

THE INFLUENCE OF TREATMENT TEMPERATURE ON SURFACE PROPERTIES OF INORGANIC-ORGANIC FILMS

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The paper deals with the treatment temperature influence of inorganic-organic films on their surface properties. Inorganic-organic films were prepared by sol-gel method in “tetraethoxysilane – triethoxy(octyl)silane – water – nitric acid – isopropyl alcohol” system, and they were treated at temperatures of 140, 160, 180, 200 and 220 °C. The atomic force microscopy and sessile drop technique were used for characterization of film surface. The morphology, rms-roughness, and surface wettability (hydrophobicity) were evaluated. Surface free energy and its polar and dispersion component were calculated by Owens-Wendt-Rabel-Kaelble (OWRK) method, using contact angles of water and diiodomethane. On the basis of results of all studied properties, the films can be divided into two groups. The first group is represented by films prepared at temperatures of 140, 160 and 180 °C because there is the evaporation of present solvents. The second group is represented by films prepared at temperatures of 200 and 220 °C because the degradation processes of inorganic-organic components are in progress in films.

INTRODUCTION

The inorganic-organic nano-materials are defined as materials which connect the inorganic and organic components with dimensions in nanometres. This connection leads to the formation of “hybrid” which has the properties of both used components [1, 2]. Inorganic components in hybrid films strengthen the properties of organic components and increase the hardness, abrasion resistance [3], stiffness, refractive index, and porosity of thin films [4]. The presence of organic components in inorganic network causes that the thin film is more flexible and less inclinable to cracking during thermal treatment [3]. Moreover, the inorganic components increase the adhesion of film to substrate and they influence the surface free energy of film [4]. The material with desired properties can be achieved by controlling of the preparation conditions [1].

Inorganic-organic materials are prepared as bulks, fibres, powders, and films [2]. Inorganic-organic films have the applications as antireflective films [5, 6], anti-corrosive films on metal and glass [7-10], hydrophobic, oleophobic and self-cleaning films on glass [6, 11-15], protective films on historical buildings [16], antibacterial films [17, 18], and optical films which combine high

transparency and high flexibility [19]. They are also used in microelectronics [20].

For preparation of inorganic-organic films, many techniques are used, such as plasma etching [21], electrospinning [22], chemical vapor deposition [23] and sol-gel process [24]. In comparison to mentioned techniques, the sol-gel process has a great advantage in preparation of inorganic-organic films, because:

- it allows the control of chemical composition of product;
- it is appropriate method of deposition on polymers which have the melting temperatures between 150 and 300 °C;
- the uniform films can be prepared easily by dip-coating or spin-coating method;
- it is the low-cost technique;
- the films are easily deposited on ceramics, glass, metals and plastics [2, 24].

The properties of inorganic-organic materials prepared by sol-gel method are influenced by the controlling of individual processes which take place during sol preparation, sol-gel transition, and gel-xerogel-product transition, i.e. during the thermal treatment of materials.

The sols properties are influenced by the controlling of hydrolysis reactions of alkoxides in solutions and the subsequent reactions of oligomers formed by hydrolysis. The important parameters, which influence the reactions (hydrolysis and condensation) and their rate, are type of precursor, pH value (OH^- or H^+ catalysis), alkoxy group : water ratio for alkoxide precursors, type of solvent, presence of electrolytes, temperature, relative and absolute concentration of components in precursors mixture, and other parameters [2, 25]. The parameters mentioned above are closely connected with the rate of polymer particles growth and the reaching the state of their mutual interconnection in order to form the steric gel. The given state refers to the increasing of viscosity, which is increased rapidly in the final phase and gel is created.

In next phase, after gelation, the evaporation of solvent takes place and then, the gel is dried and subsequently transformed to xerogel. In this process, the dehydration of gels and their subsequent shrinking, i.e. densification, are crucial and important factors. During preparation of monoliths, the drying of gels is quite problematic and depends on development of pores during densification and decomposition of present organics. In the case of films and fibres, the transition to product is less complicated because they have thickness in the scale of micrometres. Besides densification of xerogels during the thermal treatment of films, the interactions with substrate take place and they markedly influence the surface properties of films [2, 25, 26]. For preparation of inorganic-organic films, the controlling of their thermal treatment is important mainly from the point of properties of prepared film, and it is also important to avoid the degradation of organic component in inorganic-organic film.

Many papers, which studied the relationship between composition of sols and properties of inorganic-organic films, have been published [1, 24, 27-30]. In paper [28], the relation of surface free energy to composition of sols in “tetraethoxysilane (TEOS) – triethoxy(octyl)silane (OTES) – water – nitric acid – isopropyl alcohol” system was studied. The films were prepared on glass and they were treated at temperature of 140 °C for 2 hours. In paper [1], the authors studied how the chemical structure of inorganic-organic film influences the film behaviour during scratch tests. In paper [29], the influence of OTES amount on contact angle and roughness of silica films was studied. The films were treated at temperature of 120 °C for 2 hours. Authors found out, that the increasing of OTES amount (0 - 15%) leads to the increase of roughness and contact angle.

The influence of thermal treatment of monoliths and aerogels on their properties is studied by many authors [31-34], however only a few works deal with the influence of thermal treatment on properties of inorganic-organic films [35-37]. In paper [35], the authors studied the properties of organic-inorganic thin SiO_2

films modified with polydimethylsiloxane, while the given films were deposited on glass and aluminium alloy and treated at temperatures of 100, 200, 300 and 400 °C. They observed the influence of temperature on quality of films, their hardness and hydrophobicity. In paper [36], the hydrophobic films based on TEOS and hexadecyltrimethoxysilane as precursors were prepared. Films were thermally treated at 100 and 150 °C and they were characterized by scanning electron microscopy, Fourier transform infrared spectroscopy as well as measurements of surface roughness and contact angle of water.

The aim of this paper is determination of thermal treatment influence of inorganic-organic films in “tetraethoxysilane (TEOS) – triethoxy(octyl)silane (OTES) – water – nitric acid – isopropyl alcohol” system on their surface properties, namely morphology, roughness, surface wettability by water (hydrophobicity) and surface free energy (SFE).

EXPERIMENTAL

Materials

For preparation of inorganic-organic sol in “TEOS – OTES – H_2O – HNO_3 – IPA” system, the following chemicals were used: tetraethoxysilane (TEOS, 98 %, Sigma Aldrich), triethoxy(octyl)silane (OTES, 97 %, Acros Organics), distilled water (H_2O , FPT), nitric acid (HNO_3 , 65 %, Lachema), isopropyl alcohol (IPA, 99.93 %, Centralchem).

Preparation of inorganic-organic sol

The inorganic-organic sol was prepared from three solutions (RA, RB and RC) by sol-gel method according to procedure shown in the Figure 1. The RA solution contained the tetraethoxysilane and 40 % of total IPA amount, the RB solution contained the nitric acid, distilled water and 40 % of total IPA amount, and the RC solution contained the triethoxy(octyl)silane and 20 % of total IPA amount. When the RB solution was added to the RA solution, the prepared RAB solution was mixed for 30 minutes. Then, the RC solution was added to mixture and final inorganic-organic sol was also mixed for 30 minutes. By the given procedure, the sol in “TEOS–OTES– H_2O – HNO_3 –IPA” system was prepared, in which the following molar ratios were: $x(\text{H}_2\text{O}) / (x(\text{TEOS}) + x(\text{OTES})) = 6$ and $x(\text{OTES}) / (x(\text{TEOS}) + x(\text{OTES})) = 0.3$. The molar composition of sol is shown in the Table 1.

Table 1. Molar composition of inorganic-organic sol.

$x(\text{TEOS})$	$x(\text{OTES})$	$x(\text{H}_2\text{O})$	$x(\text{HNO}_3)$	$x(\text{IPA})$
0.035	0.015	0.300	0.005	0.645

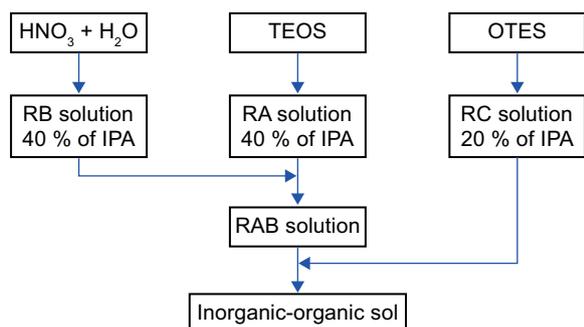


Figure 1. Preparation scheme of inorganic-organic sol.

Preparation of inorganic-organic films

By “dip-coating” technique, the inorganic-organic films were prepared with coating speed of 60 mm·min⁻¹ on the microscope slide glasses which were cleaned using procedure in [28]. After sol deposition, 2 hours treatment was performed at temperatures of 140, 160, 180, 200 and 220 °C for individual films, with following free cooling to room temperature.

Atomic force microscopy

The atomic force microscope (AFM) by Bruker Innova[®] was used for observation of films surface at room temperature as well as humidity. Measurements were carried out in tapping mode using RTESPA-300 tip with spring constant of 40 N·m⁻¹ at frequency of 300 kHz. The measured area has the size of 10 × 10 μm, and each film was measured five times at randomly chosen places. Results were processed by NanoScope analysis 1.50 software.

Surface wettability by water

On the basis of determination of contact angles of water, the wettability (hydrophobicity) of films surface was evaluated. The contact angles were determined by sessile drop technique [38]. For each film, the 12 drops of testing liquid with volume of 10 μl were randomly dropped on the surface of film. Optical equipment with camera was used for capturing of drop profile, and contact angle was calculated by nonlinear least squares method using Matlab software.

Determination of surface free energy

For calculation of surface free energy and its polar and dispersion component, the Owens-Wendt-Rabel-Kaelble (OWRK) method was used. This method is based on Fowkes method [39] and it is connected with the dispersion and polar component of solid and liquid for description of surface tension and surface free energy. According to this method, the surface energy (γ) is sum of dispersion (γ_L^D) and polar (γ_L^P) component of surface free energy:

$$\gamma = \gamma_L^D + \gamma_L^P \quad (1)$$

By the extension of Fowkes equation [40] by Equation 1, the surface free energy of solid-liquid interface (γ_{SL}) can be calculated from the equation:

$$\gamma_{SL} = \gamma_s + \gamma_L - 2\sqrt{\gamma_s^D \gamma_L^D} - 2\sqrt{\gamma_s^P \gamma_L^P} \quad (2)$$

The Equation 4 is considered as the base of OWRK method, and it is result of combination of Equations 2 and 3:

$$\gamma_s = \gamma_{SL} + \gamma_L \cos \theta \quad (3)$$

$$\gamma_L (1 + \cos \theta) = 2\sqrt{\gamma_s^D \gamma_L^D} + 2\sqrt{\gamma_s^P \gamma_L^P} \quad (4)$$

where γ_L is surface free energy of liquid with its individual components, and γ_s is surface free energy of solid. Dispersion (γ_s^D) and polar (γ_s^P) component of surface free energy of solid are determined from measurement of contact angle (θ) for a given surface, using at least two different liquids with known γ_L^D and γ_L^P values [41-43]. For determination of SFE, the distilled water and diiodomethane were used as testing liquids. The distilled water is polar liquid, because the value of its polar component of surface energy predominates the value of dispersion component ($\gamma_L^D = 21.8 \text{ mJ}\cdot\text{m}^{-2}$ and $\gamma_L^P = 51.0 \text{ mJ}\cdot\text{m}^{-2}$). Diiodomethane is dispersion liquid, because its polar component of surface energy is equal to zero ($\gamma_L^D = 50.8 \text{ mJ}\cdot\text{m}^{-2}$).

RESULTS AND DISCUSSION

On the basis of results of thermal analysis of xerogel, which was prepared by drying of sol to constant mass at temperature of 80 °C, the temperatures for treatment of inorganic-organic films were chosen. In the Figure 2, TG/DTA curves of xerogel measured in air with heating rate of 10 °C·min⁻¹ are shown.

The DTA curve shows, that the exothermic processes start at temperature near to 190 °C, and these processes correspond to the starting processes of decomposition and oxidation of present organics. These processes

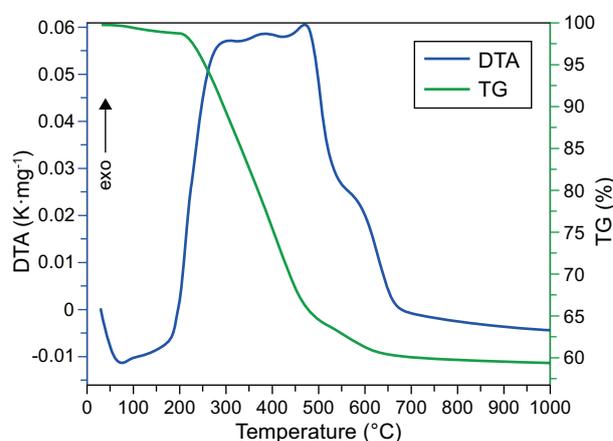


Figure 2. TG/DTA curves of inorganic-organic xerogel.

are connected with the change of mass in TG curve. The evaporation of present solvents takes place up to the mentioned temperature [44]. On the basis of the given fact, the temperatures for films treatment below and above the mentioned temperature were selected.

The influence of treatment temperature of inorganic-organic films on their surface properties was evaluated on the basis of morphology, surface wettability by water, surface free energy and its polar and dispersion component.

Morphology of films surface

Using AFM, the surface morphology of films prepared from inorganic-organic sol was observed. The Figure 3 shows 2D images of surface of inorganic-organic films which were treated at temperatures of 140 °C (a), 160 °C (b), 180 °C (c), 200 °C (d and e) and 220 °C (f). The relationship between *rms*-roughness of films and temperature for films treatment is shown in the Figure 4.

The surfaces of films which were treated at temperatures of 140 °C (Figure 2a), 160 °C (Figure 2b) and 180 °C (Figure 2c) are visually similar and they consist of uniformly distributed spherical particles and cavities. In comparison with films treated at temperatures

of 160 a 180 °C, some ridged longitudinal shapes on the surface of film treated at temperature of 140 °C occur and these shapes cause the increasing of *rms*-roughness value (Figure 4). When the temperature of films treatment increases, there is the reduction in the size of spherical particles, and the surface of film treated at temperature of 180 °C seems to be the most uniform in comparison with all other prepared films, and its value of *rms*-roughness

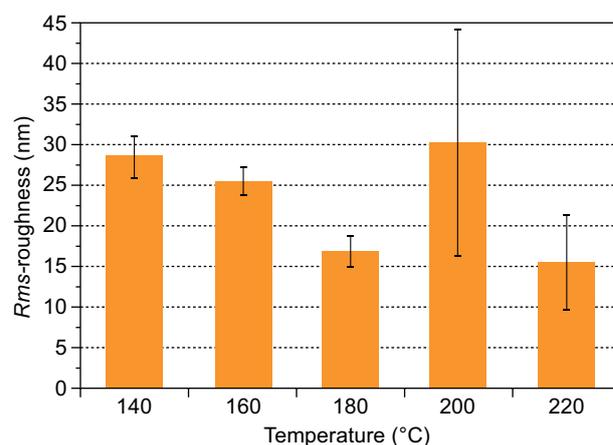


Figure 4. The dependence of *rms*-roughness on temperature of films treatment.

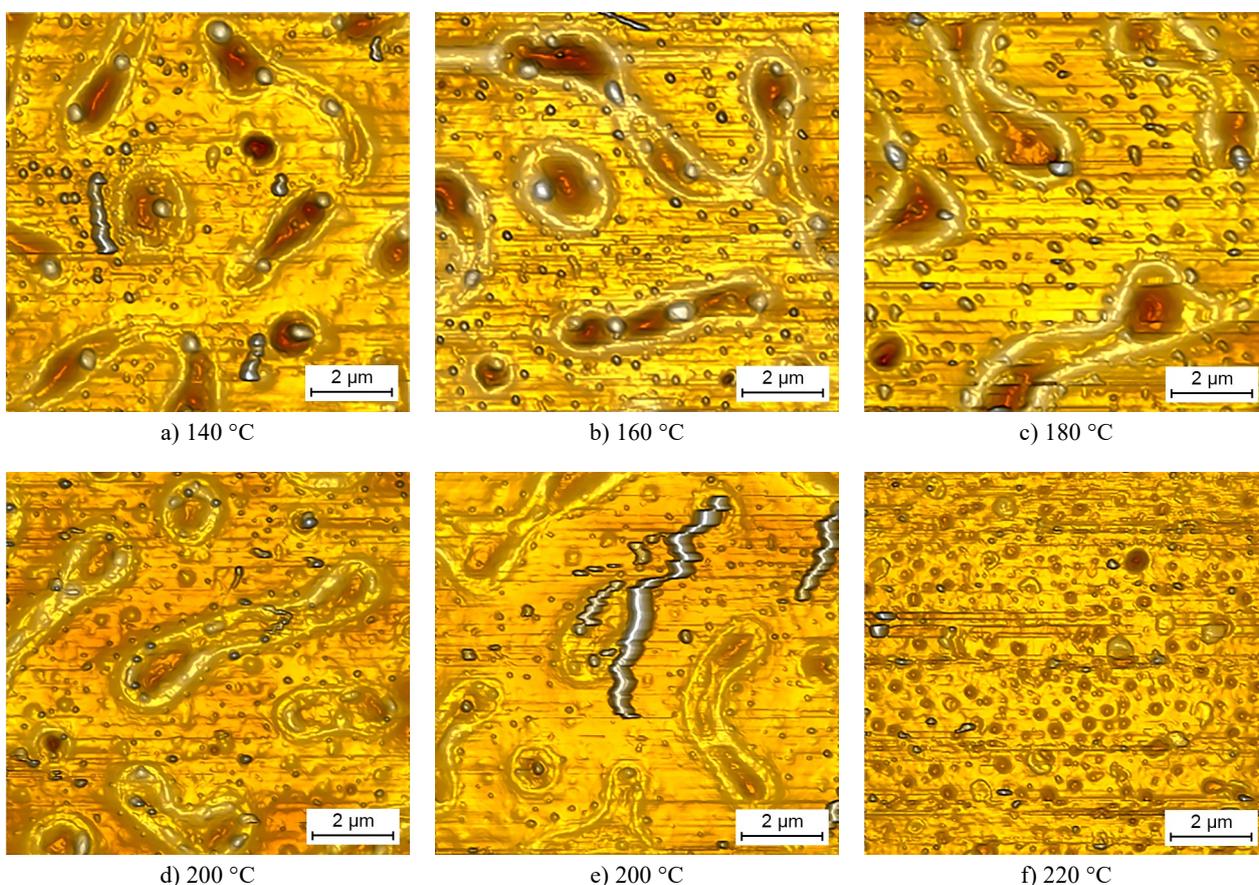


Figure 3. 2D AFM images of surface for inorganic-organic films treated at temperatures of: a) 140 °C, b) 160 °C, c) 180 °C, d-e) 200 °C, f) 220 °C.

is the lowest (Figure 4). The increasing of temperature to 200 °C causes that the film has the different morphology within the given film surface areas. Some areas of surface consist of little spherical particles and circular cavities of various sizes, but these cavities are shallower in comparison with cavities on the surfaces of films prepared at lower temperatures (Figure 3d). However, on the other surface areas of given film, the ridged longitudinal shapes occur also randomly, and they cause the increasing of *rms*-roughness value (Figure 3e). Surface non-uniformity of film treated at temperature of 200 °C is confirmed by high value of standard deviation of *rms*-roughness and it is probably caused by starting process of decomposition of organics in film. Inorganic-organic film treated at temperature of 220 °C consists of little circular cavities as well as several non-uniformly located ridged oval shapes but these shapes do not influence the *rms*-roughness value (Figure 3f). The surface of film treated at 220 °C is visually different from surfaces of films which were treated at lower temperatures.

Surface wettability of films – hydrophobicity

The relationship between contact angle of water and temperature of films treatment is shown in the Figure 5. All inorganic-organic films which were treated at chosen temperatures are hydrophobic. When the temperature of films treatment increases up to the temperature of 180 °C, the hydrophobicity gently increases, however the further increasing of temperature leads to the gently decreasing of film hydrophobicity. The film which was treated at temperature of 180 °C has the highest value of contact angle (98.5°) and film treated at 220 °C has the lowest value of contact angle (93.3°).

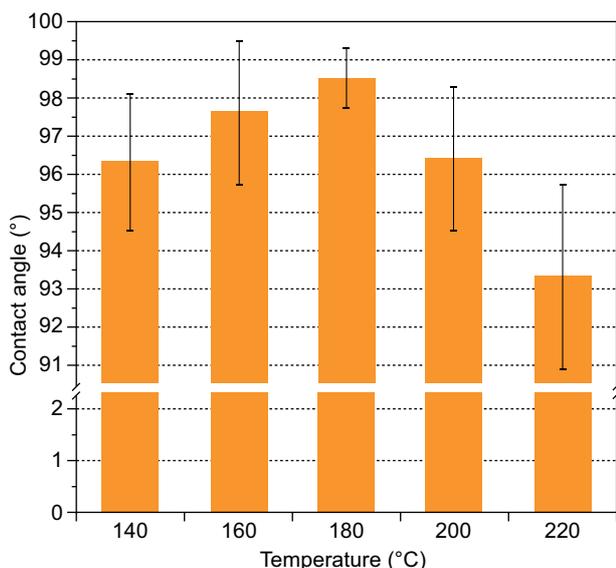


Figure 5. The dependence of contact angle of water on temperature of films treatment.

The wettability can be characterized as state when the liquid is in the contact with surface of solid. It is consequence of adhesive and cohesive forces as well as bonds between liquid and solid phase. Wetting process is influenced by the structure and surface of wetted material, i.e. its roughness, type of liquid and ambient conditions [43].

In the temperature range from 140 °C to 180 °C, when the evaporation of present solvents takes place, the dependence of contact angle on temperature has the increasing tendency, while the dependence of *rms*-roughness on temperature has the decreasing tendency. At temperature of 200 °C, the surface of film is non-uniform, and *rms*-roughness as well as contact angle have the significant standard deviations and this fact is related to starting processes of decomposition and oxidation of organics present in film. We can assume that the start of mentioned processes was specified, while it is necessary to point of that they have the significant influence on the film surface. At temperature of 220 °C, the higher conversion of mentioned processes occurs in comparison with other studied films. The morphology of film surface at 220 °C is completely different (Figure 3) and it has the lowest contact angle of water (hydrophobicity) as well as *rms*-roughness.

Surface free energy of films

SFE was determined by OWRK method, using the contact angles of water and diiodomethane. The relations of films treatment temperature to calculated average values of surface free energy, its polar and dispersion component for prepared films are shown in the Figure 6.

Surface free energy, which consists of polar and dispersion component, represents the physico-chemical

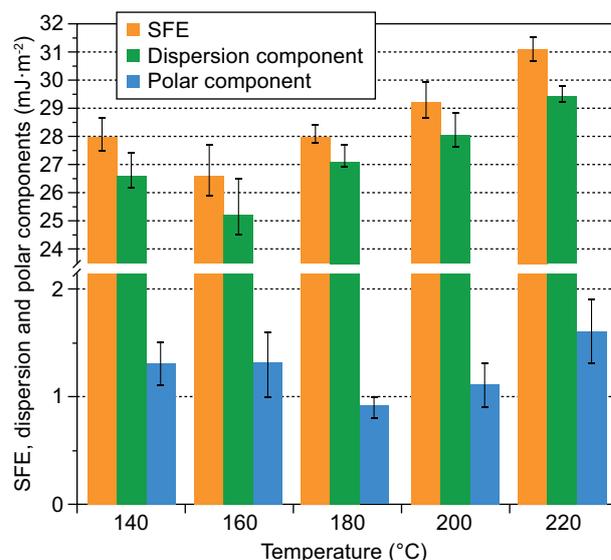


Figure 6. The dependence of SFE and its components on temperature of films treatment.

characteristic of surface. Dispersion component is connected with London forces which act between molecules and these forces occur in all types of matter and their action between adjacent atoms is always attractive. Polar component is known as sum of hydrogen, acidic/basic and induction interactions, and it provides the information on polarity, i.e. about distribution of polar forces [43, 45].

With respect to representation of polar and dispersion components of calculated SFE, we can state that for all films, the dispersion component is predominant in comparison with the polar component, i.e. their surface is nonpolar. When the temperature of films treatment increase, the SFE and its dispersion component decrease at first but subsequently, they gently increase above the temperature of 160 °C (Figure 6). The polar component of SFE is not changed when the temperature increases to 140 °C and 160 °C, but it decreases from value of 1.3 mJ·m⁻² (for 140 and 160 °C) to value of 0.9 mJ·m⁻² for temperature of 180 °C. The further increasing of treatment temperature causes the gentle increase of polar component value (Figure 6). It is connected with processes which are in progress during thermal treatment of films – the evaporation of polar solvents, up to the temperature of 180 °C, leads to the decrease of polar component value. At temperatures over the 180 °C, when the degradation processes of inorganic-organic components in films start (Figure 2), the number of OR groups on the films surface is reduced and polar Si–O groups are still present. At temperatures over the 180 °C, polar Si–O groups already predominate and polar component of SFE is gently increased.

CONCLUSION

In presented paper, the influence of treatment temperature of inorganic-organic films prepared by sol-gel method in “TEOS–OTES–H₂O–HNO₃–IPA“ system on their surface properties was studied. The inorganic-organic films were treated at temperatures of 140, 160, 180, 200 and 220 °C. Surface properties were evaluated on the basis of morphology, *rms*-roughness, surface wettability by water (hydrophobicity), surface free energy and its polar and dispersion component.

It was observed that temperature of films treatment has the influence on properties of studied inorganic-organic films. The films treated at temperatures of 140, 160 and 180 °C, when the evaporation of present solvents takes place, have the visually similar surface morphology. When the temperature increases the *rms*-roughness decreases but hydrophobicity increases, and for temperature of 180 °C, the wettability of film surface is the highest from all studied films. The polar component of SFE decreases up to the temperature of 180 °C, and it is due to evaporation of polar solvents.

For temperature of 200 °C, the film surface is only partially visually similar to films which were treated at temperatures of 140, 160 and 180 °C. Non-uniformities on the film surface cause its higher *rms*-roughness but hydrophobicity of film gently decreases. For temperature of 220 °C, when the decomposition and oxidation of substances in film take place, the morphology of film surface is different from the surfaces of other films. *Rms*-roughness of this film decreases, and its hydrophobicity has the lowest value in comparison with all studied films. The polar component of SFE gently increases when the temperature increases above 180 °C.

For all temperatures of films treatment, the dispersion component of SFE has predominant character in comparison with the polar component, i.e. the surface of films is nonpolar.

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