The influence of corrosion of inorganic-organic films on their surface properties

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Abstract: The work deals with the influence of water corrosion on the surface properties of inorganic-organic SiO₂ films, which were prepared from the sols in "tetraethoxysilane-isopropyl alcohol-water-nitric acid-triethoxy(octyl)silane" system. The atomic force microscopy and sessile drop technique was used on the characterization of surface properties. The morphology, rms-roughness, adhesion force and stiffness of prepared films were evaluated. Surface free energy and its polar and dispersion component were calculated by Owens-Wendt method using contact angles of distilled water and diiodomethane. The influence of corrosion on all of the studied properties of films was significant in the case of films prepared from sol with molar ratio of \( x(H₂O) : x(SiO₂) = 2 \).

1. Introduction

The hybrid inorganic-organic materials have recently attracted a considerable attention because they can provide the desired properties which are obtained by combination of inorganic and organic parts at the nano as well as molecular level.

Due to the extensive difference in processing temperatures of inorganic and organic parts, it is quite difficult to synthesize hybrid materials because in general, the processing temperature of organic materials is quite low (from room temperature to 200 °C) in comparison with the inorganic materials, where the given processing temperature can be more than 1000 °C [1]. Hybrid inorganic-organic materials can be prepared in several ways, including solvothermal method, microwave method, ionothermal or sonochemical method [2]. In addition, it is important to point out that the utilisation of the sol-gel method represents the most widely used technique for preparation of hybrid materials because the given sol-gel method is one of the best methods for preparation of hybrid materials at low temperatures [3–7]. In relation to the hybrid materials, the other advantage of this method is based on simple preparation, easy processing resulting in desired shapes and usage for many applications. The processing of these materials also enables the preparation of transparent films, which are deposited on various substrates, such as glass, metals and ceramics [8].

Inorganic components in hybrid films enhance the properties of organic components, including increase in hardness, abrasion resistance [9], stiffness, refractive index and porosity of thin films [8]. The presence of organic components in the inorganic network makes the thin film more flexible and less susceptible to rupture during heat treatment [10]. In addition, organic components increase the adhesion of the thin film to the substrate and the wettability of the thin film surface – hydrophobicity [8, 11, 12].
The alkylalkoxysilanes represent the basic precursors for the preparation of inorganic-organic materials because they contain the hydrolysable C-O-Si bonds as well as covalent Si-C bonds. The covalent bonds are resistant to hydrolysis and therefore, they are also remained in the final product in the case of adequate heat treatment. The inorganic polymer network consists of silicon alkoxides and alkylalkoxysilanes which provide hardness, thermal stability and low thermal expansion of the material. Non-reactive organic groups, such as phenyl or methyl, increase elasticity. Reactive organic groups (vinyl, methacrylic or epoxy groups) in alkylalkoxysilanes can be polymerised to form an organic polymeric network which provides elasticity and increases the thermal expansion of the resulting material [13].

Inorganic-organic films, which are prepared from alkoxides by the sol-gel method, have wide-spectrum applications, such as the films for protection of metallic materials against oxidation or corrosion [11, 14, 15], and films for protection of various types of glass [12], including ancient glass [16], historical window glass [17]. Furthermore, the given films can be also used as the low-refractive index films for reflective coatings [18], the anti-reflective films [19] and durable self-cleaning films [20].

The properties of surfaces of these films (morphology, hydrophobicity, \( \text{rms} \)-roughness, surface free energy, adhesion force and stiffness) play a crucial role in applications mentioned above. In the presented work, the sol-gel method was used for preparation of sol, using TEOS as an inorganic precursor and OTES as a modifying organoalkoxysilane. The effect of the water content in sols, expressed as the \( x(\text{H}_2\text{O}) : x(\text{SiO}_2) \) ratio and the effect of corrosion (in distilled water) on the properties of surface for prepared inorganic-organic films were studied.

2. Experiment

2.1. Preparation of substrates
The microscope slide glass samples were used for investigation and they were cleaned in such a way which is introduced in [21].

2.2. Preparation of inorganic-organic sols
The sols were prepared from three solutions in the "TEOS-IPA-H\(_2\)O-HNO\(_3\)-OTES" system. The process of sol preparation is shown in figure 1. The first solution (RA) was prepared from TEOS with 40% of IPA amount. The second solution (RB) was prepared from H\(_2\)O, HNO\(_3\) with 40% of IPA amount. The third solution (RC) was prepared from OTES with 20% of IPA amount. The RA solution was added drop by drop into the RB solution and obtained mixture (RAB) was stirred for 30 min. Then, the RC solution was also added drop by drop into the solution and obtained mixture was stirred for 30 min. In comparison with the work [22], the difference of sol preparation is not only in the method of solutions mixing (RB solution was added to the RA solution), but also in the conditions during the corrosion of prepared films.

![Figure 1. The process of sol preparation.](image-url)
Three different sols compositions were prepared (table 1). The difference between individual sols was based on the different H2O content, which can be expressed in the following molar ratio: x(H2O) : x(SiO2) [23].

| Sample   | x(TEOS) | x(OTES) | x(H2O) | x(HNO3) | x(IPA) | x(H2O) : x(SiO2) |
|----------|---------|---------|--------|---------|--------|------------------|
| BA16001  | 0.04375 | 0.00625 | 0.1    | 0.005   | 0.845  | 2                |
| BA16002  | 0.04375 | 0.00625 | 0.2    | 0.005   | 0.745  | 4                |
| BA16003  | 0.04375 | 0.00625 | 0.3    | 0.005   | 0.645  | 6                |

2.3. Preparation of films

The next day after the sol preparation, the films were applied to the precisely cleaned microscope slide glasses by dip-coating method, using the withdrawing speed of 60 mm min\(^{-1}\). The given applied films were dried for 2 hours at temperature of 140 °C [23]. After the slide glasses had been brought out from the drying oven, they were left to be cold at laboratory temperature and subsequently, they were placed into the specific environment with the relative humidity of 52.9 %.

2.4. Corrosion of films

Corrosion of the prepared films was based on the procedure mentioned hereinafter. Firstly, the films on a teflon plate were inserted into beaker with water. The distilled water was used as a corrosion medium. Then, the films were left to corrode for 5 hour at the temperature approximately 98 °C. After 5 hours, the films were precisely cleaned with isopropyl alcohol and they were left to dry on the air.

2.5. Surface properties measurement

The investigation of the surface properties for inorganic-organic films was based on the observation by NT-206 atomic force microscope (Micro test Machines Belarus) which was operating at the contact mode. Moreover, the sessile drop method was also used for investigation in order to specify the contact angle.

2.5.1. Morphology and topography measurement

The Si3N4 tip (MicroMasch NSC11/A1BS) was used for measurement of morphology as well as topography and the force constant was 48 N m\(^{-1}\). The given measurement process was performed for randomly selected sites of each one film under the laboratory conditions. The images of the individual surfaces with proportion of 10 × 10 μm were obtained and the morphology and topography were evaluated in the special Surface Xplorer 1.0.8.65 software.

2.5.2. Adhesion force and stiffness measurement

The measurement of the adhesion force as well as stiffness of inorganic-organic films was based on the usage of spectroscopy in point, using Si3N4 tip (MicroMasch NSC11/A1BS) and force constant was 48 N m\(^{-1}\). The measurement procedure was performed for at least 100 randomly selected sites of each one film under the laboratory conditions.

2.5.3. Contact angle measurement

The sessile drop method was applied for determination of the contact angle on the surface of the inorganic-organic films before and after corrosion. Diiodomethane and water were used as the measurement liquids. The distilled water is considered as the liquid with the dominant polar component and diiodomethane represents the liquid with the dominant dispersion component. Relating to the measurement process, 10 drops with the volume of 10 μl were dropped on the film surface, while the drop arrangement on the film surface was uniform. Using the obtained images of the water
and diiodomethane drop profiles, the values for contact angle were calculated by help of special mathematical software. In addition, the obtained results were processed in a statistical way.

2.5.4. Surface free energy determination
Referring to the results from the water and diiodomethane contact angles and using Owens-Wendt method [21, 24, 25], the values of the surface free energy and its polar and dispersion component were calculated for inorganic-organic films before and after corrosion.

3. Results and discussion
3.1. Surface topography and morphology
During topography evaluation, using AFM method, height irregularity values at certain points of the surface were determined. A set of height values was obtained, on the basic of adjustment where the obtained height values were based on the plane passing through the three lowest values for the given image and it leads to the measurement output. A similar adjustment was also used in the fast scan direction where the obtained height values were related to the line assigned to the two lowest values for given scan. With these adjustments, the most relevant surface image to reality is obtained. From the obtained set of height values \( z_i \), the values of the mean square deviation of the measured values \( z_{ij} \) around – so-called \( \text{rms} \)-roughness of surface were calculated using the following equation [26]:

\[
\text{rms} = \sqrt{\frac{1}{n.m} \sum_{i=1}^{n} \sum_{j=1}^{m} (z_{ij} - \bar{z})^2}
\]

(1)

where \( n \) is the number of rows and \( m \) is the number of columns corresponding to the AFM raster image, and \( z_{ij} \) is the height for point \( ij \) and \( \bar{z} \) is the average of measured height values of \( z_{ij} \):

\[
\bar{z} = \frac{1}{n.m} \sum_{i=1}^{n} \sum_{j=1}^{m} z_{ij}
\]

(2)

The surfaces of all films have a granular structure, while the given granular formations are relatively evenly distributed on the entire surface of the film. From the figures 2a, 2b and 2c, it is clear that the increase of the water content in the sol or in other words, the increase of \( x(\text{H}_2\text{O}) : x(\text{SiO}_2) \) molar ratio affects the surface morphology of the prepared films. In relation to the \( x(\text{H}_2\text{O}) : x(\text{SiO}_2) \) molar ratios which are 4 and 6, the surface morphology of the films is almost identical but in the case when the \( x(\text{H}_2\text{O}) : x(\text{SiO}_2) \) molar ratio is 2, the different morphology can be observed in comparison with molar ratios which are 4 and 6. The difference in film morphology is also reflected in the \( \text{rms} \)-roughness value (figure 3) and it is slightly higher for films prepared from a sol where the \( x(\text{H}_2\text{O}) : x(\text{SiO}_2) \) molar ratio is 2 in comparison with films where the molar ratios are 4 and 6.

After the corrosion of the films in the water, "cavities" were observed for all films, representing corrosion sites in the film (figures 2d, 2e, 2f). The effect of corrosion is most significant on the surface of films prepared from sol with a molar ratio of \( x(\text{H}_2\text{O}) : x(\text{SiO}_2) = 2 \). The morphology of these films (figure 2d) is different noticeably in comparison with the other films (figures 2e and 2f). Corrosion also significantly influenced the \( \text{rms} \)-roughness value of the films prepared with the lowest \( x(\text{H}_2\text{O}) : x(\text{SiO}_2) \) molar ratio – the \( \text{rms} \)-roughness of the films was almost by 5 times higher than the \( \text{rms} \)-roughness value of the given films before corrosion. High \( \text{rms} \)-roughness and high standard deviation correspond to more rugged surface. Observing the corrosion effect for higher \( x(\text{H}_2\text{O}) : x(\text{SiO}_2) \) ratios, there was not significant change in \( \text{rms} \)-values for investigated films.
Figure 2. 2D AFM images of the surface of inorganic-organic films:
a, b, c – before corrosion and d, e, f – after corrosion in distilled water.

Figure 3. The dependence of $rms$-roughness of inorganic-organic films on $x(H_2O) : x(SiO_2)$ ratio in sol.

It is well known that preparation conditions such as pH, character and concentration of catalyst, $H_2O : SiO_2$ ratio and temperature have a crucial effect on the hydrolysis as well as polycondensation reactions during the preparation of sols and thus, they have effect on the resulting film structure. The
change of the $\text{H}_2\text{O} : \text{SiO}_2$ molar ratio in the range from 1 to 50 leads to the high variability of the solid skeleton structures in gel [27]. Based on different morphology and higher $\text{rms}$-roughness of films prepared from sol where the $x(\text{H}_2\text{O}) : x(\text{SiO}_2)$ ratio is 2, we can assume that in the studied system, the sol with the lowest $x(\text{H}_2\text{O}) : x(\text{SiO}_2)$ molar ratio is formed in a different way (mechanism) in comparison with sols with a higher water content and it also affects the properties of the films. In relation to sol in which the $x(\text{H}_2\text{O}) : x(\text{SiO}_2)$ ratio is 2, the differences in the film surface were also observed for the other properties discussed hereinafter.

3.2. Adhesion force and stiffness
The adhesion force and stiffness of the prepared films were determined from the shape of the force-displacement curves measured by spectroscopy in point. The adhesion force was calculated from the retraction curve and the stiffness was obtained from the approach curve. The stiffness was obtained from the aspect of the force constant of the AFM tip [28].

At first, the set of values obtained for a given property was tested for outlying values and after that, the investigation was closely connected with determination of distribution type for the given set of values – whether it is a monomodal or bimodal distribution. Subsequently, it was specified whether the given distribution was normal (Gaussian), log-normal, Weibull or extreme values. Estimation of the mean value and estimation of variance were obtained as a result of this analysis. It was found out that the obtained sets of values had a monomodal distribution for both properties and all films (before and after corrosion process). Using the log-normal distribution, the best fit was found out.

| Sample before corrosion | Adhesion force (nN) | Stiffness (nN nm$^{-1}$) | Sample after corrosion | Adhesion force (nN) | Stiffness (nN nm$^{-1}$) |
|-------------------------|---------------------|--------------------------|------------------------|---------------------|--------------------------|
| BA16001                | 551753 ±584456$^*$  | 43931 ± 5620$^*$         | BA16001_k              | 205203 ±101864$^*$  | 38650 ±1547$^*$          |
| BA16002                | 753029 ±559454$^*$  | 45452 ± 3093$^*$         | BA16002_k              | 586942 ±299886$^*$  | 38988 ±3564$^*$          |
| BA16003                | 332064 ±131618$^*$  | 40701 ± 5327$^*$         | BA16003_k              | 548662 ±252391$^*$  | 41922 ±4091$^*$          |

$^*$estimation of variance

Based on the adhesion force values for inorganic-organic films before and after corrosion with distilled water (table 2), there is not significant difference in the estimation of the mean adhesion force value before corrosion (samples BA16001, BA16002, BA16003) and after corrosion (samples BA16001_k, BA16002_k, BA16003_k). Regarding all the investigated films, a high value of estimation of variance for adhesion force was observed and it shows the unevenness (non-uniformity) of the films in terms of the distribution of adhesion forces on the surface. When the $x(\text{H}_2\text{O}) : x(\text{SiO}_2)$ ratio is 2, the adhesion force as well as the estimation of variance for adhesion force values are the lowest after corrosion and it is closely connected with the fact that for the given films, there is the better evenness (uniformity) of the surface of the corroded films from the aspect of adhesion forces.

From the dependence of film stiffness on the $x(\text{H}_2\text{O}) : x(\text{SiO}_2)$ ratio in the sol for corroded and non-corroded films, it can be seen that there is not any significant change in value for stiffness of films with increasing water content in the sol and the stiffness of films was only slightly decreased after the water corrosion process.

3.3. Contact angle and surface free energy
Figure 4 shows the dependence of contact angles on $x(\text{H}_2\text{O}) : x(\text{SiO}_2)$ ratio in sol. It can be seen that the prepared inorganic-organic films have the contact angle of distilled water in the range from 90° to 101° and therefore, they are hydrophobic. The effect of sol composition on the contact angle of measurement liquids was reflected in a slight increase in the values for the contact angles with the increasing $x(\text{H}_2\text{O}) : x(\text{SiO}_2)$ molar ratio from 2 to 4 in sol. In addition, there was negligible change in values for contact angles after the further increase of molar ratio to 6.
Figure 4. The dependence of contact angle of inorganic-organic films on $x(H_2O) : x(SiO_2)$ ratio in sol.

After the corrosion process, the hydrophobic character was retained for all tested films. After corrosion, the contact angles of distilled water and diiodomethane were slightly increased for films prepared from sol where the $x(H_2O) : x(SiO_2)$ molar ratio was 2, while in the case of 4 and 6 ratios the contact angles of distilled water and diiodomethane were slightly decreased after corrosion.

Figure 5. The dependence of surface free energy and its dispersion and polar component of inorganic-organic films on $x(H_2O) : x(SiO_2)$ ratio in sol before and after corrosion.

From the dependence of surface free energy and its dispersion and polar component of inorganic-organic films on $x(H_2O) : x(SiO_2)$ ratio in sol (figure 5), it can be seen that surface energy values are slightly decreased with increasing $x(H_2O) : x(SiO_2)$ ratio in the sols, which were used for preparation of the films. Since the values of the polar surface free energy component are low and they are almost not changed with the $x(H_2O) : x(SiO_2)$ ratio, the dependence of the dispersion component on $x(H_2O) : x(SiO_2)$ ratio in sol has the comparable course to surface free energy.

Considering the contact angles, the same effect was observed for corroded films prepared from sol where the $x(H_2O) : x(SiO_2)$ ratio was 2. There was the decrease in values for surface energy (and its dispersion component) in comparison with the values before the corrosion process. For films prepared from sols where the $x(H_2O) : x(SiO_2)$ molar ratio was 4 and 6, the values of surface energy (and its dispersion component) are higher after the corrosion process.

The values of the polar surface energy component were the same even after corrosion. Based on the low values of the polar surface energy component before and after corrosion, the surface of the films
can be specified as the surface with the dominant dispersion component or in other words, it is non-polar surface. It can be also stated that the presence of polar groups on the surface of inorganic-organic films is minimized and there is not any increase in their concentration on the surface as a result of the corrosion.

4. Conclusion
The work deals with the investigation of the influence of sols composition ("TEOS-IPA-H2O-HNO3-OTES" system), while the given sols were used for the preparation of films and moreover, the given work also includes the influence of corrosion on surface properties of inorganic-organic films.

Based on the investigation, it was found out that the sol composition has the most significant effect on the surface properties of the films only when the x(H2O) : x(SiO2) molar ratio is changed from 2 to 4. The given films have a higher roughness, lower contact angle and higher surface energy. There was not any effect on the surface properties of the films after change of the x(H2O) : x(SiO2) molar ratio from 4 to 6.

The influence of corrosion in water on the films was observed only when the x(H2O) : x(SiO2) molar ratio was changed from 2 to 4. In relation to the films prepared from sol where the x(H2O) : x(SiO2) molar ratio was 2, there was a higher roughness, a higher contact angle and lower surface energy after corrosion, while the films prepared from sols where the x(H2O) : x(SiO2) molar ratio was 4 and 6 exhibited a lower roughness, a lower contact angle and a higher surface energy after corrosion.

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