Journal of Engineering and Applied Sciences 13 (22): 9715-9719, 2018
ISSN: 1816-949X

Anti-Corrosion Study of Polymer Nanocomposite Derived from Acrylonitrile with Manganese and Nickel Chloride

Rawaa Abbas, Nada M. Abbass and Mazin A. Abbas
Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq

Abstract: The goal of the research is to improve the corrosion resistance by using coating polymer nanocompsite which prepare from acrylonitrile and manganese chloride and nickel chloride on carbon steel (45) alloy in saline water (3.5% Nacl) at different temperature (293, 303, 313, 323) K. The inhibition efficiency (PE) reaches 89% at 303 K. Several examinations have been conducted for nanocomposite such as (FT-IR) Fourier Transformation Infrared spectroscopy, (XRD) X-rays Diffractions and (AFM) Atomic Forces Microscopy. The outcomes of X-rays and AFM revealed that the nano composite was hybrids of the metal oxides nanoparticle and the polymer that had been uniformly dispersed in general. Spectra of oxide of FTIR appear in the ranges 400-600 cm^{-1} that reveals the formations of single phases spinal structures that have tetrahedral, octahedral site and two sub lattices. One of the peaks appearing in the ranges of 1100-1130 cm^{-1} are because of C-O stretching by an hydride groups in the metal oxide, emphasize the acrylonitrile constituted as a polymer with spinal oxides.

Key words: Polymer composites, acrylonitrile, manganese and nickel chloride, corrosion, XRD, AFM

INTRODUCTION

Nano structures materials (1-100 nm) have been recognized for their special physical and mechanical features because of their highly fine grains sizes and high grains boundaries volumes fractions (Hameed *et al*., 2013; Sophia *et al*., 2012). Important progresses have been accomplished in different forms of syntheses of nanoscales material. Concentrations are changing now from syntheses to manufactures of substantial structure and coating possessing bigger corrosion and wear resistances. Nanocomposites show such advantage when improvements of environmental impacts are added. Lately, nano technologies have played substantial roles in aiding technological innovative improvements for managing the corrosions of steels (Khaled *et al*., 2007). The polymer metal nanocomposites were synthesized by polymerizing acrylonitrile and manganese and nickel chlorides. Polymer nano composite were utilized as coatings, paint and adhesive because of their outstanding performances of filmformation and good cohesiveness (Coan *et al*., 2013), good weather abilities, excellent dimensional stabilities and high strengths (Yeh *et al*., 2002). Nano technologie's uses in the corrosions protections of metals have lately added momentums (Nalwa, 2000). Polymers nanocomposites coatings could join the benefit of the organic polymers, like water resistances and elasticity to that of developed inorganic compound such as penetrability and hardness. As well as, environmental effect can utilize nano structure practically corrosion inhibition, coating and eliminating the accessories of toxic solvents (Rout *et al*., 2003). In this study in order to improve the corrosion inhibitions of carbon steels magnetite nano structure composites thin film was utilized as corrosions inhibitor. The corrosions resistances of coated carbon steel were tested in the water of the sea (3.5%) media by polarizations measurements.

MATERIALS AND METHODS

Corrosion measurement was conducted in three electrodes potentiostatic system of Bank Elek. Model MLab 200. Platinum rode as silver/silver chloride, counter electrode as reference electrode and the working electrodes were made of circular pieces (2.5 cm*0.2 mm) of carbon steel (45) alloys these electrodeswere polished with SiC emery papers in varied size (600, 800, 1200 and 2000), then the polished samples degreased in ethanol washed with water and finally dried in stream of N_2 gas then introduced into the measuring cell.

Standard solution preparation: Acrylonitrile watery solutions (acrylonitrile: water: 3:1) and 5% ammonium persulphate solutions have been arranged for experiments. The standards solutions were arranged by melting stoichiometric amount of the metals salt in refined

Corresponding Author: Rawaa Abbas, Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq

water. Sodium hydroxides solutions were regulated against solutions of oxalic acids as primary standards solutions and they were titrated as dibasic acids. About 25 mL of oxalic acids and 8 drips of phenolphthalein drop were titrated with NaOH solutions, more often, neutralization of acids, more stable pink colors were showed, stirred often additions of the final drops of NaOH.

Complexes syntheses: The complex was made according to the methods detailed by Singh *et al.* (2012). Figure 1 shows the preparations of the polymer nano composite.

Solution of ferric chlorides (10 mL, 0.1 N) have been added to 10 mL of solutions of acrylonitrile (acrylonitrile: water: 7:3) with moving. At 70-90°C, 5% $(NH_4)_2S_2O_8$ 5 mL poured to the mentioned solutions for 2 h. The solutions

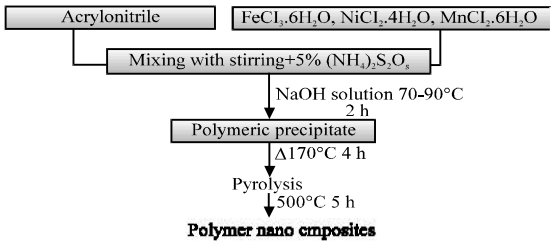

Fig. 1: Polymer nano composite preparation rote

are dried to produce the poly acrylonitrile that was dehydrated at 90-100°C over nights and was heated at 170°C about 4 h to obtain the amorphous natures of salts. The final saltwas heated at 500°C for 5 h in air, collected and cooled quietly.

FT-IR spectroscopy: FT-IR is used to reveal the incorporated nano metal oxides in the structure of the filled poly acrylonitrile materials. The FI-IR Fig. 2 offered the (v_{c-o}) stretching was as sured because of the aspects of peak at 1100-1130 cm^{-1} which refers to the an hydride groups in the metal oxides that confirm the metal bonding with the polymer and the (v_{c-c}) stretching which appears at 1140, refers to the polymer formation. The band in the regions 400-600 cm^{-1}, especially, the formations of single phases spinal structure (Sanchez *et al*., 2005).

Diffractions of X-rays: X-rays diffractions pattern of polymer nanocomposite shows in Fig. 3. It revealed that this oxide crystallize in cubic crystals at sharp peak at 2θ of 31° and crystal size (40.8 nm) by using (Scherer's equation) (Krehula and Music, 2011).

Morphology and structure of polymer nanocomposite: AFM images exhibit that polymer's surfaces of the brushes were so, soft because they contain polymer chin that have the same height. It has been noted that the hole

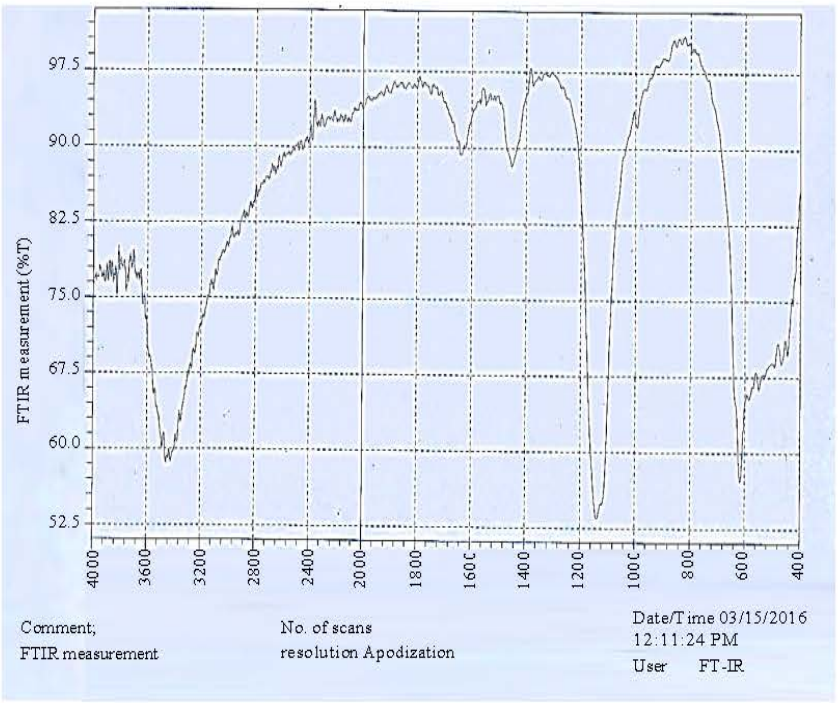

Fig. 2: FT-IR spectra of polymer nanocomposite

ismade by oxygen evolution shappening during the processes of oxidations. Surfaces of the nano oxide layer was soft and didn't reveal divergences in height by more than 6 nm Fig. 4 and 5 shows the topographic structure in 2 and 3D visions of AFM image of polymer nano composite layers builded on carbon steel specimen (Oliveira *et al*., 2009; Yuan *et al*., 2012)

Corrosion rate measurements: Electrochemical corrosion kinetics of any system can be described by determining 3 parameter of polarizations includes, corrosions currents densities (i_{corr}) corrosions potential (E_{corr}) and Tafel slope, anodic regions (β_a) and cathodic regions (β_c) by the polarization curves (E vs. i). Evaluations of this parameter results in the determinations of the polarization Resistance (Rp), Eq. 1 and 2 (Bardal, 2004) and the corrosions rates as which is sometimes converted into Faradaic corrosions rates having a unit of (mm/y).

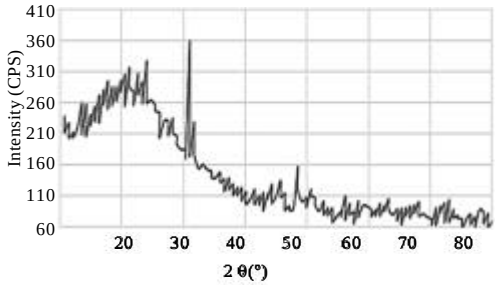

Fig. 3: XRD of polymer nanocomposite

$$R_p = \frac{B}{i_{corr}} \quad (1)$$

Where:

$$B = \frac{B_a B_c}{2.303(B_a + B_c)} \quad (2)$$

The corrosion protection abilities in saline water (3.5% NaCl) media of the CS coated with polymer composite samples were estimated from Tafel extrapolation plots and compared with the uncounted ones, the effect of rising temperature up to 50°C on corrosion rates also investigated, the Tafel parameters includes corrosions possible (E_{corr}), corrosions currents densities (icorr) and the slops β_a and β_c. The relation determining the inhibition efficiency (PE %) using Eq. 3 (Xue *et al*., 2011; Uhliy and Revie, 2011):

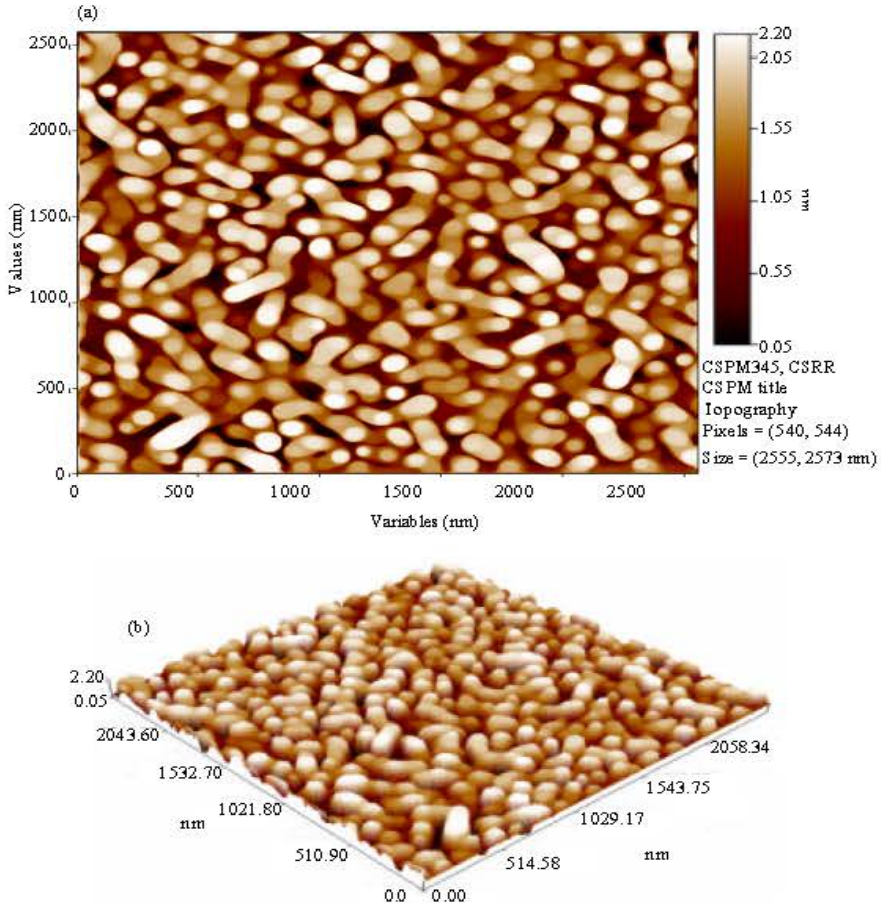

Fig. 4: 3 and 2D view of the AFM image of polymer nanocomposite layer constructed on carbon steel specimens

Table 1: Corrosions measurement parameter for uncoated carbons steels specimen in 3.5% NaCl at different temperature

T(K)	E_{corr} (mV)	i_{corr} (μA/cm^2)	B_c (mV/Dec)	β_a (mV/Dec)	R_p Ω.cm^2	CR (g/m^2.d)	CP (mm/y)	PE(%)
Uncoated CS								
293	-531.2	127.51	166.4	79.0	182.4	31.9	1.48	-
303	-578.6	173.03	206.9	98.6	167.6	43.3	2.01	
313	-592.7	213.72	334.5	97.0	151.5	53.4	2.48	
323	-614.2	241.95	344.3	93.6	132.1	60.5	2.81	

Table 2: Corrosions measurement parameter for uncoated carbons steelsspecimen in 3.5% NaCl at different temperature

T(K)	E_{corr} (mV)	I_{corr} (μA/cm^2)	Bc/(1)(mV/Dec)	B_a/(2) (mV/Dec)	CR (g/m^2 .dl)	R_p Ω.cm^2	CP (mm/y)	PE (%)	ρ(%)
Coated CS									
293	-513.08	16.04	123.08	149.7	4.13	1792.7	0.192	87.01	2.1
303	-522.06	18.06	131.07	156.4	4.62	1666.7	0.214	89.03	
313	-544.05	23.08	134.02	165.9	5.95	1352.9	0.276	88.09	
323	-558.05	27.05	137.04	195.7	6.87	1272.7	0.320	88.06	

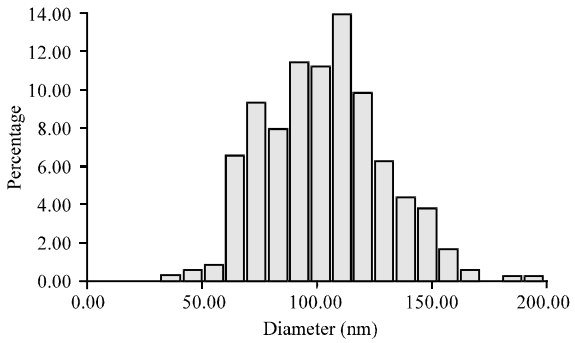

Fig. 5: AFM reprint report for statistical calculating particles sizes and their distribution of polymer nanocomposite layer on CS specimens

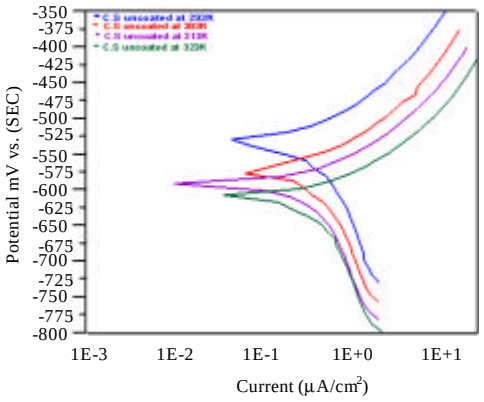

Fig. 6: Tafel plot of uncoated carbon steel in 3.5% NaCI with different temperatures

$$PE\% = \left[1-\frac{i_{corr}}{i^{0}_{corr}}\right] \quad (3)$$

where, i^{0}_{corr} and i_{corr} represent the corrosions currents densities of uncoated and coated specimen, respectively, determined by extrapolations of the cathodic Tafel line to the possible corrosions.

The potentiostatic polarizations curve for coated and uncoated carbon steel in 3.5% NaCl solutions at temperatures range (20-50)°C are shown in Fig. 6 and 7 and Table 1, respectively.

The porosity of polymer composite layers was estimated using the following equation (Lorenzetti *et al*., 2014):

$$\rho\% = \frac{R_{p,s}}{R_p}10^{-\left(\frac{\Delta E_{corr}}{\beta_a}\right)} \quad (4)$$

where, $R_{p,s}$ and R_p are the polarizations resistance of the bare substrates and substrates/coatings pair, respectively, ΔE_{corr} is the possible differences between them and β_a is the substrate's anodic Tabe 1 coefficients.

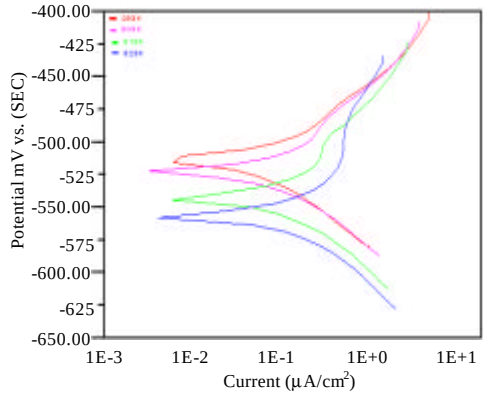

Fig. 7: Tafel plot of coated carbon steel in 3.5% NaCl with different temperatures

The potentiodynamic polarizations curve of CS specimen under investigation with and without polymer nano composite coatings immersed in the water of the sea at four temperatures: 293, 303, 313 and 323 K are shown in Fig. 6 and 7.

Table 2 shows the shifts in E_{corr} of the coated nano composite with comparisons of the uncoated samples to

more positive potential (noble direction) which indicate the resistant corrosions feature of the coatings, also, it is seen the value of corrosions current densities (i_{corr}) for nano composite coated CS are smaller than the corresponding value for bare CS. The most important evaluated parameter is the PE% of the nano composite coated sample which reflects the effects of coatings processes on sample, the best protections abilities were observed for CS metals at 303 K. The value of porosity of polymer composite-CS in saline water is 2.1 and reflects the small pores of the polymer coating.

CONCLUSION

The polymer nano composite was made by the ferric chlorides reaction, acrylonitrile and metal chloride. FT-IR analyses revealed that the acrylonitrile polymerizes at lower temperatures and form spinal ferrites. Studies of AFM images and XRD powders patterns compose spinal crystals with crystalline. The polymer nanocomposites coatingthe metal under investigations undergorising of the corrosions protections property at 303 K.

REFERENCES

Bardal, E., 2004. Corrosion and Protection. Springer, Berlin, Germany, Pages: 315.

Coan, T., G.S. Barroso, G. Motz, A. Bolzan and R.A.F. Machado, 2013. Preparation of PMMA/hBN composite coatings for metal surface protection. Mater. Res., 16: 1366-1372.

Hameed, R.A., A.A.H. Abu-Nawwas and H.A. Shehata, 2013. Nano-composite as corrosion inhibitors for steel alloys in different corrosive media. Adv. Appl. Sci. Res., 4: 126-129.

Khaled, M., B. Abu-Sharkh, E. Amr, B.S. Yilbas and A. Manda *et al*., 2007. Corrosion properties of 316L stainless steel coated with polyelectrolyte multilayers of varying anionic acidity. Corros. Eng. Sci. Technol., 42: 356-362.

Krehula, S. and S. Music, 2011. Hydrothermal synthesis of Platinum Group metal nanoparticles. Croatica Chem. Acta, 84: 465-468.

Lorenzetti, M., E. Pellicer, J. Sort, M.D. Baro and J. Kovac *et al*., 2014. Improvement to the corrosion resistance of Ti-based implants using hydrothermally synthesized nanostructured anatase coatings. Mater., 7: 180-194.

Nalwa, H.S., 2000. Handbook of Nanostructured Materials and Nanotechnology. Academic Press Inc., San Diego, California, USA., Pages: 75.

Oliveira, M.A.S., J.J. Moraes and R. Faez, 2009. Impedance studies of poly (Methylmethacrylate-co-acrylic Acid) doped polyaniline films on Aluminum alloy. Prog. Org. Coat., 65: 348-356.

Rout, T.K., G. Jha, A.K. Singh, N. Bandyopadhyay and O.N. Mohanty, 2003. Modified poly (Ethylenterphthalate) as Corrosion inhibitors for C-steel in 1M HCl. Surf. Coat. Technol., 157: 16-247.

Sanchez, C., B. Julian, P. Belleville and M. Popall, 2005. Applications of hybrid organic-inorganic nanocomposites. J. Mater. Chem., 15: 3559-3592.

Singh, B., J.P. Singh and S. Shruti, 2012. Synthesis and characterization of Inorganic polymen nano-composites. Der Chem. Sinica, 3: 521-526.

Sophia, I.A., G. Gopu and C. Vedhi, 2012. Synthesis and characterization of poly anthranilic acid metal nanocomposites. Open J. Synth. Theory Appl., 1: 1-8.

Uhliy, H.H. and R.W. Revie, 2011. Uhligs Corrosion Handbook. 3rd Edn., John Wiley of Sons, Hoboken, New Jersey, USA., ISBN:978-0-470-87285-7, Pages: 1254.

Xue, B., Y. Jiang and D. Liu, 2011. Preparation and characterization of a novel anticorrosion material: Cu/LLDPE nanocomposites. Mater. Trans., 52: 96-101.

Yeh, J.M., S.J. Liou, C.Y. Lin, C.Y. Cheng and Y.W. Chang *et al*., 2002. Anticorrosively enhanced PMMA-clay nanocomposite materials with quaternary alkylphosphonium salt as an intercalating agent. Chem. Mater., 14: 154-161.

Yuan, X.Y., L.L. Zou, C.C. Liao and J.W. Dai, 2012. Improved properties of chemically modified graphene-poly (methyl methacrylate) nanocomposites via. a facile in-situ bulk polymerization. Express Polym. Lett., 6: 847-858.