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Enhancing the Anti-corrosion and Reinforcing Properties of Epoxy Coatings using Modified Graphene oxide

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ABSTRACT

The present study deals with the synthesis and anticorrosion behavior of new modified graphene oxide. Superior corrosion resistance property was exhibited by graphene oxide and modified graphene oxide on mild steel and copper substrates. Along with the corrosion resistance behavior, the reinforcing nature of epoxy coating also improved. Graphene oxide was synthesized by Hummer's method. Graphene oxide (GO) modified with ethanol extract of *Kedrostis foetidissima* (KF) plant leaves. Gas chromatography-mass spectrometry (GCMS) analysis was selected to identify the chemical constituents present in the plant. GO, KF, and modified GO (GO-KF) were characterized by Fourier transforms infrared spectroscopy (FTIR) and Field Emission Scanning Electron Microscope (FESEM). Corrosion protection behavior of epoxy coating on mild steel and copper with GO and modified Graphene Oxide were studied using, Salt spray test, Peel test, and Contact angle measurements. Results revealed that the modified GO sheets act as a good reinforcing agent for epoxy coating on mild steel and copper substrate in a 3.5% sodium chloride (NaCl) environment.

Keywords: Epoxy coating, Mild steel, Copper, Graphene oxide, *Kedrostis foetidissima*, Sodium chloride.

INTRODUCTION

Metals and alloys are the most useful materials for industries, construction, marine, and engineering purposes. They easily combine with their environment (acid, alkali, and atmosphere) and undergo degradation. This continuous degradation is known as corrosion. Metals cannot be completely protected from corrosion. But it can be reduced in many ways, such as inhibitors[1–10], cathodic protection[11–13], and surface coating[14–19]. Mild steel is the most widely used shipbuilding material due to its good mechanical properties and low cost. Copper is another metal that plays an important role in the shipbuilding industry. It is used for saltwater cooling systems, evaporates in ships, steam lines, and numerous other equipment like pumps, feed heaters, valves, etc. Extraordinarily complex electrical equipment in ships has been built using copper and its alloys. Surface coating is the most common and useful method to protect metallic materials from their surrounding environment, which creates corrosion. The surface coating acts as a barricade between the surface of the metallic material and the corrosive environment. Among various types of coatings, the epoxy coating on the metal surface is preferable due to its high cross-linking density, act against corrosive agents, stability towards temperature and chemicals, less shrinkage, and good adhesion strength. Due to high brittleness and poor flexibility, it produces some tiny pores and cracks during solvent evaporation. Corrosive agents like oxygen, water, and electrolyte penetrate the metal coating interface through the diffusion channel through tiny pores and cracks. This leads to the weakening of the structure due to breakage of hydrogen bonding and hence adhesion is lost. To diminish this problem, many of the researchers investigated many curing agents and pigments[20, 21] to enhance the performance of epoxy coating against deterioration. But the use of nanoparticles has played a significant role in the research field for the past few years. Graphene, graphene oxide modified graphene oxide nanoparticles have good thermal, electrical, and mechanical properties. It is also impermeable to water and oxygen. The corrosion protection performance of epoxy coatings has been studied by many researchers. Bahar Nikpour et.al reported the adsorption behavior of Urtica Dioica leaf extract on GO nanoparticles and their corrosion protection performance of epoxy coated against artificial sea water[22]. Hong Peng Zheng *et al.,* modified GO using poly (Urea –formaldehyde)[23]. This composite has a good barrier performance with an epoxy coating for carbon steel. Abdul Kareem Mohammed Ali Al Sammarraie and Mazin Hasan Raheema examined electrodeposited film of reduced graphene oxide on various metals and Stainless steel[24], Carbon steel[25]. This electrodeposited GO has good protection efficiency against artificial seawater. Peimin Hou et al studied the anti-corrosion performance of epoxy coating enhanced with GO nanocontainers on carbon steel[26]. Yuwei *et al.,* studied the anti-corrosion performance of epoxy coating with modified GO (POSS-GO) in the marine environment. They have concluded that the addition of POSS–GO enhanced the barrier effect of epoxy coating[27]. Prem Anandh Senthilvasan and Murali Rangarajan investigated the corrosion protection performance of GO coating on mild steel. This study confirmed the 61% corrosion inhibition efficiency of epoxy coating on mild steel[28]. In the above-mentioned research, it was clear, that coatings GO and adding epoxy resin improved the corrosion resistance property. When the coating is damaged barrier protection of GO has been removed. To improve the barrier protection performance, GO sheets are treated with green corrosion inhibitors. In this work, it was aimed to add green inhibitors to the GO sheets. Plant extracts were selected, which are friendly to the environment, cheap, and easily available. *Kedrostis foetidissima* (KF) plant leaves were selected to extract the inhibitor. The fresh leaves have different organic compounds with aromatic rings, nitrogen, oxygen, and sulfur. Corrosion inhibition performance of GO-KF was studied in the coating phase. GO-KF was blended with epoxy resin and coated on mild steel and copper panels. The coated panels were examined by a Salt spray test (5% Sodium chloride), Contact angle measurement, and Peel test.

EXPERIMENTAL

Materials

Graphite powder, Sodium nitrate, Potassium permanganate, Sulphuric acid, Hydrogen peroxide, Hydrochloric acid, Sodium chloride, Ethanol, Acetone, and Dimethyl formamide (DMF).

Kedrostis foetidissima leaves were collected at Coimbatore, Tamilnadu, India. All the chemicals and solvents were purchased from Sigma-Aldrich and used without purification. The mild steel panels (composition 99.67% Fe, 0.09% C, 0.2% Mn, 0.01% S, 0.02% P and 0.01% N) and Copper panel (99%) were purchased from J. R Engineering works, Coimbatore. Epoxy resin and polyamide hardener were purchased from Covai Seenu & Company. The epoxy value solid content and density of epoxy resin were 0.1477-0.1665, 75-79%, and 0.96 g/cm^3 respectively.

Synthesis of graphene oxide

Hummer's method[29–31] was adopted to prepare Graphene oxide. 23 mL of concentrated Sulphuric acid was added to 1 g of graphite powder. The mixture was stirred for 2 h at room temperature. Then 0.5 g of sodium nitrate was added slowly and the temperature was minimized to 0°C and 3 g of potassium permanganate was added gradually and the temperature of the suspension was maintained to 2°C. Reaction vessel was transferred to a water bath of 35°C and stirred for 30 minutes. Then 50 mLof deionized water was added and the solution was stirred for 15 min at 90°C. 166 mL of deionized water was added to the mixture and 5 mL of hydrogen peroxide was added. The yellow-colored mixture turns into brown color. Then it was filtered and rinsed with 4% HCl. Then the resulting residue was washed with distilled water to remove impurities.

Preparation of the extract

Kedrostis foetidissima (KF) is a medicinal plant known as Appakovai in Tamil. It is a Cucurbitaceae family climber found growing near the fence. It is a herbaceous perennial that grows up to 3 meters long and gives an offensive odor when crushed. About 100 g of the plant leaves were washed with tap water and then with distilled water and allowed for some time to drain the water. To the washed leaves about 180 mL of ethanol was added and kept for 24 h at room temperature. Then extract was collected and utilized for further studies.

Preparation of the Composite

GO was dispersed in 120 mL of deionized water and sonicated for 15 min, and about 80 mL of KF extract was added. Then the GO-KF mixture was stirred magnetically for 3 hours. Then the mixture was centrifuged. The precipitate was washed with distilled water. Therefore, the untreated free KF molecules were removed. The residue was specified as GO-KF and used for further studies. 2 g of GO was dispersed in 10 mL of deionized water. The dispersion was achieved effectively by sonication. Then 30 g of epoxy resin was added. The GO and epoxy resin were sonicated for 15 min to disperse the nanoparticles into the resin phase. Then it was kept in an oven at 60°C for 24 hours. In this way, the GO/epoxy composite was prepared. Using this same procedure, a GO-KF/epoxy composite was prepared. A small amount of DMF (6 mL) was also added to the composites to enhance the dispersion of the coating. To enhance the drying process, 6 mL of polyamide hardener was added to the GO epoxy and GO-KF/epoxy composite. Fig.1. represents the structure of graphene oxide. The mild steel and copper panels were abraded by silicon carbide papers of grades 600, 800, and 1200 and then degreased with acetone. Then the abraded panels were washed with deionized water and dried. Pre-treated mild steel and copper panels were coated with GO-Epoxy and GO-KF/Epoxy. Simultaneously, neat epoxy-coated panels were also prepared as a reference. Pretreated mild steel and copper panels were coated with GO/epoxy, GO-KF/epoxy, and epoxy. Epoxy was taken as a reference. Finally, coated panels were dried in an oven for 3 h at 100°C.

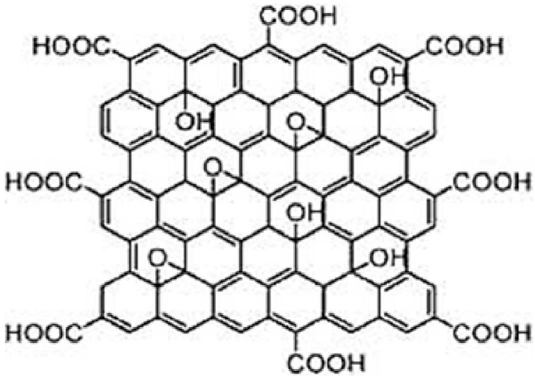


Fig. 1. Structure of Graphene oxide

Characterisation

Characterisation of GO, KF, and GO- KF

FT-IR analysis was used to elucidate the bonding and functional groups present in GO, KF, and GO-KF. A Shimadzu spectrometer was used in the FT-IR analysis with a wave number range of 4000-400 cm^{-1} and 1 cm^{-1} resolution. The field emission scanning electron microscope technique was used to identify the microstructure of GO and GO-KF with the support of the ZEISS instrument.

Chemical compounds of KF were found using a GCMS analyzer. For this, the ethanol extract was prepared and analysed using an Agilent GCMS analyzer. FESEM and GCMS analysis were carried out at the South Indian Textile Research Association (SITRA), Coimbatore, Tamilnadu.

The ASTM B117 standard salt spray test was carried out at SGS India Private Ltd, Chennai, Tamilnadu, India. To study the surface modification of mild steel and copper panels, sizes of 4 cm x 5 cm x 0.5 cm were used. An artificial defect(X mark) was created on the coated (epoxy, GO/ Epoxy, GO-KF/Epoxy) panel using a sharp knife. 5 wt% NaCl was constantly sprayed on the panels placed at a 45° angle in the salt spray chamber at a temperature of 35±2°C.

Wettability characteristics were evaluated using the contact angle measurement system model OCA20 Video-based Contact Angle Measurement Unit by Data physics, GmbH, Germany. In this test, the static contact angle of distilled water was measured on a sample at a room temperature of 25 2°C. For this purpose, a single drop of distilled water (2-3 μL) was dropped on the surface of the sample. After 10 seconds, the shape of the water droplet was recorded. The peel-off test was used to measure the force required to debond the coating from the substrate. The stickiness of epoxy and modified epoxy coating on the panels were measured. A Mark-10 Peel tester (ESM-303, USA) was used to measure the adhesion strength (peel strength) values of epoxy, GO/epoxy, and GO-KF/epoxy coatings. The Peel test was measured at an angle of 90°.

RESULTS AND DISCUSSION

Characterization of GO and GO-KF

The chemical structure and microstructure of GO, KF, and GO-KF nanosheets were characterized by FTIR, GCMS, and FESEM analysis respectively. The results received from GCMS confirmed the presence of many compounds. Semioxamazide ($C_2H_5N_3O_2$), N-(Cyanomethyl)- acetamide ($C_4H_6N_2O$), Succinic acid 3methyl but -2-yl-4-fluoro-2-methoxy phenyl ester ($C_{16}H_{21}FO_5$), ^{1}H [Isoindole-1,3 (2H)-dione, 2-phenyl ($C_{14}H_9NO_2$), Dibutyl phthalate ($C_{16}H_{22}O_4$), 5-(4-Hexyloxy benzyloxy)-2-(4-nitrophenyl) pyrimidine ($C_{23}H_{23}N_3O_5$), and 1H-1,2,4,-Triazole 3-(2-methyl propyl) ($C_6H_{11}N_3$) were the few compounds. Table 1 represents the structure of the above-mentioned compounds. The FTIR spectrum received for the GO, KF and GO-KF are shown in Fig. 2. Various peaks has be seen in the FT-IR spectrum of GO. It shows the presence many functional groups, namely -OH (3321 cm^{-1}), $-CH_2$ (2939 cm^{-1}), C=O (1685 cm^{-1}), C=C (1577 cm^{-1}) and C-O-C (1265 and 1138 cm^{-1}). The FTIR spectrum of KF reveals the presence of many functional groups. Peaks near 3365 show the presence of - NH group, C=N (2206 cm^{-1}), C=O (1722 cm^{-1}) C=C (1543 cm^{-1}) NO_2 (1510 cm^{-1}) C-O (1193 cm^{-1}) and aromatic ring (1415 cm^{-1}). FTIR spectrum of GO-KF has adsorption peaks relevant to both GO and KF. The peaks at 3543 cm^{-1} (-NH), 3458 cm^{-1} (-OH), 2283 cm^{-1} (C=N), 1660 cm^{-1} (C=O), 1139 and 1190 cm^{-1} (C-O-C) and 1479 cm^{-1} (aromatic ring) confirmed the functional groups. This confirms the absorption of KF on the surface of GO. The absorption of the compounds of KF on GO nanosheets may occur in two ways; (a). Formation of salt linkage between the functional groups of KF and the carboxylic groups present in GO. (b) Adsorption of KF on the basal plane of GO through π-π interactions.

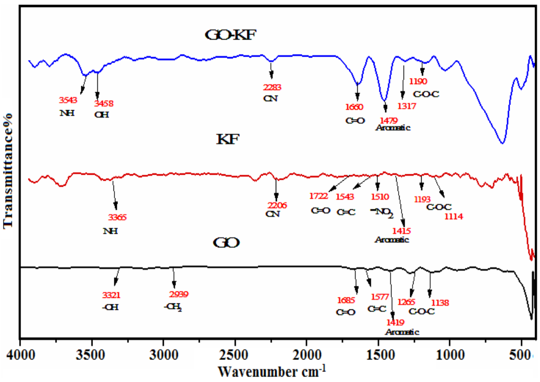


Fig. 2. FT-IR spectra of GO, GO-KF and KF

FESEM analysis

FESEM analysis was used to study the surface morphology of GO and GO–KF. Fig. 3 (a1 and a2) and (b1 and b2) represent the FESEM analysis of GO and GO-KF. Micrographs received from the FESEM analysis showed that the surfaces of GO were irregular, folded, and layered. However, the layers were captured with van der Waals's interactions. The crumpled structure of GO-KF proved that deformation occurs during the exfoliation process. From the results, it was clear that the modification of GO has a great effect on structural changes.

Salt spray tests

Mild steel and copper panels coated with epoxy, GO/epoxy, and GO-KF/epoxy was subjected to a salt spray test for 300 h continuously. The visual performances of mild steel and copper substrates are given in Fig. 4. indicates that the corrosion product was found after 144 h in the scratched area. The time of exposure to 5% sodium chloride increases to 300 hours. The corrosion product is also noted more. This may be due to the diffusion of corrosive agents to the metal and coating interface. But in the case of GO-KF added epoxy coatings, less corrosion product was observed for mild steel and copper. This proved that the epoxy modified with GO-KF has better corrosion protection properties for mild steel and copper.

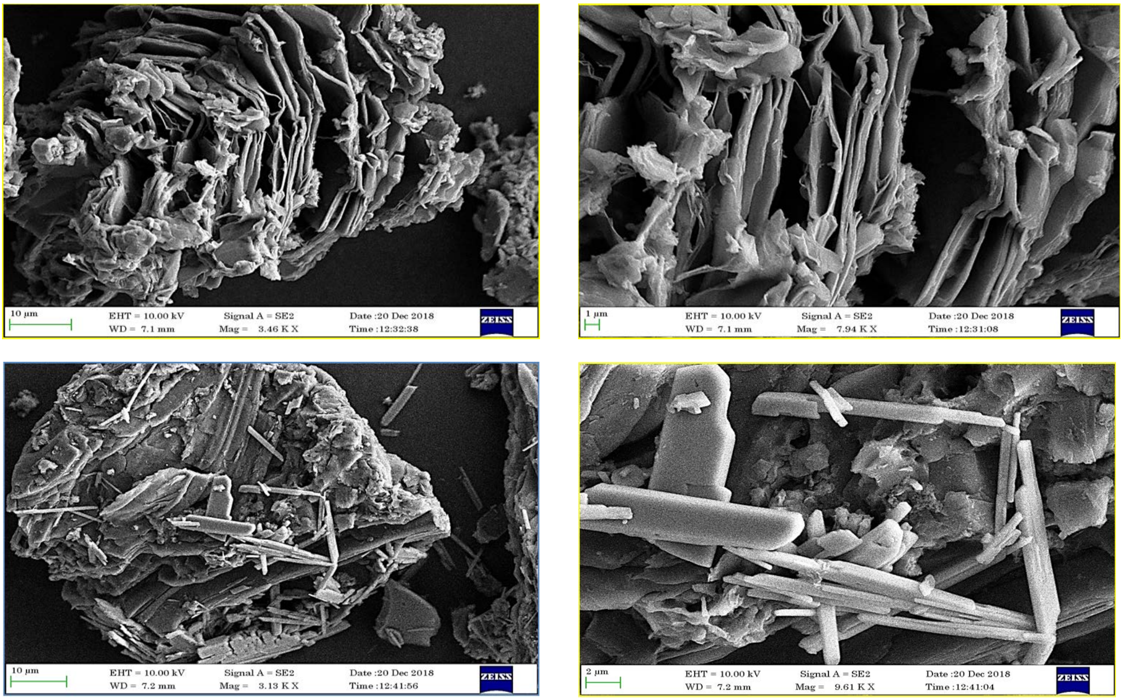


Fig. 3. a1, a2 FESEM images of GO and b1, b2 FESEM images of GO –KF a2, b2 – magnified images of GO and GO-KF

Fig. 4. Visual performances of salt spray test of mild steel and copper samples exposure to 5% NaCl solution at the initial time, after 144and 300 hours.(a): Untreated epoxy /ms,(b) : GO-epoxy/ms,(c) :GO-KF-epoxy/ms(d): Untreated epoxy /Cu , (e) : GO-epoxy/Cu,(f) :GO-KF-epoxy/Cu

Contact angle measurements

The contact angle value of a surface decides the wet ability of the metal substrate. This was measured to find the corrosion protection behaviour of epoxy coatings. The contact angle value of the epoxy coating on mild steel and copper surfaces was the same. The contact angle value of epoxy/GO and epoxy/GO-KF was a little high. Fig. 5: Pictorial representation of the contact angle measurements of epoxy, epoxy/GO, and epoxy/GO-KF coated panels. The contact angle value shows that epoxy and epoxy/GO coated substrates are hydrophilic. In general, hydrophobic surfaces have high contact angle values of 32–38 (range 90°–120°). Here, epoxy and epoxy-GO coated substrates have a high contact value compared to epoxy and epoxy-GO. This shows that epoxy/GO-KF coated mild steel and copper substrates have low surface energy and wet ability. This result reveals that the interaction of GO and KF molecules produces a hydrophobic surface.

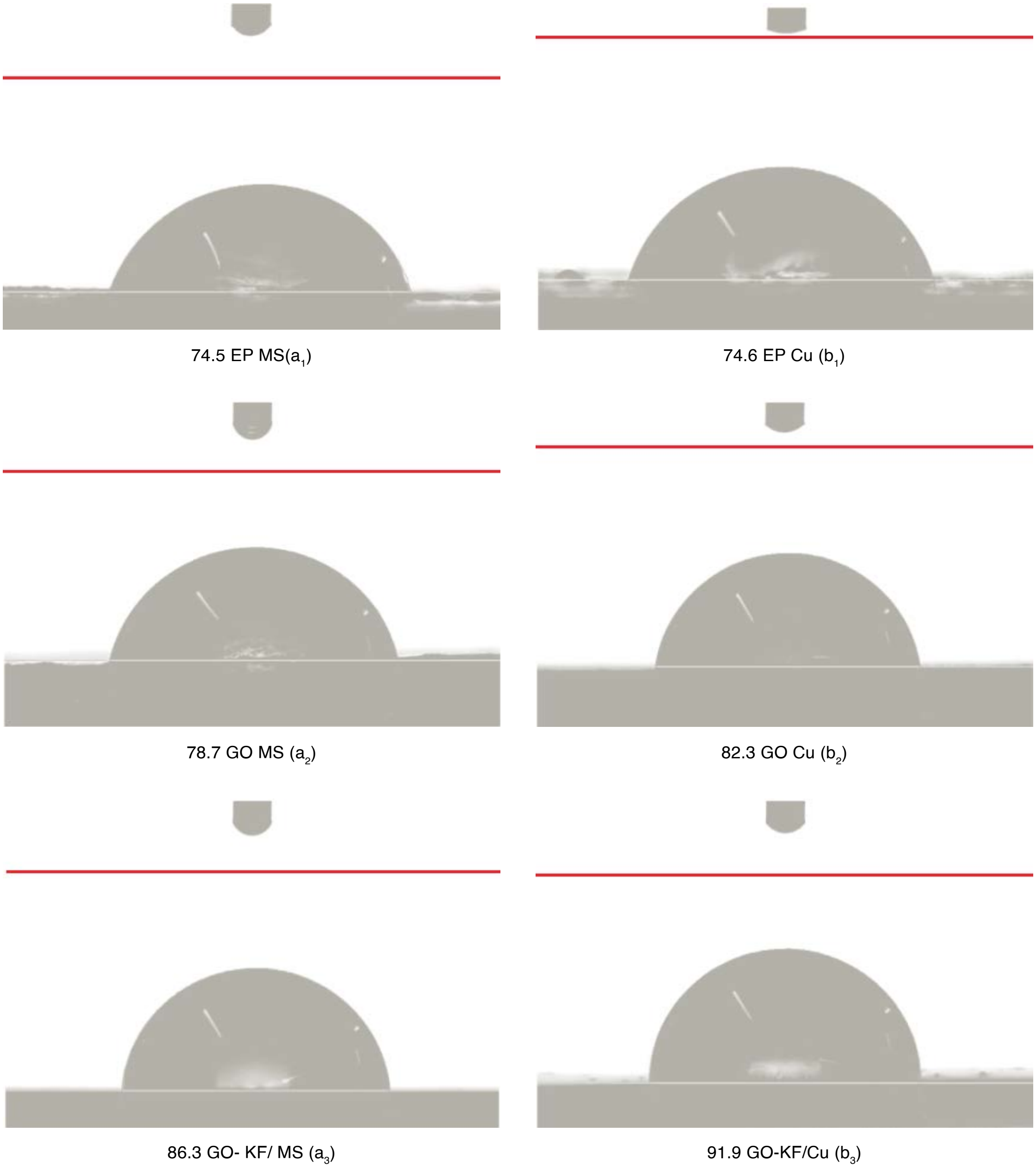


Fig. 5. Contact angle images of EP, GO, GO-KF coated mild steel (a_1, a_2, a_3) and Copper (b_1, b_2, b_3)

Peel-off test

The peel-off test was performed to determine the adhesive strength (stickiness) of the coating. Peel-off test results are given in Fig. 6. a1, a2, a3. The average forces required to debond the coatings were 1.228 (epoxy), 1.105(epoxy/GO), and 1.357(epoxy/GO-KF) for mild steel substrates. The average forces required to debond coatings were 1.031 (epoxy), 0.67 (epoxy/GO) and 1.373 (epoxy/GO-KF) for copper substrates. The peel strength data received for mild steel and copper indicated that the addition of modified GO (GO-KF) enhanced the peel strength of the epoxy coating.[39] This proved that modified GO acts as a good reinforcing agent.

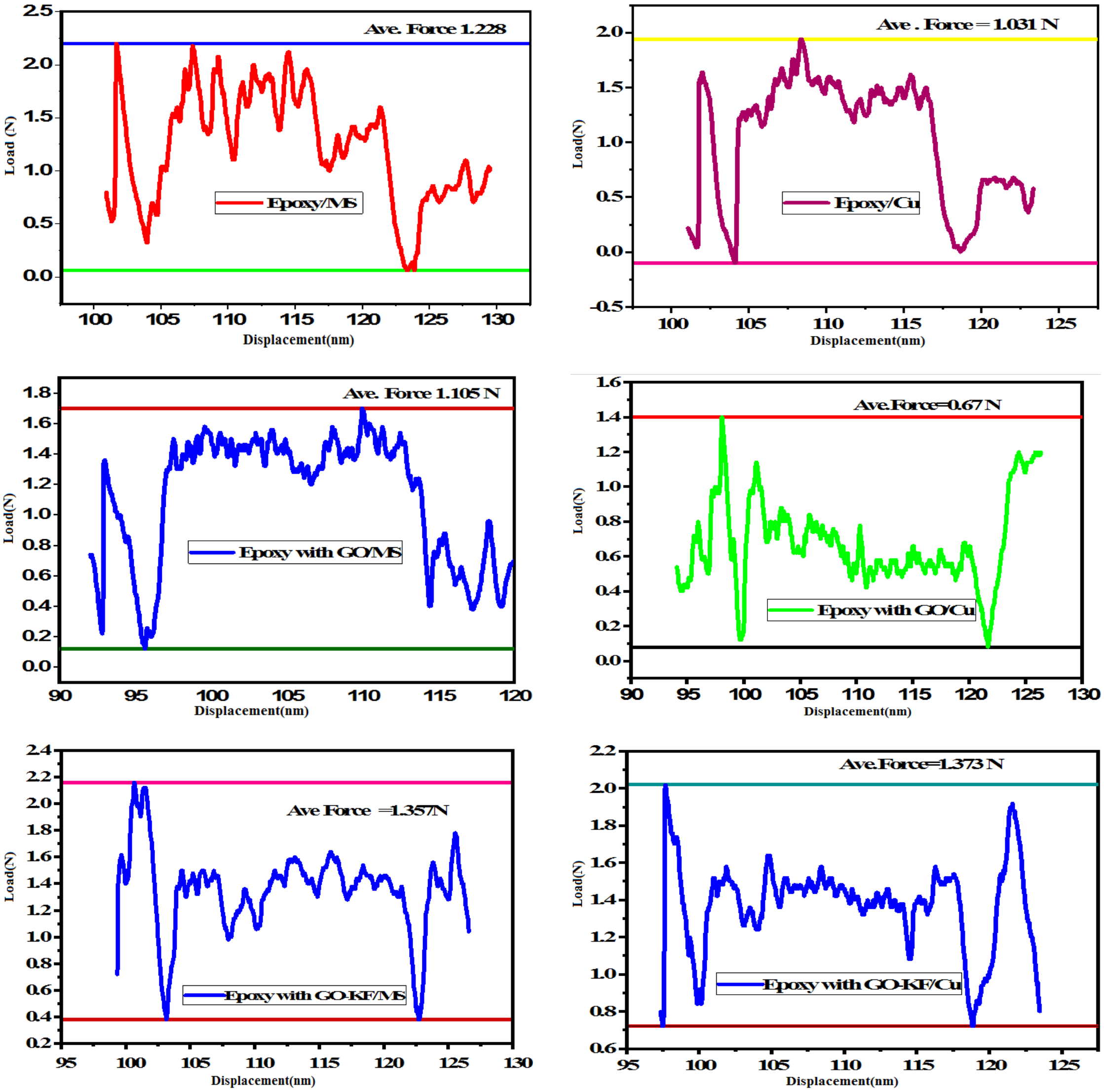


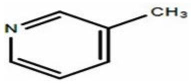
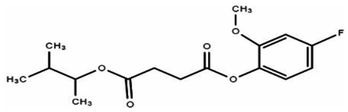
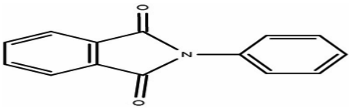
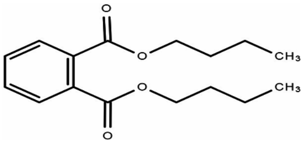
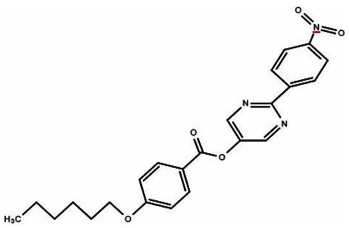
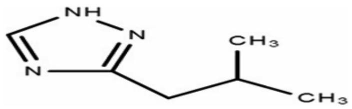
Fig. 6. Images of Peel off test for EP, GO, GO- KF coated mild steel and Copper

The corrosion protection mechanism of epoxy coating without any reinforcing agent is simple. Epoxy acts as a barricade between the metal substrate and the electrolyte. When an artificial defect is made in the coating, the electrolyte penetrates the coating and metal interface through pores and the coating defects. As a result of the penetration, the bonding between the coating and the metal is damaged. Metal dissolution occurs at the coating/metal interface. An oxygen reduction reaction occurs at the cathode and creates OH-.

$$M \longrightarrow M^{n+} + ne^{-}$$

$$nH_2O + O_2 + ne^{-} \longrightarrow nOH^{-}$$

Table 1: Structural formula of some organic compounds existed in extract of Kedrostis Foetidissima

S.No	Name of the compound	Structure
1	Pyridine , 3- methyl-	
2	Succinic acid 3methyl but -2-yl-4-fluoro-2-methoxy phenyl ester	
3	1H [Isoindole-1,3 (2H)-dione,2-phenyl	
4	Dibutyl phthalate	
5	5-(4-Hexyloxy benzoyloxy)-2-(4-nitrophenyl) pyrimidine	
6	1H-1,2,4,-Triazole3-(2-methyl propyl)	

This leads to an increase in pH. This leads to delamination of the coating, whereby adhesion is lost. When an artificial defect is created on a coating, it does not show protection performance. Reinforcing the GO sheets with KF extract improves the protection and inhibition properties of the epoxy coating. In this case, the organic molecules of KF are adsorbed on the GO sheets. These molecules form complexes with the metals (Fe/Cu). These complexes block the active sites of the electrolyte (Cl^-, O_2). Hence, treating GO-KF with epoxy provides an effective barrier performance in artificial seawater. Organic compounds present in the KF contain heteroatom like N and O. These elements are electron-rich centres and have a tendency to share the lone pair electron with the empty orbital metal ions. The complexes are formed to cover the metal surface and block the anodic and cathodic areas. In this way, the addition of GO–KF to the epoxy coating protects the metal system.

CONCLUSION

Based on the results obtained from FT-IR and FE-SEM analysis, it can be concluded that KF molecules are adsorbed on the GO sheets. Contact angle measurement results prove the hydrophobic nature of the epoxy coating containing GO-KF. Salt spray tests are in good agreement with contact angle measurement. The peel-off test result reveals that the epoxy coating containing GO-KF is a good reinforcement for the epoxy coating. Hence, GO-KF reinforces the epoxy coating for both mild steel and copper.

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Conflict of Interest

There is no conflict of interest.

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