Rheological characterization of anticorrosion coatings based on 1,2bis(trimethoxysilyl)ethane and trisilanol-heptaisooctyl POSS molecules

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ABSTRACT

In order to find the most appropriate time for application of compact and dense protective coatings, a detailed rheological characterization of sol-gel process was performed. The effect of the addition of POSS on time of gelation was evaluated and the rheological results were combined with IR, electrochemical and surface characterization.

INTRODUCTION

In recent years organosilanes have been a subject of various research studies due to high variability of possible precursor structures, which are composed of inorganic and organic moieties. Appropriate tailoring of precursors can lead to multifunctional materials with desired electrical, optical, mechanical or protective properties¹. Bissilanes are promising organic-inorganic hybrids as an interesting key to either functionalization of metal surfaces or formation of protective coatings. Namely, bis-silanes possess reactive alkoxysilyl groups on both sides of the precursor molecule, which enables an establishment of an extensive cross-linking, bonding to the metal substrate, as well as to the eventual upper-coat. For this reason a simple and short-chain bis-silane 1,2-bis(trimethoxysilyl)ethane (BTMSE)^{2,3} was used for the preparation of anticorrosion coatings for metals. Three silanol groups of trisilanolheptaisooctyl polyhedral oligomeric silsesquioxane (POSS) enabled its covalent bonding into the sol-gel network. Various concentrations of POSS were added to the BTMSE in order to evaluate the influence of POSS to rheological, electrochemical and surface properties of protective coatings.

The protective coatings on the base of BTMSE were prepared through sol-gel process. This is the process of transition from colloidal sol to solid gel, which represents a change in molecular mobility of the polymer matrix⁴. The initial sol (as usually exhibits Newtonian prepared) character with low viscosity. As the sol-gel process continues the Newtonian character of the sol changes to gel, which exhibits altered mechanical rheological and properties. When the sol-gel process is followed continuously (in situ) with rheological measurements, a precise insight of the gelation process, especially the transition from sol to gel structure could be obtained. As a result the exact time of the transition, i.e. gelation time, structural changes and rheological properties of formed gel can be determined. Moreover, the viscoelastic properties of formed gels, i.e. the proper balance between elastic and viscous contribution is particularly important in order to achieve the best barrier efficiency tested electrochemical by techniques. Accordingly, the application of the coating on the substrate has to be performed at precise time of gelation

process, which can be exactly determined from continuous rheological measurements.

EXPERIMENTAL

Preparation of sols and coatings

Four sols were prepared and applied on the aluminium substrate. In Table 1 weight masses of all components for the preparation of the sols are presented. Trisilanolheptaisooctyl POSS was added to BTMSE precursor in three concentrations, i.e. in weight ratios BTMSE:POSS = 1:0, 1:0.5,1:1 and 1:1.5, respectively. The sol-gel catalyst, i.e. 0.1 M HCl, was added with regard to the quantity of methoxy groups in organic-inorganic hybrid BTMSE. The sols were stirred up to 30 min in order to get a homogeneous mixture. The coatings were deposited on AA 2024 aluminium alloy via dip-coating technique with pulling velocity of 10 cm/min. After the application the coatings were thermally treated at 150 °C for 30 min.

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	BTMSE:POSS					
Component	1:0	1:0.5	1:1	1:1.5		
BTMSE [g]	1.35	1.35	1.35	1.35		
TS-iOc ₇ -POSS [g]	/	0.68	1.35	2.03		
2-PrOH [g]	5	5	5	5		
0.1 M HCl [g]	0.5	0.5	0.5	0.5		

Spectroscopic measurements

IR absorbance spectra were measured on a Bruker model IFS 66/S spectrometer. The sols were deposited on partly IR transmissive silicon wafers and the spectra were recorded in several time intervals in order to follow sol-gel reactions of hydrolysis and condensation. The spectra were recorded before the addition of 0.1 M HCl catalyst (t=0) and at t=5 min and t = 30 min after the addition of catalyst. Similar spectroscopic measurements were performed also on the coatings after thermal treatment (150 °C for 30 min).

Potentiodynamic (PD) measurements

Electrochemical potentiodynamic polarisation of the coatings on the AA2024 substrates was performed on Autolab PGSTAT302N potentiostat-galvanostat in a cell K0235 (Princeton Applied flat Research). 0.5 M NaCl was used as an electrolyte, while the working, reference and counter electrodes were on the investigated coatings on AA 2024, Ag/AgCl/KClsat and Pt grid. The coatings were held at open circuit potential 1800 s prior to the linear sweep of the potential with a scan rate 0.5 mV/s from -1 V to more positive direction.

Contact angle measurements

The contact angle measurements were performed at ambient temperature on a Theta tensiometer from Biolin Scientific with three different liquids (water, diiodomethane, formamide). A 4 μ l droplet of liquid was gently deposited on the sample with a micro-syringe. The surface free energy value was determined on the basis of the measured contact angles. Acid-base model was used for the calculations.

Rheological measurements

Rheological characterization was performed with controlled rate rheometer Physica MCR 301 (Anton Paar) equipped with a cone-plate geometry sensor system (CP50/2°). Standard rotational flow tests were performed with a triangular method by changing shear rate from $1 - 500 - 1 \text{ s}^{-1}$. Oscillatory stress sweep tests at constant frequency of oscillation (1 Hz) were used in order to determine the linear viscoelastic range (LVR).

The transition from sol to gel was followed continuously through small amplitude oscillatory tests (in LVR) at constant frequency of oscillation ($\omega = 1$ Hz). In order to avoid solvent evaporation during gelation process the sensor system was protected with a special cover. The temperature of all measurements was kept constant at 23 °C. ANNUAL TRANSACTIONS OF THE NORDIC RHEOLOGY SOCIETY, VOL. 24, 2016

RESULTS AND DISCUSSION

IR absorbance measurements

The IR absorbance spectroscopy was used in order to follow hydrolysis and condensation reactions in the sols. The results of spectroscopic measurements for all sols, used in the study, are presented in Fig. 1. The most striking change in the set of spectra appeared immediately after the addition of the sol-gel catalyst, i.e. 0.1 M HCl. Namely, the bands of the methoxy groups (2944, 2840, 1193, 1087 and 809 cm^{-1})⁵ of the BTMSE precursor disappeared from the spectrum, which was recorded 5 min after the catalyst addition. The band of the silanol groups at 910 cm^{-1} evolved instead⁵. The most intensive bands of 2-propanol solvent contribute at 3346, 1162, 818 cm⁻¹, which can be observed in all four sols⁵. In the sols, where POSS molecules were added, the symmetric v_s (Si-O-Si) stretching of POSS cubes at 484 cm⁻¹ could be observed. The influence of $v_a(Si-$ O-Si) stretching of POSS cubes at 1105 cm⁻¹ is less obvious due to the overlapping with siloxane modes of condensed methoxy BTMSE3,5,6,7 precursor of groups Additionally, the bands of POSS appeared at 1226, 1365, 1475, 2950 cm⁻¹ and increased intensity with the content in of 1)8 cubes (Fig. silsesquioxane The spectroscopic measurements give a lot of information about chemical changes that occur during sol-gel process, however, they don't enable any information about the structural changes and the progression of the sol-gel process. That was obtained with in situ rheological measurements.



Figure 1. IR absorbance spectra of BTMSE sols before and after the addition of 0.1 M HCl. The spectra of thermally treated coatings are also added.

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Rheological measurements

The initial sols were characterized with rheological measurements immediately after the preparation. All sols as prepared exhibited Newtonian flow behaviour with low viscosity (Fig. 2) and absence of elastic contribution. The sols were prepared by the same procedure and were measured at the same time after the preparation. The sol POSS without molecules (BTMSE) exhibited the lowest viscosity, while the viscosities of the sols with the addition of POSS molecules gradually increased as the amount of POSS increased.



Figure 2. Flow curves for initial BTMSE sols with and without POSS.

The initial sols were immediately after the preparation applied into the sensor system of the rheometer Physica MR 301. The sol-gel process was followed in situ in linear viscoelastic range at constant frequency of oscillation 1 Hz. The results of time dependence of viscoelastic moduli (G' and G") are presented in Fig. 3. For all the samples the initial sols exhibited only viscous contribution (loss modulus G'') to behaviour, viscoelastic which at the beginning of the sol-gel process only slightly increased with time. At certain time, depending on the sample, the elastic contribution (storage modulus G') became noticeable. Furthermore, a sudden increase of G' was noticed in a short time. At this point also the loss modulus strongly increased, but, compared to the storage modulus, less intense increase was observed. For all the samples the crossover point could be detected. At this point, the gelation time, i.e. the transition from sol to gel, was determined. Gelation time was defined as the time, when the values of dynamic moduli equalled (G' = G'').



Figure 3. *In situ* rheological measurements in linear viscoelastic range.

Since the vViscoelastic behaviour of the sols during sol-gel process could be presented also with phase shift angle δ (Fig. 4).



shift angle for BTMSE sols.

The Newtonian behaviour of all initial sols is expressed as $\delta = 90^\circ$, while the formed gels exhibited δ close to 0° , regardless of the amount of POSS molecules added. We can conclude that the addition of POSS molecules to BTMSE sols decreased the time, required for sol to gel transition; however, the structure of the formed gels remained similar. All formed gels exhibited viscoelastic solid-like and brittle gel structure with high elastic modulus G' and negligible viscous contribution G''.

The viscosities of initial sols and the times, determined as the gelation times, are presented as a function of the addition POSS molecules to BTMSE mixtures (Fig. 5). As the amount of POSS added to the BTMSE mixture increased, the gelation time significantly decreased. Consequently, the gelation started faster and hence the viscosity of the initial sols increased.



Figure 5. Viscosities of initial sols and gelation times for BTMSE sols with various amounts of POSS.

Electrochemical and surface characterization of the coatings

Surface characterization of the coatings, applied on the AA2024 substrate and thermally treated at 150 °C, showed that the increasing amount of POSS increased the contact angles for water, regardless of the amount of POSS (Table 2). Similarly, in the same order, the contact angles increased also for formamide and diiodomethane. The comparison of the total surface energy of AA2024 alloy and deposited BTMSE coatings showed that the surface energy was for all coatings lower compared to the AA2024 substrate. The addition of TS-iOc7-POSS molecules significantly decreased the total surface energy, which was the lowest for the coating with BTMSE:POSS = 1:1 (25.68 mJ/m²). The highest amount of POSS (weight ratio 1.5) caused slightly higher total surface value, which indicates the excessive addition of the POSS.

Table 2. Contact angles of BTMSE coatings.

Coating	θ (°)				
	H ₂ O	CH_2J_2	HCONH ₂		
AA 2024	100.4	51.0	71.9		
BTMSE	77.7	61.0	63.3		
BTMSE-0.5 TS-iOc ₇ -POSS	104.4	60.3	84.9		
BTMSE-1.0 TS-iOc ₇ -POSS	104.9	63.4	86.2		
BTMSE-1.5 TS-iOc ₇ -POSS	103.9	60.4	87.1		

Table 3. Surface energy values of BTMSE coatings.

Coating	τ+	τ	$\boldsymbol{\tau}^{\mathrm{LW}}$	$ au^{AB}$	$\mathbf{\tau}^{\mathrm{tot}}$
AA 2024	0.2	0.4	33.7	0.1	33.8
BTMSE	0.4	10.2	28.0	4.2	32.2
BTMSE-0.5 TS-iOc ₇ - POSS	-0.5	1.0	28.4	-1.0	27.4
BTMSE-1.0 TS-iOc ₇ - POSS	-0.5	1.0	26.6	-0.9	25.7
BTMSE-1.5 TS-iOc ₇ - POSS	-0.8	1.3	28.3	-1.9	26.4

Potentiodynamic polarisation measurements (Fig. 6) showed that the increasing content of POSS positively influenced the protective properties of BTMSE coatings. The cathodic current density decreased by about one and half order of magnitude for BTMSE, while these decrease increased to three orders of magnitude for the coatings with the highest amount of POSS (BTMSE-1.5 TS-iOc7-POSS). The drop in anodic current densities

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could also be noted, specifically for the samples with weight ratios BTMSE:POSS = 1:1 and 1:1.5. For these samples the anodic current densities decreased for six orders of magnitude.



Figure 6. Potentiodynamic curves for BTMSE coatings on AA2024 alloy.

CONCLUSIONS

The results showed that POSS molecules had a great impact on the sol-gel process as well as on electrochemical and surface properties of the protective coatings. For BTMSE coatings higher amount of POSS decreased the sol to gel transition time, while the viscoelastic properties of formed gels with various POSS amounts were comparable. The increasing amount of POSS raised the contact angles for water to 104° for the coating with higher amount of POSS. Similarly, in the same order, the contact angles were also increased for formamide and diiodomethane. Potentiodynamic polarization measurements showed that the increasing content of POSS positively influenced the electrochemical properties of BTMSE coatings.

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