

# Diglycidyl Ether of Bisphenol a based Epoxy Polymer Doped with ZnO Nanoparticles for Enhanced Abrasion and Corrosion Resistance to Protect Carbon Steel

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**ABSTRACT:**The DGEBA based epoxy polymer was doped with zinc oxide nanoparticles (ZnO-NPs) to synthesize zinc oxide epoxy nanocomposite (ZnO-ENC) coating by mechanical stirring method at 0-2% concentrations of ZnO-NPs. The chemical identification and surface morphology were studied by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) techniques respectively. The coating performance properties viz. abrasion and corrosion resistance were evaluated for different concentrations of ZnO-ENC coating. The characteristic FTIR peak of ZnO-NPs was obtained at  $421\text{ cm}^{-1}$ . Abrasion resistance of ZnO-ENC coating were found increasing with increase in concentration of ZnO-NPs, best result was observed at 0.5% concentration of ZnO-NPs in current study. Surface morphologies of the nanocomposite films revealed by SEM micrographs illustrate the continuous dispersion of the ZnO-NPs inside epoxy matrix, minor agglomeration of particles are also observed at higher magnification. Significant enhancement was observed in corrosion resistance property of ZnO-ENC film with incorporation of ZnO-NPs evaluated by salt fog resistance method.

**KEYWORDS:**Corrosion; abrasion; nanocomposite; ZnO.

## I. INTRODUCTION

The developments and study of nanoparticles modified coating materials have been receiving significant attention in recent years due to improvements in physico-chemical and engineering properties of the modified polymeric coatings. Epoxy is a widely used polymer for high performance coatings due to its proven protective properties. However, the durability of epoxy coatings is often hampered by surface abrasion and wear [1, 2], poor resistance to the initiation and propagation of cracks [3] and lower permeability resistance. Furthermore, being hydrophilic in nature, epoxy coatings experience large volume shrinkage upon curing and can absorb water from surroundings [4, 5]. The carbon steel surfaces are prone to be attacked by aggressive species such as water, oxygen and ions during service life. There are various reports concerning improving protective properties of epoxy coatings using various nanoparticles including zinc oxides, aluminum, iron oxides, clays and other metal & metal oxides. Zinc-rich epoxy coatings with 2 wt.% concentration of aluminum nanoparticles illustrated better performance than the standard zinc-rich epoxy coating [6]. The ZnO-NPs have potential to be used as an antimicrobial agent [7, 8], better anticorrosive in epoxy-PANI coating on steel substrates [9] and photocatalytic activity [10] application. The biocompatibility and antibacterial properties of nanocomposites advocate them for medical application too [11]. Graphene oxide alumina nanocomposite hybrid were evaluated for improved anticorrosion property inside epoxy polymer [12]. The long term protection of metals and carbon steel in particular have been a very important problem from the economical point of view. To obtain a highly durable protection from an applied surface coating, an end user of coating material expects high corrosion resistance, excellent abrasion resistance and high bond strength with substrate etc.

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In this paper, we have fabricated and evaluated DGEBA based zinc oxide epoxy nanocomposite (ZnO-ENC) coating for enhanced abrasion resistance and corrosion protection with respect to variation in concentrations of ZnO-NPs. To evaluate these parameters in current ZnO-ENC coatings, Taber abrasion resistance and Q-Lab salt fog analysis were performed as per ASTM D4060 and ASTM B117 respectively. The ZnO-NPs and ZnO-ENC coatings at various concentrations have been characterized by spectroscopy and electron microscopy methods.

## II. MATERIAL AND EXPERIMENTAL METHODS

### 1.1 Synthesis of Zinc Oxide nanoparticles (ZnO-NPs)

Synthesis of ZnO-NPs were done following the precipitation method. A two-step process was followed to synthesize the ZnO-NPs, in step one the ZnO precursors were synthesized followed by calcination in step two. Solution of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  was taken as the starting material and NaOH as precipitant. NaOH solution was added dropwise to the vigorously stirred solution of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  to adjust the pH to about 7. After this process, a large amount of white slurry was formed. The resulting slurry was continuously stirred for 12 Hours, and then washed with deionized water. The wet powder was dried at  $90^\circ\text{C}$  for 6 Hours to form the precursor of ZnO. The precursor then was calcined for 2 Hours in air at a  $400^\circ\text{C}$  to produce the ZnO-NPs. The synthesized nanoparticles were characterized by FTIR and TEM methods, an average particle size of 32 nanometer was reported by TEM analysis.

### 1.2 Epoxy resin and curing agent:

The epoxy resin and its curing agent used in this research were obtained from Huntsman Corporation and Airproducts respectively. The epoxy resin is based on Diglycidyl ether of Bisphenol A (DGEBA) and curing agent is a modified aliphatic amine with high reactivity based on Mannich base chemistry. The weight ratio of the epoxy resin to the curative was kept 4:1.

### 1.3 Synthesis of ZnO-ENC coating material

The ZnO-NPs were added into the epoxy resin gradually under stirrer and homogeneous dispersed ZnO-ENC were synthesized using high speed dispersion (HSD) machine. The dispersion processes were carried out for 30 minutes at 1000 rpm and homogeneity were verified by Hegman gauge. The concentrations of ZnO-NPs in the epoxy so prepared were kept at 0, 0.25, 0.5, 1 and 2 wt.%. The curing agent was added to the mixture at 4:1 by weight mixing ratio and solutions were stirred until homogeneity was achieved. After the mixing completed, coating materials were applied on carbon steel coupons of dimension 75mm x 150 mm x 2mm.

### 1.4 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 while the composite coating films of ZnO-ENC were analyzed by Nova Nano FEG-SEM 450. Corrosion resistance of the coated specimen were tested by salt fog resistance test using Q-FOG Q-Lab corporation salt fog chamber using 5% NaCl concentration,  $35^\circ\text{C}$ , 100% relative humidity (RH) in accordance with ASTM B-117 [13]. Abrasion resistance of the applied coating were tested on Taber abrasion tester (Taber USA) as per ASTM D4060 using CS-17 wheels after 7 days curing at  $23^\circ\text{C}$  [14]. Fourier Transform Infrared (FTIR) spectroscopic study was performed to characterize the ZnO-NPs using Thermoscientific Nicolet i-S10 instrument. Coating thicknesses were measured by Elcometer 456 gauge.

### III. RESULT AND DISCUSSION

#### 2.1 Spectroscopic Study

Fourier transform infrared spectroscopic (FTIR) scan was carried out by KBr powder pellet method to characterize ZnO-NPs. The spectroscopic scan of the synthesized ZnO-NPs (Fig.1.) at wavenumbers 400 - 4000  $\text{cm}^{-1}$  depicted a characteristic peak of Zn-O absorption bond at 421  $\text{cm}^{-1}$ . A few other peaks of the scan observed can be assigned to possible surface impurity of sulphates and hydroxides during synthesis. The peaks observed at 1100  $\text{cm}^{-1}$  is due to the stretching of the sulphates (of sodium). Hydroxyl peaks are observed due to possible moisture in the sample and environment.

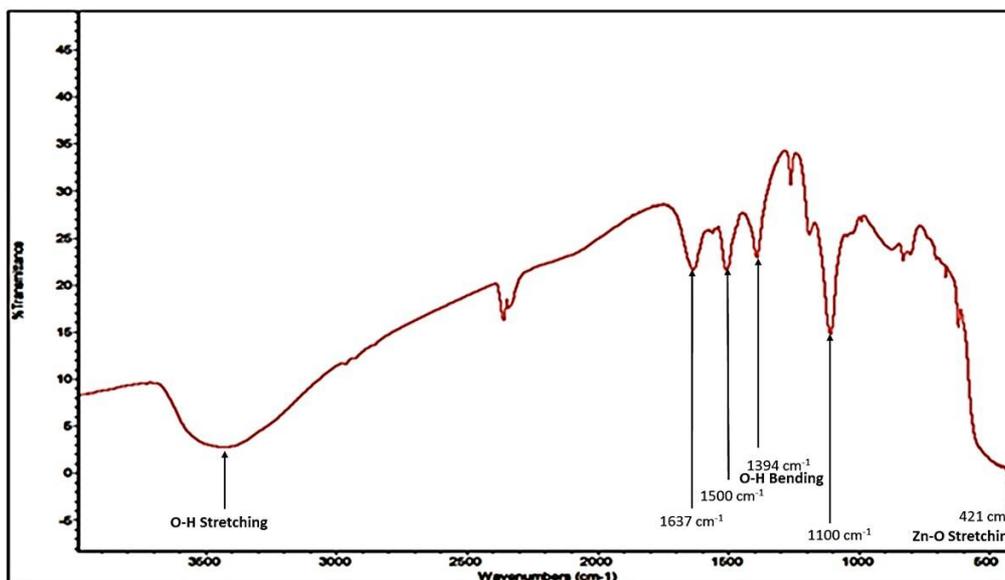


Fig.1. FTIR scan of ZnO-NPs 400 - 4000  $\text{cm}^{-1}$  depicting a characteristic peak at 421  $\text{cm}^{-1}$  of ZnO stretching.

#### 2.2 Morphological study of ZnO-NPs and ZnO-ENC coating film

The surface morphology of ZnO-NPs were studied by Scanning Electron Microscopy (SEM) & Transmission electron microscopy (TEM) and that of the nanoparticles doped composite epoxy polymer matrix were studied by Field Emission Gun Scanning Electron Microscopy (FEG-SEM) 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.2.A (SEM) and Fig.2.B (TEM). The images of the synthesized ZnO-NPs appear like continuous flakes of zinc oxide nanoparticles having irregular shape. It is clearly visible in the SEM image at 10  $\mu$  scale (Fig.2.A) that the nanoparticles in powder form have made some agglomeration. The TEM image is taken at a very small scale of 50 nm and the size of the particles were measured. It is observed that the particle size of the ZnO-NPs are 32 nm.

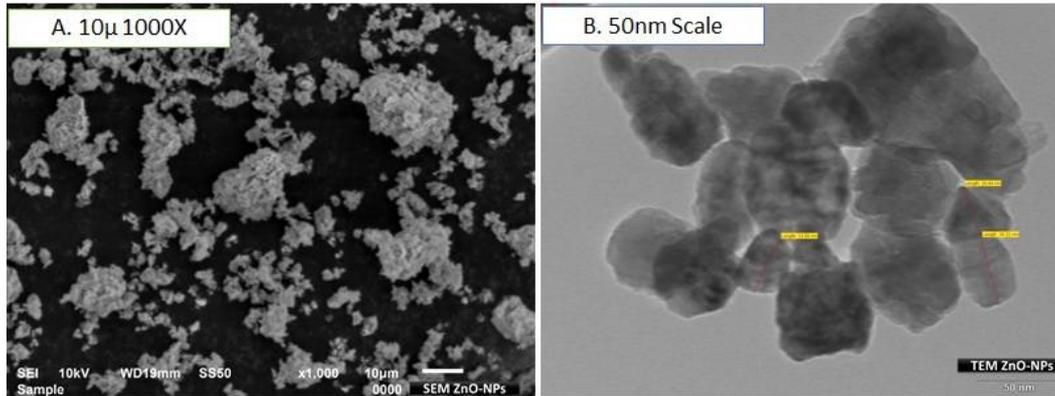


Fig.2. A. SEM micrograph of ZnO-NPs, a flake like structure is visible with minor agglomeration of particles visible at 10 $\mu$  scale. B. TEM micrograph of ZnO-NPs at 50 nm scale, average particle size measured were ~ 32 nanometers.

The surface morphology of the ZnO-ENC coating was investigated at various magnifications & scales using field emission gun scanning electron microscopy (FEG-SEM), are illustrated in Fig.3.A, B, C, D, E and F. It is evident from the FEG-SEM scans that a continuous dispersion of ZnO-NPs was achieved inside epoxy matrix with uniform distribution and coverage at most of the areas. At some areas, the scans are resembling as dusty cakes inside the composite coating film (Fig.3.A. 50 $\mu$ , 1500X) with outward protrusion from the surface which might be formed due to changes in the shear force during coating application. At higher magnifications, (Fig.3.B, C, D & E), the uniformity of nanoparticles distribution is more clearly visible. Fig.3.D and Fig.3.E are scans taken at same scale and magnifications (20 $\mu$  scale and 5000x magnification) but at adjacent locations of the film for comparison of the possible changes in nanoparticles arrangements within same film. This illustrates that there are minor change in the pattern of the nanoparticles arrangement inside the matrix at two different locations. At very high magnification of 10000X (Fig.3.F), some light reflective white bead like structures are visible which might be appearing due to possible minor agglomeration of the ZnO-NPs inside the polymer matrix.

### 2.3 Abrasion resistance analysis

The mechanical damage resistance due to friction between two surfaces were studied by Taber abrasion method (ASTM D-4060) for the synthesized ZnO-ENC coatings and the mass losses were calculated. Evaluations were done at 500 and 1000 cycles under CS-17 Taber abrader wheel and 1Kg load, results are illustrated in Fig.4. It is evident that the neat epoxy coating resulted into maximum mass loss as compared to any concentration of ZnO-ENC coatings in current study. Mere introduction of ZnO-NPs at as low as 0.25% concentration improved the abrasion resistance of the coatings from 14.9 mg (500 cycles) and 25.8 mg (1000 cycles) to 13.8 mg and 21.8 mg respectively. Highest abrasion resistance observed at 0.50% concentration of ZnO-NPs with mere 7.4 mg loss at 500 cycles. This is approximately > 50% lower abrasion compared to neat epoxy coating. Further increase in the concentration of ZnO-NPs in ZnO-ENC coating has shown saturation level and mass loss slightly increased at 1.0 and 2.0% concentrations. The phenomena of decrease in mass losses of coating on introduction of ZnO-NPs inside coating system may be attributed to possibly strong molecular interaction between the dispersed ZnO-NPs and polymer matrix as well as well dispersion of the ZnO-NPs. This result might be further be attributed to the formation of higher cross link density due to catalytic effect of ZnO-NPs which is improving the mechanical property of the coating system providing better resistance to surface abrasion during friction.

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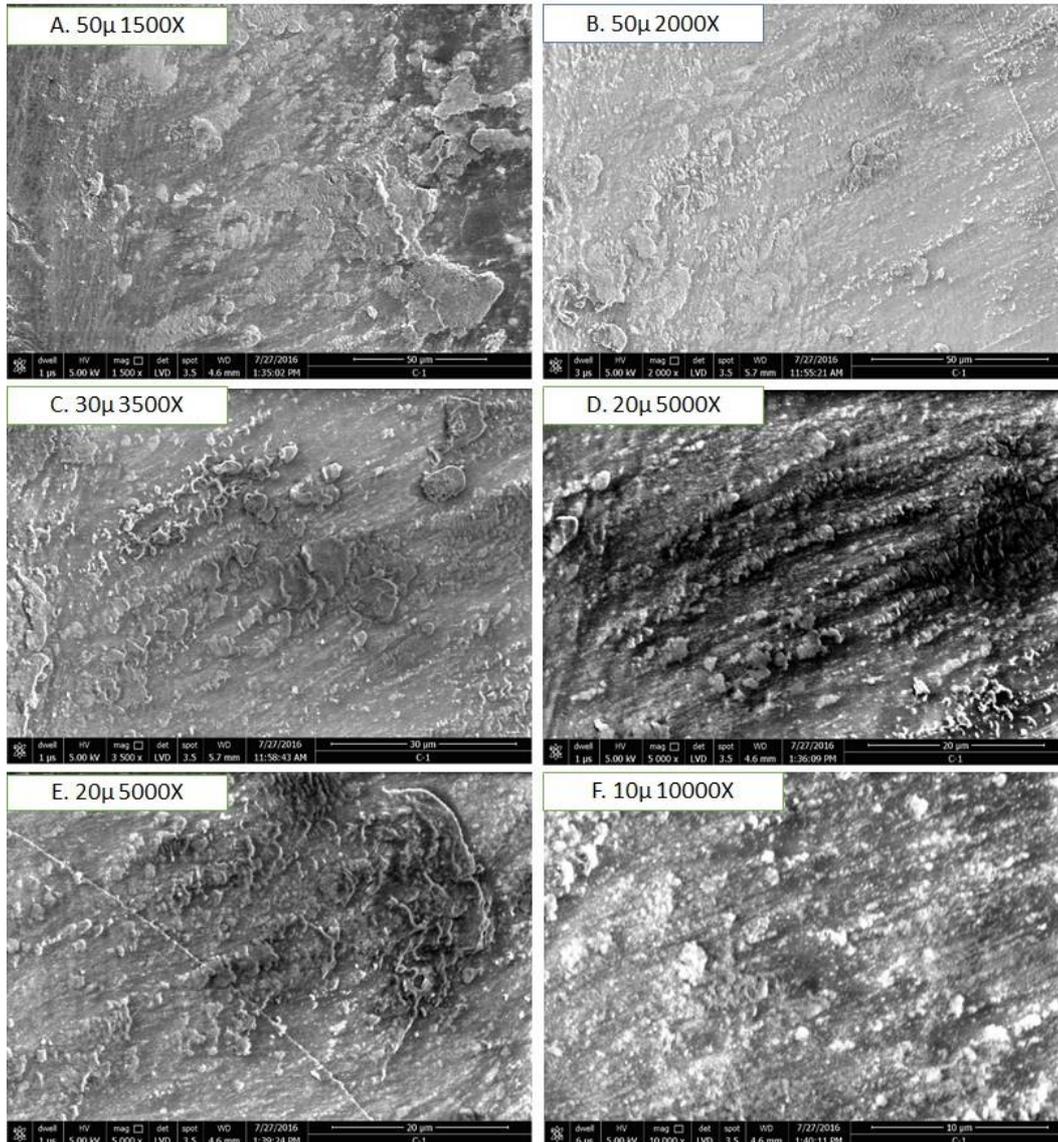


Fig.3.FEG-SEM micrographs of ZnO-ENC coating with decreasing scales and increasing magnifications to investigate the surface morphology A. 50 $\mu$  scale, 1500X magnification, B. 50 $\mu$  scale, 2000X magnification, C. 30 $\mu$  scale, 3500X magnification, D. 20 $\mu$  scale, 5000X magnification and E. 20 $\mu$  scale, 5000X magnification and F. 10 $\mu$  scale, 10000X magnification.

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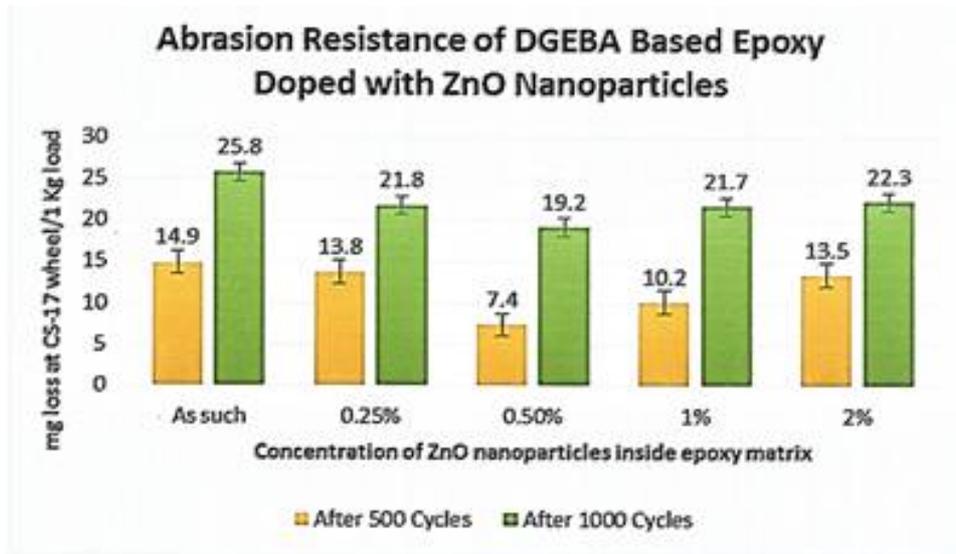


Fig.4. Abrasion resistance of ZnO-ENC coating after 500 and 1000 cycles, the mg loss of material found decreasing up to 0.5% concentration followed by minor increase.

## 2.4 Salt Fog analysis

The salt fog analysis was performed on the carbon steel coupons of dimension 75mm x 150mm x 2mm coated by neat epoxy and various concentrations of ZnO-ENC coatings at 100 $\mu$  thickness. The coated specimens were exposed for 480 Hours in the salt fog chamber at 30° angle from the vertical inside 5% NaCl salt fog [pH 7] and 100% relative humidity (RH) and examined for corrosion spread, face blistering and coating defects (ASTM D-1654). The result revealed that there is gradual improvement in corrosion resistance with increase in concentration of ZnO-NPs inside epoxy matrix. The salt fog tested coupons are illustrated in Fig.5.A, .B, C, D and E for 0, 0.25, 0.50, 1.0 and 2.0% concentrations of ZnO-NPs respectively. The decrease in the creepage of corrosion along scar and gradual lowering in the number of spot rust & blistering observed from 'A' to 'E' specimens after 480 Hours of exposure. The statistical data for spot rust and millimeter of creepage observed are given in Table.1. The surface of salt fog tested specimen found in extremely good condition in case of 2% ZnO nanoparticle concentration with no spot rust and negligible spread of corrosion along scar.

Table.1 Spot rust count and corrosion spread rating (ASTM D 1654) from scar after 480 Hours of salt fog test. It is noticed that the number of spot rust and spread of corrosion from scar reduced gradually with increase in concentration

Property/Concentration	Neat Epoxy (nE)	0.25%	0.50%	1%	2%
No. of spot rust	>50	15	12	2	NIL
Spread from scar (mm)	3.5	3	2.5	2	2

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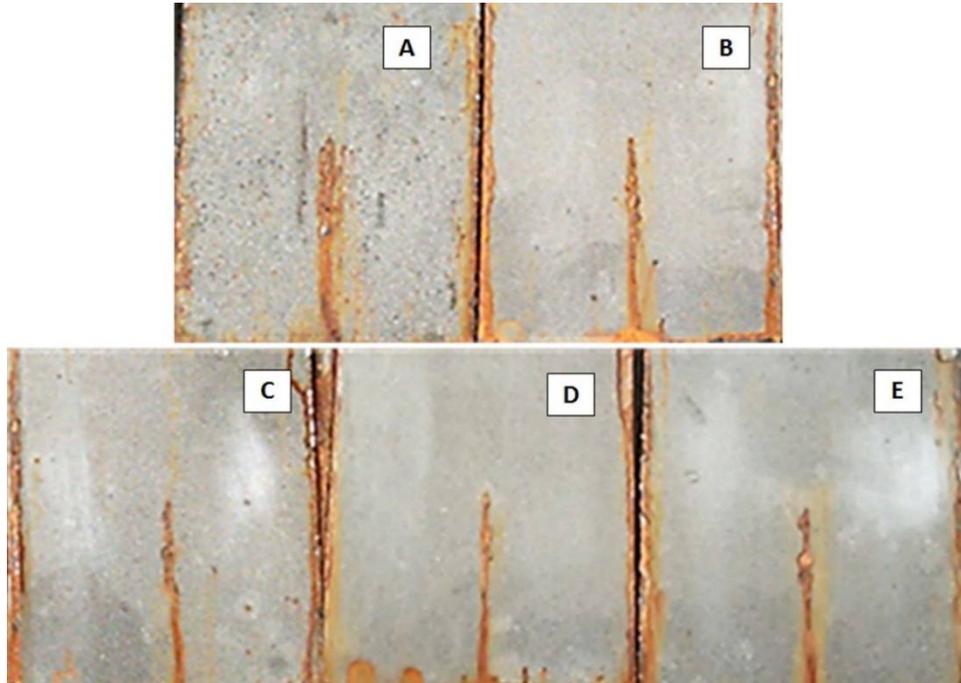


Fig.5 Salt fog evaluation results of ZnO-ENC coatings at various concentrations evaluated as per ASTM B-117 for 480 Hours at 100  $\mu$ -m dry film thickness. A. Neat epoxy B. 0.25% ZnO-NPs C. 0.5% ZnO-NPs D. 1% ZnO-NPs E. 2% ZnO-NPs.

Improvement in the salt fog corrosion resistance with increase in the concentration of ZnO-NPs inside epoxy matrix might be attributed to gradual increase in film integrity and higher electrolyte permeation resistance due to possible higher interaction between ZnO-NPs and epoxy amine molecules and a compact ZnO-epoxy nanocomposite matrix formation.

#### IV. CONCLUSION

Zinc oxide nanoparticles doped epoxy nanocomposite (ZnO-ENC) coating was successfully prepared for enhanced corrosion protection and abrasion resistance for the protection of carbon steel. The synthesized coatings were analyzed for various properties at different concentration of ZnO-NPs. We found that the abrasion and corrosion resistance of the ZnO-ENC coating increased by addition of optimum concentration of ZnO-NPs. The coating with 0.50 wt. % ZnO-NPs resulted into the best abrasion resistance while that of 2% provided best corrosion protection studied by Taber and Salt fog test methods respectively during current study. The trend of improvement in abrasion resistance illustrates that high cohesive force is developed between dispersed ZnO-NPs and epoxy amine molecule at 0.5% concentration which prevented the coating material maximum from abrasion. Based on the salt fog resistance evaluation it can be concluded that with increase in the concentration of ZnO-NPs inside epoxy matrix, an increase in film integrity and higher water permeation resistance resulted due to possible higher interaction between ZnO-NPs and epoxy amine molecules. This might also be attributed to continuous and dense ZnO-epoxy matrix formation visible in SEM analysis. The salt fog analysis result showed gradual improvement in corrosion resistance of ZnO-ENC coating with increase in concentration of ZnO-NPs which is again due to compact nanocomposite matrix formation. It is also reported from the SEM results that the dispersion of the nanoparticles in the polymer matrix is homogeneous.

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