The modification of silicon surface by selected aminophosphonates to improve its tribological properties

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Abstract

In biomedical applications, the use of materials such as silicon has certain limitations resulting from the formation of a partially oxidized layer on top of the surface, causing corrosion and wear. Therefore, there is a need to modify the surface with non-toxic compounds that are tolerated in the human body. In this study, the thin films of aminophosphonate have been successfully formed on the silicon surface. The resulting monolayers were characterized by Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM) and contact angle goniometry. Additionally, the tribological behavior was examined for their potential use. It was demonstrated that the adhesive force, the work of adhesion and the wear influence the value of the friction coefficient in microscale. Moreover, the experimental data showed that the modification of silicon substrate via aminophosphonates caused a crucial decrease in the friction coefficient about 50%, the adhesive force about 85% and wear about 80%. The presented results prove the potential of aminophosphonates films in biomedical and frictional applications from the point of view of their excellent tribological properties.

1. Introduction

The aminophosphonic compounds are characterized by biological activity so that exhibit protective, antibacterial or anti-cancer properties [1–3]. These behaviors are extremely desirable, so it is therefore expectable that the C-aryl substituted derivatives of phosphonoglycine compounds (i.e. polyyclic aromatic hydrocarbons [4], heteroaromatic compounds [5, 6] and even ferrocene [7] and pyrene [8–11]) may to have similar biological properties. Due to the fact that phosphonic analogs of phenylglycine exhibit their herbicidal activity [12], they are applied as plant growth regulators [12] especially in modern agriculture and horticulture and agrochemical fungicides [13, 14]. The application of aminophosphonates in the chemistry of nanomaterials is less explored but it is a domain, which develops very intensively. Hameau et al [15] reported the functionalization of polyphosphorhydrazone dendrimers grafted on silica nanoparticles. Their surface amino functions were converted to aminophosphonic moieties giving materials hosting silver and silver oxide nanoparticles, which exhibited antibacterial activity [15]. Aminophosphonates bonded to silica were reported to give potentially more efficient and versatile ion-exchanger for separation of transition and heavy metal ions at low pH [16]. Derivatization of the nanoparticle surface with terminal functional, primary amine groups (from 2-aminooethyl phosphonic acid) [17] provided nanomagnetic platforms for therapy. Indium tin oxide, dysprosium oxide (Dy₂O₃), hafnium oxide (HfO₂), nickel ferrite (NiFe₂O₄), zinc oxide and copper oxide nanoparticles were described too [18]. Kafarski et al [19] described the modification of the surface of the iron oxide nanoparticles with aminophosphonic acids using the classic hydrophosphonation reaction. Magnetic nanoparticles with a modified surface were obtained to provide the new possibility to deliver therapeutic agents [19].
Aminophosphonates next to thiols, silanes, and phosphonic acids are also create self-assembled monolayers (SAMs) on various types of materials. By creating a thin layer on the surface of the material, changing its properties. For example, the aluminum surface which is commonly used for various micro-/nanoelectromechanical systems (MEMS/NEMS) with SAMs of phosphonic acid improves its tribological properties and stability and also provides the efficient lifetime longevity of devices [20]. SAMs on the surface can also serve another functions such as surface coverage protecting against corrosion resistance, wear and also as target carriers of a drug. The formation of a self-assembly monolayer of aminophosphonate on the surface of silicon can be an alternative to other materials used in medicine and biomedicine, which was presented in our previous works [10, 11].

In our studies, aminophosphonates compounds were synthesized and deposited on the silicon surface. Then, their effect on morphological, wettability, adhesion and friction properties in microscale were investigated. The presence of thin layers on the surface and its topography were characterized by atomic force microscopy (AFM). The wettability of the samples was studied by water contact angle and surface free energy analysis, whereas friction and adhesion properties were analyzed by a microtribometer T-23. The wear traces for all surfaces after tribological tests were monitored by scanning electron microscopy (SEM). The obtained study indicates that aminophosphonates can be used to reduce adhesion force, work of adhesion, coefficient of friction and wear for silicon surface in tribological systems.

2. Experimental

2.1. General
All solvents were applied routinely and dried previous to use while commercial reagents were used as received. NMR spectra were recorded by using a Bruker Avance III 600 MHz apparatus which operated at 600 MHz (1H NMR), 150 MHz (13C NMR) and 243 MHz (31P NMR). Melting points were measured using a MelTemp II apparatus in a capillary and were not corrected.

2.2. Preparation of aminophosphonates 2a-f
Schiff bases were prepared by refluxing equimolar quantities (2 mmol) of pyrene-1-carboxaldehyde with an amine in methanol (1a) or hexane (1b-d) under stirring for 24 h and were used for further conversions as obtained. This harsh method to prepare imines had to be used to provide satisfactory results. The reaction completion was monitored by 1H NMR and obtained imines 2a-d were isolated by removed the solvent under reduced pressure.

Pyrene-derived aminophosphonates 2a-d were synthesized using the procedure based on the aza-Pudovik reaction [10, 21] by the addition of the diethyl phosphate (3 mmol) to the Schiff bases 1a-d (1 mmol), as shown in figure 1. The mixture was heated with stirring on a water bath for 5 min until all the imine was dissolved. Dimethyl aminophosphonates 2a-d were isolated and purified by dissolving the crude reaction mixture in a minimum amount of diethyl ether and by triturating until formed a yellow precipitate. This operation was repeated several times. This procedure was followed by column chromatography on silica gel with chloroform as eluent which allowed to afford pure products in satisfactory yields. Samples were compared to the previously prepared ones [10] and were found identical. Spectral data are available in our previous paper [10] and scans of spectra are collected in the supplementary material to that article.

In the case of benzaldehyde-derived compounds 2e-f, they were synthesized using the procedure based on the Kabachnik-Fields reaction [22–24] (figure 1). The three-component reaction consisting of benzaldehyde (5 mmol), benzylamine or p-anisidine (5 mmol), and anhydrous magnesium sulfate (MgSO4) without any catalyst was carried out in toluene. The mixture was stirred at room temperature for 15 min Then dimethyl phosphite (5 mmol) was added and stirred vigorously at 100 °C, afterwards was filtered and the solvent was removed under reduced pressure. Products 2e-f were isolated by added dichloromethane (CH2Cl2) and washing with saturated sodium hydrogen carbonate (NaHCO3) aqueous solution. The organic phases were dried sodium sulfate (Na2SO4) and dichloromethane (CH2Cl2) was removed by evaporation to obtain residue containing almost pure aminophosphonates 2e-f. Product 2e was purified by column chromatography on silica gel eluted with ethyl acetate-hexane (4:1) solvent system. The pure product 2 f was obtained by crystallization from ethyl acetate and hexane (1:3) [22]. Aminophosphonates 2e-f were also identified by melting point (2 f) and 1H and 31P NMR spectroscopy (both 2e–f) and data were compared to literature values [22, 25–27]. Scans of spectra of compounds 2e–f are collected in Supplementary Materials to this paper.

2.2.1. Dimethyl N-benzylamino(phenyl)methyl-phosphonate (2e)
Y = 70% (1.07 g). Yellow oil. 1H NMR (CDCl3, 600 MHz): δ (ppm) 7.45–7.43 (m, PhH, 2 H); 7.40–7.37 (m, PhH, 2 H); 7.34–7.30 (m, PhH, 3 H); 7.27–7.24 (m, PhH, 3 H); 4.06 (d, J 1H, = 20.1 Hz, CHP, 1 H); 3.81 (d,
2.2.2. Dimethyl N-(4-methoxyphenyl)amino(phenyl)methyl-phosphonate (2 f)

Y = 54% (0.87 g), mp = 99 °C-101°C; lit [26, 27] = 100 °C-101°C. ¹H NMR (CDCl₃, 600 MHz): δ (ppm) 7.47–7.45 (m, PhH, 2 H), 7.35–7.32 (m, PhH, 2 H), 7.29–7.27 (m, PhH, 1 H), 6.70-6.68 (m, p-C₆H₄, 2H), 6.58 (approx d, ³J₃H₁ = 8.9 Hz, p-C₆H₄, 2H), 4.73 (d, ³J₃H₁ = 23.7 Hz, CH₃P, 1 H), 3.76 (d, ³J₃H₁ = 10.6 Hz, POCH₃, 3 H), 3.68 (s, OCH₃, 3 H), 3.49 (d, ³J₃H₁ = 10.5 Hz, POCH₃, 3 H). ³¹P NMR (CDCl₃, 243 MHz): δ (ppm) 25.72 [22, 25].

2.3. Materials and deposition procedures

The substrate used to modification was commercial p-type Si wafer. To remove potential surface contaminations silicon pieces were immersed for 15 min in a glass container filled with ethanol, placed in an ultrasonic cleaner (rinsed several times) and after that dried by using the stream argon (Ar) gas. To activate the surface before modification by aminophosphonates, the Si pieces were placed in an oxygen plasma. The emerging plasma reacts chemically with the Si treated surface and causes to increase the number of hydroxyl groups on the Si which are necessary for the reaction with aminophosphonate compound.

The deposition process was carried out using liquid phase deposition (LPD) technique for all aminophosphonate compounds which are present in powder form. The deposition procedure was as follows: the silicon piece activated by oxygen plasma was immersed in the solution of aminophosphonate compounds. In this method, the aminophosphonate compounds were dissolved in ethyl alcohol at room temperature to give solutions of concentrations: C₁ = 0.1%, C₂ = 0.05%, and C₃ = 0.01%. The Si surface was kept in the solution for 60 min. After this time, the samples were removed from the solution and then rinsed several times in ethanol in order to remove the physisorbed molecules from the surface. Finally, Si with a self-assembled layer of aminophosphonate compound was heated at 50 °C for 24 h.

2.4. Characterization of modified samples

2.4.1. AFM analysis

The surface of the samples was analyzed using atomic force microscopy (AFM) Smena apparatus (NT-MDT). The AFM topography was characterized using a rectangular Si₃N₄ cantilever. The scanning area was 10 μm × 10 μm and the scan rate was 0.5 Hz.

2.4.2. FTIR spectroscopy

The GATR-FTIR spectra were obtained with 4 cm⁻¹ resolution at 64 scans on a Nicolet iS50 spectrometer equipped with a grazing angle attenuated total reflectance (GATR) and a mercury-cadmium-telluride (MCT)
detector cooling by liquid nitrogen. The measurement was carried out in a dry air atmosphere and room temperature (25 °C). Each spectrum was recorded in the range 3600–600 cm \(^{-1}\). FTIR spectra of aminophosphonates were recorded after its drying at 60 °C for 24 h. The clean silicon substrate was used for background spectra.

2.4.3. Contact angle measurements and surface free energy (SFE)
Static contact angles were investigated by using deionized water, glycerine, and diiodomethane, working on DSA-25 Drop Shape Analysis System (KRÜSS GmbH) equipped with the automatic syringe which volume of the drops was 2 μl. The measurements of the modified silicon substrate were performed at humidity 45 ± 5% and room temperature 22 ± 2 °C. For each sample, at least three drops of each liquid were made. The surface free energies of the aminophosphonate compound deposited on Si surfaces were calculated by Van Oss-Chaudhury-Good method [28].

2.4.4. Frictional tests in microscale
The friction tests were measured by equipment T-23 (ball-on-flat microtribometer) [29, 30]. A steel ball with a diameter of 5 mm served as a counterpart for each conducted measurement. The applied normal load on counterpart during the measurement was range from 30 to 80 mN. The measurement lasted 6 cycles, where the road of each cycle was 5 mm up and 5 mm down. The friction coefficient was measured 3 times for each sample at the same environmental conditions and the final result is the average of all measurements.

The adhesive force is the value read from the curve of dependence of the friction force on the applied load [29, 31].

3. Results and discussion

3.1. The optimization of deposition parameters and the physicochemical properties of aminophosphonates 2a-f on the silicon surface
The deposition parameters such as immersion time, the concentration of solution or gas pressure have an important influence on the static contact angle value [20, 32–35]. In our studies, the effect of concentration of the solution on the values of the water contact angle was investigated. Based on the measured contact angle, the optimum concentration of aminophosphonate compound solutions were selected. By using the static contact angle technique it is possible to determine the ordered of a thin layer on the silicon surface obtained by deposition. The high water contact angle indicates that well-ordered thin layers were obtained, reducing the penetration of the water drop into the layer. The contact angle is plotted against the solutions concentration for diethyl N-phenylamino(pyren-1-yl)-methylphosphonate (2d). For unmodified silicon, the water contact angle is 53 ± 2°. The analysis of the obtained data showed that after the surface modification by the aminophosphonate (2d) the water contact angle increased. It was found that the sample immersed in a lower concentration solution exhibits lower contact angle values than the same sample immersed in a higher concentration of aminophosphonate compound solution. Therefore, for further investigations was used Si prepared in a higher concentration solution of 0.1%. Based on the obtained data, were observed the sensitivity of the aminophosphonates formation process to the solution concentrations.

The contact angle values for Si modified in higher concentration solution with all the aminophosphonate compounds are shown in figure 2. Silicon substrate exhibits hydrophilic properties as evidenced by the low contact angle. After modification by phosphonate compounds, an increase in the contact angle in comparison with silicon (max ±20°) is observed. As shown in figure 2, none of the measured water contact angles exceeds 90°, thus all of the tested surfaces should be classified as more or less hydrophilic. The fact is that changes in the hydrophilicity of the between silicon and modified silicon are related to the presence of thin layers on the surface. However, the pyrene-derived aminophosphonates 2a-d are sterically hindered compounds, where a large, pyrene group forces the rotation restriction [36, 37]. Regardless of substituents on amine groups, both values of the contact angle and surface free energy (figure 3) were rather comparable for all four aminophosphonates 2a-d. In a case of N-benzyl derivative 2a, the rotation restrictions are the most significant (figure 5(a)) [36, 37], which is well reflected in a contact angle value slightly lower than those of 2b-d as well as in higher values of both components of surface free energy: dispersion and acid-base interactions (figure 4). The significant differences in values of the contact angle and surface free energy observed for compounds 2e and 2f, undoubtedly result from the different substituents on amine groups. A benzyl group, which is present in aminophosphonate 2e causes the flexibility of its molecule and makes it possible to adopt the most convenient conformation by the molecule (figure 5(b)) when linked to a surface. Therefore, contact angle and surface free energy measured for these compounds were respectively: significantly higher and lower. The methoxyphenyl derivative 2f is more rigid (figure 5(c)), moreover it bears a methoxy group, which causes much better placement
Figure 2. The contact angles from distilled water for Si and Si after the deposition process of aminophosphonates 2a–f.

Figure 3. Surface free energy of aminophosphonate 2a-f layers.

Figure 4. Polar and disperse components of surface free energy of aminophosphonate 2(a)–(f) layers.
of the molecule on a surface, and thus, significantly elevated values of contact angle and lower value of surface free energy.

Based on the presented data, it can be stated that the substrate properties are related to the SFE values. It follows that the higher the contact angle value, the lower the SFE value is. Depending on the aminophosphonates compounds deposited on the silicon, the SFE has different values. The lowest value of SFE and both components were obtained for the substrate modified by dimethyl N-(4-methoxyphenyl)amino(phenyl)methylphosphonate (2f). The molecule of the aminophosphonate 2f due to its construction (small size and the presence of a methoxy group) formed on a substrate flexible thin layer.

In this research, the van Oss Chaudhury-Good method was chosen to calculate the SFE [28] because allows getting information about polar $\gamma_{\text{p}}^{AB}$ and dispersive $\gamma_{\text{d}}^{1W}$ interaction of studied aminophosphonates. Generally, the dispersive component of the SFE is associated with interactions which are very weak and are known as London forces. The polar part of interaction is related to the polar, induction (Debye), hydrogen and acid-base forces. Molecules with a dipole moment can form polar interactions with one another [38]. In the case of surfaces possessing more hydrophobic character, the lower contribution of polar components is observed. Many studies have shown that for more hydrophobic surfaces (i.e. showing higher contact angle), a smaller contribution of polar component is observed. The modification process has a strong influence on the interaction between liquid molecule and compound which creates a layer and in consequence also on the SFE value. Also, in our research, it was found that the changes in the hydrophilicity of the modified surfaces are related to the varying polar component of SFE. The low value of the polar component of SFE is the results presence of a large number of non-polar groups in the molecule of aminophosphonate 2f. The C-H bonds present in molecules are characterized by quite low dipole moments, which means that they bind weakly with dipolar liquids. For this reason, a low contact angle and the value of the polar component are obtained. An interesting remark related to the observed the dispersive part of SFE is that there were almost no changes in dispersive components after modification for all compounds. The dispersive component of SFE is comparable for all studied surface, irrespective of the aminophosphonates used. The fabrication of thin layers on the surfaces results in a change of wettability and surface the roughness [39]. Describing the physicochemical properties of the modified surfaces by aminophosphonates, it is especially important to consider the roughness of the investigated samples.

The root mean square (RMS) surface roughness values and topography were characterized by AFM and they are shown in figure 6. The silicon surface before the deposition was smooth and its RMS value was 0.15 nm. Whereas after the functionalization of Si with aminophosphonic compounds 2a-f, an increase in roughness to maximum value 6.59 was observed (figure 6). On the AFM images, it is visible the presence of molecules of modifiers. Depending on the compound used, these molecules are arranged differently on the surface of silicon and create as islands-like structures. The largest changes in topography are observed in the case of compounds 2e and 2f. Comparing the aminophosphonate molecules deriving from benzaldehyde but with different substituents at the amino group, it was found that the molecule bearing a N-methoxyphenyl group (2f) is characterized by higher roughness than its N-benzyl equivalent (2e) and amount to 6.59 and 3.59, respectively. The obtained test results are reflected in the values of the water contact angle described earlier. As a result, it was confirmed that morphology of surface affects on roughness, while it, in turn, has a pronounced impact on wettability.

![Figure 5.](image)

Figure 5. (a) Restricted rotation in N-benzyl derivative (2a), (b) free rotation in dimethyl N-benzyl-amino(phenyl)-methylphosphonate (2e) and (c) indimethyl N-(4-methoxyphenyl)amino-(phenyl)methyl-phosphonate (2f).
3.2. FTIR characterization of aminophosphonates layers

The effectiveness of carried modification was investigated using FTIR spectroscopy. The FTIR spectra of aminophosphonates were illustrated in figure 7. At first, for all investigated modified surface, the P-O stretching...
region between 1300–800 cm\(^{-1}\) were analyzed (figure 7(b)). The large intensity of the peaks in this region shows that a strong interaction of the phosphonate head group with the silicon surface is present. The presence of the peaks characteristic for P\(=\)O bond at \(\sim 1200\) and for P–O bond at 1000 cm\(^{-1}\) was observed [40]. The occurrence of these two bands was interpreted as evidence for a monodentate bonding mode between aminophosphonate and silicon surface. Next, the characteristic N–H stretching bands at 3300 cm\(^{-1}\) were visible for all studied samples (figure 7(a)). Their occurrence indicates that the self-assembled layer of aminophosphonates is present on the silicon surface. Additionally, the surfaces with organic molecules display characteristic bands in the typical region at \(\sim 1600\) cm\(^{-1}\) for the aromatic C–C oscillation and the aromatic C–H stretching vibration at \(\sim 3050\) cm\(^{-1}\) [41]. The peaks derived from C–C bonds in aromatic systems and P–O bonds in the phosphoric group were lower intensity compared to spectra of 2e and 2f compound. The changes in intensities of FTIR signals for 2a-d compounds may be related to the presence of a large group of pyrene which restricted rotation causing to form less ordered layers on the surface. It is also worth noting that the aminophosphonates 2a-d are characterized by the higher molecular weight than their benzyl analogues. This can affect on the thickness of the layer and thus also on contact angle and coefficient of friction. The lack of order on the surface results in obtaining a relatively thick layer with not very good tribological properties.

In the case of surfaces modified with compounds 2e-f, the clear and high intensity peaks suggest that the thin layer is well-ordered on the surface. In consequence, these modified surfaces exhibit better physicochemical properties compared to pyrene-derived aminophosphonates 2a-d which will be discussed in more detail in the next chapter.

3.3. Tribological properties
Using the microtribometer, the coefficient of friction and adhesive force for silicon modified by aminophosphonate compounds was measured (figure 8). Based on microscale studies, the presence of aminophosphonate compounds adsorbed on silicon substrate results in a reduction in the coefficient of friction and adhesive force. As we can see in figure 8, all aminophosphonate compounds exhibit improved friction behavior than the silicon surface. In the case of the modified silicon substrate, the friction coefficient is reduced by about 50% relative to the value obtained for the silicon. Moreover, the differences in the frictional behavior after deposition are due to the structure of compounds forming the self-assembly layer. As previously mentioned, pyrene-derived aminophosphonates compounds 2a-d used for modification to the silicon have a steric hindrance which determines their adsorption to the substrate and the formation of a bond (figure 5). All four compounds (2a-d) form a more or less ordered layer on the silicon but the positioning of the particles on the surface is similar enough that the values of both water contact angle, SFE and friction coefficient are similar. In the case of aminophosphonic compounds 2e and 2f, the coefficient of friction changes significantly. In this scale, the 2 f compound presents the best tribological properties. It was found, that compound with the methoxy group (2 f) exhibits the lower coefficient of friction and adhesive force than a molecule with a benzyl group. After
the deposition of 2f compounds on the silicon, the − OCH3 group interact with each other to form a layer, which acts as a lubricant. Among all of the compounds, the aminophosphonate 2f showed the lowest adhesive force and also friction coefficient. These differences are caused by the higher stiffness of the methoxy groups and the fact that the backbone structure rotation of methoxy groups is much lower than benzyl ones. The layer consisted of methoxy groups is more rigid in comparison to the layer with benzyl groups. Bhushan et al in their research showed that the SAM with a stiffer backbone structure is more durable and resistant to wear because it need more energy for the elastic deformation [42–44]. The decrease of the adhesive force and coefficient of friction is due to the occurrence of elastic deformation of the methoxy group present on the surface of silicon.

Additionally, a significant reduction in obtained values of adhesion and coefficient of friction is also connected with the fact that in the microscale, friction forces are dominated by surface interactions, especially adhesive connections and plastic deformation (as seen in figure 9). In milinewton load range, adhesive force and also work of adhesion plays a crucial role and their values are the sum of van der Waals force, electrostatic and chemical covalent bonding and capillary force between two contacting surfaces. The most influence on the adhesion has capillary forces related to the presence of water on the surface. The electrostatic force and also chemical bonding can be neglected because in our study measurements are performed with uniform movement and with 25 mm min−1 speed. In these measurement conditions, no charges are presented and no chemical covalent bonding is formed. For surfaces, it is possible to determine the meniscus force (Fm), which affects the adhesion and work of adhesion values. The meniscus force was calculated from the following equitation:

\[ F_m = 4\pi R^*\gamma \cos \theta \]

where: R* - radius of the contact between two solids in the presence of surface forces, γ - surface tension, θ - water contact angle.

The radius of the contact in the presence of surface forces was appointed by:

\[ F_{adh} = -\frac{3}{2}\pi R^*W \]

where: W - surface free energy and Fadh - adhesion force.

The radius of the contact in the presence of surface forces depends on the surface forces, including the pressure force. In our study, we calculated the average value of the radius, which varied depending on the type of surface. Modified surfaces showed a smaller radius of the contact between two solids in the presence of surface forces compared to silicon (table 1). Also, there is a noticeable effect of adhesion and work of adhesion on the value of radius at the friction node. Surface 2f, characterized by the lowest adhesion and work of adhesion, also shows the smallest radius between the two surfaces in the presence of surface forces. Knowing the value of the radius, the meniscus force was calculated. For this parameter, we also observe a change in the value of meniscus force before and after the deposition of aminophosphonates on the surface of silicon. The reduction of meniscus force indicates that the surface’s functionalization led to the formation of a layer that counteracts the formation of water. It is most visible for surface 2f, for which the value of the meniscus force is the smallest. This results in obtaining the lowest adhesion and work of adhesion values, which was presented in our research.

In the case of modified silicon surfaces, adhesion is due to capillary interactions. Therefore for all aminophosphonates, we obtained decrease work of adhesion (as seen in figure 10(a)) and coefficient of friction reduction than for silicon surface. The 2f aminophosphonate, exhibiting the lowest SFE value, is characterized
by the lowest adhesion, work of adhesion and in consequence coefficient of friction. It is related to a decrease in the value of the capillary forces in frictional contact for such a system. Additionally, the benzaldehyde-derived compounds 2e-f exhibit better tribological properties in compared with the pyrene-derived aminophosphonates 2a-d, because their coefficient of friction and work of adhesion are lower.

In microscale, next to the adhesive component resulting from the shearing of the adhesive bonds between the friction elements, can also occur surface wear related to the plastic deformation. The pressure exerted by the counterpart during the friction process causes cracking or destruction of the surface layer. In our research, next to the adhesive force component also friction force component has a significant influence on the coefficient of friction and wear. The surfaces with a thin film that acts as a lubricant reduce the coefficient of friction and in consequence wear (figure 10(b)). In our study, the lowest wear is for 2f aminophosphonate which the value of the friction coefficient is 0.139. The diameter of wear trace is 5.41 μm while for 2a-2e compounds characterized by higher values of friction coefficient the trace of wear is 17.5 μm for 2a compound and gradually decreases to the value 7.26 μm for 2e compound. This means that the adhesion and wear forces have an influence on microscale friction for compounds with a benzyl and pyrene group.

Table 1. The radius of the contact in the presence of surface forces and meniscus force calculated for silicon surface before and after modification via aminophosphonates.

| Sample | R*[m]      | Fm[mN]      |
|--------|------------|-------------|
| Si     | 0.126 × 10⁻³ | 90.51 × 10⁻³|
| 2a     | 0.049 × 10⁻³ | 37.04 × 10⁻³|
| 2b     | 0.043 × 10⁻³ | 34.94 × 10⁻³|
| 2c     | 0.025 × 10⁻³ | 20.99 × 10⁻³|
| 2d     | 0.022 × 10⁻³ | 18.98 × 10⁻³|
| 2e     | 0.019 × 10⁻³ | 16.56 × 10⁻³|
| 2f     | 0.015 × 10⁻³ | 13.32 × 10⁻³|

Figure 9. Components affecting the value of the coefficient of friction.

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It can, therefore, be concluded that the surface with low SFE and high contact angle values shows small values of the adhesive forces, work of adhesion, coefficient of friction and wear.

4. Conclusions

In summary, using the modification we received the aminophosphonate films on the silicon surface. Water contact angle, AFM and FTIR characterizations confirmed that the layers of aminophosphonates were successfully prepared on the silicon surface. Moreover, the water contact angle and SFE results illustrate that the wettability of modified samples changes which is related to the construction of aminophosphonate compounds and their large pyrene and benzyl groups. Additionally, by investigating the coefficient of friction, adhesive force and wear in microscale in ambient air, we confirmed that self-assembled layers of aminophosphonates act as a lubricant thus improving tribological properties of the unmodified silicon surface. Moreover, we revealed the influence of adhesive, wear and deformation components on the friction force. It follows that the low values of adhesive force, work of adhesion and wear caused obtainment low value of friction coefficient. After modification by aminophosphonates, the coefficient of friction value was reduced about 50% while the adhesive force about 85% and wear about 80% in comparing to unmodified silicon. Because the friction coefficient and adhesion extremely decrease for the surface with aminophosphonates it could be concluded that modified surfaces could have applications across a wide range of tribology and biomedicine.

Conflict of interest

The authors declare no potential conflict of interest in preparing and publication of this article. The founding sponsors had no role in the creation of this publication (to the design of the studies; in the collection, analyses, or interpretation of data and the writing of the manuscript).

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Figure 10. Work of adhesion (a) and diameter of wear trace (b) values obtained for Si and the aminophosphonates 2a-f on Si.
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