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Comparative Studies of Wear and Corrosion Behaviors of Conventional and Nano Filler Based Solvent Free Tar-free Epoxy-amine Coatings

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Abstract

Tar-free epoxy coatings aid in protecting intact of Mild Steel (MS) substrate immersion condition of atmosphere. From lot of study revised and assorted that tar free (light colour) epoxy amine coating developed which give better performance for protection in long term. By ASTM method, wear behaviors as well as mechanical properties of quartz (micro silica) and organosiliane (nano silica) based tar-fee epoxy coatings were studied. DETA cured epoxy composites coatings were characterized by FTIR spectroscopic technique, powder X-Ray Diffraction (XRD), SEM and FESEM analysis. Transmission Electron Microscope (TEM) confirmed the size of nano particles. The data of wear index of nano fillers based epoxy coating was observed 8.3mg/1000cycles which indicate such an improvement of of abrasion behavior. Corrosion behaviors of the coated MSspecimens were evaluated by Cathodic Disbondment (CD) test immersion in 3.5% NaCl solution. Water absorption and chemical resistance also studied of composite coatings. All over tar-free epoxy-amine nano composite coating shows good result.

Keywords: *Composite, Corrosion, Mechanical, Tar-free Epoxy, TEM*

1.0 Introduction

Corrosion formed by chemical or electro-chemical action between metallic substrate and its circumstance, as a result material goes to destruction or degradation. These are serious harmful and enormous waste of resources from metallic corrosion. To mitigate the problem of corrosion of degradation of metallic substrate and implement of high performance, free from pollution and also economical anticorrosion has become a new trend in the field of protective coatings[1-2]. Polymeric *i.e* organic coatings plays important role as a physical barrier to protect the metallic surface from complex environments of corrosion[3-6]. Kind of corrosive species such as metal ions, anions, oxygen and water can come by the quantities of enter through the polymeric segments[7-11].

As example, it is considered adhesion of coating to the metal surface to be dangerous, water molecules penetrate to the interface between metal and coating then give product as metallic corrosion. The coating

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behaviors of the painted system often rely on the entity of intermediate layers and metallic substrate[12-15]. Silica nanoparticles use for different purpose of multifunctional area of nanocomposite systems from last decade. Because it has low refractive index (1.46), high hardness (7 Mohs), scratch resistance, transparent, hydrophobic in nature and also cost effective properties[16-18].

In this research work reported below, SiO_2 nanoparticles treated as nano organosiliane particles which have diacritic chain lengths and numerous of hydrophobic groups on their periphery during the formation of coating. Developed of different properties along with their characterization based on tar-free epoxy composite coating (micro and nano) silica particles are reported.

2.0 Experimental

2.1 Materials

Tar-free epoxy resin is used in the study, Diethylene Tri Amine (DETA) is used for the curing of epoxy resin. Aerosil 972 organo siliane used as SiO_2 nano particles[17]. Tar-free epoxy-DETA based cured composite coatings were formulated by using SiO_2 and soap stone as additives. The size of of additives particles formulation was within 40-70 micron, Xylene act as solvent. These are all obtained from Vijoy Solvent and Thinner, Madhyamgram, Kolkata - 700132. Conventional silica named as qurtz silica powder is used for study from same company. Organo nonasiliane is formed by treatment of SiO_2 with Dimethyl Dichloro Silane (DDS) which has Primary Particle Size (PPS) in the range of 50-30 nm and specific surface area (BET) of 115 ± 25 m^2g^{-1} [17]. This type of fumed silica used as flow ability of powder, water resistant systems and anticorrosive coatings.

2.2 Sample Preparation

Tar-free epoxy resins are very viscous and high volume solid so mixing processes have to be carried out quickly. There is no need of heating the mass. The mixture will be subjected to high speed mixer 4000-6000 RPM for 2.5 to 3 hours at 40^0-50^0C. Good dispersion will be achieved by mechanical stirring with high speed continuously. Samples are prepared of C1 for epoxy resin with conventional SiO_2 fillers and C2 for epoxy resin with nano SiO_2 fillers. Weight percentage of resin, extenders, additives, solvents and both type of fillers were varied.

2.3 Preparation of the Mild Steel (MS) Coated Panels and Rods

MS panels (6″ × 2″), (6″ × 4″), (5″ × 2½″), and MS rods of size (8 mm × 6″) were de-greased, sand blasted and cleaned, prior to coating. Both conventional silica and nano-silica containing epoxy resin with hardener was sprayed using spray painting gun onto the MS panels and rod substrates to develop uniformly coated samples achieve uniform coating thickness is 200-250 micron on MS specimen as per ASTM standard.

2.4 Prepation of Composite Film

Both conventional silica-tar-free epoxy resin and nano-silica-tar-free epoxy resin films were prepared using spray painting gun onto the hard plastic substrate and then samples were cured at room temperature for 24 hrs. to achieve uniform film thickness of 200-250 microns as per ASTM standard. After putting off from the substrates, films were post cured at 60°C for 2 hours. The composite films were then allowed to stabilize for 15 days at 28±5°C within desiccators and 50% relative humidity, before any testing was carried out.

2.5 Testing

As per ASTM D-1400 standard a dry film thickness gauge used to measure the Dry Film Thickness (DFT). Adhesion behaviors test was evaluated on coated MS panels as per ASTM D-4541 and ASTM D-3359. Here "Pull off" and "Cross-cut" methods are used for adhesion testing. "Pull off" test was studied before and after Salt Spray Test (SST) of 2200 hrs of MS coated panel. In this study, the test dolly was bonded to the coating using an appropriate adhesive. The test is done by Caltech Pull Off tester machine. The flexibility of the coatings was carried out with regard to the 'crack resistance' and these experiments were performed on coated MS panel by standard conical mandrel tester as per ASTM D-4145.

The pencil hardness test was studied on coated MS panels using pencils 6B to 6H range, as per ASTM D-3363. Scratch hardness of the coated MS panels was carried out

as per ASTMD-3363 method. Falling ball impact test was performed by impact tester dropping a 0.9 kg weight from a maximum height of 50.8cm and from 6.35cm on MS coated panels. When falling the ball was dropped onto a MS coated surface of panel i.e. 'intrusion' and on the back side of uncoated panel with reference to the coated surface i.e. 'extrusion' as per ASTM D-2794. The measurements were covering the specular illustration of the specimens of paint for gloss meter geometry of 60^{O} on a flat, homogeneous and clean surface as per ASTM D-523. Using Taber Abraser (Model: 5153) for 1000 Cycles as per ASTM D-4060 for resistance of abrasion was studied.

2.6 Characterization of Nano SiO_2

Fourier Transform Infrared Spectroscopy (FTIR) studies recorded by IR Prestige in the range between 400 and 4500 cm^{-1}. The powder XRD (X-Ray Diffraction) figures of nano organo siliane particles were reported using PANalytical Netherlands, Model: X'Pert PRO.

Images of Transmission Electron Microscopy (TEM) are taken from model name JEM-2100, 200KV, jeol. Scanning Electron Microscope (SEM) images taken from FEI Quanta 200 F SEM, Netherland and field emission scanning electron microscope (FESEM) images taken from model name INSPECT F50, GERMANY.

2.7 Cathodic Disbondment (CD) Experiments

Immersion of 3.5% NaCl electrolyte solution two individual cells made to MS coated panels were subjected to cathodic disbond test for 28 days at −1.5V and at 30 ± 5^{0}C. 6mm diameter hole drilled at the centre of each coated panel to remove the coating material up to the base MS substrate as a pre-damaged area, which acts as cathode. In this study Pt-electrode used as anode and reference calomel electrode immersed in each cell to measure continuous potential for 28 days.

2.8 Water and Chemical Resistance Behaviors

The degree of water absorption *i.e.* water swell evaluated by preserving of film with in water. The swell (%) of water was calculated by universal technique. By using acids (5% H_2SO_4 and 5% HCl) and alkali (5% NaOH) immersion test for 65 days the chemical resistance prominency of the cured coating composite were studied.

3.0 Results and Discussion

3.1 Physico-Mechanical Properies of Coating on MS Substrates

Here, with regard to the mixing ability of the formation viscosity play significant role, it is observed that with the addition of nano organosiliane resulted increases viscosity as compared to addition of conventional qurtz silica due to the silica nano-particles have interfacial interaction with highest surface area for contact with the polymer chains. The others mechanical properties like DFT (Dry Film Thickness), flexibility, scratch hardness, pencil hardness, adhesion, falling ball impact and abrasion resistance of composite coatings were studied and evaluated and the results are provided below. DFT of composite coating is 200-250 micron. It is seen by C2 is more flexible than C1. Composite coating of C2 shows better results of scratch and pencil hardness than C1 due to hardness and cross linking density are proportional of the coating of

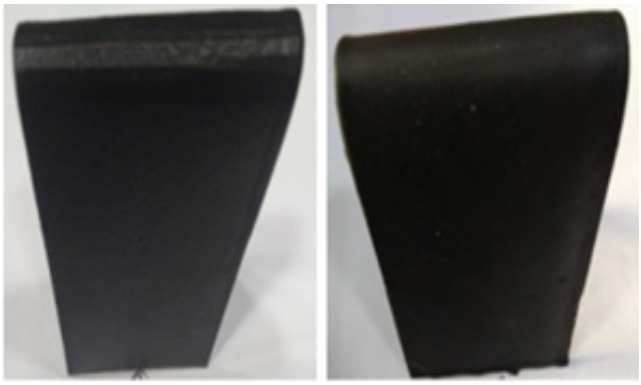
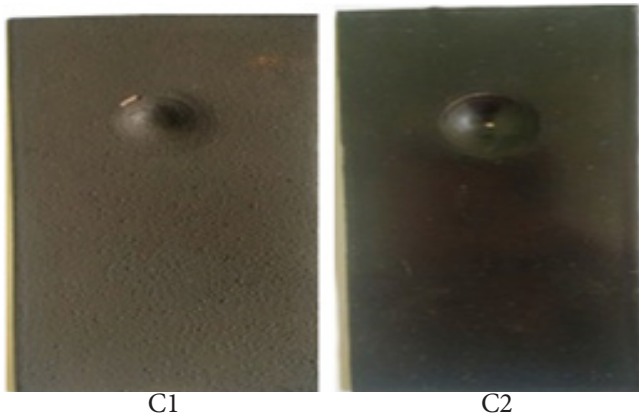


Figure 1. Images of flexibility test.

composite. Falling ball impact test shows good because dispersion of nano fillers are uniformed which give more cross link elastomeric rigid structure.

Table 1. Result of pencil hardness

Sample Name	Hardness (6B to 6H)
C1	Failed (2H)
C2	Passed



C1 C2

Figure 2. Images of falling ball impact test.

Table 2. Result of scratch hardness

Sample Name	500gm Weight	1000gm Weight	1500gm Weight
C1	Passed	Passed	Failed
C2	Passed	Passed	Passed

In the tar-free-epoxy coating incorporated nano silica remarkably improve abrasion resistance with the minor weight loss than dispersion of silica micro particles in polymer matrix. It is calculated weight loss from wear index data 31.7 mg/1000 cycles for conventional composite coating. Since in nanosilica composite coating, it is observed 8.3 mg/1000cycles which indicate uniform distribution of nano particles in polymer chains give more tough three dimensional network structure. The adhesion properties of before and after salt spary test C2, nanocomposite coatings show excellent than C1 due to distribution of nano particle increases more crosslink density in polymer matrix.

In adhesion test by "Cross-cut" method, all type by epoxy with conventional filler coatings reported 1B rating as per ASTM standard. But with nano filler coating reported 3B rating.

Table 3. Impact properties of silica based composite coatings on ms substrate

Samples Names	Impact (kg.m)	
	instrusion	Extrusuin
C1	>0.8	>0.7
C2	>0.2	>0.2

Table 4. Mechanical bheviors of SiO_2 particles embedded epoxy composite coatings on ms substrate

Name of the tests	Micro silica based composite coating (C1)	Nano organosiliane based composite coating (C2)
1. Wear index	31.7mg/1000cycles	8.3mg/1000cycles
2. Adhesion (Before Salt Spray Test)	15.3N/mm^2	28.5N/mm^2
3. After 2200 hrs Salt Spary Test	9.1N/mm^2	23.3N/mm^2

3.2 Gloss Study

In this method, the visual observation of coating periphery shininess made at roughly corresponding angles correlate with measurements. Reflection of specular also rely on the coating's refractive index ground. It measured change of gloss ratings because the surface refractive index defects. At 60^o angel C2 displays better gloss than C1 *i.e.* C2 of nano silica particles has high refractive index than conventional of C1.

Table 5. Gloss results

Samples Names	At 60^O Angle
C1	80
C2	110

3.3 FTIR Spectroscopy

Figure 3 shows C—H stretching bands are observable in regions (2850 to 3200 cm^{-1}). These bands are very closely associated to alkyl groups of the organo silane alterer on the surface of silica nanoparticles.

Two types coating structure revel a peak at 1215 cm^{-1} which suggested —C—N— bond. At 1585cm^{-1} for —C—C—linkages for aliphatic and 1460 cm^{-1} for aromatic backbone bands are confirmed. Transmission peaks are confirmed at 2926/2854 and 3008 cm^{-1} make sure aliphatic and aromatic —CH— linkages respectively. Cured films of tar-free epoxy composite undergo stretching vibration —C—O—C— oxirane ring at 826 cm^{-1}, —C—O—

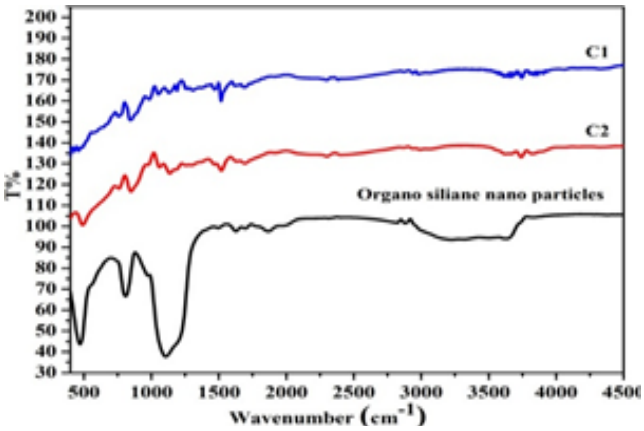


Figure 3. FTIR spectroscopy of nano R972 SiO_2 particles, composite coatings of C1 and C2

at 1181 cm^{-1} and also —N—H— at 3287 to 3289 cm^{-1} [19-20]. The IR spectrum DETA indicate characteristics peaks are at 2850 cm^{-1} for alkyl group, 1620—1500 cm^{-1} for aromatic —C=C— and 1276 cm^{-1} for aliphatic —C—N— stretch[21-22].

3.4 XRD Patterns Analysis

The XRD peaks of organo siliane particles and composite coating of cured film seen in Figure 4. A broad pattern obtained at 2θ=20.4 with d spacing 4.5 compared to the presence of SiO_2 crystalline particle. It correlates that particles are amorphous in nature mostly. In nano composite additives of broad peaks of anatase TiO_2 are observed at angles of 2θ = 25.80, 32.20, 38.02, 48.55, 55.43, 66.78, 72.84 and 75.02°. The peak at 2θ=20.10° represented nano silica particles composite of epoxy coating[23].

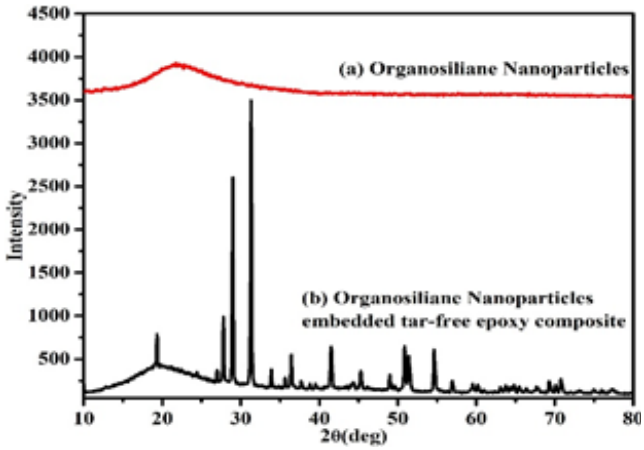


Figure 4. XRD pattern of organo siliane nano particles and tar-free epoxy composite.

3.5 Morphology Study

For better corrosion performance of resultant nano coating it is very important to good wetting necessary of particles in nano sized in composite. TEM studies determine degree of dispersion tread SiO_2 nonoparticles in the morphology which will clearly get into better corrosion performance of the nano composite coating. Used of ImageJ software organo silane particle size is less than 50nm detected. Figure 5 shows TEM images of C2 composite coating with different magnificatons.

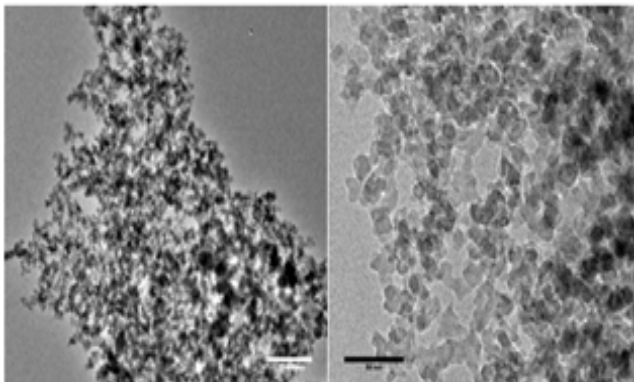


Figure 5. Transmission electron images of R972 organosilane base tar-free epoxy composite coating (C2).

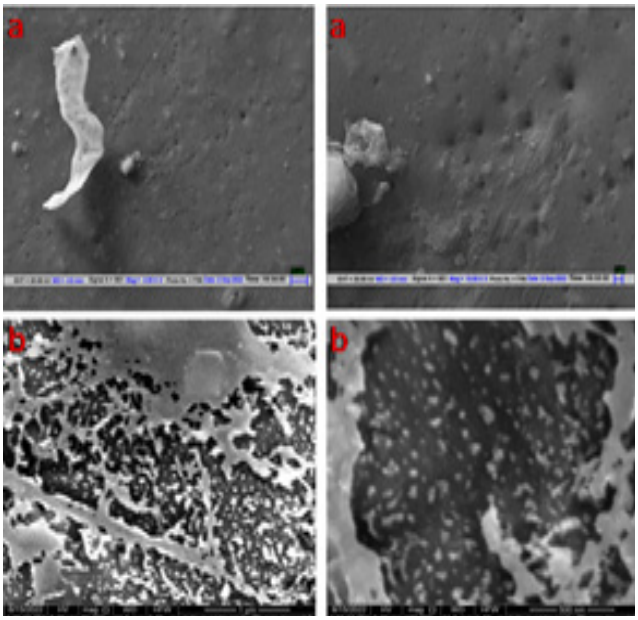


Figure 6. SEM images of (a) is C1 and FESEM images of (b) is nanosilica particles incorporated in the epoxy matrix.

Figure 6 shows at two different magnifications SEM images of C1 in (a) where some particles are observed at micro level and FESEM micrographs of dispersed nano silica in (b). FESEM images displays the nano particles are homogeneously dispersed in the polymer matrix during the formation of composite coating. Here at two different magnifications of images 3µm for C1 and 300nm used for C2 coating observation.

3.6 Corrosion Studies

3.6.1 Cathodic Disbondment (CD) Study

Complete of experiment then poured phenopthalein indicator on drilled hole at the centre of each cell. There was change of violet colour observed which indicate violet colour zone has been corroted area shown in Figure 7. Here temperature is related to disbanding of coating. An increase of the current, a greater expansion of disbonded area observed at higher temperature due to rate of disbonded area (mm/day) and temperature are proportional to each other[24,25]. There are no such experiments measured by temperature effect on the transport of water and ions. At high vapor pressure of water increase vapor of water through surface of composite coating and porosity of coating grows as a result of chemical attack with thermal expansion.

Figure 7. Images of MS coated panels after cathodic disbond test for 28 days.

3.7 Water and Chemical Resistance Study

The degree of water absorption has been evaluated by using formula of % swell test for 65 days. The nano filler based cured film (C2) showed excellent water resistant than conventional cured film (C1). As result, absorption of water C1 is 26.53% and whereas C2 is 5.76%. The resistance behaviors of chemicals of the cured films were studied byin solution of acids (5% H_2SO_4 and 5% HCl) and alkali (5% NaOH) immersed for 65 days. The studies exposed that the films, acid and alkali immersion test showed damages and weight loss in acid medium is 30-40% and loss of gloss in alkali of C1. On the other hand, small damages and weight loss in acid (8-19%) and little loss of gloss in alkali of C2 observed. C2 shows better water and chemical resistance than C1 due to nano particles completely wetted by tar-free epoxy and adduct of aliphatic chain from DETA give cured highly crosslink density rigid molecule structure presence of hydrophobic groups of nano organosiliane, etc.

4.0 Conclusion

In summary, we have developed the nano organosiline epoxy composite material by simple method and successfully showed excellent result of all experiments. Composite material of nanoparticles has been confirmed by FTIR, XRD, TEM, SEM and FESEM studies. More importantly, the composite coating with nano composite material displays excellent wear resistance and corrosion resistance than conventional one. Nano base composite coating has low water absorption and high chemical resistance than conventional one.

Table 6. Corrosion study (CD)

Composite Coating	Voltage (V)	Current (mA)	Temp (^oC)	Duration (Day)	Disbondment (mm)
C1	−1.5	90-110	30-45	28	30.3
C2	−1.5	90-110	30-45	28	10.7

5.0 Acknowledgment

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