Supporting Information for

Nanoparticle Dispersion in Polymer Nanocomposites by Spin-Diffusion-Averaged Paramagnetic Enhanced NMR Relaxometry: Scaling Relations and Applications

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References

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Figure S1. Normalized magnetization, $M(t)/M_0$, versus recovery time, $t$ for pure poly(vinyl alcohol) and poly(vinyl alcohol)/montmorillonite (PVA/MMT$_{STx-1b}$) nanocomposites at weight ratios (PVA/MMT$_{STx-1b}$) of 100/1, 100/2, 100/4, 100/6, 100/8, and 100/10. The inset displays the same data plotted as $\ln[1 - M(t)/M_0]$ versus recovery time, $t$, the slopes of which reflect the inverse $T_1$s. The relaxation rate increases upon increasing the MMT$_{STx-1b}$ content; all nanocomposites exhibit faster relaxation (shorter $T_1^H$) than the corresponding pure PVA. The calculated $T_1$ values are $11.64 \pm 0.23$ s, $9.38 \pm 0.23$ s, $9.21 \pm 0.11$ s, $7.01 \pm 0.07$ s, $6.67 \pm 0.12$ s, $5.00 \pm 0.11$ s and $3.10 \pm 0.23$ s for weight ratios from 100/0 to 100/10, respectively.

Model analysis: sinks with infinitely fast relaxation

As discussed in the main text, we recently reported an analytical relationship between NMR magnetization growth and interparticle spacings (IPS) in lamellar polymer/paramagnetic clay nanocomposites:\(^1\)

$$
\frac{M(t)}{M_o} = 1 - \left( \frac{4D}{\beta \Delta^2} \right)^{1/2} \tan \left( \frac{\beta \Delta^2}{4D} \right)^{1/2} \exp(-t / T_{1,H}) \\
- \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \left[ \frac{1}{1 - (2n+1)^2 \pi^2 D / (\beta \Delta^2)} \right] \exp \left[ - \left( \frac{(2n+1)^2 \pi^2 D}{\Delta^2} + \frac{1}{T_{1,m}} \right) t \right]$$

(5)
where \( M_0 \) is the total equilibrium magnetization, \( D \) is the bulk spin diffusion coefficient (uniform, not a function of spatial position), \( 1/T_{1,m} \) is the bulk matrix nuclear relaxation rate, \( 1/T_{1,s} \) is the relaxation rate of the clay surface nuclei, and \( \beta \) is the difference between \( 1/T_{1,s} \) and \( 1/T_{1,m} \) (i.e., \( \beta = 1/T_{1,s} - 1/T_{1,m} \)). In the case of the sinks with infinitely fast relaxation (e.g., \( T_{1,s} \to 0 \), i.e., \( \beta \to \infty \)), we can simplify eq 5:

\[
\frac{M(t)}{M_0} = 1 - \sum_{n=0}^{\infty} \beta_n^{-1} \exp \left[ \left( \frac{8\beta_n D}{\Lambda^2} + \frac{1}{T_{1,m}} \right) t \right] \tag{S1}
\]

where \( \beta_n = (2n + 1)^2 \pi^2/8 \). The summation in eq S1 converges quite rapidly with \( n \); numerical calculation using just two iterations yields errors less than 5% (see Figure S2). Taking only the first term of the summation, equation S1 can be recast:

\[
\frac{M(t)}{M_0} = 1 - \frac{8}{\pi^2} f(t) \exp \left[ \left( \frac{\pi^2 D}{\Lambda^2} + \frac{1}{T_{1,m}} \right) t \right] \tag{S2}
\]

where \( f(t) = 1 + 1/9 \exp(-8B \ t) + 1/25 \exp(-24B \ t) + \ldots \), and \( B = \pi^2 D/\Lambda^2 \). The value of \( f(t) \) approaches 1 if \( t > (8B)^{-1} = 8\Lambda^2/(\pi^2D) \). Note that this approximation is valid when spin diffusion lengths, \((D \times 5T_1)^{1/2}\), are greater than interparticle separations, \( \Lambda \). In other words, the interparticle distance is such that magnetization throughout the entire sample may equilibrate due to spin diffusion during the \( T_1 \) relaxation process. Thus, samples must be characterized by \( T_1 > \Lambda^2/(20D) \). Since this is approximately \((8B)^{-1} = 8\Lambda^2/(\pi^2D)\), eq S2 should sufficiently describe long-time relaxation behavior for \( f(t) = 1 \) (i.e., \( n = 0 \) in summation of eq S1). This was
confirmed by numerically generating relaxation curves for the first four $n$ values of the summation ($n = 0, 1, 2$ and $3$) using parameter values similar to those for a PCN with 5 wt% MMT and a spin diffusion coefficient, $D = 0.7 \text{ nm}^2/\text{ms}$. These are shown in Figure S2(a) and reveal no difference in the long-time relaxation behavior when $t > \sim 180 \text{ ms} \approx 8A^2/(\pi^2D)$. Although differences are observed in the short-time behavior, Figure S2(b) shows that these do not significantly affect the overall $T_1$ values determined from plots of $\ln[\pi^2/8(1-M(t)/M_0)]$ versus recovery time. As a result, from eq S2 with $f(t) = 1$, the observed $1/T_{1,PCN}$ can be obtained

$$\frac{1}{T_{1,PCN}} \approx \frac{\pi^2D}{A^2} + \frac{1}{T_{1,m}}$$  \hspace{1cm} (S3)$$

Equation S3 can be compared to the semi-empirical equation used to compute the paramagnetic contribution to the spin-lattice relaxation rate\(^{2-4}\)

$$R_{1,para} = 1/T_{1,para} = 1/T_{1,PCN} - 1/T_{1,polymer}$$  \hspace{1cm} (S4)$$

if the relaxation rate of the pure polymer, $1/T_{1,polymer}$, is taken to be the relaxation rate of the bulk polymer in the nanocomposite, $1/T_{1,m}$. In this case, the paramagnetic contribution to the relaxation is

$$R_{1,para} \approx \pi^2D/A^2$$  \hspace{1cm} (S5)$$

Thus, $R_{1,para} \sim A^2$, for sinks with infinitely fast relaxation (e.g., $T_{1,s} \to 0$, i.e., $\beta \to \infty$).
**Figure S2.** Relaxation curves numerically calculated using eq S1 and the first four terms of \( f(t) \), corresponding to eq S2 (first term of summation only) and \( n = 0, \leq 1, \leq 2 \) and \( \leq 3 \): (a) \( M(t)/M_0 \), and (b) \( \ln[\pi^2/8(1 - M(t)/M_0)] \) versus recovery time. The following parameters were used in the calculation: spin diffusion coefficient, \( D = 0.7 \) nm\(^2\)/ms, bulk polymer relaxation time, \( T_{1,m} = 1.635 \) s, \( \Delta = 50 \) nm and recovery time range from 0.5 to 10000 ms. Calculated values of \( T_{1,\text{PCN}} \) in (b), 296 ms \( (n = 0) \), 293 ms \( (n \leq 1) \), and 292 ms \( (n \leq 2 \) and \( \leq 3) \), are consistent with the relaxation constant of 296 ms determined by fitting the data points in (b) to a conventional exponential recovery.

**Figure S3.** X-ray diffraction patterns of octadecylamine-modified MMT\( _{STx-1b} \) (C18-MMT\( _{STx-1b} \)) and a PVA/MMT\( _{STx-1b} \) nanocomposite (PVA/MMT\( _{STx-1b} = 100/10, \) w/w). This PVA/MMT\( _{STx-1b} \) nanocomposite contains 10 wt% clay and does not exhibit a basal peak (001) reflection, indicating the clay is exfoliated.
Figure S4. Normalized magnetization, $M(t)/M_0$ versus recovery time for octadecylamine-modified MMT$_{STx-1b}$ (C18-MMT$_{STx-1b}$) measured at 300 MHz. $T_1 T = 21.4 \pm 1.3$ ms.

Figure S5. (a) Normalized and corrected magnetization versus the square root of recovery time for poly(vinyl alcohol)/montmorillonite (PVA/MMT$_{STx-1b}$) nanocomposites with different clay contents. PVA/MMT$_{STx-1b}$ weight ratios are 100/x where x = 1, 2, 4, 6, 8 and 10. The data were measured at 300 MHz and are vertically displaced to prevent overlap. Lines are linear least-square fits. Slopes of these lines, $S$, are plotted in (b) as a function of clay content, $w_c$. These initial slopes, which reflect the effective clay/polymer interfacial area, are linearly proportional to the clay weight fraction and therefore suggest similar degrees of exfoliation in these samples.
References


