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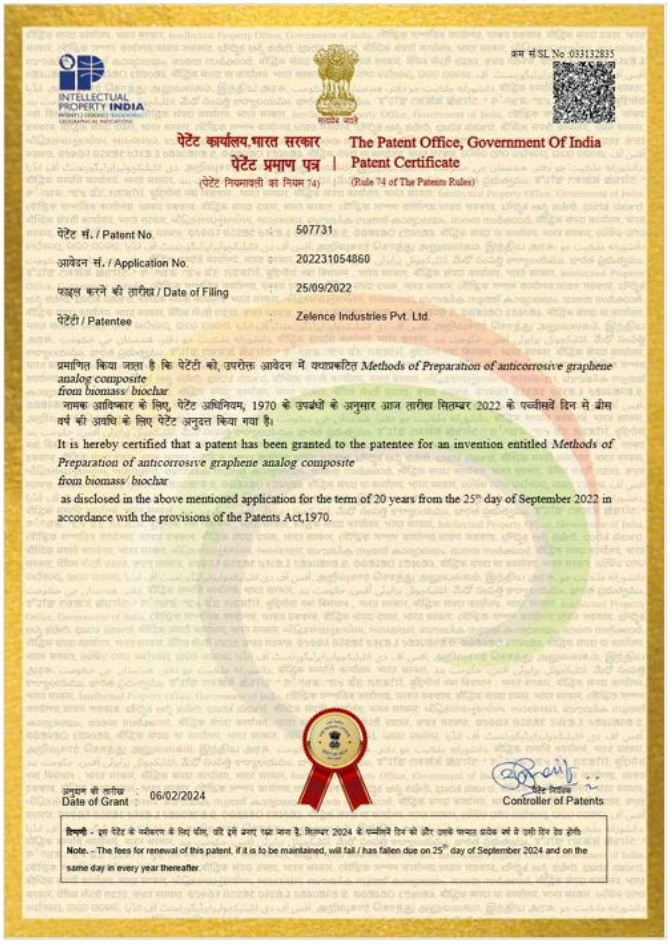
Patent Report TM

Methods of Preparation of Anticorrosive Graphene Analog Composite from Biomass/Biochar

Anu Verma, Bidus Kanti Das, Chandra Sekhar Tiwary and Jayanta Bhattacharya

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Certificate



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फाइल करने की तारीख / Date of Filing : 25/09/2022

पेटेंटी / Patentee : Zelence Industries Pvt. Ltd.

प्रमाणित किया जाता है कि पेटेंटी को, उपरोक्त आवेदन में यथाप्रकटित *Methods of Preparation of anticorrosive graphene analog composite from biomass/ biochar* नामक आविष्कार के लिए, पेटेंट अधिनियम, 1970 के उपबंधों के अनुसार आज तारीख सितम्बर 2022 के पच्चीसवें दिन से बीस वर्ष की अवधि के लिए पेटेंट अनुदत्त किया गया है।

It is hereby certified that a patent has been granted to the patentee for an invention entitled *Methods of Preparation of anticorrosive graphene analog composite from biomass/ biochar* as disclosed in the above mentioned application for the term of 20 years from the 25th day of September 2022 in accordance with the provisions of the Patents Act,1970.

अनुदान की तारीख : 06/02/2024
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Controller of Patents

टिप्पणी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, सितम्बर 2024 के पच्चीसवें दिन को और उसके पश्चात प्रत्येक वर्ष में उसी दिन देय होगी।

Note. - The fees for renewal of this patent, if it is to be maintained, will fall / has fallen due on 25th day of September 2024 and on the same day in every year thereafter.

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Date of Grant	06/02/2024

1.0 Field of the Invention

This disclosure relates to an eco-friendly corrosion inhibitor derived from carbonaceous biomass, which can be used to protect different components from environmental degradation.

2.0 Background/Prior Art

The preparation of anticorrosive graphene analog composites from biomass or biochar is a promising area in green materials science. This approach harnesses renewable sources to synthesise functional materials with corrosion-resistant properties. Here's an overview of prior art methods commonly found in patents and scientific literature:

2.1 Pyrolysis of Biomass to Produce Biochar

- *Process*: Controlled thermal decomposition of biomass (*e.g.*, agricultural waste, wood chips, coconut shells) in an oxygen-limited environment.
- *Temperature range*: 300-900°C.
- *Goal*: To obtain biochar with high carbon content, aromatic structure, and residual functional groups.

Reference

- Patents: CN107601653A, US20170275794A1
- Tan X-f, Liu S-b, Liu Y-g, Gu Y-l, Zeng G-m, Hu X-j. Biochar as a precursor of activated carbon. Renew Sustain Energy Rev. 2016; 227:359-372.

2.2 Chemical Activation of Biochar

- *Chemicals used*: KOH, H_3PO_4, $ZnCl_2$.
- *Purpose*: To increase porosity and surface area; facilitates graphitisation.
- *Typical Process*:
  - Mix biochar with the activating agent.
  - Heat under inert atmosphere (N_2 or Ar).
  - Wash and dry.

Reference

- CN104432455A – Activated carbon from rice husk biochar
- Effect of activation on biochar properties for composite applications. Carbon. 2015.

2.3 Graphitisation to Produce Graphene-like Structure

- *Catalytic Graphitisation*: Using metal catalysts (*e.g.*, Fe, Ni, Co) to promote graphene layer formation.
- *Thermal Graphitisation*: High-temperature treatment (>1200°C) in inert atmosphere to convert amorphous carbon into more crystalline graphene-like domains.

Reference

- US10822632B2 – Biochar-derived graphene nanosheets
- *Materials Chemistry and Physics* (2017)

2.4 Functionalisation of Graphene Analog

- *Purpose*: Introduce polar groups to enhance dispersibility in polymer matrices and corrosion resistance.
- *Methods*:
  - Oxidation (*e.g.*, HNO_3/H_2SO_4 treatment).
  - Silanisation.
  - Amidation for polymer compatibility.

Reference

- US10294365B2 – Functionalised graphene oxide from biochar

2.5 Composite Formation for Anticorrosive Coatings

- *Matrix materials*: Epoxy, polyurethane, polyaniline, or water-based paints.
- *Process*:

- Disperse graphene analog (modified biochar) into polymer matrix.
- Apply to metal surfaces by spray or dip-coating.
- Cure under controlled conditions.

Reference

- CN110135936A – Biochar-graphene composite anticorrosive coating
- *Progress in Organic Coatings* (2020)

2.6 *In situ* Synthesis Methods

- *Approach*: Integrate biomass pyrolysis and polymerisation in one-pot or two-step processes.
- *Advantage*: Better integration of graphene analogs into the matrix; reduces aggregation.

3.0 Summary Table

Step	Method	Output	Purpose
1	Biomass pyrolysis	Biochar	Carbon precursor
2	Chemical activation	Activated biochar	High surface area
3	Graphitisation	Graphene analog	Electrical and barrier properties
4	Functionalisation	Modified graphene	Compatibility and dispersion
5	Composite blending	Polymer coating	Corrosion resistance
6	*In situ* methods	Integrated composite	Efficiency

4.0 Object of the Invention

The object of the present invention is to describe a process to prepare silica-graphitic structure and graphene analogs-based composite from waste biomass in a single or combination. Another objective of the current innovation is to describe the process of making an emulsion of the prepared silica-graphitic structure and graphene analogs-based composite.

Further objective of the present disclosure is to prepare an anti-corrosion coating on metal/ceramic surface with the silica-graphitic structure and graphene analogs-based composite emulsion and its application process.

5.0 Summary of the Invention

Carbon-containing components of agricultural/forest/any other biomass containing either lignin, cellulose, hemicellulose or any one of their combinations have been converted to value added carbon-containing composite of graphitic structure. The present invention concentrates on the synthesis process of silica-graphitic structure and graphene analogs-based composite from agricultural/forest/any other biomass using a combined chemical treatment followed by pyrolysis and grinding/milling/exfoliation. The processed composite is further reinforced into a polymer/ceramic composite emulsion for coating. The corrosion inhibition efficiency of the composites at different concentrations was examined using electrochemical methods like potentiodynamic polarisation. The composites show multi-fold enhancement in anti-corrosion and anti-wear properties. It could be inferred from all the tests that the inhibition efficiency of silica-graphitic structure and graphene analogs-based composites (from 0.01 wt.% - 20 wt.%) by above mentioned process shows enhancement with respect to the uncoated metal/ceramic sample. The corrosion inhibition seems to occur by both cathodic and anodic protection. The same shows superhydrophobic behaviour.

6.0 Background of the Invention

Every year, approximately 1,40,000 million metric tons of biomass is generated as waste worldwide; in India, this amount is around 400-500 million metric tonnes. Conversion of this huge biomass into value-added material is a recent pattern worldwide. Carbonisation of biomass is one of the processes to make it more useful. The desired end product through the carbonisation process depends on the processing parameters like temperature, pressure, residence time, reactor type, raw materials, *etc*. In a normal pyrolysis process, charcoal and bio-oil are the end products in most cases. The amount of these end products also depends on process parameters. The parameters of the charcoal materials can be manipulated by altering the process parameters. To get the desired surface structure, sheet length, functional groups, conjugated minerals, *etc*., the raw materials may need pre-treatment before carbonisation; also, the carbonisation process may be optimised. A graphitic

structure and graphene analogs like material with silica associated with it as a composite can be resulted by proper processing and controlled carbonisation of the biomass and its subsequent processing. Exfoliation of carbonised biomass can be done by chemical as well as physical/mechanical processes. Silica-graphitic structure and graphene analog (s) like composite prepared by this process can be made soluble in desired solvents by altering the surface functional groups, maintaining sizes, *etc*. Once soluble in the desired solvent, the same can be used for different applications.

The global cost of corrosion is around 3-4% of Global GDP. India loses 5-7% GDP every year due to corrosion. Though corrosion is primarily associated with metallic material, polymeric insulating coating and ceramic materials can undergo corrosive degradation. Mitigation of corrosion has been a serious concern for a long time now. Among all the corrosion mitigation techniques, the use of corrosion inhibitor/coating is reported to be the most preferable since only a smaller amount of the material serves the purpose. The use of synthetic organic or inorganic corrosion inhibitors has been reported to cause more harm to the environment than benefit. This invites the application of eco-friendly/green organic corrosion inhibitors as a coating on metal surfaces.

In paint industries, additives like solvents, resins and curing agents are added along with the inhibitor material for a better adhesion and life span of the coating on the surface of metal. There are various kinds of resins like acrylic, alkyds, polyamides, and polyurethanes, among which, epoxy resin is the most widely used resin in the preparation of paints and coatings. This is due to the properties like high adhesion, superior toughness, thermal stability, chemical and corrosion resistance. Epoxy resin is formed by a condensation reaction between diphenylol propane derivatives and epichlorohydrin. An amine curing agent is reported to be compatible with epoxy resin.

7.0 Detailed Description of the Invention

This invention concerns the following:

(i) A combined chemical, thermal and mechanical process to synthesise silica-graphitic structure and graphene analog (s)-based composite material from agricultural/forest/any other biomass.

The biomass source ranging from crop residue (straw, husk, stalk) of cereal, horticultural, pulses, oilseeds, sugarcane any other like cotton, jute fibre, jute stalk/stick, bamboo, any wood, bio manure and other biomasses containing either lignin, cellulose, hemicellulose or any one of their combinations. The sources of cereals range

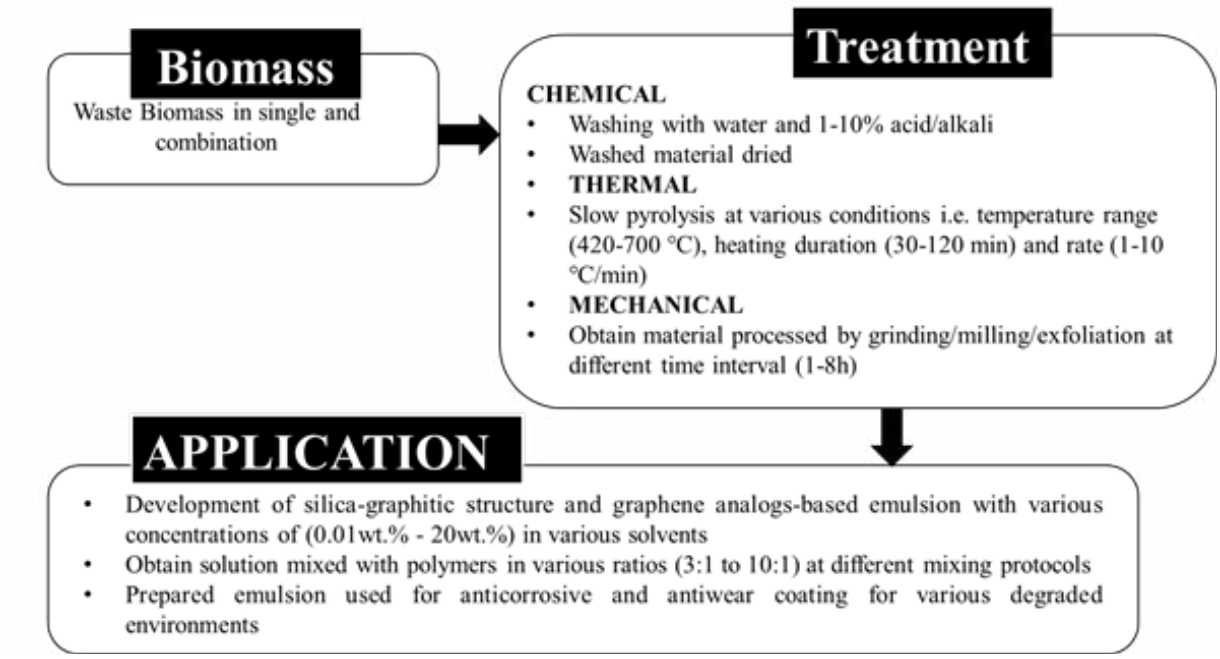


Figure 1. Process flow diagram of the invention.

from rice, wheat, paddy, sorghum, millet, barley, maize, jowar, bajra, ragi. The wood or non-wood portion of a flowering or non-flowering plant, wood chips or wood dust of any origin. The chemical process may include the treatment with acids, alkali in single or in combination. The acids used are both organic and inorganic, preferably inorganic acids, including HCl, H_2SO_4, HNO_3, H_3PO_4, H_3BO_3, *etc.*, and organic, including short-chain (less than 10 carbon) fatty acids. The alkali used are strong alkali salts NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$, $Na_2H_3CO_6$, *etc*. The thermal process here means dry heating or hydrothermal heating. The atmosphere of the heating is preferably in an anoxic condition. The energy source in the thermal process may come from electric, solar or biomass. The mechanical processes associated with this invention include grinding/milling. The milling process includes, but is not limited to, ball, jet, vertical, impact, roller, centrifugal, in single or in combination. The final material size ranged from 0.5µm to 100µm. The chemical treatment before or after the thermal process may be followed. Examples of the biomass and its chemical and thermal processes are described in Indian Patent No. 350457, Chinese patent no 101343292B, and International Patent No. WO2013152337A1. Preparation of graphitic structure and graphene analog (s) from cellulosic material is described in Chinese patent no 104724699A, each of which is incorporated herein by reference.

(ii) The synthesis of polymer/ceramic coating using silica-graphitic structure and graphene analog (s) based composite in 0.01 wt.% till 20% wt.% (as mentioned in point (i)) as a reinforcement.

The synthesis process includes dispersion of the prepared silica-graphitic structure and graphene analog (s) based composite into the proper solvent in different dispersion methods.

The solvents used may be polar or non-polar. They range from H_2O, to xylene, mixed xylenes, benzene, toluene, ethylbenzene, ethanol, methanol, butanol, isopropyl alcohol, mineral turpentine oil, 2-ethoxyethyl acetate, dimethyl sulfoxide, dimethylformamide, n-methyl-2-pyrrolidone, tetrahydrofuran, acetone, acetonitrile, in single or in combination.

The dispersion methods applicable are high-speed dispersion, ball milling, stirring, sonication, and ultrasonication in single or in combination.

The duration of the dispersion process may range from 15 min to 1200 min. The resin for polymer/ceramic emulsion may be used for the coating material preparation, are alkyd, epoxy, polyurethane, polyamides, polydimethylsiloxanes, and acrylic.

The dispersed silica-graphitic structure and graphene analog (s) based composite may be mixed along with other materials like additives, hardener, pigments, stabilisers, in single or in combination to prepare the final coating material.

(iii) The polymer/ceramic coating (Mentioned above) shows enhanced anticorrosive, anti-wear properties under different environmental degradation conditions of heat, salinity, acidic/alkaline stress and various conditions of duress like pressure, sharp and impregnated surfaces.

Example 1

Agricultural waste biomass was taken and washed with water and hydrochloric acid (10% HCL), and dried. The dried biomass was chopped into pieces with dimensions (1mm x 1mm) and thermally treated (pyrolysis). The pyrolysis was done at a slow mode with a 1-10°C increment of temperature per minute. The temperature was kept at 420-700°C for 30 to 120 min. The cooling was done at 5-20°C per min for the first 300°C, then at 1-5°C per min up to the end temperature of 35°C. Synthesised material was processed through a ball mill for different time intervals (1-8h). Processed material was taken in various range (0.01g-10.0g), and is dissolved it in 50 -1000 mL of ethanol and other in combinations of solvents (H_2O or dimethylformamide (DMF) or Ethanol or Methanol or Dimethyl sulfoxide (DMSO) or N-Methyl-2-pyrrolidone (NMP), and ultrasonicated at 70-250Hz for 15-120 min to obtain the silica-graphitic structure and graphene analog (s)-based nanosheet composite. Obtain solution is filtered, washed with distilled water, and dried in a hot air oven at 105°C for 5 h (as shown in Figure 1) to get the coating material. Phase analysis of the composite has been confirmed by X-Ray diffraction in (Figure 2a), and the presence of functional groups has been observed by FT-IR in (Figure 2b). Synthesised silica-graphitic structure and graphene analog (s)-based composite have been characterised by different techniques. Scanning electron microscopy has revealed the morphological characteristics of the composite in Figure 3.

Example 2

The metal coupon was pre-treated before coating. Each coupon was first ground sequentially using emery sheets of size 180, 240, 320, 600, and 1000. The coupon was then polished in alumina of sizes 0.3 and 0.1µ µm,

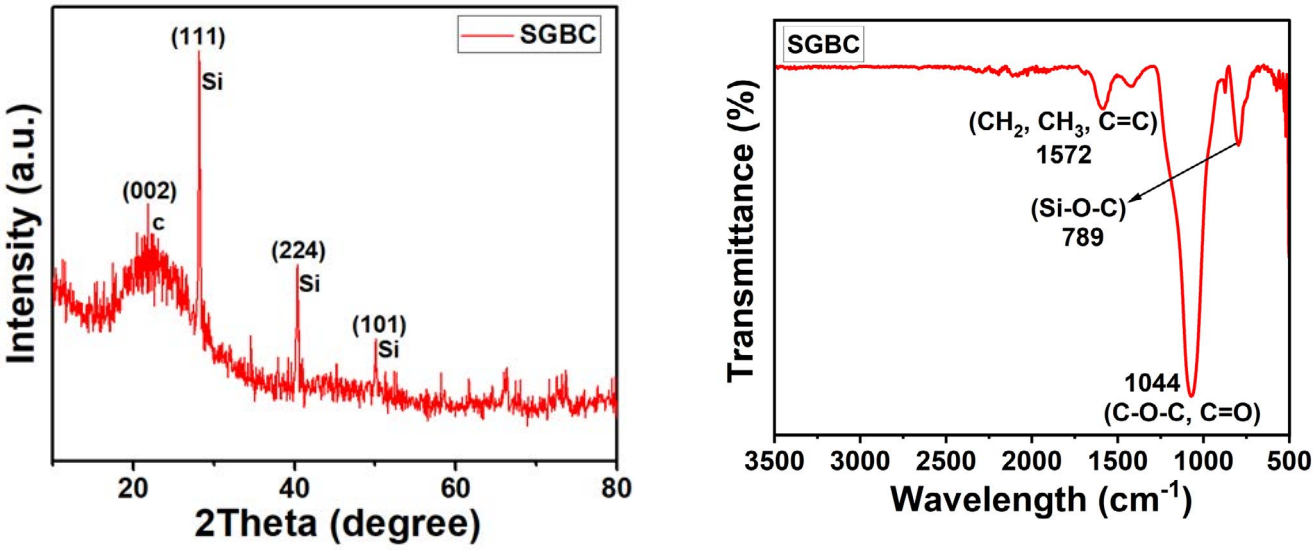


Figure 2. **(a)** XRD pattern of silica-graphitic structure and graphene analog (s)-based composite (SGBC), **(b)** FTIR pattern of silica-graphitic structure and graphene analog (s)-based composite (SGBC).

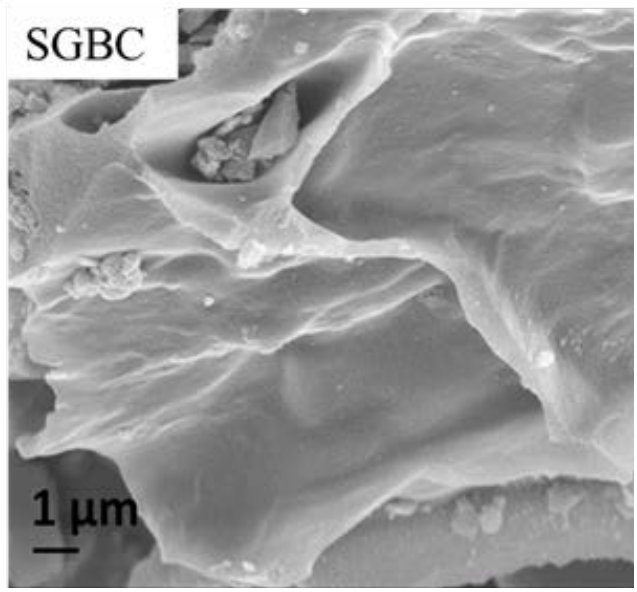


Figure 3. Scanning electron microscopy image of silica-graphitic Structure and Graphene analog (s)-Based Composite (SGBC).

rinsed, and sonicated in ethanol, followed by drying. The polished and dried coupon was then taken for coating. The coating was done using the dip coating method. Once coated, the specimen was then kept for drying for 48 hours. The quantities of the coating material (as discussed in Example 1) taken in this work are 0.01-20% (w/w). The SEM images of the coatings are shown in Figure 4.

Example 3

Electrochemical measurement, like potentiodynamic polarisation, was performed to investigate the corrosion or corrosion inhibition behaviour of the coated metal specimens at room temperature. A three-electrode system having carbon steel coupons, Ag/AgCl (3 M KCl), and Pt wire as working, reference, and counter electrodes, respectively, is connected to a potentiostat. The electrolyte used here was 3.5 wt.% NaCl solution. OCP measurements indicated that the system was stabilised in 1800 s. After stabilisation of the system, potentiodynamic polarisation was performed in a potential range of -100 mV to +100 mV with a scan rate of 1 ms^{-1}. The Ecorr (Corrosion potential), Icorr (corrosion current density), and Corrosion Rate (CR) were calculated from the polarisation plot and are listed in Table 1.

The results indicate that the corrosion rate of the coated metal decreases with respect to the uncoated specimen up to 1 wt.% of SGBC coating, and then the corrosion is seen to increase at 5 wt.%.% SGBC. The metal specimen coated with 1 wt.% material shows the highest inhibition efficiency of 50%. From the polarisation plot (Figure 5), it can be implied that the decrease in corrosion rate occurs mainly due to the increase in reduction reaction in the cathode as well as a decrease in the anodic current density. This result proves that the coating prevents the metal from dissolution in the solution.

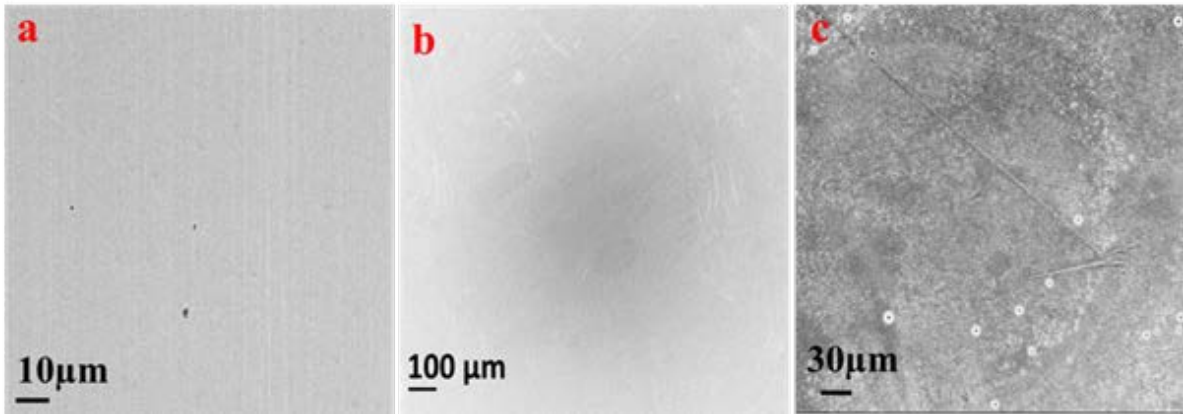


Figure 4. Scanning electron microscopy images **(a)** uncoated carbon steel, **(b)** epoxy coated, and **(c)** Silica-graphitic Structure and Graphene analog (s)-Based Composite (SGBC) coated on the carbon steel.

Table 1. E_{corr}, I_{corr} and corrosion rate values obtained from the polarisation plot

	E_{corr} (V)	I_{corr} (Acm^{-2})	Corrosion rate (mmpy)	Inhibition Efficiency (IE in %)
Uncoated	-0.39	7×10^{-5}	0.46	-
epoxy	-0.36	6.4×10^{-5}	0.36	22
0.01 wt.%	-0.28	5.8×10^{-5}	0.35	24
0.1 wt.%	-0.32	5.2×10^{-5}	0.34	26
1 wt.%	-0.32	5×10^{-5}	0.23	50
5 wt.%	-0.38	5.1×10^{-5}	0.24	48

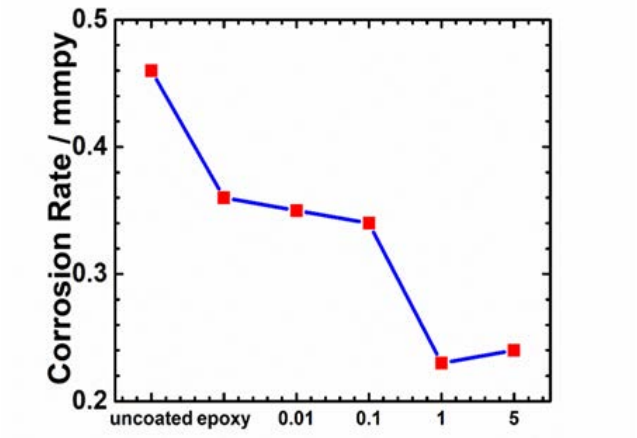


Figure 5. Corrosion rate with respect to the concentration of silica-graphitic Structure and Graphene analog (s)-Based Composite (SGBC) of metal surface obtained from the polarisation plot. X-axis values are in wt.%.

The surface roughness was studied using profilometry (Figure 6). It was found that the smoothness of the silica-graphitic structure and graphene analog (s)-based composite coated metal surface increases with respect to the uncoated and epoxy coated with a roughness coefficient (Ra) as low as 1.2 µm. Surface roughness indicates a high surface area, porous surface or uneven surface, which could increase the rate of corrosion of carbon steel. Therefore, the coated sample showing the least roughness would contribute to the inhibition of corrosion of the metal.

The surface was studied visually after 25 days of immersion in 3.5 wt.% NaCl solution (Figures 7, 8) and found that the uncoated metal surface seems to corrode, while the coated metal shows a good coating adherence on the metal surface, inhibiting the corrosion.

Example 4

A coating material was prepared as in example 1 with high-speed dispersion grinding and ball mill grinding route. Salt spray resistance test (ASTM B117) was done with 500 h exposure. There was no blister found in the X cut area or other area, even after 500 h in both cases. No flash rust was found. The external creep was found to be <1 mm.

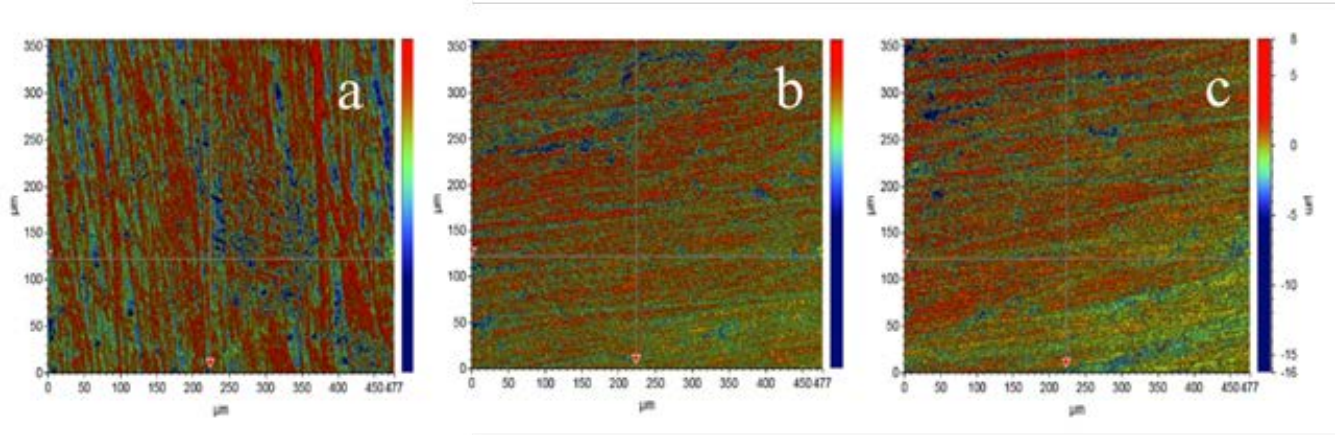


Figure 6. Profilometry images of **(a)** uncoated (Ra = 3.7 µm), **(b)** epoxy coated (Ra = 2 µm), and **(c)** 1 wt.% SGBC coated (Ra = 1.1 µm), metal specimen to estimate the surface roughness coefficient.

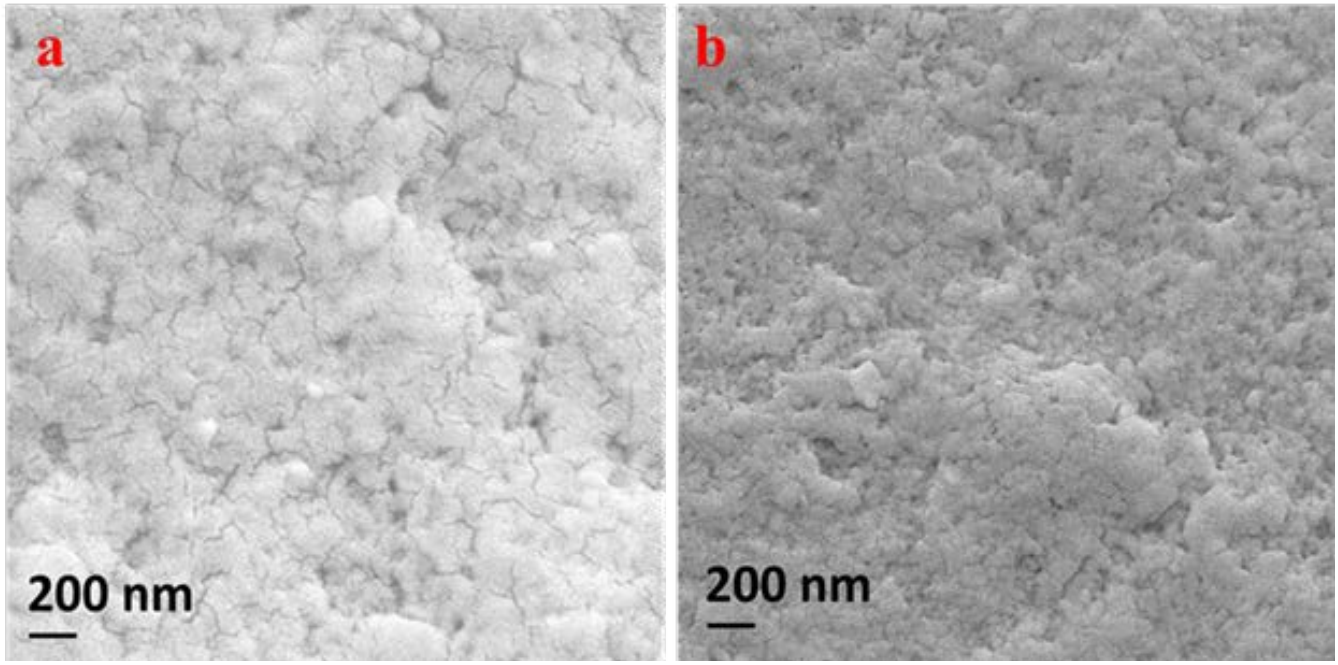


Figure 7. Scanning electron microscopy images after immersion for 25 days **(a)** Epoxy coated, and **(b)** Silica-Graphitic structure and Graphene analog (s)-Based Composite (SGBC) coated on the carbon steel.

8.0 Claims

(i) A combined chemical, thermal and mechanical process to synthesise silica-graphitic structure and graphene analog (s)-based composite material from agricultural/forest/any other biomass.

(ii) The silica-graphitic structure and graphene analog (s)-based composite in claim 1 is prepared from biomass wherein the biomass sources include but not limited to crop residue (straw, husk, stalk) of cereal (rice, wheat, paddy, sorghum, millet, barley, maize, jowar, bajra, ragi), horticultural, pulses, oilseeds, sugarcane any other like cotton, jute fibre, jute stalk/stick, bamboo, any wood, bio manure and other biomasses containing either lignin, cellulose, hemicellulose or any one of their combinations.

(iii) The chemical process in Claim 1 may include the treatment with acids, alkali or any other solvent. wherein the acids, alkali, or any other solvent includes, but is not limited HCl, H_2SO_4, HNO_3, H_3PO_4, H_3BO_3, short chain

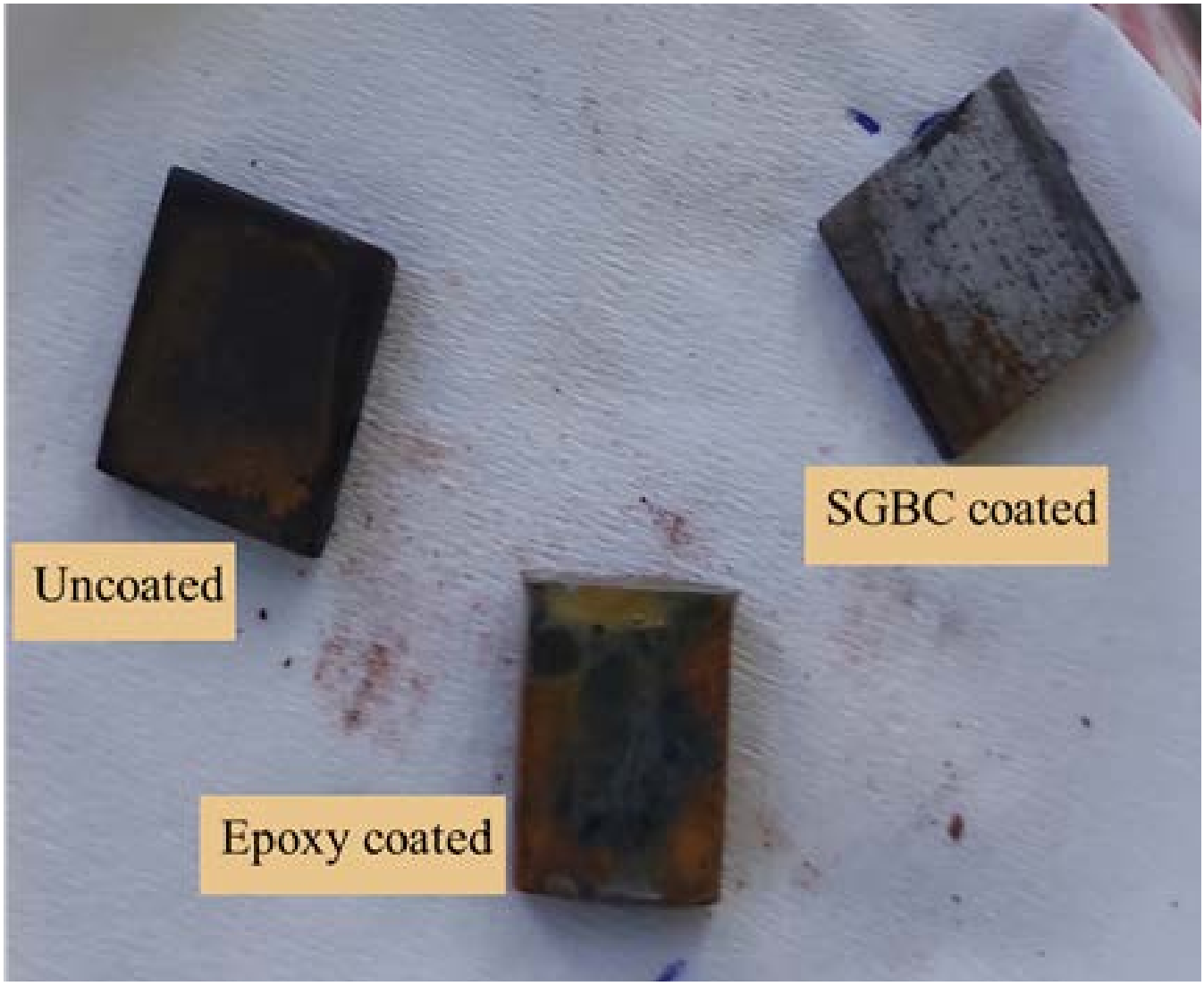


Figure 8. Images of uncoated and SGBC-coated metal specimens taken after immersion in 3.5 wt.% NaCl solution for 25 days.

(less than 10 carbon) fatty acids, NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$, $Na_2H_3CO_6$

(iv) The thermal process in claim 1 includes pyrolysis of the material as in claim 2 and after treatment as in claim 3. The pyrolysis process includes a temperature increment of 1-10°C of temperature per minute. The carbonisation temperature ranged from 300-900°C for 10 to 300 min.

(v) The mechanical process in Claim 1 includes grinding, milling by ball milling or cryogenic milling, sonication, ultra-sonication, sieving in single or in combination.

(vi) The synthesis of polymer/ceramic coating using silica-graphitic structure and graphene analog (s) based composite as in Claim 1 in a concentration of 0.01 to 20% (w/w) as a reinforcement for anticorrosive and anti-wear coating.

(vii) The size of silica-graphitic structure and graphene analog (s) based composite for synthesising polymer/ceramic as in Claim 5 ranged from 0.5µm to 100µm

(viii) The silica-graphitic structure and graphene analog (s) based composite prepared as in Claim 1 is dispersed in solvents includes but not limited to xylene, mixed xylenes, benzene, toluene, ethylbenzene, ethanol, methanol, butanol, isopropyl alcohol, mineral turpentine oil, 2-ethoxyethyl acetate, dimethyl sulfoxide, dimethylformamide, n-methyl-2-pyrrolidone, tetrahydrofuran, acetone, acetonitrile, in single or in

combination to synthesise polymer/ceramic coating as in Claim 5

(ix) The synthesis process of polymer/ceramic coating using silica-graphitic structure and graphene analog (s) based composite as in Claim 5 was done with dispersion into the solvent as in Claim 7 by high-speed dispersion, ball milling, stirring, sonication, and ultrasonication in single or in combination.

(x) The dispersion time as in Claim 8 may range from 15 min to 1200 min.

(xi) The synthesis process of polymer/ceramic coating using silica-graphitic structure and graphene analog (s) based composite as in Claim 5, wherein the resin includes, but is not limited to, alkyd, epoxy, polyamides, polyurethane, polydimethylsiloxanes, acrylic resins.

(xii) The synthesis process of polymer/ceramic coating using silica-graphitic structure and graphene analog (s) based composite as in Claim 5 may include additives, hardener, pigments, stabilisers in single or in combination along with silica-graphitic structure and graphene analog (s) based composite prepared as in Claim 1 dispersed in solvents as in Claim 7.

(xiii) The polymer/ceramic coating prepared as in Claim 5 provides enhanced anticorrosive, anti-wear properties under different environmental degradation conditions of heat, salinity, acidic/alkaline stress and various conditions of duress like pressure of sharp and impregnated surfaces.