INTERNATIONAL JOURNAL OF CURRENT ADVANCED RESEARCH

ISSN: O: 2319-6475, ISSN: P: 2319-6505, Impact Factor: 6.614

Available Online at www.journalijcar.org

Volume 13; Issue 12; December 2024; Page No.3452-3459

DOI: http://dx.doi.org/10.24327/ijcar.2024.3459.1732

Research Article

ANTI-CORROSIVE EFFECT OF GRAPHENE IN BIO-BASE PAINT-COATING

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ARTICLE INFO

Article History:

Received 25th October, 2024

Received in revised form 15th November, 2024

Accepted 22nd November, 2024

Published online 28th December, 2024

Key words:

corrosion, cardanol, epoxy, graphene, Mechanical properties, Anticorrosive properties.

ABSTRACT

The exceptional physical, mechanical, and chemical properties of graphene make it a highly applicable anticorrosive coating.Graphene has a beneficial effect on paint coatings, by improving their anticorrosion capabilities. The paint composition uses cardanol epoxy with 1.0% weight of graphene along with other pigments and fillers. Polyamines are used as the hardener. The anti-corrosion ability of the paint coating sample was assessed after it had been applied both with and without graphene. It was found that the anticorrosive properties of graphene-epoxy–cardanol resin based paints are superior to that of the paints formulated with the unmodified epoxy resin. Paints based on graphene and graphene oxide will help to reduce corrosion and improve anticorrosive characteristics for future generations.

INTRODUCTION

Metals deteriorate through a process called corrosion when chemicals are exposed to the environment.It was lead toseveral environmental and economic issues at very high cost. Numerous films, including premium paint, pigment, corrosion inhibitor, nanocomposite, and organic coating agent, were used to prevent metal corrosion [1-11]. Bisphenol A (BPA) is an organic chemical that is widely used in epoxy resin and other industrial products. However, BPA has negative effects on the immune and reproductive systems, causes dermatitis, causes cancer, and is a strong skin sensitizer [12-22]. A wide range of bio-based epoxy resins, such as cardanol[23-26], rosin[27-28], vegetable oil[29-31], eugenol[32], vanillin[33-41], and Isosorbide[42]were available to replace BPA epoxy. Moreover, acid like gallic acid[43], and cinnamic acid[44] base epoxy resinswere also useful.

A significant discovery following fullerene and carbon nanotubes is graphene (GR). Graphene was making the greatest impact in the corrosion industry because of its phenomenal mechanical power, chemical strength and compactness[45-47]. It is composed with compact sp^2 hybridized carbon atom in to honeycomb crystal structure[48]. It was first isolated by micromechanical cleavage of graphite[49]. The theoretical specific surface area of graphene is 2600 m^2 /g [50]. It has outstanding thermal conductivity (3000 W/(mK)), as well as high speed electron mobility (15000 cm^2 /(Vs)) at room temperature. Its mechanical stress reaches to 1060 Gpa, while the density is only 2.2 g/cm and it was 100 times stronger than that of the best steels in the world[51].

Graphene was utilized in many different materials, including (i) single-layer Graphene (SLG), (ii) multi-layer Graphene (MLG), (iii) Graphene platelets, (iv) Graphene oxide (GO), and (v) Reduced Graphene oxide (RGO)[52]. These materialswere good anticorrosive agent because of their superior barrier properties [53-54]. Graphene and graphene oxides coated with organic compounds, nanocomposites [55-60] and ionic liquids [61-62] enhanced anticorrosive property and reduce corrosion. Their composites have extensive application in various fields like solar cell[63-65],energy preservers[66-69],conductors[70-72], optoelectrical devise[73-76], and bio-medico[77-80]. Additionally, Graphene oxide also offers a diverse array of environmental uses, such as removal of toxic gas[81-82], water purification treatments[83-84], and so forth.

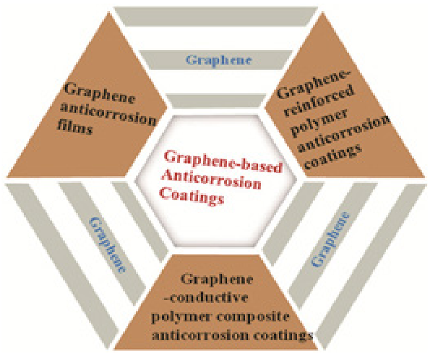

Fig.1 Different type of application for graphene base anticorrosive coating.

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Cardanol is available from the byproduct of cashew nut shell liquid(CNSL)[85].various types of phenolic compounds, such as anacradic acid, cardanol, and cardol with varying proportions, are found in CNSL [86]. Cardanol contain long aliphatic chain at meta-position of phenolic benzene ring, whichis responsible for good processability and high solubility in organic solvents that influences numerous chemical transformations. It is an intriguing alternative to BPA[87]. Furthermore, cardanol augmented mechanical attributes like tensile strength, modulus, elongation, and thermal properties when used as a modifying agent with BPA-epoxy[88-90]. Their physico-mechanical characteristics, chemical resistance, and corrosion protection efficiency were improved by the use of modified cardanol-BPA epoxy with pigment and polyamide as hardeners in anticorrosive coatings[91].

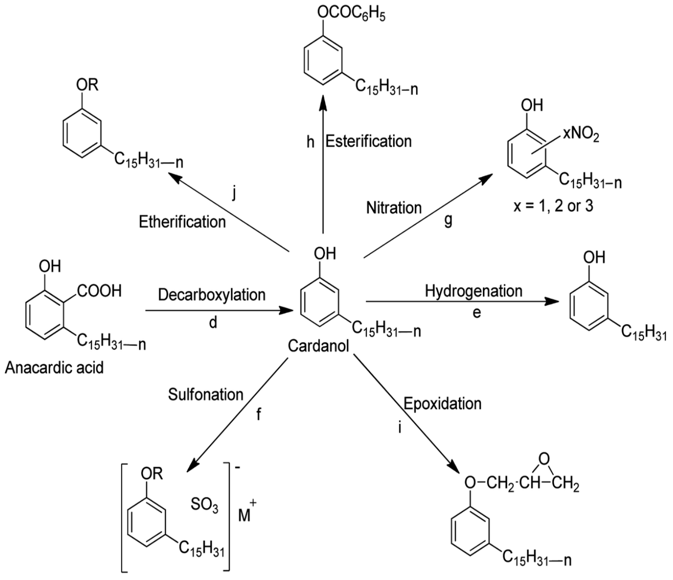


Fig. 2 possible substitution reaction of cardanol.

we are discussed in this study about paint coating and formulation with addition of graphene which was help to increases physico-mechanicalproperties of paint coating and enhance anticorrosive performance of coating. Paint sample was prepared by IS:101methodand tested by according ASTM and British Standard method.

MATERIALS AND METHODS

Cardanol,Epichlorohydrin, caustic soda, tetra-n-butyl ammonium bromide (TBAB), dichloromethane, were supplied by Thakor reductant private limited, surat, Gujarat. polyamine use as hardener.Mild Steel plates (150 mm x 100 mm) were obtain from Thakor reductant private limited, surat, Gujarat. All the chemical are of analytical grade.

synthesis of cardanol epoxy.

A 1 Lthree necked flaskwas filled with anexcess solution of epichlorohydrin (2 mol) and 20 mL of water to dissolve 1 mol of cardanol. The flask equipped with Liebig's condenser, a thermometer, and a mechanical stirrer. The mixture was gradually heated until the epichlorohydrin started to boil. A fresh dose of alkali (1 mol) was applied when the reaction had subsided. The reaction mixture was refluxed for a 1 h, as the reaction mixture became viscous, the heating was turned off. Vacuum distillation was used to eliminate the spare epichlorohydrin and DCM.The products were characterised by spectroscopic analysis, and epoxide equivalent[91].

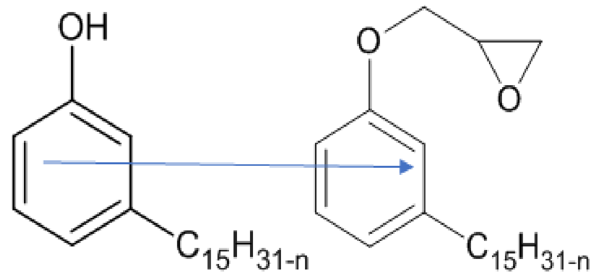


Fig.3 Epoxidation of cardanol.

Characterization of epoxy.

spectroscopy study

IR spectra were recorded on a Jasco FT/IR-6600typeA spectrophotometerusing potassium bromide pellets, the frequencies are expressed in cm^{-1}.The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance Neo 400 MHz by using tetramethyl silane as the internal references,with DMSO as solvent.Scanning electron microscopy (SEM) was usedtoobserved morphology of composite coating sample.

Epoxide Equivalent weight (EEW).

Cardanol epoxy Equivalents wt. was determine by the ASTM D-1652standard. It is simple titration method against 0.1N solution of perchloric acid solution by using crystal violet indicator blue [92].

Preparation of test samples.

Mild steel panels of size 150 mm x 100 mm were used and prepared as per the method given in IS: 101 Part 1/Sec. 3: 2001 [93]. The steel frames were degreased by washing with xylene and polished with #180 IS emery cloth. Sand dust is removed by wiping with a cotton cloth. It is then bleached with an organic solution to remove stains. Two coats of each resin are applied by brush to the iron and thoroughly cleaned rims. The rims are dried to remove traces of dampness. The paint coated panels are left in the lab for 7 days to fully dry and cure the films. The edges of the iron plates are sealed with beeswax to prevent edge attack. At least three iron panels were prepared for each chemical test. Drying time and layer thickness for different colours are shown in Table 1.

Formulation of paint

Paint was formulated by using titanium dioxide powder, zinc phosphate(ZnP), talcpowder, calcium carbonate, pigments and organic solvent. After the paint form, 1% graphene was added and continuestirring about 15-30 min.Cardanol epoxy resin with the aromatic polyamine adduct based hardener and Graphene-cardanol epoxy resin with the same hardener were used as binders.

Mechanical and Physical Properties of paint coating

A paint coating properties such as tensile strengthASTM C-638, pull of adhesionASTM D-4541, humidity test ASTM D-2247, salt spray test ASTM B-117, tabor testASTM D-4060, flexibilityASTM D-522-93and scratch hardness British Standard BS 3900 test was measurement by different standard testing method[94].

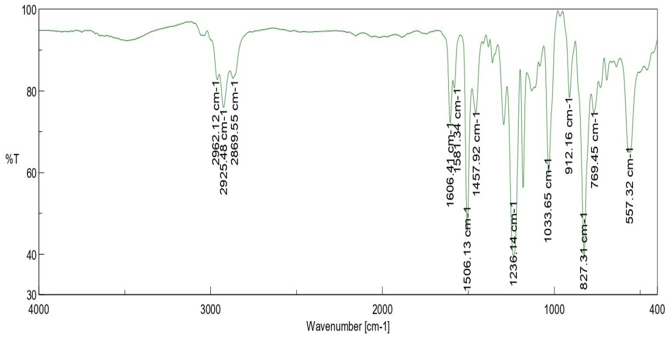


Fig. 4 FTIR data of cardanol epoxy.

FT-IR data

The IR spectra of compound exhibited sharp peak in region of 912 – 827cm^{-1}due to the presence of the Epoxied group. The C-H scratching bands were observed at 2962-2869 cm^{-1}. The C=C stretching of aromatic ring was observed at 1606-1581cm^{-1} . The appearance of peak at 1236 cm^{-1} showed presence of C-O-C group in compound.

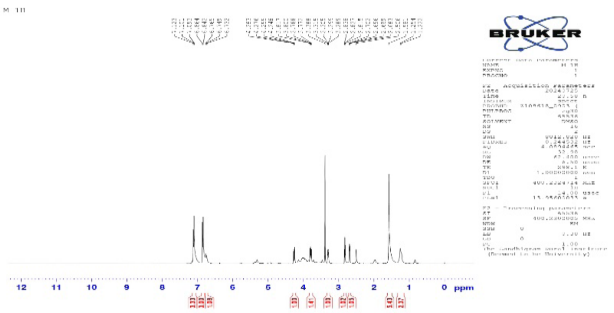


Fig. 5 ^{1}H-NMR data of cardanol epoxy

^{1}H&^{13}C-NMR data.

^{1}H-NMR sprectrum exibited two proton doublet at 1.22 ppm confriming the presences of CH_2 of epoxied. Adittionally, sceond signal was apper at 3.78 ppm indicating proton neighbouring to electronegative atom. The proton of aromatic ring was observed between 6.73-7.12 ppm.

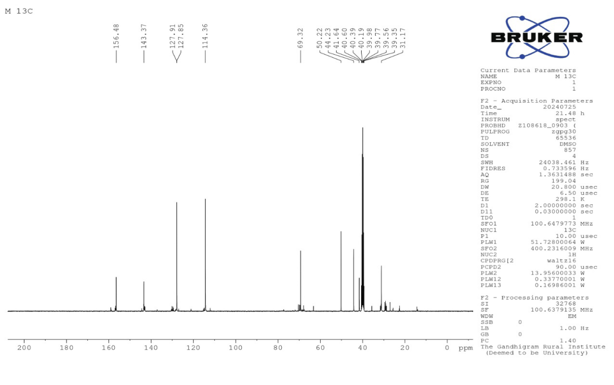
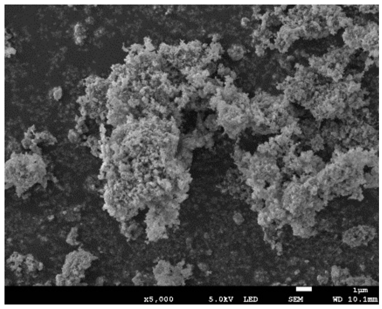
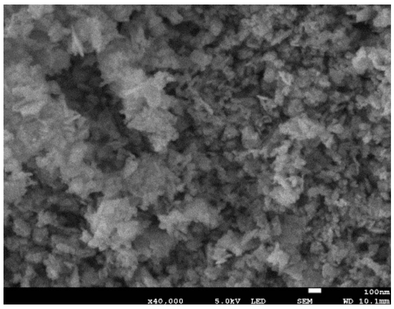


Fig. 6 ^{13}C-NMR data of cardanol epoxy.

^{13}C NMR spectra at 50.22 and 69.32 ppm confirming the presence of Epoxy carbon. Between the rage of 31.17 to 44.23 ppm spectra showed presences of alkyl carbon chain. Morover, at signal 156.48 ppm displayed aromatic moiety with electronegetive atom.singan between 114.36 to 143.37 ppm was observedas aromatic carbon.



A



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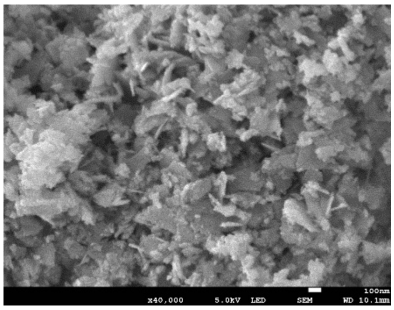
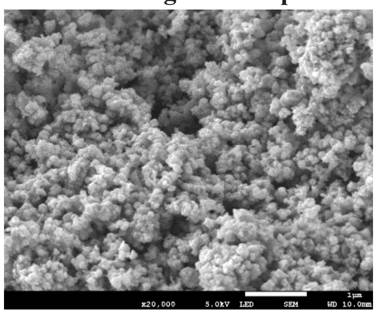
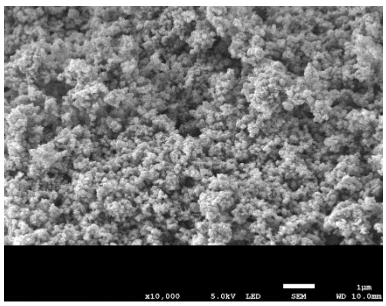


C

SEM images of sample.



D



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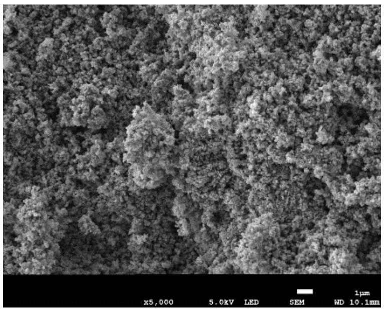


F

Fig .7 SEM images of paint sample cardanol-epoxy (A,B,C) and Graphene-cardanol epoxy (D,E,F).

Epoxy Equivalents wt.(EEW).

The epoxy equivalentswt. of cardanol epoxy was found to be 463.45. it is mean of 3 various similarwt. of epoxy sample. Calculation was done by below equation.

EEW= (W*1000)/(V*N).

Mechanical and Physical Properties of paint coating.

Physical properties of the paints like drying time, and film thickness are given in Table 1. It can be noted that the panels were coated with a similar thickness of the paints as dry film thickness of all the paints was 0.260 ± 5mm. The touch dry time for different paints varied from 35 to 50 min, while hard dry time varied from 45 to 55 h.

Table 1 properties of different paint.

Paint	Thickness of sample mm	Dry time Touch dry(min) hard dry(hr)	
Cardanol epoxy	0.260	35-40 min	48hr
1.0%Graphene-cardanol epoxy	0.260	45-50 min	54hr

Tensile strength

The tensile strength and elongation of both sample was given below table 2. Which was measure by According section 2.6. Tensile strength of paint sample was in the range between 21–25Mpa. Graphene-cardanol epoxy give better tensile results than the unmodified graphene sample and which was increased up to 27%. Moreover, elongation of both sample are also shows better results in favour of graphene sample which was also increases up to 33%. Dut to graphene properties which is increases tensile and elongation properties.

Table 2 tensile properties of sample.

Paint	Tensile strength (Mpa)	Elongation (%)
Cardanol epoxy	21.9± 0.5	4.1± 0.5
1.0%Graphene-cardanol epoxy	23.5± 0.5	5.9± 0.5

Pull of adhesion test

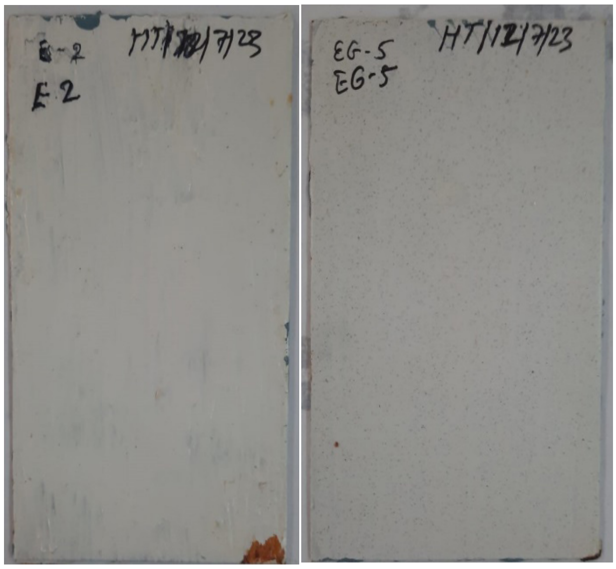
Pull adhesion test results was give the idea about what is a resistance of a coating to separation from a subtract when perpendicular tensile force is applied. Cardanol epoxy composite Adhesion strength was 10.34Mpa and 1.0wt% graphene\cardanol-epoxy composite Adhesion strength was 11.40Mpa. The average adhesion strength was 11.37 Mpa. Results was clear that addition of graphene wt.% give better adhesion property.

Table 3 pull of adhesion test results.

paint sample	Adhesion (Mpa)
Cardanol epoxy	10.34± 0.5
1.0wt% graphene\epoxy	11.40± 0.5

Humidity test.

A humidity test provided insight into the potential reactions between graphene and epoxy composites under specific environmental conditions. The cardanol-epoxy sample showed more blisters on the steel substrate after 100 hours, and it also had a higher hydrophobicity characteristic than the other sample. The paints' capacity to effectively resist corrosion is dependent on the strength and permeability of their coating. In this study, the paint containing 1% graphene-cardanol epoxy exhibited the least amount of blistering in immersion and humidity cabinet testing. It also had the highest strength and lowest permeability among the created paints.



(A)Cardanol epoxy paint sample. (B) 1.0%Graphene-cardanol epoxy paint sample.

Fig. 8 sample after humidity test.

Salt spray test

The salt spray test is the most widely used and regarded corrosion test. Salt spray testing yields data on the corrosion resistance of the materials and the failure of the coating film. For two and a half days, the sample was examined with a NaCl solution in a salt spray chamber. The outcomes of the salt spray test are displayed below. Large rust patches on the steel specimen are visible in the sample An examination. On the steel subtract, sample B exhibited very little corrosion resistance and spots.Consequently, the addition ofgraphene could improve the epoxy composite coating's anticorrosion effectiveness.

(A) Cardanol epoxy paint sample. (B) 1.0%Graphene-cardanol epoxy paint sample.

Fig. 9 sample after 2500 hr salt spray test.

Tabor abersion test and flexibility test and scratch hardness.

Table 4 results of flexibility and tabor and scratch hardness test.

Paint	Adhesion and flexibility	Tabor test (1000gm) 500 cycle	Scratch Hardness (1500g)
Cardanol epoxy	No failure	No failure	No failure
1.0%Graphene-cardanol epoxy	No failure	No failure	No failure

Using a 3.2 mm diameter mandrel, the coated panels were bent for the adhesion and flexibility tests. The findings for each paint type are shown in Table 4. Following the test, there were no visible indications of damage, separation, or cracking on the paint films, suggesting adequate flexibility and elongation. When tested with a weight of 1000 gm, all of the paints pass the scratch hardness test (Table 4), demonstrating good abrasion resistance.

Scratch hardness test, a hard hemisphere needle of the diameter of 1 mm was allowed to run on the test panel at the rate of 30-40 mm s^{-1}. A specified load was placed on the top of needle and the panel was examined for sign of bare metal.The scratch hardness was found to be in the range 1500-1700g. All the coatings on mild steel panels passed the scratch performance test up to 1.5 kg load. As the addition of graphene increased, the scratch hardness of the coating films of cardanol-Graphene based coating films was found to be also increased.

CONCLUSIONS

The Graphene cardanol epoxy resin-based paints have better anti-corrosion abilities compared to paints made with cardanol epoxy resin, regardless of the components such as pigments, fillers, and additives. Graphene plays an important role in corrosion prevention and enhanced adhesion is attributed to its outstanding characteristics, such as flexibility to confirm by various surfaces, chemical inertness, and impermeability. Graphene base coated sample tensile and elongation was much better than such epoxy sample. In the humid atmosphere graphene coated sample have highest strength and lowest permeability. From the salt spray test we conclude that graphene sample show list amount of corrosion spots.

Acknowledgement

We are grateful to Department of Chemistry, V. S. Patel College of Arts and Science, Bilimora, Gujarat for providing necessary laboratory facilities. We also thank SVNIT-Surat, Gandhi gram rural insitute-Gandhigram and PR testing agency-Delhi, Thakor reductant private limited-Surat for providing chemicals and instrumental facilities. Further, coating analysis was carried out at Surface Engineering & Coating Consultant, Mumbai.

Funding

This research was funded by major/minor project,Veer Narmada South Gujarat University,Surat.

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