Studying the Effect of Nano Filler on Epoxy Properties used in storage tank Low Carbon Steel Protection

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Abstract:

In this study a nano epoxy coating had been prepared to be used for the protection of the internal and external surfaces of storage tank (low carbon steel) from corrosion. A polymeric coating was reinforced with fillers such as red iron oxide, Zinc phosphate and nano titanium dioxide (TiO_2) which have been used as anticorrosion. Pieces from low carbon steel was picked from storage tank and coated with two layers, the first layer was prepared from organic polymer (epoxy) with red iron oxide, the second layer was prepared from epoxy with (a nano titanium dioxide and Zinc phosphate).

The fillers weight percentages were (0, 7, 10 and 13 % wt). The nano epoxy coating gave good results in limiting the corrosion, the corrosion rate results show that the best percentage of additives was (13,10 % wt) in salt solution 1.0 %wt (NaCl, Na_2SO_3 and KCl).The coating samples were immersed for 3 month at 25 ^{O}C in gas oil and cutting oil then was characterized using spectroscopic method (FTIR), physical and chemical tests add to characterization of particles size was done by SEM. The samples of TiO_2 were characterized by XRD and evaluation of corrosion was made by using static potential test.

Keywords: Nano Filler, Epoxy, Low Carbon Steel, Protection and Storage Tank.

دراسة تأثير الحشوة النانوية على خصائص الايبوكسي المستعمل في طلاء الفولاذ واطئ الكاربون

الخلاصة :

في هذه الدراسة تم تحضير طلاء الايبوكسي النانوي المستعمل في حماية السطوح الخارجية والداخلية لخزان الوقود (فولاذ واطئ الكاربون) من التأكل وتم تقوية الطلاء البوليمري بحشوات مثل اوكسيد الحديد الاحمر وفوسفات الزنك مع ثاني اوكسيد التيتانيوم النانوي (TiO_2) والتي تم استخدامهم ضد التاكل وتم اخذ قطع من فولاذ واطئ الكاربون من خزان الوقود وطلية بطبقتين، اول طبقة كانت محضرة من بوليمر عضوي (ايبوكسي) مع اوكسيد الحديد الاحمر، ثاني طبقة تم تحضيرها من الايبوكسي مع (ثاني اوكسيد التيتانيوم وفوسفات الزنك) وكانت النسب الوزنية للحشوات (0 , 7 ,10 ,13) %. الطلاء الايبوكسي النانوي أعطى نتائج جيدة في الحد من التاكل ونتائج التاكل اظهرت بان استعمال احسن نسبة للمضافات كانت % (10, 13) في المحلول الملحي 1.0 % لكل من(NaCl و Na_2SO_3 مع KCl) وتم غمر نماذج الطلاء لمدة ثلاثة اشهر في درجة 25^0C في زيت الغاز وزيت القطع ثم تم تشخيصها باستخدام طريقة (FTIR) وفحوصات كيميائية وفيزياوية و تشخيص الحجم الحبيبي بواسطة SEM وتشخيص نماذج TiO_2 بواسطة (XRD) حيود الاشعة السينية وتم قياس التاكل بواسطة أستعمال جهاز المجهاد الساكن.

الكلمات المفتاحية: حشوة نانوية، الايبوكسي، حماية، فولاذ واطئ الكاربون و صهريج الخزن.

1. Introduction:

Corrosion is one of the most common problems in petroleum industry. It happen mainly in storage tanks and pipelines.Thus considered as the biggest engineering and economic problem in the world [1]. The rate of corrosion is the speed of the metal deterioration in a specific environment. The rate or speed is dependent upon environmental conditions as well as the type, and condition, of the metal. Corrosion is prevented by insulating the metal material from the corrosion agents through the work of a protective layer such as epoxy resin and nano materials that can be used as protective coating for an iron or steel.

Nano fillers widely used in reinforcing the epoxy material to improve the efficiency of the polymeric material performance [2] which is used especially in composites, adhesives and coating as a protective coating for storage tank and pipes surfaces [3], this coating have many properties such as good resistance to chemical materials.

The use of nano fillers for anticorrosion coatings has a significant importance. Several researchers have that shown nano fillers perform well in anti-corrosion coatings with polymers and composites [4]. Many nano materials are used as a thin film in petroleum industry such as Al_2O_3, SiO_2, CuO and TiO_2.Among all nano coatings using TiO_2 considered to be as the most common [5] corrosion protection thin films due to their unique chemical, electrical and optical properties. TiO_2 thin films possess high dielectric constant, wide optical band gap, high refractive index, photo catalytic, low absorption and high transparency with high thermal and chemical stabilities. Titania or titanium dioxide (TiO_2) is a semiconductor material, and the best known crystal forms of TiO_2 are the anatase, rutile and brookite [6, 7].

While the anatase and rutile, which is a thermodynamically stable phase and is the best known polymorph of TiO2, have the tetragonal crystal system, the brookite has the orthorhombic crystal structure [8].

The anatase and brookite are metastable phases and these are converted the rutile phase after heating [9]. Nano-TiO_2 particles also provide acceptable protection especially for carbon steel and stainless steel [10]. Also, nano materials were used as catalysts in petroleum refining reactors in petroleum refining industry and as coating materials to the storage tanks [11].

TiO_2 nano particles and epoxy resin was applied on low carbon steel surface as coating. Nano fillers with epoxy can significantly improve the properties of epoxy resin [12], so the reinforcement efficiency is strongly depend on particle size, volume fraction of nanoparticles in epoxy structure and dispersion of nanoparticles [13].

The use of polymeric material such as epoxy resin in the protection of metals is significantly reducing the rate of corrosion. Epoxy resins are the basic material in the coating, these resins are poly ethers contain an epoxy rings at the end of the chain, known as (oxiranes) [14]. Epoxy resins are used in coatings such as protective coating for pipes and the internal surface of tank [15]. It is an excellent adhesive coating, strong, abrasion resistant, and is a good resistance to moisture and chemicals [16]. Composites material is made of (polymer such as epoxy resin) with (fillers such as zinc phosphate and red iron oxide) as a rust resistant layer. It has high adhesion properties on metal [17]. It is suitable for use in marine and petroleum industrial whether immersed or not immersed [18].

The main purpose of the polymer coating is to protect the internal and external surfaces of the storage tank (low carbon steel) by using reinforce- ment materials like micro (Fe_2O_3, $Zn_3(PO_4)_2$) and TiO_2 nanoparticles.

2. Experimental Part:

2.1 Materials:

The epoxy resin (EP405) was used from Fosroc, Jordan .The ethylene diamine was used as a cross-linking for the epoxy resin. Titanium dioxide nano particles (rutile) purity 99.5% with average particle size a round (30) nm, was obtained from Riedelde Haen, Germany. Micro particles were red iron oxide (Fe_2O_3) and $Zn_3(PO_4)_2$ by (Cristal Global pharma, France) with particle size (10-25) µm . Castor oil (Iraq) has been added as a plasticizer which improves from the elasticity of polymer coatings. The products were painted on pieces of the metal at thickness (150) microns and left to dry for (7 - 10) days. Gas oil and cutting oil were used from AL-Dora refinary to test the chemical resistance of the coating layer**.** Chemical analysis of pipeline material (low carbon steel) Wt% (C 0.196%, Mn 0.461% , Si 0.215% , S 0.0173% , P 0.0107% , Fe Balance % low carbon steel were used from the Petroleum Pipeline Company/ Ministry of Oil-Iraq.

2.2 Samples preparation method:

The first layer was prepared from organic polymer (EP405) with red iron oxide and hardener. The second layer was prepared from epoxy with a nano titanium dioxide and Zinc phosphate [19]. Hardener was added to mixture. The mixing ratio for (EP405) and the ethylene diamine (hardener) was (3:1). Castor oil was added in a small percentage (0.2) % to each layer. The composite material was mixed at 25ºC using a magnetic stirrer for one hour. The fillers weight percentages were (0, 7, 10 and 13) wt%. All samples componte were coated on pieces of low carbon steel with thickness (150) micron, the samples were left to dry for (7) days. Various salt solutions were prepared at 1.0 wt% for each of (NaCl, Na_2SO_3 and KCl). Determination of corrosion rate was by weight loss method and the corrosion rate was calculated for each piece using the initial and final weights. The rate can also be calculated as follows [20].

$$CR\ (g/m^2d) = \square W/\ (At)$$

CR = Corrosion rate = g / m^2 .day

□W (g) = W_0 (initial) – W (final)

t = Time taken for the loss of metal (day)

A = The surface area of the alloy (m^2)

2.3 Characterization:

FT-IR spectra were recorded using KBr disc by Shimadzu (FT-IR 8300) . FT-IR spectra were recorded for all samples of epoxy resin, gas oil and cutting oil before and after immersion, for the coating layers which composed of epoxy resin with nano filler at weight percentages (0, 7, 10 and 13) wt%. In the present investigation, different measuring techniques and instruments were used to characterize of nano materials such as X-ray diffraction (XRD) using [Shimadzu 6000 - XRD (JAPAN)]. Particles size performed by scanning electron microscopy (SEM). Corrosion resistance were measured by Galvanostatic test by using potential static device (potentiostat), [(MIab200of Bank Elec) GERMANY], currents were recorded (nA,µA) /cm^2, potentials were recorded (mV) and determination of corrosion rate by weight loss method. The coating layers roughness was measured by surface roughness of material tester [(model TR-100 Dakota altrasonics) (CHINA)].

3. Results and Discussion:

FTIR and XRD analysis:

The FT-IR spectrum of (sample [1]), showed the absorption bands at (1247) cm^{-1}, due to ν (C-O) ,ν (1184) cm^{-1} for ν (C-O-C), (2925-2964) cm^{-1}, due to ν (CH_2). FT-IR spectra of samples [2] and [3] showed the absorption bands at (1246) cm^{-1}, due to ν (C-O) and (1183) cm^{-1} for ν (C-O-C), absorption bands at (2964-2926) cm^{-1}, due to ν (CH_2) ,showed the absorption bands as in the Table (1). Also the sample [4], Figure (1) shows the FT-IR spectrum of (sample [4]), showed the absorption bands at (1245) cm^{-1}, due to ν (C-O) and ν (1184) cm^{-1} for ν (C-O-C), absorption bands at (2966-2925) cm^{-1}, due to ν (CH_2) ,showed the absorption bands as in the listed in Table (1).

By comparison between (FT-IR) spectrum of samples [2], [3] and [4] with (FT-IR) spectrum of sample [1], showed the absorption of similar bands which means that nano TiO_2 didn't change the structural formula of the epoxy when compared with sample [1].

Table (1) (FT-IR) spectrum data of samples [1], [2], [3] and [4]

No.	Samples	υ CH_2	υ C-O-C	Others
[1]	Epoxy	2925 2964	1184	υ C-H aromatic (3037), υ C-O (1247)
[2]	Epoxy + nano (7%)	2926 2964	1183	υ C-H out of plane (732) υC=C (1600-1602), υ C-O (1246)
[3]	Epoxy + nano (10%)	2926 2964	1183	υ C-H out of plane (820) υ (C-O) (1246)
[4]	Epoxy + nano (13%)	2925 2966	1184	ν (C-O) (1245) υ C=C (1606)

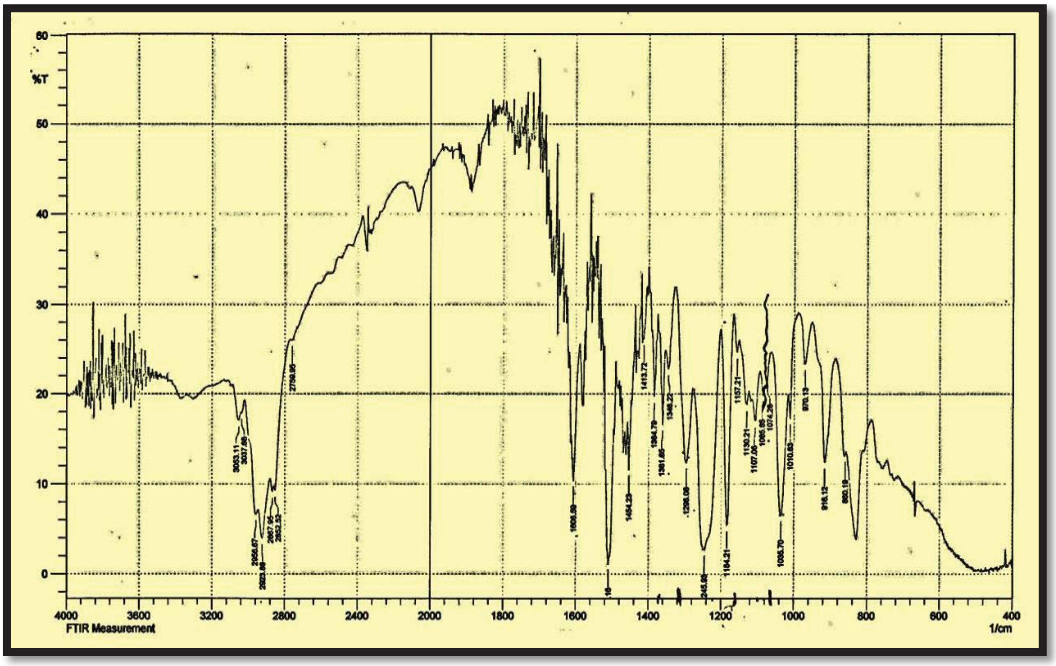

Fig. (1) (FT-IR) spectrum of epoxy resin and nano filler (13 %)

Figure (2) shows the FT-IR spectrum of cutting oil after immersing the coating layer for 3 months, it was observed from the absorption sites that the effective groups of epoxy resin was not shown, indicating that the coating layer has not been affected by the cutting oil and gas oil and it acquired a stability and chemical resistance against these substances.

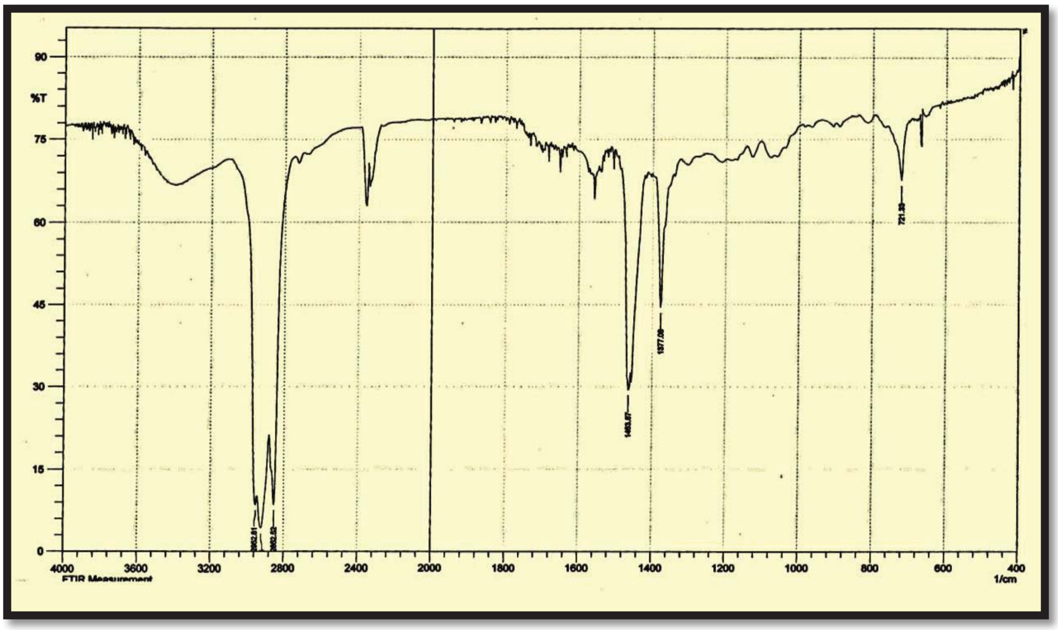

Fig. (2) (FT-IR) spectrum of cutting oil after immersing the coating layer

X-ray diffraction (XRD) technique was used to analyze the coating layer components chemically, XRD results of the (anatase and rutile) phase of (TiO2) nanoparticles with epoxy coatings target Cu wave 1.54060 at speed of 5 deg. / min. range from (5 – 60) deg. Figures (3) and (4) showed the X-ray diffraction of crystalline structure of TiO_2. Figure (3) showed a strong three peaks at angles 13.705°, 27.121° and 9.025° crystal size showed (24.41, 39.23 and 21.06) nm with tetragonal structure (101) of nano TiO_2 coatings at weight percentage (13) % wt. (Ref. 21-1276) which indicate the rutile structure of TiO_2 [21].

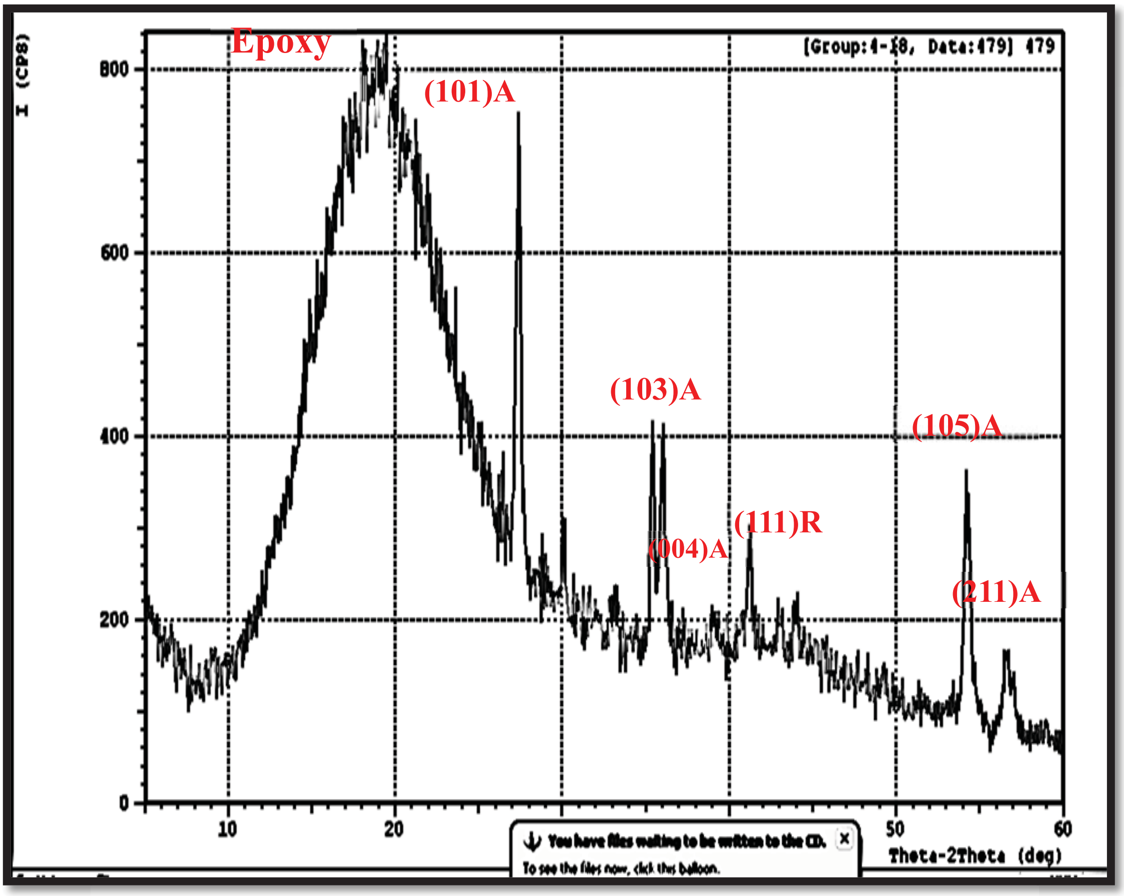

Fig. (3) (XRD) of crystalline structure of nano TiO_2 (13%)

Figure (4) showed the strongest three peaks at angles 13.70°, 17.71° and 27.13° and crystal size showed (24.41, 28.15 and 34.25) nm with tetragonal structure (101) of nano TiO_2 coatings at weight percentage (10) % wt. (Ref. 21-1276) which indicate the rutile structure of TiO_2 (Debye -Scherer) equation : is equation calculate the crystal size, as follows [22]:

$Cs = k . \lambda / \beta \cos \theta$

Cs = Crystal size (nm)

$k = 0.9$

$\lambda = 0.1540$ nm

β = Maximum width at the middle of the summit.

Θ = Diffraction angle

$\cos \theta$ = Angle of x-ray fall (deg).

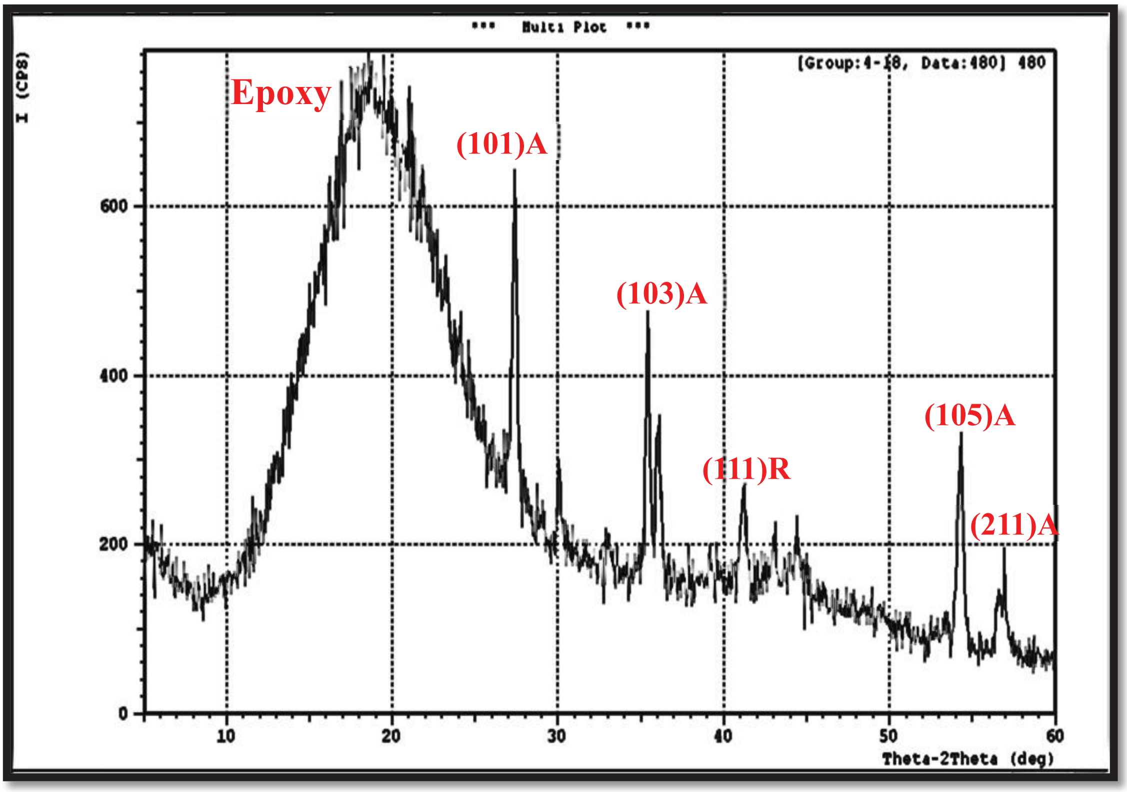

Fig. (4) (XRD) of crystalline structure of nano TiO_2 (10%)

Figure (5) showed the strong peaks at angles 22.287° and 22.565° corresponding to the iron in low carbon steel substrate without coatings sample [5].

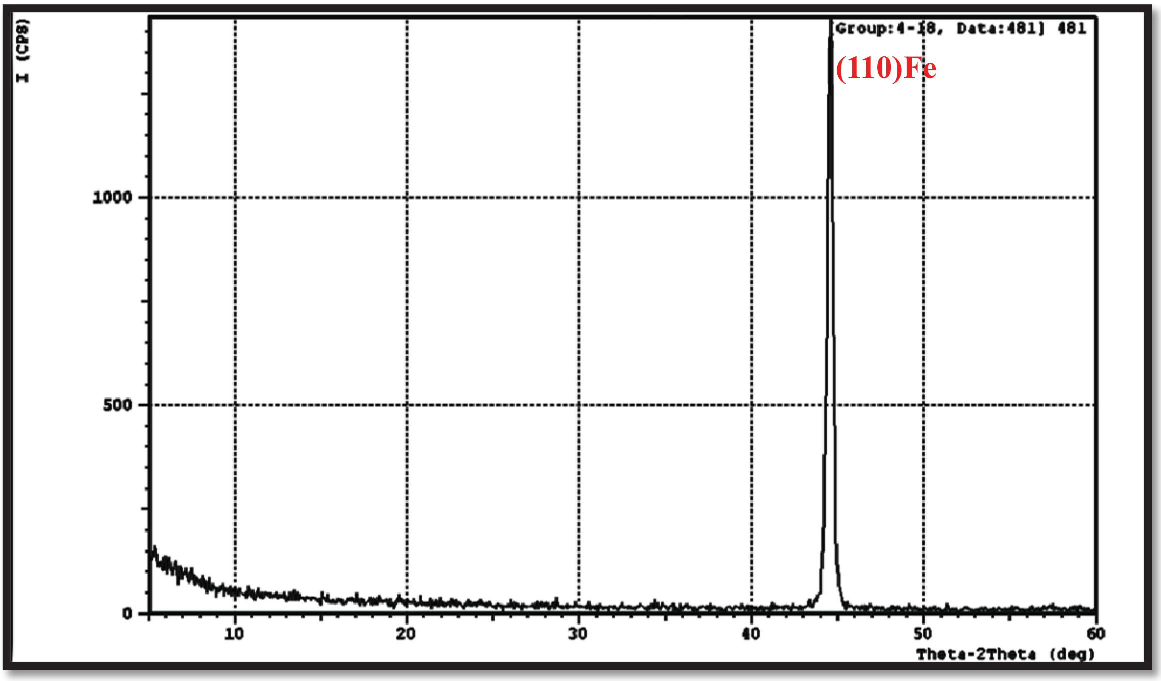

Fig. (5) (XRD) of iron in low carbon steel substrate without coatings

Crystal size showed as in the listed in table (2), the XRD results showed that the major phase in coating of TiO_2 rutile and epoxy) also were polycrystalline

Table (2) (XRD) test data of samples [2], [3], [4] and [5]

No.	Sample	θ (deg)	Intensity (counts)	Crystal size (nm)
[2]	Epoxy + nano filler (7 %)	9.31° 9.50 ° 9.33°	969 188	21.10 21.15 21.12
[3]	Epoxy + nano filler (10 %)	13.70° 17.71° 27.13°	133 102 99	24.41 28.15 34.25
[4]	Epoxy + nano filler (13 %)	13.705 ° 27. 121 ° 9. 025 °	169 102 99	24.41 39.23 21.06
[5]	low carbon steel	22.287 ° 22.565 °	588 22	30.42 32.50

Corrosion Rate:

The corrosion behavior was characterized at 40°C in salt solution 1.0 % wt (NaCl, Na_2SO_3 and KCl). by Galvanostatic tester by using Potential Static Device, (0) %wt sample [1], Figure (6), showed resistance to corrosion and record the current corrosion (I corr.) about (16.23) µA /cm^2 compared with the nano TiO_2 coatings with weight percentage (10) % wt of sample [3], Figure (7) showed resistance to corrosion and record the current corrosion about (14.30) µA /cm^2. The iron in low carbon steel substrate without coatings sample [5] Figure (8), shows non-corrosion resistance and record the current corrosion, about (47.01) µA /cm^2. Table (3), it can be noticed the Epoxy – TiO_2 composite increased corrosion inhibition with increasing nano TiO_2 weight percentage in tested samples compared with Epoxy- low carbon steel sample. Also, The most effective addition of (TiO_2) nano partical was with 13% (sample [4]), with least current corrosion compouned [1] with absence of the nano filler and [5] without coting at all. Also, results show that using the nano TiO_2 weight percentage (7, 10, % wt) in increased corrosion inhibition, as shown in Table (3).

Table (3) resistance to corrosion of samples [1-5]

No	Samples	current corrosion (I corr.) μA/cm^2	Potential Corrosion (E corr.) Mv
[1]	Epoxy resin	(16.23)	- 317.6
[2]	Epoxy + nano filler (7 %)	(14.07)	-361.4
[3]	Epoxy + nano filler (10 %)	(14.30)	-298.7
[4]	Epoxy + nano filler (13 %)	(5.36)	- 430.0
[5]	low carbon steel	(47.01)	-522.3

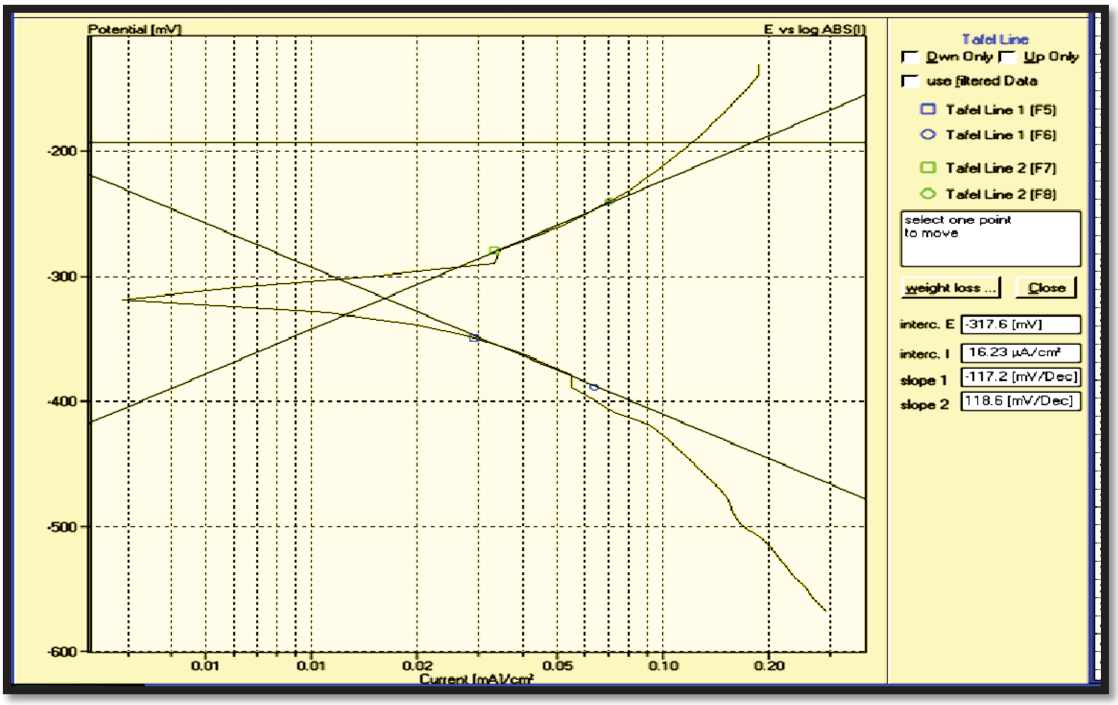

Fig. (6) Polarization curve of epoxy resin (sample [1])

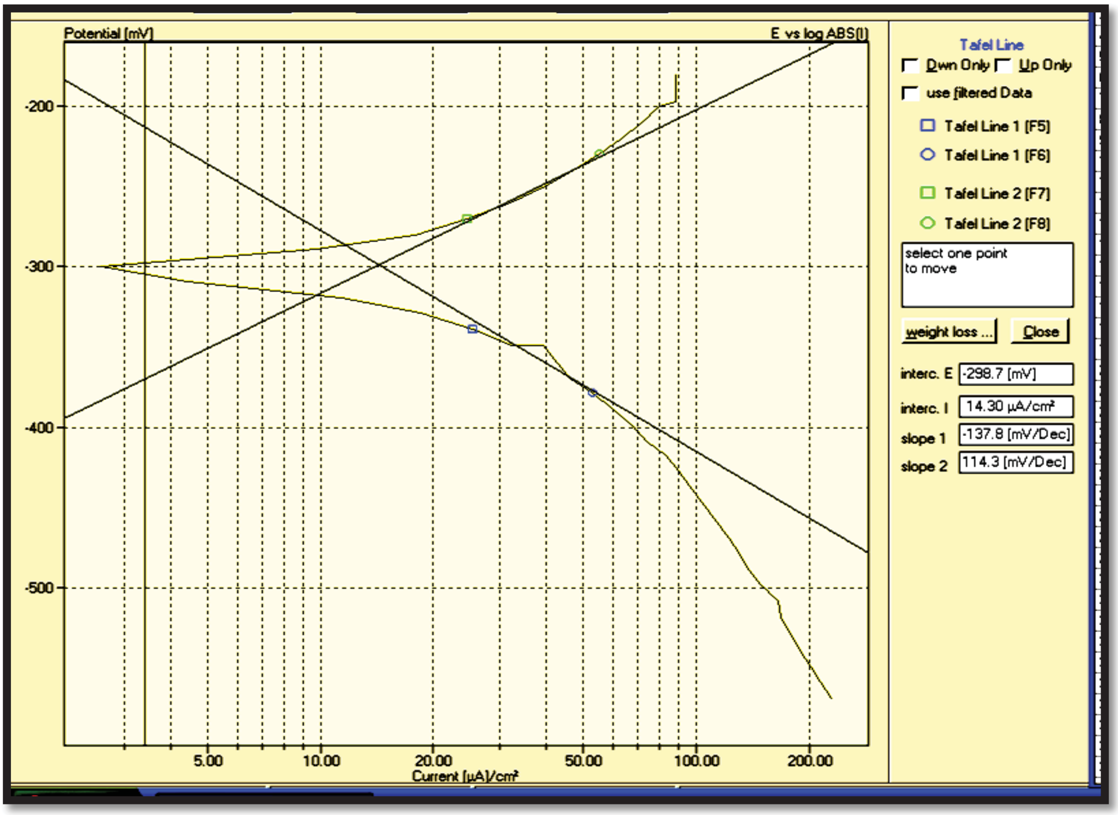

Fig. (7) Polarization curve of epoxy resin (sample [3])

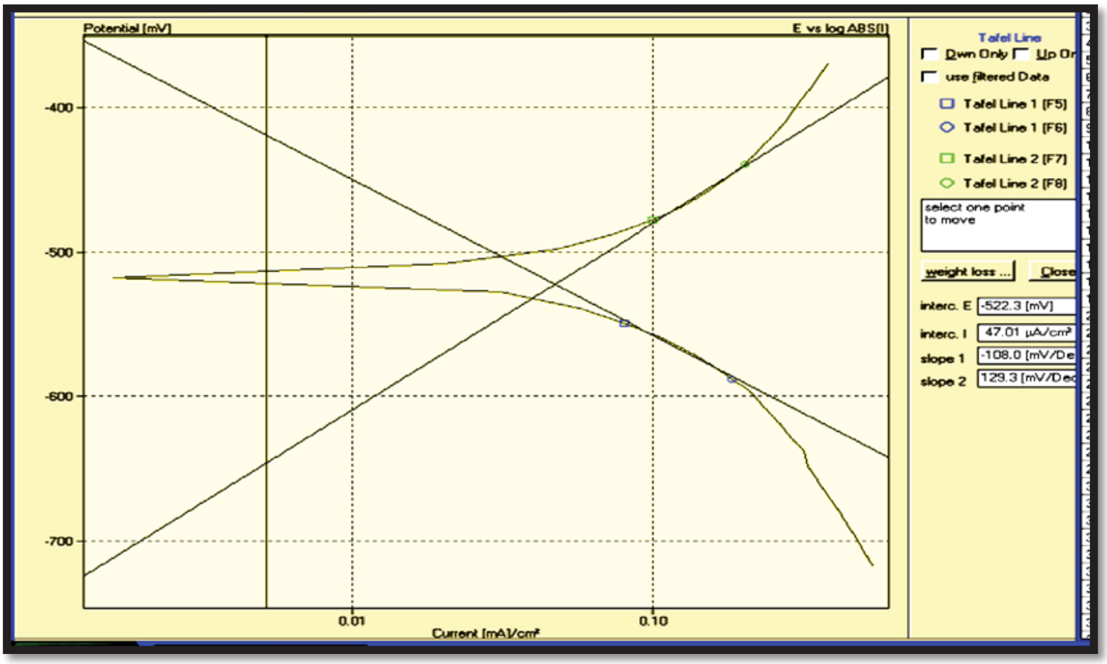

Fig. (8) Polarization curve of low carbon steel (sample [5])

Determination of corrosion rate by weight loss method as a simplest method of measuring the rate of corrosion or called immersion method, was done for low carbon steel without and samples of with coated nanoparticles coating at thickness (150) microns in (gas oil and cutting oil (fuel tank)) .The weights of the samples were measured by a sensitive balance and the surface area was calculated before and after immersion. Weight loss is calculated as follows: $CR\ (g/m^2d) = \Delta W/\ (At)$

The results showed that the low carbon steel without coating suffered from little corrosion. While the nanoparticles coating (7,10 and 13) % wt no suffered weight loss because the nanoparticles protected the alloy from corrosion as shown in Figure (9), the weight loss of samples [2-5] showed in Table (4).

Table (4) Weight loss of samples [2-5] in the different oil types

Time	Weight Loss (g / cm^2) in the cutting oil and gas oil			
Days	Nano TiO_2 7%	Nano TiO_2 10%	Nano TiO_2 13%	Low carbon steel
15	0	0	0	0.01
30	0.00001	0.00001	0.00001	0. 42
60	0.000016	0.000015	0.000013	0.82
90	0.000037	0.000033	0.000031	1.64

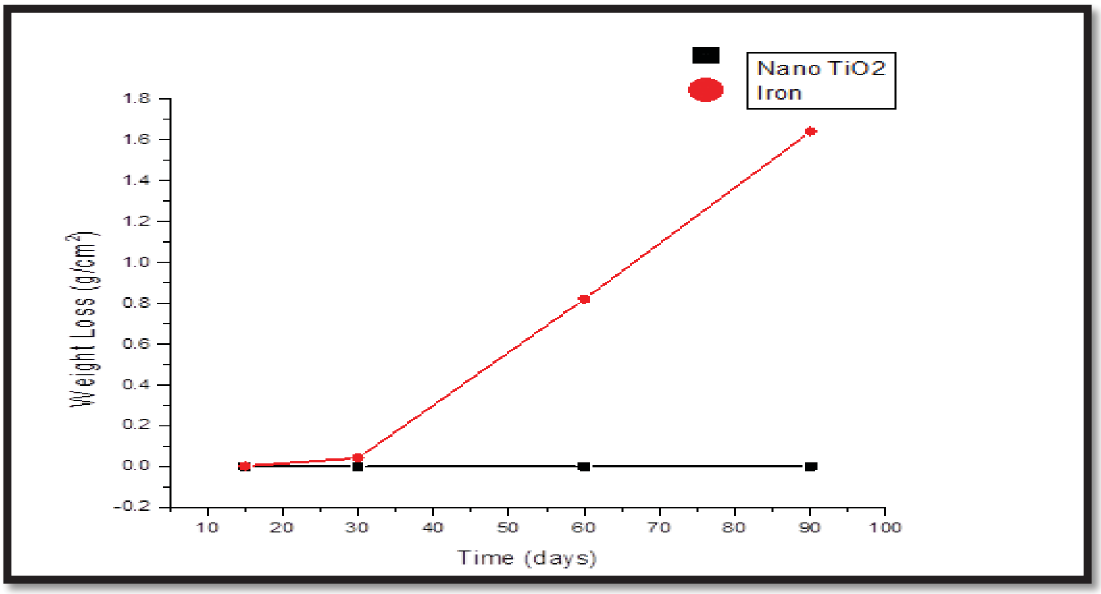

Fig. (9) Weight loss of low carbon steel and nano TiO_2 coating in the cutting oil and gas oil

SEM and Microscopic:

(SEM) Scanning electron microscopic characterization of nano TiO_2 particles, Figure (10), shows the SEM of nano-TiO_2 with average particle size around (30) nm.

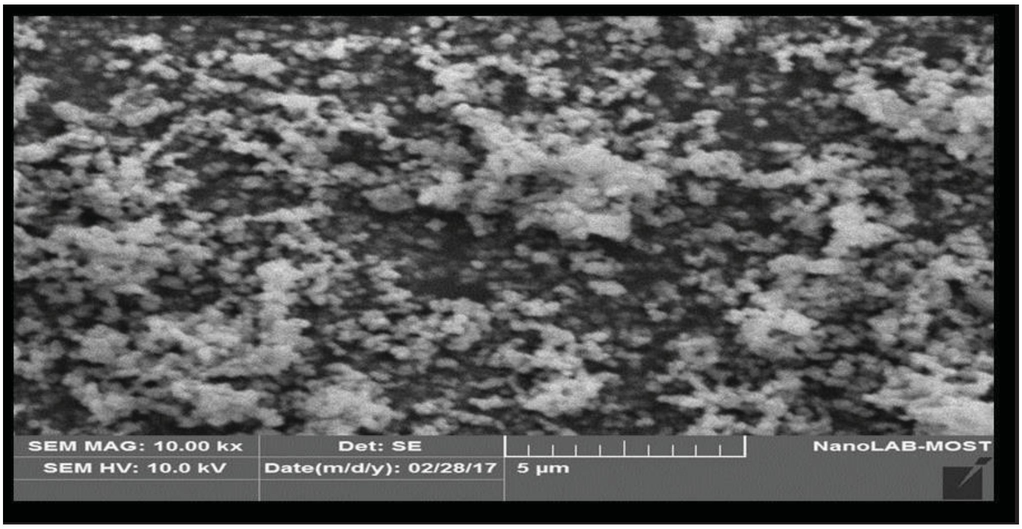

Fig. (10) (SEM) Scanning electron microscopic of nano -TiO_2

The Surface Roughness:

The coating layers roughness was measured by surface roughness of material tester, which is the equipment that used to measure the surfaces roughness of material (metal and non-metal) for a distance of 6 mm and the sample dimensions are (1 cm x 1 cm). Sample [5] showed more roughness in the surface because of steel without coating, recorded 0.78 μm. Sample [2], [3] and [4] showed low roughness, recorded (0.34, 0.3 and 0.275) μm because of the nanoparticles coating.

Conclusion:

The properties of polymer (epoxy) with filler to configure composites depend on the particles size, shape, interfacial bonding, and surface treatment of the fillers. The dispersion of fillers in polymer matrix has influence on the mechanical ,physical and thermal properties of polymers .The addition of nano fillers (3 ,7,10)% to epoxy resin cause the increase in the corrosion resistance and polymer nano composites have many advantages over micro composites in the properties such as corrosion resistance bonding strenght. So it is perfect for many uses, as adhesives, protective coating for metal, water pipes and storage tank.

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