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Research Article

Investigation of the Effect of SiO_2 Nanoparticles on Corrosion-Wear-Impact Resistance, and Bending Strength of Acrylic Coating Applied to Steel Substrate

S. Arzani [1], **H. R. Pakzaman** *[2]

Department of Research and Development, Iran Alloy Steel Company, Yazd, Iran

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ABSTRACT

This study applied a nanocomposite coating to a plain carbon steel substrate using the air spray method. Various amounts of SiO_2 nanoparticles (2-6%) were incorporated into the acrylic polymer-based coatings, and the results of corrosion, wear, impact, bending, hardness, and adhesion tests on coatings with and without nanoparticles were compared. The results indicated that coatings containing SiO_2 nanoparticles exhibited significantly higher wear, impact, and bending resistance than coatings without nanoparticles and showed better adhesion to the steel substrate. Moreover, increasing the SiO_2 nanoparticles content in the coating considerably improved the coating's hardness and resistance to corrosive agents in 3.5 wt% NaCl solution. The enhanced properties of the nanoparticle-containing coating were attributed to factors such as increased coating density and cohesion and higher average stress required to damage the coating due to the addition of SiO_2 particles. Considering economic factors and the issue of particle agglomeration, 4% SiO_2 nanoparticles were determined as the optimal filler content for the nanocomposite coating. It was found that adding 4% SiO_2 nanoparticles to the polymeric coating led to a reduction in the corrosion rate and weight loss due to wear by 93% and 29%, respectively, compared to coatings without nanoparticles. Furthermore, the coating's adhesive strength and impact resistance increased by 20% and 50%, respectively.

1. Introduction

Two types of steel, plain carbon and stainless, are widely used due to their mechanical strength and corrosion resistance, respectively. However, even stainless steel is susceptible to corrosion under severely corrosive environmental conditions [1, 2]. Therefore, issues related to the protection and extended service life of steel components and surfaces are of great importance and have drawn considerable attention. One of the most cost-effective methods to prevent corrosion of steel components and structures is coating [3, 4].

Organic polymer coatings such as polyurethane and acrylic resins are widely used for corrosion protection [5]. The resin acts as a barrier, physically protecting the metal from direct contact with the corrosive environment. However, it has been shown that the barrier properties of resins are insufficient, and corrosive ions can penetrate through the resin's porosity [6]. In other words, due to their inherent porosity, the organic coatings are susceptible to mechanical degradation or tend

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* *Corresponding Author*
Email: hr.pakzaman@gmail.com
Address: Department of Research and Development, Iran Alloy Steel Company, Yazd, Iran
1. M. S., 2. Ph. D

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to create channels for corrosive species [7]. As a result, new methods, such as polymer matrix nanocomposites reinforced with organic/inorganic fillers, have recently gained significant attention for protecting steel against corrosion [8-19]. These coatings act as a waterproof barrier, effectively preventing water absorption and extending the service life of the steel. The most notable feature of nanocomposites is the enhancement of properties with small amounts of reinforcement. For example, adding 5% by volume of nanoparticles to a polymer can improve its physical and mechanical properties by up to 70% [9].

In nanocomposite coatings, nanoparticles such as Al_2O_3, TiO_2, SiO_2, and ZrO_2 are typically used to improve the coating's performance [10-17]. Benea et al. [10] have investigated the effect of TiO_2 embedded epoxy paint on the corrosion properties of naval steel plates immersed in seawater. The corrosion rate of a nanocomposite of TiO_2 and epoxy has been reported by these researchers to be 0.141 μm per year, compared to 386.79 μm/year for uncoated steel. Zhou et al. [11] used a polybenzoxazine nanocomposite coating containing SiO_2 nanoparticles on plain steel and found that the incorporation of 1-5 wt% SiO_2 nanoparticles into coating enhanced the corrosion resistance of plain carbon steel in 3.5 wt% NaCl solution. The corrosion rate value of the coated sample with 3 wt% and 5 wt% SiO_2 nanoparticles showed a reduction of 10 and 15 times, respectively, compared to the uncoated samples under the same conditions. In another study, the authors stated that incorporating SiO_2 nanoparticles into a polyurethane coating enhanced the wear resistance of the coating significantly [12]. A study on the coating of Poly(vinylpyrrolidone)/acrylate/silane polymer nanocomposites with SiO_2 filler on metal substrate of mild steel was successfully carried out. The nanocomposite coating showed a corrosion protection efficiency of 83.4% using electrochemical impedance spectroscopy measurements at the addition of 0.5% SiO_2 nanoparticles [13]. Poorraeisi and Afshar [14] used ZrO_2 in combination with TiO_2 and hydroxyapatite to improve the overall performance of the applied coating on 316 stainless steel. They found that the synergistic contribution from corrosion resistant hydroxyapatite and TiO_2, mechanically strong ZrO_2, resulted in an increase in corrosion resistance of 316 stainless steel. The minimum corrosion current density ($I_{corr.}$) of composite coating was reported 0.007 $I_{corr.}$ of bare substrate. Xavier [15] revealed that the polyurethane/SiO_2-Al_2O_3 nanocomposite coating on mild steel exhibited significant resistance properties against corrosion as well as enhanced mechanical properties compared to pure polyurethane coating. The $I_{corr.}$ Value for nanocomposite coating was 0.142 $I_{corr.}$ of pure polyurethane coating. Another study employing epoxy resin nanocomposite coating using CeO_2 nanoparticles on metal substrate of Q235 steel was conducted. It was demonstrated that adding 3% nanorod or nanosphere CeO_2 resulted in a significant increase in the corrosion resistance of the coating in 3.5% NaCl solution. The corrosion rate of the nanocomposite coating after one week immersion was reported about one order of magnitude lower than the pure epoxy coating [16].

Acrylic coatings offer environmental stability, good transparency, and relatively decent corrosion resistance [3], but their mechanical properties are not ideal. SiO_2 is one of the most effective nanoparticles used in corrosion-resistant coatings. Due to its high hardness and wear resistance, along with outstanding optical properties resulting from its small size and refractive index close to that of commonly used resins, SiO_2 is an ideal choice for improving the properties of acrylic coatings. Moreover, its cost is relatively lower than that of other nanoparticles [2, 4, 7, 13, 15]. Obtaining optimal properties from composites is a challenge due to the non-uniform dispersion of nanoparticles in the matrix. Proper mixing and homogeneity of nanoparticles within the coating matrix are crucial to prevent the agglomeration of particles [12]. There are ongoing efforts to overcome this problem and improve the interaction between nanoparticles and polymeric matrix [2, 4, 14, 18]. Chen et al. [18] used intense stirring to produce a polyurethane-acrylic nanocomposite containing SiO_2 nanoparticles and demonstrated that particle distribution in this method was highly favorable.

The composites' fracture toughness or impact resistance is determined by the size and concentration of the reinforcing particles, the nature of the particle-matrix interface, and the properties of the polymer matrix and the filler particles. It has been demonstrated that the fracture toughness rises with the reduction in particle size, even at low-volume fractions of particles. This goes to show why nanometric reinforcing particles should be used in composite materials and coatings [19]. Additionally, weight fraction of the filler materials plays an important role in determining the overall performance of the composite [2, 4]. Limited research has been conducted on optimizing the amount of SiO_2 nanoparticles in acrylic coatings applied to steel sheets to simultaneously enhance both corrosion resistance and mechanical properties.

In the present study, various amounts of SiO_2 nanoparticles were used to improve wear-corrosion-impact resistance, bending and adhesion strength of acrylic coatings applied to plain carbon steels and compared with the properties of coatings without nanoparticles. The aim of this experimental work is to optimize the amount of nanoparticles in the coating while considering economic factors and the issue of particle agglomeration.

2. Material and Experimental Procedures

This study used plain carbon steel sheets with a thickness of 0.7 mm and the chemical composition shown in Table 1. as substrate and a coating paint with an acrylic polymer matrix containing SiO_2 nanoparticles (with specifications shown in Table 2.). An as-received traffic marking paint based on acrylic resin with the specifications in Table 3. was used as coating paint. The sheets were cut to the dimensions of 7x17 cm and degreased with acetone after grinding. To prepare the nanocomposite coating, different amounts of SiO_2 nanoparticles (2, 4, and 6 wt%) were added to 100 g of acrylic, and a high-speed disk mixer with a speed of more than 3000 rpm was used for 60 minutes to uniformly distribute the particles, and prevent their agglomeration. The nanocomposite coating was applied to the surface of steel sheets using a conventional air spray method, and the coating thickness after drying was measured to be 100±10 µm. The hardness of the resulting coating, as well as its resistance to wear, impact, bending, and corrosion, and its adhesion to the steel substrate were investigated and compared under two conditions: the coating containing SiO_2 nanoparticles and the coating without SiO_2 nanoparticles. All the tests were conducted under room temperature conditions. Steel samples coated with acrylic containing 0, 2, 4, and 6 wt% SiO_2 nanoparticles were designated as St-0%SiO_2, St-2%SiO_2, St-4%SiO_2, and St-6%SiO_2, respectively.

The corrosion resistance evaluation was made by using the electrochemical polarization test by Potentiostat-Galvanostat device. The possible variation rate was specified at 1 mV/s in the range of ±300 mV relative to the open-circuit potential. Using the Tafel test, tangents were drawn to the anodic and cathodic branches and the point of their intersection was found. The corrosion current density was defined, and the corrosion rate was calculated using ASTM G102. Further, a salt spray test, according to ASTM B-117, was used to determine the corrosion protection of the coatings. In this test, grooves were first made on the coated surface as per ASTM D1654, and the samples were exposed to an aqueous salt solution of 5±1 wt%. The result of this test was done qualitatively depending on the degree of corrosion on the surface of the sample.

Pin on disk test was carried out as per ASTM G99 to assess the wear resistance of the coating. The test was performed using 3 cm diameter disc samples, pin rotation speed at 0.042 m/s, and force applied on the samples was set about 2 N. The weight loss of the samples was measured after a distance of about 100 m. The reported results are the average of at least three pin on disk tests. Images of the wear test specimens were taken using a scanning electron microscope (SEM), which enabled the evaluation and comparison of the wear mechanism in various samples.

The hardness of the coating was identified using a Koopa microhardness tester (model MH1). A load application of 25 g was applied and maintained for a duration of 10 s. For each sample, at least five locations selected and the average microhardness is presented and discussed. The hardness of each coating was also gauged by performing a pencil scratch test according to the ASTM D3363 standard procedure. Pencils with hardness ranging from 6H to 6B were used, starting with the hardest and gradually moving to softer ones. Each pencil was drawn over the coating surface for approximately 6.5 mm with constant force until one produced a visible black line [20]. Based on the degree of pencil penetration or the scratch made by the pencil on the coating surface, the hardness is determined. In this test, the coated steel sheet must be placed horizontally in a fixed position, and the pencil is drawn across the coating at a 45-degree angle relative to the horizon. The hardness of the last pencil that does not cause a scratch on the coating is reported as the scratch hardness of the coating [20, 21].

The adhesion of the coating to the steel substrate was determined by using the pull-off test with reference to ASTM D4541. For this test, specific dollies were then applied on the coating surface. After the standard time had been counted, the device parted the dollies, and the coating adhesion strength was measured in MPa.

Table 1. Chemical composition of the used plain carbon steel sheet as substrate (in wt%).

C	Si	Mn	P	S	Fe
0.14	0.19	0.52	0.023	0.027	Balance

Table 2. Specifications of the SiO_2 nanoparticles used.

Average grain size (nm)	Specific surface area (m^2/g)	Ultraviolet reflectivity (%)	Weight loss due to drying (%)	Weight loss due to heat (%)	Fe (ppm)	Co (ppm)
80	>800	>85	<1.4	<1.8	0.2	0.8

Table 3. Characteristics of the acrylic paint.

Specific gravity (kg/lit)	Volume solid (%)	Flash point (°C)	Coupling agent
1.5 ± 0.05	50 ± 2	35	Soya lecithin

The average of three pull-off test results are reported as the adhesion strength.

In order to measure the ability of the coatings to resist the impact, an impact test was performed according to ASTM D-2794. In this test, the coated sheet is placed under a piston with a spherical end. With the help of a lever, the piston is lifted to a certain height and allowed to drop freely onto the coating. Therefore, by gradually incrementing the drop height, one can identify the threshold for coating cracking. The condition of the cracks can also be assessed with the help of a microscope and copper sulfate indicator.

For the evaluation of the flexibility and to check the possibility of crack formation as a result of the bending forces, the bending test was carried out according to ASTM D522-88(b). In this test, the uncoated side of the sheet is placed on a steel rod of a standard diameter in the range of 1-0.125 inch and bent to a 180-degree angle. Subsequently, an amount of force is applied to the sheet which is immediately lifted off the rod and examined for macroscopic fractures. If there is no crack formation on the coating, the bending test is done with a steel bar of lesser diameter until cracks are observed on the coating. Test results are expressed as the diameter of the rod that leads to cracking of the coating during the bending test [21]. For the bending test in this investigation, steel rods of 1, 0.75, and 0.5 inch in diameter were employed.

3. Results and Discussion

The typical optical micrograph on the cross-section of the St-6%SiO_2 sample is shown in Fig. 1. indicating a coating without pores and good adhesion to steel substrate. The coating thickness was measured as 100±10 μm.

3.1. Corrosion Resistance Evaluation

3.1.1. Electrochemical Polarization Corrosion Test

The corrosion test results, including Tafel polarization curves and corrosion rates, are presented in Fig. 2. and Fig. 3(a) respectively. It is observed that the corrosion rate is highest in the St-0%SiO_2 sample and lowest in the St-4%SiO_2 sample, with a slight difference compared to the St-6%SiO_2 sample. In fact, as the amount of SiO_2 nanoparticles increases from 0 to 4%, the corrosion rate decreases significantly and then slightly increases as nanoparticles are further increased to 6%. Overall, the addition of SiO_2 nanoparticles to the acrylic coating has resulted in a decrease in corrosion current density and an increase in the corrosion potential of the coating. The nanocomposite coating, due to its strong adhesion to the steel surface, exhibits greater corrosion resistance compared to the pure acrylic coating (without nanoparticles). Also, if SiO_2 nanoparticles, with increasing density, are not agglomerated, they can act as a barrier to the corrosive agents penetrating through the steel substrate [2, 4, 14]. Garcia et al. 's research [22] shows that a suitable coating can cover active sites on the steel surface, preventing the formation of micro-cells on the substrate surface. However, if the SiO_2 nanoparticles are not well dispersed in the coating, agglomerated regions of the particles form, which creates porosity and allows penetration, thereby

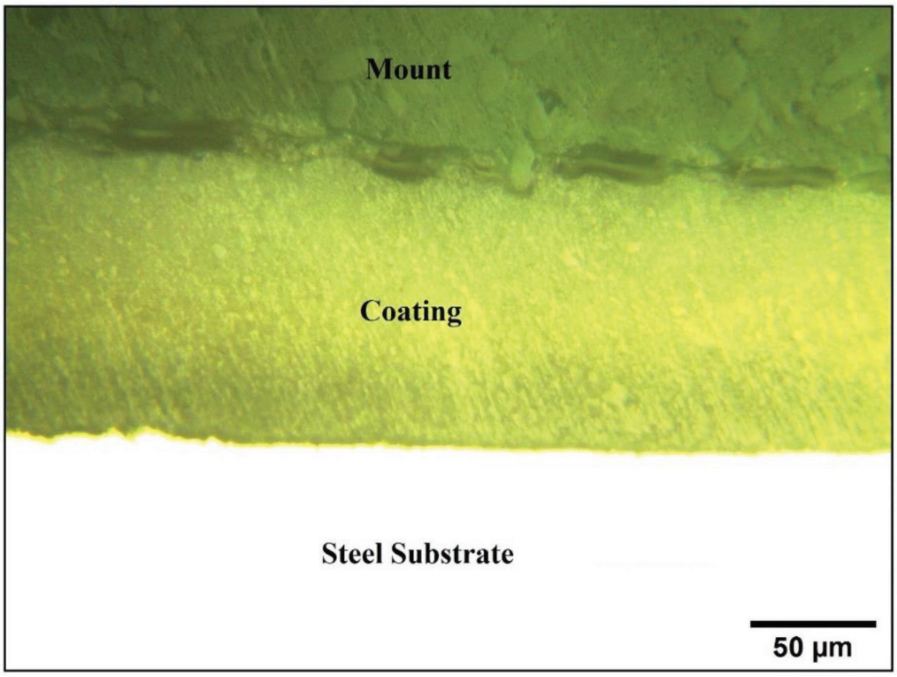

Fig. 1. Optical micrograph of the cross-section of the acrylic/6%SiO_2 nanocomposite coated steel.

increasing the corrosion rate on the substrate surface.

3.1.2. Salt Spray Corrosion Test

Fig. 4. shows the results of the salt spray test in graphical form. It can be observed that the addition of SiO_2 nanoparticles to the coating has influenced and reduced the intensity of corrosion. In the St-0%SiO_2 sample (Fig. 4(a).), corrosion effects and its products, especially around the scratches, are clearly visible. However, in the various nanocomposite coatings, particularly in the St-4%SiO_2 and St-6%SiO_2 samples, the intensity of corrosion and accumulation of products around the scratch area is less pronounced. Additionally, the initiation time of pitting and corrosion on the surface of the St-0%SiO_2 sample was shorter than the other samples; corrosion signs appeared on this sample approximately 4 hours after the start of the test. The corrosion initiation time for the St-2%SiO_2 sample occurred 4 hours and 25 minutes after the start of the test, while for the St-4%SiO_2 and St-6%SiO_2 samples, it was longer than that of the St-2%SiO_2 sample. The results of the salt spray test indicate that SiO_2 nanoparticles have good compatibility with the polymer coating. Better salt spray resistance in the St-4%SiO_2 and St-6%SiO_2 samples can be attributed to the better dispersion of SiO_2 nanoparticles, which filled the voids of polymeric matrix, thereby increasing the barrier properties of the coatings against intruding corrosive agents [23-25].

3.2. Wear Resistance Evaluation

The weight loss percentage of the samples after the pin-on-disc wear test is depicted in Fig. 3(b). From the

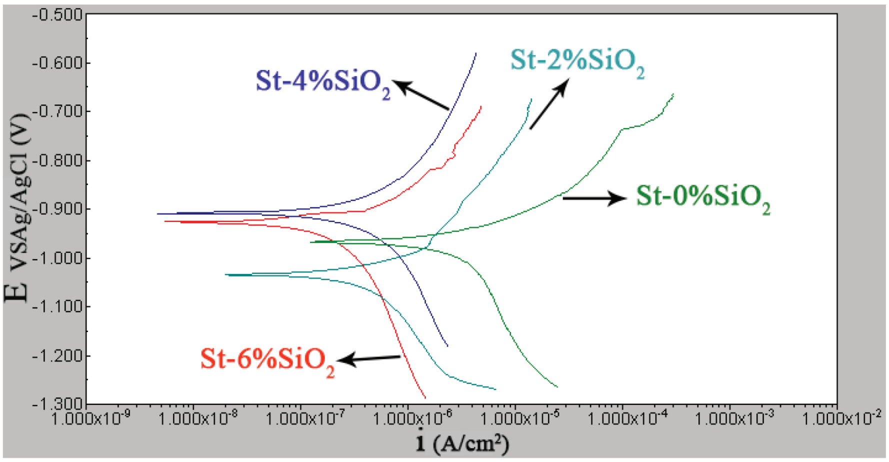

Fig. 2. Polarization curves of steel substrate corrosion with an acrylic coating containing varying percentages of SiO_2 nanoparticles in 3.5 wt% NaCl solution.

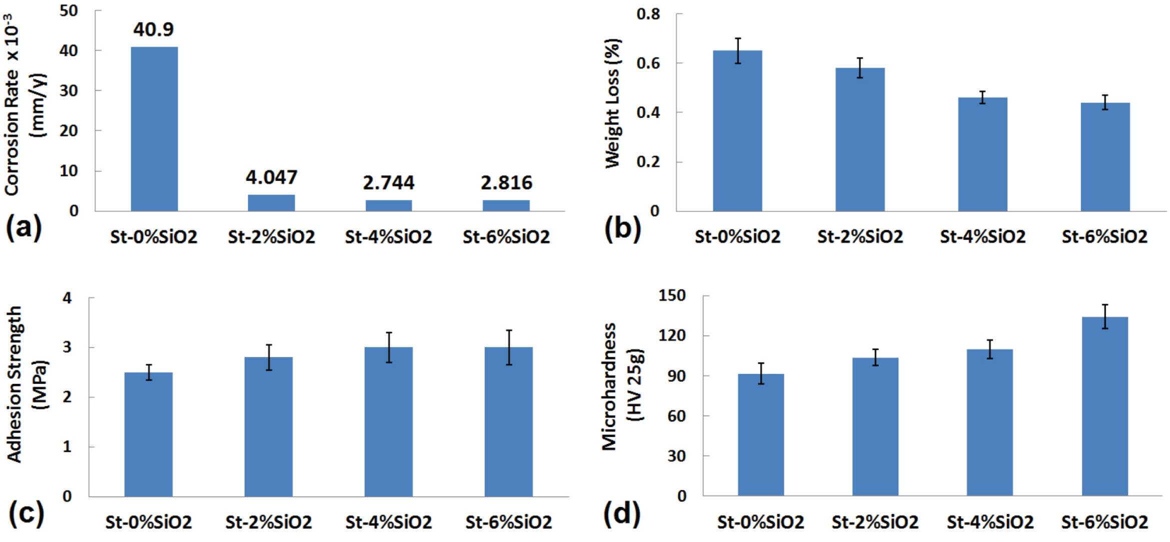

Fig. 3. Properties of the acrylic coating with different SiO_2 nanoparticle percentages applied on the steel substrate; the parameters used for the evaluation of the performance of the coatings were (a) corrosion rate, (b) weight loss from wear test, (c) adhesion strength and (d) microhardness.

results obtained, it is seen that as the weight percentage of SiO_2 nanoparticles in the coating increases, the weight loss of the samples decreases, which, in turn, increases the wear resistance of the coating. As it has been demonstrated in [26], the increase in the concentration of filler nanoparticles in polymer coatings leads to a decrease in the severity of the surface fatigue wear mechanisms. In this mechanism, because of the repeated forces applied, the surface of the material becomes vulnerable. Micro-cracks are formed and grow periodically; finally, the material is detached from the surface. Further, Fig. 5. presents the coefficient of friction for the coatings with different concentrations of SiO_2 nanoparticles obtained from the pin-on-disc test. The coefficient of friction for the St-0%SiO_2, St-2%SiO_2, St-4%SiO_2, and St-6%SiO_2 samples was about 0.4, 0.4, 0.3, and 0.4, respectively.

The lower coefficient of friction in the St-4%SiO_2 sample is due to the higher surface quality of this sample, while the presence of fine and scattered surface porosity in the St-0%SiO_2 and St-2%SiO_2 samples acts as protrusions and depressions, leading to a rougher surface. Additionally, these fine porosities cause issues for the movement of the pin when it encounters them, as they act like pits. However, regarding the higher coefficient of friction in the St-6%SiO_2 sample compared to the St-4%SiO_2, research findings by other investigators also indicate that an excessive increase in the percentage of nanoparticles results in undesirable properties [26, 27]. In other words, the lowest coefficient of friction in the coating is achieved at an optimal nanoparticle concentration. SEM micrographs (Fig. 6.) were used to investigate the wear mechanism of the coating further. According to Fig. 6(a)., the pure coating in the St-0%SiO_2 sample undergoes severe plastic deformation during wear, forming relatively large cracks. Additionally, the width of the wear track in this sample is larger compared to other samples, which justifies the higher weight loss of the St-0%SiO_2 sample during the wear test (Fig. 3(b)). With the addition of SiO_2 nanoparticles to the polymer matrix, these particles, due to the creation of appropriate

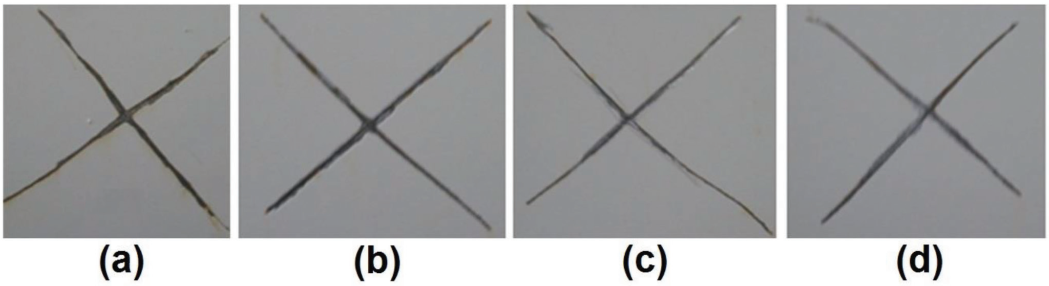

Fig. 4. Salt spray test results after 24 hours for: (a) St-0%SiO_2; (b) St-2%SiO_2; (c) St-4%SiO_2; and (d) St-6%SiO_2.

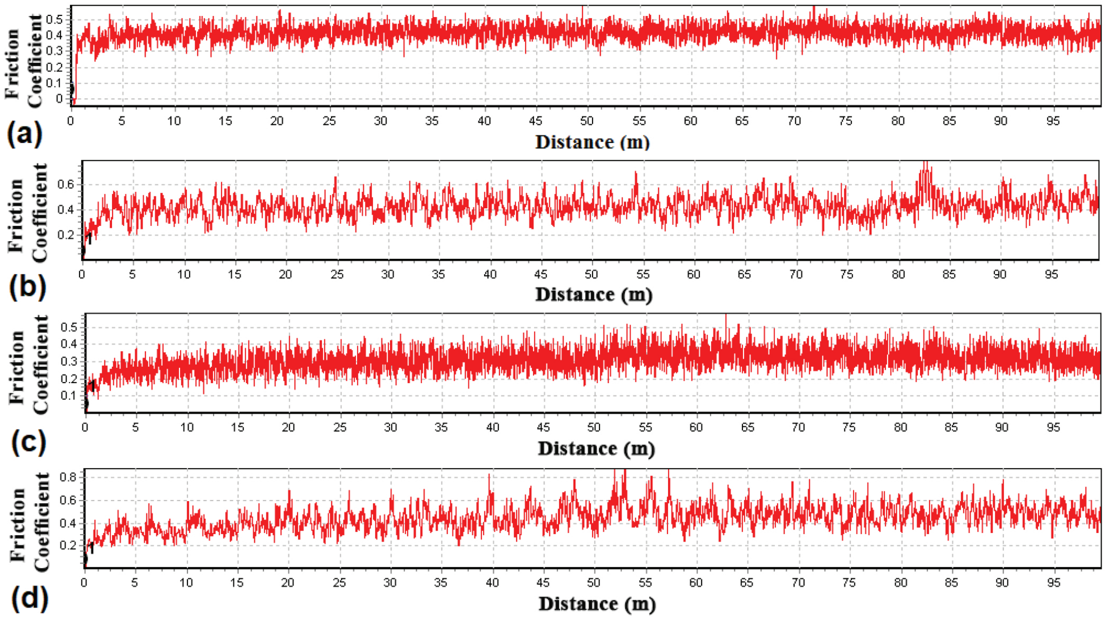

Fig. 5. Coefficient of friction versus distance diagram for: (a) St-0%SiO_2; (b) St-2%SiO_2; (c) St-4%SiO_2; and (d) St-6%SiO_2.

interface and adhesion to the matrix, largely prevent the growth and propagation of fatigue cracks. As shown in Fig. 6(b). the amount of cracks, pores, and wear track width is reduced compared to the pure coating, which correlates with the lower weight loss during wear in the St-2%SiO_2 sample compared to the St-0%SiO_2 sample (Fig. 3(b)). The St-0%SiO_2 and St-2%SiO_2 samples do not reach their maximum coating density, and as a result, they contain some fine and scattered surface and subsurface porosity. These porosities are the main cause of surface fatigue, acting as crack initiators under cyclic loading and, if large enough, functioning as cracks themselves [28]. As shown in Fig. 6(c). by adding 4% SiO_2 nanoparticles, no significant cracks or pores are observed in the wear track, and the narrowest wear track belongs to this sample. In fact, with the increase in SiO_2 nanoparticles, the coating density increases, and the amount of fine and scattered porosities, which are the source of crack initiation, decreases [19]. The SEM micrograph of the St-6%SiO_2 sample (Fig. 6(d)) is very similar to that of the St-4%SiO_2 sample. In this sample, the weight loss during wear is also significantly reduced (Fig. 3(b)).

Increased hardness, stiffness, and modulus of coatings in the presence of SiO_2 nanoparticles are key factors in enhancing fatigue wear resistance, as they prevent surface deformation and the resulting cyclic stresses. Moreover, due to their very small size, SiO_2 nanoparticles can cover a large area of the coating, resulting in a larger effective contact surface with the abrasive pin, thus reducing the pin's surface effects, which plays a crucial role in reducing wear [29].

3.3. Adhesion Test

Many properties of the coating, such as wear and corrosion resistance, are dependent on the adhesion strength of the coating to the substrate. One of the prominent features of acrylic coatings is their strong adhesion to various substrates, especially steel substrates [30]. In Fig. 3(c). the adhesion strength of the coating applied to the steel substrate is presented for different SiO_2 nanoparticle contents. The results show that increasing the weight percentage of nanoparticles enhances the adhesion of the coating to the steel substrate. The adhesion test results indicated that in the St-0%SiO_2 sample, separation and failure occurred at the coating/substrate interface. However, in the other samples, the failure occurred within the coating itself. The use of nanoparticles can reduce porosity and enhance the adhesion of a material by filling cavities [4, 31]. It has been suggested that higher structure density improves the adhesion and internal cohesion of the coating [20]. The results show that the presence of fillers increases this density. In the presence of SiO_2 particles, the hydroxyl groups (O-H) on the surface of SiO_2 particles form hydrogen bonds with the carbonyl groups (C=O) of the acrylic, creating a physically cross-linked

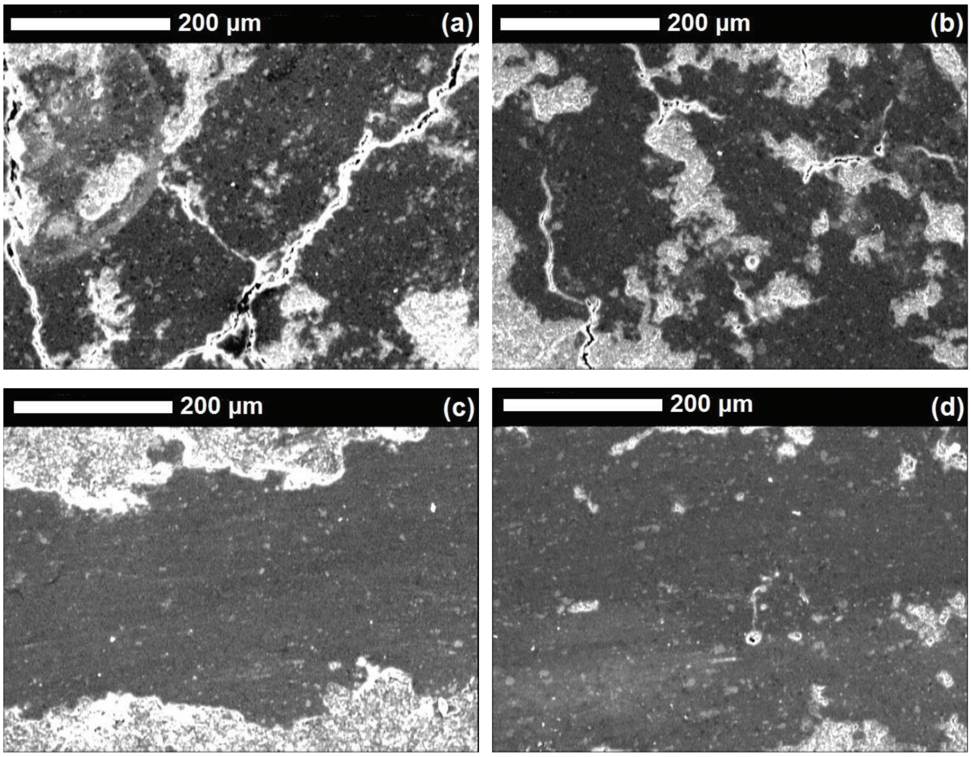

Fig. 6. SEM micrographs of sample surface after wear test for: (a) St-0%SiO_2; (b) St-2%SiO_2; (c) St-4%SiO_2; and (d) St-6%SiO_2.

structure alongside the polymer structure, which increases the coating structure density (Fig. 7.). Low molecular weight chains typically adhere to the filler particle body, forming a suitable interface between the coating and substrate with polymer chains. This process strengthens the coating's adhesion to the steel substrate while also improving the filler-matrix adhesion [4, 32-34].

3.4. Coating Hardness Evaluation

3.4.1. Microhardness Test

In Fig. 3(d). the microhardness results of the coating for different samples are reported. As the SiO_2 nanoparticle content increases from 0% to 6%, the hardness of the coating continuously increases. It has been reported that polymers' yield strength and hardness increase in the presence of SiO_2 nanoparticles. This increase in hardness is due to the high modulus of the SiO_2 nanoparticles and the increase in cross-linking from hydrogen bonds between the nanoparticles and the coating [35]. Since compressive stresses are predominantly involved in hardness tests, stiffness and modulus are more significant than the bonding conditions between the nanoparticles and the matrix. In general, at higher nanoparticle percentages (more than 4 wt%), due to the hard nature of SiO_2 and its suitable interfacial conditions with the matrix, a significant increase in the hardness of the coating is observed. These results are consistent with those of previous studies that have shown the improvement of hardness in organic coatings by using different nanoparticles [13, 15, 36].

3.4.2. Scratch Hardness Test

The results of the pencil scratch hardness test are presented in Table 4. It is evident that with increasing SiO_2 nanoparticle content as filler in the acrylic coating, the surface's resistance to surface scratches caused by the pencil increases, with the highest hardness observed in the St-6%SiO_2 sample. The findings of this study are consistent with the reports by other researchers [32, 37]. Chen et al. [37] demonstrated that in sol-gel coatings applied to polycarbonate substrates, both the coating thickness and SiO_2 content significantly improve scratch resistance. A study on nanocomposite coating using Fe_3O_4 as a filler in epoxy-acrylate resin on metal substrate of mild steel resulted in enhancement of scratch hardness of coating [32].

3.5. Impact Test

It is observed from Table 4. that the impact strength of acrylic coatings increases as SiO_2 nanoparticle content rises. Moreover, in the area impacted by the piston on coatings of St-4%SiO_2 and St-6%SiO_2, no cracks or breaking of the coating was observed despite significant plastic deformation occurring in these parts of the sample. By reducing the filler particle size to the nanometer scale, the total surface area for bonding increases, while the formation of filler aggregates decreases. These

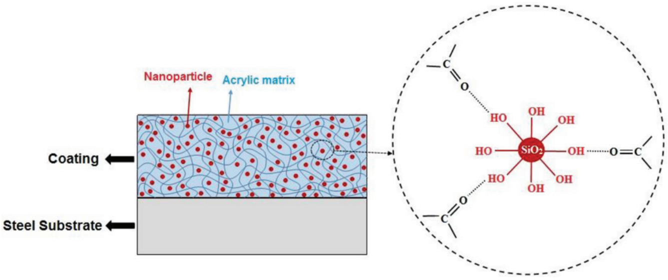

Fig. 7. Schematic illustration of the increase in density and adhesion of the acrylic coating due to the use of SiO_2 nanoparticles, which leads to improved adhesion of the coating to the steel substrate.

Table 4. Results of various tests performed on steel sheets coated with acrylic containing different percentages of SiO_2 nanoparticles.

Sample code	Hardness		Impact resistance (kg.cm)	Result of bending test with different rod diameters		
	Pencil hardness grade	Scratch hardness		Rod diameter (1 in)	Rod diameter (0.75 in)	Rod diameter (0.5 in)
St-0%SiO_2	B	2H	24	Failed	Failed	Failed
St-2%SiO_2	HB	4H	30	Passed	Failed	Failed
St-4%SiO_2	H	5H	36	Passed	Passed	Failed
St-6%SiO_2	3H	>6H	36	Passed	Passed	Passed

factors enhance energy absorption during abrupt deformation. The increased flexibility is indicated by the presence of fine-mesh pores (below the critical crack length) at the interface between the filler particles and the matrix, allowing the polymer components to penetrate into these regions. Spherical SiO_2 nanoparticles were also shown to reduce the stress concentration around themselves compared with the plate-like particles of sharp edges, thus rendering toughness higher [19]. In addition, the presence of nanoparticles also decreases the free volume in the coating, which absorbs much energy by distorting themselves and provides a space for the polymeric chain to move segmentally during impact test [38].

The reinforcing effect of SiO_2 nanoparticles is related to altering the threshold stress at the crack tip by releasing and redistributing these stresses across multiple microcrack growth centers. This process increases the average stress required to fracture the coating, thereby enhancing its toughness. In other words, matrix-origin microcracks are halted upon encountering the SiO_2 filler nanoparticles, requiring higher stress to continue growing. Therefore, the higher the SiO_2 content in the coating, the greater the barriers for microcracks, resulting in improved toughness [19].

3.6. Bending Test

The qualitative results of the bending test for different samples are reported in Table 4. The pure acrylic coating (St-0%SiO_2 sample) exhibits very low flexibility; in all three bending tests, large cracks appeared on the surface, and the coating completely peeled off in sheets. In the St-0%SiO_2 sample, separation and failure occurred at the coating/substrate interface. With the addition of SiO_2 nanoparticles as a filler in the acrylic coating, the flexibility against bending forces improved. As the SiO_2 nanoparticle weight percentage increased from 0% to 2%, flexibility increased, but in both bending tests with rods of 0.5 and 0.75 inches in diameter, macroscopic cracks were observed. These cracks started in the middle of the coating width and extended to the ends of the sample. In other words, in the St-2%SiO_2 sample, failure occurred within the coating. With the addition of 4% and 6% by weight of SiO_2 nanoparticles, the flexibility of the acrylic coating significantly increased, and in the St-6%SiO_2 sample, no macroscopic cracks were observed on the surface during the bending test. A possible explanation for this might be that higher structure density leads to better internal cohesion of the coating [34]. Consistent with our experimental results, Ahmed et al. [39] have also reported an improvement in the flexibility of the polyurethane based nanocomposite coating on steel substrate.

4. Conclusions

This study applied an acrylic-based coating with various amounts of SiO_2 nanoparticles (2-6%) as a filler to the surface of plain carbon steel. Various properties of the coating, including corrosion, wear, impact, bending resistance, and hardness, were evaluated and compared with those of the coating without nanoparticles. Considering economic factors, the agglomeration issue, and the results obtained, SiO_2 nanoparticle composite coatings with 4% by weight were determined to be the optimal nanoparticle content. The results indicated that adding 4% SiO_2 nanoparticles to the polymeric coating led to a reduction in the corrosion rate and weight loss due to wear by 93% and 29%, respectively, compared to coatings without nanoparticles. These improvements are attributed to increased structure density, modulus, orderly arrangement of polymer chains, and the barrier properties of the nanoparticles. Furthermore, the coating's adhesion strength and impact resistance in the St-4%SiO_2 sample improved by 20% and 50%, respectively, compared to the St-0%SiO_2 sample. The presence of nanoparticles raised the average stress required for coating failure, thereby improving toughness. These particles acted as obstacles to microcrack growth originating from the matrix, increasing the stress needed to propagate them.

References

[1] Meng Q, Frankel G.S, Colijn H.O, Goss S.H, Stainless-steel corrosion and MnS inclusions, Nature. 2003; 424:389-390.

[2] Radhamani A.V, Lau H.C, Ramakrishna S, Nanocomposite coatings on steel for enhancing the corrosion resistance: A review, J. Compos. Mater. 2020; 54:681–701.

[3] Goyal A, Pouya H.S, Ganjian E, Claisse P, A review of corrosion and protection of steel in concrete, Arabian J. Sci. Eng. 2018; 43: 5035–5055.

[4] Randis R, Darmadi D.B, Gaspari F, Sonief A.A, Akpan E.D, Ebenso E.E, The potential of nanocomposite-based coatings for corrosion protection of metals: A review, J. Mol. Liq. 2023; 390:123067.

[5] Joshi M, Adak B, Butola B.S, Polyurethane nanocomposite based gas barrier films, membranes and coatings: a review on synthesis, characterization and potential applications, Prog. Mater. Sci. 2018; 97: 230–282.

[6] Corvo F, Perez T, Dzib L.R, Martin Y, Castaneda A, Gonzalez E, Perez J, Outdoor–indoor corrosion of metals in tropical coastal atmospheres, Corros. Sci. 2008; 50: 220–230.

[7] Nazari M.H, Zhang Y, Mahmoodi A, Xu G, Yu J, Wu J, Shi X, Nanocomposite organic coatings for corrosion protection of metals: A review of recent advances, Prog. Org. Coat., 2022; 162: 106573.

[8] Guan L.Z, Zhao L, Wan Y.J, Tang L.C, Three-dimensional graphene-based polymer nanocomposites: preparation, properties and applications, Nanoscale. 2018; 10: 14788-14811.

[9] Guo Z, Yu J, Grafting of dendritic polythers onto

nanometric silica surface, J. Mater. Chem. 2002; 12: 468-472.

[10] Benea L, Mardare L, Simionescu N, Anticorrosion performances of modified polymeric coatings on E32 naval steel in sea water, Prog. Org. Coat. 2018; 123: 120-127.

[11] Zhou C, Lu X, Xin Z, Liu J, Zhang Y, Polybenzoxazine/SiO_2 nanocomposite coatings for corrosion protection of mild steel, Corros. Sci. 2014; 80: 269-275.

[12] Barna E, Bommer B, Kürsteiner J, Vital A, Trzebiatowski O.V, Koch W, Schmid, Graule T, Innovative, scratch proof nanocomposites for clear coatings. Composites. Part A. 2005; 36: 473–480.

[13] Eduok U, Faye O, Ohaeri E, Szpunar J, Akpan I, Synthesis and characterization of protective silica reinforced hybrid poly(vinylpyrrolidone)/acrylate/silane nanocomposite coatings, New J. Chem. 2020; 44: 1117–1126.

[14] Poorraeisi M, Afshar A, The study of electrodeposition of hydroxyapatite-ZrO_2-TiO_2 nanocomposite coatings on 316 stainless steel, Surf. Coat. Technol. 2018; 339:199–207.

[15] Xavier J.R, Electrochemical and dynamic mechanical studies of newly synthesized polyurethane/SiO_2-Al_2O_3 mixed oxide nanocomposite coated steel immersed in 3.5% NaCl solution, Surf. Interfaces. 2021; 22: 100848.

[16] Zhang W, Wang H, Lv C, Chen X, Zhao Z, Qu Y, Zhu Y, Effects of CeO_2 geometry on corrosion resistance of epoxy coatings. Surf. Eng. 2020; 36:175-183.

[17] Ledwig P, Dubiel B, Microstructure and corrosion resistance of composite nc-TiO_2/Ni coating on 316L steel, Arch. Metall, Mater. 2017; 62: 2455–2460.

[18] Chen G, Zhou S, GU G, WU L, Modification of colloidal silica on the mechanical properties of acrylic based polyurethane/silica composites, Colloids Surf, A. 2007; 296: 29-36.

[19] Zhou S, Wu L, Sun J, Shen W, The change of the properties of acrylic-based polyurethane via addition of nano-silica, Prog. Org. Coat. 2002; 45: 33-42.

[20] Johns G, Annual book of ASTM standards, paints, related coatings and aromatics, West Conshohocken, PA: ASTM International; 1989.

[21] Moayed S.H, Fatemi S, Pourmahdian S, Synthesis of a latex with bimodal particle size distribution for coatings applications using acrylic monomers, Prog. Org. Coat. 2007; 60: 312-319.

[22] Gonzalez-Garcia Y, Gonzalez S, Souto R.M, Electrochemical and structural properties of a polyurethane coating on steel substrates for corrosion protection, Corros. Sci. 2007; 49: 3514-3526.

[23] Verma G, Weathering, salt spray corrosion and mar resistance mechanism of clay (nano-platelet) reinforced polyurethane nanocomposite coatings, Prog. Org. Coat. 2019; 129: 260-270.

[24] Jafari D, Shishesaz M, Zaarei D, Danaee I, Nanocomposite coating based on thermoplastic acrylic resin and montmorillonite clay: preparation and corrosion prevention properties, Iran, J. Oil Gas Sci. Technol. 2017; 6: 63-76.

[25] Song W, Dayu X, Mingxing L, Ansari K.R, Singh A, Insight into the anticorrosion performance of synthesized novel nano polymeric material of SiO_2 for the protection of J55 steel in 3.5 wt% NaCl solution saturated with carbon dioxide, J. Nat, Gas Sci. Eng. 2022; 106:104758.

[26] Friedrich K, Zhang Z, Schlarb A.K, Effects of various fillers on the sliding wear of polymer composites, Composites Science and Technology. 2005; 65: 2329-2343.

[27] Patnaik A, Satapathy A, Chand N, barkoula N.M, Biswas S, Solid particle erosion wear characteristics of fiber and particulate filled polymer composites: A review, Wear. 2010; 268:249-263.

[28] Lima da Silva R.C, Henrique da Silva C, Medeiros J.T.N, Is there delamination wear in polyurethane? Wear. 2007; 263: 974-983.

[29] Adachi T, Osaki M, Araki W, Kwon S.C, Fracture toughness of nano- and micro- spherical silica -particle-filled epoxy composites, Acta Mater. 2008; 56: 2101-2109.

[30] Jesionowski T, Zurawska J, Krysztafkiewicz A, Surface properties and dispersion behavior of precipitated silicas, J. Mater, Sci,. 2002; 37: 1621–1633.

[31] Aung M.M, Li W.J, Lim H.N, Improvement of anticorrosion coating properties in bio-based polymer epoxy acrylate incorporated with nano Zinc oxide particles, Ind. Eng. Chem. Res. 2020; 59: 1753–1763.

[32] Rahman O.U, Kashif M, Ahmad S, Nanoferrite dispersed waterborne epoxy-acrylate: Anticorrosive nanocomposite coatings, Prog. Org. Coat. 2015; 80: 77–86.

[33] Atta A.M, Ezzat A.O, El-Saeed A.M, Tawfeek A.M, Sabeela N.I, Self-healing of chemically bonded hybrid silica/epoxy for steel coating, Prog, Org, Coat. 2020; 141: 105549.

[34] Fabbri P, Singh B, Leterrier Y, Manson J.A.E, Messori M, Pilati F, Cohesive and adhesive properties of polycaprolactone/silica hybrid coatings on poly (methyl methacrylate) substrates, Surf. Coat. Technol, 2006; 200: 6706-6712.

[35] Dasari A, Yu Z.Z, Mai Y.W, Fundamental aspects and recent progress on wear/scratch damage in polymer nanocomposites, Mater. Sci. Eng. R. 2009; 63: 31-80.

[36] Xavier J.R, Electrochemical, mechanical and adhesive properties of surface modified NiO-epoxy nanocomposite coatings on mild steel, Mater. Sci. Eng. B. 2020; 260: 114639.

[37] Chen Z, Wu L.Y.L, Chwa E, Tham O, Scratch resistance of brittle thin films on compliant substrates, Mater. Sci. Eng. A. 2008; 493: 292-298.

[38] Yang J.P, Chen Z.K, Yang G, Fu S.Y, Ye L, Simultaneous improvements in the cryogenic tensile strength, ductility and impact strength of epoxy resins by a hyperbranched polymer, Polymer. 2008; 49: 3168-3175.

[39] Ahmed M.A, Shohide M.A, El-Saeed A.M, Naguib H.M, Coating effect of polyurethane-layered double hydroxide nanocomposite on steel, Discover Mater. 2024; 4: 42.