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Preparation of a Reinforced Polymeric Coating with Inorganic Nano Additives as UV-Stabilizers and Protect Oil Pipelines from Corrosion

Abstract- *In this research a nano polymeric coating has been prepared to be used for the protection of the external surface of oil pipelines (medium carbon steel (CK50)) from corrosion in salt water (3.6% NaCl) . This coating is reinforced by inorganic (nano and micro) additives to apply a high resistance against chemicals and salts. These oxides protect the epoxy resin from degradation by preventing the epoxy molecules and active functional groups from absorbing ultraviolet light in the range (290-315) nm strongly.This coating is also resistant to the high and low temperatures, humidity, scratch and water. This coating was prepared from the reaction of 2-[[4-[2-[4-(Oxiran-2-ylmethoxy) phenyl] propan-2-yl] phenoxy] methyl] oxirane (Diglycidyl Ether of Bisphenol A) and the hardener (EDA). The mixing ratio of the two parts was (4:1). Reinforced with inorganic (nano and micro) additives such as titanium dioxide (TiO_2) and zinc oxide (ZnO) which have been used as an anticorrosion. These additives are non-toxic, thermally stable and have a high degree of the miscibility with epoxy. The weight percentages of the mixing are (0 and 10 % wt). The corrosion rate results show that using (nano and micro) coating give good results in increasing the corrosion resistance compared with the (non additives) epoxy.This coating was characterized using different spectroscopic methods (FT-IR, UV/Vis). Several tests were conducted ، including differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) , mechanical tests and evaluation of corrosion resistance was made by using static potential test.*

Keywords- *Epoxy Coating, Nano Additives, UV-Stabilizers, Protect, Oil Piplines, Corrosion*

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1. Introduction:

A polymeric coating is a material which made from two or more different materials having different physical and chemical properties. Epoxy resins are the basic material in the polymeric coating [1] .Epoxy resins are poly ethers contain an epoxy groups at the end of the chain, known as (ethylene oxide) These resins undergoes polymerization reactions through its ring opening and its participation in a process known industrially as curing, using curing agent such as the amine compounds [1]. The amine groups react with the epoxy groups to form a covalent bond and each NH group can react with an epoxy group, so that the resulting polymer is from thermosets materials, and is thus rigid and strong. Epoxy resins are used in industrial applications, such as floor coating adhesives, composites such as protective coating for pipes [2], and also have many properties as good chemical, excellent adhesion to a variety of sur- faces and good corrosion resistance [3]. The main problems with epoxy resins are low impact strength, highly brittle and low stiffness.The main problem of the epoxy is with the passage of time suffered from degrade by sun light because of the breaking of covalent bonds of epoxy resins. Therefore the addition of inorganic additives like nano TiO_2 / ZnO particles to the epoxy will absorb ultraviolet light in the range (290-315) nm strongly [4], leading to non-absorption of these rays by the active functional groups. Nano (TiO_2) / ZnO particles which are a good material due to their versatile characteristics which include resistance to chemical and physical effects [5]. Inorganic metallic oxides like zinc oxide and nano TiO_2 are best used as UV-stabilizers. These oxides basically, increase thermal stability, protect the epoxy resins from degradation [6] and long pot life period. Nano fillers can change shape during formation and

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produce modified proper- ties of the epoxy, so the reinforcement efficiency is strongly depend on particle size, dispersion of nanoparticles and volume fraction of nanoparticles in epoxy structure.The thermo, mechanical properties of the cured epoxy / nano TiO_2 / ZnO particles (composites) positively characteristics [7] such as mechanical performance, thermal stability properties, and also have many advantages as good corrosion , good scratch resistance [8]. The composite materials were characterized by Ultraviolet spectra the have been recorded by using (UV-Visible) within the range (200-900) nm and FT-IR spectra were recorded using solid KBr disc by testing Shimadzu (FT-IR 8300), the number of wave form (400-4000) cm^{-1} range.Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) of the compounds were carried out by Linseis (STA TT-1000) instrument. Scanning electron microscopy (SEM) was performed by AIS 2300 C Angstrom Advanced Inc. New York. Shore-D durometer was used for measuring surface hardness fabricated by time company, model TH 210, ITALY. Compressive strength) Tinius OL SeN-H50KT) .Evaluation of corrosion resistance after different protection methods were measuring performed by Galvanostatic test by using potential static device. Current were recorded (nA,μA) /cm^2 and potential were recorded (mV).

2. Experimental Part

I. Materials Used.

The epoxy resin (2-[[4-[2-[4-(Oxiran- 2-ylmethoxy) phenyl] propan -2 – yl] phenoxy] methyl] oxirane) matrix used that was Nitocote, from Fosroc Comp- any .The amine hardener, (ethylene diamine) was used as a cross-linker for the epoxy [7]. The mixing ratio 4:1, specific gravity 1.09, gelation time 45 minute at 35^oC, mixed viscosity 1.22 poise at 35^oC and fully cured at 35^oC is 5 days. Nano-TiO_2, with average particle size around 100 nm, was obtained from Riedelde Haen (product code: 14027), Germany. While density 0.67 g/cm^3, the purity of titanium nano particles ≥ 99.8, titanium micro particles by (Cristal Global pharma) with particle size 50 μm density 1.297 g/cm^3. The products were painted on glass slides of quartz and the metal at thickness (200-250) microns and left to dry for (7-10) days.

II.Samples preparation method

Epoxy resin and hardener were used in this study in ratio of 4:1 for with nano TiO_2 (100nm) / ZnO and micro TiO_2 (50μm) / ZnO to form nano and micro composites .Weight percentages of the mixing are (0 and 10) % wt. Careful mixing of epoxy resin with TiO_2 / ZnO and the composite then was mixed at 35ºC using a high speed magnetic stirrer for one hour. The amine hardener was added and used as a cross-linker for the epoxy resin [9].

III. Characterization

All samples of epoxy resin, epoxy resin-nano TiO_2 / ZnO particles and epoxy resin-micro TiO_2 / ZnO particles ware subjected to the following analysis ultraviolet spectra were recorded using (UV-Visible) within range (200 -900) nm and FT-IR spectra were recorded using solid KBr disc by testing (FT-IR). Shore-D was used for measuring surface hardness of epoxy and polymer matrix composite. Thermal stability of the compounds were analyzed by thermo- gravimetric analysis that discusses the measurement of the change in the weight for a material as a function for temperature by subjecting the material to a heating process.The measurements were performed on weight (7-20) mg, were heated in the thermo balance at heating rate (10^{0}c / min) in an inert atmosphere at the existence of air. Differential Scanning Calorimetry is the relationship between heat flow rate (dH/dt) on the vertical-axis and the temperature on the horizontal-axis. Corrosion resistance was measured performed by Galvanostatic tester by using potential static device.

3. Results and Discussion

The epoxy resin and hardener were mixed in ratio of 4:1 to form compound [1].Some physical properties for this compound were listed in table (1). Epoxy resin and hardener (EDA) (compound [1]) were characterized by (FT-IR) spectrum; The FT-IR spectrum of (compound [1]), showed the absorp- tion bands at (3460) cm^{-1}, due to ν (O-H) and ν (1245) cm^{-1} for ν (C-O). Absorption bands at (1114) cm^{-1}, due to ν (C-O-C) [10] and strong bands (2956-2922) cm^{-1} for ν (CH_2). We have strong peaks for the ν (NH) group from the (EDA) at (3053) cm^{-1}.Figure 1 shows the FT-IR spectrum of epoxy/nanoTiO_2/ZnO(compound [2]) the absorption band at (3437) cm^{-1},due to υ (OH),absorption band at(1172) cm^{-1} ,due to υ (C-O-C) [10] and showed the absorption band at (3251) cm^{-1}, due to υ (NH) group. Also the FT-IR spectrum of epoxy resin/micro TiO_2/ZnO particles (compound [3]), showed the absorption bands as in the listed in table (2). By comparison between (FT-IR) spectrum of (compounds [2] and [3]) with (FT-IR) spectrum of (compound [1]), showed the absorption of similar bands which means that TiO_2, wasn't changed from the structural formula of the epoxy (compound [1]) , as shown in table (2) .

Some physical properties for these (compounds [2] and [3]) were listed in table (1). The (UV/Vis) of (compound [1], Figure 2, showed the low absorbance (- 0.100) These rays can break through the polymer surface and cause cracks in the surface, and the color fades. Also (compound [2]) was characterized by (UV/Vis) spectroscopy ; Figure 3, it showed the high absorbance (0.495). Also compound [3]) was characterized by (UV/Vis) spectroscopy; it showed the high absorbance (0.295). Through the (UV/Vis) spectrum of (compounds [2] and [3]), shows the high absorbance .this means that (micro and nano) TiO_2 improve the properties of the epoxy through protecting it from UV ray, the addition of additives inorganic like TiO_2 nanocomposite and TiO_2 micro particles to the epoxy resin will absorb ultraviolet light in the range (290-315) nm strongly [11], leading to non-absorption of these rays by active functional groups and the epoxy molecules.The thermogravimetric analysis (TGA) for the (compounds [1] and [2]), Figures 4 and 5, showed curves for initial dissociation degree for each compound and final dissociation degree by drawing tangents to these curves at the beginning and the end of the disintegration, the maximum disintegr -ation degree, then account the loss percentage in weight [12] . The thermal functions values showed, that the thermal stability of the epoxy resin that has disintegrate more than the rest of the compounds[13],as shown in table (3). The (compounds [2] and [3]) are the most thermally stable compounds, due to the presence of inorganic additives (such as nano and micro TiO_2) they worked to increase the thermal stability of the compounds , the initial dissociation degree was recorded about 170 ºC and this is the highest initial dissociation degree than the epoxy resin (compound [1]), as shown in table (3).

Figures. 5 and 6, shows the Differential Scanning Calorimetry (DSC) of epoxy/ nano TiO_2/ZnO (compound [2]) and epoxy resin (compound [1]),it measures the produced or absorbed heat, gives information on the enthalpy and other functions of polymer matrix composites and Other values the Differential Scan- ning Calorimetry (DSC) were recorded of (compounds [1] and [2]) as shown in table (3). Some the mechanical properties of (compounds [1], [2] and [3]) such as hardness tester, the hardness strength Shore-D was recorded of (compound [1]) (70-71) N/mm^2. Also the hardness strength (Shore-D) was recorded of (compounds [2],[3]) (85-87) and (78-79) N/mm^2. Other mechanical properties of compounds were listed in table (4).The corrosion behavior was characterized at 40ºC by Galvanostatic tester by using Potential Static Device, (compound [1]), Figure 7, shows non-corrosion resistance and record the current corrosion (I. corrosion) about (2.9) $\mu A/cm^2$. The (compounds [2] and [3]). Figure 8 and 9, showed resistance to corrosion and record the current corrosion (I. Corrosion) about (310.4 and 128.5) nA $/cm^2$,as shown in table (5) . Because the paint layer contains the anti-corrosion materials which are working to make the metal surface resistant to corrosion.Figure 10, shows the Scanning electron microscopic SEM character-ization of nano TiO_2 particles. SEM was recorded of nano-TiO_2 with average particle size around 100 nm.

Table1: shows the physical properties of compounds [1],[2]and[3

No	Comp.	Viscosity	Drying time at 25ºC Touch dry	Fully cured	Colour
[1]	Epoxy resin	1.22 Poise	6 hours	7days	transparent
[2]	Epoxy / nano TiO_2/ZnO	5.0 Poise	6 hours	5days	green
[3]	Epoxy/ micro TiO_2/ZnO	5.5 Poise	6 hours	5days	green

No.	υ OH	υ CH_2	υ C-O-C	Others

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

[1]	3460	2956 2922	1184	υ C-H aromatic (3037) υ N-H (3053), υ C-O (1245)
[2]	3437	2947 2950	1172	υ C-H out of plane (820) υ N-H (3251)
[3]	3440 3410	2943 2923	1170	υ C-H out of plane (732) υC=C (1600-1602) υ C-O (1249)

Table 3:Thermo gravimetric analysis (TGA) and DSC of the compounds [1],[2]and[3]

No	Step	TGA				DSC		Total mass loss%
		Ti /ºC	Tf / ºC	$T_{TGA\ max}$	Weight mass loss%	T_{DSC}	H △	
[1]	Stage 1	133	298	258	38.6	148	End	83.24
	Stage 2	370	580	520	44.6	528	Exo	
[2]	Stage 1	153	297	251	17.718	252.0	Exo	42
	Stage 2	310	517	416	11.421	495	End	
	Stage 3	520	600	551	13.129	576.1	Exo	
[3]	Stage 1	160	285	235	9.7	137	End	17
	Stage 2	358	600	429	6.82	428	Exo	

Ti = Initial dissociation degree Tf = Final dissociation degree H = Enthalpy △

Table 4: shows the mechanical properties of (compounds [1],[2]and[3])

No	Comp.	Hardness Shore-D	Tear Resistance at weight 1 kg	Compressive Strength N /mm2
[1]	Epoxy resin	(70-71)	resistant	(90)
[2]	Epoxy / nano TiO2/ZnO	(85-87)	resistant	(100-110)
[3]	Epoxy/ micro TiO2/ZnO	(78-79)	resistant	(100)

Table 5: shows resistance to corrosion of (compounds[1],[2],[3])

No	Comp.	current corrosion (I corr)	Potential Corrosion (E corr)

[1]	Epoxy resin	(2.9) µA/cm2	412.9 mV
[2]	Epoxy / nano TiO2/ZnO	310.4 nA /cm2	146.3 mV
[3]	Epoxy/ micro TiO2/ZnO	128.5 nA /cm2	115.9 mV

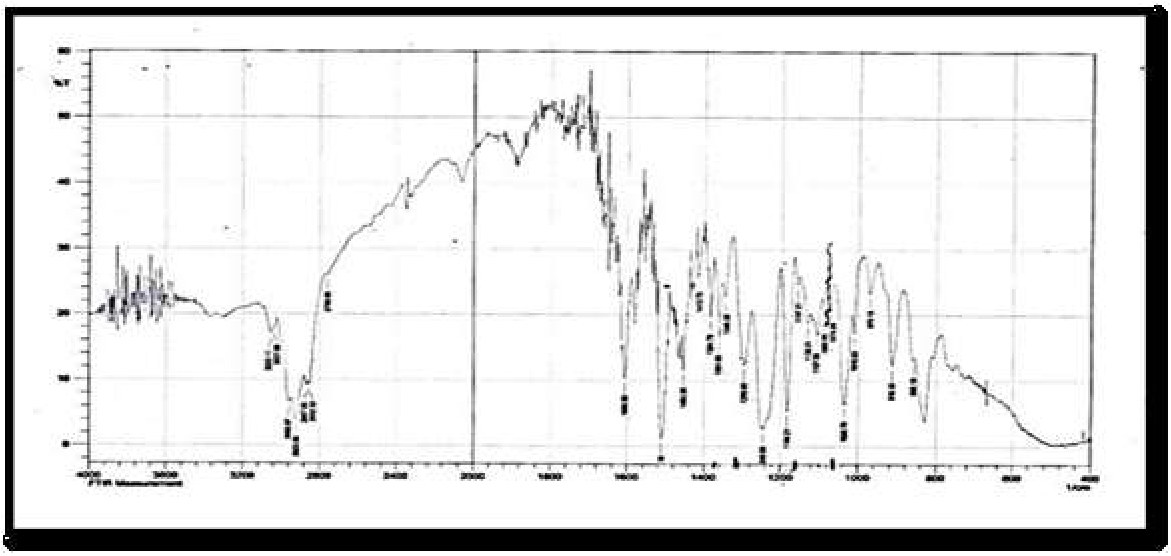

Figure 1: FT-IR spectrum of epoxy- nano TiO_2/ZnO particles

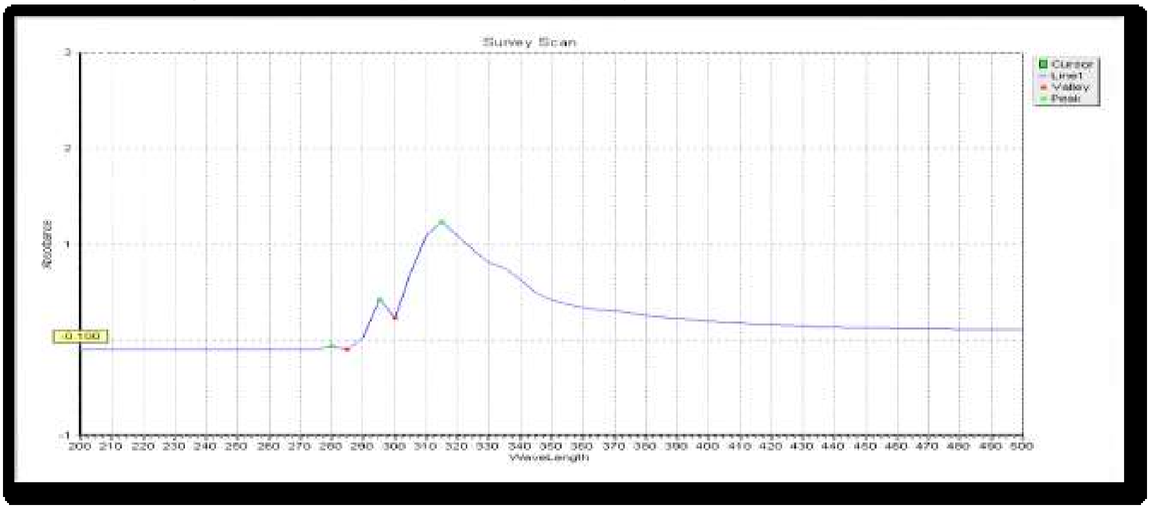

Figure 2: UV-Vis spectrum of epoxy resin (compound [1]

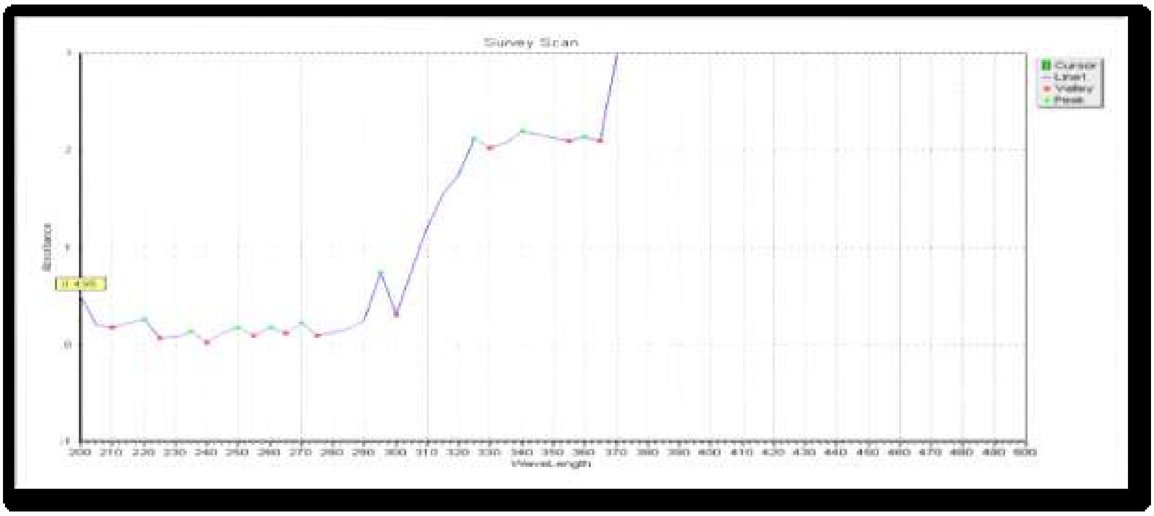

Figure 3: UV-Vis spectrum of epoxy - nano TiO_2 / ZnO (compound [2])

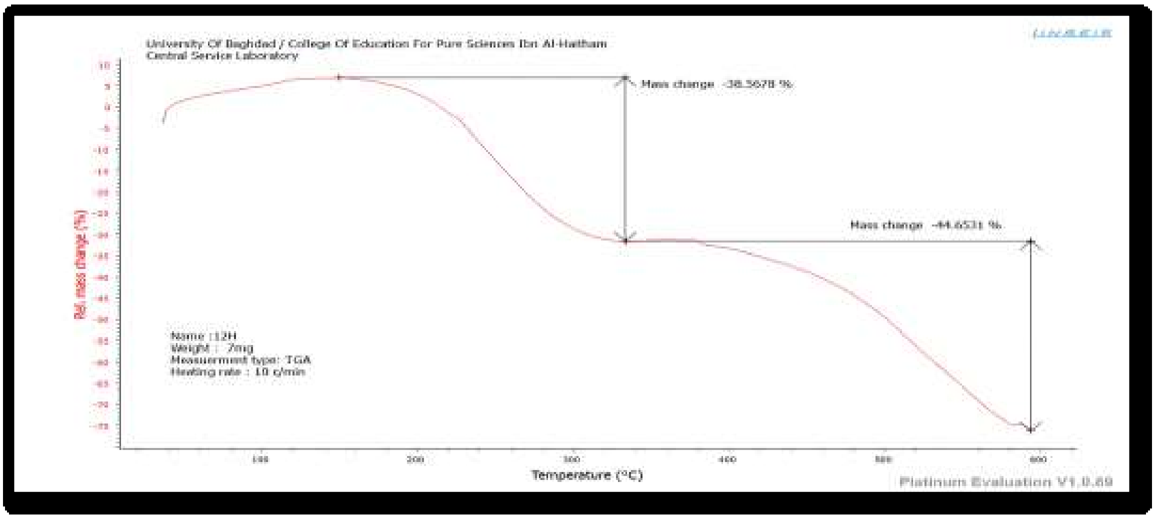

Figure 4:Thermal gravimetric analysis (TGA) of(compound [1]

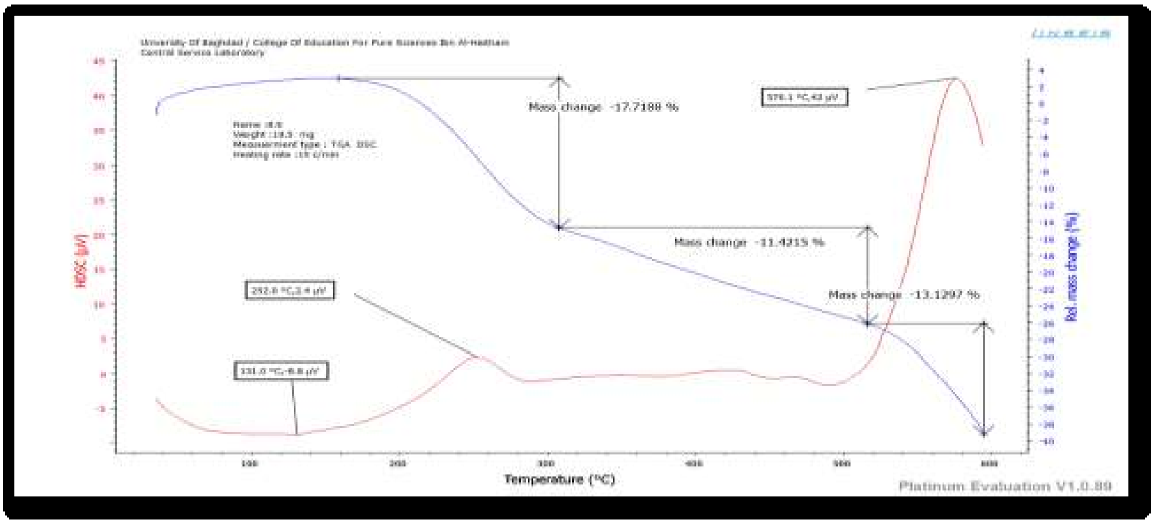

Figure 5 : Thermal gravimetric analysis (TGA), (DSC) of (compound [2])

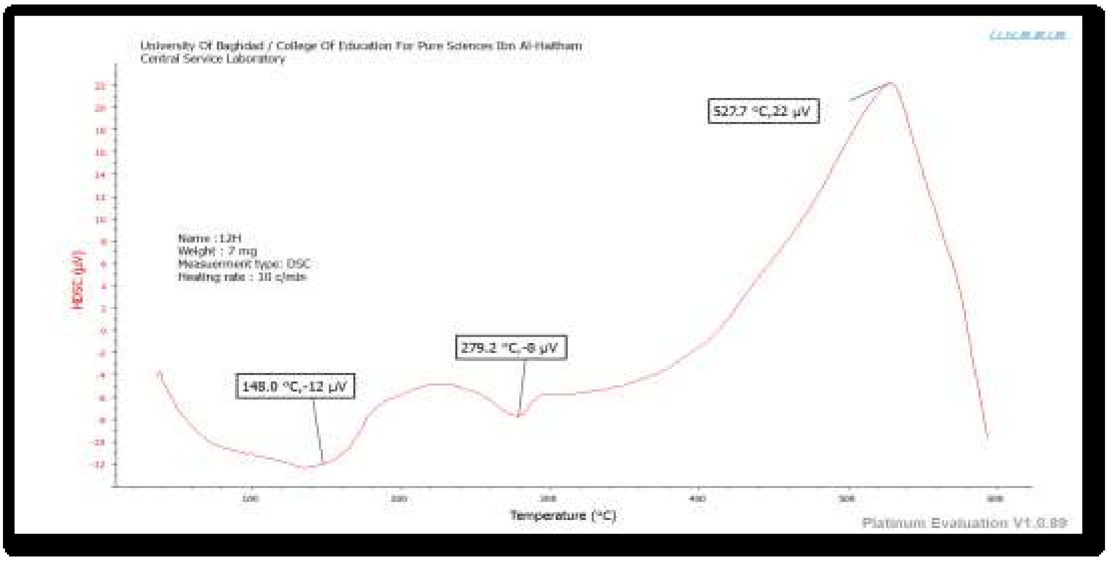

Figure 6:The Differential Scanning Calorimetry (DSC) of (compound [1])

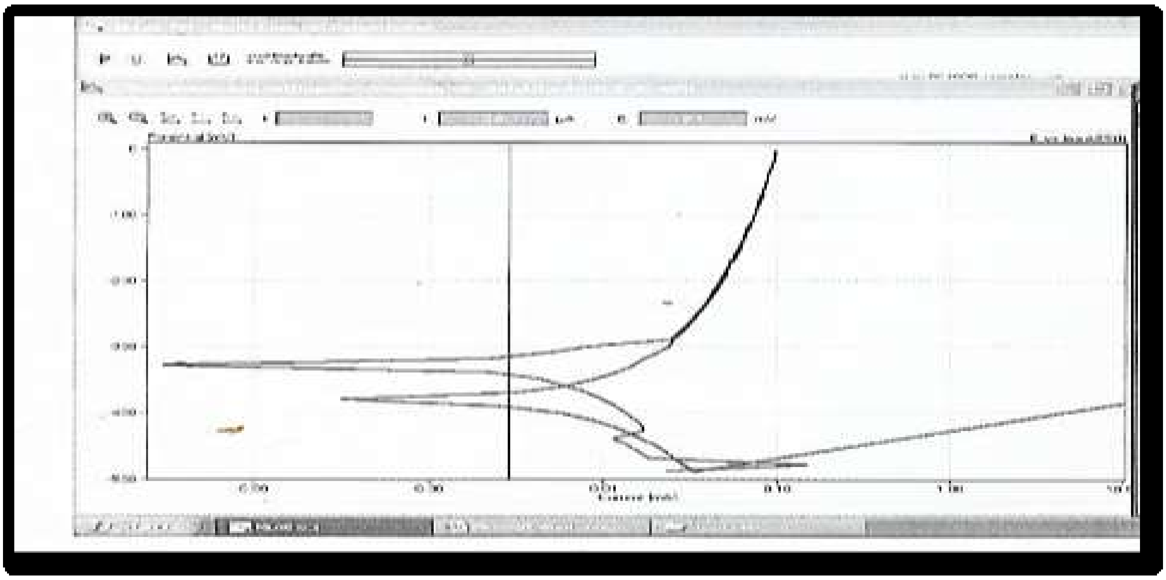

Figure 7: Shows polarization curve for epoxy resin (compound [1])

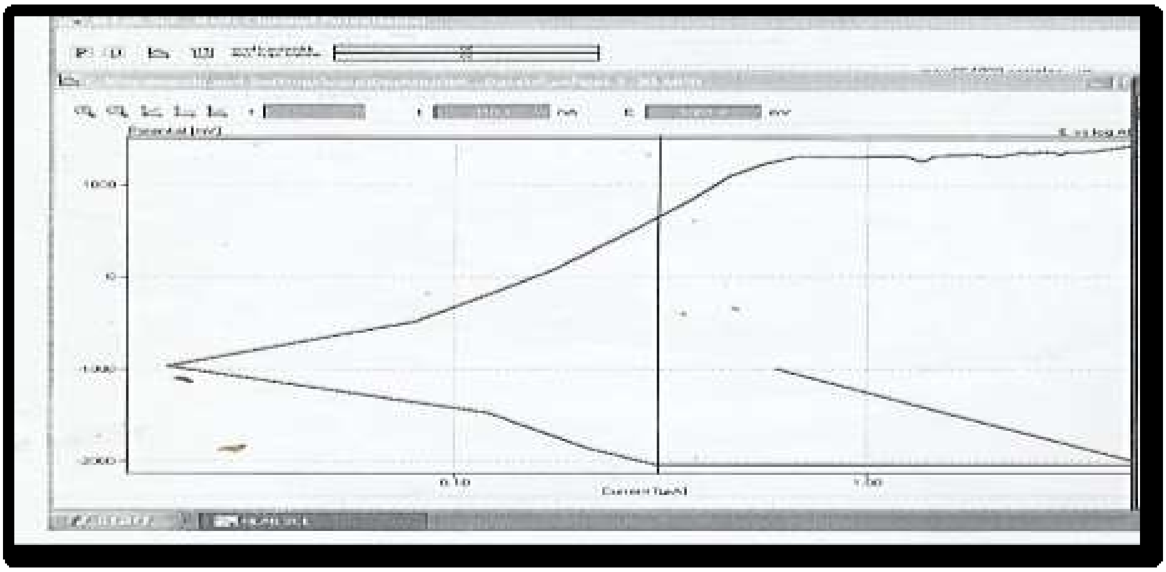

Figure 8: Shows polarization curve of (compound [2])

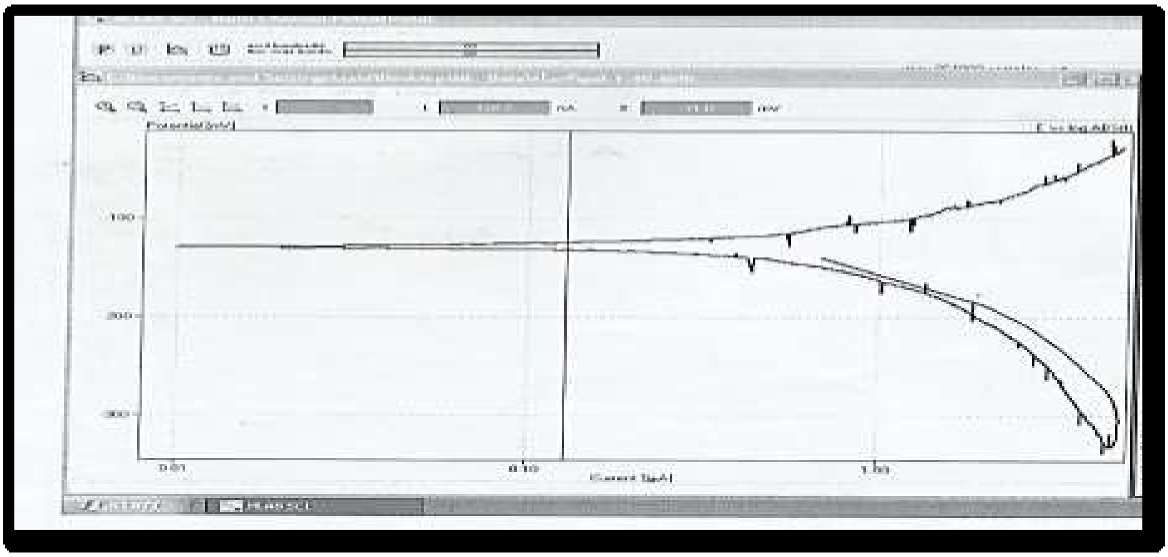

Figure 9: Shows polarization curve of (compound [3])

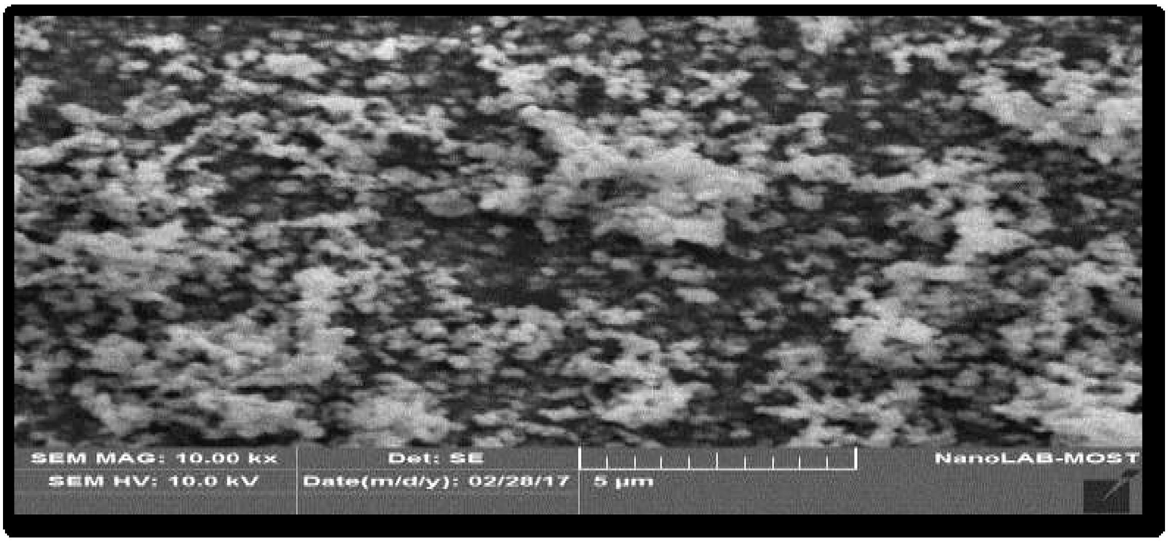

Figure 10 : micrograph of (SEM) for nano -TiO_2.

Conclusion

Improving the properties of epoxy resin against ultraviolet light and give it thermal stability can be achieved by using inorganic fillers such as (micro TiO_2/ Zinc oxide and nanoTiO_2 / Zinc oxide).NanoTiO_2 is an effective reinfor- cement for epoxy system for high per- formance applications.

The addition of nano fillers to epoxy resin cause the increase in the corrosion resistance and the protection of the epoxy resins from degradation, also increase of mechanical properties while the TGA value of nano-composite TiO_2 was higher than that of epoxy resin and micro composites. So it is perfect for many uses, such as comp-osites, adhesives, protective coating for metal, water pipes and oil pipelines

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