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The Effect of Zinc Oxide Nanoparticles on Cohesive and Adhesive Bond of Epoxy/Amine Coating on Carbon Steel Substrate

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Abstract: *The zinc oxide epoxy nanocomposite (ZnO-ENC) coating were synthesized by the mechanical stirring method at different concentrations of zinc oxide nanoparticles (ZnO-NPs) in epoxy matrix. The chemical interactions, surface characterization and thermal properties were investigated by Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and Differential scanning calorimetry (DSC) techniques respectively. The cohesive and adhesive bond analysis were carried out using pull-off adhesion test method (ASTM D4541). Results revealed that the epoxy coating containing 0.5% concentration of ZnO-NPs had maximum effect on improving bonding both cohesively and adhesively in current study. The characteristic FTIR peaks in ZnO-ENC coating revealed interaction between ZnO-NPs and epoxy amine molecular chain. The shift in glass transition temperature (Tg) with addition of ZnO-NPs towards higher scale confirmed the catalytic behavior of ZnO-NPs and decreased molecular chain mobility. A detailed mechanism of adhesion between epoxy and carbon steel surface has been proposed in presence of zinc oxide nanoparticles.*

Keywords: *Adhesion; nanocomposite; ZnO; cohesive, pull off.*

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I. Introduction

Prevention from corrosion is of prime importance when protective coating is applied over the metal surface, however the durability of the coating is highly dependent on the adhesion of the coating material on the substrate which is lost under harsh environmental condition [1-3]. The epoxy coating films are prone to diffusion of corrosive species like oxygen, water and ions, which results in the coating degradation at long exposure times. The hydroxyl ions (OH^-) created at the cathode sits beneath the coating resulting in the increase of pH. This may result into the decrease of coating adhesion with substrate, and thus accelerating corrosion of the metal beneath the coating [4-7]. Thus, investigation of the strength of bonds formed at the interface of metal and organic coating could play important role in characterizing protective properties of organic coatings on a metal substrate.

The adhesion of polymeric materials to metallic surfaces has been explained by many researchers extensively for bond formation and is a very complex phenomenon. It might involve chemical as well as physical interactions to form bonding between metal and polymers and polymeric filler ingredients. Numerous research works have been carried out to explain the probable bond formation and adhesion between coating materials and the metal involving various chemical moieties including micro and nano metal oxides inside epoxy polymer coated on steel, aluminum or other metallic substrates. The formulation of epoxy primer has a great influence both on the adhesion and corrosion resistance of protective systems. The presence of zinc and chromate pigments in epoxy primer coatings led to enhancement of adhesion values, as well as of corrosion stability [8]. The incorporation of ZnO particles with cyclic carbonate silane functional groups in non-isocyanate based polyurethane coatings resulted in improved scratch hardness and abrasion resistance compared to those without any particles and with untreated ZnO particles [9]. The increase in apparent surface energy and roughness promote the enhancement of the mechanical interlocking effect in fully wet state, resulting in the improvement of adhesion property studied between aluminum alloy sheet and epoxy [10]. The mechanism of adhesion of an epoxy adhesive (DGEBA) on a Fe (100) surface using DFT were studied, the results indicated that the adhesion energy of the epoxy adhesive depends on the molecular orientation of the epoxy adhesive and the stability of a particular geometry was due to the strong interaction between the aromatic rings and the hydroxyl group of the epoxy adhesive and the Fe surface [11]. The epoxy coating adhesion studied by pull off adhesion force measurement to the steel surface found enhanced after surface treatment by Ce and Ce–Zn conversion coatings [12]. The impressive improvement of thermo-physical properties of epoxy resin were observed with ZnO nanoparticles for application in epoxy anticorrosion protective coating [13]. The influence of organophosphonic acid on adhesion property of sol-gel films coated with silane illustrated higher adhesion strength than samples uncoated specimen. No reduction in adhesion force observed even after 60 days of immersion for the system which contained organophosphonic molecules [14]. The pull off adhesion test performed with variation of silane content in water based epoxy silane hybrid coating showed increase in adhesion value from 1% to 3% however, with increase in the concentrations, it had negative impact on adhesion which might be attributed to over curing and incompatible coating networks [15].

There might be various ways to improve or influence the adhesion of organic coatings, in this work the epoxy amine system was formulated with different concentrations of ZnO-NPs applied on carbon steel substrates and adhesion of the coating were evaluated. Although, various works have been reported in past with probable mechanism of adhesion of epoxy on steel or interaction of ZnO with carbon double bonds, no works are reported on combined mechanism of improvement of adhesion and cohesion by ZnO nanoparticles formulated inside epoxy coating. Here, an attempt has been made to explain a less explored bond formation among epoxy amine chain, ZnO nanoparticles and metal substrate based on the analytical results. The influence of ZnO-NPs with variation in concentrations, on adhesive and cohesive forces of ZnO-ENC coatings were investigated in detail by pull off adhesion force measurements and the results reported at various concentrations have been correlated with calorimetric, spectroscopic and electron microscopic findings. Based on the analytical findings, a mechanism of cohesion inside epoxy matrix and adhesion with carbon steel substrate has been proposed in presence of ZnO-NPs.

II. Material and experimental methods

2.1. SYNTHESIS OF ZNO-NPS:

The synthesis of ZnO-NPs was carried out using wet precipitation method [nano-ZnO precursor formation] followed by calcination. 2.875 g $ZnSO_4.7H_2O$ was dissolved in 200 mL distilled water in a round bottom flask. 0.4 g NaOH solution was prepared in 80 mL distilled water in a beaker to be used as a precipitant. NaOH solution was added dropwise to the vigorously stirred zinc sulfate solution to adjust the pH to about 7, a slurry was obtained with progress in reaction, which was filtered and washed with distilled water. The product obtained was dried at 90^0C for 6 h to form the precursor of nano-ZnO. The precursor was then calcined for 2 h in a muffle furnace at 400^0C to remove hydroxides and produce the white colored ZnO-NPs. The process flow of complete synthesis has been illustrated in Fig.1. The ZnO-NPs so synthesized was characterized by DLS, FTIR, SEM and TEM methods, a mean particle size of 32 nm was reported.

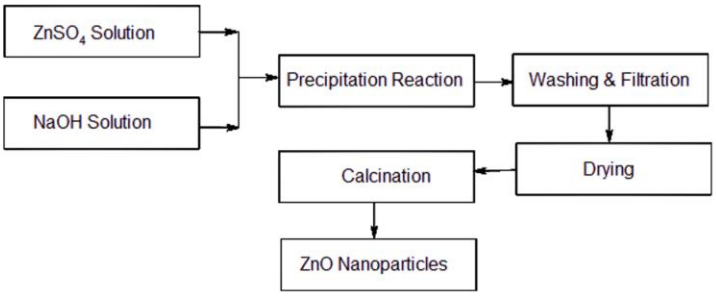

Fig.1 Process flow diagram of ZnO-NPs synthesis

2.2 EPOXY RESIN AND CURING AGENT:

The epoxy polymer used in this research was 2, 2-Bis [4-(glycidyloxy) phenyl] Propane based commercially known as Araldite GY 250 obtained from Huntsman Advanced Materials (Switzerland) GmbH having EEW 190 and a viscosity of 12000 cps, 25°C. The curing agent used was a modified aliphatic amine (typical Mannich base) commercially known as Ancamine 1856, with high reactivity obtained from Air Products and Chemicals, Inc. (Hamilton Boulevard, Allentown, PA) having amine value (mg/KOH/g) 460 and equivalent weight/[H] 73.

2.3 SYNTHESIS OF ZNO-ENC COATING MATERIAL:

The ZnO-NPs were added into the DGEBA epoxy polymer gradually under stirrer to obtain homogeneously dispersed ZnO-ENC using high speed dispersion machine, Dispermill (HSD, ATP Engineering B.V. The Netherlands). The dispersion process were carried out for 30 minutes at 1000 rpm and homogeneity were verified by hegman gauge for every batch preparation. The concentrations of ZnO-NPs in the epoxy so prepared were kept at 0, 0.25, 0.5, 1 and 2 wt.%. The polyamine curing agent was added to the synthesized ZnO-ENC composite phase in 4:1 weight ratio and the solutions were stirred until homogeneity was achieved before coating application.

2.4 STEEL COMPOSITION AND SPECIMEN PREPARATION:

The chemical composition of steel coupons under study was determined by spectroscopic method having Fe – 99.117%, C – 0.239%, Si – 0.034%, Mn – 0.468%, P – 0.019%, S – 0.012%, Cr – 0.002%, Cu – 0.060%, V – 0.001%, Al 0.042%, Co – 0.006%. The standard size of the coupons prepared were of 100x150x2 mm for salt spray resistance and 100x150x6.4 mm for pull off adhesion evaluation. All coupons were blast cleaned to SA-3 (ISO-8501-1) i.e. white metal before coating. Coatings were done by brush application method using no solvent/thinner during application, dry film thickness (DFT) were kept at 100 µ-m and cured for 7 days at standard laboratory conditions (23°C, 55% RH) in all cases.

2.5 CHARACTERIZATION TECHNIQUES:

Scanning electron microscopy (SEM) of JEOL-Tokyo model JSM-6510 LV, voltage 15kV was used to characterize the surface morphology of ZnO-NPs. The surface morphology of composite coating films of ZnO-ENC were analyzed by Nova Nano FEG-SEM 450. The size of the ZnO-NPs were analyzed by Dynamic Light scattering (DLS) method using Malvern zeta sizer NanoZS 90, UK model in methanol solvent. Pull off adhesion test were performed as per ASTM D-4541 [16]. Fourier Transform Infrared (FTIR) spectroscopic study was performed to investigate the interaction of ZnO-NPs with epoxy matrix in various concentrations using Thermoscientific Nicolet i-S10 instrument. Differential scanning calorimetry (DSC) were performed to determine glass transition temperature (Tg) by Universal V4.7A TA instruments, keeping rate of heating 20°C/minute in three different cycles viz. 1st cycle of 20-60°C, second cycle 20-275 and 3rd cycle of 20-200°C as per CSA-2006 method [17]. The objective to run the test in three cycles were to preheat at 60°C (moisture removal) followed by 1st Tg for as such cured specimens and heating for curing completion of epoxy amine system (up to 275°C) and 2nd Tg after complete curing (up to 200°C). Optical micrographs were taken by Axiovision microscope and coating thickness were measured by Elcometer 456 gauge. The failed coating area under dolly (14 mm) of pull off adhesion test were determined using area determination formula [πr^2] and is based on approximate measurement done using digital vernier caliper.

III. Results and discussions

3.1 SPECTROSCOPIC STUDY (FTIR):

Fourier transform infrared spectroscopic (FTIR) scan were carried out by KBr powder pellet method for ZnO-NPs and ZnO-ENC coatings for 0 to 2% concentrations. The spectroscopic scan of ZnO-NPs taken between wavenumbers 400 - 4000 cm^{-1} depicted a characteristic peak of ZnO at 421cm^{-1} (Fig.2). The FTIR scan of ZnO-ENC coating for various concentrations of ZnO-NPs, taken between wavenumbers 400 - 1700 cm^{-1} has been illustrated in Fig.3.

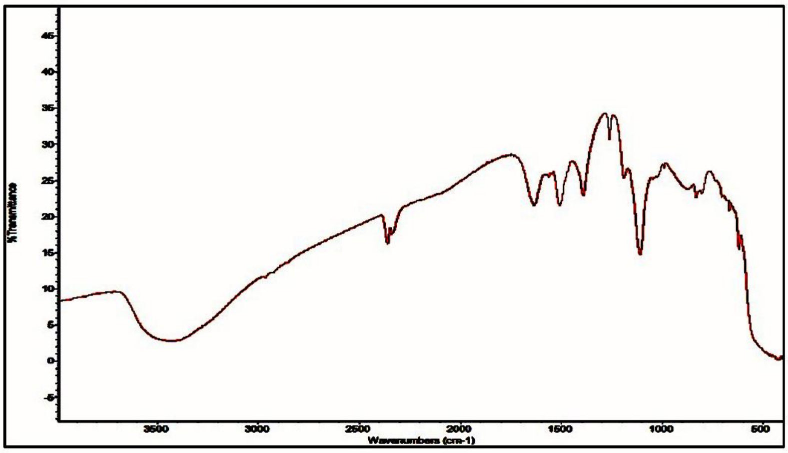

Fig.2. FTIR scan of ZnO-NPs 400 - 4000 cm^{-1} characteristic peak of ZnO observed at 421cm^{-1}

The FTIR analysis of ZnO-NPs confirms that there is a stretching frequency of Zn-O at 421cm^{-1} which gets prominently visible in NiO-ENC coating having concentration of 0.25% of ZnO-NPs. Increase in concentration of ZnO-NPs in the epoxy matrix at 0.50% level, the FTIR comparative graph [Fig.3] depicts that the peak further increases with higher intensity confirming high level of chemical interaction including possible chemical bond formation with epoxy amine chain at this concentration. Analysis of nanocomposite coatings containing increased concentration i.e. 1% and 2% of ZnO-NPs also shows peak at 421 cm^{-1} but the peak intensity is comparatively lower compared to 0.5% concentration. For distinct illustration of FTIR interactions, inset of Fig.3.A has been shown in Fig.3.B.

Table.1 Peaks appeared in FTIR scans of ZnO-ENC coatings and the respective groups representing the peak 400-1700 cm^{-1}

Groups present	Wavenumber (cm-1)
ZnO interaction with epoxy-amine molecule	421
-CH, -NH Bend	557
-AR=C-H, C-H Bending out of plane (polyamide adduct)	754
1, 4- substitution of epoxy	828
-C-O-R Ether	1035
-C-N absorption of amine	1105
-C-N absorption of amine	1182
-C-C-O-C-Stretching	1248
Aromatic -C=C- H Vibration	1457
Aromatic -C=C- H Vibration	1508
Aromatic -C=C- H Vibration	1540
Aromatic -C=C- H Vibration	1608

Various group frequencies for stretching and bending vibrations observed during infra-red analysis are listed in Table.1. Decrease in the peak intensity at higher concentrations might be attributed to poorer dispersion of nanoparticles and formation of agglomeration resulting into lower chemical interactions.

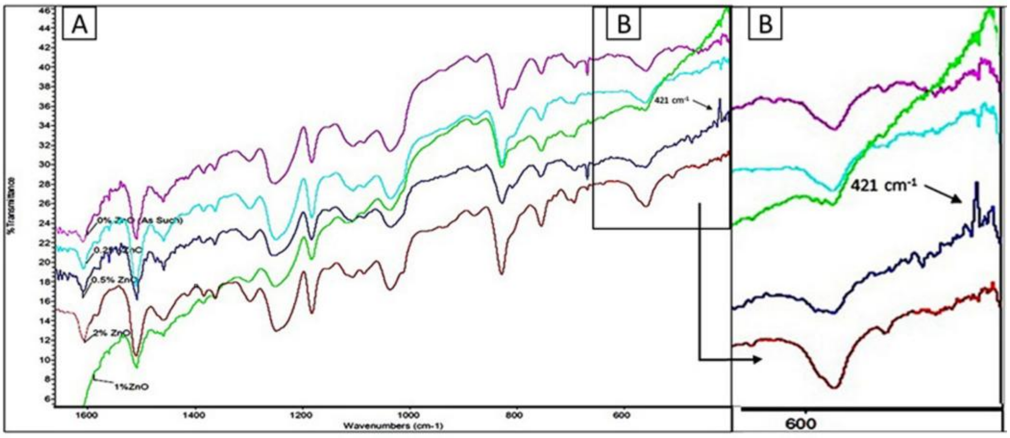

Fig.3.A. FTIR scan of ZnO-ENC coating 400-1700 cm^{-1} in various concentrations, ZnO interaction observed at 421 cm^{-1} and B. Inset of A, enlarged to visualize ZnO interaction at 421 cm^{-1} wavenumber.

3.2 SURFACE MORPHOLOGY OF ZNO-NPS AND ZNO-ENC COATING:

The surface morphology of ZnO-NPs and ZnO-ENC coatings were studied by scanning electron microscopy (SEM) and field emission gun scanning electron microscopy (FEG-SEM) methods respectively and size of the particles were determined by dynamic light scattering (DLS) and transmission electron microscopy (TEM) methods. A thin layer of gold was coated on the sample in order to avoid charging before the observation by SEM. The scans of the synthesized nanoparticles have been illustrated in Fig.4.A, B, C and D at different magnifications and scales. It is evident from the figure that at 100 & 50µ-m scales [Viz. 4.A & 4.B] that the appearance of the nanoparticles are irregular and in the form of continuous flakes. At 20µ-m scale and higher magnifications [Viz. 4.C & 4.D] agglomerates of the nanoparticles powder are prominently visible. The average size of the ZnO-NPs measured by DLS method was 32.9 nm which is nearly same as size measurement observed by TEM (~ 35 nm).

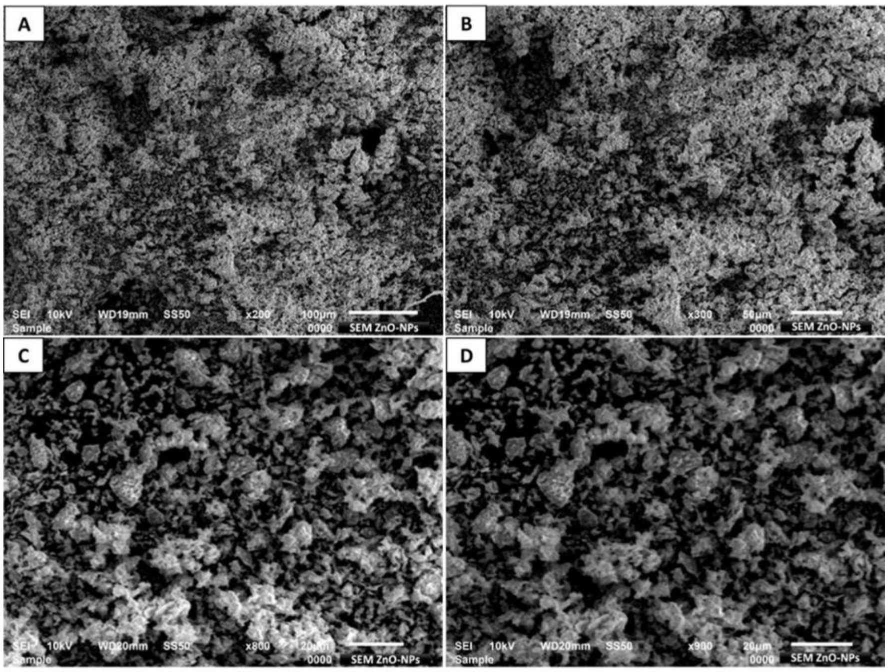

Fig.4. SEM images of ZnO-NPs at A. 200x magnification, 100μ scale B. 300x magnification, and 50μ scale C. 800x magnification, 20μ scale and D. 900x magnification, 20μ scale.

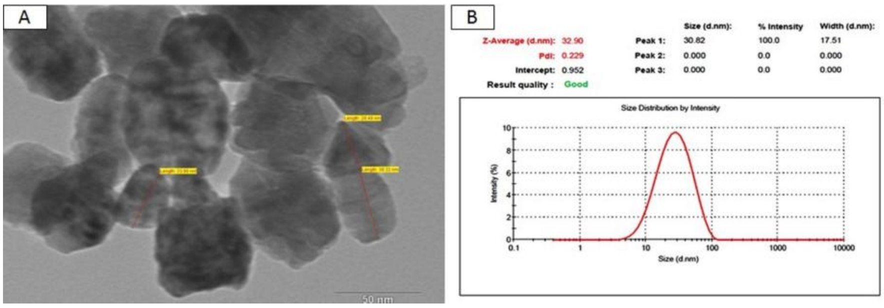

Fig.5.A. TEM image of the ZnO-NPs and B. DLS of ZnO-NPs, average size observed is 32.9 nanometer measured by Malvern zeta sizer NanoZS 90, UK in methanol solvent.

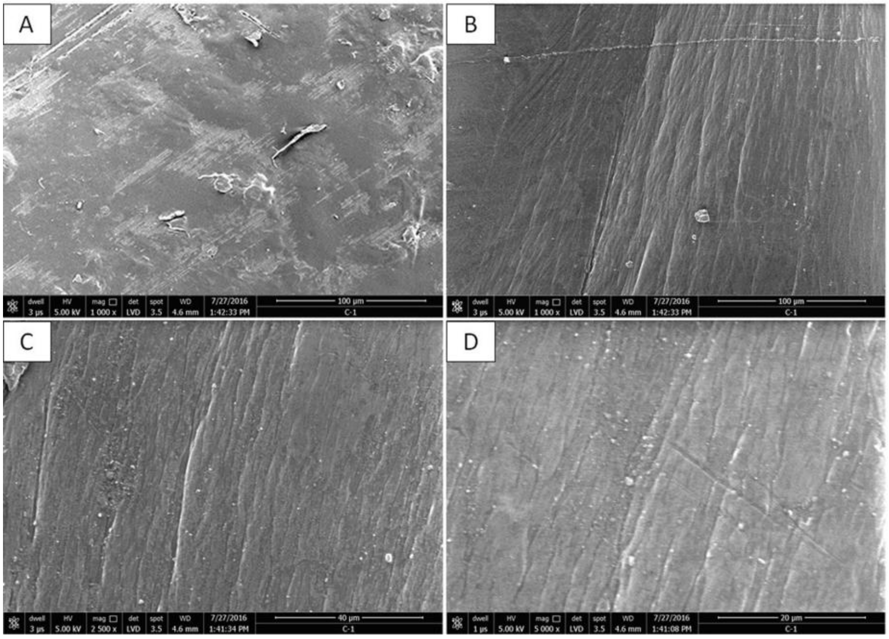

Fig.6. FEG-SEM images of A. neat epoxy (n-E), 1000x magnification, 100μ-m scale, and 0.5% concentration ZNO-ENC at B. 1000x magnification, 100μ-m scale C. 2500x magnification, 40μ-m scale D. 5000x magnification, 20μ-m scale.

The field emission gun scanning electron microscopic (FEG-SEM) scans of neat epoxy coatings (n-E) is illustrated in 6.A and that of 0.5% concentration ZnO-ENC coating are illustrated in Fig.6.B, C & D for various magnifications & scales. It is evident from the FEG-SEM scans that the surface morphology of n-E (Fig.6.A) is flat with no surface protrusion when compared to the composite coating film containing ZnO-NPs (Fig.6.B). It further depicts that the composite film is having a compact and continuous smooth layer of well dispersed ZnO-NPs throughout the surface. The ZnO-ENC coating film surface at higher magnifications viz. 2500x and 5000x illustrated in 6.C and D respectively, depicts a few agglomerated particles which might remained undispersed during the composite synthesis process.

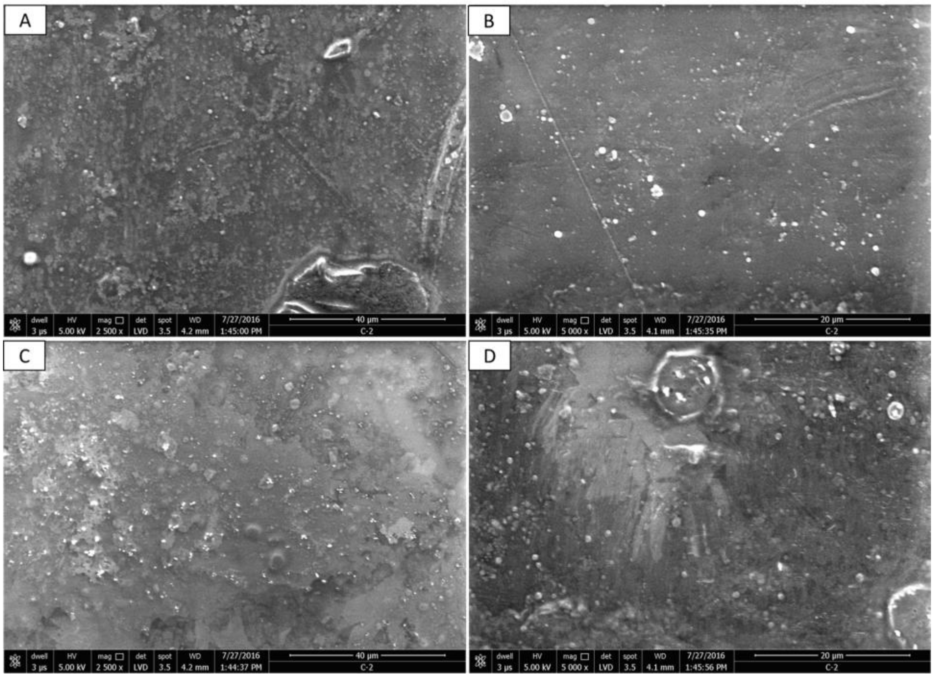

Fig.7. FEG-SEM images of ZnO-ENC coating with 1% concentration of ZnO-NPs A. 2500x magnification, 40µ-m scale, and ZNO-ENC at B. 5000x magnification, 20µ-m scale; and with 2% concentrations of ZnO-NPs C. 2500x magnification, 40µ-m scale D. 5000x magnification, 20µ-m scale.

The surface morphologies of ZnO-ENC coatings containing 1% and 2% of ZnO-NPs concentrations studied by FEG-SEM scans are illustrated in Fig.7.A & B and 7.C & D respectively at various magnifications and scales. It is clearly evident from FEG-SEM scans that the ZnO-NPs are not dispersed homogeneously as well as there are lots of agglomerates present in both the concentrations (1% &2%). In case of 2% concentrations illustrated in 7.C & D, it is observed that the particles have formed bigger clusters of the nano powders imbedded inside epoxy matrix as well as undispersed white colored particles visible on the surface. The resulted morphology can be attributed to insufficient mechanical shear force applied by machine and simultaneous addition of higher quantity of ZnO-NPs into epoxy resin for dispersion at a time resulting into agglomerate formation.

3.3 THERMAL ANALYSIS (DSC):

Differential Scanning Calorimetry (DSC) technique was used to evaluate the curing behavior of the ZnO-ENC coating by measuring glass transition (Tg) temperatures. The Tg measured during various cycles conducted is summarized in Table.2. It is observed that with the increase in the concentration of ZnO-NPs, both Tg-1 and Tg-2 increases. Remarkable differences are observed in case of 0.25% and 0.50% ZnO-NPs concentrations compared to neat epoxy coating. The glass transition temperature (Tg) appears to be stabilized when concentration of ZnO-NPs are increased above 0.5%. The enhancement of Tg due to incorporation of ZnO-NPs is indicator of improved thermal resistance of the nanocomposite coating.

Table.2 Glass transition temperature of ZnO-ENC coating.

Description	Neat epoxy	0.25% ZnO-ENC	0.50% ZnO-ENC	1.0% ZnO-ENC	2.0% ZnO-ENC
Tg1	85.12	87.05	95.16	95.39	96.25
Tg2	111.41	113.79	115.05	115.29	115.68

It is evident from the Table.2 that the glass transition temperature (Tg) of the sample having 0.50% concentration of ZnO-NPs has shown very high shift in Tg-1 and marginally high in Tg-2 compared to neat epoxy. The Tg-1 and Tg-2 of 1% and 2% concentrations are close to 0.5% concentration and also comparable to each other. The phenomena of higher shift in Tg-1 at 0.50% concentration can be attributed to high catalytic effect on epoxy amine cure reaction as well as higher interaction of ZnO-NPs with epoxy chain respectively (observed during FTIR analysis) which facilitated restricted epoxy chain mobility in similar cure condition compared to neat epoxy (n.E). This phenomena can also be attributed to a very high degree of dispersion of the nanoparticles inside epoxy matrix and filling spatial gaps making compact nanocomposite film observed during FEG-SEM scan analysis. The phenomena of shift in higher glass transition temperature observed here also correlates with the results observed for increased pull off adhesion bond strength [Sec. 3.5] of the ZnO-ENC coating system. No significant increase in Tg-2 (maximum attainable Tg) in case of 1.0% and 2.0% concentrations further implies that the catalytic effect or increase in cross link density has got limitation up to 0.5% concentration of ZnO-NPs, as well as dispersion of ZnO-NPs are poorer in case of higher concentrations as observed in FEG-SEM scans.

3.4 PULL OFF ADHESION:

The pull off adhesion analysis of ZnO-ENC coating formulations at various concentrations were done according to ASTM D 4541 test method using PosiTest AT-A fully automatic pull off adhesion tester (DEFELSKO). Carbon steel coupons of similar composition (size -150x100x4.4 mm) were blasted by automatic blast cleaning machine using metal grits with 60-70 µ-m profile creation. Surface cleanliness rated as SA 3 (ISO 8501-1) white metal cleaning (Fig.9.F). The aluminum dollies were glued on the surface of the epoxy coating using a two-part 3M adhesive Scotchweld DP 460. Samples were then kept at ambient temperature for 48 h to ensure that the glue is fully cured. Slots were made around the dollies to separate the test area followed by pull rate of 150psi/s normal to the coating surface until the epoxy coating was detached from the steel substrate. The adhesion tests were carried out in triplicate for each set of specimen (concentrations) to ensure the measurements repeatability. It is interestingly noted that with increase in the concentration of nanoparticles, the pull off adhesion increased up to 0.5% concentration (Fig.8) followed by decrease in the pull off adhesion force at higher concentrations. A set of test specimens is illustrated in Fig.9 to depict the pattern of failure of coating from film (cohesive) and the substrate (adhesive). It is observed that the increase in pull off force resulted with increased failure of surface area (Fig.10) under test dolly, which corroborates that with addition of ZnO-NPs at 0.25% and up to concentration of 0.5%, the epoxy-ZnO film integrity improves due to higher interaction of ZnO and epoxy molecule as well as with metal surface, thereby provides higher cohesive as well as adhesive force within the film. For the sake of simplicity, entire test results can be explained by adhesive bond force based on pull off adhesion values and cohesive film integrity based on failed area analysis.

3.4.1 Adhesive force between coating film and metal surface:

The pull off adhesion forces observed under the current study for various concentrations of ZnO-NPs containing epoxy coatings have been illustrated in Fig.8. It is observed that the adhesive force between metal substrate and the coating layer has increased with the introduction of ZnO-NPs inside epoxy matrix. The pull off adhesion force observed for neat epoxy is 34.32 MPa, which increased to 36.32 MPa at 0.25% of ZnO-NPs concentration. The pull off adhesion force value increased further with increase in concentration (0.5%) of ZnO-NPs and reached to 39.76 MPa, the highest value observed during current study. The result observed might be explained by continual increase in the adhesive force between metal surface and film due to possible physical and chemical interactions of ZnO-NPs present inside coating and metal oxide of the coated substrate. This increase in the adhesive force might also be attributed simultaneously to increase in cohesive force inside the epoxy film which facilitated to keep larger surface area bonded together, explained in later section.

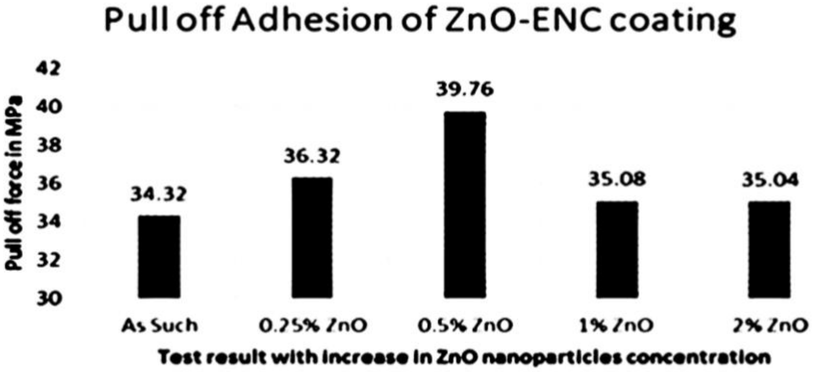

Fig.8. Pull off adhesion test for various concentrations of ZnO-ENC coating

With further increase in the ZnO-NPs concentrations, it is observed that the pull off forces have decreased to 35.08 and 35.04 MPa for 1% and 2% concentrations respectively. This decrease in the adhesion forces might be attributed to excess ZnO-NPs inside the epoxy matrix producing hindrance in the physical and chemical interactions, where limited sites for interactions are available at metal surfaces and on epoxy amine molecules. Other possible reason of decrease in adhesion force might be imparted to increase in the agglomeration of nanoparticles and comparatively poorer dispersion of particles at higher concentrations. Agglomerated particles are clearly seen in FEG-SEM images of epoxy amine coating film at 1% and 2% concentrations [Fig.7].

3.4.2 Cohesive force in the epoxy film

During pull off adhesion force test, we observed an interesting phenomenon of increase in the % age detached/failed surface area from substrate with increase in concentration of ZnO-NPs. The failed surface areas were measured and compared with each other considering total surface are under dolly as 100%. The increase in the detached area with increase in ZnO-NPs corroborates increase in cohesive force among film having similar condition of test. The correlation between coating failure area and increase in cohesive force within film and increase in pull off adhesion force has been illustrated through schematic diagram shown in Fig.10 ‘A’ to ‘E’. A cohesive bond failure in case of neat epoxy ‘A’ where only 6.25% area under dolly failed indicates that the actual bond strength between coating and substrate is higher but film has limited cohesive force resulting into failure at 32.32 MPa. Incorporation of 0.25% concentration of ZnO-NPs ‘B’ has improved cohesive force inside coating film where bond strength fails at 36.32 MPa with higher area failure of 37.75%. The maximum cohesive force and optimum bond strength between coating film and substrate found at 0.50% concentration with approximately 90% coating failure but improving bond strength to 39.76 MPa. The increase in ZnO nanoparticle concentration further (1.0% and 2.0%) inside coating has shown limitation with decrease in adhesive force as well as higher area failure compared to 0.25% concentration. At higher concentrations of ZnO-NPs viz. 1% and 2%, adhesion force between coating material and the substrate found decreased compared to that of 0.5% concentrations while the cohesive force (indicated by total failed surface area) of coating film found intact to some extent. The pull off forces of 1.0 and 2.0% concentrations resulted are 35.08 and 35.04 MPa respectively while that of neat epoxy is 34.32 MPa which shows no much improvement in adhesion between metal surface and coating film. However, the area detached from the surface is significantly higher viz. 72.55 and 73.25% in case of 1% and 2% concentration respectively while 6.25% in case of neat epoxy. This result ascertains that the cohesive force or film integrity could be improved only with low concentration of ZnO-NPs (for overall improved adhesion over substrate), while higher concentration (≥1%) might be masking – OH groups (responsible for adhesion with metal) of the epoxy amine system as well as interfering between epoxy and substrate due to excess ZnO resulting into reduced coating substrate attractive interactions and the adhesive force.

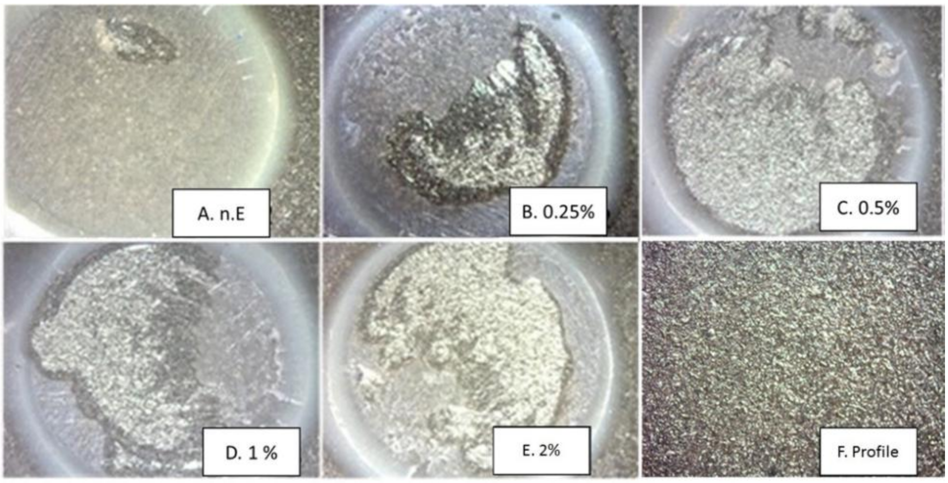

Fig.9. Optical micrograph with 6.5X magnification of the surface area under test dolly after pull off adhesion test from A to E and Blasted steel surface profile in F.

This might be attributed to masking –OH groups responsible for adhesion when the ZnO-NPs are in excess amount. It can further be interpreted that high level of dispersion of ZnO-NPs in case of ‘B’ and ‘C’ might have resulted into better physical and chemical interactions with metal surface resulting into higher bond strength, while dispersion is poor with agglomerate formation when the concentrations are higher in ‘D’ and ‘E’ observed during FEG-SEM scans.

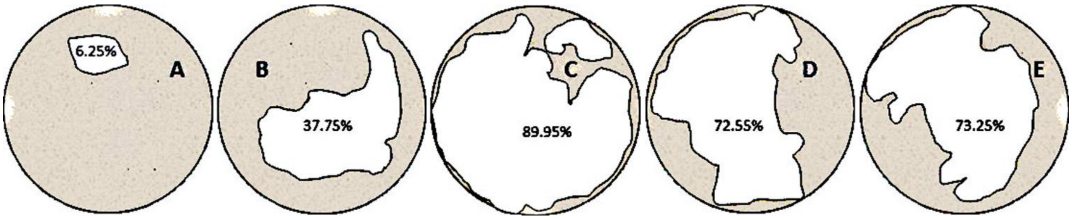

Fig.10. Schematic illustration of area detached (shown in blanc) during pull off adhesion test, ‘A’ ‘B’ ‘C’ ‘D’ and ‘E’ represents neat epoxy, 0.25%, 0.5%, 1% and 2.0% concentration respectively. ZnO-ENC coating resulted into higher cohesive force at 0.50% concentration with increase in pull off force

3.5 Mechanism of Adhesion & Cohesion in Zinc oxide-Epoxy Nanocomposite coating:

The improvement in the cohesive bond force with incorporation of ZnO-NPs in the current study might be attributed to chemical interaction and probable bond formation between ZnO and epoxy molecules. Schematic diagram has been illustrated in Fig.11 to explain the adhesion behavior of coating failure during pull off adhesion test. Cohesive forces are developed due to higher affinity and increased integrity within same surfaces. In this study, cohesive forces are developed inside epoxy coating layer. Adhesive forces are developed between two dissimilar surfaces, here bonding between epoxy coating layer and the carbon steel surface forms adhesive bonding. In case of epoxy amine coating system, an interaction of ZnO molecules is possible with epoxy molecules to provide increased cohesive bonding. This was corroborated during current study depicted by increased surface area failure (increased film integrity) with introduction of ZnO-NPs and further increase in detached surface area with increase in concentration of ZnO-NPs. Based on surface area detachment it can be interpreted that the cohesive forces found maximum in case of 0.5% concentration, and it very similar in 1% and 2% concentration.

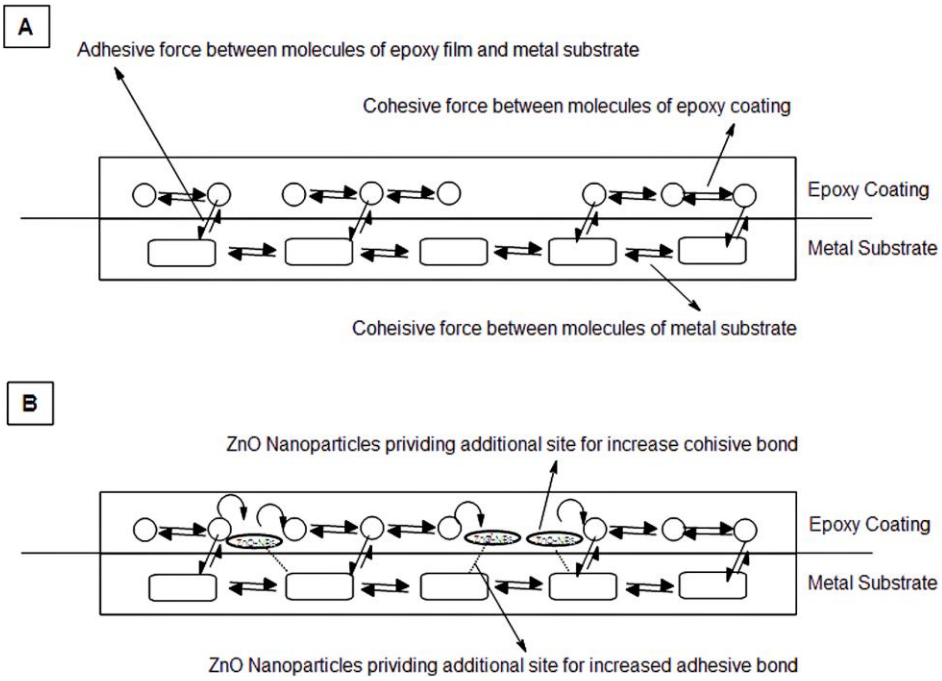

Fig.11. Schematic representation of (A) cohesive and adhesive bonding between molecules of epoxy film and that of metal substrate, (B) Introduction of ZnO-NPs created additional site for interaction and bonding to increase cohesive force among epoxy film and adhesive force between epoxy and metal substrate. Interaction of ZnO-NPs with epoxy and that of metal surfaces are shown by semicircular arrow and broken line respectively.

As shown in the schematic representation, the ZnO-NPs play important role in increasing adhesive bond site on the metal surface resulting into increased bond strength. Based on the strong increase observed in pull off adhesion force with introduction of ZnO-NPs, it can be stated that probability of chemical bonding of ZnO-NPs with epoxy amine chain is high which is also supported by interaction observed during FTIR study.

A surprisingly very high enhancement in glass transition (Tg) values (which might result due to restricted chain mobility) and high interaction of ZnO-NPs confirmed by FITR scans (highest interaction seen at

0.5% concentration) observed during the characterization of ZnO-ENC coating indicates that there are high possibilities of atomic interaction including chemical bonding among ZnO, epoxy and substrate metal oxide. There are probabilities of three different interactions and chemical bonding between epoxy & Zn-O molecules and Zn-O & metal oxide molecules illustrated in Fig.12, are summarized as below:

3.5.1 Interaction of zinc atom of ZnO with delocalized electrons of benzene ring

Interactions of zinc atom of the Zn-O molecules might take place towards the delocalized electrons of benzene molecules through van der walls force of attractions. This kind of interaction can provide additional cohesive force inside epoxy Zn-O film.

3.5.2 Interaction of zinc atom of ZnO with oxygen atom of oxirane ring

Interactions of zinc atom towards oxygen atom of the oxirane ring after opening of the ring (in presence of –NH_2) and formation of chemical bond at the open oxirane site is possible. This may be a case of formation of ZnO_2 molecule. This mechanism which is postulated based on higher interaction of ZnO-NPs confirmed by FTIR during current study, is further supported by earlier work reported by Robert D. Batch et al (1994), for surface interactions of ZnO with organic molecule, where it was concluded that insertion reactions of carbon-carbon double bonds in Zn—O should be quite feasible due to relatively low activation energy for aminolysis and hydrolysis which further suggests that amines, water or alcohol functional groups should be capable of forming covalent bond with ZnO surface [18]. This phenomena can provide enhancement in cohesive force inside epoxy matrix.

3.5.3 Interaction of zinc oxide molecule with oxygen atom of metal oxide

Some of the metal oxides might be bonded through hydrogen bonding from epoxy molecules while others might involve into interaction with Zn atom of ZnO molecules. This phenomena can impart additional adhesive bond improvement between coating film and the substrate. With introduction of 0.25% concentration of ZnO-NPs, an increase in bond strength observed which reached to saturation level at 0.5% concentration.

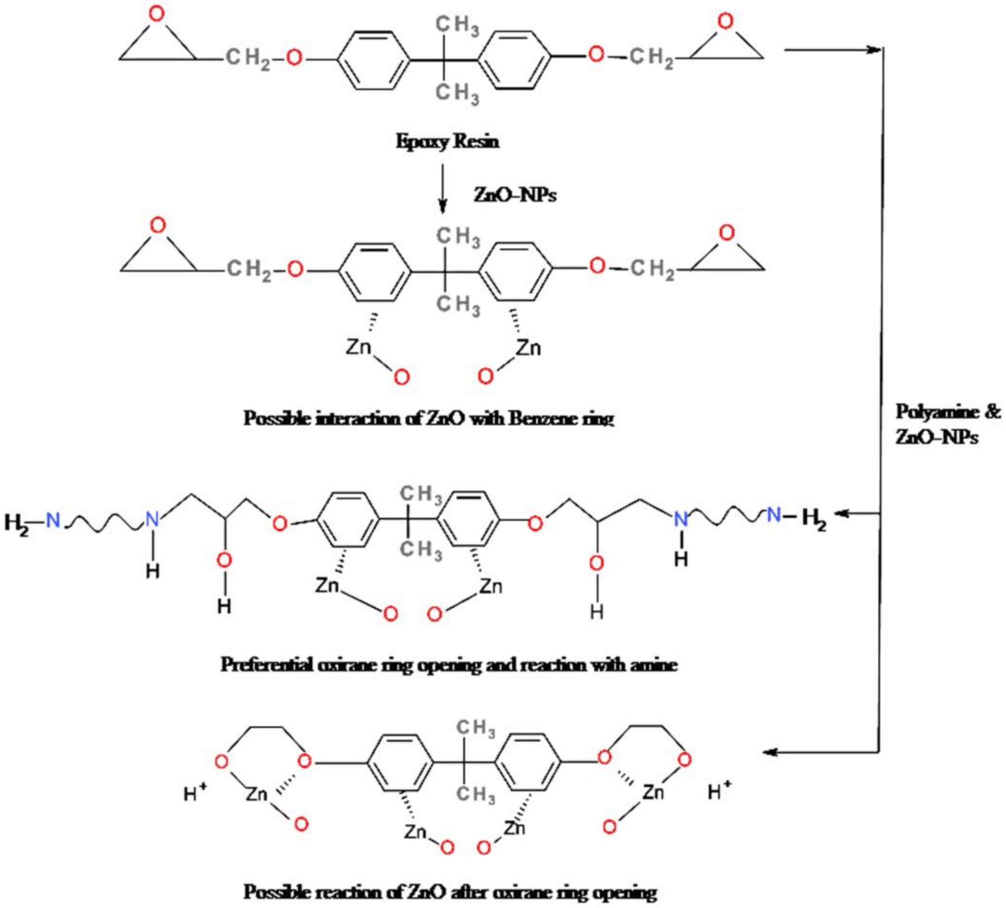

Fig.12. Probable mechanism of interaction of ZnO nanoparticles with Epoxy chain formation of bond in presence of polyamine.

Based on the possible interactions and mechanism proposed, a schematic representation has been illustrated in Fig.13 to demonstrate the cohesive and adhesive bond forces of epoxy coating containing ZnO-NPs on carbon steel surface.

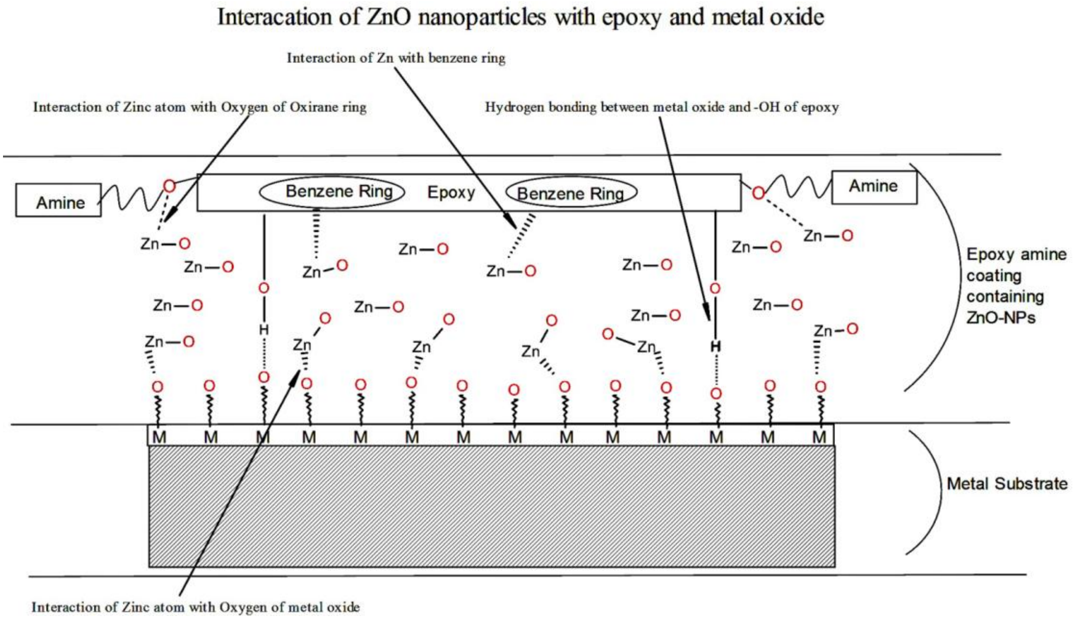

Fig.13. Mechanism of adhesion between epoxy resin and metal surface through hydrogen bond and probable interaction of ZnO-NPs.

IV. Conclusion

Zinc oxide nanoparticles [ZnO-NPs] and zinc oxide epoxy nanocomposite (ZnO-ENC) coatings were synthesized for the study of cohesive and adhesive properties of the synthesized coating on carbon steel. The ZnO-ENC coatings were investigated for various concentration of ZnO-NPs for bond strength using pull off adhesion test. We found that the adhesive bond force increases by adding ZnO-NPs and illustrated highest bonding with substrate at 0.50 wt.% ZnO-NPs concentration during current study. Also, with increase in the ZnO-NPs concentration, the cohesive force found increasing, analyzed by surface area detachment study. The trend of improvement in bond strength found correlating with Tg observed during DSC analysis. Also, based on shifts in Tg-1 and Tg-2 of ZnO-ENC compared to neat epoxy, it is concluded that the incorporation of ZnO-NPs provides restricted chain movement and catalytic effect on the reaction between epoxy and polyamine. Increase in the film integrity and cohesive force observed with incorporation of ZnO-NPs due to interaction or probable chemical bond formation between ZnO and epoxy amine molecules. It is also observed during SEM analysis that the dispersion of the nanoparticles in the polymer matrix is homogeneous with a few agglomerates up to 0.5% concentration while at increased concentrations (1 & 2%) higher agglomeration and discrete layer of ZnO-NPs observed. A mechanism of interaction of epoxy amine coating in presence of ZnO-NPs has been proposed and is explained for possible bonding among epoxy, ZnO-NPs and carbon steel surface to enhance cohesive and adhesive forces.

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