

PROPERTIES OF HYBRID COATINGS BASED ON 3-TRIMETHOXYSILYLPROPYL METHACRYLATE

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Hybrid coatings were prepared by sol-gel method from sols on the base of TMSPM ((3-(trimethoxysilyl)propyl methacrylate) – TEOS (tetraethylorthosilicate) on glass, corundum, polished steel and subsequently heat treated at 90°C/3 h or at 150°C/3 h. The morphology and microstructure of hybrid coatings were described by SEM and AFM. Properties like refractive index and thickness were measured with spectrophotometry. The abrasion resistance of hybrid coatings highly depends on the temperature of heat treatment. The tests of chemical resistance and measurement of porosity using nitrogen adsorption confirmed that the hybrid coating prepared from 100 % TMSPM is lightly porous. Therefore the hybrid material is not suitable as a protective barrier coating on the metal materials.

INTRODUCTION

Inorganic-organic hybrid materials have been receiving considerable attention as a new class of materials for their new, original properties based on a combination of organic and inorganic polymer. Inorganic-organic hybrid materials can acquire properties that purely inorganic or organic materials can not give. The hybrid networks can be conveniently divided into two classes [1]. Class I corresponds to hybrid systems, in which the two components are combined only by weak interactions like hydrogen bonding. In class II the organic and inorganic components are combined by covalent chemical bonds. In case of Ormocer (organically modified ceramics [2]) and Ormosil (organically modified silica [3]), more specifically, these are hybrid inorganic-organic copolymers belonging to the so-called class II of hybrid materials with strong covalent bonds between the inorganic and organic segments. During the sol-gel process, the first is formation of inorganic network. The organic cross-linking is the final step in the process of preparation of hybrid coating [4,5]. The formation of both networks must proceed in parallel, otherwise the steric problems will come, i.e. problems with spatial coordination of individual segments in cross-linking.

Sol-gel chemistry offers a versatile route to design chemically a great variety of hybrid inorganic-organic materials. Organic polymer components bring good elasticity, tenacity, ductility and low density, while the inorganic components increased hardness, stiffness and resistance to elevated temperature. Together, these components can create hybrid materials, which hold well on metal, polymer and glass substrates. Hybrid materials are chemically stable and they have good abrasion resistance. These features make the hybrid materials very attractive, for example, for the preparation of coatings as protective inhibitor of corrosion for special usage, for face shields or for covers of aircraft cockpit. To achieve an optimum balance of properties of hybrid materials, the separation of phases between organic and inorganic components may not occur. The organic component provides ductility and also allows to increase the thickness of the coatings without cracks significantly and release coating from the surface [6]. On the other hand, excess organic component or poorly developed organic network can cause degradation of mechanical properties of hybrid coatings.

In recent years, a wide variety of papers dealing with enhancement of the mechanical properties of hybrid coatings was reported. Mammeri et al. [7]

studied the inorganic-organic thin coatings, prepared by the condensation of f-PMMA (triethoxysilane functionalized poly(methylmethacrylate)) and a pre-hydrolyzed (in acidic conditions) solution of TEOS (tetraethylorthosilicate). The mechanical properties (indentation modulus and hardness) of the prepared PMMA-SiO₂ hybrid thin coatings measured with nanoindentation depend on the inorganic-organic ratio of PMMA and TEOS [7]. Soloukin et al. [8] described possibility of enhancement of mechanical properties with using of the hybrid cross-linked coatings consisting of polymer methacrylate matrices with dispersed nano-sized silica inorganic particles layed on polycarbonate substrate. Yano et al. [9] investigated a mechanical properties and structure of hybrid systems, which they modified by the polyvinylalcohol/ silica. In the concrete they described, micro-Brownian motion of the organic polymer that was strongly restricted by the inorganic silica network combined with the hybrid matrix on a molecular scale. Thus the mechanical strength of the hybrid coating increased with the content of the silica in the matrix. Huang et al. [10] prepared hybrid material on the base of 3-aminopropyltriethoxysilane with very good mechanical and chemical properties. They mentioned, that the structure and mechanical properties of the hybrid material were significantly affected by the process conditions, such as the amount of catalyst, molecular ratio of inorganic-organic compounds and molecular weight of organic compound. Ochi et al. [11] described possibility of enhancement mechanical properties of hybrid coatings using of epoxy-based inorganic-organic hybrid materials prepared with bisphenol-A type epoxy resin and alkoxy silane as the organic and inorganic sources, respectively. Mechanical properties (hardness and elastic modulus) of hybrid coatings on base TMSPM – TEOS (in original paper for TMSPM used abbreviation MPMS) were investigated [12]. Coatings of 600-800 nm on glass substrates were obtained by dip-coating from hybrid sols with BPO (dibenzoylperoxide) as free-radicals organic initiator of the polymerization and thermal treated to 120 °C. Hybrid materials based on TMSPM with 20-30 wt% TEOS exhibited a good combination of intrinsic values of hardness (0.50 GPa) and brittle index (0.06-0.07), that makes them suitable for coatings of plastic substrates.

Advanced hybrid inorganic-organic materials are currently being intensively studied for their variety of technological applications such as electroluminescent diodes, hybrid liquid crystals, antifogging coatings, abrasive resistant coatings, micro-mechanical systems, anticorrosion coatings, decorative coloured coatings, or composites for dental applications. Ormocers based on light-curable dental composites have been commercially available for use in dentistry since 1988 [13].

The aim of this study was preparation of sols and hybrid coatings on the base of TMSPM and measuring their properties for purpose to apply them as a protective barrier coatings on different types of substrates.

EXPERIMENTAL

Sol synthesis

Inorganic-organic sols were experimentally prepared from TMSPM (3-(trimethoxysilyl) propyl methacrylate, Sigma-Aldrich, 98 %), TEOS (tetraethylorthosilicate, Merck, 98 %) isopropanole (p.a., Penta, 99.9 %), hydrochloric acid, acetic acid and phosphoric acid (2 mol dm⁻³) and deionized water. BPO (dibenzoylperoxide, Sigma-Aldrich, 75 % and 25 % of water for stabilisation) was used as initiator of the free-radicals organic polymerization. Four series of hybrid inorganic-organic sols and one comparative SiO₂ sol were prepared at different molar ratios TMSPM:TEOS 100:0, 75:25, 50:50, 25:75 and 0:100.

In the first step of preparation, used amount of BPO (0.1 g) was dissolved in 24.5 ml of isopropanole being stirred at room temperature for 1-1.5 h. Abreast with dissolving of BPO, calculated amount of TMSPM and/or TEOS (on the resulting content 5.35 g of product as dry matter /100 g of sol) was added to 12 ml of isopropanole in the bulb in aparature and stirred for 30 minutes under the atmosphere of dry synthetic air. Then 0.2 ml of hydrochloric acid (acetic acid or phosphoric acid) of concentration 2 mol dm⁻³ and calculated amount of deionized water (the total volume of water was selected in order to correspond to the molar ratio $[H_2O] / [TMSPM + TEOS] = 2.16$) were mixed with remaining volume of isopropanole (on the general volume of sol 52.5 ml) and this mixture was added at intensive stirring to the solution of TMSPM - TEOS.

The hydrolysis process was performed by a solution of acid and water. The total volume of water was selected in order to correspond to hydrolysis only slightly more than two out of three alkoxide groups formed mainly of linear macromolecules. The process of hydrolysis is followed by much slower process of polycondensation, which forms inorganic 3D network. The obtained mixture was stirred for 30 minutes at room temperature under the atmosphere of synthetic air and the formation of primary macromolecules with bonds Si-O-Si gradually passed in the initial state of the primary sol. After 30 minutes the solution of 0.1 g BPO and 24.5 ml isopropanole was put into the prepared primary sol and the obtained mixture was stirred for 30 minutes at room temperature. Afterwards, the bulb was heated with solution in oil bath (95°C) under the reflux condenser and from this moment the polymerization of methacrylate group of TMSPM started by BPO catalysis at the boiling point of isopropanole at 82°C. Upon reaching the desired level prepolymerization, which is necessary for obtaining of high quality coatings from hybrid sol, the bulb with hybrid sol was cooled in cold water. Then the sol was poured into the polyethylene bottle and stored in the dark place. The stability of sol after its preparation is three weeks.

Preparation of coatings

Hybrid sols were applied on different types of substrates as glass (slide microscopic), corundum (plate from optical material) and metals (polished steel, aluminium foil). All substrates were cleaned before coating in ultrasonic bath with isopropanole. For coating of hybrid sol, method of dip-coating was used. Substrate was dipped into sols and then it was taken out from the sol by defined speed 4 cm min^{-1} . Coatings on the substrates were left for 45 minutes at room temperature. Finally, the substrates with coatings were heat treated at 90°C and 150°C for 3 h. The polymerization was completed by radical mechanism using BPO as the catalyst at 90°C , whereas at 150°C polymerization was completed purely due to the heat treatment.

Measurement of properties

The surface of the prepared coatings was studied with a microscope Field emission SEM Hitachi S4800 at the European Institute of Membranes, Montpellier, France. The thickness and optical properties of hybrid coatings prepared by dip-coating on the plates of optical corundum were calculated from the measured dependence of transmission on the wavelength of light. UV/VIS spectrophotometer GBC Cintra 202 was used for this purpose. The substrate (optical corundum) was chosen for its suitable difference of refractive index between substrate and hybrid coating. Measurements of all types of samples were repeated five times and arithmetic mean was calculated from the obtained results. Differences of refractive index among analogous samples were found up to the value of 0.004. Error of determination of the thickness of hybrid coating reached up to the value of 3 nm. These results were validated by ellipsometry VASE (J. A. Woollam Company) from which we received comparable values and experimental

uncertainties. Mechanical properties of hybrid coatings were tested by ELCOMETER 1720 Washability tester. The charge of frictional segment was 675 g and the speed was 37 cycles per minute. The number of cycles was determined by the control of the moment wearing through coating by means of optical microscope. The morphology of the surface coatings was studied with atomic force microscope NT-206 (Micro Test Machines, Belarus) in contact mode with MikroMasch CSC21/AIBS Si_3N_4 tip (force constant $k = 2 \text{ N m}^{-1}$). For measurement of specific surface and distribution curve of pore size, apparatus Autosorb IQ-MP (Quantachrome Instruments, USA) was used. It was based on nitrogen or krypton adsorption at the temperature of liquid nitrogen.

RESULTS AND DISCUSSION

The properties of prepared hybrid coatings depend on the sol synthesis and subsequent heat treatment and they do not depend on the type of substrate. This fact was confirmed by experiments of chemical and mechanical resistance and FTIR spectroscopy on the different types of substrates. The results obtained from FTIR spectroscopy will be published separately.

Electron microscopy

The samples of coatings prepared on glass, aluminium foil and polished steel after the heat treatment at 90°C or at 150°C were observed by SEM. All of the prepared coatings were of the same appearance and they reproduced surfaces of used substrates. The coating was visible only in the sites where it was mechanically infringed. The example of the coating dipped on the glass substrate and mechanically infringed is documented in Figure 1.

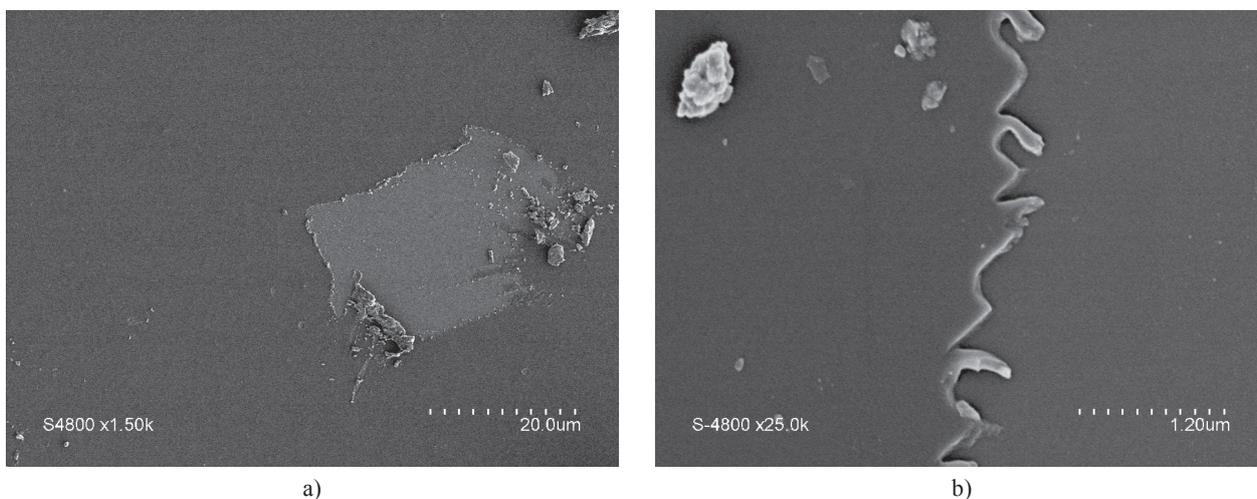


Figure 1. SEM images of coating obtained from the sol of 100 mol % TMSPM (150°C) on glass, purposely infringed coating and detail of edge of infringement.

Thickness and refractive index of hybrid coatings

Concurrently prepared coatings onto optical corundum were used for assesment of refractive index and thickness from the measured dependence of transmission on the wavelength of light on the UV/VIS spectrophotometer. The measurement on the glass substrate was very problematic, the glass substrate has very similar refractive index as the prepared hybrid coating. The results of measurements refractive index of coatings from the sol prepared by acid-catalysis with HCl are summarized in Figure 2. The thickness of these coatings is mentioned in Table 1. Figure 2 clearly shows that the refractive index of coatings for two temperatures of heat treatment slightly decreases with decreasing of content of the TMSPM in the initial sols of TMSPM – TEOS. After the transition to the coating from pure TEOS, the step change starts up. The refractive index of the corresponding coatings from TMSPM that were heat treated at 150°C is higher than in case of the coatings that were heat treated at 90°C. However, refractive index of coatings prepared from the pure TEOS is approximately identical for both temperatures.

The diference of thickness between the corresponding coatings heat treated at 90 °C or 150°C is significant too, and proves the compaction of structure at the completion of polycondensation of inorganic network and polymerization of organic network at 150 °C. In case of the coatings prepared from sols containing TMSPM and heat treated at 150°C, the thickness of the coatings is about 15 to 25 % less than in case of the coatings heat treated at 90°C. In case of the pure silica coatings (100 % TEOS), the difference in thickness is only 3 %, which is at the limit of detection. Table 2 compares the refractive index and thickness of coatings obtained from sols of pure TMSPM.

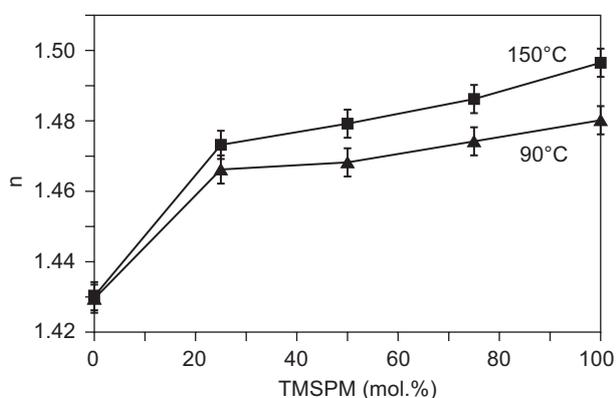


Figure 2. Dependence of the refractive index n (for $\lambda = 500$ nm) on the content of TMSPM in the initial sols of TMSPM - TEOS catalyzed with HCl by different temperature (90 and 150°C) of heat treatment.

The sols were acid-catalyzed by addition of hydrochloric acid, acetic acid and phosphoric acid. The comparison of results shows that the phosphoric acid promotes hydrolysis and polycondensation of alkoxy silane groups similarly as hydrochloric acid, whereas acetic acid is much less effective. The lower degree of polycondensation, sols prepared under identical conditions and catalyzed by acetic acid is strongly reflected in the less thickness of coating (probably thanks to a lower grade of aggregation in sol and also lower viscosity of sol).

Table 1. Thickness of coatings prepared from the sols catalyzed with hydrochloric acid.

content of TMSPM (mol%)	90°C thickness (nm)	150°C thickness (nm)
100	178	154
75	174	144
50	179	143
25	165	138
0	150	145

Table 2. The refractive index n (for $\lambda = 500$ nm) and thickness of coatings obtained from the sols of 100 mol% TMSPM catalyzed with different acids.

acid	90°C		150°C	
	n	thickness (nm)	n	thickness (nm)
hydrochloric	1.480	178	1.496	154
phosphoric	1.491	169	1.496	154
acetic	1.480	94	1.502	85

Abrasion resistance of the coatings

Coatings prepared on the glasses were tested for the abrasion resistance. In the first series, samples that were heat treated at 90°C were tentatively measured. However, as shown, the abrasion resistance of these coatings was very low. Figure 3 shows the results for coatings prepared from the sols catalyzed with hydrochloric acid. Similar values showed the samples that were prepared from the sols catalyzed with phosphoric acid or acetic acid (around 9 cycles). The course of the dependence of the number of cycles on the composition of the initial sol (Figure 3) proves no perceptible dependence.

Much interesting results were obtained in the second series where the samples were thermally processed at 150°C. The results for coatings prepared from the hydrochloric acid catalyzed sols are shown in Figure 4. The samples with coatings that were prepared from the phosphoric acid catalyzed sols (83 cycles) and acetic acid catalyzed sols (130 cycles) also showed similar values. The number of cycles depending on the composition of the sol in Figure 4 shows that the values are similar for the coatings prepared from sols containing

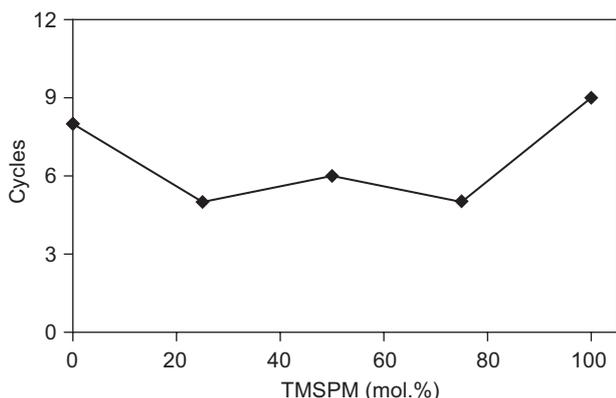


Figure 3. The abrasion resistance of coatings prepared from the acid-catalyzed sols with HCl after heat treatment at 90°C (tentatively measured).

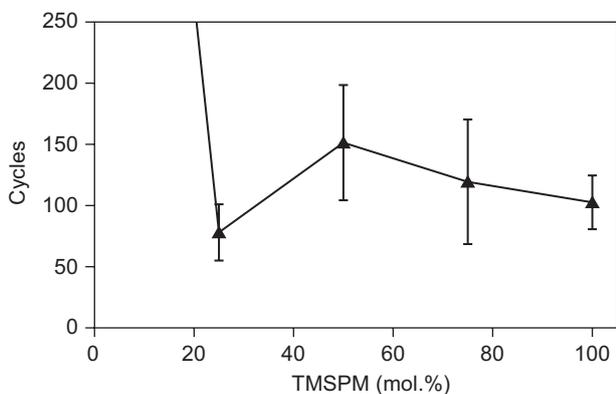
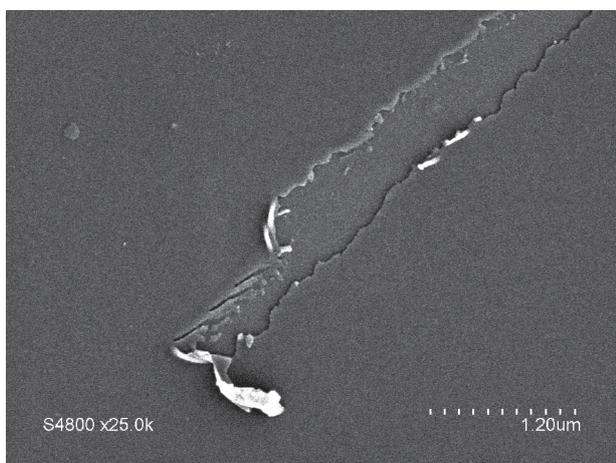


Figure 4. The abrasion resistance of coatings prepared from the acid-catalyzed sols with HCl after heat treatment at 150°C (number of measurements $n = 5$, error abscisse corresponds to the value uncertainty of average on the level of 95 %, the value for pure TEOS is bigger than 1000 cycles).

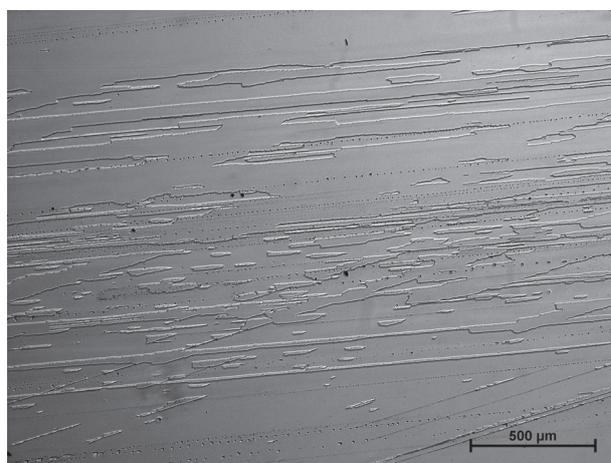
50 mol % TMSPM : 50 mol% TEOS to 100 mol% TMSPM. The coatings prepared from sol containing 25 mol% TMSPM : 75 mol% TEOS are specific with the decrease of resistance, probably evoked due to insufficient interconnected 3D organic network during the disruption of inorganic 3D network. Pure silica prepared from TEOS is again very stable (more than 1000 cycles). In Figure 5, there are documented grooves in the coating after reaching subbase of glass substrate.

Chemical properties of hybrid coatings

In addition to mechanical properties, a chemical resistance of coating prepared from sol of 100 % TMSPM was statically tested at laboratory temperature against various organic and inorganic chemicals. Changes of appearances of coatings were observed visually. The chemical resistance of prepared coatings after the heat treatment at 150 °C on glass and polished steel was excellent against organic solutions (toluene, acetone, isopropanole) for 15 minutes. During the contact with hydrofluoric acid (1:1) or 30% aqueous NaOH solution, the coatings on the both substrates (steel and glass) started to degrade. The coatings on the both substrates were dissolved approximately in 15 minutes. Coating on glass was at least 15 minutes resistant to 96% H₂SO₄, HNO₃ (1:1) or HCl (1:1). On the contrary, the coating on the polished steel was after 5 minutes completely removed after it came in touch with 96% H₂SO₄ or HCl (1:1). The vigorous reaction occurred in about 30 seconds after inserting coated steel into the solution of HNO₃ (1:1). The coating prepared on glass substrate was resistant to 96% H₂SO₄, HNO₃ (1:1) or HCl (1:1), therefore the permanent removal of a coating from polished steel with contact those acids



a)



b)

Figure 5. SEM image of coating obtained from sol of 100 mol % TMSPM (150°C) dipped on the glass after the test for abrasion resistance (on the left). On the right is image the same sample, that has been obtained from the optical microscope.

must be attributed to the penetration of acids through the coating to the surface of metal and the subsequent degradation of metal under the coating. This is also proven by 30-second-reaction delay between the insertion of coated steel in the solution of HNO_3 (1:1) and the beginning of vigorous response.

Surface quality and porosity of the coatings

The surface quality was monitored by SEM (Figure 1) and was already mentioned earlier. According to these images, the coatings were prepared without perceptible defects. AFM was used as another method for

observing the surface quality of coating. Most of the area of coatings showed a very smooth surface with Ra values of 0.4 to 0.9 nm without apparent defects (Figure 6a). These values of Ra are close to the size of atoms and that is why it can be stated that the smoothness of the surface of coating is at the atomic level (more precisely at a few atomic layers). Only a few sites have been identified with defects like pores (Figure 6b), which acids could get into the surface of steel through.

Part of sol 100 % TMSPM was applied in the form of thick coating on the Teflon plate and processed in the same way as coatings (150°C/3 h). Subsequently, the material was removed from the Teflon plate and used for the measurement of specific surface and porosity using nitrogen adsorption. Figure 7 shows the observed

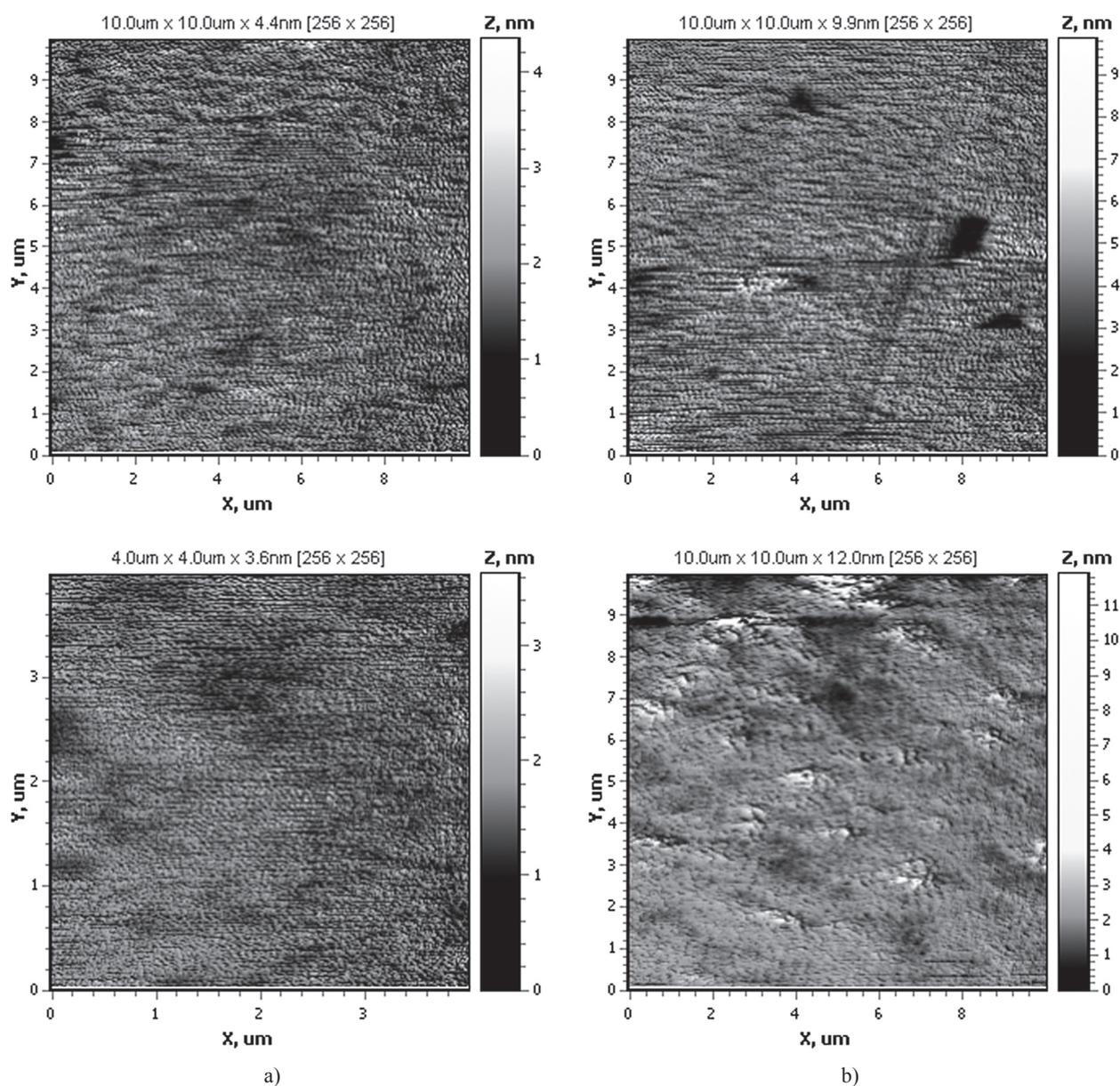


Figure 6. AFM images of coating obtained from sol of 100 mol % TMSPM (150°C) on glass. a) typical appearance, b) dark places present at the hybrid coating were identified as pores.

pore size distribution (BJH method from desorption curve). Diameter range of detected pores is from 3 to 30 nm, with a maximum at 4 nm. The total volume of pores was very small ($1.2 \text{ mm}^3 \text{ g}^{-1}$, balance to the final volume of $1.4 \text{ mm}^3 \text{ g}^{-1}$, it is volume among the particles). The total surface area (determined with the method of multi-point BET) was $1.44 \text{ m}^2 \text{ g}^{-1}$. From the calculations of the porosity (for proper pores) by the BJH method, the value of porosity is $0.8 \text{ m}^2 \text{ g}^{-1}$. For the outer surface of the sample, it remains $0.6 \text{ m}^2 \text{ g}^{-1}$. This value for the broken sample is consistent with the AFM observation of a smooth surface. Checking krypton adsorption measurements gave a value of specific surface $1.58 \text{ m}^2 \text{ g}^{-1}$ (determined with the method multi-point BET) and this value corresponds to the value of nitrogen adsorption.

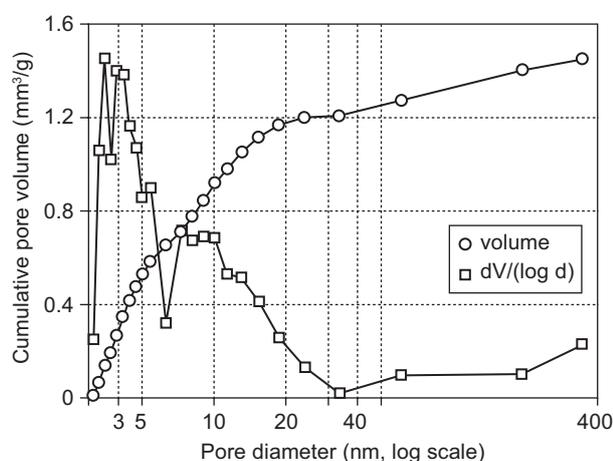


Figure 7. Cumulative volume of pores and the distribution of pore size of the sample obtained from the sol of 100 mol % TMSPM after heat treatment 150°C . Nitrogen adsorption method, BJH method from desorption curve.

CONCLUSION

Coatings on different substrates (glass, corundum and polished steel) were obtained from sols based on TMSPM - TEOS by acid-catalyzed hydrolysis. Subsequently the samples were heat treated at 90°C or 150°C . According to SEM microscopy, the coatings were of high quality, smooth and without perceptible defects. Refractive index of coatings dipped on the corundum substrates is in the range from 1.43 to 1.50 and depends on temperature of heat treatment. The thickness of prepared hybrid coatings is in the range from 85 nm to 180 nm.

The samples prepared from sols containing 50 or more mol% TMSPM and heat treated at 150°C had abrasion resistance around 150 cycles. Coatings dipped on the glass, prepared from 100 mol% TMSPM sol and heat treated at 150°C , had good resistance to various organic and inorganic chemicals, but during the 15 minutes they were destroyed by hydrofluoric acid (1:1) or 30 % NaOH solution. In case of the coatings dipped on the steel, it was found out that they are porous and tested acids can get onto the substrate.

Using AFM, very smooth surface of coatings was confirmed but with isolated defects reminiscent of pores. The existence of small pores (average from 3 to 30 nm) confirmed the determination of pore size distribution from nitrogen adsorption.

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