

## The effect of chemical modifications with spherosilicates of nanocomposite waterborne polyurethane hydrophilic coatings on anti-icing properties

Katarzyna Ziętkowska<sup>1</sup>, Rafał Kozera<sup>1,2\*</sup>, Bartłomiej Przybyszewski<sup>1,2</sup>, Anna Łabęda<sup>1</sup>, Anna Boczkowska<sup>1,2</sup>, Bogna Sztorch<sup>3</sup>, Robert E. Przekop<sup>3</sup>, Monika Pilz<sup>4</sup>, Christian W. Karl<sup>5</sup>

<sup>1</sup> Technology Partners Foundation, ul. Bitwy Warszawskiej 7A, 02-366 Warszawa, Poland

<sup>2</sup> Faculty of Materials Science and Engineering, Warsaw University of Technology, ul. Wołoska 141, 02-507 Warszawa, Poland

<sup>3</sup> Centre for Advanced Technologies, Adam Mickiewicz University in Poznań, ul. Uniwersytetu Poznańskiego 10, 61-614, Poznań, Poland

<sup>4</sup> SINTEF Industry, Department of Process Technology, Forskningsveien 1, 0373 Oslo, Norway

<sup>5</sup> SINTEF Industry, Department of Materials and Nanotechnology, Forskningsveien 1, 0373 Oslo, Norway

\* Correspondence: [rafal.kozera@technologypartners.pl](mailto:rafal.kozera@technologypartners.pl)

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### Abstract

A guarantee of safe and efficient power production by the means of green energy sources is an extremely important task, necessary to the popularize environmental-friendly solutions. Ice accumulation and water droplet erosion are some serious obstacles to increasing the power output of the wind energy sector. A proposed solution to minimize the effects of severe weathering on composite wind turbine blades is the use of anti-icing hybrid coatings. One of the strategies is to utilize protective polyurethane coatings, none of which exhibit icephobic properties. In this paper waterborne polyurethane coatings modified with nanocompounds from the group of spherosilicates were investigated in terms of water repellent and anti-icing behavior. The roughness of the surface was measured as it significantly influences the aforementioned characteristics of the material. The hydrophobicity was evaluated by means of water contact angle (*WCA*) at room temperature, roll-off angle (*RoA*) and contact angle hysteresis (*CAH*) measurements. All of the modifiers increased the contact angle, modifying the reference material from hydrophilic to slightly hydrophobic. The ice adhesion strength (*IA*), which was used to characterize the icephobic behavior was decreased even by 45% in comparison to the unmodified reference material.

**Keywords:** anti-icing coatings, waterborne polyurethane, spherosilicates, ice adhesion, chemical modifiers

### Introduction

Icephobic coatings have attracted widespread interest for many years regarding the elimination or reduction of the problem of ice formation and accumulation on many structures used in industry and our daily lives. There is a large number of accidents and failures caused by ice accumulation in various sectors of industry such as wind power, aviation, construction and telecommunications [1].

Icephobic surfaces are characterized by a delay in the freezing of water droplets, a reduction in the contact area between the droplet and the substrate (minimizing heat transfer), and the lowest possible ice adhesion strength upon ice build-up. They should also exhibit durability of their properties against mechanical, chemical and environmental damage [2,3]. Among the main types of coatings with high anti-icing potential are hydrophobic and superhydrophobic polyurethane (PU) based coatings. PU based coatings are characterized by, among others, good adhesion to substrates, high resistance to chemicals and extreme weather conditions (wind, rain and intense UV radiation), as well as excellent mechanical strength, hardness and durability. However, due to the presence of many polar groups on the surface, PU surfaces are rather hydrophilic. For this reason, obtaining hydrophobic, and consequently, icephobic PU coatings, is an important issue for current development and research [4].

In many publications, icephobicity is closely correlated with wettability [5-8]. It is assumed that a material that is poorly wettable by water can maximally reduce the contact time/area between the substrate and the cooled droplet, and consequently, increase the anti-icing performance. As reported by Mishchenko et al. [9], a supercooled droplet on a superhydrophobic surface can withstand temperatures as low as  $-30^{\circ}\text{C}$  without changing its ground state. In addition, Wang et al. [10] reported that a hydrophobic surface coated with polydimethylsiloxane (PDMS) exhibits low ice adhesion. Nevertheless, the above relationships are not necessarily true in all conditions, especially for rough substrates in humid environments as there may be anchoring of ice in the micro/nanostructure of the surface [11]. In [12], Ling et al. proved that the ice adhesion of a superhydrophobic surface increases by 67% compared to a polished coating. Bharathidasan, Susoff, et al. [13,14] proposed that a smooth, slightly hydrophobic surface may be a potential candidate for achieving low ice adhesion values, while superhydrophobic surfaces may exhibit low anti-icing performance. Thus, when developing icephobic surfaces, it is important to consider the fact that wettability does not determine icephobicity, but can influence it.

The chemical modification of coatings with low surface energy compounds is one mechanism to obtain an increased water contact angle, and thus anti-icing properties. Commonly used in the field of hydro- and icephobicity are organosilicon compounds from the polyhydrosiloxane group (PHS), which, in addition to their hydrophobic nature, are also characterized by high durability. It has been reported in the literature that surfaces based on this material can achieve very low ice adhesion (below 1 kPa). In 2023 [15], by modifying a silicone-epoxy resin with functionalized polysiloxanes, a 69% reduction in ice adhesion and a 17-time increase in the freezing time of water droplets was obtained compared to the unmodified coating.

Silsesquioxanes with the general formula  $\text{RSiO}_{3/2}$  are classified as hybrid organosilicon compounds capable of forming one-, two- or three-dimensional structures. They consist of an inorganic core containing Si-O-Si building units and attached organic groups, which may be inert or reactive ( $\text{R}$  = hydrogen atoms, alkyl, amino, aryl, hydroxyl groups, etc., or their derivatives) [16]. The core is responsible for the stiffness, chemical resistance, and thermal stability of the structure. At the same time, the functional groups determine the physicochemical properties of the compound (such as solubility, density, melting point, moisture resistance, hydrophilic-hydrophobic properties, reactivity, and compatibility in polymers and composites), and in the case of reactive groups, they enable further modifications [17]. Recently, there has been growing interest in organosilicon compounds as modifiers and nanofillers in polymers. In the case of silsesquioxanes with specific functional groups attached, it

is possible to give polymers hydrophobic properties, which in turn ensures their resistance to moisture and water [18].

Kannan et al. developed new hybrid fluoropolyurethanes that contain fluorinated polyhedral oligomeric silsesquioxane. They used fluoro(13)isobutyl-POSS (FluoroPOSS), short-chain fluorodiol and diisocyanate to create hybrids intended for thin-film applications. The obtained thin films were characterized by ultrahydrophobicity, having a water contact angle of approximately  $107^\circ$ , and low contact angle hysteresis, as well as resistance to solvents [19].

Zhao et al. presented the synthesis of silsesquioxane with dihydroxyl groups and two triethoxy groups (m-POSS), and then the use of SSQ in a reaction with diisocyanate, which allowed them to obtain aqueous polyurethane nanocomposites (APU)/m-POSS. The dihydroxyl groups facilitated the dispersion of m-POSS in the APU main chain, while the two triethoxy groups served as cross-linking sites. APU/m-POSS nanocomposite film containing 8 wt% m-POSS, exhibited high hydrophobicity, achieving a water contact angle of up to  $121^\circ$  because of Si migration to the surface [20].

Kim et al. in [21] prepared hybrid nanocomposite films of vinyl group-containing silsesquioxane (POSS) and polyurethane acrylate (PUA) by adding POSS to PUA employing free radical photopolymerization. The addition of POSS resulted in an increase in flexibility, the glass transition temperature, and thermal stability by means of an increased cross-linking density and a strengthening effect of the POSS molecules. Additionally, the surface free energy of the film decreased with an increase in the POSS content, which increased the water contact angle. In the case of a high POSS content, the mechanical properties of the film deteriorated owing to the aggregation of POSS molecules. Tan et al. presented the synthesis of linear polyurethane (PU) elastomers by dispersion in organic solvents containing various amounts of functionalized silsesquioxane with hydroxyl groups (diol-POSS) in the range of 2–10 wt%. The introduction of diol-POSS into the systems raised the glass transition temperature and improved the stability compared to pure PU. Additionally, the contact angle measurements showed significant improvement in surface hydrophobicity and a reduction in surface free energy after the introduction of diol-POSS into the synthesized PU [22].

In the present work, waterborne PU-based nanocomposite coatings with enhanced anti-icing performance were developed. Chemical modifications with compounds from the group of functionalized spherosilicates were used to achieve the desired properties. The modifiers contained more than one functional group, which is an innovation compared to previous studies regarding icephobicity. The purpose of the functionalization of the organosilicone compounds was to ensure compatibility with the polymer matrix and to induce hydro- and icephobic properties. Ice adhesion was determined by measuring the shear strength. The hydrophobicity and roughness of the produced surfaces were analyzed. In addition, an attempt was made to clarify the correlation between the surface properties.

### **Materials and testing methods**

The chemical modifications of the waterborne polyurethane coatings presented in this article were performed with chemical modifiers from the group of multifunctionalized organosilicon compounds (MOD) synthesized in-house. A spherosilicate core was used and functionalized with three different functional groups with varying molar ratios, presented in Table 1. Additionally, a pure polyurethane coating without any modifications was utilized for comparison purposes as a reference sample.

### *Synthesis and analysis of chemical modifiers*

The procedure of synthesis as well as the collected analytical data were presented in our earlier paper [6]. The purity and the degree of conversion were examined by FTIR and  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  NMR spectroscopic methods, as in the previous work. The studies showed a complete conversion of the reactants to the desired reaction product.

### *Preparation of samples*

The samples employed for testing were fabricated by adding 2 wt% of one of the chemical modifiers to the waterborne polyurethane matrix. The coatings were deposited by spraying with a pressured gun. The topcoat consisted of Aerowave 5001 base (AkzoNobel), Curing Solution 6002 (AkzoNobel) and water. The proportions were 100:33:20 by weight.

Each chemical modifier was assigned a letter symbol. The composition of each chemical modifier (core type, functional groups, and their ratio to each other) is presented in Table 1.

*Table 1. Composition of chemical modifiers (OSS – organo spherosilicate), OFP- octafluoropentyl propyl group, HEX-hexyl group, OCT-octyl group.*

No.	Sample designation	Core	Olefin 1	Olefin 2	Olefin 3	Molar ratio O <sub>1</sub> :O <sub>2</sub> :O <sub>3</sub>
1	MOD1	OSS	OFP	OCT	AGE	02:02:04
2	MOD2	OSS	OFP	OCT	VTMS	02:02:04
3	MOD3	OSS	OFP	OCT	AGE	03:03:02
4	MOD4	OSS	OFP	AGE	-	05:03
5	MOD5	OSS	OFP	AGE	-	03:05

#### **a. Roughness tests**

The roughness was investigated by utilizing an optical profilometer Sensofar S Lynx in interferometric mode. An objective with magnification of 20x/0.40 was used. The  $R_a$  parameter was determined.

#### **b. Wettability tests**

The wettability of the samples was analyzed by means of the contact angle ( $WCA$ ) at room temperature and roll-off angle ( $RoA$ ). A 5- $\mu\text{l}$  droplet was applied by the sessile drop method. The results presented in this paper are the average of five measurements. The values were measured using Goniometer OCA15 and SCA software from DataPhysics Instruments (DataPhysics, Filderstadt, Germany).

#### **c. Ice adhesion**

Samples with the dimensions of 100 x 25 mm were utilized for ice adhesion ( $IA$ ) testing. After fabrication, they were put in a metallic handle, which was then filled with water. The samples were kept at  $-10^\circ\text{C}$  for 24 h. The frozen samples were then mounted in a Zwick/Roell Z050 testing machine in such a way that the handle was locked in the upper grip. Six samples for each chemical composition were tested. The conditions during the measurements were room temperature and a relative humidity of 50%. The details of the ice adhesion test procedure were described in a previous paper [6]. The presented values were achieved based on five measurements.

## Results

### Roughness

The results of the roughness measurements by means of the profilometer are displayed in Table 2 and in Figure 1.

Table 2. Results of roughness measurements

No.	Sample designation	Core	Olefin 1	Olefin 2	Olefin 3	Molar ratio O <sub>1</sub> :O <sub>2</sub> :O <sub>3</sub>	R <sub>a</sub> [μm]	SD. [μm]
1.	REF	-	-	-	-	-	0.25	0.02
2.	MOD1	OSS	OPF	OCT	AGE	02:02:04	0.17	0.01
3.	MOD2	OSS	OPF	OCT	VTMS	02:02:04	0.15	0.02
4.	MOD3	OSS	OPF	OCT	AGE	03:03:02	0.14	0.02
5.	MOD4	OSS	OPF	AGE	-	05:03	0.68	0.03
6.	MOD5	OSS	OPF	AGE	-	03:05	0.41	0.03

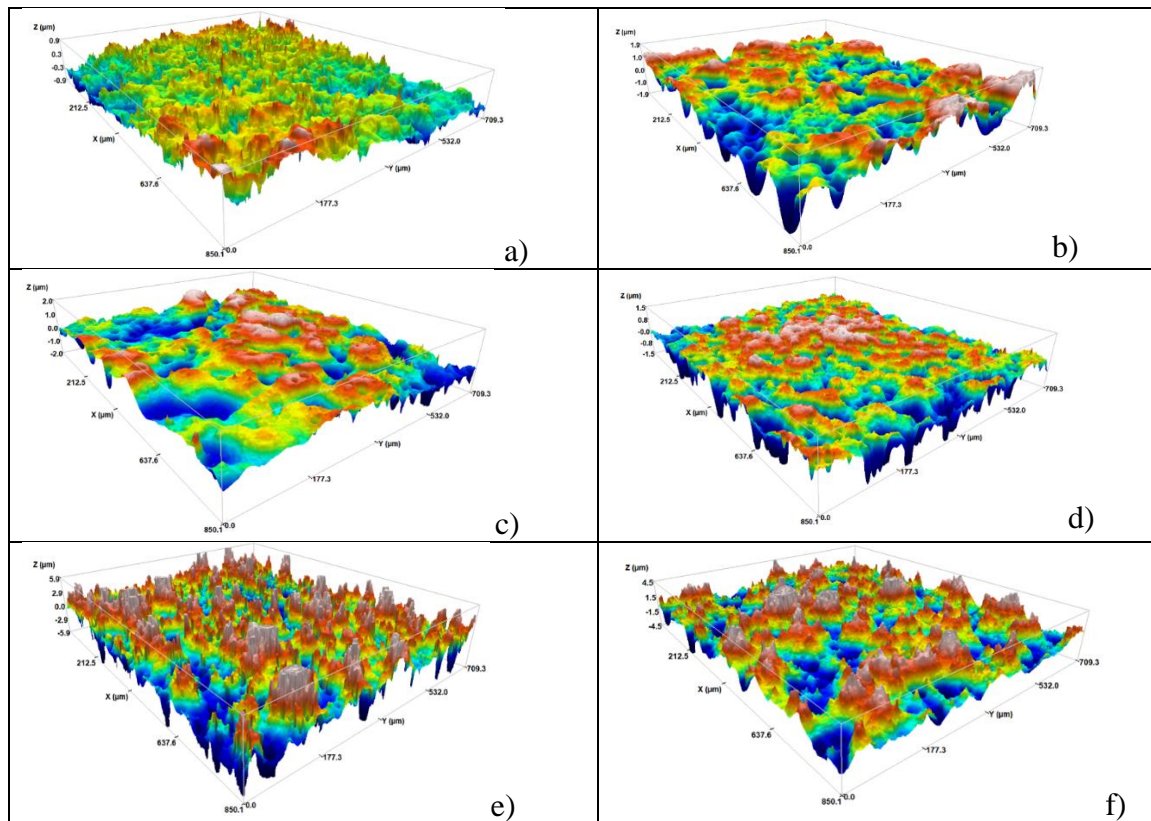


Figure 1. 3D visualization of fabricated surfaces by means of profilometer: a) REF, b) MOD1, c) MOD2, d) MOD3, e) MOD4, f) MOD5.

The R<sub>a</sub> parameter, determines the surface roughness of the modified waterborne polyurethanes and the reference sample (Fig. 1). The unmodified sample, i.e. the waterborne polyurethane coating, exhibited an R<sub>a</sub> equal to 0.25 μm. The rest of the samples with chemical modifiers indicated values between 0.14 μm and 0.68 μm. The MOD1-MOD3 samples which contained only double functionalized groups,

indicated slightly lower roughness in comparison to the reference sample, i.e. 0.14 - 0.17  $\mu\text{m}$ , while the roughness of MOD4 and MOD5 was visibly higher, i.e. 0.41-0.68  $\mu\text{m}$ . It should be noted that in the case of MOD1-MOD3 containing the AGE and OCT groups, no significant changes were observed between those three samples.

### Wettability

Table 3 presents the values of the wettability parameters.

*Table 3. Results of wettability parameters investigations of modified coatings*

No.	Sample designation	WCA [°]	SD. [ $\mu\text{m}$ ]	CAH [°]	SD. [ $\mu\text{m}$ ]	RoA [°]	SD. [ $\mu\text{m}$ ]
1.	REF	80	2	15	2	>90	3
2.	MOD1	75	2	20	3	22	2
3.	MOD2	78	1	22	2	30	4
4.	MOD3	87	1	21	4	45	3
5.	MOD4	84	2	31	3	>90	5
6.	MOD5	76	1	28	3	>90	4

Parameters such as water contact angle (WCA), contact angle hysteresis (CAH) and roll-off angle (RoA), are indicative of the wettability of the fabricated coating samples. The reference sample shows a WCA of 80°, which indicates a hydrophilic nature (Table 3). The modification of the waterborne polyurethane coatings did not lead to a significant increase in the value of this parameter in most of the studied materials except MOD3, where the WCA value grew by 7°. The WCA values of the surfaces were in the range between 75° to 87°. The highest difference in the WCA value compared to the reference sample was found for the sample modified with a spherosilicate functionalized with the OFP, OCT and AGE groups (MOD3) where there was an increased content of the OCT functional group. Moreover, only in the case of this sample did the WCA value reach almost 90°, becoming slightly hydrophilic, which suggests the OCT group as the primary factor to raise the WCA parameter. It is also worth mentioning that despite a noticeable increase in roughness in the case of MOD4 and MOD5, no growth in wettability was observed. This indicates their stronger hydrophilic character even with increased roughness, which usually provides increased WCA values.

The reference sample indicates no sliding effect at coating surface tilting values even greater than 90°. In contrast, the values of the roll-off angle changed significantly in the MOD1-MOD3 samples. The modifications containing OCT together with the AGE functional groups significantly influence the RoA values, leading to a drop from 45° (MOD3) down to 22° (MOD1). This suggests that the most optimal molar ratio for the lowest sliding angle is 2. What is also interesting is the fact that the MOD4 and MOD5 samples containing only the AGE functional group did not exhibit any changes in RoA in comparison to the reference sample.

The value of the contact angle hysteresis for the reference sample is 15°. The recorded values of CAH for the modified samples increased from 20° to 31°, which means they were higher in comparison to the reference sample values. The highest increase in CAH was noted for the samples with MOD4 and MOD5 modifications, where only double functionalization was applied. For those two samples, CAH stayed in good agreement with the RoA value changes. No variations in the samples containing MOD1-3 was observed, while the values were slightly higher than in the case of the reference sample.

## Ice adhesion

The results of ice adhesion are given in Table 4.

Table 4. Results of ice adhesion investigations for modified and reference samples

No.	Sample designation	Core	Olefin 1	Olefin 2	Olefin 3	Molar ratio O <sub>1</sub> :O <sub>2</sub> :O <sub>3</sub>	IA [kPa]	SD [kPa]
1	REF	-	-	-	-	-	306	67
2	MOD1	OSS	OFP	OCT	AGE	02:02:04	214	56
3	MOD2	OSS	OFP	OCT	VTMS	02:02:04	223	94
4	MOD3	OSS	OFP	OCT	AGE	03:03:02	170	15
5	MOD4	OSS	OFP	AGE	-	05:03	548	23
6	MOD5	OSS	OFP	AGE	-	03:05	653	33

One of parameters that determine the anti-icing properties of a surface the most extensively described in the literature is ice adhesion (IA). The obtained values of this parameter recorded for the reference and MOD1-MOD5 samples with modifiers are shown in Table 4. In the case of reduced IA values, the surface is characterized by improved icephobic properties, i.e. it has better anti-icing properties.

The MOD1-MOD3 samples showed a noticeable decrease in IA values, which reached 170 kPa for the MOD3 sample. What is significant is that the samples with the OSS core functionalized with OCT indicated significantly lower values in comparison to the MOD4-5 samples. This indicates the positive influence of the presence OCT functional groups on the icephobic performance i.e. the ice adhesion values. The samples containing double functionalized groups with AGE (MOD4-5) exhibited ice adhesion values almost two times higher (MOD4) and over two times higher in comparison to the reference sample with 306 kPa. This confirms the significant and positive influence of the OCT functional groups.

## Discussion

### Relationship between roughness and wettability

The relationship between the water contact angle (WCA) and roughness parameter  $R_a$  is shown in Figure 2. Based on the graph, no direct correlation between wettability and roughness can be seen for the developed coatings. The WCA values for similar  $R_a$  values differ. The coating with a WCA of 75° (the lowest WCA among the samples) has an  $R_a$  of 0.17  $\mu\text{m}$ , while the coating with a WCA of 87° (the highest WCA among the samples) has an  $R_a$  of 0.14  $\mu\text{m}$ . The samples with similar surface textures exhibit different wettability. Moreover, the two surfaces with the highest WCA values (MOD3 and MOD4) exhibited extreme  $R_a$  values, differing by more than 0.5  $\mu\text{m}$ . Thus, it can be concluded that for the developed polyurethane coatings, surface wettability is not directly determined by surface development. The low energy of the employed organosilicon compounds is likely a decisive factor that affects the obtained wettability.

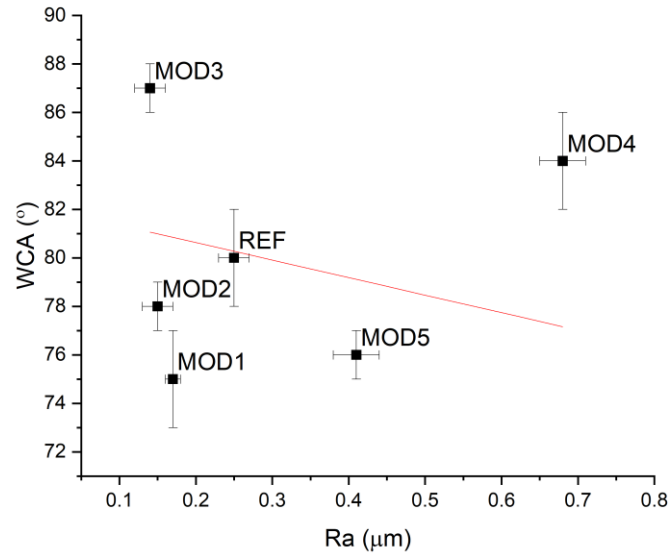


Figure 2. WCA as a function of  $R_a$ .

### Relationships between ice adhesion and roughness/wettability

For many years, researchers have been trying to determine the relationship between surface roughness/wettability and ice adhesion as one of the parameters describing anti-icing performance [23-24]. These correlations are not clear, as they involve a large number of different factors such as the type of ice formed or different surface texture (number and depth/height of pits/rises), which can affect the surface/time contact between the overcooled droplet and the substrate differently. To date, direct correlations occurring in icephobicity have not been fully determined.

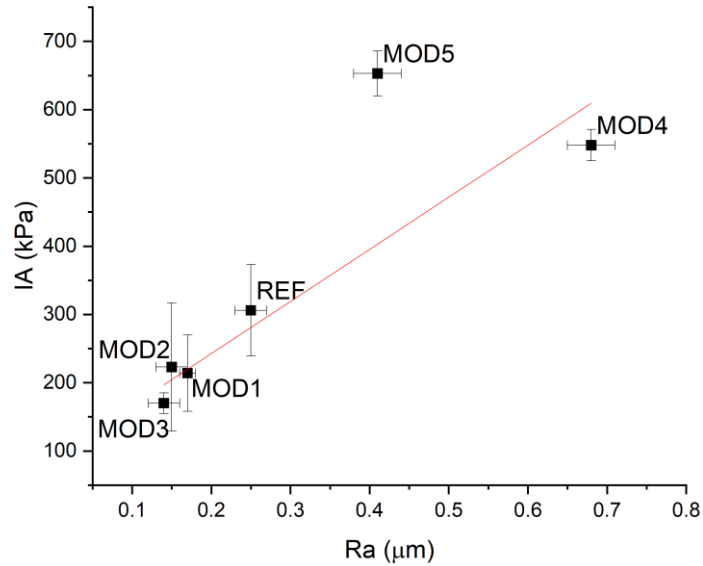
By analyzing the graph in Figure 3, one can see a certain trend between the  $R_a$  values and IA values. As the surface roughness increases, the ice adhesion also grows. The coatings with the highest  $R_a$  values exhibited an increment in ice adhesion compared to the unmodified surface, i.e. their anti-icing performance deteriorated. Increases in the ice adhesion strength to substrates with high surface roughness were also noted in many other research works [10, 13, 14,]. Such phenomena can be explained by the fact that high roughness leads to growth in the contact area between the forming ice and the coating, and consequently results in the anchoring of ice in the surface texture and the creation of a mechanical blockage. This results in an increase in ice adhesion strength. By comparing the IA value of a polished metal substrate with the IA value of a textured superhydrophobic substrate, it was shown that the difference in the value of this parameter between the above surfaces can reach up to 67% [25].

Figure 3 shows the relationship between the water contact angle and ice adhesion. For the researched surfaces, the IA values do not directly depend on the WCA values. The coatings that exhibited the lowest IA values, and thus a reduction in value compared to the unmodified coating, obtained WCA values in the range of  $75^\circ$  to  $87^\circ$ . In addition, the samples with nearly identical WCA values (MOD1

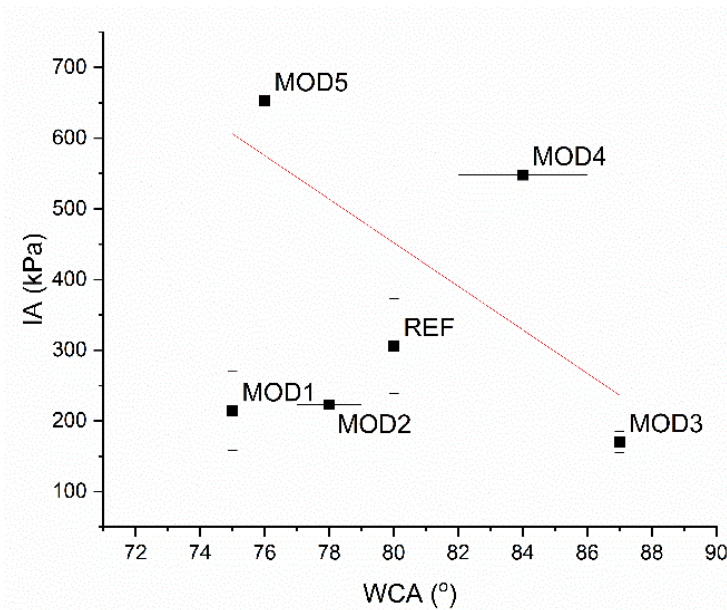


and MOD5) obtained extreme IA values that differed by a factor of three. The studied coatings likely obtained differences in the WCA values too low to determine how they affect the IA values. According to the available literature, organosilicon compound-based coatings exhibiting low ice adhesion strength (lower than 100 kPa) can exhibit WCA values from about 80° to 110° [26].

Summarizing the above discussion, for the developed polyurethane coatings, the ice adhesion strength was the lowest for the coatings with the lowest surface roughness. In addition, the surfaces that achieved a reduction in ice adhesion values were of a hydrophilic nature, obtaining a WCA in the range of 75°-87°. Thus, the attainment of hydrophobicity by a surface (WCA>90°) is not necessary to obtain an improvement in anti-icing performance.



(a)



(b)

Figure 3. Ice adhesion values as a function of (a)  $R_a$ ; (b) WCA.

## Conclusions

Waterborne polyurethane coatings were fabricated and investigated. Different functional groups were applied in order to determine which of them are dominant regarding wettability and icephobicity.

- Roughness: The MOD1-MOD3 samples which contained only double functionalized groups (AGE and OCT) achieved slightly lower roughness in comparison to the reference sample, while MOD4 and MOD5 had visibly higher roughness.
- WCA: Only in the case of the MOD3 sample did the WCA value reach almost 90°, attaining a slightly hydrophilic character, which suggests the OCT group as the primary factor to increase the WCA parameter. Despite a noticeable increase in roughness in the case of MOD4 and MOD5, increase in wettability was not observed. This indicates their stronger hydrophilic character even with increased roughness, which usually results in increased WCA values.
- RoA: Modifications containing OCT together with AGE functional groups significantly influenced the RoA values, leading to a drop in their values. On the other hand, the MOD4 and MOD5 samples containing only the AGE group did not exhibit any changes in RoA in comparison to the REF sample.
- CAH: The recorded values of CAH for the modified samples increased in comparison to the reference sample values. The highest growth in CAH was noted for the samples with the MOD4-5 modifications, where only double functionalization was applied. No variations in the MOD1-3 samples was observed, although their values were slightly higher than in the case of the REF samples.
- IA: The samples functionalized with OCT exhibited significantly lower IA values in comparison to the MOD4-5 samples, while the samples containing double functionalized functional groups with AGE (MOD4-5) exhibited ice adhesion values almost two times higher (MOD4) and over two times higher (MOD5) than the reference sample with 306 kPa ice adhesion, which indicated and confirmed the significant and positive influence of the presence of the OCT functional groups.
- The ice adhesion strength was lowest for the coatings with the lowest surface roughness. In addition, the surfaces that showed a reduction in ice adhesion values were hydrophilic in nature. Thus, the attainment of hydrophobicity is not necessary to achieve an improvement in anti-icing performance.

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