Self-healing Anticorrosion Coatings for Gas Pipelines and Storage Tanks

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In the present study, chitosan based self-healing anticorrosion coatings were prepared by layer by layer (lbl) addition of chitosan (Ch) and polyvinyl butyral (PVB) on mild carbon steel substrate. Chitosan coatings exhibited enhanced coating stability and corrosion resistance in aggressive environments by the application of a PVB top layer. Chitosan layer in the lbl coatings have been modified by using glutaraldehyde (Glu) and silica (SiO_2). Performance of different coatings was tested using electrochemical impedance spectroscopy and immersion test. The best anticorrosion performance was observed in case of 10 % Ch_SiO_2_PVB coatings, which withstand immersion test over 25 days in 0.5 M salt solution without visible corrosion. 10 % Ch _SiO_2 coatings without the PVB top layer didn't last more than 3days. Application of PVB top layer sealed the defects in the chitosan pre-layer and improved its hydrophobic nature as well. Raman spectra and SEM of steel surfaces after corrosion study and removal of PVB_Ch/Glu_PVB coatings showed a passive layer of iron oxide, attributing to the self-healing nature of these coatings. Conducting particle like graphene reinforcement of chitosan in the lbl coatings enhanced corrosion resistance of chitosan coatings.

Keywords : *self-healing, chitosan, glutaraldehyde, silica, anticorrosion, layer by layer coatings*

1. Introduction

Corrosion of metals is one of the main destruction processes resulting in huge economic losses, especially in the petroleum industries, aerospace and automotive. The need for replacement of hazardous chromates in barrier coatings has led tremendous interest to a new generation of "self-healing coatings". They are able to reconstruct the mechanical integrity of the polymer matrix after it has been damaged or at least capable of stopping the development of corrosion processes at formed defects. The application of natural polymeric materials is an attractive approach for the development of "green" self- healing coatings. Chitosan is one such interesting candidate due to its good film- forming properties, superior adhesion to metallic surfaces as well as to many organic polymers, and the ability to reversibly form complexes with natural fillers and corrosion inhibitors[1-5].

Chitosan is very similar to cellulose and is classified as a linear polyamine (poly D- glucosamine)[1]. In terms of chemical characteristics, chitosan is insoluble in aqueous solution but in protonated amine form it is soluble at pH < 6.5. Chitosan adheres to negatively charged surfaces and might be expected to spontaneously adsorb on metal or oxide surfaces under certain conditions. It can form complexes with metal ions and gels with poly-anions[1]. The hydroxyl and amine groups on chitosan are reactive and can be used to make a range of interesting chemical derivatives. Many of these chemical attributes make chitosan an attractive candidate as a film former on metals[2]. However, the major critical issue in using CS as a corrosion-preventing barrier is that it absorbs a large amount of moisture from the atmosphere, and then forms a hydrogel. This transformation not only leads to biodegradation of the film, but also allows moisture to infiltrate easily into the film, causing its failure as a protective coating[6-8].

Attempts to exploit chitosan as a coating material are limited. Perhaps the most significant instance demonstrated so far is the work of Sugama[6,7], who reported that aluminium substrate, dip-coated in a chitosan solution withstood 700 hours of salt spray exposure. They prepared water-insoluble chitosan biopolymer by grafting synthetic poly (itaconic acid) (PIA) polymer onto the liner chitosan chains and to crosslink between the chitosan chains. Carneiro et. al used chitosan as a smart container for the storage and controlled release of corrosion inhibitor 2-Mercptobenzothiazole[3,10].

The aim of present work was to develop stable chitosan

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coatings capable of providing self-healing nature by the layer by layer addition of chitosan and hydrophobic polymer like PVB. Chitosan modification with glutaraldehyde and silane coupling agent like tetraethoxysilane have also been tried to improve the adhesion strength and corrosion resistance of coatings. Reinforcement of chitosan coatings with conducting particle like graphene (Gr) was studied. Immersion test and electrochemical impedance spectroscopy measurements were conducted for corrosion analysis.

2. Experimental Part

2.1. Materials

Polyvinyl butyral (PVB), 98 % tetraethoxysilane (TEOS), isopropanol, hydrochloric acid and 95 % methyltrimethoxysilane (MTMS) was purchased from Aldrich, Germany and used as received. Chitosan ($M_v = 1.7 \times 10^5$, degree of deacetylation (DD) = 90 %) was purchased from Sea Food Pvt. Ltd. India.

2.2. lbl coatings of chitosan and PVB

0.5 mg chitosan was dissolved in 10ml of 2 %acetic acid. This mixture was stirred for 24 h to ensure complete dissolution of chitosan in acetic acid. 0.5 mg of PVB was dissolved in 10ml of methanol. lbl coating was applied on 5 cm x 3 cm x 2 cm carbon steel coupons by using a dip coater. One layer of PVB was applied first followed by two layers of chitosan. After drying at 75 ˚C for 2h a final PVB layer was applied. Final coating wwas cured for 2h at 90 ˚C.

2.3. PVB_Ch/Glu_PVB coating

5 ml of 1 % glutaraldehyde were added to 0.5 mg of chitosan dissolved in 10ml of 2 % acetic acid and stirred for 15 minutes. Carbon steel coupons coated with PVB first layer were dip coated two times in the chitosan/glutaraldehyde solution. After drying at 75 ˚C for 2h a final layer of PVB was coated. Final coatings were cured at 90 ˚C for 2 h. Chitosan/Glutaraldehyde/Graphene formulation were prepared by adding 5 % of graphene in the chitosan/glutaraldehyde solution. This mixture was sonicated for 6h and dip coated on the carbon steel coupons using the lbl approach described above.

2.4 Ch_SiO₂_PVB coatings

Chitosan_SiO₂ hybrid coatings were prepared by sol gel method. Silica sol was prepared first by mixing 0.6 g TEOS with 7.9 g isopropanol and 9.5 g 0.001M HCl (1:4:16 molar ratio)[11]. The stirring was continued for 1.30 h at 30 ˚C. 10 % of chitosan dissolved in 2 % acetic acid was added to silica sol under constant stirring. Stirring

was continued for 10min and MTMS, 2 times the molar ration of TEOS, was added to this mixture drop by drop to prepare hydrophobic Chitosan_silica hybrid. This precursor sol was dip coated two times on the carbon steel substrate and kept at 80 ˚C for 2 h to obtain the gel. One top layer of PVB was coated on this Chitosan _silica hybrid coating and cured for 2 h at 90 ˚C.

2.5. Immersion test

Four sides of all the coupons were sealed using Nippon epoxy primer. After 24 h drying in room temperature PVB_Ch_PVB and PVB_Ch/Glu_PVB coatings were immersed in 0.3 M salt solution for standard corrosion analysis, whereas Ch_SiO₂_PVB coatings were immersed in 0.5 M salt solution.

2.6. Electrochemical measurements

Tafel plot and impedance measurements of PVB_ Ch_ PVB and PVB_Ch/Glu_PVB coatings were carried out in 0.3 M salt solution and for Ch_SiO₂_PVB coatings 0.5 M salt solution were used as electrolyte. All measurements were performed on computerized electrochemical analyzer (supplied by BioLogic, France). Carbon steel coupons with Chitosan_PVB lbl coatings were used as working electrode while Pt and SCE were the counter and reference electrodes respectively. 1 cm² area of working electrode was exposed to electrolyte and impedance measurements were performed as a function of open circuit potential (E_{OCP}). Tafel plots were recorded at a scan rate of 0.166 mV/s.

2.7. FTIR and Raman spectroscopy

Structural characterization of chitosan crosslinking with glutaraldehyde and silica was investigated using a Bruker VERTEX 70 FTIR spectrometer attached with a DRIFT accessory. Raman spectra were recorded using LabRAM HR spectrometer (Horiba Jobin Yvon). Laser light from He/Ne source with wavelength of 633 nm was used for excitation. A long working distance objective with magnification 50X was used to collect the scattered light as well as to focus the laser beam on the sample surface.

3. Results and Discussion

Self-healing anti corrosion coatings of chitosan were prepared by layer by layer addition of chitosan and PVB on mild carbon steel surface. One layer of PVB was applied first followed by two layers of chitosan and one final layer of PVB. For comparison PVB alone, chitosan alone and PVB_Ch coatings were prepared and corrosion resistance behaviour of these coatings was assessed by
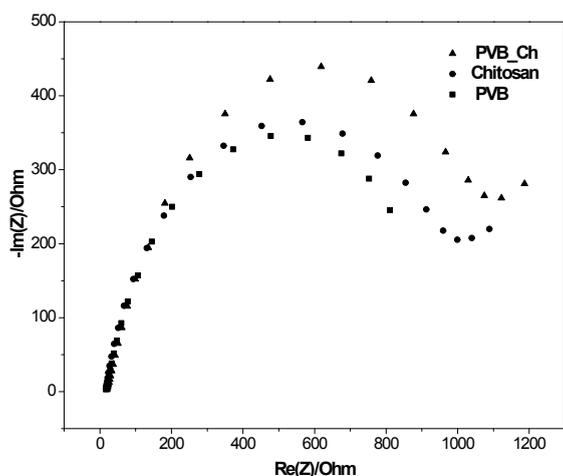
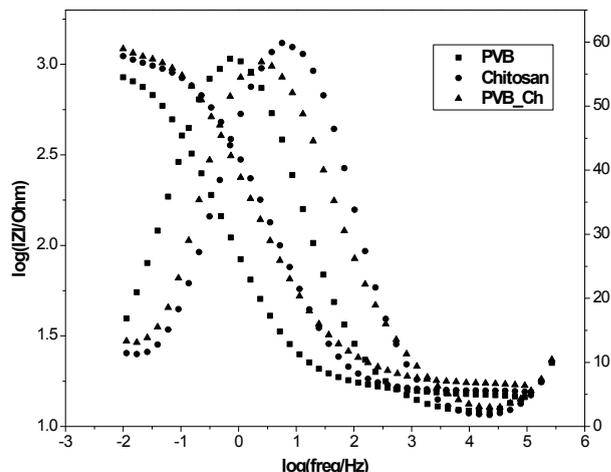**Fig. 1.** Nyquist plot of PVB, Chitosan and PVB_Ch coatings in 0.3 M salt solution.

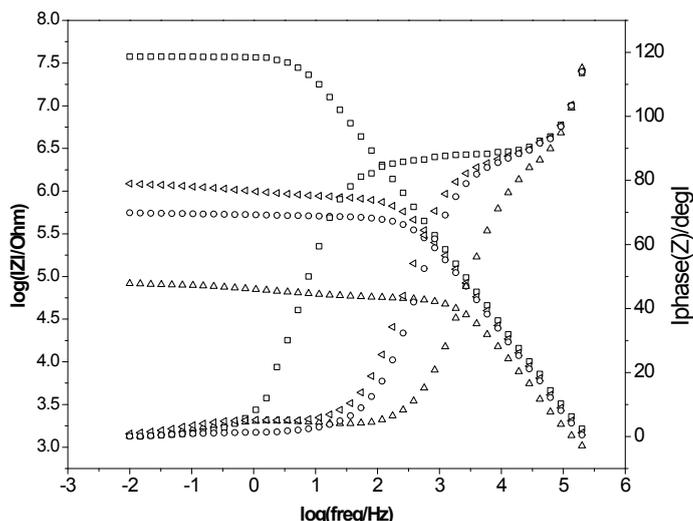**Fig. 2.** Bode plots of PVB, Chitosan and PVB_Ch coatings in 0.3 M salt solution.

Fig. 3. Bode plots of (△) PVB_Ch_PVB, (◎) PVB_Ch/1% Glu_PVB, (◁) PVB_Ch/5% Glu_PVB and (○) PVB_Ch/10% Glu_PVB.

EIS studies. Fig. 1 & 2 show Nyquist and Bode plots of PVB alone, chitosan alone and PVB_Ch coatings immersed in 0.3 M salt solution for 2h. As seen in Fig. 1 & 2 electrode impedance is higher for chitosan coatings than PVB coatings which attributed to the anticorrosion property of chitosan. Since these coatings were not stable in the corrosive medium for more than one day, lbl coating of PVB one layer and chitosan two layers were prepared. EIS spectra of this coating showed an increased low frequency impedance in the Bode plot (Fig. 2). Loop diameter of the Nyquist plot (Fig. 1) also increased for the PVB_Ch coatings which indicated that the layer by layer addition of PVB and Chitosan improved stability and corrosion resistance of chitosan coatings.

Addition of a top layer of PVB on PVB_Ch coatings, to avoid the direct contact of chitosan with the corrosive medium, enhanced significantly the coating stability and corrosion resistance of lbl coatings as shown in Fig. 3 where low frequency impedance (logZ) in the Bode plot of PVB_Ch_PVB coating increased to 4.9 ohm cm^2 compared with PVB_Ch coatings which exhibited a low value of 3.1 ohm cm^2.

3.1. Chitosan modification with glutaraldehyde

PVB_Ch_PVB coatings were modified by incorporating glutaraldehyde in the chitosan layer. The Nyquist and Bode plots of PVB_Ch/Glu_PVB coatings given respectively in Fig. 4 and Fig. 3 showed a tremendous in-
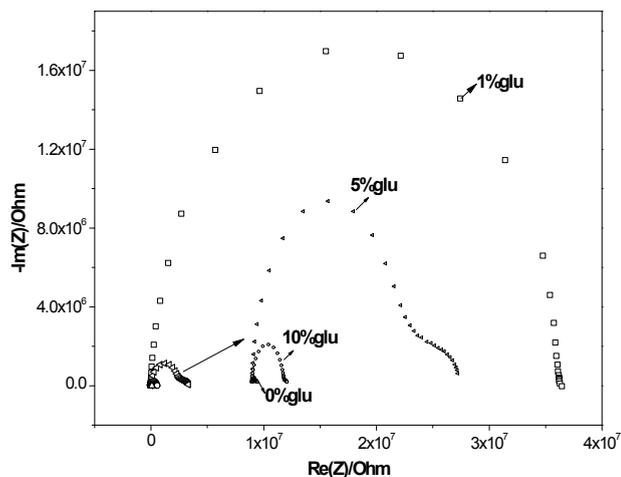
Fig. 4. Nyquist plots of PVB_Ch/Glu_PVB coatings with different percentages of glutaraldehyde in the chitosan layer.
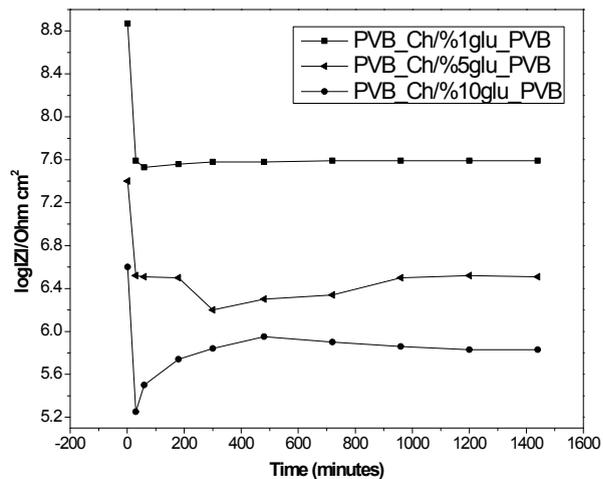

Fig. 5. Variation of loglZl calculated from Bode plot with respect to time of immersion in 0.3 M salt solution.
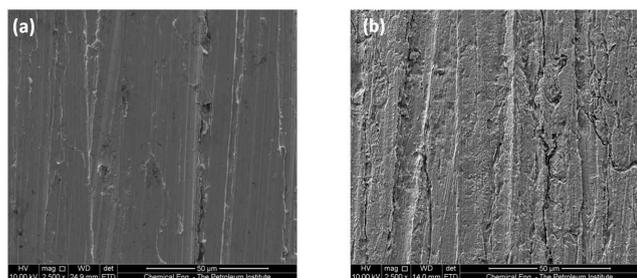

Fig. 6. SEM images (a) bare steel surface and (b) steel surface after corrosion study and removal of PVB_Ch/1 % Glu_PVB coating.
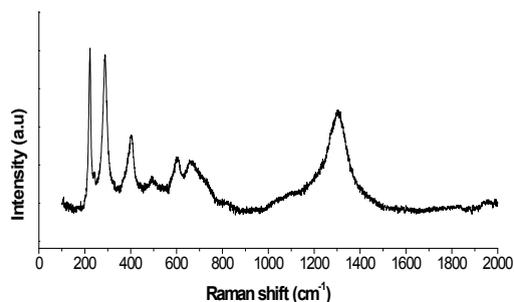

Fig. 7. Raman spectra of the passive layer formed beneath PVB_Ch/1 % Glu_PVB coating.

crease in the impedance values compared with PVB_Ch_PVB coating. Furthermore, the real part of semicircle i.e. diameter of Nyquist plot also increased with the addition of glutaraldehyde in the chitosan layer (Fig. 4).

This leads to an assumption that glutaraldehyde activated chitosan crosslinking, which was observed in the FTIR spectra of PVB_Ch/Glu_PVB coatings where amide 1 and amine bands of chitosan at 1664 cm^{-1} and 1560 cm^{-1} shifted to a single broad band centered at 1570 cm^{-1}. This cross-linked chitosan restricts the penetration of corrosive species by acting as a physical barrier and thus improves the corrosion resistance. Increasing the percentage of glutaraldehyde in the chitosan layer decreased corrosion resistance of PVB_Ch/Glu_PVB coatings. The low frequency impedance values derived from Bode plots (Fig. 5) continue to remain high for PVB_Ch/1 % Glu_PVB coatings even after 24 h exposure to the corrosive environment. This is a clear indication of the protection against corrosion. It can also be observed in Fig. 5 that after an initial decrease, impedance value increased slightly which suggests that

there is a self-healing process taking place in PVB_Ch/Glu_PVB coatings. SEM images of steel surfaces after the removal of film given in Fig. 6 showed a passive layer formation and Raman spectra of these layers (Fig. 7) showed bands characteristic to α-Fe$_2$O$_3$ and Fe$_3$O$_4$ at 220 cm^{-1}, 292 cm^{-1}, 1308 cm^{-1} and 696 cm^{-1} respectively. This leads to an assumption that the passive layer formed on the surface of carbon steel coated with PVB_Ch/Glu_PVB are composed of α-Fe$_2$O$_3$ and Fe$_3$O$_4$.

It can be suggested that crosslinking of chitosan with glutaraldehyde enhanced coating stability and this coating provided self-healing by the formation of a passive layer on the metal surface. Incorporation of conducting particle like graphene in the chitosan layer enhanced corrosion resistance of PVB_Ch/1 % Glu_PVB coatings. E$_{corr}$ of PVB_Ch/1 % Glu/5 % Gr_PVB coatings calculated from Tafel plots measured after 6 h immersion in 0.3 M salt solution showed a more positive value (-370 mV) than that of PVB_Ch/1 % Glu_PVB coatings (-606 mV), which indicated the enhanced corrosion resistance of graphene re-
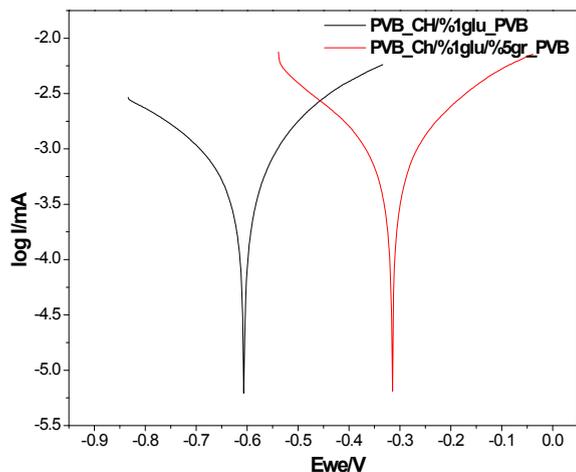
Fig. 8. Tafel plot of PVB_Ch/1 % Glu_PVB and PVB_Ch/1 % Glu/5 % Gr_PVb coatings after 6 h immersion in 0.3 M salt solution.

Fig. 9. Bode plot of PVB_Ch/1 % Glu/5 % Gr_PVB coating after 2 h immersion in 0.3 M salt solution.

inforced coatings (Fig. 8). Even though, unequal distribution of graphene in chitosan layer resulted in a decreased low frequency impedance (loglZl: 6.6 ohm cm^2) in the Bode plot (Fig. 9).

3.2. Chitosan modification with silica

Chitosan-PVB lbl coatings have been modified by incorporating silica in the chitosan layer and the final coating consist of a first layer of chitosan_silica hybrid coating and a PVB top layer. Chitosan_silica hybrid coating wwas prepared by sol gel method using TEOS. FTIR spectra of this coating given in Fig. 10 confirmed chitosan cross linking with silica.

The characteristic peaks of chitosan at 1664 cm^{-1} and 1560 cm^{-1} corresponded respectively to amide 1 and NH$_2$ bending vibrations were shifted to lower wavenumbers of 1635 cm^{-1} and 1550 cm^{-1} respectively for Ch_SiO$_2$ hybrid coating. Si-O stretching of silanol observed in pure silica at 973 cm^{-1} have been shifted to 960 cm^{-1} in the Ch_SiO$_2$ coating. These peaks shifts are due to hydrogen bonding of silanol hydrogen with carbonyl and amine groups of chitosan[11]. The hybrid gel structure of Ch_SiO$_2$ coating was confirmed from the peaks at 1279 cm^{-1} corresponded to Si-O-Si symmetric stretching which were observed in pure SiO$_2$ at 1318 cm^{-1}. Note only that antisymmetric stretching vibration of C-O-C bridge present in pure chitosan at 1169 cm^{-1} and skeletal vibrations involving C-O stretching at 1126 cm^{-1} have been shifted to 1229 cm^{-1} and 1175 cm^{-1} respectively. It can be say from the changes in the FTIR band vibrations that chitosan in the first layer is existing as cross-linked with SiO$_2$.

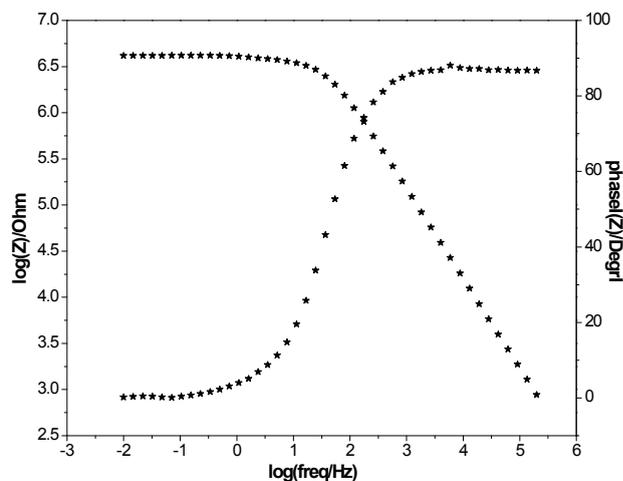Corrosion analysis of these coatings was conducted by

EIS measurements and immersion test in 0.5 M salt solution. Fig. 11 shows EIS spectra of 10 % Ch_SiO$_2$ hybrid coatings after 1h and 1day immersion in 0.5 M salt solution. After one day of immersion the Nyquist plot showed two loops. The loop at high frequency region is attributed to coating response and the second loop at low frequency region is ascribed to the charge-transfer resistance associated with corrosion processes occurring at the metal/solution interface[12]. This assignment was supported by the presence of red pits observed in Fig. 12a. It is interesting to see that lbl coatings of two layers of 10 % Ch_SiO$_2$ hybrid and one top layer of PVB showed corrosion indications after 30 days of immersion in 0.5 M salt solution (Fig. 12b). Single loop in the Nyquist plot of this coating, measured after 1 week of immersion, are
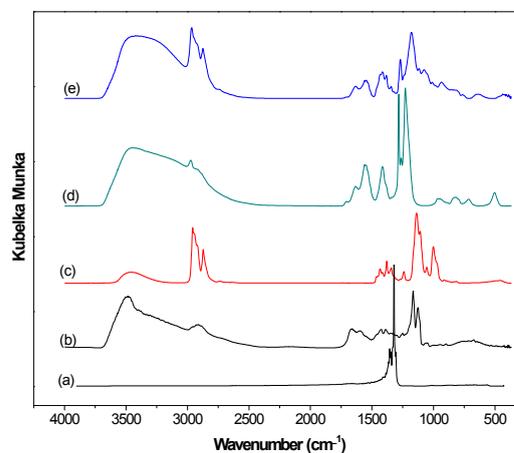

Fig. 10. FTIR spectra of (a) SiO$_2$, (b) Chitosan, (c) PVB, (d) Ch_SiO$_2$ hybrid coating and (e) Ch_SiO$_2$ PVB coating.
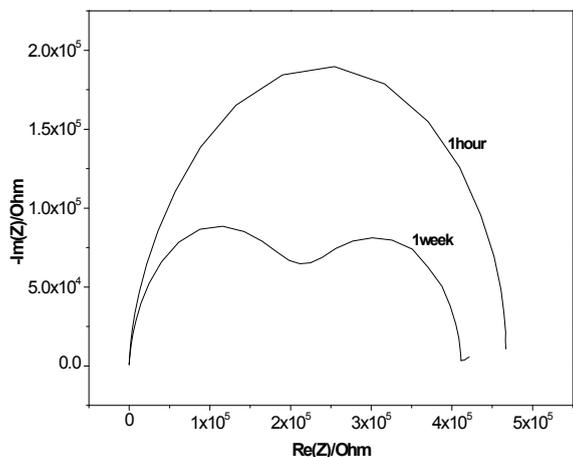
Fig. 11. Nyquist plot of 10 % Ch_SiO$_2$ coating after 1h & 1 week of immersion in 0.5 M salt solution.
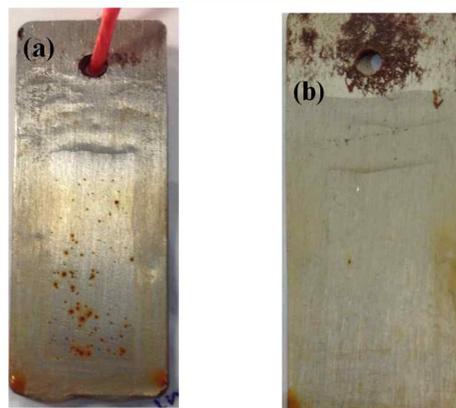

Fig. 12. Optical photographs of (a) 10 % Ch_SiO$_2$ (b) 10 % Ch_SiO$_2$_PVB coatings after 3 days and 30 days respectively in 0.5 M salt solution.
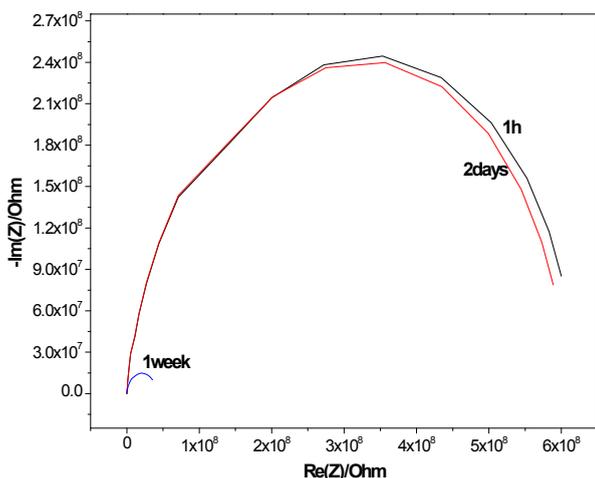

Fig. 13. Nyquist plot of 10 % Ch_SiO$_2$_PVB coating at different time of immersion in 0.5 M salt solution.
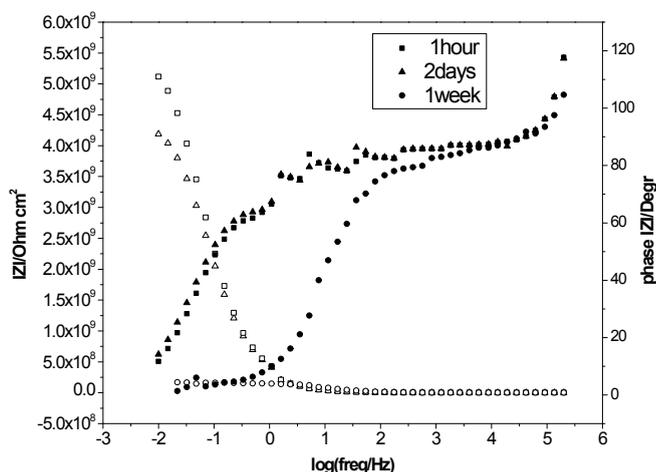

Fig. 14. Bode plots of 10 % Ch_SiO$_2$_PVB coating at different time of immersion in 0.5 M salt solution.

attributed to the coating resistance (Fig. 13). Though the loop diameter decreased with time of immersion, the −Im (Z) at f_{max} was still high ($6.0 \times e^7$). Note only that, the low frequency impedance in the Bode plot (Fig. 14), obtained after 1week immersion, was also high enough ($1.6 \times e^8$) to support the fact that the application of organic top layer increases the stability and corrosion resistance of Ch_SiO$_2$ hybrid coatings. It can be assumed that curing of final PVB coating at 90 ^{O}C might have been sealed all the defects in the Ch_SiO$_2$ hybrid coating which resulted in improved coating stability and corrosion resistance of Ch_SiO$_2$_PVB coatings.

Increasing the percentage of chitosan in the Ch_SiO$_2$_PVB coating decreased coating stability and corrosion resistance. Black pits of corrosion were started to form on 20 % Ch_SiO$_2$_PVB coatings after 15 days of im-

mersion and corrosion products were observed on 50 % Ch_SiO$_2$_PVB coatings after 2 days immersion in 0.5 M salt solution. These observations were supported from the low frequency impedance of Ch_SiO$_2$_PVB coating calculated from Bode plot at different time of immersion, which decreased with increase of chitosan content. After 1 week of immersion in 0.5 M salt solution low frequency |Z| modulus of 10 % Ch, 20% Ch and 50 % Ch_SiO$_2$_PVB coatings decreased respectively to $1.6 \times e^8$ ohm cm^2, $4.5 \times e^7$ ohm cm^2 and $3.5 \times e^6$ ohm cm^2. It is generally considered that coatings with low frequency impedance higher than 10^6 ohm cm^2 are giving a good corrosion resistance[13]. Therefore we can suggest that chitosan concentration up to 20 % in the Ch_SiO$_2$_PVB hybrid coatings is stable enough to provide an active corrosion protection.

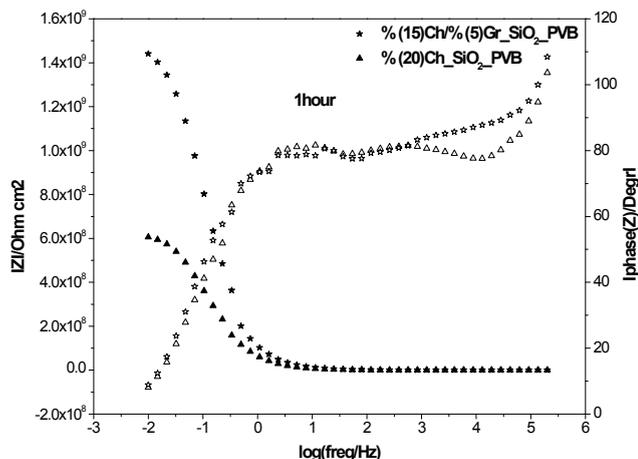In order to study the effect of conducting particle re-

Fig. 15. Bode plots of 20 % Ch_SiO2_PVb and 15 % Ch/5 % Gr_SiO$_2$_PVB coatings after 1 h immersion in 0.5 M salt solution.
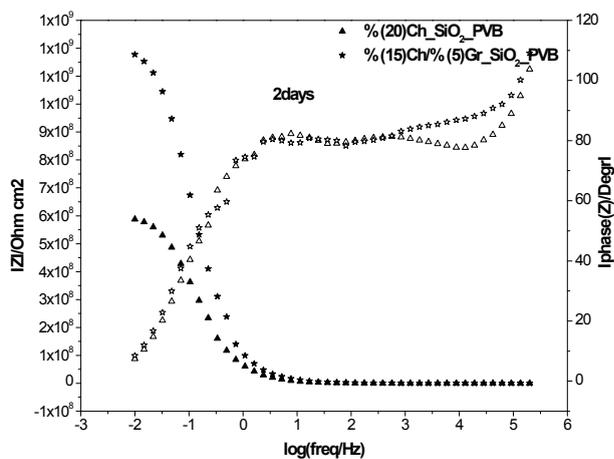

Fig. 16. Bode plots of 20 % Ch_SiO$_2$_PVb and 15 % Ch/5 % Gr_SiO$_2$_PVB coatings after 2 days immersion in 0.5 M salt solution.
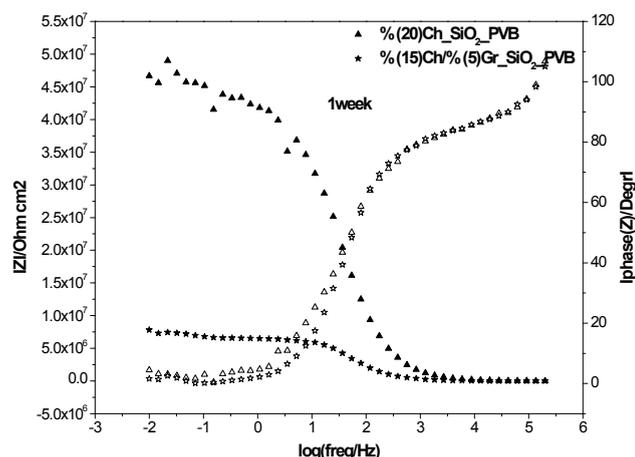

Fig. 17. Bode plots of 20% Ch_SiO$_2$_PVb and 15 % Ch/5 % Gr_SiO$_2$_PVB coatings after 1 week of immersion in 0.5 M salt solution.

Fig. 18. Optical photograph of 15 % Ch/5 % Gr_SiO$_2$_PVB coatings after 1 week immersion in 0.5 M salt solution.

inforcement, Graphene were incorporated in the Ch_SiO$_2$ hybrid layer of 20 % Ch_SiO$_2$_PVB coatings. Any visible agglomerates of graphene particles was not observed in the optical images of 15 % Ch/5 % Gr_SiO$_2$_PVB coatings indicating the good dispersion of the graphene particles in the Ch_SiO$_2$ hybrid coating. Graphene reinforcement in the Ch_SiO$_2$ hybrid layer enhanced coating stability and corrosion resistance as observed in the Bode plot given in Fig. 15, where |Z| modulus of 15 % Ch/5 % Gr_SiO$_2$_PVB coatings increased to $1.4\times e^9$ compared with 20 % Ch_SiO$_2$_PVB coatings which showed a low frequency |Z| modulus of $6.0\times e^8$ after 1hour immersion in 0.5 M salt solution. Even though, continuous immersion reduces low frequency impedance. Bode plot obtained after 2 days and 1 week immersion showed |Z| modulus

as $1.0\times e^9$ ohm cm^2 and $7.5\times e^5$ ohm cm^2 respectively (Fig. 16 & 17). It was supported by the black pits observed on the optical photographs of 15 % Ch/5 % Gr_SiO$_2$_PVB coatings given in Fig. 18.

4. Conclusions

Self-healing anticorrosion coatings of chitosan were prepared by layer by layer addition of PVB and Chitosan on carbon steel substrate. Incorporation of glutaraldehyde in the chitosan layer enhanced coating stability and corrosion resistance of PVB_Ch_PVB coatings. Increased chitosan crosslinking with glutaraldehyde decreased coating performances as observed in the Bode and Nyquist plots of PVB_Ch/Glu_PVB coatings where both impedance values and diameter of Nyquist plot decreased with in-

crease of glutaraldehyde in the chitosan layer. These coatings provided self-healing by forming a passive layer of iron oxide in between the metal substrate and PVB_Ch/Glu_PVB coating. Graphene reinforcement in the chitosan layer of PVB_Ch/1 % Glu_PVB coatings shifted corrosion potential to -370 mV, though, unequal distribution of graphene in the chitosan layer reduced low frequency impedance. Chitosan modified with silica through sol gel process was stable in 0.5 M salt solution over 25 days. Increasing the percentage of chitosan in the Ch_SiO$_2$_PVB coatings decreased coating stability and corrosion resistance. Black pits of corrosion were observed on 20 % Ch_SiO$_2$_PVB coatings after 15 days and on 50 % Ch_SiO$_2$_PVB coatings after 2 days immersion in 0.5 M salt solution. Low frequency |Z| modulus of 10 % Ch, 20 % Ch and 50 % Ch_SiO$_2$_PVB coatings calculated from Bode plot decreased respectively to $1.6 \times e^8$ ohm cm^2, $4.5 \times e^7$ ohm cm^2 and $3.5 \times e^6$ ohm cm^2 after 1 week of immersion in 0.5 M salt solution. Reinforcement of chitosan layer in 20% Ch_SiO$_2$_PVB coatings with graphene particles increased low frequency impedance values. It can be concluded from these results that chitosan crosslinking with glutaraldehyde and silica increased the stability and corrosion resistance of chitosan coatings. Conducting particle like graphene reinforcement of chitosan in the lbl coatings enhanced corrosion resistance of chitosan coatings. Moreover, the lbl method of chitosan_PVB coatings was found to be promising as a temporary coating for active corrosion protection of carbon steel substrates.

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