# Modifying the Anticorrosion and Chemical Resistance of Epoxy Composites Used for Surface Coatings

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## ABSTRACT

Epoxy coatings have been widely used for the protection of steel structures. In the present study a new type of protective coatings is developed for use in coating of marine utilities. Nanocomposite coating was successfully prepared by incorporating Chitosan and zinc oxide nanoparticles (ZnO NPs) into epoxy coating with different concentrations to enhance its protection role against aggressive environments. ZnO NPs were synthesized via direct precipitation method. Chitosan is manufactured from locally available shrimp shells. Chitosan, ZnO NPs and epoxy nanocomposite are characterized through various techniques such as Fourier Transform Infrared (FTIR), Scanning Electron Microscope (SEM), elemental analysis and Transmission Electron Microscope (TEM). The manufactured coatings are applied on carbon steel panels. The resistance to corrosion of the nanocomposite coated panels was investigated by the salt spray test after 500 hours according to ASTM D1654-92. Results indicated that the performance of the epoxy composite resin is modified with increasing percentage of ZnO NPs and with increasing percentage Chitosan. The highest performance was shown by a composite having 3% ZnO NPs + 5% Chitosan; where its evaluation parameters were 1% disbanded area and 9 rating number. The corresponding values for the blank sample were 19% disbanded area and 5 rating number. The resistance of these coatings to chemicals such as NaOH, HCl and Acetone solvent was studied. The results showed that incorporation of 5% Chitosan and 3% ZnO NPs to epoxy matrix led to better protective performance towards these materials in comparison to blank epoxy resin. Thus ZnO NPs-Chitosan-epoxy composite coating is a promising methodology for developing corrosion and chemical resistant of surface coatings.

**Keywords**: Epoxy coating, Chitosan, Nanoparticles, Corrosion, Chemical resistance.

## Abbreviations and Acronyms

| | |
|---|---|
| ASTM | American Society for Testing and Materials |
| DD | Deacetylation Degree |
| FTIR | Fourier Transform Infrared Spectroscopy |
| PANI | Polyaniline |
| SEM | Scanning Electron Microscopy |
| TEM | Transmission Electron Microscopy |
| ZnO NPs | Zinc Oxide Nanoparticles |

## 1. INTRODUCTION

Epoxy resins, because of their interesting chemical properties, low price, good adhesion properties, limited shrinkage and corrosion resistance are extensively used in different coating purposes. The properties of the epoxy coating can be adjusted by curing [1, 2, 3].

Epoxy resins are a category of organic macromolecules which are largely used in different industrial uses. These types of resins give good surface coverage and resistance to corrosive activities more than some other organic materials used as corrosion inhibition materials. The

resins polar functional groups act as adsorption cites during the interaction of metal-inhibitor. Many epoxy resins; either in a pure or cured form are used as anti-corrosive coating materials. A special use is for coating carbon steel which is used in acidic and salty solutions. Many epoxy resins work as an interface and are a mixture of more than one corrosion inhibitor. The anticorrosive nature of epoxy resin coatings can be further enhanced by adding inorganic and organic components. The function of the additives is to block the surface micropores present in the epoxy resin coating through which the corrosive components can diffuse and damage the coating structure [4].

A study is made and focused on the manufacture of a functionalized silane coupling agent for the object of modifying the surface of graphene oxide and enhancing the anticorrosion properties of the epoxy resin coatings. This takes place by adding functionalized graphene oxide to the coating. Experimental results indicated that this addition process improves the corrosion resistance properties of the modified epoxy resin composite [5].

In another study, the authors prepared epoxy nanocomposites to which is added magnetite clay (B) at various filler loading. The results clarified high improvement in corrosion inhibition properties. This is accomplished by using electrochemical impedance spectroscopy. Besides, the oil sensing test showed a great response [6].

Later on, a study announced a strategy for mixing both inorganic fillers and organosilanes for the object of enhancing the ability of silicon nitride to disperse in the coating formed of epoxy resin. Results indicated that by increasing the immersion time, the corrosion resistance and consequently the performance towards adhesion of the coating of epoxy resin and the unmodified silicon nitride coating decreases greatly. They explained the high corrosion resistance properties to be because of the chemical interactions which takes place between the silicon nitride powders and the functional groups [7]. This is assumed to be a result of the formation of Si-O-Si bonds. Besides, the developed silicon nitride coating is considered a strong barrier for the corrosive electrolyte because of the hydrophobic characteristics of the modified silicon nitride powder having increased bonds.

Other researchers prepared a polyurethane modified epoxy emulsion which is highly corrosion resistant. They tested the rate of salt spray effect, water absorption and the flexibility of the coatings. Standard methods are used in the tests. They applied this coating on tinplate sheets and tested it. It had good flexibility and it could resist the effect of the salt spray test for 60 days [8].

Researchers also blended the acrylate epoxy coating with zinc oxide in the nano-sized range to form a combined nanocomposite to improve the coating anticorrosion performance. A coating formed of Jatropha-oil based epoxy acrylate (AEJO) resin blended with ZnO (AEJO/ZnO) was used with mild steel panels and it had good performance with respect to corrosion resistance when tested through the salt spray tests and impedance spectroscopy. Addition of 5 wt % ZnO showed significant improved corrosion resistant [9].

A group of researchers conducted a chemical reaction between cyanate ester and graphene oxide to modify the properties of the epoxy coating. The improvement of corrosion protection properties was tested with sulfuric acid solution. Results indicated that the epoxy coating which is modified with cyanate ester has slower diffusion for electrolyte. Besides, addition of 1% (by weight) of graphene oxide into CE/EP apparently enhanced the stability of polymer and the anti-corrosion properties [10].

A research team conducted a study to synthesize polyaniline/graphene oxide nano-composites. The results indicated that nanocomposites give better crystallinity, dispersibility, conductivity and thermal stability. Besides, the composites formed is tested for its characteristics as anti-corrosive coating [11].

In coatings based on polymers, addition of various nanoparticles such as titanium oxide, zinc oxide and layered silicates in the matrix of poly aniline (PANI) has proved to guarantee better resistance towards the electro-chemical corrosion of the coating [12].

Conductive graphene has been used for developing the anti-corrosion paints [13, 14]. it is used in its reduced form or through covalent functioning with inorganic nano-particles; such as Al2O3 [8,15]. This nano paint formulation is considered to be formed by the crosslinking of the graphene oxide with the chains of alkyd resin lipid in order to satisfy corrosion resistance and to be used in antibacterial applications [16].

The present study is concerned with modifying the anticorrosion and chemical resistance of epoxy coatings used in the marine environment. This is accomplished by introducing ZnO NPs and Chitosan into the composition of the epoxy coating. Epoxy composites modified with different concentrations of the additives will be tested against the corrosive action of salt solution and some chemicals such as HCl, NaOH and Acetone. The performance of the modified composite as an anti-corrosion coating is evaluated through the salt spray test according to ASTM D1654-92.

## 2. EXPERIMENTAL WORK

This section presents all issues related to the experimental work of the study

### 2.1. Materials and Method

The materials used in the study and the procedure followed are mentioned herein:

### 2.1.1. Materials

The materials used in the present study are: The commercial grade of epoxy resin, its hardener and thinner (are used as a base for the epoxy resin), obtained from Trans- Ocean Company, Egypt; Ethyl alcohol (used for rinsing zinc carbonate to obtain pure ZnO NPs), it was brought from El-Nasr Company for Chemicals (in Egypt); HCl (is used for chitosan extraction and evaluating chemical resistance of epoxy nanocomposite) and is purchased from Sigma- Aldrich Company; Zinc nitrate hexa-hydrate (is used for preparation of Zinc oxide NP) and is purchased from Sigma- Aldrich Company; Acetone (is used for chitosan extraction and evaluating solvent resistance of epoxy nanocomposite); Ammonium carbonate (is used for preparation of Zinc oxide NP) and Sodium hydroxide (is used for chitosan extraction and evaluating chemical resistance of epoxy nanocomposite) and these materials were purchased from El-Gomhouria Company for Trading Chemicals, Egypt.

### 2.1.2. Method

The method here is concerned with the manufacture of ZnO nanoparticles, extraction of Chitosan from shrimp shell wastes, synthesis of epoxy- Chitosan- ZnO nanoparticles composite and preparation of panel followed by application of the modified composite on it.

### 2.1.2.1. Manufacture of Zinc Oxide Nano-particles [17]

ZnO nano-particles are manufactured by the direct precipitation method; which is followed by thermal decarbonation. Zinc nitrate hexahydrate, Ammonium carbonate, ethanol and deionized water were used as the raw reagents for preparing ZnO NPs. Firstly, Zinc nitrate hexahydrate and Ammonium carbonate were dissolved in deionized water to make solutions with concentrations of 1.5 and 2.25 mol/L, respectively. Subsequently, the Zinc nitrate solution was slowly dropped into the vigorously stirred Ammonium carbonate solution for 1 h at 40℃. The reaction between Zinc nitrate and Ammonium carbonate solutions produces the Zinc carbonate white precipitate:

$$Zn(NO_3)_2 + (NH_4)_2CO_3 \rightarrow ZnCO_3\downarrow + 2NH_4NO_3 \qquad (1)$$

After that; the resulting precipitates were collected by utilizing a micrometer filter paper then rinsed many times with de-ionized water and ethanol respectively. The washed precipitates were dried at 80℃. Finally, the precipitates were calcined at 550℃ for 2 h in the muffle furnace to get white nano-sized Zinc oxide particles. Zinc carbonate turns into Zinc oxide by the following thermal decarbonation reaction:

$$ZnCO_3 \rightarrow ZnO + CO_2\uparrow \qquad (2)$$

### 2.1.2.2. Extraction of Chitosan from shrimp shell wastes

#### A. De-proteinization and demineralization of shrimp shells

The shrimp shells were de-proteinized by using 3.5% (w/w) NaOH solution for 2 h at 65°C, then demineralized by a solution of 1N HCl for 1 day at room temperature. After that acetone was used for decolorizing stage 2 h at 50°C. Finally, the extract was dried at room temperature for 2 h [18].

#### B. De-acetylation of shrimp shells

Acetyl groups removing from the extracted Chitin as shown in Figure (1) was accomplished via mixing with NaOH (50%) with agitating at a temperature of 115°C for 2 h keeping the solid to solvent ratio at 1: 10 (w/v). Then the obtained Chitosan was washed till it is neutral under faucet water, after that rinsed with deionized water, subsequently filtered, and finally dried at 60°C for 24 hours [18].
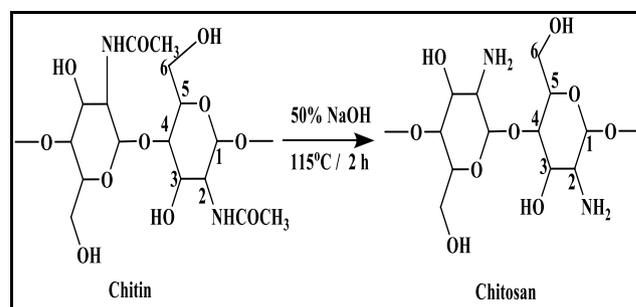


Figure (1): De-acetylation of Chitin to get Chitosan

### 2.1.2.3. Synthesis of Epoxy- Chitosan - ZnO nanocomposite

ZnO NPs were sonicated in thinner solvent for 30 minutes, then both ZnO NPs. and Chitosan were mixed and agitated for 15 minutes at speed up to 800 rpm, then both epoxy resin and the hardener were diluted separately by thinner. After that, the mixture of ZnO NPs. and Chitosan was added to the resin-thinner solution, followed by agitating for 15 minutes at speed up to 500 rpm. Subsequently, the hardener thinner solution was added to the mixture, and stirred for 15 minutes. Finally, the prepared coatings were applied on the surface prepared steel panels by using air spray gun [19].

### 2.1.2.4. Preparation of panel and application of epoxy nanocomposite

Steel panels surface were prepared to achieve acceptable roughness and cleanliness. Scrubbing was used to remove mill scale and for roughening the surface. Surface was cleaned from any dirt or oil by thinner. All epoxy nanocomposite samples were sprayed on steel panels with thickness of about 100 microns. The epoxy nanocomposite coating thickness was measured with an Elcometer 456 electromagnetic induction coating thickness gauge. The percentages of ZnO NPs used in the nanocomposite coatings were (0.1, 0.5, 1, 2 and 3%) and

Chitosan concentrations used were 1, 2, 3, 4 and 5%. The coated panels were air-dried at room temperature for 24h (touch dry), and then they are left in a dry place for 7 days to achieve full curing [5].

## 2.2. Characterization of ZnO NPs., Chitosan and Epoxy nanocomposites

The following paragraphs explain the characterization tests run for characterization of ZnO nanoparticles, characterization of Chitosan and characterization of nanocomposite.

### 2.2.1. Characterization of ZnO NPs

The particle size of ZnO NPs. was characterized by TEM (model JEM 2100 LaB6, Japan). The surface morphology of the synthesized epoxy ZnO NPs-Chitosan nanocomposites was investigated by SEM (JEOL JSM530, Japan). Chitosan chemical structure was characterized by FTIR Spectra recorded with Nicolet iS10 spectrometer, thermo Fisher scientific, USA. Mass percentages of C, N, H were estimated by CHN elemental analysis using a Perkin Elmer analyser, model 2400, USA.

Figure (2) shows an overall view of ZnO NPs, revealing a large quantity of nanoparticles with small size

distribution. The particles diameters are nearly uniform about 15–65 nm.
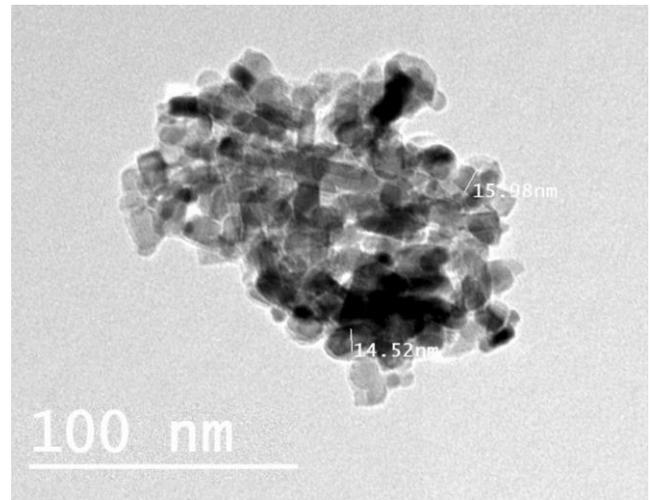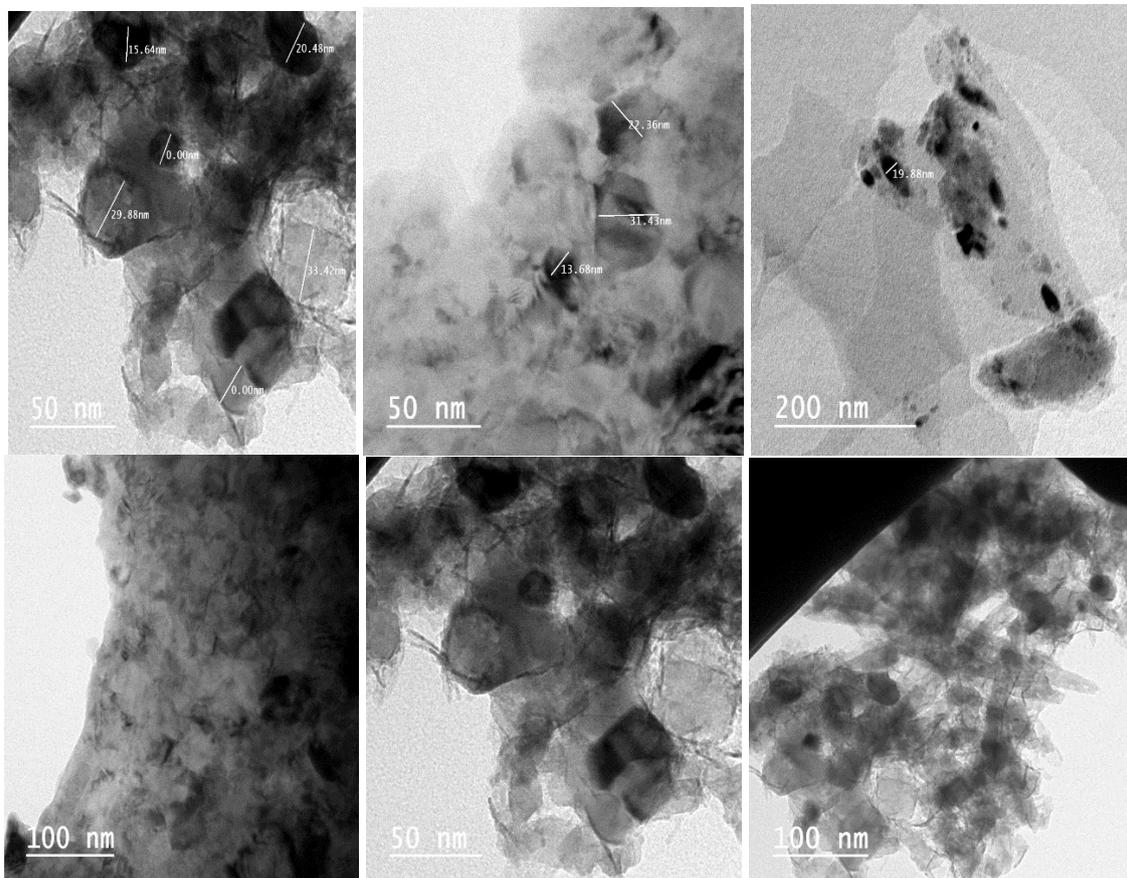


Figure (2): TEM of ZnO NPs structure



Figure (3): SEM for ZnO-Chitosan Epoxy nanocomposite coating

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Figure (3) shows the SEM micrographs which is got from the fractured surface of the prepared nanocomposite coating films containing ZnO nanoparticles and Chitosan. An observation is made for some white particles which are embedded in the epoxy matrix and this may be attributed to the incorporation of Chitosan and ZnO NPs into the epoxy resin. The number of these particles increased by increasing ZnO NPs and chitosan concentrations. ZnO NPs addition proved to be beneficial for a ratio up to 3.0 wt.%, and for Chitosan concentration of up to 5%. The embedded white particles into the epoxy matrix showed uniform and well dispersed distribution. The particle size of white particles was around 40 nm. This elucidated that the ZnO NPs were successfully dispersed without undergoing agglomeration.

### 2.2.2. Characterization of extracted Chitosan

*A. Fourier transform infrared spectroscopy*

FTIR spectrum of extracted Chitosan is shown in Figure (4). It can be observed that the peaks at 1634 cm-1 and at 1562 cm-1 are related to the presence of the C=O stretching of the amide bond. Besides it is also related to the bending vibrations of the N−H amide bond, respectively. The peak at 1415 cm-1was assigned for the C−H bending vibrations of methyl group. Peaks 1088 cm-1 and 1024 cm-1 may be associated with the C−O stretching vibration. The band 588 cm-1 ascribed C−H stretching of the polysaccharide backbone [20].

*B. Elemental analysis of extracted Chitosan*

Elemental analysis is used as rapid test to differentiate between Chitin and Chitosan. It is based on the nitrogen content of the material. It is assumed that the nitrogen content is higher than 7% for the purified Chitosan and it is lower than 7% for the raw Chitin [21].

Results of the elemental analysis of the produced Chitosan were 42.85, 6.54 and 7.93 for the C, H and N content, respectively. The value of nitrogen content obtained guarantee a successful purification process for Chitosan extract.

*C. The determination of the de-acetylation degree of the produced Chitosan (DD)*

In order to characterize the extracted chitosan, it is required to determine its DD, because it affects the performance of chitosan in various applications [22]. The DD was calculated from this equation [23].

$$DD = \left[ 1 - \frac{\frac{C}{N} - 5.145}{6.861 - 5.145} \right] * 100 \qquad (3)$$

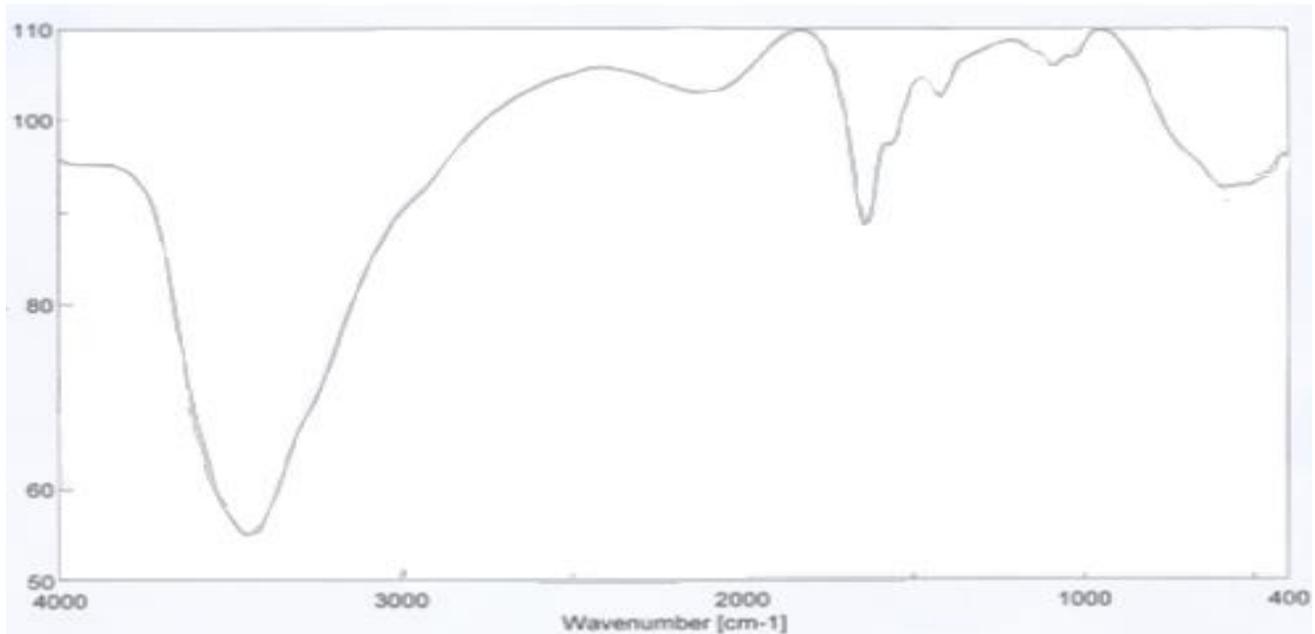$$= 84.93 \%.$$

where, C/N is carbon to nitrogen ratio.



Figure (4): FTIR spectrums for extracted Chitosan

### 2.2.3. Corrosion resistance of Chitosan epoxy nanocomposite coated panels (Salt spray test)

The Salt Spray Test is the suitable test to examine the corrosion behaviour of coating films [23]. Panels coated with the epoxy resin are evaluated for their resistance to

salt-spray in accordance with the ASTM B117 test. The test is conducted by spraying the panels with 5 wt.% NaCl solution in a type of closed cabinet; Model SF/450, which is especially manufactured for that purpose. At the beginning of the procedure, the test panels are covered on its edges and the uncoated side with paraffin wax. A cross mark line is made on each steel panel for allowing the salt solution to penetrate through the scratched panel. The panels were observed periodically and were examined after 500 hours. The results of salt-spray test are evaluated according to ASTM D 1654 testing system. Panels are evaluated with regard to its size, the number and the distribution of blisters and according to the location and number of the corrosion pits which resulted from exposure to corrosive action of salt solution.

2.2.4. Effect of acid and alkali on the coated panel

The alkali and acid chemical resistances of coated panels were rated according to ASTM D1647-89 and D 3260-01, respectively. Panels are coated at their edges and back surface and are immersed partially in 10% HCl, 5% Panels are coated at their edges and back surface and are immersed partially in 10% HCl, 5%NaOH solutions or acetone; separately for 90 days at 25°C. The panels are

next removed from the test solution, it is rinsed under running tap water, wiped carefully and then it is allowed to dry at ambient temperature. Panels are then visually inspected for any change like discoloration, blistering, peeling, flaking and cracks to determine the degree of durability and resistance against chemicals.

## 3. RESULTS AND DISCUSSION

The following paragraphs outlines the experimental results obtained from the present study as well as its discussion and analysis

### 3.1. Corrosion resistance of Chitosan epoxy nanocomposite films

Coated epoxy panels were evaluated after 500 hours from exposure to corrosion environment by visual inspection of coating performance appeared on surface of panels as shown in Figures (5- 9) and the panels were rated according to ASTM D 1654–92. Rating number and failed area percentage of all coated epoxy samples are shown in Tables (1-5).



Blanck          0.1%NPs          0.5% NPs

1%NPs          2%NPs          3% NPs

Figure (5): Salt spray images for 1% Chitosan with different concentrations of NPs

0.1%NPs        0.5%NPs        1% NPs
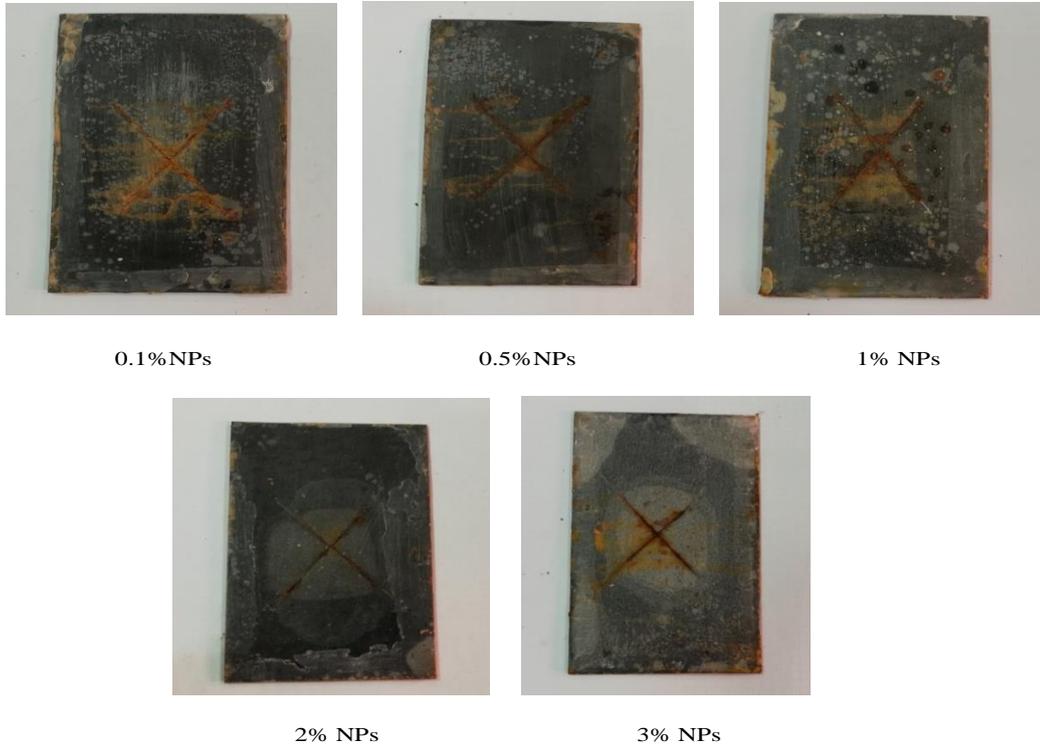
2% NPs        3% NPs

Figure (6): Salt spray images for 2% Chitosan with different concentrations of NPs



0.1%NPs        0.5%NPs        1% NPs
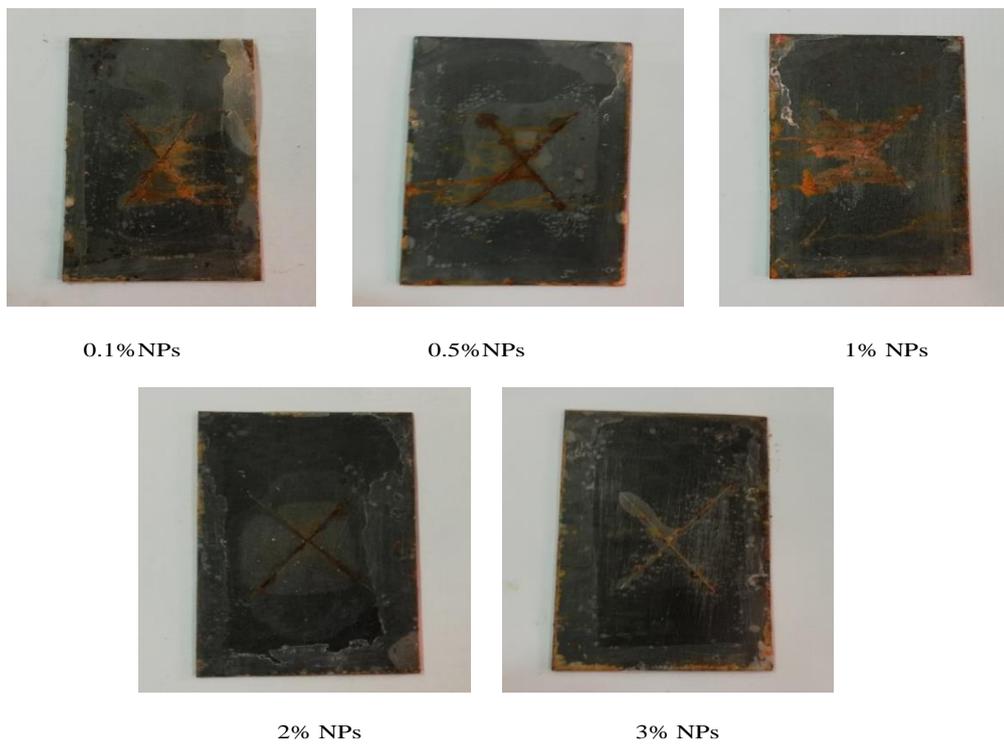
2% NPs        3% NPs

Figure (7): Salt spray images for 3% Chitosan with different concentrations of NPs

0.1%NPs        0.5%NPs        1% NPs

2% NPs        3% NPs

Figure (8): Salt spray images for 4% Chitosan with different concentrations of NPs

0.1%NPs        0.5%NPs        1% NPs

2% NPs        3% NPs

Figure 9: Salt spray images for 5% Chitosan with different concentrations of NPs

Table 1: Resistance to salt spray of epoxy coated panels (1.0% Chitosan–ZnO NPs)

| Nanoparticles % in the composite | Time of Exposure, (hours) | Disbanded area % | Rating Number (ASTM D1654) |
|---|---|---|---|
| Blank sample | 500 | 19 | 5 |
| 0.1NP | 500 | 15 | 5 |
| 0.5 NP | 500 | 14 | 5 |
| 1.0NP | 500 | 13 | 5 |
| 2.0 NP | 500 | 9 | 6 |
| 3.0 NP | 500 | 7 | 6 |

Table 2: Resistance to salt spray of epoxy coated panels (2.0% Chitosan–ZnO NPs)

| Nanoparticles % in the composite | Time of Exposure, (hours) | Disbanded area % | Rating Number (ASTM D1654) |
|---|---|---|---|
| Blank sample | 500 | 19 | 5 |
| 0.1NP | 500 | 6 | 7 |
| 0.5 NP | 500 | 6 | 7 |
| 1.0NP | 500 | 5 | 7 |
| 2.0 NP | 500 | 5 | 7 |
| 3.0 NP | 500 | 4 | 7 |

Table 3: Resistance to salt spray of epoxy coated panels (3.0% Chitosan–ZnO NPs)

| Nanoparticles % in the composite | Time of Exposure, (hours) | Disbanded area % | Rating Number (ASTM D1654) |
|---|---|---|---|
| Blank sample | 500 | 19 | 5 |
| 0.1NP | 500 | 4 | 7 |
| 0.5 NP | 500 | 4 | 7 |
| 1.0NP | 500 | 3 | 8 |

| Nanoparticles % in the composite | Time of Exposure, (hours) | Disbanded area % | Rating Number (ASTM D1654) |
|---|---|---|---|
| Blank sample | 500 | 19 | 5 |
| 0.1NP | 500 | 2 | 8 |
| 0.5 NP | 500 | 2 | 8 |
| 1.0NP | 500 | 2 | 8 |
| 2.0 NP | 500 | 2 | 8 |
| 3.0 NP | 500 | 1 | 9 |
| 2.0 NP | 500 | 3 | 8 |
| 3.0 NP | 500 | 2 | 8 |

Table 4: Resistance to salt spray of epoxy coated panels (4.0% Chitosan–ZnO NPs)

Table 5: Resistance to salt spray of epoxy coated panels (5.0% Chitosan–ZnO NPs)

| Nanoparticles % in the composite | Time of Exposure, (hours) | Disbanded area % | Rating Number (ASTM D1654) |
|---|---|---|---|
| Blank sample | 500 | 19 | 5 |
| 0.1NP | 500 | 1 | 9 |
| 0.5 NP | 500 | 1 | 9 |
| 1.0NP | 500 | 1 | 9 |
| 2.0 NP | 500 | 1 | 9 |
| 3.0 NP | 500 | 1 | 9 |

Results showed that, after exposure to salt spray, the failure of coating becomes more distinct in the blank epoxy coated panels than it is in the coating which is modified with Chitosan and ZnO NPs.

As shown in table (1) the lowest rating number was determined for blank coating and it has a value of 5 that means blank coating failed after 500 h, such that the area of corrosion spots and blisters represented approximately 19% of total area of the coated panel.

The salt spray image in fig. (4) shows the appearance of blisters, loss of adhesion and rusting to a high degree for the epoxy coated blank panel. This proves that the epoxy coating on the blank sample has suffered deep chemical changes during exposure to the salt solution and this led to coating failure.

**Role of ZnO in reducing the corrosive action on epoxy coated panels**

The results of the test given before indicate that incorporation of ZnO NPs. into epoxy resin improved the corrosion resistance effect of the epoxy coating. This could be a result of the good dispersion of nanoparticles in the epoxy resin; an action which in turns hinders corrosive electrolyte diffusion into the composite coating films. This helps the coating to work as a powerful barrier.

There are two mechanisms explaining the barrier effect of ZnO NPs:

The first one is that the well dispersed ZnO NPs. into epoxy matrix are characterized with a high surface area and a small particle size. The nano particles absorb a noticeable amount of resin on its surface and this increases the composite film density. Besides, they also fill the cracks and micro porosities of the coating and the free volume existed in the epoxy matrix. This leads to decreasing the transport paths required by the corrosive electrolyte for passing through the coating; thus, it reduces its corrosion rate [25].

The second mechanism assumes that the electrolyte penetrates into the paint film and when it reaches the surface of metal the corrosion reaction starts and produces some corrosion products. These resulting products in conjunction with the added nanoparticles serve to fill the lately produced channels which resulted from the penetration of the electrolyte, and hence blocking it against any further transformation of ions. At certain time this will stop the corrosion reaction [26].

**Role of Chitosan in reducing the corrosive action on epoxy nano- composite coated panels**

The results in tables (1-5) show that adding Chitosan to the epoxy coating composite enhances its anticorrosion performance. This improvement in corrosion resistance properties may be a result of the chitosan molecular structure which contain nitrogen and oxygen atoms. These can be extensively adsorbed on surface of the metal. This leads to the formation of new bonds between the Nitrogen /Oxygen electron pairs and the π-electrons and the surface of metal, thus blocking the corrosion active sites [27].

The best result of corrosion resistant panel was that given by the panel coated by epoxy- Chitosan ZnO NPs composite containing 3% ZnO NPs. and 5% Chitosan. This sample showed rating number 9 which indicates an excellent corrosion resistance whereas the failed area was only about 1% of the total area.

To conclude, we can notice that the combination of Chitosan and ZnO NPs. reinforced the epoxy matrix. These filler materials enhance the adhesion property of coating to the metal surface. Adhesion of composite to metal surface increased by increasing percentage of both Chitosan and ZnO NPs., thereby corrosion resistance also increased.

## 3.2. Chemical resistance of Chitosan epoxy nanocomposite films

The results of chemical resistance tests are shown in Figures (7:11) and photos of the test samples are given in figures (12:14). Chemical resistance against acid, alkali and a solvent are tested. Figure (7) shows the change of chemical resistance for the nanocomposites having 1% Chitosan, with different concentration of NPs. The modified coating resisted the action of acid for 6 days and the action of alkali for 17 days and showed good resistance to solvent (acetone). Thus, this figure indicates that resistance to acid and alkali improves as the concentration of NPs in the composite increases. This improvement which may be due to addition of ZnO NPs, which act as inert lamellar filler, which orientate themselves parallel to the substrate surface and inhibit corrosion by acting as effective barrier element to acid and alkali solutions.
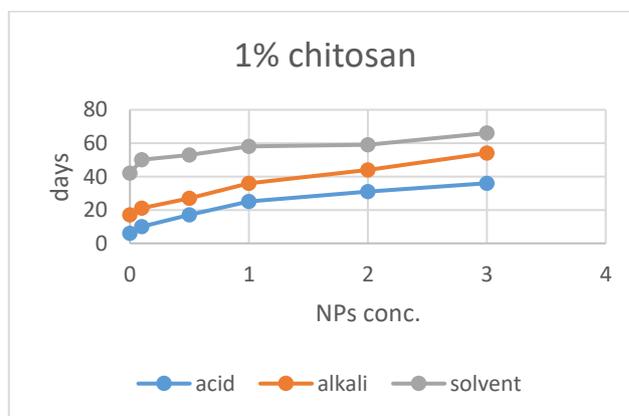


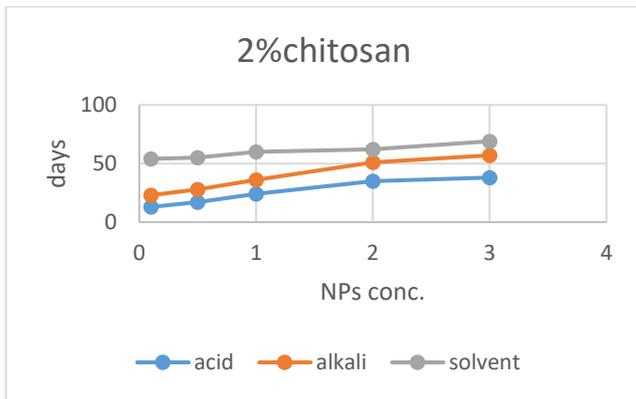Figure (7): Chemical resistance of 1% Chitosan epoxy nanocomposite

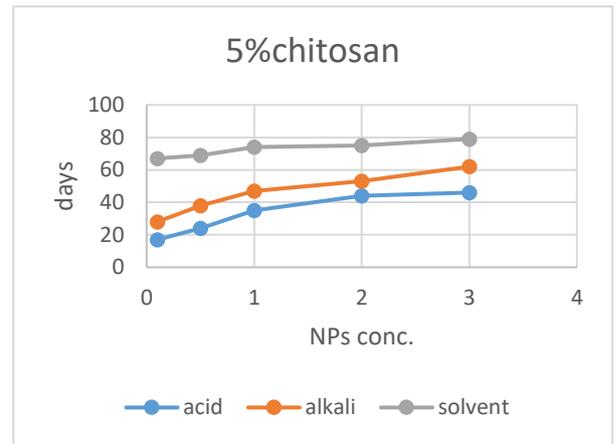Figure (8): Chemical resistance of 2% Chitosan epoxy nanocomposite

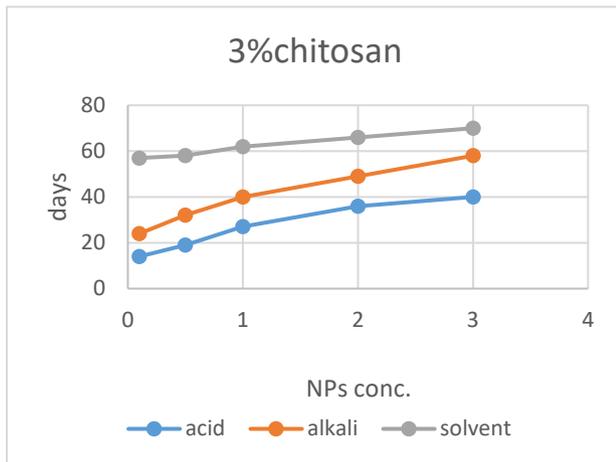

Figure (9): Chemical resistance of 3% Chitosan epoxy nanocomposite



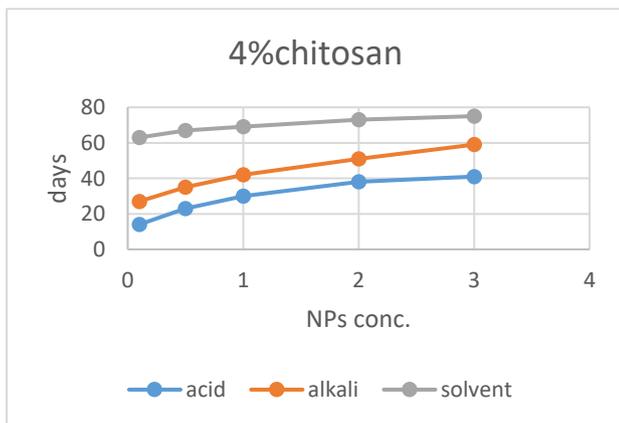Figure (10): Chemical resistance of 4% Chitosan epoxy nanocomposite



Figure (11): Chemical resistance of 5% Chitosan epoxy nanocomposite



Figure (12): Blank epoxy coated sample after 42 days of Acetone exposure



Figure (13): Blank epoxy coated sample after 17 days of NaOH exposure



Figure (14): Blank epoxy coated sample after 6 days of HCl exposure

The corresponding results for 2% Chitosan composite are represented in Fig. 8. This figure indicates that increasing the percentage of Chitosan raised the resistance to acids to 10 days and to alkali to 20 days. Increasing the chitosan concentration increases the amino group which

react with epoxy resin forming the amide bond led to improve the crosslinked density which enhance the chemical resistance Further increase in resistance is noticed with increasing Chitosan concentration to 3, 4 and 5% as given in Figures (9-11).

Neat epoxy coating film showed poor chemical resistance results up to 6 days in HCl, 17 days in NaOH and showed good resistance against organic solvent; Acetone; as shown in figures (12-14). Blank coating showed cracks, flakes and lost its adhesion with steel panels after short exposure periods compared to other nanocomposite coatings. Blank coating was assigned as the weakest chemical resistant coating in comparison with other modified coatings.

The results given by the previous test could be explained as follows:

### Role of ZnO NPs. in modifying the chemical resistance of the epoxy nanocomposite

The data in figures (7-11) elucidated that increasing ZnO NPs concentration in the epoxy nanocomposite enhanced the chemical resistance of coated panels. This may be because the incorporation of ZnO NPs. enhances the adhesion forces formed between the polymeric epoxy coating molecules and the metal substrate and prevented coating delamination. ZnO NPs. also enhanced the cohesive forces between the epoxy molecules, which reduced the grain boundaries size; so that the cracks initiation and propagation was prevented.

### Role of Chitosan in improving the chemical resistance of the epoxy nanocomposite

It is noted that the epoxy coating which is cured with nano-particles mixes well in different percentages with chitosan. It has high chemical resistance; for all percentages of chitosan as shown in figures (7-11). This may be due to the increase in the number of crosslinks which increases when the chitosan ratio in the epoxy coating is increased. The resistance to chemicals and solvents attack is directly related to the crosslinking density of the polymer matrix. This may be related to the thermodynamic relation between the polymer net-work structure and solvent [28]. A greater crosslinking degree means less free volume; and the segmental mobility remains available in the polymer. So that the solvent molecules find difficulty to penetrate the crosslinked network. Thus, 5% Chitosan nanocomposite samples gives excellent resistance for chemicals and solvents as indicated in Figure (11). Coating nanocomposites with 3% ZnO NPs. and 5% Chitosan showed excellent results for chemical resistance; up to 46 days in HCl solution, 62 days in NaOH solution and 79 days in Acetone solvent. It was determined as being the highest chemical resistant and the most durable coated panel.

### 4.CONCLUSION

### The following conclusions could be made from the present study:
- Nanocomposite coating is developed by blending epoxy resin, ZnO NPs and chitosan with different concentrations to improve the anti-corrosion and chemical resistance characteristics of the epoxy coating resin.
- The obtained results elucidated that the improvement of coating performance increase with increase in both Chitosan and ZnO NPs concentrations.
- The results of salt spray and chemical resistance tests proved that the addition of Chitosan beside ZnO NPs into epoxy matrix results in an enhancement in the anticorrosion and the chemical resistance properties of the epoxy composite coating for deterioration in aggressive environment. The highest performance was accomplished with nanoacomposite having 3% ZnO NPs + 5% chitosan. The evaluation parameters for the salt spray test were 1% disbanded area and 9 rating number for the modified composite. The corresponding values for the blank sample were 19% and 5 for the disbanded area and rating number, respectively.
- Thus ZnO NPs-Chitosan-epoxy composite coating is a promising methodology for developing corrosion and chemical resistant of surface coatings.

### Credit Authorship Contribution Statement
**Aghareed M. Tayeb**: Conceptualization, Review and editing, Investigation and Supervision.
**Ashraf M. ElSaeed**: Methodology, Investigation and Supervision.
**Ali S. Mehany**: Methodologyand Writing original draft.

### Declaration of Competing Interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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