

Synthesis of bio-based epoxy resin from gallic acid with various epoxy equivalent weights and its effects on coating properties

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Abstract The bio-based epoxy resins for coating application were synthesized from gallic acid (GA) in various molar ratios with epichlorohydrin (ECH). The reaction was carried out in the presence of sodium hydroxide (NaOH) and phase-transfer catalyst tetrabutylammonium bromide. The reaction progress rate at various molar ratios as 1:8, 1:12, and 1:16 with respect to time was monitored by calculating the epoxy content. The epoxy content value increases in the product as the molar ratio of GA to ECH increases. Epoxy equivalent weight of products was evaluated by physiochemical method and structure illustrated by Fourier transform infrared and ¹H-nuclear magnetic resonance spectroscopy. This bio-based epoxy resin was cured with polyamide hardener, and the coating properties such as mechanical, chemical, and solvent resistance were studied. The cured films have been evaluated for glass transition temperature (T_g) and thermal behavior by a differential scanning calorimeter and thermogravimetric analysis, respectively. The biobased epoxy coatings show interesting mechanical, chemical, and thermal properties as compared to the conventional epoxy resin. The gel and water absorption of polyamide-cured coatings has also been evaluated.

Keywords Bio-based, Epoxy resin, Gallic acid, Epoxy equivalent weight, Coating properties

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Introduction

Epoxy resins are recognized for their thermal stability, superb chemical resistance as well as excellent mechanical properties. Hence, they are considered as one of the most important thermosetting resins for coating applications, and are characterized by a three-member ring known as the oxirane ring.^{[1,2](#page-9-0)} Epoxy resins have applications in various fields such as surface coatings, adhesives, flame retardants, automotive and structural insulating materials for electronic devices. $3-5$ The synthesis reactions of epoxy resins are followed by dehydrohalogenation reaction between the active hydrogen-containing compounds and epichlorohydrin (ECH) in the presence of sodium hydroxide (NaOH). 6 Commercial epoxy resins are available with a wide range of molecular weights in aliphatic, cycloaliphatic, or aromatic backbones depending on monomers used to synthesize. Most of the commercially available epoxy resin is synthesized from BPA (>85% of resin sales volume). However, BPA may lead to several negative health effects such as reduced sexual desire, heart disease, or endocrine disruptors.^{[7](#page-9-0)} In 2010, the US Environmental Protection Agency reported that over one million pounds of BPA are released into the environment annually.⁸ Due to the recent awareness regarding BPA toxicity and high cost of fossil resources, there is an increasing interest from the chemical industries to replace BPA with eco-friendly material that is easy to handle or is nontoxic.⁹ Most of the biomaterials are comparatively easy to handle with no toxicity and health-related issues; these are abundantly available in nature, and these are one of the good replacement solutions to BPA in epoxy resin synthesis.¹⁰ The utilization of bio-based materials as such or by chemical modifications for epoxy resin synthesis has been reported over the past two decades by numerous researchers.¹¹ To date, epoxy resin has been synthesized from various biomaterials such as vegetables oils, $12-14$ $12-14$ isosorbide, 15 cardanol,^{16–19} vanillin,^{[20,21](#page-10-0)} glucose,^{[10](#page-9-0)} catechin,¹¹ and

lignin.^{22,23} Bio-based aliphatic monomer-based polymers which are mainly obtained from long fatty acids of plant oils have low T_g and are found to be unsuitable for highperformance applications. Overcoming the natural limitations imposed by the aliphatic nature and limited functionality of long fatty acids of plant oils is needed. A variety of methods are used to achieve a number of derivatized plant oils with higher reactive group.²⁴ The heat resistance and mechanical and electrical performance properties of coatings are generally attributed to the aromatic ring structure. In this sense, Shieh et al. synthesized it by the condensation of a hydroxybenzaldehyde with phenol followed by epoxidation with a halohydrin. The trifunctional epoxy resin provides a densely crosslinked protective layer with excellent mechanical and thermal properties. The incorporation of higher functional epoxy resin into the resin enhanced the properties. $25,26$ A number of the bio-polyphenols have more than two phenolic hydroxyl functional groups that are in high demand in resin synthesis, and polymer based on it could offer high heat resistance with good mechanical properties. 27.28 In this context, Nouailhas et al. synthesized bio-based glycidyl ether of catechin (GEC) by reacting catechin with ECH in alkaline medium. The synthesized GEC was characterized by FTIR and NMR spectroscopy. The GEC was mixed with glycidyl ether of BPA (BPADGE) in various weight proportions (50:50, 75:25) and successfully cured with amine hardener at 60° C for 24 h. GEC resin content coatings had induced a low swelling percentage as compared to GEB coating, and that suggested GEC enhanced crosslinking density in the epoxy resin network. The synthesized GEC coating exhibited good thermal and mechanical properties in comparison with the GEB coating.¹¹ In the current work, bio-based epoxy resin from GA with various epoxy equivalent weights (EEW) was synthesized by reaction with various molar ratios of ECH in the presence of sodium hydroxide catalyst. The EEW of products has been calculated by physiochemical method, and products were cured with polyamide hardener. The obtained GAbased epoxy coatings were characterized for various coating properties and compared with conventional BPA-based epoxy coatings.

Experimental

Raw materials

Gallic acid (99.5%) was used as phenolic compound purchased from Loba Chemie Pvt. Ltd., India. Epichlorohydrin, tetrabutylammonium bromide (TBAB), and sodium hydroxide (NaOH) were laboratory-grade chemicals procured from SD Fine Chemicals Ltd., Mumbai, India. The conventional petroleumbased epoxy monomer used was a diglycidyl ether (DGEBA) supplied by Grand Polycoat Pvt. Ltd., India. Polyamide hardener (amine value 190–230 mg KOH/g) was purchased from Jayant Agro-organics Ltd., India. Acetone, butanol, and xylene solvents were purchased from SD Fine Chemicals Ltd., Mumbai, India, and used as solvent as supplied.

Synthesis of epoxy resin

Bio-based epoxy resin derived from gallic acid was synthesized according to procedure described by Tomita et al.^{[29](#page-10-0)} A four-necked flask equipped with mechanical stirrer was charged with gallic acid (0.02 mol) and ECH (0.016 mol) and the mixture stirred for 30 min. Afterward, phase-transfer catalyst (TBAB) was added to reaction mixture, the temperature was gradually increased to 105° C within a span of 1 h, and the reaction was allowed to proceed for the next 5 h. After this, the reaction mixture was cooled to room temperature (RT), an aqueous solution of NaOH was added, and the mixture was stirred for 90 min at RT. The completion of the reaction was monitored by the EEW of product. After the completion of the reaction, the mixture was washed with deionized water and ethyl acetate. The organic layer was dried over anhydrous sodium sulfate and the product filtered. Ethyl acetate and excess ECH were removed by using a rotary evaporator. The structure of synthesize GA based epoxy resin is shown in Fig. 1. A series of GA-based epoxy resin formulations are given in Table [1.](#page-2-0)

Fig. 1: Synthesis of bio-based epoxy resin

Table 1: Formulation of epoxy resin

Fig. 2: Curing reaction of epoxy resin with polyamide

Preparation of substrate coating application

The synthesized bio-based epoxy resins were mixed with polyamide hardener on an equivalent weight basis and applied on a metal panel. The oxirane rings react with the active hydrogen atoms of polyamide and convert the liquid epoxy resin into an infusible, solid, and hard material. The curing reaction was carried out for 1.5 h at 80 \degree C and is shown in Fig. 2. The coatings were evaluated for various coating properties such as mechanical, chemical, thermal, water absorption, and solvent resistance compared with the BPA-based conventional epoxy coating.

Characterization

Physiochemical analysis

The EEW of the obtained epoxy resins were calculated according to ASTM D-1652 by using equation (1) . A known weight of epoxy resin sample was taken in a glass stopper Erlenmeyer flask, and it was completely dissolved in 25 mL of hydrochlorinating agent. The mixture was kept at ambient temperature for about 20 min. This mixture was then titrated against methanolic 0.1 N NaOH solution using bromocresol red as an indicator. The blank titration was carried out under the same conditions.^{[30](#page-10-0)}

$$
EEW = \frac{W_s \times 100}{(B - S) \times N} \tag{1}
$$

where B is blank titration reading, S is sample titration reading, N is normality of NaOH, and W_s is the weight of the sample.

Instrumental analysis

FTIR analysis

The chemical structure of epoxy resin was identified by a Fourier transform infrared Spectrophotometer (FTIR) on a Bruker ATR spectrophotometer, USA. The spectra were observed in the $600-4000 \text{ cm}^{-1}$ wavelength range.

¹H-NMR analysis

The supportive conformation of chemical structure was given by ¹H-nuclear magnetic resonance (¹H-NMR) spectroscopy. ¹H-NMR spectra of product were analyzed using a Bruker DPX 800 MHz spectrophotometer with dimethyl sulfoxide (DMSO) as solvent.

DSC analysis

The glass transition temperature (T_g) of cured films was estimated using differential scanning calorimetry (DSC) TA Q100 analyzer (T.A. Instrument, USA). The film sample was accurately weighed in an aluminum pan and heated in the $40-120$ °C temperature range with a heating rate of 10° C/min under nitrogen atmosphere.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) of cured films was conducted on a PerkinElmer TGA 4000 instrument under nitrogen and air atmosphere. Thermal analysis was monitored in the $40-600^{\circ}$ C temperature range with a 20° C/min heating rate.

Coating characterization

Mechanical properties

Coating adhesion on metal substrate was determined by crosscut (ASTM D-3359) and pull-off tests (ASTM D-4541). In the crosscut test, a lattice marking of 1 sq.cm on coating was made until the metal surface was exposed, and adhesive tape was then applied over the lattice marking. The adhesive tapes were pulled out, and lattice marking of coating was examined for adhesion failure as per the ASTM standard. Further, in the pull-off adhesion test, a dolly was attached to the coating by using adhesive. Tensile force was applied perpendicularly by a pull-off adhesion tester onto the coating surface until a dolly was removed from the surface. The force attained at failure was reported as a result. Flexibility (ASTM D-522) and impact resistance (ASTM D-2794) properties of the coating were determined by conical mandrel and impact tester, respectively. To check the coating flexibility, the coating was fixed before the rotator arm of the mandrel with the coated surface facing away from the cone. The rotator was then softly rotated 180° causing the panel to deform. Impact test was carried out by dropping a 2 lb weight ball from the maximum height of 60 cm. The test was done on both sides of the metal: the coated side (intrusion impact) and the uncoated side (extrusion impact). Scratch hardness (IS-104) of the coating was measured by a hardness tester. The MS panel was fixed onto a movable base with the coated surface facing upward. A needle rested on the coating and moved: if the needle makes contact with the metal substrate, then the coating is said to have failed at that point for that weight. Pencil hardness was also used to study the hardness of coating according to ASTM D-3363. The 6B–6H range of pencils was used for the test.

Chemical resistance

Chemical resistance property of the coatings has been evaluated according to the ASTM D-1308. The coated panel was immersed in 5% w/w aqueous sodium hydroxide (NaOH) solution and 5% v/w hydrochloric acid (HCl) solution separately for 24 h at ambient temperature, and the edges of it were sealed with adhesive tape or wax. The coated panel was monitored for any visible defect like the softening of film, blistering, and separation of film from substrate.

Solvent resistance

Solvent resistances of the coatings were evaluated by a spot and rub resistance (ASTM D-4752) test by using xylene, acetone, and methanol. Solvent rub resistance of cured coatings was studied by rubbing the coating with a piece of white cotton saturated with solvent, and maximum rubbing cycles were 200. To perform the spot test, cotton saturated with solvent was placed on cured coating and the change examined in the coating after 6 h.

Gel content

Gel content of the cured epoxy coatings was determined by putting a known weight of coating sample (W_i) into xylene/DMF solvent (50:50 by volume) for 24 h. On the next day, coatings were removed from solvent and the residue was dried in an oven to achieve

$$
Gel content (%) = \frac{W_r}{W_i} \times 100
$$
 (2)

where W_i and W_r are the initial weight and residual weight of sample, respectively.

Water absorption

Water absorption of cured coatings was measured by ASTM D-570. The cured coating was dried in oven until a constant weight was achieved (W_1) and then dipped into water at room temperature for 24 h. The coating film was removed from the water and dried with a paper towel and weighed (W_2) . Water absorption was calculated from the difference in the weights of the sample before and after soaking in the water according to equation (3).

Water absorption (
$$
\% = \frac{(W_1 - W_2)}{W_2} \times 100
$$
 (3)

where W_1 is the weight of the sample after immersion in water and W_2 is the weight of the sample before immersion in water.

Results and discussion

Physicochemical analysis

In the conventional process of epoxy resin synthesis, sodium hydroxide was used as catalyst to promote two reactions: forming phenoxide ions and dehydrohalogenating the intermediates. It simultaneously affected basic hydrolysis of epichlorohydrin and dehydrohalogenation of the addition reaction products. It decreased the amount of epichlorohydrin in the reaction mixture and increased the amount of oligomer. Phasetransfer catalysts (PTC) were introduced to accelerate the ring-opening reaction for producing an epoxy monomer with low molecular weight, narrow polydispersity, high yield, and elevated purity and to prevent side reactions. Epoxy resin was synthesized from gallic acid in the presence of sodium hydroxide (NaOH) and phase-transfer catalyst tetrabutylammonium bromide (TBAB), and the progress of reaction with respect to time was monitored by calculating the epoxy content (Fig. 3). A series of epoxy resin from GA have been synthesized by changing the molar ratio of GA to ECH such as 1:8, 1:12, and 1:16. The reaction always was carried out with an excess of ECH, resulting in resin having an epoxy ring as an end group. 31 Initially, the ECH was reacted with the carboxylic group of GA in the presence of TBAB causing the addition reaction of ECH to carboxylic group of GA. Hence, the initial

Fig. 3: Epoxy content vs time

three and half hours did not allow any epoxy content in the reaction mixture and it is due to the halohydrin being formed, not an oxirane ring.^{[29](#page-10-0)} After that, aqueous NaOH solution was added drop-wise into the reaction mixture and a sudden increase in epoxy content was observed. The complete conversion of phenolic hydroxyl into the oxirane ring did not occur due to the steric hindrance.

FTIR analysis

The structure of GA-based epoxy resins is illustrated by FTIR spectra, as shown in Fig. [4.](#page-5-0) The spectrum shows peaks at 1429 and 1708 cm^{-1} which is attributed to C=C aromatic ring vibrations and C=O stretching vibration, respectively. The peak at 1355 cm^{-1} was assigned to the stretching of $CH₃$. The aliphatic and aromatic C–H stretching shows sharp bands at 3008 and 2930 cm^{-1} . The broad absorption peak was observed at around $3500-3200$ cm⁻¹ for the hydroxyl group. The characteristic band observed at 912 cm^{-1} was attributed to the presence of oxirane ring in epoxy ring.[32](#page-10-0) The FTIR result showed that bio-based epoxy resin was successfully synthesized from GA and ECH.

¹H NMR analysis of GA-based epoxy resin

¹H-NMR spectrum of GA-based synthesized epoxy resin is shown in Fig. [5.](#page-5-0) The recognized tall singlet at 7.25 ppm (A, 2H) corresponded to the de-shielded aromatic proton. The peaks at 4.2 ppm (B, 6H) and 4.8 (B, 2H) ppm correspond to the doublet of aliphatic proton having a different chemical environment. The peak was shifted to the higher value due to the higher shielding by oxygen of carboxylic group. The epoxy ring proton resonates at 2.82 and 3.58 ppm for the doublet (C, 4H) and multiplet (B, 8H), respectively. Thus, from the ¹H-NMR spectrum data, it may be concluded that GA-based epoxy resin was successfully synthesized.

Fig. 4: FTIR spectra of CE, GE1, GE2, and GE3 resins

Fig. 5: H-NMR spectra of GA-based epoxy resin

Differential scanning calorimetry

The DSC analysis of cured coatings is shown in Fig. [6.](#page-6-0) The DSC analysis shows the T_g (midpoint) of CE, GE1, GE2, and GE3 values as 47.53, 53.94, 55.97 and

62.85°C, respectively. It was observed that $T_{\rm g}$ of the cured coatings shifted to the higher value with the higher crosslinked and aromatic content structure. The crosslink density depends on the functional groups present in molecules, and the higher the functional

Fig. 6: DSC analysis of CE, GE1, GE2, and GE3 coatings

groups present, the higher the crosslinked threedimensional structure. The dense crosslinked structures have a higher value of T_g than less crosslinked cured coatings. In same line, the number of epoxy rings present in the molecule of epoxy resin would directly affect the T_g values. Thus, the higher the number of epoxy ring present, the higher the crosslinked structure and hence the higher the T_g value. Therefore, the GE3 coating showed higher T_g as compared to the GE2, GE1, and CE coatings.^{[33](#page-10-0)}

TGA analysis

Thermal degradation of the cured coating was characterized by TGA under nitrogen and air atmosphere, and the result is shown in Fig. [7](#page-7-0). From Fig. [7](#page-7-0), the result was recorded as a weight loss of coating as functions of temperature. Initially, 10% degradation of GA-based epoxy coatings occurred at around 275° C, whereas in the case of CE coating occurred at around 290° C and a sharp weight loss was observed at higher temperatures. GA-based epoxy coatings show a two-stage degradation, and CE coating shows a one-step degradation graph. GA-based epoxy coatings consist of ester linkage in the backbone, and this linkage was degraded at a low temperature compared to the rest of the crosslinked structure. Thermal stability of the cured resins was characterized by the statistic heat-resistant index temperature (T_s) . The temperatures at 5% (T_{d5}) and 30% weight loss (T_{d30}) of the cured coating

obtained in thermogravimetric analysis were used to calculate the T_s (equation (4)). The calculated value of statistic heat-resistant index (T_s) of cured GA-based coatings was a lower value than that of cured CE coating. The faster heat degradation of cured GAbased epoxy coatings was due to the degradation of ester bond linkages at lower temperature.^{[27](#page-10-0)}

$$
T_s = 0.49[T_{d5} + 0.6(T_{d30} - T_{d5})]
$$
\n(4)

where T_s is the statistic heat-resistant index temperature.

The GA-based coatings have higher char value as compared to CE coatings at 600° C, and this observation is given in Table [2.](#page-7-0) The crosslinked density of coating increases with the functional group, and the highly crosslinked network has high thermal stability. GA molecules have nearly four epoxy rings per aromatic ring, which leads to higher crosslinking structure and less chain lengths as compared to the CE network. This higher crosslinking density may enhance the higher thermal char formation. In addition, the aromatic ring of gallic acid enhanced the thermal properties of the coating.³

Gel content

The gel content of cured epoxy-polyamide coatings was studied in xylene/DMF solvent mixture for 24 h, and result is shown in Fig. [8](#page-7-0). The gel content of coatings was 93.2, 92.43, 94.92, and 94.02 for CE, GE1,

Fig. 7: Thermogravimetric analysis of coatings

Table 2: Thermogravimetric analysis of CE, GE1, GE2, and GE3 coatings

| Resin sample | T_{d5} (°C) | T_{d30} (°C) | $T_{\rm S}$ (°C) | Char-600 (%) |
|-----------------|---------------|-----------------------|------------------|--------------|
| CE | 208.42 | 395.12 | 157.01 | 4 |
| GE ₁ | 204.3 | 358.41 | 145.41 | 15 |
| GE ₂ | 209.21 | 365.4 | 148.43 | 16 |
| GE ₃ | 210.2 | 370.6 | 150.15 | 18 |

Fig. 8: Gel content of CE, GE1, GE2, and GE3 coatings

GE2, and GE3, respectively. The gel content is correlated to the crosslinked structure of the cured coating structure. The crosslinked density of coating was related to the number of functional groups present in the resin structure, and the higher the functional groups, the higher the crosslinked structure. GE3 resin has the larger number of epoxy rings than the other epoxy resins, which form highly crosslinked structure. Hence, penetration or diffusion of solvent mixture in GE3 coating was difficult.

Water absorption

The behavior of a coating toward water is a most important property, which can determine the end application of coatings. The water absorption test was performed to evaluate the migration of water in a cured polyamide epoxy coating. The coatings were immersed in water for 24 h, and the observations are shown in Fig. [9.](#page-8-0) The percentage of water absorption for CE, GE1, GE2, and GE3 is 2.0, 2.9, 2.1, and 1.8, respectively. GE3 coating showed less water absorption than any other coating, and it may be attributed to the highly crosslinked network which has less free space for water absorption. GE1 coating has higher percentage of water absorption due to a number of hydroxyl groups along the main chain; hence, this results in more affinity toward the water.

Coating characterization

Mechanical properties

The coatings were characterized for various mechanical properties, and the obtained results are given in Table [3](#page-8-0). The coating hardness was checked by a pencil

and scratch hardness tester. The excellent pencil and scratch hardness properties were observed for CE- and GA-based epoxy coatings. GE3 coating showed high hardness properties as compared to the GE1 and GE2 coatings. The trend observed could be correlated to the fact that the higher the number of epoxy rings present, the greater will be the crosslinked structure network and the higher the hardness properties. All coatings showed the pencil hardness above 4H, and this could be attributed to the high crosslinked density. Coating adhesion with metal substrate was determined by crosscut and pull-off adhesion tests. The coatings showed 100% adhesion to the metal substrates as measured by the crosscut adhesion method. The adhesion strength of coating on metal substrates was also evaluated with the pull-off adhesion test. The GE3 resin has a lower number of secondary hydroxyl groups present in the molecules that create hydrogen bond with metal substrate and improve the adhesion properties as compared to other epoxy resins. Hence, the GE3 coating was given a lower value of pull-off adhesion test as compared to the remaining epoxy coatings. Further, the flexibility of CE, GE1, and GE2 coatings was observed to be excellent with no crack development during testing on conical mandrel apparatus. This could be attributed to the presence of long aliphatic chains in polyamide and also the presence of hydroxyl group along the chain length of epoxy resin.

Fig. 9: Water absorption of CE, GE1, GE2, and GE3 coatings

In the impact resistance test, all coatings had a good response to the high-speed load for intrusion impact test. This could be attributed to the excellent balance maintained between the softer segments of long aliphatic chains of polyamide and the hardness offered from highly crosslinked structure of epoxy coating. For the extrusion impact test, all epoxy coatings showed poor results as compared to the intrusion impact test. From the above study, GA-based epoxy coatings have shown good performance for all mechanical properties when compared to the BPA-based conventional epoxy coating.

Chemical resistance properties

Acid (5% HCl) and alkali (5% NaOH) resistances of GA-based epoxy resin coatings were evaluated by immersion method for 24 h, and results are reported in Table 4. No GA-based epoxy coating showed defects on the coating surface such as loss of gloss or blistering. Here, the chemical resistance properties in the coating system can be attributed to the highly crosslinked structure. The aromatic structure also enhances the chemical resistance.

Solvent resistance

Solvent spot and rub resistance tests were conducted using xylene, methanol, and acetone. The change in coating properties after the completion of the spot test is shown in Fig. [10](#page-9-0). In the case of he spot test except for the GE1 resin coating, all resin coatings showed good resistance to the solvent. The highly crosslinked networks have high resistance to the solvent penetra-

Table 4: Chemical resistance properties

Fig. 10: Solvent spot test

Table 5: Solvent rub resistance analysis of CE, GE1, GE2, and GE3 coatings

| Sample code | Xylene | Methanol | Acetone |
|-----------------|--------|----------|---------|
| CE. | 7 | 7 | Z. |
| GE ₁ | x | 7 | 7 |
| GE ₂ | | Z. | 7 |
| GE ₃ | 7 | | |
| | | | |

x, poor; y, satisfactory; z, excellent resistance

tion, and in addition, the secondary hydroxyl groups present in the molecules create a hydrogen bonding in it or with other molecules, which can be considered as effective physical crosslinks. Hence, penetration or diffusion of solvent into the cured films became difficult and improved the solvent resistance properties. The solvent rub resistance test was also carried out with same solvent as in the spot test, and the observation is reported in Table 5. All coatings showed more or less same resistance to solvent rub, but in the case of xylene, the loss of gloss of coatings was observed after 200 cycles. From the above study, it may be concluded that the coatings have sufficiently crosslinked network.

Conclusion

Bio-based epoxy resins with various epoxy equivalent weights were successfully synthesized from gallic acid. The synthesis of bio-based epoxy resin involved a onestep reaction between GA and ECH in the presence of the phase-transfer and sodium hydroxide catalysts. They were cured with polyamide hardener in 1:1 equivalent weight basis and coating properties were studied. The GA-based epoxy coatings show interesting mechanical, chemical, and thermal properties as compared to the conventional epoxy resin. GE2

coating showed the good balanced coating properties as compared to the GE1 and GE3 coatings. These studies disclose the feasibility of GA-based epoxy coating as a good alternative candidate for the conventional bisphenol A epoxy resin.

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