Supplementary Material

Degradation of sol-gel acrylic coatings based on Si and Zr investigated using electrochemical impedance, infrared and X-ray   
photoelectron spectroscopies

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**Figure S1** shows the *real-time* FTIR spectra of the chelating process with a specific molar ratio (ZTP/MAA=1) to briefly explain the chelating mechanism. ZTP dissolved in the 1-propanol shows six characteristic absorbance bands located at 1157, 1130, 1003, 909, 888 and 860 cm−1, Figure S1. MAA is characterised by bands at 1691 cm−1 (C=O), at 1634 cm−1 (C=C), at 1455 cm−1 (CH3), at 1298 and 1203 cm−1 (C–O stretching in acid), at 944 cm−1 (COO−) and 810 cm−1 (C=C) (**Figure S1**) (Rodič et al., 2014a). After the drop-wise addition of MAA to ZTP, the chelating reaction occurred spontaneously and took a few minutes. These spectra combine the spectral characteristics of both substances, ZTP and MAA, **Figure S1b**. The bands characteristic for ZTP at wavenumber between 860 and 909 cm−1, and between 1003 and 1157 cm−1 remained visible in Sol 2 as well. Bands related mainly to MAA are located at higher wavenumber (>1350 cm−1), although they may overlap with the CH3 bands originating from ZTP (1381 and 1460 cm−1), **Figure S1b**. There were significant differences between the spectra for Sol 2 and MAA. Except for the bands in the CH3 range, all bands characteristic of MAA (C=O band at 1691 cm−1, C=C band at 1634 cm−1) were almost completely absent in the spectrum for Sol 2. Their intensity after stirring can be taken as an indication of the degree of the chelating process. In addition to bands related to the initial reagents, ZTP and MAA, two new bands appeared at 1555 and 834 cm−1 in the spectrum of Sol 2 (**Figure S1b**), thus proving that no free MAA remained after mixing with ZTP but was consumed in the chelation with ZTP and in MAA polymerisation. These new bands followed the same trend as other bands originating from MAA or ZTP. Hence, we assume that these bands are related to a new compound formed while stirring the ZTP and MAA, presumably through the bonding of Zr–O with the carbonyl group of MAA. The complete absence of the band at 1691 cm−1, related to the non-conjugated carboxylic group, additionally confirms that, in Sol 2, the MAA is completely consumed by chelating with ZTP and polymerisation.

After few minutes, the constant spectra of the Sol 2 were observed, **Figure S1a, c**. The wavenumber of the C=C band in MAA was shifted from 1634 to 1646 cm−1. Analysis of the FTIR spectra provides clear evidence for forming a zirconium complex with an organic ligand (MAA).



FIGURE S1. a) 3-D FTIR spectra (increment 3 min) b) individual FTIR spectra and c) band intensity recorded during the chelation process of ZTP during the addition of MAA to obtain the Sol 2   
(ZTP : MAA = 1 : 1).

**TABLE S1.** Impedance parameters of the TM and TMZ coatings deposited on aluminium substrate after 1, 4 and 6 days immersion in 0.1 M NaCl. EIS data and EECs are presented in Figure 6. *R*Ω = 30 Ω cm2.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Immersion  time | Impedance parameters | | | | | | | | |  |
| *Q*outer × 106  (Ω−1 cm−2 sn) | nouter | *R*outer  (kΩ cm2) | *Q*intermed × 106  (Ω−1 cm−2 sn) | ninterrmed | *R*intermed  (kΩ cm2) | *Q*dl × 106  (Ω−1 cm−2 sn) | ndl | *R*ct  (MΩ cm2) | *R*p  (MΩ cm2) |
| TM coating | | | | | | | | | |  |
| 1 day | 0.016 | 0.849 | 42.5 | 0.096 | 0.699 | 210 | 2.18 | 0.715 | 6.25 | 6.46 |
| 4 days | 0.057 | 0.764 | 1.8 | 0.453 | 0.672 | 9.2 | 4.65 | 0.685 | 2.03 | 2.01 |
| 6 days | 0.796 | 0.586 | 1.95 | 3.89 | 0.534 | 3.8 | 4.50 | 0.792 | 1.98 | 1.98 |
|  | | | | | | | | | |  |
|  | *Q*outer × 109  (Ω−1 cm−2 sn) | nouter | *R*outer  (MΩ cm2) | *Q*intermed × 106  (Ω−1 cm−2 sn) | nintermed | *R*intermed  (MΩ cm2) | / | / | / | *R*p  (MΩ cm2) |
| TMZ coating | | | | | | | | | |  |
| 1 day | 1.76 | 0.941 | 2.95 | 2.43 | 0.720 | 5.40 | / | / | / | 8.35 |
| 4 days | 3.46 | 0.897 | 1.13 | 2.94 | 0.455 | 3.85 | / | / | / | 4.98 |
| 6 days | 4.20 | 0.884 | 0.75 | 3.64 | 0.462 | 4.07 | / | / | / | 4.82 |

TABLE S2. Experimental atomic ratios of TM coatings were determined from high energy resolution XPS spectra before (TM) and after immersion in 0.1 M NaCl for 1 day (TM1), 4 days (TM4) and 6 days (TM6).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Experimental ratios | | | |
| TM | TM1 | TM4 | TM6 |
| C/Si | 5 | 5 | 5 | 7 |
| O/Si | 3 | 3 | 3 | 5 |
| O/C | 0.6 | 0.6 | 0.6 | 0.7 |

TABLE S3. Experimental atomic ratios of TMZ coatings were determined from high energy resolution XPS spectra before (TMZ) and after immersion in 0.1 M NaCl for 1 day (TMZ1), 4 days (TMZ4) and 6 days (TMZ6).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Experimental ratios | | | |
| TMZ | TMZ1 | TMZ4 | TMZ6 |
| C/Si | 8 | 6.3 | 12.1 | 8.0 |
| O/Si | 11.8 | 12.4 | 12.5 | 11.5 |
| O/C | 1.4 | 2.0 | 1.0 | 1.4 |
| C/Zr | 11.8 | 8.3 | 16.4 | 10.4 |
| O/Zr | 16.2 | 16.4 | 16.9 | 15.0 |