

## Control of glass surface wettability via esterification with n-alkyl alcohols

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**Abstract:** Surface wettability plays an essential role in many processes and materials applications. It depends mainly on the surface roughness and chemical composition, thus through a controlled modification of these parameters, the wettability can be restrained. Glass is an inorganic solid material, composed mainly of amorphous silica, which surface, due to the presence of reactive hydroxyl groups, can be quite easily chemically modified. This feature can be used to control the wettability of glass by reaction with organic compounds. In this study, the esterification of glass silanol groups with n-alkyl alcohols ( $C_nH_{2n+1}OH$ ,  $n=3, 4, 6, 8, 10$ ) was employed to modify its wettability. The effect of such modification on the physicochemical properties of glass surface was comprehensively investigated and characterised by the water contact angle, surface free energy, zeta potential, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) measurements. We demonstrate that the wettability of the esterified glass surface is strongly dependent on both the chain length of used alcohol and modification time. The alcohol molecule binds to the glass surface through a Si-O-C bond, leading to the formation of a monolayer that does not significantly affect the surface morphology and zeta potential. Conducted studies provided a broader view of the influence of this technique for modifying surface wettability on its physicochemical properties.

**Keywords:** hydrophobicity, surface free energy, contact angle, zeta potential, roughness

### 1. Introduction

The wettability of surfaces by liquids is an essential aspect in many fields of science. It is a crucial parameter in many processes applied in the industry. Wetting of surface is characterised by the value of equilibrium contact (wetting) angle ( $\theta$ ) formed between a liquid drop placed on a solid surface (i.e., sessile drop technique) at the solid-liquid-gas interface. The sessile drop technique is the most commonly used for contact angle determination as it is relatively fast, simple and provides reliable information on the wettability of the flat, smooth and homogeneous surfaces. According to the Young equation (Eq. 1) (Young, 1805), the cosine of the equilibrium contact angle is related to interfacial tensions between liquid and vapour (gas)  $\gamma_{lv}$ , liquid and solid  $\gamma_{sl}$ , and the free energy of the solid surface  $\gamma_{sv}$ :

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (1)$$

According to this equation, a hydrophobic material has a water contact angle greater than  $90^\circ$ , and the value of this angle for a hydrophilic material is below  $90^\circ$ . This distinction has been used for a long time in surface chemistry. However, there is an exception to this ninety-degree threshold applied in mineral processing (especially in flotation science and technology). Here, hydrophilic surfaces are those with a contact angle of  $0^\circ$  (complete wetting). On the other hand, surfaces with a larger value of angle are called naturally hydrophobic. Due to a considerable range of contact angle of hydrophobic surfaces, an additional subdivision into weakly hydrophilic and weakly hydrophobic surfaces for contact angles

between  $0-56^\circ$  and  $56-90^\circ$  is used, respectively (Drelich et al., 2011; Drelich and Marmur, 2018). Therefore, the exact definition of the terms hydrophilic and hydrophobic depends on the particular field of science in which the surface is being considered.

The wettability, expressed as the contact angle, depends on the surface chemical composition, and can be adjusted by different treatment methods leading to introducing new functional groups. Silica is one of the most popular materials used by researchers as a model substrate, thus a large number of available studies focus on the modification of its surface properties. It owes this to its chemical and mechanical stability, broad availability, and low price. A characteristic attribute of silica is that there are reactive silanol groups ( $\equiv\text{Si-OH}$ ) on its surface. The presence of silanol groups allows the modification of the surface properties through reactions with various organic compounds, including silanes and alcohols, to obtain strongly bonded organic layers (Ossenkamp et al., 2002). Therefore, this property provides a route to effectively control the surface properties of such material (Iler, 1979).

One of the methods used for the silica surface modification (e.g. its wettability) involves the treatment with of organosilicon compounds, such as octadecyltrichlorosilane ( $\text{CH}_{17}\text{SiCl}_3$ ). The use of silanes, in addition to their advantages, which include simplicity of implementation and relatively short time of surface treatment, also has some disadvantages. The main one is the difficulty in obtaining the monolayer surface coverage. It depends on a number of variables that appear in this method of modification, such as type of solvent, concentration, temperature, time and curing conditions (Zhu et al., 2012). In the case of silane application, side reactions that occur cause the formation of oligomeric silane networks on the surface. These multiple layers also result in increased surface roughness (Biggs and Grieser, 1994). In addition, silanes are most often used as solutions in organic solvents such as hexane, toluene (beside vapour phase deposition), which is also a disadvantage for both the user and the environment regarding the waste generated. Also, the final surface coverage effect depends on the solvent used and especially the amount of moisture that may be in it. Silanes are molecules that are sensitive to the presence of water, which causes hydrolysis of the alkoxy group, resulting in the formation of a hydroxyl group which, on the one hand, allows the silane to bind to the surface of the substrate but, on the other hand, excess moisture can lead to a violent reaction with water and polymerisation of molecules, in effect leading to the formation of lumps and aggregates (McGovern et al., 1994; Issa and Luyt, 2019).

An alternative to silanisation, in the context of modifying wettability, is the method that involves the esterification of surfaces with alcohol. This technique has been used by various researchers (Ballard et al., 1961; Bournival et al., 2021; Feng and Nguyen, 2017; Hampton et al., 2009; Hunter et al., 2009; Li et al., 2020; Sygusch and Rudolph, 2021). This method is also based on the use of exposed reactive hydroxyl groups of silans on the surface. Hydrophobisation by esterification leads to covalent attachment of alcohol molecules to the surface (Ossenkamp et al., 2002), and produces very stable, uniform, and monolayer hydrophobic surfaces without the formation of reagent patches or domains. It is a significant advantage of esterification over silanisation. This surface is also characterised by resistance to hydrolysis (Ossenkamp et al., 2001).

Biggs and Grieser (1994) compared the layers formed by trimethylchlorosilane and 1-dodecanol on the glass surface. Silanisation, depending on the deposition method, led to layer thicknesses ranging from two to three molecules (vapour deposition) to as much as 60 nm (solution deposition), while the monolayer coverage was observed for esterification with alcohol. This method is considered to form a monolayer, and the extent of hydrophobicity is dedicated to the length of alkyl chain. The authors proposed the following esterification mechanism (Fig. 1). In the first step, the alcohol molecule is physically adsorbed on the surface of silica through a hydrogen bond between the alcohol and silanol groups, and then a condensation reaction results in the formation of a covalent bond and a water molecule. This mechanism was also confirmed by Ossenkamp et al (2002).

Soda-lime glass is often used instead of pure silica in many studies as a model substrate. The main component of this type of glass is silica ( $\text{SiO}_2$ ). Therefore, it can be used as a low-cost silica-based structure (i.e., plates, beads, and irregular particles) in applications where the high purity material is not required. In addition, glass has a high mechanical and chemical resistance, making it a widely used material in many engineering applications. Due to the high silica content, the glass surface is very similar to the silica surface, and both have numerous siloxane groups (Zhuravlev, 2000). However, these

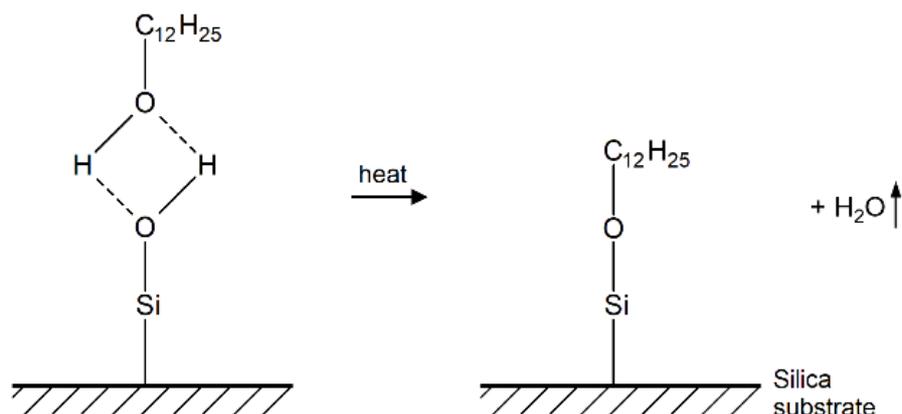


Fig. 1. Assumed mechanism of the esterification reaction after physisorption of the alcohol on the silica surface (Biggs and Grieser, 1994)

materials differ significantly in the structure, with silica being a crystalline material, while glass is an amorphous material that contains other atoms in its structure in addition to silicon and oxygen. The typical composition of soda-lime glass is 70-75% SiO<sub>2</sub>, 12-16% Na<sub>2</sub>O, 10-15% CaO, 0-5% MgO, 1-2% Al<sub>2</sub>O<sub>3</sub>, and small amounts of iron oxides (Hubert, 2019).

Esterification with alcohol seems to have several advantages over silanisation in terms of obtaining a monolayer of the modifying agent on the surface. It is also more convenient to carry out; however, it may require a longer modification time. Although this method has been in use for more than 60 years, there are still far fewer publications on the effect of such modification on surface properties than for silanes. Therefore, this paper investigates the effect of glass surfaces esterification with n-alcohols of different chain lengths in the context of surface wettability modification. The main goal of this study was to provide complementary information on the effect of esterification on the modified surface in terms of its wettability and other physicochemical properties. To achieve this objective, it was necessary to know the surface chemistry (functional groups present) and the surface energy. This was attained by using several known methods to enable detailed surface characterisation. Glass substrate surfaces were characterised by the water contact angle, surface free energy, atomic force microscopy and X-ray photoelectron spectroscopy. The wettability and surface properties (e.g., chemical composition, zeta potential, and morphology) of both pristine and modified glass were compared. Acquired data and results will increase the knowledge about the influence of alcohol esterification of glass surface (which is very often used as a substrate in many scientific studies and applications) on its wettability and surface properties.

## 2. Materials and methods

### 2.1. Materials

Soda-lime glass microscope slides (Chemland, Poland) were used as substrates. The chemical composition of the slides was obtained by X-ray fluorescence spectroscopy (XRF, Epsilon 3X, PANalytical, USA). The main chemical component was SiO<sub>2</sub>, which was 79.7±0.2%, and CaO, Na<sub>2</sub>O, MgO, K<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and others in the amount of 10.9, 4.1, 3.4, 0.6, 0.4, 0.2, 0.7%, respectively.

Esterification was performed with n-alkyl alcohols 1-propanol (99+%), 1-butanol (99%), 1-hexanol (99%), 1-octanol (99%) and 1-decanol (98+%) purchased from Alfa Aesar (MA, USA). Methanol, acetone, sulphuric acid (95%), hydrochloric acid (35-38%) used in glass cleaning and hydrochloric acid (0.1 M) and potassium hydroxide (0.1 M) for pH correction in zeta potential measurements were analytical grade purchased from Avantor Performance Materials Poland S.A. (Poland) Diiodomethane (99%, stab.) and formamide (99.6%) for surface free energy determination were purchased from Alfa Aesar (MA, USA) and Acros Organics, respectively. The ultrapure water was supplied by the Millipore Simplicity-UV purification system (Merck Milipore, Burlington, MA, USA) with a conductivity of 0.05 μS cm<sup>-1</sup> (at 25 °C).

## 2.2. Methods

### 2.2.1. Cleaning procedure

To expose the hydroxyl groups, the organic compounds must be thoroughly removed from the glass surface prior to esterification. Therefore, the cleaning procedure was based on the method described elsewhere (Cras et al., 1999). First, the glass slides were sonicated in acetone for 15 min. After sonication, the slides were rinsed with methanol, and then immersed in a 1:1 HCl-methanol mixture for 2 h. The HCl treatment helps removing nonbinding metal ions, such as calcium, sodium, and potassium (Hermanson, 2013) ; while methanol facilitates wetting of the surface by the solution. Then, the slides were cleaned in sulfuric acid for next 2 h to remove organic contaminants. Each step was followed by exhaustive rinsing with water. After cleaning, the slides were dried at 80 °C, and directly used for the esterification.

### 2.2.2. Esterification

Esterification of the glass surface was performed with n-alkyl alcohols  $C_nH_{2n+1}OH$ , with  $n=3, 4, 6, 8$  and 10. The glass slide was mounted on a Teflon holder and placed in a cylindrical bottom glass vessel filled with alcohol. The glass vessel was equipped with a reflux condenser with a drying tube at the top filled with glass wool and  $CaCl_2$  desiccant. The alcohol was refluxed for the desired time. After esterification, the slide was rinsed with acetone immediately without prior cooling, dried in a dryer at 80 °C, and stored in a desiccator.

### 2.2.3. Surface composition

The surface chemical composition of the glass surface was characterised by X-ray photoelectron spectroscopy (XPS), which is a highly sensitive surface analysis method with a probing depth of ~1–10 nm (Tougaard, 2013). Spectra were obtained by a multi-chamber UHV analytical system equipped with a monochromatic hemispheric analyser (R4000; VG Scienta). The Casa XPS program was used for the data processing of XPS spectra and the quantitative analysis of surface properties of examined samples. The XPS measurements were carried out for non-modified and esterified with 1-decanol glass surface.

### 2.2.4. Surface morphology and roughness

The surface of the glass slides was imaged with the SEM/Ga-FIB FEI Helios NanoLab 600i electron microscope. The samples were attached to aluminium mounts with double-sticky carbon-based conductive tape and coated with a carbon layer to 30 nm thickness to enhance conductivity.

Topographical analysis of the surface was performed using the Flex-Axiom (Nanosurf) atomic force microscope (AFM), followed by roughness analysis. AFM scans were performed in contact mode using a silicon cantilever (CONTR-20, NanoWorld) with a spring constant of 0.2 N/m and a resonance frequency of 13 kHz. All samples were first scanned with a  $20 \mu m \times 20 \mu m$  field of view to ensure even surface coverage and to avoid damaged and contaminated areas, before selecting  $10 \mu m \times 10 \mu m$  areas for scanning and analysis. The roughness of each surface was quantitatively characterised by the root mean square (RMS) (Eq.2), which is a standard height (Z) deviation for the image area analysed.

$$RMS = \sqrt{\frac{\sum_{i=1}^N (Z_i - Z_a)^2}{N}} \quad (2)$$

where  $Z_a$  is the average Z value within the analysed area,  $Z_i$  is the current Z value, and N is the number of points in the given area. All roughness data presented in this study are an average of two scans.

### 2.2.5. Surface wettability

The water contact angle on the glass surface was measured by a sessile drop method using the OCA 15 EC contact angle meter (DataPhysics Instruments GmbH, Germany). Water droplets of 0.2  $\mu l$  were deposited at ten random locations on each slide surface for each measurement. The droplet images were recorded and analysed using the SCA 20 shape analysis software (DataPhysics Instruments GmbH, Germany).

The surface free energy (SFE) and its components of glass slides were determined based on the Owens-Wendt-Rabel-Kaelble (OWRK) method (Kaelble, 1969; Owens and Wendt, 1969; Rabel, 1977). In ORWK method the surface free energy of solid was calculated based on the contact angle created by at least two liquids placed at the solid surface, where the polar and dispersive components are known. The surface free energy ( $\gamma_s$ ) is a sum of polar ( $\gamma_s^p$ ) and dispersive ( $\gamma_s^d$ ) components (Owens and Wendt, 1969):

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (3)$$

In ORWK model the interactions are interpreted as the geometric mean of a disperse and a polar part of liquid surface tension and of the solid surface energy (Owens and Wendt, 1969):

$$\gamma_{SL} = \gamma_s + \gamma_L - 2 \left( \sqrt{\gamma_s^d \gamma_L^d} + \sqrt{\gamma_s^p \gamma_L^p} \right) \quad (4)$$

where  $\gamma_s^L$  is interfacial tension,  $\gamma_L^d$  and  $\gamma_s^d$  are the dispersive parts, and  $\gamma_L^p$  and  $\gamma_s^p$  are the polar parts of liquid and solid surface free energies, respectively, whereas  $\theta$  is the contact angle between the surface of the sample and the standard liquid.

Combining Eq. 4 with Young's equation (Eq. 1), gives:

$$\frac{\gamma_L(1+\cos\theta)}{2\sqrt{\gamma_L^d}} = \sqrt{\gamma_s^p} \cdot \sqrt{\frac{\gamma_L^p}{\gamma_L^d}} + \sqrt{\gamma_s^d} \quad (5)$$

Equation 5 can be expressed in the slope-intercept form, where variables value depends on either the contact angle, polar and dispersion components of the liquid used. Therefore, plotting this linear equation allows calculating  $\gamma_{sp}$  from the slope of the fitted line and  $\gamma_{sd}$  from the intersection with the vertical axis.

As a test liquid water, diiodomethane, and formamide (Table 1) were used. The measurement of the contact angle for diiodomethane and formamide was performed in the same way as for pure water. The values obtained were used to determine the surface free energy using the SCA 21 software (DataPhysics Instruments GmbH, Germany).

All measurements were carried out in a saturated vapour atmosphere.

Table 1. Specific surface free energy components of standard test liquids used in this study from SCA 21 software database (DataPhysics Instruments GmbH, 2019)

Liquid	Total surface tension, $\gamma_l$	Polar component, $\gamma_l^p$	Dispersive component, $\gamma_l^d$	Values adopted from
	[mJ m <sup>-2</sup> ]			
water	72.3	53.6	18.7	Rabel (1977)
diiodomethane	50.0	2.6	47.4	Busscher et al. (1984)
formamide	58.2	18.7	39.5±7.0	Fowkes (1964)

### 2.2.6. Zeta potential measurements

Zeta potential measurements were performed using a SurPASSTM 3 analyser (Anton Paar GmbH, Austria). Before the measurement, the apparatus was calibrated (pH electrode and conductivity sensor) and checked for correct operation using a cotton cloth, according to the procedure recommended by the manufacturer. For measurement, the sample glass slide and the polypropylene film, serving as a reference material, were mounted in a clamping cell, and the gap height was set at  $100 \pm 10 \mu\text{m}$ . The pH correction was carried out using either 0.1 mol/l HCl or 0.1 mol/l KOH solutions. KCl (1 mM) was used as an electrolyte. During the analysis, pH was automatically measured with a pH electrode. To remove CO<sub>2</sub> from the solution, the electrolyte was purged with nitrogen throughout the analysis. The tests were conducted at room temperature (22 °C). At each pH value, the measurement was performed three times. Each slide was analysed at least twice, and the results are presented as an average value.

### 3. Results and discussion

#### 3.1. Surface composition

The zeta potential measurements allow determining the surface charge, and thus the character of functional groups. However, they cannot provide precise information about the chemical composition of functional groups (Bellmann et al., 2019). This can be achieved by, for instance, X-ray photoelectron spectroscopy (XPS). Data provided by the XPS analysis allowed for more depth insight to the chemical composition of surface layer, and therefore its impact on the wettability. The result of the XPS spectrum survey for the unmodified slide and esterified with 1-decanol is shown in Fig. 2, and the quantitative results are listed in Table 2. The spectra indicate that the main elements on the glass slide surface were oxygen (O) with the strongest absorption peak, silicon (Si) and carbon (C). In addition, bands of other elements are present, such as calcium (Ca) and sodium (Na), which occur in glass in relatively high amounts (10.9% CaO, and 4.1% Na<sub>2</sub>O based on XRF results).

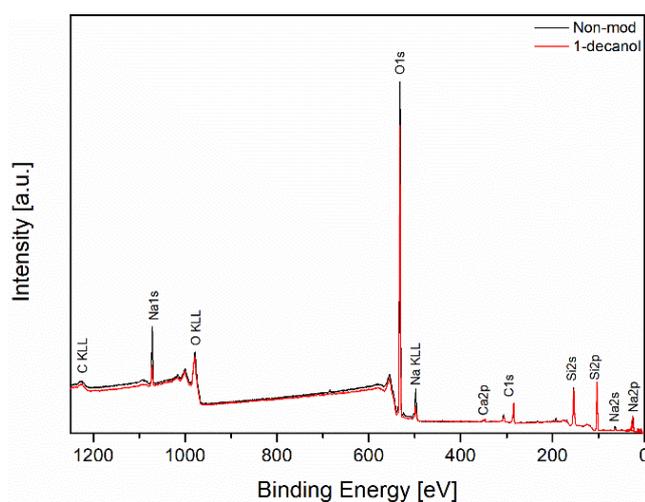


Fig. 2. XPS survey spectrum of glass surface before (non-modified) and after esterification with 1-decanol

Table 2. Elemental surface composition of glass surface before (non-modified) and after esterification with 1-decanol, calculated from XPS spectra

Sample	Component				
	C1s	O1s	Si2p	Na1s	Ca2p
	Atomic concentration [%]				
Non-modified	7.8	58.3	29.3	3.42	0.58
1-decanol	16.1	51.8	29.1	2.55	0.45

The XPS analysis revealed that the carbon content on the glass surface after esterification increased from 7.8% to 13.3%. This indicates that the alcohol molecules used for the modification permanently adsorbed on the slide surface. The narrow scan spectra of the C1s peaks were obtained, and peak fitting was performed for further analysis to identify chemical groups (Fig. 3).

The binding energy of C-C/C-H; C-OH; C-OC; C=O; O-C=O, and carbonate corresponded to 284.7; 286.2; 287.7; 288.1 and 290.2 eV, respectively. The number of differently bonded carbon atoms obtained from the deconvolution of the C1s spectrum is shown in Table 3. These results also indicate that the carbon-containing function groups on the surface were mainly C-C and C-H, with a relative content of 85%, i.e. they are the alkyl chains of the alcohol.

The relatively high content of C1 on the non-modified surface may be either due to insufficient cleaning or attributed to the presence of carbonaceous material contamination from environmental air (adventitious carbon) since the time between sample preparation and measurement was several days. The air contains small, low-energy organic molecules, such as fatty acids and esters, which can be

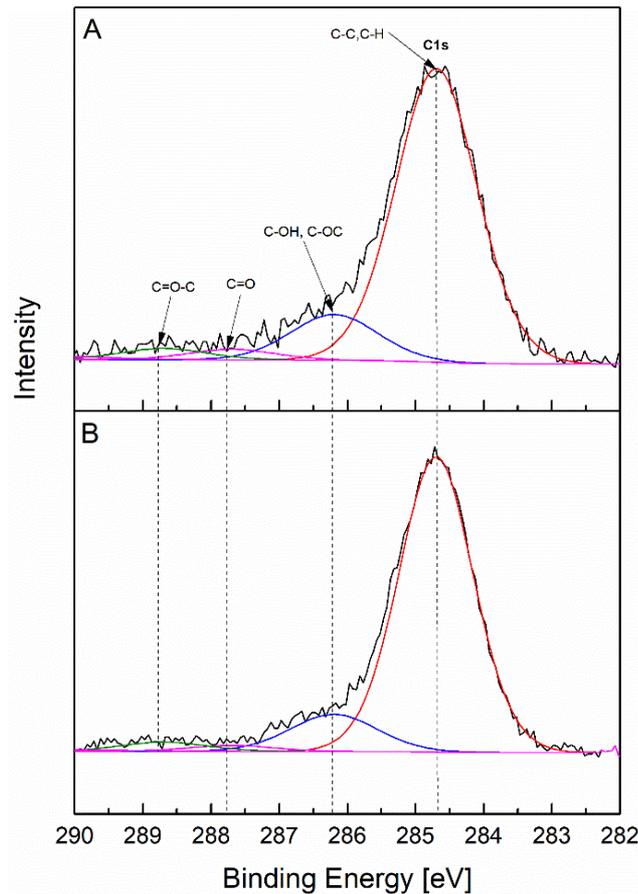


Fig. 3. High resolution XPS spectra and fitting curves of the C1s peak for glass before (A) and after (B) esterified esterification with 1-decanol

Table 3. Concentration of different chemical bonds on the glass surface

Sample	Atomic concentration (%)				
	Functional groups				
	C-C, C-H	C-OH, C-OC	C=O	O-C=O	carbonate
Non-modified	70.8	19.4	4.3	2.6	3.0
1-decanol	85.4	9.4	2.4	2.3	0.5

attracted by glass as high surface energy material to reduce its surface energy. The XPS data indicate that both singly and doubly bound oxygen functionality (C=O/O-C=O/O-C-O) could be possible for adsorbed either CO or CO<sub>2</sub> (Barr and Seal, 1998). It was observed that the surface of almost all air-exposed materials, even those cleaned and stored under moderately high vacuum conditions, contained carbon (Miller et al., 2002).

The Si2p electron orbital spectra of a non-modified slide consist of two peaks (103.0 and 103.6 eV), which can be attributed to the Si-O bond (Fig. 4). The spectra for the modified surface also consist of two peaks (102.8 and 103.8 eV), which can be assigned to the Si-O-C and Si-O bonds, respectively. Previous works (Avila et al., 2000; Li et al., 2013) reported that the 102.5 eV position is a strong indicator of Si-O-C linkage.

A curve fitting analysis of XPS O1s spectra affords only one peak for each sample located in the range of 532.6-532.9 eV (Fig. 5), which can be attributed to the Si-O-Si bond, as a large part of the sample is SiO<sub>2</sub> (Avila et al., 2000). The intensity of the Si-O-C signal may be very weak and completely masked

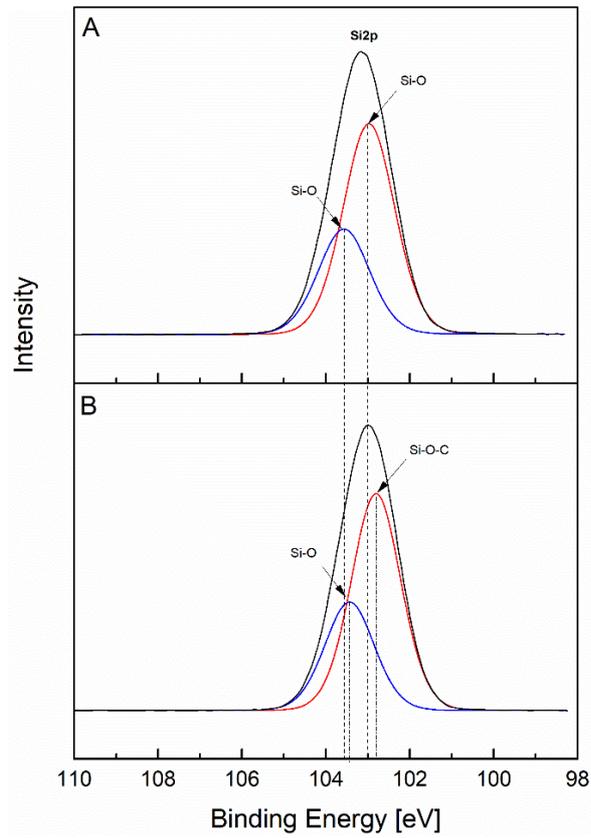


Fig. 4. High resolution XPS spectra and fitting curves of the Si2p peak for glass before (A) and after (B) esterified esterification with 1-decanol

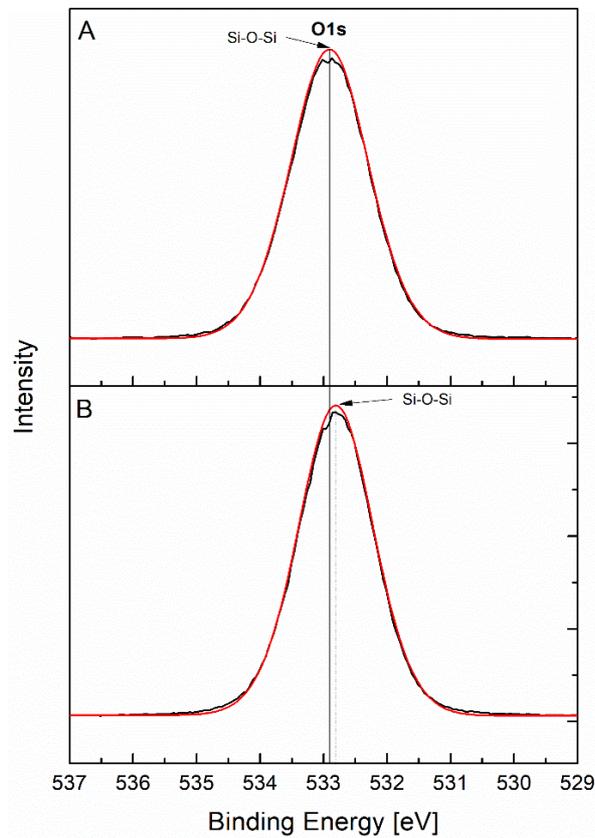


Fig. 5. High resolution XPS spectra and fitting curves of the O1s peak for glass before (A) and after (B) esterified esterification with 1-decanol

by the O-Si signals (Li et al., 2013). This can be explained by the fact that the thicknesses of the created layer are much smaller than the penetration depth of XPS (typically 5–10 nm), and thus the Si-O of the glass has a significant contribution to the result. Therefore, the Si-O-C bond is difficult to detect in the O1s spectra compared to that in the Si2p spectra.

The XPS results confirm that esterification of the glass surface with the n-alkyl alcohol resulted in the formation of a stable Si-O-C bond. Figure 6 shows schematic representation of such chemical functionalisation. The molecule of 1-decanol, having a chain of methylene groups terminated by a methyl group (1), is bonded to the structure (3) of glass through Si-O-C bond (2).

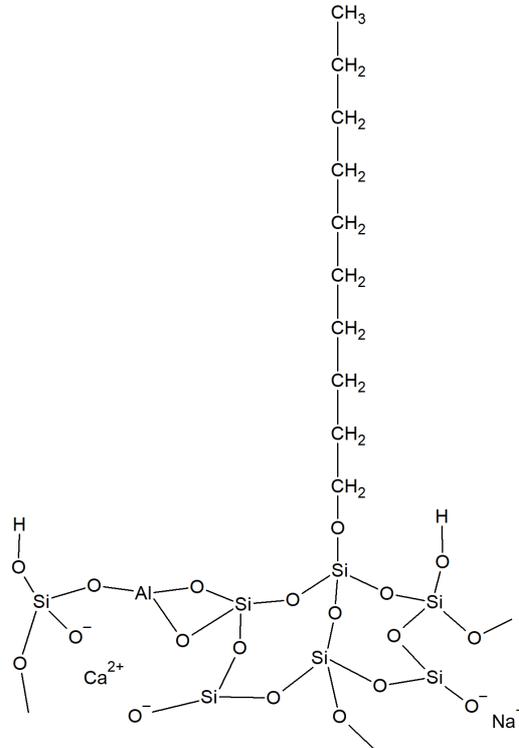


Fig. 6. Schematic representation of glass surface modification with 1-decanol

### 3.2. Surface morphology and roughness

Chemical modification of the solid surface might change not only its composition but also the morphology/topography (Bellmann et al., 2019). Additionally, when modifying surface properties, it is often crucial to keep the physical structure of surface unchanged with respect to the raw material. Figure 7 shows SEM micrographs of the glass slide surface before and after esterification. As can be observed, the surface was relatively homogeneous and smooth. No significant changes in the surface morphology were observed due to the treatment.

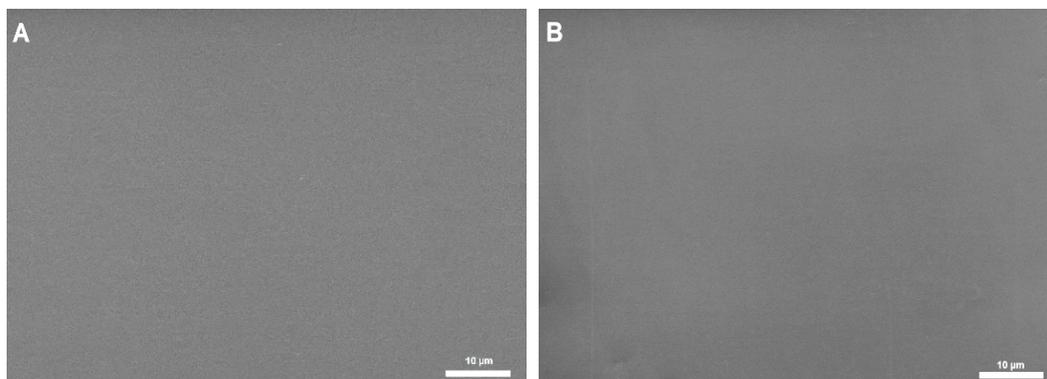


Fig. 7. SEM images of the non-modified (A) and esterified with 1-decanol surface (B)

The AFM images of the glass surface (non-modified and esterified with 1-decanol) are presented in Fig. 8. One can see that the pristine glass had a quite heterogeneous topography. There are, however, individual surface irregularities visible. The esterification of the surface results in a noticeable, but a few-nanometre, change in its roughness. The quantitative results of the analysis are presented in Table 4. The untreated surface was the least rough, with an RMS value of 0.9 nm (Table 4). In the case of esterified surfaces, the RMS value increased within the range of 1.22 to 1.59 nm.

Table 4. Root mean square roughness of glass

Sample	RMS [nm]
Non-modified	0.89 ± 0.05
1-propanol	1.22 ± 0.03
1-butanol	1.38 ± 0.11
1-hexanol	1.42 ± 0.14
1-octanol	1.53 ± 0.03
1-decanol	1.59 ± 0.04

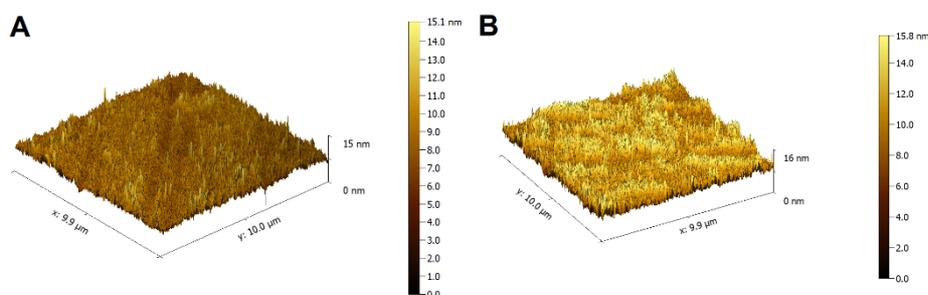


Fig. 8. AFM images of slide surface – non-modified (A), esterified with 1-decanol (B)

The results obtained from the analysis of the morphology and surface roughness allow us to state that the esterification of the glass surface only slightly changed its physical properties, which is undoubtedly an advantage of the method used. This method certainly does not lead to the formation of larger accumulations of alcohol molecules on the surface. There are no visible large peaks on the surface, suggesting a greater amount of alcohol. The RMS roughness values for created alcohol layers are extremely low (nanoscopic scale) and for all practical purposes they can be considered smooth.

### 3.3. Surface wettability

The water equilibrium contact angle measured on the freshly cleaned glass surface was  $9 \pm 1^\circ$ , which indicates that the pristine glass has high affinity to water. That is because the glass surface is occupied by silanol groups ( $\equiv\text{Si-OH}$ ). Zhuravlev (1987) experimentally determined that the surface density of -OH groups on the glass surface was practically constant and about ca. 5 groups per  $\text{nm}^2$ . Exposed by chemical cleaning, the surface hydroxyl groups are known to form hydrogen bonds with water molecules, which is why the cleaned glass surface shows such a good wettability by water (Cyran et al., 2019). Although a low value of contact angle indicated that the surface of the glass was cleaned of organic contaminants, it cannot be guaranteed that the surface was entirely free of contamination, which was shown by XPS.

As it can be seen from Fig. 9, the water contact angle, measured by the sessile drop method, increased with the chain length of alcohol and esterification time. The longer the chain, the more hydrophobic the surface. Similar results were obtained by Chen et al. (2021) when investigating the effect of silane chain length on the hydrophobicity of spherical silica nanoparticles. They showed that the alkyl chain length was essential for controlling the hydrophobicity (wettability). The greatest changes in the surface hydrophobicity were observed up to ca. 60 min. With a further increase in the

esterification time, the dependence became almost a plateau. This is related to the decreasing available number of silanol groups over time (Zhuravlev, 1987). Ossenkamp et al. (2002) showed that the process of alcohol chemisorption on to the silica surface can be described by the Langmuir adsorption model, allowing one to conclude that an alcohol monolayer was formed on the surface of the modified material.

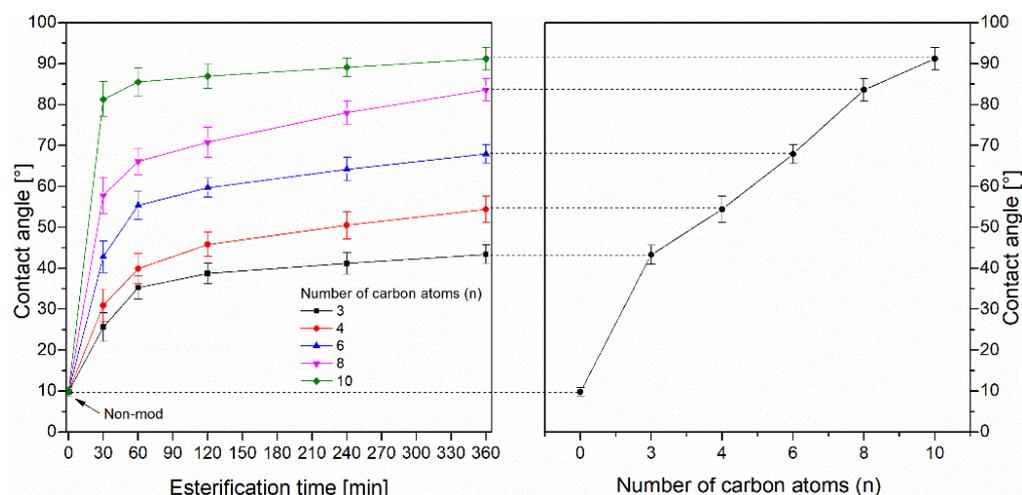


Fig. 9. Dependence of equilibrium water contact angles on the glass surface versus (A) esterification time for different chain lengths of alcohols, and (B) number of carbon atoms in alcohol chain after 6 h of esterification

As the surface properties of solid are mainly influenced by its interfacial molecular layer, the analysis of the total surface energy and its components also provides valuable information on the wettability, as well as how the surface reacts against different chemical/physical interactions (such as hydrogen bonds and long-range interactions). Determination of the surface free energy (SFE) may be performed by a number of methods, e.g. Owens-Wendt-Rabel & Kaelble, van Oss-Good, Fowkes, Zisman, Neumann, or Wu (Żenkiewicz, 2007). They differ mainly in their theoretical interpretation, and thus in the way they are calculated. However, the most commonly used surface free energy theory, OWRK, subdivides the total surface energy ( $\gamma_s$ ) between two components: polar ( $\gamma_{ps}$ ) interactions such as hydrogen bonds, dipole moments, and dispersive ( $\gamma_{ds}$ ) interactions which are the results of nonpolar interactions based on the London forces (fluctuations in electron density). An example of a highly polar surface is glass due to a large number of hydroxyl groups. In contrast, alkanes are examples of molecules in which only dispersive interactions occur.

The calculated values of the total surface energy and its components are shown in Fig.10. It is clearly visible that the surface energy decreases with increasing the chain length (number of carbon atoms, n) of the alcohol used. The esterification with 1-decanol (C=10) resulted in reduction of 57% in the total surface energy (from 70 to 30 mJ m<sup>-2</sup>) compared to the non-modified glass surface. It was mainly attributed to the decrease of the polar component from 51 to 4 mN m<sup>-1</sup>. The value of the SFE dispersive component remained relatively constant (within the range of 20-27 mN m<sup>-1</sup>) regardless of the length of the alcohol chain used for the surface esterification.

Sygyusch and Rudolph (2021) studied the surface energy of esterified glass particles (spheres, fragments, and fibres) by inverse gas chromatography (iGC), and showed that SFE decreased with an increasing chain length of the alcohol used. A notable reduction was observed for the surfaces esterified with 1-octanol (n=8) and 1-decanol (n=10) compared to the unmodified surface. However, in their studies, the decrease in SFE was due to both a reduction in the dispersive and polar components. These distinctions may result from differences in the measurement methods used. The surface energy measurement method used in our study was based on the measurement of the contact angle formed by drops of reference liquids. Such drop covers a relatively large area of the sample compared to the size of the -OH groups and hydrocarbon chains. As the chain length of the alcohol used for esterification increases, the -OH groups remaining on the surface are increasingly shielded by the chains (Chen et al., 2021). When the measurement is carried out by inverse gas chromatography (iGC), the probe molecules can directly interact with the functional groups on the surface, in this case -OH groups.

In our study, for the non-modified glass, mainly polar interactions occur (71% of total SFE) due to the presence of free silanol groups, what means that the solid surface was strongly polar. With decreasing wettability, their contribution decreased (to 12%) in favour of dispersive interactions. The decrease in the proportion of polar interactions was due to the decrease in the number of hydroxyl groups that form bonds with alcohol molecules during esterification. Also, Sygusch and Rudolph (2021) attributed the decrease in the polar component during esterification.

The minor increase in the dispersive component was most likely due to the increase in the concentration of methylene groups on the glass surface. Rueckriem et al. (2012) carried out the iGC studies on the porous glass modified by different chain length chlorosilanes. They indicated a positive correlation between the concentration of trimethylsilyl groups and the dispersive surface energy. In our study, the difference in the number of methylene groups between the alcohols used is very small, hence there was a slight difference in the SFE dispersive component value.

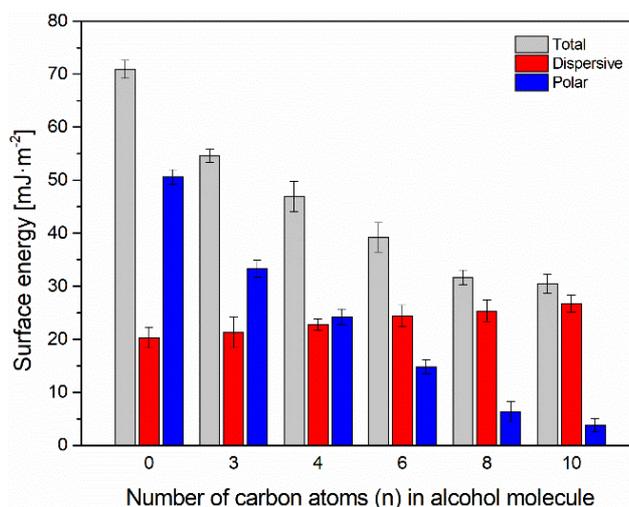


Fig. 10. Total surface energy and its components of glass surface – non-modified (n=0) and esterified (for 6 h) with the n=3-10 alcohols

### 3.4. Zeta potential

When a material comes into contact with an aqueous solution, a surface charge is developed at the interface (Luxbacher, 2014). The resulting charge has a key role in any process where the solid material is found in an aqueous medium (e.g., flotation), due to the fact that it is the source of such interactions as electrostatic attraction and repulsion. The information about this charge is provided by the zeta potential analysis – an indicator of the charge forming on the surface of a solid in an aqueous solution. Besides the fact that zeta potential analysis can provide information about the chemical groups present on the surface of a material, it can also be used a complementary technique to characterise its wettability (Luxbacher, 2014). This parameter also depends closely on the properties of solution and mainly on its pH and electrolyte concentration. Depending on the pH of solution, the groups present on the surface may undergo ionisation and become either positively or negatively charged. In case of glass, which the main component is silica, most of the surface charge comes from the ionisation of silanol ( $\equiv\text{Si-OH}$ ) groups in contact with the solution, giving it either negative or positive charge according to pH (Behrens and Grier, 2001).

The pH dependence of glass zeta potential is shown in Fig. 11. For unmodified and modified samples, the isoelectric point ( $\text{pH}_{\text{iep}}$ ) was found at pH of about 5.2. The difference in the value of isoelectric point for glass compared to pure silica, which  $\text{pH}_{\text{iep}}$  is ca. 2-3, comes from the presence of other metals in the glass structure (Matisons, 2012). Below the isoelectric point (pH 2-5) the value of zeta potential did not exceed +10-15 mV, while above  $\text{pH}_{\text{iep}}$  (pH 5-11) the value decreased very rapidly and reached a value of ca. 50-70 mV already at pH 7.5. Such a high negative value, even for esterified surfaces, is due to the presence of -OH groups. Although the -OH groups bind to the alcohol molecules during glass functionalisation, it is highly unlikely that all free silanol groups (-SiOH) were eliminated.

In case of organosilicon compounds, it was shown that up to 50% of the silanol groups can remain unreacted during the surface modification (Vansant et al., 1995). Whereas during chemisorption of aliphatic alcohols on the surface of fumed silica three n-butoxy groups are sufficient to cover area occupied by 8 hydroxyl groups, making the remaining two thirds of the groups inaccessible for further reaction (Ballard et al., 1961). The esterification did not lead to other chemical changes on the glass surface, apart from the binding of silanol groups to the alcohol molecule. Therefore, the zeta potential remained almost unchanged. For samples esterified with longer chain alcohols ( $n=6-10$ ), the value of the zeta potential was less negative in the pH region of 7.5-11.5, compared to non-modified and modified with shorter chain ( $n=3,4$ ) alcohols. This may be related to mentioned earlier isolation of the surface from the solution by chains of longer alcohols.

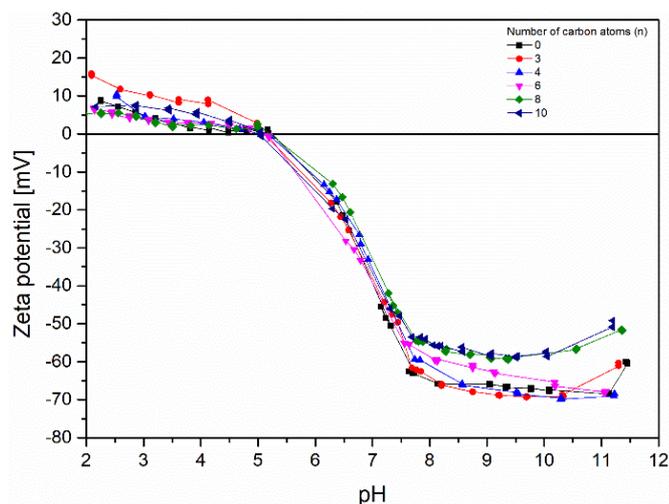


Fig. 11. pH dependence of zeta potential for non-modified and esterified glass surface for alcohols with different carbon chain length ( $n$ )

#### 4. Conclusion

In this study, an effect of esterification with  $n$ -alkyl alcohols ( $n=3, 4, 6, 8, 10$ ) of soda-lime glass surface on its wettability was presented. The XPS analysis revealed that this type of modification led to the binding of the alcohol molecule to the glass surface through Si-O-C bond, which resulted in the formation of a layer of alkyl carbon chains on the surface, and thus affected its wettability. Based on AFM surface roughness measurements as well as SEM images of glass substrates before and after esterification, it can be concluded that the created layer of hydrocarbon chains was relatively homogeneous.

The water contact angle measurements showed that implemented esterification allowed to control wettability of glass surface, and the degree of this modification depended on the chain length of the alcohol used as well as the modification time. The surface esterified with shorter-chain alcohols ( $n=3-6$ ) showed low to moderate hydrophobicity (ca.  $40-60^\circ$ ), while longer chains ( $n=8, 10$ ) resulted in a surface wetting angle of approximately  $90^\circ$ .

The zeta potential of glass substrate was not significantly affected by the esterification. This indicates that despite the binding the alcohol molecules to the part of -OH groups, the remaining silanols had a strong influence on the potential value. This is of considerable importance in cases where the solid is immersed in an aqueous medium and it is crucial that surfaces with different degrees of wettability have the same potential characteristics (e.g. in a flotation process research).

In general, the advantage of the esterification with the  $n$ -alcohol method over silanisation is that this is a simple and low-cost method and does not require the use of hazardous solvents. Obtained results provided valuable information which allowed for a comprehensive and broader view of the influence of this technique for modifying surface wettability on its physicochemical properties. Glass model surfaces modified with this method can be used in many different types of tests concerning the influence of wettability of solid surfaces in processes occurring at solid-liquid-air interfaces.

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