Eng. &Tech.Journal, Vol. 33,Part (A), No.4, 2015

Characterization of sherardized low carbon steel used in oil pipelines coated with polymer blends layers

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Received on:25/6/2014 & Accepted on:2/4/2015

Abstract

Oil pipelines of low carbon steel were coated by sherardizing process at 400°C for different treatment times (15, 30, 60, 120, 240) min and then the sherardizing samples coated by polymer blend unsaturation polyester resin with butadiene rubber (UP:BR) and unsaturation polyester resin with nitrile butadiene rubber (UP:NBR) with different percentage weight ratio of BR and NBR (0, 5,10 and 15 %) in the blends. The thickness of sherardizing coated, hardness, surface roughness and adhesive strength were studied. The results of this research showed that the thickness of sherardizing coated and hardness value increase with increasing time treatment. The adhesive strength of sherardizing surface coated with polymer blends layer increases with increasing surface roughness of sherardizing coated with two mixed group of polymers blends [(UP:BR) and (UP:NBR)] samples, as well as the adhesive strength decreases with increasing percentages weight of BR or NBR in the blend. The higher values of adhesion force reach to (2.761 KN) and (0.848 KN) for polymer blends (95%UP:5%NBR) and (95%UP:5%BR) respectively. Whereas coating sherardizing surface by unsaturated polyester only having the high value of adhesion force (2.921 KN) at surface roughness (2.29µm). As well as the results show the sherardizing surface coated by mixed polymers blend (UP:NBR) having higher values of adhesion force compared with other samples coated by mixed (UP:BR) polymer blend.

Key words: sherardizing, Adhesion force, metal, polymer blend, NBR and BR.

خصائص الفولاذ المنخفض الكاربون المطلي بالخارصين والمستخدم في خطوط انابيب النفط وطلائها بطبقات من الخلائط البوليمرية

الخلاصة:

في هذا البحث أجريت عملية الطلاء بالخارصين لأنابيب النفط الصلب منخفض الكربوني في درجة حرارة 400 درجة مئوية لأزمان مختلفة (15، 30، 60، 120، 240) دقيقة ثم طلاء هذه العينات بالخليط البوليمري المتمثل

https://doi.org/10.30684/etj.33.4A.9
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براتنج البوليسر الغير مشبع مع مطاط البيوتاتين والخليط الاخر متمثل المتمثل براتنج البوليسر الغير مشبع مع مطاط نترال البيوتاتين وبنسب مختلفة من المطاط (0،5،10 و 15٪) في الخليط البوليمري. وتم قياس سمك العينات المطلية باخارصين,الصلادة, خشونة السطح وقوة الالتصاق. وتناظرت النتائج بأن سمك الطلاء والصلادة تزداد مع زيادة وقت المعاملة . إضافة إلى ان الصلادة تزداد مع زيادة سمك العينات المطلية بالخارصين . تتزداد قوة التصاق السطح المطلي بالخارصين وطبقة طلاء الخليط البوليمري تزداد مع زيادة خشونة السطح للعينات المطلية بالخارصين ولكلا نوعين الخلائط الوليمرية , إضافة إلى ان قوة الالتصاق تتناقص مع زيادة النسب الوزنية للمطاط في الخليط واعلى قيم تصل اليها هي 2.761كيلو نيوتين لل(95%بوليستلر:5% مطاط نترال بيوتايتين) و0.848كيلو نيوتين لل(95% بوليستلر:5% مطاط بيوتايتين) للخلائط البوليمرية على التوالي. في حين سطح المعدن المطلي بالخارصين ثم طلاءه بالبوليستر الغير مشبع فأن له اعلى قوة التصاق تصل الى 2.921 كيلو نيوتين للعينات التي لها خشونة 2.29مايكرون . كما يمكن ان نلاحظ نتائج سطح المطلي بالخارصين مع الخليط البوليمري(بوليستر :مطاط نترال بيوتايتين) له قيم التصاق اعلى مقارنة مع الخليط البوليمري (بوليستر :مطاط بيوتايتين).

INTRODUCTION

Adhesion bonding refers to the bond (chemical or physical) between two adjacent materials, and is related to the force required to affect their complete separation. Adhesion is a macroscopic property which depends on three factors: 1) bonding across the interfacial region, 2) type of interfacial region (including amount and distribution of intrinsic stresses) and 3) the fracture mechanism which results in failure [1].
Adhesion of a coating to its substrate is critical to its function. Mechanical, chemical, and metallurgical factors may contribute to such adhesion. For a coating to be retained and to perform its function, its adhesion to the substrate must tolerate mechanical stresses and elastoplastic distortions, thermal stress, and environment or process fluid displacement.

Good adhesion performance of a coating depends on a variety of the attributes of the interface region, including its atomic bonding structure, its elastic moduli and state of stress, its thickness, purity and fracture toughness [2].

Although no single material is suitable for all applications, usually there are a variety of materials that will perform satisfactorily in a given environment. carbon steels are the most common materials of construction, not because of their corrosion resistance, which is usually fair to poor, depending on carbon content and its impurties but because of their excellent mechanical properties, weldability, and low cost. When used in corrosive environments, steels usually require some form of corrosion protection, such as protective coatings, cathodic protection, or a combination of these corrosion prevention methods [3].

Sherardizing is the coating of iron or steel with zinc/iron alloy. coating by polymeric blends also can be used as protective layer against corrosion [4].

J. W. Cook, *et al.* [5] studied two aspects of the adhesion produced by the vulcanisation bonding of a simple natural rubber (N.R.) compound to mild steel. Adhesion was measured using a 45° peel test. Arnaud Chichea, *et al.* [6] studied the debonding of a soft adhesive from a hard flat surface is initiated by the formation of cavities which extend in the volume of the adhesive. Adherent's surface properties, surface topography and chemical composition have an important influence on these associated micromechanisms. Dennis Bankmann, *et al.* [7] A process of bonding a metal substrate to a non-halogenated polymer, especially of bonding a polyolefin overcoat to a metallic tube or pipe, using an epoxy-based adhesive which comprises at least one salt of a metal ion M in an oxidation state of n which has a standard reduction potential $E^0{}_M$ more positive than the standard reduction potential of the surface of the metal substrate.

Current work focus on the preparation of different layer of coating (sherardizing coating and polymers blend coating) to protect low carbon steel used in oil pipelines.

Experimental part

Material :

Low carbon steel pipes were taken from the oil pipelines of the Midland Refineries Company for high temperature service type A 106 made according to an American society for testing and materials (ASTM) and were supplied by Daura refiner , Chemical composition analysis has been performed in General Company for examination and rehabilitation engineering. Table (1) gives the chemical composition of low carbon steel which was used in this search. This inspection was performed in General Company for Examination and Rehabilitation Engineering (S.I.E.R).

Table (1) Chemical composition of low carbon steel.

Element	**C**	**Mn**	**Si**	**S**	**P**	**Fe**
Wt %	0.195	0.460%	0.215%	0.0173%	0.0107%	Balance%

Zinc powder has purities about 99.9%, the chemical composition of zinc powder. shown in Table (2)

Table (2) Chemical composition of zinc powder.

Element	**Fe**	**Heavy metals**	**As**	**Cd**	**Sn**	**Zn**
Wt %	0.005%	0.01%	0.00001%	0.005%	0.001%	Balance%

The particle size analysis of zinc powder was carried out in a laser diffraction , particles size analyzer type (SHIMADZU SAID -2101) was used in (Ministry of Science and Technology) . The result particle size distribution is shown in Figure (1). The mean diameter for the zinc particles was (29.317) µm and the medium value was (31.686) µm.

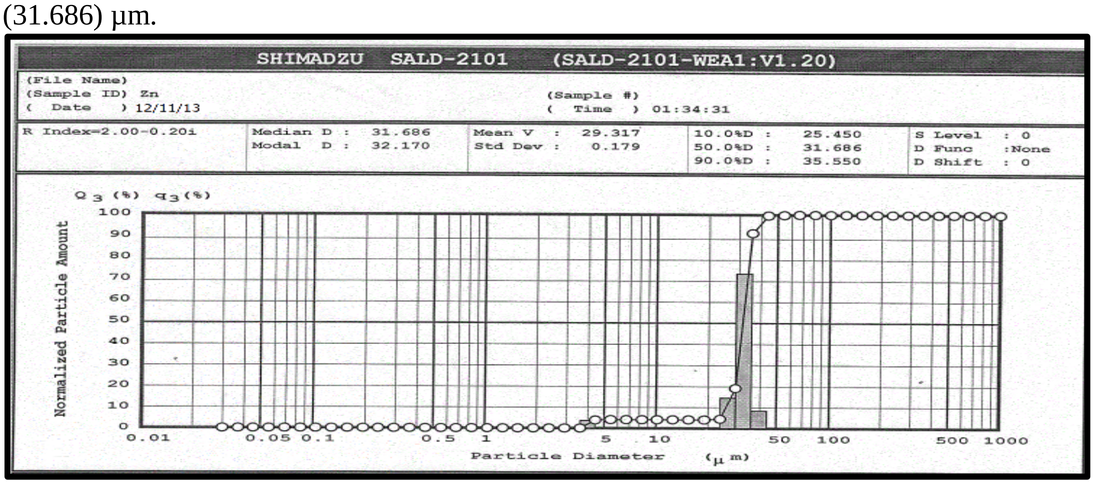


Figure (1) Particles size distribution of zinc powder

The sand used is Iraqi silica sand from Al-ardhimah region. it is chemical composition shown in Table (3) , the analysis was done in (geology survey & mining in ministry of industry & minerals in Baghdad), using atomic absorption spectrophotometer type, type Unicom England .

Table (3) The chemical composition of the Al-ardhimah sand.

Element	SiO_2 %	CaO %	MgO %	Al_2O_3 %	Fe_2O_3 %	SO_3 %	Cl %	Na_2O_3	K_2O%
Wt %	97.85	0.56	0.06	1.06	0.16	trace	0.04	0.12	0.15

The particle size of sand is in the range (100-250) µm that is done in the using sieves shaker (FRITSCH – Germany) .

Unsaturated polyester resin (UP) was used as coating materials, supplied by Saudi company SIR . it is a viscous liquid transparent at room temperature , It is one type of polymer thermally hardened, was mixed with hardener (supplied by the company itself , which is a methyl Ethylketon peroxide. The weight ratio between hardener and resin was 2gm of hardener per 100gm of the resin. The properties of the resin which was used are shown in Table (4). It was be cured at room temperature .

Table (4) The properties of unsaturated polyester resin according to product company.

Material name	Density gm /cm^3	Tensile strength MPa	Modulus of elasticity GPa	Percent Elongation El%	Fracture toughness MPa.√m	Specific heat J/Kg.K
polyester resin	1.2	41.4-8.7	2.06-4.11	< 2.6	0.6	710-910

The NBR and BR, ASTM D-2000 are obtained from (National Company for the tire industry in Najaf), the properties of NBR and BR are shown in Table (5)

Table (5) Mechanical and physical properties of NBR and BR.

material	Hardness	Tensile strength Mpa	Elongation%
NBR	20-95	1.379-24.13	350-650
BR	45-80	3.442-13.79	450-650

NBR: meaning Nitrile Butadiene Rubber
BR: meaning Butadiene Rubber

Samples preparation before coating: Surface preparation is the essential step for coating purpose, and as the first stage treatment of a substrate before the application of any coating, a low carbon steel pipe was prepared by cutting the pipe into samples according to inspection used and then cleaning by using hydrochloric acid (HCL) in 20% to remove the outer oxide layer (it is formed after annealing process at 800 º C for 2 hour) and to obtain a clean surface. Then, the samples were first washed by water, equaled the acid with hydroxide sodium (NaOH) and then washed with water again. The work surface of samples was abraded with silicon carbide abrasive paper down from 320 grit to

800 grit to obtain smooth surface, and then the samples rinsed with deionized water and degreased in acetone. Then, the coating was directly begun to avoid the samples from oxidation which encourages the failure of coats.

Sherardizing process

The sherardizing process was done by mixing zinc powder with sand at ratio (50:50) % the mixer was done for 15minutes period. The samples and mixture are placed inside containers together, then these containers are closed and placed inside furnace. The containers are left inside the furnace at 400 C° for different treatment times (15, 30, 60, 120, 240 min). Finally the coated samples are cooled to room temperature inside a switched off furnace.

Coating by Polymer

The coating process by polymeric blends was done before and after sherardizing process, The steps of polymeric blends coating was done by Solving the rubber material (BR or NBR) in the solvent (Toluene), solution is mixed with unsaturated polyester resin by different percentages ratio (0,5,10 and 15%wt) of BR or NBR .was poured into the glass mold to cover the samples at room temperature (27°C), And then left to solidify for 24 hr all the polymeric blends plated samples were then post cured in an electrical oven at 55 °C for 2hr.

Inspection and Tests

Micro Structure Examination:

has been accomplished on cross section of samples (low carbon steel and sherardized sample), micro structure of samples was observed with magnification range of 50X. This test done by use Optical microscope type (Reflected metallurgical microscope (XJL-101).

Coating Thickness Measurement:

The thickness of coating was measures after sherardizing process by using Automation machine (made in Germany by posiTector 6000 Company) . Measurement was performed by fixing the coated sample on a plane surface and applying the probe of the device on the sample and more than five readings of coating thickness were taken, and then the average value of these readings was adopted.

Hardness:

The Rockwell instrument type C has been used to measure the hardness for sherardized samples , the indentation load is (1471 N) for loading time 15 sec. the Rockwell hardness have been taken according to ASTM (D785) .

Adhesion Test:

Adhesive examination for coating polymer layer with low carbon steel and sherardizing low carbon steel was made by using tension machine (microcomputer controlled electronic universal testing machine (WDE-200E).

Procedure of adhesion test: After coating harden, A thick layer of polymer blends(1cm) was put on the surface of coated sample (sherardized) in once side. One side (polymer coated side) it was fixed on top of jaws tensile machine and the other side (sherardizing low carbon steel) fixed in bottom of jaws tensile machine the test was conducted at velocity of (1mm/min) at ambient temperature tension load was applied till the failure of the coated specimen and the failure force was obtained from stress-strain curve. Each sample was tested three times and the average results have been reported.

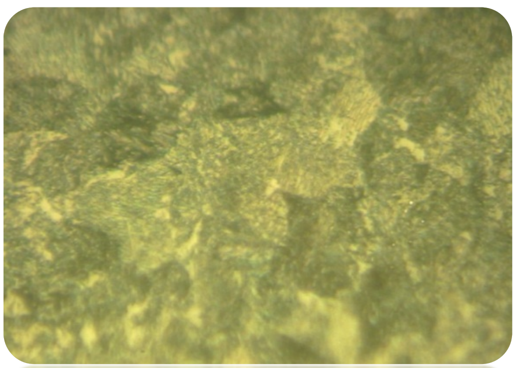
Scanning Electron Microscopy Inspection:

scanning electron microscope (SEM) model (Tescan VEGA-SB made in Belgium by TESCAN Company. With a field emission gun operating at 30 KV, was used to assess the microstructure of samples.

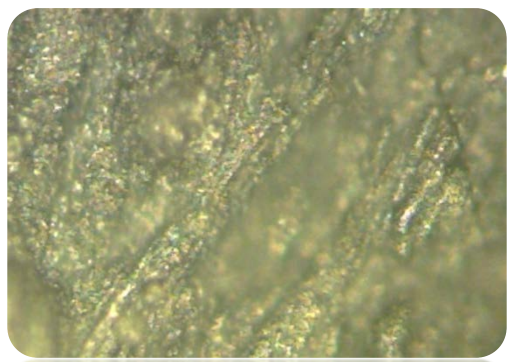
Result and discussion:

Microstructure:

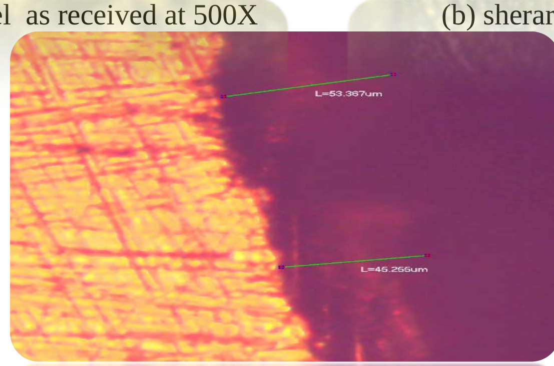
The Microstructure of low carbon steel and sherardizing coating shown in Figure (2 a, b and c). Microstructure of sherardizing coating Figure 2 (c) show the coating thickness is 50µm. Microstructure characterization of sherardizing coating do not show a distinct crystal structure (unlike hot dip galvanizing where coating is formed initially by solidification from a melt) [8].



(a) Low carbon steel as received at 500X



(b) sherardizing surface at 200X



(c) sherardizing thickness

Figure (2) Optical micrographs of as received (low carbon steel) sample and sherardizing coating. A: Low carbon steel as revised at 500X magnification, B: Sherardizing surface at200X magnification, C: Sherardizing thickness.

The coating thickness of sherardizing process increases with increased treatment time as shown in Figure (3) .The coating thickness increase from 21µm when treatment time 15 min to 52 µm when the time reach to 240 min at 400°C that due to diffusion of zinc powder increase as time coat increase that due to the required coating thickness is achieved by combination of time and temperature [8].

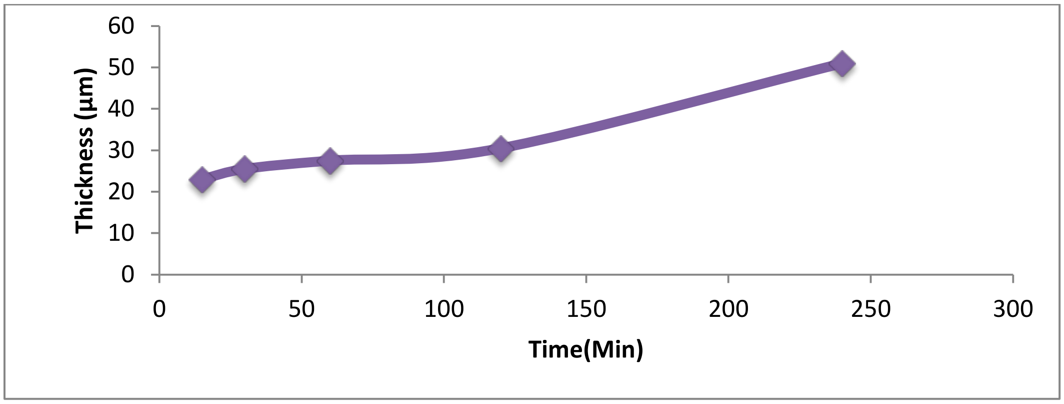


Figure (3) Sherardizing thickness as a function of treatment time.

Hardness

The effect of treatment time of sherardizing coating on Rockwell hardness values shown in Figure (4), hardness value of sherardizing coating surface increase as treatment time increase . Furthermore, it is noticed that the hardness value of low steel alloy (surface without coating) is smaller value (48.5) compared with sherardizing coating surface , that due to increase diffusion time of zinc powder and the sherardizing coating is harder than that of other zinc [9].

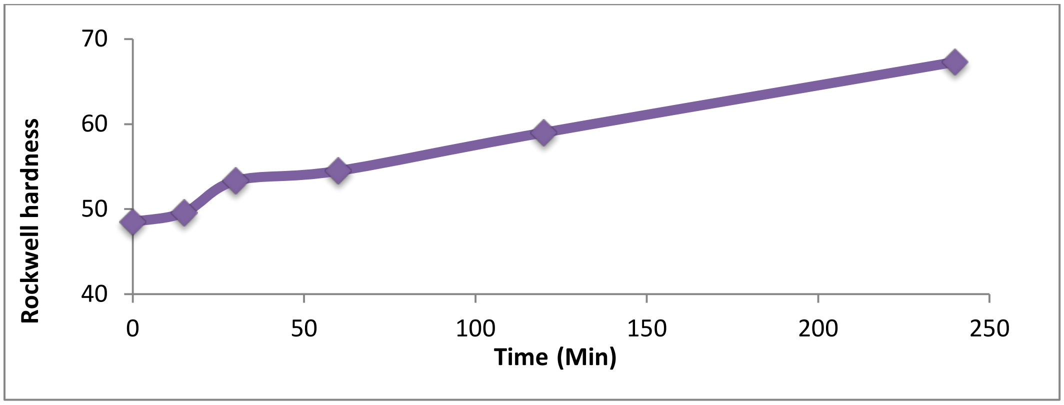


Figure (4) Hardness value of the sherardizing coating surface increases as treatment time increases.

Shore D hardness was investigated for both types of polymer blends (NBR: UP, BR:UP) . It was found that there are decreases in hardness values with increase in rubber content in polymer blend coating as shown in Figure (5). Furthermore, It was observed the hardness values of the polymer blend coating which contains nitrile butadiene rubber has higher hardness values compared with that contains butadiene rubber .This is due to the difference between both types of rubber in molecular chain structure [10].

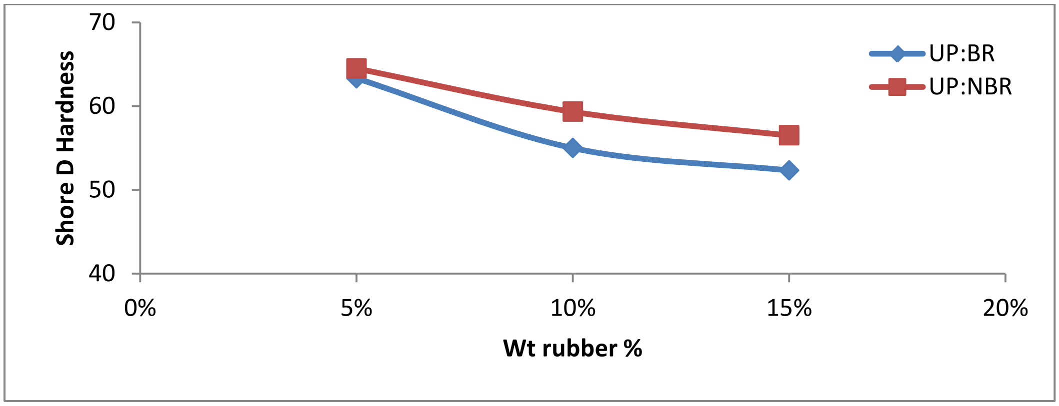


Figure (5) Hardness of the polymers blend coated low carbon steel as a function of BR or NBR content in the polymers blend (UP: rubber (BR or NBR)).

Adhesion force and Surface Roughness

Figures (6) and (7) Adhesion force between sherardizing coating low carbon steel and polymer blends coating (UP: NBR) and (UP: BR) respectively as a function the surface Roughness of sherardizing coating , it was shown that the adhesion force increases with increase surface roughness for all coating polymer blend and the adhesion force decreases with the increased NBR or BR content in the blend .As well as the coating layer prepared from 100%wt unsaturated polyester resin have higher adhesion force compared to the other coated by polymer blend layer , as well as from these figures and Figures (8 and 9) it was notice that the adhesion force of samples decrease as the rubber (NBR or BR) content in the blend of coating layer increase.

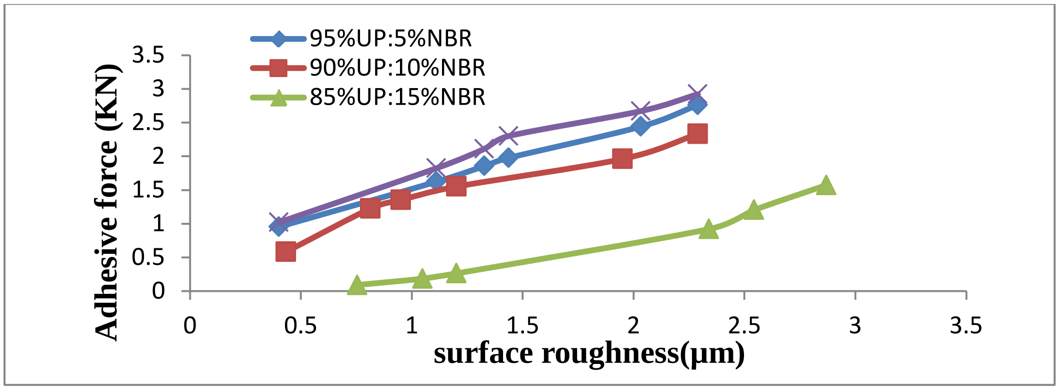


Figure (6) Adhesion force of sherardizing coating low carbon steel and polymer blends (UP:NBR) as a function of surface roughness and polymer blend content.

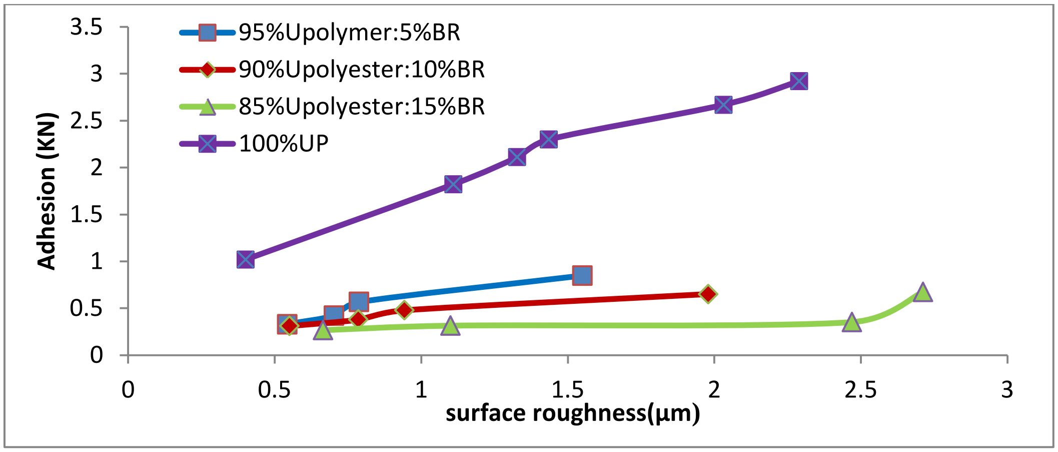


Figure (7) the effect of surface roughness of sherardizing coating on adhesion force for (UP: BR) blend and sherardizing coating low carbon steel.

The effect of type of polymer blends (UP:BR) and (UP:NBR) on adhesion force it was found from Figure (6) and (7) that the samples coated by polymer blends (UP:NBR) which have the same thickness (1.15 cm) having the higher values of adhesion force as compare to the other samples coated by polymers blend (UP:BR) and having the same thickness and that attributed to the nature of copolymer NBR which is product of copolymerization of acrylonitrile and butadiene, the high electronegativity of the nitrile group on every other carbon atom of the main chain of acrylonitrile exert mutual electrical repulsion, causing the molecular chains to be force extended, stiff and good abrasion resistance[11].

Figures (8) and (9) indicated adhesion force as a function of the surface roughness of (UP : NBR) and (UP : BR) blends with different rubber content respectively. It is shown that the adhesion force is decreases with increased rubber contents (NBR or BR). This is due to the nature molecular chain structure of butadiene rubber and copolymer nitrile butadiene rubber which having high flexibility structure compare to high cross-link of up thermosetting polymer. Layer so the high addition of rubber cause more increase in the flexibility of coating polymer to decrease the interfacial adhesion between layer coated and sherardized low carbon steel . And from these figures also it was found the adhesion force is decreases with increase in the surface roughness of all coating polymer blend layer and that related to the same causes previously mentioned[11].

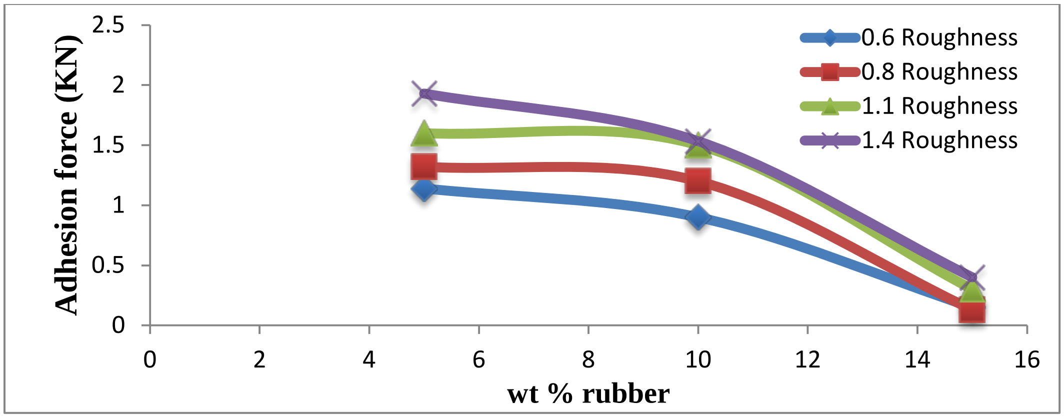


Figure (8) The effect of rubber content on adhesion force for different values of surface roughness (UP : NBR).

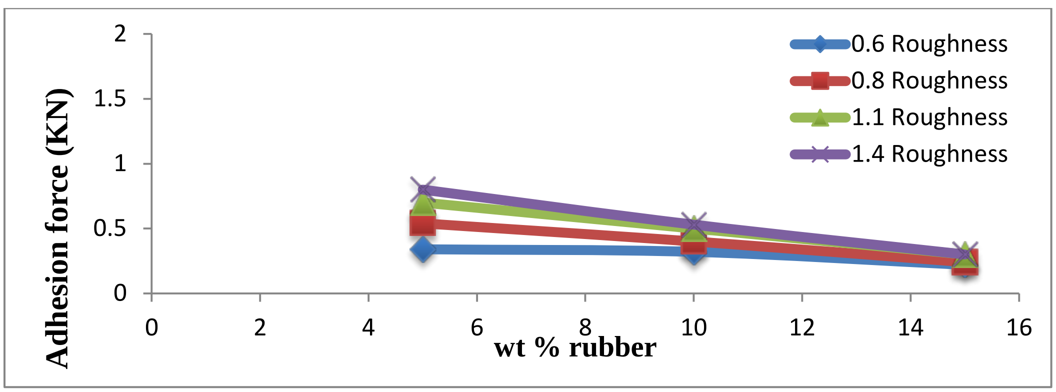


Figure (9) The effect of rubber content on adhesion force for blend (UP: BR) for different of surface roughness.

Bending Test results

From bending test and according to the relationship the flexural strength of sherardized low carbon steel coated with polymer blend layer (UP:NBR or UP:BR) exhibited in Figures (10 and 11) for flexural strength and the maximum shear stress respectively. This Figure indicates that the of sherardized low carbon steel coated with polymer blend layer (UP: NBR) has higher flexural and the maximum shear stress than (UP : BR), as well these figures show the addition of rubber material to the polymer blend coating layer increases the flexural strength and the maximum shear stress values of sherardized low carbon steel , except the samples which are coated with polymer blend (UP : BR) layer .The flexural strength and the maximum shear stress reaches a maximum value at BR 10%wt then sharply decreases with increased BR ratio to 15%wt. The above results may be related to the difference in the molecular chain structure of nitrile butadiene rubber and butadiene rubber because nitrile rubbers are copolymers of butadiene and acrylonitrile .The presence of the nitrile groups increase the degree of polarity in the main chains and the hydrogen bonding between adjacent chains. The nitrile groups provide good resistance to solvents and oils as well as improved abrasion and heat resistance [12] as well as the compatibility between component substances in polymer blend (Un saturated polyester , BR and NBR) which increases the interfacial adhesion [13].

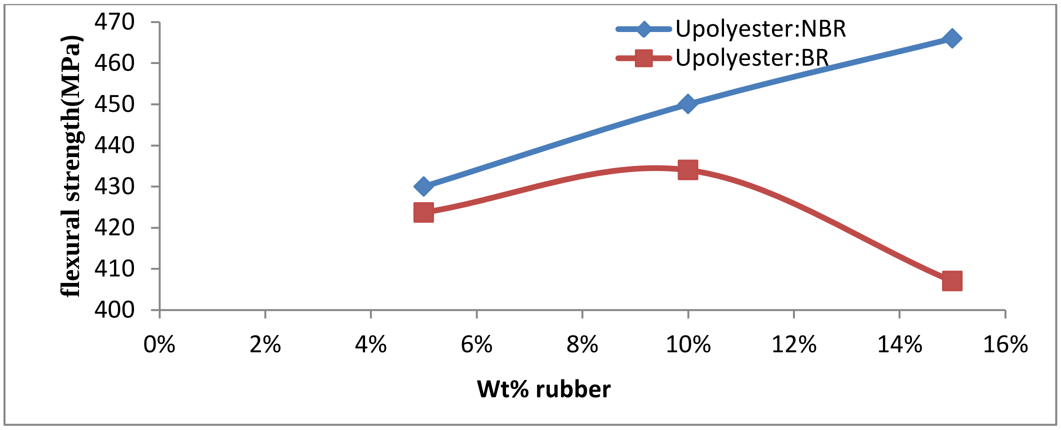


Figure (10) The flexural strength of sherardized low carbon steel as a function of BR or NBR content in the polymer blends coating layer.

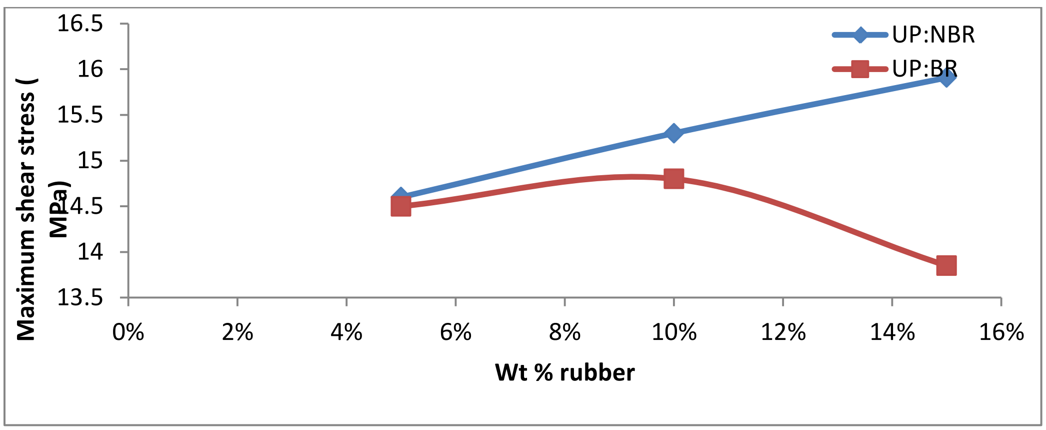


Figure (11) The maximum shear stress of sherardized low carbon steel as a function of BR or NBR content in the polymer blends coating layer.

Figure (12) shows the surface morphology of the sherardizing coating which showing a good distribution zinc powder. It can be seen from Figure (11a) free pores morphology of sherardizing coating, free pores which is assisted by the good mechanical properties as hardness as shown in Figure (2).

The surface morphology of polymer coated samples (10%BR: 90%UP) and (10%NBR:90%UP) are shown in Figure 13. The morphology show immiscible polymers blend which depends on the components, ratios, component melt viscosities and processing conditions. In most heterogeneous system, a morphology where by one phase distributed in another phase is observed [14].

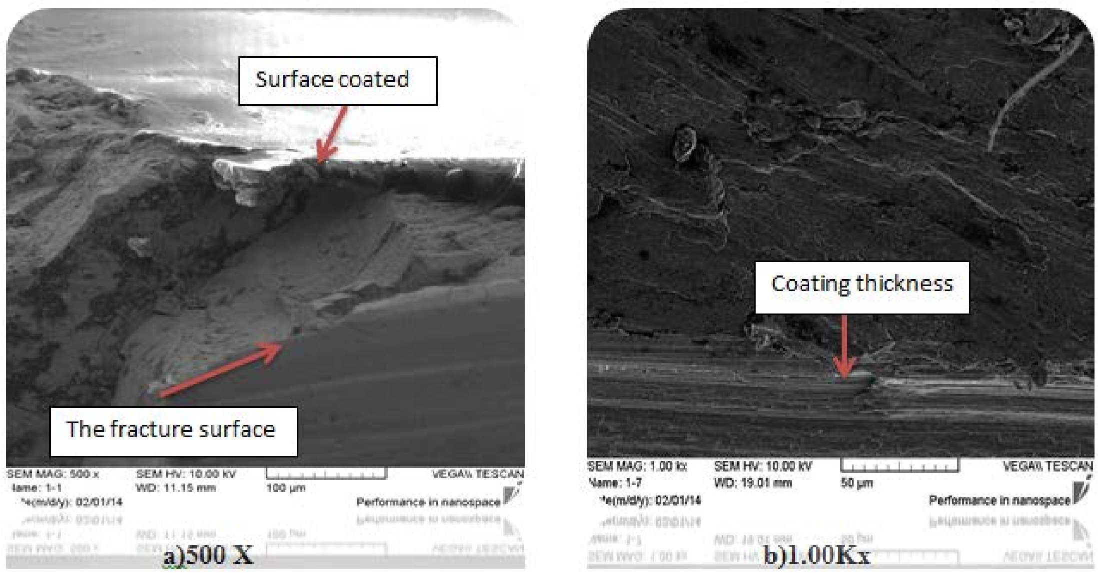


Figure (12): SEM of sherardizing coating at different magnifications.

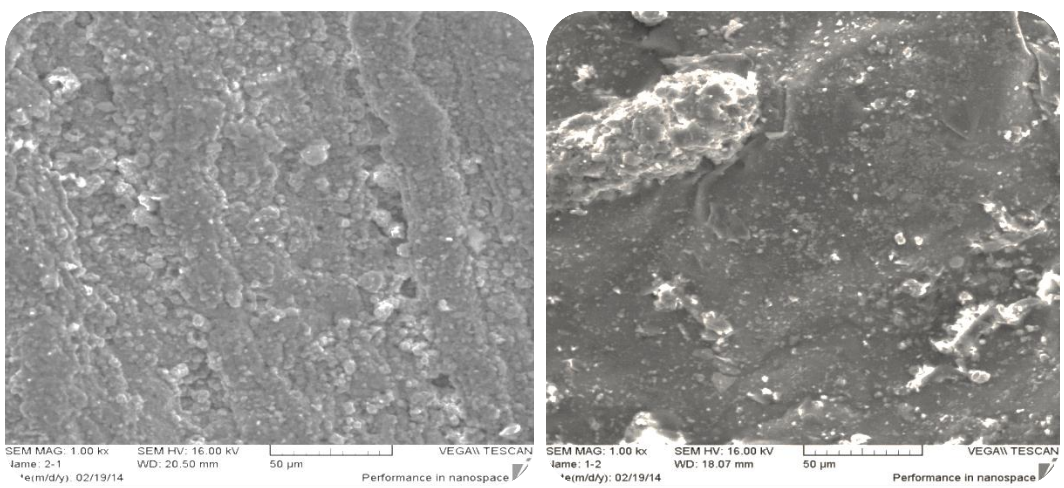


Figure (13) surface morphology of coating samples by polymer blends (a) (90%UP: 10%BR) and (b) (90%UP:10%NBR) at 1000X magnifications.

Conclusions

1.The sherardizing coating thickness increases with treatment time. The coating thickness increases from 21μm to 52 μm when treatment time increased from 15 min to 240 min.

2.Hardness values of sherardizing coating surface are increased with treatment time.

3.There are decrements in hardness values with the increment in rubber content in polymer blend coating .Furthermore, hardness values of the polymer blend coating which contains nitrile butadiene rubber (UP:NBR) has higher values than that containing butadiene rubber (UP:BR).

4.Adhesive force between sherardizing coating of low carbon steel and polymer blends are increased with increment of surface roughness for all coating polymer blends and decreased with the increased NBR or BR contents in the blend.

5.Sherardized low carbon steel coated with polymer blends layer (UP: NBR) has higher flexural and maximum shear stress than (UP : BR). Addition of rubber material to the polymer blends coating layer increases the flexural strength and the maximum shear stress values of sherardized low carbon steel , except the samples which are coated with polymer blend (UP : BR) layer.

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