

DEVELOPMENT AND CHARACTERIZATION OF CORROSION RESISTANT
COATINGS USING NATURAL BIOPOLYMER CHITOSAN

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ABSTRACT

In the present study, chitosan, a derivative of naturally abundant biopolymer chitin, was used as the basis for corrosion resistant coating. Chitosan suffers from two inherent weaknesses as a coating material namely its high hydrophilicity and its poor adhesive strength with Al 2024 T3 alloy. In the present study, chitosan structure was modified using epoxy functional silane and vanadate. Performance of different coatings was tested using electrochemical impedance spectroscopy, adhesion testing and salt spray testing. The best salt spray performance was observed in case of chitosan-(3-Glycidoxypropyl)-trimethoxysilane-vanadate coatings, which lasted 450 hours in salt spray chamber without visible corrosion. UV/Visible spectroscopy measurements showed release of vanadate by chitosan increases with increasing solution pH. This property of chitosan provides self-healing characteristics to these coatings. When the solution pH is readjusted to a lower value, chitosan can re-adsorb released vanadate. FTIR spectra of chitosan gel showed adsorption of vanadate at protonated amine sites. Chitosan showed a maximum in the vanadate adsorption capacity in the pH 3 to 5 range.

INTRODUCTION

Many corrosion resistant coatings used in aerospace systems are dependant on corrosion inhibiting compounds that contain hexa-valent chromium and solvent-borne organic resins. Chromate species in solution undergo reduction at active corrosion sites to form insoluble oxides, which form a barrier for the permeation of other corrosive species like water, oxygen and/or aggressive anions. Chromates inhibit both anodic and cathodic reactions and are among the most potent inhibitors of Al corrosion known. Organic resins provide a wide range of mechanical, barrier, and aesthetic properties that make them attractive for meeting many different service demands placed on aircraft coatings.

Unfortunately, chromates and many solvents in resins are toxic. Reduction of Cr^{6+} to Cr^{5+} is responsible for DNA damage[1]. Federal regulations are underway to control the use of chromate containing compounds due to their known carcinogenic effects. Many compounds either inorganic (cerium, vanadate, molybdate, phosphate) or organic (sodium

sebacate, potassium hydrogen phthalate) are under consideration for use as a suitable replacement for chromates. Water-borne resins are being introduced in non-critical applications, but their performance is not usually as good as that as the solvent-borne resins they are intended to replace. In the present study, the use of chitosan doped with environmentally friendly inhibitors as a non-toxic component in coating systems has been investigated.

Chitosan is very similar to cellulose and is classified as a linear polyamine (poly D-glucosamine) [2]. In terms of chemical characteristics, chitosan is insoluble in aqueous solution but in protonated amine form it is soluble at $\text{pH} < 6.5$. 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 polyanions. 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. However, attempts to exploit chitosan as a coating material are limited. Perhaps the most significant instance demonstrated so far is the work of Sugama [3, 4], who reported that aluminum substrate, dip-coated in a chitosan solution withstood 700 hours of salt spray exposure.

We have based our work with inhibitor-modified chitosan on structure-property relations on the general understanding of the function of chromate conversion coatings. Chromate conversion coatings form a strongly adherent protective $\text{Cr}(\text{OH})_3$ film on the metal substrate through a sol-gel process. Adsorbed onto that gel is a releasable chromate inhibitor. Therefore, alternative coatings modeled after chromate conversion coatings should have:

- a. A strongly adherent film former, to form a barrier type surface film.
- b. A releasable inhibitor, to provide anodic and/or cathodic protection and self-healing capacity.

Any protective coating system should have good adhesive strength with metal substrate and barrier properties that are consistent with needed protective properties and mode of corrosion protection. Poor adhesion has been a potential weakness of as-cast chitosan coatings in our studies until now. Additionally, previous studies [3-5] have indicated that chitosan coatings are hydrophilic and take up water and electrolyte readily. This behavior can result in poor coating protection. In the literature, some treatments and additives have been specifically aimed at improving chitosan coating bond strength (e.g. silane gluteraldehyde modification to improve the bond strength with Ti substrate) [5], and some treatments have been aimed at decreasing the hydrophilicity of chitosan coatings (e.g. dextrine modification) [3]. But no attempts have been made to overcome both these weaknesses simultaneously. Moreover, no attempts have been made to incorporate inhibitors in the coating system. Therefore, in the present study, our aim is to develop a corrosion resistant coating by modification of chitosan structure by simultaneous addition of an inhibitor and an adhesion promoter. Inhibitors are intended to provide anodic/cathodic and self-healing characteristics to these coatings apart from reducing hydrophilicity. Coupling agents should act as adhesion promoters. In the present study, vanadate was used as the inhibiting compound in the coating system. Silanes, known coupling agents that facilitate the bond formation between organic and inorganic compounds, have also been incorporated in our formulations [6, 7]. There are number of available silanes and proper selection is a prerequisite for proper functionality. Due to the

presence of amine functional group on chitosan, epoxy functional silanes appeared as a suitable candidate. Further, silanes used in the present study are stable over a wide range of pH. Based on the above two criteria, (2-(3,4-epoxycyclohexyl)-ethyltrimethoxysilane (ECET) and (3-Glycidoxypropyl)-trimethoxysilane (GPTS) silanes were chosen as coupling agents.

EXPERIMENTAL PROCEDURE

Materials and Preparation of Coatings

Coatings containing chitosan in its pure and modified form were applied to aluminum alloy 2024-T3 (Al 4.4Cu-1.5Mg-0.6Mn) substrates. Before application of coatings, Al 2024-T3 substrates were degreased and deoxidized using standard methods. An initial solution of chitosan was prepared by dissolving 1 g of 85% deacetylated chitosan in 100 ml of DI water and 1 wt% of acetic acid. Some of the coatings were applied using soft brush on degreased and deoxidized Al 2024-T3 panels. Later, different amounts of two different silanes (GPTS and ECET) were added to the chitosan solution and allowed to cross-link for 24 hours. Coatings using these solutions were applied using a soft brush. These coatings were dried in ambient atmosphere for at least 24 hours before testing. In the final treatment, some of the coatings made using previous two methods were treated in 2.38 wt% NaVO₃ solution for 15 seconds. These coatings were also dried in ambient atmosphere for at least 24 hours before further testing.

Effect of processing variables on performance was assessed on coatings made with chitosan-1.5 wt% GPTS at different viscosity. The change in viscosity of chitosan solution was measured using Anton Parr modular compact rheometer. Shear rate ranging from 0.01 sec⁻¹ to 1000 sec⁻¹ was applied between two rotating plates at 25 °C. These coatings were applied using soft brush as before and treated for 15 seconds in 2.38 wt % NaVO₃ solution ranging from pH 3 to 10. These coatings were dried in ambient atmosphere for at least 24 hours before further handling.

EIS testing

Electrochemical impedance spectroscopy (EIS) was carried out on the coated panel using three-electrode configuration. Panels were tested using a Gamry PTC1TM paint test cell, which exposed well-calibrated surface area of 14.6cm². A glass body saturated calomel electrode (SCE) reference electrode and a graphite rod counter electrode were used in all measurements. Impedance spectra were collected over a frequency domain ranging from 10kHz to 10mHz. A sinusoidal voltage modulation of 10mV was used for all measurements. Panels were exposed in 0.5M NaCl solution and impedance spectra were collected up to 48 hours of exposure.

Adhesion Testing

Adhesion testing on these coatings was carried out using Elcometer 110 PATTI (pneumatic adhesion tester) tester. An aluminum pull stub was glued to the test panels using a commercial two-part epoxy Araldite™. The epoxy was cured for 24 hours prior to testing. The tester applies a true axial tensile stress and this value quantitatively measures the bond strength between a coating or adhesive and the test surface.

Salt spray testing

ASTM B117 salt spray corrosion resistance testing was carried out in 5% NaCl solution. A panel was considered to have failed when 5 corrosion spots per 30in.² of exposed area were observed. Test temperature was at 95⁰ F. Coated panels were observed at a regular interval and digital images of the panels were taken.

UV/Visible spectroscopy

Chitosan gels, obtained by mixing 1 wt% chitosan solution with 2.38 wt% NaVO₃ solution, were allowed to dry in ambient air. One-half gram of dried gel was then exposed in 40 ml of deionized water at different pH values. Aliquots of samples were withdrawn periodically and UV/visible spectroscopy was performed at regular intervals. UV/Visible spectroscopy was performed using Lambda EZ201 spectrophotometer on solution using 1 cm quartz cuvettes. These samples were later returned to the original containers.

FTIR Spectroscopy

To understand the mechanism of chitosan gel formation, release of vanadate inhibitor into solution and possible mechanisms of adsorption of inhibitor by chitosan, Fourier transform infrared spectroscopy (FTIR) was performed. Polymeric gels were obtained by mixing 1 wt% chitosan solution with 2.38 wt% NaVO₃ solution at different pH. The resulting gels were allowed to dry in ambient air. FTIR spectroscopy was performed on the dried gels using a Perkin Elmer FTIR 1600 series. Gel samples were mixed with potassium bromide (KBr) in powder form and pressed into discs. The scan resolution was 2.0 cm⁻¹ and 16 scans were made per sample.

RESULTS AND DISCUSSION

Effect of Silane And Vanadate Addition

Impedance spectra of chitosan-silane coatings collected after 1-hour in 0.5 M NaCl are shown in Figure 1. In spectra exhibiting a resistive plateau at the lowest measured frequency, the total impedance of the corroding system at lowest frequency is due mainly to the impedance of coating defects and can be taken as a measure of coating protectiveness. A defect-free coating will give rise to a purely capacitive response at beginning of experiment and generally exhibits a large impedance. With passage of time, latent discontinuities will give rise to ionic conducting pathways through the coating resulting in a loss of capacitive response at low frequencies [8, 9]. The resistivity of these paths will decrease as degradation of coatings increases resulting in further decreases in the low frequency coating impedance[8]. Therefore the rate of decrease of the total impedance at low frequencies can be used as an indicator of coating degradation.

ECET additions to chitosan solutions resulted in a decrease in coating resistance as compared to neat chitosan coatings (5×10^4 ohm-cm²) after 1-hour exposure in 0.5 N NaCl solution (Fig. 1a). On the other hand, GPTS additions resulted in improved total impedance values (3×10^5 ohm-cm²) after a 1-hour exposure in 0.5 M NaCl solution as compared to neat chitosan coatings (Fig. 1b). ECET-modified coatings showed capacitive behavior over a smaller frequency domain (Fig 1a) compared to GPTS-modified coatings (Fig. 1b). This observation is another indicator of better performance of GPTS-modified coatings compared to ECET-modified coatings. Figure 2 shows the EIS spectra of chitosan, chitosan-vanadate and chitosan-GPTS silane-vanadate coating collected after 1-hour exposure in 0.5 M NaCl solution. Clearly, the vanadate modification resulted in an improvement by one order of magnitude in coating resistance. Such large improvements in coating resistance were not possible with silane additions alone. Further improvement in the coating resistance of chitosan-vanadate-modified coating was observed with GPTS additions.

For a more quantitative comparison, equivalent circuit modeling was performed on impedance spectra collected from these coatings during exposure. An equivalent circuit model with single time constant was selected (Figure 3). After fitting, coating resistance and coating capacitance were obtained. Figure 4 shows corrosion resistance values of different coatings studied. These corrosion resistance values were obtained after averaging over 2 to 3 measurements. Most coatings showed considerably better coating resistances than bare Al 2024-T3. The highest corrosion resistance was observed for vanadate-and GPTS-silane-treated coating. None of the coatings approach the coating resistance of a chromate conversion coating.

The adhesive strength of different coatings is shown in Figure 5. The addition of silanes to chitosan coatings generally resulted in an improvement in adhesive strength of these coatings. Increase in amount of ECET silane in coating resulted in decrease in adhesive strength of the coatings. There is a direct correlation between adhesive strength and coating corrosion resistance value with the amount of ECET added to the coatings. Increasing the amount of GPTS resulted in increase in adhesive strength of these coatings. Adhesive strength of chitosan-1% GPTS silane-vanadate coating was comparable to adhesive

strength of that of epoxy coatings. This indicates the effectiveness of silane in increasing the adhesive strength of coatings. However, the performance of these two silanes in coating system is completely different and reasons behind it are under investigation.

- a) is a coupling agent that increases the adhesive strength of these coatings.
- b) increases the corrosion resistance of these coatings.

Effect of Solution pH in Vanadate Post Treatment

Impedance spectra collected after 24- and 164-hour exposures in 0.5 M NaCl are shown in Figure 6 for several chitosan-1.5 wt% GPTS silane coatings post-treated by immersion in a sodium metavanadate solution of different pH (pH values indicated in the figure). The impedance spectrum for the coating prepared using NaVO₃ solution at pH 10 was collected after a 120-hour exposure instead of 164-hours. After 24 hours in 0.5 M NaCl, the coating treated using NaVO₃ solution at pH 10 showed a capacitive response over a larger frequency range and demonstrated a higher total impedance (10^6 ohm-cm²) (Fig. 6a) compared to the coatings made at lower pH (pH < 10). However, for longer exposure times (164 h), impedance spectra of coatings prepared using pH 6 to 8 post-treating vanadate solutions performed better on the basis of higher coating resistances (1×10^6 ohm-cm²) and a larger capacitive regions. Visual observation of panels after immersion in 0.5 M NaCl supports an independent observation that panels prepared with vanadate solutions in the pH 6 to 8 range perform better over the long term in salt spray exposure testing. There was no evidence of pitting in panels post-treated pH 6 and 8 solutions even after 312 hours of exposure. On the other hand, panels post-treated at pH 10 started showing pitting only after 120 hours of exposure. All the exposure test results are generally consistent with the impedance results. Clearly, the pH of the post-treatment solution plays a significant role in the evolution of corrosion resistance of these coatings.

Effect of Crosslinking

Figure 7 shows the EIS spectra of chitosan-1.5 wt% GPTS silane-vanadate coatings obtained after a 2 ± 1 hours exposure in 0.5 M NaCl solution. In this case, coated panels were prepared using chitosan-silane solution at different viscosity while post-treating the coatings using a sodium metavanadate solution at pH 8.67. Corrosion resistance of different coatings was not very different. Coatings prepared using intermediate viscosity (0.96 Pa-s) showed the highest coating resistance (4×10^6 ohm-cm²). Increasing or decreasing the solution viscosity from this value resulted in a slight decrease of the coating resistance.

Adhesive strength of these coatings prepared from chitosan solutions of different viscosity is shown in Figure 8. An increase in adhesive strength of coatings was observed with increase in viscosity of chitosan-silane solution. Adhesive strength of coating was highest at higher viscosity (0.96 Pa-s) and remained almost constant with further increases in viscosity (7 Pa-s). From the present discussion, it is clear that viscosity of the solution plays a major role in electrochemical and adhesive behavior of these coatings. Among the

coatings tested, the best solution viscosity for coating application appears to be around 0.95 Pa-s. Clearly, the interaction of chitosan, silane and vanadate and their interaction with aluminum substrate need to be understood mechanistically.

Salt Spray Exposure Testing

Three sets of test panels were made for salt spray exposure testing. Panels were prepared as described previously. Conditions of the coating preparation are given in the Table 1. The neat chitosan coated sample failed only after 48 hours of exposure in salt spray, while vanadate-modified samples withstood around 200 hours of exposure. Silane- and vanadate-modified chitosan coated panels demonstrated better salt spray performance than the vanadate-modified chitosan coated panels. Salt spray performance of these coatings has been tabulated and shown in Table 1. Further improvement in the salt spray performance of coated panels was observed with increased viscosity and by post-coating aging at 50°C. Which step in the coating process is controlling performance in salt spray exposure--increased viscosity or ageing at higher temperature or both, is not properly established at this stage. The best salt spray performance was always observed when chitosan-silane coatings were modified using NaVO₃ solution in the pH 6 to 8 range.

Table 1: Salt spray performance of different coatings

Coating Type	Time (Hrs)
Chitosan	48
Chitosan-vanadate	200
Chitosan-1.5 wt% GPTS silane-vanadate Viscosity= Not measured	
pH=6.0	72
pH=6.67	225
pH=8.0	72
Chitosan-1.5 wt%GPTS silane- vanadate Viscosity=1.5 pa-s Aged for 24 hour at 50 °C	
pH=6.0	450
pH=6.67	400
pH=8.0	400

UV/Visible Spectroscopy

Calibration curve determination. Vanadium, being a transition metal that forms complexes in aqueous solution, will absorb light in the UV (ultra violet)/Visible region of the electromagnetic spectrum [10]. This enables the qualitative and quantitative study of vanadate species using UV/Visible spectroscopy. The optical absorbance vs. concentration spectrum of vanadate solutions is complicated due to the presence of ortho- (VO_4^{3-}), meta- (VO_3^-) or pyrovanadate ($\text{V}_2\text{O}_7^{4-}$) species. These species form complexes of higher order by reacting further among themselves. Appropriate speciation diagrams show the presence or absence of different species in solution over a range of pH and concentration [11]. These diagrams show the dominant species present in the solution at a particular pH and concentration. For the present work, combined concentration of all these species present in the solution at a particular pH is indicated as “vanadate concentration”.

To determine vanadate concentration in solution by UV/Visible spectroscopy, a calibration curve was prepared. For calibration curves, solutions of sodium metavanadate at different concentrations ranging from 2.3×10^{-4} to 0.2×10^{-4} M were prepared and adjusted to different pH values by NaOH and HNO_3 . In case of vanadate solutions with pH values greater than 3, absorption spectra are pH-independent as shown in Figure 9(a). All these spectra are unique and show a shoulder in the 260-270 nm wavelength range. Figure 9b shows different UV/Visible spectra of vanadate solutions at different concentrations maintained at pH 10. Since all these spectra are pH-independent, absorbance at any particular wavelength can be used to make a calibration curve. A calibration curve was made for pH greater than 3 by selecting the absorbance value at 265 nm. UV/Visible spectrum at pH 3 was found to be different from other spectra collected from solutions at higher pH. This spectrum still shows the shoulder in wavelength range 260 - 270 nm but absorbance values are lower. This necessitates the formation of a separate calibration curve for pH 3. UV/Visible spectrum at different concentrations of vanadate at pH 3 is shown in Figure 9c. These spectra also follow a Beer's law relation and calibration curve was made using absorbance value at wavelength 265 nm. These two-calibration curves are shown in Figure 9d. Using these calibration curves, and by knowing the absorption value at wavelength of 265 nm, the concentration of vanadate in solution was determined.

The molar absorptivity in terms of total vanadate concentration was $1.59 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ at 265 nm for pH greater than 3 and $0.792 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ for pH 3.

Release and readsorption of vanadate. One-half gram of dried gel was exposed in 40 ml of deionized water at different pH values. Aliquots of samples were withdrawn periodically and UV/visible spectroscopy was performed at regular intervals. These samples were later returned to the original containers. From the absorbance values at 265 nm, vanadate concentration in solution was determined using the calibration curves made previously. Vanadate concentrations in solution increased with time. Solutions contained different vanadate species depending on concentration and pH, which had not been identified, and was not an aim of the present study. Increase in vanadate concentration indicated the release of vanadate inhibitor by the chitosan gel. All release curves shown in Figure 10 eventually reached at a constant vanadate concentration value after several days. Release kinetics of vanadate was pH dependent and increased with increasing pH. The total amount of vanadate released was highest at highest pH values. The greatest release of vanadate was

observed at solution pH 10, and lowest (negligible) release was observed in case of solution pH 3.

After vanadate concentrations in solution reached constant values, solution pH was readjusted to pH 3. After pH readjustment, the vanadate concentration in solution was again measured as a function of time. In this case, a time-dependant decrease in vanadate concentration was observed as shown in Figure 11 indicating that vanadate was re-adsorbed back on the chitosan polymer gel.

Release and readsorption of Cr (VI) in chromate conversion coatings are also pH driven and imparts self-healing characteristics to these coatings. The mechanism of release and readsorption of Cr (VI) is well established and documented[12]. Release and readsorption of inhibitors may provide self-healing characteristics to these coatings.

Fourier Transform infrared spectroscopy

Figure 12 shows the FTIR spectrum of chitosan, chitosan gel obtained using sodium metavanadate solution at pH 6, and sodium metavanadate. The chitosan spectrum shows a band at 1640 cm^{-1} , which corresponds to the overlap of an amide I band due to the residual acetylated residues and -OH bands corresponding to the pyranose structure[13]. There are many other small bands in the range of 1600 to 1300 cm^{-1} . A second band near 1575 cm^{-1} corresponds to free amine form of glucosamine residues [3, 4, 13]. A few smaller bands corresponding to the amide II band were detected near 1560 - 1520 cm^{-1} . In the case of the FTIR spectrum of the chitosan gel, two bands at 1620 cm^{-1} and 1511 cm^{-1} were observed. These bands are attributed to -NH^{3+} deformation. Simultaneously, the band corresponding to amine functional group disappeared. The presence of such a band can be explained by assuming adsorption of vanadate on protonated -NH_2 functional group of chitosan. There are some other important bands identified in the FTIR spectra of chitosan gel. Bands at 1154 , 1072 and 1026 cm^{-1} correspond to the stretching vibration of C-O-C linkages in the glucosamine rings. Similarly, the band at 947 cm^{-1} is attributed to VO_2 symmetrical stretch. The FTIR spectrum of sodium metavanadate shows a band at 950 cm^{-1} , which corresponds to a VO_2 symmetrical stretch reported by Onodera et al.[14]. There is no band at 950 cm^{-1} in neat chitosan spectrum. This spectroscopic evidence supports the notion of vanadate adsorption on the chitosan polymer backbone. Furthermore, it can be concluded that amine functional group in its protonated form is the receptor site for vanadate on chitosan.

According to Beer's law, absorbance is directly proportional to concentration of the absorbing species. Since the peak corresponding to the VO_2 symmetrical vibration and that corresponding to C-O-C stretching vibration of glucosamine ring are well established, the ratio of their absorbance values can be used to qualitatively determine the change in amount of vanadate on chitosan backbone with change in pH of sodium metavanadate solution used to introduce vanadates into the coating. FTIR spectroscopy was carried out on the gels formed using sodium metavanadate solution at different pH. From their FTIR spectra, ratio of absorbance at 952 cm^{-1} , which corresponds to VO_2 symmetrical stretch and that at 1072 cm^{-1} , which corresponds to C-O-C linkage in glucosamine ring has been calculated. Figure 13 shows this absorbance ratio for different chitosan gels formed with NaVO_3 solution of varying pH. This ratio is taken as a measure of the vanadate adsorption

capacity of chitosan. From the figure, vanadate adsorption capacity of chitosan decreases with increase in solution pH. Chitosan adsorbs maximum amount of vanadate in solution pH range 3 to 5.

Although the FTIR results shown in Figure 13 are qualitative in nature, they are very helpful in understanding important trends observed in the behavior of vanadate-modified chitosan. Speciation diagram of chitosan shows below pH 4.5, the amine functional group on chitosan is fully protonated but with continuous increase in pH it starts deprotonating [11]. Above pH 8.5, amine functional groups on chitosan are fully deprotonated. On the other hand, the vanadate speciation diagram shows the presence of various anions depending on its pH and concentration. From FTIR spectroscopy, it has been concluded that amine functional group in its protonated form is responsible for vanadate adsorption. With continuous increase in solution pH, the deprotonated amine group loses its ability to adsorb vanadate anions. Therefore, the maximum adsorption capacity of vanadate occurs at lower pH where the amine functional group on chitosan is protonated (NH_3^+).

Results from UV/Visible spectroscopy are also consistent with the speciation diagrams. Gel in high pH solutions demonstrated fast vanadate release kinetics. Additionally, the total amount of vanadate released in the solution was greater at higher pH. There was almost no release of vanadate at a solution of pH 3 because of the stability of the bond between vanadate and the protonated amine site. From the speciation diagram of chitosan, it is possible to estimate the fraction of amine functional groups that can be deprotonated. This value determines the amount of vanadate that can be adsorbed by chitosan and the amount that can be released into solution. Certainly, this value is pH-dependent and is highest at high pH.

UV/Visible spectroscopy also demonstrates the stability of chitosan matrix after long exposure times. Once the solution pH is readjusted to pH 3, chitosan re-adsorbs vanadate. At lower pH, protonation of amine functional group on chitosan is possible leading to re-adsorption of vanadate. After re-adsorption, amount of vanadate in solution is similar to that of the amount of vanadate released at pH 3. This indicates reversibility in the absorption of vanadate by chitosan gels.

SUMMARY

- A novel environmentally friendly corrosion resistant coating has been developed based on the following components:
 - chitosan - biopolymer network
 - (3-Glycidoxypropyl)-trimethoxysilane - adhesion promoter
 - vanadate - releasable corrosion inhibitor
- Additions of (3-Glycidoxypropyl)-trimethoxysilane silane to chitosan coating formulations increases in adhesive strength.
- Vanadate inhibitors can be stored and released by chitosan coatings leading to self-healing type corrosion resistance.
- Adsorption and desorption of vanadate onto chitosan is reversible.
- In terms of overall corrosion protection, vanadate inhibited chitosan coatings compare to conversion coatings rather than to primers.

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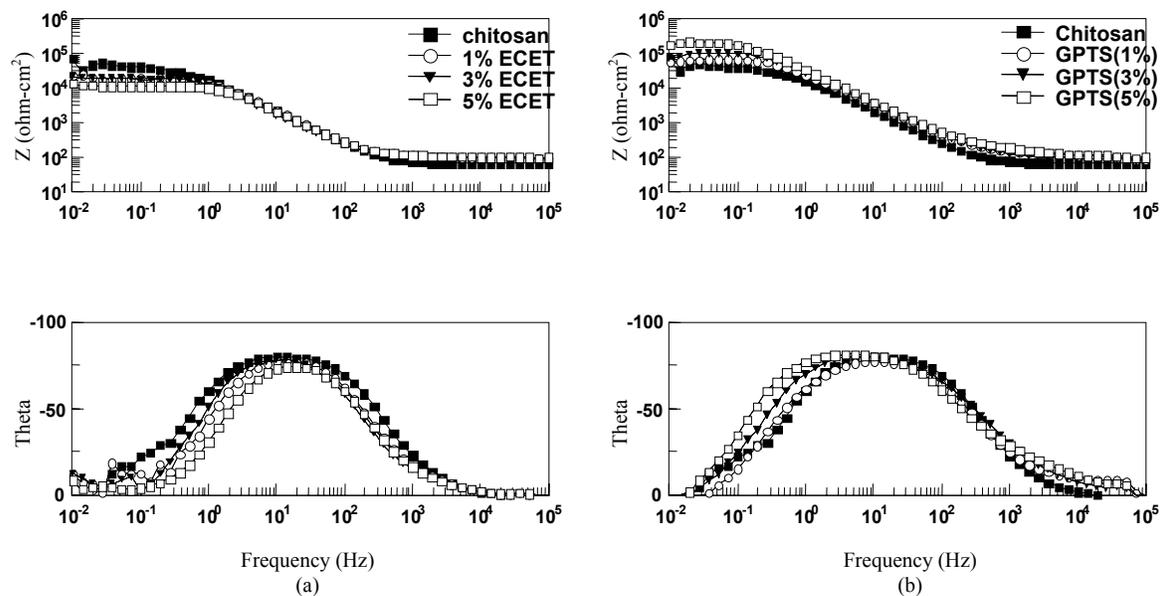


Figure 1(a): Effect of ECET silane addition on impedance spectra of chitosan coatings. 1(b) Effect of GPTS silane addition on impedance spectra of chitosan coating.

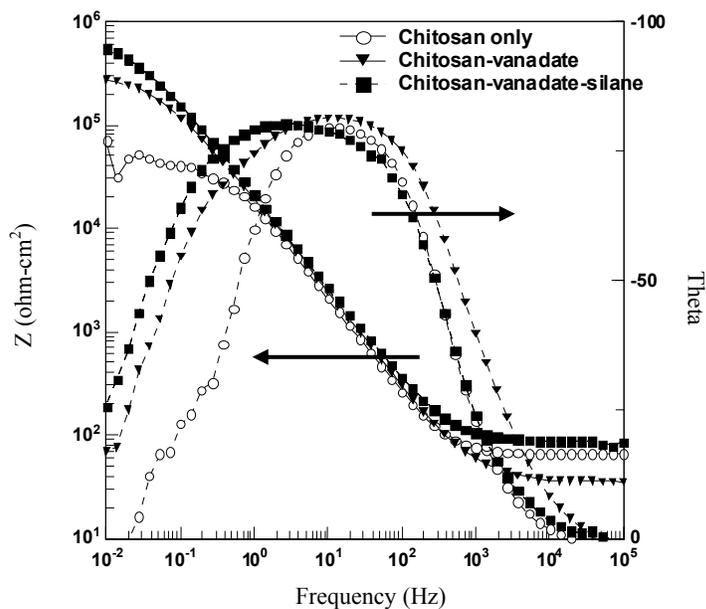


Figure 2: Effect of vanadate and GPTS silane-vanadate addition on impedance spectra of chitosan coatings.

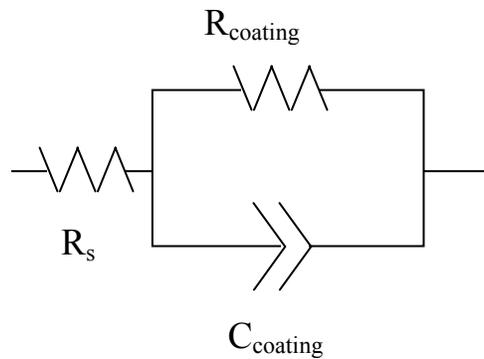


Figure 3: Equivalent circuit used for fitting EIS data.

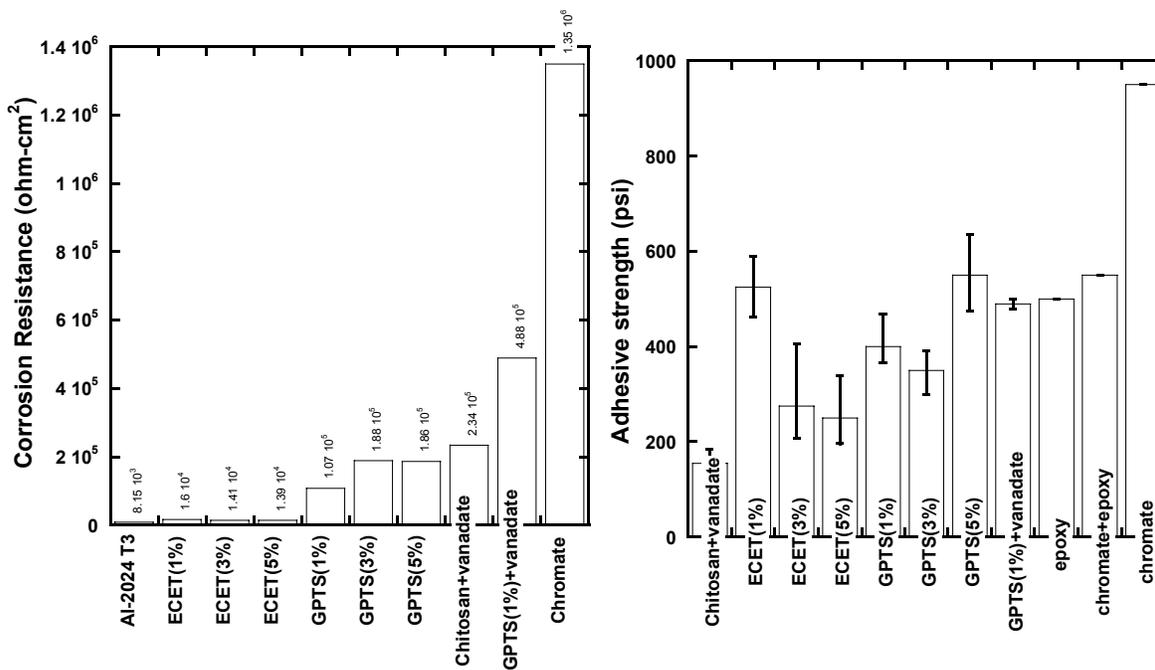


Figure 4: Corrosion Resistance values of different coatings. Figure 5: Adhesive strength of different coatings

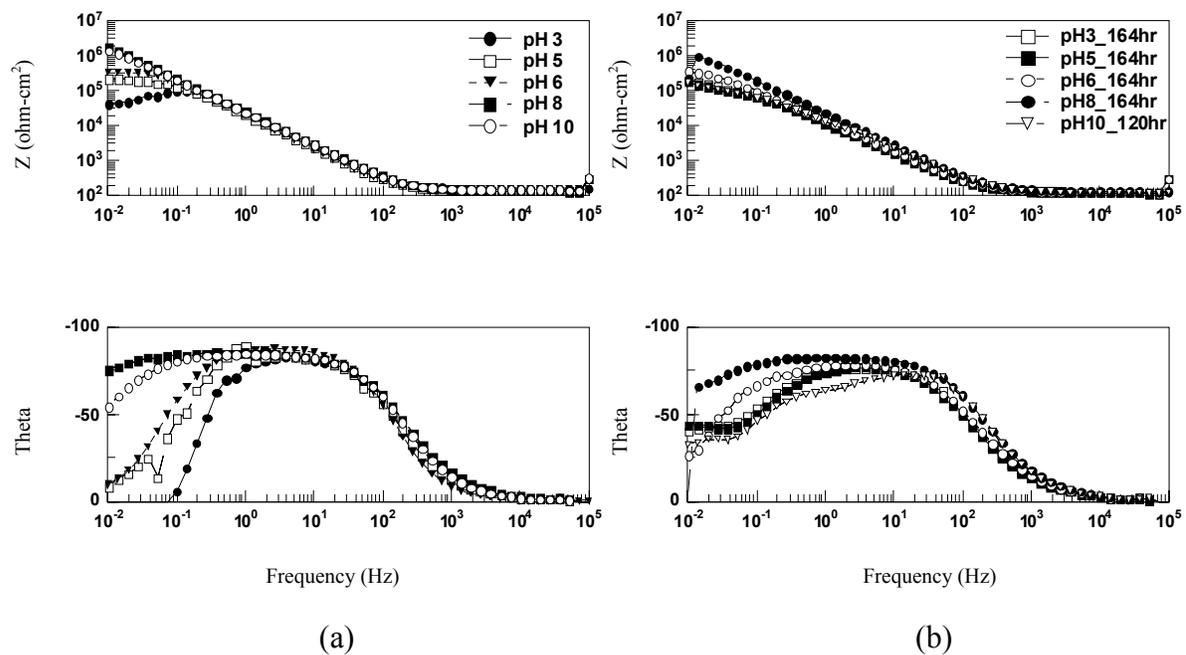


Figure 6: (a) EIS spectra of chitosan-vanadate-GPTS silane coatings after 24 hour exposure in 0.5 M NaCl solution. Chitosan-silane coatings were treated using sodium metavanadate solution at different pH. (b) EIS spectra of the same coatings after 164 hours of exposure in 0.5 M NaCl solution. Note: coatings made using a sodium metavanadate at solution at pH 10 were exposed for only 120 hours.

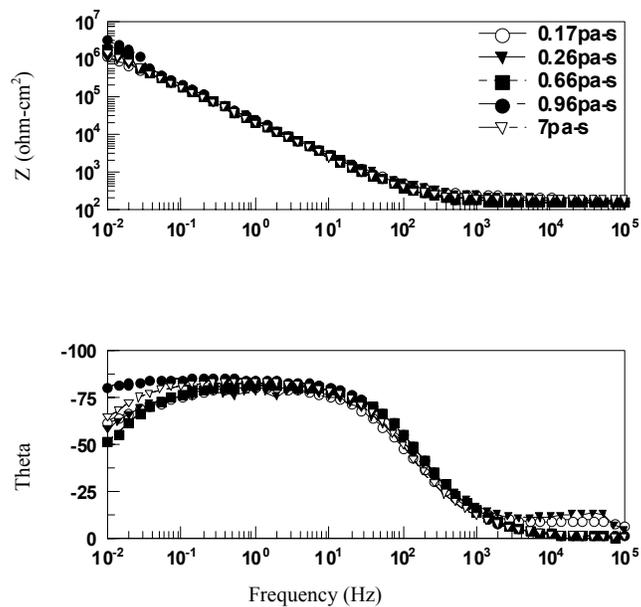


Figure 7: EIS spectra of chitosan-silane-vanadate coatings. These coatings were made using chitosan-silane solution at different viscosity.

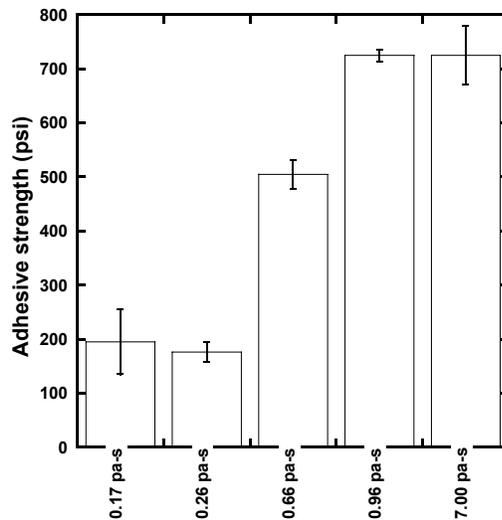


Figure 8: Adhesive strength of chitosan-silane-vanadate coatings. Different coatings were prepared using chitosan-silane solution at different viscosity.

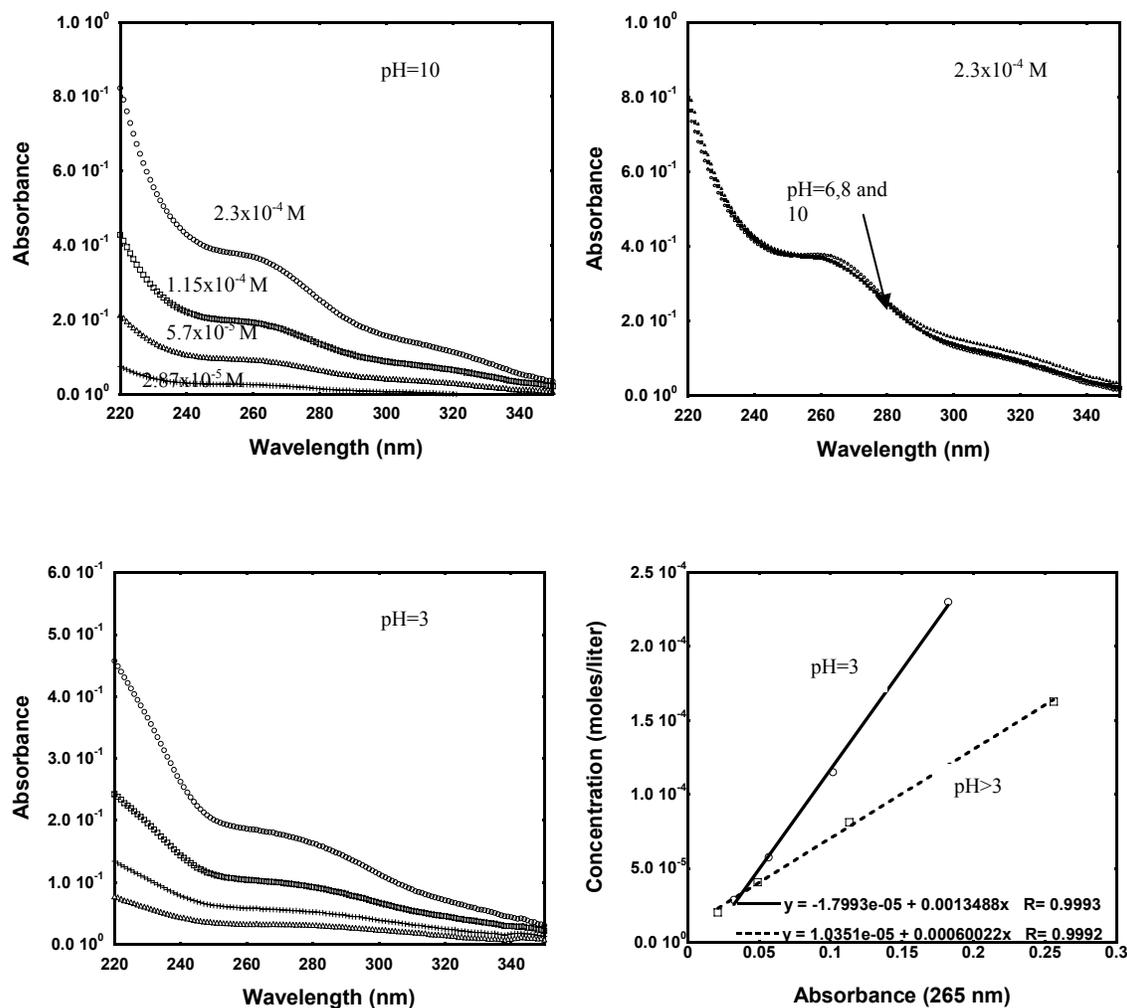


Figure 9: (a) UV/Visible spectra of vanadate at pH 10 for different concentrations. (b) UV/Visible spectra of vanadate at fixed concentration but at different pH. (c) UV/Visible spectra of vanadate at pH 3 for different concentrations. (d) Two different calibration curves, one for vanadate solution pH greater than 3 and another for solution pH 3.

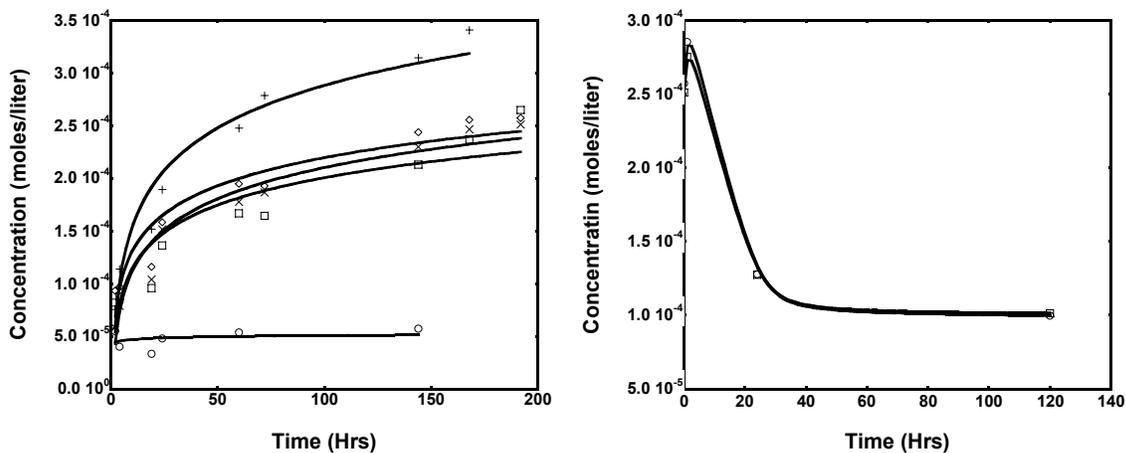


Figure 10: Release of vanadate by chitosan-vanadate gel with time. Figure 11: Readsorption of vanadate by chitosan gel with time.

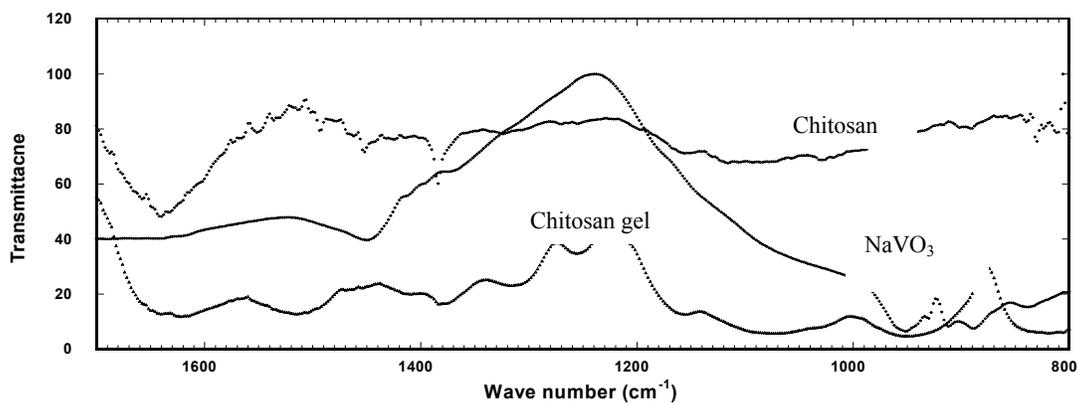


Figure 12: FTIR spectra of chitosan, chitosan gel (chitosan-vanadate) and reagent grade NaVO_3

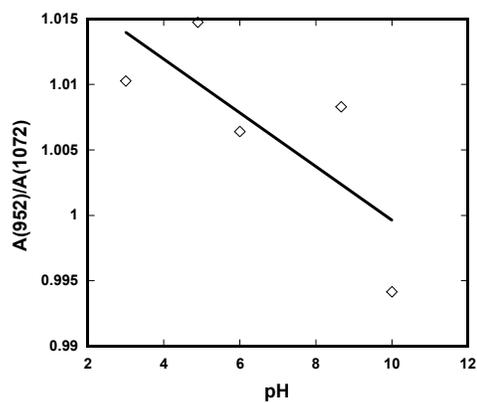


Figure 13: Ratio of absorbance at 952 cm^{-1} , which corresponds to VO_2 symmetrical vibration and 1072 cm^{-1} , which corresponds to C-O-C stretching vibration of glucosamine linkage, for chitosan gel prepared using sodium metavanadate solution at different pH.