



# Graphene/Epoxy based barrier coatings for corrosion protection: A Review

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**Abstract:** Due to the excellent properties like including flexibility that allows it to adjust to the substrate surface, chemical inertness, and impermeability, Graphene play key role to preventing of corrosion and improved adhesion property. Its distinctive band structure and physical properties determine its wide range of applications. In this, review article we describe how different study shows the effect of graphene in anti-corrosion system protection. It provides detailed information about the graphene coatings by different methods, graphene-based organic coatings, the modification of graphene-based coatings, and the effects of graphene functionalization on the corrosion resistance of protective coatings.

**Key word:** Corrosion, Graphene, Modified Graphene Oxide, Corrosion Resistance, Polymer Composit

**Introduction:** Corrosion is degradation process of metal, when chemicals are exposed in the environment. In the another word corrosion is simple electrochemical reaction<sup>1-3</sup>. Metal corrosion leads the economic and environmental losses. Corrosion is not only restricted with air but also saw in various type of water, and gases in environment. Organic coatings are the majority used method to prevent metallic corrosion from environment<sup>4-5</sup>. Metal surface is coated generally by thin films, as consequence corrosive agents are stopped from reaching the metal surface<sup>6-9</sup>. Moreover, Pigments could act as anticorrosive inhibitor to increase the corrosion resistance of metallic surface. Based on the anticorrosion mechanism, pigments are widely use for coating agent.<sup>10-13</sup> Active inhibitor<sup>14-16</sup> and sacrificial<sup>17</sup> which are used to develop coatings with outstanding performance on metallic substrate.

Graphene (GR) is a very important discovery after fullerene and carbon nanotube. In the field of corrosion, it is creating greatest impact in world because of it has some fantastical chemical and physical properties. Graphene containing material are the good anticorrosive agent because of their superior barrier property<sup>18-20</sup>. Graphene is a monolayer of graphite sheet which shows the great mechanical power, chemical strength and compactness<sup>21-23</sup>. It is composed with compact sp<sup>2</sup> hybridized carbon atom in to honeycomb crystal structure<sup>24</sup>. The graphene was first isolated by micromechanical cleavage of graphite<sup>25</sup>. For improvement of this method second method was developed, which is a chemical cleavage of graphite<sup>26</sup>. Single/multi-layered Graphene and

chemically implemented and Graphene have an extensive research<sup>27-29</sup>. Graphene is used as various materials like (i) single-layer Graphene (SLG), (ii) multi-layer Graphene (MLG), (iii) Graphene platelets, (iv) Graphene oxide (GO), (v) Reduced Graphene oxide (RGO)<sup>30</sup>. The theoretical specific surface area of graphene is up to 2600 m<sup>2</sup>/g<sup>31</sup>. It has outstanding thermal conductivity (3000 W/(m\$K)), as well as high speed electron mobility (15000 cm<sup>2</sup>/(V\$S)) at room temperature. Its mechanical stress reaches to 1060 GPa<sup>32</sup>, while the density is only 2.2 g/cm and it was 100 times stronger than that of the best steels in the world. Graphene and graphene base coating (fig-1) have long range application in various filed like photovoltaic device, solar-cells, use as catalysts like electro catalyst, carbon catalyst, use as energy storage device in batteries, use as antibacterial and drug delivery in biomedicine<sup>33</sup>.

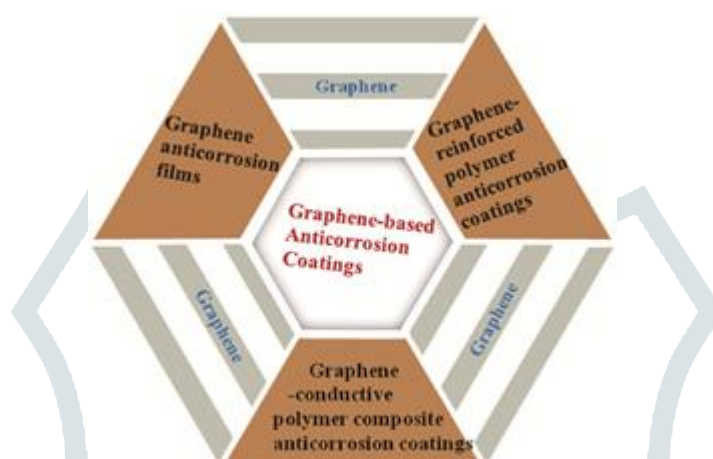


Fig 1 application of graphene base coating.

This paper systematically summarizes the great potential applications of graphene in the field of metal corrosion protection, graphene anticorrosion films, graphene/organic anticorrosion coatings, graphene/Inorganic anticorrosion coatings and graphene/polymer anticorrosion coatings. In spite to corrosion protection, graphene coatings have been applied as flame-retardant coatings, wear/scratch-resistant coatings, antifouling coatings, pollutant-adsorption coatings, and antiseptic coatings.

### Graphene-based anticorrosive coatings:

Pourhashem et al. studied that polycrystalline graphene (PG) use as anti-corrosion agent with epoxy coating. The result saw that the using nanocomposite coating give better results than the pure epoxy. Also results saw PG sheet has some good property and increase of hydrophilicity. Theory approach like quantum and DFT calculation are also give better results in PG than pure epoxy<sup>34</sup>.

Chen et al. try to make a new petter on graphene base nanocomposite and epoxy polymer combine with organic coating and get a good physicochemical property over pure polymer. they use organic material such as poly(2-butylaniline) (P2BA) and act as dispersing agent. In between Graphene nanosheet and P2BA has saw the non-covalent  $\pi$ - $\pi$  interactions. The graphene structure was identified in SEM(fig-2), TEM, XRD and AFM. On results of XRD was very clear about remarkably improved anticorrosion performance and wear resistance

properties and high mechanical and barrier properties of well-dispersed graphene nanosheets in the epoxy material<sup>35</sup>.

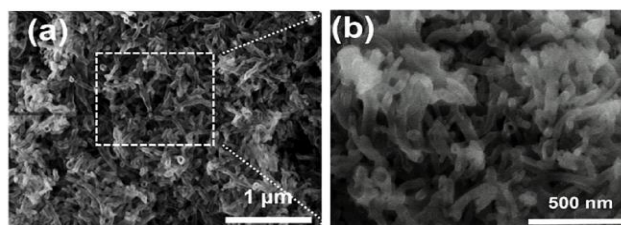


Fig 2 Morphology and texture of P2BA.

The anticorrosive effect of graphene oxide and reduce graphene oxide (RGO) with waterborne polyurethane (PU) use as anti-corrosive agent has been studied. Different type of % solution with PU coating are determined in Electrochemical Impedance Spectroscopy (EIS) (fig-3,4) and salt spray tests(fig-5). composite coatings showed improved anticorrosive properties, compared to neat PU coatings. Reduce graphene oxide have better anti-corrosive property. The EIS graph show that mixture of GO and PU has good barrier property.

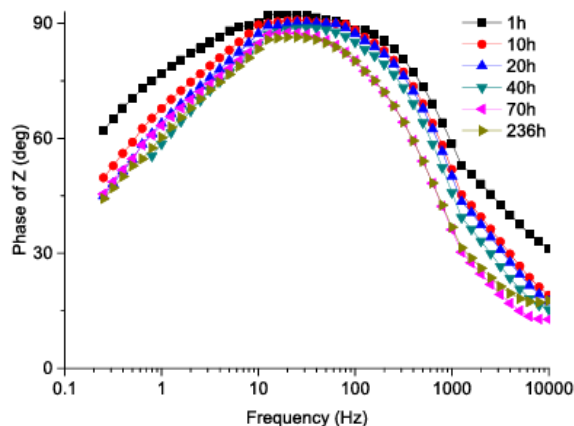


Fig 3 EIS spectra of 0.2 wt % GO reinforced PU composite coatings.

RGO had lower surface functionality and hydrophilicity than GO, which was further improvement by anticorrosive properties for RGO/PU coatings, compared with GO/PU coatings. Salt spray test are also confirmed that RGO/PU are better anti corrosion behaviour than the GO/PU coating<sup>36</sup>.

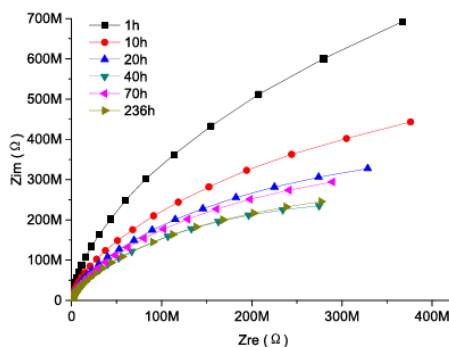


Fig 4 EIS spectra of 0.2 wt % RGO reinforced PU composite coatings

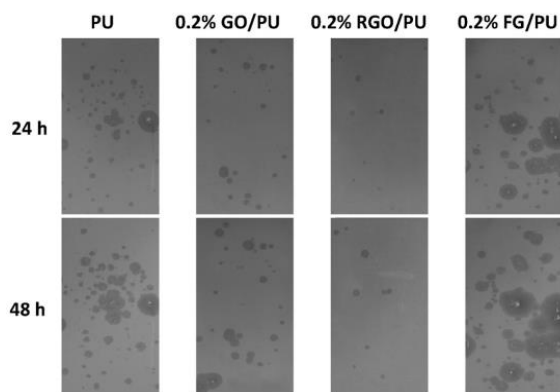
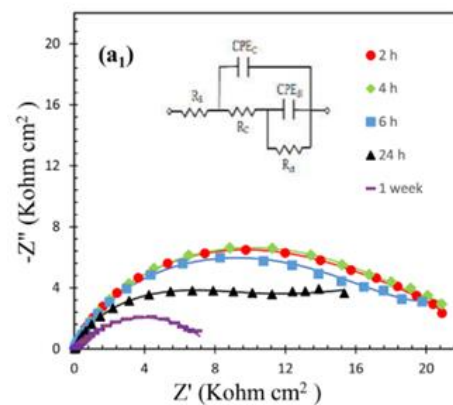


Fig 5 images of coated EG samples.

Saurav et al. Devalope New functionalized graphene oxide [FGO] nanocomposite of graphene oxide (GO) was coated by 4-nitro aniline ans it was characterised by SEM, FT-IR, RAMAN, NMR and XRD. The anticorrosion property was studied by using electrochemical impedance spectroscopy (EIS) and Thermogravimetric-Differential Thermal Analysis (TG-DTA) technique use for monitoring of thermal property of FGO. The FGO and epoxy coating are increase barrier property and ionic resistance of coating. Moreover, they reduce corrosion performance and electrolyte diffusion into the coating<sup>37</sup>.

Yang et al. used carboxylic acid with epoxy coating 3, 4, 9, 10- perylene tetracarboxylic acid-graphene (PTCA-G) composite was prepare by using by graphene and carboxylic acid. In composite saw  $\pi$ - $\pi$  interactions and hydrophobic forces between PTCA-G and graphene. This was confirmed by FT-IR. They are use PTCA-G/epoxy in different ration and examine the chemical and anticorrosion behaviour. In 10:4 volume ratio of PTCA-G/epoxy give best results and it is analysis by SEM, TEM. The Electrochemical measurement get results in favour of PTCA-G/epoxy then the pure epoxy coating. The PTCA-G/EP showed most superior corrosion protection efficiency<sup>38</sup>.

Graphene oxide(GO) nanosheets/polyaniline/zinc composite was synthesis route show in fig-6 and than it characterized by SEM,FE-SEM,X-ray diffraction (XRD) analysis and Raman spectroscopy. Anticorrosion study was examining by the EIS and salt spray test. Filling the epoxy coating with GO-PAni-Zn resulted in the coating active inhibition and barrier properties enhancement simultaneously<sup>39</sup>.



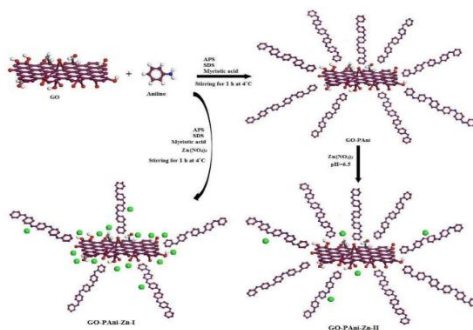


Fig 6 preparation digram of the GO-PAni, GO-Pani-Zn-I, GO-PAni- Zn-II.

Electrochemical measurements were applied on the epoxy coatings without defect to investigate their barrier anticorrosion properties in saline electrolyte after 48 h, 1, 5, 6, 9, 10, and 11 weeks. by this technique the scratched coatings protection properties were analysed after 2, 4, 6, 24 h and 1-week immersion (fig -7).

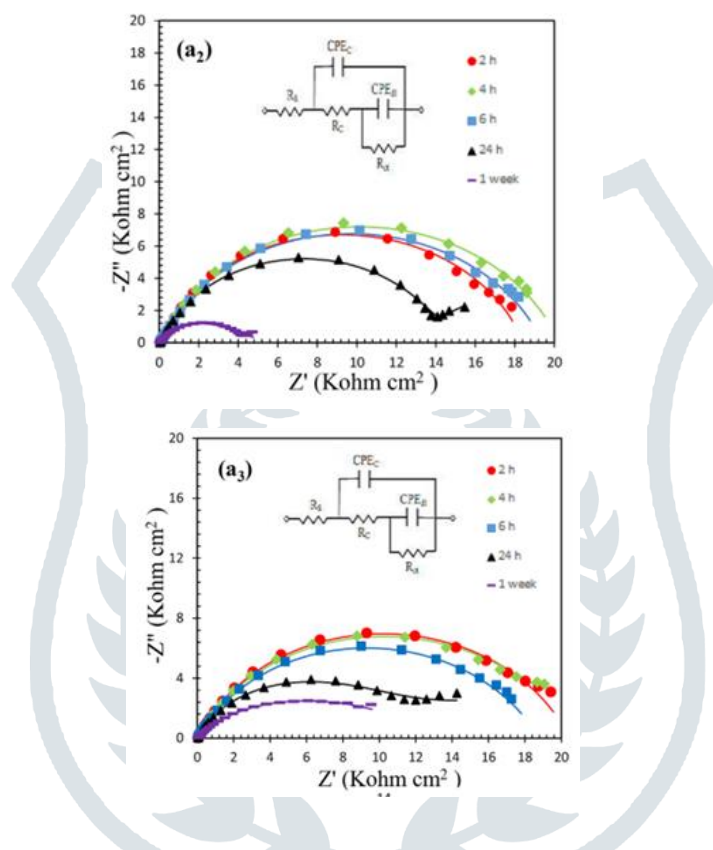


Fig 7 coating system (a1) EP, (a2) EP-GO, (a3) EP-GO-PAni, and with an artificial defect immersed in the 3.5 wt % NaCl solution for different immersion times.

GO-nanosheet modified with silane coupling reagents such as 3-aminopropyl triethoxysilane (APTES) and 3-glycidyloxypropyl trimethoxysilane (GPTMS) with amine and epoxy groups. Characterization of f-GO nanosheets done by FTIR, FS-SEM XRD. Results are very clear about that silane coating was improve adhesion metal and enhance water angle. Electrochemical analysis is also confirmed APTES-GO increases corrosion resistance property. Salt spray test results was show in fig-8. Moreover, the type of silane coupling agent based on different functional groups have great effect on the properties of coatings<sup>40</sup>.

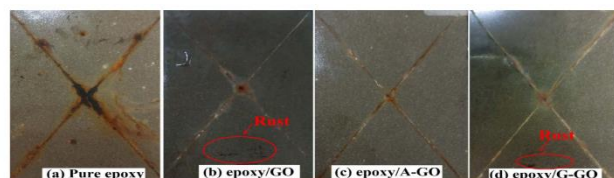


Fig 8 (a) pure epoxy, (b) epoxy/GO, (c) epoxy/A-GO, and (d) epoxy/G-GO coatings after 300 h exposure to salt spray test.

A series of SiO<sub>2</sub>-GO hybrids (fig-9) with anchoring silicon dioxide (SiO<sub>2</sub>) on graphene oxide. Furthermore, it was assembled with 3-aminopropyltriethoxysilane (ATPS) and 3-glycidypropyltrimethoxysilane (GTPS) and study anticorrosion behavior. Morphology was studied by EIS, UV-visible, HR-TEM. Results show that SiO<sub>2</sub>-GO ratio of (1:5) give better anticorrosive performance of epoxy coatings<sup>41</sup>.

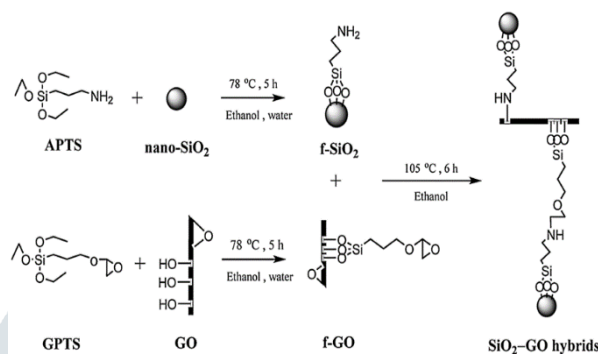


Fig 9 preparation of SiO<sub>2</sub>-GO hybrids.

Cerium oxide (PANI-CeO<sub>2</sub>) was modified by polyaniline (PANI) with graphene oxide and increases the performance of epoxy as anticorrosive agent. Further it was synthesized Layer-by-Layer. epoxy matrix was characterized by FTIR, FE-SEM (fig-10), XRD, X-ray photoelectron spectroscopy, and Thermal gravimetric analysis (TGA). EIS and salt spray test results of GO-PANI-CeO<sub>2</sub> matrix gave better performance against corrosion and improved barrier property of mild steel<sup>42</sup>.

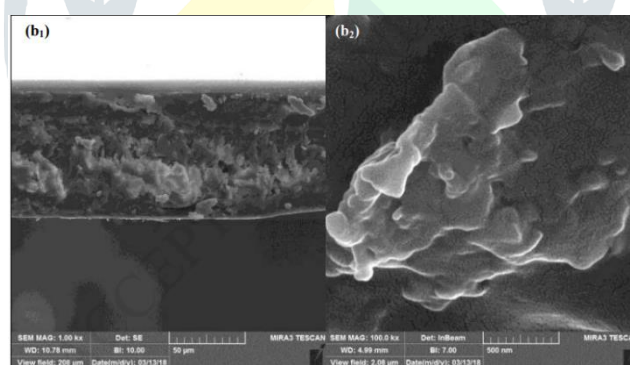


Fig 10 FE-SEM images GO-PANI-CeO<sub>2</sub>/Epoxy.

Graphene oxide mixed with poly(urea-formaldehyde) and GUF composites was prepared in different five wt % solution. GUF with epoxy (GUF/EP) was studied under the transmission electron microscopy TEM, SEM, FTIR, and sedimentation test. Results were clear at 8.6 wt % sample gave high barrier property against corrosion. Electrochemical impedance spectra give results in favour of 8.6%wt GUF/epoxy. Experimental results proved that the novel GUF composites enhanced the barrier property of epoxy coating<sup>43</sup>.

Bautin and co-workers used graphene oxide (GO) as an additive in the process of phosphating of 08YU (DC04) to improve its corrosion properties. It was found that the increasing of GO concentration in

phosphating solution was improve the anticorrosion properties of the phosphate coatings in neutral NaCl solutions at optimal concentration 0.3g/L of GO. But in acidified ( $\text{Na}_2\text{SO}_4$ ) solution corrosion rate of 08YU steel was increased<sup>44</sup>.

Composite coating containing three different percentages of reduced graphene oxide particles were compared with pure epoxy and bare samples. It showed more anticorrosive property compared with pure epoxy coating<sup>45</sup>. The OCP and EIS results revealed that 1.0 wt% reduced graphene in epoxy coating showed better anticorrosive characteristic in pure solution medium containing 0.5 M NaCl solution showed in fig 11.

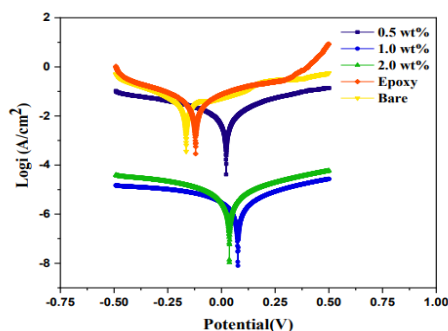


Fig 11 Polarization graph of mild steel coated with EP.

The bioinspired graphene epoxy (B-G-EP) coating in homogeneous distribution and alignment showed greatly increased anticorrosion performance. Because of It's construction of nacre like structure, and B-G-EP exhibits the corrosion promotion activity<sup>46</sup>.

Polypyrrole functionalized graphene oxide (GO-PPy) had been synthesized by situ process to grow polypyrrole (PPy) film on graphene oxide (GO) surface. They introduced in- situ polymerization process to synthesize nanoscale additive for waterborne epoxy (WEP) coatings. Morphology was of matrix image was show in fig-12 by SEM technology. Among the combination of two mass ratio of GO-PPy nanocomposite into the WEP coatings, GP0.05% coating convey the best impermeable and anticorrosive performance compare to other coatings<sup>47</sup>.

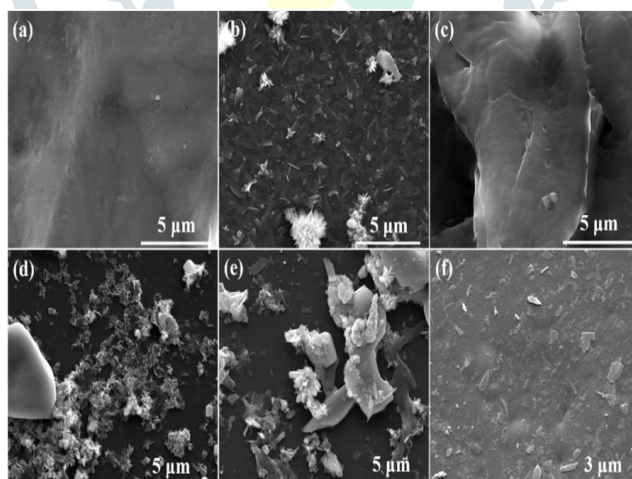


Fig 12 SEM images of mild steel beneath (a) pure epoxy, (b) PPy0.05%, (c) GO0.05%, (d)G2P0.05% and (e-f) GP0.05%.

Zhiyi et al. Reduce Graphene oxide was modified by Polyvinylpyrrolidone which could be scattered and revealed good adherence property with epoxy resin matrix with 0.7 wt % loading of PVP- rGO. The mechanical and thermal properties of epoxy resin coating were significantly improved, with increase in Young's modulus and thermal stability of around 21.3% and 73°C respectively. Furthermore,

erosion resistance of graphene nano sheet based epoxy resin coating was also investigated by the electrochemical measurements and immersion corrosion experiment in NaCl solution respectively and it showed that the graphene nanosheet based epoxy resin coating with greater mechanical and thermal properties was more resistance to erosion<sup>48</sup>.

Ambrosi and Pumera revealed that graphene is highly promising, low-cost, and transparent anticorrosion coating material that has just emerged. But it is demonstrated here that a multilayer graphene sheet formed on Ni by chemical vapour deposition fails suddenly under galvanic corrosion condition<sup>49</sup>.

Hung et al. synthesized polypyrrole-based nanocomposites doped with graphene oxide, molybdate, and salicylate (PPy/GO/Mo/Sal) via in situ electrochemical polymerization to increase the anti-corrosion property of polymer coatings. The results showed that the morphology of the nanocomposites were changed when GO was incorporated into polymer coatings with the presence of both molybdate/salicylate and GO in the PPy matrix which reveal the excellent anticorrosive property against corrosion for low carbon steel. In addition the doping of both salicylate/molybdate and GO resulted in improved wrapping of GO by PPy spheres, there for it show better dispersion of GO in Polymer matrix<sup>50</sup>.

The functionalys graphene oxide (TDPG) was prepared by using polymer like triethylene tetramine-polyethylene glycol diglycidyl ether. For improving anti-corrosion property of waterborne polyurethane (WPU) coating was modified by TDPG. The anticorrosion ability of composite coating was evaluated by EIS and salt pray test<sup>51</sup>.

GO/PANI composite was synthesized by in-situ polymerization of aniline on the surface of GO. The prepared composite showed the excellent water dispersion ability, remarkable electrochemical properties, outstanding water barrier effect and thermal stability, which made them appropriate as a corrosion inhibitor for waterborne anticorrosion coatings. Compared with pure waterborne epoxy (WEP) and WEP/PANI coating, the synthesized GO/PANI/WEP coatings exhibited remarkably strengthen anticorrosion performances, which were confirmed by the results of the polarization curves and electrochemical impedance spectroscopy (EIS). The presence of PANI can provide electroactive protection<sup>52</sup>.

Sun et al. Studied conductive GNSs were prepared by a controlled Fe powder reduction process and a microwave-assisted fast thermal reduction process. Scanning probe technologies including localized electrochemical impedance spectroscopy (LEIS) and scanning vibrating electrode technique (SVET) were used to investigate the influences of GNSs preparation process on the CPA of GNSs/epoxy nanocomposite coatings<sup>53</sup>.

Chaudhry et al. studied corrosion reduction mechanism by using different concentration of graphene oxide such as 0,3,9,12,15 ppm in saline media. SEM technology use for study of GO surface. As pr results rate of corrosion was decreases with increases concentration of GO<sup>54</sup>.

Zhu et al.<sup>55</sup> use water dispersible graphene and amino group which was synthesis by nucleophilic ring-opening reaction with epoxy. First they graphene acrylic modified by alkyd resin coating and which is known by AMAR(fig-13). They use as Amino group like 3-(1-(2-aminopropoxy) propan-2-ylamino) propane-1-sulfonate sodium (PPS) with epoxy. The structure of graphene/amar is characterized by FTIR, XRD, XPS, TEM, and AFM. Results was very clear about the modified graphene/Amar has improved anti-corrosion



behaviour. 1wt% of (graphene\Amar) coating get best barrier and anodic protection properties results then other.

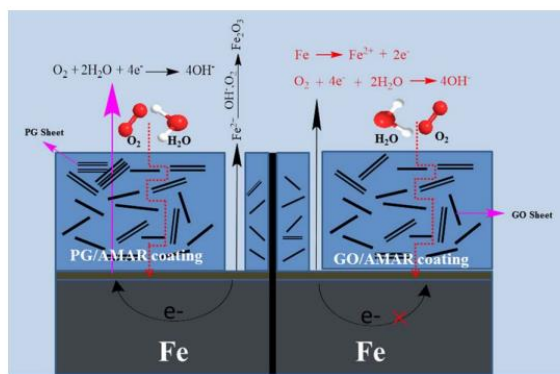


Fig 13 Schematic anticorrosion mechanism for PG/AMARs coatings.

Sun et al. reported devalope new corrosion protection systhesis by using graphene/peirngranine composites (GPCs) for copper. GPCs was modified with help of polyvinylbutyral coating (PVBC). Systhesis was create by situ-polymerzation. PVBC Modified GPCs was give better corrosion protection than peirngranine or reduced graphene oxide (rGO) modified PVBC<sup>56</sup>.

Yu et al.<sup>57</sup> use nanocomposite of vinyl/graphene base polymer in corrosion protection. They use polystyrene and modified graphene oxide by using situ polymerization process. This nanocomposite behaviour of anticorrosion property was compared with pure polystyrene. Functionalised GO was characterised using FT-IR, XPS, XRD, and TEM. However, modified graphene oxide with polystyrene at 2% wt.(fig-14) solution was give better results in anti-corrosion property like thermal stability and mechanical properties. Resultants show that corrosion protection efficiency of matrix was improved up to 99%.

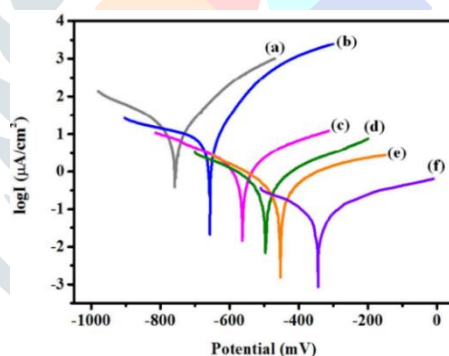


Fig 14 Tafel plots of (a) steel, (b) PS, (c) PS/pv-GO 0.5 wt.%, (d) PS/pv-GO 1 wt.%, (e) PS/pv-GO 1.5 wt.%, and (f) PS/pv-GO 2 wt.% measured in 3.5 wt.% NaCl aqueous solutions.

Monetta was incorporated graphene nano flakes into a water-based epoxy resin, and then the hybrid coating was applied to Al 2024-T3 samples. Electrochemical Impeectectdance Spectroscopy (EIS) analysis showed the addition of graphene significantly improved barrier properties of epoxy resin. When graphene is added to a non anticorrosive coating system, it has significant effect on the corrosion performance of material<sup>58</sup>.

Sun et al. use graphene nanosheet (GNS) with polydimethylsiloxane(PDMS) and prepared new matrix (GNS-PDMS) via chemical vapor deposition method and investigated by respectively spectroscopy technique. Results was show that the thickness of GNS-PDMS was increases up to 0.23nm compare to GNS. They also conclude that anticorrosion behaviour of GNS-PDMS was improved with help of epoxy coating<sup>59</sup>.

Ramezanzadeh et al. try to new approach with functional group like polyisocyanate(PI) and modified surface of graphene oxide (GO). PI-GO matrix results was compare with polyurethane(PU) matrix with graphene oxide. Investigation was done by X-ray photo electron spectroscopy, thermal gravimetric analysis and X-ray diffraction analysis. Anticorrosive property of PI-GO was much higher than the PU-GO from the results. Moreover, this route enhancing barrier performance and ionic resistance of PI-GO<sup>60</sup>.

Raza et al. work on corrosion study and develop new route by using graphene oxide with copper metal coating. Graphene oxide was prepare by using Hummer's method. Results was analysis by atomic force microscope (AFM), Electrophoretic deposition, XRD, SEMetc.GO coatings on copper acted as anodic barrier and reduced the corrosion rate of Cu metal by compared to bare Cu. EIS results are consistent with the Tafel analysis(fig-15), which showed that the charge transfer resistance (Rct) of EPD-GO was significantly increased<sup>61</sup>.

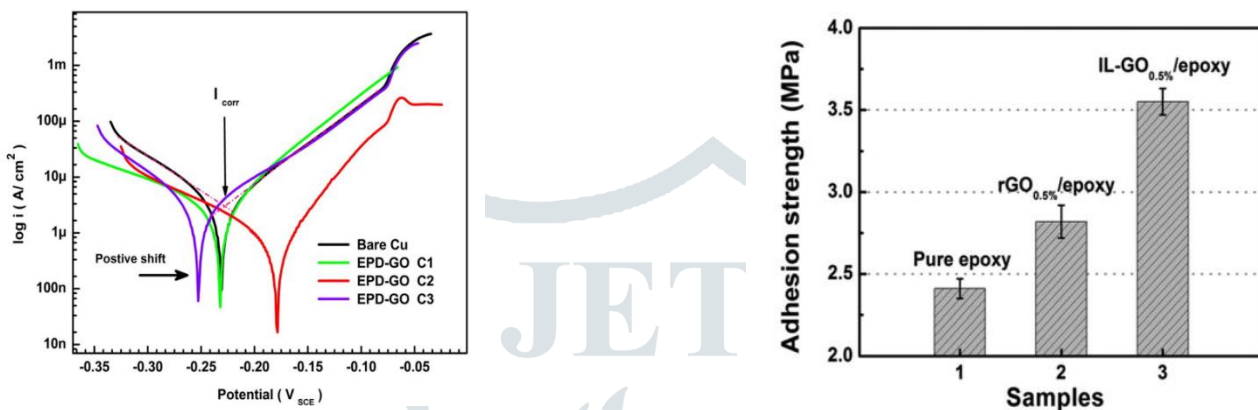


Fig 15 show that Tafel curves of EPD-GO studied in 0.6 M NaCl solution.

Liu et al. try to make new novel route by using ionic liquid(IL) with graphene oxide and create new nano matrix(IL-GO). N-(3-aminopropyl)-3-decylimidazolium bromide liquid use as ionic liquid and FT-IR, RAMAN, XPS,SEM spectra was successfully investigated imidazol liq mixed with graphene oxide surface.This kind of New synthesis (IL-GO) was effectively improved adhesion strength(fig-16),and anticorrosion performance of epoxy-based waterborne coatings.<sup>62</sup>

Fig 16 Adhesion strength calculated pull-of test. From the graph results was very clear IL-GO give better adhesion strength than other composite.

This route provide much better application rang in coating And enhance the anticorrosive performance of polymer matrix.

Cui et al. study New eco-friendly coating like water borne epoxy and ethanol which is increases the anticorrosion property. Modified Graphene oxide(GO) with polydopamine(PDA) both are combined (GO-PDA) each other and show  $\pi$ - $\pi$  interactions. Morphology of matrix was study by SEM,TEM,FT-IR,RAMAN etc. Three type of matrix was use in experiments which are GO-EP, GO-PDA, GO-PDA-EP. The GO-PDA-EP(fig-17) coating matrix have a much better corrosion properties and barrier property than other two matrix<sup>63</sup>.

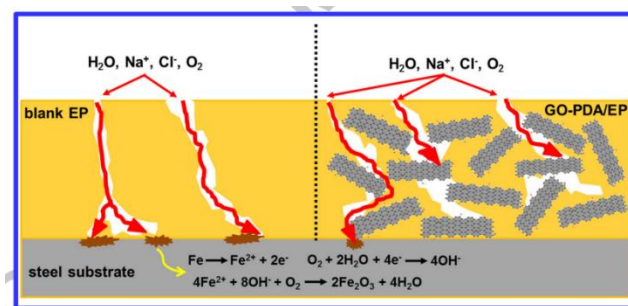


Fig 17 Corrosion protection mechanism of GO-PDA/EP.

Ding et al. reported that Study of Graphene with bio base epoxy monomer which is helpful to reduce the corrosion of metal With the help of Diels alder reaction they have prepared nonconductive graphene which is known as FMG. FMG have distracted organic solvent and better compatibility in polymer matrix. Three type of sample was examine by various technique which is contain FMG/EP 1%wt, 0.2% wt, 0.5% wt. According to the results 0.2wt and 0.5% wt sample have excellent corrosion resistance which was determine by electro chemical series. It is Good idea and excellence work provide better and great potential application of EP coating in field of corrosion resistance <sup>64</sup>.

Change et al. reported that Study of conductive filler by using 4-aminobenzoyl group-functionalized graphene sheets (ABF-G).they have also use other two composite like polyaniline/graphene(PAGC) and polyaniline/clay(PACC).Electrophilic substitution reaction and P2O5 medium give ABF-G in PANI was good coating behaviour in steel because of good barrier property.The high conductivity enable PAGCs to have a great potential for various electronic and optoelectronic applications. The corrosion protection depend on value of Ecorr, Icorr, Rp, Rc. Higher Ecorr and lower Icorr, Rp, and CR give better corrosion protection. Generally Rp vule was calculated by Tafel plot from the Stearn-Geary equation<sup>65</sup>.

Yu et al. reported that Study of graphene oxide and alumina (Al2O3) with epoxy coating as anticorrosiveagent. 3-aminopropyltriethoxysilane with alumina and GO combined and generate new matrix. Further, matrix was investigated by FT-IR, XPS, XRD, SEM and TEM. Various sample like GO, Al2O3, and GO-Al2O3 hybrids was prepared and all of them GO-Al2O3 hybrids much better corrosion resistance with low content of epoxy<sup>66</sup>.

Zhan et al.<sup>67</sup> make new route of developing anticorrosive coating with help of bio-inspired co-modification and graphene oxide/Fe<sub>3</sub>O<sub>4</sub> hybrid with epoxy coating. Which is lead to increases anticorrosive performance up to 71.8% than pure epoxy coating. 0.5% wt sample matrix give best anticorrosion performance at different time(fig-18) and micro-hardness than other sample like 1wt% and 2wt%.

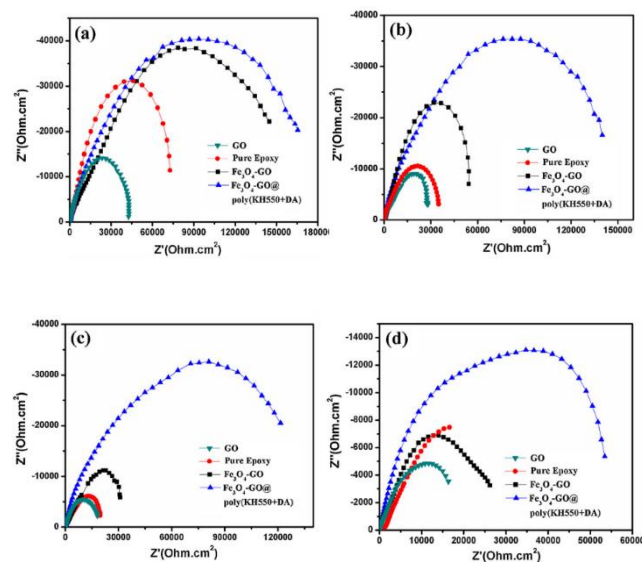


Fig 18 Impedance spectra of various epoxy composite coatings (with 0.5wt %) after soaking for different times: (a) 12 h, (b) 24 h, (c) 72 h, and (d) 144 h.

Yu et al.<sup>68</sup> also study Calcium carbonate nanoparticles (nano-CaCO<sub>3</sub>) and graphene oxide with epoxy as anticorrosive coating. This matrix was prepared by a curing process. Morphology and analysis of results show GO-CaCO<sub>3</sub>/epoxy much higher corrosion resistance effects than other matrix like GO/epoxy and pure epoxy.

Zhou et al. studied anticorrosive effect of graphene oxide(GO) with phytic acid(PA) and waterborne epoxy(WEP) as anticorrosive coating. PA molecule help to increases closeness between GO and WEP. Sample was investigated by different spectroscopy like FT-IR, SEM, TEM etc. Electrochemical measurements and salt spray test(fig-19) PA-GO/WEP sample give better adhesion and anticorrosive property than other sample like pure epoxy and GO/WEP<sup>69</sup>.

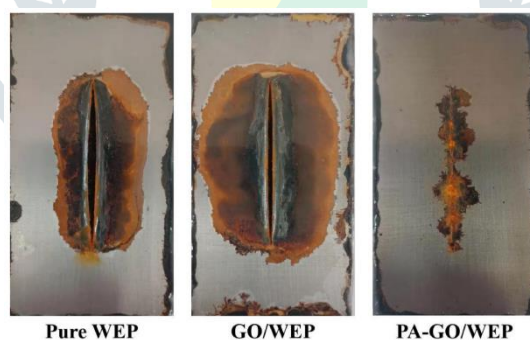


Fig 19 images of samples after 450 h salt spray test.

Gu et al. studied graphene and carboxylated aniline trimer derivative (CAT) by reacting aniline trimer with succinic anhydride and proved for the first time that CAT derivatives could be used as dispersing agents to disperse commercial graphene in water. G-CAT hybrid graphene sheet demonstrated strong conductivity (1.5S/cm) good electroactivity and improved electrochemical stability. The addition of well-dispersed graphene into waterborne epoxy solution (G-CAT/epoxy) significantly improved corrosion protection compared with pure waterborne epoxy coating.<sup>70</sup>

Zhou et al.<sup>71</sup> studied effect of corrosion by used graphene powder and epoxy coating. With epoxy they prepared different sample of graphene oxide(GO) powder and graphene slurry(GS), respectively Ga and Gb. sample anticorrosion resistance performance was investigated by electrochemical test. from results of EIS and SVET was confirmed that the barrier property of matrix was improved. Moreover, this work provide better application potential in corrosion filed.

Ye et al. Synthesised epoxy matrix with Super-hydrophobicity polyhedral oligomeric silsesquioxane and modified graphene oxide (POSS-GO). Reaction take place between graphene oxide and aminopropylisobutyl polyhedral oligomeric silsesquioxane (POSS-NH<sub>2</sub>) and create new matrix PG/EP. Morphology of GO sheet was characterized by FT-IR, SPM, TEM and XSP. help of EIS measurement show that the PG/EP better anticorrosion ability than pure epoxy coating. Moreover, from the results of EIS confirmed that 0.5wt% PG\EP coating give much higher corrosion potential at low current density by using 3.5wt% NaCl solution. The synergistic effect of good dispersion and super-hydrophobicity promoted the enhancement of anticorrosion ability for composite coatings<sup>72</sup>.

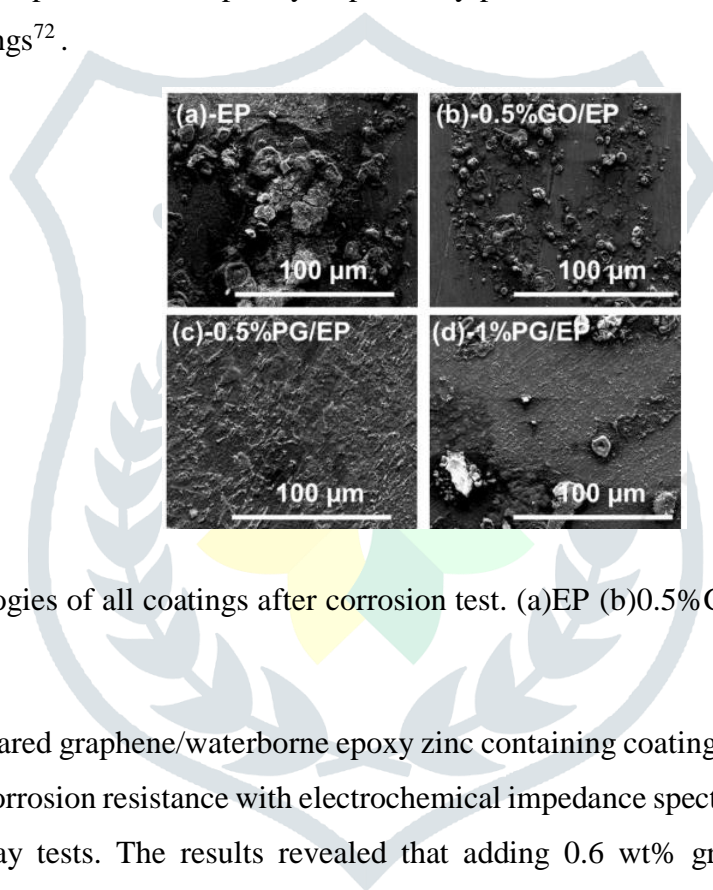


Fig 19 Corrosion morphologies of all coatings after corrosion test. (a)EP (b)0.5% GO/EP (c) 0.5%PG/EP (d) 1%PG/EP.

Shiyu and coworkers prepared graphene/waterborne epoxy zinc containing coatings with varying amounts of graphene and tested their corrosion resistance with electrochemical impedance spectroscopy (EIS), immersion tests, and neutral salt spray tests. The results revealed that adding 0.6 wt% graphene into the coatings considerably increased their corrosion resistance. They discovered that the zinc particles in the upper part of the coating deteriorated second after those close to the interface between the steel substrate and the coating. Graphene slowed the corrosion process and decreased the amount of corroded zinc particles<sup>73</sup>.

Mohammad et al. synthesized Graphene polyindole (Gr-PIn) nanocomposite different wt%content of graphene via an in-situ redox polymerization doping technique. In 3.5 wt. % NaCl, Gr-PIn coating was found to be an efficient anti-corrosion coating for LCS (Low Carbon Steel) substrate. Gr-PIn nanocomposite suggested that more graphene contents in PIn provide higher anticorrosion property<sup>74</sup>.

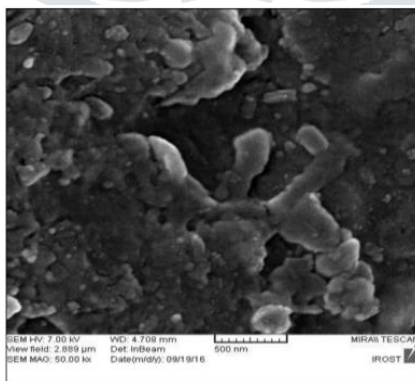
Xiao and coworker designed a spin coating method and fabricated highly orientated graphene/epoxy (OG/EP) coating with long-term corrosion resistance performance. The orientation of graphene, which maximize its

barrier effect and prevents the development of graphene conductive network, is thought to be protective mechanism of OG/EP coating<sup>75</sup>.

Morteza et al. used various combination of GO and Cloisite 20A montmorillonite (MMT) nanoclay (NC) particles modified with aminosilane and 1,4-butanediol diglycidyl ether (BDDE) molecules to develop an epoxy based nanocomposite coating with improved corrosion protection properties. Corrosion resistance greatly improved when MNC and MGO particles were added to the epoxy coating compared to clean particles. It was shown that the coatings loaded with MGO particles shown better resistant to corrosion than the coatings filled with MNC particle. The results established that the greatest improvement of the coating barrier and corrosion protection properties from the combination of MNC-MGO at ratio of 30:70 w/w<sup>76</sup>.

Xi-Zi et al. studied the creation of a novel anticorrosive pigment comprised of graphene oxide (GO) and hydroxyapatite (HAP). The pigment is created via the in-situ bonding technique, resulting in a strong and stable contact between the GO and HAP. On the metal surface, the GO/HAP Nano composite forms a dense and impermeable barrier, preventing corrosive species from contacting the metal. The HAP in the Nano composite can react with corrosive species like chloride ions to generate stable compounds that are not harmful to the metal surface. According to the findings, the GO-HAP nanocomposite pigment is a potential novel material for corrosion prevention<sup>77</sup>.

The anticorrosive effect of functionalizing graphene oxide (GO) nanosheets with ionic liquid (IL) on the mechanical properties of an epoxy coating is investigated by A. Khalili Dermani and his colleagues. They discovered that 1-Butyl-3-methylimidazolium chloride (BMIM-Cl) IL was successfully adsorbed on the GO surface via physical or chemical bonding. The incorporation of 0.09% GO-BMIM nanosheets into the epoxy matrix enhanced the glass transition temperature (T<sub>g</sub>), storage modulus, tensile strength, and energy at break substantially. They further postulated that the BMIM molecules operate as cross-linkers between the GO nanosheets and the epoxy matrix, enhancing interfacial adhesion and load transmission even more. The SEM micrographs obtained from the cross-section of the coatings<sup>78</sup> (Fig 20).



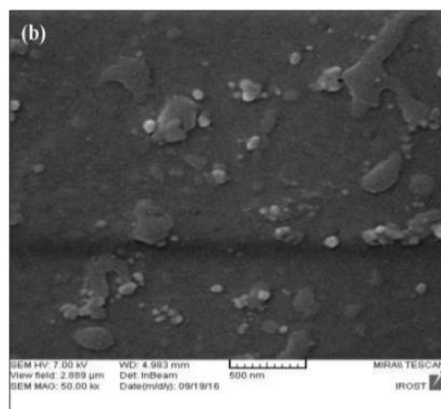


Fig 20 SEM micrograph obtained from the cross-section of the epoxy coatings filled with (a) GO and (b) GO-BMIM nanosheets.

Wang and partners studied the application of graphene oxide/ZSM-5 hybrids (ZSM-5-NH-GO) as nanofillers in aqueous epoxy coatings to improve corrosion resistance. ZSM-5 is a form of zeolite, which is a porous crystalline substance with a large surface area. The ZSM-5-NH-GO hybrids were then mixed in various quantities with aqueous epoxy coatings. ZSM-5-NH-GO (0.7% wt) hybrids are promising nanofillers for enhancing the corrosion resistance of aqueous epoxy coatings<sup>79</sup>.

Qiu et al. described a method for non-covalently exfoliating graphene by using poly(2-aminothiazole) (PAT) in organic solvent. and prepare subsequent fabrication of a composite coating with PAT functionalized graphene(PAT-G). It is concluded that the PAT-G composite coating is a promising material for protecting metals from the corrosion and wear<sup>80</sup>.

Rajabi et al. work on graphene oxide and epoxy coating which was prepared by various wt% amount of graphene like 0.125wt%, 0.25wt% and 0.5wt% by mechanical and sonicator process. Anticorrosive properties of matrix was analysis by electrochemical test. from the results 0.25wt% GO/epoxy sample was give much better anticorrosion resistance than other sample<sup>81</sup>.

Chang et al. studied anticorrosive effect by using thermally reduce graphene oxide (TRG) and carboxylic group. which was improved anticorrosive properties. poly(methyl methacrylate) (PMMA) mix with TRG and generate new poly matrix PTC. In this experiment carboxylic group play vital key role to enhance anticorrosion property. PTC coating TRG with high amount of carboxylic group which is help to enhance anticorrosive properties and barrier property compare to lower amount of carboxylic group content<sup>82</sup>.

Park and coworkers work on deposited graphene oxide (GO) on to carbon steel by using electrophoretic deposition (EPD) from a GO water suspension. Deposited mass of GO on carbon steel was determined by comparing the weights before and after deposition. With increasing applied voltage and deposition. Results was clear that EDP yield rise linearly. potentiodynamic polarization method was used to evaluate corrosion protection performance of the GO-EDP layer on mild steel<sup>83</sup>.

N. Parhizkar et al. study corrosion protection properties of modified graphene oxide/epoxy with amino group like 3-aminopropyltriethoxysilane. Modified of graphene oxide was prepare by hummer's method and Chareterazation was done by FE-SEM, EIS and XPS. Results of EIS was very clear that epoxy coating on

steel surface give better barrier properties and enhance adhesion property due to modified graphene oxide was reduce epoxy delamination rate on steel <sup>84</sup>.

## **Acknowledgements:**

## **Conclusion:**

The current review paper highlights the salient research works, carried out in the last few years, where the research was done to achieve higher mechanical, thermal and anticorrosion properties in Graphene/epoxy, Graphene/Organic filler and Graphene/Inorganic filler nanocomposites. It is proved that graphene-like materials are not the only existing solution to all the technological challenges in the field of protective coatings, especially in cases where more cost-effective additives exist and give similar performances. Although the anticorrosive property of graphene composites has been widely studied and some progress has been made, this field is still in the early stage of development and there is still a lot of work to be carried out. The development of anticorrosive graphene-composite coating shows good application prospects. The development trend will be more toward the green, high-quality, large-scale preparation and multifunctional integration of graphene. In the future, industrial resources will be further integrated and will continue to be widely applied in industry, new energy, and other fields.

Further developments in polymer coatings containing carbon-based nanomaterials will be obtained via improving the nanofiller dispersion in polymer matrix via simple low-cost methods. The carbonbased nanofillers will be used extensively in different industries for providing corrosion resistance coatings with long lifetime and low cost. The proposed nanocomposite coatings will be loaded with significantly low amounts of carbon nanofillers, leading to decrease in the anticorrosive pigment usage while increase in the strength-to-weight ratio.

## **Scope:**

Since the addition of Graphene Oxide in MWCNTs/Epoxy coating increases the properties of the composite coating. The work can be extended by studying the effect of graphene in this as epoxy coating with MWCNTs nanocomposite. The resulting composite should be analysed to find its mechanical, thermal, and anticorrosive performance.

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