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Novel Sustainable Polymeric Coatings for Protection of Copper and Steel Alloys from Metal Deterioration

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Abstract

New protective transparent polymeric coatings were used in this study based on the presence of 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA); Vinyl chloride vinyl acetate copolymer (VCVACO); Ormocer; Nitrosal (Hydroxy ethyl cellulose HEC) as polymers, to protect copper and iron alloys from corrosion. The protection efficiency of these polymeric coatings on copper and iron alloys was measured by electrochemical impedance spectroscopy (EIS) technique. The electrochemical impedance results were confirmed by scanning electron microscopy (SEM) technique. The results showed that vinyl chloride-vinyl acetate copolymer and trimethoxysilyl-propyl methacrylate can be used as protective coatings for copper alloys due to their high protection efficiency 98 and 92 %, respectively. On the other hand, ormocer polymeric coating showed mild protection efficiency for copper alloys with protection efficiency 57.7 % and did not show any protection efficiency towards corrosion of iron alloys. Vinyl chloride vinyl acetate copolymer showed the highest protection efficiency for iron alloys, 91.6 %. While, 3-(trimethoxysilyl)propyl methacrylate showed only 75.9 % protection efficiency. On the other hand, nitrosal did not show any protection behavior against corrosion for both copper and iron alloys.

Keywords: *Trimethoxysilyl-propyl methacrylate; Vinyl chloride vinyl acetate copolymer; Ormocer; Nitrosal; Metal deterioration.*

1. Introduction

Carbon steel and copper alloys have a significant consideration due to their wide range of uses either in industry, buildings, bridges, furniture or metallic heritage. Hence, their protection from deterioration is crucial in order to lessen their economic loses [1,2]. The use of polymers for the inhibition of corrosion of metals and metal alloys gained a wide acceptance during the last decades. Polymeric coatings have the preference than other methods of corrosion protection due to their low cost, stability to aggressive media. The protection efficiency of protective coatings can be explained by taking into consideration the presence of multiple adsorption sites, the capability of forming metal complexes by their function groups and the metal ions on the metal surfaces. The formed complexes and/or adsorbed layers act as blanketing to the surface, extending the path route of aggressive ions preventing them from attaining the metal surface [3,4]. The impact of chemical structure of organic polymers on their corrosion inhibition behavior is very strong. Recent studies manifested that the presence of highly electronegative atoms, such as: O, N, S and P in addition to unsaturated bi bonds, have an important role in corrosion inhibition properties of organic polymers [5-7]. Numerous articles reported detailed description on these polymers. Among the polymeric coatings that can be used in metal protection from corrosion polyacrylamide, carboxymethyl cellulose are widely used for different environments and different metals [8-11]. Previously, we studied the use of polydimethylsiloxane modified with long-chain alkyl silane groups, as insulating material to protect bronze artifacts from corrosion [12].

The aim of this study was to investigate the effect of different polymeric coatings based on the presence of 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA); Vinyl chloride vinyl acetate copolymer (VCVACO); Ormocer; Nitrosal (Hydroxy ethyl cellulose HEC), as protective coatings for copper and iron alloys, which were found overlapped in an old heritage originated in Alexandria, Egypt from 19th century. During this study, comparison between the efficiency of the different polymers as protective coatings will be carried out and discussed.

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2. Materials and Methods
2.1 Materials.

Four different polymers were studied in this article. i) Nitrosal (Hydroxy ethyl cellulose HEC). Hydroxyethylcellulose is a gelling and thickening agent derived from cellulose, soluble in methanol. It is widely used in cosmetics, cleaning solutions and other house hold solutions (fig 1a). ii) Vinyl chloride vinyl acetate copolymer (VCVACO). It has the molecular formula $C_6H_9ClO_2$ and dissolved in ethyl acetate. Vinyl chloride vinyl acetate copolymer is modified resin that combines the toughness and chemical resistance of vinyl chloride, the strong adhesiveness and plasticity of vinyl acetate, that enhance adhesive properties (figure 1b). iii) Ormocer is an acronym for "organically modified ceramic technology". Ormocers are a new type of hybrid (organic-inorganic) dental composite material. Ormcer materials contain: (i) inorganic, (ii) organic copolymers in addition to the (iii) inorganic silanated filler particles (polysiloxanes) (fig 1c) [13]. iv) 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA). It has the molecular formula $C_{11}H_{20}O_5Si$. TMSPMA is commonly dissolved in xylene. TMSPMA is a hydrophobic monomer, it contains trialkoxy groups (figure 1d). It is widely used in the application of modern clinical dentistry.
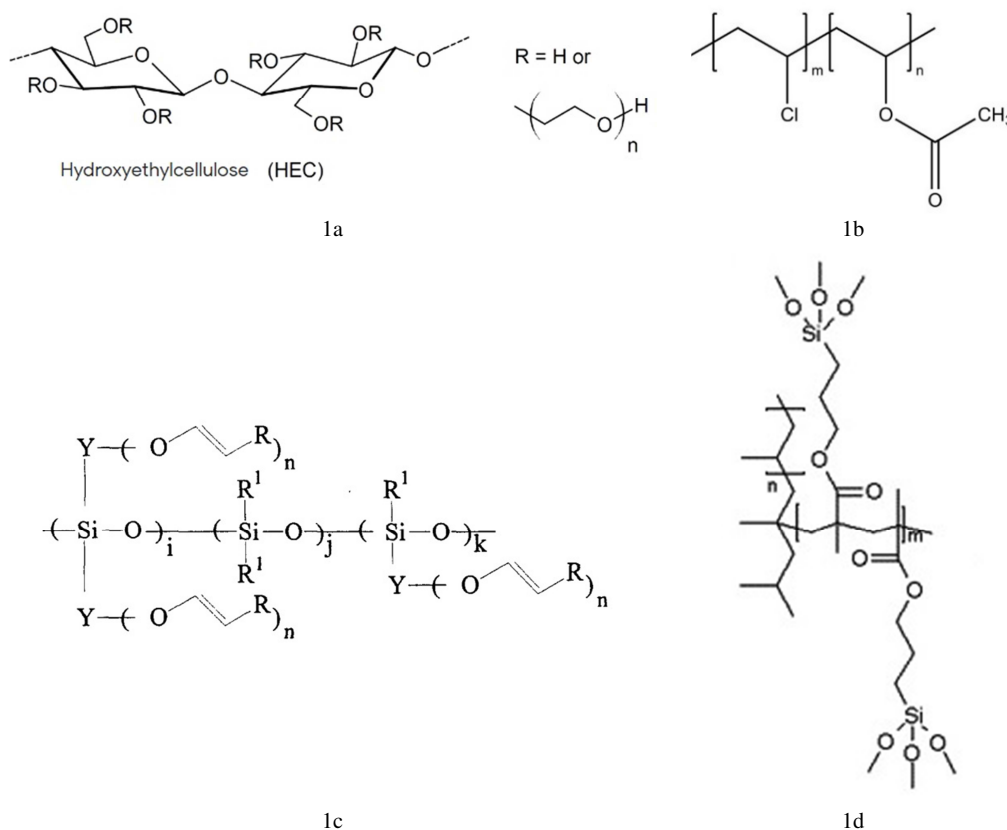

Figure 1: Chemical composition of polymers: a) Nitrosal (Hydroxy ethyl cellulose HEC); b) Vinyl chloride vinyl acetate copolymer (VCVACO); c) Ormocer; d) 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA).

All chemicals used in this study, were purchased from Sigma Aldrich Company. The coatings were prepared by dissolving the required polymeric resins in the corresponding solvent with continuous stirring at room temperature until complete dissolution. The specimens used in this study where made of iron and copper based alloys. The iron alloy used in this study has chemical composition (% wt): Fe 95.3 ; C 4.7, while the copper alloy used in this study has chemical composition (% wt): Cu 54.3; Zn 33.8; Al 0.8; Pb 2.6; C 8.5. They washed with double distilled water, then rinsing with ethanol and finally dried in air prior to coating. Coating of the specimens was carried out by dipping the samples for three times, in order to obtain uniform film thickness of approximately 65 µm, in a container containing 250 mL of the previously prepared polymeric coating solution. The samples were kept for a while to drain the excess coat. The samples were hanged perpendicularly for nearly an hour after coating in room temperature until complete drying. Coating thickness gauge, Minitest 300FN, Elektrophysik, Erichsen Testing Equipment was used to measure the thickness of the coated samples [14]. The criteria used to evaluate and compare the different polymeric coatings as a conservative material for iron and copper based alloys was the impedance spectroscopy (EIS), scanning electron microscopy (SEM) techniques.

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2.2 Electrochemical impedance measurements

Impedance experiments were performed in aqueous solution containing 3.5 % sodium chloride simulating sea water composition. The conditions of testing were maintained similar to the coastal environment at which the artefacts under study were found. The relative humidity RH is normally between 55 and 60 % simulating the coastal environment and the temperature ranged from 20 to 30 ^{0}C. The impedance were measured by Metrohm Autolab Potentiostate by using container contains three electrodes with: (i) either iron or copper samples as working electrodes; (ii) platinum sheet as counter electrode; (iii) Calomel electrode (SCE) as reference electrode. The dimensions of the working electrode were 5 cm x 5 cm x 0.5 mm, and the exposed area to solution: 26.0 and 23.75 cm^2 for copper and iron alloys respectively. Regarding the impedance measurements, the frequency range used was 0.01 to 10^4 Hz. Zisimpwin 3.2 program was used to analyse the experimental data by fitting the data to different equivalent circuits simulating the solution chemistry and choosing the best fit equivalent circuit with minimum percentage error. The results were validated by taking into consideration, the low Chi Square value ($\approx$ 0.001) during all impedance measurements which is a good indication about the fitting between the obtained results and data obtained by analysis.

2.3. Morphologies of polymeric coating materials.

Scanning Electron Microscopy (SEM) technique using JOEL instrument was used to study the morphologies of the polymeric coating materials on iron and copper alloy samples. Scanning electron microscopy (SEM) was done on films deposited on a Tracor Northern Microanalysis Addessory Electrodes, coated with a thin gold film, with conditions: magnification 1500x at 20 kV.

2.4 Characterization of iron and copper alloys based samples

The iron and copper based alloys samples studied, were investigated by SEM-EDAX analysis unit for elemental analysis. The SEM micrographs of iron and copper alloys used in this study are presented in Fig. 2.
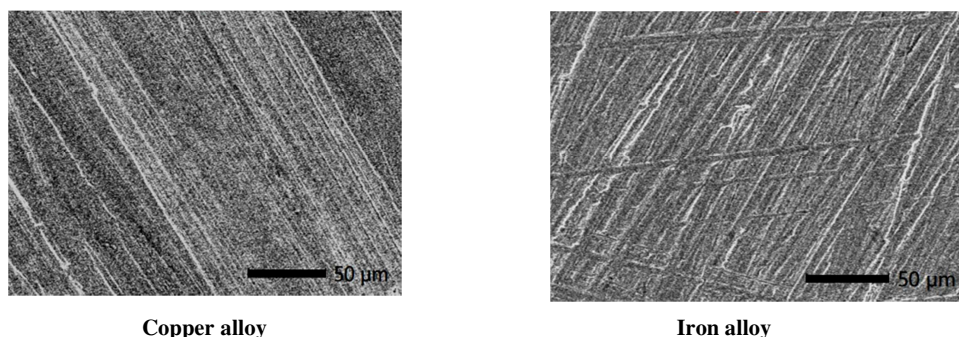

Copper alloy   **Iron alloy**

Figure 2: SEM for copper and iron alloy samples (magnification 500X, 20 kV)

2.5. Surface analysis of copper and iron alloys

The chemical analysis of the corrosion products formed on the iron and copper based samples under this study was performed by XRD X-ray diffraction. Samples were used from three different places are analyzed by using X-ray Powder Diffraction, Bruker-Germany Diffractometer. Fiures 3 showed the analysis of samples of both iron and copper based alloys.
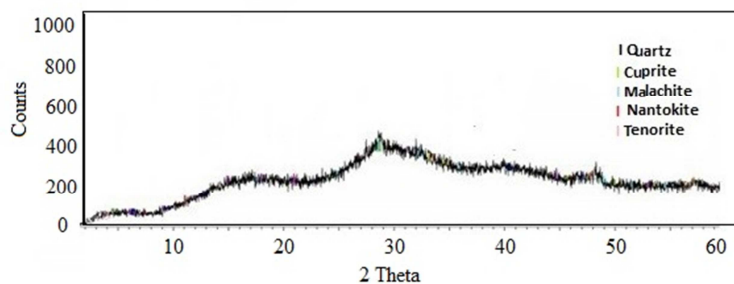

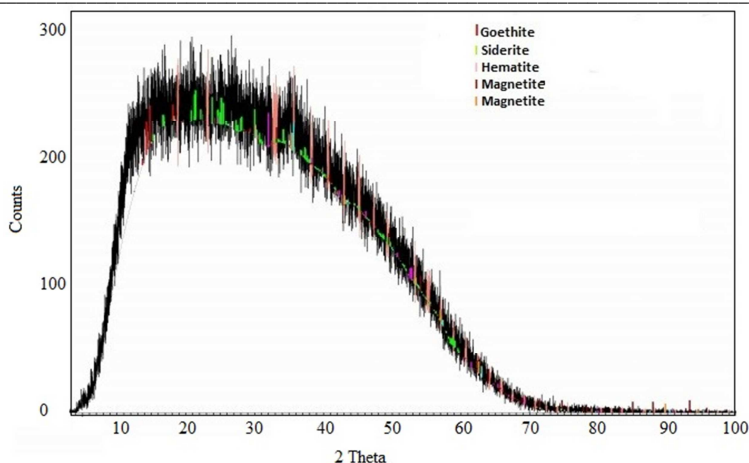**Figure 3a:** XRD for copper based alloy

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Figure 3b: XRD for iron based alloy

The XRD spectra showed the presence of rust products, in which a layer of copper oxide (cuprite) Cu_2O, with dispersed spots of basic copper carbonate which called malachite. Other copper compounds were formed as a result of the ions available in the surrounding medium. Black rust products of copper oxide (CuO) in addition to black patina are presented due to the presence of copper sulfide from pollution by hydrogen sulfide gas H_2S present in the environment. Also, copper chloride (Cu_2Cl_2) (Nantokite) found. The iron alloy takes multiple forms of rust begin with ferrous oxide FeO as a coherent layer. In presence of oxygen, the ferrous oxide converted to magnetite Fe_3O_4, which turns into hematite Fe_2O_3 and continues to progress. These minerals interact with the surrounding environment dispersing the corrosion products on the surface forming basic oxides: brownish yellow limonite in addition to brown to reddish brown (OH)FeO goethite, especially in presence of moisture and polluting gases represented in sulfur dioxide gas.

3. Results and discussion
3.1. Electrochemical Impedance Spectroscopy EIS technique
It is worth telling that impedance measurement is the most widely method used for the evaluation of polymeric organic coatings due to its accuracy and it is non-destructive for either the metal or the coating material. Impedance performed in this study to assess the efficiency of 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA); Vinyl chloride vinyl acetate copolymer (VCVACO); Ormocer; Nitrosal (Hydroxy ethyl cellulose HEC), as insulating materials to protect the iron/copper specimens from corrosion. The area exposed to the aggressive environment was 26.0 for copper and 23.75 cm^2 iron based alloys. Blank samples, in addition to samples coated with: 3-(Trimethoxysilyl) propyl methacrylate (TMSPMA); Vinyl chloride vinyl acetate copolymer (VCVACO); Ormocer; Nitrosal (Hydroxy ethyl cellulose HEC) were constructed. All the polymers used were in solutions with concentration 4 % by mass from each in the suitable solvent for each polymer. The impedance carried out in aggressive solution simulating sea water with concentration 3.5 % by mass sodium chloride.
3.1.1   Impedance results of copper
Nyquist plots for copper samples both coated and uncoated measured in 3.5 % NaCl solution are showed in figures 4 a & b.
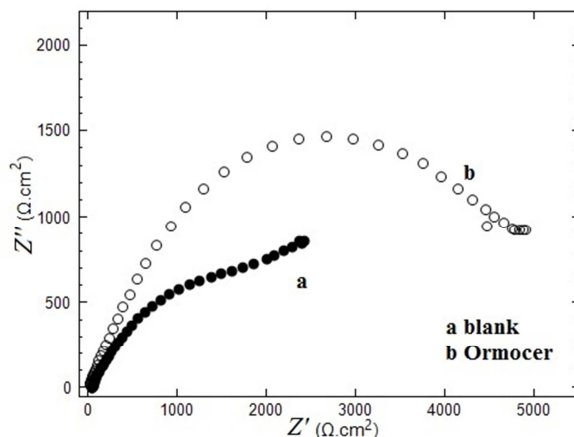

Figure (4a): Nyquist plot measured for copper sample in absence and presence of ormocer polymeric coating in 3.5 % NaCl solution.
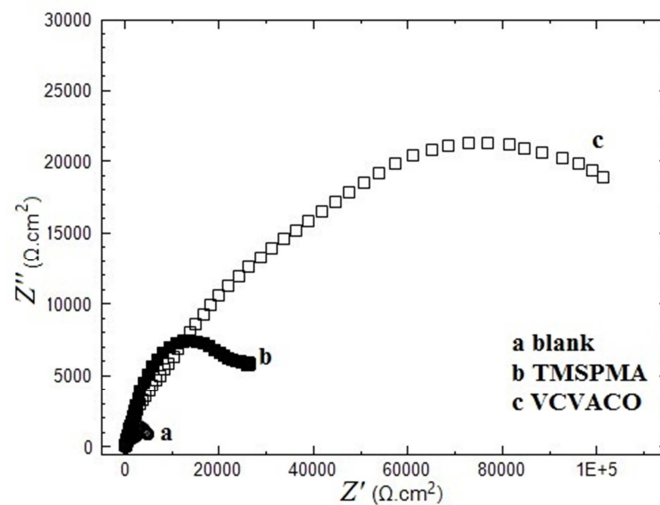
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Figure (4b): Nyquist plot measured for copper samples in absence and presence of 3-(Trimethoxysilyl) propyl methacrylate (TMSPMA) and Vinyl chloride vinyl acetate copolymer (VCVACO) polymeric coating in 3.5 % NaCl solution.
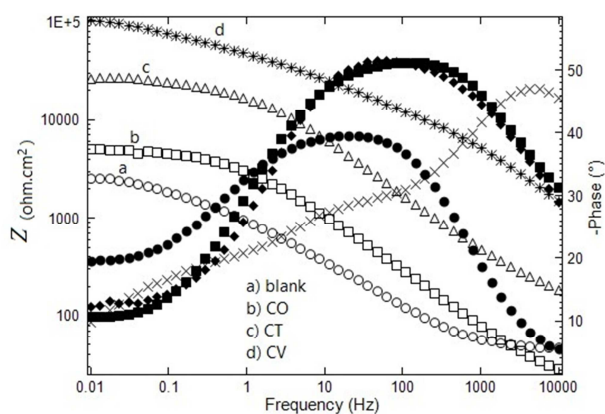

Figure 4c: Impedance and theta plots measured for copper samples with and without polymeric coatings in 3.5 % NaCl.

The behaviour of nyquist was found to be capacitive which is indicative of the presence of charge transfer resistance in addition to the effect of capacitance ionic double-layer. The impedance measurements were examined by fitting the experimental data to Zsimpwin program by applying to different equivalent circuits and choosing the best fit Eq. Cir. Fig 5.

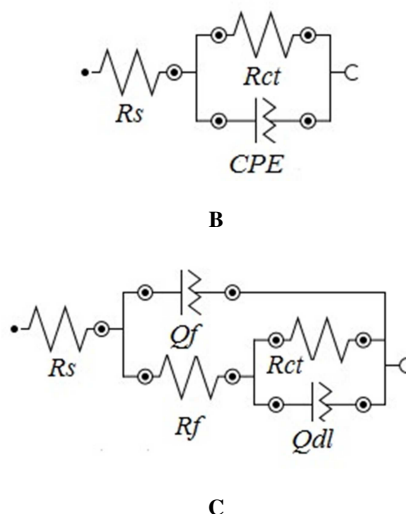

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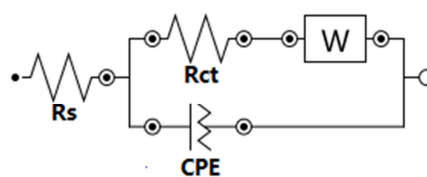
Figure 5: Equivalent circuits used in copper alloy coatings

The equivalent circuit chosen simulates the chemical reactions takes place at the interface area between the patina of the copper based sample, which is of cuprite (Cu_2O), and the saline bulk solution. Generally, the equivalent circuit consists of solution resistance R_s, constant phase element Q, charge transfer resistance element R_{ct} placed in parallel to Q. Q usually placed in the equivalent circuit to interchange the capacitor in the equivalent circuit. Q represents the non-homogeneity in the solution. Q is accompanied to n value, where; $0 \leq n \leq 1$. If $n = 1$, the Q will be exchanged by the pure capacitance C. The best fit of nyquist plot of copper blank obtained by introducing Warburg constant W (fig. 5a). W is indicative of the diffusion behaviour of ionic species at the interface between the copper specimens and bulk solution. In the meantime, fitting the experimental data of the coated copper by either Ormocer or TMSPMA polymeric coatings were found best by applying the equivalent circuit in fig. 5b. Contrary, copper samples coated by VCVACO polymeric coatings were fitted only by adding, to the previously mentioned simple equivalent circuit, R_f component (film resistance) and C_{dl} (capacitance of double layer). The equivalent circuit used to fit the results of VCVACO coating represented in fig. 5c. The electrochemical parameters acquired from EIS for copper samples with and without coatings and the percentage inhibition is given in table 1. The percentage inhibition calculated from the following equation:

$$\% E. = [(R_{CT} - R_{CT}0) / R_{CT}] \times 100 \qquad (1)$$

Where; R_{CT0} is the charge transfer resistance of blank copper, while R_{CT} represents the charge transfer resistance of the coated copper. Bode and theta plots for copper and coated copper are shown in fig. 4c.

Table 1: Impedance parameters for copper, coated with ormocer; TMSPMA; VCVACO insulating material in 3.5 % NaCl solution at room temperature

Coating	R_s ohm.cm^2	Q_F µF/cm^2	n_f	R_f ohm.cm^2	Q_{dl} µF/cm^2	n_2	R_{ct} ohm.cm^2	W	% inhibition
Copper (uncoated)	39				2.68E-4	0.56	2242.8	0.086	-------
Ormocer	14.6				6.54E-5	0.62	5309.2		57.7
TMSPMA	102.7				1.08E-5	0.62	28306.2		92.1
VCVACO	868.4	2.078E-6	0.54	47242	1.99E-5	0.62	70228.6	----	98.1

Inspection the data in table 1, revealed that the charge transfer resistance R_{ct} and the percentage inhibition of coated samples showed higher values than blank copper. The given results showed that the three polymeric coatings can be used as protective coatings for copper based alloys. The variation of the inhibition efficiency of the polymeric coatings used in this study, is in the order: VCVACO > TMSPMA > Ormocer. It was found that, nitrosal organic coating has no effect on the protection efficiency of copper alloys from corrosion.

3.1.2   Impedance results of iron alloy

Nyquist plots for iron samples in uncoated and coated samples with TMSPMA and VCVACO polymeric coatings measured in 3.5 % NaCl solution are showed in figures 6 a & b.
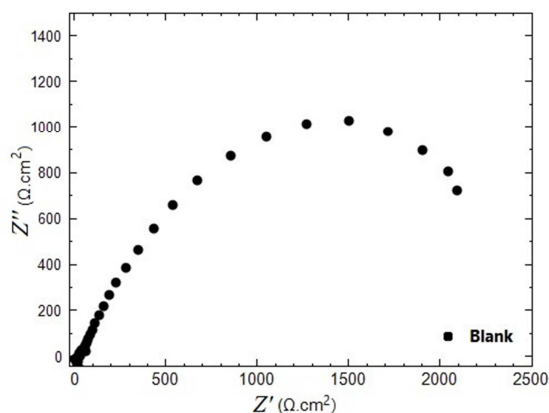
Figure 6a: Nyquist plot measured for iron sample in absence of polymeric coatings in 3.5 % NaCl solution.
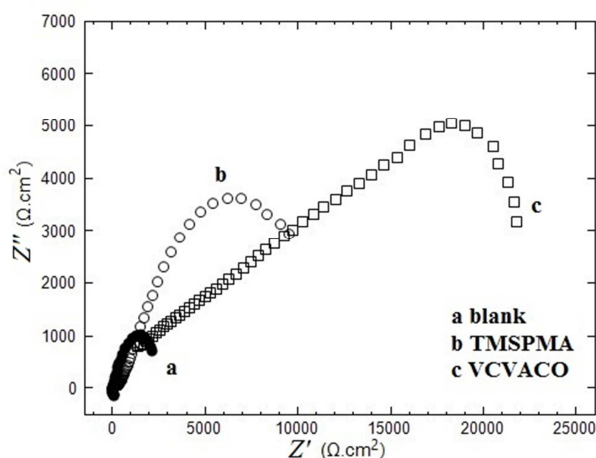

Figure 6b: Nyquist plots measured for iron samples in absence and presence of 3-(Trimethoxysilyl) propyl methacrylate (TMSPMA) and Vinyl chloride vinyl acetate copolymer (VCVACO) polymeric coating in 3.5 % NaCl solution
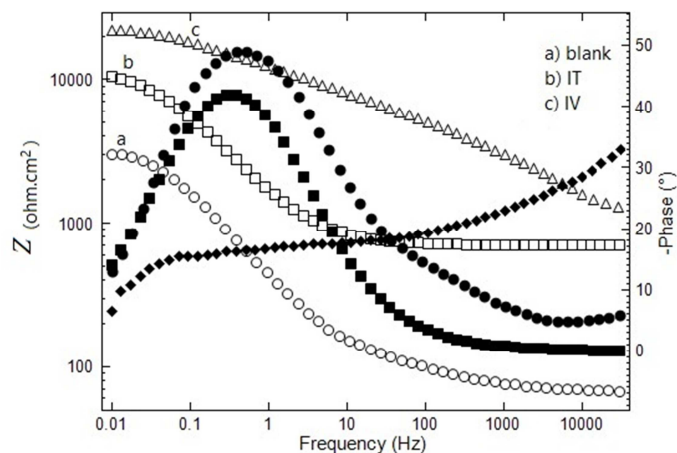

Figure 6c: Impedance and theta plots measured for iron samples with and without polymeric coatings in 3.5 % NaCl.

The behaviour of nyquist was found to be capacitive which is indicative of the presence of charge transfer resistance in addition to the effect of capacitance ionic double-layer. The impedance spectra were analysed by fitting the experimental data to equivalent circuit model (fig 7).
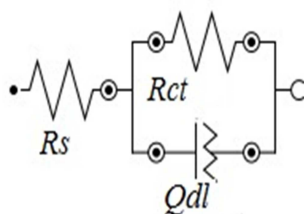
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Figure 7: Equivalent circuit used in iron alloy coatings.

The inhibition efficiency is calculated by equation 1, similar to that in case of copper alloy. The impedance data and the inhibition efficiency are shown in table 2.

Table 2: Impedance parameters for steel coated with TMSPMA and VCVACO insulating material in 3.5 % NaCl solution at room temperature

| Coating	R_s ohm.cm^2	Q_{dl} μF/cm^2	n_2	R_{ct} ohm.cm^2	% inhibition
Iron (uncoated)	36.1	1.06E-3	0.68	2817.93	-------
TMSPMA	695.9	2.08E-4	0.70	11739.6	75.9
VCVACO	254.1	3.16E-5	0.27	33511.3	91.6

It is clear from the data in table 2, that R_{ct} and the percentage inhibition of coated iron with polymeric materials are higher than blank iron specimens. The data revealed that both vinyl chloride vinyl acetate copolymer and trimethylsilyl propyl-methacrylate polymers can be used as protective coatings for iron alloy from corrosion. While ormocer and nitrosal have negative effect on the corrosion protection of iron alloys. The inhibition efficiency of the vinyl chloride vinyl acetate copolymer is higher than the trimethsilyl propyl-methacrylate polymeric coatings. Fig. 6c, showed bode and theta figures for iron alloy in absence and presence of polymeric coatings.

3.2 Scanning electron microscopy SEM
Scanning electron microscopy (SEM) technique gives a superficial vision of the solid surface by magnification of the surface to many thousands times. SEM used in this study to shed the light on the importance of surface analysis and its agreement with the electrochemical measurements. Figures 8 and 9, showed the SEM microphotography for the copper and iron alloy samples with and without insulating materials, respectively.
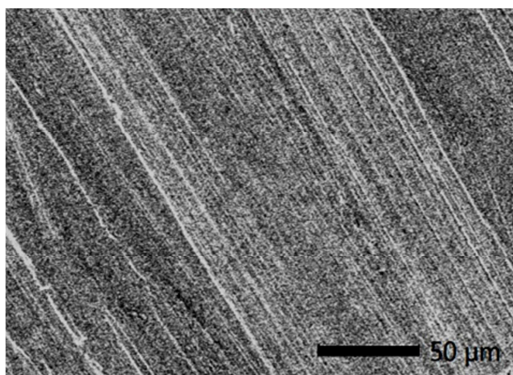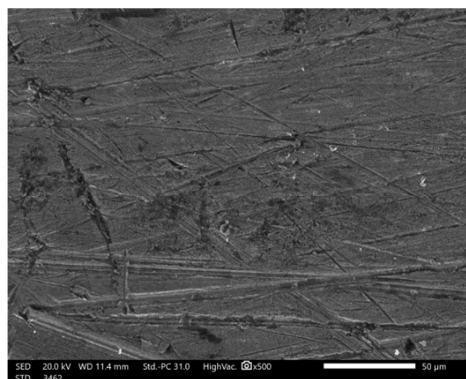
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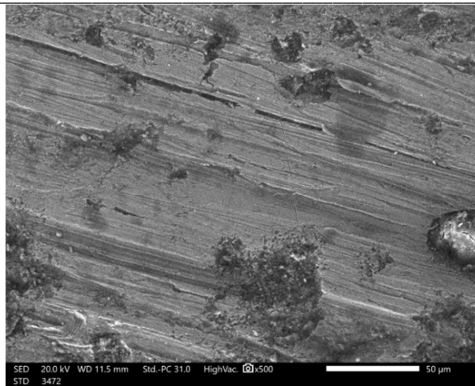
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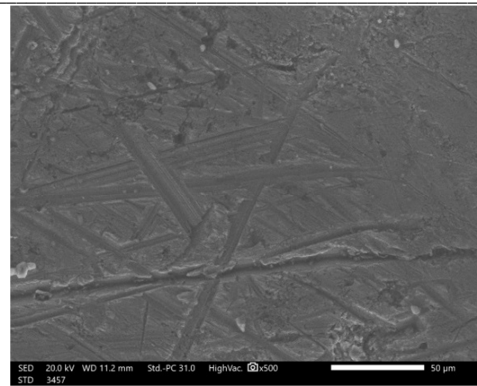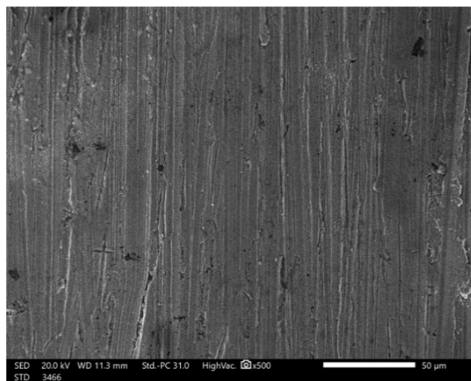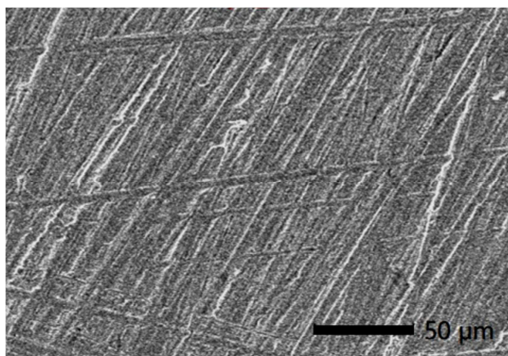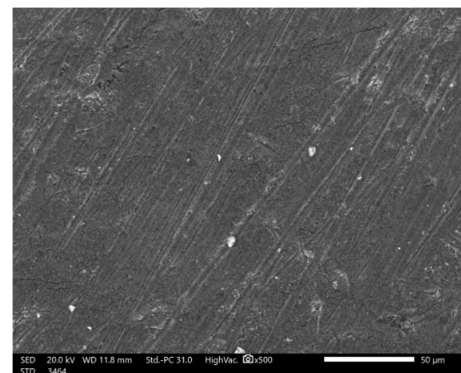**Figure 8:** SEM micrographs for a) copper sample; copper samples coated with b) Ormocer; c) TMSPMA; d) VCVACO; e) Nitrosal insulating polymeric coatings after insulation.
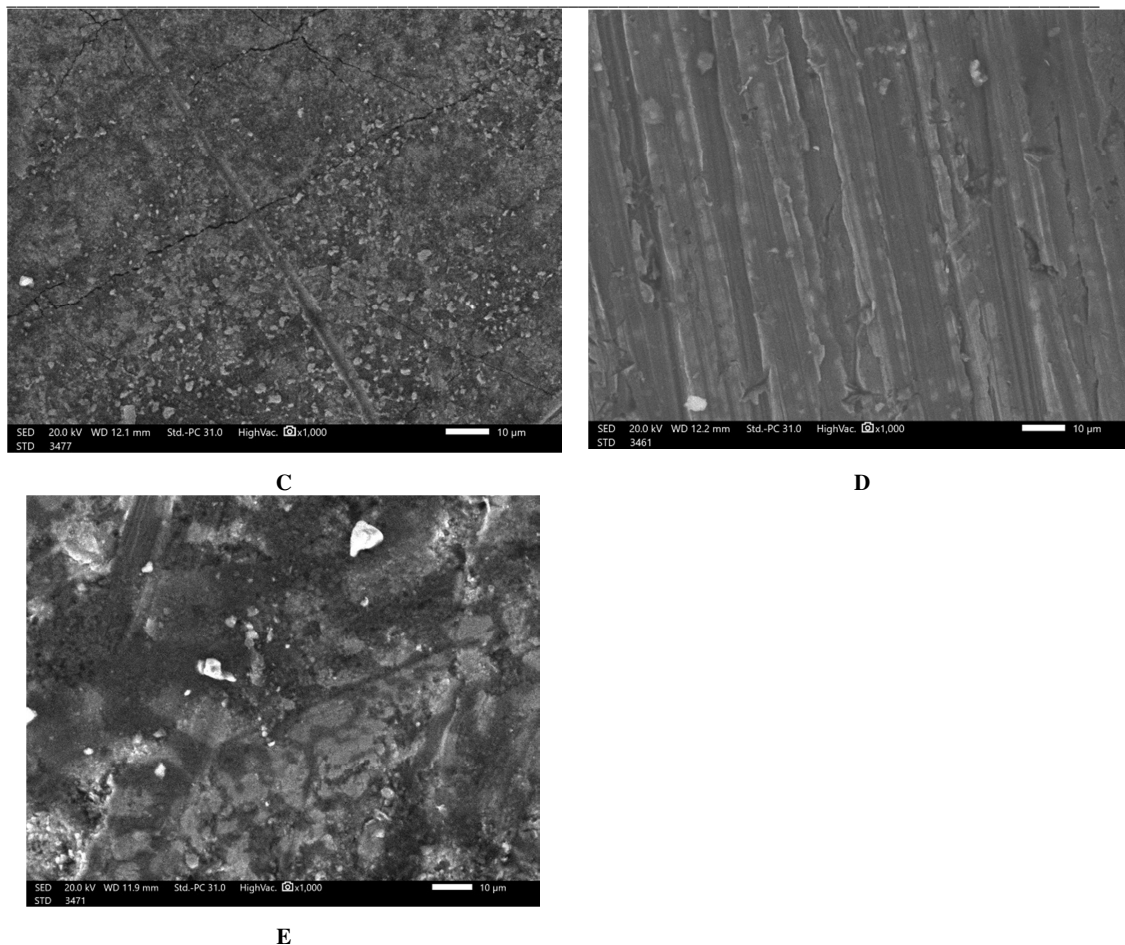

A

B

C

D

E

Figure 9: SEM micrographs for a) iron sample; iron samples coated with b) Ormocer; c) TMSPMA; d) VCVACO; e) Nitrosal insulating polymeric coatings after insulation.

The SEM micrographs for the blank samples of copper and iron in figures 8a and 9a, showed scratch marks of copper and iron samples which result from abrasion of the samples during surface preparation. The SEM micrographs in figures 8(b, c and d), revealed that the layers formed on copper samples covers nearly all the surface homogeneously and fill even the tiny gaps in the insulating material, indicating that vinyl chloride vinyl acetate copolymer, trimethylsilyl propyl-methacrylate and ormcer can be used as protective coatings for copper samples. On the other hand, figure 8e showed that the polymer coating covered all the surface of copper sample with the appearance of some aggregates of rust products, appeared as spots on the surface. This means that nitrosal polymeric coating did not have the potential for corrosion protection of copper samples. These results are in accordance with the results obtained from impedance measurements. The SEM micrographs in figures 9(c and d), revealed that the layers formed on iron samples covers nearly all surface homogeneously and fill even the tiny gaps in the insulating material, indicating that both vinyl chloride vinyl acetate copolymer and trimethylsilyl propyl-methacrylate polymeric coatings can be used as protective coatings for iron samples. Figure 9b, showed scratch marks of the surface, this means that ormocer polymeric coating did not cover the metallic surface totally or did not adhere firmly, this confirms the negative effect of ormocer on the corrosion protection of iron sample. On the other hand, figure 9e indicated that the polymer coating used did not cover all the surface of iron samples, in addition to, the rust products that appeared much, as spots on the micrographs. This means that nitrosal polymeric coating did not have the potential for corrosion protection of iron samples. These results are in accordance with the results obtained from impedance measurements. The enormous protection efficiency detected for vinyl chloride vinyl acetate copolymer can be elucidated by considering the chemical and mechanical properties of the resin. Vinyl chloride-vinyl acetate copolymer is considered a modified resin. VYHH has high degree of crosslinking and wear resistance combined to the toughness and chemical resistance of vinyl chloride resin. The strong adhesiveness and plasticity of vinyl acetate enhances the adhesive properties of the copolymer. VYHH has high degree of transparency and low fisheye level. VYHH resin has high resistance to water absorption. All these, led to its use as excellent surface protection coating [15-17]. Trimethylsilyl propyl-meth acrylate has hydrophobicity properties formed from trialkoxy group's monomers. The main application of TMESPMA polymer is the implementation of clinical dentistry referring to its very high adhesion power. Extra adhesion properties are gained due to the presence of dissimilar materials organic polymer/metal surface due to

the silane coupling agent. The trialkoxy silane groups shape the most powerful and extensive properties. This causes the slowing of the penetration of the aggressive ions regarding to its high crosslinking structure [18]. Ormocers is a type of hybrid (organic and inorganic) composite materials combined with inorganic silanated filler particles (polysiloxanes) [19]. The ormocer organic part is a polymer. Ormocer has high ability of crosslinking. Ormocer has good optical properties, its hardness and abrasion resistance properties are confirmed. The chemical stability of ormocer and its thermal expansion depend mainly on the inorganic part of the copolymer. Its elasticity and interface properties are referred to the polysiloxane part of ormocers. The physical and mechanical properties of ormocers are low compared to other hybrid composite materials. Ormocers show a little wear resistance, so, its application as adherent groups was found so limited. The alkoxysilyl groups led to the formation of an inorganic Si=O=Si strong network by polycondensation and hydrolysis reactions. The presence of (meth) acrylate groups are assigned for the photochemical induced organic polymerization. A strong covalent bonds exist between inorganic and organic moieties of ormocers [20]. The volumetric and mechanical behaviours of ormocers during the curing process studied in order to stimulate the development and the spatial distribution of residual stresses. It was found that, a continuous decrease of the specific volume of polymer reaching – 1.2 % ± 0.1 % observed revealing the occurrence of polymerization shrinkage with time [21]. All these facts should be considered to explain the low efficiency of ormocers as protective coating for metal and alloys although it has potential for other very good applications as dentistry restorative materials and the use of other applications regarding its strength. The mechanism of adsorption of these polymeric coatings can be explained by taking into consideration the presence of multiple adsorption sites, the capability of forming metal complexes by their function groups and the metal ions on the metal surfaces. The formed complexes and/or adsorbed layers act as blanketing to the surface, extending the path route of aggressive ions preventing them from attaining the metal surface [22-27]. The negative effect of nitrosal as corrosion protective coating for metallic surfaces can be explained by elucidating the physical and mechanical properties of the resin. Hydroxyethyl cellulose is used mainly in gelling and thickening agent in cosmetics. Hydroxyethyl cellulose is also applied in capsule formulations in drug industry, to improve drug dissolution. Also it is used in oil and gas industry as a drilling mud additive. Hydroxyethyl cellulose is used in paints and coatings, ceramics, adhesives, emulsion polymerization, inks, welding rods, pencils and joint fillers. Its application in paint and coating formulations is to increase the viscosity of paints and to enhance its flow properties. There is no evidence in the literature found about the hardness and adhesion properties of the hydroxylethyl cellulose. This means that, its applications can be limited to improve the paint application on metallic surfaces but has no potential for its use as protective coating for metallic surfaces. It is reported that polyamide polymeric coatings showed high protection efficiency against corrosion of iron artefacts. The experiments were carried out by using coupons simulating iron window which is the artefact under study. The protection efficiency of polyamide coatings were assessed by using electrochemical impedance spectroscopy (EIS) and polarization resistance (RP) electrochemical techniques. The results showed sufficient protection and good inhibition of corrosion of the iron window [28]. Polyaniline coating were assessed for the corrosion inhibition of ancient steel spearheads from Al Qala military museum in Egypt. Characterization of the chemical composition and microstructure of the spreaheads were done by X-ray diffraction XRD, scanning electron microscope SEM and energy dispersive X-ray spectroscopy EDX. Electrochemical impedance EIS and potentiodynamic polarization spectroscopy techniques were used to evaluate the polymeric coatings used in this study. Significant increase in the corrosion resistance of the spredheads was found out. The results explained on basis that the coat acts as barrier, blocked out water and other aggressive ions from reaching the surface of the metal [29].

Conclusions

The efficiency of 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA); Vinyl chloride vinyl acetate copolymer (VCVACO); Ormocer; Nitrosal (Hydroxy ethyl cellulose HEC) as protective coatings for iron and copper alloys were studied by electrochemical impedance spectroscopy EIS and scanning electron microscopy SEM techniques. The results indicated that 3-(Trimethoxysilyl)propyl methacrylate, Vinyl chloride vinyl acetate copolymer and Ormocer polymers can be used as protective coatings for copper based alloys. The order of increasing their inhibition efficiency is: VCVACO > TMSPMA > Ormocer. It was found that, nitrosal organic coating has no effect on the protection efficiency of copper alloys from corrosion. The results also showed that, only vinyl chloride vinyl acetate copolymer and trimethylsilyl propyl-methacrylate polymeric coatings can be used as protective coatings for iron alloy from corrosion. The inhibition efficiency of vinylchloride vinyl acetate copolymer is higher than trimethylsilyl-propyl methacrylate polymeric coating. Ormocer and nitrosal has negative effect on the corrosion protection of iron alloy. The results obtained from impedance spectroscopy are in good agreement with that obtained from scanning electron microscopy technique.

Statement and Declarations
- Conflicts of interest/Competing interests
Submission of this manuscript implies: that the work described has not been published before; the manuscript is being submitted exclusively for the Corrosion Engineering Science and Technology Journal; it is not under consideration for publication anywhere else; and its publication has been approved by all the co-authors.

- Ethics approval and consent to participate
     NA

- Consent for participate
     Participants of the research are full informed about publication in your journal.

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- Consent for publication

        All participants in the research agree to my authorization to publish.

- Author contributions (Ensure all authors are referred to in the statement)

        *Professor Mohamed M. Megahed***:**

        Assigning the point; revision of data, revision of manuscript.

        *Professor Mohamed K. Khalaf***:**

        Assigning the point; revision of data, revision of manuscript.

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        Assigning the point, research plan, practical work, analysis of data, writing the manuscript.

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        Practical work, analysis of data, revision of the manuscript.

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