Received: 28 September 2019 | Revised: 31 December 2019 | Accepted: 2 January 2020
DOI: 10.1002/pc.25510

RESEARCH ARTICLE

Polymer COMPOSITES
WILEY

Development of cashew nut shell carbon reinforced thiourea based biophenolic benzoxazine-epoxy composites: High performance biobased coating materials

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Abstract

The research work focused on the preparation of biobased eugenol benzoxazine (EUBz) using thiourea as amine resource and their conversion into EUBz-epoxy (EUBz-EP) blend matrix and EUBz-EP blend composites. In the present work, thiourea-based eugenol-benzoxazine monomer was synthesized using eugenol as phenolic compound, thiourea as amine resource and paraformaldehyde. The molecular structure of monomer was confirmed by FTIR, NMR, and Maldi mass studies. The thiourea-based EUBz properties were enhanced by the blending of EP resin and reinforced with varying weight percentages of amine functionalized cashew nut shell carbon (*f*-CSC). The thermally cured *f*-CSC/EUBz-EP composites possesses a higher glass transition temperature of 202.9°C when compared to that of the EUBz matrix (104.2°C), which might arise due to the higher crosslinking density resulted from the reinforcement of EP resin with *f*-CSC. In addition, the hydrophobic behavior of the prepared composite materials is improved by blending the EUBz with EP resin and reinforcing with *f*-CSC. The enhancement of the value of contact angle from 80.3° to 105.9° infers the improvement of hydrophobic behavior of *f*-CSC reinforced EUBz-EP blend composites. The corrosion rate and protection efficiency of 5 wt% *f*-CSC/EUBz-EP composites exhibits 0.814 (mm/year) and 99.97%, respectively. Data obtained from different studies suggested that the *f*-CSC reinforced EUBz-EP blended composites can be used in the form of sealants, encapsulants, adhesives, and coatings for different industrial and engineering applications.

KEYWORDS

biobased polymer composites, cashew nut shell carbon, corrosion resistant coating, hydrophobic behavior, thiourea-based bio-benzoxazine

1 | INTRODUCTION

Recently, those researchers working in the field of polymers have been devoting their attention to utilize bioresources as raw materials for substituting the majority of synthetic polymer building blocks. Some of the polymers with partial replacement of biobased constituents are also available in the markets,[1,2] which are also tempting the researchers to devote their time for the development of biobased polymers towards high-performance applications utilizing straight and facile synthesis through the process like Mannich condensation.[3] Although benzoxazine (EUBz)-based polymers offer several advantages, they have not yet become very attractive to industry due to some of the deficient characteristics associated with EUBz-based materials. They have the brittleness behavior and require high temperature for curing and the most of the EUBz monomers are solid, which limit their process ability and their conversion into polymer films or complex structures.[4]

The choices of precursors with competitive cost and renewable natural resource are the essential parameters to reduce the cost of the materials produced for commercialization process. Among the renewable monomers, EUBz monomers can be prepared using cost competitive sustainable bioresource precursor as starting materials.[5,6] A eugenol is one of the bioresources/plant oil with relatively low cost and rigid aromatic ring with an allyl, hydroxyl, and methoxyl groups. Eugenol-based thermosets are getting attracted and eugenol-based EUBzs were reported with improved specific properties.[7] Clove is cultivated in various countries like India, Indonesia, Madagascar, South China, and Srilanka, from which eugenol is derived. Eugenol is responsible for the spicy aroma in clove and also it is one of the main components present in the clove oil with 72% to 90%. In addition, it is a clear pale yellow oily liquid extracted from certain essential oils, especially from clove, nutmeg, cinnamon, basil, and bay leaf, which are slightly soluble in water and soluble in organic solvents. Clove oil is widely used for flavoring pastry, special sauces, condiments, and medicines for the preparation of gums and teeth.[8]

Further, the thermal withstanding capacity, and anticorrosion properties of the polymers are improved with the addition carbon material for high-performance applications.[9] Commercially available activated carbons are usually derived from natural materials such as wood or coal, which is still expensive and the processing are also highly expensive. Hence, low-cost agricultural solid waste-based activated carbon have been studied for a long time and activated carbons were prepared from agricultural wastes such as bamboo, coconut shell, cassava peel, plum kernels, jute fiber, bagasse, rice husks, palm-tree cobs, date pits, olive stones, nutshells, fruit stones, peach stones, rattan sawdust, orange peel carbon, oil palm shell, corn shell, and vegetable fiber,[10–15] which are widely used as adsorbent due to large surface area and they have been suggested as an effective adsorbent for the removal of pollutants. India is the largest producer, processor, and exporter of cashew nuts (*Anacardium occidentale* Linn) in the world and producing 400 kilotonnes of raw cashew nuts. The activated carbon prepared from cashew nut shell (CNS) has large specific surface area, high adsorption capacity, and low cost.[16,17]

Thiourea and its derivatives are thermally stable compounds, and review articles were published relating to its applications in the pharmaceutical sector, plant protection, and the synthesis of heterocyclic compounds.[18,19] However, the thiourea has not attracted much attention in the preparation of complex and composite materials in EUBz chemistry. Hence, a new attempt was made to prepare thiourea-based thermosets, which may be interesting and competitive with petroleum-based resin materials for real time potential applications in near future.

The EUBz was synthesized using eugenol (as a phenolic source), thiourea (as an amine source), and paraformaldehyde via a simple wet chemical method. The synthesis of EUBz from thiourea is a very simple, high yield reaction and EUBzs obtained from thiourea and eugenol is partially biobased material. The EUBz is also blended with EP through *in situ* thermal curing process to get EUBz-EP blended polymer matrix. In addition, the present work focused on the preparation of amine-functionalized cashew nut shell carbon (*f*-CSC) reinforced thiourea-based eugenol EUBz-EP matrix composites. The prepared composites are characterized for thermal, surface, and corrosion resistant properties. The synthesized monomers were also systematically analyzed by nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR), and MALDI-mass to confirm the formation of thiourea-based eugenol-EUBz monomer. The systematic characterization results of the prepared composite studies suggest that the obtained composites can be used for high-performance thermal and corrosion resistant applications.

2 | EXPERIMENTAL

2.1 | Materials

Concentrated sulphuric acid (Con.H_2SO_4), sodium bisulphate, triethylenetetramine, and methanol were procured from Merck, India. Thiourea was bought from Loba Chemie. Paraformaldehyde, chloroform, sodium hydroxide, and sodium sulphate were purchased from Alpharm fine chemicals. Diglycidyl ether of bisphenol-A and polyamide imidazoline were obtained from Hindustan Ciba Giegy Ltd. Mumbai, India. Eugenol was acquired from Avra synthesis Pvt. Ltd. Hyderabad, India.

2.2 | Characterization

^1H and ^{13}C NMR spectra were recorded using Bruker EXT 40618 spectra at 400 MHz and 25°C in $CDCl_3$ solvent. FTIR spectra were measured by Thermo Nicolet

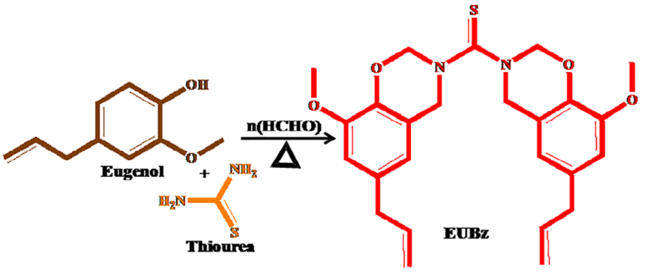
Model: 6700 with a wave number ranges from 4000 to 500 cm^{-1} at the resolution of 0.1 cm^{-1}. Scanning electron microscope (SEM) images were obtained using Hitachi, Model S-3400 N. The Bruker Ultrafle Xtreme (MALDI-Mass) was used to find the molecular weight of the prepared EUBz monomer. The Perkin Elmer Diamond TA/TGA instrument was used to study stability of the compounds with a heating rate of 10°C min^{-1} under nitrogen flow. Differential scanning calorimeter (DSC) analysis of polybenzoxazine and its composites were carried out using Hitachi DSC7020 at a heating rate of 10°C min^{-1} under nitrogen atmosphere. The hydrophobic natures of the composites were studied using a contact angle instrument Model OCA EC15 from Data Physics, GmbH, Germany. The anticorrosion properties were studied using biologic VSP2 multichannel (France) workstation analyzer.

2.3 | Preparation of amine functionalized cashew nut shell carbon

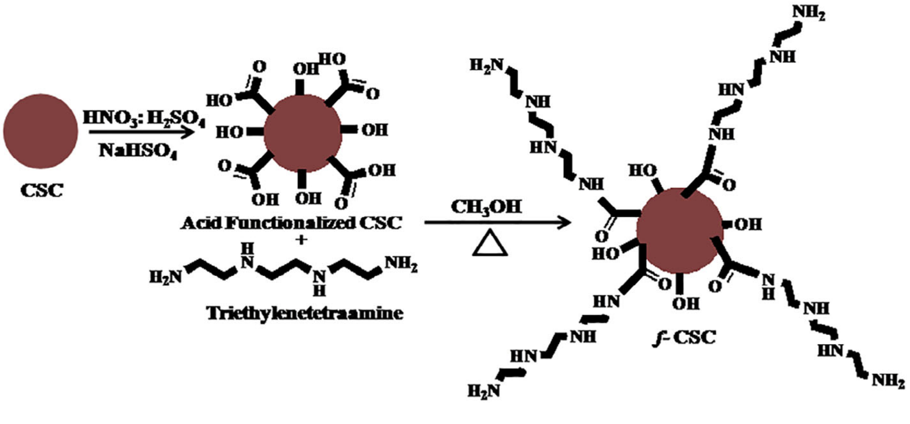
A 250 g of sunlight dried cashew nut shell (*Anacardium occidentale* linn shell) was taken in a silica crucible and heated at 300°C for 2 hours to obtain carbon (CSC). The carbon resulted was ground into a fine powder for surface activation and the chemical activation was carried out by immersing 5 g of CSC in Con.HNO_3 and Con.H_2SO_4 (3,1) solution and the resulted reaction mixture was refluxed at 100°C for 24 hours.[20] Then, the solid was filtered and dried, which was then soaked in 1 wt% sodium bisulphate prepared in 100 mL distilled water for 24 hours in order to remove the adsorbed acid molecules in the carbon material. Finally, the reaction mixture was filtered and washed with distilled water and then dried at 100°C for 24 hours. *f*-CSC was further prepared according to the previous work reported.[21] In brief, 2 g of acid treated cashew nut shell carbon was dispersed in 15 mL of methanol and stirred for half an hour at 40°C. A 4 mL of triethylene tetramine (TETA) was added in drop wise to the reaction mixture and sonicated for 20 minutes towards uniform dispersion. After sonication, the reaction mixture was refluxed under stirring for 24 hours. The obtained solid product was filtered and washed with methanol and then dried at 80°C for 24 hours to get moisture-free carbon for the preparation of composite materials (Scheme 1).

2.4 | Synthesis of thiourea-based eugenol benzoxazine monomer

A 14.2 g of eugenol was mixed with 2.8 g of paraformaldehyde and refluxed at 80°C for 1 hour. Then, 10 g of thiourea was added and the temperature was raised to 110°C and the reaction was continued under stirring for 12 hours at the same temperature. The completion of reaction was checked using thin-layer chromatography spot. The reaction product was poured in 2 N sodium hydroxide and separated using $CHCl_3$.[22] The collected organic layer was dried over anhydrous sodium sulphate and filtered. The dark-brown color gel of thiourea-based EUBz obtained after the removal of the chloroform solvent under reduced pressure (Scheme 2).



SCHEME 2 Synthesis of thiourea-based eugenol benzoxazine monomer [Color figure can be viewed at wileyonlinelibrary.com]



SCHEME 1 Preparation of triethylene tetramine functionalized cashew nut shell carbon [Color figure can be viewed at wileyonlinelibrary.com]

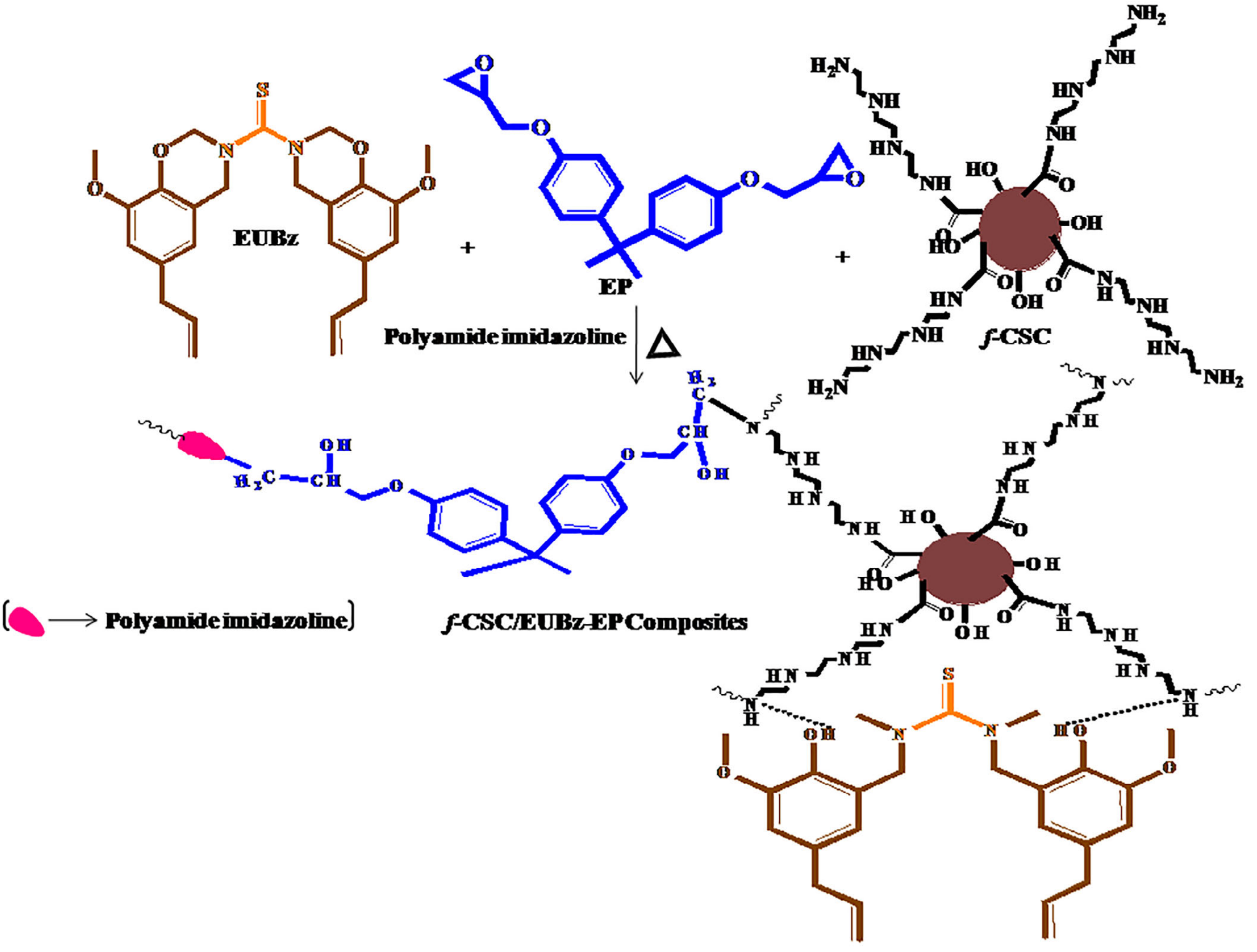
2.5 | Preparation of EUBz polymer, EUBz-EP matrix, and *f*-CSC/EUBz-EP composites

The thiourea-based EUBz polymer, EUBz-EP matrix, and *f*-CSC/EUBz-EP composites were prepared according to the Scheme 3. For the preparation of thiourea-based EUBz polymer, 2 g of thiourea-based EUBz monomer in 15 mL of chloroform was stirred for 3 hours to get homogeneous solution, which was then poured into a silane coated glass plate for the curing process. The temperature was raised slowly to avoid air bubbles. The EUBz monomer was cured at 40°C, 60°C, 80°C 100°C, 120°C, 160°C, and 180°C for 1 hour at each temperature to obtain EUBz polymer film. The same procedure was repeated to optimize the EUBz and EP ratio such as 0.75:0.25, 0.50:0.50 (or 1:1), and 0.25:0.75 with a constant weight ratios of 0.25 polyamide imidazoline to form stable polymer films. The optimized 0.50:0.50 or 1:1 weight ratio of EUBz and EP blend was used for the preparation of composites. Varying weight percentages of (1, 3, and 5 wt%) *f*-CSC was incorporated to the reaction blend containing 1:1 ratio of EUBz and EP as well as a calculated quantity of polyamide imidazoline hardener, and then, the resulting blend solution was poured in the silane coated glass plate for the curing. The EUBz-EP-based composites were also cured at the same temperature of 40°C, 60°C, 80°C 100°C, 120°C, 160°C, and 180°C for 1 hour at each temperature (Scheme 3).

3 | RESULTS AND DISCUSSION

3.1 | Molecular studies of *f*-CSC and benzoxazine monomer

The *f*-CSC and eugenol-based EUBz monomer were characterized by FTIR, NMR, and MALDI mass. The peak



SCHEME 3 Preparation of *f*-CSC incorporated thiourea-based EUBz-EP (*f*-CSC/EUBz-EP) composites. EUBz-EP, eugenol benzoxazine-epoxy polymer matrix [Color figure can be viewed at wileyonlinelibrary.com]

(Figure 1A) corresponding to —C═O was observed at 1720 cm^{-1} along with OH vibration at 3431 cm^{-1} are confirming the —OH group present in the acid treated cashew nut shell carbon.[23] The peaks appeared at 2939 and 2808 cm^{-1} in *f*-CSC similar to TETA confirms the presence of —CH_2 group. In addition, functionalization of CSC with TETA was also ascertained by the appearance of absorption bands at 3310 cm^{-1} for —NH_2 group stretching vibration along with the peaks observed at 2939 and 2808 cm^{-1} in *f*-CSC reinforcement.[24]

The FTIR spectrum of eugenol-based EUBz (Figure 1B) shows the characteristic absorption bands at 1273 cm^{-1} (asymmetric stretching of C—O—C), 1076 cm^{-1} (symmetric stretching of C—O—C), and 913 cm^{-1} (N—C—O stretching), which are the typical vibration peaks of EUBz ring structure. The peaks appeared at 2923 and 2846 cm^{-1} are owing to the stretching vibrations of —CH_2 group in the oxazine ring as well as the alkyl side chain of eugenol.[25] The absorption peak appeared at 745 cm^{-1} is due to rocking vibration of the C═S bond of thiourea present in the EUBz monomer.[26] Therefore, FTIR results ascertain the formation of eugenol-based EUBz monomer.

The molecular structure of EUBz monomer was characterized by ^{1}H (Figure 2) and ^{13}C NMR studies (Figure 3). The chemical shift from Figure 2 appeared at 6.10 ppm is due to —CH_2 protons connected with the oxazine ring.[27] The signals observed at 3.73 and 4.93 ppm are corresponding to —O—CH_3 and —CH═CH— protons, respectively.

The signal appeared at 89.8 ppm in ^{13}C NMR spectrum (Figure 3) is corresponding to the oxazine ring (—O—CH_2—N—) carbon in the EUBz monomer. The

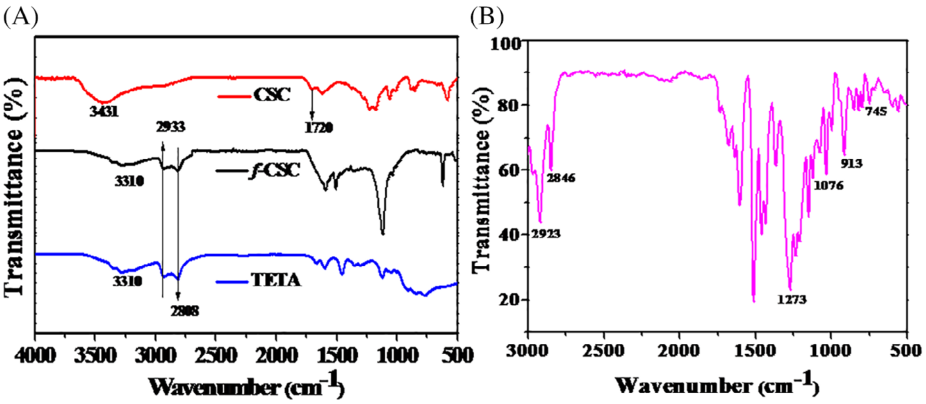


FIGURE 1 FTIR spectra of TETA, CSC, *f*-CSC, and thiourea based EUBz monomer. EUBz, eugenol benzoxazine [Color figure can be viewed at wileyonlinelibrary.com]

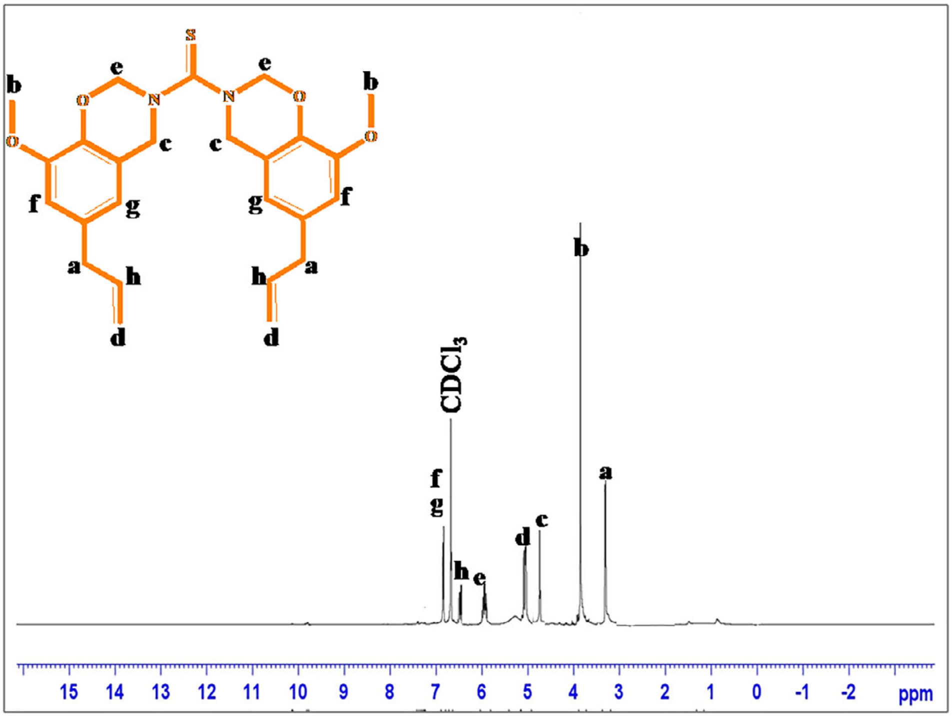


FIGURE 2 ^{1}H NMR spectrum of EUBz monomer. EUBz, eugenol benzoxazine [Color figure can be viewed at wileyonlinelibrary.com]

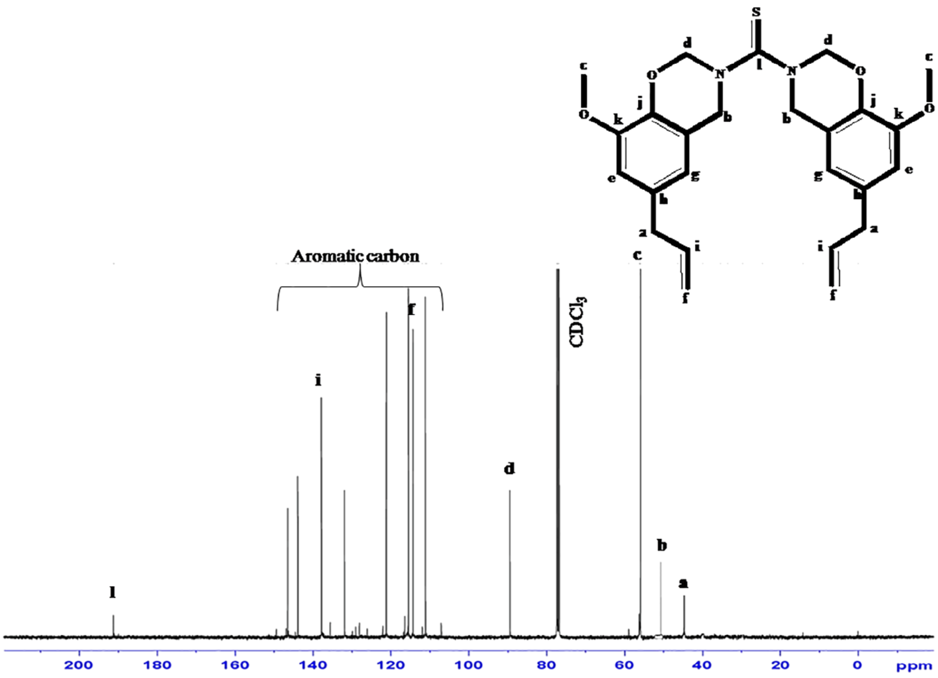


FIGURE 3 ^{13}C NMR spectrum of EUBz monomer. EUBz, eugenol benzoxazine [Color figure can be viewed at wileyonlinelibrary.com]

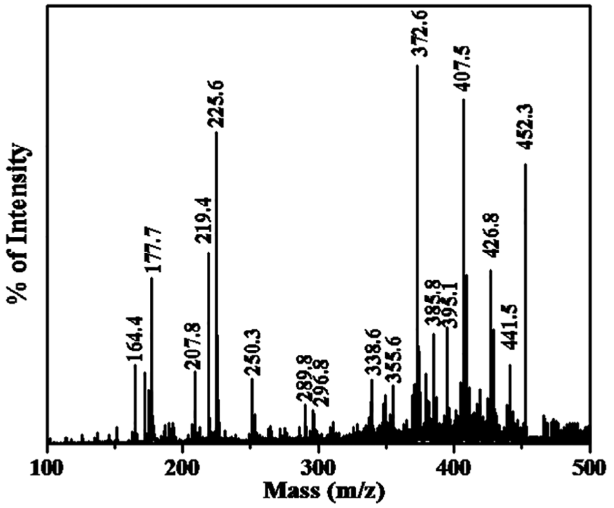


FIGURE 4 MALDI-Mass spectrum of thiourea-based EUBz monomer. EUBz, eugenol benzoxazine

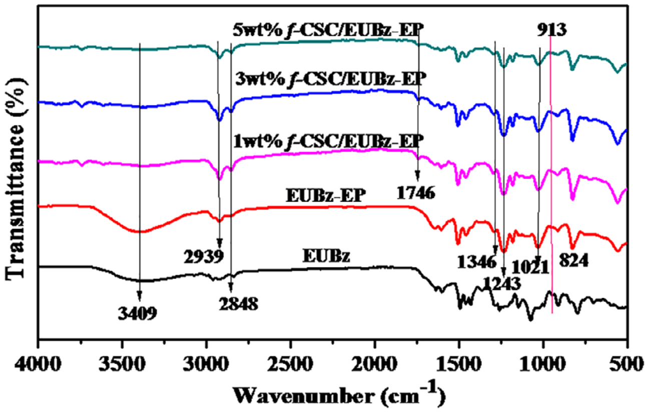


FIGURE 5 FTIR spectra of EUBz polymer, EUBz-EP matrix, and *f*-CSC/EUBz-EP composites [Color figure can be viewed at wileyonlinelibrary.com]

methoxy carbon (—O—CH$_3$) was observed at 56.2 ppm.[28] The chemical shift signal observed at 117.2 ppm indicates the presence of HC═CH carbon. Thus, the NMR data along with FTIR results confirm the formation of thiourea-based eugenol EUBz monomer.

Maldi mass study (Figure 4) was also carried to find the molecular weight of the EUBz monomer from molecular ion peak (M-1). From MALDI-Mass spectrum, it was noticed that the molecular ion peak (M-1) was obtained at 452.3 m/z value, which coincides with the theoretical value of molecular weight calculated for thiourea-based eugenol EUBz ($C_{25}H_{28}N_2O_4S$).

3.2 | Polymerization behavior of EUBz polymer, EUBz-EP matrix, and *f*-CSC/EUBz-EP composites

Figure 5 shows FTIR spectra of thiourea-based EUBz matrix, thiourea-based EUBz-EP matrix, and *f*-CSC/EUBz-EP composites. The absorption peak of oxazine group disappeared at 913 cm^{-1} indicates the ring-opening and crosslinking reaction via alkene bond formation.[29] The other characteristic absorption peaks observed at 1746 cm^{-1} (—C═O), 1346 cm^{-1} (C—N bond), 2939 and 2848 cm^{-1} (—CH$_2$—), 1243 cm^{-1} (asymmetric stretching of C—O—C), and 1021 cm^{-1} (symmetric stretching of

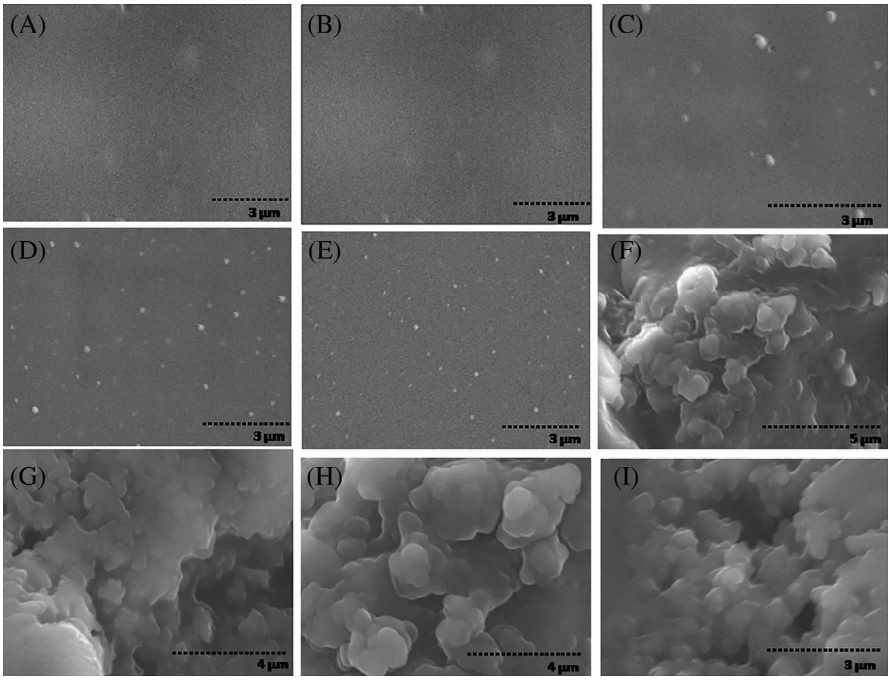


FIGURE 6 SEM images of (A) EUBz matrix, (B) EUBz-EP matrix, (C) 1 wt% *f*-CSC/EUBz-EP, (D) 3 wt% *f*-CSC/EUBz-EP, (E) 5 wt% *f*-CSC/EUBz-EP and cross-sectional images of 5 wt% *f*-CSC/EUBz-EP composite at different magnifications (F-I)

C—O—C)[30] confirm the network formation between the EUBz and EP resin in the polymeric matrix. The absorption peak obtained at 3409 cm^{-1} indicates the presence of —H—O···H hydrogen bonding[31] present in the EUBz and EUBz-EP polymer matrices.

3.3 | Surface morphological studies

Morphological structure of EUBz-EP matrix and varying weight percentages of *f*-CSC reinforced EUBz-EP composites were presented in Figure 6. The SEM pictures of both the EUBz polymer (Figure 6A) and EUBz-EP matrices (Figure 6B) exhibit homogeneous surfaces. The roughness of the EUBz-EP blended matrix-based composites were increased with respect to the increased weight percentage quantity of *f*-CSC reinforcement in the blended matrix (Figure 6C-E), which ascertains the formation of composites. In addition, the cross section of SEM images (Figure 6F,I) of 5wt% *f*-CSC/EUBz-EP composites at different magnifications clearly show the formation of 3D network structure due to the interconnected crosslinked polymeric matrix structure with *f*-CSC reinforcement and also shows the dense morphology that reflecting the corrosion resistant performance of the prepared 5 wt% *f*-CSC/EUBz-EP composites.[32,33] Further, it was noticed from the SEM pictures that the reinforcements are uniformly dispersed throughout the matrix, which might be due to the efficient physicochemical compatibility of *f*-CSC reinforcement with EUBz-EP polymer matrix. In addition, a good retention of EUBz-EP structure was noticed from the SEM images after reinforcing *f*-CSC, which suggests that the resulted composite materials could exhibit good thermal stability and strong durability.[34,35]

3.4 | Optimization of EUBz and EP resins by DSC analysis

The EUBz and EP resin blends were prepared with ratios such as 0.25:0.75, 0.75:0.25, and 0.50:0.50 (1:1) on weight basis and their curing behavior was studied using DSC analysis. Figure 7 presents the curing temperature of different weight ratios of EUBz and EP (0.25:0.75, 0.75:0.25, and 0.5:0.5 [1:1]) blends. The data obtained from DSC analysis infer that the curing temperature of the EUBz-EP blend samples of 0.25:0.75 and 0.75:0.25 weight ratios exhibit two exothermic peaks with one broad major peak with one small minor peak, where as that of the blend with 1:1 (0.50:0.50) weight ratio of EUBz: EP possesses only one clear broad major peak (Figure 7). The 0.25:0.75 and 0.75:0.25 (EUBz:EP resin) weight ratios have unequal weight percentage concentration of either EP resin or EUBz which in turn contributes to mild splitting characteristic exothermic peaks at 169.3°C and 160.4°C when curing proceeds with ring-opening polymerization of EUBz prepolymer.

However, DSC thermograms of 0.50:0.50 or 1:1 (EUBz:EP) weight ratio show a single and well-defined exothermic peak at 179.7°C, which is corresponding to

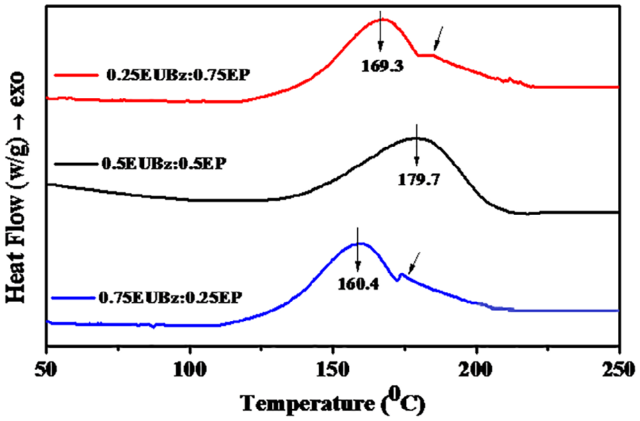


FIGURE 7 DSC analysis of different ratios of benzoxazine-epoxy premixture to study the cure behavior temperatures [Color figure can be viewed at wileyonlinelibrary.com]

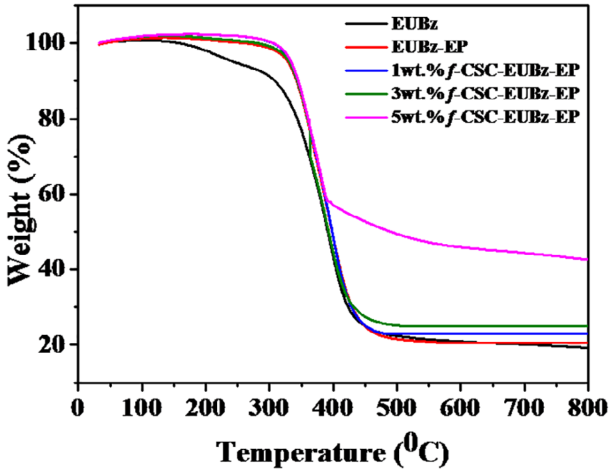


FIGURE 8 TGA curves of EUBz polymer, EUBz-EP matrix, and *f*-CSC/EUBz-EP composites [Color figure can be viewed at wileyonlinelibrary.com]

the characteristic cure temperature for the ring-opening self-polymerization of EUBz and EP resins.[36] The data obtained from curing behavior are considered as an important parameter in the cases of both EUBz and EP resin. It was ascertained that equal weight percentage concentration of EUBz and EP resin was the most probable blend combination to obtain balanced physicochemical, thermal, and surface properties suitable for coating applications. Further, it is well known that the EP resin with its rigid molecular structure possesses the higher crosslinking density and brittle behavior of the material, when cured with hardener, which also results in lower curing temperature. In addition, the blend of 0.50:0.50 expected to improve the glass transition temperature (Tg) and crosslink density with improved toughness and better thermal, hydrophobic, and anticorrosion properties of the resulted blended material-based composites. Hence, 0.50:0.50 blend ratios were used in the present study.

3.5 | Thermal studies of EUBz polymer, EUBz-EP matrix, and *f*-CSC/EUBz-EP composites

The thermal stability of EUBz matrix, EUBz-EP matrix, and varying weight percentages of *f*-CSC/EUBz-EP composites were studied using thermogravimetric analysis (Figure 8). From TGA results (Table 1), it was noticed that the initial degradation temperature and char yield are improved by increasing the weight percentage of reinforcement in the EUBz-EP blended matrix. The thermal degradation temperature at 5% weight loss was increased from 238.4°C to 332.8°C and also significant enhancement for thermal degradation temperature were also noticed at 10% weight loss while moving from EUBz matrix to 5 wt% *f*-CSC/EUBz-EP composites (Table 1). The prepared 5 wt% *f*-CSC/EUBz-EP composite was started to degrade slowly at higher temperature compared to that of eugenol-based EUBz-EP (EUBz-EP) resin blended matrix and other prepared wt% *f*-CSC/EUBz-EP composites. In addition, the thermal stability was also indirectly confirmed by the char yield and it was increased from 19.42% to 45.28%, which is confirming enhanced thermal stability of the prepared 5 wt% *f*-CSC/EUBz-EP composite compared to other composites and polymer matrix. From Table 1, it was concluded that *f*-CSC incorporated EUBz-EP matrix shows good thermal stability and char yield, which might be due to high crosslinking network between the reinforcement *f*-CSC and EUBz-EP polymer matrix.[37,38]

The Tg of EUBz matrix, EUBz-EP matrix, and *f*-CSC/EUBz-EP composites were obtained through DSC analysis (Figure 9). From Figure 8 and Table 1, it was observed that the Tg value of EUBz matrix is 104.2°C and it was improved with the incorporation of EP and *f*-CSC reinforcement, which is due to increase in network structure and complexity of the materials.[39,40] In the other words, the addition of EUBz to EP reduces the brittleness of EP matrix, increases the toughness and improved flexibility, which in turn contributes to an enhanced values of Tg.

3.6 | Contact angle analysis of polybenzoxazine

The contact angle values obtained for EUBz matrix, EUBz-EP matrix, and *f*-CSC incorporated EUBz-EP composites are shown in Figure 10. The contact angle values were increased from 95.1 to 110.8° with the addition of

TABLE 1 Glass transition temperatures and thermal properties of the prepared materials

S. No.	Samples	T_g (°C)	5 wt% loss (°C)	10 wt% loss (°C)	T_{max} (°C)	Char yield % at 800 °C
1	EUBz	104.2	238.4	303.9	387.1	19.42
2	EUBz-EP	132.4	312.6	337.7	391.5	20.56
3	1 wt% *f*-CSC/EUBz-EP	166.2	328.3	339.9	396.0	22.84
4	3 wt% *f*-CSC/EUBz-EP	191.5	330.6	342.2	400.6	24.74
5	5 wt% *f*-CSC/EUBz-EP	202.9	332.8	346.7	591.6	45.28

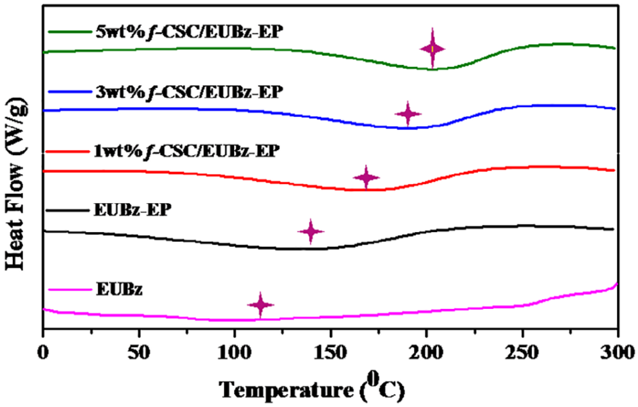


FIGURE 9 DSC thermograms of EUBz matrix, EUBz-EP matrix, and *f*-CSC/EUBz-EP composites [Color figure can be viewed at wileyonlinelibrary.com]

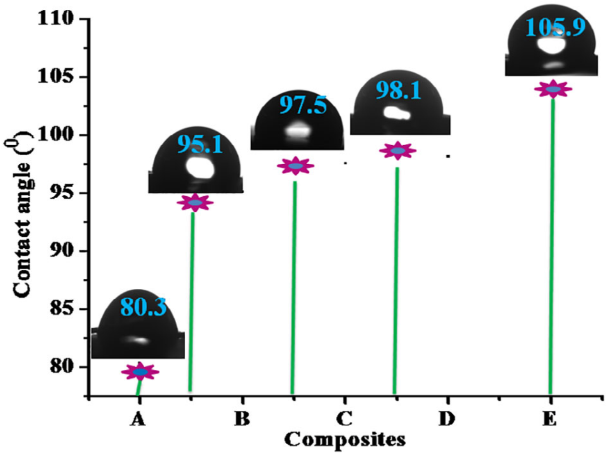


FIGURE 10 The contact angle of (A) EUBz matrix, (B) EUBz-EP matrix, (C) 1 wt% *f*-CSC/EUBz-EP, (D) 3 wt% *f*-CSC/EUBz-EP, and (E) 5 wt% *f*-CSC/EUBz-EP composites [Color figure can be viewed at wileyonlinelibrary.com]

both EP and reinforcements.[6] Furthermore, the water droplets on *f*-CSC/EUBz-EP films surface remained nearly spherical in shape after 30 minutes, which indicates stable and super hydrophobicity of the prepared *f*-CSC/EUBz-EP composites.[41]

3.7 | Anticorrosion properties of benzoxazine polymer

The EUBz matrix, EUBz-EP blended matrix, and different weight percentages of *f*-CSC incorporated EUBz-EP composites were coated on mild steel plate with the surface area of 1 cm × 1 cm. The coated mild steel was cured at different temperature as provided in the experimental part. Ag/AgCl electrode was used as a reference electrode, and uncoated as well as coated mild steel plates were used as working electrodes. The corrosion measurements were conducted in 3.5% NaCl solution at ambient temperature.

The corrosion currents were obtained from Tafel plots (Figure 11) by superimposing a straight line along the linear portion of the corrosion current and corrosion potentials were obtained through extrapolating method. The corrosion rate and protection efficiency can be calculated quantitatively from I_{corr} values (Table 2). The bare steel shows E_{corr} potential of about −1.1160 mV and the corrosion potential was increased to −0.2820 mV for 5 wt% *f*-CSC/EUBz-EP composite, that is, moving towards zero potential. Moreover, the obtained E_{corr} result concludes that the prepared 5 wt% *f*-CSC/EUBz-EP composite also shows better anticorrosion property (Table 3) compared with other previously reported literatures.[42,43] In addition, the corrosion current (I_{corr}) decreased from −3.2784 to −7.2570 Acm^2. These results conclude that *f*-CSC/EUBz-EP composites have a better anticorrosion property than the uncoated steel and EUBz-EP polymer matrix. The protection efficiency and corrosion rate were also calculated using Equations (1) and (2).

$$\eta\,(\%) = \frac{I^0{}_{corr} - I_{corr}}{I^0{}_{corr}} \times 100 \qquad (1)$$

where $I^0{}_{corr}$ is a current density of the bare mild steel and I_{corr} is the current densities of the materials coated on the mild steel plates.

$$\text{Corrosion Rate} = \frac{K \times EW \times I_{corr}}{\rho A} \qquad (2)$$

where K is a corrosion rate constant (K = 3272 mm/year), EW is an equivalent weight of mild steel plate (EW = 27.9 g), ρ is a density of the mild steel plate ($\rho = 7.85\ gcm^{-3}$), and A is the sample area ($A = 1 \times 1cm^2$).

Protection efficiency and corrosion rate results indicate that EUBz-EP blend also shows better corrosion protection performance. The *f*-CSC/EUBz-EP composites have shown protection efficiency greater than 98%, which is higher than the value recorded with EUBz and EUBz-EP matrices. In addition, the prepared composite shows the corrosion protection efficiency of 99.97% and minimized corrosion rate (0.814 mm/year), which is due to the result of high crosslinked network structure, occurrence of hydrogen bonding, which reduces the porosity and also decreases the penetration of oxygen and water/moisture molecules into the steel and thus, the composites have a good barrier properties against corrosion behavior.[44,45]

Generally, the corrosion or rust formation takes place on steel through the redox reaction in the presence of oxygen and water or moisture in the air. The different types of reaction may be involved in the corrosion or rust formations in the steel and the following reactions are expected to undergo during the rust or corrosion formations.

$$Fe \rightarrow Fe^{2+} + 2e^{-} \qquad (1)$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-} \qquad (2)$$

$$O_2 + 2H_2O \rightarrow 4OH^{-} \qquad (3)$$

$$Fe^{3+} + 3OH^{-} \rightarrow Fe(OH)_3 \qquad (4)$$

$$2Fe^{2+} + 4OH^{-} \rightarrow 2Fe(OH)_2 \rightarrow Fe_2O_3.H_2O \qquad (5)$$

$$2Fe^{2+} + O_2 + 2H_2O \rightarrow 2FeOOH + 2H^{+} \qquad (6)$$

The above reaction mechanisms conclude that the H_2O/moisture and oxygen or moisture in the air are the important components to cause corrosion or rust

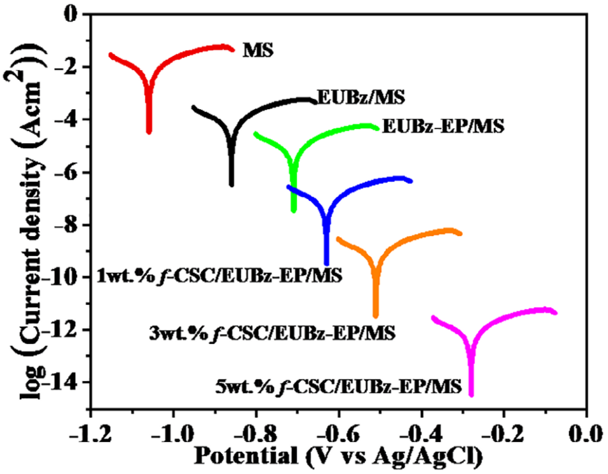


FIGURE 11 Tafel graph of MS, EUBz/MS, EUBz-EP/MS, and *f*-CSC/EUBz-EP/MS samples. MS, mild steel [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 3 Comparison of anticorrosion behavior-based on E_{corr} value for the prepared 5 wt% *f*-CSC/EUBz-EP/MS composite with the previous reports

Benzoxazine polymer	Tafel plot; E_{corr} value (mV)	Reference
Rubber-modified polybenzoxazine-based polyaniline composites	−0.542	[42]
Polybenzoxazine (poly[BA-aptms]) incorporated epoxy	−0.450	[43]
Silica (SiO_2) nanoparticles into the rubber modified polybenzoxazine (PB_Z)	−0.583	[46]
PANI/graphene composite (PAGC)	−0.584	[47]
5 wt% *f*-CSC/EUBz-EP/MS	−0.282	Present work

TABLE 2 Corrosion properties of mild steel, EUBz/MS, EUBz-EP/MS, and *f*-CSC/EUBz-EP/MS electrodes

Samples	I_{corr} (Acm^{-2})	E_{corr} (mV)	Corrosion rate (mm/year)	η (%)
MS	−2.6490	−1.1160	82.218	-
EUBz/MS	−3.2784	−0.8601	43.725	98.58
EUBz-EP/MS	−3.5243	−0.7094	34.189	98.89
1 wt% *f*-CSC/EUBz-EP/MS	−4.2325	−0.6328	16.862	99.45
3 wt% *f*-CSC/EUBz-EP/MS	−5.2869	−0.5143	5.814	99.81
5 wt% *f*-CSC/EUBz-EP/MS	−7.2570	−0.2820	0.814	99.97

Abbreviation: MS, mild steel.

formation process in the steel material. In the other words, the corrosion can take place only in the presence of O_2 and H_2O/moisture in the air. Hence, the corrosion or rust formation can be decreased if these components impeded to reach at the steel surface. Similar to the previous report,[47] the diffusion of oxygen and water or moisture in the air may be expected to decrease with increasing the content of *f*-CSC in the polybenzoxazine-EP composites. Hence, the corrosion or rust formation was reduced and the contact angle study also confirms the effective water/moisture repellent behavior of composites. Hence, the biobased composites developed in the present work can be used as coating for high-performance corrosion resistant materials including microelectronic applications.

4 | CONCLUSION

The thiourea-based eugenol-EUBz monomer was prepared and blended with EP via copolymerization process. The composites of *f*-CSC incorporated EUBz-EP matrix were prepared, and structure of the EUBz monomer was confirmed by FTIR, ^{1}H NMR, ^{13}C NMR, and MALDI-TOF spectroscopy. The ring-opening polymerization of EUBz matrix, EUBz-EP matrix, and *f*-CSC/EUBz-EP composites are confirmed by FTIR spectra. The composite prepared in the present study makes a conclusion that the biobased EUBz blended EP composites showed enhanced thermal stability, higher char yield, and improved Tg values. Further, the *f*-CSC/EUBz-EP composites including EUBz blended EP matrices are showing good hydrophobic and anticorrosion properties. Data resulted from different studies can be concluded that the eugenol can be considered as a very attractive renewable biosource for the preparation of EUBz monomers as well as its composites with high corrosion resistant behavior using biobased cashew nut shell carbon material as reinforcement.

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How to cite this article: Vaithilingam S, ThangavelRavivarman R, Muthukaruppan A. Development of cashew nut shell carbon reinforced thiourea based biophenolic benzoxazine-epoxy composites: High performance biobased coating materials. *Polymer Composites*. 2020;1–12. https://doi.org/10.1002/pc.25510