

# Evaluation of hydrophobic properties of organic layers modified with graphene flakes

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The paper presents the results of our research on graphene composites with organic polymers in various media. The following composites have been tested: PVDF/DMF/GR, PVDF/NMP/GR, PVDF/acetone/toluene/GR and PMMA/GR. The main purpose of this study is to evaluate hydrophobic properties of the selected materials by the contact measurements angle using the static method. The highest obtained value of the contact angle approached 180° for a superhydrophobic composite PVDF/acetone/toluene/GR.

**Key words:** hydrophobic surface, contact angle, PMMA, PVDF, graphene



## Ocena właściwości hydrofobowych pokryć organicznych modyfikowanych grafenem płatkowym

W artykule przedstawiono rezultaty prac dotyczących kompozytów grafenowych z polimerami organicznymi w różnych ośrodkach. Badano PVDF/DMF/GR, PVDF/NMP/GR, PVDF/acetone/toluene/GR i PMMA/GR. Główny przedmiot badań stanowiła ocena właściwości hydrofobowych wytypowanych materiałów. Weryfikowano je za pomocą pomiarów kąta zwilżania metodą statyczną. Najlepszymi parametrami charakteryzował się kompozyt PVDF/acetone/toluene/GR, który wykazywał właściwości superhydrofobowe z wartościami kąta zwilżania wodą zbliżonymi do 180°.

**Słowa kluczowe:** powierzchnia hydrofobowa, kąt zwilżania, PMMA, PVDF, grafen

## 1. Introduction

Wettability is defined as the ability of a liquid to maintain a contact with the surface of a solid. It is characterized by the contact angle (CA), whose value results from an equilibrium between the adhesion forces, which are of the surface origin, and the cohesion forces, i.e. the intermolecular interactions inside a drop of water. This state causes the appearance of the surface tension at the A/B interface. A low value of the surface tension indicates that cohesive forces (A-A and B-B types of cohesion) exceed the adhesion forces at the A/B interface. In this case the value of CA becomes very high and the surface of the solid is defined as hydrophobic.

Theories concerning superhydrophobic and superhydrophilic surfaces are currently being investigated by different groups of scientists representing such fields of science as material science, botany, physics and chemistry. The discovery of the lotus effect by Wilhelm Barthlott and Christoph Neinhuis initiated a rapid increase in the interest in these phenomena, although the relationship between the surface roughness and wettability had been already demonstrated in the 1940s by Cassie and Baxter [1 - 3]. Over the recent decades, due to the development of the technologies and methods, such as scanning electron microscopy, the investigations on biological surfaces revealed the existence of complex microstructures. The observation of the natural phenomena, and their combi-

nation with the possibilities offered by nanotechnology [4], have enabled the ways to obtain surfaces with the desired properties.

The functionalization consists in the chemical and physical treatment of a given material in order to make it applicable in various branches of industry, from the textile and aircraft industries to the armaments industry. The surfaces are modified towards the desired properties. For instance, the hydrophobic surfaces are obtained by combining the proper morphology in a micro- or nano-scale with the specific properties of polymers [5]. There is a demand for highly hydrophobic layers, which are the basis of the technologies relying on antistatic and nonadhesive phenomena, and using the self-cleaning and anti-pollution mechanisms. The hydrophobic layers can also be used for protection against the accumulation of ice crystals, e.g. on the surfaces of airplanes, highways or various types of building structures. The accumulation of water on the bearing surfaces and in the gaps or pores results in the change of aerodynamic properties, an increase in aerodynamic resistance, weight, and also in cracking and disintegration of the structures from the inside. In addition, these materials become useful in biomedical applications [6 - 9].

In 2013, Dong and Yao [10] reported in *Scientific Reports* on hydrophobic layers obtained from a composite: graphene - octadecylamine (ODA), characterized by the contact angle value of 152°. The authors also showed

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the examples of other hydrophobic graphene composites utilizing such organic compounds as PVDF-HFP, i.e. polyvinylidene fluoride-co-hexafluoropropylene or MEH-PPV, i.e. poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]. The attention was also paid to the differences in the quality of the layers covering smooth surfaces and those with microstructures. The obtained values of contact angles were as high as  $152^\circ$  [10]. Rafiee et al. in the text entitled *Superhydrophobic to Superhydrophilic Wetting Control in Graphene Films* [11] described the material properties dependent on the type of the support. The properties of graphene flakes, suspended in water and acetone, and then transferred onto a substrate, varied from superhydrophilic to superhydrophobic, with the contact angle values (for wetting by water) ranging from  $0^\circ$  to  $160^\circ$ . The authors studied the mixture of water and acetone in various proportions, and determined an exact relationship between the composition of the support and the contact angle values. The higher got the water content in the mixture, the lower CA values and the stronger hydrophilic properties were observed.

The article entitled *Hydrophobicorganic layers on smooth and 3-dimensional developed surfaces* [9] presented the results which confirmed a very strong effect of the support on the parameters of the tested materials. The contact values angle for PVDF polymer (polyvinylidene fluoride) dispersed in various media, wetted by water, varied from  $4^\circ$  in an NMP solution (N-methylpyrrolidone), through  $90^\circ$  in DMF (dimethylformamide) to  $133^\circ$  in an acetone-toluene mixture. The authors explained that the significantly different CA values were related to the polarity and dipole moment of the solvents used. It was also noticed that covering the structured surfaces with layers enhanced the properties of a given material. The best parameters were exhibited by PVDF in the acetone/toluene medium, with the CA values reaching  $133^\circ$  on the smooth substrates and increasing up to  $150^\circ$  on the structured surfaces.

The use of graphene and the introduction of an additional heterogeneity is expected to reduce further the surface energies of the low-energy polymers and it allows obtaining materials with superhydrophobic properties.

On the basis of the previous studies on the organic polymers [9], the most optimal solutions selected for the modification were those with the use of graphene flakes. Besides the contact angle value, the composite ability to form a homogeneous layer both on smooth and structured substrates was the decisive parameter in qualifying a given material for further experiments. The obtained graphene composites were tested in a goniometer and the contact angles were determined by a sitting drop method, while the quality of the obtained samples was evaluated by optical microscopy. In order to verify the hydrophobic properties, the experimental results presented in this article were compared with the previously published data concerning the polymers not modified with graphene [9].

## 2. Experimental

### 2.1. Reagents used and method of their preparation

#### 2.1.1. Samples of reduced graphene oxide (rGO)

Asbury graphite was subjected to the expansion process. Then it was oxidized using the Hummers method [12], in the medium of sulfuric acid, potassium nitrate and potassium permanganate. The obtained graphene oxide was purified during centrifugation, which was followed by the exfoliation using an ultrasonic probe. Next, the graphene oxide suspension was reduced by the additive of hydriodic acid and again purified by filtration. After sonication, a stable suspension in N-methylpyrrolidone was obtained from the prepared rGO.

#### 2.1.2. Preparation of PVDF samples

##### 2.1.2.A. PVDF/DMF/rGO (1BGR solution)

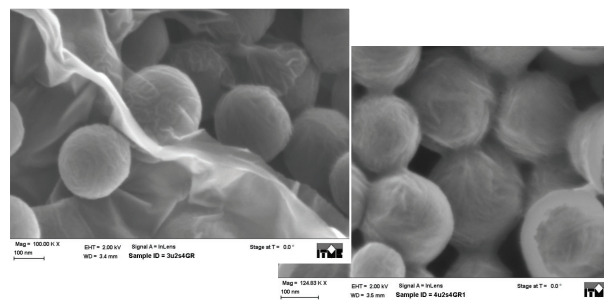
Solution 1 was prepared by dissolving 10 g of PVDF in 100ml of dimethylformamide and followed by sonication for 20 minutes. The homogeneous solution was then diluted in a voluminal ratio of 1:2 (r1: DMF = r1B). The solution denoted as 1B was used to prepare a composite with reduced graphene oxide flakes. The suspension of graphene in N-methyl-2-pyrrolidone was mixed with the polymer solution in a 1:1 voluminal ratio and again sonicated for 20 minutes (1BGR solution).

##### 2.1.2.B. PVDF/NMP/rGO (2GR solution)

Solution 2 was prepared by mixing 2.5 g of PVDF with 50 ml of N-methylpyrrolidone and then holding it for 20 minutes in an ultrasonic bath. This solution was a basis for the preparation of a composite of a fluoropolymer and graphene, in NMP (solution 2: rGO / NMP = 1: 1  $\leftrightarrow$  2GR) as the support.

##### 2.1.2.C. PVDF/acetone/toluene/rGO (4GR solution)

During the preparation of solution 4, acetone was mixed with toluene (5:3) and added to 2.5 g of PVDF. The homogeneous mixture was subjected to sonication for 20 minutes. After adding the additive of toluene,



**Fig.1.** SEM image of the structure of a PVDF/acetone/toluene/GR composite.

**Rys. 1.** Obraz, z mikroskopu elektronowego, struktury kompozytu PVDF/aceton/toluen/GR.

the suspension of reduced graphene oxide in acetone was dispersed in solution 4, again by applying the ultrasonic for 20 minutes (solution 4: rGO/acetone/toluene = 1:1 ↔ 4GR). Fig. 1 shows the SEM images of the structure of a PVDF/acetone/toluene/rGO composite.

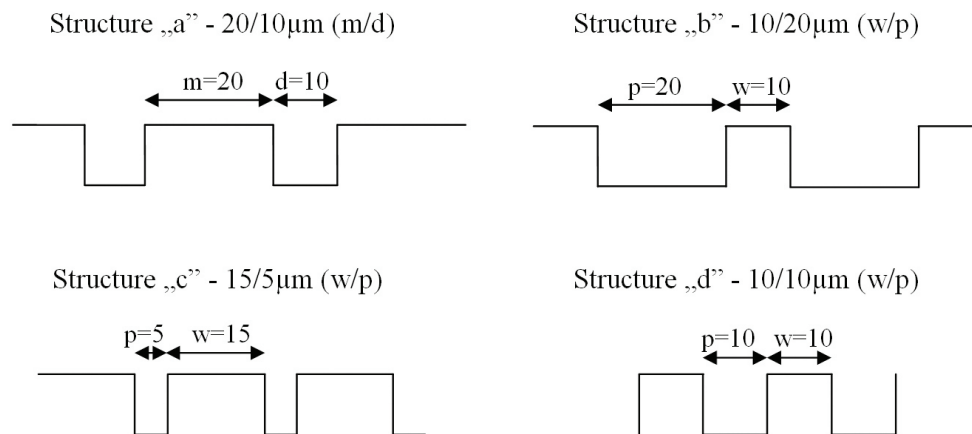
### 2.1.3. Preparation of the samples from PMMA/rGO (PMMAGR solution)

Graphene from the rGO/NMP solution was directly dispersed by sonication (20 minutes) in poly(methyl methacrylate) (PMMA) in a 1:1 voluminal ratio (PMMAGR).

## 2.2. Experimental methods

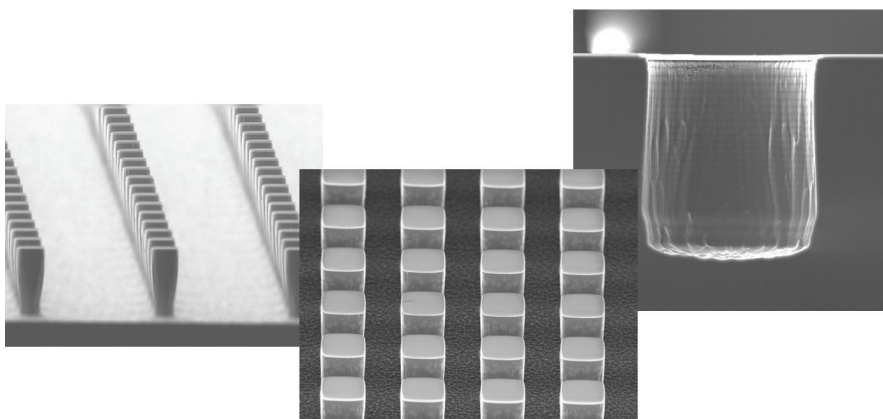
The process of covering the polymer layers modified with graphene was carried out directly on the four-inch silicon wafers (ITME) with (100) crystallographic orien-

tation. The desired geometry was obtained by photolithography, wet treatment and cryogenic plasma etching of silicon. The first step to obtain such profiles in the substrate was the deposition of SiO<sub>2</sub>. Silicon oxide was prepared by a thermal oxidation of silicon wafers in PEO 603 furnace. Next, silicon oxide was etched with a NH<sub>4</sub>F: HF: H<sub>2</sub>O etching mixture, using the light sensitive emulsion as a mask. The obtained oxide was then used itself as a mask for plasma etching. The cryogenic process was carried out in the atmosphere of the mixed SF<sub>6</sub> and O<sub>2</sub> gases of 5N purity with the etch rate of ~ 1 μm/min. The produced structures were characterized by the following dimensions: 20/10 (m/d, closed structure); 10/20 (m/d, open structure); 15/5 (m/d); 10/10 μm (m/d) and a depth of ~ 10 μm (Fig. 2 and Fig. 3), where: "m" is the distance between the holes etched into the



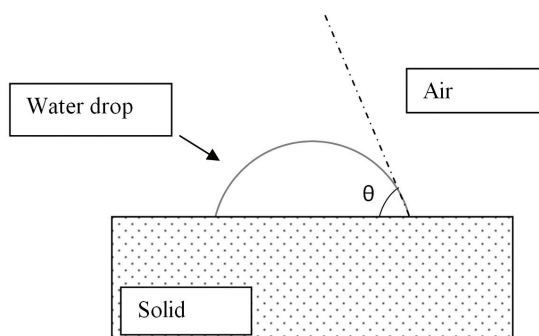
**Fig. 2.** Geometry of the structures obtained by cryogenic etching of silicon. „a” - 20/10 (m/d); „b” - 10/20 (w/p); „c” - 15/5 (w/p); „d” - 10/10 μm (w/p), where: "m" is the distance between the holes etched into the surface, "d" – the hole diameter; "w" - the side of the square of the hillock, "p" – the distance between the hillocks.

**Rys. 2.** Geometria struktur uzyskana w procesie kriogenicznego trawienia krzemu. „a” - 20/10 (m/d); „b” - 10/20 (w/p); „c” - 15/5 (w/p); „d” - 10/10 μm (w/p), gdzie: m/d - "m" oznacza odległość między otworami wytrawionymi w głąb powierzchni, a "d" średnica tego otworu; w/p - "w" to bok kwadratu wzgórek, a "p" przerwa - odległość między wzgórkami.



**Fig. 3.** Example SEM images of the structures which allow obtaining the lotus effect.

**Rys. 3.** Przykładowe zdjęcia SEM obrazujące struktury pozwalające na uzyskanie efektu „liścia lotosu”.



**Fig. 4.** The principle of the static method of the contact angle measurement.

**Rys. 4.** Zasada pomiaru kąta zwilżania metodą statyczną.

surface, "d" – the diameter of that hole; "w" - the side of the square of the hillock, "p" – the distance between the hillocks.

The composites were overlaid onto the smooth or structured silicon surfaces by sedimentation and centrifugation. Rotational speed and time varied from 400 to 3000 rpm and from 20 to 80 s, respectively. The substrates were prepared from poly(fluorovinylidene) - PVDF,  $(-\text{CH}_2\text{CF}_2)_n$ ,  $M_w = 534$ , Sigma Aldrich, poly(methyl methacrylate) - PMMA (H5%), and modified with reduced graphene oxide flakes (ITME). Various compositions of solvents, such as N-methyl-pyrrolidone - NMP, acetone, toluene, N, N-dimethylformamide - DMF, were used.

### 2.3. Measurement of contact angle by static method

An optical goniometer coupled with a computer system served as the basic diagnostic tool that enabled the

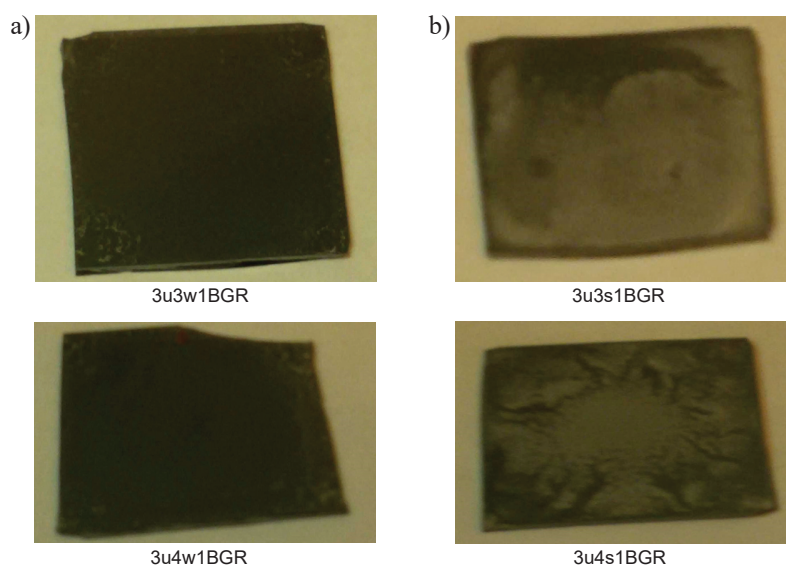
contact angle measurements by the drop shape analysis after wetting the surface with water. The volume of a water drop dosed with a syringe was of the order of 5  $\mu\text{l}$ . The principle of the contact angle measurement using the static method is shown in Fig. 4.

The contact angle ( $\theta = \text{CA}$ ) is the angle between the tangent to the surface of the drop that is set on a solid at the point of a contact of three phases: solid, liquid and gas phase. The higher the contact values angle, the more hydrophobic are the properties of the material tested.

## 3. Results and discussion

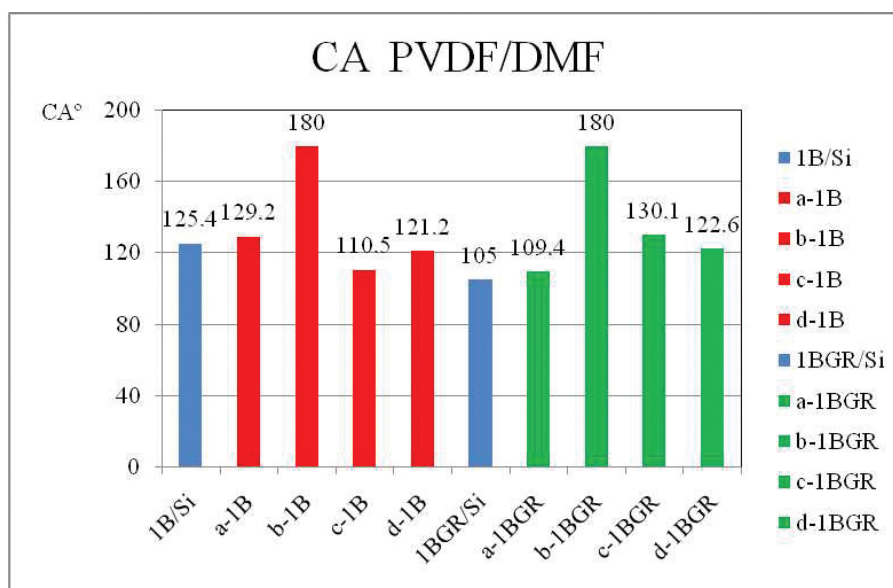
The role of the additive of graphene to organic polymers has been verified by measuring the angle values contact. The graphene composites with PVDF/DMF, PVDF/NMP, PVDF acetone/toluene and PMMA have been tested.

The method of covering with layers was dependent on the properties of polymers [9], i.e. their viscosity. The images in Fig. 5 show the 1BGR samples with a PVDF/DMF solution as a support. This composite was overlaid onto a developed surface using two methods: centrifugation at low speed (Fig. 5a) and sedimentation (Fig. 5b). Only in the former case, the DMF-based composites, whose viscosity is of the order of 0.8 cP, lead to the silicon surface functionalization, giving homogeneous, smooth substrates. For the solutions characterized by the value of viscosity lower by a half, low-speed centrifugation does not guarantee a good quality of the substrate. In the latter case, the satisfactory layers are obtained by the deposition of the graphene composites by sedimentation (PVDF/acetone/toluene/rGO-solution 4GR).



**Fig. 5.** Images showing the quality of the graphene/PVDF composite layers obtained by centrifugation (left pictures) and sedimentation (right pictures).

**Rys. 5.** Obrazy ilustrujące jakość uzyskiwanych warstw kompozytów polimerowo-grafenowych w zależności od metody nakładania: zdjęcia po lewej stronie a) wirowanie; zdjęcia po prawej stronie b) sedymentacja.



**Fig. 6.** The values of CA for PVDF/DMF and PVDF/DMF composites with graphene (1B i 1BGR solution) deposited by centrifugation on of the smooth (blue color) and developed silicon substrates (red color - 1B, green color – 1BGR): "a" - 20/10 (m/d); "b" - 10/20 (w/p); "c" - 15/5 (w/p); "d" - 10/10  $\mu\text{m}$  (w/p), where: "m" is the distance between the holes etched into the surface, "d" – the hole diameter; "w" - the side of the square of the hillock, "p" – the distance between the hillocks.

**Rys. 6.** Wartości kąta zwilżania (CA) dla PVDF/DMF i kompozytów PVDF/DMF z grafenem (roztwór 1B i 1BGR) osadzanych metodą wirowania na podłożach krzemowych gładkich (kolor niebieski) i ze strukturami (kolor czerwony 1B, zielony 1BGR): "a" - 20/10 (m/d); "b" - 10/20 (w/p); "c" - 15/5 (w/p); "d" - 10/10  $\mu\text{m}$  (w/p), gdzie: m/d - "m" oznacza odległość między otworami wytrawionymi w głąb powierzchni, a "d" średnica tego otworu; w/p - "w" to bok kwadratu wzgórek, a "p" przerwa - odległość między wzgórkami.

When applying this method, we can avoid the cleavage of the intermolecular bonds, which are weak in those solutions, and do not cause the formation of any unfavorable clusters or agglomerates on the surface.

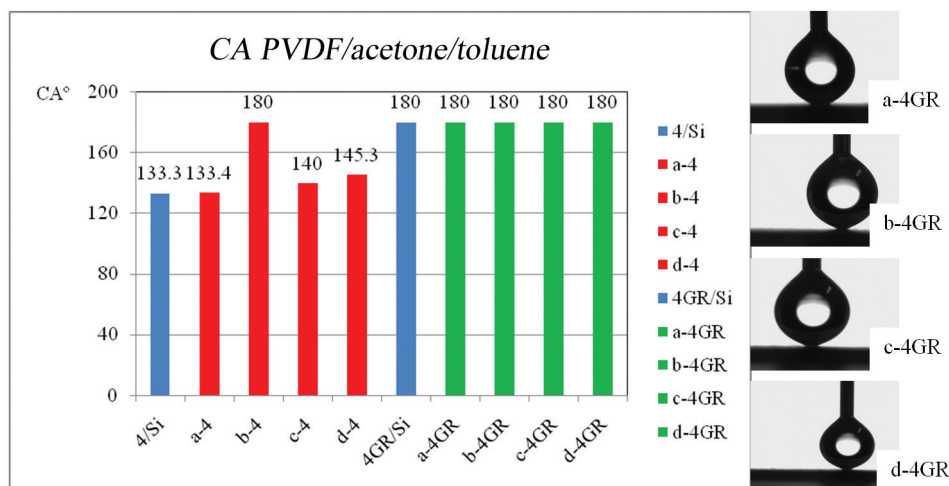
Fig. 6 presents the contact angle values for wetting with water of PVDF dispersed in DMF (solution 1B-red color in Fig. 6) and its composite with graphene (1BGR solution - green color in Fig. 6), overlaid onto silicon. The analysis of this diagram shows that either the surface development (Figs. 6a, c, d) or the additive of rGO do not improve significantly the hydrophobic properties of the obtained surfaces. For both 1B and 1BGR polymers the average values of CA (calculated for the structure types: a, b, c, d) are  $\sim 135^\circ$ . Only for the structure b - 10/20 (w/p), the polymers and their composites cause the repulsion of the water drop and the values of CA reach  $180^\circ$  ( $CA = 180^\circ$  is a limiting value, which is difficult to be determined and therefore conventionally assumed in this article).

Similar hydrophobic properties were observed for the material of graphene in PVDF/NMP/GR (2GR solution), obtained according to the procedure described in section 2.1.2.B. For this composite, the values contact angle were  $\sim 130^\circ$ , while the PVDF/NMP material not modified with graphene was characterized by strong hydrophilic properties.

The graphene composite in a PVDF medium, distributed in a mixture of acetone/toluene (4GR solution, according to section 2.1.2.C), exhibited a superhydrophobic character.

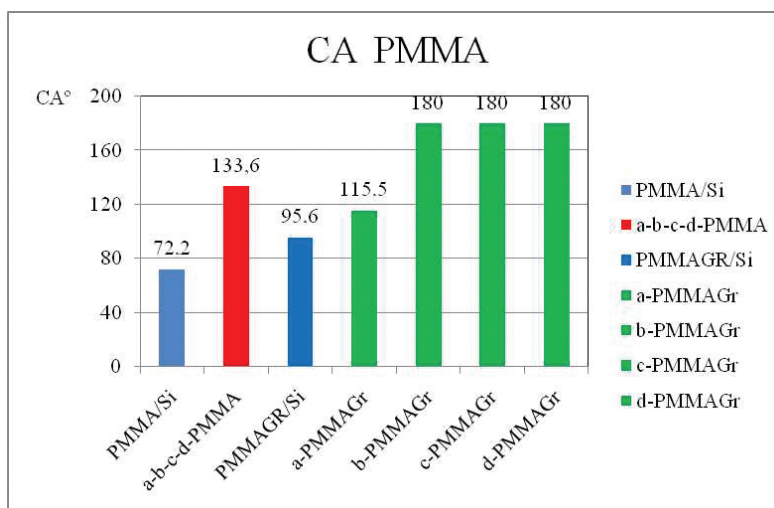
Fig. 7 shows a collection of the contact angle values for both the smooth and developed surfaces covered with the solution of PVDF polymer/acetone/toluene (taken from Ref. [9]) and its composite with graphene. The fact that the CA values equal to  $180^\circ$  for all surfaces with the additive of graphene composite, i.e. both the smooth and developed ones, demonstrates the unique properties of this material (blue and green color in Fig. 7). The comparison of the above parameters with those for a pure polymer confirms this hypothesis. The high CA values, ranging from  $130 - 150^\circ$  for PVDF/acetone/toluene (red color in Fig. 7), reach the maximum values after the modification. The additive of graphene to a pure polymer enhances the hydrophobic effect of the obtained surfaces and causes a complete repulsion of the water drop.

Similar superhydrophobic properties were exhibited by a poly(methyl methacrylate)/graphene composite. The importance of the graphene additive to the polymer is demonstrated by the comparison of the average CA values for PMMA and PMMAGR, overlaid onto the smooth and developed surfaces (Fig. 8). These values are, respectively:  $72^\circ$  and  $96^\circ$  for the smooth surfaces (blue color in Fig. 8), and  $134^\circ$  and  $165^\circ$  for the developed surfaces (green color in Fig. 8). However, it should be noted here that the value  $165^\circ$  is an average of the following four individual CA values:  $115.5^\circ$ ,  $180^\circ$ ,  $180^\circ$  and  $180^\circ$ , obtained on four types of the structures, namely: a - 20/10 (m/d), b - 10/20 (w/p), c - 15/5 (w/p) and d - 10/10  $\mu\text{m}$  (w/p). The analysis of these four CA values is consistent with



**Fig. 7.** The values of CA of PVDF/acetone/toluene (solution 4) and PVDF/acetone/toluene/GR, deposited by sedimentation on the silicon smooth (blue color) and structured substrates (red and green colors, respectively): "a" - 20/10 (m/d); "b" - 10/20 (w/p); "c" - 15/5 (w/p); "d" - 10/10  $\mu\text{m}$  (w/p), where: "m" is the distance between the holes etched into the surface, "d" – the hole diameter; "w" - the side of the square of the hillock, "p" – the distance between the hillocks.

**Rys. 7.** Wartość kąta zwilżania (CA) dla PVDF/acetone/toluen (roztwór 4) oraz PVDF/acetone/toluen/GR osadzanych metodą sedymentacji na krzemowych podłożach gładkich (kolor niebieski) i ze strukturami (odpowiednio kolor czerwony i zielony): "a" - 20/10 (m/d); "b" - 10/20 (w/p); "c" - 15/5 (w/p); "d" - 10/10  $\mu\text{m}$  (w/p), gdzie: m/d - "m" oznacza odległość między otworami wytrawionymi w głąb powierzchni, a "d" średnica tego otworu; w/p - "w" to bok kwadratu wzgórkka, a "p" przerwa - odległość między wzgórkami.



**Fig. 8.** The values of CA for PMMA (red color – an average calculated for the structures a, b, c, and d) and PMMAGR composites (green color) deposited by centrifugation of the smooth (blue color) and structured silicon substrates (red color - 1B, green color - 1BGR): "a" - 20/10 (m/d); "b" - 10/20 (w/p); "c" - 15/5 (w/p); "d" - 10/10  $\mu\text{m}$  (w/p), where: "m" is the distance between the holes etched into the surface, "d" – the hole diameter; "w" - the side of the square of the hillock, "p" – the distance between the hillocks.

**Rys. 8.** Wartość kąta zwilżania (CA) dla kompozytów PMMA (kolor czerwony - średnia wartość obliczona dla struktur a,b,c,d) i PMMAGR (kolor zielony) osadzanych metodą wirowania na podłożach krzemowych gładkich (kolor niebieski) i ze strukturami: "a" - 20/10 (m/d); "b" - 10/20 (w/p); "c" - 15/5 (w/p); "d" - 10/10  $\mu\text{m}$  (w/p), gdzie: m/d - "m" oznacza odległość między otworami wytrawionymi w głąb powierzchni, a "d" średnica tego otworu; w/p - "w" to bok kwadratu wzgórkka, a "p" przerwa - odległość między wzgórkami.

the conclusions presented in the article *Hydrophobic organic layers on smooth and 3-dimensional developed surfaces* [9]. The closed structure of "a"-type does not guarantee an improvement in the hydrophobic properties and the adsorption on that surface proceeds similarly as on the smooth surface, which is illustrated in Fig. 8. For the smooth surface of PMMAGR/Si, the measured CA value

was 95.6°, while for the PMMAGR surface of "a"-type the values of CA reached 115.5°.

In most cases, the use of the reduced graphene oxide improved the hydrophobic properties of the prepared composites. Such behavior is due to the fact that the reduced graphene flakes are non-polar. The rGO flakes are free from oxygen atoms and the covalent bonds

between carbon atoms are unpolarised. They exhibit a strong affinity for the alkyl groups and combine easily with the hydrophobic PVDF polymer on various supports. The non-polar solvents additionally ensure a good dispersion of the flakes in the composite.

#### 4. Conclusions

The article presents the results of the studies on graphene composites with organic polymers in various media. The following materials have been tested: PVDF/DMF/rGO, PVDF/NMP/rGO, PVDF/acetone/toluene/rGO and PMMA/rGO. The main subject of the research was the evaluation of the hydrophobic properties of the selected materials. These properties depend markedly on the medium, in which the material is dispersed, and on the way of coating the substrate with the material. The homogeneity of the composite layer was accepted as the evaluation criterion. The layers were deposited on the smooth and developed substrate surfaces. The composite of PVDF/acetone/toluene/rGO was characterized by the best parameters, i.e. by the contact angle value equal to  $180^\circ$  (superhydrophobic properties), for the material covering both smooth and structured surfaces. The CA value of  $180^\circ$  means that no adsorption of the water drop occurred on the composite during the measurement on the goniometer. This value did not depend on the type of the structure and was significantly greater than that obtained previously for a pure polymer. Graphene introduces an additional inhomogeneity and surface roughness, and combines well with the medium of PVDF/acetone/toluene, ensuring a good distribution of graphene film and a reproducibility of the deposition process. Because of the intermolecular interactions in the composite, the surface tension appearing at the interface is so small (the high values of CA are observed) that the water drop is repelled from the surface and superhydrophobic layer is formed.

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