ELECTRONIC SUPPLEMENTARY INFORMATION

Fitting – Laponite RD Suspensions

The scattering from the Laponite RD suspensions in D_2O were fit to the Monodisperse Rigid Cylinder form factor model[1] in IGOR Pro. The disk can be represented by the cylinder model with the length, L (= $2H$), according to Figure S1, being smaller than the radius, R, of the cylinder. This model calculates the form factor, $P(q)$, for a monodisperse right circular cylinder with uniform scattering length density. The form factor is normalized by the particle volume, Vol, such that $P(q)$ = scale*$<\phi^2>/Vol$ + bkg, where < > is an average over all possible orientations of the cylinder and bkg is the incoherent background term. The function calculated is:

$$P(q) = \frac{scale}{V_{cyl}} \int_0^{\pi/2} f^2\,(q,\alpha) \sin\alpha\, d\alpha$$

$$f(q,\alpha) = 2\big(\rho_{cyl} - \rho_{solv}\big) V_{cyl} j_0(qH\cos\alpha) \frac{J_1(qr\sin\alpha)}{(qr\sin\alpha)}$$

$$V_{cyl} = \pi r^2 L \text{ and } j_0(x) = \sin(x)/x$$

where $J_1(x)$ is the first order Bessel function. The angle between the cylinder axis and the scattering vector, q, is defined as α. The integral over alpha averages the form factor over all possible orientations of the cylinder with respect to q. The returned value is in units of cm^{-1}, on an absolute scale. The scattering contrast is defined as $(\rho_{cyl} - \rho_{solv})$ = SLD (cylinder) - SLD (solvent). The scale and scattering length densities (the contrast) are both multiplicative factors in the model and are perfectly correlated. One or both of these parameters must be held fixed during model fitting.

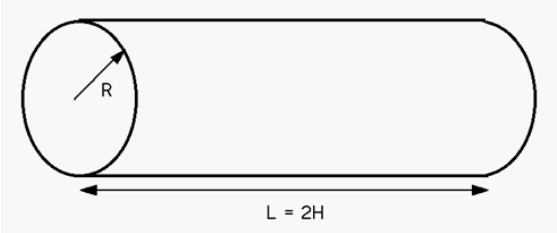
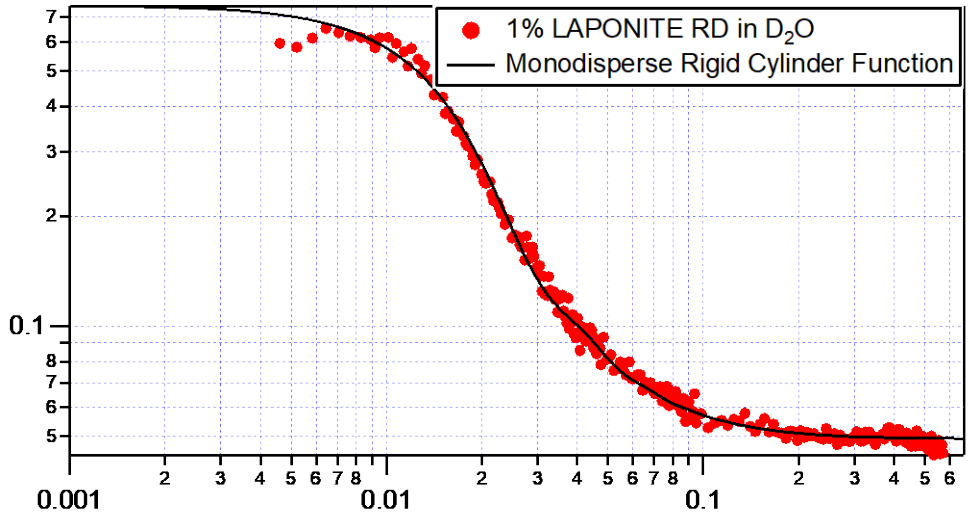


Figure S1. – Schematic of Rigid Cylinder defining parameters used in model fitting.

If the scale factor is set equal to the particle volume fraction, ϕ, the returned value is the scattered intensity per unit volume, $I(q) = \phi * P(q)$. However, no interparticle interference effects are included in this calculation. There are six parameters in the functional form: 1) The scale factor; 2) the radius of the cylinder; 3) the length of the cylinder; 4) the scattering length density of the particle; 5) the scattering length density of the suspending medium and 6) the incoherent background intensity. The volume fraction and scattering length density of the clay (= 4.18×10^{-6} Å^{-2}) are known assuming the density of the clay reported by Nelson and Cosgrove[2] of 2.35 g/cm^3. The scattering length density of pure D_2O is also well known (= 6.3×10^{-6} Å^{-2}). Therefore, the IGOR Pro non-linear regression routine has three unknown parameters, the clay particle dimensions (radius and length) and the incoherent background term. An example of the fitting results for one run on the Laponite RD suspension data is shown in Figure S2 along with the extracted fit parameters. The specific fit values for the Laponite RD from each experimental set were used for the core parameters in PolyCoreShell Cylinder model fits described below.



Parameter	Value	Hold
scale	0.00377	1
radius (Å)	132.066	0
length (Å)	7.59351	0
SLD cylinder (Å^-2)	4.18e-06	1
SLD solvent (Å^-2)	6.3e-06	1
incoh. bkg (cm^-1)	0.0492114	0

Figure S2. - Scattering data from a 1% suspension of Laponite RD in D_2O. Curve representing best fit to monodisperse rigid cylinder model in black

Fitting – PEO/Laponite RD Mixtures

For the PEO/Laponite RD samples, a core-shell cylinder with polydisperse radius (PolyCoreShell Cylinder) model[Error! Bookmark not defined.] was found to best represent the scattering. This function calculates the scattering for a polydisperse, right circular cylinder with a core-shell scattering length density profile. The shell thickness on the flat ends of the cylinder is independent of the shell thickness on the radial surface. The polydispersity of the cylinder core radius is modelled using a log-normal distribution. The overall intensity is obtained by calculating the scattering from each particle size present and weighting it by the normalized distribution.

The function calculated is:

$$I(Q) = bkg + \frac{scale}{V_p}\sum_{R_p} n(R_p, \sigma_p)P(q, R_p, R_l, H_p, H_l, \rho_p, \rho_l, \rho_{solv})$$

with the normalized log-normal distribution:

$$n(R_p) = \frac{exp\left(-\frac{1}{2}\left[\frac{ln(R_p/R_0)}{\sigma_p}\right]^2\right)}{\sqrt{(2\pi)}\sigma_p R_p}$$

and

$$P(Q) = \int_0^{\pi/2} \sin\theta\, d\theta \left[V_l(\rho_l - \rho_{solv})\frac{\sin\left(\frac{QH_l\cos\theta}{2}\right)}{\frac{QH_l\cos\theta}{2}}\frac{2J_1(QR_l\sin\theta)}{QR_l\sin\theta} + V_p(\rho_p - \rho_l)\frac{\sin\left(\frac{QH_p\cos\theta}{2}\right)}{\frac{QH_p\cos\theta}{2}}\frac{2J_1(QR_p\sin\theta)}{QR_p\sin\theta}\right]^2$$

$$V_x = \pi R_x^2 H_x$$

where $J_1(x)$ is the first order Bessel function. The variable θ is defined as the angle between the cylinder axis and the scattering vector, Q. The integral over θ averages the form factor over all possible orientations of the cylinder with respect to Q. The core radius = R_p, core length = H_p (the mean core radius is R_o). Note that the shell radius and shell length incorporate the dimensions of the bare particle (i.e. $H_l = H_p + 2\cdot$face thickness and $R_l = R_p +$ radial thickness). The quantity σ is equivalent to the standard deviation of the log-normal distribution.

The form factor *P(Q)* is normalized by multiplying by scale/V_p. If the scale represents the volume fraction of the core particles then the multiplication factor is the number density of particles and an absolute intensity is returned. The PolyCoreShell Cylinder model contains 10 adjustable parameters:

1) Scale factor;

2) Core (clay) radius);

3) Core polydispersity;

4) Core thickness;

5) Radial shell thickness;

6) Face shell thickness;

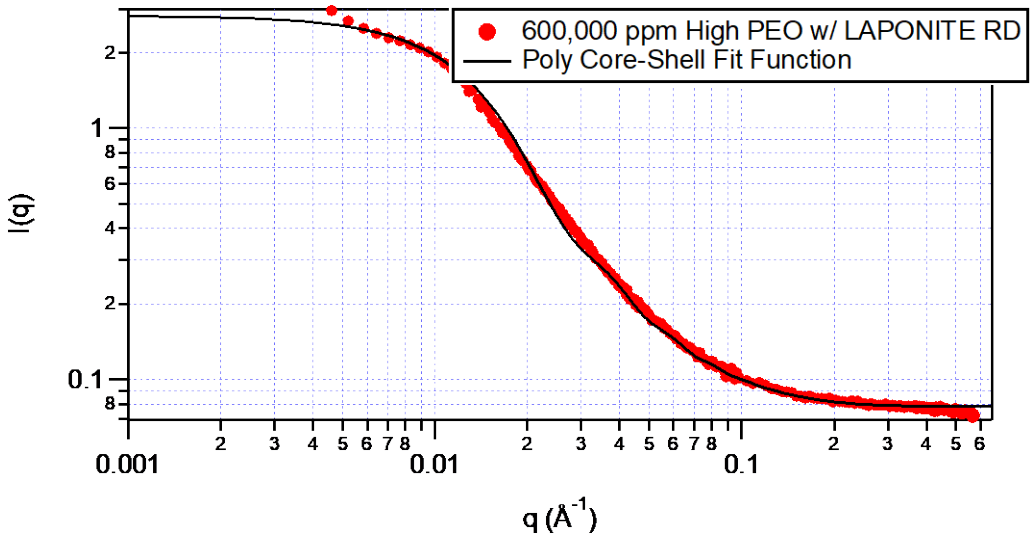
7) Scattering length density of the core;

8) Scattering length density of the shell;

9) Scattering length density of the suspending medium; and

10) Incoherent background scattering term.

The scale factor is known from the initial clay concentration, and the dimensions of the core were measured directly from the suspensions of the pure Laponite RD. Since the Laponite RD was fit to a monodisperse, rigid cylinder model, the polydispersity value is arbitrarily fixed to 0.01. The scattering length densities of the core and suspending medium are also known; therefore, four of the ten parameters (in bold), the radial shell thickness, the face shell thickness, the scattering length density of the shell, and the incoherent background terms are extracted from the fit. The scattering length density of the shell is allowed to be a fit parameter in contrast to Nelson and Cosgrove,[2] who fix the shell scattering length density to the scattering length density of the bulk polymer. By allowing the scattering length density of the shell to be a fit parameter, the composition of the shell is presumed to be a layer of polymer swollen by the suspending medium (D_2O), instead of a layer of pure polymer. We believe this to be a better representation of the structure of the polymer adsorbed to the clay surface. An example of the fit to a PEO/Laponite RD mixture and the associated fit parameters are shown in Figure S3. Summaries of the fit values for the different molecular weight PEO polymers with Laponite RD are given in Tables S1 – S3.



Parameter	Value	Hold
scale	0.001885	1
mean CORE radius (Å)	130.191	1
radial polydispersity (sigma)	0.01	1
CORE length (Å)	7.7881	1
radial shell thickness (Å)	14.2218	0
face shell thickness (Å)	2.92943	0
SLD core (Å^-2)	4.18e-06	1
SLD shell (Å^-2)	6.4e-07	0
SLD solvent (Å^-2)	6.3e-06	1
incoh. bkg (cm^-1)	0.0784185	0

V_chisq = 5077.91

Figure S3. - Fit to 600,000 ppm high molecular weight PEO with respect to Laponite RD (0.5% by mass) in pure D_2O. Data represented by colored data points and fit to PolyCoreShell Cylinder model depicted by solid black line. Fit parameter values in table.

Table S1. – High Molecular Weight PEO Average Fitting Results

Polym Conc. (ppm)	Radial Shell Thick (Å)	Radial Shell Std. Dev (Å)	Face Shell Thick (Å)	SLD Shell x10^6 (Å^{-2})	Apparent Polym. Vol Fract.
1,000	20.5	1.1	-	2.948	0.592
2,000	24.9	4.8	-	4.056	0.396
3,000	8.4	0.1	-	2.016	0.757
5,000	14.1	5.4	0.15	3.710	0.458
10,000	15.7	2.8	-	2.223	0.720
20,000	13.2	2.0	0.010	3.203	0.547
30,000	13.9	2.7	0.17	1.648	0.822
100,000	18.6	6.0	0.85	1.718	0.810
200,000	28.6	9.9	2.11	2.262	0.713
300,000	22.2	2.7	3.03	1.688	0.815
400,000	34.6	2.8	9.80	3.321	0.526
600,000	24.2	11.6	7.26	3.562	0.484

Table S2. - Medium Molecular Weight PEO Average Fitting Results

Polym Conc. (ppm)	Radial Shell Thick (Å)	Radial Shell Std. Dev	Face Shell Thick (Å)	SLD Shell x10^6 (Å^{-2})	Apparent Polym. Vol. Fract.
1,000	12.0	1.2	-	2.592	0.655
2,000	15.8	9.8	-	3.708	0.459
3,000	17.8	0.2	-	3.273	0.535
5,000	25.8	14.2	-	3.582	0.480
10,000	19.5	11.7	-	2.844	0.611
20,000	13.8	1.3	0.08	2.117	0.739
30,000	16.3	2.0	0.23	2.019	0.756
100,000	18.7	1.9	1.27	2.748	0.628
200,000	26.1	7.3	2.41	1.920	0.774
300,000	33.0	5.3	3.45	1.709	0.811
400,000	32.8	NA	4.56	2.100	0.742
600,000	40.2	8.8	5.37	1.628	0.825

Table S3. – Low Molecular Weight PEO Fit Results

Polym Conc. (ppm)	Radial Shell Thick (Å)	Radial Shell Std. Dev.	Face Shell Thick (Å)	SLD Shell x10^6 (Å^{-2})	Apparent Polym. Vol. Fract.
1,000	21.8	2.9	-	4.487	0.320
2,000	19.4	2.4	-	3.961	0.413
3,000	10.6	2.3	-	2.158	0.732
5,000	11.4	1.9	-	1.663	0.819
10,000	10.4	1.7	-	0.640	1.000
20,000	11.5	1.4	0.20	LoBnd	1.000
200,000	30.8	0.5	1.78	1.552	0.839
300,000	43.9	0.4	2.89	2.038	0.753
600,000	30.5	0.3	2.83	LoBnd	1.000

Fitting – HPAM/Laponite RD Mixtures

The Fractal Cylinder model gives a satisfactory fit to the high concentration HPAM/Laponite RD data and is described as follows. Starting with a spherical core, the basic fractal model for hard sphere building blocks, the scattering intensity, $I(q)$, is calculated by

$$I(q) = P(q)S(q) + bkgd$$

where *S(q)* is the scattering structure factor, $P(q)$ is the scattering from randomly distributed spherical "building block" particles (“particle form factor”), having radius, R_0, volume fraction, ϕ, scattering length density difference between the particle and surrounding medium, $\Delta\rho$, and background scattering contribution, *bkgd*. Scale parameters and contrast parameters are multiplicative factors in the model and are perfectly correlated. Only one of these parameters should be left free during model fitting.

$$P(q) = \phi V_p \Delta\rho^2 F(qR_0)^2$$

where $V_p = (4/3)\pi R_0^3$ and

$$F(x) = \frac{3[\sin(x) - x\cos(x)]}{x^3}$$

In the fractal aggregate scattering model, the spherical building blocks aggregate to form fractal-like clusters. The clusters have a correlation length, ξ, corresponding to their overall size, and self-similarity

dimension, D_f. From Teixeira,[3] the interference from the building blocks of the fractal-like cluster can be calculated as:

$$S(q) = 1 + \frac{\sin\left[\left(D_f - 1\right)\tan^{-1}(q\xi)\right]}{(qR_0)^{D_f}} \frac{D_f \Gamma\left(D_f - 1\right)}{\left[1 + 1/(q^2\xi^2)\right]^{(D_f-1)/2}}$$

where $\Gamma(x)$ is the gamma function. The number density of building blocks is calculated as $N_0 = \phi/V_p$, and the mean number of blocks per cluster, or aggregation number, $G = S(0) = \Gamma\left(D_f + 1\right)(\xi/R_0)^{D_f}$, and the Guinier radius of cluster, $R_G^2 = D_f\left(D_f + 1\right)\xi^2/2$.

By substituting the form factor for a sphere with the form factor for a right circular cylinder (given in the Section "Fitting-Laponite RD Suspensions"), the scattering from fractal clusters of cylinders (discs) is obtained. Overall, the Fractal Cylinder model contains nine parameters:

1) Volume fraction of cylinders

2) Fractal dimension of the aggregates

3) Correlation length of the aggregates (Å)

4) Scattering length density of the cylinder

5) Scattering length density of the solvent

6) Radius of a single cylinder (Å)

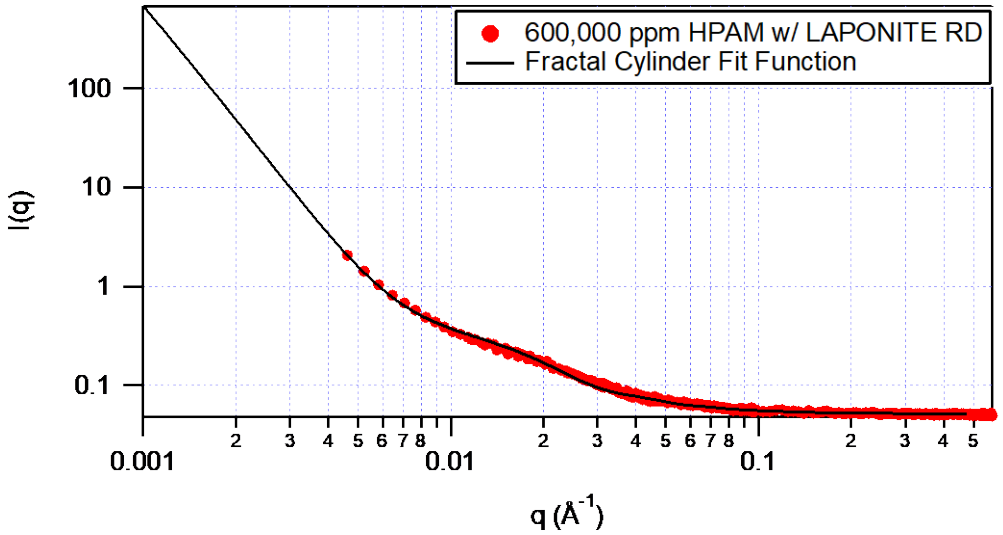
7) Length of a single cylinder (Å)

8) Polydispersity of the radius

9) Incoherent background.

Of the nine parameters, five are known (Volume fraction, SLD of cylinder, radius of cylinder, length of cylinder and polydispersity) and are fixed during the non-linear regression fit. The same disk dimensions extracted from the Laponite RD solution scattering for each set of experiments were used for the Fractal Cylinder model. The extracted fit parameters are the fractal dimension and correlation length of the aggregate, the SLD of the solvent, and the incoherent background term (in bold above). The Fractal Cylinder model does not account for polymer adsorption on the surface of the disks. By allowing the SLD

of the solvent to be a fit parameter, we assume that the HPAM polymer resides primarily in the solvent, altering the SLD from the value of pure D_2O. An example of the fit using the Fractal Cylinder model to a HPAM/Laponite RD mixture at high HPAM concentration and the associated fit parameters are shown in Figure S4.



Parameter	Coeff	Hold
Volume Fraction (scale)	0.001885	1
fractal dimension	3	0
correlation length (Å)	3274.1	0
SLD cylinder (Å-2)	4.18e-06	1
SLD solvent (Å-2)	6.28798e-06	0
Cylinder radius (Å)	130.191	1
Cylinder length (Å)	7.7881	1
polydisp of Radius	0.01	1
bkgd (cm^-1 sr^-1)	0.051739	0

V_chisq = 1097.55

Figure S4. - Fit to 600,000 ppm HPAM with respect to Laponite RD (0.5% by mass) in pure D_2O. Data represented by colored data points and fit to Fractal Cylinder model depicted by solid black line. Fit parameter values in table. Concentration in legend represents polymer solution concentration.

Table S4. – HPAM Average Fitting Results

Poly Core-Shell Cylinder Model

Polym Conc. (ppm)	Scale	Radial Shell Thick (Å)	Radial Shell Std. Dev (Å)	Face Shell Thick (Å)	SLD Shell x10^6 (Å^{-2})	Apparent Polymer Vol. Fract.
1,000	0.001885	18.4	2.7	-	4.134	0.383
2,000	0.001885	5.7	3.3	-	0.641	1.0
3,000	0.001885	13.5	4.2	-	4.419	0.332
5,000	0.001885	11.1	6.3	-	3.089	0.567
10,000	0.001885	17.3	3.4	-	4.271	0.358
20,000	0.001885	9.4	1.6	-	2.752	0.627
30,000	0.001885	18.8	6.2	-	4.042	0.399
100,000	0.001885	10.4	0.8	-	2.741	0.629

Fractal Cylinder Model

Polym Conc. (ppm)	Scale	Fractal Dim.	Fractal Dim. Std. Dev	Corr. Length (Å)	Corr. Length Std. Dev.	SLD Solv. x10^6 (Å^{-2})	Poly. Vol. Fract.
100,000*	0.001885	2.980	0.010	5e+08	5e+08	6.25	0.010
200,000*	0.001885	2.971	0.009	3e+09	4e+09	6.181	0.025
300,000	0.001885	2.954	0.004	6e+06	6e+06	6.081	0.045
400,000	0.001885	2.968	0.007	24,000	12,000	6.070	0.048
600,000	0.001885	2.935	0.075	3,700	2,000	6.020	0.058

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1) Guinier, A.; Fournet, G. Small-Angle Scattering of X-Rays; 1st ed.; Wiley: New York, 1955.
2) Nelson, A; Cosgrove, T, A Small-Angle Neutron Scattering Study of Adsorbed Poly(ethylene oxide) on Laponite, *Langmuir*, **20**, (2004), 2298-2304.
3) Teixeira, J, Small angle scattering by fractal systems, *J. Appl. Cryst.*, **21**, (1988), 781.