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AGING ANALYSIS OF TEXTURED WATER-REPELLENT COATINGS UNDER ULTRAVIOLET RADIATION AND WATER

The object of research in this work is a coating based on styrene butyl methacrylate binder and calcium carbonate modified with stearic acid. The existing problem is that the stability of the properties of superhydrophobic coatings when interacting with environmental factors – ultraviolet radiation, water vapor or dynamic action of water is limited. Establishing the relationship between the change in the chemical composition and texture of structured water-repellent surfaces under the influence of environmental factors is an essential step towards creating a stability model for such coatings. The work carried out is aimed at establishing the nature of the loss of water repellency of textured organo-mineral coatings under exposure to ultraviolet radiation in the UV-A range and water.

UV resistance testing was performed in accordance with ASTM D 4329. The surface texture was examined using electron microscopy. The study of the change in chemical composition was performed using the IR spectroscopy method.

As a result, it was shown that, under UV radiation, the most vulnerable component of organo-mineral coatings consisting of styrene-butyl methacrylate polymer and calcium carbonate modified with stearic acid is the polymer matrix, the oxidation of which leads to surface hydrophilization. The action of water in both static and dynamic modes leads to the loss of the upper layer of microparticles which forms the structure. It was found that in the surface layer of the polymer, upon irradiation with ultraviolet, the formation of polar carboxyl groups occurs at the initial stages of irradiation, which is accompanied by noticeable hydrophilization. Based on the obtained results, one of the ways to increase the resistance of additive water-repellent coatings to environmental factors can be the use of polymers that are more resistant to UV radiation. An alternative way is to use the optimization of the interfacial contact, which will ensure the slowing down of the loss of texture elements in the water environment.

Keywords: *water contact angle, UV resistance, water repellent coatings, superhydrophobicity.*

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1. Introduction

The stability of the ability of textured surfaces to water repellency is one of the important practical properties that determine their possible areas of application. However, as noted in [1], the stability of their properties when interacting with environmental factors – ultraviolet radiation, water vapor or the dynamic effect of water, including supercooled water, is limited. Other problems also include the limited scalability of such surfaces [2], which in some cases can be overcome by using laser texturing [3], and when obtaining superhydrophobic surfaces, for example, for architectural purposes, due to additive coatings applied using air spraying.

It is known that the Cassie state is provided by the joint action of the surface geometry, as well as its chemical composition, namely, polarity, the ability to form van der Waals bonds [4]. The latter is due to the presence of polar surface groups that can form during the oxidation of polymers used as matrices for additive coatings, as well as modifier layers if relatively polar organic particles are used as texture-forming elements.

The action of liquid water as one of the main environmental factors also plays a significant role, since the filler matrix adsorbed at the phase separation boundaries can weaken the interaction within the system. It is also known that polar polymers have a certain tendency to hygroscopic absorption of air moisture [5].

The combined action of these two factors is a typical attribute of the environment under operating conditions and is taken into account when determining the resistance of coatings to aging in atmospheric conditions [6].

Thus, establishing the relationship between the change in the chemical composition and texture of structured water-repellent surfaces under the influence of environmental factors such as ultraviolet aging and exposure to liquid water is an essential step towards creating a stability model for such coatings.

Thus, *the object of research in this work* is a coating based on styrene butyl methacrylate binder and calcium carbonate modified with stearic acid. *The aim of this work* is to establish the nature of the loss of water repellency of textured organo-mineral coatings under the influence

of UV radiation and water. To achieve this aim, the problems of studying the process of binder photooxidation are solved, the loss of water-repellency of coatings is fixed, and morphological changes in their texture are determined.

2. Research methodology

Styrene-butyl-methacrylate copolymer NeoCryl B-880 (DSM, Netherlands) was used as a polymeric binder. To create the texture, ground calcium carbonate brand Normcal 2 (Som Calcite, Turkey) was used, followed by modification with stearic acid in accordance with the procedure described in [7]. The process was carried out in 1 wt. % ethanol solution. Calcium carbonate was kept for 24 hours at 1 wt. % solution of stearic acid in ethanol, then the particles were washed with ethanol and filtered.

UV resistance testing was carried out according to ASTM D 4329. The UV source was a fluorescent lamp (340 UV-A, 400 W). The temperature of the samples was kept within 60 ± 2 °C.

The contact angle was determined by the sessile drop method using a digital camera and appropriate software.

The photo of the surface of the samples was taken on a scanning electron microscope REM-106 (Selmi, Ukraine). The IR spectrum of the styrene-butyl-methacrylate copolymer was obtained on a SPECTORD 75IR (Zeiss, Germany) in the range $4000\text{--}400$ cm^{-1} .

3. Research results and discussion

The polymer matrix based on styrene butyl methacrylate (Fig. 1) contains an aromatic ring, which is confirmed by the presence of absorption bands with coordinates 3045 and 3015 cm^{-1} , corresponding to the stretching vibration of the C–H bond [8]. The aliphatic part of the polymer (side isobutyl substituents and the main chain) can be identified by the absorption bands at 2950 , 2910 and 2850 cm^{-1} . A well-differentiated peak of stretching vibrations of the C=O group has coordinates of 1713 cm^{-1} . The band with coordinates 1449 cm^{-1} corresponds to the deformation vibrations of the C–H bond, and the complex of bands with coordinates 1375 and 1172 cm^{-1} corresponds to the ether group [9].

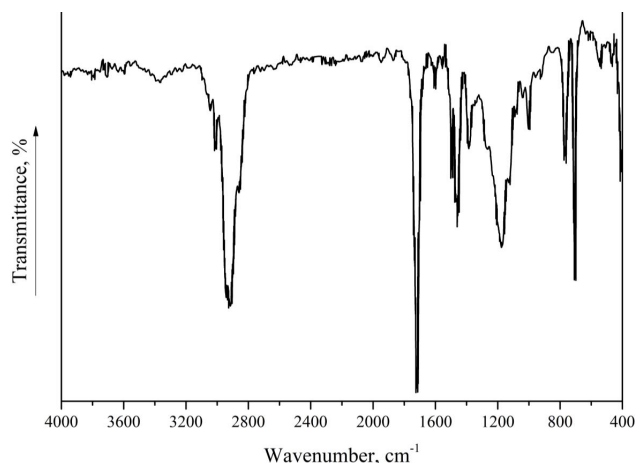


Fig. 1. Styrene-butyl methacrylate spectrum

Under conditions of light aging, an additional band with coordinates 1731 cm^{-1} appears in the spectra, which is related to the formation of a wide range of carboxyl

groups characteristic of acrylate oxidation products [10]. In order to quantify the process, the value of the carbonyl index, C.I., was used [11], which is the ratio of the intensities of the absorption bands with coordinates 1731 cm^{-1} and 2950 cm^{-1} .

Considering that the film thickness in the system under study was about 4 μm , the volume concentration of carboxyl groups formed in the surface layer was quite noticeable, which is confirmed by the rapidly growing value of the carbonyl index at a fairly short exposure time (Table 1).

Table 1

Band intensity and carbonyl index of the polymer matrix film after exposure to UV radiation

Irradiation time, min	I_{1731}	I_{2950}	C.I.
0	0	2.03	0
10	1.26	1.4	1.11
20	0.63	0.98	1.56
30	0.32	1.05	3.28
45	0.21	0.88	4.19

By the time the exposure time reaches 60 minutes, the film spectrum ceases to be distinguishable and merges with the baseline.

The water contact angle is a practical measure of the polarity of a surface. For example, the value of this parameter for the polymer before irradiation is 92° , 15 minutes – 75° ; 30 minutes – 59° , and 45 – about 33° . With an increase in the exposure time for a sample in a relatively thick layer, the contact angle remains within $25\text{--}30^\circ$ after 1 and 2 hours of testing.

When considering the UV stability of the filler for such systems – calcium carbonate hydrophobized with stearic acid [12], it was shown that it retains stable contact angle values for 2 hours, after which the modifier layer is destroyed. Therefore, it can be expected that the surface layer of the matrix will oxidize much faster than the oxidation of the modifier layer.

Compositions containing stearic acid modified filler were deposited on an aluminum substrate and exposed to liquid water under static and dynamic conditions in combination with ultraviolet light.

Long-term exposure (8 hours) of coating samples in liquid water leads, first of all, to washing out of the upper layer of texture-forming elements (Fig. 2, a), which is illustrated by the appearance of black areas on the surface of the sample – depressions left from the removed particles. With the combined action of ultraviolet radiation and dynamic water flow, this effect is significantly enhanced (Fig. 2, b), which is probably caused by ultraviolet ablation of the remaining polymer.

The contact angles of the surface of the compositions reflect changes in its texture and chemical composition (Fig. 3). Removal of part of the texture-forming particles after soaking in water causes a slight decrease in the contact angle with water. However, due to the fact that the surface roughness does not decrease significantly, but a significant change is the replacement of the contact surface from the modifier layer to the textured polymer, the Cassie state is preserved to some extent. According to the classical Cassie equation [13], this is possible only if 90° is exceeded for the intrinsic contact angles of the material, which indicates the preservation of the relatively unoxidized state of the polymer.

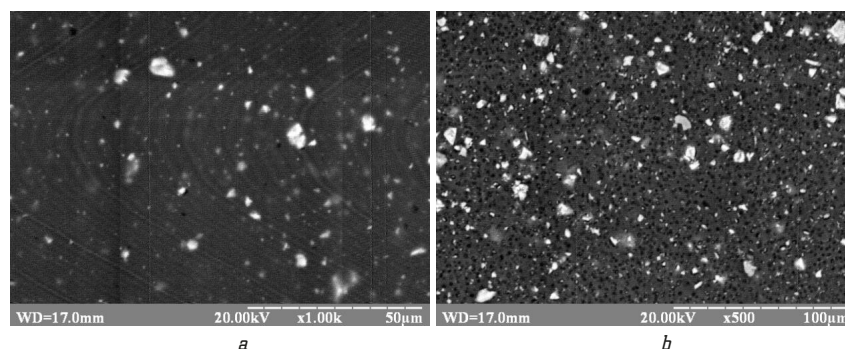


Fig. 2. The surface of the coatings exposed: *a* – under the conditions of static action of water; *b* – under conditions of combined action of UV light and dynamic water flow

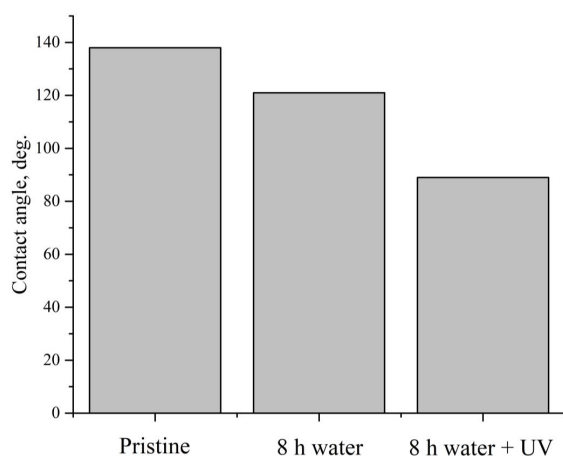


Fig. 3. Static water contact angles of surfaces

When exposed to UV radiation and the removal of structural elements from the surface, its hydrophilization is also observed, which is accompanied by a decrease in the contact angle to 89°, that is, the Wenzel state is observed and, accordingly, a significant decrease in water repellency.

The limitation of this study is to consider stability factors only for additive structures based on polymeric materials intended for outdoor use, however, not having maximum UV resistance and non-polarity. Also, only UV radiation and water factors are considered in the work, and for the design of more stable coatings, environmental factors such as salt fog, acid gases, etc. should also be considered.

A promising direction for the development of this study should be the use of more UV-resistant polymers, as well as the optimization of interfacial contact, which slows down the loss of texture elements in the aquatic environment.

4. Conclusions

It has been shown that, under UV radiation, the most vulnerable component of organo-mineral coatings consisting of styrene-butyl methacrylate and calcium carbonate modified with stearic acid is a polymer matrix, the oxidation of which leads to surface hydrophilization. At the same time, the action of water in both static and dynamic modes leads to the loss of the upper layer of microparticles that form the structure.

It has been established that in the surface layer of the polymer during ultraviolet irradiation, the formation of polar carboxyl groups occurs at the initial stages of irradiation,

which is accompanied by noticeable hydrophilization already during the first 15 minutes of the experiment.

Therefore, ways to increase the resistance of additive water-repellent coatings to environmental factors can be outlined: the use of more UV-resistant polymers, as well as the optimization of interfacial contact, which slows down the loss of texture elements in the aquatic environment.

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Conflict of interest

The author declares that they have no conflict of interest in relation to this study, including financial, personal, authorship or other, which could affect the study and its results presented in this article.

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