ACRYLAMIDE-BASED MAGNETIC NANOSPONGES: A NEW SMART NANOCOMPOSITE MATERIAL

SUPPORTING INFORMATION.

Small Angle Scattering Fitting Procedure used for the nanocomposite samples.

For polarized neutrons, where the neutron spins are aligned anti-parallel (+) or parallel (-) to the magnetic field vector **H**, the scattering cross-sections depend on the polarization of the incident neutrons $I^{+}(Q)$ and $I^{-}(Q)$, respectively. The scattering intensity relationships (denoted here as SANSPOL) has been previously derived.[1,2] When the magnetic moments and neutron polarization are fully aligned along the external field, the SANSPOL intensities perpendicular to the applied field are given for the two states by:

$$I^{(-,+)}(Q\perp H)\propto\left[P_N \pm P_M\right]^2 S(Q) \qquad (1)$$

where P_N and P_M represents the nuclear and magnetic form factors, respectively, and $S(Q)$ is the inter-particle structure factor.

The arithmetic mean of the parallel and anti-parallel intensities perpendicular to the applied field corresponds to the cross-section for un-polarized neutrons:

$$\left[I^{-}(Q\perp H)+I^{+}(Q\perp H)\right]/2 = I^{unpol}(Q\perp H)\propto\left[P_N^2+P_M^2\right]S(Q) \qquad (2)$$

The scattering cross-section parallel to **H** is independent of the polarization state since it depends from pure nuclear contrast and is given by:

$$I(Q//H) \propto P_N^2 S(Q) \quad (3)$$

The difference between the two intensities represents a magnetic-nuclear cross term, allowing the magnetic contrast with respect to the nuclear contrast to be determined:

$$I^{-}(Q,\alpha) - I^{+}(Q,\alpha) \propto P_N P_M S(Q) \quad (4)$$

where α is the azimuth angle between the magnetic field vector **H** and the scattering vector **Q** ($\mathbf{Q} = \mathbf{k_i} - \mathbf{k}_s$), where $\mathbf{k_i}$ and $\mathbf{k_s}$ are the incident and scattered wave vectors, respectively).

Both the perpendicular and the parallel intensities have been calculated in two separate ways, obtaining identical results: i) by adjusting the 2-D pattern to the $\sin^2\alpha$ dependence, and ii) by averaging the 2-D pattern only over sectors with a width of 5º respectively centred at α = 90° and 270º for the perpendicular intensities, and centred at α = 0° and 180º for the parallel intensities. As expected, the parallel intensities for the two flipper states resulted identical: in fact, as indicated by equation 4, these intensities account only for the nuclear scattering.

SANSPOL results on the magnetic gel have been fitted according to the following equation:

$$I(Q) = I_{Lorentz}(Q) + I_{excess}(Q) + I_{MagNP}(Q) + bkg \quad (5)$$

where *bkg* is the incoherent background.

The only contribute that is dependent on the magnetization is $I_{MagNP}(Q)$.

The Lorentzian component can be described as:

$$I_{Lorentz}(Q) = \frac{I_{Lorentz}(0)}{1 + Q^2\xi^2} \quad (6)$$

where $I_{Lorentz}(0)$ is the Lorentzian intensity at Q=0, Q is the scattering vector, and ξ is the mesh size of the gel network.

According to the Debye-Bueche theory,[3] an excess scattering term has to be introduced to account for the inhomogeneities due to strand-strand interactions:[4]

$$I_{excess}(Q) = \frac{I_{excess}(0)}{\left(1 + Q^2a^2\right)^2} \quad (7)$$

where $I_{excess}(0)$ is the Debye-Bueche intensity at Q=0 and a is the inhomogeneity domains' size.

The scattering intensity due to the MagNPs ($I_{MagNP}(Q)$) was modeled according to the formalism introduced by Bartlett and Ottewill for polydisperse spherical particles.[5] In this approach, the particles are described as spherical objects with a Schultz distribution of radii.[6,7] The contribute to the total scattering intensity arising from these objects was calculated according to the following equations:

$$P(Q) = \frac{1}{V_p}\int_0^\infty G(r_c)F^2(Qr_c)dr_c \quad (8)$$

$$F(Qr_c) = \frac{4\pi}{Q^3}\left(\rho_{shell} - \rho_{core}\right)\left\{\rho_{scaled}\, j\left(Qr_c + \frac{t}{r_c}Qr_c\right) - j\left(Qr_c\right)\right\} \quad (9)$$

$$\rho_{scaled} = (\rho_{solv} - \rho_{shell})(\rho_{core} - \rho_{shell}) \quad (10)$$

$$j(Qr_c) = \sin(Qr_c) - (Qr_c)\cos(Qr_c) \quad (11)$$

where r_c is the core radius, t is the shell thickness, V_p is the particle volume, and ρ_{core}, ρ_{shell} and ρ_{solv} are the scattering length densities (SLDs) of core, shell and solvent, respectively.

The function $G(r_c)$ is the normalized probability of finding a particle with a core radius between r_c and r_c+dr_c, and it accounts for the polydispersity of the cores according to a Schultz distribution:[6,7]

$$G(r_c) = \frac{r_c^Z}{\Gamma(Z+1)}\left(\frac{Z+1}{\langle r_c \rangle}\right)^{Z+1} \times \exp\left[-\frac{r_c}{r_{avg}}(Z+1)\right] \quad (12)$$

where $\Gamma(Z+1)$ is the gamma function and the parameter Z is related to the polydispersity σ_c of the core radius by the expression:

$$\sigma_c = \frac{\sqrt{\langle r_c^2 \rangle - \langle r_c \rangle^2}}{\langle r_c \rangle} = \frac{1}{\sqrt{Z+1}} \quad (13)$$

The fitting routine has been constrained to globally fit all the SANSPOL curves for each sample: i.e. the fitting parameters are the same for the SANSPOL intensities parallel and perpendicular (flipper ON and OFF) to the magnetic field, excepted for the core scattering length density that changes as a function of the polarization of the neutrons and the angle between **Q** and **H**. This is summarized in equation 14 where the nuclear part of the core scattering length density is the same for all the SANSPOL intensities, while the magnetic contribution is null for the parallel direction and it has the same value for the two perpendicular curves:

$$\rho_{core} = \rho_{core}^{nucl} \pm \rho_{core}^{mag} \quad (14)$$

Small Angle Scattering Fitting Procedure used for the microemulsion, before the uploading into the nanosponge and after the recovery.

In the fitting model we assume the microemulsion as composed of polydisperse core-shell spheres with a mean aggregation number, N_{agg}, and an effective charge Z. The external hydrophilic shell having dimension t is formed mainly by the SDS polar heads, the OH groups of the 1-pentanol molecules, the first methylene group of both 1-pentanol and SDS,[8] the hydration water, and a fraction of counterions. The hydrophobic core of spherical shape, with a radius r_c, contains the surfactant hydrocarbon tails (i.e. $C_{11}H_{23}$ and C_4H_9 of SDS and 1-pentanol respectively) and the molecules of p-xylene and nitrodiluent.

Within these assumptions the scattering intensity can be written as:[9]

$$I(Q) = A\ \phi P(Q)S(Q) + bkg \qquad (15)$$

where A is a constant accounting for the instrumental factor (intensities are not in absolute scale), ϕ is the microemulsion volume fraction, P(Q) is the averaged intraparticle structure factor for polydisperse spherical particles as already described by equations 9-13 considering the SLD profile in the microemulsion case, S(Q) is the averaged center-center interparticle structure factor, and *bkg* the instrumental background.

$$S(Q) = 1 + \frac{\langle F(Qr_c)\rangle^2}{\langle F(Qr_c)^2\rangle}\left[S_{MM}(Q) - 1\right] \qquad (16)$$

where $\langle F(Qr_c)\rangle$ represents an average over the size distribution and $S_{MM}(Q)$ has been calculated, as described by Liu et al.[9] by solving the Ornstein-Zernicke equation for the pair correlation function within the non-additive radius multicomponent mean spherical approximation closure that yields analytical solutions.

For each sample the adjustable parameters were the core radius r_c, the shell thickness t, the micellar charge Z and the background contribution bkg; the amplitude A was

assumed to be equal for all the samples so that the two scattering curves have been simultaneously fitted under this constraint. In the case of the microemulsion before the incorporation in the gel the volume fraction has been calculated by its chemical composition. After the recovery from the gel this parameter has been left free to vary.

Table 3. Parameters resulting from the fit of SAXS intensities on microemulsions.

Coefficient	**Before Loading**	**After Recovery**
volume fraction	0.150	0.134
average core radius	28.8 Å	25.3 Å
core polydispersity	0.283	0.293
shell thickness (Å)	5.3 Å	5.7 Å
SLD core ($Å^{-2}$)	$7.3x10^{-6}$	$7.3x10^{-6}$
SLD shell (A-2)	$1.11x10^{-5}$	$1.10x10^{-5}$
SLD solvent (A-2)	$9.37\ x10^{-6}$	$9.37\ x10^{-6}$
Micellar charge	28.1	27.4
Monovalent salt (M)	0	0
Temperature (K)	298	298

dielectric const.	78	78
bkg (cm^{-1})	2.472	2.266
Amplitude	49.5542	49.5542

Thermal analysis. Thermogravimetric analysis was performed with an SDT Q600 apparatus (TA Instruments, Milan, Italy). The temperature range was 25–800 °C, with a scan rate of 20 °C/min. The run was performed with alumina pan and under a nitrogen flux of 100 mL/min. Two weight losses are clearly visible: the first one due to water evaporation and the second one due to the burning of the organic matrix of the gel. Therefore, the constant residual weight from 700°C can be ascribed to the solid metallic content of the gel, equal to 0.65 %wt as inferred from TGA data analysis.

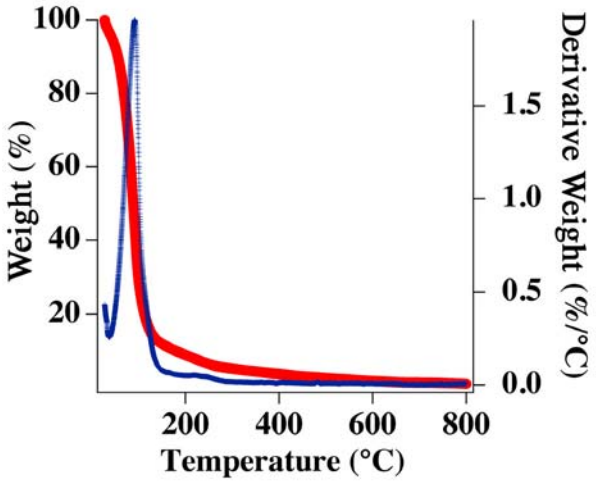

Figure 1. TGA plot of the hydrated gel; continuous line, sample weight; markers, derivative weight.

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