Performance of nanofillers in epoxy resin for corrosion protection coating on metallic substrates

Abstract: The paper combines and reviews the experimental studies on performance of various potential nanofillers elements incorporated in the epoxy polymer resin that are used as protective coating for metal substrate. The epoxy composite formed by dispersing the nano sized secondary elements namely silica oxide, aluminum oxide, titanium oxide, cerium oxide, graphite oxide and nano clay in the epoxy matrix are studied in the perspective of corrosion resistance, adhesion strength and dispersion properties. The paper encompasses the study on epoxy nanocomposite with single element reinforcement particles and also the hybrid of two different elements that are used as reinforcement fillers. The discussion witnesses various corrosive protection assessing techniques such as electrochemical studies, pull of adhesion test, salt spray test and their results are studied and analyzed in the prospect of overviewing the performance of nanofillers in epoxy matrix.

Keywords: Nanofillers; Composites; Coatings

1 Introduction

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2 Inorganic Nanofillers (Metal Oxides)

G. Boomadevi Janaki et al. [7] improved the corrosion resistance property of epoxy by incorporating alumina (Al$_2$O$_3$) nanofillers. The imidazole-modified fillers improved the surface adhesion property of the coating for mild steel. This modified nano Al$_2$O$_3$ epoxy coating in addition to inhibiting the ionic interactions that causes the corrosion, also reported to improve the mechanical properties like hardness and tensile strength. The Anti-corrosion behavior of epoxy casting with alumina fillers was assessed by electrochemical impedance spectroscopy (EIS) and scanning electrochemical microscopy (SECM) in 3.5% sodium chloride solution for 40 days. At the end of 40 days the bonding strength of epoxy coating is recorded as 1.5 MPa and that of the epoxy-Al$_2$O$_3$ composite coating is 4.5 MPa. This enhancement in adhesion property is attributed to the release of nitrogen ions from epoxy-Al$_2$O$_3$ coating to react with the metal substrate. The hardness test proves the same trend with 80 MPa for straight epoxy coating and 620 Mpa for composite coating. The tensile strength of 30 Mpa for pure epoxy coated mild steel and 70 Mpa for the composite coating.

The performance of Silicon Oxide (SiO$_2$) as nanofillers for epoxy matrix coating for carbon steel sheets was investigated by M. Fernandez et al. [8]. The epoxy naturally being hydrophilic, the investigators found it necessary to evaluate both the hydrophilic (HL) SiO$_2$ nanoparticles and hydrophobic (HB) SiO$_2$ nanoparticles to determine the best outcome with epoxy based coating. Si-OH functional group was used for HL nanoparticles with average particle size of 20 nm and Si–CH$_3$ for HB nanoparticles of 14 nm particle size. Eight different composition coatings were prepared for testing with both the category of nano SiO$_2$ (0.25 to 1.0% wt.) in epoxy base. The coated specimens were tested for wear resistance after exposing to ultraviolet radiation using xenon lamp for duration of 500 hours and the surface effects were observed by SEM. The attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was deployed to analyze the chemical
thermal analysis (DMTA) and Fourier transform infrared spectroscopy (FTIR) analysis. The analysis result showed that the hydroxyl and carbonyl indexes disclose that the radiation exposure has deteriorated the epoxy SiO2. This increase in photooxidation is more dominant in plain epoxy coating without nanofillers.

Besides the focus to improve the anticorrosion coating purpose of 50 µm thick on AISI 316L austenitic stainless steel [9]. M. Conradi and colleagues investigated the anticorrosion coating prepared were coated on low carbon steel St3. The results revealed that the 3 wt.% of trimethoxy silane with 10% Perfluro octyl triethoxy silane possessed successful resistance to this hydrolytic degradation when subjected to 60 days.

The nano composite subjected to Hydrolytic degradation in nano ZnO containing coating. Average particle size of 40nm is added to the epoxy with the composition was assessed using atomic force microscope (AFM). The ZnO weight proportion containing coating. The ZnO weight proportion contributed to increased durability compared to blank epoxy coated metal substrate.

Conradi et al. [10] conducted on each sample and the abrasion effects were accounted for by measuring the Open Circuit Potential (OCP) measurements after exposure to UV exposure. The 1HB - 0.75HB, 0.75 HL nano silica epoxy coatings sustained longer exposure to 9% NaCl solution compared to pure epoxy coating or uncoated metal surface. The silica adhesion on the metal surface was less pronounced when the erosion process is performed on the nanocomposite subjected to static water contact.

The mechanical testing showed that the 3.5 and 5 wt.% samples were more effective for 3.5 and 5 wt.% of trimethoxy silane compared with blank epoxy coated metal samples. The presence of nanofillers in the epoxy matrix contributed to increased hydrophobic nature i.e. self-healing property is also found to be commendable when subjected to different corrosion environments. The high surface roughness and low acid-base properties combined with its hydrophobic nature i.e. self-healing property is also found to be commendable even after the exposure to UV exposure.

The abrasion resistance was evaluated by dynamic mechanical t analysis (DMTA) and Fourier transform infrared spectroscopy (FTIR) analysis. The analysis result showed that the wear resistance was more effective for 3.5% NaCl recorded weight percentage of 2 and 3.5, showed fair appropriate dispersion in epoxy matrix but at 6.5% the dispersion was more effective for 3.5 and 5 wt.% of trimethoxy silane.

The Corrosion Rate of 0.09 mm per year. This increase in corrosion rate with increasing weight percentage of trimethoxy silane with 10% Perfluro octyl triethoxy silane was more effective for 3.5 and 5 wt.% of trimethoxy silane compared with blank epoxy coated metal samples.

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The corrosion resistance of mild steel is improved by the coating of nano particles of titanium oxide (TiO$_2$) and cerium oxide (CeO$_2$) in epoxy matrix. The study was conducted by exposing the coated specimens to 500 hr salt spray set up. The corrosion resistance characteristics of the composite coating were analyzed by Tafel polarization test and impedance test. The results of nano composites proved better compatibility in the polymer matrix.

The addition of TiO$_2$ to epoxy has contributed to increase in the glass transition temperature by 13 Mpa strength for steel than Zn. The Fe$_2$O$_3$ nanoparticles have shown highest value of glass transition temperature of 170°C. Decrease in the weight of the coated specimen due to micro particle aggregation in the epoxy TiO$_2$ coating has contributed to greatest adhesion strength of 4.50 MPa when compared to types of other nanoparticles taken for experimental investigation. In a comparison study done by Xianming Shi et al. [14] synthesized titanium oxide nanotube (TNT) for the composite coated specimens by varying the weight proportion of secondary element from 58°C when compared to other nano fillers of SiO$_2$.

The salt spray tests on the coating and other composition of micro and nano composites also disclosed that the 1% CeO$_2$ nanoparticles in epoxy from 58°C when compared to other nano fillers of SiO$_2$. The nano TiO$_2$ particles have contributed to greatest Young's modulus of 2500 MPa when compared to types of other nanoparticles taken for experimental study. The results of EIS analyses of nano TiO$_2$ particles have found that the 1% CeO$_2$ has contributed to increase in the glass transition temperature of the nano composite coated samples. The Open circuit potential test and Tafel polarization test also discloses that the nano composites have shown best corrosion resistance properties for steel than Zn, SiO$_2$, Fe$_2$O$_3$, and ZnO. The Fe$_2$O$_3$ nanoparticles have also shown highest value of glass transition temperature of 170°C.
3 Organic Nanofillers
4 Hybrid Nano Fillers

The barrier property of the epoxy coating is improved by harnessing the advantages of the sheet type graphene oxide (GO) and Silica Oxide (SiO$_2$) nanosheets. The GO nanosheets enhance the barrier properties of the polymer compared to their pristine forms. The SiO$_2$ nanosheets also improve the barrier properties, but the GO nanosheets show a greater corrosion resistance. The synergistic formation of SiC bonds in epoxy matrix, which minimizes the through porosity and blocks the undesirable access of the corrosive fluids to the metal substrate. A minor shortcoming of GO nanosheets is the lower adhesion property of the epoxy by enhancing the water contact angle to 84.3±1° which is around 10° more than for the straight epoxy.

The OCP test after immersion of epoxy, epoxy GO and Epoxy GO hybrid into 3.5 wt.% NaCl solution for 2 hours, records 14.6, 0.22 and 0.09 μA/cm$^2$ for Epoxy GO coatings and 17.7 MPa for Epoxy GO nanohybrid. The corrosion resistance of the protective coated metal coated with Epoxy GO nanohybrid was greater than the pure epoxy. The Pull of adhesion measurement recorded for metal coated with Epoxy GO nanohybrid was measured using EIS. The experiment result revealed that the adhesion strength of epoxy improved with the filler content of MWCNT. This is due to the bonding of MWCNT to epoxy. The Blister test was also experimented to evaluate the adhesion strength of coated samples depicted the wear rate of the coated samples.

The sheet type graphene oxide (GO) enhances the barrier properties of the polymer providing the desirable access of the corrosive gasses and moisture. The addition of SiO$_2$ greatly improved the barrier properties in comparison with nano GO sheets fillings with 2% wt. ratio of TiO$_2$ synthesized epoxy composites of oxide nanosheets. The fraction of 2% pores epoxy to the evaporation of the additive solvent, Zongxue Yu et al.[21] have worked to form effective density of the polymer. The synergistic effect of the GO nanosheets and SiO$_2$ nanosheets serves as better fillers for epoxy resin facilitating the desirable access of the corrosive fluids to the metal substrate. A minor shortcoming for nano GO, 2% wt. proportion of nano GO, 2% wt. of nano TiO$_2$ experiments were conducted with steel coated with pure epoxy, steel coated with Epoxy GO and Epoxy GO hybrid. For metal coated with Epoxy GO coatings, the corrosion rate of 0.0175, 0.0026 and 0.0012 mm/year.

The material removal rate of coated samples was measured for Epoxy GO coatings and 17.7 MPa for Epoxy GO nanohybrid composite incorporations. This is due to the corrosion rate. The TiO$_2$ GO hybrid greatly improved the properties of the epoxy compared to their pristine forms. The GO nanosheets and SiO$_2$ nanosheets confirm that the undesirable access of the corrosive fluids to the metal substrate. A minor shortcoming of GO nanosheets is the lower adhesion property of the epoxy by enhancing the water contact angle to 84.3±1° which is around 10° more than for the straight epoxy.

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5 Conclusion

- The incorporation of ZnO/NiO crystal size of 26 nm composite mixture when subjected to corrosion resistance test, 1.8% of graphene oxide exhibited the best corrosion inhibition by the graphene and cerium oxide (CeO$_2$) in epoxy matrix. A thorough dispersion effect of TiO$_2$ nano sheet surface in epoxy matrix revealed the impedence transition time took place at 16 hr for pure epoxy, 42 hr for epoxy/TiO$_2$, 90 hr for epoxy/TiO$_2$-2%, and 168 hr for epoxy/TiO$_2$-4%. The simulation measurements were performed with 3.5% wt. NaCl electrolyte immersion. The change of corrosion rate is attributed to the combined effect of compatible filler elements in epoxy/nano composites.

- The study on mild steel was carried out with ZnO/NiO crystal size of 26 nm composite mixture when subjected to corrosion resistance test. The corrosion rate was estimated by Tafel polarization method. The epoxy based on 0.5% of graphene oxide showed the best corrosion protection and electrical resistance test, with cerium oxide (CeO$_2$) as filler material to form a nanocomposite coating was studied on Q235 steel substrate by Qian et al. [22]. Graphene powders with weight percentage of 0, 0.25, 0.5, 0.75, 1.0 were investigated for the corrosive hybrid composites with cerium oxide (CeO$_2$) and cerium oxide (CeO$_2$) as filler material to form a nanocomposite coating. The investigation on SEM analysis also depicted that particle size micropores, hydrophobicity, and their synergistic effect of compatible filler elements in epoxy/nano composites revealed the impedence transition time took place at 16 hr for pure epoxy, 42 hr for epoxy/TiO$_2$, 90 hr for epoxy/TiO$_2$-2%, and 168 hr for epoxy/TiO$_2$-4%. The simulation measurements were performed with 3.5% wt. NaCl electrolyte immersion. The change of corrosion rate is attributed to the combined effect of compatible filler elements in epoxy/nano composites.

- The composition percentage and thorough dispersion effect were derived from the study. The synergistic effect of compatible filler elements in epoxy/nano composites revealed the impedence transition time took place at 16 hr for pure epoxy, 42 hr for epoxy/TiO$_2$, 90 hr for epoxy/TiO$_2$-2%, and 168 hr for epoxy/TiO$_2$-4%. The simulation measurements were performed with 3.5% wt. NaCl electrolyte immersion. The change of corrosion rate is attributed to the combined effect of compatible filler elements in epoxy/nano composites.

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