SUPPORTING INFORMATION for:

Generalized vs. Fractional: A Comparative Analysis of

Maxwell Models Applied to Entangled Polymer Solutions

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1. FMM Material Functions

The material functions of the fractional Maxwell model (FMM) all exhibit two power law regions. The behavior in the short-time / high-frequency limit is characterized by a power law with the lower of the two exponents, β , while the behavior in the long-time / low-frequency limit is described by a power law with the higher of the two exponents, α . The equations for some of the material functions, their limiting behavior and the intersection points of the two limiting power laws are given in Table S1 and shown in Fig. S1.



Fig. S1: FMM material functions plotted together in one graph. In this example, $\alpha = 0.75$, $\beta = 0.25$, $\mathbb{V} = 1$ Pa s^{0.75}, $\mathbb{G} = 1$ Pa s^{0.25}. To make them comparable to the material functions in the time domain, the frequency-dependent moduli are plotted as functions of ω^{-1} . All material functions show α -scaling for long times (low frequencies) and β -scaling for short times (high frequencies). The empty circles indicate the interception point of the limiting power laws of each material function.

Tab. S1

All equations for the material functions of the Fractional Maxwell Model (FMM). All material functions scale as α or β -power laws in the limit. The intersection of the two limiting power laws are given by (x-intersection, y-intersection).

Material Function	α -scaling	β -scaling	x-intersection	y- intersection
$G(t) = \mathbb{G}t^{-\beta}E_{\alpha-\beta,1-\beta}\left(-\frac{\mathbb{G}}{\mathbb{V}}t^{\alpha-\beta}\right)$	$G(t \to \infty) \\\approx \mathbb{V}(1-\alpha)t^{-\alpha}$	G(t o 0) $\approx \mathbb{G} (1 - \beta) t^{-\beta}$	$\left(\frac{\mathbb{V}(1-\alpha)}{\mathbb{G}(1-\beta)}\right)^{\frac{1}{\alpha-\beta}}$	$\left(\frac{[\mathbb{G}(1-\beta)]^{\alpha}}{[\mathbb{V}(1-\alpha)]^{\beta}}\right)^{\frac{1}{\alpha-\beta}}$
$\begin{aligned} G'(\omega) &= \\ \frac{\left(\mathbb{G}\omega^{\beta}\right)^{2} \cdot \mathbb{V}\omega^{\alpha} \cos(\alpha \pi/2) + \left(\mathbb{V}\omega^{\alpha}\right)^{2} \cdot \mathbb{G}\omega^{\beta} \cos(\beta \pi/2)}{\left(\mathbb{V}\omega^{\alpha}\right)^{2} + \left(\mathbb{G}\omega^{\beta}\right)^{2} + 2\mathbb{V}\omega^{\alpha} \cdot \mathbb{G}\omega^{\beta} \cos((\alpha - \beta)\pi/2)} \end{aligned}$	$ \begin{aligned} &G'(\omega \to 0) \\ &\approx \mathbb{V} \cos(\alpha \pi/2) \omega^{\alpha} \end{aligned} $	$G'(\omega \to \infty)$ $\approx \mathbb{G} \cos(\beta \pi/2) \omega^{\beta}$	$\left(\frac{\mathbb{G}\cos(\beta\pi/2)}{\mathbb{V}\cos(\alpha\pi/2)}\right)^{\frac{1}{\alpha-\beta}}$	$\left(\frac{\left[(\operatorname{Gr}\cos(\beta\pi/2)\right]^{\alpha}}{\left[\operatorname{V}\cos(\alpha\pi/2)\right]^{\beta}}\right)^{\frac{1}{\alpha-\beta}}$
$\begin{aligned} G^{\prime\prime}(\omega) &= \\ \frac{\left(\mathbb{G}\omega^{\beta}\right)^{2} \cdot \mathbb{V}\omega^{\alpha} \sin(\alpha \pi/2) + \left(\mathbb{V}\omega^{\alpha}\right)^{2} \cdot \mathbb{G}\omega^{\beta} \sin(\beta \pi/2)}{\left(\mathbb{V}\omega^{\alpha}\right)^{2} + \left(\mathbb{G}\omega^{\beta}\right)^{2} + 2\mathbb{V}\omega^{\alpha} \cdot \mathbb{G}\omega^{\beta} \cos((\alpha - \beta)\pi/2)} \end{aligned}$	$G''(\omega \to 0) \approx \mathbb{V} \sin(\alpha \pi/2) \omega^{\alpha}$	$G''(\omega \to \infty)$ $\approx \mathbb{G} \sin(\beta \pi/2) \omega^{\beta}$	$\left(\frac{\mathbb{G}\sin(\beta\pi/2)}{\mathbb{V}\sin(\alpha\pi/2)}\right)^{\frac{1}{\alpha-\beta}}$	$\left(\frac{[\mathbb{G}\sin(\beta\pi/2)]^{\alpha}}{[\mathbb{V}\sin(\alpha\pi/2)]^{\beta}}\right)^{\frac{1}{\alpha-\beta}}$
$\frac{ G^*(\omega) =}{\sqrt{\left(\mathbb{V}\omega^{\alpha}\right)^2 + \left(\mathbb{G}\omega^{\beta}\right)^2 + 2\mathbb{V}\omega^{\alpha} \cdot \mathbb{G}\omega^{\beta} \cos((\alpha - \beta)\pi/2)}}$	$\begin{aligned} & G^*(\omega\to 0) \\ &\approx \mathbb{V}\omega^\alpha \end{aligned}$	$\begin{aligned} G^*(\omega \to \infty) \\ \approx \mathbb{G}\omega^\beta \end{aligned}$	$\left(\frac{\mathbb{G}}{\mathbb{V}}\right)^{\overline{\alpha-\beta}}$	$\left(\frac{\mathbb{G}^{\alpha}}{\mathbb{V}^{\beta}}\right)^{\frac{1}{\alpha-\beta}}$
$H(\tau) = \frac{1}{\pi} \tau^{-\beta} \frac{\mathbb{V}\mathbb{G}^{2} \sin(\pi\alpha)\tau^{\alpha-\beta} + \mathbb{V}^{2}\mathbb{G} \sin(\pi\beta)}{\mathbb{G}^{2}\tau^{2(\alpha-\beta)} + 2\mathbb{V}\mathbb{G}\tau^{\alpha-\beta} \cos[\pi(\alpha-\beta)] + \mathbb{V}^{2}}$	$H(\tau \to \infty) \\\approx \frac{\mathbb{V}\sin(\pi\alpha)}{\pi} \tau^{-\alpha}$	$H(\tau \to 0) \\\approx \frac{\mathbb{G}\sin(\pi\beta)}{\pi} \tau^{-\beta}$	$\left(\frac{\mathbb{V}\sin(\pi\alpha)}{\mathbb{G}\sin(\pi\beta)}\right)^{\frac{1}{\alpha-\beta}}$	$\left(\frac{[\mathbb{G}\sin(\pi\beta)]^{\alpha}\pi^{\beta}}{[\mathbb{V}\sin(\pi\alpha)]^{\beta}\pi^{\alpha}}\right)^{\frac{1}{\alpha-\beta}}$

2. Estimation of critical concentrations

The transition from dilute to semi-dilute non-entangled takes place at the overlap concentration c^* , which is defined as the concentration, where polymer coils start to overlap. It is given by

$$c^* = \frac{3M_w}{4\pi N_A R_a^3} , \qquad (S1)$$

where R_g is the radius of gyration and N_A is Avogadro's constant. Using an empirical relation between R_g and M_w from literature for PEO:¹

$$R_a = 0.215 M_w^{0.583} \text{ Å}, \qquad (S2)$$

 c^* can be estimated for the molecular weights employed in this paper. The onset of the semi-dilute entangled regime occurs beyond the critical entanglement concentration, c_e . At concentrations above c_e , the dynamics of the polymer solution are governed by entanglement effects. For $c^* < c < c_e$, the solutions are semi-dilute but not entangled.^{2,3} The critical entanglement concentration can be approximated as $c_e \approx$ $10c^*$ for neutral polymers in good solvents.⁴ The onset of the concentrated regime (iv) is given by another critical concentration, c^{\ddagger} . At c^{\ddagger} , the excluded-volume repulsions are cancelled out by screening.⁵ c^{\ddagger} is not easy to predict theoretically. Ebagninin et al. determined the values of c_e and c^{\ddagger} experimentally for PEO of similar molecular weight as used in our work.⁶ The experimental values as well as the predicted values are tabulated in **Table S2**. No experimental data for 2000 kDa PEO are available. Since c_e and c^{\ddagger} are often given as multiples of c^{\ast} and since we can safely assume that 2000 kDa PEO will have intermediate properties between 1000 and 4000 kDa PEO, we calculate the missing c_e value for 2000 kDa according to

$$c_{e,2000} = \frac{1}{2} \left[\left(c_{e,1000} / c_{1000}^* \right) + \left(c_{e,4000} / c_{4000}^* \right) \right] \cdot c_{2000}^* .$$
(S3)

 c_{2000}^{\ddagger} is determined in an analogous fashion. According to these considerations, the PEO solutions used in this work fall either in the semi-dilute entangled regime or in the concentrated regime. An overview of the samples is shown in Tab. 1 in the main text.

Table S2:Values for the critical concentrations c^* , c_e and c^{\ddagger} . Theoretical values were calculated using
equations (S1) and (S2) as well as the assumption that $c_e \approx 10c^*$. Experimental values are
taken from ref ⁶. The two values marked with * were determined using the procedure shown in
equation (S3).

	Theoretical		Experimental	
M _w [kDa]	<i>c</i> * [wt%]	<i>c</i> _e [wt%]	<i>c</i> _e [wt%]	<i>c</i> [‡] [wt%]
1000	0.13	1.28	1.6	4.9
2000	0.08	0.76	1.0^{*}	3.0^{*}
4000	0.05	0.45	0.65	1.8

3. Amplitude Sweeps

Amplitude sweeps were performed to determine the extension of the linear viscoelastic regime by varying the strain amplitude of oscillation γ_0 between 0.1 and 20 rad/s at a constant frequency of 6.28 rad/s. The results are shown in Fig. S2. The linear viscoelastic regime extends to values clearly beyond 20%. For the subsequent frequency sweeps, the strain amplitude was kept fixed at $\gamma_0 = 5\%$.



Fig. S2: Amplitude sweeps for solutions of A) 1000 kDa, B) 2000 kDa and C) 4000 kDa PEO. Filled and open symbols denote G' and G'', respectively. The vertical dashed lines indicate the strain amplitude chosen for the subsequent frequency sweeps.

4. Frequency Sweeps

Frequency sweeps were performed on all PEO solutions at a constant strain amplitude of 5%. For each PEO solution, three separate samples were prepared containing 192, 109 and 69 nm polystyrene particles, respectively. The particles have a negligible impact on the rheological measurements. For one sample, 4000 kDa PEO, 2 wt%, the frequency sweep results from the three particle-containing samples and one sample without particles are shown in Fig. S3. Very small differences between the four measurements can be seen at low frequencies.



Fig. S3 Frequency sweep results for a PEO solution with three differently sized polystyrene particles and without particles.

The fractional Maxwell model (FMM) was fitted to all frequency sweep data. For the 1000 and 2000 kDa samples, the α -parameter was fixed to 1. In this case, the corresponding spring-pot reduces to a regular dashpot and \mathbb{V} becomes η , which is a regular viscosity with units of Pa s. For some samples at lower concentrations, G' approaches a plateau at low frequencies. This is an instrumental artefact that can be attributed to phase angle

uncertainties.⁷ For samples, 1000 kDa, 2 wt%, 2000 kDa 2 wt% and 4000 kDa, 1 wt%, only data points for frequencies above 1 rad/s were considered for the fit. All frequency sweep data and fits are shown in Fig. S4. For the GMM, usually at least 4 modes are necessary to yield a better description than the FMM. The advantage of the FMM is particularly strong for samples at high M_w and high concentrations, where G' and G'' exhibit a low frequency dependence. The fit residuals of the 3 wt% of 1000, 2000 and 4000 kDa are shown in Fig. S5.



Fig. S4: Frequency sweep data for all samples fitted with the FML (1000 and 2000 kDa) and the FMM (4000 kDa). Full lines indicate G' and broken lines indicate G''.



Fig. S5: Fit residuals for the 3 wt% solutions of A) 1000 kDa, B) 2000 kDa and C) 4000 kDa PEO.

5. Zero-shear viscosity

The zero-shear viscosity is fully defined by the relaxation modulus:⁸

$$\eta_0 = \int_0^\infty \mathrm{d}t \ G(t) \,. \tag{S4}$$

For this discussion, the relaxation modulus of the FMM may be approximated by two power-laws (neglecting the transition from one to the other)

$$G(t) = \begin{cases} G_{\text{FMM}} t^{-\beta} \text{ for } t \le \tau_{\text{FMM}} \\ G_{\text{FMM}} t^{-\alpha} \text{ for } t > \tau_{\text{FMM}} \end{cases}$$
(S5)

where

$$\tau_{FMM} = [(1 - \alpha) \mathbb{V}/\mathbb{G}]^{1/(\alpha - \beta)}$$
(S6)

is the time, where the two power-laws intersect and

$$G_{\text{FMM}} = \mathbb{G}[(1-\alpha)\mathbb{V}/\mathbb{G}]^{\beta/(\beta-\alpha)}$$
(S7)

is the value of *G* at $t = \tau_{\text{FMM}}$. A simple approximation as such can be used to explore the properties of the zero-shear viscosity of the FMM:

$$\eta_0 = \int_0^{\tau_{FMM}} \mathrm{d}t \ G(t) + \int_{\tau_{FMM}}^\infty \mathrm{d}t \ G(t) \,, \tag{S8}$$

which rearranges into

$$\frac{\eta_0}{G_{\text{FMM}}\tau_{\text{FMM}}} = \int_0^{\tau_{\text{FMM}}} \frac{\mathrm{d}t}{\tau_{\text{FMM}}} \left(\frac{t}{\tau_{\text{FMM}}}\right)^{-\beta} + \int_{\tau_{\text{FMM}}}^{\infty} \frac{\mathrm{d}t}{\tau_{\text{FMM}}} \left(\frac{t}{\tau_{\text{FMM}}}\right)^{-\alpha}$$

$$= \frac{1}{1-\beta} + \frac{1}{1-\alpha} \lim_{(t/\tau_{\text{FMM}})\to\infty} \left(\frac{t}{\tau_{\text{FMM}}}\right)^{1-\alpha} - 1 = \lim_{(t/\tau_{\text{FMM}})\to\infty} \left(\frac{t}{\tau_{\text{FMM}}}\right)^{1-\alpha}.$$
(S9)

According to equation (S9), the zero-shear viscosity of the FMM diverges for values of $\alpha \neq 1$. Such behaviour is expected for materials at the gel point,^{9–11} but not for solutions of non-permanently crosslinked polymers. Steady shear experiments were performed for one of the three sets of PEO solutions as shown in Fig. S6. All measured apparent viscosities approach a plateau value at low shear rates indicating the presence of a plateau modulus η_0 . The exception is the 4 wt% solution of 4000 kDa PEO, where in the experimental shear rate range, no true plateau can be seen, but can be presumed to appear at lower shear rates. The data are well described by the Cross model:

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (k\dot{\gamma})^m} \tag{S10}$$

where η_{∞} is the infinite shear viscosity, k is a characteristic crossover time and m describes the sharpness or cooperativity of the shear-thinning transition. Since the infinite shear viscosity plateau is not seen within the range of our data, η_{∞} is kept fixed at 0.



Fig. S6: Steady shear experiments for one of the three sets of PEO solutions: A) 1000 kDa, B) 2000 kDa and C) 4000 kDa. The determined apparent viscosities approach a plateau at low shear rates which corresponds to the zero-shear viscosity. The data were fitted with the Cross model (black lines).

6. Determination of Shift Factors

The horizontal shift factor, a_c is determined by aligning $\tan \delta = G''/G'$ of the curve that is to be shifted with the reference curve. For a given shift factor, a_c , the overlapping frequency range is determined. Only shift factors for which the number of overlapping data points is larger or equal to 2 are considered. In the overlapping frequency range, cubic splines (denoted S(x)) are used to interpolate both curves (N = 100 points). The final minimized quantity is

$$E = \frac{1}{100} \sum_{i=1}^{100} [S(\tan \delta)_i - S(\tan \delta_{\text{ref}})_i]^2.$$
 (S11)

After horizontal shifting is completed, vertical shifting is performed. G' and G'' are shifted in horizontal direction with the ideal value of a_c . In the overlapping frequency range, cubic splines are used to interpolate G', G'', G'_{ref} and G''_{ref} (N = 100 points). The final minimized quantity is given by

$$\bar{E} = \frac{1}{100} \sum_{i=0}^{100} [S(G')_i - S(G'_{\text{ref}})_i]^2 + [S(G'')_i - S(G''_{\text{ref}})_i]^2.$$
(S12)

The shifted tan δ and G', G'' curves for the PS-109 containing samples are shown in the main text in Figure 7. The shifted curves for the remaining two samples sets are shown in Figures S7 and S8.



Fig. S7: Time-concentration superposition results for the PS-69-containing samples. Firstly, horizontal shifts are obtained by shifting the loss tangents (left column). Secondly, vertical shifts are obtained by shifting G', G'' (right column). A)-B) 1000 kDa, C)-D) 2000 kDa, E)-F) 4000 kDa.



Fig. S8: Time-concentration superposition results for the PS-192-containing samples. Firstly, horizontal shifts are obtained by shifting the loss tangents (left column). Secondly, vertical shifts are obtained by shifting G', G'' (right column). A)-B) 1000 kDa, C)-D) 2000 kDa, E)-F) 4000 kDa.

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