CORROSION INHIBITION OF PEKTIN C ON ST-34 IN HYDROCHLORIC ACID

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ABSTRACT:
Construction materials in the form of any products are subject to unintentional or harmful changes, occurrences and processes that reduce their usability. The destruction of construction materials is aimed to be slowed down or prevented by measures and procedures of a special technological discipline - material protection, which is usually called surface protection, since harmful occurrences and processes mostly begin on the surface of the product. In addition to the many protective methods that are used, corrosion inhibitors have a special place due to their specificity and widespread use. Based on the performed tests and their analysis, it was determined that the inhibition efficiency obtained by electrochemical measurements is in good correlation with the results obtained by the FTIR method. Impedance measurements of steel St 37-4 Pectin C in the tested media show corrosion resistance. Pectin C in 3.5% HCl at a concentration of 2.0 g / l increases the value of the charge transfer resistance and the increases of the size of the absolute impedance in the Bode diagram, which further confirms the improved resistance to corrosion of steel.

KEYWORDS: Corrosion, Pectin C, EIS, FTIR

INTRODUCTION

Corrosion is a natural process that shortens the life of structures, causes losses in production, endangers human health and affects environmental disasters. In order to reduce, various protective measures are applied. Due to the prevalence and specificity of application, corrosion inhibitors have a special place. With the development of techniques and technology, environmentally friendly inhibitors are gaining importance.

Table 1. Development of corrosion inhibitors and main parameters of their choice [2]

Time period	Required property	Type of the inhibitor
Before 1960	Efficacy	Chromates, phosphates, nitrates, borates, silicates, zinc inhibitors
1960-1980	Economy	Polyphosphates, gluconates, molybdates, vitamins
Since 1980	Ecological acceptability	Tannins, natural polymers, vitamins

Adding inhibitors to aggressive environments in small concentrations, it can greatly reduce the corrosion rate. The use of inhibitors has established itself today and has wide application. When choosing the type of inhibitor bear in mind the metal to be protected, the environment in which the metal is located, the conditions, toxicity and economy of the inhibitor [1]. Table 1. provides an overview of the development of inhibitors that have been used and which inhibitors should be used, and the main parameters of their selection:

Research by Mohammad M. Faresa et all has proven that the use of a promising green eco-friendly pectin is a natural polymer on the surface of an aluminum metal in an acidic medium. The highest inhibitory efficacy obtained at 10 ° C using pectin at a concentration = 8.0 g / L was 91%, while at 40 ° C it dropped markedly to 31%. As the pectin concentration increased, higher activation energy, enthalpy of activation, and entropy of activation were obtained. In the presence of 2.0 M HCl, the aluminum sheet showed longitudinal parallel grooves along with a huge amount of irregular deep voids distributed along the sheet, while in the presence of inhibitors and acid medium the number of deep voids decreased [3].

Adsorbed inhibitors in acidic solution act by stopping the cathodic hydrogen excretion reaction or the anodic dissolution of the metal or even both reactions. This effect occurs as a consequence of the influence on the electrical bilayer, reduction of metal reactivity, partial precipitation of inhibitors and formation of a physical barrier. The decrease in the reactivity of the metal occurs as a result of the adsorption of the inhibitor on the active sites of the electrode, and not on the entire surface, reducing the area of the cathodic or anodic reaction or both.[6]

EXPERIMENTAL

The material used for the test is St 37-4, and the chemical composition is shown in Table 2.

The condition for conducting and the accuracy of the analysis depends on the surface preparation of the tested steels. The preparation of steel was performed by mechanical and chemical processes.

To perform the experimental part, in addition to the mentioned steel, the eco inhibitor Pectin C in an acidic medium of 3.5% HCl was used.

Table 2. Chemical composition St 37–4

Sample	Fe	C	Si	Mn	P max	S max	Cr	Ni
St 37-4	99,39 – 99,63%	≤0,17	≤0,04	≥0,35	0,04	0,04	-	-

Pectin is a polysaccharide, made up of galactouronic acid units. Pectins differ from each other in the length of the polymer chain, complexity, as well as the structure of the monosaccharide unit. One third of the dry cell wall is represented by pectins, and the highest concentrations of pectin are found in the middle lamella of the cell wall with a gradual decrease through the primary wall, towards the plasma membrane. Most commercial pectins are obtained from lemon peel or soup pomace. Apple puree contains 10-15% dry matter-based pectin, and citrus korar 20-30%. [4]

According to the chemical structure shown in Figure 1, pectin has a large amount of associated D-galctrouronic acid residues. D-galactouronic acid is a cyclic monosaccharide with one carboxylic acid on the side and four hydroclic groups. A small proportion of the carboxyl groups in the D-galactouron residues are esterified and on the side arcs the residue can deprotonate and form anions.

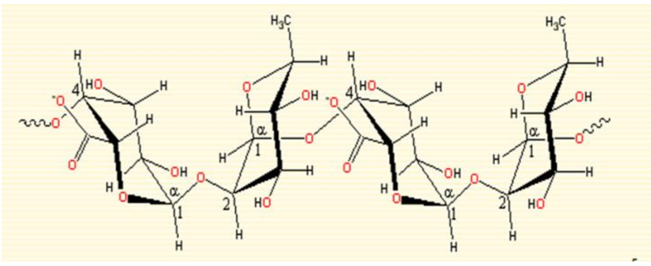

Figure 1. Chemical structure of Pectin C

Electrochemical methods were used to determine the corrosion behavior of St37-4 steel in 3.5% HCl without and in the presence of inhibitors. Electrochemical measurements were performed on Potentiostat / Galvanostat Model 263A in a corrosion cell (Figure 24) model K47 with a saturated calomel electrode as a reference electrode, graphite electrodes as counter-electrodes and steel (DIN 2391 St 37.4 and X5 CrNi 18-10) as the working electrode. [2]; [8]

Alternating current methods are non-destructive methods, because there is no disturbance of the system, so the methods of electrochemical impedance spectroscopy (EIS) are preferred when testing at the phase boundary. The method is based on the response of a circuit to alternating voltage or current as a function of frequency.

In addition to the electrochemical method, the FT-IR spectroscopic technique (Fourier Transform Infrared Spectroscopy Technique) was used. FTIR spectrum of Mimosa tannin and Pectin C was measured on Nicolet iS10 FTIR Spectrophotometer-Thermo Fisher Scientific.

RESULTS AND DISCUSSION

The aim of the measurement is to determine the mechanism of dissolution of St 37.4 steel in 3.5% HCl without and in the presence of tested inhibitors. The pictures show Bode's diagrams (Figure 2 – 3). The points on the diagrams represent the experimentally obtained test results while the lines represent the simulated curves corresponding to the constructed models of the electrical circuit shown in the figure.

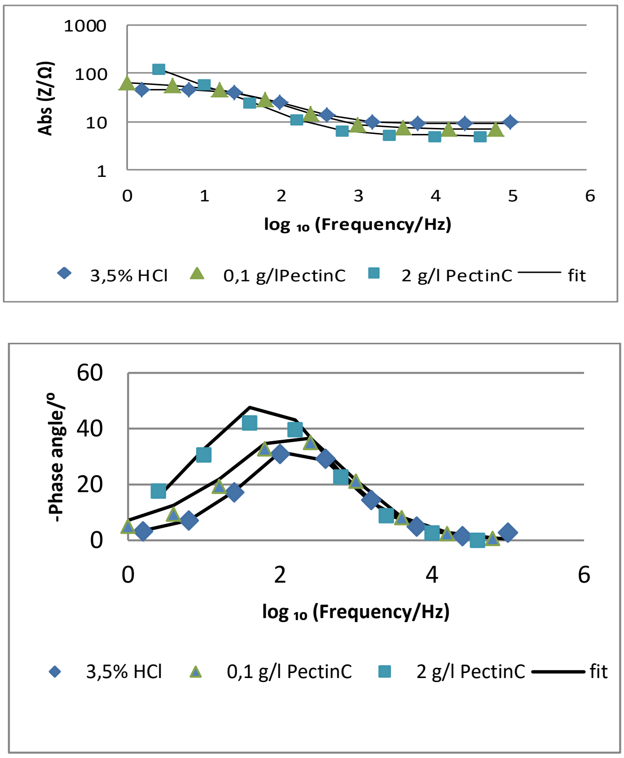

Figure 2. Bode curves St 37.4 steel in 3.5% HCl with and without PectinC inhibitor

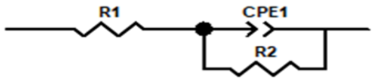

Figure 3. Equivalent electrical circuit for modeling experimental impedance measurement results

The resistance and capacitance values shown in Table 3. obtained by adjusting the experimental results and the equivalent circuit parameters show that PectinC caused an increase in the R2 value, which is also noticeable with the increase in the magnitude of the absolute impedance in the Bode diagram, ie. PectinC improves the corrosion resistance of steel St 37-4.

Table 3. Electrochemical impedance parameters of corrosion St 37.4 steel in 3.5% HCl with and without the presence of Pectin C inhibitors

	R_1 (Ω)	CPE			R_2 (Ω)
		Q	n	C (μF)	
without inhibitor	8,645	0,0002136	0,8096	64,67	38,64
0,1 g/l	6,856	0,00032234	0,77275	102,0	52,73
2 g/l	5,055	0,00041232	0,81371	191,1	79,84

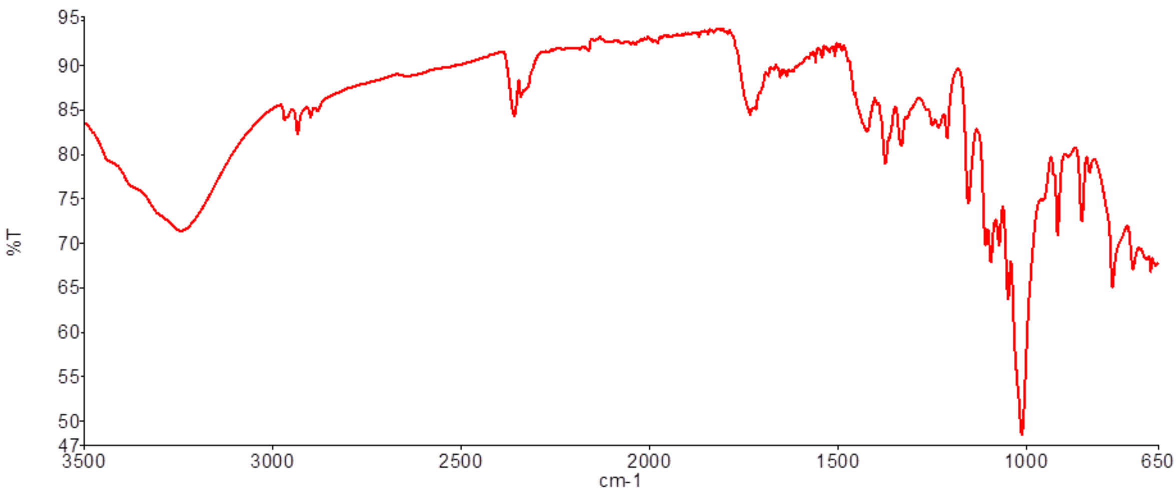

Figure 4. FTIR spectrum of pectin C

The presence of carboxyl and hydroxyl groups in the pectin molecule, as well as the glycosidic bonds, makes the FTIR spectrum of pectin relatively complex, especially in the region below 1500 cm-1. The stretching vibration of the O – H bond was recorded at 3244 cm – 1 as a broad band of medium intensity. Several bands of low intensity in the range of 2970-2900 cm-1 correspond to the vibrations of the C-H bonds. The band of lower intensity at about 1733 cm-1 corresponds to the stretching vibration C = O and indicates the presence of an acetyl group in the pectin. The band of strong intensity at 1011 cm-1 corresponds to C-O-C symmetrical vibrations.

Table 4. presents the results of the analysis of adsorption bonds and intensities of functional groups of commercial Pectin from apples.

Table 4. Overview of adsorption bonds and intensities of functional groups of commercial Pectin from apples determined by FTIR technique [10]

Adsorption binding	Functional groups	Intensity
3438,0	O-H stretching	Strong bond
2923,9	C-H stretching symmetrically, asymmetrically	Sharp
1750,3	C=O esterified	Strong
1636,1	COO^- asymmetric stretching	Strong
1446,4	COO^- asymmetric stretching	Weak
1381,7	C-H bending	Weak
1300-1000	C-O elongation	Weak

CONCLUSION

The concentration range used for the assay was 0.1 to 2 g / l of eco inhibitor. Inhibitors have been found to reduce the rate of corrosion. Impedance measurements of steel St 37-4 Pectin C in the tested media show corrosion resistance. Pectin C in 3.5% HCl at a concentration of 2.0 g / l increases the value of the charge transfer resistance and increases the size of the absolute impedance in the Bodeo diagram, which further confirms the improved resistance to corrosion of steel.

FTIR results of PectinC indicate the presence of functional groups -OH and -COOH which contain oxygen atoms with solitary pairs that act as adsorption centers in order to reduce corrosion, ie. represent places where the formation of chelates is possible.

REFERENCES

[1] A. D. Merzer, Corrosion Inhibitors: Principles and Practice, (Shreir, L. L. Ed), Butterworth, London, 1976.

[2] Ema Stupnišek-Lisac, Korozija i zaštita konstrukcionih materijala, Zagreb 2007, str.133

[3] Mohammad M.fares, A.K. Maayta, Mohammad M.Al-Qudah, Pectin as a promising green corrosion inhibitor of aluminium in hydrochloric acid solution, C.Science 60 (2012) 112-117

[4] May CD (1990) Industial pectins: Sources, Prodaction and application Carbohyd Polym12: 79 - 99

[5] G. Jelić Mrčelić, Korozija i zaštita materijala okoliša, Digitalni udžbenik, Pomorski fakultet, Split, 2012.

[6] INTECH – Corrosion inhibitors – Principles, Mechanisms and Applications, Chapter 16

[7] N.Saidi, H. Elmsellem, M.Ramdani, A.Chetouani, K.Azzaoui, F.Yousfi, A.Aouniti and B.Hammouti. Using pectin extract as ecofrendly inhibitor for steel corrosion in 1M HCl media

[8] Southampon Electrochemistry Group, Instrumental Methods in Electrochemistry, Ellis Horwood London, 1990

[9] Pornsak Sriamornsak, Chemistry of Pectin and Its pharmateuticals Uses: A Review

[10] Saviour A. Umoren, Ime B.Obot, A. Madhankumar, Zuhair M. Gasem, Performance evaluation of pectin as ecofrendly corrosion inhibitor for X60 pipeline steel in acid medium: Experimental and theoretical approaches, Elsevier, Carbohydrate Polymers 124 (2015) 280-291

[11] M. Victoria Fiori-Bimbi, Patricia E. Aalvarez, Hugo Vaca, Claudio A. Gervasi, Corrosion Inhibition od mild steel in HCL solution by pectin, Manuscript

[12] Andrzej Lasia, Electrochemical Impedance Spectroscopy and its Applications, Modern Aspects of Electrochemistry, B. E. Conway, J. Bockris, and R.E. White, Edts., Kluwer Academic/Plenum Publishers, New York, 1999, Vol. 32, p. 143-248.

[13] E. McCafferty, Introduction to Corrosion Science, Springer New York Dordrecht Heidelberg London

[14] Mark E. Orazem, Bernard Tribollet , Electrochemical Impedance Spectroscopy, Published by John Wiley & Sons, Inc., Hoboken, New Jersey.