Physical Properties of Low Carbon Steel Coated with Iraqi Clay-Reinforced Epoxy Composites

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Coatings with polymeric composite materials are one of the most used methods in recent times among other methods, to provide a physical barrier that prevents the metal from direct contact with the environment, Examples of this are epoxy/clay composites because they have excellent chemical resistance, high adhesion to the substrate In this research, polymeric composites reinforcement by local clays were prepared as insulating coatings for chemical corrosion. using a low carbon steel alloy coated with materials consisting of epoxy as a matrix material and reinforcement by clay particles (MK and M) by weight percentage of 2, 4, 6, 8, and 10 wt.%. The result of the mechanical properties tests of the composite epoxy coating in the microhardness was (160.38 MPa) at a ratio of 8 wt.%. Also, the wear rate and corrosion decreased at 6 wt.%. The adhesion strength improved after reinforcement of the epoxy coating with particles, and its highest value was 2.26165 MPa at 4 wt.% for (M-epoxy) composite coating

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1. Introduction

Corrosion is one of the major problems faced by many industries such as marine, aviation, automobile and petrochemical industries. This causes economic problems all over the world. Economic losses may exceed 100$ million annually. In addition to environmental contamination (such as air, water, and soil, as well as toxic gases arising from fuel combustion) [1,2], (H_2S, CO_2) and various salts (Ca^+, K^+, Cl_2, and Na^+) [3]. Therefore, many methods have been developed to protect the barrier from corrosion, such as cathodic protection, anodic protection and protection with polymeric coatings [1,4]. Epoxy resin has interesting mechanical properties, such as high modulus of elasticity, good adhesion strength, and creep resistance. Thus, epoxy coating is a good barrier to protect against the corrosion for many corrosive environments; however, when it is exposed to an aggressive environment, it will corrode for long periods and may cause penetration of corrosive electrons containing oxygen and water from the coating to the substrate. Therefore, inorganic fillers are considered as one of the methods used in the corrosion resistance of organic coatings, as it was found that small particles improve the properties of the coating [4-6]. Clay particles are widely used because of the plate's shape and aspect ratio, as well as unique properties, such as mechanical properties, good thermal stability and low cost. These properties provide great attraction in polymer science and technology over the commercialization of clays [7]. Olivein et al. studied the effect of adding alumina particles to epoxy coatings on the adhesion and mechanical and chemical corrosion properties of undersea oil and gas production systems. They reported an increase in the rate of wear and adhesion after adding Al_2O_3 particles by 30% and 50%, as well as a decrease in the corrosion rate [8]. Tasew and Thotdri prepared an epoxy coating with metakaolin clay particles to improve the corrosion resistance of galvanized carbon. The results showed a decrease in water absorption and acid resistance at a percentage of 7% reinforcement, as well as an improvement in thermal stability at 5% [1]. Abenojar et al. studied the effect of adding silica (SiO_2) particles to improve the mechanical and thermal properties and corrosion resistance [9]. Chen et al. investigated the corrosion resistance of epoxy coatings enhanced with non-covalent functional graphene nanoparticles. The results revealed that adding 3.5% graphene nanoparticles considerably increased the corrosion resistance [10]. Mathiazhagan et al. prepared an epoxy coating containing nanotexten particles to improve the chemical corrosion resistance of the copper-zinc alloy. The results depicted that the copper samples covered with epoxy/WO_3 are corrosion resistant [2]. Conradi et al. applied an epoxy coating containing 2% homogenous silica particles with a thickness of 50 µm on the austenitic stainless steel type ALS316L. The results revealed an increase in hardness and surface roughness, an improvement in the coating's microstructure, and a considerable drop in corrosion rate [12,13].

The current work investigates how adding particles (MK, M) to epoxy composite coatings can enhance their mechanical qualities while utilizing the spray painting method.

2. Experimental Part

Epoxy resin, a low-density liquid produced by Sikadur (type E52) with methphenylene diamine (MPDA) as a hardener and a 2:1 mixing ratio, was utilized as the matrix material. Reinforcement materials include metakaolin (M.K.), which is a pozzolanic material made in a lab from Iraqi kaolin clay ($Al_2O_3.2SiO_2.2H_2O$), which is burned for three hours at 750 °C in an electric furnace as shown in Fig. (1). Also, mullite (M) was used as a reinforcement material. This aluminosilicate was produced in a lab using Iraqi kaolin clay ($Al_2SiO_5(OH)_4$) and heated to 1050 °C for three hours in an electric oven. To verify the conversion of kaolin clay into mate kaolin and mullite as shown in Fig. (2). The x-ray diffraction analysis was used as in shown figures (3) and (4).

Fig. (1) Meatakoline clay

Fig. (2) Mullite clay

Table (1) displays the chemical composition of low carbon steel, which served as the substrate for the coating procedure. Using a cutting tool, specimens with a 1.2 mm thickness were sliced into two different sizes (5x5 cm and 1x5 cm) in accordance with the necessary inspections.

Two types of composite coatings were prepared in addition to pure epoxy coated. The epoxy resin was prepared by preheating at a temperature of 60°C to reduce the viscosity so that it is easy for the clay particles to disperse. Metakaolin (MK) and Mullite (M) clay particles in weight percentages (0, 2, 4, 6, 8, and 10 wt.%) were added to the epoxy resin and mixed by a magnetic stirrer device for 60 min, then, by ultrasonic for 60 min for further dispersion and homogeneity of the clay particles in epoxy. The hardener was added to the mixture (ratio 2:1 of resin to hardener) based on the data sheet and factory specifications and mixed for 5 min using a magnetic stirrer. The obtained mixture composites were applied as coating with thickness for 1μm by using a paint spry gun.

Table (1) Chemical composition of low carbon steel

Elements	C%	Si%	Mn%	P%	S%	Cr%
Carbon steel wt%	0.0587	0.0069	0.171	0.0077	0.0078	0.0173

Elements	Mo%	Ni%	Al%	Co%	Cu%	Fe%
Carbon steel wt%	<0.0020	0.0237	0.0266	<0.0015	0.0057	Bal.

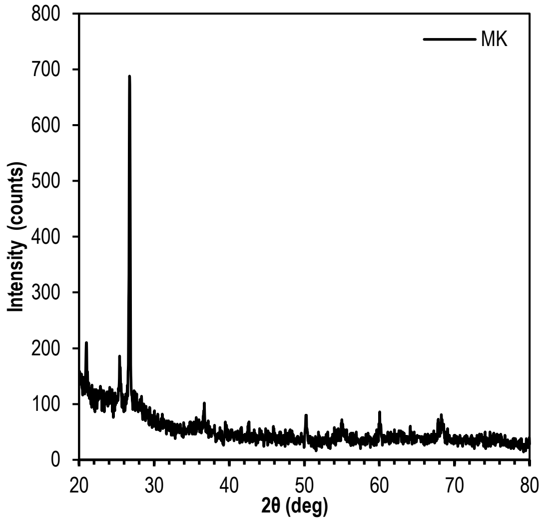

Fig. (3) XRD of Meatakoline clay

Fourier-transform infrared spectrum (FTIR) studies were carried out using a conducted using a spectrometer (I.R. Prestige-21). Microhardness of the coating was tested using a Vickers microhardness tester (type HVS-1000 MTI) using applied load 25 g and a time of 15 s. The adhesion pull-off test was used to evaluate the adhesion strength of epoxy specimen using a tensile testing machine according to the standard (ASTM-D638).

To determine the wear rate, a wear device was used based on the principle of a (ball on a disc) and according to the standard specification (ASTM G99-95a), the applied load was 300 g and the time was one minute. The wear rate was calculated from the following equation [14]

$$\textit{Wear rate}\ (g/cm) = \Delta W/SD \qquad (1)$$

where ΔW is the weight loss, SD is the sliding distance

Electrochemical corrosion was examined by means of a device (potentiostat/galvanostat) (DY2323) made by Digi-ivy, Inc. The corrosion resistance was determined after immersing the specimen in 3.5% NaCl solution as a medium. The experimental data were recorded using the Tafel extrapolation method

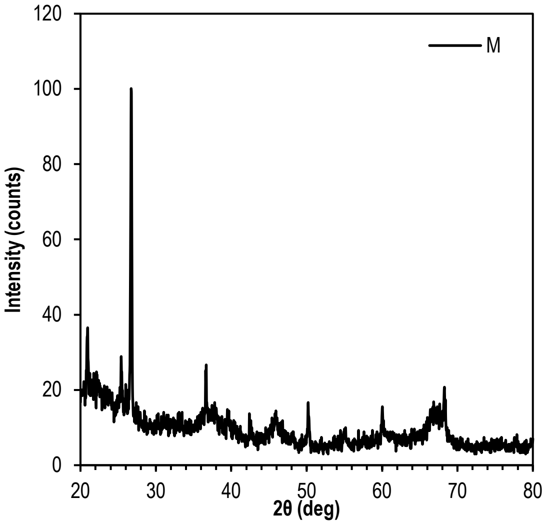

Fig. (4) XRD of Mullit clay

3. Results and Discussion

The absorption spectra for both pure epoxy and epoxy composite coatings (MK, M) is displayed in figures (5-7). Three bonds can be found in pure epoxy at the following locations: bonds aliphatic C-H at 2927.37 and 2996.15 cm^{-1}, the vibration bond C=O at 1647.21, 1606.70, 1508.33, and 1462.97 cm^{-1}, the bond vibration C-O at 12946.02, 1182.36, 1112.93, 1037.70, and 829.39 cm^{-1}, and the bending bond C-H at 761.88 and 700.16 cm^{-1}. A shifting occurred when the pure epoxy coating was mixed with MK and M clay particles. Due to the formation of a bending bond (CH_2) upon the addition of clay to the epoxy matrix, all of this evidence is adequate to show the presence of a chemical bond with clay (MK, M) and the epoxy matrix [15,16].

The results in Fig. (8) showed the addition of MK clay particles to the epoxy coating rise the microhardness compared to the pure epoxy coating while the addition of MK and M clay particle rise microhardness by about 60-160 MPa. As weight percentage of clay particles increase for both (M, MK) in the epoxy composite form a more cross-linking between epoxy and clay particles that while distributed among the epoxy chains which led to an increase in the microhardness as the clay weight percentage increase microhardness of the (Epoxy/M) composite coating was higher than that of the (Epoxy/MK) composite coating, because the mullite clay particles had a high compressive property and a stable structural composite compared to the MK clay particles [11,14,17].

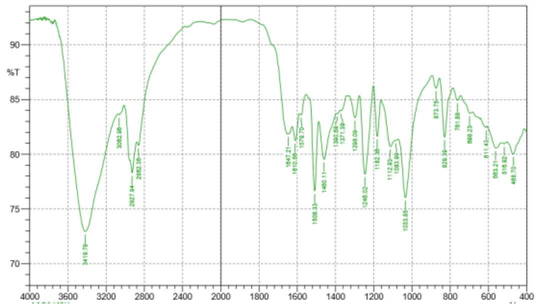

Fig. (5) FTIR spectrum of (epoxy/MK)

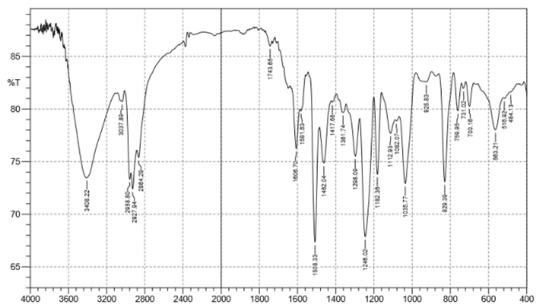

Fig. (6) FTIR spectrum of (epoxy/M)

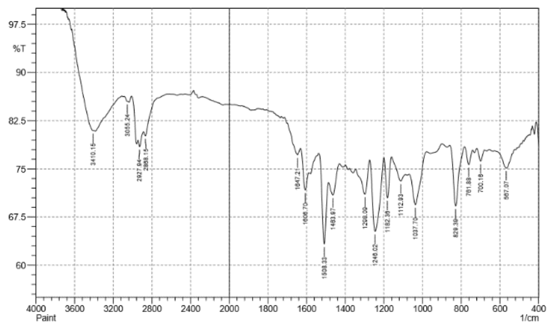

Fig. (7) FTIR spectrum of epoxy

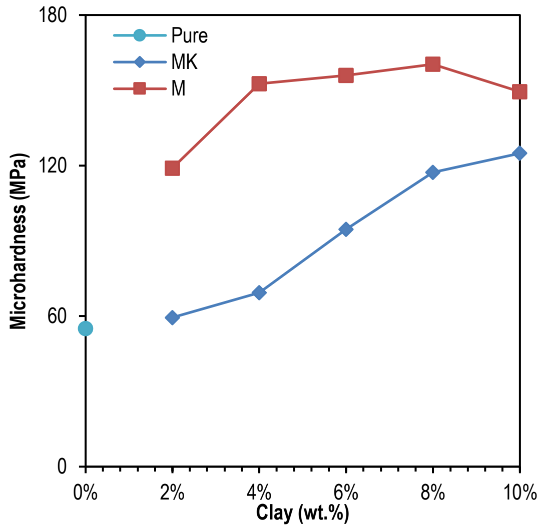

Fig. (8) Effect of adding MK and M clay particles on the microhardness of epoxy coatings

Since epoxy adheres to metal substrates well, it supports the coating domain that enhances the characteristics, both chemically and mechanically. When compared to a pure epoxy coating, the adhesion strength of the coating is enhanced by the addition of clay particles, as figure (9) illustrates. Low reinforcement ratio (2 and 4 wt.%) of both MK and M clay particles; respectively, adhesion strength reduced for both MK and M clay particles as the amount of reinforcement clay particles is increased (6, 8, 10 wt.%). The uniform distribution of clay particles in the matrix improves bonding within the epoxy matrix, which leads to an increase in adhesion strength at low reinforcement ratios (2 and 4 wt.%). Although the adhesion strength decreases at large clay particle aggregation, the epoxy matrix acts as a barrier and reduces bonding, therefore the failure change to cohesion mode. Furthermore, the reinforcement with M clay particles increases the adhesion strength when compared to the MK clay particularly about 2.46165 MPa because mullite clay has better bonding with epoxy than clay (MK) [17] as indicated in table (2). The same situation was observed for the reinforcement with (M) clay particles but with higher adhesion strength as compared with MK reinforcement.

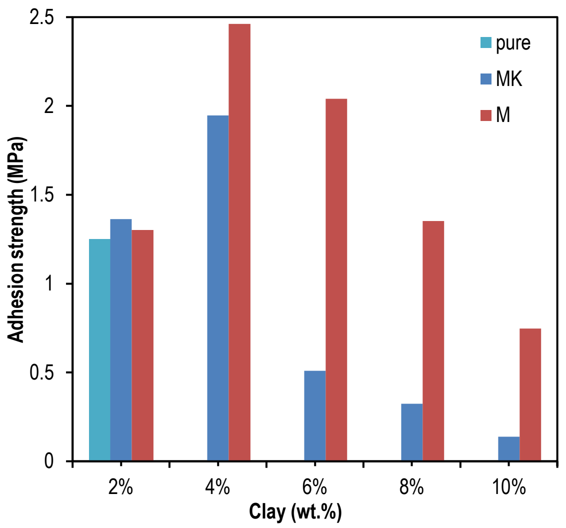

Fig. (9) The adhesion strength of the epoxy coating reinforced with MK and M clay particles

The result showed a decrease in wear rate of composite coating as the weight percentage of addition clay particles (MK and M) increase up to 6 wt.% then the wear rate increase as weight percentage addition clay particles increase. The reinforcement with M clay particle had a lower wear rate than to composite coating reinforce with MK clay particle which (Epoxy/MK) had high wear rate when compared to pure epoxy. The decrease in wear rate of epoxy composite coating reinforce with low eight percentage of M clay particle due to increase in the hardness of composite coating as find in hardness result as shown in Fig. (10).

Table (2) The adhesion strength of the epoxy coating reinforced with Metakaoline clay once and Mullite once again, monitoring notes

Sample	Adhesion (MPa)	Notes
Epoxy (puer)	125.051	A
Epoxy + Mk2%	136.29	B
Epo xy + Mk4%	264.69	A-B
Epoxy + Mk6%	50.908	B-C
Epoxy + Mk8%	32.38	B
Epoxy + Mk10%	13.85	B-C
Epoxy + M2%	30.126	A
Epoxy + M4%	246.165	A
Epoxy + M6%	203.956	C-B
Epoxy + M8%	135.165	C-A
Epoxy + M10%	074.751	C

A: Adhesion, B: Adhesive, and C: Cohesive

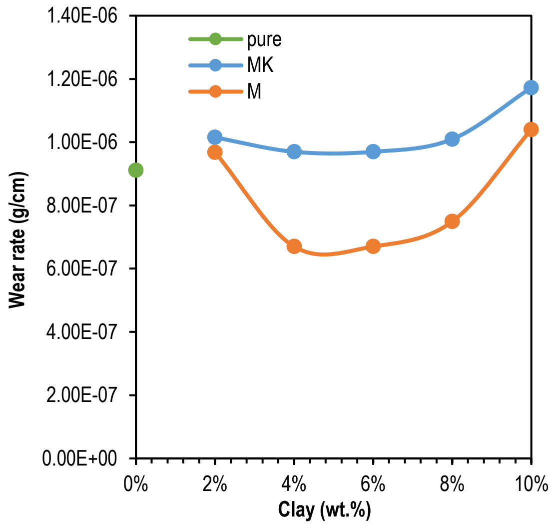

Fig. (10) Effect of adding Mk and M clay particles on the wear resistance rate of epoxy coating clay particles

While reducing in the wear rate of composite coating as the reinforcement increase may be attributed to lowering the bond between epoxy and clay particle that result from aggregation of clay particle which lead to lowering the bond between the epoxy polymer as shown in FE-SEM image (figures 11a and b) that lead to the removal of the particles from the surface, as in the adhesion strength test [19,20]. The same situation was noted for the reinforcement with the M clay particles, but with a lower wear rate as compared with Mk, because M has a high friction resistance [16].

Effect of adding Mk and M clay particles on the corrosion rate of epoxy coating is depicted in Fig. (12). Figures (13) and (14) reveal the polarization curves of the coated and uncoated low carbon steel samples.

It was also noted that the uncoated sample gave a higher corrosion rate than the pure epoxy coated sample as displayed as shown in Fig. (12) when the MK clay particles were added to the pure epoxy. A decrease in the corrosion rate was noticed due to the high electrical resistance of the composite coating at low percentages, because the addition of clay particles reduces the defects of the epoxy as well as effectively increases the length of the paths for the diffusion of water and oxygen, and thus the permeability decreases [2,21]. However, it started to rise at higher percentage due to the slurry agglomeration. The same situation was seen for the reinforcement with the M clay particles but with a lower corrosion rate as compared with the MK, because of the chemical stability of mullite clay and its corrosion resistance [16]. The corrosion rate and electric resistance of pure epoxy and after coating with the reinforcements MK and M clay particles are evinced in table (3).

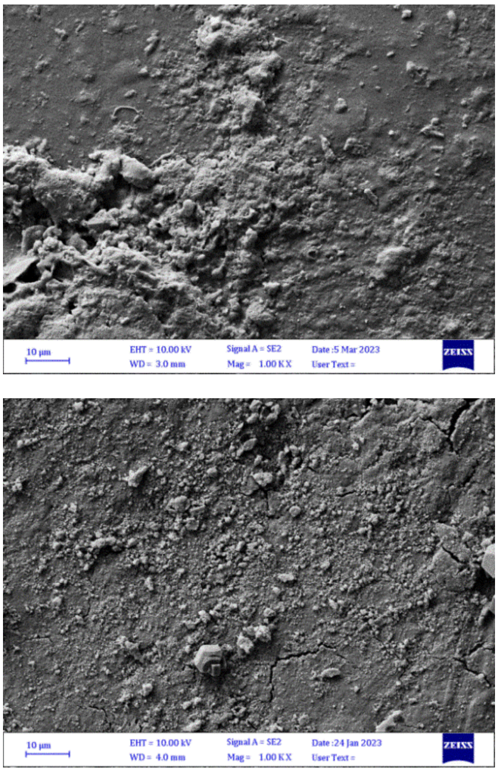

Fig. (11) FE-SEM images of (A) MK-epoxy and (B)M-epoxy composite coating

Table (3) The corrosion rate and electric resistance of pure epoxy and after coating with the reinforcements (Mk and M) clay particles

Sample	Corrosion rate (mm/years)	Electric resistance R(Ω)
Base	0.3625	820
Epoxy (pure)	0.2849	1040
Epoxy + MK2%	0.1350	8800
Epoxy +MK4%	0.1260	1600
Epoxy + MK6%	0.3050	4220
Epoxy + MK8%	0.3650	815
Epoxy + MK10%	0.4220	360
Epoxy + M2%	0.0407	7300
Epoxy + M4%	0.0243	12000
Epoxy + M6%	0.0198	880
Epoxy + M8%	0.00264	110000
Epoxy + M10%	0.3350	15000

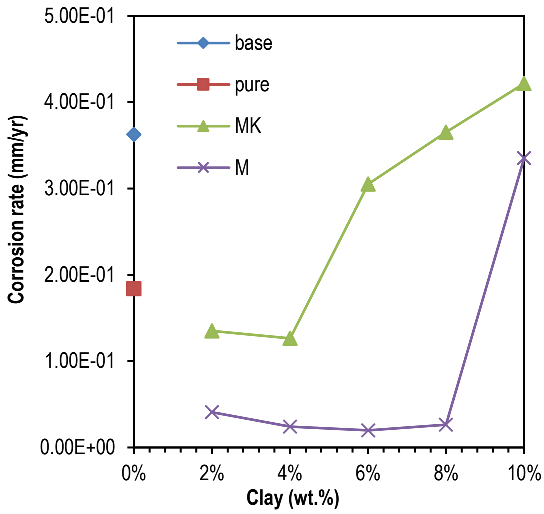

Fig. (12) Effect of adding Mk and M clay particle on the corrosion rate of epoxy coating

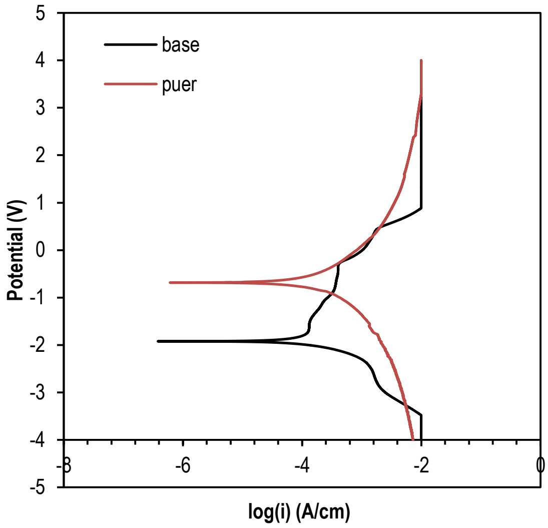

Fig. (13) Polarization curves of low carbon steel samples before and after epoxy coating

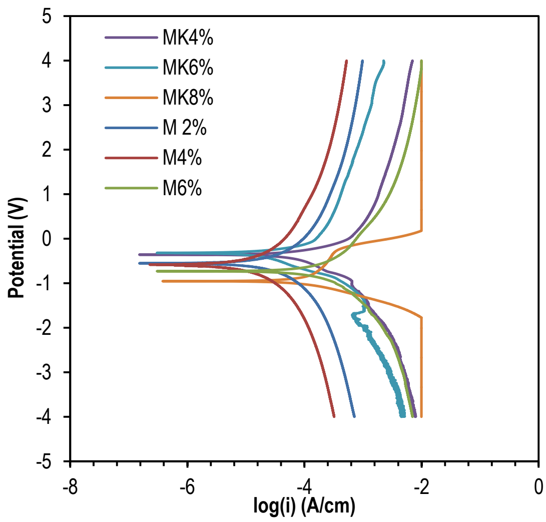

Fig. (14) Polarization curve of low carbon steel sample epoxy after coating with the reinforcements Mk and M clay particles

4. Conclusion

In this work, epoxy-based composite coatings containing different compositions of metakaoline and mullite clay were prepared. The addition of metakaolin and mullite clay particles to the pure epoxy coating. The results showed that there was a bond between the epoxy and the clay. This improved both the mechanical properties (microhardness, wear, and adhesion) as well as the chemical corrosion of the epoxy. Especially when adding mullite clay particles to the epoxy (epoxy/M).

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