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Effects of Substrate Surface Characteristics on the Adhesion Properties of Geopolymer Coatings

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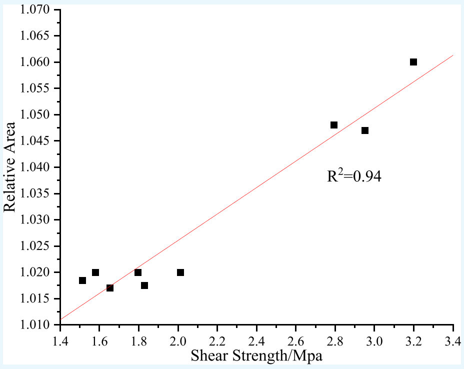
ABSTRACT: Geopolymer is a kind of material with a better ability of high-temperature and corrosion resistance. Poor adhesion could easily lead to problems such as coating cracks, peeling at an early stage, and inability to work with the substrate. The adhesion depends on many factors such as chemical composition of the raw materials, the formulation of the geopolymer, the type of substrate, surface roughness of the substrate, etc. The higher the Si/Al ratio, the greater the shear strength of the coating. This is because geopolymers synthesized with different Si/Al ratios have different phases in the geopolymer binder. Each study uses different multi-parameter combinations selected by itself, which is not uniform and has no universal applicability. As the parameter Ra is determined by the profile centerlines of the substrate surface, it is difficult to get an appropriate value of Ra to represent the roughness of the substrate surface. The parameter-relative area, determined by area scale fractal analysis, can effectively characterize the surface roughness, predict the texture component of bond strength, and establish a connection between which and the bonding performance of the geopolymer coating at a high level of confidence. The bonding strength reduces with the decrease in the value of the relative area. The magnitude of scale employed should be seriously determined when characterizing the surface roughness.



1. INTRODUCTION

Building structures often suffer various natural or man-made disasters, such as fire, during its whole service circle, with serious casualties and property loss. Building materials will get damaged and even fail in fire; to be specific, wood structures tend to burn down, the strength of steel of the reinforced concrete structures will deteriorate at high temperatures, and concrete will burst therein. Engineers usually apply fire-resistant coatings on the structure, in practice, to improve the high-temperature/fire-resisting performance of building materials.

Geopolymer is a kind of material with the same mechanical properties as ceramics, and it has a better ability of high-temperature and corrosion resistance than most polymer materials. Wide raw materials, easy-to-use technology, conservation of energy, and environmental protection are also marked as the main advantages of geopolymer materials. The behavior of geopolymer coatings with respect to being fire protective and corrosion resistant has been studied,[1−5] concentrating mainly on the fire-resistant time, thermal conductivity, and thermogravimetric analysis of the geopolymer coating by far. Few literature works were reported in terms of the surface adhesion properties of geopolymer coatings to substrates.

The surface characteristics and contact angle of the substrate have important impacts on the adhesion properties, which is the key to endow geopolymer coatings with well resistance to corrosion and heat. Poor adhesion could easily lead to problems such as coating cracks, peeling at an early stage, and inability to work with the substrate.

The adhesion depends on many factors between the matrix and the geopolymer, such as chemical composition of the raw materials, the formulation of the geopolymer,[1] the type of substrate, surface roughness of the substrate, etc.

An important factor affecting the bond strength is the surface treatment method. Chemical and mechanical treatments (silanization and nitrophosphoric acid) were conducted on metallic substrates, e.g., aluminum and steel plates, to improve the adhesion. The tests of pull-out, single-and double-shear, and the mixed mode flexural were used to confirm the value of bonding strength. A chemical interaction of Al−O−Fe bonds between geopolymer gel and mental substrates was found.[2] Nevertheless, it is indicated that[1] the bonding is physical rather than chemical. It is recognized[1] that the

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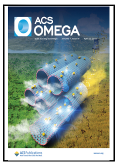

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Table 1. Composition of Metakaolin

metakaolin	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	moisture content	loss on ignition
chemical composition, wt %	53.90%	42.02%	1.52%	0.07%	0.06%	0.07%	0.22%	0.09%	0.33%	0.18%

geopolymers of chemical Al−O−Fe bonds with a higher Al/Si ratio should have better adhesion, but this is not supported[1] by the experimental results that the geopolymers of Si/Al ratio = 2.5 with fewer Al atoms have better bond strength than the geopolymers of Si/Al ratio = 1 and 2. De Barros et al.[3] also believe that mechanical treatments are more effective than chemical treatments when geopolymers are used as adhesives for both steel and aluminum joints.

Temuujin et al.[1] pointed out that though all metal substrates are pretreated in a standard way, the adhesion of geopolymer coatings are different, which is not caused by surface roughness. The roughness of each substrate surface is also different due to a number of affecting factors, e.g., the treating times and power of grinding. A large number of scholars have been studying the relationships between the roughness of the substrate surface and bonding strength, providing valuable contributions to the literature on geopolymers as coating materials.

Generally, the bond strength will increase with the increase in roughness because it will increase the contact area between the two substrates and increase the adhesion through mechanical anchoring. Therefore, we should not only pay attention to the surface treatment methods but also determine the correct surface parameters to characterize the surface roughness.

Many parameters have been used to characterize the roughness, among which the most common one is the profile centerline roughness, Ra.[4] In the macro-scale, the relationship between Ra and the mechanical properties, e.g., splitting strength, bending strength, and shear strength, can be established at a confidence level of approximately 0.85.[5] The relationships between Ra and friction coefficient,[6] ultimate load,[6−9] and wear rate[10,11] were also developed on a micro-scale by researchers. De Barros et al.[3] studied the relationship between substrate roughness and bonding strength; from the results, multi-parameters are more effective than a single parameter to study this relation, and the confidence level of the multi-parameter formula can reach 0.99.When characterizing roughness by multiple parameters, a relationship between it and the bonding performance can be better specified.[3,12−14] However, each study uses different multi-parameter combinations selected by itself, which is not uniform and has no universal applicability. Additionally, due to the difference of each experiment, the value of the same parameter is not the same.

As the determination of Ra is determined by the profile centerlines of the substrate surface, it is difficult to obtain an appropriate value of Ra to represent the roughness of the substrate surface. As alternatives, numerous studies have been attempted to find better parameters.[15,16] The roughness of the substrate is expressed by the average radius of curvature of the roughness of the substrate.[15] A dimensionless coating parameter was proposed by Goltsberg et al.,[16] which is able to explain the relationship in a better way. It is given by the following equation:

$$\lambda' = \left(\frac{t}{R}\right)\left(\frac{P_{c\_co}}{P_{c\_su}}\right)^{-0.507} \tag{1}$$

The main objective of this study is to evaluate the influence of substrate surface roughness on the shear strength of geopolymer coatings and to determine the parameters that can better characterize the substrate surface roughness. Geopolymers based on metakaolin with different mixing ratios are used as an adhesive for steel substrates.

2. EXPERIMENTS

2.1. Raw Materials. The primary aluminosilicate source material used in preparing geopolymer specimens for property tests is metakaolin. The metakaolin was provided by Advanced Cement Technologies, LLC, and its chemical composition is shown in Table 1.

The desired composition of the alkaline-silicate activator was formulated by blending commercial sodium silicate solution with 10.60 wt % Na_2O, 26.50 wt % SiO_2, 62.90 wt % H_2O, and 50% sodium hydroxide with 50.00 wt % NaOH and 50.00 wt % H_2O, which are given in Tables 2 and 3. The specification of the substrate is low carbon steel, as shown in Table 4.

Table 2. Composition of Sodium Silicate Solution

solution	Na_2O	SiO_2	H_2O	density (g/mL)
sodium silicate solution	10.60%	26.50%	62.90%	1.39

Table 3. Composition of Sodium Hydroxide

solution	NaOH (wt %)	H_2O (wt %)	density (g/mL)
50% sodium hydroxide	50.00%	50.00%	1.53

Table 4. Specification of the Substrate

	material	carbon steel standards	temper	size
substrate	low carbon Steel	ASTM A36	cold finish	101.6 mm × 25.4 mm × 1.6 mm

2.2. Geopolymer Synthesis. The recipe of synthesizing geopolymer employed in this study is given in Table 5. In all the procedures, sodium silicate solution and silica fume were first mixed at room temperature to prepare the alkaline activator. The mixed solution was stirred at a speed of 350 rpm for 30 min, then mixed with metakaolin, and stirred for 30 min again, and eventually the mud was poured into a mold. The mold was vibrated for 30 min to remove air bubbles inside the mixture.

The paste was poured on the top of a steel plate and spread using a rectangular trowel, with proper maintenance in keeping the coating uniform thickness. The coated steel plates were covered with a clean plastic sheet and then placed in an oven at a temperature of 70 °C for curing for 7 days.

2.3. Surface Treatment and Surface Characterization. The surface of the steel plates were treated by corundum abrasive paper (grade 60#, 120#, 240#, and 800#) and then washed with distilled water and acetone. In order to

Table 5. Synthesizing Recipe

recipe	metakaolin (g)	sodium silicate (mL)	50% NaOH (mL)	silica fume (g)	Si (mol)	Al (mol)	Na (mol)	Si/Al (molar ratio)	Na/Al (molar ratio)	L/S (mass ratio)
MK2	150	147	30	15	2.47	1.24	1.27	2	1.03	1.67
MK2.5	150	174	90	45	3.09	1.24	2.55	2.5	2.06	2.53
MK3	150	238	120	60	3.71	1.24	3.43	3	2.77	3.42

characterize the roughness of the treated substrate, the surface analysis was conducted on steel substrates by a three-dimensional (3D) confocal microscope (Sensofar Metrology). The test area is 5 mm × 5 mm. The main quantitative parameters of surface roughness are listed in Table 6.

Table 6. Roughness Quantitative Parameters

parameters	description
Ra	arithmetic mean deviation of the roughness profile
Rt	total height of the roughness profile
Rz	maximum height of the roughness profile
Rv	maximum valley depth of the roughness profile
Rp	maximum peak height of the roughness profile
Rsm	mean width of the roughness profile elements
Sa	arithmetic mean height of the surface
Sq	root-mean-square (RMS) deviation of the surface
Sp	maximum height of summits
Sv	maximum depth of valleys
St	total height of the surface
Sz	10-point height of the surface

2.4. Adhesion Test. Based on ASTM D 1002-10, the shear strength was obtained by a single-lap joint test. The metallic plates (101.6 × 25.4 × 1.6 mm) were assembled with 12.5 mm of overlap length, as shown in Figure 1. The tests were conducted on an INSTRON universal testing machine (Massachusetts, USA), with a max load of 30 kN, at a speed of 0.05 mm/min at room temperature. Three samples are tested under different given roughness conditions, specifically.

3. RESULTS AND DISCUSSION

3.1. Roughness Parameters and Test Results. The 3D surface profile of the substrate is presented in Figure 2. S60 (S120, S240) represents a sample treated by 60 (120, 240) mesh sandpaper.

It can be seen from Figure 2 that the surface of the steel polished by 240-mesh sandpaper is quite smooth, while that by 60-mesh sandpaper has relatively deep ravines. One side of the figure is blue, the other red, indicating that the specimen itself has a micron-level height difference; nevertheless, this does not affect the characterization of roughness based on fractal geometry. Based on fractal geometry analysis, we can get the surface roughness parameters of the samples (shown in Table 6).

3.2. Specimens Sanded by Sandpaper with 120# Grits. From Figure 3, the histogram represents the relative area and the dot diagram represents Sa. Based on ASTM D 1002-10, each unidirectional shear specimen consists of two separated steel plates. For MK2−1, in which −1 represents the first steel plate, MK2 is the number of recipe. Sa is a height parameter and closely related to the selected face, representing the arithmetic average height of the selected face. The relative area is a function that resulted from area scale analysis. Brown and Siegmann[17] pointed out that the bonding strength will be underestimated at a larger scale by the model, while below the basic scale, the value of the correlation coefficient could be very low and the bonding strength will be overestimated.

All the samples were sanded by sandpaper of 120# grits. From Figures 3 and 4, the values of the relative area are almost 1.04, but the values of Sa are considerably different. Hence, the roughness parameter, Sa, is inappropriate to measure the adhesion because the obtained values for the same surface are quite different. The relative area is a better alternative to evaluate the adhesion. In conclusion, the literature works on characterizing the surface roughness of the structure and establishing the relationship with the shear strength by using the parameters, Ra and Sa, need re-evaluations.

When the relative area is used as the indicator of roughness, the values of the specimens are equal, closing to 1.04. It can be seen from Figure 5 that the higher the Si/Al ratio, the greater the shear strength of the coating.

The effects of the silicon-to-aluminum ratio on compressive strength and bond strength are different. From Figure 3, the bond strength increases with the increasing of the Si/Al ratio, which is consistent with the literature (23).

The strength, reaction, and microstructure of MK-based geopolymers vary in relation to the individual N-A-S-H gel; they were compared at different Si /Al ratios by Wan et al.[18] As most of the nuclei were not dispersed, a small amount of geopolymer binder and some zeolite cores were manifested when Si/Al = 1, and at this moment, macro-pores were formed. It was also observed that geopolymers present a feature of high contents of crystalline phase. When Si/Al = 2 and 3, a homogeneous geopolymer binder and derivatives of soluble silicates, such as nesosilicates and silicic acid, were observed, respectively. In reference to Si/Al = 4, a large number of micropores/mesopores were observed, but the geopolymer binder was not.

3.3. Results of Samples Sanded by Sandpaper of 60# Grits, 240# Grits, and 800# Grits. *3.3.1. Roughness*

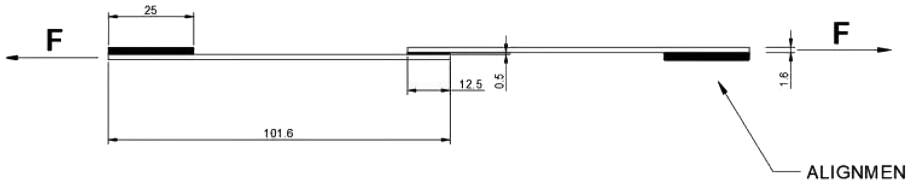

Figure 1. Samples' geometry (dimensions in mm).

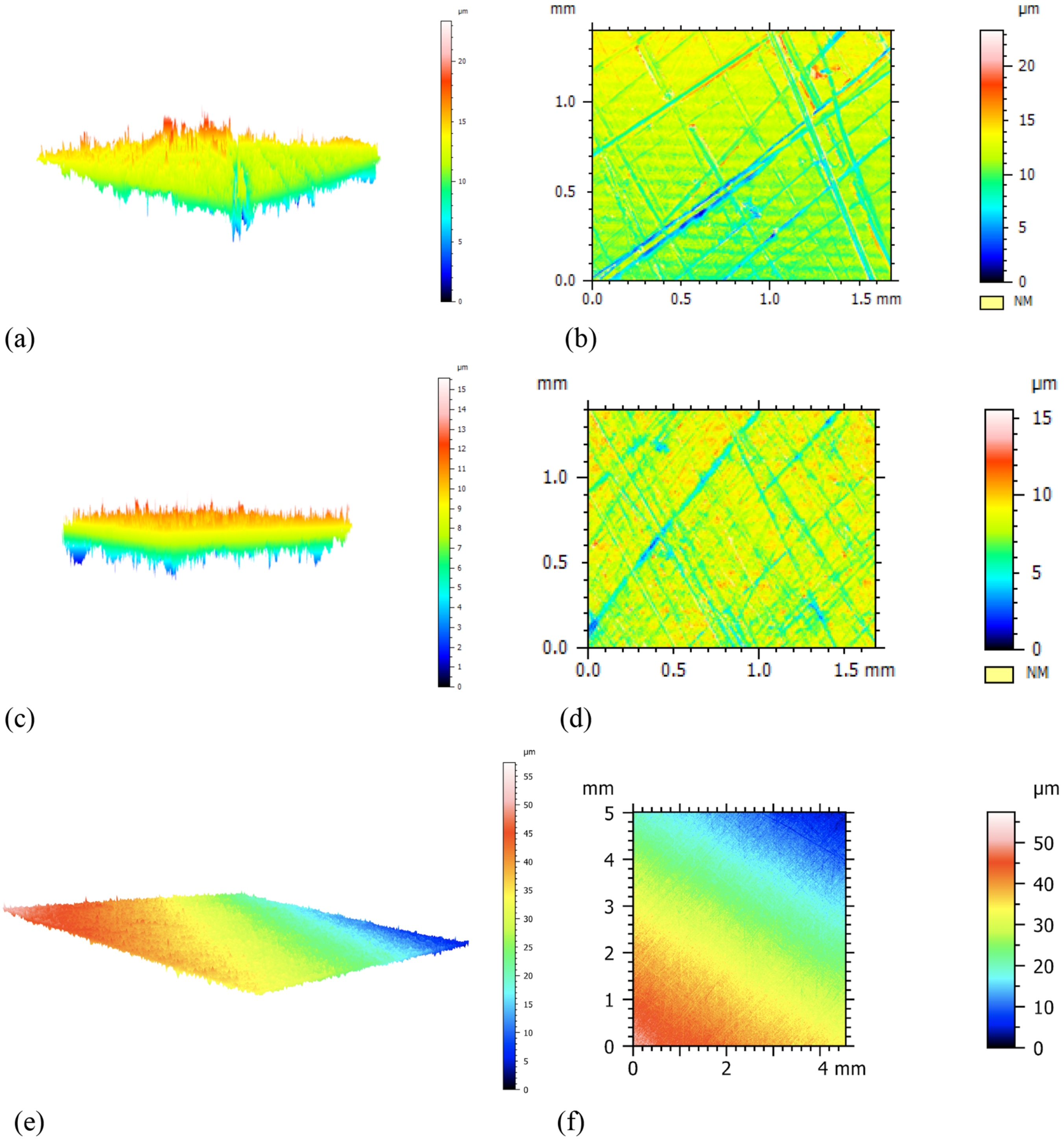

Figure 2. 3D surface profile and topography of samples. (a) 3D surface profile of S60. (b) Topography of S60. (c) 3D surface profile of S120. (d) Topography of S120. (e) 3D surface profile of S240. (f) Topography of S240.

Characterization. In order to exclude other influencing factors and ensure that only the interface roughness affects the bond strength, the geopolymer recipe used in this section is MK2.

It can be seen from Figure 6 that the value of the relative area is close when three points on the sample are taken arbitrarily for testing. Therefore, we can take a certain small area (5 mm × 5 mm) to represent the whole sample.

With the increase in the number of sandpaper grits, the surface of the treated specimen gets smoother and the value of its relative area decreases. When the amount of grit is over 240, the value of the relative area almost remains constant, indicating that the surface roughness of the specimen does not change much.

From Figure 7, the relative area depends on the area scale. When the scale is larger than 10,000 um^2, although the samples are processed by sandpaper of different grits, the values of the relative area remain 1. Therefore, the magnitude of scale employed should be seriously determined when characterizing the surface roughness. The volatility gets larger after grinding

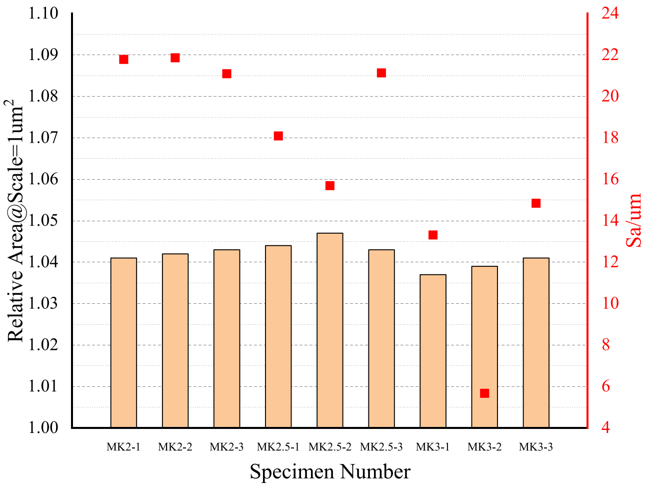

Figure 3. Surface roughness parameters. (Left: relative area; right: Sa).

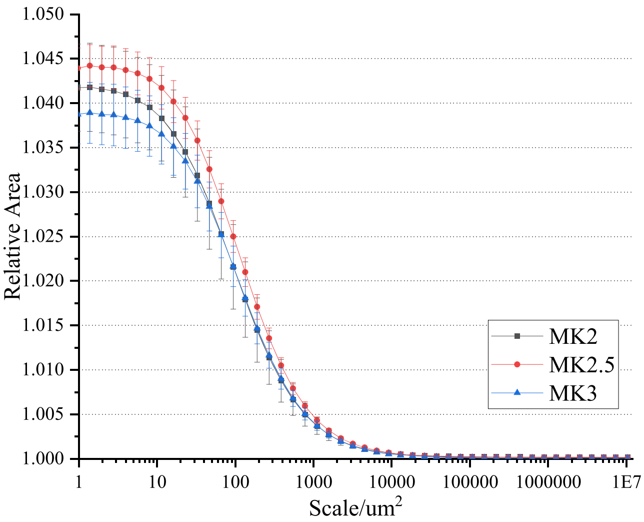

Figure 4. Scale-sensitive fractal plot.

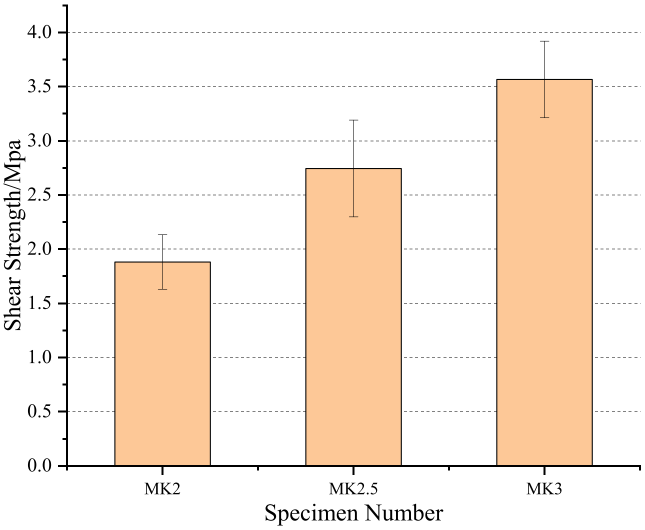

Figure 5. Effect of Si/Al ratio on shear strength of the geopolymer coating.

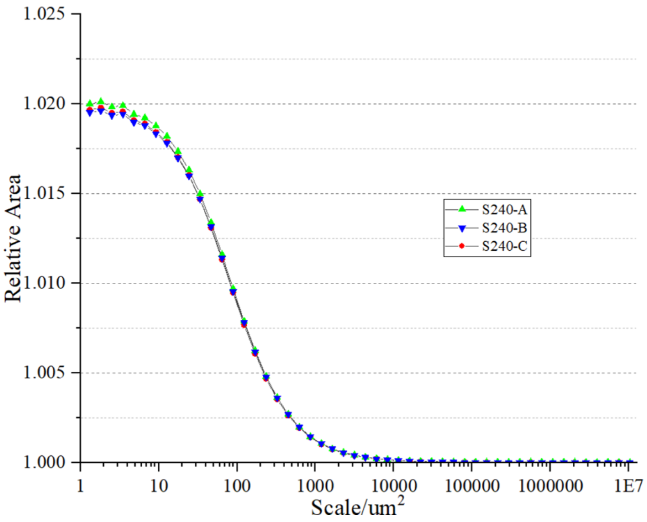

Figure 6. Scale-sensitive fractal plot of samples used in the unidirectional shear test; S240-A means a sample treated with 240-mesh sandpaper, in which -A stands for any test area A.

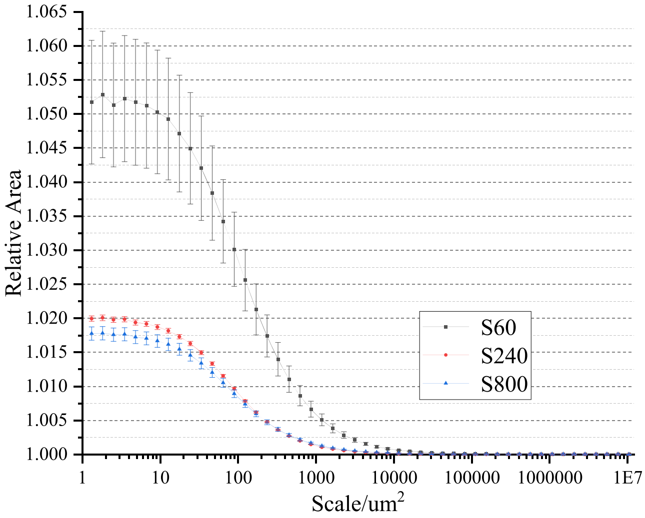

Figure 7. Scale-sensitive fractal plot of samples used in the unidirectional shear test; S60 (S240, S800) represents a sample treated with 60 (240, 800) mesh sandpaper.

the steel plate due to the coarser particles of 60# sandpaper; in this way, the error bar is higher.

3.3.2. Bond Strength Analysis.

The results of surface scanning after pretreatment are presented in Table 6. From Table 7, the value of the relative area decreases and the changes of the value of Sa are irregular with the increase in the number of sandpaper meshes, which is consistent with the previous analysis. It is inappropriate to characterize the surface roughness and establish strength relationship by using the height parameter as the bond strength also depends on occlusion and contact angle of the cross section.

Table 7. Roughness Parameter of Samples

specimen number	S60	S240	S800
relative area	1.052	1.020	1.018
Sa	8.96	7.75	8.02

The bonding strength reduces with the decrease in the value of relative area, shown in Figure 8. When the sandpaper mesh number is greater than 240, the bonding strength does not change much. The bonding strength of the steel plate treated with 60-mesh sandpaper is significantly higher than that treated with 240- and 800-mesh sandpaper. Therefore, the sandpaper with a mesh number less than 240 is recommended when processing the steel surface.

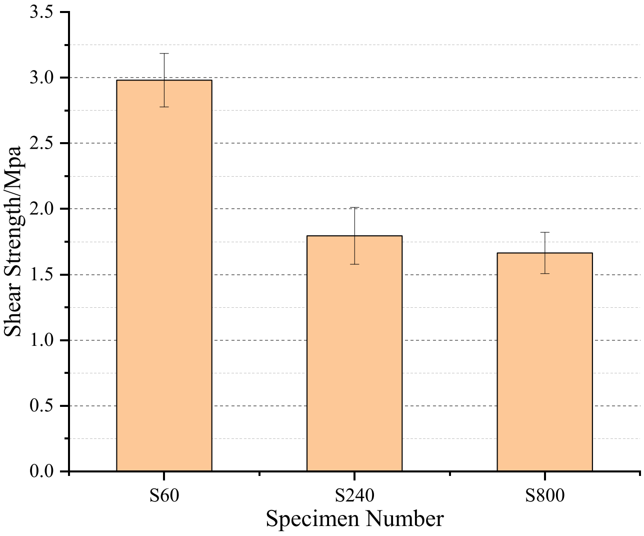

Figure 8. Effect of relative area on shear strength of the geopolymer coating.

For the geopolymer muds with the same composition ratio, the shear strength rises with the increase in the relative area, with a confidence of 0.94 (as observed in Figure 9.). As can be seen in Figure 10, the correlation between the shear strength and Sa is unobvious as it is not a generally admitted parameter.

4. CONCLUSIONS

In this work, the effects of substrate surface roughness on the adhesion of geopolymers to metal substrates are studied, and parameters that can be used to characterize the roughness are proposed.

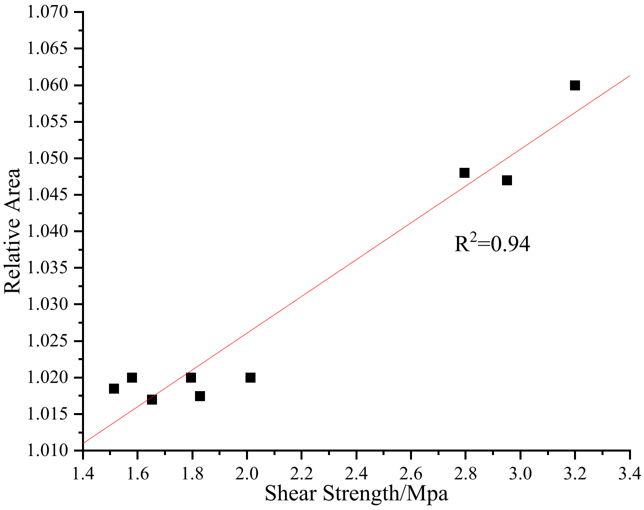

Figure 9. Relative areas versus adhesive strength.

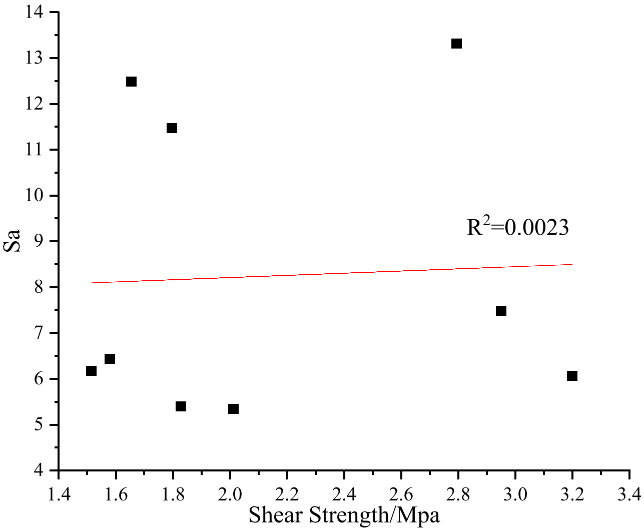

Figure 10. Sa versus adhesive strength.

1. As the parameter Ra is determined by the profile centerlines of substrate surface, it is difficult to get an appropriate value of Ra to represent the roughness of the substrate surface. The relationship between roughness and bonding strength based on the parameter Ra is unreliable.

   Sa is a height parameter and closely related to the selected face, representing the arithmetic average height. Although the parameter Sa is better than the parameter Ra, it is not accurate enough to characterize surface roughness and evaluate the adhesion because the obtained values even for the same surface are quite different. The parameter-relative area, determined by area scale fractal analysis, can effectively characterize the surface roughness, predict the texture component of bond strength and establish a connection between which and the bonding performance of the geopolymer coating at a high level of confidence.
2. When the relative area is used as the indicator of roughness, the values of the specimens are equal, closing to 1.04. The higher the Si/Al ratio, the greater the shear strength of the coating. This is because geopolymers synthesized with different Si/Al ratios have different phases in the geopolymer binder. The formation of geopolymer binders is of great significance for controlling mechanical strength.
3. The relative area depends on the area scale. When the scale is larger than 10,000 um^2, although the samples are processed by sandpaper of different grits, the values of the relative area remain 1. Therefore, the magnitude of scale employed should be seriously determined when characterizing the surface roughness. The bonding strength reduces with the decrease in the value of relative area. The sandpaper with a mesh number less than 240 is recommended when processing the steel surface.

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Notes

The authors declare no competing financial interest.

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