

ELECTRONIC SUPPORTING INFORMATION

1. WAXD analyses

The WAXD spectra are shown in Fig. S1 for the neat organo-clay and three as-extruded polymer/clay samples at $\Phi \approx 0.93\%$. The interlayer spacing between the silicate layers, d_{001} , was estimated by applying the Bragg's condition to the low-angle peak ($2^\circ < 2\theta < 4^\circ$) of the scattering intensity, which corresponds to the {001} basal reflection of the montmorillonite aluminosilicate.

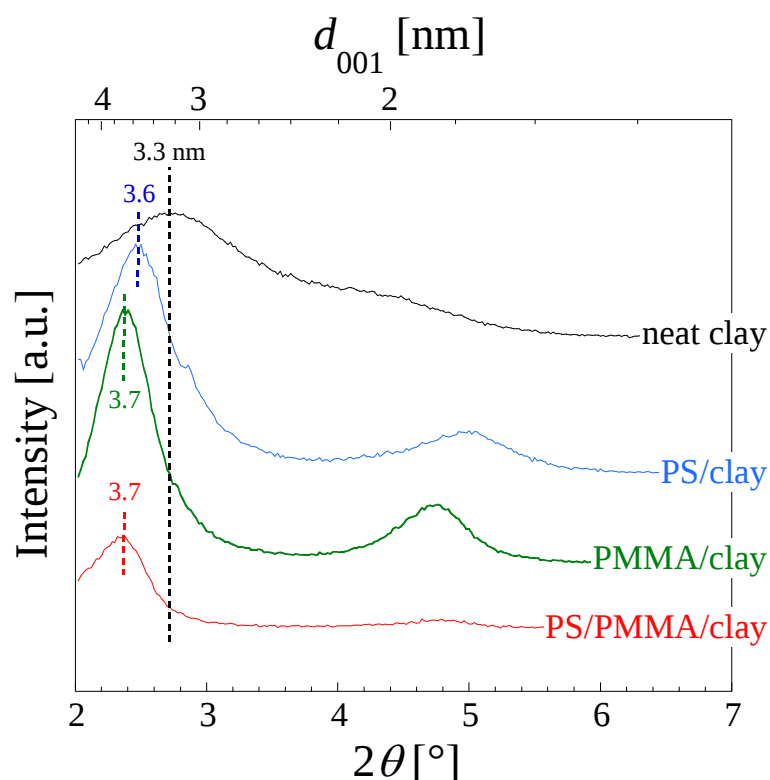


Fig. S1 WAXD patterns for: neat organo-clay, PS/clay, PMMA/clay and PS/PMMA/clay samples at $\Phi \approx 0.93\%$. The interlayer spacing computed through the Bragg's condition are reported as well.

Although PMMA seems having somewhat better interaction with the organo-clay, the diffraction peaks of the three polymer nanocomposites are too wide and too close to draw unambiguous conclusions about which of the polymers preferentially intercalates the filler. The most reasonable deduction is that both PS- and PMMA-intercalated tactoids can exist. In addition, as sometimes proposed to explain the presumed compatibilizing action of organo-clays,¹ the presence of interfacially-located stacks simultaneously intercalated by both polymers is also possible. Similar conclusions exactly reflect the criterion adopted to select the materials: since the rational was promoting the positioning of the filler at the polymer-polymer interface, we have deliberately selected an organo-clay that does not exhibit preferential interactions with none of the polymers of the blend (please see ref. #20 of the manuscript for the underlying thermodynamics calculations).

2. Rotary diffusivity of the clay particles in the PS/clay samples

To estimate the rotary diffusivity of the clay particles the viscosity of the suspending medium, η , and the disk diameter, d , are needed.

For the PS/clay samples we set $\eta \approx 3000 \text{ Pa}\cdot\text{s}$, which is the zero-shear rate viscosity of PS. Concerning the clay diameter, the single silicate layers on which commercial organo-clays are based are intrinsically variable in lateral dimension.² In addition, the platelets may be skewed relative to one another within the tactoids, which results in further variability in the distribution length.³ Consequently, the lateral dimension of organo-clays typically ranges between 100 nm and 300 nm, with occasional big tactoids more than 1 μm long in case of bad dispersion of the pristine clay aggregates.

The rotational relaxation time D_{r0}^{-1} is reported in Fig. S2 as a function of d .

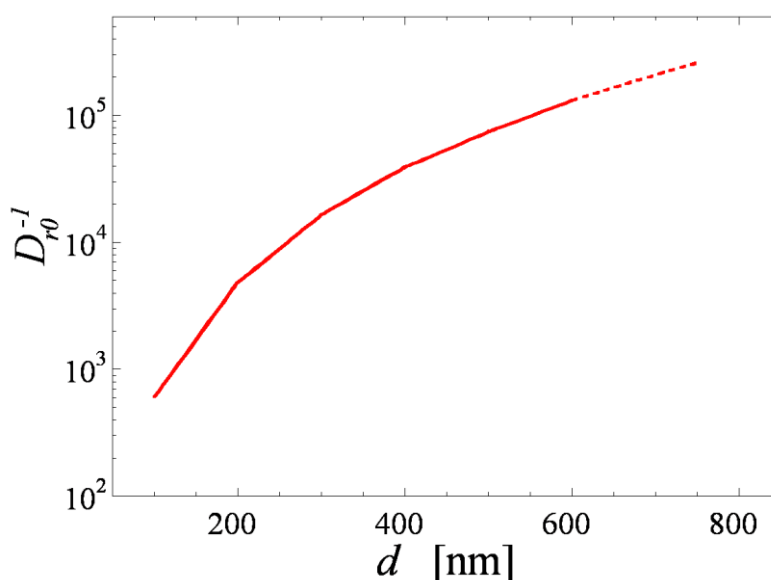


Fig. S2 Rotational relaxation time as a function of the clay lateral dimension.

Considering that the duration of time scans is about 10^4 s , the timescales for particle rearrangements in the PS/clay system are consistent with the observed dynamics of G' .

3. Frequency-dependent loss moduli

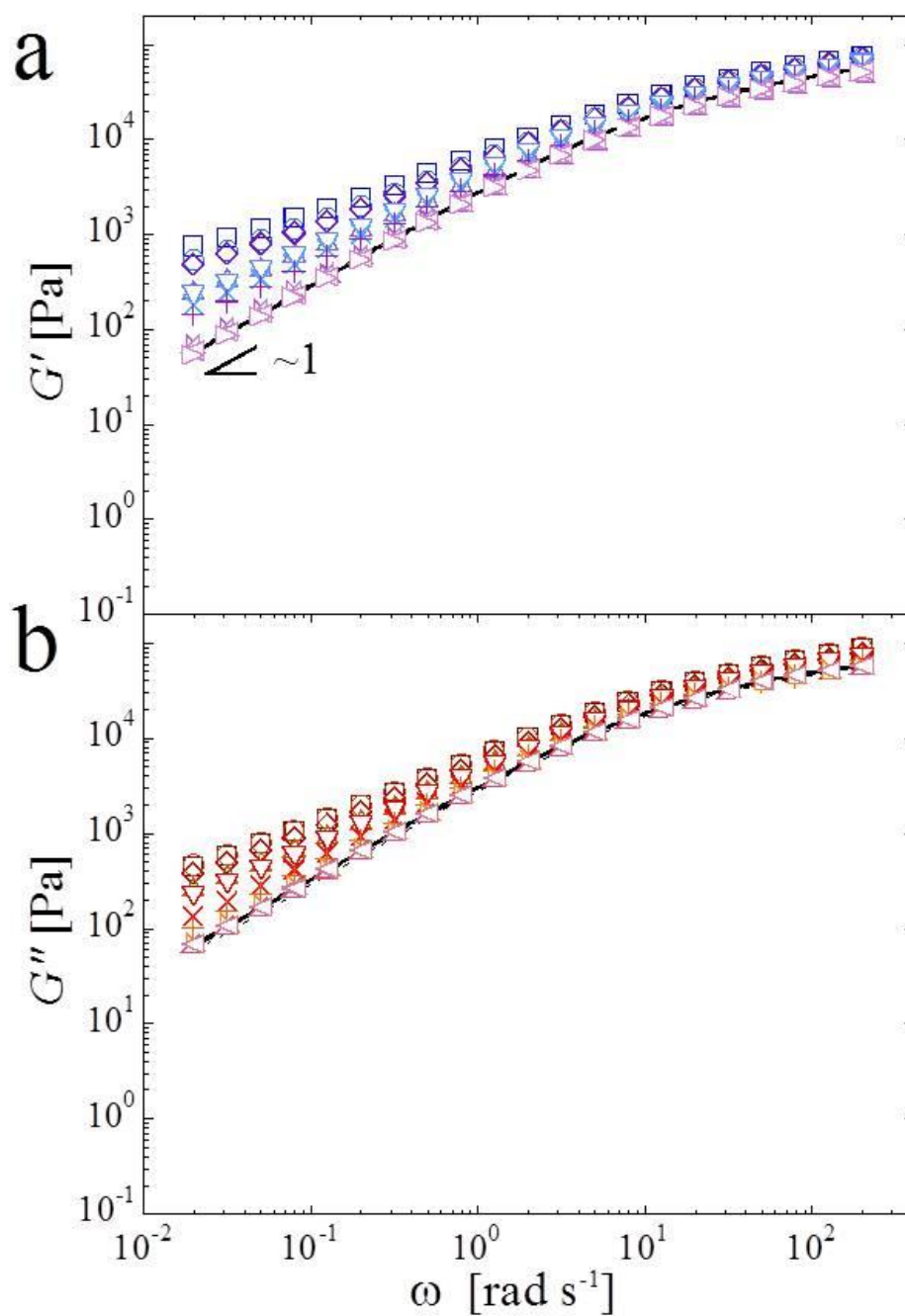


Fig. S3 Frequency dependence of the elastic moduli: (a) neat PS (solid line) and PS/clay samples at $\Phi = 0.07\%$, 0.25% , 0.44% , 0.60% , 0.94% , 1.10% , 1.27% , 1.32% , 1.63% , 1.89% and 2.65% (bottom to top); (b) unfilled blend (solid line), neat PS (dotted line) and PS/PMMA/clay samples at $\Phi = 0.18\%$, 0.32% , 0.61% , 0.75% , 0.93% , 1.32% , 1.66% , 2.05% , 2.12% , 2.24% (bottom to top).

4. Predictions of the Palierne model

The frequency-dependent values of G' and G'' measured for the unfilled PS/PMMA blend have been compared with the expectations of the Palierne model, which predicts the linear viscoelastic moduli of a blend with drop-matrix morphology once the interfacial tension (σ) and the radius of the dispersed phase (R) are known.⁴

A value $\sigma=1.16$ mN/m has been taken from the literature for the pair PS-PMMA.⁵ The size of the PMMA drops has been estimated by analyzing micrographs of the PS/PMMA blend obtained by scanning electron microscopy (SEM, Phenom by FEI), according to the procedure described below. SEM analyses have been performed on the cryo-fractured surface of a sample previously etched with formic acid to selectively remove the PMMA phase. About 10^3 holes, corresponding to the removed PMMA drops, have been manually selected from several micrographs (see Fig. S4).

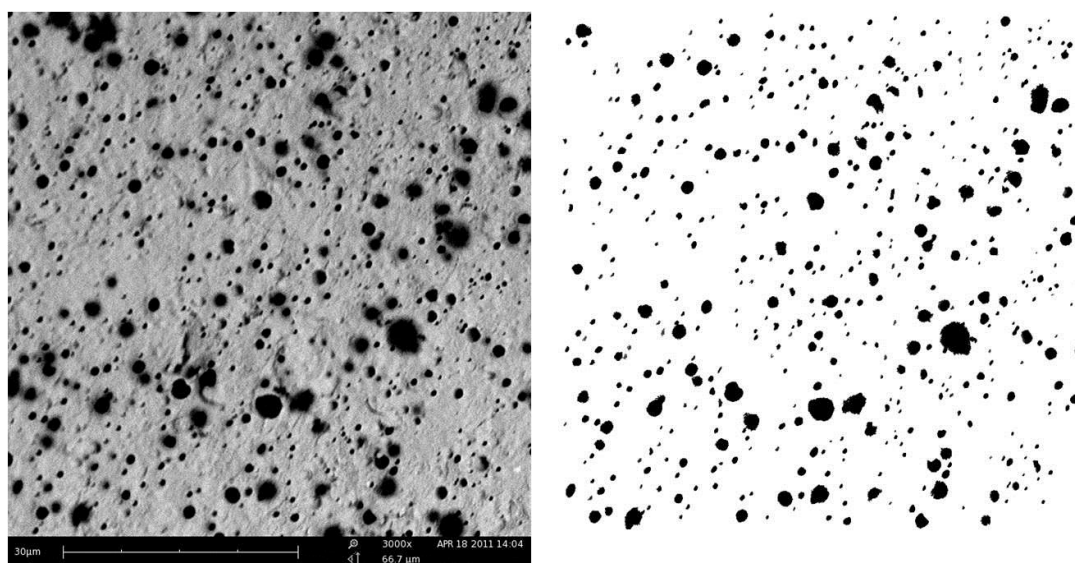


Fig. S4 Original SEM micrograph of a PS/PMMA blend (left) and binary image obtained by manually detecting the PMMA inclusions (right).

The so-obtained binary images have then been analyzed by means of a public domain Java image processing program (ImageJ 1.42q). The radius of the i -th inclusion has been evaluated as $R_i = \sqrt{\bar{A}_i / \pi}$, where $\bar{A}_i$ corresponds to the measured area of the inclusion amplified by a factor $4/\pi$ in order to account for the systematic underestimation of the dimensions of an object from its print on a flat surface.⁶ The number-average drop radius R_n and the volume-average drop radius R_v have been then estimated as:

$$R_n = \sum_i \left(\frac{n_i}{n_{tot}} \right) R_i ; \quad R_v = \sum_i \left(\frac{V_i}{V_{tot}} \right) R_i$$

where n_i/n_{tot} and V_i/V_{tot} are the numerical and volumetric fractions of drops with radius R_i , respectively. The image analysis leads to $R_v=0.895$ μm and $R_v/R_n = 1.94 < 2$. Thus, the volume-average radius can be used as representative size of the PMMA drops.⁷

Fig. S5 shows the comparison between the predictions of Palierne model and the experimental moduli of the unfilled blend. A good agreement exists between predicted and measured moduli, which supports the reliability of our rheological measurements.

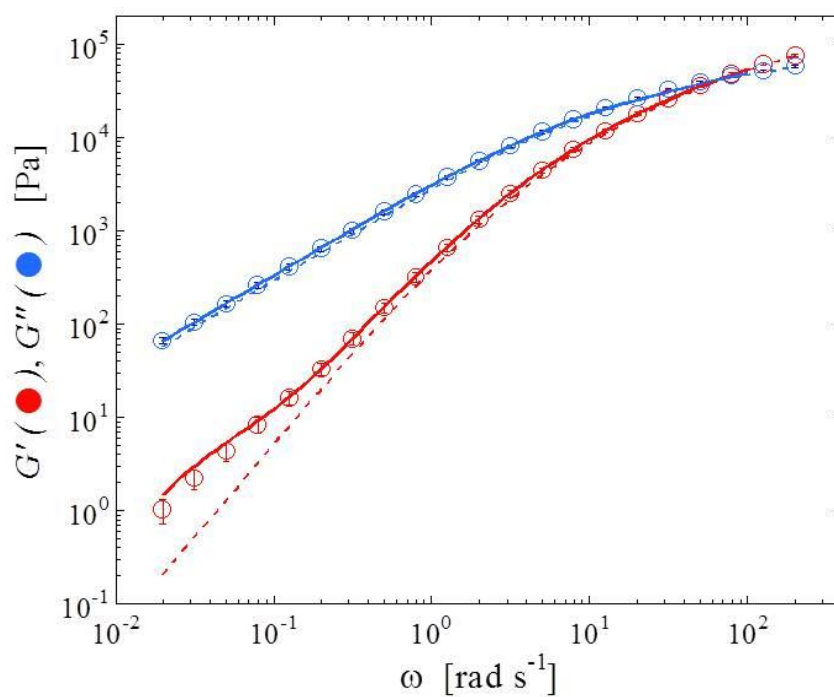


Fig. S5 Comparison between the measured (circles) and predicted by the Palierne model (solid lines) viscoelastic moduli. The error bars represent the standard deviations over three independent measurements. The dashed lines are the moduli of the neat PS.

5. Amplification and shift factors for the building of the master curves of G'

The key steps for identifying the horizontal (a_ϕ) and vertical (b_ϕ) shift factors for the building of the master curve of G' can be summarized as follows:

- 1) account for hydrodynamic effects related to the presence of the filler by introducing an amplification factor $B(\Phi)$; it represents the ratio between the complex modulus $G^*(\Phi)$ of the filled sample and that of the neat matrix (neat PS for the PS/clay systems, unfilled PS/PMMA blend for the PS/PMMA/clay ones) in the high-frequency range;
- 2) amplify the viscous modulus of the pure matrix $G''(\omega)$ by $B(\Phi)$;
- 3) identify a_ϕ and b_ϕ as the coordinates of the point at which the network elasticity, identified as the low-frequency plateau of the elastic modulus, G'_0 , equals the amplified viscous modulus of the pure matrix, $B(\Phi)G''(\omega)$.

The previous procedure only applies to samples above the percolation threshold, which should be identified first. Actually, the physical constraints of the two-phase model allow to reliably identify the samples which exceed Φ_c : once the master curve has been built by referring to samples with a clear low-frequency plateau, the scalability of the G' curve of a sample at lower Φ unequivocally certifies the crossing of Φ_c .

The amplification and scaling factors are resumed in Table S1 for both the PS/clay and PS/PMMA/clay samples at $\Phi > \Phi_c$.

System	Filler volume fractions of the scaled G' curves [%]	$B(\Phi)$	a_ϕ [rad s ⁻¹]	b_ϕ [Pa]
PS/clay	0.94 ± 0.07	1.126	0.004	13.6
	1.10 ± 0.01	1.153	0.012	42.7
	1.27 ± 0.05	1.185	0.025	88.3
	1.32 ± 0.08	1.194	0.051	171.5
	1.63 ± 0.01	1.256	0.223	812.7
	1.89 ± 0.10	1.313	0.332	1256.3
	2.65 ± 0.01	1.500	0.454	1942.2
PS/PMMA/clay	1.32 ± 0.03	1.227	0.024	94.8
	1.66 ± 0.04	1.321	0.044	185.0
	2.05 ± 0.11	1.448	0.113	525.7
	2.12 ± 0.03	1.472	0.143	674.3
	2.24 ± 0.08	1.518	0.157	763.3

Table S1. Amplification factors, $B(\Phi)$, and shift factors, (a_ϕ ; b_ϕ) of each scaled G' curve of Fig. 5 of the manuscript.

6. Strain sweep experiments

The viscoelastic moduli have been recorded at increasing oscillation amplitude at $\omega = 0.1 \text{ rad s}^{-1}$. We have conventionally set γ_c as the strain at which $\log G'$ decreases by about 5% with respect to its low-strain plateau value. The log-log plots of G' vs. γ are shown in Fig. S6 for the PS/clay and PS/PMMA/clay samples used to apply the Wu-Morbidelli model. The abscissae of the points indicated by the arrows are the estimated values of γ_c on logarithmic scale.

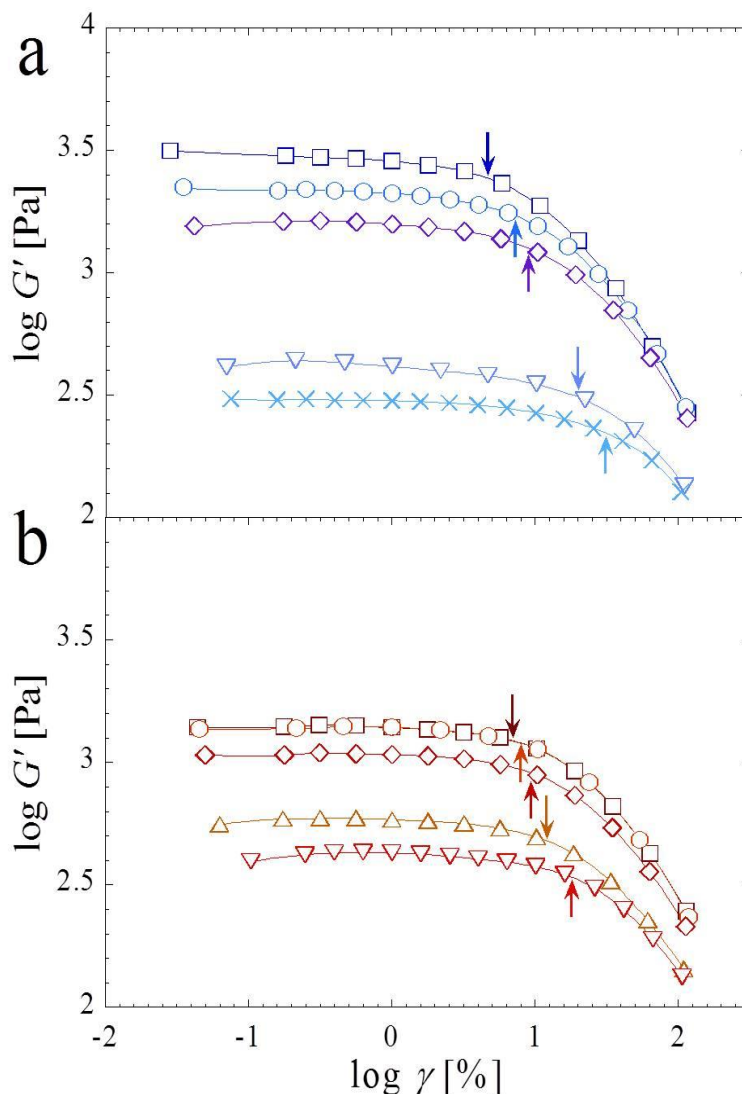


Fig. S6 Log-log plots of the strain-dependent G' for (a) the PS/clay samples at $\Phi = 1.10\%$, 1.27% , 1.63% , 1.89% and 2.65% , and (b) the PS/PMMA/clay samples at $\Phi = 1.32\%$, 1.66% , 2.05% , 2.12% , 2.24% . The filler volume fractions are reported from bottom to top. The estimated values of γ_c correspond to the abscissae of the points indicated by the arrows.

7. Image pre-processing and fractal analysis

Before being analyzed, the TEM micrographs have been preprocessed to isolate the dark pixels associated with the clay particles. First, the images have been adjusted and equalized to their basic tones. Then, the position of the dark pixels has been obtained through the indices of the low tone image. The preprocessing step are summarized by the montage reported as Fig. S7.

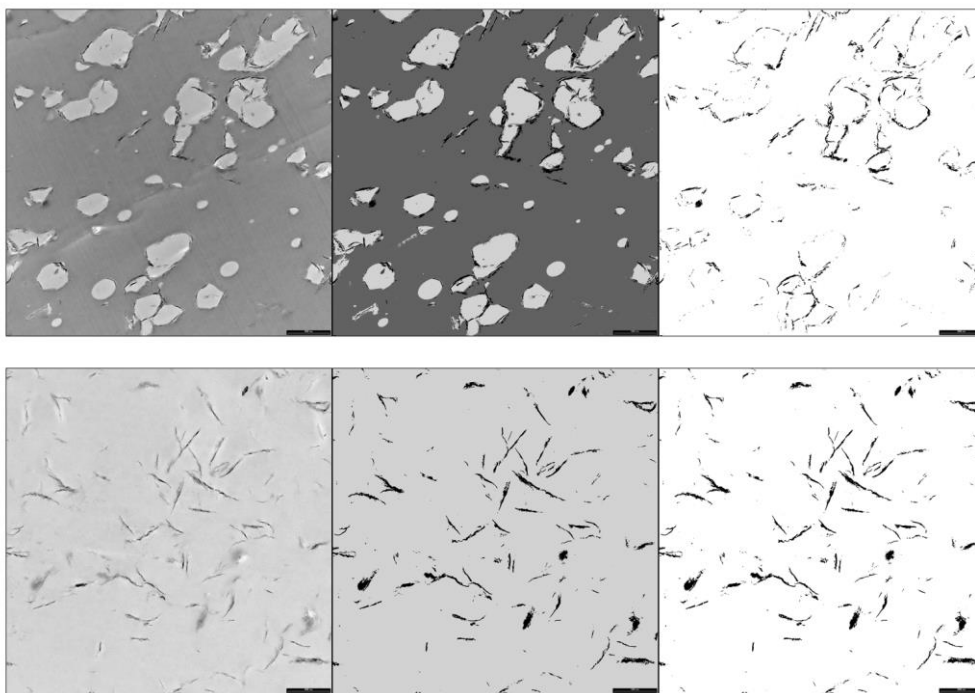


Fig. S7 Example of the preprocessing step for two representative samples at $\Phi = 1.32\%$ (top row: PS/PMMA/clay; bottom row PS/clay). The original micrographs (left) have been adjusted and discretized to the most frequent tones according to the image histogram (center). The resulting channel of dark pixels is shown on the right.

The following step has been the identification of the flocs. It has been assumed that two clay tactoids belong to the same floc if their minimum distance is smaller than 100 nm, i.e. about one tenth of the average lateral dimension of the tactoids. An example of outcome of the floc identification step is shown in Fig. S8.

Each identified floc has been isolated, extracted from the image and subjected to fractal analysis. The 2D box counting fractal dimension D_f has been estimated through the counting boxes algorithm. The algorithm divides the image into equal-sized square blocks, and then it tests each block to check if it meets some user selected criterion. In our case, the presence in the box of a fraction of black pixels higher than 25% is considered a positive correspondence. This procedure is repeated for all possible image tessellation, collecting the total number of positive correspondences, generally named as counts.

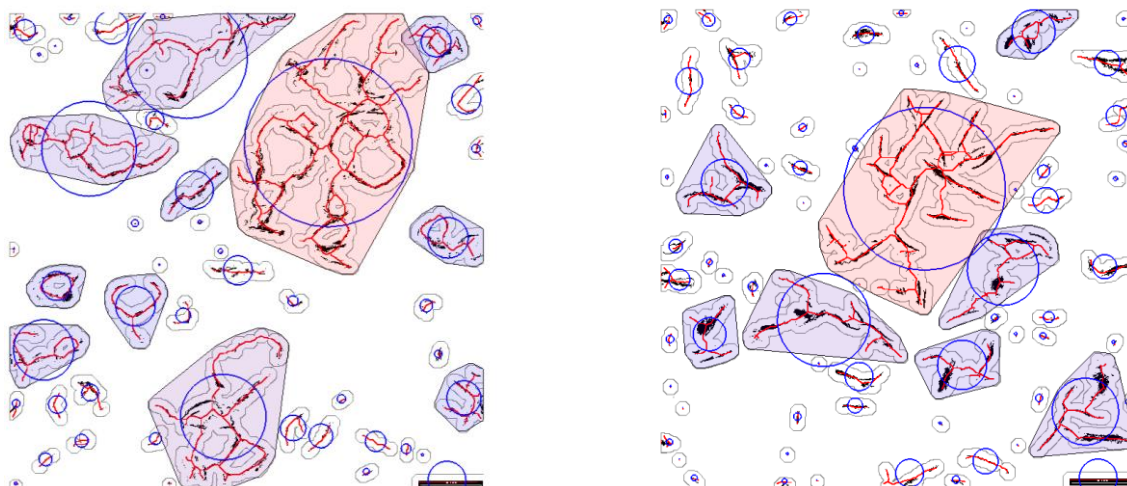


Fig. S8 Identification of the flocs and image segmentation. The shaded areas display the convex circumscribing the floc, which also represents the mask used to extract the objects from the image. Note that small objects have not been considered in the fractal analyses.

The result of the box counting algorithm is shown in Fig. S9. The 2D box counting fractal dimension corresponds to the linear regression of the log-log plot reporting the total counts (N_{box}) versus box length (L_{box}).

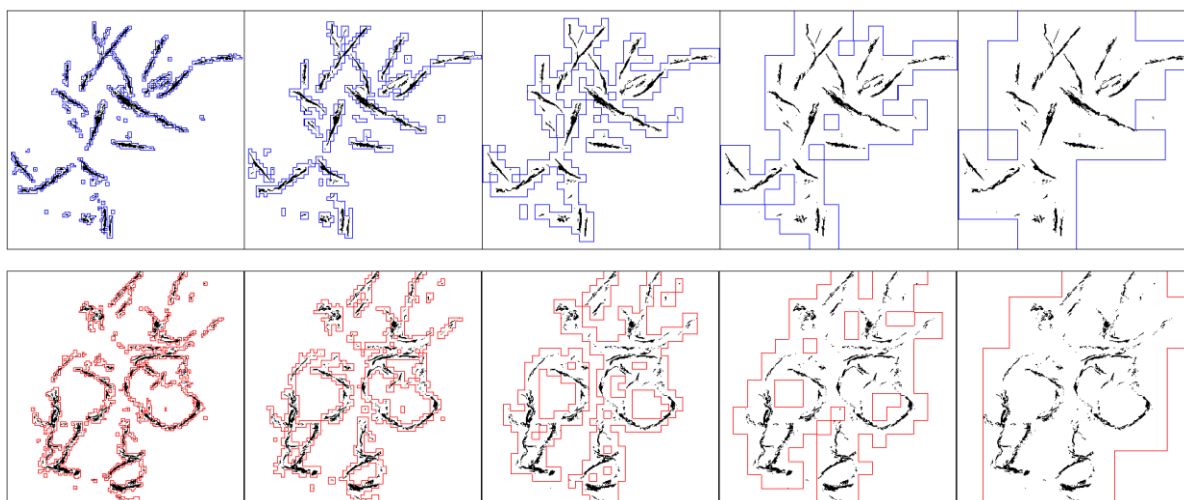


Fig. S9 Counting box snapshots at several box lengths (from left to right: 8, 16, 32, 64, and 128 pixels). The size of the region of interest was 1024x1024 pixels wide. Only the boxes containing a fraction of dark pixels greater than the overall content of the image are shown.

References

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