

BIO-RESOURCE-DERIVED SELF-HEALABLE VITRIMERS FOR ANTI-CORROSION COATINGS

A thesis submitted to the
UPES

For the award of
DOCTOR OF PHILOSOPHY

in
Department of Chemistry

By
POONAM SINGH
September 2024

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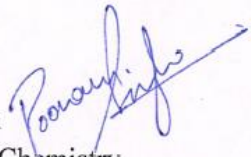
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DECLARATION

I declare that the thesis entitled “**Bio-resource Derived Self-healable Vitrimers for Anti-corrosion Coatings**” has been prepared by me under the guidance of **Dr. Sravendra Rana**, Professor (Supervisor), Applied Science Cluster (Chemistry), School of Advanced Engineering (SoAE), UPES and **Dr. Pankaj Thakur**, Professor (Co-Supervisor), Applied Science Cluster (Chemistry), School of Advanced Engineering (SoAE), UPES.

No part of this thesis has formed the basis for the award of any degree or fellowship previously.

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ABSTRACT

Corrosion is the most destructive natural phenomenon, where the conversion of metal into a more stable oxide state takes place, which possesses lower mechanical and structural properties of the designed material. The high maintenance due to corrosion alone costs 3.6% of global GDP. There are wide range of anti-corrosive coatings available in the industry to address the various shortcomings in protective coatings, however, conventional coating materials are susceptible to failure after fracture or damage during service, leading to a decrease in materials safety and lifetime. Therefore, a smart coating, capable of repairing itself along with protecting the assets from corrosion is highly desirable. In addition, the emergence of bio-resource-derived polymers and their composites signifies the major initiative toward sustainable development for cutting-edge applications. Among extensive resources (cellulose, starch, sugar, etc.) available, vegetable oils are potential starting materials because of their favorable chemical structure, cost-effectiveness, and advantages in designing/modifying the molecules as per the desired properties. Nonetheless, there is another provocation in designing the vegetable oil-derived epoxy coatings is their low mechanical strength and durability to deal with severe environmental conditions, which can be effectively addressed with vitrimer-derived self-healing chemistry in polymeric matrices and controlled by the incorporation of suitable nano-filler (e.g. GO, rGO, CNT, etc.). The current study focuses on the detailed investigation of bio resource-derived vitrimer self-healable composites for anti-corrosive application. This report is categorized into four parts as follows: (A) a comprehensive literature survey of recent advancements in sustainable vegetable oil-derived self-healable anti-corrosive coatings, (B) Linseed oil acquired microwave-assisted vitrimer coatings for anti-corrosion application, (C) Comparative study of ortho and para position of amine-based crosslinking agent on various properties of vitrimer coating (D) Nickel dopped biochar filler based thiol frameworks for the application of self-healable coating systems.

Herein, Linseed oil-derived epoxy self-healable composites were developed using 4,4'-diphenylamine-disulfide (4-AFD) for crosslinking with the inclusion of rGO as nano-filler. In this approach, microwave-triggered smart vitrimer coatings were generated with remarkable anti-corrosion protection. The composite exhibits excellent self-healing and shape memory properties due to embedded disulfide covalent adaptive chemistry in the network which facilitates the dynamic bond exchange reaction. The network demonstrates improved in thermomechanical properties with 20.8 GPa and a low activation energy of 78 KJ/mol,

indicates a fast dynamic exchange reaction. In addition, anti-corrosive properties were also impressive due to presence of the amine group which also helps to attain high hydrophobic properties (131° contact angle). Further, the impact of amine group position (ortho & para) present in moiety was examined, where a thorough study of epoxy-828 based 4,4'-diaminophenyl disulfide (4-AFD, para) and 2,2'-diaminophenyl disulfide (2-AFD, ortho) crosslinking agents is provided. In the study, systematic comparative study of self-healing efficiency, thermomechanical properties and anti-corrosion inhibition properties are conducted. These microwave radiation-responsive systems were also embedded with GO as the nano-filler to enhance the various characteristics. This part of the study covers the investigation of mechanical strength (storage modulus-129GPa and loss modulus-83GPa for 2-AFD), stress relaxation, and low activation energy(63KJ/mol) due to fast dynamic disulfide exchange reaction, furthermore, the low corrosion rate of 1.20×10^{-3} mm/y was observed for the 2-AFD coating network.

The report is further extended to utilizing the bio-char/nickel-doped bio-char as a nano-filler and its impact on the vitrimer coating system. The study has shown that addition of biochar in epoxy/thiol coatings has remarkable impact on thermomechanical properties, self-healing efficiency as well as hydrophobic properties. The incorporation of WBC shows increment in thermomechanical properties with 17.2 GPa storage modulus and withstands 5.7 MPa stress at 1.9 strain%, in addition, the composite shows fast relaxation with the activation energy of 49KJ/mol. The properties of the composite were further enhanced with the incorporation of Ni-doped WBC into the matrix with 24.2 GPa storage modulus and withstand the stress of 18.8 MPa at 1.9 strain% along with activation energy of 39 KJ/mol exhibiting fast transesterification exchange reaction in the matrix. The composite coatings material shows excellent hydrophobicity with a 120.4-degree contact angle along with reliable corrosion protection tested with the help of salt spray testing.

Therefore, the current study comprising epoxy-based vitrimer materials responsive towards microwave heating has immense potential in self-healable coating materials. Microwave-triggered vitrimers need minimal effort to make the coating functional and enhance the life span of the coating and article coated with it. This study reveals the pathway for corrosion-specific engineered composite coating materials for protection against corrosion and various possible damages.

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ABBREVIATIONS

ADCAN	Associative Dynamic Covalent Adaptive Networks
AFD	2-Aminophenyle Disulfide; 4-Aminophenyle Disulfide
AFM	Atomic Force Microscopy
ATR-FTIR	Attenuated Total Reflectance-Fourier Transform Infrared
BC	Bio-char
DCAN	Dynamic Covalent Adaptive Networks
DDCAN	Dissociative Dynamic Covalent Adaptive Networks
DETA	Diethylenetriamine
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimeter
E _a	Activation Energy
ELO	Epoxidized Linseed Oil
ELA	Epoxidized Linseed Oil-AFD Composite
FT-IR	Fourier Transform Infrared Spectroscopy
GO	Graphene Oxide
IR	Infrared
Ni@BC	Nickel doped Biochar
rGO	Reduced Graphene Oxide
SEM	Scanning Electron Microscopy
TA	Thermal Analysis
T _g	Glass Transition Temperature
TMP-MP	Trimethylolpropane tris-(3-Mercapto Propionate)
TGA	Thermal Gravimetric Analysis
THF	Tetrahydrofuran
TMA	Thermomechanical Analyzer
UV-Vis	Ultraviolet-Visible Spectroscopy
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-ray Diffraction Spectroscopy

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CHAPTER 1

General Introduction

Sustainable development has been the main concern globally in the highly technical era. Thus, it is important to promote renewable resources to fulfil the sustainable development goals (SDGs) by the UN. The polymers attained from renewable resources, including starch, lignin, vegetable oils, etc. have enticed the attention of the researchers. The synthesis of bio-polymers from various vegetable oils starts emerging with different properties to give rise to a strengthened system. Conventional coating materials are susceptible to non-performance after damage during working, which leads towards a sharp decrease in the material's lifetime. Therefore, an intelligent coating able to repair itself and protect the assets from corrosion, and improve durability is highly desirable. The main idea of self-healing coatings is inspired by nature, given how natural mechanism helps heal the wounds in living species. The concept of the self-healing matrix is gradually settling, in which the macro/micro-damages in materials can be repaired on their own, and the scratches on the designed materials can be repaired to seal up with a complete original property's restoration.

The vitrimer is a contemporary concept, which represents a significant endowment to improving the recycling as well as repairability properties of thermoset networks. The idea of associative dynamic covalent adaptive networks (ADCAN) is about the thermoset vitrimers. The concept reveals an excellent degree of stress relaxation which leads to self-healable properties. In "vitrimers" the dynamic crosslink bonds allows reprocessing of the matrix without losing inherent properties due to active associative exchange reactions. The reprocessing and repairability of the material can be achieved by dynamic bond exchange reactions, which is lead by kinetic processing, and altered with the use of suitable catalysts. An understanding of the recyclable and healable properties of thermoset polymer materials is required. Self-healing materials would overcome limitations connected to damage diagnosis which include interference to restore and recyclability of the functional composite materials. This proposed work aims to reduce costs and labour associated with coating maintenance for offshore applications, where inspection and maintenance are complex due to the location of the asset. Vegetable oils (bio-resource) are potential starting materials with scope of functional modification according to the application required. The vegetable oils such as sunflower oil, castor oil, linseed oil, palm oil, Karanja oil, yellow oleander, jatropha curcas, Nahar seed oil, tung oil, etc are excellent examples of oils that can be used for polymer synthesis. Vegetable

oil-based materials are a cost-effective alternative to petroleum-based products and offer a range of properties, given self-healability, shape-memory, recyclability, and protection against solvents and ion attack. They also provide reliable mechanical strength and self-adhering properties (Hu et al., 2018). Among different types of vegetable oils, linseed oil is a popular choice due to its high degree of unsaturation and fast-drying nature. (Ghasemi Rad et al., 2019). This oil allows for the formation of auto-oxygenated polymeric networks with high crosslinking, resulting in thermal adaptive behavior, shape reconfiguration ability, and excellent crosslinked networks in linseed oil-based epoxy matrices. (Selim et al., 2018). Epoxy-based networks with reversible covalent bond exchange are functional at moderate temperature conditions, even without any catalyst loading, which makes them more beneficial for screening surfaces from corrosive conditions. Vitrimer coatings have the ability to restore the mechanical and physical properties of the material after healing. However, bio-derived matrices have a common drawback, which is their lack of mechanical strength. To enhance mechanical strength and create a prolonged passive barrier towards the substrate, 2D-nano-fillers are used. However, non-dispersive or agglomeration of these nanofillers can restrict the corrosion inhibiting behaviour and accelerate the electrochemical reaction, leading to accelerated corrosion (H. Li et al., 2021; X. Li et al., 2023). Herein, this study focusses on the detailed literature comprehensive followed by designing and development of epoxy based vitrimer coating systems validated in terms of thermal stability, thermomechanical properties, self-healing/ shape memory efficiency along with corrosion inhibition properties. The networks have also been investigated with hydrophobic character and various range of characterisation techniques in order to validate the particulars of the coating composite materials.

PROBLEM STATEMENT

Corrosion is known to be a highly destructive natural phenomenon, which not solely results in a considerable economically degrading but also known to be life-threatening. The key reason related to the corrosion activity is the reduction of Gibbs free energy, which promote the metal to convert to its most stable oxide form (Habib et al., 2021). The provided types of damages create micro-scale rifts. In the latest advances, self-healable smart composite coatings are capable of repairing cracks automatically or with lesser external mediation. Self-healable composites are going to have immense importance as polymeric coatings materials because of

their improvement in the shelf-life of coating as well as maintenance cost(Mahajan & Gite, 2022b).

Vegetable Oil-Based Polymer

Vegetable oils(VOs) based polymers demonstrate excellent properties including biocompatibility. (Siyanbola et al., 2019). VOs can be classified as two wide categories, edible vegetable oils (EVO) and nonedible vegetable oils (NEVO). Among all, NEVOs are mostly opted for the development of polyols, as they help to preserve the global food supply. In addition, the conversion of NEVOs into polyols, using various chemical conversion methods, for example, epoxidation reaction, thioene conversion, ozonolysis reaction, hydrogenation process, hydroformylation reaction, transesterification reaction, and amidation conversion(C. K. Patil et al., 2021) Based on percentage of unsaturation present, vegetable oils can also further categorized as drying oils, non-drying oils, and semi-drying oils. If long fatty acid chains in oil start crosslinking and become hard upon exposure to air for a certain time period, it is drying oil. Based on various parameters, the characteristic profile of oil like acid value to determine the acidity or free fatty acids present, saponification value give notion about average molecular weight of fatty acid whereas rancidity can be discovered with peroxide value but iodine value calculates the unsaturation present in different oil(Islam et al., 2014)(Liang et al., 2018)(Akbar et al., 2009)(Galúcio et al., 2011)(Abdalla et al., 2014)(Azcan & Danisman, 2007)(Silva et al., 2021). Linseed oil (LO) is the most widely used vegetable oils due to its fast-drying property, causing a high degree of unsaturation, which make oxygen molecules to react with these natural resins and create a polymer network. Dry oil demonstrates better properties in order to facilitate self-healable property including anti-corrosion coatings(Selim & Shenashen, 2018). Along with the inherent properties of vegetable oil, external materials can be grafted on the polymeric network with the intention of enhancement and according to the demand of properties needed in the coating. These grafted materials are known as fillers, can be obtained from very diverse sources and methods. Carbonized material can be useful in several applications such as CNT, Graphene, and mesoporous carbon structures due to their chemical, thermal, electrical, and mechanical properties. Incorporation of these materials in polymeric coatings leads to the enhancement of mechanical, corrosion, and antimicrobial properties(Siyanbola et al., 2019).

Concept Of Self-Healing Properties

Conceptually, vitrimers fall under the category of resins with the advantageous behaviour of rearranging their topology *via* dynamic covalent bond exchange, which makes them attractive

for further studies(Nardeli et al., 2020). Basically, there are two ways material can demonstrate their qualities of self-healing made them classified into two categories: intrinsic and extrinsic coatings. Intrinsic coatings possess self-healing quality due to presence of function groups that exchange bonds among them and result in healing process. Extrinsic coatings have microcapsules incorporated into polymeric matrix which get busted when experience mechanical stress result into release of healing material and address the purpose (Materials et al., 2018). The terminal bond rearrangement in the network and dynamic bond disassociation temperature can be controlled by adjusting modifying phenol-carbamate matrix networks with various known electronic effects(J. Zhang et al., 2022) For self-healing properties to be there in polymer, the phenolic group must present to support the self-crosslinking, resulting into self-damage reparation(Chakraborty & Chatterjee, 2020). Some of the phenolic biomolecules are known for their accord towards the modification of VO-based polymers for coating applications. The molecules containing -OH (hydroxyl group) like flavones, tannin, and flavonoids act as good corrosion inhibitors. Taking Tannin biomolecules for this purpose provide effective corrosion protection as well as self-healing abilities. Tannins are mostly found in various range of natural extracts as well as various organic components. Because of the self-healing properties of the smart coatings, the corrosion do not propagate from the infected surface to the whole surface(Nardeli et al., 2020). Promising shape-memory property, self-healing, and reprocessing properties of these networks lead to sustainable and eco-friendly research in the domain of polymers. (Yang et al., 2020) Self-healable materials take immediate action after the generation of cracks in the matrix, but the rate of the recovery of inherent mechanical properties is reported to be not that rapid, which can be achieved through either extrinsic stimuli or intrinsic stimuli healing strategy. For the fast recovery to occur, chemical or physical interactions within the network and planes of crack are expected to develop within a very short span of time.(Ye et al., 2014)

The recovery by self-healing material can occur autonomously or non-autonomously which can be activated due to external initiators such as heat and radiation. An ideal self-healing material is able to sense and respond to damage on the surface of the polymeric asset and restore the material's performance. Therefore, the material is expected to be reliable, safer, and durable besides the costs and maintenance will be reduced.(Krishnakumar et al., 2022)

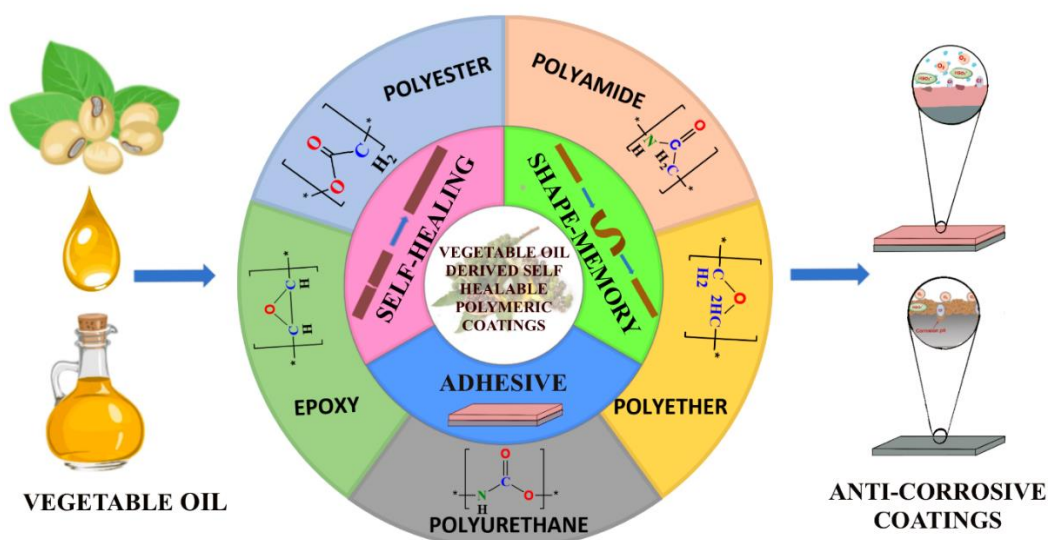


Figure1.1. schematic illustration of vegetable oil derived polymers for application of anti-corrosive application

Anti-Corrosion Properties

In nature, usually, pure metals are not extracted directly; because most metals are extracted in their most stable oxidized forms, and in the same state present in the ores. Therefore, thermodynamically, most of the metals tend to corrode and easily convert back to their stable naturally encountered oxide form. Metals are familiar for their strong mechanical properties, for example, steels, are prone to corrosion if they are not protected. (Pottschmidt, 2019) Theoretically, corrosion is an easy to occur electrochemical reaction, which requires four parts to occur: a metal site to be oxidized (an anodic site), a conductive electrolyte, a reduction site for species to be reduced (a cathodic site), and one metallic interrelation between the anodic and cathodic parts.(Jones, 1996) Epoxy coatings are commonly used for the mitigation of corrosion. (Pottschmidt, 2019) Polymeric coatings derived from vegetable oil are generally found to show poor anti-corrosion protection as compared to mineral or petroleum-based polymeric coating when corrosion-inhibitor or any filler is absent. To prepare a better anti-corrosion protective system, good adhesive properties must present between the coating material and the metal surface. Nano-fillers used in the matrix could lead towards better wettability and resistance against acid and alkaline medium, which in turn give anti-corrosion property to the coating system(Nadine et al., 2021). Considering principal material in aircraft production, aluminum alloy is best for the study of the application of anti-corrosion coating. Aluminum alloys are susceptible towards corrosion of Cu and Mg-rich S phase. The coating

prepared can be characterized by using electrochemical impedance spectroscopy (EIS), localized electrochemical impedance spectroscopy, and scanning vibrating electrode technique for corrosion resistance technique. Collectively all these tests are suitable for corrosion testing. Taking a call on waterborne polyurethane in the coating industry, it is known that waterborne polyurethane coatings show poor corrosion resistance whereas organic solvent polyurethanes are comparatively better along with excellent adhesion properties found in tape pull-off tests. Generally, Chromate pigments can be used along with organic coating in order to minimize corrosion(Nardeli et al., 2020). On the other hand, vegetable-derived metal-containing polymers are considered to enhance anti-corrosion as well as anti-fungal properties and the Incorporation of the metal to these polymeric moieties modify the coating to give crosslinking properties which enhance other aspects of the coating film. Whereas the aliphatic tri-ester moiety of oils provides a hydrophobic nature and inherent flexibility to the coating. (Akram et al., 2008) In coming future, bio-resource derived polymer coatings are going to gradually replace naturally occurring fossil-based coating materials. The crosslinking of the chains presents in the thermosetting polymer restrict the bond exchange, flow and repressibility which are prime necessities for the self-healing property of the polymer (Krishnakumar, Sanka, et al., 2020)(Chakma & Konkolewicz, 2019).

Irradiation

In recent years, various methods for rapid heating or localized targeted heating for healing of the components have been explored. These include Joule or resistive heating(Chien et al., 2014), induction heating(Lucia et al., 2014), vibrational heating(Bates et al., 2001), ultrasonic heating and welding(Benatar & Gutowski, 1989)(Villegas, 2019), Infrared heating(Zou et al., 2018), and electromagnetic heating(Herren et al., 2020). Particularly, electromagnetic heating in the network is a rapidly emerging domain of study, which has various advantages counting fast, non-contact, rapid non-invasive, and based on material-selectivity as well as volumetric heating. Recently it is found in study that microwave can be used for heating through exciting carbonaceous materials like CNT(Sweeney et al., 2018), carbon black(Gruener et al., 2020), graphene, graphene oxide(Debnath et al., 2020), carbon fibers(Vashisth et al., 2020). Radiation based healing provide localised healing just at the location of damage occur on the material. Carbonaceous material incorporated coating system as a nanofiller to induce the dielectric effect, making the system compatible with microwave radiation and potentially enhancing its healing and mechanical properties. There is a relationship between heating rate of matrix and

concentration of filler loading; given concentration of added filler enhances the conductivity (due to percolation) and hence enhances the heating rate of the material. (Gruener et al., 2020)

MOTIVATION

1. To innovate a coating system to provide better protection for the offshore sector, thus a longer product produces less waste.
2. Utilization of bio-resource in synthesis of self-healing polymers would lead towards the development of green materials/coatings.
3. Maintenance requires even more attention economically (long down-time, manual intervention, need of skilled persons. etc.), but Vitrimers require less attention in terms of maintenance.
4. The Self-healing function of vitrimers requires particular temperature/pressure, etc. (but difficult to provide self-healing conditions based on the working environment), Implementation of radiation-active materials in the vitrimer coating could provide a solution in this direction.

OBJECTIVES

1. Development of advanced self-healable hydrophobic anti-corrosion coatings using vegetable oils.
2. To develop a novel method to create self-healing coatings working in absence of conventional heating source.
3. Validation of anti-corrosive and healing properties for the developed bio-derived coatings.

The multi-functional coating system will be developed with the aim of overcoming the following drawbacks of coating materials:

- ❖ Poor corrosion resistance and impact damage resistance (which significantly affect the integrity of the coating system)
- ❖ Improving the number of “healing-cycles” by investigating the dynamic-processes of healing, to repeatedly heal the damage occur at the same position of the network.
- ❖ Addressing and understanding the timescale of self-healing process. Usually, self-healing systems based on “reactive covalent chemistry/capsule-based system” can

display only one healing cycle, whereas vitrimeric systems allow multiple healing cycles as the chemical reactivity is not used up.

- ❖ The self-healable coatings to repair various products, to make them economic and reduce waste.

Overview of research approach/model

The main focus of this research work is to develop and validation of bio-based self-healable vitrimeric for the application of anti-corrosive coatings. This approach involved in investigation of this work involves the characterization of developed composite and the study of dynamic covalent chemistry along with the efficiency of coating material.

Phase 1: Phase 1 involves the detailed literature survey and selection of material to be used for development of bio-resource-derived vitrimeric composites. Linseed oil-based epoxy resin was chosen because of its optimum drying character and non-edible for the common food industry. The range of crosslinking agents was also listed based on their performance in terms of mechanical and anti-corrosive properties. In addition, the mechanism behind the self-healing mechanism (e.g. disulfide chemistry, transesterification chemistry etc.) was also identified. The methodology protocols were established to conduct the systematic research along the objectives.

Phase 2: Phase 2 involves the synthesis of bio-based epoxy resin from the selected vegetable oil and modification as per the requirement of applications. Based on the literature linseed oil (LO) was sorted out to be used as a renewable starting material because of its drying nature and being non-edible oil which will not interrupt the food supply of oil used. In addition to it, Graphene oxide and reduced graphene oxide were also synthesis following established methodology. Furthermore, the linseed oil-based epoxy was synthesized followed by the development of LO-based vitrimeric composites.

Phase 3: In this phase, the synthesized vegetable oil base epoxy, nano-filler, and developed vitrimeric composites were characterized using various characterization techniques like, TGA, TMA, and optical microscope.

For chemical composition analysis: FT-IR, NMR, XRD, XPS, and Raman spectroscopy was conducted.

For thermal and thermomechanical properties: TGA, DSC, TMA were conducted.

Phase 4: In this part, rigorous testing conditions were established to test vitrimeric, hydrophobic, and anti-corrosive properties. Along with that in order to support the surface information AFM was also lead.

Self-healing tests: for self-healing materials were coated on a glass slide and healing of the cracks were observed in optical microscope. In addition, relaxation time was also calculated support the healing of the composite.

Hydrophobicity test: the contact angles were observed for each composite in a drop shape analyser (DSA).

Corrosive properties: the corrosion inhibition properties were examined *via* Tafel plot in electrochemical analysis, where the rate of corrosion and efficiency was calculated along with optical image analysis using microscope.

Phase 5: This phase concludes the carried-out research work in the terms of systematically arranging the specifics. Validation in terms of publications and recording all the details of research work in the form of thesis.

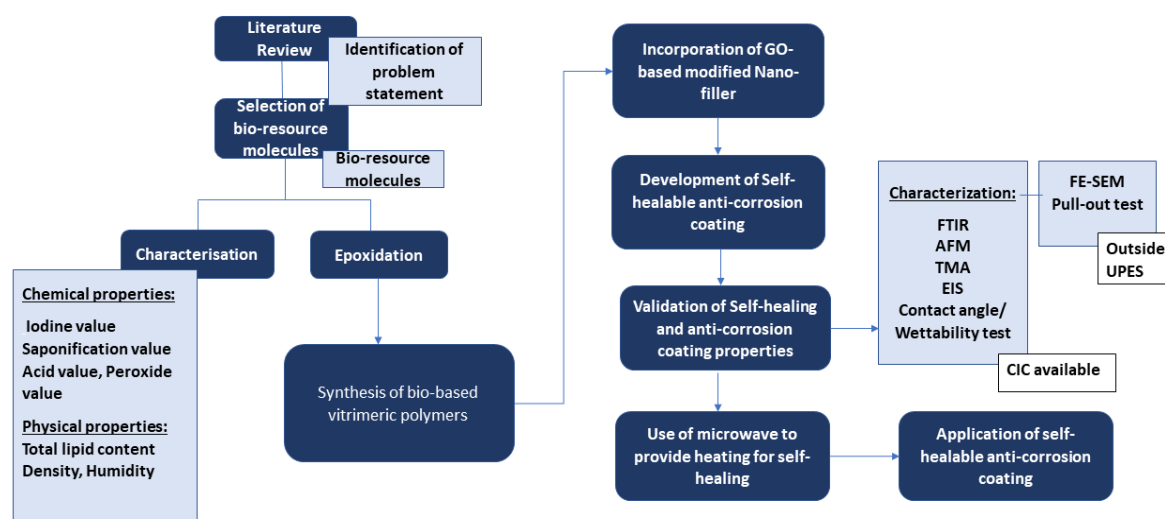


Figure 1.2. Systematic representation of methodology followed to carry out research work

Contribution of Research

The development of bio-resource derived self-healable vitrimeric coatings has been designed with keeping wide economic and environmental benefits upfront. The detailed contribution and benefits have been summarized below:

- ❖ **Sustainability and environmental impact:** the use of bio-resources as starting materials such as vegetable oil, lignin, or starch promotes sustainability by reducing

the utilization of petroleum-based products. The coating materials are designed to minimize the ecological footprints and are biodegradable.

- ❖ **Enhancement in performance and longevity:** The self-healing properties in the coating network allows it to repair all minor damages automatically and hence extend the lifespan of the protective film. In addition, microwave-responsive coatings are selective with localized healing at the area of damage without much manual intervention and extensive downtime.
- ❖ **Economic and Industrial Impact:** The self-healing properties in the composite significantly minimize the maintenance cost by reducing the frequency of repair. Other than maintenance cost, bio-derived materials are more abundant and cheaper as compare to petroleum-based materials which eventually lower the cost for industrial production.
- ❖ **Corrosion performance and durable technology advancement:** The developed coatings provide impressive protection against corrosion by creating a barrier from moisture and corrosive agents even in harsh environmental conditions like salt territory, temperature fluctuation etc. The microwave assistance in healing of composite makes significant advancements as smart coating materials. In addition, the developed coating systems are adaptable and scalable for various industrial applications e.g. marine applications etc.
- ❖ **Research contribution:** The contribution to broadening the scientific understanding of radiation-responsive dynamic covalent bond exchange chemistry which facilitates the self-healing mechanism. Other than that this interdisciplinary work collaborated between the field of materials science, polymer chemistry, material engineering and bio material science.

CHAPTER 2

Recent Advancements in Sustainable Smart Anticorrosion Coating Materials Derived from Vegetable Oil Derivatives

2.1. Background

Although so many polymeric protective coatings are present in the market, approx. 3.6% of total GDP (total gross domestic product) is being spent on the maintenance of structural substrates and instruments caused by destruction due to corrosion(Asif et al., 2022)(Mahajan & Gite, 2022a). Therefore, an intelligent coating able to repair itself and protect the assets from corrosion and improve durability is highly desirable. The concept of self-healing coating is inspired by nature itself, given how natural healing of wounds occurs in various living species. The concept of self-healing matrix is gradually settling, in which the macro/micro-damages in materials can be repaired on their own, and the scratches on the designed materials can be repaired to seal up with a complete original properties restoration. In particular, self-healing coatings are helpful to reduce costs and labor associated with coating maintenance for offshore application, where inspection and maintenance are complex due to the location of the asset. However, due to geopolitical challenges, coating industry need to shift its focus from conventional petroleum-based polymers to bio-chemicals derived polymers. Lined up from the biomaterial to smart protective coatings, vegetable oil is worth to utilize for the synthesis of high-performance material, given that oils provide a wide range of fatty acids like oleic acid, linoleic acid, palmitic acid and stearic acid. Leaving an impression of interest, sustainable polymeric protective coatings have been in prime focus for corrosion inhibition of metallic surfaces and thus explored in this report(Dutta & Karak, 2022)(Deka & Karak, 2009). Along with the inherent properties of vegetable oils, external materials/groups can be easily coupled due to the presence of different functional moieties in oil, as required for different coating applications(Mahapatra & Karak, 2004)(Dutta & Karak, 2022)(Kar & Karak, 2022)

2.2. Polymers derived from different vegetable oils (for coating applications)

2.2.1. Castor oil-based polymers

Castor oil, a readily available organic chemical can be extracted *via* solvent extraction or mechanical pressing. In the case of solvent extraction, the main constituent obtained is ricinoleic acid, which is present at around 90% of the whole oil and comes under the euphorbiaceous group. The different components, including oleic acid, linoleic acid, stearic

acid, as well as palmitic acid, etc. are also occur in trace amounts.(Chakraborty & Chatterjee, 2020)(Morales-Cerrada et al., 2021) The presence of carboxylic groups in castor oil facilitates esterification as well as amidation, where double bonds react to hydrogenation and epoxidation. Other than that, hydroxyl groups promote the acetylation and alkoxylation, leading to the formation of a different range of polymers, which also includes polyether, polyurethanes, polyesters, and polyamides, etc. discussed in Table 2.1.

Table 2.1: castor oil-derived polymeric networks synthesis reaction conditions and applications

S. No.	Resultant polymer	Catalyst/chain extender (conditions)	Polymerization technique/ crosslinking	Filler used	Research findings	References
1.	Polyester-amide	poly (styrene co-maleic anhydride) (SMA) copolymer	Cured at ambient environment	-	• N, N-bis-2-hydroxy ethyl linseed oil fatty amide diol (HELA) derived from linseed oil with ambient cured polyesteramide (AC-PEA) shows thermal stability. • The SMA copolymer resin present in ambient cured polyester-amide resin gives good physico-mechanical and corrosion inhibition performance on mild steel.	Manawwer Alam et al,2011(Alam & Alandis, 2011)
2.	Poly-ester-amide resins	N-phthaloyl-glutamic acid(NPGA)	Esterification	-	• Modified polyester amides (PEA) resins can be used successfully for the development of many anticorrosive paint formulations and which lower the costs • Advantage of the binders is that based on nitrogenous compounds they combine the properties of both polyester and polyamide resins • Introduction of N-phthaloylglutamic acid, elevates the performance of the film and enhances the corrosion inhibition properties of PEA resins.	H. Abd El-Wahab et al,2012(Abd El-Wahab et al., 2012)

3.	Alkyd resin	3-isocyanatopropyl-triethoxysilane (IPTES)	Sol-gel reaction	Organo-silane as nano-filler	- linseed oil and 3 iso-cyanato-propyl-triethoxy silane (IPTES) derived organic-inorganic bio hybrid coatings using sol-gel technique exhibits a high transparency. - The highly crosslinked network enhances mechanical, thermal, hydrophobicity along with flexibility as well as anticorrosive properties on mild steel. - The presence of high number of less polar Si-O-Si linkages (NLA-IPTES-III) reduces the surface free energy resulting on water repellency.	Shabnam Pathan et al, 2016(Pathan & Ahmad, 2016)
4.	Waterborne alkyd resin	dibutyltin di laurate (DBTDL)+ p-toluene-sulfonic acid (PTSA) used as catalyst	-	3-iso-cynato-propyl tri-ethoxy silane (IPTES)	- APS-treated microcapsules in formulated self-healing epoxy nanocomposites in order to restored the mechanical properties carbon steel. - Impact resistance, scratch hardness, thermal stability and anti-corrosion properties improved on crosslinking alkyd, Melamine formaldehyde (MF) and 3-isocyanatopropyltriethoxysilane (IPTES)	Shabnam Pathan et al, 2018(Pathan & Ahmad, 2018)
5.	Hyperbranched alkyd resin	dibutyltin oxide as catalyst	Polycondensation reaction	Cu ₂ O nano-cubes as nano-filler	- Hyperbranched polyester synthesized by A₂ +B₃ approach, minimize VOC emissions which is resulted from the large-terminal functionality as well as reduced viscosity of the alkyd matrix. - Incorporating Cu₂O nano-cube as fillers in the matrix provided enhanced adhesion, mechanical, and hydrophobicity, along with anticorrosion performance comparatively. - High nanofiller loading concentrations of 3 wt% reduce the Cu₂O nano-cube surface area and alkyd/Cu₂O interfacial bond strength due to of particle clustering.	Mohamed S. Selim et al, 2018(Selim & Shenashen, 2018)

6.	Epoxidized Alkyd resin	Amberlite, 3-Amino propyl-trimethoxy-silane (APTMS)	Esterification	-	- To overcome limitation on high-performance applications, alkyd resin can be modified to oxirane ring through epoxidation reaction. - Increase in 3-amino propyl-trimethoxy-silane (APTMS) conc. enhances the anti-corrosive properties of coatings due to highly cross-linked structure on mild steel.	Deepak M. Patil et al, 2018 (D. M. Patil et al., 2018)
7.	Epoxy resin	3-aminopropyl-trimethoxy silane (APS) as coupling agent	Sol-gel technique	Microcapsules filled with linseed oil	- APS-treated microcapsules were used to formulate self-healing epoxy nanocomposites in order to restore the mechanical properties. - Epoxy films containing both linseed oil microcapsules and nanoclay particles exhibit excellent anticorrosion and self-healing properties.	S.M. Mirabedini et al, 2020 (Mirabedini et al., 2020)
8.	Epoxy resin	NaNO ₃ as corrosion inhibitor, linseed oil as a healing agent	-	Talc nanoparticles and urea-formaldehyde microcapsules, sodium nitrate-NaNO ₃	- Talc nanoparticles in epoxy matrix reinforced with fixed conc. Of urea-formaldehyde microcapsules (UFMCs) and linseed oil loaded with NaNO₃ exhibit promising self-healing properties. - Tempting corrosion inhibition efficiency of 99.9% and 99.5% shown by polymeric nanocomposites containing 3 and 1 wt% TNPs.	Shrish Habib et al, 2021 (Habib et al., 2021)
9.	Polyurethane	-	Epoxidation and carbonation	-	Bio-based non-isocyanate polyhydroxy-urethane (NIPHU) resin exhibit good Hydrophobic and anti-corrosion properties.	J. Pouladi et al, 2021 (Pouladi, Mirabedini,

					Increasing the carbonation content improves the adhesive strength because of presence of urethane linkage and polar hydroxyl group.	Mohammadlo o, et al., 2021)
10.	Acrylated-epoxy resin	(3,4-dihydroxyphenetyl) acrylamide as adhesion promoter	Copolymerization	1,10-dibutoxyethyl-sebacate (DBES)	- The incorporation of DBES lower down Tg and the water uptake (higher hydrophobicity) in linseed oil based matrix. - The ability of DBES to induce cross-linking with latent epoxide under thermal treatment leads to self-healing character on 3003 aluminum alloy. - Significant adhesion of this anti-corrosion coatings on the AA3003 substrate	David Boucher et al,2021(Nadine et al., 2021)
11.	Polyurethane	Resorcinol as cross linker, DBTDL as a catalyst	Condensation polymerization	Microcapsules	- Linseed oil loaded cardanol-formaldehyde microcapsules provides a thermal stability of 230 °C - Increment in the microcapsules loading up to 16%, Coatings on mild steel surfaces would show enhancement in self-healing and corrosion inhibition performances. - Eugenol-based coating exhibited reliable solvent resistance, flexibility, along with desired gloss values as well as excellent adhesive properties on mild steel.	Mahendra S. Mahajan et al,2022(Mahajan & Gite, 2022a)

12.	Poly-urethane	-	Amide linkage	Carbonized nanoparticle s	- Carbonized nanoparticles can be obtained by burning the eucalyptus leaves in atmospheric oxygen - Incorporation of these materials in polymeric coatings leads to enhancement of mechanical, corrosion, antimicrobial properties on mild steel. - With 2% CNM, Hydrophobicity was found to increase with highest degree of contact angle	T.O. Siyanbola et al, 2019(Siyanbola et al., 2019)
13.	Poly-urethane	2,2'-disulfanediyl dianiline (DTDA) or 4,4'-disulfanediyl dianiline (paraDTDA)	Di-Sulfide linkage	Nano-hybrid graphene oxide	- Banana and Colocasia esculenta leaves extract can be used to produce nano hybrids graphene oxides. - Crystallinity and self-healing ability of castor oil derived nanocomposites increases with concentration of nano-hybrid concentration upto 99%.	Chaoqun Zhang et al, 2021(C. Zhang et al., 2021)
14.	Poly-urethane	Stannous octoate as catalyst, trimethylolpropane (TMP)	Poly-esterification	-	- Taking Tannin biomolecules provide effective corrosion protection as well as self-healing abilities - Hydrogen bonding between tannin -OH group and polyurethane matrix lead to repair of coating, which in turn inhibits corrosion - Due to self-healing properties of coating, corrosion do not propagate from infected surface to whole surface	Nardeli et al, 2019(Nardeli et al., 2020)
15.	Poly-urethane	-	Esterification	-	- wide set of polyurethanes can be obtained from cross reaction between different poly-isocyanates and different polyols - network was found to be non-homogenous, which lead to unreacted sites and affect the mechanical properties.	R. M. Cerrada et al., 2021(Morales-Cerrada et al., 2021)

16.	Poly-urethane	poly(epichlorohydrin-triol)(PECH-triol) as crosslinker	Cationic ring-opening polymerization (CROP)	-	- polyurethane matrix and can be blended with different crosslinkers like poly chlorohydrin-triol (PECH-triol) to get better anti-corrosion results. - Increase in % of PECH-triol in the system crosslinking density and thermal stability increases due to presence of –OH group in the network.	T.O. Siyanbola et al, 2021(Siyanbola et al., 2021)
17.	Poly-urethanes	-	-	-	- The interaction between the clay and polymer enhances the thermal and physical stability along with the mechanical properties. - Addition of nanofillers, decrease the glass transition temperature and thereby improve the elastic characteristics.	Amit Shirke et al, 2015(Shirke et al., 2015)
18.	polyurethane	di(1-hydroxyethylene) diselenide (DiSe) as chain extender	diselenide bonds	-	- Exhibit excellent triple-shape-memory effect, the shape fixation and recovery above 99.3% and 60.6% after three cycles, respectively - excellent self-healing efficiency while retaining high flexibility (468%) and mechanical strength (6.5 MPa)	Ruitong Liu et al,2021(R. Liu et al., 2022)

19.	waterborne polyurethane	Titanium Carbide, 2-aminophenyl disulfide	disulfide exchange	Ti3C2Tx nanosheets	• Ti3C2Tx nanosheets mixing results in mechanical property elevated to 15 MPa and exhibiting the self-healing and shape memory performance at given low elongation at break (~30%) due to the disulfide exchange. • composite perform an excellent EMI shielding property (51 dB) which is due to the analogic segregated structure of the matrix to absorb up the EM waves within the material	Jingyi Lu et al, 2021 (Lu et al., 2021)
20.	Poly-imine	-	Imine exchange reaction	multi-walled carbon nanotubes (MWCNT)	• 3D network based biomass polymer crosslinked via multiple H-bonds as well as dynamic covalent imine bonds. • by incorporating Multiwalled CNTs retain the inherent properties of the polymer and enhanced adhesion properties, which can be used as conductive, adhesives and wires	Fei Song et al, 2019 (F. Song et al., 2019)
21.	elastomer	-	metal-ligand coordination	-	• zinc-carboxylate bonds were found weaker, which facilitated the self-heal ability in polymeric films • metal-ligand coordination act as cross-linking junctions, which helps to achieving excellent improvement in thermomechanical properties.	Meghan E. Lanm et al, 2019 (Lamm, Song, et al., 2019)
22.	Acylated epoxy	2-methylimidazole as catalyst	free radical polymerization	-	• The obtained polymers are water insoluble and various common organic solvents. • highly transparent, and shows glass transition temperatures near room temperature	Emanuel Hernández et al, 2020 (Hernández et al., 2020)

23.	Alkyd resin	Dibutyltin dilaurate (DBTDL) as catalyst	Urethane linkage	-	polyurethanes formed have good coating properties with mechanical thermal stability as well as appreciable anti-corrosion efficiency on mild steel panels.	M. Patil. et al., 2020(A. M. Patil & Jagtap, 2021)
24.	Poly(urethane-malonic-esteramide) (PUMEA)	-	Ester-amide linkage	multi-walled carbon nanotubes (MWCNTs)	- The PUMEA-0.8 resin exhibit the great coating effectiveness among prepared samples, where physicomechanical properties deteriorated with further increment in content of MWCNTs further - the 0.8 wt% MWCNTs based PUMEA-0.8 composite coating was found to be uniformly dispersed in developed PUMEA matrix	Manawwer Alam et al,2021(Alam et al., 2021)
25.	polyurethane acrylate	N, N-dimethylethanola mine as a catalyst, glycidyl methacrylate and hydroquinone as an inhibitor, DBTDL was added as catalyst.	Urethane linkage	itaconic acid acrylate (IAG), ricinoleic acid acrylate (RAG), oleic acid acrylate (OAG)	- Highly effective strategy for the development of bio-polyurethane-based photosensitive oligomers exhibited excellent performance, and has reliable application potential in the coating industry - The IAG content was increased twice, due to which the glass transition temperature (T_g) of the cured film reached 75.62 °C, and where the others were found to be RAG (60.21°C), OAG (54.65°C) and CO (21.52°C)	Jinqing Huang et al,2021(Huang et al., 2022)

To enhance coating properties, filler incorporation is highly advantageous.(W. Zhang et al., 2019) Deewan and coworkers studied the effects of incorporating boron-based nanofillers in polyester and polyurethane matrix during synthesis.(Akram et al., 2008) The reaction involves esterification of hydroxyl group of castor oil (BCPE) followed by polyaddition between BCPE and Toluene,2,4-diisocyanate (TDI). The coating results in highly effective anti-corrosion properties with no weight loss in the basic medium for 50 hours, whereas a loss in weight was observed in the acidic medium. Good thermal stability ($\sim 220^\circ\text{C}$) and physio-chemical properties were observed for boron-polyurethane-based coatings. To understand the significance of castor oil-based shape memory PUs, Karak and coworkers discussed the advantages of using sulfur-containing reduced graphene oxide-based coatings (SRGO)(Thakur et al., 2015). The presence of functional groups on the graphene surface gives better dispersion properties in polymeric matrix than to pristine graphene nanosheet. In addition, poly(ϵ -caprolactone)-diol(PCL) and SRGO were mixed to get the final hyperbranched PU/SRGO (HPU/SRGO) hybrid. Due to the strong interaction between pre-polymer and functionalized GO, improvement of thermal stability as well as mechanical properties was observed. The presence of PCL helped to achieve excellent shape recovery and shape-healing properties (due to crystalline character) under sunlight and microwave. In addition, authors have reported microwave radiation-assisted SH composites.(Thakur & Karak, 2015) The microwave radiation incidence oscillates the dipoles, and hence helpful in transferring the energy to respective the polymer matrix. This absorbed energy is beneficial to raise the temperature of the matrix above T_g and as consequences facilitates the repairing of the damages on reported coatings. The synthesis mechanism and exclaimed properties of nanocomposite are substantiated in the schematic diagram in [Figure 2.1(A)(B)]. Hyperbranched polyurethane iron oxide reduced graphene oxide (HPU-IO-RUO) nano-composites were prepared using different compositions of nanohybrids. The healing efficiency of the coating was judged by cutting scratching the surface and calculating the recovery in tensile strength [Fig 2.1 (C)(D)(E)]. Urethane linkages can be obtained *via* reacting isocyanates and alcohols catalyzed by tertiary amines (with low steric hindrance to facilitate the reaction), or Pb, Sn-based catalysts, e.g. N, N-dimethyl cyclohexylamine or stannous octoate (Shirke et al., 2015). Reacting pre-urethanes along with another polymeric matrix results in the formation of interpenetrating polymer networks (IPN) possessing impressive thermal stability. By controlling the composition of isocyanates and polyols, the matrix demonstrated adhesive properties and is beneficial for vast applications including coatings. Shahidul and coworkers have reported the TiO_2 dispersed hyperbranched poly-(ester amide)(HBPEA) nanocomposites derived from castor oil using A2+B3

approach.(Bhat & Ahmad, 2018) In this process, firstly, N, N- bis (2-hydroxy ethyl) castor amide (HECA) was synthesized by reacting diethanol amine and sodium methoxide at 110 °C and the addition of castor oil was performed dropwise, which was further used for the synthesis of hyperbranched poly (ester-amide). The reported composite was found to have hydrophobic properties (due to the hydrophobic surface of TiO₂ increasing cross-linking density) with contact angle in the range of 89° to 107°, and thermal stability of 452 °C. Moving further, eucalyptus leaves were used to synthesize the carbonized nanoparticles as bio-resourced nano-fillers (Siyanbola et al., 2019). These carbonised nanoparticles were obtained by burning the leaves in atmospheric oxygen and treating them with piranha solution, which leads to delignified carbon nanoparticles. Further, biobased hybrid polyurethane was synthesized by reacting polymeric 4,4'-methylene diphenyl diisocyanate, carbonized nano particles (CNM-COOH) and 4-methyle pentene-2-one along with castor oil. The study found that with increasing the percentage of CNM doping, cross-linking power of urethane and thermal stability (399 °C) was enhanced. The corrosion resistance of the composite coating was improved with $E_{corr}=12.4\text{mV}$, $I_{corr}=4.4 \times 10^{-4} \text{ Acm}^{-2}$, $R_p= 7.02 \times 10^4 \text{ K ohm cm}^2$ and $R_{corr}=5.1 \times 10^{-6} \text{ ohm}$ on mild steel. Kashif and coworkers investigated corrosion inhibition behaviour of castor oil-derived polyurethane, synthesised by reaction of the castor oil with diethanol-amine and sodium methoxide followed by the addition of toluene2,4-diisocyanate(TDI).(Kashif & Anjum, 2020) The reported polymer matrix possesses high hardness due to TDI (because of aromatic moiety), impact resistance 200 lb/inch, and corrosion inhibition efficiency of 94% & 90% in acidic and alkaline environments, respectively. In another study, it was observed that castor oil-derived alkyd resin has a good affinity towards corrosion inhibition (A. M. Patil & Jagtap, 2021).

In order to strengthen the anti-corrosion and hydrophobic properties; lotus leaves inspired self-cleaning coatings is highly advantageous. Wei and coworkers has developed anti-smudge bio-based polymeric coatings ncorporated with poly(dimethyl-siloxane) (PDMS))(Wei et al., 2021). Hyperbranched polyol was synthesised by a transesterification reaction between CO, 2,2-bis (hydroxymethyl)propionic acid (DMPA) and p-toluene-sulfonic acid (P-TSA) under nitrogen environment [Fig 2.2 (A)(B)]. PDMS-OH was applied to the coating surface to provide the low surface tension and change in contact angle [Fig 2.2 (C)]. A study found that it inhibits the deposition of dirt on the surface, and no trace of liquid was left behind.

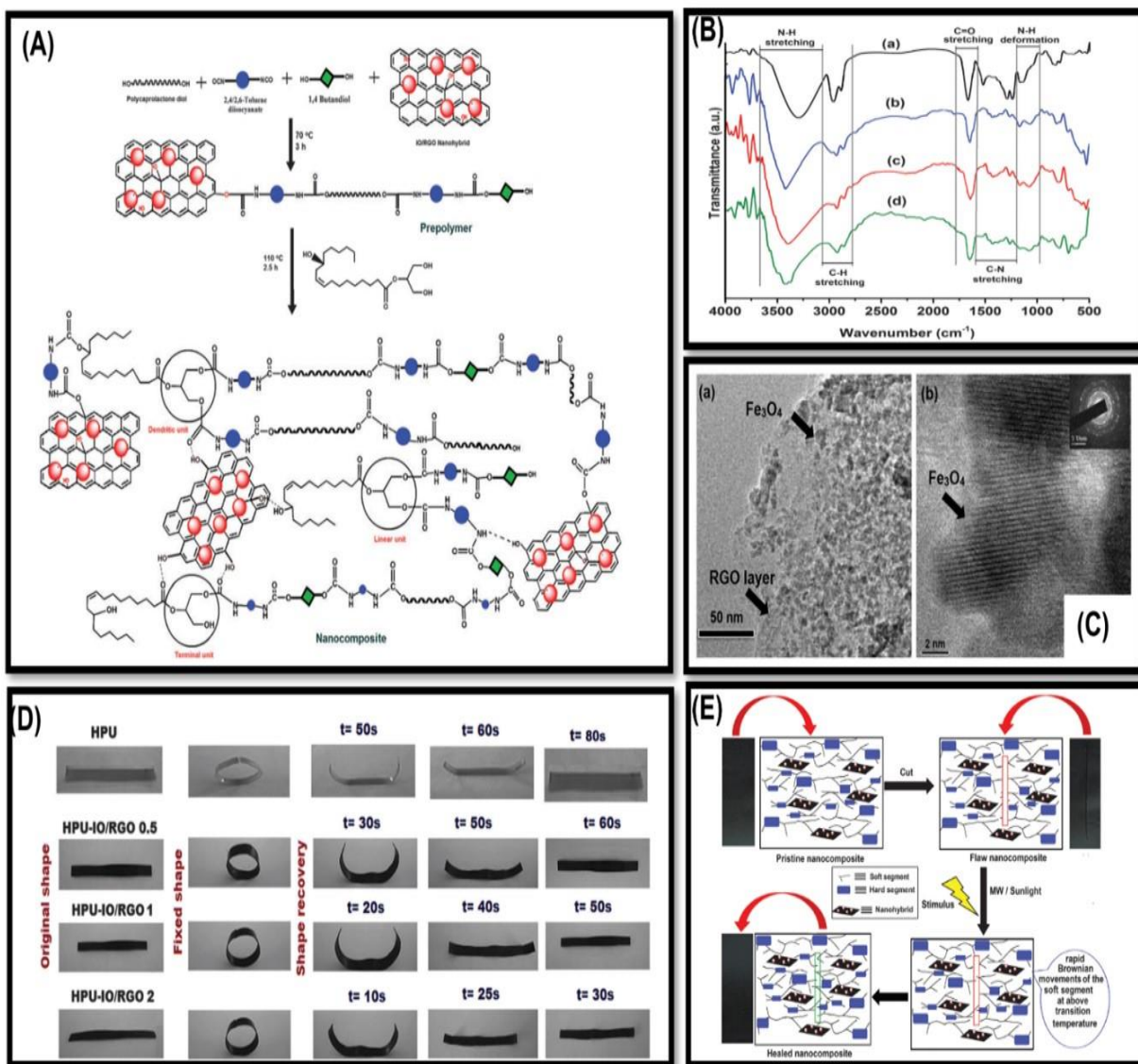


Figure 2.1. (A) Reaction scheme demonstrated the synthesis of HPU-IO-RGO composite. (B) FTIR spectra of different compositions of Iron-oxide- Reduced graphene oxide a) HPU b) HPU-IO-RGO(0.5) b) HPU-IO-RGO(01) c) HPU-IO-RGO(02) (C) Images of HRTEM showing Iron oxide nanoparticle incorporation in RGO-HPU layer: (a) at low resolution and (b) at high resolution (inset displays SAED patterns) (D) Clear representation of composite exhibiting properties of shape-memory under MW radiation. (E) Self-healing mechanism representation of nanocomposite. (Thakur & Karak, 2015)

The reported coating was found to repel water, inks, and other organic solvents; thus, it can be used for anti-graffiti as well as anti-fingerprint purposes [Fig 2.2 (B)]. Mechanical and excellent adhesive properties were observed with considerable flexibility and transparent, robust qualities in the coating. Recently, there has been a high demand for electromagnetic interference (EMI)

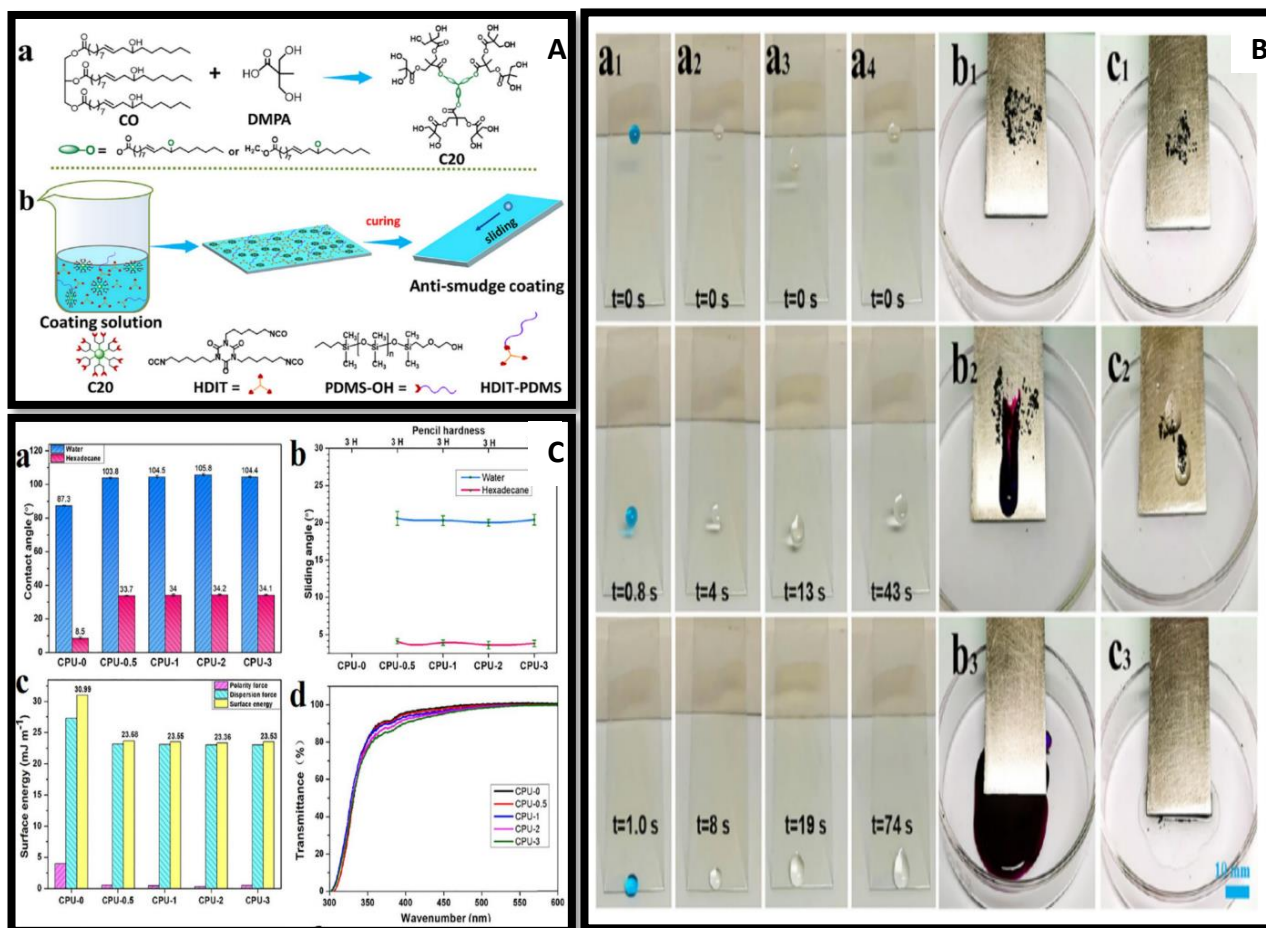


Figure 2.2: (A)(a) Schematic representation of Castor Oil derived hyper branched C20 development. (b) pictorial representation of anti-smudge coating synthesis polymer of HDIT and PDMS-OH (B) pictorial representation of flow of (a1) blue-dye water drop, (a2) hexadecane drop, (a3) peanut oil, and (a4) pump oil on the CPU-0.5 coating with 40, 15, 40, and 40 μL of drop volume respectively at 25.0° angle inclined. Rhodamine B stain was removed with water and hexadecane droplets(b1-b3&c1-c3) at 30.0° inclination. (C) (a) Comparative study of Water and hexadecane contact angles, (b) Pencil hardness as well as study of sliding angles of various compositions of CPU-0, 0.5, 1, 2, and 3 coatings with both the media. (d) Transmittance study of the samples optically measured and (c) Detailed comparative study on calculated surface energy of the various compositions of coatings.(Wei et al., 2021)

shielding materials. Jingu lu and coworkers worked on castor oil-based polyurethanes coating films with properties like self-healing and EMI shielding(Lu et al., 2021). Castor oil was treated with Iso-phorone diisocyanate (IPDI) to synthesize the water-borne polyurethane network. Afterwards, titanium carbide was grafted on the polymer moiety in different proportions along with 2-aminophenyl disulfide (AD). The film prepared was mechanically robust due to the presence of H-bonding. Though ADWPU polymeric film synthesized is very effective against electromagnetic waves, as after adding Ti_3AlC_2 , about 99.9% of waves were found to be blocked either by reflecting, scattering, or absorbing the radiations.

2.2.2. Soybean oil-based polymers

Soybean oil has majorly been used in the polymeric coating industry for the last decade. Despite high T_g and low strength causing limitations, epoxidized soybean oil has remained magnificent feed stock for the synthesis of polymers with functional properties (Yang et al., 2020). Bio resource-derived acrylic monomers exhibit high hydrophobicity, which is beneficial for the application as anti-corrosion coating (Lamm, Song, et al., 2019). For exploring soybean oil for synthesizing self-healable coating systems, Altuna and coworkers developed the epoxy resin embedded with gold nanoparticles (Altuna et al., 2016). In this study, citric acid was used to synthesize an epoxy-based polymer network followed by the incorporation of gold nanoparticles, where gold NPs were prepared in situ through the Turkevich poly(vinyl-pyrrolidone) (PVP) medium. The prepared network is a non-toxic and biologically compatible polymer. The presence of PVP facilitates the linear alignment of the NPs in the polymeric matrix, which promotes stress relaxation and self-healing properties of the nanocomposite. The tensile strength of the coating was quite good, and stress relaxation at 60°C and self-healing properties were well facilitated through localized healing with green laser radiation to ease the reach of the thermal effect for the crack healing process. Thiol-ene click reactions are currently in vogue in the self-healing coating industry as it is very economical to carry out at very high-speed kinetics. Prakash and coworkers used a photo-induced thio-ene click reaction approach to synthesize the castor oil polyol(MCO) and soybean oil(MSO) polyol in the presence of DMPA and ME followed by the formation of thermoplastic PU from MCO and MSO using chain extender 1,4-butanediol (BD) and dibutyltin dilaurate (DBTDL) (Altuna et al., 2016). The prepared thermoplastic PU was found to have excellent transparency, elasticity and high mechanical strength. Altogether, Kocaman suggested the use of coconut-based bio-fillers to enhance the coating properties (Kocaman et al., 2017). Acrylated and epoxidized soybean oil (AESO) based epoxy resins can be fused with bio-fillers generated from grinded coconut waste (CW) particles. Coconut waste particles were

functionalized with poly(hexafluoro butyl acrylate) (PHFBA) which is hydrophobic in nature. This modification in polymeric matrix benefits the material with several properties like water

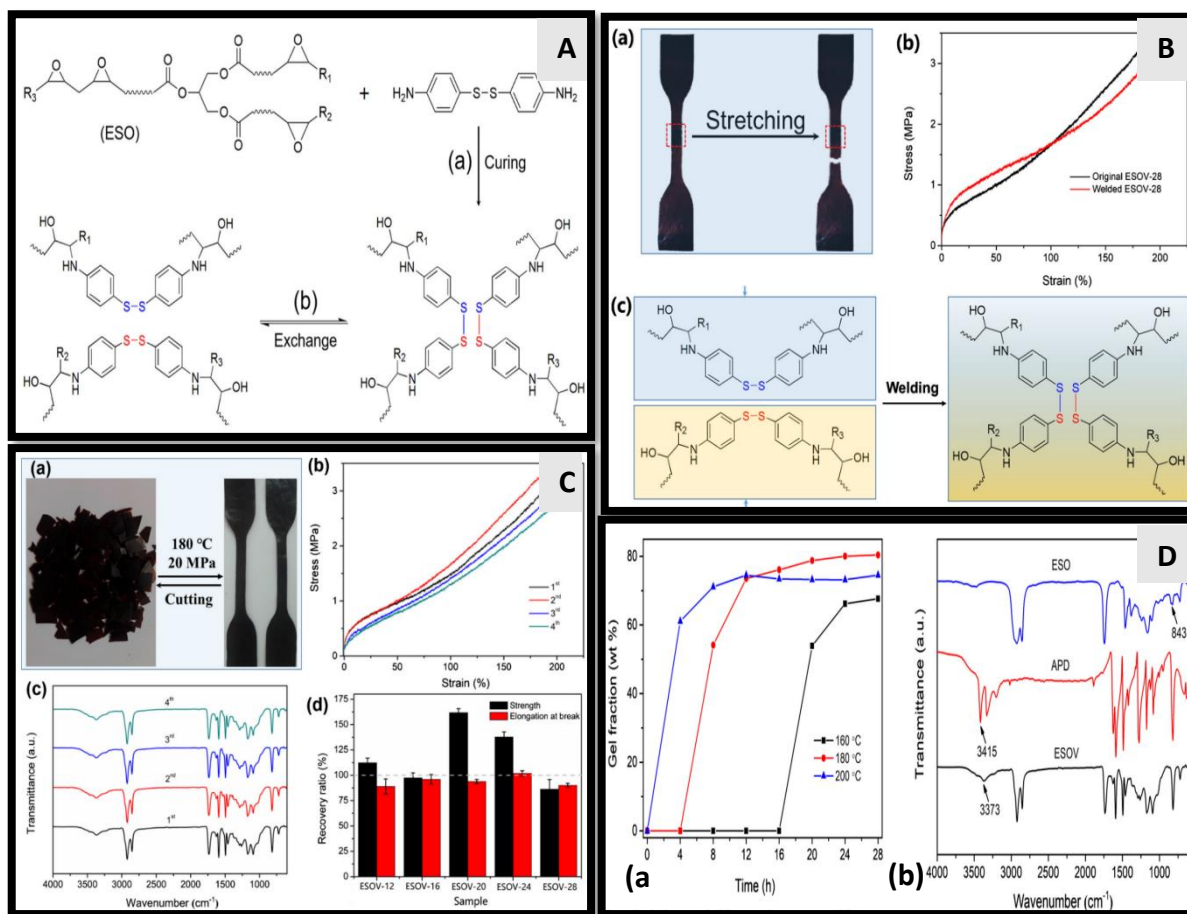


Figure 2.3: (A) (a) Preparation of ESOV using ESO with APD and (b) Topological representation of ESOV network (B) (a) Digital illustration of welded sample bars before and after tensile testing, (b) stress-strain curves of ESOV-28, and (c) Structural representation of ESOV based reaction (C) (a) Recycle process of ESOV-28 via compression molding, (b) stress-strain curves and (c) FT-IR spectra after each healing cycle of cutting and given compression molding, and (d) recovery ratios of each tensile strength of samples after 4 times recovery (D) (a) Graphical illustration of gel fraction concerning curing time. (b) FT-IR spectra of ESO sample, APD sample and ESOV samples respectively (Y. Y. Liu et al., 2020).

repellence, high thermal stability, flammability, good acid and alkali resistance which exhibit anti-corrosion properties. The results show that with high cellulosic content, the flammability of the material increases as lignin content is high. Prakash and coworkers suggested that soybean polyols can be prepared through a thio-ene reaction between soybean oil and 2-mercaptoethanol (ME) in the presence of DMPA and THF (Alagi et al., 2018). The soybean-based polyol was further used for the formation of polyurethane coating by reacting it with toluene 2,4-

diisocyanate (TDI) and DBTDL at room temperature. The resultant coating was found to have good anti-corrosion properties on mild steel panels (tests conducted in 3.5% NaCl and 0.5N HCl aqueous solution). The coating provides excellent tensile strength and barrier properties against corrosion, due to notable high H-bonding in methane linkage between PU coating where no damage or fracture was observed on the coating surface.

According to thermal studies, first degradation was observed at 250 °C and second degradation start at 390°C due to breakage of ester linkage.

Generally, imine-based polymers show good mechanical properties and irretrievability, where due to lower in bond energies and easy dissociation, H- bonds provide efficient self-healing properties. Initially, epoxidized soybean oil was treated with trivanillyl-phosphate (TVP), which was further used to prepare the multilayer-CNT (MWCNT) composites. With the increase in TVP concentration H- bonding abundancy increases while stable imine bonds go down, which results an increase in cross-linking, thus enhances the rigidity of polymer. With the elevation in temperature multi-exchange of network come in existence to achieve self-healing and re-processibility. With a low TVP concentration polymer show rubbery character above T_g , however, a further increase in TVP concentration T_g increase from 40 °C to 75 °C. Aynur ÖZŞEKER and coworkers performed silylation of epoxidized soybean oil (ESBO) to functionalised the polymeric network with silicon(F. Song et al., 2019). Silylation of oil occurred by ring-opening reaction using two coupling agents, 3-mercaptopropyltrimethoxysilane (MPTMS) and 3-aminopropyltriethoxysilane (APTES)

followed by synthesis of polyurethane from the polyol prepared. The prepared polyurethane exhibits properties like flame retardancy, which can have multiple applications in the coating industry.

Vitrimeric polymers can be synthesized from the epoxidized oil in the absence of the catalyst.

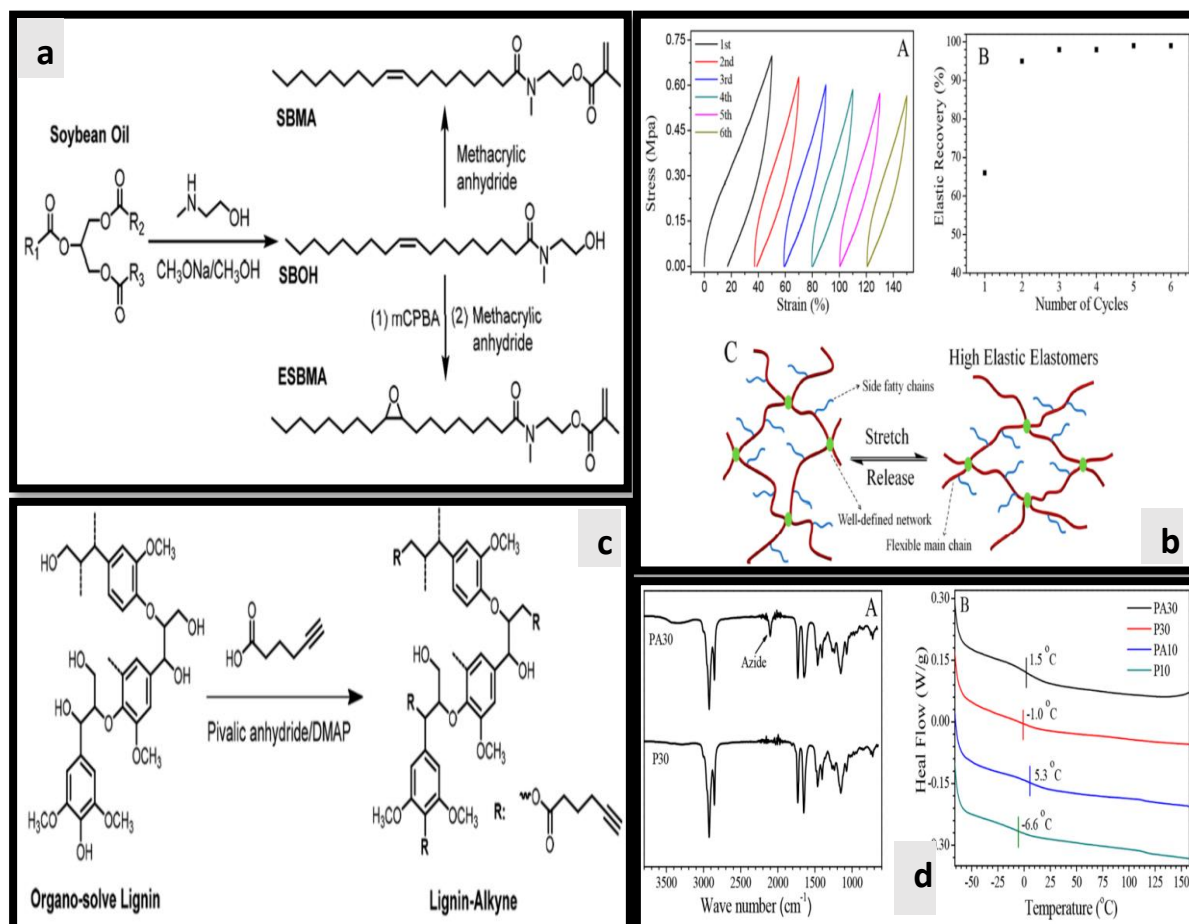


Figure 2.4. (a) Reaction schematics of soybean oil generated SBMA and ESBMA composites. (b) (A) Illustration of Stress–strain plots of PA30-L10 samples. (B) Representation of elastic recovery even after many cycles for the PA30-L10 composites. (C) The microstructure modeling at the stretched as well as relaxed samples state. (c) Reaction scheme representation of Alkyne-grafted lignin development reaction (d) (A) FT-IR spectra of various compositional samples of P30, PA30 polymers and DSC plots of soybean oil-based copolymer (A and B) (Yuan et al., 2019).

Liu and coworkers developed a catalyst-free epoxy-based vitrimeric network using soybean oil and 4,4'-dithiodiphenylamine (APD) as curing agents [Figure 2.3 (A)]. The polymer composite shows excellent tensile strength, re-processability bonding strength, and super high stretchability [Figure 2.3 (B)(C)(D)]. (Y. Y. Liu et al., 2020) Kamal and coworkers produce three different types of novel polyester resins by reacting mono-glyceride (from soybean oil) with phthalic and maleic anhydride. The monoglyceride was obtained by glycerolises of oil via a reversible ester

interchange reaction. (Aly et al., 2020) Yuan and coworkers have reported the synthesis of lignin and soybean oil-based azide-functionalized sustainable elastomers via controlled thermal azide-alkyne cycloaddition (TAAC) [Figure 2.4 (a)(c)] along with the flexibility and appreciable mechanical strength prepared elastomer exhibits excellent elasticity with T_g less than 5 °C [Figure 2.4 (b)(d)]. Alongside this, a catalyst-free bio-based vitrimer from soybean oil was done by Guillermina and coworkers. The thermal and mechanical behaviour of the material was found to be controlled by the content of the precursor used. (Capiel et al., 2020)

Despite limited application due to water resistance, methacrylate gelatine can be used in bio-coating to improve moisture resistance. Being able to perform photo-crosslinking reactions and be prepared from renewable resources, methacrylate gelatine is found to enhance hydrophobicity and mechanical properties. Single layer application is reported to be very useful and spontaneously stratifying into layers, whereas multilayer application is quite complex, expensive and energy consuming. Self-stratification is blending incompatible polymers to form a collective multilayer structure. Sahar and coworkers reported that to enhance the mechanical properties and breathability, this self-stratifying light curable AESO-based coating material could be formulated (Abdollahi Baghban et al., 2021).

2.2.3. Linseed oil-based polymer

Due to its rich inherent properties, linseed oil is one of the highly utilised vegetable oils in the coating industry. Linseed oil has been widely used among researchers because it is eco-friendly, economical, available, and suitable to form the polymeric network. (Selim & Shenashen, 2018) Drying oil Linseed oil-derived polymers are known for their self-healing abilities, and the recent advance in properties and applications for the same has been discussed in Table 2.2. Due to the drying ability of linseed oil has been used as a healing component within the microcapsules in self-healable polymeric coatings. However, temperature curing is one of the major challenges with the vegetable oil-based polymeric coating. Manawwer and coworkers has synthesized a linseed oil-based polyester-amide for anti-corrosion applications (Alam & Alandis, 2011). The reported coating prepared was cured at the ambient environment, which possess appreciable anti-corrosion and physio-mechanical properties. Initially, linseed oil was used to form N, N-bis 2-hydroxy ethyl linseed oil fatty amide diol (HELA), followed by the formation of hydroxyl-terminated polyester-amide (Ed-PEA) by treating with ethylenediaminetetraacetic acid (EDTA). The resultant material was cured while reacting with

poly (styrene co-maleic anhydride) (SMA) at ambient temperature. Polyester-amide coating was thermally stable upto 150°C and possesses significant corrosion inhibiting properties. Subsequently, polyester amines have also been known for their uses in anti-bacterial and anti-corrosion coatings. To improve the anti-bacterial properties, durability and anti-corrosion properties, H. Abd El-Wahab and coworkers modified polyester amine with N-phthaloyl-glutamic acid (Abd El-Wahab et al., 2012). In this study, linseed oil and diethanolamine (DEA) reacted to get N,N-bis-(2-hydroxyethyl)linseed oil fatty acid amide (HELA) which was made to react with phthalic anhydride (PA) and N-phthaloyl-glutamic acid (NPGA) (synthesised in situ) to obtain modified resin for coating. The reported coating exhibits notable chemical resistance and anti-corrosion properties along with excellent mechanical properties. The coating was tested to have less permeability for water, oxygen, and other ions to pass, owing to enriching the adhesion of the hydroxyl group connected to metal surfaces. Although bio-oil-based nanocomposites are potential alternatives for replacing petroleum coatings, advancing the properties of composite polymers can do wonders to address the issues like corrosion, optical transparency, and flexibility. Shabnam Pathan and team attempted to address these noted issues by tailoring the linseed oil-based water-borne alkyd resin with 3-iso-cyanatopropyl-tri-ethoxy silane (IPTES) and di-methyl-tin-di-neo-decanoate (Pathan & Ahmad, 2016). In nanohybrid composite, flexibility is due to the synergistic reinforcing effect and merging of

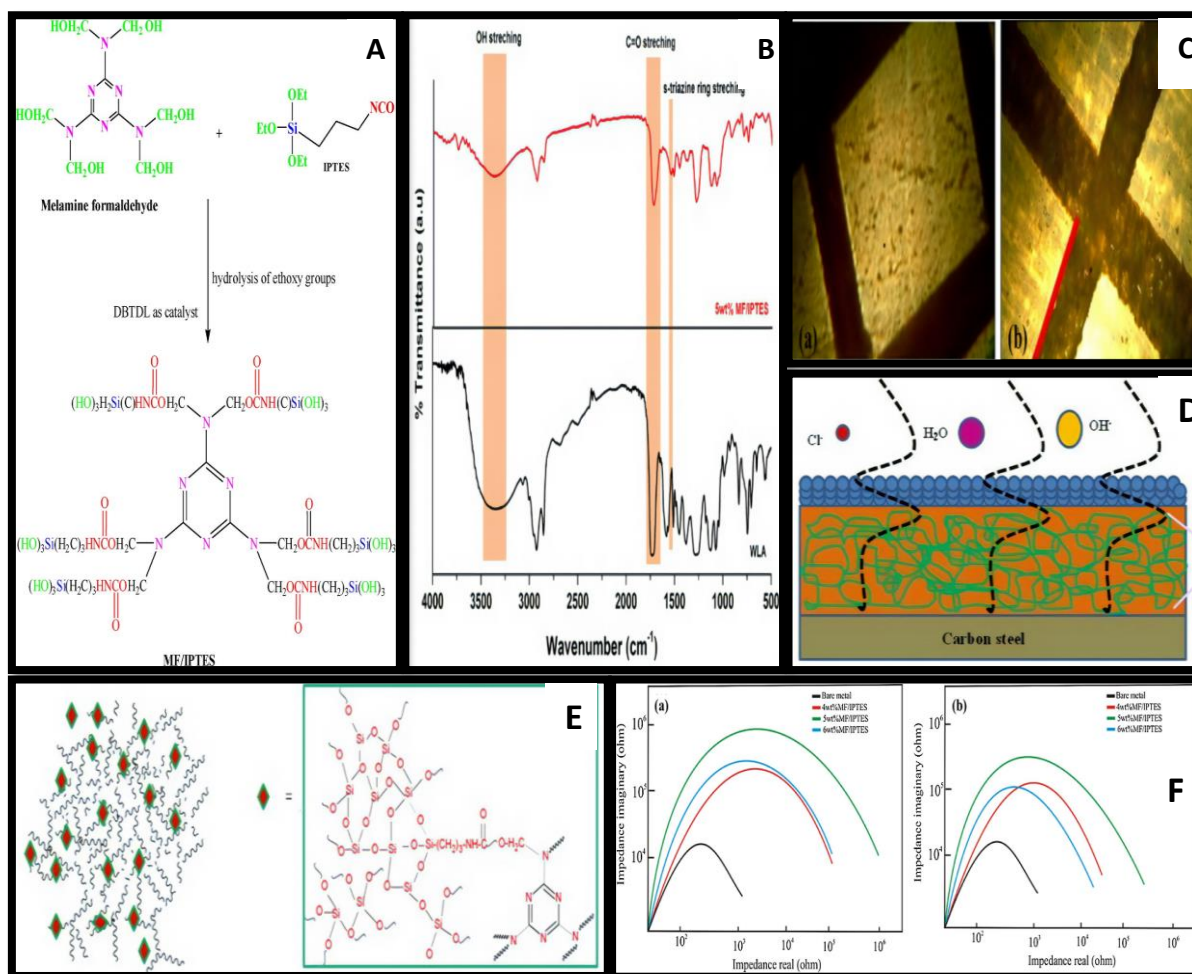


Figure 2.5. (A) Illustration diagram representing IPTES functionalization of MF. (B) FTIR spectra graph demonstration of WLA and MF/IPTES (5 wt%) (C) Optical micrographs showing cross hatch test on hybrid coating at 100 X (D) WLA coatings are represented with help of illustration as barrier created for various types corrosive ions and environment to reach metal substrate cured with MF/IPTES. (E) Structural representation of WLA cross-linked with MF/IPTES. (F) (a) Nyquist plot obtained for WLA coatings in different compositions in HCl (3.5 wt%) (b) as well as in NaOH (3.5 wt%). (Pathan & Ahmad, 2018)

organic and inorganic phases of the system. Shabnam Pathan and coworkers used water-borne linseed oil-based alkyd composites to improve the mechanical properties, (Pathan & Ahmad, 2018) where silane-based coupling agents have been used to address the limitations and escalate the interaction between two phases. Cross-linked polymer coatings derived from linseed oil using melamine formaldehyde (MF) and 3 iso-cynato-propyl tri-ethoxy silane (IPTES) exhibits great mechanical and anticorrosive performance [Figure 2.5 (A)(B)]. It was found that the prepared coating exhibits remarkable adhesive and barrier properties against chemical environment and water along with high thermal stability which comprises to corrosion inhibition [Figure 2.5 (C)(D)(E)(F)].

In another approach, Mohamed and coworkers introduced Cu₂O nano-cube-based filler into alkyd resin to achieve high thermal stability (~324 °C) along with better mechanical and corrosion inhibition properties (Selim & Shenashen, 2018). The hyper-branched poly-alkyd resin was synthesized by adopting A₂ + B₃ approach, where glycerol and adipic acid were reacted in the presence of dibutyltin oxide (catalyst). The prepared materials were further treated with linseed oil fatty acid and P-TSA as catalyst under poly-condensation reaction. The resultant resin incorporated with Cu₂O nanoparticles was used for coatings, where coating possess excellent corrosion inhibition abilities, significant mechanical features as well as stability against chemicals. The further advancement of the reported studies in domain of VO-based alkyd resin Deepak M. Patil and coworkers synthesized linseed oil based epoxidized alkyd resin using itaconic acid for the enhanced anti-corrosive properties in coating (D. M. Patil et al., 2018). In this two-step process, linseed oil (LO) was converted into mono-glyceride via an esterification reaction. Further, the unsaturated bonds exist in the alkyd moiety were further converted into oxirane bonds and later for conversion into epoxidized alkyd resin. The resultant polymer was modified by using 3-Amino propyl-trimethoxy-silane (APTMS) to obtain a coating with good mechanical and adhesive properties. It is due to its ability to form H-bonding with the metal surface. The coating was able to create a good barrier against acid as well as alkaline medium and corrosion and showed increased thermal stability up to 247 °C and high cross-linking density. Regarding microcapsule-based matrix, incompatibility of microcapsules with polymeric matrix results in poor mechanical properties of the coating (Bei et al., 2022). To address the limitations, Mirabedini and group have modified the microcapsules to enhance the surface interactions with the addition of 3-aminopropyltrimethoxy silane as coupling agent (Mirabedini et al., 2020). Microcapsules filled with linseed oil generated from polyurea-formaldehyde exhibited self-healable properties. The developed polymeric network shows improved tensile strength and anti-corrosion properties. To create a coating with enhanced anti-corrosion and self-healing properties, Sehrish and coworkers made an attempt to incorporate talc nanoparticles (TNP) and urea-formaldehyde micro (UFM) capsules (Habib et al., 2021). Talc falls into the category of mineral clay having corrosion inhibitor properties, composed of magnesium silicate. The authors observed that the composite exhibits excellent thermal stability and self-healing properties. When any damage occurs on the coating surface, it makes microcapsule breaks due to mechanical stress and linseed oil releases. Linseed oil works as a healing agent as it starts to cross-link when it interacts with air and forms a protective film with 99% healing efficiency. In combination with NaNO₃, this film inhibits corrosion from spreading on the substrate surface with a corrosion inhibition efficiency 99%. Likewise, to

extend the lifetime of the oil-based polymeric coatings. David and coworkers used acrylated epoxidized linseed oil as the base matrix(Nadine et al., 2021). Linseed oil was converted into acrylated epoxidized linseed oil and copolymerized with di-hemiacetal ester (1,10-dibutoxyethyl sebacate (DBES)) and 3,4-dihydroxyphenetyl acrylamide (DHPA) for adding desired cross-linking property to the polymeric matrix. The corrosion protection by the coating on the surface was found to be appreciable, as DBES addition to the matrix results in an increase in hydrophobic property and high thermal stability, however, it does not lead the matrix towards barrier properties. Though interesting barrier properties were observed in absence of DB.

Table 2.2: Linseed oil-derived polymeric networks synthesis reaction conditions and applications

S. No.	Monomers	Resultant polymer	Catalyst/curing extender (conditions)	Polymerization technique/crosslinking	Fillers	Properties			References
						Self-healing	Mechanical properties	Anti-corrosion	
1.	Linseed oil+ poly(styrene co-maleic anhydride) (SMA)+ ethylene glycol monomethyl ether+ sodium methoxide+ ethylene diamine-tetraacetic acid	Polyester-amide	ethylene-diamine+acetic acid (EDTA)	Cured at ambient environment	-	-	Thermal stability up to 150°, stretching hardness up to 3.7%, impact resistance- 150lb/inch, Tg- 120 °C.	Anti-corrosion in 5% NaOH and HCl up to 10 days.	(Alam & Alandis, 2011)
2.	Linseed+ diethanolamine (DEA)+ xylene+ L-glutamic acid	Polyester-amide resins	-	Esterification	N-phthaloyl-glutamic	-	Impact resistance up to 1.4 kg/m,	Anti-corrosion coating with acidic and	(Abd El-Wahab et al., 2012)

					acid(NP GA) ring		excellent stretchin g of 1 kg, and flexibility	alkaline resistance	
3.	Linseed oil+ 3- isocyanatopropyltriethoxysilane (IPTES)+ Dimethyltin dineodecanoate+ tetrahydro furan (THF)	Alkyd resin	3- isocyanato propyl- triethoxysi lane (IPTES)	Sol-gel reaction	Organo -silane as nano- filler	-	Tthermal stability- 330 ℃, Tg=90- 125 ℃, contact angle=97° , 2θ=20°	Anti- corrosion on CS with Ecorr=- 0.289V, Icorr=4.41 X10 ⁻¹⁰ A/cm ² , Rp=1.05 X10 ⁸ ohm (acid)& 1.94 X10 ⁵ ohm(alkali ne), corrosion rate-5.12 X10 ⁻⁶ mpy.	(Pathan & Ahmad, 2016)
4.	Linseed oil+ melamine- formaldehyde (MF)+ 3-iso- cynato-propyl tri- ethoxy silane (IPTES)+ phthalic acid	Water- borne alkyd resin	dibutyltin di laurate (DBTDL)+ p-toluene- sulfonic acid (PTSA) used as catalyst	Si-O-Si linkage	3-iso- cynato- propyl tri- ethoxy silane (IPTES)	-	Adhesive properti es, thermal stability, impact resistanc e, scratch hardness , 2θ=20°	Anti- corrosion coating on carbon steel	(Pathan & Ahmad, 2018)
5.	Linseed oil+ adipic acid+ glycerol+ CuSO ₄ + sodium hydroxide+ ascorbic acid+	Hyperbr anchored alkyd resin	dibutyltin oxide as catalyst	Polycond ensation reaction	Cu ₂ O nano- cubes as nano- filler	-	Thermal stability up to- 325 ℃, Contact angle-	Anti- corrosion inhibition on carbon steel with 500 hour	(Selim & Shenash en, 2018)

	manganese actuate+ cobalt octoate+ lead octoate						120°, pull off test 26 MPa, impact resistanc e=18 joule	spray resistance test in NaOH & HCl.	
6.	Linseed oil+ 4- methoxypheno+ triethylamine+ para-toluene sulfonic acid+ sodium hydroxide+ Itaconic acid	Epoxidiz ed Alkyd resin	Amberlite	Esterificat ion	3- Amino propyl- tri- methox y-silane (APTMS)	-	Thermal stability= 246 °C, Tg=39-46 °C, Stretch hardness -2250g, scrub test>200 and static heat resistanc e-157 °C.	Anti- corrosion properties with polarisatio n resistance= 0.089Ω, Ecorr=113 1mV, Corrosion rate=0.299 17mmpy, corrosion inhibition- 94.02%.	(D. M. Patil et al., 2018)
7.	Linseed oil+ Polyvinyl alcohol (PVA)+ sodium dodecyl sulphate (SDS)+ diglycidyl ether of Bisphenol A.	Epoxy resin	3- aminopro pyl- trimethox y silane (APS) as coupling agent	Sol-gel techniqu e	Microca psules filled with linseed oil	Self- heali ng prop erties	Tensile strength = 1.75MPa , young's modulud - 1515.4M Pa, elongati on break- 5.6%,str ess break=6 5.3MPa	Anti- corrosion properties with corrosion resistance up to 7.94 X10 ⁵ ohm cm ²	(Mirabe dini et al., 2020)

8.	Linseed oil+ NaNO ₃ + resorcinol+ polyvinyl alcohol (PVA)	Epoxy resin	NaNO ₃ used as corrosion inhibitor, linseed oil as healing agent	-	Talc nano-particles and urea-formaldehyde micro-capsules, sodium nitrate-NaNO ₃	Self-healing efficiency 99.9 %	Thermal stability up to 350 °C, phase angle=-85 to-90°	Anti-corrosion properties with Rp=0.01mΩ, corrosion efficiency-99.5%	(Habib et al., 2021)
9.	Linseed oil+ tetra-n-butyl ammonium bromide (TBAB)+ diethylenetriamine (DETA)	polyurethane	-	Epoxidation and carbonation	-	-	Contact angle=75°, thermal stability-394 °C, pull off adhesion -5.1MPa, direct impact=80in.lb..	Anti-corrosion with impedance modulus=1.85 X10 ⁶ Ω cm ²	(Pouladi, Mirabedini, Mohamadloo, et al., 2021)
10.	Linseed oil+ di-hemiacetal-ester (1,10-dibutoxyethyl-sebacate)+ N,N-dimethyl-acrylamide+ dopamine hydrochloride	Acrylate d-epoxidised resin	(3,4-dihydroxyphenetyl) acrylamide as adhesion promoter	Copolymerization	1,10-dibutoxyethyl-sebacate (DBES)	Self-healing properties	High hydrophobicity, Tg= -61°C, Thermal stability-200 °C	Anti-corrosion properties, barrier properties with Rf=-1.9 X10 ⁷ Ω cm ² , Rpore=1.3 X10 ⁵ Ωcm ²	(Nadine et al., 2021)
11.	Linseed oil+ aq Poly (vinyl alcohol) (PVA)+ sodium lauryl sulphate (SLS)+	polyurethane	Resorcinol as cross linker, DBTDL as a catalyst	Condensation polymerisation	Microcapsules with 87%	self-healing	hydrophobic nature with contact	Anti-corrosion properties with corrosion	(Mahajan & Gite, 2022a)

	cardanol+ methylene di phenyl diisocyanate(MDI) + Diethanolamine				release core		angle- 98.3°, Cross cut adhesion =100%, gloss%=8 5%, thermal stability- 230 °C	inhibition efficiency= 86.92%	
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Other vegetable oils

Because of the difference in their functionality and degree of unsaturated bonds present in their molecular structures, vegetable oils exhibit their unique features and qualities to deliver specific properties. In the coating network, drying time and durability of the matrix have quite an important role, which varies oil to oil. Characteristics of neem oil are full of surprises as it delivers an enormous number of properties to the polymeric matrix. Neem oil's great potential in the coating industry as it contains anti-corrosion and anti-microbial and is highly available (in India). Exploring further, Chaudhari and coworkers studied self-healing poly(ester-amide) synthesised from neem oil (Chaudhari et al., 2013). Neem oil undergoes an amidation reaction with a diethanolamine along side PbO as catalyst, which results in Azadirachta indica juss based Fatty-amide (AIJFA), which was utilized for the synthesis of polyester amide. Microcapsules were prepared using poly-amido-amine (PAMAM) and linseed oil as core material in it and further used for the development of polyurethane coatings. The prepared coating shows thermal stability up to 221 °C, resistance against water and chemical interaction including good adhesive and anti-corrosion properties on the metal substrate. To add on to green composite materials with improved properties, Manawwer and coworkers studied corn oil-based organic coating using isosorbide (Alam, 2019). Corn fatty amide reacted with isosorbide in the presence of sulfuric acid as catalyst to get poly(isosorbide-ether-amide) (PIEtA), which was further converted into PUIEtA/fused silica nanocomposite. Prepared Silica based nanocomposite manifests excellent anticorrosion properties and barrier against chemicals with the notable thermal stability of 275 °C and increased adhesion up to 98%, impact resistance with corrosion inhibition efficiency 99%. In addition, authors have investigated corn oil-based poly(urethane-malonic-ester-amide) network to improve the properties of the matrix by

incorporating multi-walled carbon nanotubes (MWCNTs) as filler(Alam et al., 2021). N,N-bis(2-hydroxyethyl) corn oil fatty amide (HECA) was reacted with malonic acid in toluene to obtain malonic polyester-amide(MPEA) followed by the preparation of poly(urethane-malonic-ester-amide) using iso-phorone diisocyanate (IPDI) which finally get incorporated with MWCNTs. The integration of CNTs in polymeric network increases contact angle (110°) and provides hydrophobic nature to it, making it suitable for anti-corrosion coatings with excellent thermal stability and mechanical. performance. Aung and coworkers suggested that ZnO can be used as a nano-filler for corrosion inhibition in polymeric coating(Aung et al., 2020a). To synthesize the epoxy acrylate of jatropha oil (AEJO), epoxidized jatropha oil was made to react with triethylamine, 4-methoxyphenol and acrylic acid, which is further processed to prepare the composite by reacting AEJO with reactive diluent tetra-methyl-ol-propane tri-acrylate (TMPTA) and photo-initiator 2-hydroxy-2-methylpropiphenone, followed by the addition of ZnO as nano-filler in different compositions. These nano-hybrid resins possess properties to protect the metal surface from corrosion owing to the hydrophobic nature of ZnO. Incorporating a 5% weight% ZnO loading showed significant enhancement in corrosion resistance and coating performance. Tung oil is being used in polymeric coating industries for its positive impact as filler inside microcapsules. A study by Gonçalves and co-researchers reported that composites prepared from poly(urea-formaldehyde) positively impact corrosion inhibition and self-healing properties(Cordeiro Neto et al., 2020).

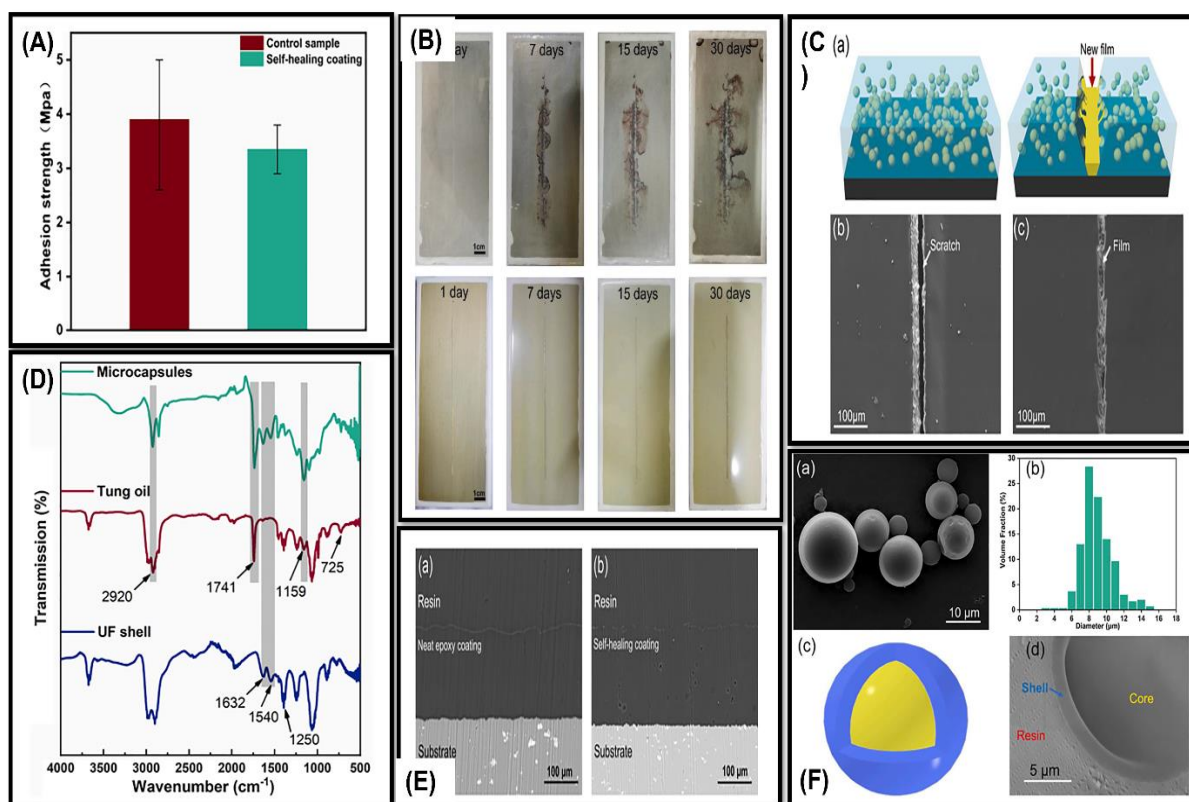


Figure 2.6. (A) Comparative bar representation of adhesion strength for the pristine epoxy sample and self-healing network. (B) Pictorial representation of AA2024-T3 plates with corrosion inhibition: AA2024-T3 plate with the pristine epoxy coating (represented up side), self-healable material coated plates (shown in downside plates) after tested and examined via salt spray test after the time period of 0 day, to 7, 15, and 30 days. (C) (a) Demonstration of the self-healing properties of the scratch on the surface. (b) SEM demo gram of the pristine epoxy coating scratched, (c) SEM demo gram of the healed self-healed coated surface scratches. (D) Comparative FTIR spectra of tung oil UF, and synthesised microcapsules. (E) SEM image in the cross-section of (a) control coating (b) self-healable material coating. (F) (a) SEM demo gram of developed microcapsules UF, (b) Study of size distribution developed microcapsules, (c) Illustrative representation of shell core structure, (d) SEM demo gram showcasing details in thickness of prepared microcapsule shells. (J. Li et al., 2021)

Zinc phosphate is being used as a corrosion inhibitor as the hydroxyl group in the base network reacts with zinc phosphate and results in an even more stable zinc oxide film, helping to protect the substrate from corrosion.

Along with all the properties of the coating, the thickness of the coating is also essential to study in polymeric coatings. Usually, in self-healing polymeric coatings, large microcapsules facilitate the release of a good amount of healing agents, which results in a thick coating. In comparison, a thin application of the coating is enough to protect the metal surface. Aiming toward the

characteristic of diameter, Li and coworkers studied the tung oil microcapsules subsumed in epoxy matrix [Figure:2.6. (A)(D)(F)](J. Li et al., 2021). Tung oil-based microcapsules were prepared in situ using formaldehyde for the formation of shell and urea, resorcinol and ammonium chloride [Figure:2.6. (B)(C)(E)]. Self-healing coating embedded with tung oil microcapsules was investigated, and found that a decrease in adhesion of coating was found, but the barrier ability of the coating was good along with self-healing and anti-corrosion properties.

Limitations and challenges

In spite of great economic and ecological values, vegetable oil based polymeric coatings are facing numerous challenges in making place in industrial market(Adekunle, 2015). One of the major issues with the vegetable oil based polymeric network is the availability of the edible oils(Silva et al., 2021). The relation of production rate of edible oils and rate of consumption makes the discussion even more crucial. Though the alternative to address the issue is the use of non-edible oils in polymer production, which will not hamper the supply to food industries.

Apart from the availability, polymeric network often possess low crosslinking density which lead towards low mechanical properties and solvent resistivity due to the triglyceride long chain structure of vegetable oil based polymeric moiety, though it also offers flexibility to the network compared to the petroleum based polymeric networks(Stanzione & La Scala, 2016)(Nayak, 2000). Mechanical properties of the VO based polymeric coatings can be improved with the addition of suitable crosslinker and also by adding the fillers. In addition, to avoid the environmental oxidation and physical stability, vegetable oil based self-healing materials can be used in encapsulated form for developing self-healable polymeric coatings. But with encapsulated networks there are limitation in terms of reusability, re-processibility and low mechanical properties(Lammari et al., 2021). Alongside, to compete with thermal stability, and mechanical properties of petroleum-based coating networks in the industry, hardener or curing agents are required to increase the crosslinking for the bio-based network(Llevot, 2017). Since for designing the coating materials, we need to modify the oil molecular structure using different reaction steps, thus, there are possibilities of free fatty acids methyl ester (FAMES) traces, those make the material less resistive towards high temperature and hence makes it less suitable towards flame resistance coating material(Silva et al., 2021)(Zhou et al., 2019).

As the low thermal stability of the VO based coating network ultimately lead towards the lower shelf life and hence the early degradation of the network, which can be answered by using the various fillers in the form of graphene based nanosheets, metal nanoparticles or metal-legend composites(Y. Zhang & Hu, 2020)(T. Song et al., 2021). On the other hand, vegetable oil based self-healing networks require particular conditions to reprocess and to reflect the characteristic behavior (like high temperature and high pressure), which is not feasible to provide at industrial level(Bei et al., 2022). Due to drastic working conditions, these materials are also not preferred in aeronautical applications (Fainleib & Purikova, 2019). To address such issues various techniques can be applied in case of advanced materials (e.g. vitrimers), where instead of conventional thermal heating electromagnetic radiation or induced heating can be used to attain the energy, required for the dynamic bond exchange reaction in order to facilitate the self-healing property at different working environment(Bei et al., 2022)(T. Song et al., 2021). To acquire the radiation heating of the system, the chemistry can be obtained with the presence of carbonaceous materials or the molecules with dielectric constant. In consideration of bio-integrated electronic devices, longer healing time of the cracks could result into failure of the device, apparently rapid healing of the network at ambient temperature would be required to avoid the damage(J. Xu et al., 2022). On the other hand, curing of the coatings at the substrate outside the laboratory is one of the major drawbacks which needs special attention, where thermal curing or curing involve hardening agents are not possible in the case of bulk and offshore application. To answer such complications, UV/ electromagnetic radiation promoted curing of coating materials can be designed (Bei et al., 2022)(J. Xu et al., 2022).

CHAPTER 3

Microwave-Assisted Self-Healable Bio-Vitrimer/Rgo Framework For Anti-Corrosion Applications

Abstract:

Microwave-stimulated smart self-healable polymeric coatings with significant protective technology against corrosion have been developed in this work. Herein, a generous approach was strategized to generate linseed oil-derived epoxy composites embedded with reduced graphene oxide(rGO) as nanofiller in the shielding network. The composite showed excellent self-healing and shape memory properties when irradiated with microwaves due to the dynamic reversible nature of the disulfide covalent bond exchange mechanism. The network also has improved thermo-mechanical properties and thermal stability, with a storage modulus of 20.8 GPa and low activation energy of 78 KJ/mol, indicating a fast disulfide dynamic exchange reaction. The amine functionality in the composite contributes to excellent corrosion protection with 99.9% protection efficiency, as validated through electro-impedance spectroscopy via the Tafel plot. The composite also showed excellent hydrophobicity, with a 131° contact angle. This study provides insight into the engineering and application of smart materials as anti-corrosive coatings.

3.1 INTRODUCTION:

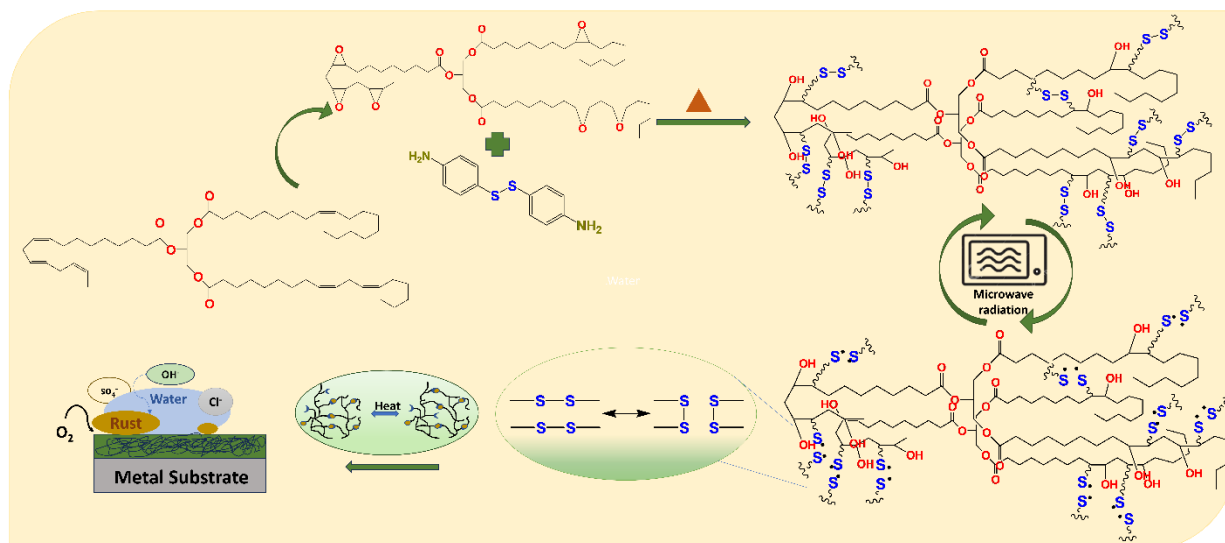
Corrosion of metal is an unavoidable destructive phenomenon that affects the workability of the metal and causes damage to the structural assets, and lethal accidents, which eventually lead to resources waste and hence economic detriments (approx. 4 trillion dollars across the worldwide) (Auepattana-Aumrung & Crespy, 2023; Koochaki et al., 2021; Mahajan & Gite, 2022a). Polymeric coatings are potential candidates in corrosion protection as it prevents the direct contact of metal with corrosion causing environment(Jiang et al., 2023). Traditional organic coatings have been used for ages to protect assets from corrosive elements and environmental conditions such as moisture, salt ions, and other substances that cause corrosion. However, prolonged exposure to harsh weather and other environmental conditions can also deteriorate polymeric coatings.(Auepattana-Aumrung & Crespy, 2023; Zafar et al., 2007; M. Zhang et al., 2022) thermoset polymers like epoxy, polyester amide, poly amide acrylates based anti-corrosive coatings display appreciable properties to screen the substrate from damages and hence have been the

favorable choice due to their chemical stability, mechanical strength and other tailorable properties(Alam et al., 2021; Alam & Alandis, 2011; Lamm, Li, et al., 2019; Materials et al., 2018).. However, thermoset coating can suffer damage from cracking, environmental conditions, and working routines. This can result in the corrosion of metal surfaces, leading to low mechanical properties and structural damage. To protect high-value metallic structures and to extend their lifetime, a smart coating is needed. This smart coating should be able to heal cracks and prevent the penetration of corrosive substances.(Sahoo et al., 2010; Wu et al., 2022). Self-healable smart materials, achieved via dynamic covalent bond exchange reactions such as di-sulfide bonds, transesterification, boronic ester, and Diels-alder reactions, are collectively known as "Vitrimers"(Krishnakumar, Sanka, et al., 2020; Winne et al., 2019). These materials require external stimuli such as pH, catalysts, or heat to make the matrix functional(Habibiyan et al., 2020; F. Song et al., 2019; F. Y. Sun et al., 2023).

Many researchers are focusing on biomass resources to achieve sustainability development goals and reduce environmental pollution caused by petroleum products. Vegetable oil-based materials are a cost-effective alternative to petroleum-based products and offer a range of properties, such as self-healing, shape-memory, recyclability, and protection against solvents and ion attack. They also provide reliable mechanical strength and self-adhering properties(Hu et al., 2018). Among different types of vegetable oils, linseed oil is a popular choice due to its high degree of unsaturation and fast-drying nature (Ghasemi Rad et al., 2019). This oil allows for the formation of auto-oxygenated polymeric networks with high crosslinking, resulting in thermal adaptive behavior, shape reconfiguration ability, and excellent crosslinked networks in linseed oil-based epoxy matrices(Selim et al., 2018). Epoxy-based networks with reversible covalent bond exchange are functional at moderate temperature conditions, even without any catalyst loading, which makes them more beneficial for screening surfaces from corrosive conditions. Vitrimer coatings have the ability to restore the mechanical and physical properties of the material after healing. However, bio-derived matrices have a common drawback, which is their lack of mechanical strength. To enhance mechanical strength and create a prolonged passive barrier towards the substrate, 2D-nano-fillers are used, due to the "labyrinth effect". However, non-dispersive or agglomeration of these nanofillers can restrict the corrosion-inhibiting behavior and accelerate the electrochemical reaction, leading to accelerated corrosion (H. Li et al., 2021; X. Li et al., 2023). 2-D materials like graphene has also been used as a nanofiller due to its high mechanical and anti-corrosive properties.

However, to endow various properties and functionalities according to the selective applications modifications are required on the surfaces. Guo and coworkers prepared and modified graphene using various exfoliation methods and functional modifications(M. Li et al., 2023). Here in this study, reduced graphene oxide (rGO) has been used as the nano-filler with intention of increasing the mechanical as well as corrosion protective properties of the composites. The rGO inclusion reinforced the composite coating system as well as shows enhanced adhesive properties and increased impact strength which interrupts the crack propagation(Aradhana et al., 2018).

The purpose of this study is to develop epoxy-based smart protective coatings originated from linseed oil. The aim is to provide hydrophobic anti-corrosive protective coatings with excellent self-healing properties. To achieve this, 4-amino diphenyl disulfide is used as a hardening agent for crosslinking the network, which provides disulfide bonds to facilitate the dynamic bond exchange reaction and self-healing properties. The amine group present in the 4-AFD serves as an excellent corrosion inhibitor toward the substrate (Cherubin et al., 2022). Additionally, reduced graphene oxide(rGO) is incorporated into the coating system as a nanofiller to induce the dielectric effect, smaking the system compatible with microwave radiation and potentially enhancing its healing and mechanical properties. A systematic study was conducted on the interaction between the epoxy matrix and microwave radiation, along with the proportional addition of reduced graphene oxide shown in scheme (Scheme 3.1). As per our knowledge, this study is the first to explore microwave-induced reparable linseed oil-based bio-vitrimer anticorrosive epoxy systems displaying disulfide covalent bond exchange.



Scheme 3.1. Schematic representation of development of microwave assisted self-healable anti-corrosive coating using linseed oil derived epoxy matrix.

3.2 MATERIALS AND METHODS

3.2.1 Materials

Linseed oil (LO, Sigma Aldrich), 4,4'-diphenylamine-disulfide (4-AFD, Sigma Aldrich), diethylenetriamine (DETA, Sigma Aldrich), sulphuric acid(H_2SO_4), hydrogen peroxide(H_2O_2), and acetic acid were procured and used in their original form.

3.2.2. Synthesis of GO and rGO:

Graphene oxide (GO) nanosheets were synthesized using a modified Hummers' method(Hummers & Offeman, 1958; Nia et al., 2014). In a 500 mL round bottom flask, 1g of graphite was mixed with 3g of sodium nitrate in 23 mL of sulfuric acid. The mixture was constantly stirred at 0 °C while gradually adding 3g of potassium permanganate, with the temperature being maintained at 0 °C throughout. The resulting mixture was washed and dried. The prepared GO was then converted into reduced graphene oxide (rGO) using a thermal exfoliation method. GO was exfoliated at 600 °C under a nitrogen environment for 2 hours to obtain rGO(Sengupta et al., 2018). The chemical structure of GO and rGO is discussed in supporting information (Figure A3.1)

3.2.3. Synthesis of epoxidized linseed oil (ELO)

Epoxidized linseed oil (ELO) was synthesized with few modifications to existing methods to prevent unwanted crosslinking due to the highly reactive allylic double bond. In a 250-mL two-neck round bottom flask equipped with a magnetic stirrer, 5g of linseed oil (LO) was mixed with 3g of glacial acetic acid (conc. 95%) and 0.25g of sulfuric acid (conc 98%) as a catalyst at 45°C for 15 minutes (500rpm). Gradually, 10g of hydrogen peroxide (conc. 30%) was added, and the temperature was raised to 70 °C for an additional 6 hours. The transparent viscous ELO was extracted by washing the product with diethyl ether and water until a neutral pH was achieved. The conversion of the epoxidation was calculated using the oxirane number (supporting information) and HBr titration with an oxirane value of 3.9 (Figure A3(d))(Ghasemi Rad et al., 2019; Karami et al., 2019).

3.2.4. Preparation of ELA (epoxidized linseed oil-AFD) vitrimer and specimen:

ELA vitrimer samples were successfully prepared using dynamic disulfide exchangeable bonds in a catalyst-free method, with 4,4'-diaminophenyl disulfide as the hardening agent. The compositional calculation is given in the supporting information. ELA samples with varying compositions of rGO as a nanofiller were also prepared. To prepare ELA-x%rGO (where $x = 0.1, 0.3, 0.5$), the synthesized rGO (50mg) was dispersed in 5 mL ethanol by sonicating for 30 minutes until it was completely dispersed (Compositional Table given in supporting information). The rGO in defined percentage was added to ELO, and 4-AFD was added to the matrix system as the hardening agent. The mixture was homogenized for 15 minutes at 80 °C followed by degassing and poured into PTFE molds. The material was also coated on a glass slide for investigation of its self-healing properties and a metal substrate (SS-216) in a spin coater (spinNXG-P2) at 1000 rpm for 60 seconds, then accelerated to 1200 for 30 seconds. The vitrimer coating and samples were cured in the following cycle: 2 hours at room temperature, 2 hours at 80 °C, 2 hours at 120 °C, and 5 hours at 180 °C in a split furnace. The thickness of the developed coating was controlled in the range of 80 μm -110 μm , as preferred for anti-corrosion study(Nabil Bassim et al., 1988). After the furnace temperature reached room temperature, the samples were extracted and characterized further.

3.2.5. Characterization techniques:

The molecular structure and composition of GO and rGO were studied using various techniques. Fourier transform infrared spectrometer (FTIR) spectra were obtained on a Perkin Elmer C94612 instrument in the wavenumber range 4000-400 cm^{-1} at 0.4 cm^{-1} resolution with KBr beam splitter

and deuterated triglycine sulfate (DTGS) detector using MIR mode. XRD spectra of GO and rGO were obtained from a Bruker D8 Advance Eco with CuK α radiation and source at 40KV $\times$ 25 mA.

Raman spectrometer of model RIMS-U-DC was used to obtain Raman spectra of GO, rGO, LO and ELO at 532nm laser wavelength with laser power 0.88 mW and S/N ratio 15000:1. Crosslinking of ELA was determined by solvent stability test. ^1H NMR spectra for LO and ELO were tested on Bruker advance NEO 500MHz nuclear magnetic resonance spectrometer (NMR) at RT using deuterium chloroform (CD_3Cl) as solvent. The thermal stability of all compositions of vitrimers were investigated on thermogravimetric analysis (TGA) using the PerkinElmer4000 thermal analyzer under nitrogen atmosphere of 3 Pa with an N_2 flow of 20 mL/min and between room temperature (RT) and 700°C temperature range.

Atomic force microscopy (AFM, NaioAFM, Nanosurf) instrument was used with tapping mode in an area range of 5 $\times$ 5 μm to study the surface topology of the coating surface. Roughness values were calculated using inbuilt Nanosurf software. To evaluate the hydrophobicity of the coating, the drop shape analyzer (DSA) instrument of Kruss was used with deionized as well as saltwater (3.5% salt water as the composition of salt in seawater). Microscopic optical images of the healing process and after-corrosion surface were observed on microscope Nikon ECLIPSE MA200 at 50X and 100X for close investigation of the process.

The thermo-mechanical properties (like storage modulus, relaxation modulus, stress vs. strain) of vitrimer samples were studied at TA-Q400em TMA in 3-point bending mode under N_2 atmosphere with 50 mL/min gas flow and 0.02N force applied along with the stress-strain curve performed at 40 °C. The anti-corrosive properties were investigated using electrochemical impedance spectroscopy CHE-660 and a 3-electrode system in a flat corrosion cell in 3.5% NaCl electrolyte consisting of Ag/AgCl (KCl) as the reference electrode, a platinum electrode as the counter electrode, and vitrimer matrix-coated substrate as the working electrode.

3.3. RESULTS AND DISCUSSION

3.3.1. Characterization of GO, rGO, ELO and ELA:

The process of synthesizing GO and rGO was analyzed using FT-IR spectroscopy. The FT-IR spectra of GO showed a broad peak at 3443 cm^{-1} , which was due to the stretching vibration of the hydroxyl (-OH) group (Figure S2(a)). A significant carbonyl stretching vibration peak was also

observed at 1724 cm^{-1} , indicating the presence of carbonyl-containing functional groups on the surface of GO. The peak observed at around 1636 cm^{-1} , corresponding to the C=C stretching is also observed which is also present in rGO spectra. On the other hand, the intensity of the 3443.0 cm^{-1} peak decreased in rGO as compared to GO. This indicates a reduction in the number of functional groups present on the surface. Moreover, the peak due to the carbonyl functional group at 1724 cm^{-1} was absent in rGO. This signifies the restoration of aromatic character in the graphene lattice and reduction of GO to rGO (Figure S2 (a))(Sengupta et al., 2018). The synthesis of GO and rGO was also confirmed through X-ray diffraction analysis. GO is a highly disordered structural form of graphene derived from graphite. It contains various oxidized functional groups on its surface, including hydroxyl and epoxy groups, which affect the structure's crystallinity. The XRD peak of graphene oxide was obtained at 11° (Figure S2(b)) (Hegde et al., 2021). The peak of GO shifted towards a lower angle compared to graphite due to an increase in interlayer spacing caused by the presence of oxidizing functional groups on the nanosheet surface, which also lowers the peak intensity. On the other hand, for rGO, the peak was observed at 23° , which is a higher 2θ angle due to its more ordered and crystalline structure. The peak observed for rGO is wider, indicating a π -conjugated structure and a more randomly arranged crystal phase after removal of functional groups (Figure S2(b)) (Hidayah et al., 2017). The Raman technique was used to analyze GO and rGO (Figure S2(c)). GO exhibits three Raman peaks. The D band appears at 1337 cm^{-1} , which is due to sp^3 hybridized carbon atom vibration. The G band appears at 1567 cm^{-1} , which is due to sp^2 hybridized carbon atom vibrational mode. The I_D/I_G ratio is 1.28. Furthermore, the 2D band appears at 2968 cm^{-1} due to second-order scattering of the G band caused by multi-layer graphene present in the lattice. On the other hand, reduced graphene oxide shows a stronger G band as compared to GO and a decrease in the D band. The I_D/I_G ratio is 0.47, which is lower than that of GO due to reduction at the surface of the nanosheet.(Hegde et al., 2021).

The FT-IR spectra were analyzed to study the conversion of ELO. Figure S3(a), linseed oil spectra show a shoulder peak of stretching ($=\text{C-H}$) at 3010 cm^{-1} , indicating the presence of a carbon-carbon double bond in the moiety. Additionally, at 2923 cm^{-1} , an aliphatic stretching vibration peak (C-H) was observed due to the aliphatic chain present in the linseed oil structure. At 1648 cm^{-1} , the ($-\text{C}=\text{C}-$) double bond stretching vibrational peak was observed in linseed oil spectra due to the unsaturated fatty acid chain. The bending vibration and wagging vibration band due to the C-H bond of the methylene group was observed at 1462 cm^{-1} and 1384 cm^{-1} respectively which are also observed in

ELO spectra. Another peak was observed at 720 cm^{-1} due to the stretching vibration of $\text{cis}(-\text{C}=\text{C}-)$ present. On the other hand, in epoxidized linseed oil (ELO) spectra (Figure S3(a, b)), peaks observed earlier at 3010 cm^{-1} and 1648 cm^{-1} due to alkene hydrogen ($=\text{C}-\text{H}$) and $(-\text{C}=\text{C}-)$ respectively vanished after conversion to epoxy (Téllez, 2009). However, the peak at 2923 cm^{-1} due to aliphatic stretching remains intact. Additionally, oxirane($\text{C}-\text{O}-\text{C}$) vibrational band were appeared at 905 cm^{-1} and 821 cm^{-1} . The intensity of the peak observed at 720 cm^{-1} due to $\text{cis}(-\text{C}=\text{C}-)$ was less due to partial conversion into oxirane ring.

The ELO crosslinked with AFD was characterized by ATR-FTIR (Figure 3.1. (a)). In ELA spectra, at 3750 cm^{-1} , a new peak emerged as compared to ELO due to N-H stretching, and at 1574 cm^{-1} peak due to C-N was observed due to the formation of the C-N bond, making the crosslinking of ELO and AFD evident. The peak at 821 cm^{-1} due to epoxy was missing as they were utilized in the formation of the C-N bond (Ramezanzadeh et al., 2016). The crosslinking status of the ELA was also verified by solvent dispersion method. The samples were allowed to disperse in acetone before and after the crosslinking cycle, followed by sonication for 10 min resulting in the stability of cured samples with no loss and dispersion (Figure 3.1. (b,c)).

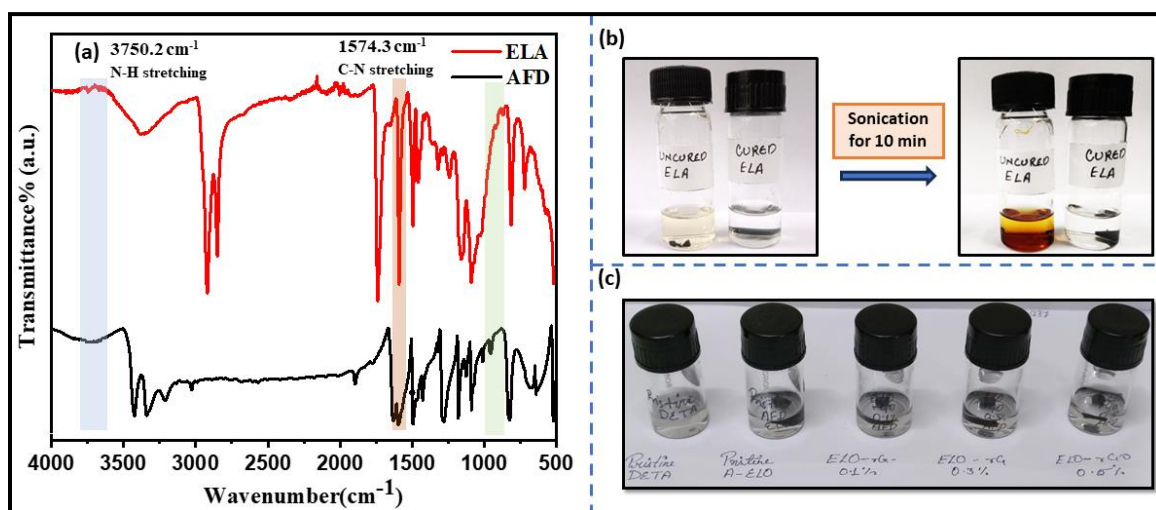


Figure 3.1. (a) ATR-FTIR of ELA vitrimer and AFD crosslinking agent (b) solvent crosslinking testing in the acetone (c) Solvent stability of vitrimer composites in acetone for 24 hours

In ^1H NMR spectra of LO (Figure S4(supporting information)), a peak due to unsaturation was observed at around $\delta\ 5.3\text{--}5.5\text{ ppm}$ which corresponds to non-conjugated $\text{cis}-\text{C}=\text{C}-$, these particular

peaks disappeared in NMR spectra of ELO due to epoxidation at these sites. The signal due to α -hydrogen of oxirane ring appears in δ 2.8-3.2 ppm (Hegde et al., 2021). H_b and H_c signal from hydrogen presented adjacent to oxirane ring appeared at δ 1.4 and δ 1.6 ppm respectively. The signal peaks at δ 4.1-4.5 ppm due to glycerol moiety of oil remained unchanged after epoxidation. In ^{13}C NMR spectra, peak appear at δ 62-65 ppm are corresponds to oxirane carbon and at δ 25-28 ppm are the signals due to carbon adjacent to oxirane ring, the both validated the successful conversion of ELO (Pouladi, Mirabedini, Eivaz Mohammadloo, et al., 2021) (Pathan & Ahmad, 2018).

3.3.2. Thermal and Thermo-Mechanical properties

The thermal degradation of vitrimer material was analyzed at different compositions of rGO over a temperature range from room temperature to 700°C. The degradation of AFD vitrimer was observed in two stages (Figure 3.2). The first stage resulted in a 5% weight loss at 300°C for the pristine material. The highest temperature value was obtained with 0.3% rGO incorporation at 306°C due to the degradation of the epoxy fragment of the matrix though $T_{5\%}$ value decreases for 0.5% rGO composite due to decrease in matrix-filler interaction as a result of agglomeration where filler-filler interaction is stronger than matrix filler interaction (weak π - π stacking interaction), hence the thermal stability decreases (Su et al., 2018). This was followed by the degradation of the disulfide bond of the network in continuity until the 500°C range of temperature. This signifies the crosslinking of the matrix (Figure 3.2) (B. Singh et al., 2023). The complete degradation of the samples was obtained in temperature range of 530°C, whereas, 5% weight loss thermal degradation of ELA-0.1-rG was observed at 305°, which is very much closer to ELA0.3-rG.

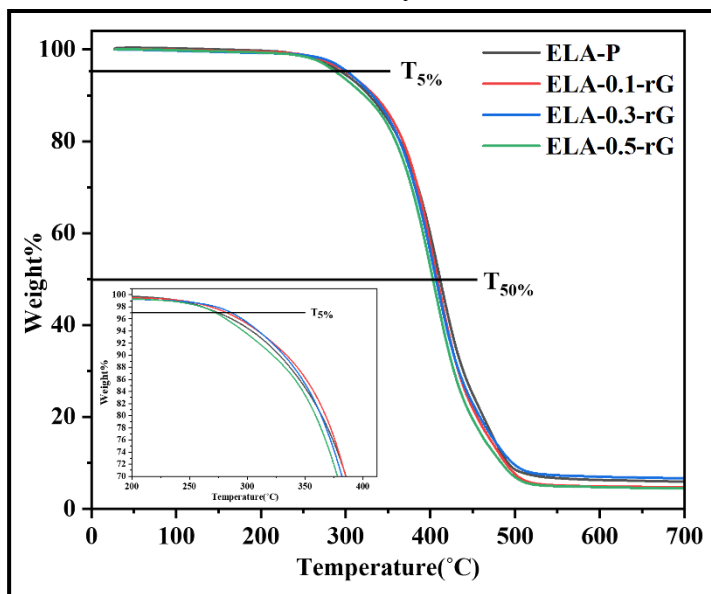


Figure 3.2. TGA analysis of various vitrimer sample ELA-P, ELA-0.1-rG, ELA-0.3-rG, ELA-0.5-rG.

Table 3.1. Glass transition temperature (T_g) through DMA and Thermal stability of vitrimer samples with 5% and 50% weight loss temperature through TGA

S. No.	Sample codes	$T_g(^{\circ}\text{C})$ (DMA)	T-5% ($^{\circ}\text{C}$)	T-50% ($^{\circ}\text{C}$)	Storage modulus (GPa)	Stress (MPa)
1.	ELA-P	33.9	300	412	10.7 $\pm$ 0.6	16.9 $\pm$ 3.2
2.	ELA-0.1-rG	36.5	305	408	20.8 $\pm$ 0.7	15.9 $\pm$ 2.3
3.	ELA-0.3-rG	32.2	306	407	8.9 $\pm$ 0.4	14.8 $\pm$ 1.5
4.	ELA-0.5-rG	31.0	292	403	8.7 $\pm$ 0.5	12.7 $\pm$ 1.8

The vitrimer composites were studied to determine their temperature-dependent properties, specifically, their glass transition temperature (T_g) using DMA, and the viscoelastic character of the matrix with rGO nanofiller (Figure S5). The addition of filler increases the chain mobility of the matrix due to the interfacial spacing between the nanosheet and resin. This allows the matrix chain to move freely and alters the T_g value (Krishnakumar, Prasanna Sanka, et al., 2020a; Park et al., 2020). However, when the filler is not well dispersed into the matrix, due to agglomeration of the nanosheets, it can affect the interaction between the filler and matrix. The higher the T_g , the stronger the interaction of the filler with the polymeric matrix, whereas T_g drops with poor interaction due to agglomeration. The agglomeration of rGO nano-filler occurs at higher concentrations due to π - π interaction between nanosheets (Deep et al., 2017; L. Li et al., 2023). The pristine vitrimer sample ELA-P had a T_g of 33.9 $^{\circ}\text{C}$, which increased to 36.5 $^{\circ}\text{C}$ when rGO was incorporated as filler in the ELA-0.1-rG composite (as displayed in Table 1) (Zhao et al., 2018). The topological freezing transition temperature (T_v) was also calculated using the Maxwell equation as well as by average modulus values. The T_v value for the prepared vitrimer composites was found -12.06 $^{\circ}\text{C}$ (for sample ELA-0.1-rG). The viscoelastic properties of bio-vitrimer were studied in terms of storage modulus at varying concentrations of rGO filler. At 0.1% rGO content, the storage modulus value was 20.8 GPa at 30 $^{\circ}\text{C}$. However, the modulus value decreased with a

further increase in nano-filler content. Table 3.1 shows the systematic study of vitrimer samples at different concentrations, and the storage modulus curves are discussed (Figure 3.3(a)).

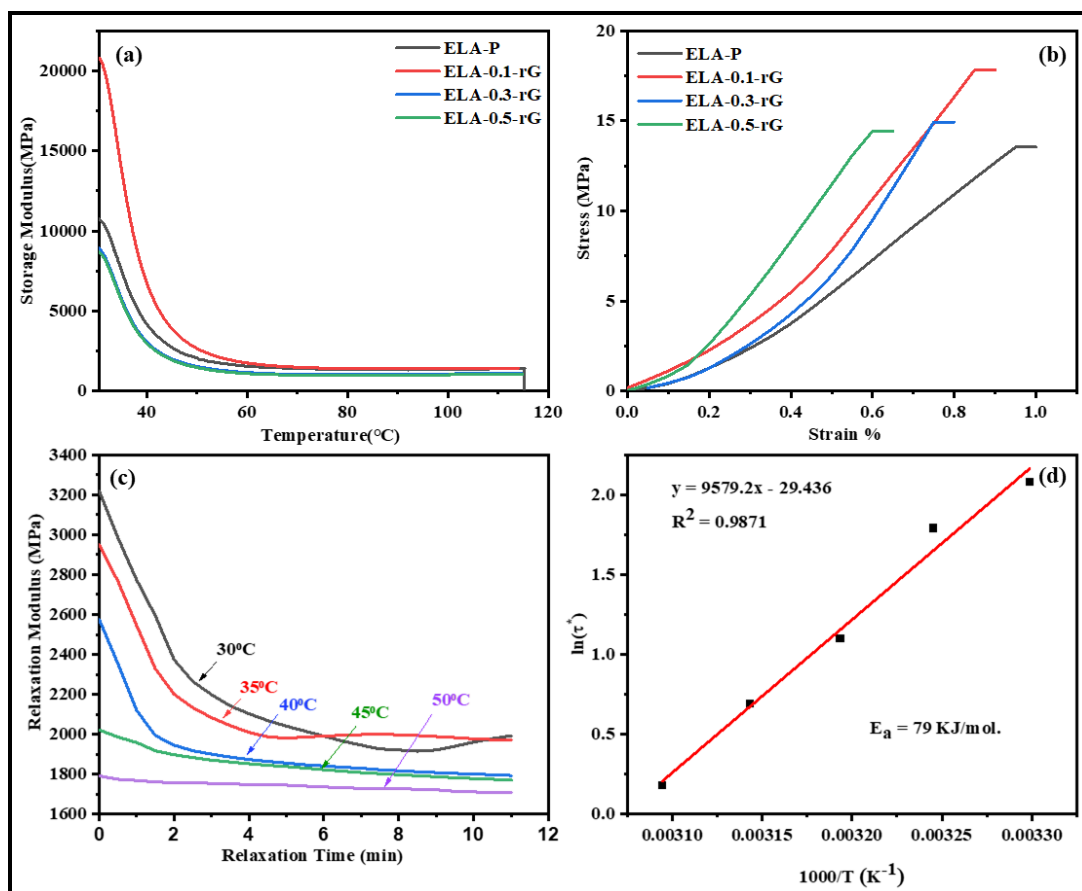


Figure 3.3. (a) Storage modulus of Vitrimer composites of different rGO concentrations.

(b) Stress-strain curves for vitrimer composites (c) Relaxation modulus of ELA-0.1-rG at 30°C, 35°C, 40°C, and 45°C. (d) Arrhenius graph plot for ELA-0.1-rG vitrimer

The incorporation of rGO enhanced the modulus value of the matrix until it started to agglomerate due to interfacial topology, but it still resisted deformation under applied load (Jenkins et al., 2019). The flexural stress-strain relation of bio-vitrimers of different compositions was analyzed at the respective T_g temperature of each sample using a 3-point bending test in TMA with force ramp mode (Figure 3.3(b)). The highest flexural strength of 15.9 MPa with flexural strain 0.9% was obtained for the 0.1% rGO concentration in vitrimer composite (ELA-0.1-rG) as compared to the pristine sample with 13.9MPa. However, with a further increase in filler concentration, the flexural strength deteriorated to 15.0 MPa with 0.5% filler incorporation. This indicates the depletion in

the strain at break, which signifies the stiffness augmentation in the composite with the increase in filler concentration (Figure 3.3(b)).

The dynamic properties of disulfide exchange reactions in bio-composite networks are determined by relaxation modulus (Figure 3.3(c)). The relaxation modulus was plotted with comparatively best thermal-mechanical properties obtained for ELA-0.1-rG at 30°C, 35°C, 40°C, and 45°C set of temperatures to observe relaxation time for each. The viscoelastic properties of the vitrimer material show a change in the topological behavior of the matrix, which can be assisted by stress relaxation experiment. In the stress relaxation experiment, the external strain of 0.66% was applied on the specimen where stress response was recorded as a function of time at four different temperatures in its T_g range (Rohewal et al., 2024). As reported, at lower temperatures, the matrix shows a slow relaxation rate with τ^* of 8 min, however as the temperature increases the matrix shows a fast relaxation rate with τ^* of 2 min with classic vitrimer topological behavior. The relaxation time was determined using Maxwell's model for viscoelastic fluid, which states that it is the time required to relax the initial stress up to 63% for each test. The activation energy (E_a) was determined using the Arrhenius equation, which is given below (Ruiz de Luzuriaga et al., 2022).

$$\tau(T) = \tau_0 \exp\left(\frac{E_a}{RT}\right) \quad (1)$$

As calculated from the Arrhenius equation, E_a value 78 KJ/mol was obtained (Figure 3.3(d)) (Krishnakumar, Prasanna Sanka, et al., 2020b).

3.3.2. Self-healing and shape memory

The self-healing properties ELA vitrimer samples were studied using both conventional thermal methods and microwave radiation. Both methods demonstrated significant self-healing. To study the self-healing behavior, the matrix was coated on a glass slide and scratched with a blade. The samples were then observed using an optical microscope at 50x magnification. When the vitrimer-coated samples were exposed to microwave radiation, all the samples were found to be healed completely within 2 minutes, whereas healing via thermal stimuli took 10 minutes at 80°C. It was observed that ELA-coated samples were self-healed even without the incorporation of rGO. However, the efficiency of healing in samples containing rGO in the matrix was enhanced and quicker as compared to ELA-P (Figure 3.4. (a) and Table A2). The healing properties in the matrix

are due to the disulfide dynamic bond exchange reaction. The amine group at the para position of the sulfide group enhances the associative bond exchange reaction due to neighboring group participation. The amine functional group, being an electron-donating group, provides stabilization to the sulfenyl radical, and hence promotes the terminal bond exchange, facilitating the self-healing process in the network (Ruiz de Luzuriaga et al., 2022). The thermos-mechanical properties of healed ELA-0.1-rG composites were studied in terms of stress-strain curves up to 2 healing cycles. Where the flexural strength shown after the first healing cycle is 15.8 MPa and 12.35 after 2nd healing cycle with 0.9% strain (Figure S6). The cured vitrimer samples demonstrate excellent shape memory (100% recovery; as calculated in supporting information) within 1 minute at 80°C (Figure 3.4(b)) (J. Chen et al., 2024). The linseed oil-based vitrimer sample has also demonstrated self-adhering properties. The samples were cut into two pieces and placed together with the help of tweezers, and allowed to bind at 80-90°C within 20 min. However, in presence of microwave radiation, composite specimens took 7-10 min to repair themselves completely (Figure 3.4(c)). The samples were able to bind themselves with highly efficient adhering properties and withstand the weight of 200g, which is 200 times more than the weight of the sample itself (J. H. Xu et al., 2021).

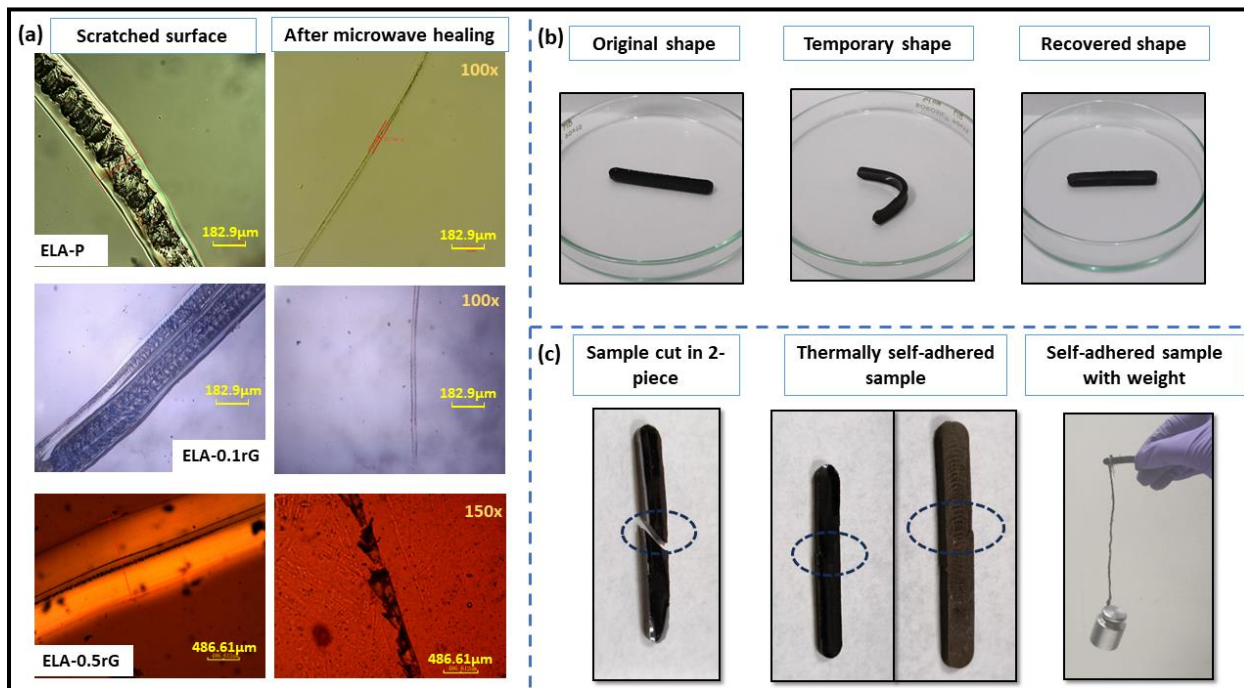


Figure 3.4. (a) Microscopic images of the scratched and microwave-healed coatings for ELA-P, ELA-0.1-rG, ELA-0.5-rG (b) Optical images of shape memory properties of the vitrimer sample.

(c) self-adhering properties of vitrimer composite as it is cut into pieces and thermally repaired which can uplift the 200g of weight.

3.3.3. Hydrophobic property of vitrimer coating

The hydrophobic nature of ELA vitrimer composites was evaluated using a contact angle analyzer. Two mediums were used: deionized water and salt water, as the prepared coating could potentially be applied on offshore facilities. The vitrimer coating displayed excellent hydrophobic properties in DI water, with a contact angle of 102.8° observed on the coated surface without the incorporation of carbonaceous fillers (Figure 3.5(a)). As the percentage of rGO in the network system increased, the contact angle gradually elevated up to 109.3°. Further, the study of DI water contact angle has been studied in detail with respect to time up to 600 sec, which reports the gradual reduction in rate of decrease in contact angle with time as well as with incorporation of filler (Figure 3.5(a) and supporting information: Figure A7). The bio epoxy backbone and AFD-based crosslinking present in the matrix contribute to its hydrophobic character. The introduction of reduced graphene oxide (rGO) increases the roughness of the surface, providing enhanced hydrophobicity to the matrix, as observed in the AFM images in (Figure A9(a)).(Berendjchi et al., 2016). AFM is a technique that explains the surface topology of a material. The dark regions on the surface represent valleys, while the bright regions represent hills. To determine the surface roughness, nanosurf software calculates the root mean square (RMS) and arithmetic average. It is known that roughness and contact angle are directly related, meaning that the higher the roughness, the greater the contact angle and the more hydrophobic the surface. According to the Wenzel theory, surface wettability and surface roughness are interconnected factors. In vitrimer coating, ELA-0.1-rG has shown a roughness of 37.37nm, which is higher compared to other compositions, as presented in Table 3.4. The increased filler content in the matrix contributes to the higher roughness, and consequently, improved hydrophobicity and hence corrosion inhibition (Khun & Frankel, 2013; Valadez-Martínez et al., 2023).

It has been observed that the contact angle with salt water is higher and more stable than that with DI water. This is because of the charge balancing ions present on the surface and the presence of salts in water which form an ion hydration cell. This weakens the interaction of water with the surface, thereby enhancing the hydrophobicity (Figure 3.5(b, c))(Meng et al., 2022; P. Singh, Umamaheshwara, et al., 2024). The highest contact angle recorded in the presence of salt water is

131.3° (as shown in Table 3.5) (Figure 3.5 (b, c)) and supporting information: Figure A8). However, a further increase in rGO concentration creates opposite effect on contact angle because of agglomeration and considerable decrease in roughness of coating surface. The higher concentration of filler leads towards stacking and overlapping of the sheet and hence gradually decreases the hydrophobicity (Chau et al., 2009; Swain & Bahadur, 2014). Contact angle and roughness are correlated with each other as hydrophobicity increases with the increase in surface roughness, stated as Lotus' effect (Figure A9 (a, b)) (Zheng & Lü, 2014). Therefore, the filler concentration causing a change in surface topology due to the formation of labyrinth structures exhibits variation in surface roughness and hence the contact angle. Subsequently, an increase in filler concentration results in agglomeration of the same which causes a gradual decrease in roughness as well as contact angle (Figure A9) (Drelich & Miller, 1994; Hooda et al., 2017).

Table 3.2. Average arithmetical and RMS values of the roughness obtained for various vitrimer composite surfaces from AFM

S. No.	Samples	R _a (nm)	R _{RMS} (nm)
1.	ELA-P	1.8	3.8
2.	ELA-0.1-rG	30.3	37.3
3.	ELA-0.3-rG	2.3	3.3
4.	ELA-0.5-rG	1.6	2.4

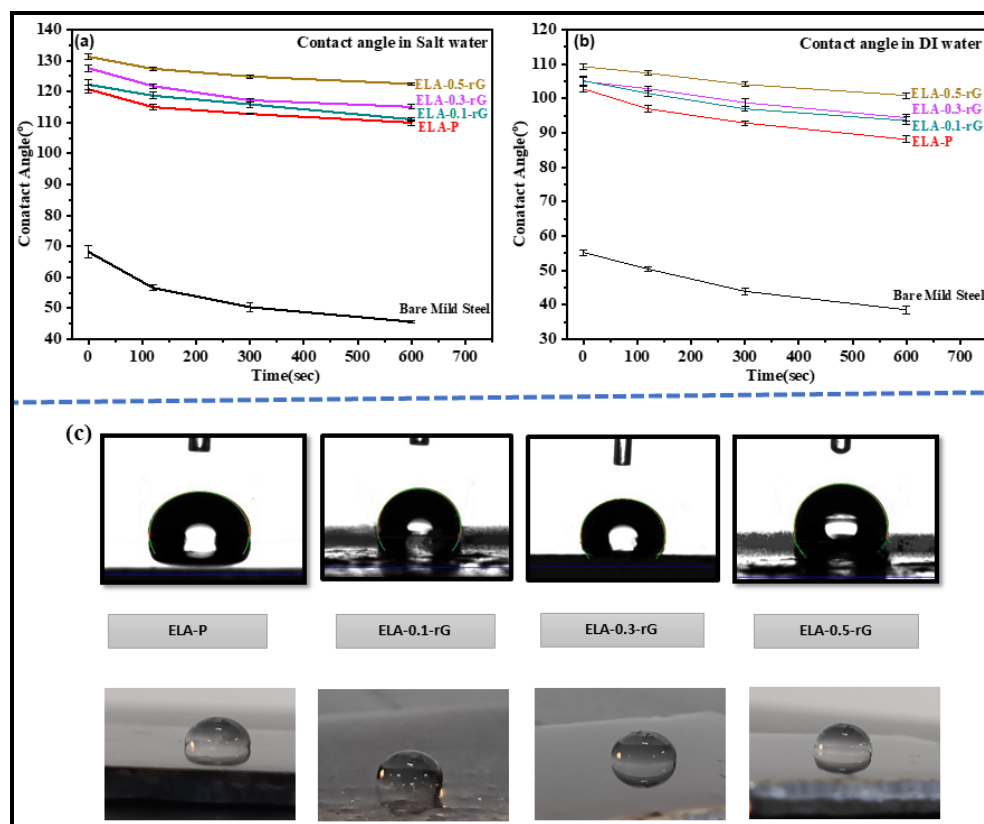


Figure 3.5. (a) Graphical representation of contact angle study using DI water with respect to time. (b) Graphical representation of contact angle study using salt water with respect to time
(c)Optical images of the droplets on the surface of vitrimer coating using DSA instrument
(Upper) and actual images of the droplet on coating (Lower).

Table 3.3. Contact angles DI water at coated substrate and salted water with respect to time.

S.No.	Samples	DI water contact angle (°)				3.5% Salt water contact angle (°)			
		0 Sec	120 Sec	350 Sec	600 Sec	0 Sec	120 Sec	350 Sec	600 Sec
1.	Mild steel	55.2±0.8	50.4±0.7	43.9±0.9	38.5±1.1	68.2±2	56.6±0.8	50.3±1.3	45.6±0.3
2.	ELA-P	102.8±0.8	97.0±0.9	92.9±0.6	88.1±1.0	120.8±1.2	115.0±0.9	112.8±0.8	110.0±1.1
		8				2	9	6	0
3.	ELA-0.1-rG	109.3±0.8	107.4±0.9	104.1±0.9	100.9±0.9	131.3±0.9	127.4±0.9	124.9±0.9	122.5±0.9
		7	6	6	8	9	6	5	4
4.	ELA-0.3-rG	105±1.2	102.9±0.9	98.8±1.1	95.4±0.9	127.6±1.1	121.6±0.9	117.2±0.9	115.1±0.9
			8			1	7	6	8

5.	ELA-0.5- rG	105.2±1. 4	101.5±0. 9	97±0.7	93.6±1.0	122.3±1. 6	118.7±1. 1	115.9±0. 9	111.0±0. 6
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3.3.4. Corrosion studies:

The effectiveness of a self-healing coating made from linseed oil in inhibiting corrosion was studied using a Tafel polarization test on an electrochemical workstation. The coating was applied to mild steel SS-216 substrate, with and without reduced graphene oxide.

The study immersed the coated substrate in 3.5% NaCl electrolytes for 1 hour before conducting electrochemical tests using a three-electrode flat corrosion cell, consisting of an Ag/AgCl/KCl reference electrode and a mesh platinum counter electrode. Optical images of the substrate surface were taken before and after corrosion immersion. The potentiodynamic polarization plot of the sample data is presented in (Figure 3.6 (a)). The corrosion current density (I_{corr}) for coated samples reduced from -4.53A to -8.73A compared to bare samples. The corrosion potential (E_{corr}) gradually shifted towards cathodic reaction area with -1.68V. The slope of the anodic reaction curve also gradually increased with the addition of rGO incorporation, signifying considerable protection of the coating against corrosive species present in the electrolyte. The resistance potential (R_p), as calculated from the Stern-Gary equation (Equation 3.2), showed a significant increase from bare samples to coated samples(Nematollahi et al., 2010).

$$R_p = \frac{\beta_a \times \beta_c}{2.303 \times I_{corr} (\beta_a + \beta_c)} \quad (3.2)$$

Where R_p is measured in $M\Omega cm^2$ and I_{corr} in A/cm^2 , R_p values further get increased due to incorporation of rGO in to the system upto 0.1% concentration with $7.8 \times 10^8 M\Omega cm^2$, however it starts dropping for 0.3% and 0.5% compositions with $1.88 \times 10^8 M\Omega cm^2$ and $7.76 \times 10^6 M\Omega cm^2$ respectively. Further, the shift of E_{corr} towards the cathodic range imply the cathodic inhibition of the coating regardless of values first increases and then shows slight decrease due to agglomeration between rGO nanosheets(Dobruchowska et al., 2019). The results from tafel plot fitting are listed in Table 4. Corrosion rate (P_i) of coated samples can be explained by the Fraday's law as shown in equation (3)(X. Li et al., 2023).

$$P_i = 2.285 \times 10^4 \cdot I_{corr} \quad (3)$$

Where P_i is measured in mm/y, lowest P_i was obtained for ELA-0.1-rGO vitrimer composite with 0.41×10^{-4} mm/y whereas bare sample showed degradation with 0.66 mm/y. Along with that corrosion protection efficiency (PE%) of the coating system was calculated using equation(4) as stated below(Ding et al., 2019).

$$PE\% = \frac{R_p^{-1}(Bare) - R_p^{-1}(Coated)}{R_p^{-1}(Coated)} \times 100 \quad (4)$$

Where R_p^{-1} (bare and coated) is inverse of resistance potential for bare and coated samples respectively.

The purpose of using epoxy matrix here in protective film is to provide barrier against corrosive species and to minimize the penetration of electrolyte through network. The AFD as crosslinking agent provide disulfide bonds to facilitate the reversible dynamic covalent bond exchange reaction for healing process under condition of any mechanical damage in case coating get fatigue. In addition, this microwave assisted sustainable coating could reverse the damage and regain its original strength and properties and hence reduce the maintenance cost and thus maintains the long work life. Whereas amine group connected with it works as corrosion inhibiting moiety, decreasing the ionic penetration possibilities. The passive region in tafel plot, which is due to decrease in cathodic slop(β_c) as compared to anodic slop(β_a) (Figure 3.6 (a)) is due to the formation of oxidative layer (Cathodic protection effect), which isolates the coating from further deformation and act as addition shielding layer between corrosive ions and substrate(Q. Liu et al., 2016, 2019). Incorporating rGO as a filler can increase resistance against electrolyte, elongating the penetration pathway for diffusion ions. This synergistic effect improves the corrosion inhibition properties due to the formation of complex labyrinth structures inside the coating network. These structures reduce the conductivity of corrosive ions by creating a compact surface (X. Li et al., 2023). However, when the concentration of filler is increased beyond a certain point, it tends to agglomerate due to its large specific surface area. As a result, it becomes difficult to disperse the rGO. This can accelerate the corrosion rate instead of inhibiting it, as it promotes electrochemical reaction in the matrix system.(H. Li et al., 2021). Therefore, the developed coating would exhibit a significant impact as anti-corrosive coating in marine structures. As observed, the coatings are hydrophobic in nature against salt water and shows appreciable inhibition against marine corrosion (NaCl-3.5%). However, the capability of the coating composite to be healed in the presence of

microwave as well as thermal conditions makes them promising for any damage to occurs in harsh environmental conditions.

The morphology of the coated surface was also analysed before and after corrosion process *via* SEM micrograph images to understand the role of incorporated nano-fillers. Figure A10 (a) demonstrate the morphology of the surface before corrosion, where ELA-P shows no presence of nano-filler whereas ELA-0.1-rG display uniform dispersion of nano-filler in 50 μ m as well as at 20 μ m magnification, further, in ELA-0.5-rG coating, agglomeration of nano-filler can be observed at 50 μ m as and at 20 μ m magnification as marked with red circle (Figure A10). In SEM micrograph of the coatings after corrosion testing (Figure A10 (b)), ELA-P coatings shows greater damage on the surface as compared to rGO incorporated composites. In ELA-0.1-rG, it is observed that the surface was not much disturbed after NaCl electrolyte immersion and hence coating is well protected and provides barrier against penetration of corrosive ions, whereas in ELA-0.5-rG, the damage as well as deposition of corrosion product was observed on the coating surface, which supposed to protect the substrate from further propagation of corrosion and electrolyte penetration(Q. Liu et al., 2019). (Supporting information, Figure A10)

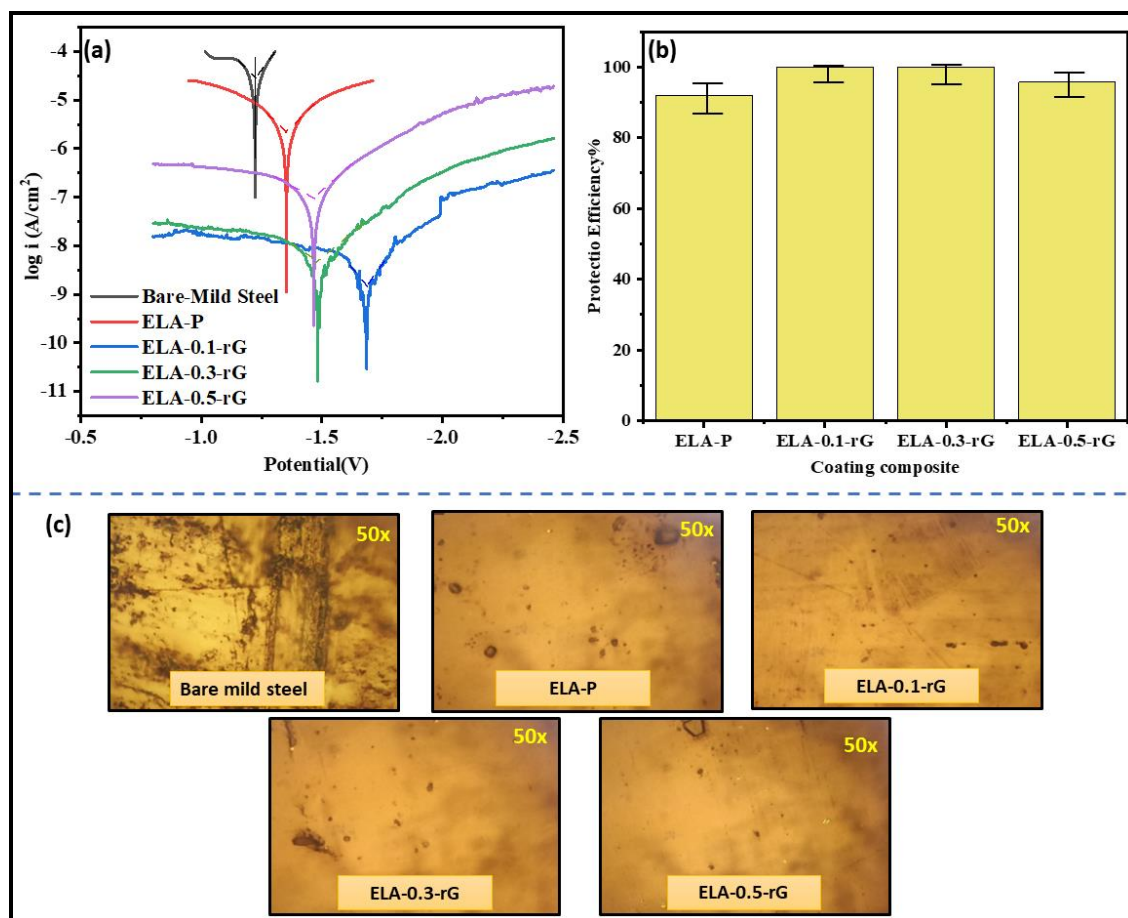


Figure 3.6: (a) Tafel plot of bare mild steel and various compositions of ELA (b) Bar chart representing protection efficiency of various compositions of ELA (c) Microscopic images of the surface of the substrate after corrosion testing.

3.3.5. Mechanism of self-healing and anti-corrosive properties:

Corrosive agents in the environment, such as water, oxygen, and various electrolytes (Cl^- , Na^+), can cause corrosion on the surface of mild steel. This results in weaker mechanical properties as it is converted into an oxidizing form. Over time, electrolytes can diffuse through coating materials *via* cracks and pores that appear when the coating quality deteriorates. This can cause corrosion and debonding of the coating from the surface. ELA Self-healable coating has dynamic di-sulfide reversibility, providing long-term protection against corrosion through active and passive functional feasibility. The disulfide bond exchange said to be occurred via [2+2] metathesis or [2+1] radical- mediated mechanism. In [2+2] metathesis disulfide bond makes and break simultaneously, whereas in [2+1] radical mechanism, homolytic breaking of disulfide bond would

lead to the formation of sulfenyl radical that further attacks other disulfide bonds *via* three membered transition state. In case of 4-AFD crosslinked matrices, the exchange reaction follows [2+1] radical mechanism (Figure 3.7)(Nevejans et al., 2016). In this mechanism the low bond energy disulfide bonds get homolytic cleavages due to the similar neighboring group participation (NGP) on both side of the bond and thus forms sulfenyl radicals which leads to chain radical reactions(Ruiz de Luzuriaga et al., 2022). The cleavage of these bonds results in increase in viscoelasticity of the matrix and provide mobility, hence allow the matrix to flow enough to mend the damage without losing the integrity of the original properties and shape. Further these radicals keep on reforming the bonds at random terminals making them dynamic in nature(Beaupre & Weiss, 2021; Nevejans et al., 2016). The pictorial images shows the healing progress with time indicating the rate of healing for ELA-0.3 rG coating in the presence of microwave radiation (Table A2).

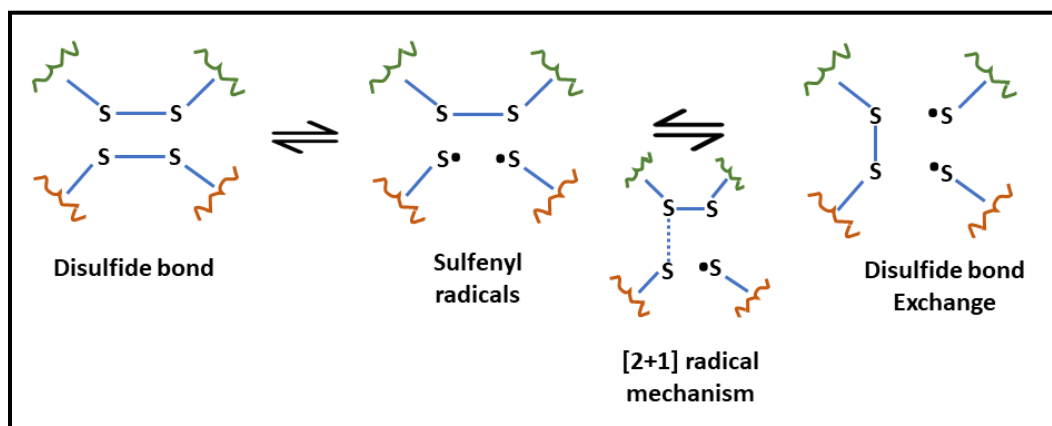


Figure 3.7: Illustration demonstrating mechanism of disulfide bond exchange reaction

The rGO incorporated vitrimer composites display reversible bond exchange reaction upon interaction with microwave radiation due to localized heating which leads to rapid healing process as compared to pristine samples(P. Singh, Umamaheshwara, et al., 2024). The incorporation of carbonaceous materials like rGO, CNT, and MXene are known to respond to electromagnetic fields because of their appreciable electrical properties as impedance of the composite will allow the radiation to be dissipated as heat, thus, provides much rapid heating temperature in composite, requires for healing purpose. As explained in modern theory of polarization, interaction of homogenous matter and EM field results in dipole, electronic and ionic polarization and these

mechanisms results in heat dissipation due to molecular and electronic collision(Vashisth et al., 2020). The presence of carbonaceous filler contributes to thermal conductivity of the composite and hence microwave radiation activates localized heating, which increases viscoelasticity of the matrix causing a disulfide bond exchange reaction and therefore self-repairability time get reduced to 1-2 min as compared to thermal healing (convention oven heating) which takes 5-10 min in healing process(Jia et al., 2022; P. Singh et al., 2023; Solouki Bonab et al., 2019).

The addition of rGO to the coating creates a more difficult path for ions to reach the surface, but the labyrinth effect enhances the passive protection of the coating even more. This reduces the corrosion rate to 0.41×10^{-4} mm/y and increases the corrosion protection efficiency to 99.99% (Figure 3.6 (b) and Table 3.6). However, the Tafel plot (Figure 3.6 (a)) shows positive corrosion potential for uncoated substrate as compared to vitrimer-coated substrate which is possibly due to the cathodic protection effect generated by the lower potential in three possible ways: thermodynamic effect, kinetic effect, and chemical effect. In thermodynamic effect metal potential has no tendency to form a corrosion product, where driving voltage is negative or zero which lowers the corrosion rate, whereas, in kinetic effect, lowering of potential can lead towards condition of passivity, therefore passivity protection system is established. Further in case of chemical effect- where the cathodic reaction at the metal-electrolyte interface produces alkalinity, this effect is most favorable for mild steel and favors the precipitation of a protective layer and passive conditions(Bai et al., 2022; Brenna et al., 2017). Moreover, the incorporation of rGO as filler enhances the corrosion inhibition by introducing labyrinth structures in epoxy matrix, which creates effective barrier for invasion of corrosive ions. This synergistic effect of cathodic protection and labyrinth effect provides eminent improvement in corrosion protection(Bai et al., 2022). However, the increase in concentration of the filler in the matrix leads towards the agglomeration which eventually affect the workability of the coating in terms of mechanical strength, decrease in corrosion inhibition efficiency as well as long term workability. The addition of rGO base nanofiller caused the enhancement of protection barrier against the corrosive ion, but, the further increment resulted in the agglomeration and hence decrease in barrier quality. The agglomeration has been identified using the optical microscopic images with 20x magnification, which has been explained with illustration demonstrating the effect of agglomeration on coating efficiency (Figure 3.8). The poor dispersity led to the defects in matrix and hence produce points of defects and stresses. The defects in the matrix create voids allow the ions and external environment to interact

with substrate and hence promotes the corrosion (Tamayo-Vegas et al., 2022). In the similar way with these clusters of defects, mechanical strength of the material also gets compromised with increasing agglomeration and voids, as discussed earlier in Section 3.3.2 (Figure 3.3). These facts conclude that the optimum concentration of rGO up to 0.1% results in shows excellent corrosion barrier as well as mechanical strength of the coating (Tamayo-Vegas et al., 2022) (Herren et al., 2020).

Additionally, the coating surface is highly hydrophobic, which is very beneficial in protecting it from water and hence, corrosion (Figure 3.9). To visually examine the effect of corrosion on the surface, optical images of the coated sample were taken at 100X magnification using a Nikon ECLIPSE microscope MA200. It was evident from the optical images that the damage on the coating surface was minimized compared to the damage on the bare sample (Figure 3.6 (c)).

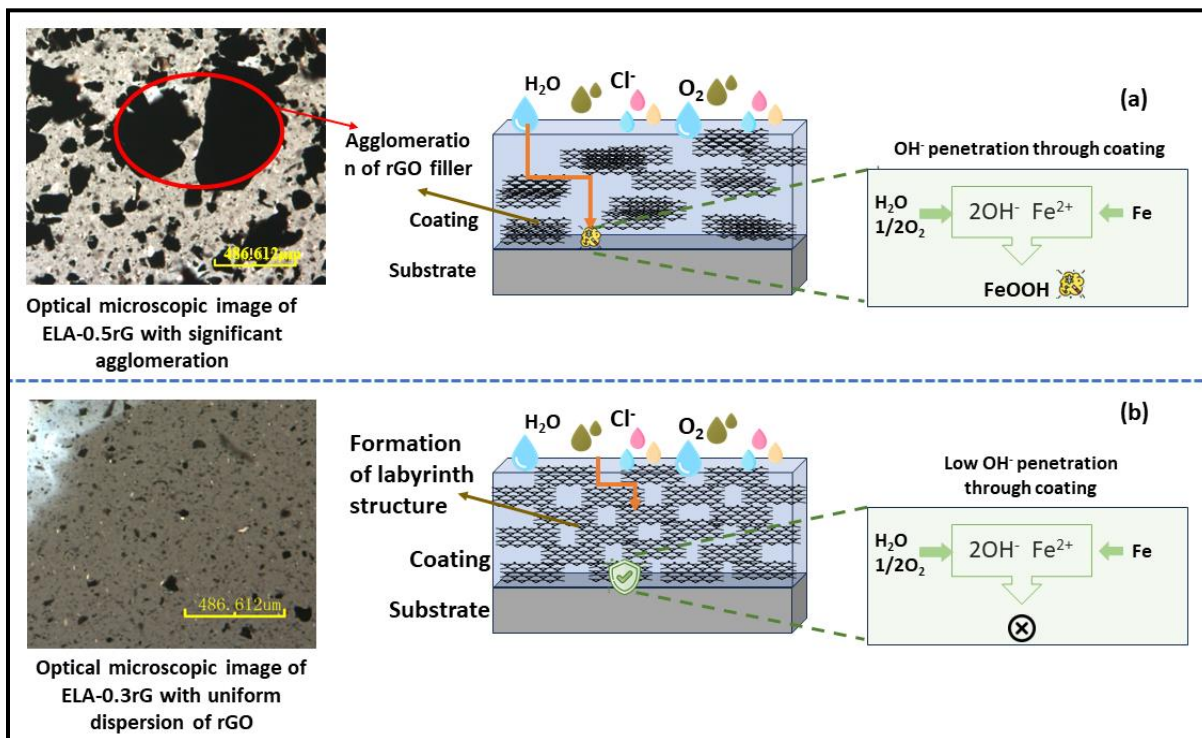


Figure 3.8: (a) Mechanism explaining the effect of agglomeration on the corrosion inhibition efficiency with the support of optical microscopic images (b) Mechanism of formation of labyrinth structure promoting the inhibition properties with well-dispersed rGO filler optical microscopic images.

Table 3.4. Electrochemical parameters and potentiodynamic polarization measurements for bio-vitrimer coatings

S.No.	Sample	E_{corr} (V)	I_{corr} (A/cm ²)	β_c (V/dec)	β_a (V/dec)	R_p (M Ω cm ²)	P_i (mm/y)	PE %
1.	Mild steel	-1.22	-4.53	7.31	5.92	4.90×10^4	0.66	-
2.	ELA-P	-1.35	-5.63	5.10	4.59	4.54×10^5	0.0528	91.9%
3.	ELA-0.1-rG	-1.68	-8.73	8.81	5.33	7.87×10^8	0.41×10^{-4}	99.9%
4.	ELA-0.3-rG	-1.48	-8.33	4.65	2.95	1.88×10^8	1.04×10^{-4}	99.8%
5.	ELA-0.5-rG	-1.46	-7.00	4.54	3.47	7.76×10^8	2.28×10^{-3}	95.6%

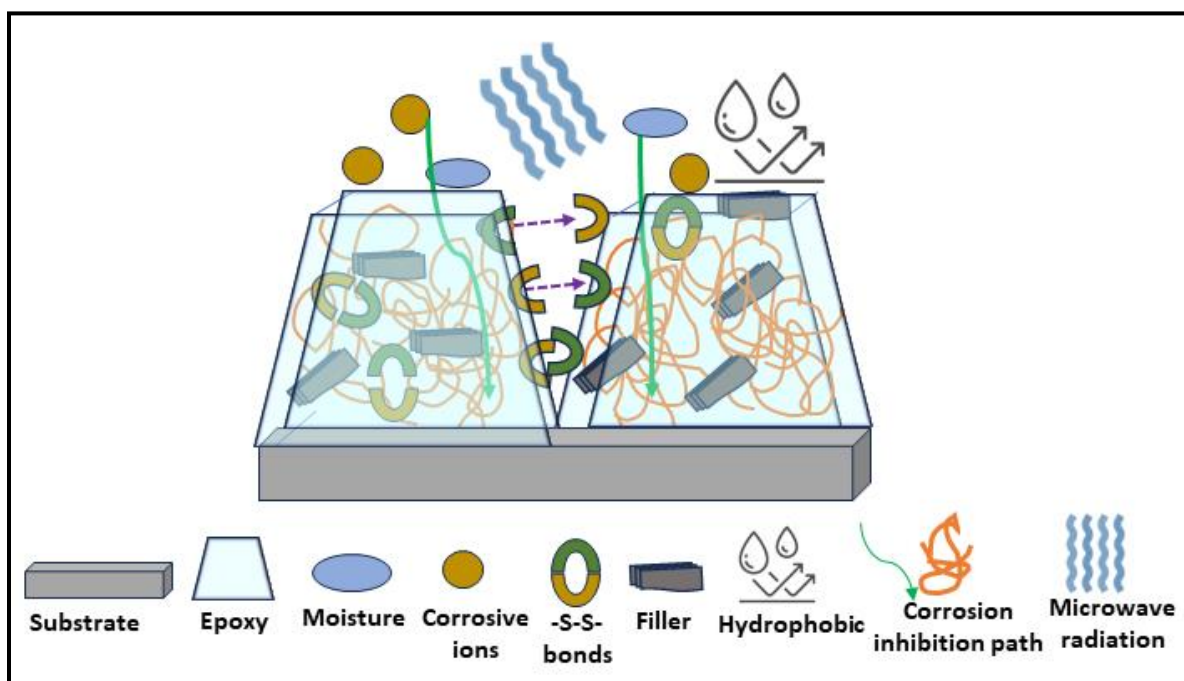


Figure 3.9. Schematic representation of self-healing protection mechanism of vitrimer composite coating against corrosion.

3.4. CONCLUSION:

In this study, a new hydrophobic self-healing coating, triggered by microwave, has been created to protect mild steel from corrosion and weathering. The bio-epoxy/rGO-based coating provides a 99.9% corrosion efficiency, reliable hydrophobicity, and radiation-assisted self-healing to facilitate long-term sustainable coating service. The dynamic disulfide metathesis and high crosslinked epoxy network facilitate the protection mechanism. The coating has a storage modulus of 20.8 GPa, 100% shape memory, and excellent self-adhesive ability that ensures the reparation of damage. The coating's corrosion protection has been measured through a Tafel plot in 3.5% NaCl, where a corrosion rate of 0.41×10^{-4} mm/y was recorded due to corrosion inhibition caused by amine-based bio-epoxy/rGO framework synergistic effect. Being derived from bio-based resources makes these coatings a competitive candidate holding the sustainability development goals as well as promising mechanical and thermal properties. The combination of characteristic properties like microwave stimuli self-healing, hydrophobicity, and anti-corrosion makes this composite coating an eminently promising alternative to petroleum-derived coatings for off-shore applications.

CHAPTER 4

Comparative Study of Ortho and Para Position of Amine In Microwave Assisted Self-Repairable Vitrimeric Coating For Anti-Corrosive Applications

Abstract

Vitrimeric coatings are revolutionary and most widely emerging materials for metal corrosion inhibition. As harsh environmental conditions damage polymer-derived protective films and results into micro cracks and corroded metal surfaces. In this work, an active microwave-responsive vitrimeric epoxy coating embedded with weathering-resistant properties is introduced along with a systematic comparative study for the effect of ortho and para position of amine in hardening agent. The developed microwave radiation responsive coating system felicitates self-healing due to the disulfide exchange mechanism and corrosion inhibition properties in marine environments. Compared to conventional coatings, prepared graphene oxide (GO) incorporated vitrimeric network showed more promising protection against corrosion in offshore applications with 95.4% protection efficiency and hydrophobicity with a 96-degree contact angle. This study covers the self-healing properties, thermal mechanical study, hydrophobicity measurement, and thorough corrosion examination of synthesized material coated on 304 grade SS substrate. The coating reports excellent self-healing efficiency, reliable mechanical strength (storage modulus-129GPa and loss modulus-83GPa), fast stress relaxation and low activation energy(63KJ/mol) for dynamic disulfide exchange reaction, furthermore, low corrosion rate of 1.20×10^{-3} mm/y was observed for the coating. Thus, demonstrates its importance for self-healable anti-corrosive application for the marine environment.

4.1. Introduction:

Polymeric coatings on metal surfaces are one of the majorly used surface protecting techniques for corrosion prevention (Y. Zhang et al., 2022). Corrosion is a major destructing phenomenon, causes micro cracks, and thermal instability thus, deteriorating the mechanical strength of the metal structure, which results in dangerous accidents and loss of major assets and lives(Peñas-Caballero

et al., 2023)(Amendola et al., 2023). Theoretically, corrosion is the conversion of metal into a more stable metal oxide form in the presence of moisture and air. This conversion keeps on increasing and start discrediting the metal structure(Pedefferri (Deceased), 2018). Polymer-based organic coatings create a barrier between the substrate and external environment (J. Wang et al., 2023). Subsequently, Polymeric coatings interact with sun radiations or any mechanical scratches while its assistance, which leads to free-radical formation and hence, systematic degradation of polymeric coatings occurs(J. Wang et al., 2023)(P. Singh et al., 2023). However, thermosetting polymers were of great use due to their unreplaceable properties like high mechanical properties, chemical resistance due to high crosslinking, but these set of polymers cannot be reshaped or reprocessed like thermoplastics, which in turn increase the environmental and waste management issues. To cease the destruction on the surface of metal substrate, self-healable polymeric coatings are most emerging solutions of the century(Cho et al., 2009). The self-healing mechanism in the matrix can be explained in terms of intrinsic and extrinsic properties(Safdari et al., 2021). In extrinsic mechanism, external healing agent collaboration is needed for the healing, e.g. microcapsules or vascular matrices(Amendola et al., 2023), whereas intrinsic matrices are functional without any external material(Sanka et al., 2019)(Rana et al., n.d.). In addition, the intrinsic polymeric network go through an internal molecular exchange reaction and restore its original dignity even after damage (Pulikkalparambil et al., 2018)(Safdari et al., 2021)(Nia et al., 2014)(Guadagno et al., 2021). To reap the best of both thermosetting and thermoplastic polymers, a new class of polymers named ‘vitrimers’ was introduced by Ludwick Labler and co-workers (Guadagno et al., 2019b)(Guadagno et al., 2021)(T. Song et al., 2021)(Guadagno et al., 2019a)[17](Winne et al., 2019)(Krishnakumar, Sanka, et al., 2020). In spite of many advantages, vitrimeric networks have one limitation as it requires external stimuli to be functional, which in the case of many applications is not easy to provide. The quoted disadvantage can be addressed by designing a coating system that can interact with various range of radiations with localized heating effects. (Electromagnetic radiation, UV radiation, IR radiation, microwave radiation, etc.)(Vashisth et al., 2021)(Gruener et al., 2020)(Vashisth et al., 2020). In this reported work, microwave radiation was used to provide required heating temperature to heal the matrix instead of conventional heating methods.

The coating system responsive towards external stimuli is to be counted under an embodiment of active properties in passive matrices(Pulikkalparambil et al., 2018)(Andreeva & Shchukin,

2008)(Grigoriev et al., 2017). However, Corrosion protective coatings can be functional either by creating a barrier between the substrate and environment or *via* corrosion inhibition reaction (Peñas-Caballero et al., 2023). Self-healing vitrimeric coatings seal the surface of the metal and recover it even after any possible damage via dynamic bond exchange reactions like transesterification reaction, Schiff base exchange reaction, Diels alder reaction and disulfide exchange reaction, etc.(Krishnakumar, Sanka, et al., 2020)(Gogoi et al., 2015)(Chong et al., 2022)(Guadagno et al., 2019b). Eventually, very extensive research has been done to strengthen the corrosion inhibition qualities of the vitrimeric coatings, including incorporation of nano fillers and corrosion inhibiting agents like MXene, carbon dot etc.(Sharma et al., 2023). On the other hand, epoxy coatings are well established corrosion inhibiting networks (Amendola et al., 2023). Previously polymeric coatings provide shielding against corrosion but cannot protect the asset once there is damage on the surface in a highly harsh marine environment(Arukalam et al., 2021).

Disulfide bonds are known for their dynamic bond exchange reaction due to their spontaneity towards cleavage and reformation of bonds under specific conditions, which is again responsible for the repairability and recyclability of the material(Krishnakumar, Singh, et al., 2020)(Park et al., 2020). The current study focuses on the comparative analysis for the corrosion inhibition study of the two matrices based on the para and ortho position of the amine group in 4,4'-diamino-phenyl disulfide and 2,2'-diamino-phenyl disulfides respectively, along with variation in concentration of nanofiller in offshore application. Both the crosslinking agents show similar chemistry of disulfide bond exchange reaction mechanism however the efficiency of these hardening agents is quite different. Studies have shown that the disulfide exchange reaction follows the [2+1] radical mechanism, which is mediated by the S-S bond cleavage and sulfenyl radical formation (Ruiz de Luzuriaga et al., 2022). Furthermore, the study shows the position of the amine group causes differences in the extent of their functionality in corrosion inhibition, thermal stability, and mechanical strength in the system. The study includes microwave radiation to facilitate the self-healing of the coating in multiple cycles, which is much easier to apply during marine applications.

4.2. Experimental Section:

4.2.1. Materials and methods: Epoxy 828 (g/mol), 4,4'-diamino-phenyl disulfide (4-AFD) and 2,2'-diamino-phenyl disulfide (2-AFD) (248.37 g/mol), Diethylenetriamine (DETA) (103.17

g/mol), Ethanol, graphene flakes were used in their original forms. PTFE sheet was used to prepare molds for sample formation.

4.2.2. Preparation of GO-based vitrimeric epoxy nanocomposite:

Graphene oxide was prepared by Modified Hummer's method. In brief graphite flakes were reacted in a 500ml Round bottom flask with sodium nitrate and sulfuric acid at 0°C for 15 min, followed by the addition of potassium permanganate. After 5 hours, the reaction was stopped by adding water and hydrogen peroxide dropwise, and systematically dried GO was used for further process. Different percentages of GO prepared were added to the matrix in concentrations 0.5 % and 1.0% (prepared by dispersing 50 mg GO in 5 ml ethanol and sonicated for 30-40 min). Pristine samples were prepared using DETA, 4-AFD, and 2-AFD with Epone-828 commercial epoxy, followed by curing at room temperature, then at 80°C followed by 120°C and 150°C. DETA was used as a standard hardener to compare the self-healing behavior imposed by 2-AFD and 4-AFD. The epoxy was prepared in two different compositions with 2-AFD-x% and 4-AFD-x% in 1:35.6 weight ratio, EP-AFD-x% (x=0.5 ,1.0) where x is denoted as GO weight percentage. GO was first dispersed in ethanol and mixed with epoxy matrix in given proportion, then the matrix was allowed to mix with constant stirring at 80 °C until ethanol-evaporated. The curing agents (2-AFD and 4-AFD) were added in GO containing epoxy resin and stirred at 80 °C for 15 min, followed by degassing in a vacuum desiccator for 10 min. The metal substrate SS-304 of dimension 2cmX2cmX2mm was sanded by 120 grit sandpaper followed by cleaning using ethanol and coated with developed vitrimeric material using spin coater spinNXG-P2 at 1000 rpm for 60 sec and accelerated to 1200 for 30sec(Foo et al., 2011). The developed coating was cured in cycle at room temperature for 1 hour, then at 80°C for 2 hours followed by precuring at 120°C for 2 hour and curing at 150°C for 5 hours. The systematic compositional details are listed in EP-AFD shown in Table 4.1. The schematic diagram of the above synthesis has been displayed in Figure 4.1.

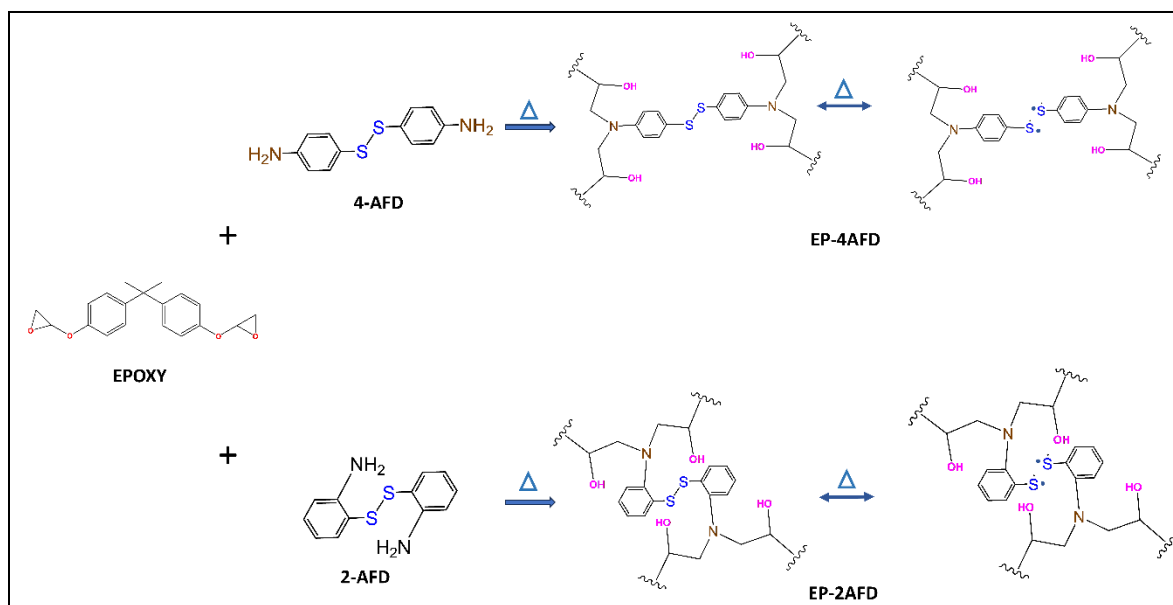


Figure 4.1. Schematic representation of molecular arrangement of epoxy based vitrimer and bond rearrangements in the presence of radiation stimuli.

Table 4.1. Composition details of developed vitrimeric composite coating material

S.NO.	SAMPLE	EXPERIMENTAL COMPOSITION OF EPOXY RESIN			
		<u>DETA</u>	<u>2AFD</u>	<u>4AFD</u>	<u>x%(GO)</u>
1	EP-DETA	1.2%	-	-	-
2	EP-2AFD	-	3.56%	-	-
3	EP-4AFD	-	-	3.56%	-
4	EP-2AFD-0.5	-	3.56%	-	0.5%
5	EP-2AFD-1	-	3.56%	-	1%
6	EP-4AFD-0.5	-	-	3.56%	0.5%
7	EP-4AFD-1	-	-	3.56%	1%

4.3. Result and Discussion:

4.3.1. Compositional Analysis:

FT-IR was done to investigate the conversion of graphene oxide from graphite. The spectrum in Figure 4.2. (A)(a) shows a broad absorption peak due to the stretching vibration of hydroxyl(-OH) group functionality at 3417 cm^{-1} and a very profound peak was observed at 1627 cm^{-1} due to carbonyl group stretching vibration at the surface of graphene oxide. The signal present at 1208 cm^{-1} was known to be corresponding to (C-O) stretching vibration. $1138, 1076$ appear due to epoxy (-COC-) stretching (B. Singh et al., 2023) (Krishnakumar, Prasanna Sanka, et al., 2020b). For vitrimeric composite material, the peak observed in uncured epoxy material at 915 cm^{-1} by oxirane bond, which gets diminished in a cured sample, indicating crosslinking of vitrimer whereas at 3394 cm^{-1} and 1104 cm^{-1} absorption peak appeared due N-H stretching vibration and C-H stretching respectively, further at 715 cm^{-1} peak due to C-S stretching signify successful curing as shown in Figure 4.2(A)(b) (Dang et al., 2005). However, the curing of the epoxy vitrimeric material was also verified with solvent stability test, where cured and uncured samples were sonicated in acetone and no loss of cured material was observed whereas uncured material was observed to be completely dissolved in acetone as shown in Figure 4.2.(B). In Raman spectroscopy analysis of graphene oxide (GO) in Figure 4.2.(A)(d) shows three Raman peaks: D band at 1340 cm^{-1} due to SP^3 hybridized carbon atom vibration, G band observed at 1570 cm^{-1} due to SP^2 hybridized carbon atom vibrational mode with I_D/I_G ratio of 0.31, and further D' band was appeared at 2697 cm^{-1} due to second order scattering of G band caused by multilayer graphene present in lattice. Whereas the XRD pattern of GO in Figure 4.2. (A)(c) shows a peak at 10.8° which significantly verifies the conversion of graphite into graphene oxide (B. Singh et al., 2023).

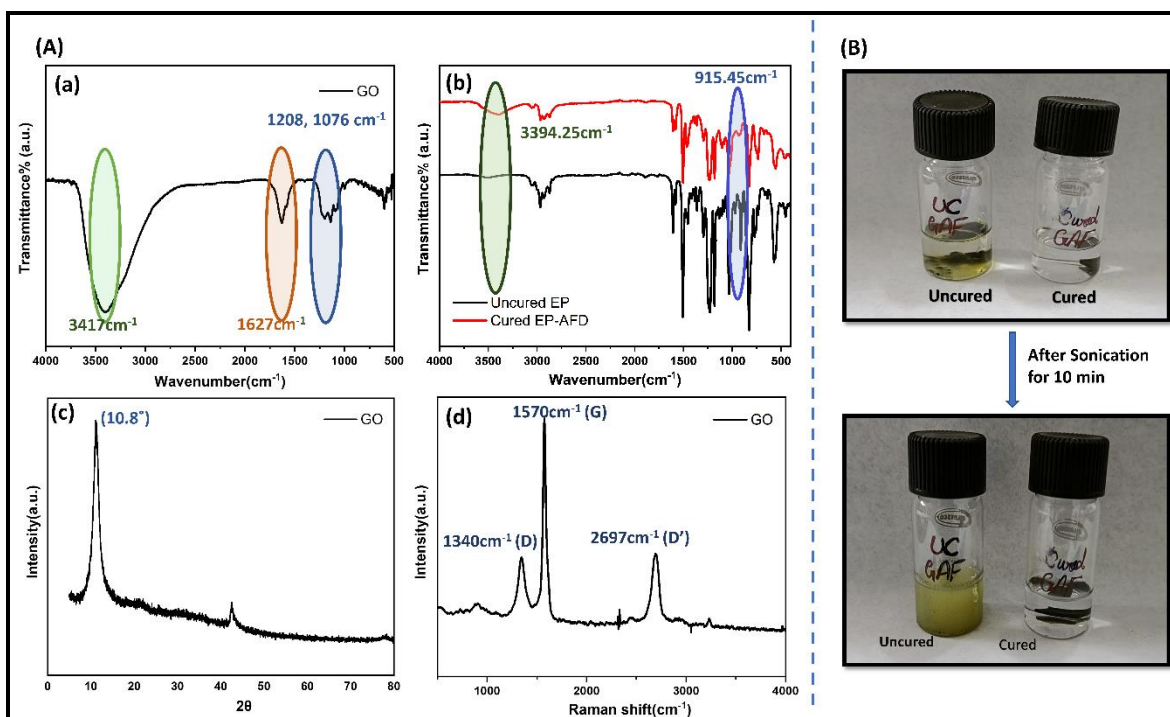


Figure 4.2. (A)(a) FT-IR spectra of GO (b) ATR-FTIR of uncured epoxy and cured vitrimeric sample of EP-AFD (c)XRD spectra of GO, (d) Raman spectra of GO. (B) pictorial representation of stability of cured sample as after sonication as compared to uncured sample.

4.3.2. Thermal and thermomechanical properties of epoxy samples:

The thermal properties of polymeric samples reveal numerous information about the composite. To study thermal properties, the glass transition temperature(T_g) and thermal stability of vitrimeric composites was analyzed using DSC and TGA data respectively for all the samples given in Table 2 and Figure3 a,b. The T_g values of 2-AFD composites were observed to be decreasing with the increase in fillers (GO), which is possibly due to the interfacial interaction between the matrix and filler. With the increase of GO concentration in the matrix, chain mobility between the matrix and filler increases due to degraded interfacial interaction, causing free motion and, in turn a decrease in lower T_g (Krishnakumar, Prasanna Sanka, et al., 2020b). This modification, however helps in attaining the self-healing and shape-memory properties of the composite easily and at lower temperatures. Whereas, in case of 4-AFD based composites the T_g value increases with increase in filler concentration which is due to the poor interfacial interaction of filler and matrix in presence of 4-AFD as well as the agglomeration of nanofiller at higher concentration which hinder the chain mobility(Figure 3(a))(Krishnakumar, Prasanna Sanka, et al.,

2020b)(Krishnakumar, Singh, et al., 2020)(B. Singh et al., 2023). To examine the thermal stability of the vitrimeric composite, TGA was performed on samples with different compositions of matrix and filler. In a study, two-step degradation was observed, which signifies degradation due to epoxy bond and second degradation due to di sulfide bond degradation(Krishnakumar, Prasanna Sanka, et al., 2020b).

In first degradation at $T_{5\%}$, which occurs at 306°C for pristine EP-2AFD and little higher at 308.0 for EP-4AFD. However. Second degradation is observed in the range of 360-380°C described by disulfide bond cleavage. With the increase in filler concentration, thermal stability of the matrix composite increases as GO provides the higher thermal stability to the matrix. As shown in Figure3(b) 50% degradation marked at 374.2°C for 4-AFD whereas 2-AFD composite shows at 378.4°C which is discussed in Table 2. The 4-AFD cured matrices are closely packed and crosslinked structures, which is indicated by above thermal study for 4-AFD and 2AFD cured composites.

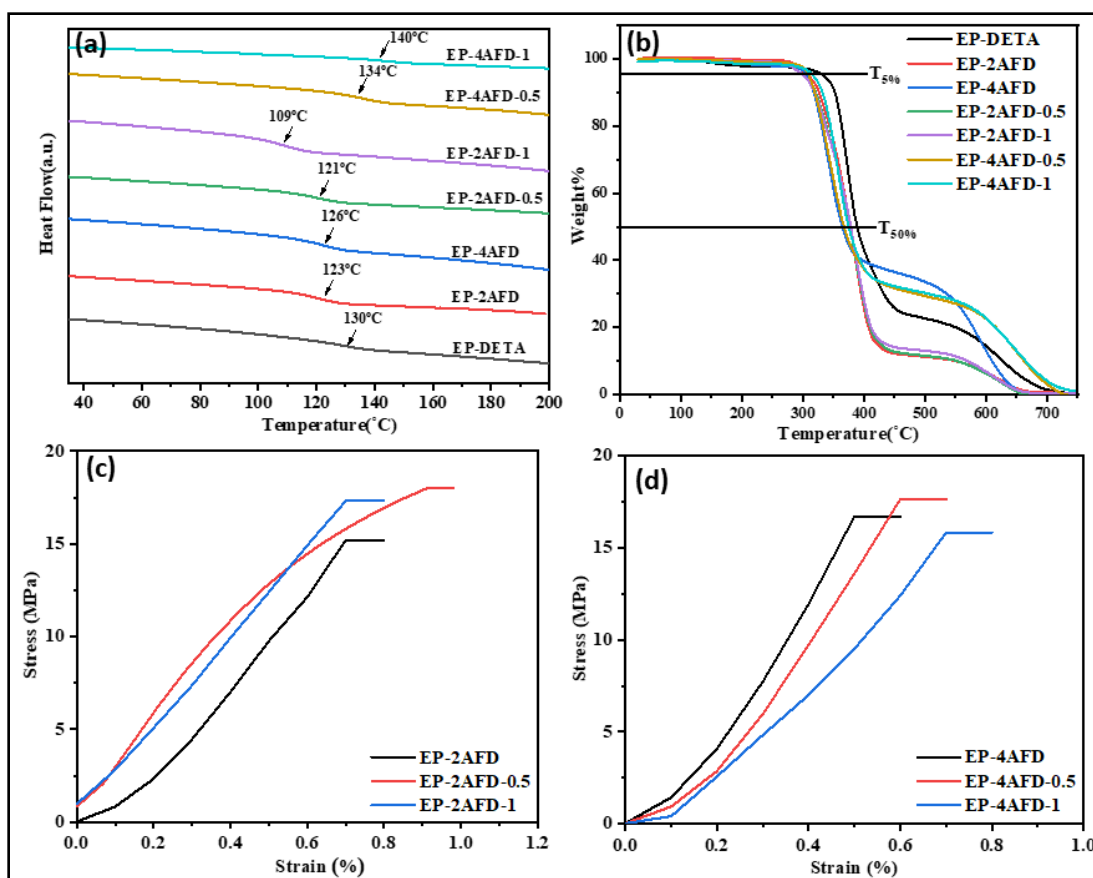


Figure 4.3. (a) DSC curves indicating T_g temperature for each composite of 2-AFD and 4-AFD. (b) TGA study curves of 2-AFD and 4-AFD based vitrimeric composites, (c) Stress vs strain plot of 2AFD vitrimers, and (d) Stress vs strain plot of 4AFD vitrimers.

Table 4.2. Glass transition temperature (T_g), Thermal analysis ($T_{5\%}$ and $T_{50\%}$), storage and loss modulus of vitrimeric composites.

S. No.	Sample codes	$T_g(^{\circ}\text{C})$ (DSC)	$T_{-5\%}$ ($^{\circ}\text{C}$)	$T_{-50\%}$ ($^{\circ}\text{C}$)	Storage Modulus(GPa)	Loss Modulus(GPa)
1.	EP-DETA	130.0	334.0	388.6	-	-
2.	EP-2AFD	123.0	306.6	376.3	78.0	43.2
3.	EP-4AFD	126.0	308.0	364.7	50.8.0	28.2

4.	EP-2AFD-0.5	121.0	300.4	377.3	129.0	82.6
5.	EP-2AFD-1	109.0	302.3	378.4	89.7	58.5
6.	EP-4AFD-0.5	134.0	310.3	367.04	121.0	73.9
7.	EP-4AFD-1	140.0	316.5	374.2	76.3	42.3

The Stress-strain relation of composite vitrimer was measured TMA via three-point bending tests using the force ramp mode at 40°C for all the compositions, as shown in Figure 3(c)(d) for 2-AFD and 4-AFD composites respectively. In 2-AFD composites, which explains that the highest flexural strength was observed in EP-4AFD-0.5. Whereas the reduced value of strain for EP-4AFD-1 affirmed the composite's stiffness increment (Krishnakumar, Prasanna Sanka, et al., 2020b). Highest flexural strength (18MPa) was observed for EP-2AFD-0.5 with 0.9% strain at break compared to pristine and EP-2AFD-1 whereas for 4AFD composites higher flexural strength(17.6MPa) was obtained for sample EP-4AFD-0.5 at 0.6% strain at break. The reduction in value of strain-at -break signify the increase in stiffness of nanocomposites with the incorporation of GO as nano fillers(Bortz et al., 2012).

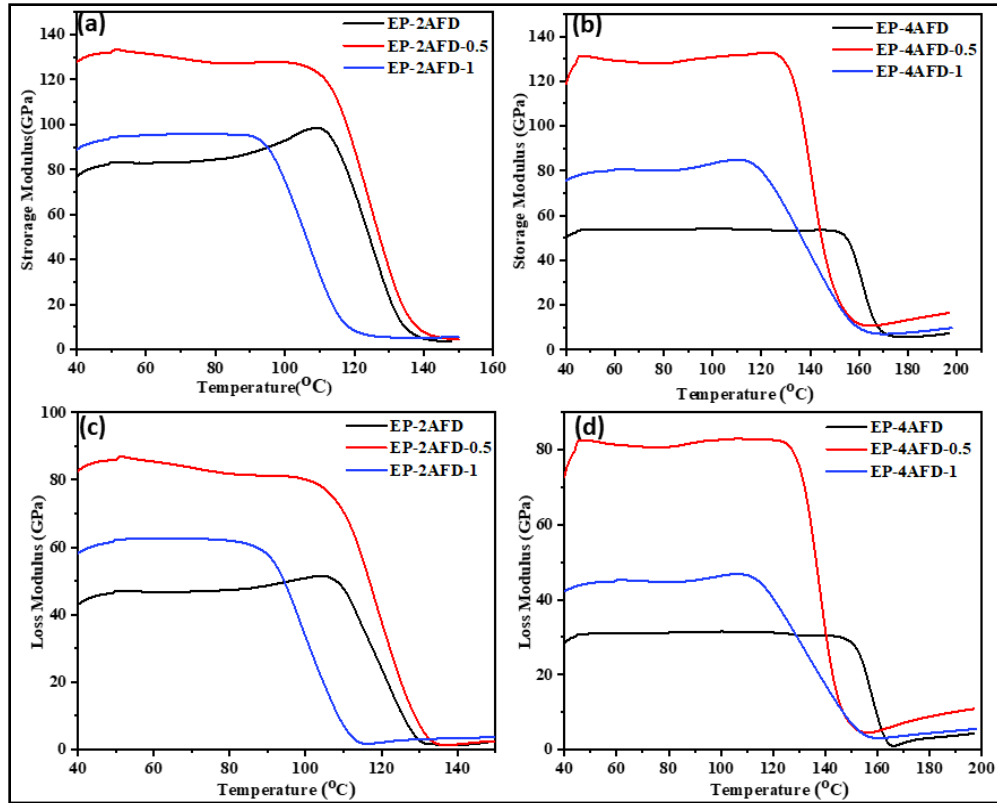


Figure 4.4. (a) Storage modulus temperature curve for 2-AFD composites (b) Storage modulus vs temperature curve for 4-AFD composites (c) Loss modulus vs temperature curve for 2-AFD composites (d) Loss modulus vs temperature curve for 4-AFD composites.

The viscoelastic behavior of vitrimeric composites were explained in the term of storage and loss modulus at 40°C as shown in Figure 4.4. the modulus values show increase with incorporation of nanofiller with highest storage modulus (129 GPa) and loss modulus (83 GPa) for EP-2AFD-0.5 composite as compare to 4-AFD composites with storage modulus (122 GPa) and loss modulus (74 GPa) (Figure 4.4 a,b,c,d). The accretion observed in modulus values are due to the wavy topology of nano-filler, which advances the efficiency of polymer interlocking explaining the viscoelastic behavior of composite. In the graph, a hump also can be observed which indicates the rubbery region (after T_g), which is attained at lower temperature in the presence of filler.

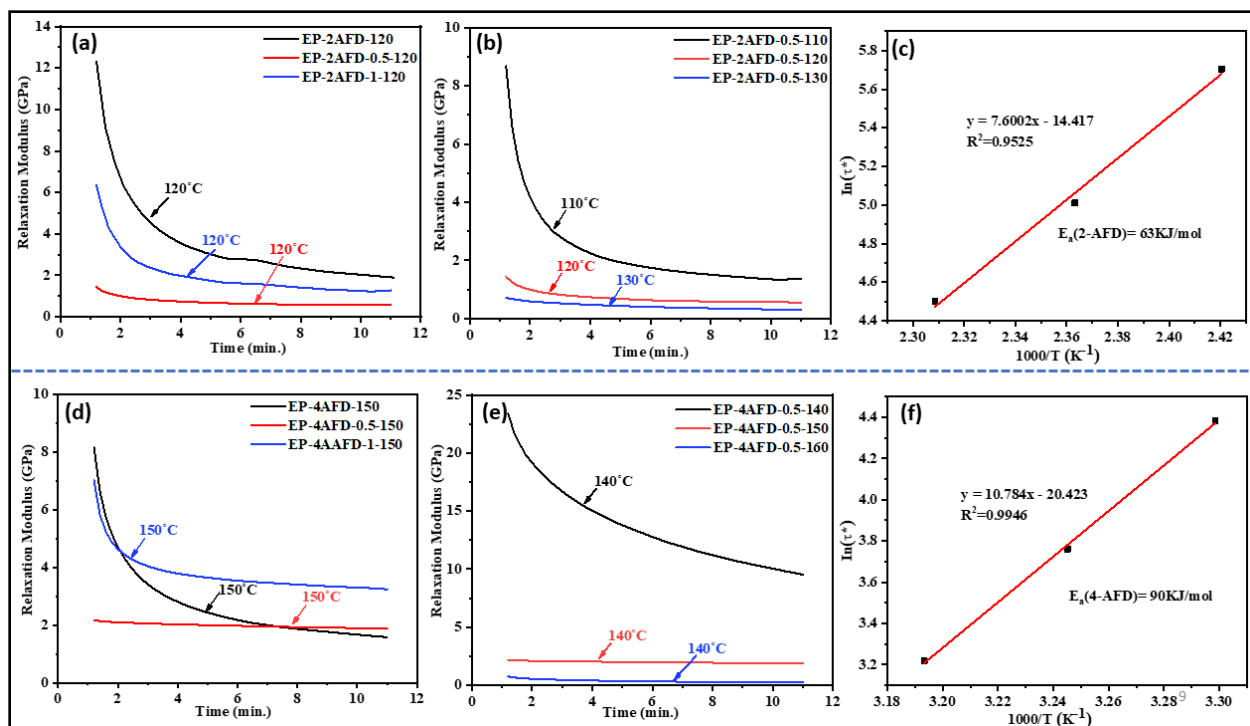


Figure 4.5. (a) Relaxation modulus vs time curve of all 2-AFD composites at 120°C temperature (b) Relaxation modulus vs time curve of 2-AFD-0.5 composite at 110°C, 120°C and 130°C temperature (c) Arrhenius linear fitting for the calculation of activation energy for 2-AFD-0.5 composite (d) Relaxation modulus vs time curve of all 4-AFD composites at 150°C temperature (e) Relaxation modulus vs time curve of 4-AFD-0.5 composite at 140°C, 150°C and 160°C temperature (f) Arrhenius linear fitting for the calculation of activation energy for 4-AFD-0.5 composite

The dynamic bond exchange efficiency which facilitates the self-healing character of nanocomposite can be explained in the term of stress relaxation modulus. The time dependent curve of relaxation modulus was plotted for 2AFD composites at 120°C (Figure 4.5 (a)) and 4AFD composites at 150°C (Figure 4.5. (d)), from which the best relaxation with time results were obtained for 0.5% nanofiller composite. Furthermore, the 0.5 filler composites relaxation modulus with time curves were plotted at 110°C, 120°C and 130°C for EP-2AFD-0.5 (Figure 4.5 (b)) and at 140°C, 150°C and 160°C for EP-4AFD-0.5 (Figure 4.5 (e)) respectively which results in fast relaxation of applied stress above T_g temperature. The high relaxation rate indicates fast disulfide exchange in the matrix, in other words decrease in relaxation time with temperature supports the quick dynamic exchange reaction. The obtained time values from curve were further fitted in

Arrhenius equation for the calculation of activation energy (Figure 4.5. (c),(f)). from the linear plot 9270 activation energy was calculated using the given equation(1) 63KJ/mol for EP-AFD and 90KJ/mol for 4AFD composites(Krishnakumar, Prasanna Sanka, et al., 2020a).

$$\tau^* = \tau^0 \exp(E_a/RT) \quad (1)$$

4.3.3. Self-healing of coating samples (optical microscope):

Self-healing tendency of developed vitrimer coating samples showed significant healing with conventional heating and microwave heating at 500GHz input frequency, which gradually increases with the concentration of GO. To study self-healing properties in detail, the coating matrix was coated on a glass slide and metal substrate as shown in Figure 4.6 (a), followed by making scratches with the blade and observing the scratches at 20x magnification using an optical microscope. At first instance, pristine AFD vitrimeric samples were observed to be healed at 110°C in 10-15 min, and then healing time was reduced to 8 min with an increase in GO% in samples EP-AFD-0.5 and EP-AFD-1. Whereas during microwave radiation exposure, pristine vitrimeric samples EP-2AFD and EP-4AFD demonstrated healing within 5 minutes. With increasing concentration of nano fillers, complete healing of the scratch occurs within 4 minutes as shown in optical images captured at optical microscope in Figure 4.6 (b). Ortho composite EP-AFD showed faster healing than para composite 4-AFD, due to the higher activation energy, ortho composites show higher temperature dependence in bond exchange reaction(Ruiz de Luzuriaga et al., 2022). Sulfenyl radical formation due to S-S cleavage reduces bond dissociation energy when the amine is present at the ortho position because of highly stable sulfenyl radical formation(Matxain et al., 2016). The healing behavior was estimated from T_g determined from the endothermic peak of the second DSC heating cycle as explained in the prepared composites, thermal properties. The composite's T_g increases with nanofiller addition due to increased interfacial interaction of the matrix and altered polymer heat flow(B. Singh et al., 2023)(Guadagno et al., 2019a). The T_g is observed to be slightly higher with an increase in GO concentration. In addition, healing efficiency of composite also increases with nano filler in the presence of microwave radiation due to feasible thermal conductivity of graphene oxide (Sánchez-Romate et al., 2021). Electromagnetic radiation can provide a wide range of energy to be converted into heat, and microwave radiation is the

convenient option to be converted into heat and facilitate the healing process. Graphene-based nanofiller increases the heat production in microwave radiation exposure(Zarepour et al., 2023).

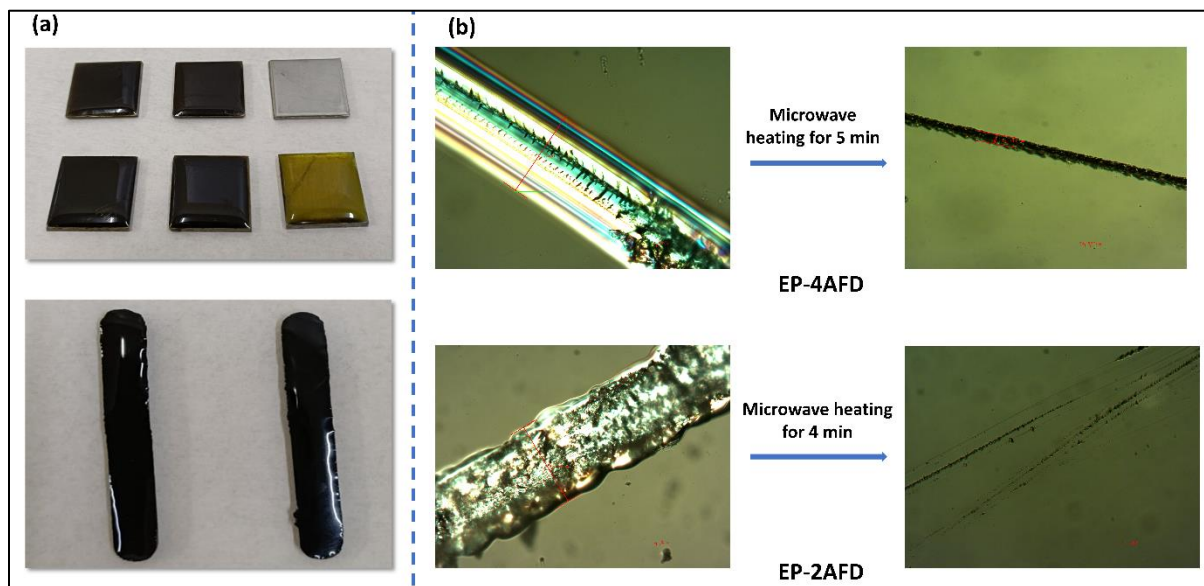


Figure 4.6. (a) Pictorial images of the vitrimer samples cured and coated on SS-304 substrate
(b) Optical microscope images of vitrimers (2AFD and 4AFD) before and after healing of mechanical scratch.

4.3.4. Surface properties of the coating:

The surface properties of the coating were studied in the terms of surface roughness and hydrophobicity. The developed coating sample EP2-AFD has shown excellent hydrophobic character, as the contact angle for the EP2-AFD-1 reported 90.51° in the case of DI water and 96.45° in the presence of salt water (3.5% of salt wt%, equivalent to seawater salt conc.), along with that EP2-AFD-0.5 also have shown hydrophobicity with contact angle of 92.65° . The contact angle has been observed to be higher with salt water due to the charge-balancing cation present on the surface, which increases the hydrophobicity of the droplet on the surface. The salts present in the salt solution form an ionic hydration cell, weakening the interaction of water molecules in the inter hydration layer and supporting the hydrophobicity enhancement(Meng et al., 2022). The contact angle of salt water with the surface was studied with time, as shown in Figure 4.7 (b) and reported in Table 4.4. The contact angle keeps decreasing with the resting time of drop for the pristine surface, whereas, the decrease in angle reduces with the increase in nanofiller concentration as shown in contact images in Figure 4.7 (c). The contact angle samples have also

shown significant increase after addition of GO nano-filler, which can be explained by the surface roughness of the coating as, explained in Wenzel's theory.

Table 4.3. Detailed description of roughness values of vitrimeric coating

S.No.	Samples	Ra(nm)	Rq(nm)
1.	EP-2AFD	10.8	12.8
2.	EP-4AFD	11.1	13.4
3.	EP-2AFD-0.5	11.9	14.1
4.	EP-2AFD-1	10.7	12.7
5.	EP-4AFD-0.5	10.9	13.3
6.	EP-4AFD-1	21.9	26.8

According to the Wenzel theory, surface wettability and surface roughness are major factors affecting each other, below 90° wettability increases with contact angle, whereas above 90° wettability decreases with contact angle. The surface roughness of the AFD vitrimeric coatings were recorded in the range of 10.8nm - 26.8 nm (Q. Liu et al., 2019)(Meng et al., 2022). The surface roughness of the coating was measured using AFM; the obtained AFM images are shown in Figure 4.7(a) and reported in Table 4.3. The roughness of the surface has been found to be lower with the addition of GO nanofiller. In addition, the smoother the surface, the greater the corrosion inhibition properties (Q. Liu et al., 2019).

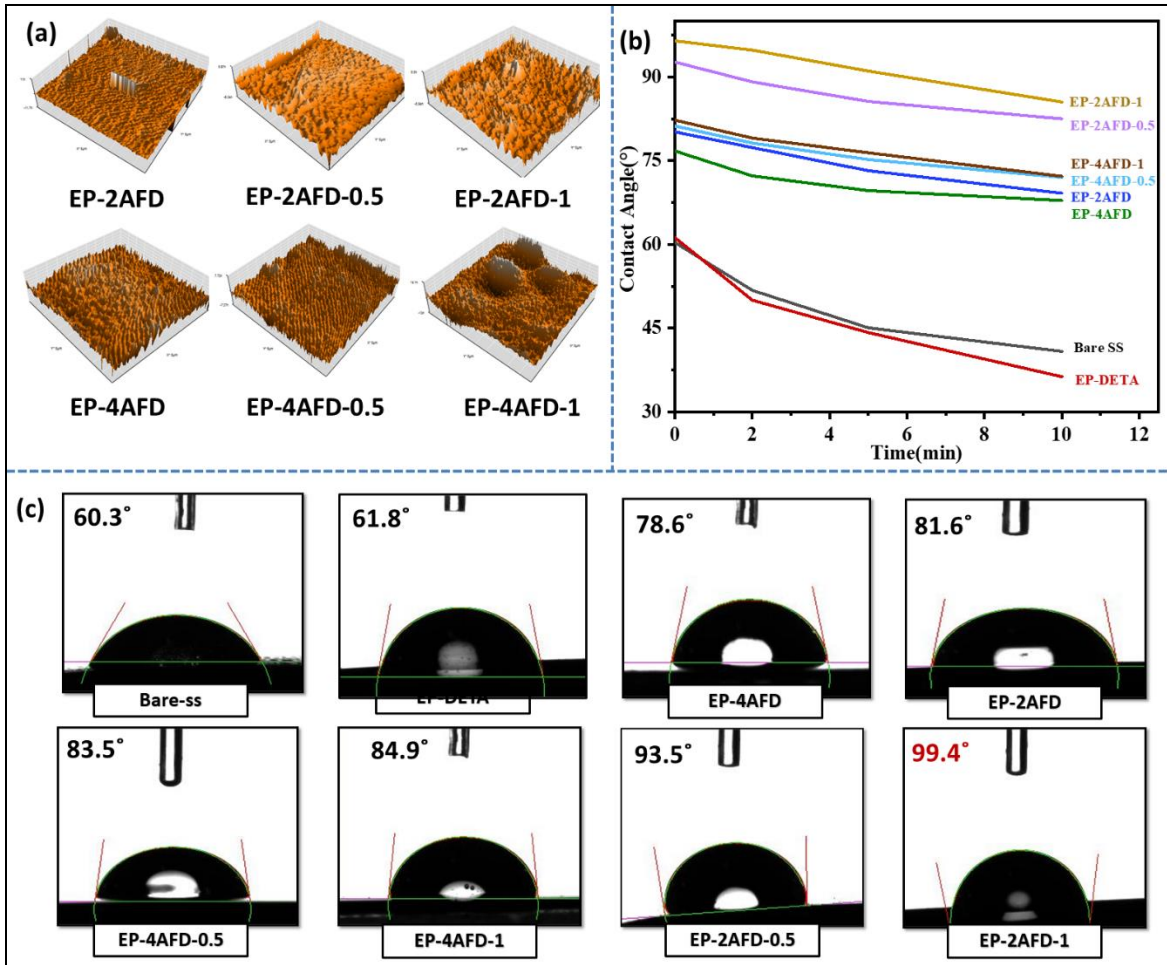


Figure 4.7. (a) AFM images of the composite coating for the surface topology study (b) Graphical representation of contact angle on coating surfaces with time using salt water and (c) Pictorial presentation of images of various composite surfaces using drop shape analyser.

Table 4.4. Contact angle of DI water and Salt water droplets on coated substrate surface

S.N	Samples	DI water contact angle (avg value)	3.5% Salt water (avg. value)			
			Initial	2min	5 min	10min
1.	Bare SS304	57.9±1.2°	60.3±2°	51.7±0.6°	45.0±0.7°	40.8±0.3°
2.	EP-DETA	55.3±1°	61.8±1°	50.0±0.5°	44.2±0.3°	36.3±0.2°
3.	EP-2AFD	70.4±1.5°	80.1±2.1°	77.3±0.9°	73.2±0.5°	69.1±0.4°
4.	EP-4AFD	65.7±1.7°	76.7±2.3°	72.2±1°	69.6±0.6°	67.8±0.5°
5.	EP-2AFD-0.5	87.9±2°	92.6±2.6°	89.1±1.1°	85.6±0.9°	82.5±0.6°

6.	EP-2AFD-1	90.5±2.1°	96.4±3.8°	94.8±2.5°	91.0±2.7°	85.5±1.2°
7.	EP-4AFD-0.5	77.3±0.7°	81.2±3.1°	78.1±0.8°	75.2±1.2°	72.0±0.9°
8.	EP-4AFD-1	79.0±0.9°	82.2±2.7°	79.0±1°	76.4±0.8°	72.2±0.5°

4.3.5. Electrochemistry characterization:

The corrosion-inhibiting efficiency of the self-healing coating was studied on an Electrochemical work station using a Tafel polarization test for bare SS-304 substrate, pristine coating, and composite developed vitrimeric coating. The electrochemical behavior of coated metal was done in the presence of 3.5% aqueous NaCl as electrolytes using electrochemical workstation CHE-660 and three electrode system in flat corrosion cell consisting of Ag/AgCl as reference electrode, a platinum electrode as counter electrode and SS-304 coated with developed material as working electrode. As shown in Figure 4.8 (A)(a) the highest corrosion potential (E_{corr}) is obtained in the case of EP2-AFD-0.5 (-0.09406V), whereas the lowest corrosion potential was observed in the case of bare SS-304 with -0.4499V. It can be seen stated in Table 4.5, E_{corr} increases with the addition of GO upto 0.5%. In contrast, a slight decrease is observed when the concentration of GO was increased up to 1%, which can be due to agglomeration of GO at higher concentrations (Ramezanzadeh et al., 2016). The decrease in value of β_c (cathodic slop) as compared to β_a (anodic slop) indicates the passive area in the tafel plot, which can be seen in Figure 4.8 (A)(b) of EP4-AFD-1 as well as EP2-AFD-1. With the increase in the concentration of GO, there is a relative decrease in β_c , suggesting that the addition facilitates the corrosion inhibition of the film due to the formation of an oxidative layer of material on the surface, which acts as shielding between the coating layer and corrosive species, as well as protects the epoxy layer from further deformation which can be seen visibly in Optical microscopic images in Figure 4.8 (B)(Q. Liu et al., 2016)(Q. Liu et al., 2019). The corrosion current density I_{corr} decreases following the same trend, the highest value obtained for Bre SS-304, which gradually decreases and the lowest values were observed for EP2-AFD-1 composite coating, suggesting thermodynamically less corrosion tendency(Nematollahi et al., 2010). Resistance potential (R_p) of bare SS-304 and pristine and composite vitrimeric coating has been calculated using the Stern-Geary equation given below as equation 2. R_p shows significant increase respectively for bare, pristine and composite samples, which were enhanced by GO-based nano filler. The detailed potential-dynamic

polarization measurements have been listed in the Table 4.5, along with calculated R_p and PE% of the vitrimeric composite coatings.

$$R_p = \frac{\beta_a \times \beta_c}{2.303 \times I_{corr}(\beta_a + \beta_c)} \quad (\text{Nematollahi et al., 2010}) \quad (2)$$

Where R_p is denoted as resistance potential, β_a is anodic slope whereas β_c is cathodic slope and I_{corr} explained as corrosion current density. Further, corrosion rate(P_i) can be calculated from I_{corr} values for each sample measured in mm/y using faraday's law given in equation (3)(X. Li et al., 2023).

$$P_i = 2.285 \times 10^4 \cdot i_{corr} \quad (3)$$

Where P_i is explained as calculation of corrosion in mm per year, the lowest value of P_i is obtained for 2-AFD-1 composite with the value of 1.20×10^{-3} mm/y, whereas for 4-AFD composite lowest value of P_i obtained is 1.25×10^{-3} . The protection efficiency % of the developed coating was calculated using the equation given in Equation 4. The protection efficiency gradually increases with an increase in GO-based nanofiller in the matrix, which protects the substrate in active and passive inhibition from corrosive ions to penetrate.

$$PE\% = \frac{R_p^{-1}(\text{Bare}) - R_p^{-1}(\text{Coated})}{R_p^{-1}(\text{Coated})} \times 100 \quad (\text{Ding et al., 2019}) \quad (4)$$

The proposed corrosion inhibition mechanism provided by the coating is due to the barrier created by the epoxy coating between substrate and corrosive ions and decreasing the penetration possibility for the corrosive ions(Q. Liu et al., 2019). The corrosion inhibition tendency of the coating is said to increase with addition of graphene- based nanofiller. GO strengthens the barrier properties of the epoxy coating due to formation of 'labyrinth structure' formation, which increases the layer spacing and cause insulation for conductivity as well corrosion medium (H. Li et al., 2021; X. Li et al., 2023). It helps to hinder the galvanized layer from corrosion ions and electrolytes by enhancing the shielding due to the elongated penetration pathway and diffusion of ions. The oxygenated surface of GO increases ionic resistance of the coating, which tends to inhibit penetration of negative corrosive ions and simultaneously, reduce diffusion of cations due to the compact surface. This synergistic effect benefits the corrosion protecting properties of the composite film(Ramezanzadeh et al., 2016). Along with torturous penetration barrier properties, the developed coating system protects from mechanical damage. For instance, if due to weathering

conditions or high salt condition, the coating surface gets fatigued or damaged, microwave triggered self-healing property of the sustainable film reverse the damage and regain the original strength and protective properties of the repaired coating, thus enabling the maintenance long life and ensures the lesser of damage of the coating(B. Zhang et al., 2022). In the coating system cured using 2AFD hardener, a passive coating region was developed in the Tafel plot of each composition, which keeps on intensifying with the addition of nano-filler, signifying the protection of substrate due to oxides formation of the material which can further be supported by P_i and PE % values with 1.20×10^{-3} mm/y and 95.4% respectively(Q. Liu et al., 2016; B. Zhang et al., 2022).

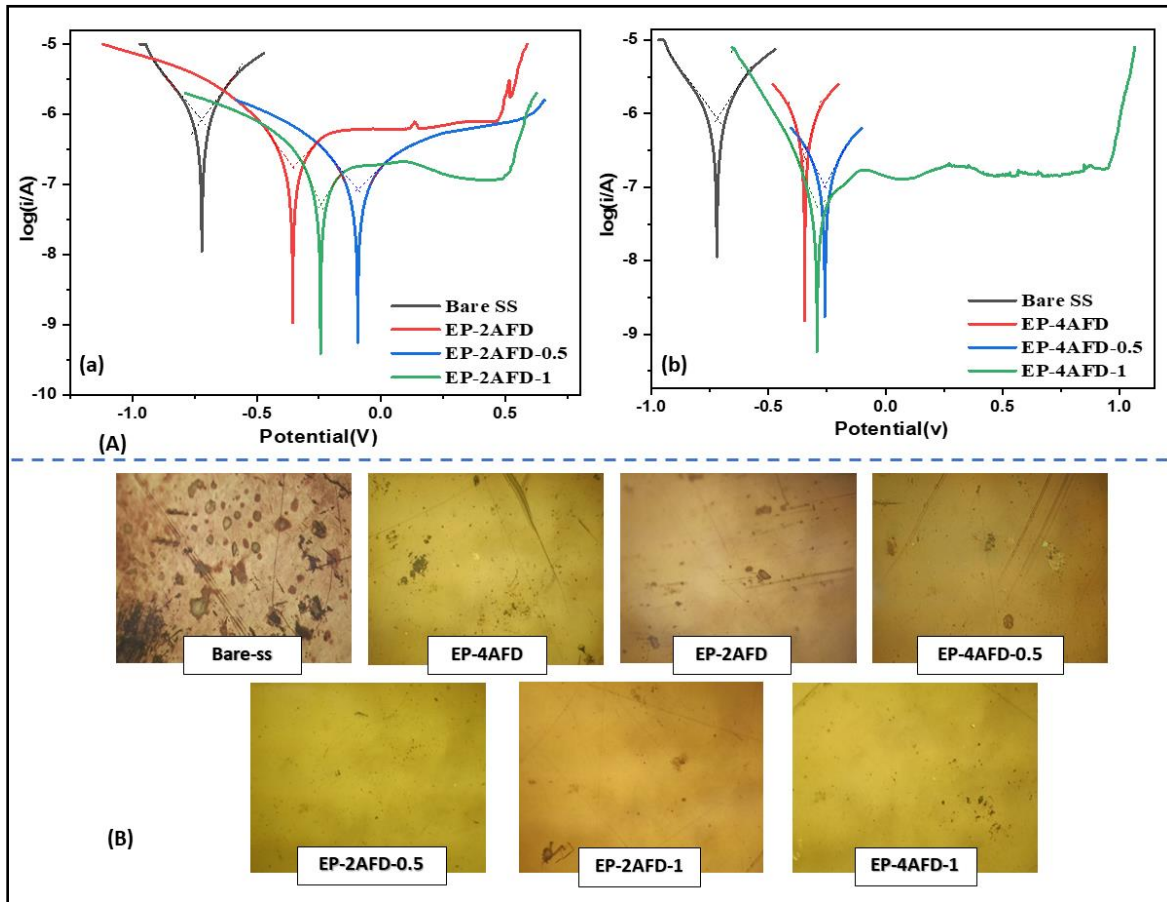


Figure 4.8. (A)(a) Tafel plot of 2-AFD based vitrimeric coating,(b) Tafel plot of 4-AFD vitrimeric coating in NaCl electrolyte respectively (B) Optical microscopic images of coated surface after the corrosion testing done

Table 4.5. Potentiodynamic polarization measurements and electrochemical parameters for composite coatings

S.No.	Sample	$E_{corr}(V)$	$I_{corr}(A)$	$B_c(V/dec)$	$B_a(V/dec)$	$R_p(M\Omega cm^2)$	Corrosion rate(mm/y)	PE%
1.	Bare SS	-0.722	-6.06	4.571	4.5658	1.14×10^6	0.0198	-
2.	EP-2AFD	-0.35	-6.73	6.705	4.57	6.3×10^6	4.25×10^{-3}	82.7%
3.	EP-4AFD	-0.34	-6.57	9.896	8.298	5.85×10^6	6.14×10^{-3}	81.2%
4.	EP-2AFD-0.5	-0.094	-7.06	7.263	5.699	1.6×10^7	1.98×10^{-3}	92.3%
5.	EP-2AFD-1	-0.24	-7.27	8.161	5.019	2.5×10^7	1.20×10^{-3}	95.4%
6.	EP-4AFD-0.5	-0.25	-6.98	7.4105	6.1727	1.4×10^7	2.37×10^{-3}	91.9%
7.	EP-4AFD-1	-0.29	-7.26	7.639	2.81274	1.62×10^7	1.25×10^{-3}	93.04%

4.4. Mechanism of self-healing and corrosion protection:

GO incorporated vitrimeric composites were observed capable of reversible bond exchange reaction with localized heating in the presence of microwave radiation. Compared to pristine polymers, the incorporation of carbonaceous materials like GO, CNT, and MXene provides much rapid heating temperature in composite, requires for healing purpose (Sosa et al., 2015). The interaction of composite with microwave radiation activates localized heating, which increases viscoelasticity of the matrix causing a disulfide bond exchange reaction and hence self-repairability time get reduced to 4-5 min as compared to thermal healing which takes 8 to 10 min in healing process (Solouki Bonab et al., 2019). The developed coating provides shielding against corrosion through active as well as passive functional protection as shown in Figure 4.9. The incorporation of GO creates more difficult path for corrosive ions to penetrate and interact with the substrate. This increases the corrosion protection efficiency up to 95.4% with corrosion rate 1.20×10^{-3} mm/y.

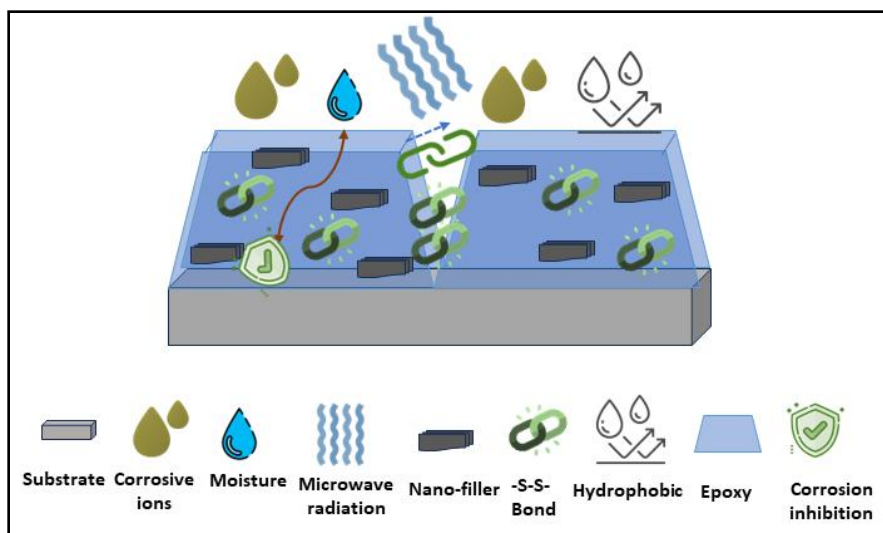


Figure 4.9. Illustration demonstrating the mechanism behind microwave triggered self-healing and corrosion inhibition of the vitrimeric coating

4.5. Conclusion:

Sustainable microwave triggered self-healable epoxy composite coatings were developed for the anticorrosive inhibition for marine applications using a composite of Epon-828 with 2-AFD and 4-AFD and GO as nanofillers. The composite coating showed excellent thermal healing property at 110°C for 10 min and microwave healing within 5 min due to reversible covalent disulfide bonds. We have observed that adding nanofiller is more efficient for the healing property as it provides high chain mobility to the matrix. The amine-disulfide moiety in the crosslinked matrix network delivers significant corrosion inhibition and appreciable hydrophobicity to the coating. The coating reported in the study showed noticeable corrosion inhibition with a protection efficiency of 96.4%. The GO-based nanofiller eventually enhanced the network by shielding the penetration of corrosive ions toward substrate. In addition, the coating sample with 1% GO shows the highest passive corrosion region, which means substrate protection from oxidized materials as a barrier. Epoxy-based vitrimeric materials responsive towards microwave heating have immense potential as the game-changer in self-healable coating materials.

CHAPTER 5

Nickel Doped Bio-Char Derived Dual Responsive Self-Healable Epoxy/Thiol Framework for Anti-Corrosive Coatings

Abstract

Nickel-doped biochar-based high-performance filler was introduced to polymeric matrix in this study for anticorrosive coatings. These microwaves triggered vitrimeric coating were developed as a pre-eminent futuristic approach for sustainable development and to promote the circular economy in the coating industry. To protect exorbitant assets from micro-cracking, damages, and getting fatigued due to prolonged use and weathering conditions, self-healable materials are the revolutionary choices. A generous strategy was introduced to modify the biochar surface with nickel to enhance the corrosive resistance as well as the mechanical properties of the coating material. The developed composites display excellent self-healing efficiency when irradiated with microwave via transesterification exchange mechanism and rapid relaxation time with excellent thermal stability (310 °C). The composite also demonstrates reliable thermo-mechanical properties (with 24.2GPa storage modulus and 18.8 MPa stress at 1.9 strain%) along with noticeable stress relaxation ability with 39 kJ/mol activation energy, indicating a fast dynamic bond exchange reaction in the network. The composites exhibit amazing shape-memory and self-adhesive properties in the presence of microwave radiation as stimuli. The excellent hydrophobicity makes these smart composites insightful into the designing and application as protective coatings in marine applications.

5.1. Introduction

One of the chief features of coating materials is to provide barrier and resistance against moisture in liquid or vapor form which determines the utility of the coating system (Bassett, 2001). Organic coatings are reliable and potential materials for creating barriers between the metal substrate and the external environment. Epoxy coatings have been known long for their robust barrier properties against various environmental as well as mechanical damages possible on the substrate surface (P. Singh et al., 2023). However, considerable efforts have been devoted in the past few years to develop robust hydrophobic coatings with high transparency. Generally, the development of transparent and hydrophobic coatings is found to be quite challenging as both properties are competitive with each other (X. Li et al., 2021). In addition, the extended exposure of conventional coating materials with harsh ecological habitats

retrograde the properties of the coating (P. Singh, Binder, et al., 2024). To address the aforementioned challenges, smart coatings with generous features of self-healing character, shape memory, and reversible dynamic interaction are the future of metal protection (Jiang et al., 2023). Self-healable vitrimers-based composites have already been game changers for the coating industry with significant attention. In the domain of matrix designing and development of advanced metal protective coatings, the challenge is protecting the metal assets economically. Self-healable vitrimer coatings play a decisive part in reducing waste, frequent maintenance, and promoting circular economy in material science (Rana et al., 2022). With the increasing concerns of environmental issues, more importantly, with the large consumption of non-renewable resources and the growing demand for biosafety of materials, bio-based materials prepared from renewable resources are favored by researchers as well as industries. Subsequently, biochar derived from biomass has opened the road map to enhance the coating properties in a sustainable and ecological manner (Aung et al., 2020b)(Pandey et al., 2018). Vitrimer polymeric coatings offer major solutions that deal with the majority of the issues (maintenance, self-reparability, strong barrier for substrate, and repressibility). Vitrimer chemistry is a breakthrough towards multi-repairing cycles and enhancement in the lifespan of the coating and hence the longer protection of valuable asset (Altuna et al., 2016)(Nardeli et al., 2020)(Thakur & Karak, 2015).

In this work epoxy vitrimer composites were prepared by using thiol click chemistry in the presence of wood biochar and nickel-doped bio-char ($\leq$ wt.%). Herein, a comparative study of biochar and nickel-doped biochar is provided with the structural and properties performance and relationship of the composite. The mechanism behind the properties exhibited by tri-functional crosslinking agent used comprising efficient dynamic transesterification exchange reaction the presence of stannous octoate as catalyst. This catalyst facilitates the crosslinking reaction between epoxy and crosslinking agent, along with promoting the dynamic transesterification exchange bond reaction by altering the activation pathway via dual responsive mechanism of the developed matrix. It is interesting to explore and report the mechanism behind the workability of this composite system with the functionality of nano-fillers incorporated.

5.2. Experimental Section

5.2.1. Materials

Epon 828, trimethylolpropane tris(3-mercaptopropionate) (Sigma Aldrich), Tin(II)2-ethylhexanoate, Sigma Aldrich), Nickel(II) Nitrate hexahydrate, ethanol were procured and used in their original form.

5.2.2. Preparation of Nickel doped wood biochar:

Nickel (II) nitrate was added in DI water along with finely grinded wood biochar (WBC) with a wt. % of 10:1 for Ni: WBC. The prepared mixture was sonicated for 1 hour followed by stirring at 500 rpm for 1 hour. Afterward, the mixture was oven-dried overnight at 60°C. When the prepared mixture was dried completely it was pyrolyzed in the presence of N₂ environment for 3 hours at 600°C. The obtained doped WBC was further washed with DI water and sonicated each time to remove extra salt present. The resultant Ni@WBC was dried and further used for characterization.

5.2.3. Preparation of vitrimer coating system:

EP-SH vitrimer samples were developed using mercaptan-based crosslinking agent trimethylolpropane tris(3-mercaptopropionate) (TMP-MP) using catalyst Tin (II) 2-ethyl hexanoate in epoxy 828. For the sample preparation epoxy and TMP-MP were used in 1:1 molarity and 5 mol% catalyst Sn(oct)₂ mixing in a homogenous mixture. The prepared homogenous mixture was degassed in a vacuum for 15 min and poured in PTFE molds to prepare a sample of desired dimensions followed by curing in a curing-cycle of 2 hours at 100°C, 3 hours at 130°C and 150°C for 4 hours. As a result, highly transparent vitrimeric material was synthesized. The matrix was coated on SS-216 grade substrate using a spin coater (spinNXG-P2) for 1 min at 1000 rpm, then spin was accelerated to 1200 rpm for 1 min. vitrimeric composite samples with varying compositions of WBC and Ni@BC as a nanofiller were also prepared. To prepare EP-SH-x%WBC/Ni@BC (where x = 0.1, 0.3, 0.5 and 1), the synthesized WBC/Ni@BC (50mg) was allowed to be dispersed in 5ml of ethanol by ultrasonication of the mixture for 30-60 minutes until it was fairly dispersed. The filler mixture was added in a defined percentage to epoxy followed by the addition of TMP-MP and Sn(Oct)₂ as the hardening agent and catalyst respectively. The prepared mixture was homogenized at 80°C for 15 minutes at 200 rpm and degassed further cured in the same curing as mentioned. The composite material was also applied on a transparent glass slide for easy self-healing investigation. The thickness of the developed coating was controlled in the range of 110µm as preferred for anti-corrosion.

5.3. Result And Discussion:

5.3.1. Characterization of Ni@BC

The organic functional groups present on the surface of WBC and Ni@WBC were analyzed using FT-IR as shown in Figure 1(a). The absorption band was observed at 3620 cm^{-1} due to -OH stretching vibration corresponding to the presence of adsorbed water. At 2926 cm^{-1} band due to C-H stretching was observed corresponding to the alkyl group. The peak at 1450 cm^{-1} corresponds to C-O stretching vibration whereas the peak at 1079 cm^{-1} is attributed to -C-O-C-/-C-OH stretching vibration. However, after doping of Nickel on WBC (Ni@WBC), the peak present at 1450 cm^{-1} intensified due to possible presence of Ni=C vibration along with at 712 cm^{-1} peak corresponding to Ni(OH)₂ observed as well as a new peak emerging at 578 cm^{-1} due to Ni-O vibration (Pham & Nguyen, 2016) (Y. Wang et al., 2017) (Mohamed et al., 2023).

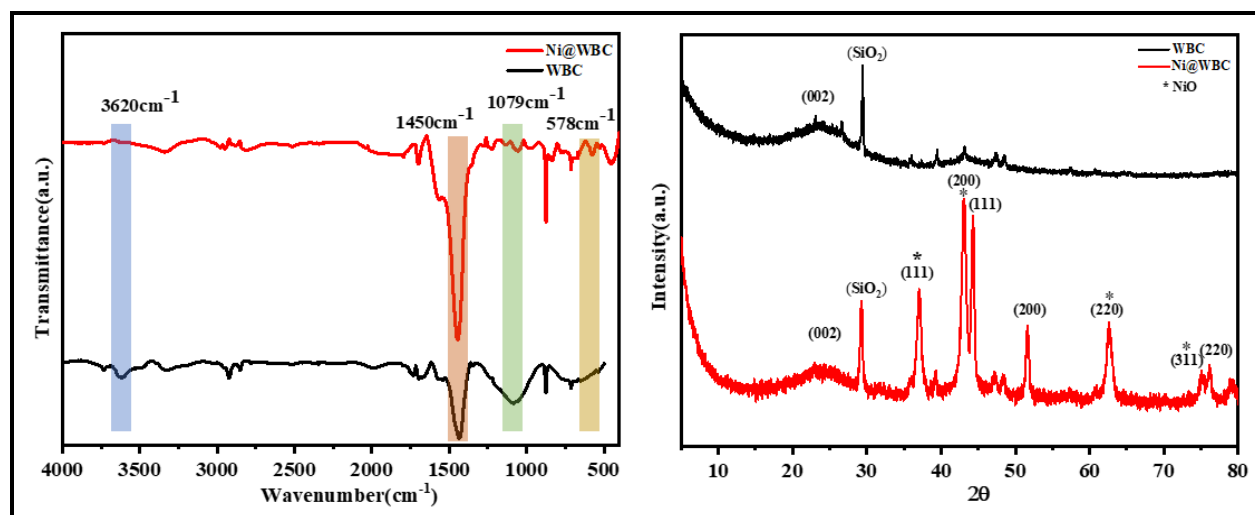


Figure 5.1. (a) FT-IR spectra of WBC and Ni@WBC (b) XRD spectra of WBC and Ni@WBC.

XRD spectra were used for further validation of Ni doping (Figure 5.1 (b)), two strong peaks have been identified, broad peak identified at 23° is due to the stacking structure of aromatic layers present (002), the broadening of the peak is due to the small crystallinity of the layers whereas a sharp peak at 29° is due to the high content of crystalline SiO₂ (Y. Liu et al., 2012). However, for Ni@WBC, the diffraction pattern exhibits multiple different sets of peaks, where 23° is due to biochar, 29° is due to SiO₂, and peaks at 45° (111), 52° (200), and 77° (220) are due to Ni doping along with 37° (*111), 43° (*200), 62° (*220) and 75° (*311) are due to Nickel oxide (Y. Wang et al., 2017). In order to understand the Ni-doped percentage and surface composition of doping was analyzed using ICP-EOS and XPS were performed, where ICP-EOS results show a good amount of Ni present on the surface of biochar with 138.7 mg/L

leached from 0.5g of Ni@WBC. XPS results also validate the successful doping of the nickel on WBC along with oxygen(O) and carbon(C). In Figure 5.2 (a) full survey scan of WBC displays the presence of O and C which is supported by high-resolution spectra of C in fitted peaks present at 284.8eV and 287eV corresponding to C 1s and C-O respectively. Similarly, in O high-resolution spectra peak at 531.5 eV and 533 eV attributed to O 1s and C-O respectively. On the other hand, Ni-doped WBC full survey spectra confirm the presence of Ni, O, C, which is again evidenced by high-resolution spectra of C and O with observed peaks at 284.8 eV due to C 1s, 285.6 eV corresponds to CO₂/Ni and 290eV due to C-O spectra. Likewise, O spectra confirm the presence of NiO 1s through the peak at 529eV, whereas the peak at 532 eV corresponds to C-O. The deconvolution of high-resolution spectra of Ni reveals the presence of 8 peaks where Ni 2p_{1/2} is observed at 873.1eV followed by its satellite peak at 880eV possibly due to the presence of NiOOH and NiO. In addition, the peaks at 855 eV attributed to Ni 2p_{3/2} with its satellite peak at 861.7 eV affirming the presence of nickel in +2 and +3 oxidation states (Figure 5.2)(Guide, 2015)(Isaac et al., 2023)(Z. Chen et al., 2019).

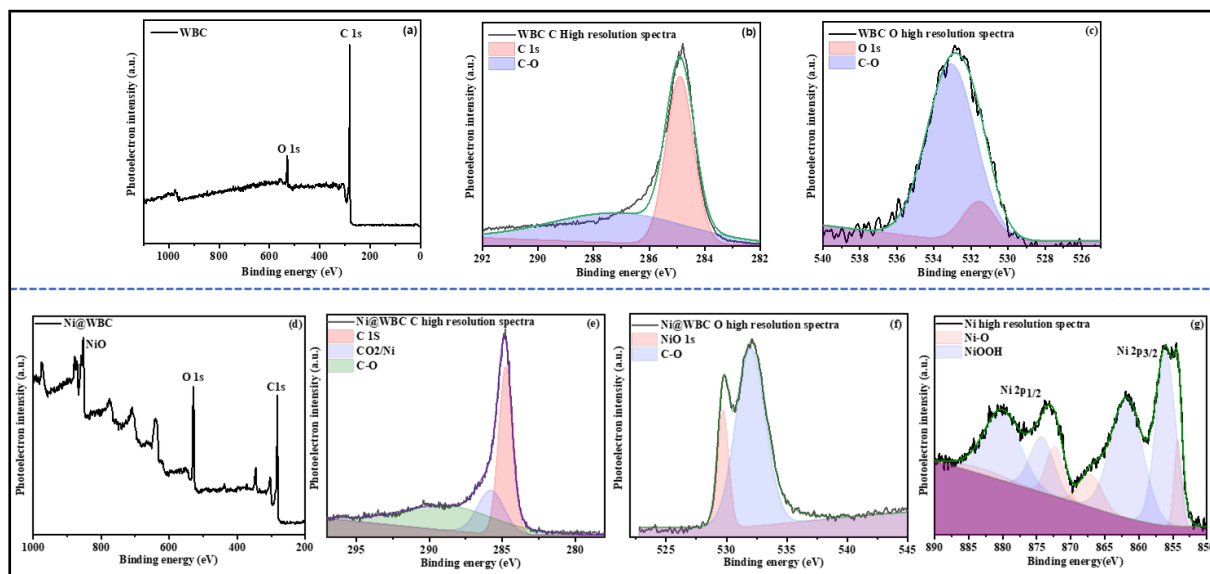


Figure 5.2. XPS spectra of WBC and Ni@WBC : (a) Complete spectra of WBC, (b) High resolution fitted Carbon spectra of WBC, (c) High resolution fitted oxygen spectra for WBC. (d) complete high-resolution spectra of Ni@WBC, (e) Carbon high-resolution fitted spectra, (f) Oxygen high-resolution fitted spectra of Ni@WBC (g) Nickel high-resolution spectra.

5.3.2. Characteristics of vitrimer composite:

The developed vitrimeric composites were analyzed using ATR-FTIR (Figure 5.3(a)). In the case of epoxy, the peak present at 1033 cm⁻¹ was known to be attributed to (C-O) stretching

vibration, and peaks at 736 cm^{-1} and 556 cm^{-1} appear due to oxirane bond ($-\text{C}-\text{O}-\text{C}-$) stretching (B. Singh et al., 2023)(Krishnakumar, Prasanna Sanka, et al., 2020b). For crosslinked vitrimeric sample, the peaks due to oxirane stretching disappeared indicating a ring-opening reaction and crosslinking of epoxy whereas a new signal at 1730 cm^{-1} emerged after crosslinking due to $-\text{C}=\text{O}$ bond (from TMP-MP) indicating bond formation between epoxy and hardening agent(Z. Sun et al., 2017). The resultant composite samples in the coating and sample form have been demonstrated in Figure 5.3 (b) along with transparency of the coating with increasing WBC concentration in the matrix(Figure 5.3)(P. Singh, Umamaheshwara, et al., 2024).

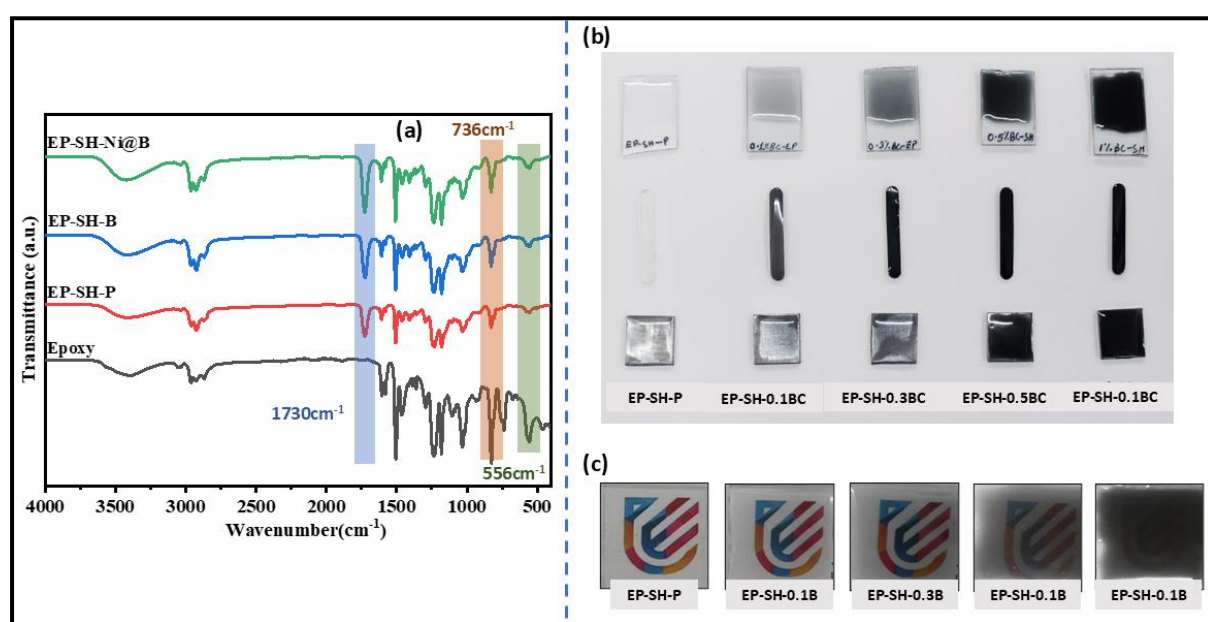


Figure 5.3. (a) FT-IR spectra of epoxy, pristine sample of EP-SH, biochar incorporated composite of EP-SH-b and Ni@WBC incorporated composite EP-SH-Ni@b (b) DCS plots of series of composites of EP-SH-B (c) pictorial images of prepared samples on the coated substrate (d) Transparency of the prepared composites with increasing concentration of nano-filler.

The temperature-dependent properties of vitrimer samples revealed several particulars about the composite material. To understand the trend of thermal properties, the glass-transition temperature (T_g) and thermal strength of EP-SH vitrimer composites were studied using DSC and TGA instrumental data respectively for all the compositions (Table 5.1) and Figure 5.4. The T_g of WBC-based composites was detected to be elevated with the increase in WBC concentration, which is due to the possible change in the interfacial interaction between the epoxy network and filler which restricts the matrix flow and mobility and resulted in T_g

elevation (Figure 5.4). With the increase in WBC-based filler concentration in the matrix, T_g increases from 30.5° C for the pristine sample to 38.4° for 0.1% concentration of WBC and 53.2 for 1% Ni-doped WBC incorporation into the matrix (Krishnakumar, Prasanna Sanka, et al., 2020b). However, this adaptation assists in achieving higher thermal as well as mechanical strength to sustain in real-life applications (Krishnakumar, Prasanna Sanka, et al., 2020b)(Krishnakumar, Singh, et al., 2020)(B. Singh et al., 2023). In order to study the thermal sustainability of the developed vitrimer composites TGA study was performed where the first degradation($T_{5\%}$) started at 285° C for the pristine sample(EP-SH-P), which increases up to 305.4° for EP-SH-0.1-BC and started to decrease with further increase in the concentration of WBC, in addition $T_{5\%}$ values reported with 296.7 incorporation of Ni@WBC incorporation (Krishnakumar, Prasanna Sanka, et al., 2020b). The second degradation ($T_{50\%}$) was observed at 366.4° C for the pristine sample and with maximum temperature stability of 382° C for EP-SH-0.1-BC and 376 for EP-SH-1-Ni@BC. The addition of WBC provides thermal stability up to optimum concentration but with further incorporation, it started to decline because of packed biochar structure (Figure 5.4).

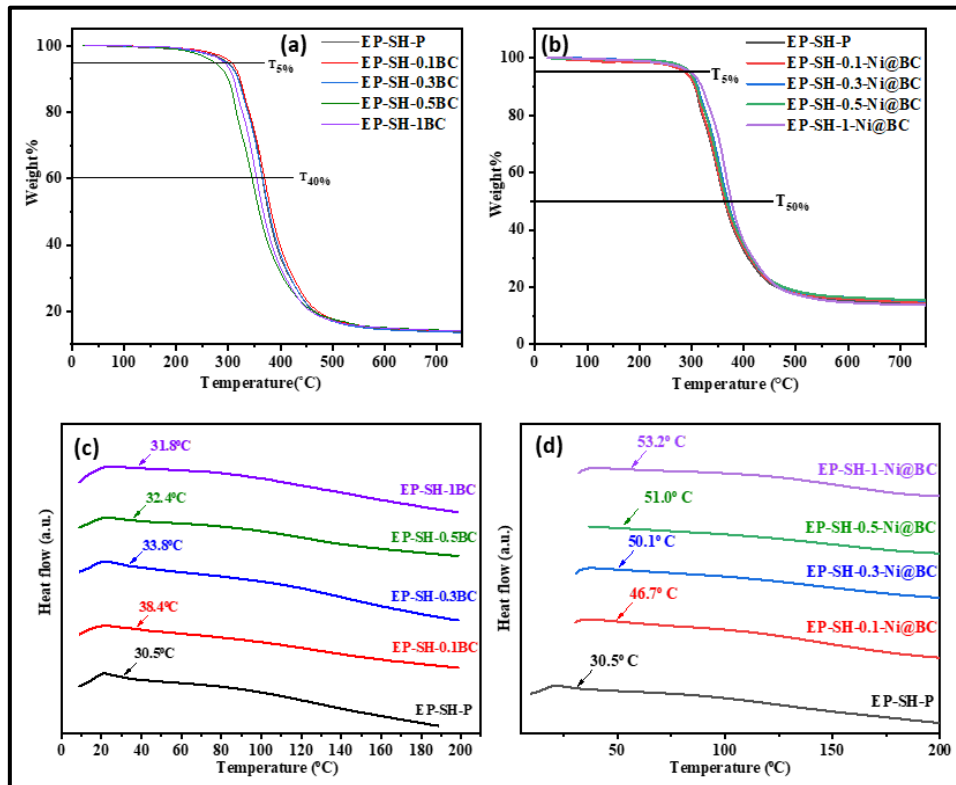


Figure 5.4. (a) TGA plots for EP-SH-BC vitrimer composite, (b) TGA plot for EP-SH-Ni@BC vitrimer composites, (c) DSC curves for EP-SH-BC composites series, (d) DSC curves for EP-SH-Ni@BC composites series

5.3.3. Thermal properties and thermo-mechanical properties:

The thermal mechanical properties in terms of viscoelasticity of developed vitrimer composites with various compositions were also examined, where storage modulus and loss modulus along with stress-strain relation with various concentrations of WBC filler were studied. The composite EP-SH-0.3-BC demonstrates the best thermo-mechanical properties with a storage modulus 17.2 GPa, loss modulus 2.5 G Pa, and stress of 5.7 MPa at 1.8 strain % in comparison to pristine sample EP-SH-P with 12.3 G Pa and loss modulus of 1.8 and stress of 1.9 M Pa at 1.4% strain at optimized 30° C temperature, whereas after the doping of Ni in biochar a drastic shift in thermomechanical properties were observed with 24.2 GPa storage modulus and 3.6 GPa loss modulus and stress of 18.8 MPa at 1.9 strain% for EP-SH-0.5Ni@BC. The values of these properties started to decline if the concentration of filler surpasses the 0.3 % for WBC and 0.5% for Ni@WBC, as at 1 % concentration of WBC shows 14.8 GPa storage modulus, 2.3 G Pa loss modulus and 2.8 M Pa stress for 1% conc. of Ni@WBC shows 17.4 GPa, 2.3 loss modulus, and 15.9 MPa stress at 1% strain due to agglomeration of nanofiller beyond a certain concentration due to change in interfacial topology (Table 1) (Figure (a-e)).

The dynamic nature of the trans-esterification exchange reaction in prepared composites were obtained by studying the relaxation modulus (Figure (e)(f)). The relaxation modulus for WBC series of compositions was mapped for the composite and showed best viscoelasticity in terms of Storage and loss modulus values (EP-SH-0.3-BC) at 40° C, 45° C, 50° C, 55° C, 60° C, and 65° C resulted into relaxation time in the range of 8 min to 1.5 min respectively. The relaxation time here was obtained by using Maxwell's viscoelastic fluid equation, which can be explained as the time essential for releasing the initial stress up to 63% of the initial modulus. Similarly, relaxation modulus was obtained for a composite series of nickel-doped WBC vitrimer where relaxation was recorded for EP-SH-0.5.Ni@BC at 35° C, 40° C, 45° C, 50° C, 55° C, and 60° C, resulted in relaxation time in the range of 7.5 min to 1.3 min. In addition, the activation energy was calculated following the Arrhenius equation as given below.

$$\tau(T) = \tau_0 \exp\left(\frac{E_a}{RT}\right) \quad (1)$$

Practicing from Arrhenius equation, activation energy (E_a) value obtained was 49 kJ/mol and 39 kJ/mol for EP-SH-0.3BC and EP-SH-0.5-Ni@BC respectively (Figure 5.5(f) and Figure 5.6(f)) (Krishnakumar, Prasanna Sanka, et al., 2020b).

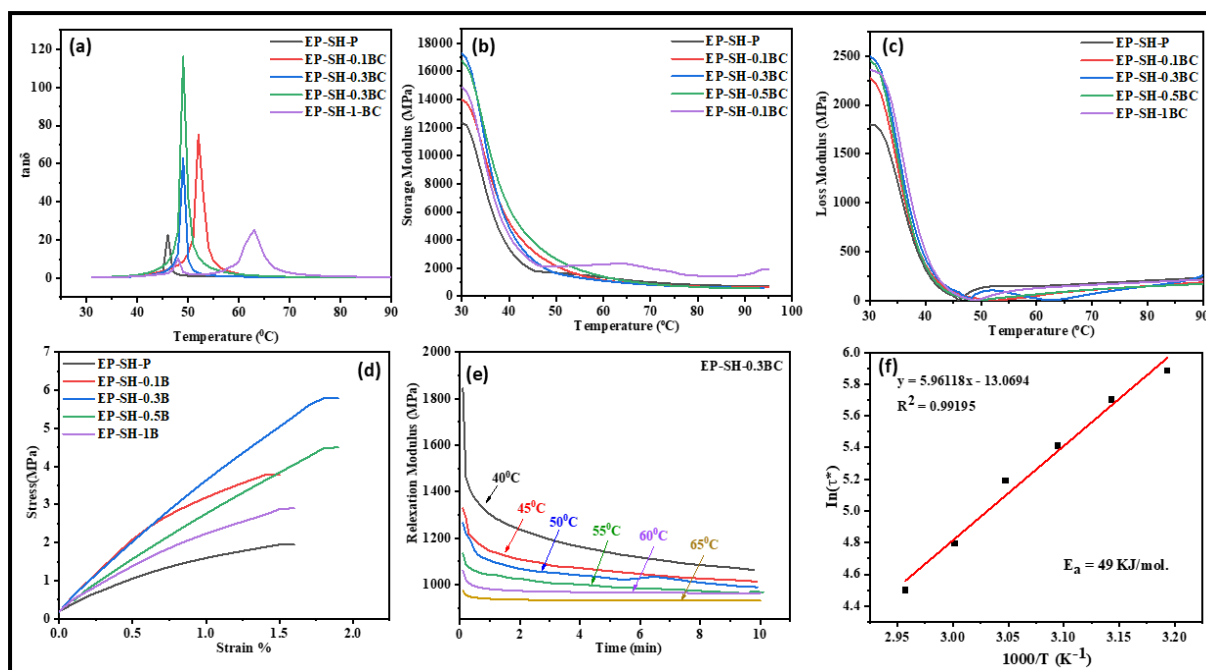


Figure 5.5. (a) Tan del graph of biochar incorporated EP-SH-BC composites, (b) storage modulus of EP-SH-BC, (c) loss modulus plots for EP-SH-BC, (d) Stress-strain graph for EP-SH-BC series, (e) Relaxation modulus for EP-SH-0.3-BC at 40°C, 45°C, 50°C, 55°C, 60°C, and 65°C, (f) Arrhenius plot for the calculation of activation energy of EP-SH-0.3-BC

Table 5.1. Thermal and thermomechanical values of biochar-incorporated composite samples

S. No.	Sample codes	T _g (°C) (DSC)	T _g (°C) (DMA)	T-5% (°C)	T-50% (°C)	Storage modulus (GPa)	Loss Modulus (GPa)	Stress (MPa)
1.	EP-SH-P	30.5	45.0	285.2	366.4	12.3	1.8	1.9
2.	EP-SH-0.1BC	38.4	52.0	305.4	382.1	13.9	2.2	3.7
3.	EP-SH-0.3BC	33.8	48.9	301.1	378.4	17.2	2.49	5.7
4.	EP-SH-0.5BC	32.4	48.8	276.5	359.7	16.7	2.45	4.4
5.	EP-SH-1BC	31.8	47.9	293.4	367.2	14.8	2.3	2.8
6.	EP-SH-0.1-Ni@BC	46.6	45.9	286.2	371.3	13.6	2.0	5.5

7.	EP-SH-0.3-Ni@BC	50.1	46.9	295.5	373.4	19.0	2.4	5.2
8.	EP-SH-0.5-Ni@BC	51.0	47.9	295.4	369.3	24.2	3.6	18.8
9.	EP-SH-1-Ni@BC	53.2	52.9	296.7	376.3	17.4	2.3	15.9

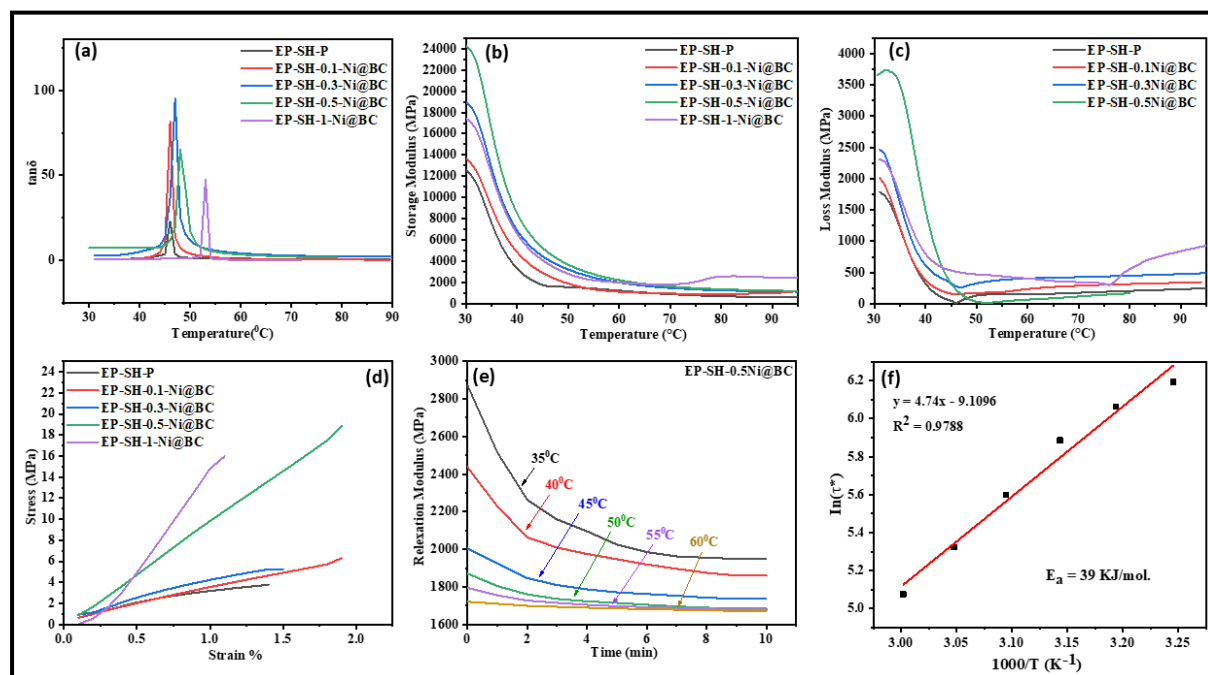


Figure 5.6. (a) Tan del graph of biochar incorporated EP-SH-Ni@BC composites, (b) storage modulus of EP-SH-Ni@BC, (c) loss modulus plots for EP-SH-Ni@BC, (d) Stress-strain graph for EP-SH-Ni@BC series, (e) Relaxation modulus for EP-SH-0.5-BC at 35°C, 40°C, 45°C, 50°C, 55°C, and 60°C, (f) Arrhenius plot for the calculation of activation energy of EP-SH-0.5-Ni@BC

5.3.4. Self-healing and Shape memory

The self-healing and shape memory character of the developed EP-SH vitrimer was examined, and coated glass samples and solid samples of 2mm×4mm×40mm dimension were used respectively. A manual cut with a blade was made on a composite coated on a glass sample and an optical image was captured (Figure 5.7(a)) followed by healing in the presence of microwave irradiation for 3-4 min for all compositions, however, WBC incorporated composites showed delayed healing due to enhanced T_g with the increasing inclusion of WBC

into the matrix. The mechanism behind the healing followed the dynamic transesterification reaction due to the presence of the ester group in the crosslinking agent which is facilitated by catalyst stannous octoate. The role of the catalyst in this reaction is not only to provide feasible activation energy for the crosslinking of epoxy and hardening agent but also to enable the dynamic exchange reaction for healing properties. In addition, as discussed in thermal-mechanical properties, relaxation time was calculated for EP-SH-0.5-B, which signifies and demonstrates the duration the material takes to relax and assist in healing. The matrix has also shown excellent shape memory properties (Figure 5.7 (b)). The developed vitrimer sample was placed in preheated oven at 70°C for 5 min, when the sample attained the desired temperature, it was manually molded into an O shape and kept at room temperature, the sample remained in the same shape as far it was at RT temperature but when it was exposed to its functional temperature(70°C), within 1 min it attained its original shape.

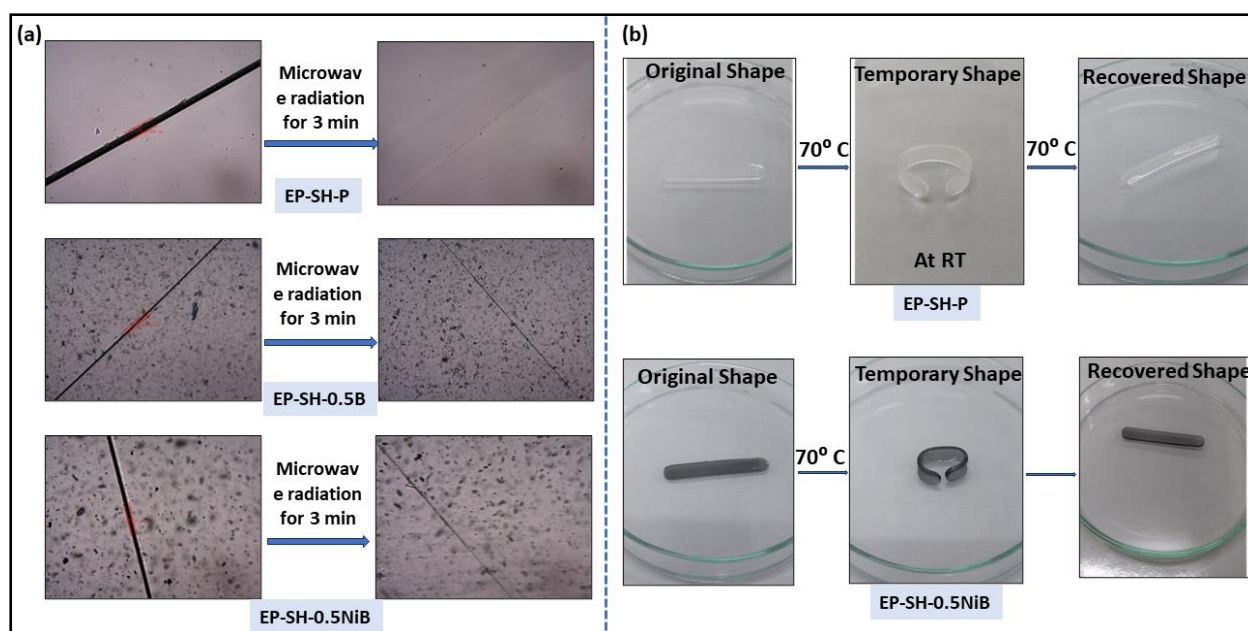


Figure 5.7. (a) Pictorial images of self-healing on the coating surface of the pristine sample, biochar-based sample, and Ni@WBC vitrimer composite samples, (b) Images demonstrating shape memory of pristine sample and Ni@WBC vitrimer composite samples.

5.3.5. Surface Properties

The developed coating sample EP-SH has shown excellent hydrophobic character, as the contact angle for the EP-SH-1Ni@BC reported 120.6° in DI water as compared to pristine coating EP-SH-P which has shown hydrophobicity with a contact angle of 96.3° as reported in Table 5.2 and Figure 5.8. The contact angle samples also showed a significant increase after

adding WBC nano-filler, which can be explained by the surface roughness of the coating, which is explained in Wenzel's theory. The contact angle increases further with the addition of Ni@BC as a nano-filler. According to the Wenzel theory, surface wettability and surface roughness are major factors affecting each other, below 90° wettability increases with contact angle, whereas above 90° wettability decreases with contact angle (Q. Liu et al., 2019) (Meng et al., 2022).

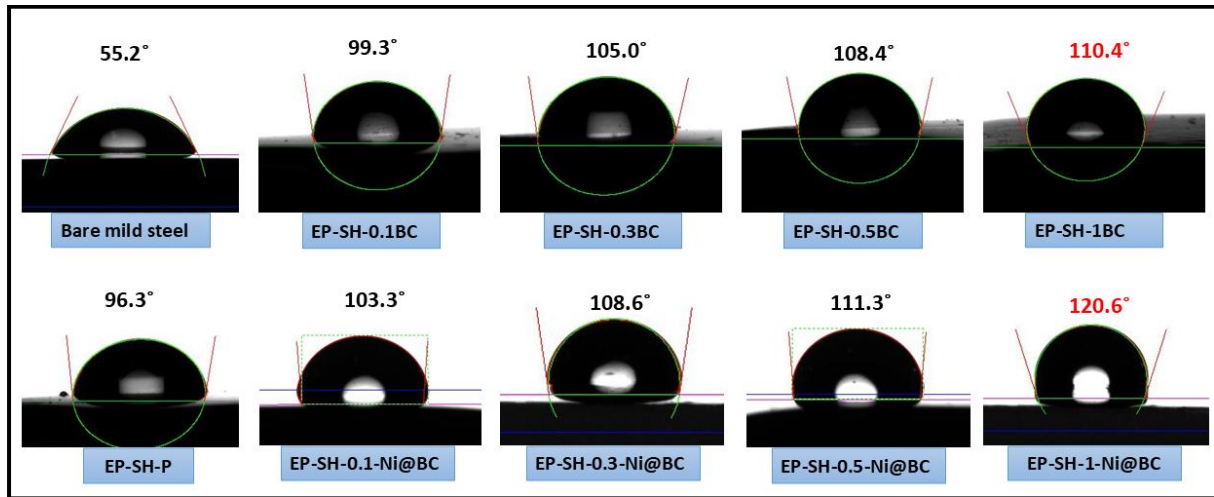


Figure 5.8. The contact angle of various compositions of EP-SH vitrimer-coated samples in DI water

Table 5.2. The contact angles listed for biochar incorporated vitrimer coating in the presence of DI water and saltwater

S. No.	Samples	DI water contact angle (°)			
		0 Sec	120 Sec	350 Sec	600 Sec
1.	Mild steel	55.2±0.8	50.4±0.7	43.9±0.9	38.5±1.1
2.	EP-SH-P	96.3±1.4	91.1±1.1	88.6±0.7	80.9±0.5
3.	EP-SH-0.1-BC	99.3±0.9	96.7±0.6	92.2±0.5	88.3±0.5
4.	EP-SH-0.3-BC	105±1.1	100.4±0.9	93.2±0.6	90.8±0.4
5.	EP-SH-0.5-BC	108.4±1.4	103.1±1.1	98±0.7	94.6±1.0
6.	EP-SH-1-BC	110.4±0.8	106.3±0.7	101.2±0.6	97.5±0.6
7.	EP-SH-0.1-BC	103.3±1.1	99.3±0.9	95.4±0.7	90.2±0.4
8.	EP-SH-0.3-BC	108.6±1.4	103.6±0.7	98.2±0.6	92.1±0.8

9.	EP-SH-0.5-BC	111.3±1.3	109.6±1.1	105.8±0.6	101.0±0.5
10.	EP-SH-1-BC	120.6±1.2	116.3±0.8	112.3±0.7	109.7±0.5

The corrosion inhibition properties of the coating composite were tested using the salt spray method where the coated samples were put in a salt spray chamber for the immersion time of one month. For the testing, a few samples were scratched with a blade and put into the chamber while a few were healed before testing. After one month duration, the coated surfaces were examined using the microscope, where it was observed that unhealed samples were highly corroded near the scratch however the healed samples were barely infected with corrosion as reported in Figure 5.9. In the images, it is observed that Ni-doped biochar-incorporated coatings were highly protected against corrosion as compared to WBC incorporation and pristine coated surfaces.

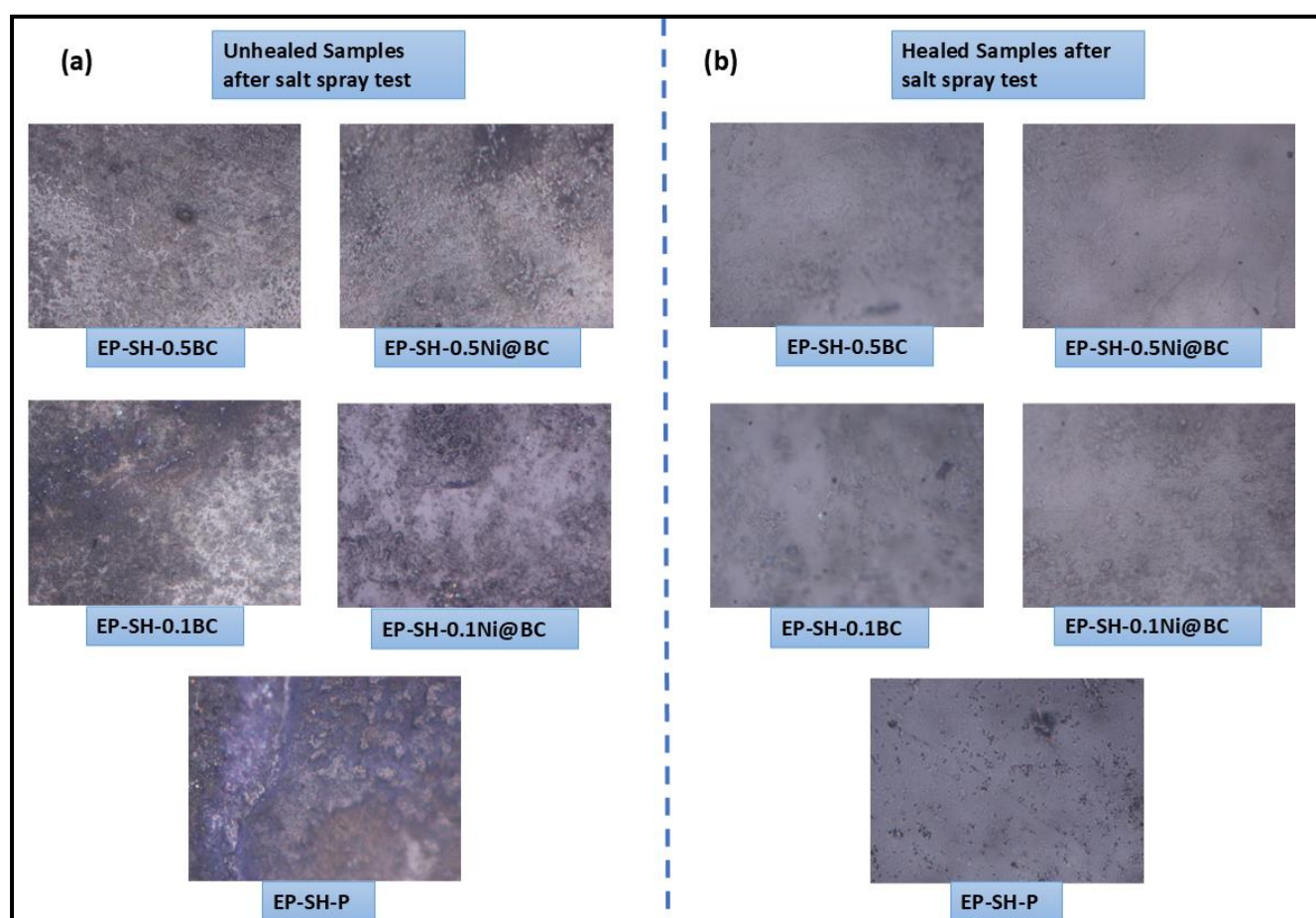


Figure 5.9. (a) Microscopic images of the coated samples when unhealed after the salt pray process (b) Microscopic images of the coated samples after healing the coating in salt spray process

5.4. Conclusion

Ni@WBC incorporated self-healable epoxy composites were developed for the protection against corrosion in marine applications. These sustainable coatings are microwave responsive, which facilitates the fast healing of the damaged area via a localized healing mechanism. The developed coatings exhibit excellent shape memory and self-repairing properties due to dynamic transesterification exchange bond reactions. The thermal stability of the prepared set of composites is reliable along with remarkable thermomechanical properties in terms of storage modulus (24.7 GPa and 17.2 GPa), and fast stress relaxation with 39kJ/mol and 49 kJ/mol for Ni@WBC and WBC incorporation as nano-filler respectively. The coating has demonstrated hydrophobic characteristics with DI water, which collectively concludes these composite coatings as revolutionary ideas for surface chemistry.

CHAPTER 6

Thesis Conclusion

As conclusion, a series of smart vitrimeric epoxy composites were developed as the coating system, which exhibits excellent self-healing properties promoting the lifespan of the network. The composites were incorporated with nano-fillers (GO, rGO, biochar, and Ni-doped biochar) with the purpose of increasing the associated properties of the composite. Self-healable vitrimeric composites comply with the circular economy guidelines of the United Nations, which ensures the effective sustainable utilization of resources, waste management, ensures recycling efficiency of the material throughout its lifespan. Herein, in this generous approach, linseed oil-derived epoxy was used as the base matrix of the composite with rGO in various compositions as the filler, the study reports the reliable enhancement in the thermomechanical properties (20.8 GPa storage modulus and 15.9 MPa stress at 0.9 strain%), where excellent microwave-triggered self-repairability due to fast relaxation via dynamic disulfide bond exchange reaction with the activation energy of 78 kJ/mol and 100% shape-memory was observed along with 99.9% of corrosion protection efficiency with a corrosion rate of 0.41×10^{-4} mm/y due to corrosion inhibition caused by amine-based bio-epoxy/rGO framework synergistic effect. The developed coatings show fast healing in the presence of microwave radiation as a stimuli response within a few seconds due to fast localized heating which facilitates the making and breaking of dynamic covalent bonds and thus forms sulfenyl radicals which leads to chain radical reactions. The incorporation of rGO as a nanofiller enhanced the healing efficiency as well as protection against the corrosive environment due to the formation of labyrinth structures within the matrix, which makes the penetration pathway for corrosive ions even more torturous. The developed coatings were found to be excellent with hydrophobic properties with a 131-degree contact angle. Being derived from bio-based resources makes these coatings a competitive candidate holding sustainability development goals due to their economical approach and recyclability as well as promising mechanical and thermal properties (412° C). To expand the deeper understanding of the crosslinking mechanism of the crosslinking agent used in this study, the work was extended to the comparative study of the ortho and para position of the attached amine group in the amine-based AFD crosslinking agent. This investigation reveals the mechanism behind the difference in the properties exhibited by two sets of composites developed with GO as a nano-filler. Though, both the crosslinking agents were excellent with their healing efficiency and protection barrier properties against harsh corrosive environments, however as the result of this study, 2-AFD was

found to be more promising towards fast self-healing of damage in the presence of microwave radiation, more efficient protection and barrier against the corrosive environment and higher thermal stability up to 320° C. 2-AFD based composite coatings show reliable hydrophobicity with 96.4-degree contact angle and corrosion inhibition properties of 95.4% corrosion efficiency with a corrosion rate of 1.20×10^{-3} mm/year. In addition to disulfide-based chemistry, thiol/transesterification chemistry was also explored as part of this work. In this record, epoxy-828 was crosslinked with a thiol/ester-based composite series and was developed with the incorporation of wood-based biochar and Ni-doped biochar to enhance the feature of these coatings. The report also provides a comparative study for both the bio-resource derived nanofillers. In addition, these networks show magnificent responsive self-healing behavior in the presence of microwave radiation as well as conventional thermal heating, accompanied by reliable thermal stability up to 307° C and thermomechanical properties with 24.2 GPa storage modulus and 18.4 MPa stress at 1.9 strain % for Ni-doped biochar composite. The composite shows notable differences in relaxation performance of composite with 49 kJ/mol activation energy for WBC as nano-filler and 39 kJ/mol for Ni@WBC along with excellent hydrophobicity with the contact angle 110.4 and 120.6 degrees respectively. The 100% shape memory of these composites in the presence of microwave radiation as well as conventional thermal conditions make these composites functional with changes in weathering conditions and protect the substrate surface even while contraction and relaxation process of the coating and crowned as revolutionary candidates for coating application. These coating composites show hydrophobic behavior which indeed helps to reduce the interaction of moisture with substrate leading towards higher corrosion protection. In addition, combining characteristic properties like microwave stimuli self-healing, hydrophobicity, and anti-corrosion makes this composite coating an eminently promising alternative to petroleum-derived coatings for off-shore applications. Microwave-triggered vitrimers need minimal effort to make the coating functional and enhance the life span of the coating and surfaces coated with it. Along with marine environment workability, these smart GO/rGO/WBC-based epoxy vitrimer composites hold potential applications in sensors, supercapacitors, EMI shielding materials, soft robotics, and electronics applications, holding the vast market in the coming future.

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List of Publications

1. **Poonam Singh**, W H. Binder, Pankaj Kumar, R Patel, G J Yin, Sravendra Rana* “Microwave-assisted Self-healable bio-vitrimer/rGO framework for Anti-corrosion applications”, *ACS-Applied materials and interface* (Accepted).
2. **Poonam Singh**, A U M Rao, H Sharma, B. S. Bohra, N G Sahoo, T Dagar, Sravendra Rana*, RajKumar Patel* “Microwave-assisted self-repairable vitrimeric coating for anti-corrosive applications”, “*Progress in Organic Coatings*”, Volume 191, June 2024, <https://doi.org/10.1016/j.porgcoat.2024.108411>
3. **Poonam Singh**, A Rana, N Karak, I Kumar, Sravendra Rana,* Pankaj Kumar,* “Sustainable smart anticorrosion coating materials derived from vegetable oil derivatives: A review”., *RSC Advances*, 13 (6), 3910-3941. DOI: [10.1039/D2RA07](https://doi.org/10.1039/D2RA07)

Other Publications

1. B. S. Bohra, **Poonam Singh**, A Rana, H Sharma, T Arya, M Pathak, A Chaurasia, Sravendra Rana, N G Sahoo, “Specific functionalized graphene oxide-based vitrimer epoxy nanocomposites for self-healing applications”, *Composites Science and Technology*, volume 241, 18 August 2023, 110143. <https://doi.org/10.1016/j.compscitech.2023.110143>
2. N Kaushik, **Poonam Singh**, Sravendra Rana, N G Sahoo, F Ahmad, M Jamil, Self-Healable Electromagnetic Wave Absorbing/Shielding Materials for Stealth Technology: Current Trends and New Frontiers, *Materials Today Sustainability*, 2024/5/16, <https://doi.org/10.1016/j.mtsust.2024.100828>
3. S Rana, SP Sanka, **Poonam Singh**, AK Mishra, P Kumar, M Singh, N G Sahoo “Self-healing nanocomposites via N-doped GO promoted “click chemistry” , *Soft Matter*, 2023, 19, 98-105. DOI: [10.1039/D2SM01423H](https://doi.org/10.1039/D2SM01423H)

Conferences

1. **Poonam Singh**, Pankaj Thakur, Sravendra Rana, "Specifically modified bio-char infused epoxy-based vitrimeric thiol frameworks for anti-corrosive coatings" in 85th Prague Meeting on Macromolecules and 11th Conference GCNPM-2024, 24-28, June Prague, Czech Republic

- 2. Poonam Singh,** Harsh Sharma, Viranchika Bijalwan, Pankaj Kumar,* Sravendra Rana* “Linseed oil derived self-healable anti-corrosion coatings” in CHEMCON-2022, **HBTI-Kanpur**
- 3. Poonam Singh,** Akula Uma Maheshwar Rao, Tanya Dagar, Aman Choudhary, Pankaj Kumar, Sravendra Rana* “Preparation and Characterization of Graphene-oxide Promoted Vitrimers for Corrosion Inhibition Coatings” in Sustainability fair-2022 in Total Environment Research Theme, **UPES, Dehradun**
- 4. Poonam Singh,** Sravendra Rana, Vegetable oil derived self-healable anti-corrosive coatings ‘International Young Researcher Conclave’-2023, **UPES, Dehradun**
- 5. Poonam Singh,** Pankaj Kumar,* Sravendra Rana* “Microwave Triggered Self-Healable Coatings for Anti-Corrosive Applications” in ICNIB-2023, **Dehradun**
- 6. Poonam Singh,** Sravendra rana*, in Sustainability Conference on HSFEA-2023, **Dehradun**
- 7. Poonam Singh,** Pankaj Kumar,* Sravendra Rana* “Microwave Triggered Vitrimeric Hydrophobic Coatings for Anti-Corrosive Applications” in Nainital two days workshop-2023, **Nainital**

APPENDICES

Compositional details of ELA-x%-rGO:

Reduced graphene oxide was dispersed in ethanol through ultra sonication for 30 min and added in different compositions in epoxidized linseed oil at 80° C with vigorous stirring (Table 1). After evaporation of ethanol and uniform dispersion of rGO in the matrix 38 wt % of 4-AFD was added to it. Further, stirred for another 15 min for uniform homogenous mixing of hardening agent and poured into PTFE mold and coated on glass and metal substrate.

Table A3.3. Compositional details of ELA-based vitrimeric composites

S.NO.	SAMPLE	EXPERIMENTAL COMPOSITION OF EPOXY RESIN	
		4-AFD	rGO%
1.	ELA-P	38%	-
2.	ELA-0.1-rG	38%	0.1%
3.	ELA-0.3-rG	38%	0.3%
4.	ELA-0.5-rG	38%	0.5%

Chemical structures of GO and rGO Structures.

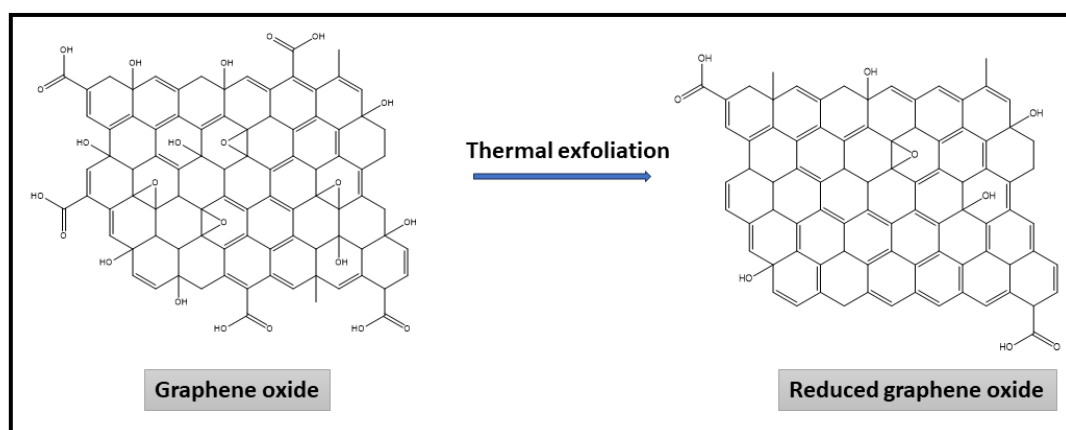


Figure A2: Chemical structure of graphene oxide (GO) and reduced graphene oxide(rGO).

Characterizations of synthesized GO and rGO nano-sheets:

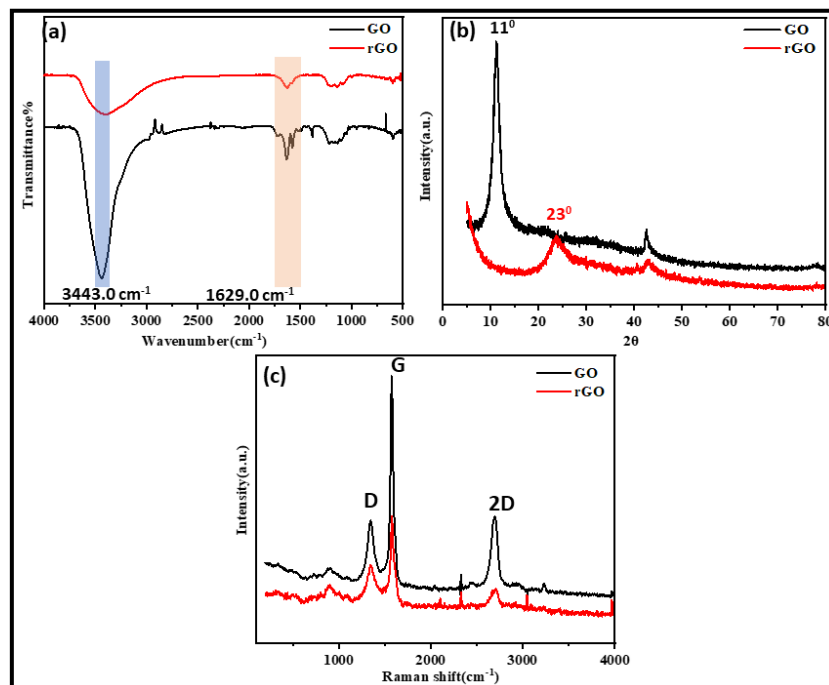


Figure A2:(a) FT-IR of synthesized GO and rGO (b) XRD spectra of GO and rGO (c) Raman analysis of GO and rGO

Oxirane Number (O.N.) Calculation:

Equation for the oxirane number calculation can be given by

$$O.N. = \frac{1.6 \times N \times (V - B)}{W}$$

Where, N is Normality of HBr used in titration, V is the volume of HBr used in titrating epoxy sample, B is Vol of HBr used in titrating blank potassium hydrogen phthalate standard solution and W is the weight of synthesized epoxy used in sample titration.

N=0.09 g/L

V=37.98 mL

B=10.9 mL

W=1 g

$$O.N. = \frac{1.6 \times 0.09 \times (38 - 10.9)}{1}$$

O.N.=3.9

Oxirane number for synthesized epoxidized linseed oil is found to be 3.9 g eq in 100 g of resin.

Synthesis of epoxidized linseed oil from linseed oil

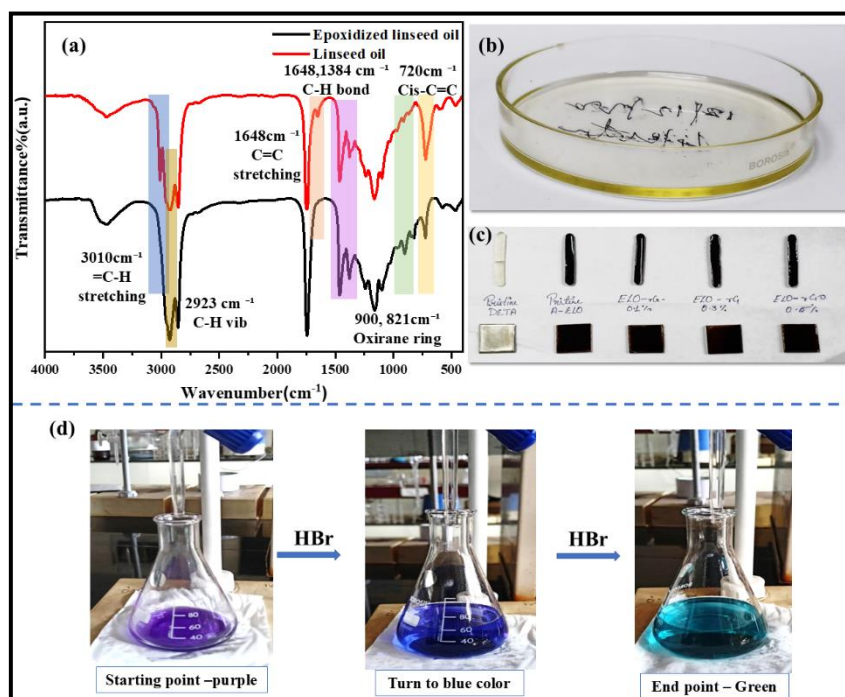


Figure A3: (a) FT-IR spectra of linseed oil and epoxidized linseed oil (b) synthesized epoxidized linseed oil (c) samples prepared from vitrimer material and coated over SS-216 (d) titration color change for oxirane number calculation for epoxidized linseed oil.

H¹-NMR spectra of Linseed oil and Epoxidized linseed oil

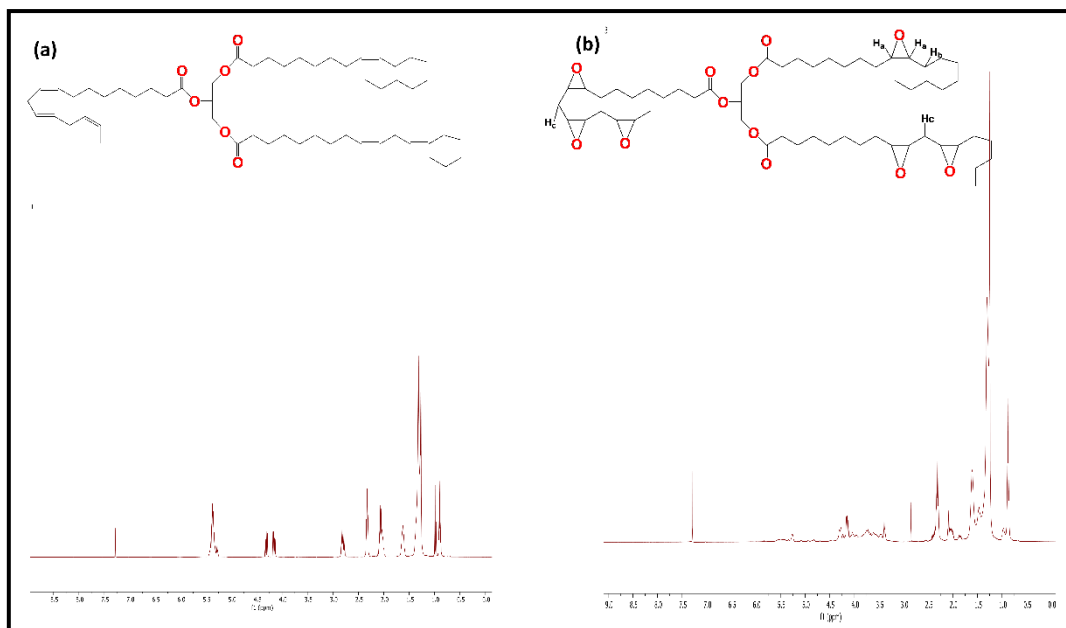


Figure A4: (a) H^1 -NMR spectra of the linseed oil and (b) epoxidized linseed oil

Tan δ vs temperature curves of Prepared vitrimeric materials:

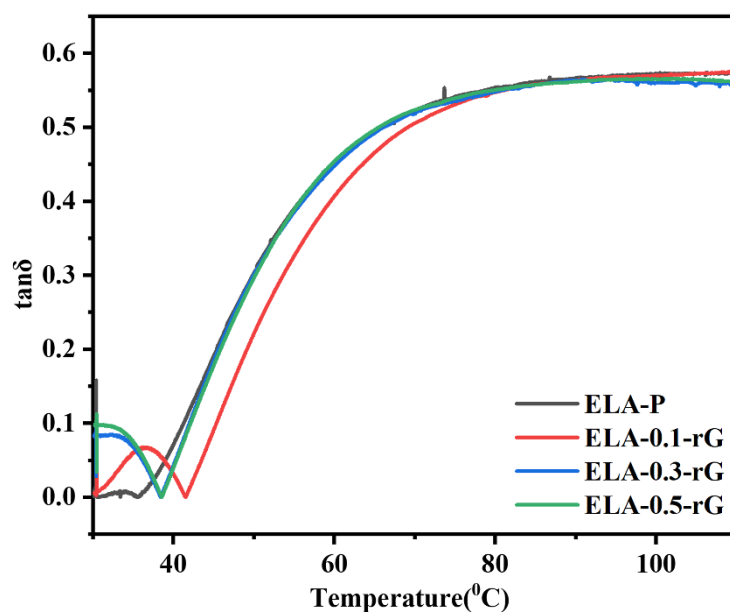


Figure S5. Tan δ vs temperature curve for various vitrimeric composite

Calculation of topological freezing transition temperature (T_v)

Maxwell equation was used to calculate T_v ,

$$\eta = G \cdot \tau^* \quad (\text{maxwell equation})$$

G- Shear viscosity modulus;

Shear modulus and tensile modulus relation is given as,

$$G = E' / 2(1+\nu) \quad (S3)$$

For rubbery materials ν - Poisson's ratio is usually 0.5, from figure 3(a) in the storage modulus plot, the average tensile modulus was reported in the temperature range 40-70°C, and the obtained value the value 2326.4 MPa.

$$\text{So, } G = 2326.47/3 = 775.49 \text{ MPa (or) } 775.49 \times 10^6 \text{ Pa}$$

To Tv calculation, viscosity value arbitrary has been taken as: $\eta = 10^{12} \text{ Pa.s}$.

$$\tau^* = 10^{12} / (775.49 \times 10^6) = 1289.50 \text{ s.}$$

$$\ln(\tau^*) = \ln(1289.50) = 7.16.$$

$$\text{Equation obtained from Arrhenius law: } \ln(\tau^*) = 9350.3x - 28.693$$

$$x = 1/T = (7.16 + 28.69) / 9350.3 = 0.00383 \text{ K}$$

$$\text{So, } T = 1/0.00383$$

$$T_v = 261.09 \text{ K (or) } -12.06^\circ \text{C}.$$

Calculation of shape memory:

$$\text{Initial Deformation angle } \theta_i = 180^\circ$$

$$\text{Change of angle } \theta_f = 0^\circ$$

So,

Recovery ratio based equation is,

$$R_r = ((\theta_i - \theta_f) / \theta_i) * 100\%$$

$$R_r = ((180 - 0) / 180) * 100\%$$

$$R_r = 100\%$$

The stress-strain plot of healed vitrimer samples up to two cycles

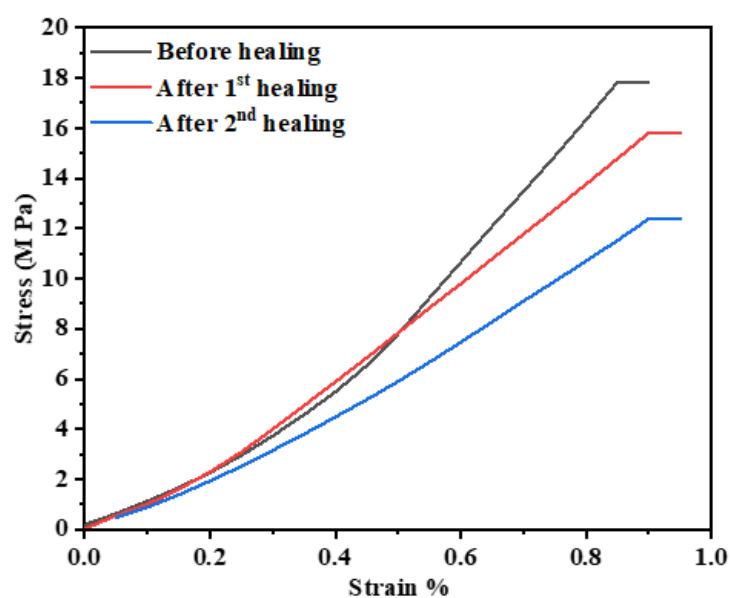
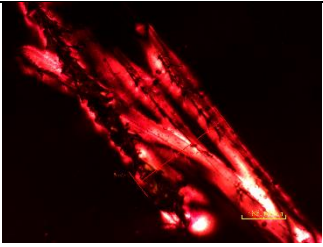
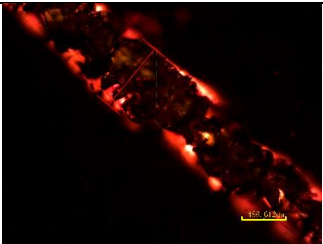
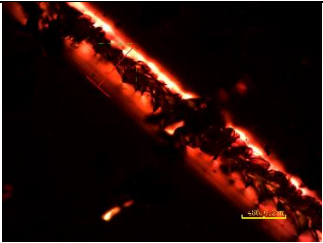
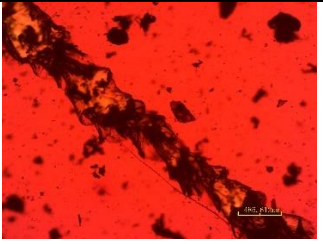
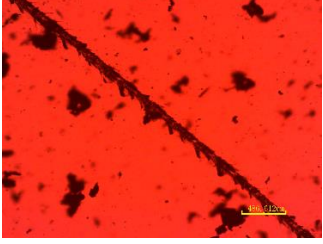
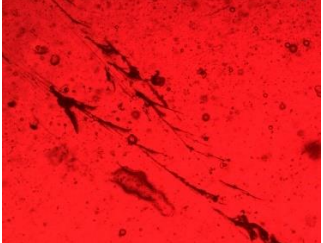


Figure A6: The stress-strain curves of ELA-O.1-rG composite after two healing cycles

Table A4: Progress in healing process of ELA-0.3rG with time in the presence of microwave radiation

S.No.	Sample healing time	Healing Progress(images)	Healing efficiency (%)
1.	0sec		0%

2.	30 sec		50%
3.	60 sec		70%
4.	90 sec		80%
5.	120 sec		90%
6.	180 sec		98%

Contact Angle of DI water on vitrimeric coating samples

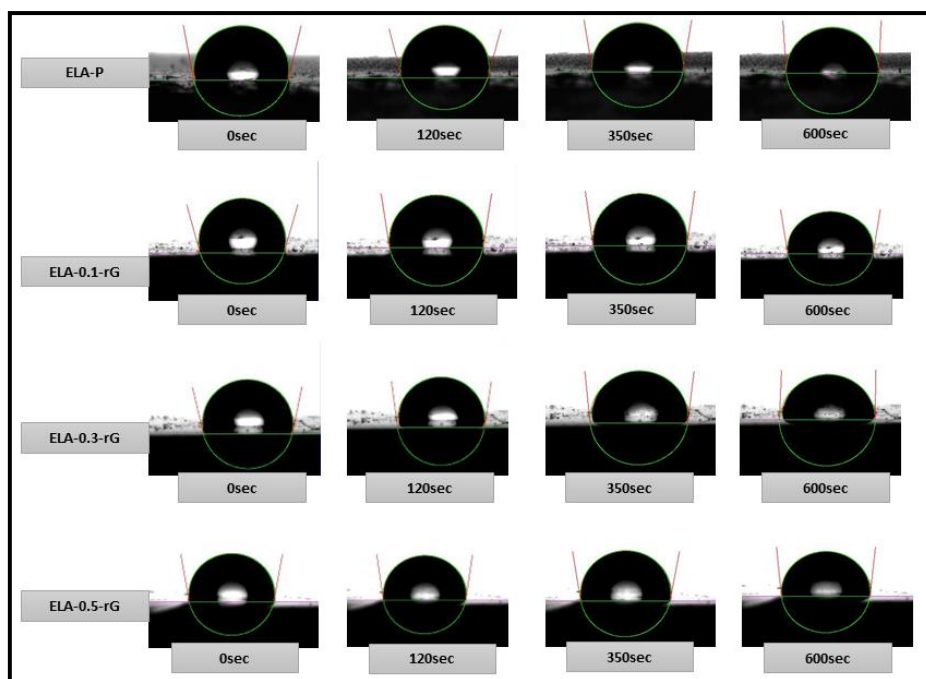


Figure A7: Microscopic images of DI water contact angle on DSA of different compositions of vitrimeric coatings with respect to time

Contact Angle of salt water on vitrimeric coating samples

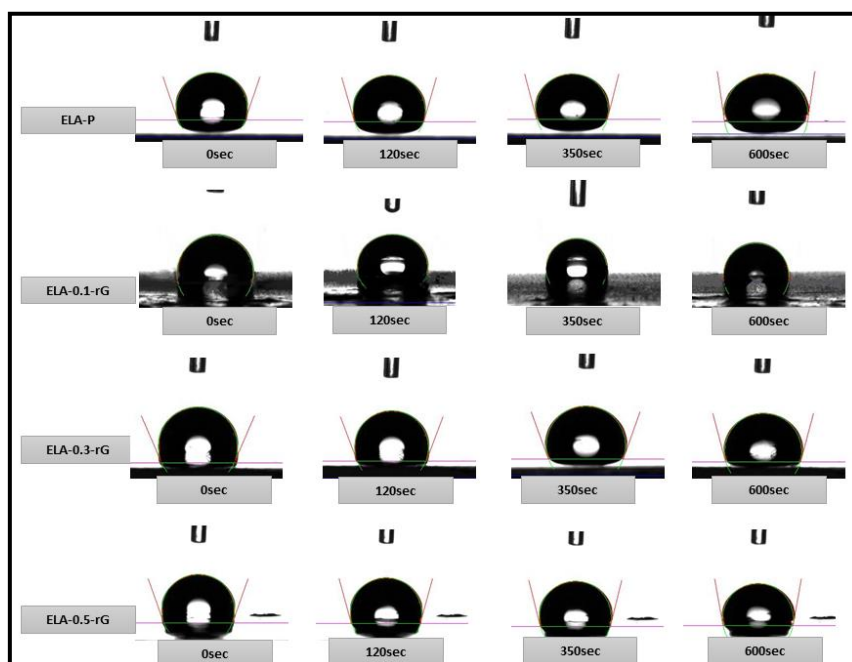


Figure A8: Microscopic images of salt water contact angle on DSA of different compositions of vitrimeric coatings with respect to time

Correlation between roughness and contact angle

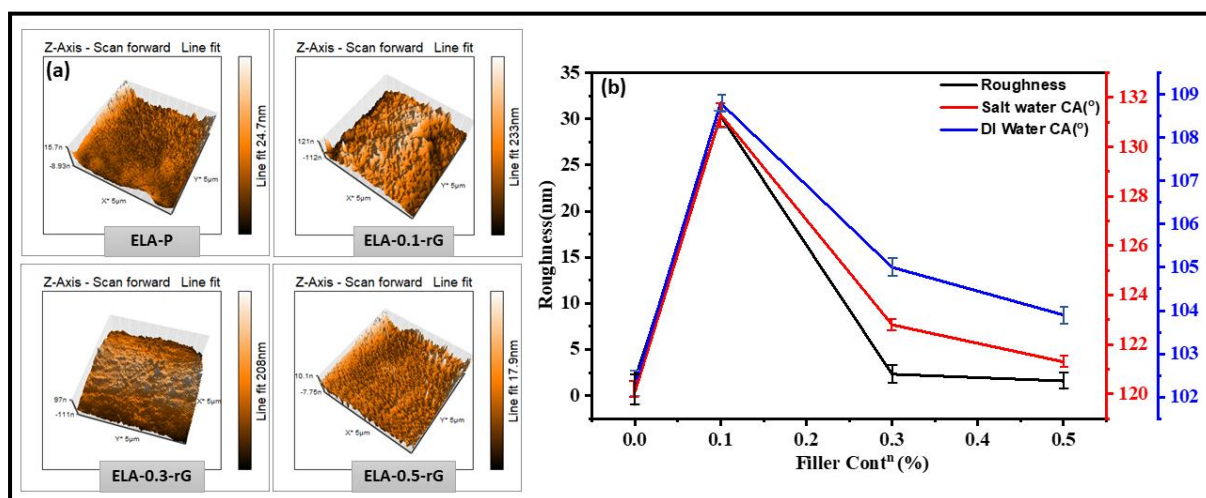


Figure A9:(a) AFM images of vitrimer coating composite for surface topology study. (b) Graphical representation of the correlation between the roughness (AFM) of coated surface and the contact angle in salt and DI water.

Morphological study of vitrimer coatings before and after corrosion

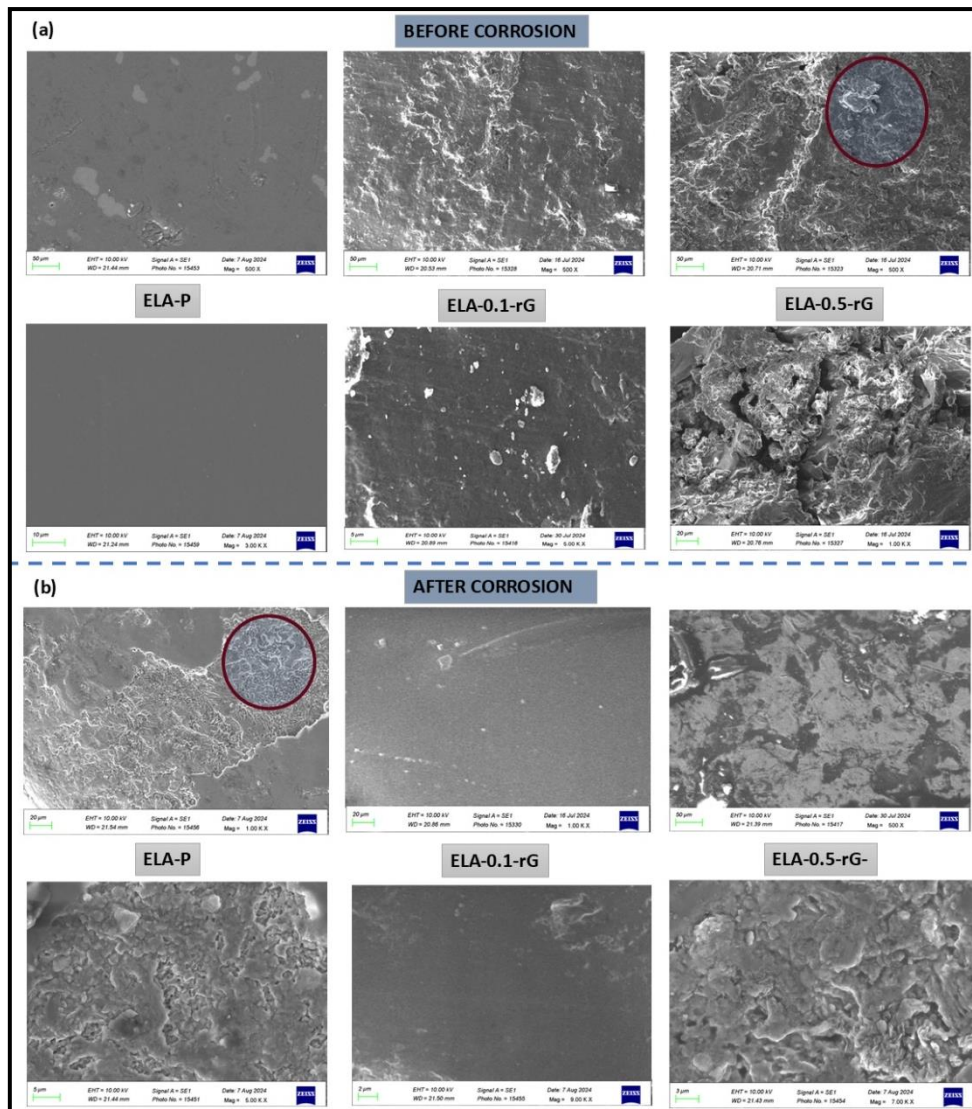


Figure A10: (a) SEM images of coating surface before NaCl immersion for corrosion test with ELA-P, ELA-0.1-rG and ELA-0.5-rG (b) SEM images of coating surface after corrosion test with ELA-P, ELA-0.1-rG and ELA-0.5-rG.

thesis

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