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Supporting Information: A structural and physical study of sol-gel methacrylate-silica hybrids: Intermolecular spacing dictates the mechanical properties

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Sol-gel hybrids are inorganic/organic co-networks with nanoscale interactions between the components leading to unique synergistic mechanical properties, which can be tailored, via a selection of the organic moiety. Methacrylate based polymers present several benefits for class II hybrids (which exhibit formal covalent bonding between the networks) as they introduce great versatility and can be designed with a variety of chemical side-groups, structures and morphologies. In this study, the effect of high cross-linking density on the structure-property relationships of hybrids generated using poly(3-trimethoxysilylpropyl methacrylate) (pTMSPMA) and tetraethyl orthosilicate (TEOS) was investigated. The complexity and fine scale of the co-network interactions requires the development of new analytical methods to understand how network evolution dictates the wide-ranging mechanical properties. Within this work we developed data manipulation techniques of acoustic-AFM and solid state NMR output that provide new approaches to understand the influence of the network structure on the macroscopic elasticity. The concentration of pTMSPMA in the silica sol affected the gelation time, ranging from 2 h for a hybrid made with 75 wt% inorganic with pTMSPMA at 2.5 kDa, to 1 minute for pTMSPMA with molecular weight of 30 kDa without any TEOS. A new mechanism of gelation was proposed based on the different morphologies derived by AC-AFM observations. We established that the volumetric density of bridging oxygen bonds is an important parameter in structure property relationships in SiO_2 hybrids and developed a method for determining it from solid state NMR data. The variation in the elasticity of $pTMSPMA/SiO_2$ hybrids originated from pTMSPMA acting as a molecular spacer, thus decreasing the volumetric density of bridging oxygen bonds as the inorganic to organic ratio decreased.

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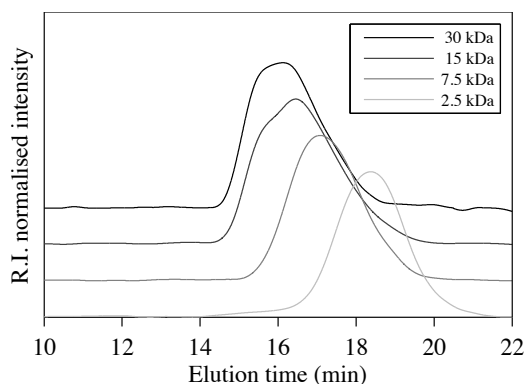
Fig. 1 Gel permeation chromatographs of pTMSPMA synthesised by regulated-free radical polymerisation using thioglycerol as chain transfer agent. Dimethylformamide with 0.075% of lithium bromide was used as eluent flowing at 0.7 ml/min, 35°C
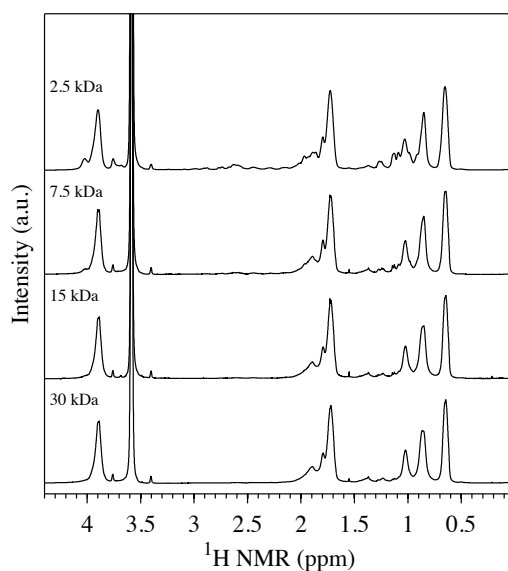

Fig. 2 ^{1}H NMR spectra of pTMSPMA at different molecular weight. All baseline were corrected and CDCl$_3$, δ_{CDCl_3} 7.27, was used as an internal reference.

Table 1 Reduced Young's modulus, E$_r$, hardness, H, and viscoelastic factor, $\alpha_3\eta_Q$, extracted from nanoindentation data using the Viscous-Elastic-Plastic model. mean and standard deviation are given on a basis of 50 measurements. The Young's modulus, E, is related to the reduced Young's modulus by $E_r = \frac{E}{1-v^2}$, where v is the Poisson's ratio.

| Hybrid	E$_r$ (GPa)	H (GPa)	$\alpha_3\eta_Q$ (10^{12} Pa.s^2)
I100	15.96±0.73	3.40±0.01	40.29±1.25
I29, 2.5 kDa	1.41±0.50	0.21±0.09	8.32±1.93
I50, 2.5 kDa	2.53±0.19	0.62±0.06	22.55±2.30
I75, 2.5 kDa	6.35±0.80	1.56±0.02	44.54±2.07
I29, 7.5 kDa	1.11±1.64	0.17±0.16	7.37±2.33
I50, 7.5 kDa	3.0±0.70	0.52±0.04	28.28±1.54
I75, 7.5 kDa	7.23±0.46	2.52±0.02	38.56±0.42
I29, 15 kDa	1.41±0.23	0.25±0.03	8.57±1.33
I50, 15 kDa	2.53±0.32	0.45±0.03	25.19±2.60
I75, 15 kDa	7.35±0.98	1.32±0.05	40.89±1.65
I29, 30 kDa	1.41±0.68	0.24±0.03	9.23±1.17
I50, 30 kDa	2.83±0.28	0.47±0.01	22.56±3.40
I75, 30 kDa	7.08±0.75	1.22±0.03	41.21±0.55
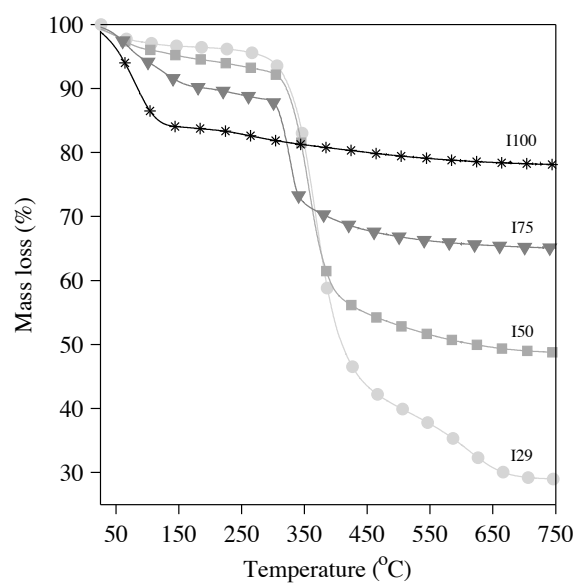
Fig. 3 Mass loss determined by TGA of hybrids made with pTMSPMA at 15 kDa using a temperature ramp of $10°C.min^{-1}$ in air. Calculations of the real inorganic to organic were made between $150°C$ and $750°C$
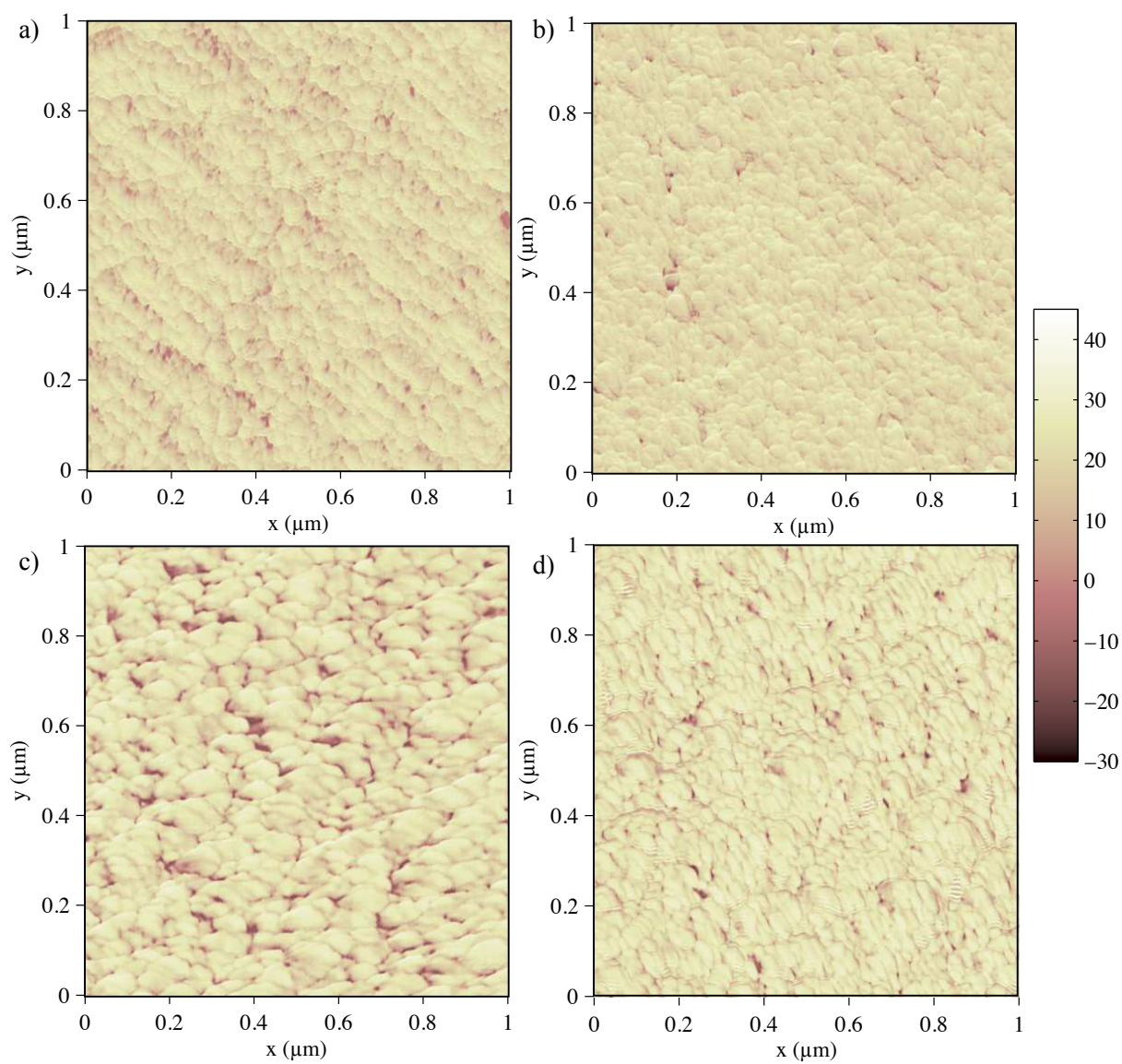
Fig. 4 Acoustic atomic force microscopy phase imaging of pTMSPMA/SiO$_2$ hybrids with pTMSPMA at 30 kDa at (a) I100, (b) I75, (c) I50 and (d) I29 over an area of 1 μm by 1 μm from -30 to 45°.
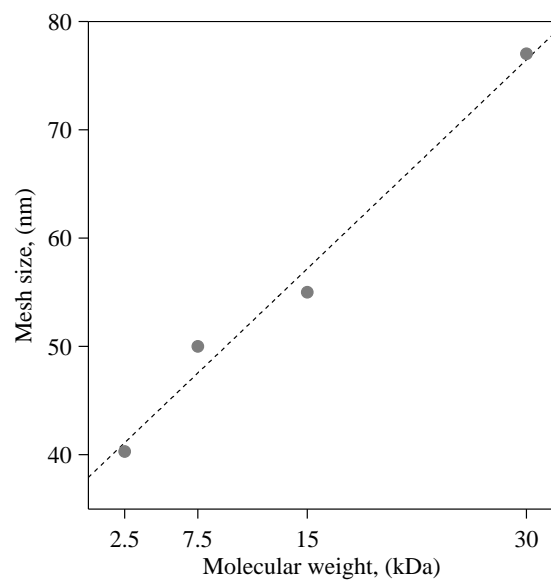
Fig. 5 Characteristic size of the polymeric mesh measured from the phase image (AC-AFM) on pTMSPMA/SiO$_2$ hybrid at I50.

$$\alpha_1 = \pi \, \tan^2 \psi$$

$$\alpha_2 = \pi \, / \, \cot \psi$$
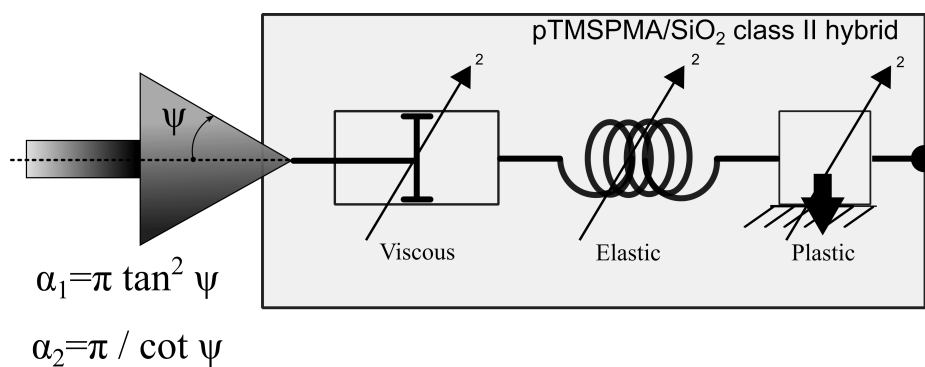
Fig. 6 Representation of the Maxwell model used to get the VEP differential equation in order to extract mechanical data from the nanoindentation measurement. The geometric parameter α_1 and α_2 are given.
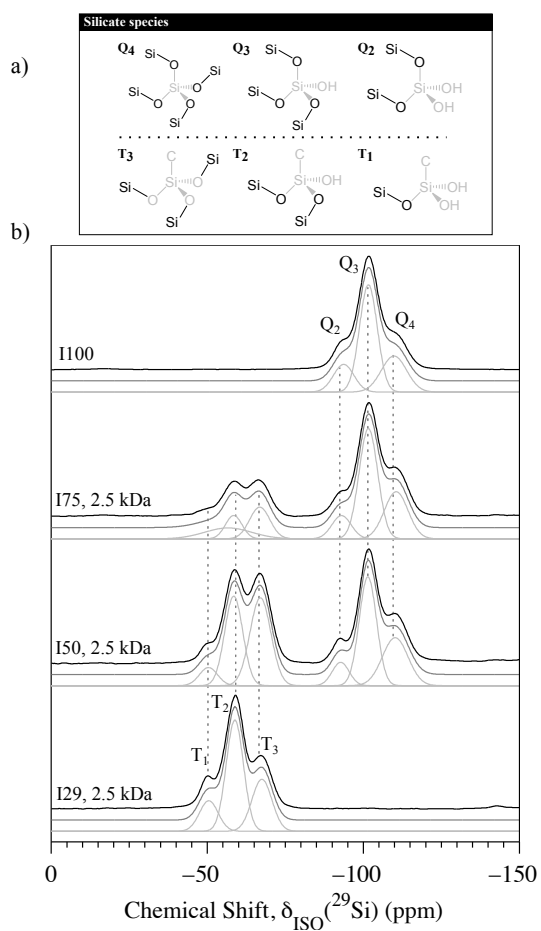
Fig. 7 a) Representation of the different silica species seen in the b) CP ^{29}Si MAS NMR spectra of hybrids synthesised with pTMSPMA at 2.5 kDa at different inorganic to organic ratio.
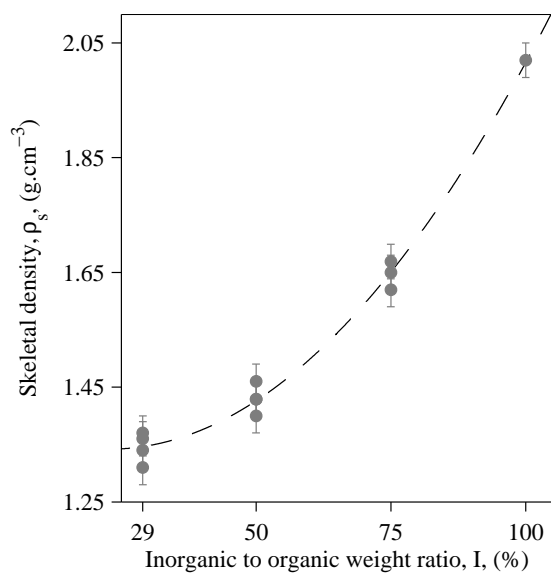
Fig. 8 Skeletal density, ρ_s, of pTMSPMA/SiO$_2$ hybrids as a function of the inorganic to organic weight ratio.