Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

On the structure of high performance anticorrosive PMMA-Siloxane-Silica hybrid coatings

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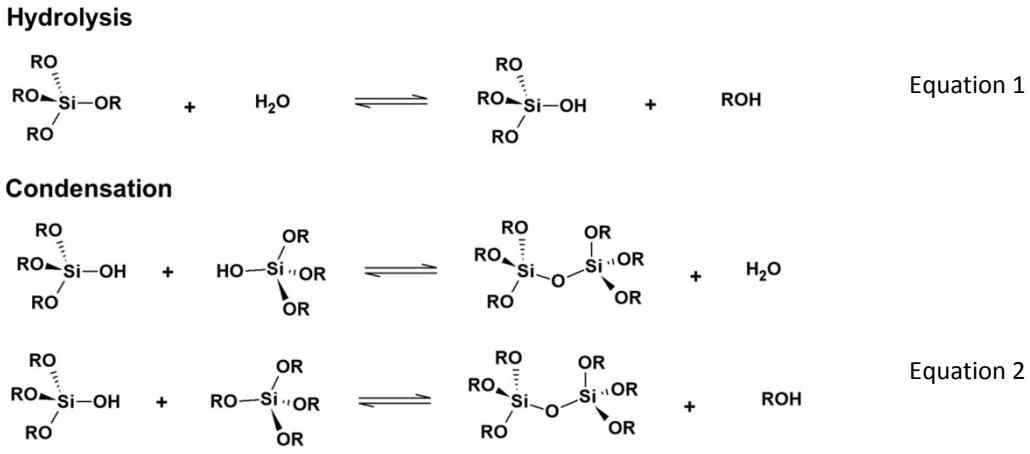

Scheme S1. Hydrolysis and condensation reactions of the sol-gel process.

Method of the SAXS analysis

Assuming an isotropic system of a set isolated silica-siloxane particles nanoparticles embedded in a homogeneous PMMA matrix, with a spatial correlation evidenced by the maximum in the ME05, the experimental SAXS intensity was fitted by the semi-empirical function proposed by Beaucage:[17]

$$I(q) = [G \exp(-q^2 R_g^2/3) + B[[erf(q R_g \sqrt{6})]^3/q\,]^{\alpha}]\, S(q) \qquad (1)$$

where R_g is the Guinier radius of gyration of the isolated nanoparticles. For a two-electron density model, G and B are are adjustable parameters given by $G = N (\rho_p - \rho_m)^2 V_2$ and $B = 2\pi (\rho_p - \rho_m)^2 A$, where N is the number of particles per unit volume, V is the particle volume, A is the interface area between the particles and the matrix and (ρ_p and ρ_m) are average electron densities of the particles and the matrix, respectively.

In Eq. (1), the asymptotic Guinier and Porod laws are merged. The *erf* function acts as a low q cut-off that brings to zero the Porod law contribution at a point depending on the R_g parameter. For a system with a diluted set of nanoparticles the interference effects of intensity scattered by each particle is absent and structure function is equal to unity $S(q) = 1$.

In the case of semi-diluted the interference effect was take accounts considering the structure-function $S(q)$ for spherical particles, in which the only correlation is a hard sphere interaction, is given by [17]:

$$S(q) = 1/(1 + k\,\theta) \qquad (2)$$

The packing factor k describes the degree of correlation that measures the number of nearest neighbour particles and is equivalent to $8V/V_0$ where V is the average "hard-core" volume and V_0 is the average available volume for each sphere. The form function, θ, depends on the average inter-particle distance, d, as follows:

$$\theta\,(q) = 3[\sin(qd) - q\,d\cos(q\,d)]/(q\,d)^3 \qquad (3)$$

where d is the average distance between nanoparticles. Equation (3) was derived for systems of identical spatially correlated nanoparticles, but it is usually also applied, to systems of correlated particles with a narrow or moderate width of size distribution.

The experimental SAXS curves were fitted with equation (1) using a no linear least square procedure, leading to the continuous lines displayed in Fig. 2.

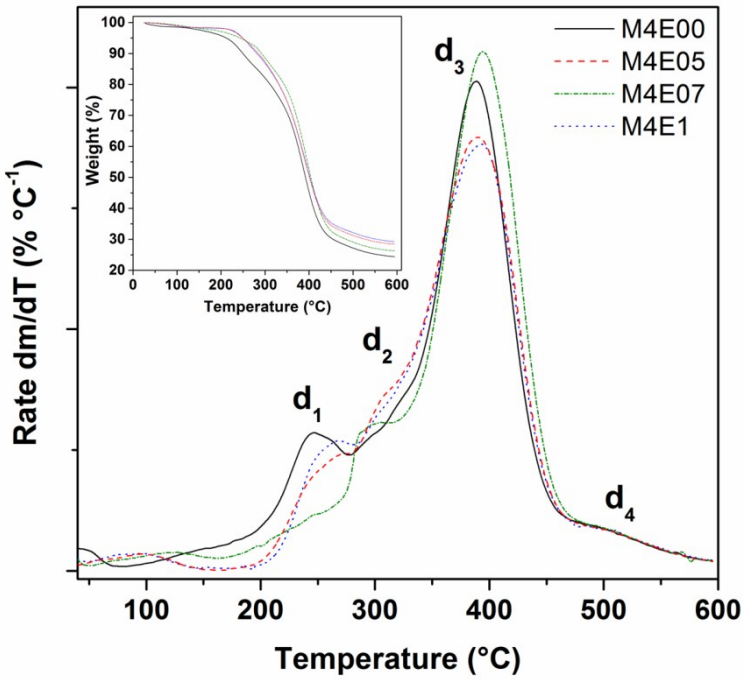

Figure S1. DTG and TG (inset) curves of PMMA-SS hybrids, prepared at EtOH/H_2O molar ratios ranging from 0.0 to 1.0, indicate the existence of four degradation stages: rupture of the head-to-head segments at ~250 °C (d_1) and to unsaturated chain ends at ~310 °C (d_2), random scissions of the polymer chains ~400 °C (d_3) and partial dehydration of residual silanol groups ~480 °C (d_4).

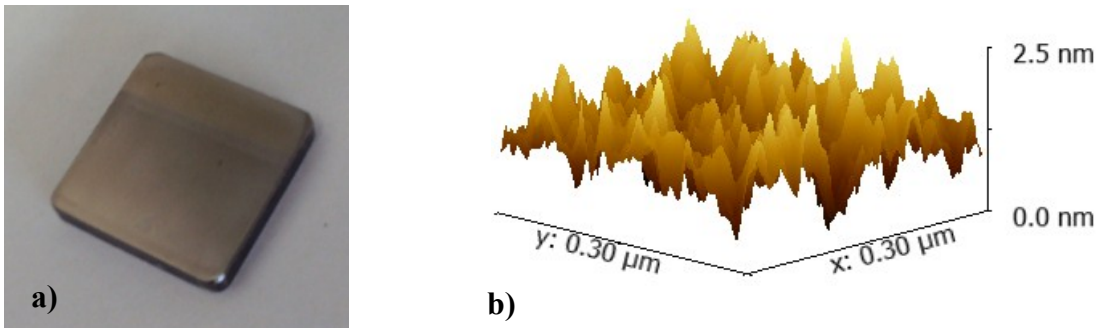

Figure S2. a) Representative image of the PMMA-SS hybrid coated carbon steel, and b) AFM topography of the flat and featureless surface of sample M4E05.

Table S1. Critical loads observed for the scratch events for hybrid films prepared with different EtOH/H_2O ratios.

	Critical loads (mN)				
Event / Sample	M4E00	M4E01	M4E02	M4E05	M4E1
Plastic deformation	1.7 ±0.6	0.4±0.1	0.4±0.1	1.0 ±0.9	0.3 ±0.1
Initial cracks	21.8 ±0.6	19.5±0.5	17.5±1.0	19.2 ±0.2	17.5 ±1.2
Film delamination	not observed	Not observed	not observed	not observed	not observed

Table S2. Parameters of the electrical equivalent circuit for sample M4E05 after 1 day exposure and M4E02 after 1 day and 196 days immersion in neutral 3.5% NaCl solution.

Sample	M4E05 (1day)		M4E02 (1day)		M4E02 (196 days)	
χ^2	1.9×10^{-4}		0.63×10^{-3}		1.6×10^{-3}	
R_1 (Ω cm^2)	1.63×10^{7}	(5.80)	2.37×10^{7}	(13.9)	2.05×10^{7}	(7.87)
CPE_1 (F cm^{-2} s^{n-1})	4.50×10^{-9}	(0.50)	2.08×10^{-9}	(1.07)	2.71×10^{-9}	(1.70)
n_1	0.97	(0.10)	0.97	(0.12)	0.95	(0.22)
R_2 (Ω cm^2)	1.68×10^{9}	(1.00)	4.59×10^{9}	(5.25)	7.26×10^{8}	(1.78)
CPE_2 (F cm^{-2} s^{n-1})	2.3×10^{-9}	(0.86)	2.19×10^{-9}	(0.75)	3.69×10^{-9}	(1.29)
n_2	0.69	(0.39)	0.56	(0.92)	0.69	(1.04)

Values between brackets represent the fitting errors (%).