is a multilayered structure that contains peptidoglycon and lipopolysaccharide layer (LPS).³¹ The LPS of the gram surface consist of two portions

core polysaccharides having a wide variety of sugars and hydroxyl functional groups which interact with the highly crosslinked structure of the IPNs resulting in the deactivation of the microbes.

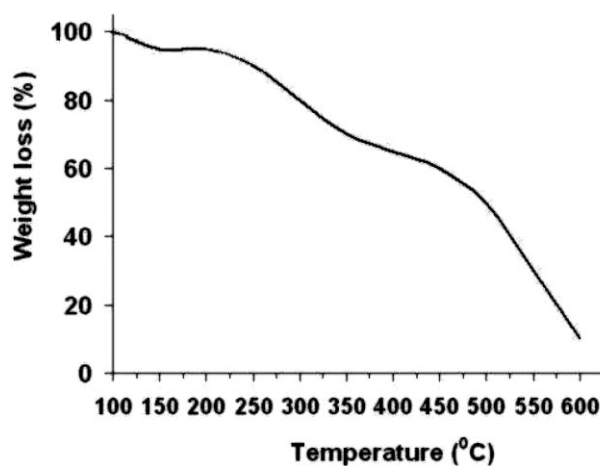


Figure 7 TGA thermogram of EpAcO-BMF-40.

TABLE III
Antimicrobial Activity of OA, Ep, EpAc, EpAcO, and EpAcO-BMF-40

Sample	<i>S. aureus</i> Inhibition zone (mm)	<i>E. coli</i> Inhibition zone (mm)	<i>Aspergillus</i> Inhibition zone (mm)	<i>Bacillus</i> Inhibition zone (mm)	<i>Salmonella</i> Inhibition zone (mm)	<i>Candida</i> Inhibition zone (mm)	<i>Fusarium</i> Inhibition zone (mm)
Amekasin (control drug)	10	11	15	15	18	15	17
OA	–	–	–	–	–	–	–
Ep	–	–	–	–	–	–	–
EpAc	–	–	–	–	–	–	–
EpAcO	12	15	–	17	–	–	22
EpAcO-BMF-40	15	22	–	20	–	25	–

CONCLUSION

The waterborne interpenetrating network [EpAcO-BMF-40] prepared from EpAc, oleic acid, and BMF showed significant enhancement in mechanical, chemical, and thermal properties over those of EpAc-MF system. The EpAcO-BMF-40 also exhibited excellent antimicrobial performance. Therefore, EpAcO-BMF-40 can be safely used as eco-friendly anticorrosive and antimicrobial coating materials up to 250°C. The creation of IPN materials from prepolymerized polymers through a simultaneous process, followed by crosslinking, is a concept applicable to many other systems and opens the possibility of creating novel IPN compositions and microstructures. The detailed investigations on the antimicrobial activity of these IPNs is in progress in our laboratory and will be published soon.

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