Supplementary Information (SI) for Soft Matter.
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Electronic supplementary information: Shear thickening in suspensions of particles with dynamic brush layers

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S1. Particle synthesis and characterization

Silica particles were purchased from Fiber Optic Center (New Bedford, MA) with diameters 300 nm, 500 nm, 1 μm, and 2 μm. The particle surface was functionalized by the procedure reported previously[1]. First, 10 g of silica particles were added to 400 mL of toluene. The suspension was sonicated for 1 hr and stirred for another 30 min to homogenize the suspension. Then 3-mercaptopropyl trimethoxysilane (MPTMS) was added to the solution. The concentration of MPTMS was kept 10 MPTMS molecules per nm^2 surface area of the added silica particles. The solution was then heated to reflux and left for 24 hr. Toluene from the final solution was completely removed using a rotary evaporator. The particle powder was washed with ethanol three times by repeating sonication and centrifugation. The final particles were left under vacuum for 24 hr.

The surface density of thiol functional groups was estimated using nuclear magnetic resonance (NMR) studies[1] using 1,3,5-trioxane as an internal standard. First, 20 mg of the silica particles was added to 0.5 M NaOD/D_2O solution. The solution was stirred at 85 °C overnight to fully dissolve the silica particle. The thiol density of the particle surface ρ_{SH} was estimated by NMR. The peak intensity of the (ONa)3SiCH2CH2C**H**2SH ($\delta = 2.43$ ppm) was compared to that of the internal standard (Table S1). The total number of the surface thiol N_{SH} at the particle with diameter d in a suspension with packing fraction ϕ is estimated by

$$N_{\mathrm{SH}} = \phi \frac{\pi d^2}{\pi d^3/6} \rho_{\mathrm{SH}},$$

and the total number of the Michael-acceptor group is estimated by

$$N_{\mathrm{MA}} = (1-\phi)\rho_{\mathrm{PPG}} N_{\mathrm{A}} n_{\mathrm{MA}} / M_{\mathrm{PPG}}$$

with the Avogadro constant N_{A}, the density ($\rho_{\mathrm{PPG}} \approx 1$ g/ml) and molecular weight ($M_{\mathrm{PPG}} = 5300$ g/mol) of (N-BCAm)-endcapped poly(propylene glycol), and the number of Michael-acceptor group $n_{\mathrm{MA}} = 2$. The

Table S1: Estimated thiol density of the particle surface.

diameter	340 nm	620 nm	870 nm	1210 nm	1930 nm
Thiol density of the particle surface	1.09 SH/nm^2	2.15 SH/nm^2	2.19 SH/nm^2	1.20 SH/nm^2	1.31 SH/nm^2

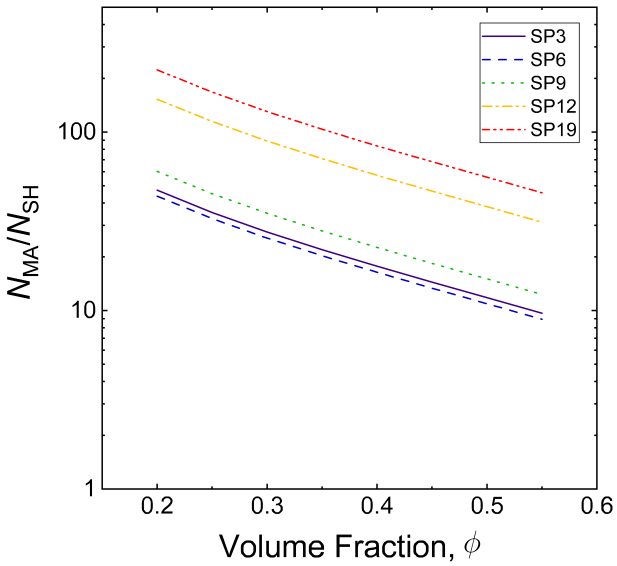

Figure S1: Stoichiometric ratio of Michael-acceptor to thiol in suspensions of different particle sizes is plotted over the particle volume fraction range studied in this study.

Table S2: Parameters from a power-law relation, $\eta = A(1-\phi/\phi_J)^{-n}$.

diameter	A	n	ϕ_J
620 nm	0.79	1.79	0.48
1210 nm	0.96	1.69	0.51
1930 nm	0.74	1.73	0.54

ratio of Michael-acceptor to thiol N_{MA}/N_{SH} in suspensions with various particle volume fractions is plotted in Figure S1.

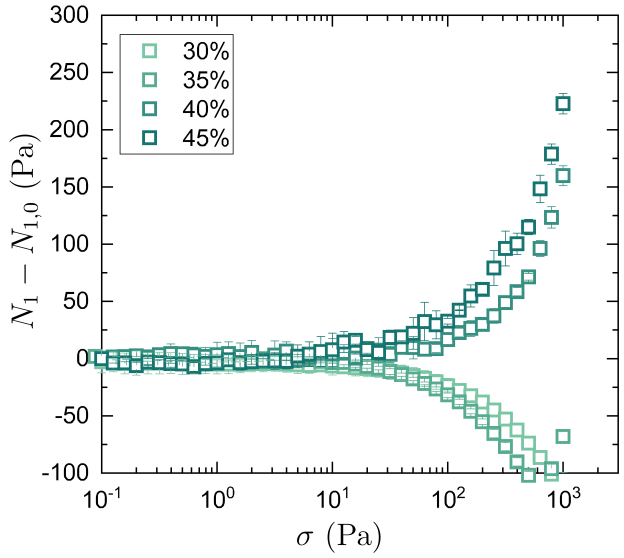

Figure S2: First normal stress difference N_1 for particles ($d = 620$ nm, SP6).

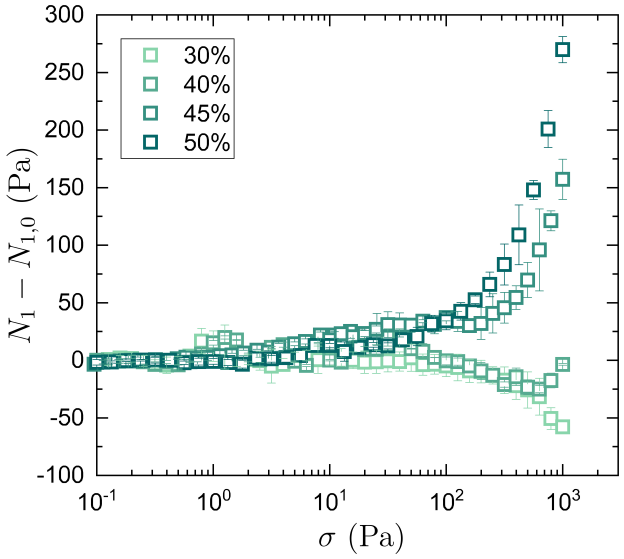

Figure S3: First normal stress difference N_1 for particles ($d = 1210$ nm, SP12).

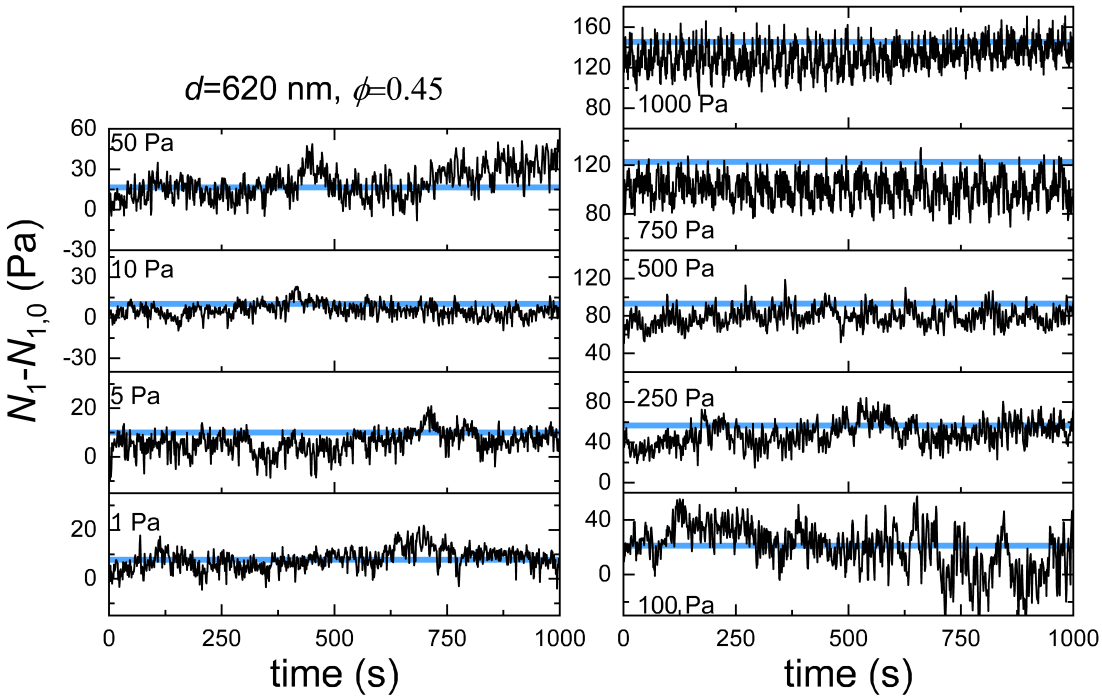

Figure S4: Time-dependent measurement of the first normal stress difference N_1 for the suspension of particles with diameter $d = 620$ nm at $\phi = 0.45$. Measurements were performed at each shear stress after the consistent preshear and relaxation steps. Blue lines indicate the N_1 at each shear stress from the stress-sweep measurement (30 s per each stress).

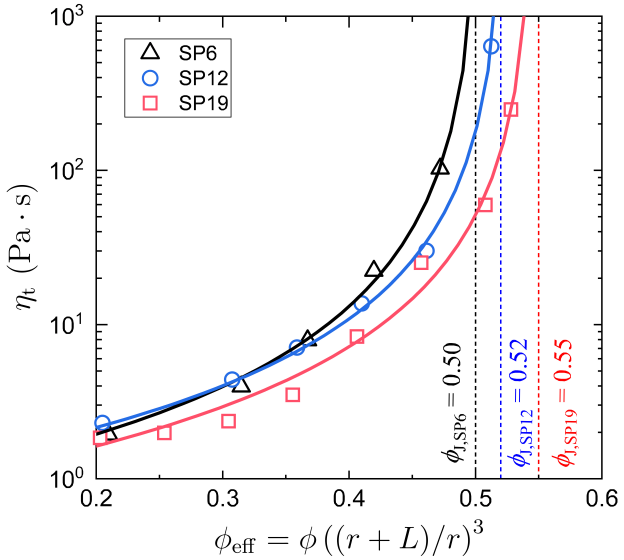

Figure S5: Viscosity η_t at the thickened state versus the effective volume fraction $\phi_{\text{eff}} = \phi(1 + 2L/d)^3$ for SP6 (black), SP12 (blue), and SP19 (red). The thickness of the brush layer is set to half of the contour length $L_c \approx 10$ nm. Lines are least-squares fits to $\eta = A(1-\phi_{\text{eff}}/\phi_J)^{-n}$. The estimated jamming volume fraction ϕ_J is $\phi_{J,\text{SP6}} = 0.50$, $\phi_{J,\text{SP12}} = 0.52$, and $\phi_{J,\text{SP19}} = 0.55$.

References

S1 Carina IC Crucho, Carlos Baleizao, and Jose Paulo S Farinha. Functional group coverage and conversion quantification in nanostructured silica by ^{1}H NMR. *Analytical chemistry*, 89(1):681–687, 2017.