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The wetting properties of Langmuir–Blodgett and Langmuir–Schaefer films formed by DPPC and POSS compounds

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ABSTRACT

The possibility of modification of surface wettability is especially desirable in implantology. This effect is achieved by coating a given material with thin films containing nanoparticles of different chemical properties. In recent years, much interest has been paid to supported phospholipid bilayers (SPBs), because they can be exploited in novel biotechnological devices such as biosensors and mimetic membrane–coated implants. In view of the above, we decided to study the modification of wetting properties of phospholipid layer by two types of polyhedral oligomeric silsesquioxanes (POSS) with different functional groups attached to the silica open–cage. The POSS and phospholipid (1,2-dipalmitoyl-sn-glycero-3-phosphocholine, DPPC) were vertically (Langmuir-Blodgett; LB) and horizontally (Langmuir-Schaefer; LS) deposited on quartz substrates to form a thin layer structure. The advancing contact angles on the modified surface coated with thin films were measured. The surface free energy (SFE) of DPPC, POSS and their mixed DPPC/POSS films was estimated by using Owens-Wendt-Rabel-Käelbe (OWRK) method. It was shown that the chemical structure of POSS used as a modifier influence the wetting properties of modified quartz surface. Incorporation fluoroalkyl-POSS into DPPC monolayer leads to obtaining a more hydrophobic film, while the addition of polyethylene glycol-POSS creates a more hydrophilic film. The transfer of the film with a more condensed structure led to a more hydrophobic material. The deposition technique (horizontal or vertical) had a particular impact on the modification of wettability of quartz surface coated with monocomponent fluoroalkyl-POSS film, whereas for the modification with mixed DPPC/POSS systems the choice of transfer method was not so significant.

1. Introduction

Solid-supported lipid bilayers (SPBs) are the systems made of a continuous lipid bilayer deposited onto a planar solid substrate. SPBs are used in many fields of biology, e.g. as stationary cell membrane mimics, for better understanding of a membrane–related cellular processes (Khan et al., 2013; Risović et al., 2016; Heath et al., 2017; Arslan Yildiz et al., 2013), for drug and bactericide delivery mechanisms (Ramadurai et al., 2017) and for prevention of biofouling (Kılıç et al., 2017). Recently, SPBs have been also extensively studied in the context of development of new biological and biomedical devices. In particular, the potential to exploit SPBs in novel biotechnological devices such as mimetic membrane–coated implants has been recognized (Khan et al., 2013; Kılıç et al., 2017). As far as implant devices are concerned, it has been proposed that supported bilayers or supported tethered monolayers (Kılıç et al., 2017) can be specifically impregnated with lipopeptides, whole proteins, and other molecules in order to increase biocompatibility and even promote new tissue growth (Khan et al., 2013; Ananthanarayanana et al., 2010; Altgärde et al., 2013). When designing new mimetic membrane-coated implants, it is important to take into account that implant affects the surrounding tissue through its surface. Topography (especially roughness) and chemical composition of the implant surface layer significantly affect the adhesion of cells to the material (Espinar-Escalona et al., 2016; John et al., 2015). The differences in chemical composition of materials influence such parameters as: surface energy, polarity, wetting and zeta potential, and consequently affect the interactions of cells with the material. Thus, an essential point is to predict and control the structure of the adsorbed layer formed on any given biomaterial. Skillful control of surface parameters allows modification of the surfaces to satisfy in the best possible way the target requirements. For example, surface free energy and roughness are the factors determining the initial bacterial colonization, a right modification may allow deceleration of the biofilm formation. For instance hydrophilic materials are desirable in dental implantology because of the threat of periodontitis caused by the pathogenic bacteria and associated with biofilm formation (Liu et al.,

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2014). On the other hand, hydrophobic materials are also desirable in implantology. When implants come in contact with blood, platelet adhesion and activation may occur, which could lead to thrombosis and sometimes failure of implants. Therefore, much attention has been paid to improving hemocompatibility by employing superhydrophobic surfaces (Movafaghi et al., 2017). The phenomenon of wettability plays a decisive role in respect to histophilic ("tissue loving") or osteolytic ("bone loving") behavior of implants (Jennissen, 2005). The above examples show how important is to prepare the material surface with adequate wettability because by tuning the wetting properties of surface layer, an implant most suitable for desired medical application can be obtained.

Our paper describes the preparation and characterization of supported lipid layers in which POSS molecules have been incorporated into the DPPC. The obtained layers were examined for changes in the wetting properties of hydrophilic surfaces.

We have chosen POSS derivatives because these substances can generally improve thermal stability, viscoelastic, chemical and mechanical properties also have good biocompatibility, are non-toxic and cytocompatible (Kim et al., 2007; Punshon et al., 2005). Moreover, POSS molecules incorporated into polymer matrix improve the oxidation resistance and enhance antimicrobial properties (Zhang and Müller, 2013; Dopierała et al., 2016). In order to check how chemical composition of the surface layer affects the properties of modified material, we studied two types of POSS derivatives with different functional groups. We chose fluorinated silsesquioxane because fluorinated compounds have many potential applications as drop—in modifiers for wetting–resistant surfaces. Moreover, the incorporation of fluorinated POSS could significantly improve the thermal stability of poly(methyl methacrylate) (PMMA). This increase in thermal stability is particularly desirable for the application in implants made of PMMA in dentistry. In addition, it has been shown that these fluorinated POSS–based copolymer surfaces could reduce the surface energy and could be used to design water–repellant nanocomposite coatings (Dai et al., 2010). We also studied POSS with poly(ethylene glycol) (PEG) moieties in chemical structure because the surfaces modified with PEG groups are widely recognized as materials resistant to protein adsorption (Harris, 1992; Goddard and Hotchkiss, 2007) and reduction of unwanted effects, for example: fouling of contact lenses, clotting on blood containing devices, triggering inflammation around artificial organs (Kawakami and Artif, 2008).

The supported lipid bilayers are usually flat and deposited on a hydrophilic solid surface (quartz, glass, mica, and silicon) (Zwang et al., 2010; Seeger et al., 2010; Spangenberg et al., 2004; Jurak et al., 2015). According to literature (Khan et al., 2013) in order to obtain high lipid mobility, the substrate should be hydrophilic, smooth and clean. For this reason, our fundamental research was carried out on the quartz surface. There are several techniques for the preparation of supported lipid bilayers: spin-coating (Rappolt et al., 2004; Jurak and Chibowski, 2007; Pompeo et al., 2005), vesicle fusion (Rossi et al., 2003; Bucak et al., 2010) and solution spreading (Jurak et al., 2015; Bucak et al., 2010; Gołąbek and Holysz, 2010; Li et al., 2004). However, the most common and often used are Langmuir–Blodgett (LB) and Langmuir–Schaefer (LS) techniques (Hianik et al., 2017; Zhu et al., 2016; Lalgee et al., 2018; Zhavnerko and Marletta, 2010; Jurak and Chibowski, 2010; Golabek et al., 2011). Langmuir techniques offer the possibility to prepare and investigate lipid monolayer under well–-defined conditions (such as subphase composition, nature of molecules and counter ions, and pressure of deposition) and to transfer it onto a solid.

In our previous paper (Wamke et al., 2015; Skrzypiec et al., 2018) it has been shown that the films (deposited by LB and LS techniques) formed by molecules of POSS derivatives effectively modify the wetting properties of glass and gold substrates. The results presented in that work show that good quality of the transferred POSS monolayer leads to desired modification of investigated substrates. Therefore, in our research we have also decided that the floating monolayers would be transferred from the liquid subphase onto solid supports by using these techniques.

The wetting properties of modified films were characterized. Moreover we estimated the SFE values of modified films, which affect the adhesion, propagation and proliferation of cells (Risović et al., 2016).

The main goal of our basic research was to show how the presence of POSS derivatives incorporated into the SPB and the type of deposition technique modified of the wetting properties of hydrophilic material.

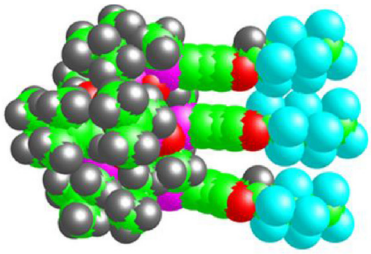
2. Experimental and theoretical methods

2.1. Materials

Two silsesquioxane derivatives with different functional groups attached to the silica open–cage used in this study were synthesized according to the method described by Maciejewski et al. (Dutkiewicz et al., 2011, 2016). Detailed information on spectral characterization and elemental analysis of the POSS derivatives used is given in our previous paper (Dutkiewicz et al., 2016). Phospholipid DPPC (≥99%) was purchased from Sigma Aldrich. The structures both of POSS compounds are presented in Fig. 1.

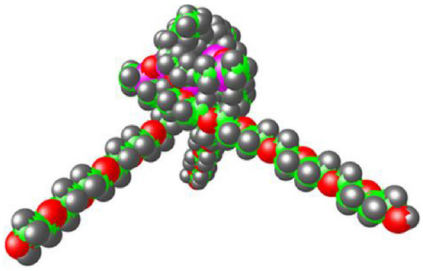
2.2. Substrate preparation

Quartz slides (purchased from PHASIS, L × W × D 25 × 25 × 1 mm)



OFP – POSS

3,7,14-Tris{[3-(2,2,3,3,3,4,4,5,5 octafluoropentyloxy) propyl] dimethylsiloxy} -1,3,5,7,9,11,14 –heptaisobutylotricyclo [7.3.3.] heptasiloxane)



PEG – POSS

3,7,14-Tris{[ω (hydroxy)(poliethoxy) propyl]dimethylsiloxy}-1,3,5,7,9,11,14-heptaisobutyl tricyclo[7.3.3.]heptasiloxane)

Fig. 1. Structural formulas of the investigated fluoroalkyl-POSS (OFP-POSS) and polyethylene glycol-POSS (PEG-POSS) substances. Molecular colors. black-hydrogen, red-oxygen, blue- fluorine, green-carbon, magenta-silicon.

were used as substrates for film deposition. Prior to starting Langmuir-Blodgett (LB) or Langmuir-Schaefer (LS) experiments, the quartz slides were heated to 75 ± 5 °C in a mixture of H_2O:NH_4OH (27% concentrated): H_2O_2 (30% by volume) at 5:1:1 v/v ratio for 0.5 h. The RCA is a standard procedure to remove organic residues from quartz wafer. At the next step, the quartz plates were rinsed with abundant amount of ultrapure water and dried in the air atmosphere. High-purity water, obtained by ultrafiltration (Elga Purelab system) of deionized water (reverse osmosis), was used. Polished quartz wafers were cut into ca. 1cm^2 pieces to serve as film substrates.

2.3. Langmuir–Blodgett (LB) and Langmuir–Schaefer (LS) deposition experiments

The quartz surface was modified with the films of POSS and DPPC/POSS using the Langmuir-Blodgett and Langmuir Schafer techniques by commercial Langmuir trough (KN 0033, KSV Nima) with a surface area of 273 cm^2 (L × W × D, 364 × 75 × 4 mm) and a subphase volume of 190 mL. LB method is a vertical lifting procedure that allows the transfer of a monolayer film onto a quartz substrate. LB deposition was performed by immersing the substrate in the water subphase and then POSS/chloroform solution was spread on the water surface. The POSS and DPPC/POSS monolayer, compressed up to selected pressure, was transferred onto the substrate by withdrawing the quartz slides from the water subphase (upstroke deposition). The dipping rates were 1 mm/min, with a fixed constant surface pressure. The compression rate when approaching the transfer substance was 5 mm/min. During all measurements the temperature of the subphase was kept constant at the level of 25.0 ± 0.1 °C with the application of Julabo water circulating baths. Langmuir-Schaefer technique is a horizontal lifting procedure. LS films were transferred in the same experimental conditions, by clasping horizontally the compressed Langmuir film and lifting the substrate upwards very slowly (0.5 mm/min). A scheme illustrating the DPPC/POSS films transfer onto the quartz substrates by LB and LS methods is presented in Fig. 2.

Layer deposition (LB and LS) of DPPC, POSS and DPPC/POSS was performed at two fixed transfer pressures: i) 10 mN/m and ii) transfer pressure corresponding to the maximum value of C_s^{-1} (Fig. 1S, Supplementary material). The compression modulus defined as $C_s^{-1} = -A(d\pi/dA)$ depends on the state of the film, taking higher values for more condensed films. The layer deposition at the transfer pressure value corresponding to the maximum value of C_s^{-1} permits transfer of a more packed monolayer and thus it ensures more effective modification of the quartz surface, a higher pressure at the transfer gives a surface of much better uniform cover with the modifier molecules. To prove the deposition efficiency by LB technique the values of transfer ratio (TR) of coated quartz are reported in Table 1S in Supplementary Material. The quality of the film can be described by the transfer ratio (TR), which is defined as the ratio of the area of the monolayer removed from the air–water interface during deposition to the area of the substrate on which it is to be deposited. For the ideal transfer, TR is equal to 1. The reported TR values apply only to LB films. Analysis of the obtained values of TR shows that the quality of the transfer depended strongly on the surface pressure (Wamke et al., 2015). For the DPPC/POSS mixtures the TR values are a little higher than 1. This suggests that for both mixtures: DPPC/PEG-POSS and DPPC/OFP-POSS the substrate was coated with a single monolayer of the material.

2.4. Contact angle measurements

The quartz surfaces modified with films of POSS or DPPC/POSS mixture were characterized by contact angle measurements. After 24 h drying of quartz plates stored in a desiccator at 25 °C and humidity 18%, the contact angle of water (WCA) and diiodomethane on the modified surface were measured using the sessile drop method with the Theta Lite Optical Tensiometer TL101 (Attension, KSV Finland). This instrument consists of a CCD video camera with a maximum resolution of 1280 × 1024 pixels and up to 60 images per second, multiple dosing/micro- syringe units, and a temperature-controlled environmental chamber. A drop (3 µl) of ultrapure water or diiodomethane (99%, Sigma Aldrich, Poland) was automatically pushed out of the capillary and deposited on a stationary surface of the sample under air atmosphere. Then the change in contact angle was recorded by a high-speed video camera over time. The software fitted the Young-Laplace equation to the shape of the drop accurately by using all of the points on the drop profile (volume of the drop and surface tension of liquid as input values). The digital drop image was processed by an image analysis system, which calculated both the left and right contact angles from the shape of the drop with an accuracy to ± 0.1°. In our study, the "static" contact angle was measured, which means that the measurements were carried out immediately after the drop was placed on the solid surface. The "static" contact angle depends on the initial kinetic energy of the drop and the dynamics of vibrations occurring after landing on the surface (Risović et al., 2016). For this reason contact

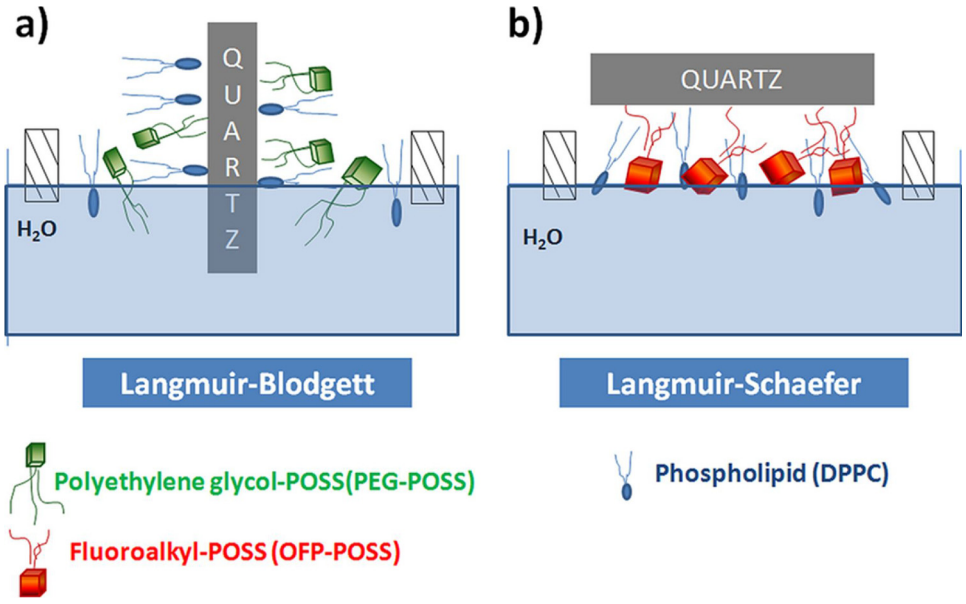


Fig. 2. The LB and LS techniques of Langmuir film deposition on the quartz plate.

angle measurements were repeated three times for each solid-liquid sample and the average values of advancing contact angle were reported. During all measurements the temperature was kept constant at a level of 25.0 ± 0.1 °C.

2.4.1. Determination of the surface free energy (SFE) by the OWRK method

The Owens–Wendt–Rabel–Kaelble (OWRK) method is one of the most commonly used for the calculation of the surface free energy (SFE) on the basis of the experimentally obtained values of contact angle (Owens and Wendt, 1969; Li et al., 2013; Borah et al., 2015; Cwikel et al., 2010; Kape et al., 2016). The polar and dispersive components of polymer surface energy were determined by this method (Eq. 1) which allows linearization of the contact angles in various liquids:

$$\sqrt{\gamma_{sv}^{d}\gamma_{lv}^{d}} + \sqrt{\gamma_{sv}^{p}\gamma_{lv}^{p}} = 0.5\gamma_{lv}(1 + \cos\theta) \quad (1)$$

where γ_{sv} and γ_{lv} are the solid-vapor and liquid-vapor surface tension, respectively; and θ is the contact angle, which is established by a tangent to the liquid droplet and the solid surface in the area of intersection of the solid-liquid-vapor phases. In the OWRK model it is possible to discriminate the surface free energy of the solid (γ_{sv}) in terms of two kinds of interactions corresponding to the dispersive type (Van der Waals interactions) and the polar type (dipole-dipole interactions and hydrogen bonds). Because there are two unknowns, γ_{sv}^{d} and γ_{sv}^{p} in the equation, two liquids with the known dispersive and polar components are needed to solve it. In our study, diiodomethane (γ_d; θ_d) was used as the dispersive liquid and double distilled water (γ_w; θ_w) as the polar liquid (Jacniacka, 2009):

$$(\gamma_{sv}^{d})^{0.5} = \frac{\gamma_d(\cos\theta_d + 1) - \sqrt{(\gamma_d^p/\gamma_w^p)}\cdot\gamma_w(\cos\theta_w + 1)}{2(\sqrt{\gamma_d^d} - \sqrt{\gamma_d^p(\gamma_w^d/\gamma_w^p)})} \quad (2)$$

$$(\gamma_{sv}^{p})^{0,5} = \frac{\gamma_w(\cos\theta_w + 1) - 2\sqrt{\gamma_{sv}^{d}\gamma_w^d}}{2\sqrt{\gamma_w^p}} \quad (3)$$

According to literature reports (Cwikel et al., 2010; Kape et al., 2016), the dispersion part of the surface tension was 21.8 mN/m for water (γ_w^d) and 50.8 mN/m for diiodomethane (γ_d^d). The polar part of the surface tension was 51 mN/m for water (γ_w^p) and 0 mN/m for diiodomethane (γ_d^p). The total surface free energy (SFE) of solid equals:

$$SFE = \gamma_{sv}^{d} + \gamma_{sv}^{p} \quad (4)$$

The surface free energy of a sample can provide very important information (e.g. on adhesion, spreading, etc.) concerning the processability of the solid product. It is therefore advisable to know this parameter in working on the formulation of a film–coated product.

Also, the work of adhesion (W_a) was calculated from Eq.5 (according to the Young-Duprè model), whose value shows the changes in the hydrophilic/hydrophobic properties of the surface.

$$W_a = \gamma_l(1 + \cos\theta_a) \quad (5)$$

where γ_l is the surface tension or surface free energy of the liquid (water or diiodomethane), θ_a – means advancing contact angle.

3. Results

3.1. The Langmuir–Blodgett films of DPPC-POSS

In our previous papers (Dutkiewicz et al., 2016; Rojewska et al., 2017; Skrzypiec et al., 2017) we have presented surface properties, morphology and rheology of mixed DPPC/POSS monolayers at the air/water interface, i.e. π–A isotherms, the miscibility and stability of the two components in the monolayer were analyzed in terms of compression modulus (C_s^{-1}), excess Gibbs free energy (ΔG_{exc}), activity coefficients (γ) and interaction parameter (ξ). Successful preparation of LB films by using the DPPC/PEG-POSS and DPPC/OFP-POSS (Skrzypiec et al., 2018) suggests that these two types of SPBs with silsesquioxanes can be good candidates for obtaining nanostructured coatings which can be applied as surface modifiers e.g. for implants. Now, we focus on the wetting properties of thin films formed by equimolar mixtures of DPPC and POSS after deposition onto quartz plates. Selection of quartz surface as a substrate resulted from our previously studies, presented in (Dutkiewicz et al., 2016). Topography AFM images of POSS films deposited on the quartz substrates using LB technique indicated that this substrates are almost completely covered with silsesquioxane films although there are some defects in the surfaces (Supplementary material, Fig. 2S). Moreover, we also have shown that the roughness of POSS films (PEG-POSS and OFP-POSS) is the same and the values of the Wenzel factor are very close to unity (Dutkiewicz et al., 2016). Therefore, considering the difference in the hydrophobicity of the surfaces covered only with POSS compounds, we can conclude that this effect comes entirely from the chemical nature of POSS and is not related to geometry of quartz.

The transfer surface pressures of thin films DPPC/POSS were set down at 10 mN/m and at the pressure corresponding to the maximum of compression modulus, according to the results presented in Fig. 1S (Supplementary material). Fig. 3 shows the values of transfer pressure at which the thin films were deposited on the substrate by both LB and LS techniques.

Fig. 4 presents the wettability curves of the surfaces modified by LB method. The wetting angle measurements of so prepared materials confirmed the successful deposition of POSS and DPPC/POSS mixed films. The addition of POSS to DPPC significantly influenced the run of the curves illustrating the changes in contact angle with time. The addition of POSS to DPPC monolayer results in obtaining quartz surface of wettability stable for much longer time as compared with that of the film formed by pure DPPC (Fig. 3). Literature (Scherer et al., 2014; Krafft, 2012)(Krafft (2012)) has demonstrated that F-chains and F-components constitute powerful tools for modifying and controlling phospholipid behavior, in particular their self-assembling properties, and, consequently, the properties of e.g. phospholipid-based films.

The WCA on the unmodified surface of polished quartz slide is 15 ± 0.1° (Dutkiewicz et al., 2016) and significantly increased when the surface was coated with DPPC monolayer or DPPC/POSS film.

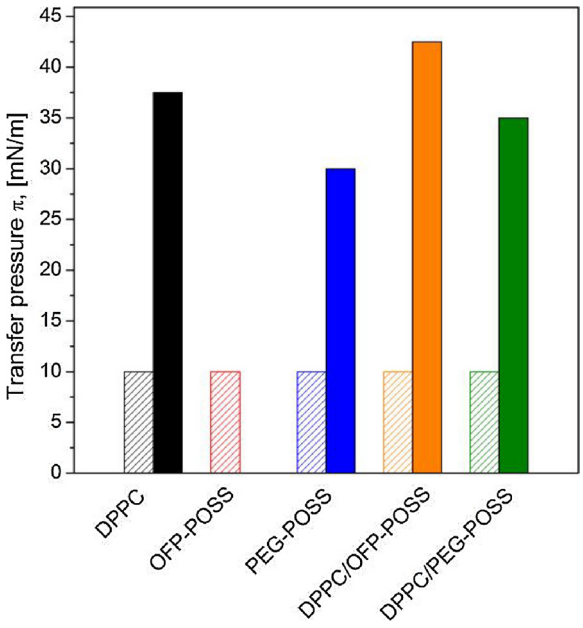


Fig. 3. The transfer pressure (π) at which thin films of DPPC, POSS and their equimolar mixtures were deposited on quartz by LS and LB methods (striped columns refer to π = 10 mN/m, black columns refer to π set down at maximum value of compression modulus).

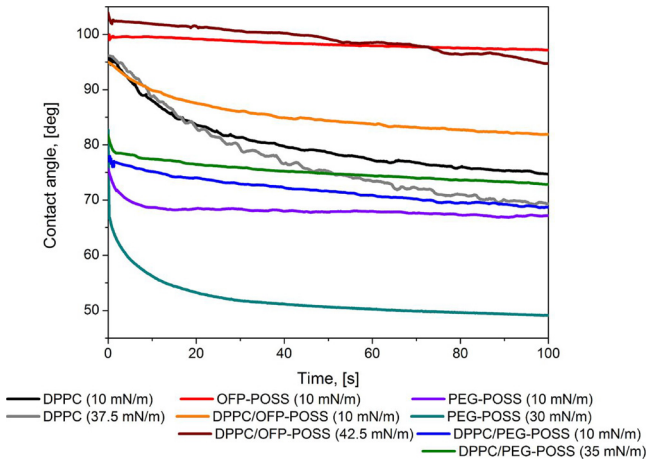


Fig. 4. The WCA vs. time measured on the quartz substrate modified by LB thin film (transfer pressure in brackets).

Strong hydrophobization of the quartz surface also proves that it is well covered with DPPC with incorporated POSS molecules. This effect is especially pronounced for DPPC/OFP-POSS film. In our previous paper (Skrzypiec et al., 2018) it was shown that the fluorine-containing compounds are good precursors for chemical modification and they increase the hydrophobicity of a material. Moreover, referring to the wettability results presented for the glass modified with OFP-POSS ((i.e. the compound with three fluorinated substituents and closed cage) (Skrzypiec et al., 2018), it can be concluded that the mixed DPPC/OFP-POSS film more effectively hydrophobized the hydrophilic surface.

As expected, the surface pressure at which the film is transferred to the solid substrate, has significant influence on the results of surface modification. For DPPC/POSS mixed monolayers transferred at surface pressures corresponding to the $C_{s,\max}^{-1}$ value, higher values of WCA were obtained. Particularly pronounced differences in the wetting properties of the surface modified with mixed DPPC/OFP–POSS film were observed between the films transferred at surface pressures of 10 mN/m and 42.5 mN/m. Undoubtedly, this effect is due to the transfer of monolayers in different phases on the quartz surface. The monolayers were prepared by spreading suitable amphiphilic molecules dissolved in chloroform on the air/water interface. Upon evaporation of the solvent, the amphiphiles self-assembled with their hydrophilic head group submerged in the water and the hydrophobic tail directed towards the air. Depending on the area per individual molecule, they arrange to form different phases. The DPPC/OFP–POSS film is found in the liquid expanded phase (LE) at the surface pressure of 10 mN/m, while at the surface pressure of 42.5 mN/m it is in the liquid condensed phase (LC) (Borah et al., 2015). This is consistent with the results of our previous studies (Wamke et al., 2015) concerning the monolayer formed by molecules of open-cage POSS and deposited on gold by different methods (LB or LS) and at different pressures. In order to assess the quality of modified surfaces, we used the FTIR spectra which showed that the higher the transfer pressure, the greater the amount of POSS molecules deposited on the modified surface (Wamke et al., 2015). In the study presented here, the value of $C_{s,\max}^{-1}$ corresponds to the maximum transfer pressure (Supplementary material, Fig. 1S) and also refers to the greatest packing of molecules at the interface. Therefore one would expect that at $C_{s,\max}^{-1}$ the largest number of molecules or domains will be transferred onto the substrate and thus the greatest modification in the wettability will be obtained.

Here, it should be emphasized that the transfer of the DPPC/OFP-POSS film at pressure of 10 mN/m and higher, corresponds to the zone in which phase separation occurs. This significantly influences the morphology and topography of transferred film and in consequence the value of contact angle. The topography of solid substrate surfaces (quartz) modified with LB and LS films was characterized and evaluated by using the atomic force microscopy [Supplementary materials Fig. 2S and Fig. 3S]. The changes in the morphology of the created films are visible as the surface pressure approaches the collapse point. Similar effects were observed for fluorinated POSS derivatives with closed cage (Skrzypiec et al., 2018). Moreover we observed formation of characteristic domain structure in the DPPC/OFP-POSS layer [42, Supplementary material Fig. 4S BAM]. Formation of nanodomains, as well as multilayer, promote the increase in the film roughness, and thus allows obtaining materials with more hydrophobic surfaces (Camacho et al., 2014; Skrzypiec et al., 2018). The presence of specific domains has also been reported in literature (Krafft, 2012; Niemelä et al., 2007)(Scherer et al. (2014)) have investigated the monolayers formed by binary mixtures of lipids: DMPE and fluorinated molecules (a derivate of itaconic acid esterified with perfluorododecanol). It has been shown that full miscibility seems unlikely regarding the different structures of the lipids and their chemical compositions, such as the presence of highly fluorinated lipid alkyl chain. Formation of two separate coexisting regions for both lipids is possible. What is worth emphasizing, the functional nanodomains (*rafts*) which result from demixing within the lipid membrane also play an important role in cellular processes such as membrane trafficking or regulation of the activity of membrane proteins (Krafft, 2012; Niemelä et al., 2007). The presence of rafts also affects the topography of the monolayer, which undoubtedly affects the surface wetting.

According to literature reports (Pi et al., 2013; Gew and Misran, 2017; Campos et al., 2011; Skrzypiec et al., 2018) we expected that after deposition and drying of condensed DPPC/OFP-POSS monolayer the film obtained could have a rougher surface than before its modification. Gew and Misran (Gew and Misran (2017)) have shown how incorporation of DOPE/PEG2000 (DP) into Langmuir monolayer of C18 fatty acids causing an increase in the roughness parameter. The deposition of a nanostructured film with micro-domains or other nanostructures increases the roughness of the coated material and thereby changes the wetting properties according to Wenzel state. The increase in the surface roughness increases the hydrophobicity of the material, therefore the surface modified by the DPPC/OFP-POSS film shows a high contact angle value. It is consistent with literature (Campos et al., 2011; Skrzypiec et al., 2018) showing that the F-POSS molecules also contribute positively to the surface hydrophobicity by increasing surface roughness of the material.

The equilibrium WCA on the quartz surface modified with DPPC/OFP–POSS mixed film at a surface pressure corresponding to $C_{s,\max}^{-1}$ (42.5 mN/m) is ca. 97° (t = 100 s), while on the quartz surface modified with DPPC/PEG-POSS at a surface pressure corresponding to the value of $C_{s,\max}^{-1}$ (35 mN/m) it is ca. 75°. The WCA measured on the quartz covered by DPPC thin LB film is lower and equal to 70° (at $C_{s,\max}^{-1}$ it is 37.5 mN/m) after 100 s. Thus, both types of DPPC/POSS mixed films cause hydrophobization of the quartz surface, but to a different degree, which extends the potential application possibilities. The film made of DPPC/OFP–POSS showed a much more hydrophobic character. The same trend was observed for the quartz surface modified only with POSS molecules, i.e. OFP-POSS is more hydrophobic than PEG-POSS (Dutkiewicz et al., 2016).

Furthermore, in our previous paper (Wamke et al., 2015; Skrzypiec et al., 2018), we have shown that modification of gold or glass substrates with LB films of POSS derivatives with open or closed cage also leads to obtaining more hydrophobic surfaces. Moreover, the WCA values obtained after the film deposition took similar values, irrespective of the type of substrate surface (glass or gold). As expected, the hydrophobic nature of the material is mainly determined by the film's chemical composition not the type of substrate.

When the quartz plate was immersed into the subphase DPPC/POSS, then its surface got negative charge density as a consequence of dissociation of silanol groups. The DPPC/POSS monolayer compressed up to an appropriate surface pressure was transferred onto the substrate

drawing the quartz slides out from the water subphase. As a result, the polar groups of DPPC and POSS molecules interacted with the quartz surface and were oriented towards the support surface, with their hydrophobic groups directed outside. The differences in the wettability of the surfaces modified by mixed films were observed to be related to the chemical structure of the POSS molecules. PEG–POSS molecules had more hydrophilic character than OFP–POSS molecules, which was also reflected in the wetting properties of mixed monolayers with DPPC. As follows from the measurements, the wettability of solid substrate modified with the deposition of DPPC/PEG–POSS monolayer was significantly higher in comparison with the quartz covered by a thin film of DPPC/OFP–POSS.

The energetic and wetting properties of tested films deposited on a quartz support can be characterized by determination of the surface free energy (SFE). The SFE magnitude depends on the type and strength of the involved intermolecular interactions, which influence interfacial adhesion processes. Surfaces with higher surface energy provide closer tissue adhesion (Anselme et al., 2010). On the basis of water and diiodomethane contact angle values, SFE was estimated by the OWRK method for modified quartz. The percentage of polarity can be derived from the surface free energy. It is the ratio of the polar part (γ_{sv}^{p}) and the total surface free energy (SFE). The results are shown in Table 1.

According to literature (Jurak et al., 2015; McClellan and Franses, 2005) the deposition of DPPC film on the quartz surface enhanced its hydrophobic properties. The hydrogen bonding and electrostatic interactions determine the adsorption of the phospholipid molecules with their polar heads oriented towards the support surface, and their hydrophobic tails outside, which makes the quartz surface more hydrophobic. The values of SFE estimated for the quartz surface modified by LB technique are in the range of 18.7 mJ/m^2 to 41 mJ/m^2. It has been shown in several papers (Aslan and Dayi, 2004; Parida et al., 2006), that cell adhesion and cell spreading display a sigmoidal dependence on the surface energy. In the hydrophobic range at critical surface energy of solid less than 60 mJ/m^2, practically no adhesion of fibroblast can be observed. This is a beneficial effect because the presence of fibroblasts at the site of injury of bone tissue leads to a slow-down the osteoinduction and osteointegration processes (Parida et al., 2006). Hydrophobic materials are employed clinically for endosseous implants. From among the films examined by us (Table 1), particularly low value of SFE was obtained for DPPC/OFP-POSS film transferred at 42.5 mN/m. On the other hand, at surface energies more than 60 mJ/m^2 a significant to strong adhesion and spreading of cells has been reported (Parida et al., 2006). The strong adhesion is desirable to increase biocompatibility of the material, but there are also some limitations. One of the limitations of the use of hydrophilic materials is the possibility of adhesion of certain bacteria strains on the surface of implants showing the maximum WCA in the range 70–90 (Parida et al., 2006). This criterion is met by the DPPC/PEG-POSS film, so the surface covered with this film may exhibit greater susceptibility to biofilm formation.

The phase state of the monolayer, which was transferred onto the substrate, influence the SFE values. The mixed monolayers DPPC/POSS in LE phase were deposited at surface pressure equal to 10 mN/m. It should be noted that LE phase is a loosely packed monolayer which could contain also molecules of the water subphase. Therefore, the interpretation made for the films transferred at a pressure corresponding to $C_{s,\max}^{-1}$ seems to be more correct.

The formation of the closest packed monolayer allows elimination of the effect of heterogeneous quartz surface coverage, which is important during SFE analysis. In our paper (Rojewska et al., 2017) we show that the hydrophobization effect of quartz surface could be improved especially by the addition of OFP–POSS molecules into DPPC monolayer. The SFE value obtained for quartz modified with DPPC/OFP–POSS mixed film, transferred at the surface pressure corresponding to $C_{s,\max}^{-1}$ (at. 47.5 mN/m) is lower than that for the substrate covered with DPPC/PEG-POSS mixed film deposited at. 35 mN/m. The disperse fraction of SFE (γ_{SV}^{d}) is greater than the polar fraction (γ_{SV}^{p}) for most surface–modified substrates studied. Polar interactions determine the affinity of a substance and its interactions to water. For the monolayer in LC state, incorporation of OFP–POSS to DPPC monolayer reduces the SFE by reducing their polar fraction. The reduction of polar fraction of SFE is caused by the addition of a highly hydrophobic compound. The addition of a fluorinated POSS derivative to DPPC causes marked decrease in polarity in comparison to the surface modified with DPPC only (approx. 30%) and hence reduces its affinity to water. Using the LB method and OFP–POSS compound as a modifier, it is possible to get surfaces with worse adhesion to water than the surfaces modified with DPPC molecules only. The incorporation of PEG–-POSS into DPPC for monolayers at the surface pressure corresponding to $C_{s,\max}^{-1}$ causes an increase in the polarity of phospholipids film (from 7.3%–25%, Table 1). Thus, the addition of POSS molecules into the DPPC monolayer leads to the appearance of new interactions between phospholipids and functionalized PEG–POSS or OFP–POSS molecules. Depending on the hydrophilicity of the POSS functional groups, one can modify the wetting properties of the DPPC monolayer by LB method in the desired direction needed for the potential applications of the material.

3.2. The Langmuir-Schaefer films of DPPC-POSS

The films formed by POSS and DPPC were also horizontally (LS) deposited onto the quartz surface to form a layer structure. Fig. 5 presents the wetting curves for the surface modified by LS method.

As follows from the data presented in the form of graphs (Fig. 4 and Fig. 5), the values of contact angles measured for the surface modified with LB and LS films deposition are different, especially when one compares the WCA values obtained for the surface coated with DPPC and OFP-POSS monolayers. The surface modified with Langmuir-Schaefer film of DPPC is characterized the greatest hydrophobicity and its WCA value is around 100°. According to literature (Oleson and Sahai, 2008; Oleson et al., 2010) the adsorption of DPPC by LS

Table 1
Estimated values of the surface free energy (SFE) for thin films prepared by LB technique, based on the OWRK method; γ_{sv}^{p} -polar and γ_{sv}^{d} -dispersive components of SEF, θ_w - the contact angle value of water (WCA at t1 s), θ_d - the contact angle value of diiodomethane (at t1 s).

No.	Film component/-s	Transfer pressure π [mN/m]	θ_w [deg]	θ_d [deg]	SFE [mJ/m^2]	γ_{SV}^{d} [mJ/m^2]	γ_{SV}^{p} [mJ/m^2]	Polarity [%]
1	**OFP–POSS**	10.0	99.5 ± 2.9	66.8 ± 2.7	27.4	24.7	2.67	9.70
2	**DPPC**	10.0	88.8 ± 0.5	77.3 ± 1.3	21.9	18.9	3.00	13.6
3	**DPPC/OFP–POSS**	10.0	94.6 ± 3.9	87.2 ± 1.1	18.7	13.5	5.18	27.7
4	**DPPC**	37.5	96.4 ± 2.7	72.5 ± 2.1	23.2	21.5	1.70	7.30
5	**DPPC/OFP–POSS**	42.5	105.6 ± 1.6	75.3 ± 3.6	21.1	19.9	1.18	5.60
6	**PEGPOSS**	10.0	73.1 ± 1.9	66.7 ± 2.2	35.8	24.7	11.1	31.0
7	**PEG–POSS**	30.0	68.1 ± 1.2	66.2 ± 1.4	39.0	25.0	14.0	35.9
8	**DPPC/PEG–POSS**	10.0	76.9 ± 3.3	64.2 ± 2.5	34.7	26.3	8.39	24.2
9	**DPPC/PEG– POSS**	35.0	79.7 ± 0.4	68.2 ± 2.4	31.8	23.9	7.97	25.0

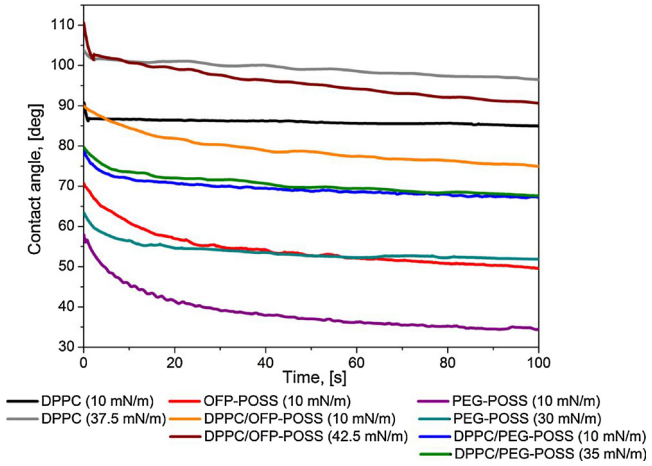


Fig. 5. The WCA vs. time measured on the quartz substrate modified by LS thin film (transfer pressure in brackets).

technique from bulk solution to quartz which is controlled by attractive van der Waals forces and further modified by electrostatic interactions of oxide surface sites with the negatively charged phosphate ester (-R (PO_4^-)R'-) portion of the DPPC headgroup. Anderson et al. (Anderson et al. (2009)) have concluded that the electrostatic interaction is the most important interaction in determining the adhesion between phospholipids and charged hydrophilic surfaces. As mentioned above, the quartz surface has been hydrophilized, so it should be expected that the polar groups of DPPC will interact increasingly stronger with the hydroxyl groups of the substrate on the monolayer approaching the quartz solid. On the basis of literature (Golabek et al., 2011; Kiessling and Tamm, 2003) we suppose that DPPC molecules reorient at the interface. The reorganization of lipid molecules may depend on the environment surrounding the film after its deposition (Solletti et al., 1996), i.e. air in our experiments. We suppose that the reorientation of DPPC molecules have changed during the film transfer at the air-quartz interface. As a result, the phospholipid molecules may reorient and expose the hydrophobic chains towards the air which gives a more hydrophobic surface. Moreover, in LS technique the quartz substrate is placed horizontally to the DPPC monolayer and away from the air/subphase interface at least by the thickness of the DPPC monolayer (in contrast to LB method). This distance between the air/subphase interface and the quartz substrate probably limits the interactions between water molecules and quartz surface and consequently, the film forming by LS technique is more hydrophobic.

Similarly as for the LB technique, the wetting properties and SFE of the surface modified by LS technique significantly depend on the transfer pressure of the monolayer. Higher values of SFE (more hydrophilic surfaces) were estimated for thin films deposited at lower transfer pressure (10 mN/m) than for pressures corresponding to the maximum compression of the monolayer (C_s^{-1}). This effect is associated with the LE phase state of the coating film and as a result fewer modifier particles are transferred to the quartz surfaces.

Table 2 presents the water contact angle values, measured on the surface modified by LS method and SFE values estimated by OWRK method. SFE values obtained for DPPC film at the transfer pressure 37.5 mN/m are very similar for both techniques used LB and LS. The polarity of the quartz surface covered with a DPPC film using the LS method is lower than that of the film formed by LB technique.

The two deposition techniques applied to modify quartz surface with DPPC, OFP–POSS or DPPC/OFP-POSS films give the surfaces with different wetting properties. This is a crucial point of our research because the results obtained evidence the impact of the deposition mechanism on the properties of the deposited layer. The occurrence of van der Waals interactions between the fluorinated groups of OFP–POSS and the quartz surface permitted the deposition of the layer made of these compounds on the quartz plate by LS method (Pellerite et al., 2002). For the film deposited by LB method the WCA on the modified surface changes in the range from 97° to 100° (Fig. 3) while for the layer deposited by LS method it varies from 52.5° to 71° (Fig. 4). The estimated value of the SFE for the surface modified with the OFP–POSS film deposited by LS method is greater than that of the SFE for films transferred by LB method. The increase in the value of SFE is mainly due to the increase in the polar component (γ_{SV}^{p}), which is also reflected by the threefold increase in the polarity of the surface modified with OFP–POSS (Tables 1 and 2). In contrast to the results obtained for OFP-POSS, the SFE values for DPPC/OFP-POSS film are the same for LB and LS techniques and moreover the decrease in the polarity of surface modified by LS method can be observed (Tables 1 and 2). The fact that the surface with the layer deposited by LS technique is more hydrophilic is probably a consequence of the mosaic structure of the OFP—POSS molecules (Dutkiewicz et al., 2016). The mosaic structure of the OFP–POSS monolayer produced at the air–water interface remained in the same form after the deposition of this film onto the solid substrate by LS method. Because of the use of LS method, OFP–POSS particles are horizontally oriented on the quartz surface, which leads to increased area occupied by POSS molecule per a unit of quartz surface and thus fewer particles OFP–POSS are able to adsorb on the solid. It can be assumed that LB technique promoted the formation of fabrication of better organized OFP-POSS based thin films

According to literature the conformation of the films when transferred onto a solid support probably changes and is dependent on the way of deposition (LB or LS).Silva et al., 2017 have suggested that the conformation of the polymer films changes when transferred by LS technique, which can also be due to the deposition of more than one layer. Probably, during the modification of quartz surface by DPPC/OFP-POSS film by LS method, a multilayer structure can be formed in which the polar groups of DPPC and OFP-POSS interact leading to a decrease in the film polarity.

In the case of surface modification with PEG–POSS or DPPC/PEG-POSS film on quartz using LS technique, the values of SFE and the surface polarity are comparable to those for the film obtained by the LB technique.

For more information about the changes in the surface free energy, Fig. 6 presents the work of adhesion of polar water and apolar diiodomethane for the layers produced by the LB and LS methods. The value of the work of water adhesion is particularly important because once the implant is inserted into a body, water molecules are adsorbed to the implant surface within the first few nanoseconds (Kulkarni et al., 2015). Therefore, understanding the wetting behavior and the wettability kinetics of the modified surface with water is really important in designing new material for implantology.

As can be seen, the work of adhesion of apolar liquid does not differ much for the monolayers containing PEG–POSS and DPPC (6-9 Fig. 6a and b) molecules, ca. 70 mJ/m^2. A similar effect is also observed for the surfaces modified by films containing OFP-POSS and DPPC (column1,4,5; Fig. 6a and b). What is also interesting, despite the differences in hydrophilicity of the POSS derivatives, the work of adhesion for diiodomethane on the surface modified with DPPC/OFP–POSS (column 5) is only slightly lower than on the surface modified with DPPC/PEG-POSS (column 9) film. Moreover, the deposition method does not significantly influence the value of the work of diiodomethane adhesion for most of investigated films (columns 1–9). Clear differences in the work of adhesion values appear with respect to the polar liquid (water). For DPPC/PEG–POSS (column 9) film a much better affinity to water was obtained than for only DPPC layer (column 4). The work of adhesion for the surface modified with LB film of DPPC/PEG-POSS (column 9; Fig. 6a) was by 38% higher than that for the surface covered with only DPPC film (column 4; Fig. 6a). Transferring DPPC/PEG-POSS films by LS method (Fig. 6b, columns 8 and 9) allows obtaining a modified surface with similar properties as that obtained by LB

Table 2
The surface free energy (SFE) for thin films prepared by LS technique, estimated by the OWRK method; γ_{sv}^{p}-polar and γ_{sv}^{p}-dispersive components of SEF, θ_w- the contact angle of water at 1 s, θ_d- the contact angle of diiodomethane at 1 (± SD, n = 3).

No.	Film component/-s	Transfer pressure π [mN/m]	θ_w [deg]	θ_w [deg]	SFE [mJ/m^2]	γ_{SV}^{d} [mJ/m^2]	γ_{SV}^{P} [mJ/m^2]	Polarity [%]
1	**OFP–POSS**	10.0	69.1 ± 2.7	61.8 ± 4.3	40.0	27.2	12.8	31.9
2	**DPPC**	10.0	88.8 ± 4.9	70.0 ± 3.3	27.2	22.9	4.3	15.8
3	**DPPC/OFP–POSS**	10.0	88.9 ± 2.6	63.3 ± 2.7	30.1	26.7	3.45	11.5
4	**DPPC**	37.5	102.4 ± 2.2	72.5 ± 1.0	22.2	21.1	1.11	5.01
5	**DPPC/OFP–POSS**	42.5	110.5 ± 0.9	73.5 ± 3.0	21.1	21.0	0.1	0.40
6	**PEG-POSS**	10	56.6 ± 0.6	63.4 ± 1.5	47.1	26.6	20.5	43.5
7	**PEG–POSS**	30.0	62.4 ± 0.3	65.0 ± 3.7	43.5	25.7	17.7	40.8
8	**DPPC/PEG–POSS**	10.0	76.7 ± 0.7	65.6 ± 1.7	34.3	25.4	8.90	25.9
9	**DPPC/PEG–POSS**	35.0	78.4 ± 0.3	67.4 ± 0.5	33.1	24.4	8.60	26.0

technique.

The use of LS method leads to an increase in water adhesion to the surface modified with OFP-POSS film (Fig.6b, column 1) by more than 40% in comparison to LB technique. While, the DPPC/OFP-POSS (column 5) film deposition method does not change the affinity of the modified surface to water, which for the films made by both LB and LS methods is ca. 50 mJ/m^2. The strongest decrease in the surface affinity to water was noted for the surface modified with DPPC/OFP–POSS film (column 5). The water adhesion is a slightly stronger for quartz surfaces modified by monolayers in the LE phase; with DPPC (column 2) or mixed films with POSS at the transfer pressure of 10 mN/m (Fig. 6, columns 3,8), than DPPC (column 4) or mixed films (columns 5 and 9). Generally, incorporation of PEG–POSS into DPPC monolayer improves the hydrophilicity of DPPC regardless of the deposition method used. However, for OFP-POSS molecules incorporated into DPPC monolayer a more hydrophobic surface was obtained than that with only DPPC film.

4. Conclusion

Fast development of new biomaterials prompts the search for new coatings in order to minimize undesirable effects and improve the biological response to an implant surface. SPBs with incorporated molecules of other compounds are extensively studied as promising coating materials. The surface properties of films containing DPPC and POSS molecules were studied as components of potential new biomimetic membrane coatings for implants. We chose two derivatives of POSS with different hydrophilicity determined by the presence of different functional groups in their molecules. As presented in our previous study (Dutkiewicz et al., 2016), PEG-POSS films were more hydrophilic than the monolayer formed by OFP-POSS. Analysis of the wetting properties of DPPC/POSS thin films has shown that the addition of a POSS derivative has ambiguous effect on the wettability. In general, the addition of PEG-POSS derivative to DPPC permits obtaining films of increased affinity to water (more hydrophilic). Moreover, the DPPC/PEG-POSS film is more hydrophilic than the DPPC/OFP-POSS, which is a result of the hydrophilic character of POSS molecules incorporated into phospholipid layer.

We also observed that the transfer pressure at which the film is deposited on the quartz surface and selection of method of deposition (LB or LS) influence the physical properties of the materials such as: wettability, surface energies, polarity, which, as known, determine a proper adhesion of material surface to the tissue. The lower the transfer pressure during the deposition of the DPPC/POSS film on the quartz surface the more hydrophilic material was obtained. The choice of deposition method is important for modification of the surface with only OFP-POSS film. The quartz surface covered with OFP-POSS using the LB technique gives a hydrophilic material, whereas the use of the LS method leads to a hydrophobic surface. The choice of deposition method does not affect the wetting properties of quartz modified by the two-component DPPC/POSS films at surface pressure corresponding to the most condensed phase.

According to our results, depending on the chemical structure of POSS and the type of deposition method (LB or LS) it is possible to get materials of different degree of surface hydrophobicity, which is much promising for the future use of POSS compounds as effective modifiers of the implant surfaces.

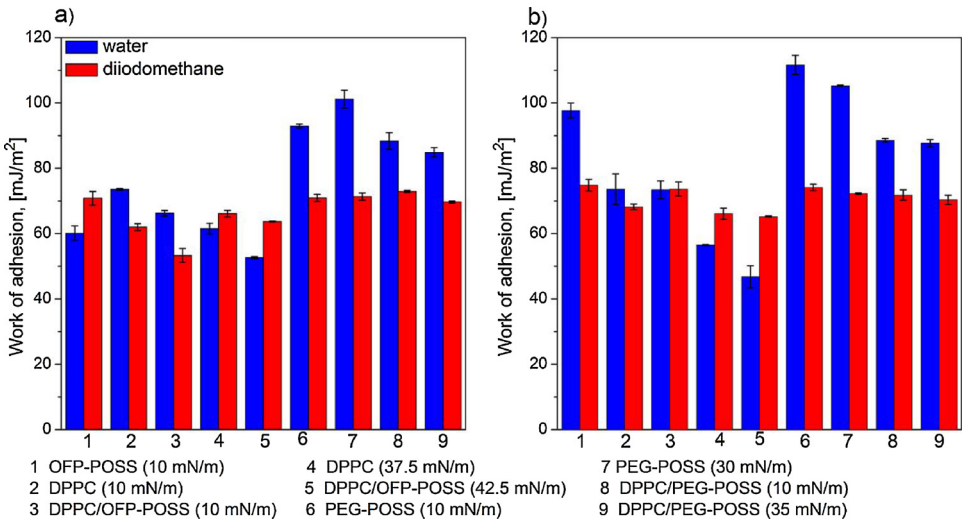


Fig. 6. Work of adhesion of water and diiodomethane on modified quartz surface by DPPC, POSS and their mixtures by a) LB b) LS technique (indicated values are means ± SD of at least three experiments).

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.chemphyslip.2019.04.004.

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