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A new double layer epoxy coating for corrosion protection of Petroleum Equipments

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ABSTRACT
Homogeneous epoxy coating containing polymer nanocomposite (PNC) was successfully synthesized and applied on carbon steel substrates by room temperature curing of fully mixed epoxy slurry. (PNC) containing both ZNO nanoparticles and epoxy hyper branched polymer (EHBP), a new double layer thin film which comprises ZNO-epoxy as a primer coat and ZNO-EHBP-epoxy as a top coat offers better corrosion protection compared to the purely inorganic ZNO-epoxy coating and hybrid ZNO-EHBP-epoxy coating. Chemical structures of synthesized compounds were confirmed by FTIR, H^1NMR spectroscopy and GPC. The surface morphology and phase structure of the produced Zno nanoparticles were characterized by scanning electron microscopy SEM, transmission electron microscopy TEM and X-ray diffraction. Chemical resistance of theses coatings to NaOH and HCL was investigated. The effect of incorporating polymer nanocomposite and new double layer coating on corrosion resistance of epoxy coated steel was investigated by salt spray test.

Keywords: double layer coating, Epoxy coatings, Hyper branched polymers, polymer nanocomposites, ZNO nanoparticles.

I. INTRODUCTION

Epoxy has been widely used as a coating material to protect the steel structures [1–3], because of its outstanding process ability, excellent chemical resistance, good electrical insulating properties and strong adhesion to heterogeneous materials. Epoxy coatings generally reduce the corrosion of a metallic substrate subject to an electrolyte in two ways: First, they act as a physical barrier layer to control the ingress of deleterious species. Second, they can serve as a reservoir for corrosion inhibitors to aid the steel surface in resisting attack by aggressive species such as chloride anions. Nonetheless, the successful application of epoxy coatings is often hampered by their susceptibility to damage by surface abrasion and wear [4, 5]. They also show poor resistance to the initiation and propagation of cracks [6], such processes introduce localized defects in the coating and impair their appearance and mechanical strength. The defects can also act as pathways accelerating the ingress of water, oxygen and aggressive species onto the metallic substrate, resulting in its localized corrosion. Furthermore, being hydrophobic in nature, epoxy coatings experience large volume shrinkage upon curing and can absorb water from surroundings [7, 8]. The pores in the cured epoxy coating can assist in the migration of absorbed water and other species to the epoxy–metal interface, leading to initiation of corrosion of metallic substrate and delamination of the coating. The barrier performance of epoxy coatings can be enhanced by incorporation of a second phase that is miscible with epoxy coating. incorporation of zinc oxide nanoparticles into epoxy resins offers environmentally benign solutions to enhancing the integrity and durability of coatings, since the fine particles dispersed in coatings can fill cavities, decreasing the porosity, zigzagging the diffusion paths for deleterious species [9–11] and cause crack bridging, crack deflection and crack bowing [12]. Nanoparticles tend to occupy small hole defects formed from local shrinkage during curing of epoxy resin and they act as a bridge interconnecting more molecules. This results in a reduction of total free volume and grain boundaries size, as well as an increase in the cross-linking density of epoxy resin matrix, so that the trend of coating to blister or delaminate is reduced [13 - 16].

The main problem with Incorporation of inorganic nanoparticles into an epoxy polymer matrix is the prevention of particles aggregation. It is difficult to produce mono dispersed nanoparticles in an epoxy polymer matrix because of agglomeration nanoparticles due to their high specific surface area and volume effects, which lead to lower dispersion stability in epoxy resin, in addition to incorporation of inorganic nanoparticles cause some of rigidity to epoxy matrix. These problems can be overcome by applying polymer nanocomposite modification where the surface of the inorganic nanoparticles is modified through core–shell structure such that inorganic nanoparticles work as core and masked by polymer which work as shell, core-shell structure improves the interfacial interactions between the inorganic nanoparticles and epoxy matrix that improve dispersion stability of nanoparticles into epoxy matrix, in addition the surfaces of nanoparticles become hydrophobic that important in miscibility and compatibility of nanoparticles with epoxy resin matrix. Polymer nanocomposite consist of two components zinc oxide nanoparticles and epoxy terminated hyperbranched polymer.

Recently, epoxy terminated hyperbranched polymers (EHBP) have been widely used for improving toughness of epoxy resin. The small dimensions of the hyperbranched polymer (HBP) molecules compared to their molecular weight and their low viscosity make them extremely suitable as toughness modifiers in epoxy resins [17-22]. EHBP can create core-shell structure with Zno nanoparticles which can improve the dispersion stability of nanoparticles in epoxy matrix [23]. Toughness implies energy absorption that causes some deformation during the curing reaction of final epoxy network, where curing reaction is exothermic reaction. incorporation of second flexible homogenous dispersed phase (EHBP) to the epoxy matrix allow better dissipation to energy evolved during curing reaction so, the stress and strain that occur up on curing were reduced [24-26]. The improvement of fracture toughness by the addition of EHBP modifiers is frequently associated with softening of the epoxy matrix due to flexibilization of final network structure by decreasing the cross linking density of epoxy matrix. Since the glassy transition temperature of the EHBP is much lower than that of the epoxy polymer [27].

According to the literature, organic–inorganic hybrid coatings improve corrosion resistance more effectively than do inorganic coatings [28], but the adhesion of inorganic coatings to metallic substrates is better than that of organic–inorganic coatings [29]. This paper presents results of a new strategy to produce a new double layer thin film coating which comprises ZNO-epoxy as a primer coat and ZNO-EHBP-epoxy as a top coat. A new double layer coating offers corrosion protection to carbon steel higher than (PNC) modified epoxy coating, such that ZNO-epoxy layer work as sacrifial layer and form strong bonds and strong adhesion with steel substrate while ZNO-EHBP-epoxy layer work as physical barrier layer, comprise high flexibility and it offer excellent mechanical properties as high impact resistance and high bending stability.

II. EXPERIMENTAL

2.1. Materials

The commercial epoxy resin and its commercial hardener used in this research were obtained from trans-ocean Company, Egypt. Methyl acrylate was purchased from (Merck A. G.), Diethanol amine, Trimethlol propane, Para toluene sulfonic acid, Zinc nitrate hexahydrate, Epi-cholrohydrine and Boron trifluoride were purchased from Sigma-Aldrich Company. Ammonium carbonate, Sodium hydroxide, Acetic acid, Ethyl alcohol, methyl alcohol and Hydrochloric acid were purchased from El-Gomhouria chemical company, Egypt.

2.2. Preparation of zinc oxide nano particles

ZnO Nanoparticles were prepared by a direct precipitation method. $Zn(NO_3)_2 6H_2O$ and $(NH_4)_2CO_3$ were firstly dissolved in de-ionized water to form solutions with a 0.5 mol/L concentration. The $Zn(NO_3)_2$ solution was slowly dropped into the $(NH_4)_2CO_3$ solution with vigorous stirring at 40°C and the mole ratio of ($CO_3{}^{2-}$) ions to (Zn^{2+}) ions kept to 1.5, The reaction between the $Zn(NO_3)_2$ solution and the $(NH_4)_2CO_3$ solution was kept for 60 minutes. Then, the precipitates derived from the reaction were collected by filtration and rinsed three times with de-ionized water and ethanol, respectively. The washed precipitate was dried at 80°C to form the precursors of ZnO. Finally, the precursors were calcinated at 500°C for 2 hours in a muffle Furnace to obtain white nano-sized ZnO particles.

2.3. Synthesis of hydroxyl terminated hyper branched polymer

The hyperbranched polymer was synthesized as mentioned elsewhere in the literature [30].

N, N-diethylol-3-amine methyl propionate (AB_2 monomer) was prepared via Michael addition of methyl acrylate and diethanolamine in methanol solvent. Faint yellow oily liquid (AB_2 monomer) was obtained. Subsequently, 0.1 mol of 1, 1, 1-trimethylolpropane, 0.3 mol of (AB_2 monomer) and 0.5 wt% of para-toluene sulphonic acid as catalyst were stirred at 120°C for 2.5 h to give hydroxyl terminated hyperbranched poly amine ester (HBP).

2.4. Epoxidation of hyper branched polymer

In a 500 ml glass reactor equipped with a mechanical stirrer, dropping funnel and condenser, 1 mol of hydroxyl terminated hyper branched polymer and 1% of $BF_3.OET_2$ (based on weight of reactants) were placed and heated at 40°C then 6 mol of Epi-cholro hydrine was added drop wise during 2h. The reaction mixture was heated at 60°C for 30 minutes and then, cooling to 40°C. Subsequently, 6 mol of NaOH 50% aqueous was added drop wise to the reaction mixture. Finally, the mixture was neutralized with acetic acid.

2.5. Polymer nanocomposite preparation and application

Firstly ZnO nanoparticles were continuously sonicated in ethanol solvent by ultrasonic waves using sonicator model (Sonics& materials, VCX-750, USA, with a frequency of 20 kHz equipped with a titanium probe with a diameter =13 mm) for 15 minutes Before mixing, secondly both ZNO nanoparticles which account for (2%) of the total weight of (resin & hardener) and EHBP that account for (3%) of total weight of (resin & hardener) were mixed and stirred at speed up to 1200 rpm for 15 minutes. thirdly both epoxy resin and its hardener were diluted separately by ethanol solvent with 20% weight by weight ratio. Subsequently, the mixture of ZNO Nanoparticles (2%) and EHBP (3%) were added to the resin-ethanol solution, followed by stirring at speeds up to 1200 rpm for 15 minutes. after that, the hardener ethanol solution was added to the mixture, followed again by stirring for 15 min. then the coating mixture was applied to steel substrate by using spray gun and then kept in a dry place at room temperature for 7 days to allow full curing, which lead to the formation of a uniform coating for the anticorrosion and surface indentation tests in this work.

2.6. New double layer thin film preparation and application

First layer (primer coat), Zno nanoparticles were continuously sonicated in ethanol solvent by ultrasonic waves for 15 minutes Before mixing, Nanoparticles which account for (2%) of the total weight of resin and hardener were added to the resin-ethanol solution, followed by stirring at speed up to 1200 rpm for 15 minutes. After that, the hardener ethanol solution was added to the mixture, followed by stirring for 15 min. then the coating mixture was applied to steel substrate by using air spray and then kept in a dry place for 7 days to allow full curing.

Double layer (topcoat), top layer containing Zno-EHBP-epoxy that prepared as mentioned above, Was applied on the first layer (primer coat) of steel substrate by using spray gun and then kept in a dry place at room temperature for 7 days to allow full curing.

2.6. Characterization of synthesized materials

The structure and functional groups of epoxy terminated hyperbranched polymer and ZnO nanoparticles were characterized by (FTIR) [Nicolet iS10 thermo scientific, (USA)]. The phase structure of the produced Zno nanoparticles was identified by the powder X-ray diffraction. [X'pent PRO (Netherlands)]. The Size of ZnO nanoparticles was characterized by high resolution transmission electron microscopy (HRTEM) [JEM 2100 LaB6, Japan]. The surface morphology of the obtained ZnO nanoparticles was characterized by (JEOL JSM530). The number average molecular weight and the polydispersity index of the HBP and EHBP were measured by GPC via GPC-1100 Agilent technologies by using polystyrene (PS) as standard and N, N-dimethyl formamide (DMF) as eluent with flow rate 1 ml/min. H^1NMR spectra were obtained by Varian Mercury VXR-300 (USA) 300 MHz where demso-d_6 was used as a solvent and tetra methyl-silane Me_4Si (TMS) as internal standard.

2.7. Evaluation of anticorrosion, mechanical and chemical resistance properties of coatings

It is common to use mild steel panels (7cm x 9 cm) to evaluate the different properties of coatings. The panels were prepared according to British standard specification 1449. The other side of the panels was coated and protected against corrosion environments by using coal tar epoxy primer. Then the panels were subjected to different testing procedures to evaluate their mechanical properties (adhesion strength, pencil hardness test, impact resistance and T-bend test) and their durability. The coated panels were evaluated for salt-spray resistance in accordance with ASTM B117. The acid and alkali resistances of coated panels were determined after immersion in 10% of HCl and 5% of NaOH solutions using distilled water. The degree of adhesion and visual inspection of blister and cracks were tested for the coated panels [31].

III. RESULTS AND DISCUSSION

application of polymer nanocomposites has increased due to their specific properties. Anticorrosion paints have considered an important industry segment where coatings should protect the surface of the artificial structures exposed to corroded environment. These structures usually made of iron are highly susceptible to corrosion in the moisture environment. Therefore, they should been protected from the corrosion. A new alternative way is to use nontoxic anticorrosion coating comprising chromate coating. In the current study, a polymer nanocomposite added to epoxy resin to increase corrosion resistance properties of epoxy coating, but a new double layer thin film coating which comprises ZNO-epoxy as primer coat and ZnO-EHBP-epoxy as atop coat was determined to has better corrosion protection properties than (PNC) coating.

A typical XRD spectrum of synthesized ZnO nanoparticles had depicted in Fig.1. In order to discuss the phase and structural characteristics, The XRD pattern well matched with the standard database library. No further peaks had observed in the XRD pattern indicating that the purity of ZnO nanoparticles is high. Sharp nature of the distinguished peaks in the XRD pattern implies high crystalline nature of ZnO nanoparticles.

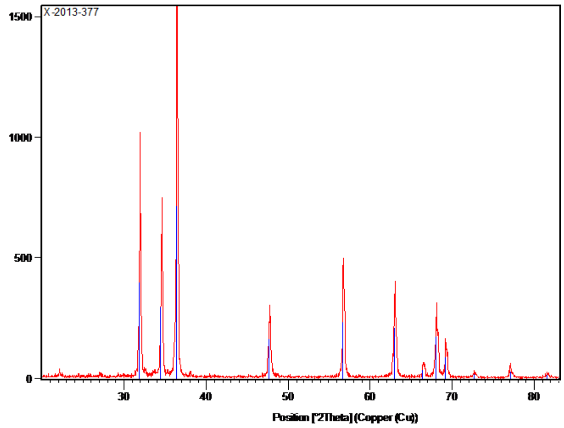

Fig.1. X-ray diffraction spectrum of ZnO nanoparticles

TEM images of ZnO nanoparticles were showed in Fig.2. The TEM analysis of ZnO nanoparticles showed that these nanoscaled materials have diameters ranging between 35 and 66 nm. The smaller of nanometer materials, the higher building block properties in the coating film can be attained. ZnO nanoparticles can reduce penetration and water absorption in paint film, therefore swelling and degradation of paint film considerably reduced.

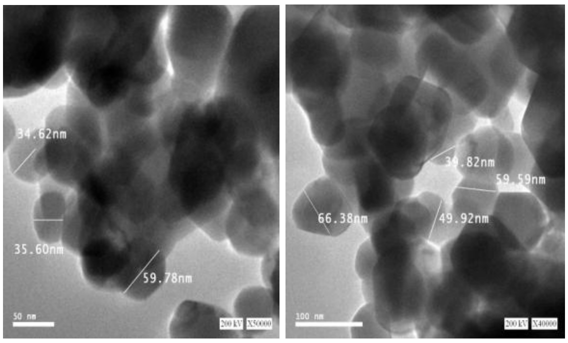

Fig.2. Transmission electron microscopy (TEM) images of ZnO nanoparticles

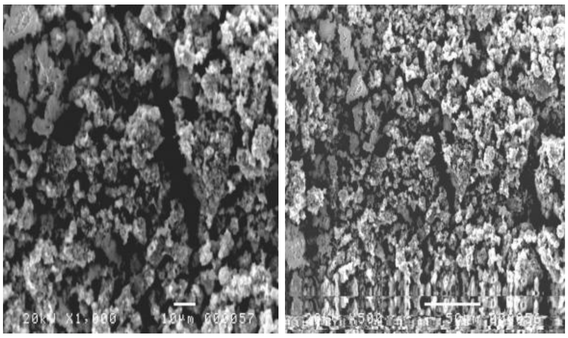

Fig.3. Scanning electron micrographs (SEM) of Zno nanoparticles

The surface morphology of the ZnO nano-particles showed in Fig.3. Represent the formation of Zinc oxide nanoparticles in single phase and the constituents are nanospheres shape.

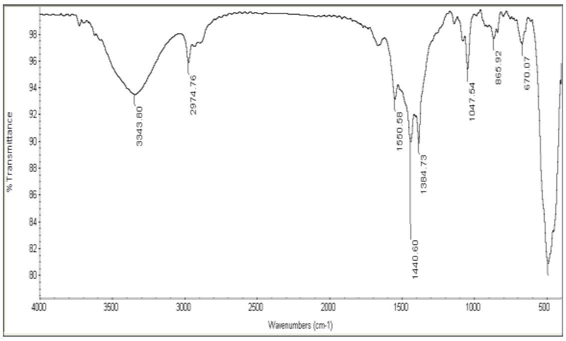

Fig.4. IR spectrum of ZnO nanoparticles

IR spectrum of the prepared Zno nanoparticles showed in fig.4. The absorption bands at about 500 cm^{-1} can be attributed to the stretching mode of Zn-O and the weak band in the range of 3343 cm^{-1} is probably attributed to the presence of water in the KBr matrix.

IR spectrum of the synthesized HBP was showed in fig.5. The two bands at 2881 cm^{-1} and 2941 cm^{-1} were due to C–H stretching of CH_3 and CH_2 respectively. The band at 1729 cm^{-1} represented the α-unsaturated carbonyl of the ester group. The broad absorption band at 3377cm^{-1} was assigned to hydroxyl groups, which were H-bonded, and those bands at 1191 cm^{-1} and 1259 cm^{-1} were attributed to C–O and C–N stretching respectively.

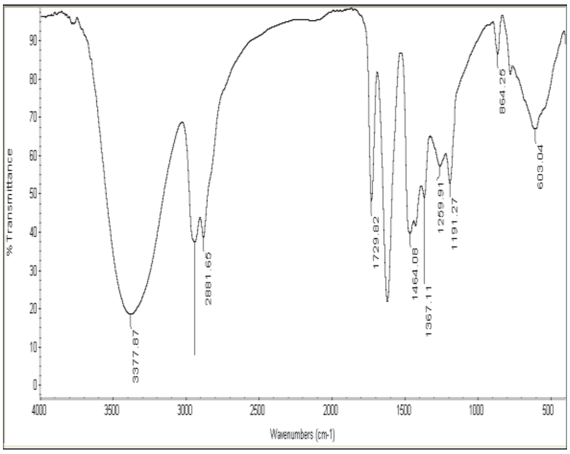

Fig.5. IR spectrum of hyper branched polymer

IR spectrum of EHBP was showed in fig.6. The intensity of peak around (3300 cm^{-1} - 3500 cm^{-1}) was decreased due to epoxidation reaction on hydroxyl groups in HBP. The peaks at about 1726 cm^{-1} are due to the presence of strong absorption corresponding to the –COO– groups resulting from the ester bond formation by the polymerization reaction. The appearance of peak at 1063 cm^{-1} was due to C-O-C stretching mode of epoxy group confirms the reaction between HBP and epichlorohydrin, and those bands at 1121 cm^{-1} and

1189 cm^{-1} were attributed to C–O and C–N stretching respectively.

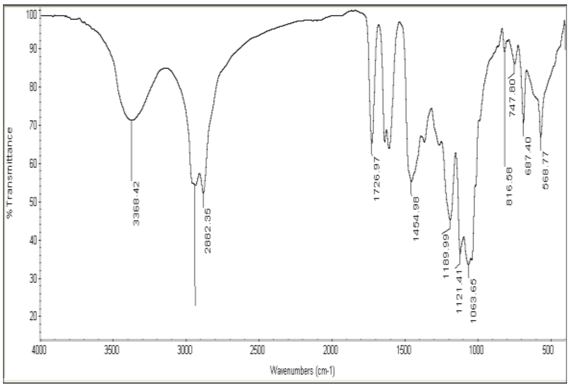

Fig.6. IR spectrum of EHBP

The molecular weight of hyperbranched polymer and EHBP was characterized by gel permeation chromatography. GPC recorded the number average molecular weight (M_n) and the poly dispersity index (PDI) for HBP as 9096.8 g/mol and 2.633 respectively, Where weight average molecular weight (M_w) is equal to 23954 g/mol. GPC recorded the number average molecular weight (M_n) and the poly dispersity index (PDI) for EHBP as 11632 g/mol and 2.259 respectively, where weight average molecular weight (M_w) was equal to 26282 g/mol.

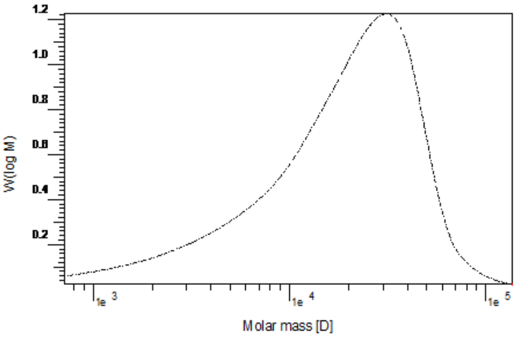

Fig.7. GPC trace of HBP

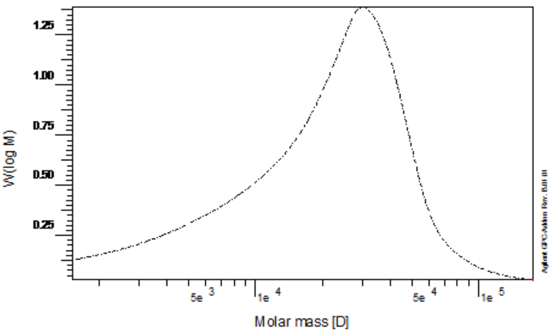

Fig.8. GPC trace of EHBP

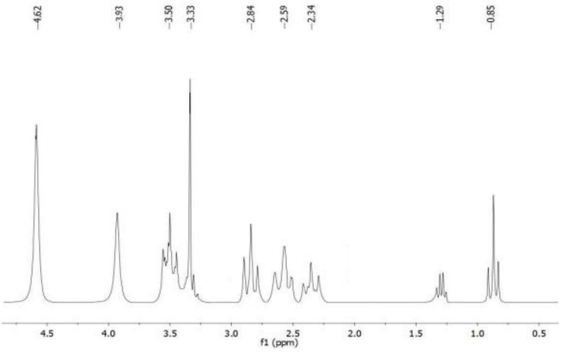

Fig.9. H^1NMR spectrum of HBP

H^1NMR spectrum of hyperbranched polymer showed in Fig.9. Distinguished signals of chemical shifts at 0.83 ppm which were associated with the methyl protons. Peaks that appeared at 1.26 ppm were due to methylene protons ($CH_3CH_2CR_3$). Peak appeared at 4.62 ppm was due to (O-H) end function groups. And peaks appeared at 2.31 - 2.80 ppm were assigned to methylene protons of ($OCOCH_2CH_2NR_2$) respectively. Peaks that appeared at 2.59 - 3.52 ppm were assigned to methylene protons (NCH_2CH_2OH) respectively. Signal at 3.92 ppm was assigned to methylene protons of (R_3CCH_2OCO).

The representative H^1NMR spectrum of EHBP is supported, as shown in Fig.10. Distinguished signals of chemical shifts at 0.86 ppm which were associated with the methyl protons. Peaks that appeared at 1.28 ppm were due to methylene protons ($CH_3CH_2CR_3$). And those from 2.32 - 2.74 ppm were assigned to methylene protons ($OCOCH_2CH_2NR_2$) respectively, 2.62 - 3.45 ppm were assigned to methylene protons (NCH_2CH_2O) respectively. Signal at 3.95 ppm was assigned to (R_3CCH_2OCO). Signal at 3.69 ppm was due to methylene protons of (OCH_2CH). Signals at 2.95 ppm and 2.51 ppm were due to protons of oxirane ring ($CHOCH_2$) respectively.

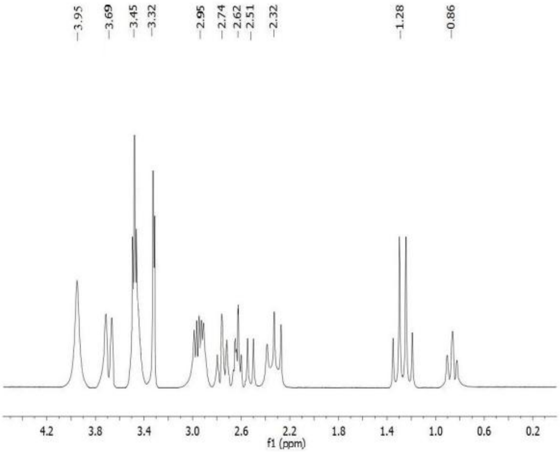

Fig.10 H^1NMR spectrum of EHBP

Anticorrosion studies

Salt spray tests are probably the most common tests applicable to corrosion resistance and the most controversial. There are two tests: the continuous salt spray test and the intermittent test. In the present work the continuous salt spray test was used to study the effect of salts on the properties of coating films. The duration times of test were determined for all cured epoxy systems. The test was stopped when the films show poor adhesion.

It is clear from salt spray images that neat epoxy coating (E-blank) show poor corrosion resistance on long term such that after 170 hours blank coating started to form cracks and micro holes that assist in migration of moisture and water molecules inside coating, after 500 h (E-blank) coating suffered from localized corrosion and corrosion product started to appear on the metal surface, after 1000 h (E-blank) coating was completely failure. Modification of epoxy resin with both Zno nanoparticles and EHBP can enhance corrosion resistance property of epoxy coating. a new double layer coating (R) offers corrosion protection to carbon steel substrate better than other coatings, where it provide protection up to 1000 h in salt spray chamber conditions, polymer nanocomposite (C) coating offer corrosion resistance higher than inorganic Zno-epoxy coating (B) due to core-shell structure that enhance dispersion stability of ZnO nanoparticles in epoxy polymer matrix, reduce grain boundaries size, cause crack bridging and crack deflection.

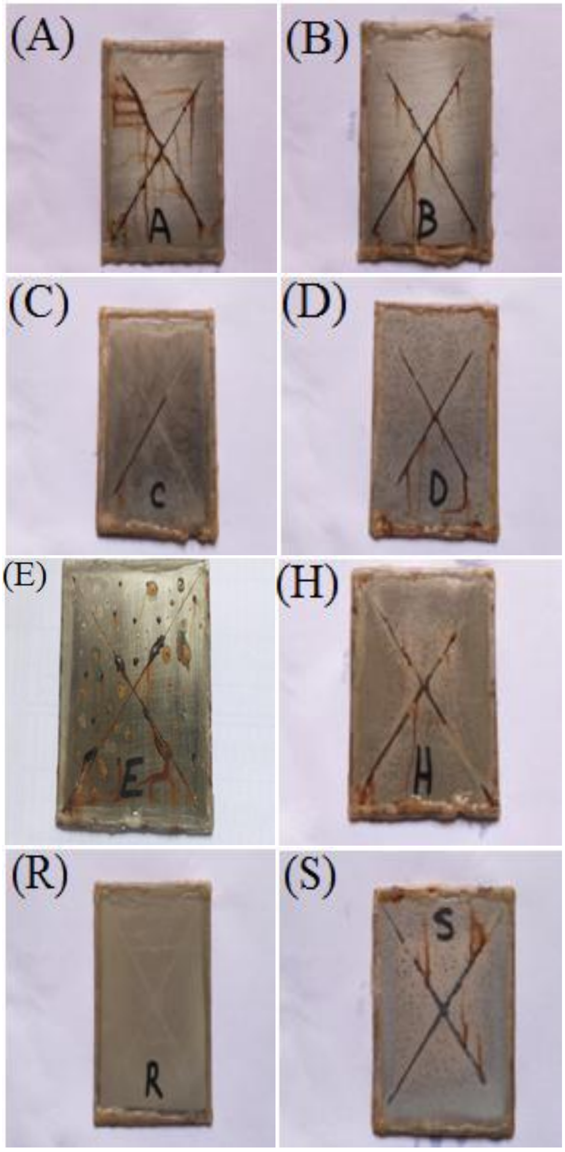

Fig.11. images of coating films after 170 h (week) in salt spray chamber. [(A: Commercial epoxy + 0.5% ZnO) (B: Commercial epoxy + 2 % ZnO) (C: Commercial epoxy + Polymer nanocomposite PNC that contain 2% ZnO + 3% EHBP) (D: Commercial epoxy + 4 % ZnO) (E: Commercial epoxy only, blank) (H: Commercial epoxy + EHBP 3%) (R: double layer) (S: Commercial epoxy + 1 % ZnO)].

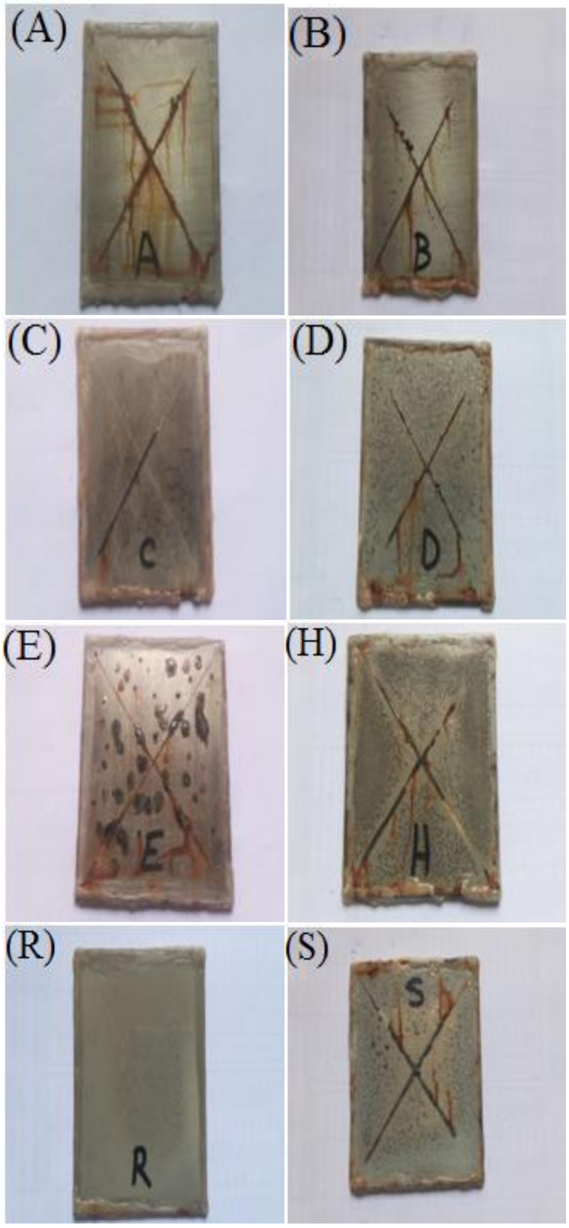

Fig.12. images of coating films after 500 h in salt spray chamber [(A: Commercial epoxy + 0.5% ZnO) (B: Commercial epoxy + 2 % ZnO) (C: Commercial epoxy + Polymer nanocomposite PNC that contain 2% ZnO + 3% EHBP) (D: Commercial epoxy + 4 % ZnO) (E: Commercial epoxy only, blank) (H: Commercial epoxy + EHBP 3%) (R: double layer) (S: Commercial epoxy + 1 % ZnO)].

The effect of Zno nanoparticles increase as its loaded percent increase until 2% (B) that represent the optimum percent at which corrosion resistance of epoxy coating is excellent, where any increase in this percent cause particles agglomeration and the effect of Zno nanoparticles is neglected as was showed in a coating (D) that contain 4% Zno nanoparticles. Modification of epoxy coating with only EHBP 3% (H) can improve corrosion resistance, such that EHBP assist in decreasing the number of hole defects that formed during the curing reaction resulting in more durable and more corrosion protection of epoxy coating to carbon steel substrate.

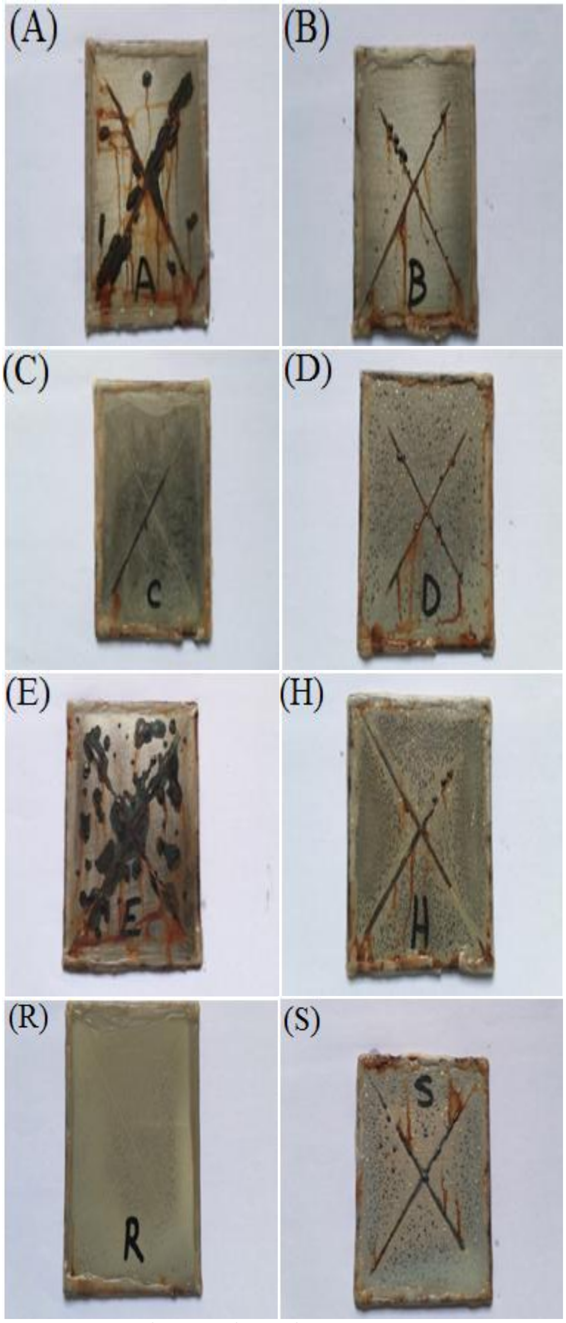

Fig.13. images of coating films after 1000 h in salt spray chamber [(A: Commercial epoxy + 0.5% ZnO) (B: Commercial epoxy + 2 % ZnO) (C: Commercial epoxy + Polymer nanocomposite PNC that contain 2% ZnO + 3% EHBP) (D: Commercial epoxy + 4 % ZnO) (E: Commercial epoxy only, blank) (H: Commercial epoxy + EHBP 3%) (R: double layer) (S: Commercial epoxy + 1 % ZnO)].

Mechanical properties

The effect of both EHBP and Zno nanoparticles modification on the hardness, impact strength, bending stability and the adhesion of epoxy coatings showed in table 1. Coatings that loaded with (2%) Zno nanoparticles [(R), (C) and (B)] showed higher hardness than other coatings. There is an enhancement in epoxy hardness with addition of Zno nanoparticles which blocks grain boundaries of epoxy matrix so the grain boundaries size between epoxy molecules decrease and resistance of epoxymatrix coating to dislocation movement under applied load increase. Coated samples were tested for their adhesion to the metallic substrate**,** according to pull off test both a new double layer coating (R) and modified Zno (2%) coating (B) were show higher adhesion to steel substrate than other coatings that because of strong bonds that formed between Zno nanoparticles and steel surface. It seemed that adhesion of inorganic modified coating (B) to

Table 1: show results of mechanical tests

Sample name	Hardness (Newton)	Impact strength (joule)	Pull off Test (Pascal)	Cross hatch test	Bending
A - (0.5%) zno	12 N	10J	4Mpa	pass	pass
S - (1%) Zno	15 N	10J	5Mpa	pass	pass
B - (2%) Zno	18 N	10J	7Mpa	pass	pass
D - (4%) Zno	10 N	10J	3Mpa	pass	pass
E - (blank)	10 N	10J	3Mpa	pass	pass
R – (two layer)	18 N	15J	7Mpa	Pass	Pass
C – (PNC)	18 N	15J	5Mpa	Pass	Pass
H – (E_{TMP} 3%)	10 N	15J	3.5Mpa	pass	pass

Table 2: show results of chemical resistance tests

Sample name	NaoH (5%) (days)	HCL (10%) (days)
A - (0.5%) zno	30	21
S - (1%) Zno	45	30
B - (2%) Zno	60	42
D - (4%) Zno	30	12
E - (blank)	21	9
R – (two layer)	90	63
C – (PNC)	72	48
H – (ETMP 3%)	39	30

metallic substrates is better than that of organic modified coatings (H) or organic-inorganic modified coating (c). Where all specimens were pass the adhesion (crosshatch) test. Coated samples were tested for their bending stability, (E-blank) neat epoxy coating show poor stability on bending such that there were some of micro cracks that appeared on bending area, where all specimens modified with EHBP (R) (C) (H) showed bending area without any cracks that prove the addition of EHBP enhance the flexibility of epoxy coating matrix and improve the bending stability. Incorporation of zno nanoparticles reflected in reinforcing effect that cause some of rigidity and restrict the impact strength of epoxy coating compared to coatings that modified with EHBP. Addition of EHBP leads to an improvement of about 50% on impact strength with respect to neat epoxy coating (E) or coatings that were modified only with ZnO nanopsrticles, that because of highly branched structure of EHBP which provide plasticizing effect and more flexibility to epoxy matrix.

Chemical resistance of epoxy coatings

Durability of coats may be defined as the capacity of a paint to endure; that is, to remain unchanged by environment and events. The coated panels have subjected to chemical environments (alkalie and acid) to study the durability of coats. The data of alkalie and acid resistance were determined for cured epoxy systems [32]. Results of chemical resistance tests showed in table 2. Blank epoxy coating (E) show poor chemical resistance up to 9 days in HCL and 21 days in NaOH, coating lost its adhesion with panels and showed cracking and flaking after short time in comparison with other coatings, where it can be considered test failure such that (E-blank) coating was the weakest chemical resistance coat. Double layer coating (R) showed chemical resistance up to 63 days in HCL and 90 days in NaOH that were higher than other coatings because of addition of ZnO nanoparticles improves the adhesion forces between polymeric epoxy coating and metal substrate that prevent coating delamination, also ZnO nanoparticles enhance cohesive forces between epoxy molecules and work as a bridge interconnecting more molecules so that, grain boundaries size was reduced which prevent initiation and propagation of cracks, where (R) coating is the most durable coating in comparison with other coatings. Coating (B) with 2% ZnO nanoparticles also showed good chemical resistance up to 42 days in HCL and 60 days in NaOH for the same reasons. Addition of EHBP to epoxy resin affect the chemical resistance of epoxy coating because of EHBP allows better dissipation to energy evolved during the curing reaction so, the stress and strain that occur up on curing were reduced resulting in decreasing the number of hole defects in epoxy matrix which lead to more durable coating. Therefore, modifications of epoxy coating (C) with PNC can improve the chemical resistance of epoxy coating up to 48 day in HCL and 72 days in NaOH.

IV. CONCLUSIONS

In this work, a new double-layer coating, comprising ZNO-epoxy as a primer layer and Zno-EHBP-epoxy as the top layer, was synthesized and applied on carbon steel substrate. According to salt spray test, double-layer coating offered better corrosion protection, compared to the purely inorganic ZNO-epoxy and hybrid ZNO-EHBP-epoxy coatings. The reason is that the primer inorganic layer provide better adhesion to the metal substrate and it work as sacrificial layer where the topcoat layer filled the physical defects in the film, there by rendering the top layer to be a denser, less porous barrier for blocking the electrochemical processes that otherwise would occur on the metal substrate also, topcoat layer improves mechanical properties of coating.

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