

Article

The Effect of the Methyl and Ethyl Group of the Acrylate Precursor in Hybrid Silane Coatings Used for Corrosion Protection of Aluminium Alloy 7075-T6

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Abstract: This study investigated polysiloxane hybrid sol-gel coatings synthesized from tetraethyl orthosilicate (TEOS), 3-(trimethoxysilyl)propyl methacrylate (MAPTMS) and two different precursors, i.e., methyl- or ethyl- methacrylate (MMA or EMA), as corrosion protection of aluminium alloy 7075-T6. The hypothesis was that the additional alkyl group might affect the chemical properties and, consequently, the corrosion properties. Synthesis of the sols proceeded in two steps, each involving either MMA or EMA in the same molar ratio. The resulting sols, siloxane-(poly(methyl methacrylate-co-MAPTMS)) or siloxane-(poly(ethyl methacrylate-co-MAPTMS)), were applied on aluminium alloy followed by characterization in terms of chemical structure and composition, topography, wettability, adhesion and corrosion resistance in 0.1 M sodium chloride solution. The chemical properties of sols, monoliths and coatings were investigated using Fourier transform infrared spectrometry, solid state nuclear magnetic resonance spectrometry, X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry. Coatings were similar in terms of surface topography, while the wettability of the coating with EMA showed 6° greater water contact angle compared to the coating with MMA. Both coatings were shown, by electrochemical impedance spectroscopy in 0.1 M NaCl solution, to act as barriers to protect the underlying substrate in which coating with EMA exhibits better protection properties after 2 months of immersion. Adhesion tests confirmed the highest grade of adhesion to the substrate for both coatings. Testing in a salt-spray chamber demonstrated excellent corrosion protection, where coatings remaining intact after more than 600 h of exposure.

Keywords: aluminium alloy AA7075-T6; methyl methacrylate; ethyl methacrylate; MAPTMS; coating; sol-gel; silane; corrosion

1. Introduction

Chromate conversion coatings have been used as common protection or primer coatings for aluminium alloys. Their use is nowadays limited and is expected to be replaced completely by other types of protective coating which are environmentally acceptable and not toxic like hexavalent chromium [1]. To achieve complete withdrawal of chromate coatings from the market, numerous studies have been dedicated to the development of alternative coatings that would exhibit

comparable anti-corrosion characteristics and add further functionalities, including self-healing, improved mechanical strength, adhesion, hydrophobicity, etc. Hybrid sol-gel coatings show promise as alternatives for corrosion protection. Most of the studies have been carried out on aluminium and steel substrates coated with siloxanes based on tetraethoxy orthosilicate (TEOS), (3-glycidyloxypropyl)trimethoxysilane (GPTMS) or 3-(trimethoxysilyl)propyl methacrylate (MAPTMS) as the most commonly used precursors [2]. The combination of MAPTMS and methyl methacrylate (MMA) leads to the formation of polymer network consisting of poly(methyl methacrylate) (PMMA) as organic component and siloxane-based component originating from TEOS [3–6]. When deposited, these polymerized networks form dense coatings which assure excellent adhesion and corrosion properties on tin coated steel [3], stainless steel [4] and carbon steel [5–7] after long-term immersion in saline solution. Combinations of inorganic (TEOS) and organic (MAPTMS and MMA) precursors have been optimized [3–6], especially with respect to the optimal molar ratios between precursors. It has been reported that the ideal ratio for TEOS to MAPTMS is 2 [4], for MMA to MAPTMS is 8 [5] and for ethanol to H₂O is 1:2 [6]. The resulting transparent coatings have, after six months in 3.5% NaCl, yielded the best corrosion performances with impedance values of around 10 GΩ cm² at frequency of 10 mHz [6]. By increasing the ratio between thermal initiator benzoyl peroxide (BPO) and MMA, the polymerization efficiency can be improved [8]. Some sol-gel coatings were doped in order to increase their cross-linking, increase adhesion to the metal substrate, or to improve scratch resistance and thermal stability [7,9–14].

The aim of the present work was twofold. The first aim was to study the chemical, physical, electrochemical and corrosion properties of hybrid methyl methacrylate-based sol-gel coatings deposited on aluminium alloy AA7075-T6. Hybrid sols have been prepared using TEOS and MAPTMS in the optimum ratio [5]. Since previous studies on these type of coatings were carried out on steel-based substrates [3–6] and less on Al-based substrate [8,15], we focused this study on aluminium alloy (AA) 7075-T6 substrate. This particular alloy was chosen because it is the least corrosion resistant among alloys used in the aviation industry. Aluminium alloys have many outstanding physical and mechanical properties, i.e., high toughness, high strength-to-weight-ratio and low density, and are used widely in a variety of industrial applications [16–18]. However, aluminium alloys are more susceptible to corrosion compared to aluminium metal, in particular to localized galvanic processes that take place between the various intermetallic particles (IMPs) within the aluminium matrix [19,20]. The AA7075-T6 contains IMPs with zinc, magnesium and copper as the main elements. These IMPs in aluminium matrix increase the strength of the material but, on the other hand, decrease the corrosion resistance due to localized galvanic effects [6].

The second aim and a further novelty compared to previous studies [3–6] was the use of two types of acrylates: not only methyl methacrylate (MMA) but also ethyl methacrylate (EMA) was used. The purpose was to determine whether addition of an alkyl group affects chemical and/or protective properties. Among the chemical properties, chemical composition, bonding and degree of polycondensation were investigated using FTIR (Fourier transform infrared spectroscopy), ¹³C and ²⁹Si CP/MAS NMR (cross polarization magic angle spinning nuclear magnetic resonance spectroscopy), XPS (X-ray photoelectron spectroscopy) and ToF-SIMS (time-of-flight secondary ion mass spectroscopy). A combination of these methods enabled the mechanism of sol-gel coating formation to be elucidated. Among the physical properties of the coatings, the water contact angle and adhesion to the substrate have also been measured. Electrochemical properties were determined using long-term electrochemical impedance spectroscopy in 0.1 M NaCl. Standard corrosion testing in a saline medium was also conducted in the form of salt spray testing in 5 wt % NaCl.

2. Materials and Methods

2.1. Preparation of Coatings

2.1.1. Substrates and Chemicals

The metal used as substrate was aluminium alloy AA7075-T6 (UNS A97075; ISO AlZn_{5.5}MgCu) in the form of 0.5 mm thick sheet (Kaiser Aluminium, Lake Forest, CA, USA). The chemical composition of substrates is given in Table 1. Samples were cut in a rectangular shape 4 cm long and 2 cm wide.

Table 1. The substrate composition of AA7075-T6, as provided by manufacturer.

Nominal Composition (wt. %)	Si	Fe	Cu	Mg	Zn	Cr	Other	Al
AA7075-T6	0.08	0.21	1.67	2.55	5.81	0.19	0.08	89.41

Samples were freshly polished with SiC emery papers (Struers, Ballerup, Denmark) of up to 4000-grit, rinsed with deionized water, cleaned ultrasonically in ethanol for 3 min, then dried in a stream of nitrogen before the deposition of sol.

The corrosive medium for electrochemical measurements was 0.1 M NaCl (pH = 5.7), prepared from analytically pure NaCl (Sigma Aldrich, ≥98%), and Milli-Q Direct water with a resistivity of 18.2 MΩ·cm at 25 °C (Millipore, Billerica, MA, USA).

The following chemicals were used for the synthesis of sols: tetraethyl orthosilicate (TEOS, ≥99%, Aldrich), (3-(trimethoxysilyl)propyl methacrylate) (MAPTMS, 98%, Aldrich), tetrahydrofuran (THF, 99.8%, Alfa Aesar), benzoyl peroxide (BPO, 97%, Alfa Aesar), methyl methacrylate (MMA, 99%, Acros Organics), ethyl methacrylate (EMA, 99%, Aldrich) and ethanol (absolute, Carlo Erba). The MMA was distilled three times to remove the inhibitor that prevents the monomer from polymerizing.

2.1.2. Synthesis of Sols

Hybrid inorganic-organic sol-gels were synthesized by mixing two separately prepared solutions in molar ratios of MAPTMS:TEOS:MMA/EMA:H₂O:BPO:EtOH:THF of 1:1.77:7:10.5:0.07:5:47. The first sol (Sol 1) was prepared by dissolving BPO in THF at room temperature. The appropriate derivative of acrylate ester and MAPTMS was then added to the flask and heated at 70 °C under reflux for 4 h. The reaction mixture was then allowed to cool down to room temperature. Meanwhile, the second sol (Sol 2) was prepared from TEOS, ethanol and water acidified to pH = 1 with nitric acid. The sol was then stirred for 20 min at room temperature [5].

The second sol was then mixed with the first sol (Sol 1 + Sol 2) and stirred for a further 1 h to give the final sol used for deposition. Depending on the acrylate ester derivative used for the reaction, the sols were denoted as siloxane-PMMA (siloxane-(poly(methyl methacrylate-co-MAPTMS))) or siloxane-PEMA (siloxane-(poly(ethyl methacrylate-co-MAPTMS))).

2.1.3. Deposition of Coatings

Immediately after synthesis, sols were deposited, by dip-coating (Bungard, RDC15), onto the substrate, which had been prepared as described in Section 2.1.1. One layer was applied at a constant immersion (10 s) and withdrawal rate of 14 cm min^{−1}. After deposition, the samples were heated on a hot plate, initially at 60 °C for 1 h and then, for a further 1 h, at 180 °C, in order to complete the polymerization/condensation process of the prepared coating. The resulting coating was homogeneous and transparent. Denotation of the coating was the same as that for the sols, i.e., siloxane-PMMA and siloxane-PEMA.

2.2. Characterization of Sols

2.2.1. FTIR

Fourier transform infrared (FTIR) spectra of the initial monomers, precursors, solvents and final sols after synthesis were recorded using a PerkinElmer Spectrum 100 instrument with the attenuated total reflection (ATR) sampling accessory, where the drops were applied on the sensor top-plate of the instrument. The spectra were recorded from 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1} , averaging 4 scans. Spectra were normalised and are presented as absorbance units (A.U.). The results are presented in the range from 1800 to 700 cm^{-1} , within which the bands of most interest appear.

2.2.2. CP/MAS NMR

^{13}C and ^{29}Si Solid-state Cross-Polarization Magic Angle Spinning Carbon-13 and Silicon-29 Nuclear Magnetic Resonance (CP/MAS NMR) spectra were recorded using a 600 MHz Varian NMR System equipped with a 3.2 mm Varian MAS probe head. Larmor frequencies for ^{13}C and ^{29}Si nuclei were 150.751, and 119.088 MHz, respectively. Chemical shifts of the two types of nuclei were reported relative to the signals of these nuclei in tetramethylsilane. Relaxation delays and sample rotation frequencies for both types of measurement were 2 s and 20 kHz. CP contact times were 4 and 5 μs for ^{13}C and ^{29}Si CPMAS measurements, respectively. The high sensitivity of the ^{29}Si and ^{13}C NMR measurements results in an uncertainty in the chemical shift values of less than 0.2 ppm.

For analysis, sols were prepared as described in Section 2.1.2, then treated thermally as described in Section 2.1.3. The dried sols (i.e., monoliths) were then ground to a powder to maximize homogeneity of the samples, as required for CP/MAS NMR analysis. The NMR analysis was carried out in at least triplicate and the representative spectra plotted.

Experimental ^{29}Si CP/MAS NMR spectra were fitted manually; each measured peak being fitted with a linear combination of three pseudo-Voigt functions, using a non-linear least squares method. The ratio of the area of each separate component to that of the total area of the fitted curve was then determined. To estimate the error incurred by the fitting procedure, the area under the fitted peak was compared with that of the experimentally measured peak. The maximum difference in area determined in this way amounted to approximately 0.3% and the average difference in the areas to about 0.1%. In this way, an error of 1% was estimated in the determination of the fraction of each constituent.

2.3. Characterization of Coatings

2.3.1. XPS and ToF-SIMS

X-ray photoelectron spectroscopy (XPS) was carried out using a PHI-TFA XPS spectrometer (Physical Electronic Inc., Chanhassen, MN, USA). The vacuum during the XPS analysis was in the range of 10^{-9} mbar. The area analysed was 0.4 mm in diameter and the corresponding depth about 3–5 nm. X-rays were produced by a monochromatic Al source at a photon energy of 1486.6 eV. Survey and high-energy resolution spectra were recorded. The high-energy resolution spectra were acquired with an energy analyser operating at a resolution of ca. 0.6 eV and pass energy of 29.3 eV. XPS spectra were analysed using Multipak software, version 8.0 (Physical Electronics Inc.). During data processing the spectra were corrected by setting the C 1s peak to a binding energy (E_b) of 248.8 eV, characteristic of C–C/C–H bonds. The accuracy of the binding energies was ± 0.3 eV. Survey XPS spectra were used to deduce the elemental composition of the coatings, based on the total intensity of particular element peaks and using values of atomic sensitivity factors, C 1s = 0.857, O 1s = 2.51, Si 2p = 0.790 [21,22].

ToF-SIMS analysis was performed using a ToF-SIMS 5 instrument (ION-TOF, Münster, Germany) equipped with a bismuth liquid metal ion gun with a kinetic energy of 30 keV. The analyses were performed under an ultra-high vacuum of approximately 10^{-7} Pa. SIMS spectra were measured by scanning a Bi_3^+ cluster ion beam over areas $200 \times 200 \mu\text{m}^2$. The beam current was 0.6 pA and the total measuring time taken to acquire the SIMS spectra, 30 s. The dose of the primary ions during

the measurements was that used in the static regime. The SIMS spectra were processed using the SurfaceLab 6.7 (ION TOF) software. The positive secondary ion mass spectra were calibrated using CH_3^+ (mass to charge ratio (m/z 15.02), C_2H_3^+ (m/z 27.02) and C_2H_5^+ (m/z 29.02), and the negative mass spectra were calibrated using C^- (m/z 12.00), C_2^- (m/z 24.00) and C_2H^- (m/z 25.01). The mass resolution $m/\Delta m$ during the SIMS measurements was ca. 10,000. For each sample, spectra were acquired at three spots to ensure reproducibility. An electron gun was used to prevent charging on the sample surfaces during the analysis.

2.3.2. Coating Thickness, 3-D Topography, Adhesion and Water Contact Angle

3-D topography was determined at the surface (1 mm $\times$ 1 mm) of uncoated and coated substrates, using a Bruker DektakXT (Vienna, Austria) profilometer with a tip diameter 2 μm . The recording resolution was 0.167 μm /per point. The instrument has a lateral resolution of 1 μm and vertical resolution of 5 nm. The surface profile was measured in one direction. Measurements were performed on at least three locations of each sample using a 1 mm² spot. Data were processed with TalyMap Gold 6.2 software to create 3-D surface topography and to calculate the mean surface roughness (S_a). Results are presented as average value $\pm$ standard deviation. Corrections were made to exclude general geometrical shape and possible measurement-induced misfits.

The same instrument was used to determine coating thickness according to the following procedure: 2 cm from the sample edge on the long, vertical side using a diamond tip with $\sim 100 \mu\text{m}$ diameter to reach the substrate surface. This initiated the delamination of the coating. Along the delaminated coating, a 3D map was made to scan the area and to determine the step which would accurately represent the coating thickness as the step height. The procedure was repeated at least five times at different spots and the reported value is given as average value $\pm$ standard deviation. Since the substrate is smooth ($S_a = 0.056 \mu\text{m}$), we can claim that area below the layer is the substrate.

The level of adhesion of the coatings to the aluminium-based substrates was evaluated using a Cross-Hatch Adhesion tester (ASTM D3359-09 [23]). Coatings were first cut with a cutter blade, making two rectangular cuts. The whole sample was then covered with a strong adhesive tape (#810 ScotchMagicTM) and tightened against the surface. The adhesive tape was then stripped off slowly. The level of adhesion was evaluated and depended on the amount of fragments removed from the coatings, according to the ASTM D3359-09 standard, on a scale from 0B to 5B, (Grade 5 signifies no detachment, Grade 4, less than 5% of the area is affected; Grade 3, the area affected is 5% to 15% of the lattice; Grade 2: the area affected is 15% to 35% of the lattice; Grade 1: the area affected is 35% to 65% of the lattice; Grade 0: the area affected is more than that signified by Grade 1). For further analysis, the cross sections were examined more closely by confocal microscopy (Axio, CSM 700, Zeiss, Göttingen, Germany) with 20 $\times$ magnification. The range of vertical measurement was 10 μm , with a resolution of 0.05 μm .

The contact angles of drops (8 to 10 μL) of deionized water were measured using the Krüss EasyDrop DSA 20E (Hamburg, Germany) instrument equipped with DropShape software (1.92.1.1). The resolution of the instrument was 0.1°. The fitting of the baseline was performed manually, and the calculation of the contact angle was performed within the program. Measurements were performed at least ten different sites to obtain the most representative value.

2.3.3. Electrochemical Measurements

Electrochemical measurements were performed at room temperature in a three electrode corrosion cell (Flat Cell, Ametek PAR, Oak Ridge, TN, USA; volume 250 mL). The working electrode was either bare or a coated aluminium-based substrate with 1.0 cm² of its surface exposed to the corrosive medium. A platinum mesh was used as a counter electrode and the reference electrode was saturated Ag/AgCl, ($E = 0.197 \text{ V}$ vs. a standard hydrogen electrode). In the text, all potentials refer to the Ag/AgCl electrode.

Measurements were carried out with a potentiostat/galvanostat Autolab PGSTAT 302 (Metrohm Autolab, Nova[®] software 2.1.3, Utrecht, The Netherlands). For each sample, measurements were

performed in at least triplicate. A representative measurement was chosen and presented in plots, the parameters being given as mean values $\pm$ standard deviation. All electrochemical experiments were performed in 0.1 M NaCl.

Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range from 100 kHz to 4 mHz at a sinusoidal AC voltage amplitude of 10 mV. The EIS spectra were recorded at the E_{oc} after 1, 35 and 65 days' immersion. Measurements were repeated three times; representative curves are presented in graphs and results reported as average value $\pm$ standard deviation. The experimental data were fitted using the complex non-linear least squares (CNLS) fit analysis software [24] using Nova 2.1.3[®] software (Utrecht, The Netherlands).

2.3.4. Salt Spray Test

A salt spray chamber with 170 L volume was used (model ASCOTT). The test was performed according to the specification of the standard ASTM B117-07a [25]. The neutral salt spray test was selected as the standard method.

The spray solution was 5 wt. % sodium chloride. The total test duration was 25 days (600 h). The brine collected in the chamber during the test had a pH between 6.5 and 7.2. The test was carried out at 35 °C. Samples were placed in the chamber at an angle of 70° and protected with tape around the edges to prevent retention of the brine.

Specimens were inspected every 24 h. At the end of each time period, all the samples were taken out, rinsed with distilled water and dried in a stream of nitrogen. Corrosion damage was evaluated by visual analysis performed according to the standard ASTM D 610-01 [26]. The rust grade ranged from 0 (more than 50% surface area rusted) up to 10 (less than or equal to 0.01% surface area rusted).

3. Results and Discussion

3.1. Chemical Composition, Bonding and Mechanism of Formation of A Sol-Gel Network

FTIR spectroscopy was used to compare the FTIR spectra of initial chemicals, i.e., monomers MMA and EMA, precursors MAPTMS and TEOS and solvents THF and ethanol, with that of siloxane-PMMA and -PEMA (Figure 1, Table 2). The aim was to differentiate the chemical composition and bonding and get an insight into the mechanism of formation of a sol-gel network. The spectra are presented in the region from 1800 to 700 cm^{-1} , where several bands reflecting the characteristic bonds for (poly)acrylates, alkyl chains and silyl/siloxane bonds are located.

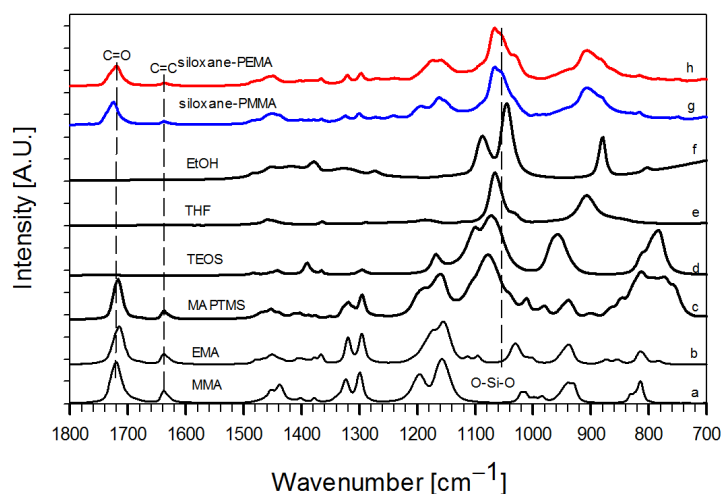


Figure 1. FTIR absorption spectra of (a) MMA, (b) EMA, (c) MAPTMS, (d) TEOS, (e) THF, (f) EtOH, (g) siloxane-PMMA and (h) siloxane-PEMA sols. Spectra were recorded for freshly prepared sols without further curing treatment.

Table 2. The main bands in FTIR spectra for initial MMA and EMA monomers, TEOS and MAPTMS precursors, siloxane-PMMA and siloxane-PEMA sols and solvents.

Monomers, Precursors, Solvents and Sols.	Wavenumber (cm ⁻¹)
MMA	1720, 1638, 1452, 1438, 1325, 1300, 1198, 1158, 1015, 939, 930, 832, 813
EMA	1715, 1638, 1452, 1405, 1364, 1318, 1298, 1173, 1158, 1032, 938, 815
MAPTMS	1720, 1640, 1455, 1407, 1323, 1297, 1190, 1162, 1081, 1014, 980, 940, 816, 792, 775, 755
TEOS	1392, 1169, 1100, 1075, 960, 812, 785
THF	1461, 1365, 1065, 1030, 908
Ethanol	1382, 1088, 1047, 880
water	1638
siloxane-PMMA	1055
siloxane-PEMA	1055

Monomer MMA exhibits several characteristic bands for carbonyl group C=O at 1720 cm⁻¹ conjugated to double bond C=C at 1638 and 815 cm⁻¹, stretching vibrations of C–O–C bond at 1198 and 1158 cm⁻¹ and the CH₂/CH₃ band at 1452, 1325, 1300 and 832 cm⁻¹ (Figure 1a,b, Table 2). EMA exhibits similar spectrum, but bands are slightly shifted for few wavenumbers (Figure 1a,b, Table 2). The only difference can be seen in the shape and in the intensity of C–O–C at 1198 and 1158 cm⁻¹ band due to a longer alkyl chain in EMA.

MAPTMS exhibits many characteristic bands similar to MMA/EMA due to the presence of acrylate group (Figure 1c, Table 2). Additionally, the band at 1081 cm⁻¹ in the spectrum is assigned to Si–O–C and C–O bonds. Band at 816 cm⁻¹ corresponds to the stretching mode of Si–C bond [27].

The most important of TEOS are bands at 1169, 1100, 1075, 960, 812 and 785 cm⁻¹ corresponding to the –CH₃ group, and those at 1100 and 1075 cm⁻¹ assigned to Si–O–C symmetrical stretching in linear structures and to C–O asymmetric stretching (Figure 1d, Table 2).

In the first step of sol-gel preparation (Sol 1), the polymerisation process between acrylate groups (MMA or EMA and MAPTMS) in the presence of BPO radicals took place. Due to dilution in THF, only the evolution of characteristic bands for acrylates (carbonyl group C=O at 1720 cm⁻¹ conjugated to double bond C=C at ~1640 cm⁻¹) was compared between initial reagents (Figure 1a,b, Table 2) and final siloxane-PMMA and -PEMA sols (Figure 1g,h, Table 2). The polymerisation process is thermally activated at 70 °C and proceeded during 4 h of mixing. According to the spectra of the final sols (Figure 1g,h), the polymerisation process occurred to a certain degree as evidenced by a lower intensity of C=C bands at 1640 cm⁻¹ and slightly shifted carbonyl group C=O to higher wavenumbers (from 1720 cm⁻¹ to 1740 cm⁻¹) due to fewer conjugated interactions between C=O and C=C [28,29]. For both siloxane-PMMA and -PEMA solutions, the characteristic bands for the polymerisation process at 1240 and 1270 cm⁻¹ (they have low intensities) assigned to asymmetric and symmetric stretching vibrations of C–O and C–O–C bonds appeared. The band at 1640 cm⁻¹ related to C=C bond was present in the spectra, confirming that the polymerisation process was not completed. Unfortunately, the polymerisation degree is difficult to evaluate due to overlapping of the C=C band with a band characteristic for water (1638 cm⁻¹) [30].

In the second step of sol-gel preparation (Sol 2), the alkoxide groups of TEOS are hydrolysed and new siloxane Si–O–Si bonds are formed during the condensation process at 1047 cm⁻¹ [31]. The addition of hydrolysed TEOS (Sol 2) into a partially polymerised solution of Sol 1 induces the hydrolysis of MAPTMS as well leading to the final FTIR structure of the two sols.

Several important differences in the FTIR spectra were observed between the initial precursors (Figure 1c,d) and siloxane-PMMA and -PEMA sols (Figure 1g,h) in the region between 1250 and 700 cm⁻¹. These differences are a result of the network formed between silicon and oxygen (Si–O) following the hydrolysis of ethoxy (TEOS) or methoxy (MAPTMS) groups, and their further polycondensation to

form oxo-bridges [31]. Diminishment of the bands characteristic of MAPTMS and TEOS occurred in the range between 750 and 850 cm^{-1} . This indicates that methoxy ($\text{O}-\text{CH}_3$) groups of MAPTMS and ethoxy ($\text{O}-\text{CH}_2-\text{CH}_3$) groups of TEOS were replaced by $-\text{OH}$ groups during the hydrolysis and condensation reactions. As a result, siloxane bands ($\text{Si}-\text{O}-\text{Si}$), appeared at the characteristic band at $\sim 1055 \text{ cm}^{-1}$ for siloxane-PMMA and siloxane-PEMA, becoming some of the main bands in the spectra for both hybrid sols [9,28,29].

In general, FTIR spectra of siloxane-PMMA and siloxane-PEMA (Figure 1g,h) are comparable and indicative of similar polymerisation degree and siloxane network formation. The only difference in the composition of freshly prepared sols can be obtained in the ratio of characteristic bands of $\text{C}-\text{O}-\text{C}$ at 1180 cm^{-1} and at 1150 cm^{-1} , which are related to spectra of initial monomers.

It is noteworthy that the final sols siloxane-PMMA and siloxane-PEMA contain ethanol and THF as a solvent; therefore, the spectra also contain their characteristic bands (Figure 1e,f, Table 2). Some of the characteristic $\text{Si}-\text{O}-\text{Si}$ bands formed overlap with the band at 880 cm^{-1} related to ethanol that formed also as a side-product of hydrolytic condensation of TEOS. Bands related to methanol formed as a side-product of MAPTMS cannot be seen in the spectra due to low concentration.

CP/MAS NMR spectra of monoliths were used to determine the chemical hybrid structures of the monoliths and to monitor the polymerization of organic groups originating from MAPTMS, MMA, EMA and TEOS. The ^{13}C spectra of siloxane-PMMA and siloxane-PEMA (Figure 2) both contain peaks characteristic of the $\text{C}=\text{O}$ group at 177 ppm (ester group), the $-\text{C}-\text{C}-\text{O}-$ group at 68 ppm, the quaternary carbon atoms at 45 ppm, the $-\text{CH}_3$ group at 22 ppm, the $-\text{C}-\text{C}-\text{C}-$ aliphatic carbon atoms at 18 ppm, and $-\text{C}-\text{Si}-$ at 9 ppm [4,5,32]. The absence of peaks characteristic of vinyl $\text{C}=\text{C}$ carbon atoms (120–140 ppm) indicates that the polymerization of the organic groups was complete for both acrylates [5,32]. In contrast, in FTIR spectra recorded for fresh sols, the $\text{C}=\text{C}$ bond at 1639 cm^{-1} was still present (Figure 1). Thus, thermal treatment resulted in complete polymerization of the $\text{C}=\text{C}$ bond. The differences in chemical structure between the two hybrid sols are related to methoxy and ethoxy groups in siloxane-PMMA and -PEMA respectively. The methoxy group exhibits a peak typical of $-\text{O}-\text{CH}_3$ at 52 ppm, while the ethoxy group shows a peak for $-\text{O}-\text{CH}_2-\text{CH}_3$ at 60 ppm, and a methyl bonded to the ethoxy group at 14 ppm.

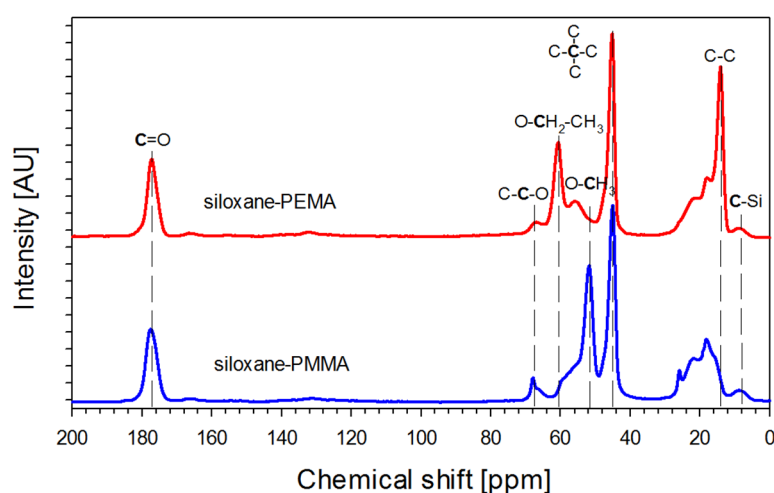


Figure 2. Solid state ^{13}C CP/MAS NMR spectra of the siloxane-hybrid monoliths prepared from TEOS, MAPTMS and two acrylates: methyl methacrylate (MMA) and ethyl methacrylate (EMA). Spectra were recorded for sols treated thermally for 1 h at 60 $^{\circ}\text{C}$ and 1 h at 180 $^{\circ}\text{C}$.

The ^{29}Si CP/MAS NMR spectra corresponding to the hybrid siloxanes PMMA and PEMA are presented in Figure 3. Each spectrum shows three peaks in the T and Q regions. In the T region, which is related to the condensation of the organic precursor MAPTMS in the hybrid network, three peaks appear for both siloxane-PMMA and siloxane-PEMA at -52 , -58 and -65 ppm, corresponding

to T^1 ($-\text{CH}_2\text{Si}(\text{OSi})(\text{OR})_2$, $\text{R}=\text{H}$ or CH_3), T^2 ($-\text{CH}_2\text{Si}(\text{OSi})_2(\text{OR})$) and T^3 ($-\text{CH}_2\text{Si}(\text{OSi})_3$) units [32,33]. Condensation of the inorganic precursor TEOS in the hybrid network is reflected in the three signals in the Q region: at -93 , -101 and -109 ppm for siloxane-PMMA, and at -93 , -101 and -109 ppm for siloxane-PEMA. These are assigned to Q^2 ($\text{Si}(\text{OSi})_2(\text{OR})_2$), Q^3 ($\text{Si}(\text{OSi})_3(\text{OR})$) and Q^4 ($\text{Si}(\text{OSi})_4$) species respectively [7,33]. No signal appeared at -85 ppm, indicating that the Q^1 ($\text{Si}(\text{OSi})(\text{OR})_3$) species were not present [7,33].

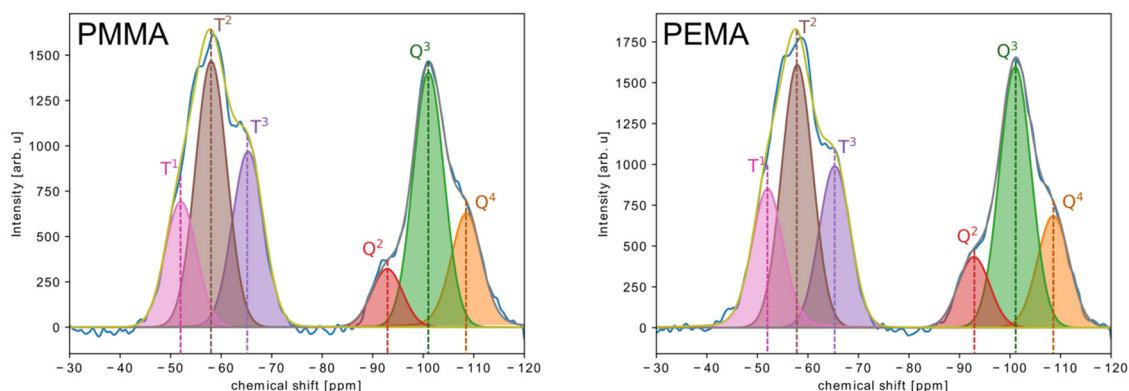


Figure 3. Fitted solid state ^{29}Si CP/MAS NMR spectra of siloxane-PMMA and siloxane-PEMA monoliths prepared from TEOS, MAPTMS and two acrylates: methyl methacrylate (MMA) and ethyl methacrylate (EMA). After synthesis, sols were treated thermally for 1 h at 60°C then 1 h at 180°C to obtain monoliths. The experimental curve (blue line), fitted curve (yellow line) and individual component peaks used for fitting the experimental curve. Experimental curves were fitted using three component peaks described by pseudo-Voigt functions, using a non-linear least squares method^a. An estimate of a 1% error in the determination of the fraction of each component peak can be predicted. Absolute and relative proportions of T and Q species obtained by deconvolution of spectra are given in Table 3. a. https://docs.scipy.org/doc/scipy/reference/generated/scipy.optimize.curve_fit.html.

NMR spectra were deconvoluted using component pseudo-Voigt peaks, as described in the Experimental section, in order to deduce the percentage of particular T and Q species in the sol. The proportions of individual species relative to total T + Q species, and relative to total of T or Q species, respectively, obtained by spectral deconvolution are presented in Table 3. The degrees of condensation of particular species, and the common degree of condensation (C_d) were then calculated according to the equation [5,34]

$$C_d = \left[\frac{T^1 + 2T^2 + 3T^3}{3} + \frac{Q^1 + 2Q^2 + 3Q^3 + 4Q^4}{4} \right] \times 100 = [D_c(\text{T}) + D_c(\text{Q})] \times 100 \quad (1)$$

with $D_c(\text{T})$ being the degree of condensation of T species, $D_c(\text{Q})$ the degree of condensation of the Q species, and C_d the common degree of condensation of both inorganic and organic species [34]. The results are presented in Table 3. Of the T units, T^2 predominated over T^3 and T^1 species, indicating a high degree of condensation. For Q units, the percentage of Q^3 species strongly prevailed over that of Q^4 and, especially, of Q^2 . The degrees of condensation of both inorganic and organic parts of the network are similar at ca. 72 %. Considering the effect of the derivative MMA or EMA, no significant difference is observed between the two sols with respect to the $D_c(\text{T})$, $D_c(\text{Q})$ and C_d (Table 3). The C_d of ca. 72%–73 % is the same for the two hybrid sols, thus indicating comparable total degrees of polycondensation for siloxane-PMMA and -PEMA sols. The obtained common degree of condensation is in accordance with that reported for similar PMMA-based coatings: 75.8%–80.9% [5], 78%–85% [4] and 84%–86% [34].

Table 3. Proportions and relative proportions of T and Q species (%), the degree of condensation (%) of the T and Q species, D_c(T) and D_c(Q), and the common degree of condensation, C_d, deduced from deconvoluted ²⁹Si CP/MAS NMR spectra recorded for polysiloxane-PMMA and -PEMA monoliths (Figure 3).

	T ¹	T ²	T ³	D _c (T)	Q ²	Q ³	Q ⁴	D _c (Q)	C _d ^c
Siloxane-PMMA									
Proportions ^a (%)	12.7	26.9	17.8	40	5.8	25.3	11.5	33.4	73.4
Relative proportions ^b (%)	22.1	46.9	31.0	-	13.6	59.4	27.0	-	-
Siloxane-PEMA									
Proportions ^a (%)	14.3	25.8	15.8	37.8	7.0	26.1	11.0	34.1	71.9
Relative proportions ^b (%)	25.6	46.2	28.2	-	15.9	59.1	25.0	-	-

^a Proportions (%): (each T (or Q) species/total T + Q species) ×100. ^b Relative proportions (%): (each T (or Q) species/total T (or Q) species) ×100. ^c Total degree of condensation calculated from Equation (1).

XPS and ToF-SIMS spectra were recorded on siloxane-PMMA and -PEMA coatings to gain additional information regarding their chemical composition and speciation. Elemental compositions of coatings deduced from XPS spectra are presented in Table 4. Coatings contain carbon, oxygen and silicon. Carbon is the most abundant element, followed by oxygen and then silicon. It should be taken into account, however, that XPS techniques always measures adventitious carbon (C–C, C–H); therefore, carbon content is overestimated compared to that of O and Si. The content of carbon is somewhat higher in siloxane-PEMA than in the siloxane-PMMA coating by ca. 4 at. %, which may be related to the additional alkyl group in -PEMA coating. Elements originating from the substrate (Al, Zn, Cu, etc.) could not be detected by XPS in such thick hybrid coatings.

Table 4. Composition [atomic %] deduced from survey XPS spectra recorded for siloxane-PMMA and siloxane-PEMA hybrid sol-gel coatings deposited on AA7075-T6. Please note that carbon content includes also adventitious carbon.

Sample	C (at. %)	O (at. %)	Si (at. %)
siloxane-PMMA	65.3	29.9	4.8
siloxane-PEMA	69.2	27.2	3.6

High energy resolution XPS C1s, O 1s and Si 2p spectra are presented in Figure 4 together with curves obtained by curve deconvolution using fitted component sub-peaks. The experimental C 1s spectra were deconvoluted using four component sub-peaks: aliphatic (C–C, C–H) at 285.0 eV, ether (C–O) at 286.3 eV, carbonyl (C=O) at 287.4 eV and carboxylic (O–C=O) at 288.6 eV. The assignment of sub-peaks is in accordance with the chemical environment of carbon as determined from FTIR and NMR spectra (Figures 1 and 2). The relative intensity of particular component sub-peaks is similar for both coatings, with the aliphatic and hydrocarbon sub-peak being the most intense (ca. 65%), followed by ether and carboxylic groups.

The experimental O 1s spectra were deconvoluted using two fitted component sub-peaks: oxygen bonded to carbon or to silicon (O–C, O–Si) at 532.1 eV and carbonyl oxygen (O=C–O) at 533.4 eV. The experimental Si 2p spectra are non-resolved doublet peaks centred at 102.6 eV. These spectra were deconvoluted using one sub-peak associated with silicon bonded to carbon and oxygen (C–Si–O) at 101.9 eV. Majority of the silicon is bonded to oxygen, as evidenced by the NMR results (Table 3). This is reflected by the sub-peak ascribed to O–Si–O bond at 102.9 eV, as proposed [35].

ToF-SIMS spectra recorded for siloxane-PMMA and -PEMA coatings are presented in Figure 5. The peak at a mass to charge ratio (*m/z*) 31.02 is related to positive CH₃O⁺ fragments, indicating the presence of a methoxy groups. This peak is very strong on the surface of PMMA coating, and negligible on the PEMA coating. The peak at *m/z* 45.03 is related to positive C₂H₅O⁺ fragments, indicating the

presence of the ethoxy groups. In contrast to the methoxy peak, the intensity of ethoxy peak is very high on the surface of the PEMA coating, and negligible on the PMMA coating. The peaks at m/z 45.00, corresponding to CHO_2^+ fragments are similar in the two samples. The ToF-SIMS results confirm that methoxy and ethoxy groups are present in the topmost layer of the siloxane-PMMA and -PEMA coatings (Figure 5).

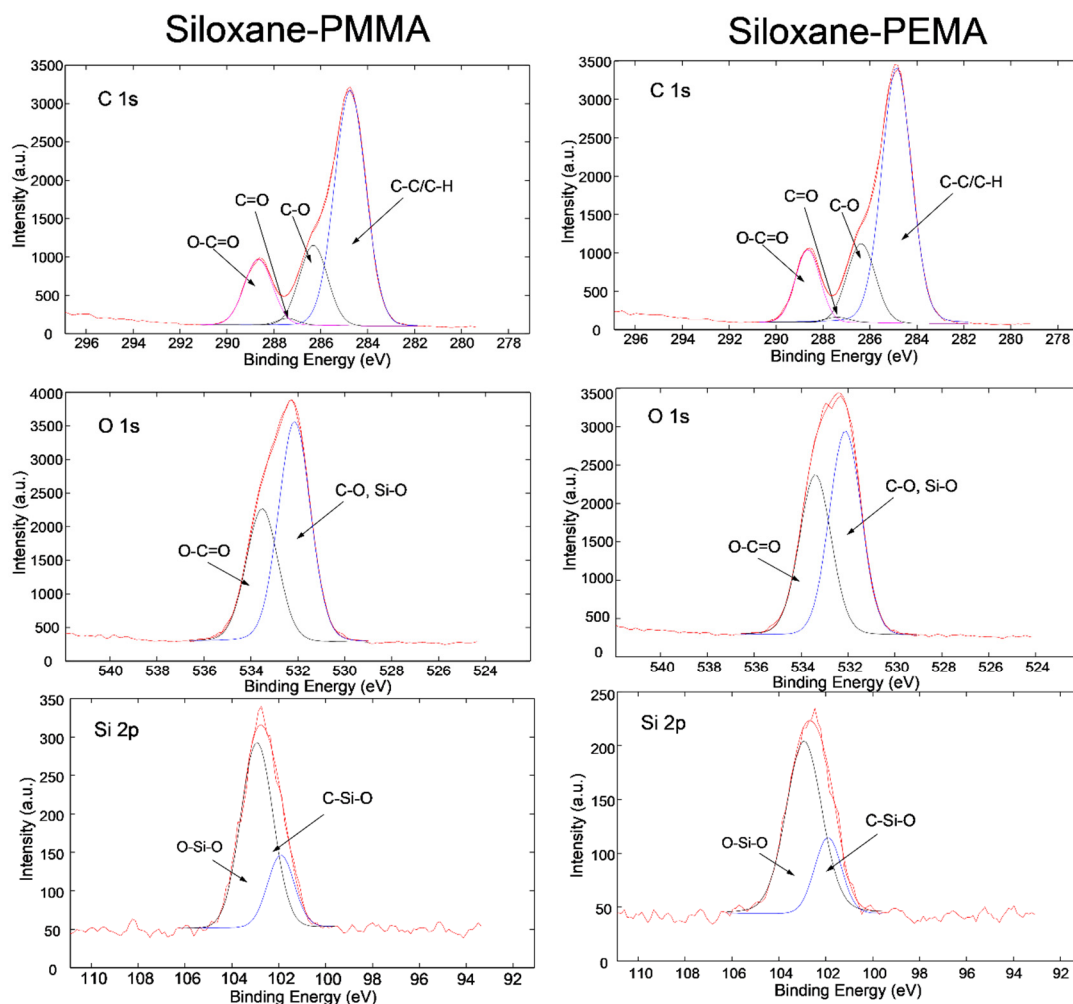


Figure 4. XPS C 1s, O 1s and Si 2p spectra recorded for siloxane-PMMA and siloxane-PEMA hybrid sol-gel coatings deposited on AA7075-T6. Spectra were deconvoluted using fitted components sub-peaks corresponding to particular species present in the coatings. The composition deduced from survey spectra is given in Table 4.

Based on the results of FTIR, NMR, XPS and ToF-SIMS analyses the mechanism of formation of hybrid siloxane-PMMA and siloxane-PEMA sols was postulated and is presented in Figure 6, which is in line with literature studies [5]. During the first synthesis step (Sol 1), when MAPTMS and MMA (or EMA) are mixed for 4 h at 70 °C, polymerization of the double carbon-carbon bond of the methacrylic group (R) takes place progressively, though it is not completed after 4 h (Figure 6a). In the second step (Sol 2), hydrolysis of TEOS is initiated by the addition of acidic solution, leading to the replacement of ethoxy with hydroxyl groups (Figure 6b). Note that the number of hydroxyl groups may vary depending on the degree of hydrolysis, as expressed by parameters Q^2 – Q^4 (Table 3, Figure 3). The process of polycondensation of TEOS also begins. In the third step (Sol 1 + Sol 2), i.e., upon addition of acidified TEOS sol to a partially polymerized mixture of MAPTMS and MMA (or EMA), hydrolysis of MAPTMS and progressive replacement of methoxy (or ethoxy) with hydroxyl groups occurs (Figure 7c). The process of condensation between hydrolysed MATPMS and TEOS begins

resulting in formation of Si–O–Si bonds and a decreased number of hydroxyl group in the organic (T^i species) and the inorganic part (Q^i species) of the network. The degrees of condensation of the inorganic part (TEOS) and the organic part (MAPTMS) are similar, with T^2 , T^3 and Q^3 being the most abundant species. At the same time, further polymerization of the C=C double bond of the methacrylic group in the organic part takes place. This process is stimulated by the thermal curing treatment.

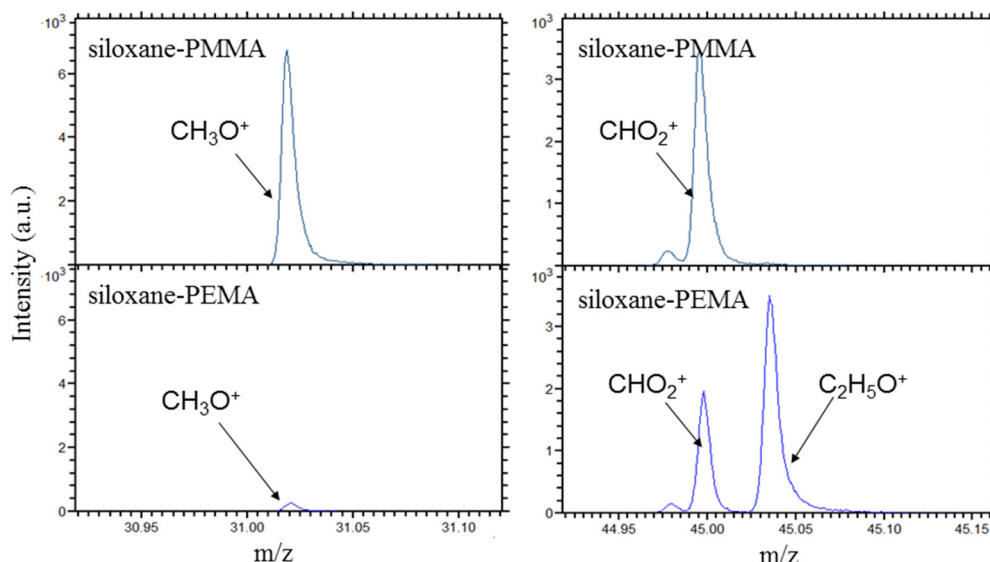


Figure 5. ToF-SIMS spectra of positive secondary ions at mass to charge ratios (m/z) around 31 and 45 with indicated methoxy CH_3O^+ and ethoxy $C_2H_5O^+$ fragments. Spectra were recorded for siloxane-PMMA and siloxane-PEMA hybrid sol-gel coatings.

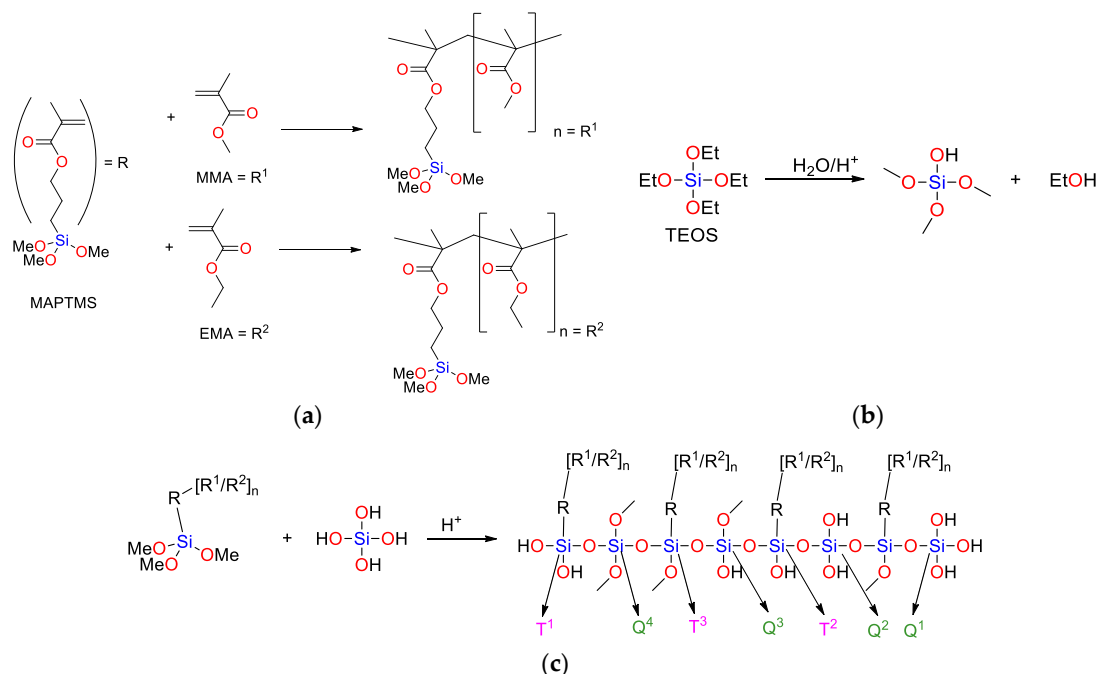


Figure 6. Postulated mechanism of polymerization, hydrolysis and polycondensation reactions in the formation of siloxane-PMMA and siloxane-PEMA sols. Different T and Q species are denoted in organoalkoxysilane (i.e., MAPTMS) with two (T^1), one (T^2) or none (T^3) silanol groups, and in inorganoalkoxysilane (i.e., TEOS) with three (Q^1), two (Q^2), one (Q^3) or no (Q^4) silanol groups. Methyl- and ethyl- methacrylate are denoted as MMA and EMA, respectively. (a) Sol 1: Polymerization; (b) Sol 2: Hydrolysis; (c) Sol 1 + Sol 2 – Network formation.

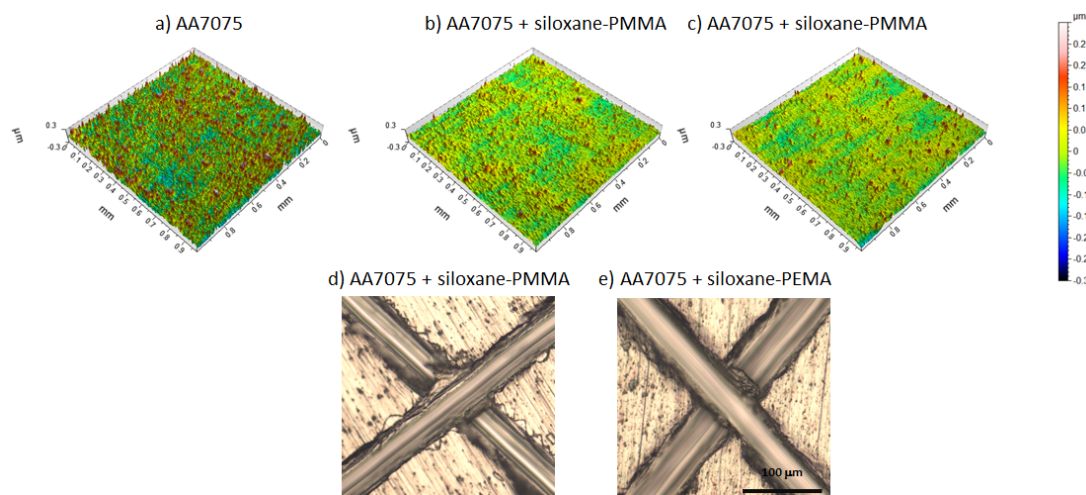


Figure 7. (a–c) 3D topography images of bare AA7075 and AA7075 coated with siloxane-PMMA and siloxane-PEMA. Colour scale bar denotes the span of $\pm 0.3 \mu\text{m}$. (d–e) X-cut surfaces of AA7075-T6 substrates coated with siloxane-PMMA and siloxane-PEMA following the adhesion test - imaged by confocal microscope.

The difference between MMA and EMA in the sol does not affect significantly the final degree of condensation (Table 3). It may be hypothesized that the additional methyl group in EMA may contribute to the formation of a denser network and increase in the coating thickness, as will be shown below. Good adhesion of siloxane Si–O–Al bonds to the aluminium substrate and the dense, polymerized organic network form the basis for the excellent protective properties of these coatings, as presented in the following section.

3.2. Thickness, Topography, Water Contact Angle and Adhesion of the Coatings

The thickness of the siloxane coatings was measured using a 3D profilometer at the step made using a diamond blade. The thickness of the siloxane-PMMA and siloxane-EMA coatings is $5.0 \pm 0.3 \mu\text{m}$ and $6.7 \pm 0.3 \mu\text{m}$, respectively. The larger thickness of the latter is related to the larger volume of EMA, compared to that of MMA, which is required to achieve the same molar ratio in Sol 1.

The topography of the uncoated and coated AA7075-T6 substrates was determined using 3D profilometry (Figure 7). The mean surface roughness (S_a) of the uncoated alloy is $0.056 \mu\text{m}$, but is less, at $0.027 \mu\text{m}$, after deposition of hybrid coatings. Both coatings cover the surface homogeneously without the presence of visible pores or defects at the surface. No significant differences are observed between the values for siloxane-PMMA and siloxane-PEMA coatings.

The values of contact angle (θ) of a water drop on uncoated Al-based substrates and on those coated with hybrid siloxane-PMMA and siloxane-PEMA coatings were measured in order to investigate the effect of coating on surface wettability (Figure S1). The surface of bare substrates is hydrophilic ($<90^\circ$), with values of θ around 55° . After application of PMMA and PEMA coatings, θ were higher, at $70^\circ \pm 2^\circ$ (siloxane-PMMA) and $76^\circ \pm 2^\circ$ (siloxane-PEMA), respectively, by about 20° than for bare samples, but still in the hydrophilic region. Higher θ values are related to the presence of organic components in the coating [14]. Longer and branched alkyl chains would make the coatings more hydrophobic due to their lower surface energy. Such coatings are expected to exhibit higher corrosion resistivity [36]. The use of an acrylate group with an additional $-\text{CH}_2$ group, i.e., siloxane-PEMA, was expected to increase the contact angle to more hydrophobic regions. Values of contact angle show that the addition of a CH_2 group to siloxane-PEMA did not significantly affect the contact angle, indicating that the addition of only one alkyl group was not sufficient to change the wettability regime and achieve values in the hydrophobic region of θ over 90° .

Adhesion between Al-based substrates and hybrid coatings was evaluated by the tape test. Both types of coatings on all substrates showed excellent adhesion classified as 5B, which is the best grade. This means that there is no delamination of the coating from the substrate at scratched sites. Microscopic images taken at magnification (20 $\times$) (Figure 7) confirmed the presence of good adhesion with no peeling or cracking of the coating.

3.3. Electrochemical and Corrosion Properties of the Coatings

3.3.1. Electrochemical Properties

Bode plots of $|Z|$ vs. f in the frequency range from 10^5 to $4 \cdot 10^{-3}$ Hz for AA7075-T6 uncoated and coated with siloxane-PMMA and siloxane-PEMA after 1 day of immersion in 0.1 M NaCl are shown in Figure 8. According to the standard interpretation used for coated metals, the time constant in the high frequency region is attributed to the hybrid coating properties at the coating/electrolyte interface, while that in low frequency region is related to the properties of the inner part of the coating present on the metal surface including the corrosion reaction which may take place at the metal/coating interface [7,37,38].

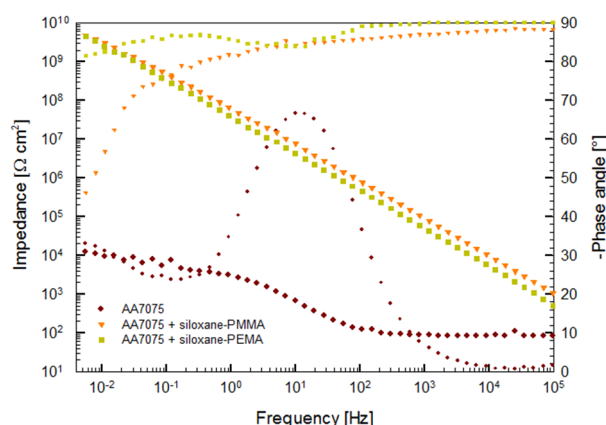


Figure 8. Bode plots of impedance magnitude and phase angle of bare AA7075-T6, and AA7075-T6 coated with siloxane-PMMA and of siloxane-PEMA coatings measured after immersion in 0.1 M NaCl for 1 day.

Compared to the uncoated substrate, both coatings exhibit very high impedance values. Starting from high frequencies, the value of $|Z|$ increases linearly with decreasing frequency and, for both coatings, reaches extremely high values in the low frequency region, i.e., up to $5 \text{ G}\Omega \text{ cm}^2$ at 4 mHz; the same value of uncoated metal is almost six orders of magnitude smaller. Value of impedance at 4 mHz was chosen as the parameter representing the corrosion resistance of the coating due to corrosion processes at the inner interface with the substrate [8]. Bode plots of Φ vs. f are similar for the two coated substrates in the region from 10^5 to 1 Hz, showing pure capacitive behaviour with phase angles of almost -90° . At lower frequencies, however, the curves for two coatings differ. Φ for siloxane-PMMA decreased to -40° , indicating that some deterioration at the inner metal/coating interface has started. In contrast to PMMA, siloxane-PEMA still acts as a pure capacitor, with Φ of about -90° achieved across the whole frequency region down to 4 mHz. This result confirms that PEMA coatings exhibit high barrier properties.

Long-term coating behaviour was monitored, for coated samples on AA7075-T6 immersed in 0.1 M NaCl for up to 2 months (Figures 9 and 10). Curves recorded after 1 day immersion, already shown in Figure 8, are repeated here for the sake of comparison. Siloxane-PMMA shows a small decrease in the value of impedance after one month, from $6 \text{ G}\Omega \text{ cm}^2$ to ca. $1.5 \text{ G}\Omega \text{ cm}^2$, and to $1 \text{ G}\Omega \text{ cm}^2$ after 65 days (Figure 9). Similar values of impedance at 10 mHz were observed for 1.5–2.0 μm thick siloxane-PMMA coatings deposited on carbon steel after 196 days in 35 wt.% NaCl [6], and 3–7 μm

thick siloxane-PMMA coatings containing graphene oxide and carbon nanotubes deposited on carbon steel after 203 days in 3.5 wt.% NaCl [6,13]. In parallel with the slightly decreasing $|Z|$ value, the phase angle at low frequencies also decreased, reaching -30° at 4 mHz after 65 days. On the other hand, after 1 month Φ of siloxane-PEMA decreased much less than that of PMMA, -70° at 4 mHz, and remained unchanged for up to 2 months (Figure 10). The results obtained confirm that a coating containing ethyl methacrylate retains its capacitive behaviour and offers even better long-term barrier corrosion protection of AA7075-T6 than that based on methyl methacrylate.

Table 5. Fitting parameters for the impedance measurements plotted in Figures 9 and 10 using denoted electrical equivalent circuit.

Sample	Siloxane-PMMA			Siloxane-PEMA		
	1 Day	1 Month	2 Months	1 Day	1 Month	2 Months
χ^2	0.0523	0.0539	0.0595	0.0129	0.0337	0.0329
R_{sol} [Ω cm ²]	11 (3.1) *	10 (4.0)	12 (2.5)	13 (2.8)	10 (1.2)	10 (2.8)
Q_1	1.92	2.12	1.99	3.90	4.99	4.81
$[n\Omega^{-1} \text{cm}^{-2} \text{s}^n]$	(23.2)	(13.6)	(7.2)	(2.5)	(3.5)	(3.6)
n_1	0.83 (4.0)	0.76 (3.9)	0.60 (6.5)	0.98 (0.3)	0.97 (0.4)	0.97 (0.4)
R_{po} [Ω cm ²]	26 (32.3)	0.9 (30.1)	0.9 (30.8)	27.7×10^6 (27.5)	2.87×10^6 (9.1)	1.73×10^6 (10.0)
Q_2	1.22	1.89	2.64	0.828	4.60	4.12
$[n\Omega^{-1} \text{cm}^{-2} \text{s}^n]$	(28.6)	(15.2)	(5.6)	(13.4)	(4.0)	(4.4)
n_2	1.0 (2.2)	0.99 (1.0)	0.97 (0.5)	0.85 (3.5)	0.89 (0.6)	0.89 (0.6)
R_2 [$G\Omega$ cm ²]	8.28 (5.6)	1.63 (2.5)	0.844 (4.2)	1100 (45.2)	6.99 (5.2)	12.9 (11.1)

* Error [%].

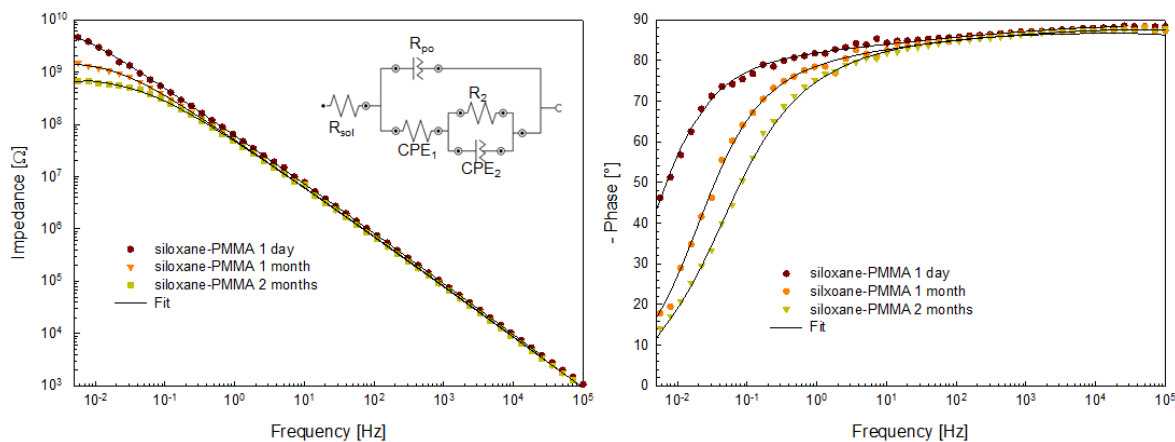


Figure 9. Bode plot of impedance magnitude and phase angle of AA7075-T6 coated with siloxane-PMMA measured after immersion in 0.1 M NaCl for up to 2 months. Symbols correspond to the experimental data and lines to the fitted curves. Electrical equivalent circuit used to fit the experimental data is given in inset; fitted parameters are presented in Table 5.

To quantitatively described the impedance parameters of the two coatings, the experimental data were fitted using electrical equivalent circuit (inset in Figures 9 and 10) with two time constants containing constant phase element (CPE) and resistance (R) and uncompensated resistance between reference and test electrode (R_{sol}). The CPE_1 and R_{po} are related to the high frequency (f) region corresponding to the coating/electrolyte interface; in other words, these parameters correspond to the coating resistance to water uptake at the outer interface resulting from the formation of ionically conducting paths across the coating (also referred to as pore resistance). The CPE_2 and R_2 are related to the low frequency region corresponding to the response of the inner layer adjacent to the metal/coating interface [8,11,14]. Fitted parameters including Q as the pseudocapacitance of CPE, R as the resistance and n as the CPE power are presented in Table 5.

Looking at the siloxane-PMMA upon 1 day of immersion the value of R_{po} is extremely small (orders of $\Omega \text{ cm}^2$), orders of magnitude smaller compared to R_2 (orders of $\text{G}\Omega \text{ cm}^2$), indicating a high capacitive character of the inner coating layer. Such a coating is assumed to be dense and impermeable to ion ingress, i.e., water uptake. With increasing immersion time, the Q_1 values somewhat increased. The value of n is expected to be smaller in the high f zone, associated with higher porosity, than in the lower f zone associated with the layer of high impedance; indeed, n_1 decreased from 0.83 down to 0.60, and n_2 remained close to 1.0. These values show that although the coating still exhibits R_2 in the range of $\text{G}\Omega \text{ cm}^2$; however, water uptake is announced by a reduced n_1 and increased Q^1 values [37].

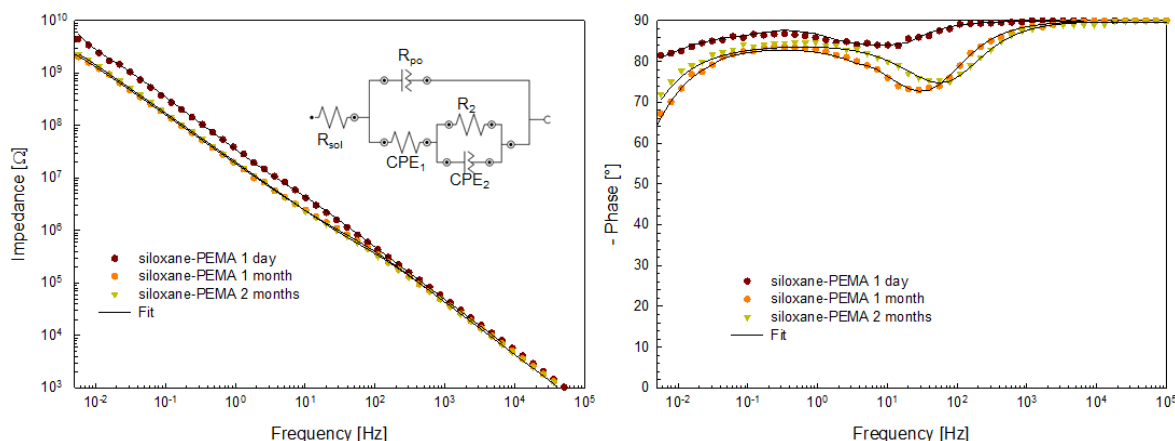


Figure 10. Bode plot of impedance magnitude and phase angle of AA7075-T6 coated with siloxane-PEMA measured after immersion in 0.1 M NaCl for up to 2 months. Symbols correspond to the experimental data and lines to the fitted curves. Electrical equivalent circuit used to fit the experimental data is given in inset; fitted parameters are presented in Table 5.

Siloxane-PEMA coating shows somewhat different behaviour. Much higher R_{po} values remained in the range of $\text{M}\Omega \text{ cm}^2$ throughout the immersion time up to 2 months (compared to small R_{po} values related to siloxane-PMMA). Similar trend is followed by n_1 values, which remained close to 1.0 even after 2 months immersion. Values of n_2 lie between 0.85 and 0.89, accompanied by R_2 values in the tera range of magnitude at the beginning of immersion, and giga range upon 2 months immersion. A highly capacitive character of the siloxane-PEMA coating is obviously related to very low permeability to electrolyte ingress and, consequently, low water uptake. Such coating represents a highly resistant corrosion barrier.

3.3.2. Salt Spray Test

The corrosion behaviour of siloxane-PMMA and -PEMA hybrid coatings on AA7075-T6 substrates was evaluated by salt spray test after exposure for 600 h in 5 wt. % salt spray at 35 °C. Images of samples before and after 24 and 600 h exposure to salt spray are presented in Figure 11. For reference, bare substrate was also tested. Uncoated AA7075-T6 was corroded completely after only one day's exposure, forming a thick layer of corrosion products.

Both coatings, siloxane-PMMA and siloxane-PEMA, show similar long-term performances and remain intact, even after 600 h, in a corrosive environment. No changes in colour or visible signs of corrosion were observed, thus showing excellent corrosion resistance, with a rust grade of 10 according to the ASTM D 610-01 [26].

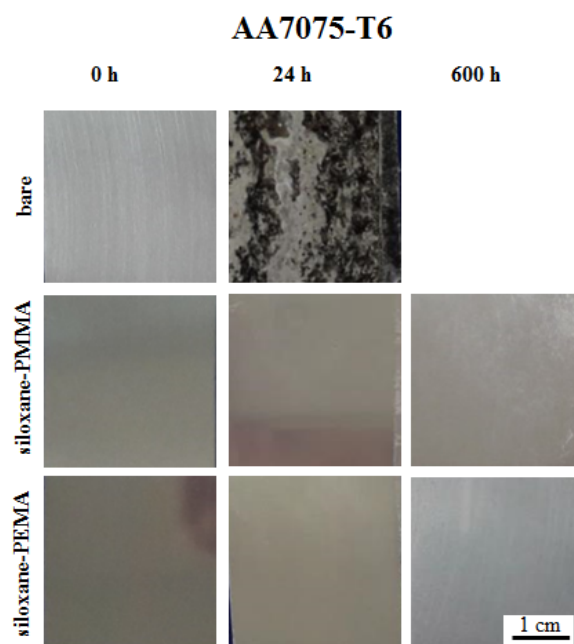


Figure 11. Images of bare and coated AA7075-T6 after 0, 24 and 600 h exposed to salt spray test (ASTM B117-07A).

3.3.3. Summary of Coatings Characteristics and Performance

Summary of representative parameters of siloxane-PMMA and siloxane-PEMA coatings is presented in Table 6.

Table 6. Representative parameters of two siloxane coatings.

Coating	Condensation Degree	Thickness	Contact Angle	Roughness	Impedance at 4 mHz After 2 Months in 0.1 M NaCl	Adhesion
siloxane-PMMA	73.2 %	$5.0 \pm 0.3 \mu\text{m}$	$70^\circ \pm 2^\circ$	$0.027 \pm 0.001 \mu\text{m}$	$0.83 \pm 0.03 \text{ G}\Omega \text{ cm}^2$	5 B
siloxane-PEMA	71.6 %	$6.7 \pm 0.3 \mu\text{m}$	$76^\circ \pm 2^\circ$	$0.027 \pm 0.001 \mu\text{m}$	$3.2 \pm 0.4 \text{ G}\Omega \text{ cm}^2$	5 B

4. Conclusions

Hybrid coatings, synthesized via the two-step sol-gel procedure from organo-siloxane, with different derivatives of acrylate monomer and inorganic siloxane, were deposited onto aluminium alloy 7075-T6. Two sols, siloxane-PMMA and siloxane-PEMA, differed in the methacrylate derivative, i.e., methyl- and ethyl-methacrylates. The mechanism of formation and chemical composition and structure of the sols were elucidated using FTIR and solid state NMR. The chemical composition of the coatings was investigated by XPS and ToF-SIMS.

On considering the effect of the derivative, no significant difference was observed between the two sols concerning the particular inorganic or organic units and common degree of condensation. The C_d values of ca. 72% are similar for both hybrid sols, indicating comparable polycondensation processes for siloxane-PMMA and -PEMA sols (Table 6).

The long-term test in a salt spray chamber revealed, after 600 h, that both coatings remained intact with no sign of corrosion. Both the methyl- and the ethyl- coatings show decreased surface wettability compared to that of the bare substrate but still within the hydrophilic regime. The coatings achieved good adhesion to the substrate and decreased the surface roughness compared to that of bare metal.

Upon immersion in 0.1 M NaCl, both coatings deposited on AA7075-T6 exhibited high barrier properties and protected the underlying substrate, as evidenced by EIS. However, siloxane-PEMA

coating exhibited high capacitive character and achieved very high impedance values in the range of $G\Omega\text{ cm}^2$, even after 2 months immersion in chloride solution. The phase angle vs. frequency curve also proves that the siloxane-PEMA coating degrades less than the PMMA-derivative. The reason lies in the extremely high resistance of siloxane-PEMA to water uptake, which makes this coating durable in chloride solution. It seems that this is related to a low coating porosity which prevents of establishing ionically conductive paths across the coating. Therefore, although both coatings show similar polycondensation degree, EIS was able to detect differences between the coatings in terms of their electrochemical activity and, consequently, corrosion resistance. Therefore, in this sense the EIS is considerably more sensitive than salt spray chamber testing.

These coatings require only one-layer application to achieve high level of corrosion protection. Despite that the ethyl-based coating is thicker than the methyl-based (Table 6), it seems that the addition of alkyl group is a more decisive factor in terms of corrosion resistance than larger thickness; this may be related to a reduced porosity of the coating attained by longer alkyl chain. In order to investigate the effect of alkyl chain length on the properties of methacrylate network in more detail, future work will be devoted to the derivatives with longer spans of chain lengths.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2079-6412/10/2/172/s1>, Figure S1: Images of water drop on bare substrate AA7075-T6 and coatings siloxane-PMMA and -PEMA.

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References

1. Abrahams, S.T.; de Kok, J.M.M.; Terryn, H.; Mol, J.M.C. Towards Cr(VI)-free anodization of aluminum alloys for aerospace adhesive bonding applications: A review. *Front. Chem. Sci. Eng.* **2017**, *11*, 465–482. [CrossRef]
2. Figueira, R.B.; Silva, C.J.R.; Pereira, E.V. Organic–inorganic hybrid sol–gel coatings for metal corrosion protection: a review of recent progress. *J. Coat. Technol. Res.* **2015**, *12*, 1–35. [CrossRef]
3. Sakai, R.T.; Di Da Cruz, F.M.L.; De Melo, H.G.; Benedetti, A.V.; Santilli, C.V.; Suegama, P.H. Electrochemical study of TEOS, TEOS/MPTS, MPTS/MMA and TEOS/MPTS/MMA films on tin coated steel in 3.5% NaCl solution. *Prog. Org. Coat.* **2012**, *74*, 288–301. [CrossRef]
4. Sarmento, V.H.V.; Schiavetto, M.G.; Hammer, P.; Benedetti, A.V.; Fugivara, C.S.; Suegama, P.H.; Pulcinelli, S.H.; Santilli, C.V. Corrosion protection of stainless steel by polysiloxane hybrid coatings prepared using the sol-gel process. *Surf. Coat. Technol.* **2010**, *204*, 2689–2701. [CrossRef]
5. Hammer, P.; Dos Santos, F.C.; Cerrutti, B.M.; Pulcinelli, S.H.; Santilli, C.V. Highly corrosion resistant siloxane-polymethyl methacrylate hybrid coatings. *J. Sol-Gel Sci. Technol.* **2012**, *63*, 266–274. [CrossRef]
6. dos Santos, F.C.; Harb, S.V.; Menu, M.-J.; Turq, V.; Pulcinelli, S.H.; Santilli, C.V.; Hammer, P. On the structure of high performance anticorrosive PMMA–siloxane–silica hybrid coatings. *RSC Adv.* **2015**, *5*, 106754–106763. [CrossRef]
7. Hammer, P.; Schiavetto, M.G.; dos Santos, F.C.; Benedetti, A.V.; Pulcinelli, S.H.; Santilli, C.V. Improvement of the corrosion resistance of polysiloxane hybrid coatings by cerium doping. *J. Non-Cryst. Solids* **2010**, *356*, 2606–2612. [CrossRef]

8. Trentin, A.; de Gasparini, A.L.; Faria, F.A.; Harb, S.V.; dos Santos, F.C.; Pulcinelli, S.H.; Santilli, C.V.; Hammer, P. Barrier properties of high performance PMMA-silica anticorrosion coatings. *Prog. Org. Coat.* **2020**, *138*, 105398. [[CrossRef](#)]
9. Tiringer, U.; Durán, A.; Castro, Y.; Milošev, I. Self-Healing Effect of Hybrid Sol-Gel Coatings Based on GPTMS, TEOS, SiO₂ Nanoparticles and Ce(NO₃)₃ Applied on Aluminum Alloy 7075-T6. *J. Electrochem. Soc.* **2018**, *165*, C213–C225. [[CrossRef](#)]
10. Suegama, P.H.; Sarmiento, V.H.V.; Montemor, M.F.; Benedetti, A.V.; de Melo, H.G.; Aoki, I.V.; Santilli, C.V. Effect of cerium (IV) ions on the anticorrosion properties of siloxane-poly(methyl methacrylate) based film applied on tin coated steel. *Electrochim. Acta* **2010**, *55*, 5100–5109. [[CrossRef](#)]
11. Rodič, P.; Katić, J.; Korte, D.; Desimone, P.; Franko, M.; Ceré, S.; Metikoš-Huković, M.; Milošev, I. The Effect of Cerium Ions on the Structure, Porosity and Electrochemical Properties of Si/Zr-Based Hybrid Sol-Gel Coatings Deposited on Aluminum. *Metals* **2018**, *8*, 248. [[CrossRef](#)]
12. Mosa, J.; Rosero-Navarro, N.C.; Aparicio, M. Active corrosion inhibition of mild steel by environmentally-friendly Ce-doped organic-inorganic sol-gel coatings. *RSC Adv.* **2016**, *6*, 39577–39586. [[CrossRef](#)]
13. Harb, S.V.; Pulcinelli, S.H.; Santilli, C.V.; Knowles, K.M.; Hammer, P. A Comparative Study on Graphene Oxide and Carbon Nanotube Reinforcement of PMMA-Siloxane-Silica Anticorrosive Coatings. *ACS Appl. Mater. Inter.* **2016**, *8*, 16339–16350. [[CrossRef](#)] [[PubMed](#)]
14. Harb, S.V.; Cerrutti, B.M.; Pulcinelli, S.H.; Santilli, C.V.; Hammer, P. Siloxane-PMMA hybrid anti-corrosion coatings reinforced by lignin. *Surf. Coat. Technol.* **2015**, *275*, 9–16. [[CrossRef](#)]
15. Trentin, A.; Harb, S.V.; Uvida, M.C.; Pulcinelli, S.H.; Santilli, C.V.; Marcoen, K.; Pletincx, S.; Terryn, H.; Hauffman, T.; Hammer, P. Dual Role of Lithium on the Structure and Self-Healing Ability of PMMA-Silica Coatings on AA7075 Alloy. *ACS Appl. Mater. Inter.* **2019**, *11*, 40629–40641. [[CrossRef](#)]
16. Davis, J.R. *Corrosion of Aluminum and Aluminum Alloys*; ASM International: Cleveland, OH, USA, 1999.
17. Vargel, C. *Corrosion of Aluminum*, 1st ed.; Elsevier: Amsterdam, The Netherlands, 2004.
18. Starke, E.A.; Staley, J.T. Application of modern aluminum alloys to aircraft. *Prog. Aerospace Sci.* **1996**, *32*, 131–172. [[CrossRef](#)]
19. Buchheit, R.G. A Compilation of Corrosion Potentials Reported for Intermetallic Phases in Aluminum Alloys. *J. Electrochem. Soc.* **1995**, *142*, 3994–3996. [[CrossRef](#)]
20. Rodič, P.; Milošev, I. Corrosion Inhibition of Pure Aluminium and Alloys AA2024-T3 and AA7075-T6 by Cerium(III) and Cerium(IV) Salts. *J. Electrochem. Soc.* **2016**, *163*, C85–C93. [[CrossRef](#)]
21. Scofield, J.H. Hartree-Slater subshell photoionization cross-sections at 1254 and 1487 eV. *J. Electron Spectrosc. Relat. Phenom* **1976**, *8*, 129–137. [[CrossRef](#)]
22. Reilman, R.F.; Msezane, S.T.; Manson, J. Relative intensities in photoelectron spectroscopy of atoms and molecules. *J. Electron Spectrosc. Relat. Phenom.* **1976**, *8*, 38–44. [[CrossRef](#)]
23. ASTM D3359-09 *Standard Test Methods for Measuring Adhesion by Tape Test*; ASTM: West Conshohocken, PA, USA, 2009.
24. Boukamp, B. A Nonlinear Least Squares Fit procedure for analysis of immittance data of electrochemical systems. *Solid State Ionics* **1986**, *20*, 31–44. [[CrossRef](#)]
25. ASTM B117-07a *Standard Practice for Operating Salt Spray (Fog) Apparatus*; ASTM: West Conshohocken, PA, USA, 2007.
26. ASTM D610-01 *Standard Test Method for Evaluating Degree of Rusting on Painted Steel Surfaces*; ASTM: West Conshohocken, PA, USA, 2001.
27. Dazzi, A.; Deniset-Besseau, A.; Lasch, P. Minimising contributions from scattering in infrared spectra by means of an integrating sphere. *Analyst* **2013**, *138*, 4191. [[CrossRef](#)] [[PubMed](#)]
28. Rodič, P.; Iskra, J.; Milošev, I. A hybrid organic-inorganic sol-gel coating for protecting aluminium alloy 7075-T6 against corrosion in Harrison's solution. *J. Sol-Gel Sci. Technol.* **2014**, *70*, 90–103. [[CrossRef](#)]
29. Rodič, P.; Iskra, J.; Milošev, I. Study of a sol-gel process in the preparation of hybrid coatings for corrosion protection using FTIR and ¹H NMR methods. *J. Non-Cryst. Solids* **2014**, *396–397*, 25–35. [[CrossRef](#)]
30. Pellice, S.A.; Williams, R.J.J.; Sobrados, I.; Sanz, J.; Castro, Y.; Aparicio, M.; Durán, A. Solutions of hybrid silica microgels as precursors of sol-gel coatings. *J. Mater. Chem.* **2006**, *16*, 3318–3325. [[CrossRef](#)]
31. Rubio, F.; Rubio, J.; Oteo, J.L. A FT-IR Study of the Hydrolysis of Tetraethylorthosilicate (TEOS). *Spectrosc. Lett.* **1998**, *31*, 199–219. [[CrossRef](#)]

32. Rodič, P.; Milošev, I.; Lekka, M.; Andreatta, F.; Fedrizzi, L. Corrosion behaviour and chemical stability of transparent hybrid sol-gel coatings deposited on aluminium in acidic and alkaline solutions. *Prog. Org. Coat.* **2018**, *124*, 286–295. [[CrossRef](#)]
33. Criado, M.; Sobrados, I.; Sanz, J. Polymerization of hybrid organic-inorganic materials from several silicon compounds followed by TGA/DTA, FTIR and NMR techniques. *Prog. Org. Coat.* **2014**, *77*, 880–891. [[CrossRef](#)]
34. Han, Y.-H.; Taylor, A.; Mantle, M.D.; Knowles, K.M. UV curing of organic–inorganic hybrid coating materials. *J. Sol-Gel Sci. Technol.* **2007**, *43*, 111–123. [[CrossRef](#)]
35. Milošev, I.; Jovanović, Ž.; Bajat, J.B.; Jančić-Heinemann, R.; Mišković-Stanković, V.B. Surface Analysis and Electrochemical Behavior of Aluminum Pretreated by Vinyltriethoxysilane Films in Mild NaCl Solution. *J. Electrochem. Soc.* **2012**, *159*, C303–C311. [[CrossRef](#)]
36. Zhang, D.; Wang, L.; Qian, H.; Li, X. Superhydrophobic surfaces for corrosion protection: a review of recent progresses and future directions. *J. Coat. Technol. Res.* **2016**, *13*, 11–29. [[CrossRef](#)]
37. Mansfeld, F. Use of electrochemical impedance spectroscopy for the study of corrosion protection by polymer coatings. *J. Appl. Electrochem.* **1995**, *25*, 187–202. [[CrossRef](#)]
38. Mitton, D.B.; Latanision, R.M.; Bellucci, F. The Effect of Post-Cure Annealing on the Protective Properties of Polyimides on Chromium Substrates. *J. Electrochem. Soc.* **1996**, *143*, 3307–3316. [[CrossRef](#)]



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