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Electronic Supplementary Information

Polymer-mediated Interaction between Nanoparticles during Hydration and Dehydration: A Small-angle X-ray Scattering Study

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Fourier Transform Infrared Spectroscopy (FTIR):

To study the molecular structures of the PVA-silica nano-composites, Infrared spectra of the samples were recorded in the spectral range of 600-4000 cm^{-1} using the Bracer Vertex 80 V FTIR spectrometer with an Attenuated Total Reflection (ATR) method.

Table S1 The assignment of major adsorption bands of FTIR spectra of composite samples

Modes	**Peak position (cm^{-1})**	**Assigned functional groups**
ν_1	650	Wagging mode of (OH) groups
ν_2	790	Si-O-Si bending
ν_3	1050, 1075	C=O stretching, Si-O-Si rocking
ν_4	1640, 1652	-OH bending, C=C stretching
ν_5	1735	C=O stretching
ν_6	3300	-OH stretching

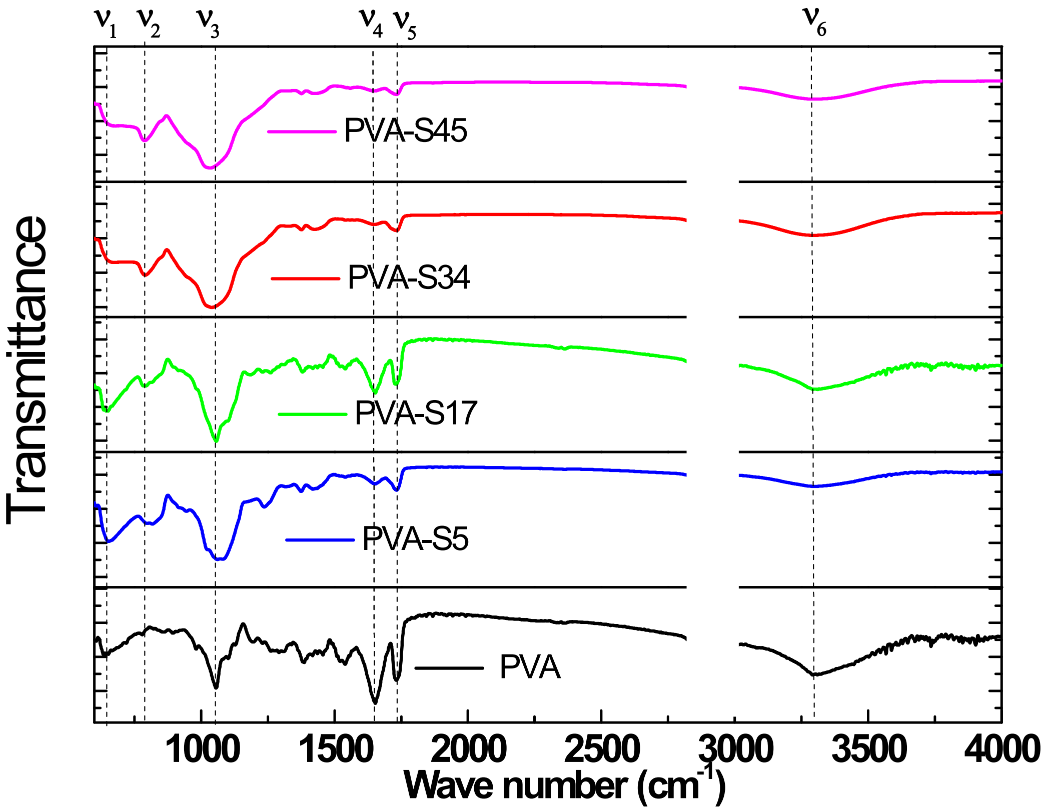


Figure S1 The IR spectra of the polymer nanocomposites. The important functional groups are marked.

The large adsorption band at around 3,300 cm^{-1} which is present in all the samples was due to the O-H stretching of the non-hydrogen bonded and hydrogen bonded O-H groups[1]. The OH groups of silanol groups on the silica nanoparticle also contribute to the mode in PVA-silica composites. Band around 1650 cm^{-1} corresponds to C=C stretching and the intensity of this mode decreases with increasing volume fraction of silica nanoparticle in the composite. Similarly, band at around 1730 cm^{-1} corresponds to the C=O stretching mode and its intensity decreases with increasing relative fraction of the silica as expected. Additional adsorption band appears ~1075 cm^{-1} due to Si-O-Si rocking mode as silica nanoparticle is introduced in the polymer nanocomposite. The modes in the range of ~ 1400 -1500 cm^{-1} appears due to CH_2

bending vibration[2]. The IR study confirms successful incorporation of the silica nanoparticles in the polymer matrix.

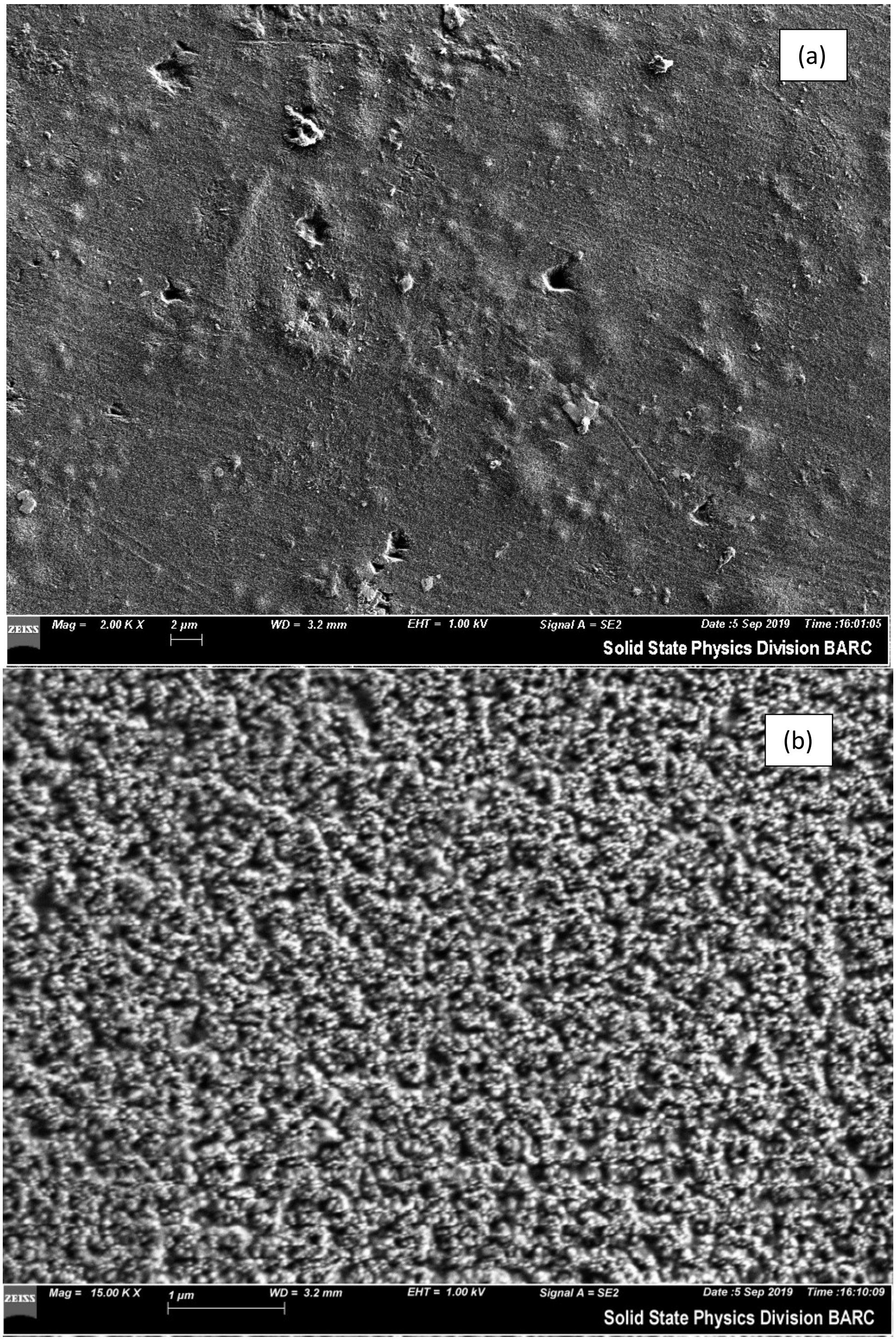


Figure S2 Micrographs of the PVA-S34

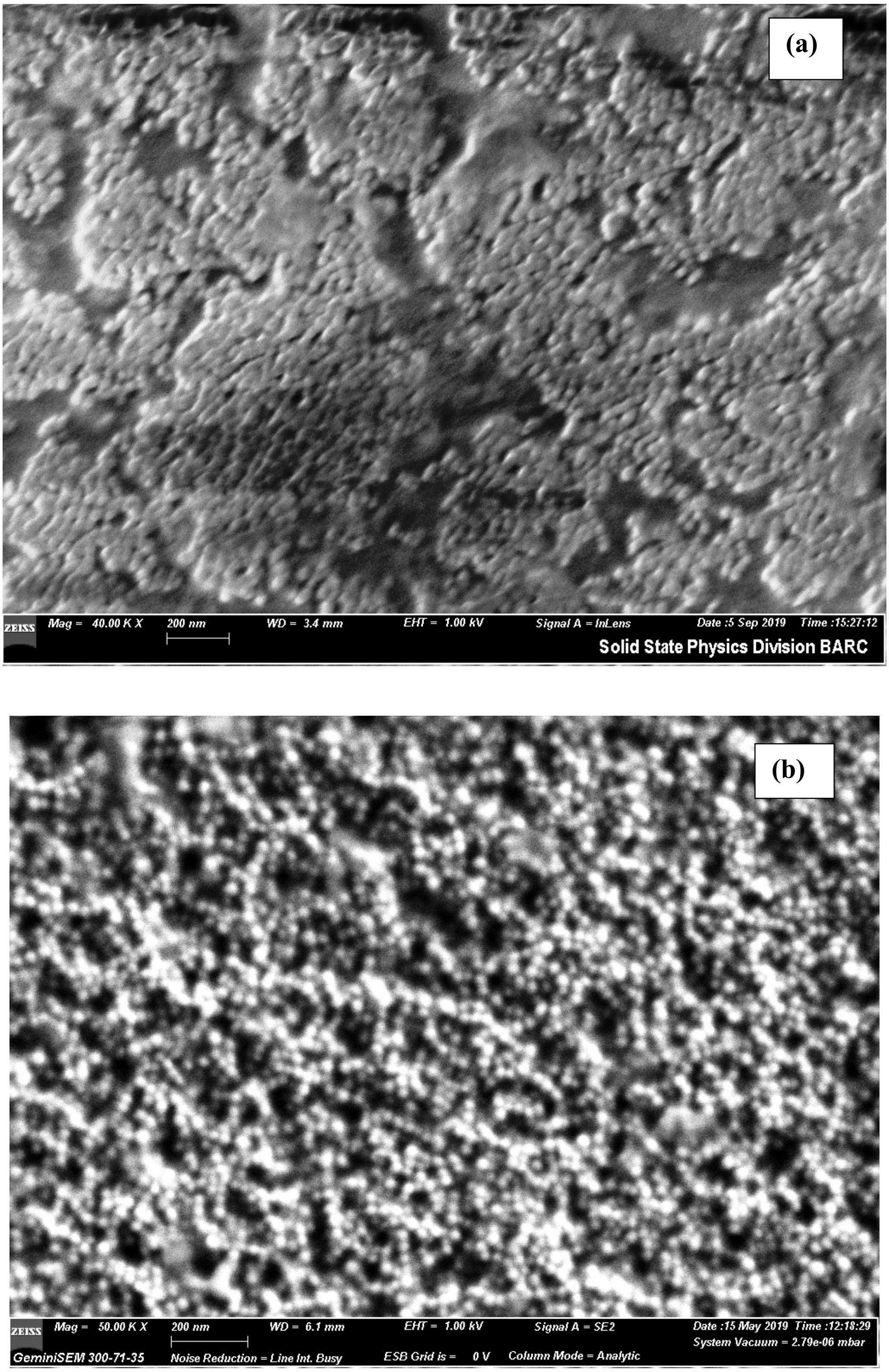


Figure S3 Micrographs of (a) PVA-S5 (b) PVA-S45 in high magnification

Modelling of SAXS and SANS data:

The SAXS profile of the PVA film is fitted using the following simple functional form that fit the broad peak feature.

$$I(q) = C_1 q^{-\alpha} + \frac{C_2}{\left(1 + \left(|q - q_0|\xi\right)^m\right)} + BKG \qquad (S1)$$

C_1 and C_2 are q-independent constants. BKG is the constant background at high q. The first term accounts the scattering contribution at low-q which is power law in nature. α is the exponent of power law scattering. The second term accounts the broad peak due to crystalline nature of the PVA polymers in the film. Here, the peak position q_0 is related to the average distance between the microcrystallites as $q_0=2\pi/D$. ξ is the characteristic length for positional correlation. The scattering intensity $I(q)\sim q^{-m}$ at $q \rightarrow \infty$, the exponent m in the eq. S1 provides information about the interface of the scattering objects. For a smooth interface, m becomes 4.

The following expression for the scattering intensity is assumed to fit the SAXS profiles.

$$I_s(q) = n\,(\Delta\rho)^2 \int V_p^{\,2}(r) N(r) P(q,r) S(q,r)\,dr + BKG \qquad (S2)$$

where n is number density of the silica nanoparticles and $(\Delta\rho)^2$ is the contrast between the silica and polymer. P(q,r) is the form factor of the sphere with radius r (eq. 3). V_p $(4\pi r^3/3)$ is the volume of a silica nanoparticle with radius r and N(r) is the lognormal size distribution of the silica particles. The expressions for P(q, r) and N(r) are shown below:

$$P(q,r) = 9\left[\frac{\sin(qr) - qr\cos(qr)}{(qr)^3}\right]^2 \qquad (S3)$$

$$N(r) = \frac{1}{\sqrt{2\pi\sigma^2 r^2}}\exp\left(-\frac{[\ln(r/r_0)]^2}{2\sigma^2}\right)$$

(S4)

S(q,r) is the structure factor corresponding to sticky hard sphere interaction[3] between nanoparticles and it depends on the volume fraction of the nanoparticles, ϕ_s. The model as shown in eq. 2 fits the SAXS data of both the dispersions and composite film quite well (Fig. 2). The SANS data is also fitted using the model shown in eq. 2 and the estimated parameters are found to be identical. The high-q part of the SANS data contains some contribution of polymer scattering which is modelled assuming Gaussian chain model and a radius of gyration of polymer is found to be ~ 4.0 nm.

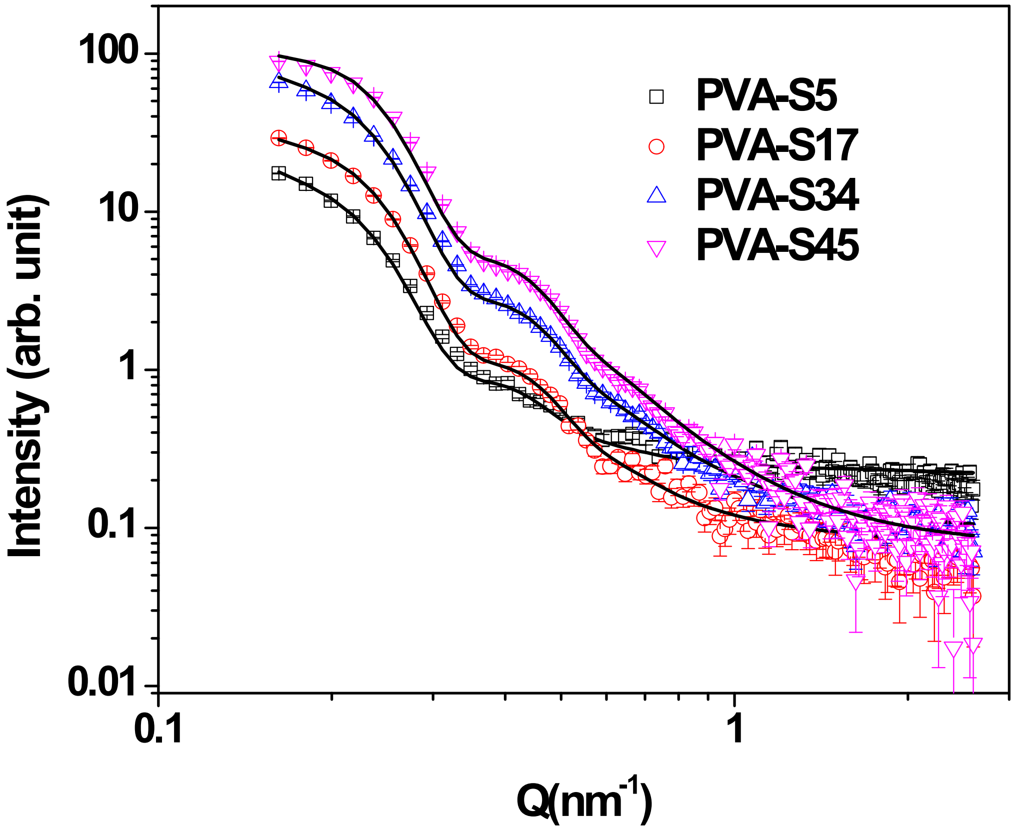


Figure S4 Experimental SANS profiles of the pure PVA and PVA-silica composite films.

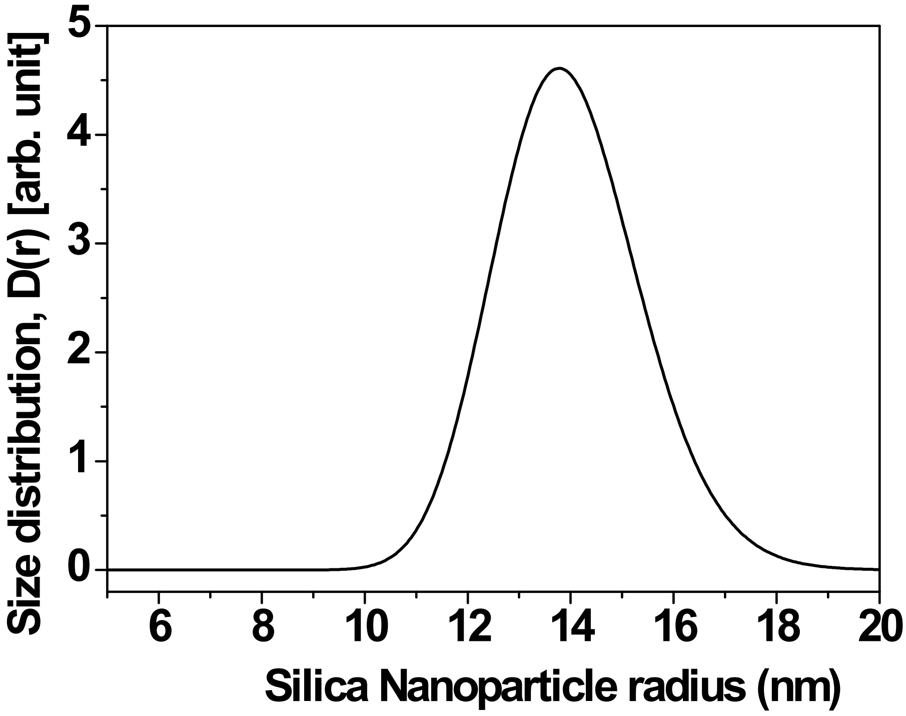


Figure S5 Size distribution of silica nanoparticles in the composite

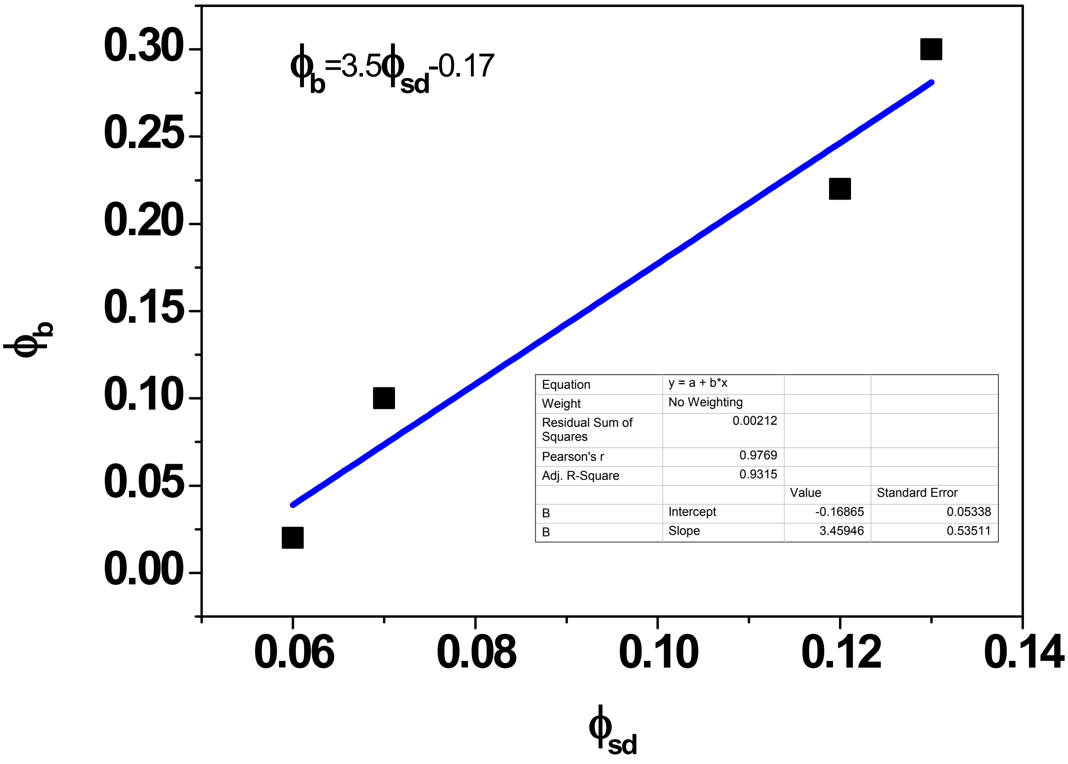
Fitting function of the temporal evolution of the dehydration kinetics

The logistic function can be expressed as below:

$$\phi(t) = \phi_f + \frac{\phi_i - \phi_f}{\left(1 + exp\frac{(t - t_0)}{\Delta t}\right)}$$

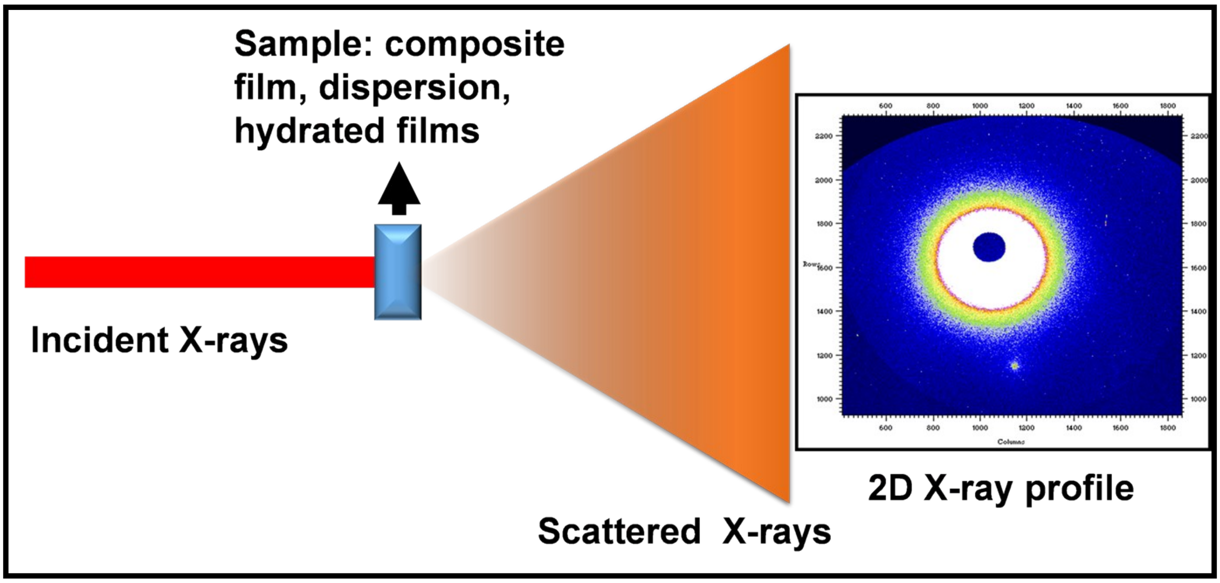
(S5)

Here, ϕ_i and ϕ_f is the initial local volume fraction for the water saturated composite and dried composites, respectively. t_0 is midpoint of the sigmoid curve and defined as the time when value of $\phi(t)$ reaches to the average value of initial and final volume fraction, i.e. $\phi(t_0) = \phi_i + \phi_f/2$. Δt is the sharpness of the logistic growth rate. It is important to note that logistic function is widely adopted for representing processes of growth in several fields such as population growth, growth of tumors, haemoglobin release and growth of bacteria etc.[4]. Logistic function is used to describe process which consists of three basic kinetics stages: nucleation, multiplication and termination. During the first stage of nucleation, clusters of products molecules with defined sizes are formed. In second stage, concentrations of cluster multiplies without growth of their sizes leading to abrupt increase in the process rate to its maximum value. In the termination stage, clusters concentrations decrease due to various processes which leads to slowing down of the process rate.

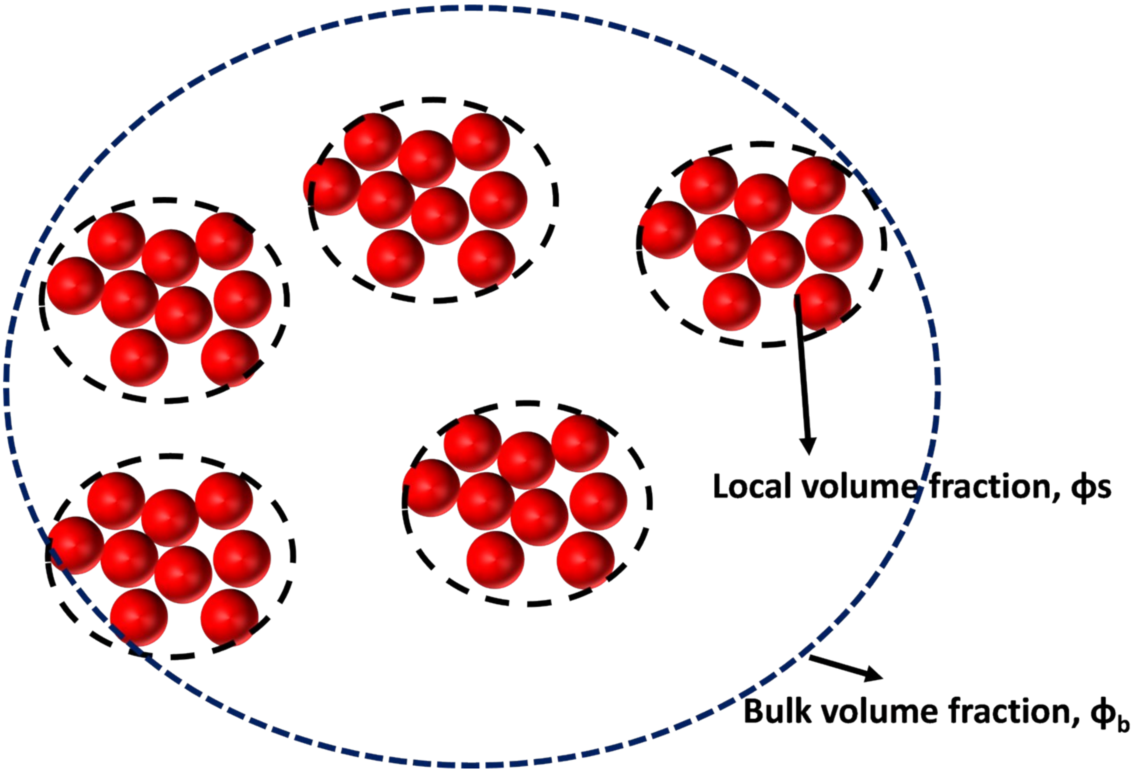


Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.00212		
Pearson's r	0.9769		
Adj. R-Square	0.9315		
		Value	Standard Error
B	Intercept	-0.16865	0.05338
B	Slope	3.45946	0.53511

Figure S6 Variation of local volume fraction in the dispersion ϕ_{sd} as a function of bulk volume fraction ϕ_b. Error bars are within the size of the legends. The solid line is a linear fit to the data



Schematic S1 Schematic showing SAXS measurements setup



Schematic S2 Schematic diagram showing the concept of local and bulk volume fraction

References:

1. M. Miya, R. Iwamoto and S. Mima, *Journal of polymer science: Polymer Physics edition*, 1984, **22**, 1149-1151.
2. G. H. Kumar, J. L. Rao, N. Gopal, K. Narasimhulu, R. Chakradhar and A. V. Rajulu, *Polymer*, 2004, **45**, 5407-5415.
3. S. Menon, C. Manohar and K. S. Rao, *The Journal of chemical physics*, 1991, **95**, 9186-9190.
4. B. Adnadjevic, G. Tasic and J. Jovanovic, *Thermochimica acta*, 2011, **512**, 157-162.