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CORROSION RESISTANCE OF POLYMER-SILICA-CALCITE TEXTURED SURFACES

Purpose. Determine the relationship between the corrosion resistance properties of the additive coatings and the fractional composition of the components that form the texture.

Methodology. In this work, an additive bifractional texture was created on the basis of a styrene-butyl acrylate copolymer as a binder and hydrophobized silica nanoparticles and hydrophobized calcium carbonate microparticles as texture-forming fillers. The coatings were applied to the substrate by pneumatic means. To assess the corrosion resistance, the samples were immersed in distilled water and salt solution. To assess the change in properties, the angle of wetting with water (the sitting drop method) was used, and scanning electron microscopy was used to observe structural changes on the surface. Electrochemical impedance spectroscopy and potentiodynamic polarization curves were used to evaluate the corrosion potential.

Findings. The results show that the obtained coatings are not completely resistant to prolonged exposure to water. The main defects are cracking and an increase in surface polarity. This leads to a drop in the angle of wetting with water. An additional deterioration in the water-repellent properties is due to a decrease in the adhesion of the polymer to the filler. According to the studies of self-corrosion potential, the sample with the largest amount of micro-sized filler and the lowest polymer content was the most stable. For this sample, no loss of hydrophobic properties was observed after prolonged immersion in a corrosive environment, although cracks formed on the surface.

Originality. For the first time, significant changes in corrosion resistance have been shown to be possible for additive coatings obtained by pneumatic spraying with a hierarchical surface structure, depending on the fractional ratio of micro- and nanosized particles that form the texture.

Practical value. The composition of an additive coating based on a styrene-acrylic polymer and structure-forming particles has been developed, which is characterized by increased corrosion resistance due to the fractional ratio, which allows forming a structure with high water repellency.

Keywords: hydrophobicity; textured coating; contact angle; water-repellent coatings; corrosion.

Introduction. The use of textured surfaces to increase the ability to repel liquids by forming anomalous wetting states – Wenzel and Cassie and it is attracting attention as a promising approach to the formation of useful properties of materials: anti-icing, increased corrosion resistance, self-cleaning, etc. [1–4]. There are many research papers that investigate methods of creating texture on a surface among which laser engraving, electrochemical etching and sol gel fusion can be mentioned, however these technologies have a scaling problem as further increasing the area of the lining requires high equipment costs [5, 6]. An alternative is additive coatings that can be applied to the surface by pneumatic means and solve one of the main problems of this technology, namely its scalability [7]. At the same time, the surface structure of such materials can be flexibly adjusted by varying their fractional composition, which ultimately allows changing their degree of water repellency. The development of a relatively technological method to adjust the texture parameters of coatings obtained by classical pneumatic spraying technology by varying their component composition is a way to solve two essential problems of textured water repellent surfaces at the same time: scalability and cost [8–10]. In this work, the effectiveness of this method is evaluated by the indicators of one of the final target properties – corrosion resistance, which illustrates the practical potential of its application.

Task statement. The literature review revealed that there is a need for resistant coatings that can provide water-repellent properties when exposed to corrosive media. For this purpose, water-repellent coatings based on the principle of bifractional fillers of the micro- and nanoscale with a depleted polymer matrix composition are effective. In this work, the method of electron microscopy

was used to evaluate the structure of the texture, and wettability anomalies were determined using the equilibrium edge angle of water wetting. The stability of the water-repellent properties was evaluated during prolonged contact with liquid water and corrosive environments.

Purpose. The purpose of this work is to establish the relationship between the corrosion properties of additive coatings and the fractional composition of the components that form the texture.

Materials and methods of the research. To form textured surfaces were used two filler types – nanoscale and microscale. As a nanoscale filler, dimethyldichlorosilane treated silica (Aerosil R972, Evonik, Germany), referred to as “R972”. As microscale filler, a commercial grade filler for plastics was used, ground calcite (Normcal 2, Som Calcite, Turkey). The polymer matrix includes the AC80 styrene-butyl-methacrylate copolymer (OMNOVA Solutions, USA), referred to as “AC”.

To reduce surface energy, the calcite surface was treated with stearic acid according to the procedure [11]. The process was carried out in 1 wt. % ethanol solution. After conditioning 5 g of calcium carbonate in 30 ml of solution for 24 h, the liquid above the precipitate was decanted and the particulate was washed with pure ethanol and filtered on a paper filter. Obtained hydrophobized calcite referred as “CaCO₃”.

The coating substrates were mirror polished aluminum plates (commercial anodized 6063 aluminum alloy). The coatings were applied by pneumatic spraying of polymer-filler solutions in xylene (a mixture of para- and ortho-xylene). The ratio of xylene and other components was 4:1, respectively. The compositions of the created samples are given in the Table 1. After spraying, the coated plates were dried in an oven for 1 hour at 100 °C. Pure polished aluminum plate and polymer coated aluminum plate were used as reference.

Table 1

Sample compositions

Sample name	Aerosil R972, wt. %	Hydrophobized calcium carbonate (CaCO ₃), wt. %	Styrene-butyl-methacrylate copolymer (AC), wt. %
AL	-	-	-
AC	-	-	100
C3	13	78	9
C4	5	90	5
C5	35	42	23

The coated aluminum plates were insulated with epoxy resin. As a result, only one side of the surface was subjected to corrosion. The test samples were immersed in 3,0 wt. % NaCl solution in water. Electrochemical impedance spectroscopy and potentiodynamic polarization curves of the samples were measured using an electrochemical workstation BP-300 (Biologic, France). In the experiment, a three electrode system was used: the working electrode was the specimens with different corrosion time; the auxiliary electrode was a 4 cm² Pt sheet; the reference electrode was a saturated calomel electrode (SCE); the working temperature was room temperature (25 °C); all the potential values were relative to the potential of saturated calomel electrode; the electrolyte used in the experiment was 3,0 wt. % NaCl solution; the frequency range of electrochemical impedance spectroscopy (EIS) was 10~100 kHz; the amplitude of disturbance AC potential applied during the test was 10 mV; the scanning potential range of the potentiodynamic polarization curve was ±0,3 V vs. E_{corr} (relative to the self-corrosion potential); the scanning speed was 1 mV/s.

Water contact angles data was obtained by sessile drop technique using an optical microscope and a digital camera with a 10x objective. Scanning electron microscopy (Sigma 300, Zeiss) was used for to observe structural changes on the surface.

Research results. Considering that polymers, especially polar polymers, can absorb liquid water, their water repellent properties and long-term stability of coatings in wet or underwater conditions may deteriorate with time. The samples did not lose Cassie condition after exposure to salt

water for 32 hours (Table 2). The wetting angle of sample C5 (35% R972 + 42% CaCO₃ + 23% AC) started to increase after 4 hours of immersion in water. A possible reason for this is the self-repair of the structure after the surface layer was removed. Also, the results showed that sample C4 (5% R972 + 90% CaCO₃ + 5% AC) was the most stable.

Table 2

Surface characterization of the water resistance (water contact angles, deg.)

Sample	Composition	Duration of immersion in water, hours					
		0	1	2	4	8	32
C3	13% R972 + 78% CaCO ₃ + 9% AC	146°	146°	130°	138°	125°	122°
C4	5% R972 + 90% CaCO ₃ + 5% AC	146°	146°	141°	140°	136°	130°
C5	35% R972 + 42% CaCO ₃ + 23% AC	146°	120°	109°	100°	110°	124°

It can be assumed that after wetting with water, the adhesion of the polymer to the filler surface decreases and water can concentrate at the boundaries between the polymer and particles. This feature is most visible for sample C3, which can be confirmed by studying the structure of such coatings (Fig. 1). The photo shows that some particles have detached from the surface, forming well-defined cavities (Fig. 1 C3a and C5a).

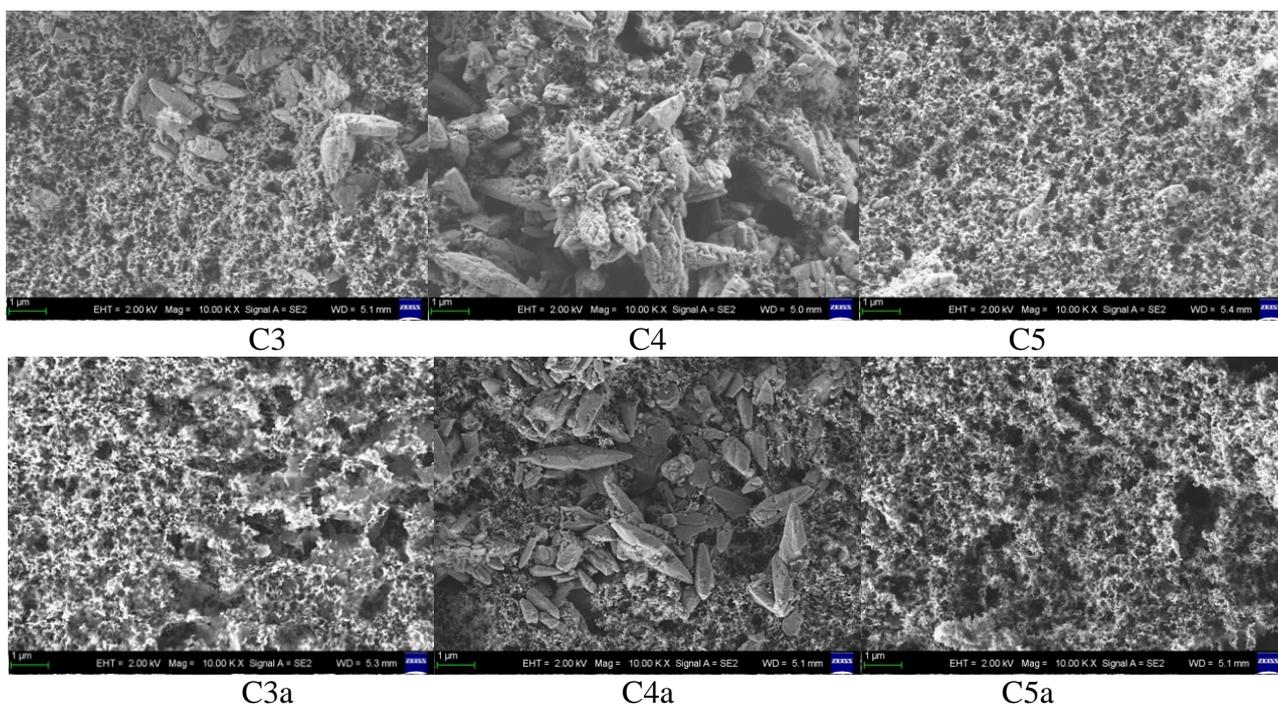


Fig. 1. SEM images of the sample surface before (C3-C5) and after (C3a-C5a) 32 hours of static water immersion

Figure 2 shows the polarization curves for samples C1-C5. Also, in table 2 are given self-corrosion potential of samples C1-C5. The polarization curves measure the corrosion rate of the surface of the samples. The lower the density of the self-corrosion current, the lower the corrosion rate, the more positive the self-corrosion potential, the less the corrosion tendency.

From the self-corrosion potential data (Table 3), it can be said that sample C4 has the strongest corrosion resistance. Sample C2 is more susceptible to corrosion than the pure aluminum plate (C1). The self-corrosion potential of sample C3 is close to that of sample C4, but it also has high corrosion resistance. The self-corrosion potential of sample C5 is close to that of pure aluminum, which may be due to the fact that water molecules easily penetrate the coating.

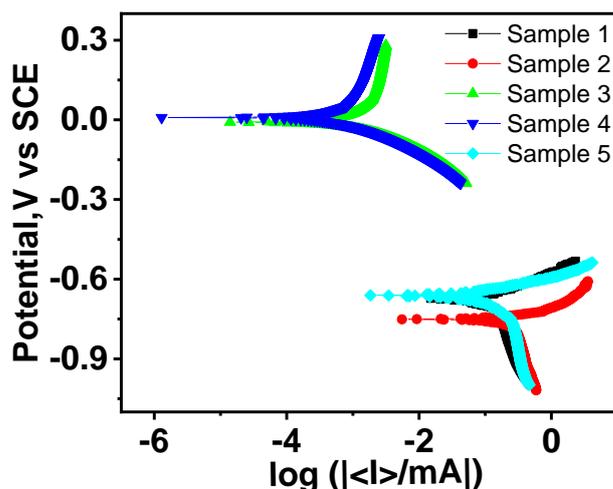


Fig. 2. Polarization curves of different electrodes, where: Sample 1 – polished aluminum plate; Sample 2 – AC coated aluminum plate; Sample 3 – 13% R972 + 78% CaCO₃ + 9% AC; Sample 4 – 5% R972 + 90% CaCO₃ + 5% AC; Sample 5 – 35% R972 + 42% CaCO₃ + 23% AC

Table 3

Surface characterization of the water resistance (water contact angles, deg.)

Sample	Composition	Self-corrosive potential, mV (SCE)
C1	-	-660
C2	100% AC	-720
C3	13% R972 + 78% CaCO ₃ + 9% AC	-6
C4	5% R972 + 90% CaCO ₃ + 5% AC	137
C5	35% R972 + 42% CaCO ₃ + 23% AC	-658

Figure 3 shows the results of the AC impedance spectra of the samples. Table 4 shows the modulus of high-frequency and low-frequency impedance of samples. The low-frequency modulus for sample C4 is much higher than that of other samples. This indicates that the corrosion resistance of the sample can be effectively improved by superhydrophobic modification. Sample C3 also exhibits high corrosion resistance. Sample C5 has properties close to the pure aluminum surface.

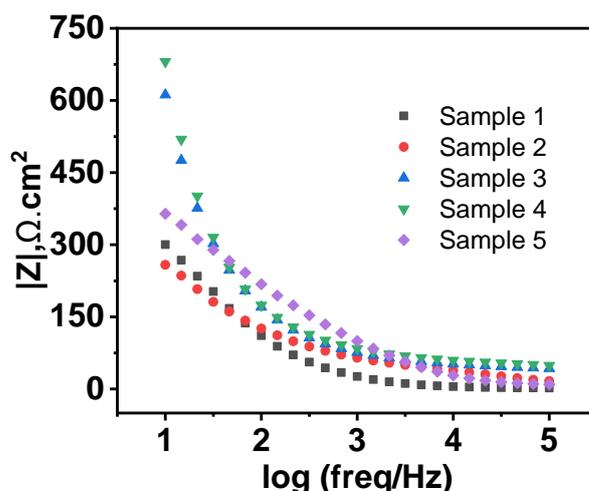


Fig. 3. Bode plots of the EIS results for different specimens, where: Sample 1 – polished aluminum plate; Sample 2 – AC coated aluminum plate; Sample 3 – 13% R972 + 78% CaCO₃ + 9% AC; Sample 4 – 5% R972 + 90% CaCO₃ + 5% AC; Sample 5 – 35% R972 + 42% CaCO₃ + 23% AC

Table 4

The modulus of high-frequency and low-frequency impedance of samples

Sample	Composition	High-frequency impedance modulus, $\Omega \cdot \text{cm}^2$	Low-frequency impedance modulus, $\Omega \cdot \text{cm}^2$
C1	-	2,149	300
C2	100% AC	16,59	258
C3	13% R972 + 78% CaCO ₃ + 9% AC	42,54	611
C4	5% R972 + 90% CaCO ₃ + 5% AC	49,06	680
C5	35% R972 + 42% CaCO ₃ + 23% AC	9,67	364

When comparing the wetting angle with water after 72 hours of immersion in a solution of 3,0 wt. % NaCl, the surface of sample C5 suffered the most severe corrosion (Table 5). It is followed by specimen C3, with specimen C4 having no obvious changes, indicating a significant improvement in the corrosion resistance of the specimens after hydrophobic treatment of the microfiller – calcium carbonate treated by stearic acid. The effect of increasing the wetting angle for sample C5, as was the case when immersed in distilled water, was not observed for NaCl solution.

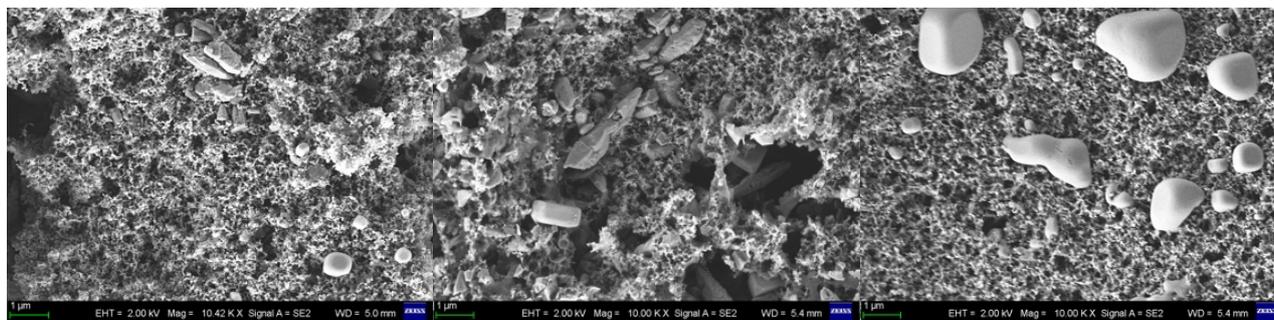
Table 5

Water contact angles (deg.) of coatings after immersion in NaCl solution

Sample	Composition	Duration of immersion in 3,0 wt. % NaCl solution, hours			
		0	24	48	72
C3	13% R972 + 78% CaCO ₃ + 9% AC	146°	120°	125°	120°
C4	5% R972 + 90% CaCO ₃ + 5% AC	146°	135°	134°	134°
C5	35% R972 + 42% CaCO ₃ + 23% AC	146°	120°	104°	89°

Figure 4 shows the SEM images of the C3-C5 samples after 72 h of soaking in corrosion medium (3,0 wt. % NaCl solution). The photo shows that many holes and uneven branches appear on the surface, and some areas fall off, indicating partial erosion of the coating on the samples during the corrosion process.

According to Figure 1 (C5) and Figure 4 (C5a), the surface of the specimens before corrosion consists mainly of spherical particles, which are generally flat but with many cracks. Figure (C5c) shows NaCl particles on the coating surface, which means that the coating was most degraded after exposure to the corrosive environment for 72 h. By comparing the surface photo of the C3a and C4a specimens after the action of water and the surface photo of C3c and C4c after the action of the NaCl solution, it can be seen that the cracks and caverns increased after the action of the corrosive medium. However, salt crystals are not observed in these samples, as in the case of sample C5c.



C3c C4c C5c
Fig. 4. SEM images of sample surfaces after corrosion C3c-C5c (immersion in 3,0 wt. % NaCl solution)

Conclusions. As a result, it is shown that coatings based on a styrene-butyl acrylate copolymer and two hydrophobic fillers nanosized silicon dioxide and microsized calcium carbonate are not resistant to prolonged residence in water. The main defects observed are cracking and an increase in surface polarity, which leads to a drop in wetting angle with water. Also, water reduces the adhesion of the polymer to the filler, further degrading the water repellent properties. The self-corrosion potential study showed that the most resistant specimen was the specimen with the highest amount of micro-sized filler and minimum polymer. For this sample, no loss of hydrophobic properties was also observed after prolonged immersion in the corrosive medium, although cracks were formed on the surface.

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КОРОЗИЙНА СТІЙКІСТЬ ПОЛІМЕР-КРЕМНЕЗЕМ-КАЛЬЦИТОВИХ ТЕКСТУРОВАНИХ ПОВЕРХОНЬ

Мета. Встановлення взаємозв'язку протикорозійних властивостей адитивних покриттів з фракційним складом формуючих текстуру компонентів.

Методика. У даній роботі адитивна біфракційна текстура створена на основі сополімеру стирол-бутил-акрилату як зв'язуючого та як текстуроутворюючі наповнювачі наночастинки гідрофобізованого кремнезему та мікрочастинки гідрофобізовано стеариновою кислотою карбонату кальцію. На підкладку покриття наносилися пневматичним способом. Для оцінювання корозійної стійкості зразки занурювалися у дистильовану воду та розчин солі. Для оцінювання зміни властивостей використано кут змочування водою (метод сидячої краплі), скануюча електронна мікроскопія для спостереження за структурними змінами на поверхні. Електрохімічна імпедансна спектроскопія та потенціодинамічні поляризаційні криві були використані для оцінки корозійного потенціалу.

Результати. В результаті показано, що отримані покриття не є повністю стійкими до тривалого перебування у воді. Основними дефектами є розтріскування і збільшення полярності поверхні. Це призводить до падіння кута змочування водою. Додаткове погіршення водовідштовхувальних властивостей пояснюється зменшенням адгезії полімеру до наповнювача. Згідно досліджень потенціалу самокорозії найбільш стійким виявився зразок з найбільшою кількістю мікророзмірного наповнювача і мінімальним вмістом полімеру. Для цього зразка також не спостерігалось втрати гідрофобних властивостей після тривалого занурення в корозійне середовище, хоча на поверхні утворилися тріщини.

Наукова новизна. Вперше показано, що для адитивних покриттів, одержаних пневматичним розпиленням, з ієрархічною структурою поверхні можливі суттєві зміни корозійної стійкості в залежності від фракційного співвідношення мікро- та нанорозмірних формуючих текстур частинок.

Практична значимість. Розроблено склад адитивного покриття на основі стирол-акрилового полімеру та структуроутворюючих частинок, яке характеризується підвищеною протикорозійною здатністю за рахунок співвідношення фракцій, що дозволяє сформувати структуру з високою стабільністю водовідштовхування.

Ключові слова: гідрофобність; текстуроване покриття; кут змочування; водовідштовхувальні покриття; корозія.