Preparing and Study the effects of Composite Coatings in Protection of Oil Pipes from the Risk of Corrosion that resulting from Associated water with Petroleum Products

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Abstract. In order to inhibit the metallic corrosion in the oil pipelines, the protection method with composite coating of Unsaturated polyester and reinforced by Caolin at weight percentage (20%) was studied. Where, the work samples were classified into two groups according to internal composite coatings layers for all group of these samples. The first group is nitrocellulose coating reinforced by nano and Micro Powder of Mgo. The second group is sodium silicate coating reinforced by nano powder of Mgo. The following weight percentages (0%, 1%, 3% and 5%) were adopted as reinforcement ratios for nano powders, as well as the weight percentages (0%, 3%, 5% and 7%) as reinforcement ratios for micro powders. Tribology properties and Electrochemical Corrosion Resistance by Polarization method (Tafel) and Adhesion Strength were studied. The results showed an improvement in the corrosion resistance of protected steel by coatings compare with uncoated steel, as well as improvement in mechanical properties and adhesion strength of composite coatings.

1-Introduction.
The problem of corrosion has received great attention from many researchers in order to arrive at effective solutions to reduce this problem. This is evident to us through research completed and worked to find appropriate solutions to reduce the problem of corrosion and the effects of it through a number of modern engineering methods that ensure addressing the problem at the lowest cost and time of possible scenarios. The risk of corrosion lies in the diversity of its forms and the multiplicity of its causes. Therefore, there are many ways and means of protecting it [1]. One of the most common ways of protecting the pipes from the risk of corrosion, which was adopted by many researchers is the protection method of coating as one of the effective methods of protection because of the distinct characteristics in the protection of steel pipes from corrosion. One of the most common ways of protecting the pipes from the risk of corrosion, which was adopted by many researchers is the protection method of coating as one of the effective methods of protection because of the distinct properties in the protection of steel pipes from corrosion.
2. Experimental part

2.1 The stage of the preparation of steel samples
Steel pipe was cut to two dimensions (15×15×3mm) and (30×30×3mm). After the cutting process, solid carbonization was done on the samples where the samples immersed in (100g coke + 4g barium carbonate). The carbonization process was done at (1.5hr) and (950°C), and then the samples coated with iron oxide as a corrosion resistant layer, and added (0.25g) of Hydrazine hydrate per (100g) of iron oxide coating in order to remove the oxygen from it. See the ‘figure 1’ and ‘figure 2’.

2.2 Coating by reinforced Sodium silicate
Group of the samples coated with a layer of sodium silicate, reinforced by magnesium oxide Nano powder. It was reinforced by (0%, 1%, 3%, and 5%). The mixture was mixed into a glass beaker by Hot Plate Stirrer, then the sodium Silicate poured on the samples and left to reach to the case of full dryness. See ‘figure 3’.

2.2 Coating by reinforced Nitrocellulose
Another Group of samples coated with Nitrocellulose reinforced by magnesium oxide Nano powder with percentages (0%, 1%, 3%, and 5%), and also reinforcement with magnesium oxide Micro powder with percentages (0%, 3%, 5%, and 7%), and used (aluminum citrate powder) by percentage (0.75g) to disperse the reinforcement powders. The coatings were mixed by use an electrical mixer type (RW-20), the samples coated by use the hand brush and left to dry. Notes ‘figure 4’.
2.3 Coating with reinforced Unsaturated Polyester

The composite polyester prepared by mixing the polyester with kaolin powder at different weight percentages (5%, 10%, 15%, 20%, and 25%) and the samples coated by using the hand brush. Notes: 'figure 5'

3. Results and discussion

3.1 Hardness Test

The results of the surface hardness test in Figure 6 and Table 1 for the composite coatings (Sodium silicate and Nitro cellulose) showed an improvement in the surface hardness values with increasing the ratio of (Nano/Micro) powder. When increasing the weight ratio of additives, this increase led to raising the hardness of sodium silicate from 68.5NO in the case of non-reinforced silicates up to its highest value 71.1NO, at weight percentage (5%). In the case of Nitro cellulose, we notice an increase in the hardness values in both of (nano /micro) powders, where the highest hardness value in the nano-reinforcement was recorded at 3% which is 87.1NO, and the value of hardness with the micro-reinforcement was recorded at 5% is 87.5NO, Compared with unreinforced case which recorded the value 84.6NO. The high surface hardness due to the reinforcement particles that improve mechanical properties of materials composite, This is consistent with Saeid and Rafiq [2], and the reinforcement particles are working on impeding dislocations movement, this confirmed by the researcher Higgins [3].
Figure 6. Effect of ratio of additives on surface hardness for prepared composite coatings.

Table 1. Hardness values for composite coatings at the best weight percentages.

| Types of composite coatings | Hardness NO. |
|-----------------------------|--------------|
| Sodium Silicate             |              |
| Non-reinforcement           | 68           |
| Reinforced with 5% MgO.Nano | 71           |
| Nitrocellulose              |              |
| Non-reinforcement           | 84.6         |
| Reinforced with 3% MgO.Nano | 87.1         |
| Reinforced with 5% MgO.Micro| 87.5         |

3.2. Wear rate test
The results of the wear rate test, Figure 7 and Table 2 showed a decrease in the wear rate of the composite coatings. The wear rate of the sodium silicate is lower compared with non-reinforced. The wear rate decreased from $7.7282 \times 10^{-6} \text{gm/cm}$ in the case of the non-reinforced sodium silicate to $0.4246 \times 10^{-6} \text{gm/cm}$ when reinforced by 5%, where the particles of magnesia which has high hardness acts to deform the matrix material and improve the toughness of the composite body. This is consistent with Samal and Bal[4]. The wear rate decreased with the increase of weight percentages reinforcement of (Nano/Micro) the magnesium for Nitrocellulose coating, where the wear rate was $5.0955 \times 10^{-6} \text{gm/cm}$ before reinforcement, and then started to decrease further to its optimum value $0.6794 \times 10^{-6} \text{gm/cm}$ at 3% the nano-reinforced and $1.1040 \times 10^{-6} \text{gm/cm}$ at 5% of the micro-reinforced. From Figure 8 shows the superiority of reinforcement by nano-particles on reinforcement by micro-particles in improve the tribological properties because of the grain size of the nano powders that allow to particles to enter inside the polymeric chains, that led to increase in compact and cohesion of the composite material. Consequently, the wear rate become lower. This confirms the interpretation of the researcher Praveen et al[5].
Figure 7. Effect of change in the ratio of additives on the wear rate of the composite coatings at fixed operating conditions.

Table 2. Wear rate for composite coatings at the best weight percentages.

| Types of composite coatings | Wear rate × 10⁻⁶ |
|----------------------------|------------------|
| Sodium silicate            |                  |
| Non-reinforcement          | 7.7282           |
| Reinforced with 5%MgO.Nano | 0.4246           |
| Nitrocellulose             |                  |
| Non-reinforcement          | 5.0955           |
| Reinforced with 3%MgO.Nano | 0.6794           |
| Reinforced with 5%MgO.Micro| 1.1040           |

3.3 The Surface hardness test of the reinforced polyester coating layer
From Figure 8 and Table 3 show the improvement in the surface hardness values of the Unsaturated polyester coating, and which reinforced by kaolin particles. Where The surface hardness increases with the increase of the reinforcement ratios to reach to the highest hardness value at 20%, which was 76.8NO. Compared with its value for unsaturated polyester which was 76.8NO. Here, show the effect of additive in the participation of the matrix to bear the stresses placed on the surface of composite. This based on the interpretation of the researcher Higgins [3].
**Figure 8.** Effect of the percentages of additives (kaolin) on the surface hardness of the unsaturated polyester coating.

| Weight percentages of kaolin | Surface hardness NO. (Shore-D) |
|------------------------------|-------------------------------|
| 0%                           | 76.8                          |
| 5%                           | 81.6                          |
| 10%                          | 84.1                          |
| 15%                          | 85.1                          |
| 20%                          | 85.7                          |

**Table 3.** The values of Surface hardness for unsaturated polyester composite reinforced with different percentages of kaolin.

3.4 The Wear rate Test of reinforced Unsaturated Polyester layer

The results of the wear test for kaolin-reinforced polyester with different reinforcement ratios, showed a significant decrease in wear rate with increase the weight percentages of kaolin as shown in Figure 9 and Table 4. The wear rate was lowest at 20% Which is 0.545*10^{-7} gm/cm and represents the lowest value compared with the value of wear at the unreinforced polyester, which is recorded at 3.639*10^{-7} gm/cm. This is consistent with the researcher Oleiwi [6]. This decrease in the value of wear is due to the role played by the particles of reinforcement in reducing the Sliding Contact between the surfaces of the objects, as described by d'Almeida et al [7]. From Figure 9 We note an increase in wear rate at percentage (25%) of kaolin because of the weakness in toughness and cohesion of the composite due to the increase of the reinforcement percentages above the required limit, that's agrees with the researcher AL-Abbasi [8].

**Figure 9.** Effect of the change in the percentages of additives on the wear rate of composite polyester.

**Table 4.** The wear rate of reinforced unsaturated polyester by different percentages of kaolin.

| Weight percentages of kaolin | Wear rate×10^{-7} |
|------------------------------|--------------------|
| 0%                           | 3.639              |
| 5%                           | 2.001              |
| 10%                          | 1.637              |
| 15%                          | 0.909              |
| 20%                          | 0.545              |
| 25%                          | 1.637              |
3.5 Electrochemical Corrosion Test after coating with composite coatings layer

The results obtained from Figure 10 and Table 5 of the electrochemical corrosion test (Tafel) show a change in the density of the corrosion current and the corrosion potential of the steel samples protected by layers of composite coatings. Where, the values of the corrosion currents and the corrosion potentials of all the coated samples decreased to be more nobleness compared with their value of the uncoated steel sample. The practical results showed improvement in the values of protection against corrosion caused by the associated water with the oil product, and this reflects the important role played by those composite layers, specifically the final layer of unsaturated polyester as a stable protection layer with high resistance to degradation in the aqueous medium. This agrees with the researcher's opinion Thair et al. [9].

![Figure 10. Change of the density of the corrosion currents for composite coatings.](image)

**Table 5.** Change of the density of the corrosion currents for composite coatings.

| Types of composite coatings                                      | I_Corr µA/cm² | V_Corr (mv) |
|-----------------------------------------------------------------|---------------|-------------|
| St.37                                                           | 5.06          | -569        |
| (Na₂SiO₃) + (polyester+20%clay)                                 | 0.29576       | 155.8 -     |
| (Na₂SiO₃+5%MgO.Nano)+ (polyester+20%clay)                      | 0.01075       | -264.3      |
| (polyester+20% clay)) +N.C.                                     | 0.00460       | -20.5       |
| 3%MgO.Nano)+(polyester+20%clay)+N.C(                            | 0.14345       | -33.7       |
| (N.C+ 5%MgO.Micro)+(polyester+20%Clay)                         | 0.00870       | -218.2      |

3.6 Adhesion strength test

From the results that obtained from Figure 11 and Table 6 of adhesion strength of the coatings, show the improvement in adhesion strength where recorded adhesion strength in the case of (pure sodium silicate + reinforced polyester) 83Pa, and reinforced sodium silicate with 5% of magnesium oxide nano particles, showed a high adhesion strength 117 Pa. As for the other model of composite coatings (pure Nitrocellulose+ reinforced polyester), recorded the value of adhesion strength 626 P. and also when reinforcing Nitrocellulose with 3% of (MgO.nano+Reinforced polyester or 5% of (MgO.micro +Reinforced polyester) where adhesion strength recorded the following values 523Pa and 482Pa respectively, but these values are low compared to their previous value (the case of the non-reinforced coating layers). The adhesion strength is attributed to several reasons, including strength of the mechanical interlock between the different coating layers on one hand, and the
coating layers and the steel surface on the other hand, as well as the forces of the Vander Wals between the different coating layers, as described by Abbas [10].

**Figure 11.** Adhesive strength values for composite coatings.

**Table 6.** Adhesive strength values for composite coatings.

| Types of composite coatings                                      | (Pa) Adhesive strength |
|------------------------------------------------------------------|------------------------|
| (Na2SiO3)+ (Polyester+20%Clay)                                   | 83                     |
| (Na2SiO3+5%MgO.Nano)+ (Polyester+20% Clay)                       | 117                    |
| (N.C) + (polyester+20%Clay)                                      | 626                    |
| (N.C+3%MgO.Nano)+ (polyester+20%Clay)                            | 523                    |
| (N.C+5%MgO.µ)+ (polyester+20%Clay)                               | 482                    |

4- Conclusions
The sliding wear resistance, as well as surface hardness are improving with the increase of additives for all composite coating. The adhesion strength of the composite coatings (reinforced Sodium silicate + reinforced Polyester) increases more than in the case of unreinforced coating layers, while the adhesion strength of the composite coatings (reinforced nitrocellulose + reinforced polyester) decreases more than unreinforced coatings. The electrochemical corrosion test of the coated samples showed the effects of these coatings on the protection of steel from the corrosion risk of associated water with the oil products when compared these results with result of steel without protection. And from results obtained we note the excellence of protection with (reinforced nitrocellulose + reinforced polyester) more than (reinforced Sodium silicate + reinforced Polyester).

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