Electronic Supplementary Information:
Dynamic-bond-induced sticky friction tailors non-Newtonian rheology

Hojin Kim, Mike van der Naald, Neil D. Dolinski, Stuart J. Rowan, and Heinrich M. Jaeger

a James Franck Institute and Department of Physics, The University of Chicago, Chicago, Illinois 60637, USA
b Pritzker School of Molecular Engineering, The University of Chicago, Chicago, Illinois 60637, USA
c Department of Chemistry, The University of Chicago, Chicago, Illinois 60637, USA
‡ E-mail: stuartrowan@uchicago.edu (SJR), jaeger@uchicago.edu (HMJ)
S1. Characterization techniques

- Dynamic light scattering (DLS): A dynamic light scattering instrument (Wyatt Technology’s Mobius™) was used to measure the hydrodynamic radius of the synthesized thiol-functionalized silica particle and silica seed particle.

- Nuclear magnetic resonance spectroscopy: A Bruker Avance nanobay III HD 400 MHz nuclear magnetic resonance spectrometer was used to characterize the functionalized silica particles and the synthesized Michael-acceptors. The residual solvent CHCl$_3$ peak at $\delta = 7.26$ ppm was used as a reference peak.

S2. Characterization of the synthesized materials

- Functionalized silica particle characterization
  The functionalized silica particles were characterized with $^1$H NMR following the method reported by Crucho et al.\textsuperscript{1}. 20 mg of silica particles was dissolved in a solution of 0.5 M NaOD in D$_2$O. To quantify the functional group density, 35 mg of 1,3,5-trioxane was added as an internal standard. The intensity of the (ONa)$_3$SiCH$_2$CH$_2$CH$_2$SH at $\delta = 2.43$ ppm was compared to that of the internal standard, giving 1.3 SH groups/nm$^2$ surface area of silica particles.

DLS was used to measure the size of synthesized silica particles suspended in water. The synthesized particle density ($\rho = 1.92$ g/mL) was measured with the bromoform ($\rho = 2.89$ g/ml) and methanol ($\rho = 0.79$ g/ml) mixture at which the particle does not sediment or float.

- Characterization of Michael-acceptors
  The synthesized 1M, 1H, and 1N molecules were characterized with $^1$H NMR (400 MHz, CDCl$_3$ in Fig. S1):
  R=–OCH$_3$ (1M): $\delta = 8.23$ (s, 1H, C=CH), 7.67 (d, 2H, Ar-H), 6.91 (d, 2H, Ar-H), 3.82 (s, 3H, Ar-OCH$_3$, 3.42–3.77 (m, -CH$_2$-CH-), 1.25 (m, -CH$_3$) ppm.
  R=–H (1H): $\delta = 8.30$ (s, 1H, C=CH), 7.73 (t, 3H, Ar-H), 7.40 (d, 2H, Ar-H), 3.42–3.77 (m, -CH$_2$-CH-), 1.25 (m, -CH$_3$) ppm.
  R=–NO$_2$ (1N): $\delta = 8.37$ (s, 1H, C=CH), 8.24 (d, 2H, Ar-H), 7.88 (d, 2H, Ar-H), 3.42–3.77 (m, -CH$_2$-CH-), 1.25 (m, -CH$_3$) ppm.

- Solvent viscosity
  The viscosity of Michael-acceptor endcapped polymer fluids was measured using MCR301 or MCR702 rheometer (Anton Paar). In the measured shear rate range (1 – 100 s$^{-1}$), the fluid viscosity exhibited Newtonian behavior.
  $\eta_{1M_{230}} = 2564$ mPa·s, $\eta_{1M_{2000}} = 579$ mPa·s, $\eta_{1M_{4000}} = 1195$ mPa·s
\[ \eta_{H_{230}} = 880 \text{ mPa} \cdot \text{s}, \quad \eta_{H_{2000}} = 528 \text{ mPa} \cdot \text{s}, \quad \eta_{H_{4000}} = 1048 \text{ mPa} \cdot \text{s} \]

\[ \eta_{N_{2000}} = 980 \text{ mPa} \cdot \text{s}, \quad \eta_{N_{4000}} = 1393 \text{ mPa} \cdot \text{s} \]

Fig. S1 \[ ^1H \text{ NMR for } 1N_{4000}, 1H_{4000}, \text{ and } 1N_{4000} \text{ (top to bottom).} \]

S3. Preparation of piperidinium acetate

Piperidinium acetate was prepared following the reaction in Scheme S1. 40 mmol of piperidine (Sigma-Aldrich, 99%) and 40 mmol of acetic acid (Thermo Fisher Scientific, \(\geq 99.7\%\)) were added to a 50 mL round-bottom flask with 12 mL of chloroform. The solution was stirred with a magnetic stirrer for 30 min at room temperature. After the reaction, chloroform was removed from the product using a rotary evaporator.

\[ ^1H \text{ NMR (400 MHz, CDCl}_3) \text{ spectrum for piperidinium acetate: } \delta = 8.50 \text{ (s, 2H, } -\text{C-NH}_2^+) \text{, 3.02 - 2.95 (m, 4H, N-CH}_2 \text{), 1.97 (d, 3H, C}_3 \text{), 1.81 - 1.71 (m, 4H, N-C-CH}_2-\text{C), 1.67 - 1.58 (m, 2H, N-C-C-CH}_2 \text{ ppm.} \]
Scheme S1  Synthesis of piperidinium acetate.

Fig. S2  Relative viscosity $\eta_r = \eta / \eta_s$ for suspensions in $1M_{2000}$ (a), $1H_{2000}$ (b), and $1N_{2000}$ (c) as a function of shear rate $\dot{\gamma}$. Closed symbols: increasing stress ramp. Open symbols: decreasing stress on the ramp’s return cycle.

Fig. S3  Confirmation of steady-state viscosity. Relative viscosity $\eta_r = \eta / \eta_s$ is plotted as a function of shear stress $\tau$ for $\phi = 0.52$ thiol functionalized silica particle suspensions in $1M_{2000}$. The viscosity is measured at three different equilibrating times (5 s, 30 s, and 90 s per each $\tau$).
Fig. S4  Viscosity as a function of time at constant shear rate $\dot{\gamma}$ for the suspension in $1H_{2000}$.

Fig. S5  The estimated fraction of bonded thiols as a function of $K_{eq}$ for $M_{PPG}=230$ (blue), 2000 (orange), and 4000 g/mol (green) at fixed packing fraction ($\phi = 0.52$).
S4. The fraction of bonded thiols to form thia-Michael bonds

The equilibrium constant of thia-Michael reaction between thiol (–SH) and Michael-acceptor (–MA) is:

\[ K_{eq} = \frac{[tMA]}{[−SH][−MA]} \]

The fraction of bounded thiol \( p \) at equilibrium suggests \([tMA] = p[−SH]_0\) and \([−SH] = (1 − p)[−SH]_0\), where \([−SH]_0\) is the initial molar concentration of thiol. Then, \([−MA] = [−MA]_0 − [tMA] = [−MA]_0 − p[−SH]_0\). Finally, the equilibrium constant is expressed by:

\[ K_{eq} = \frac{p}{(1 − p)([−MA]_0 − p[−SH]_0)} \]

Using this equation, \( p \) is solved for all Michael-acceptors (Table S1). Based on this expression, we estimated the fraction of bonded thiols as a function of \( K_{eq} \) for all molecular weights in Fig. Fig. S5.

**Table S1** The fraction of thiol reacted for the thia-Michael adduct formation.

<table>
<thead>
<tr>
<th></th>
<th>( M_{M_{PPG}} = 230 \text{ g/mol} )</th>
<th>( M_{M_{PPG}} = 2000 \text{ g/mol} )</th>
<th>( M_{M_{PPG}} = 4000 \text{ g/mol} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M_{M_{PPG}}</td>
<td>0.992</td>
<td>0.970</td>
<td>0.944</td>
</tr>
<tr>
<td>1H_{M_{PPG}}</td>
<td>0.999</td>
<td>0.996</td>
<td>0.992</td>
</tr>
<tr>
<td>1N_{M_{PPG}}</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
</tr>
</tbody>
</table>

**Fig. S6** Relative viscosity \( \eta_r \) versus shear stress \( \tau \) of \( \phi = 0.52 \) thiol functionalized silica particle suspensions in different molecular weight BCAm-endcapped poly(propylene glycol) 1N_{2000} (a) and 1N_{4000} (b).
Fig. S7  Relative viscosity $\eta/\eta_s$ as a function of shear rate $\dot{\gamma}$ of the suspension in hydroxy-terminated polypropylene glycol (2000 g/mol, PPG$_{\text{OH}2k}$) and in a mixture of PPG$_{\text{OH}2k}$ and 2,2’-(ethylenedioxy)diethanethiol (EDDT) with a 1-to-10 molar ratio. The packing fraction of suspensions is fixed at $\phi = 0.52$.

Fig. S8  A Raman spectrum of thiol-functionalized silica particles suspended in a mixture hydroxy-terminated polypropylene glycol (2000 g/mol, PPG$_{\text{OH}2k}$) and and 2,2’-(ethylenedioxy)diethanethiol (EDDT) (1-to-10 molar ratio). The packing fraction of suspensions is $\phi = 0.52$. A free thiol peak clearly appears at 2570 cm$^{-1}$, whereas there is limited-to-no disulfide formation from a peak at 510 cm$^{-1}$. 
S5. Constraint-based Wyart-Cates model fitting

We fitted the experimental rheology curves using the constraint-based model by Guy et al.\textsuperscript{2,3}, which extends an earlier model by Wyart and Cates (WC) that does not account for attractive interactions\textsuperscript{4}. This modified WC model includes frictional and adhesive force responsible for the sliding and rolling constraints, respectively. Based on the WC model, the relative viscosity is expressed by

\[ \eta_r = \left[ 1 - \frac{\phi}{\phi_J(a, f)} \right]^{-2} \]  

with the jamming volume fraction $\phi_J(a, f)$ that is a function of the fraction of adhesion ($a$) and friction ($f$). These parameters can be expressed by $f(\tau) = \exp \left[ -\frac{(\tau^*/\tau)^{\beta}}{\tau_a} \right]$ with the critical stress $\tau^*$ for dominating friction over particle repulsive interaction and $a(\tau) = 1 - \exp \left[ -\frac{(\tau_a/\tau)^{\gamma}}{\tau_a} \right]$ with $\tau_a$, the stress required to break the adhesion between contacting particles. With $a$ and $f$, $\phi_J(a, f)$ can be interpolated with all four possible constraints,

\[ \phi_J(a, f) = af\phi_{\text{alp}} + a(1-f)\phi_{\text{acp}} 
+ (1-a)f\phi_{\mu} + (1-a)(1-f)\phi_{\text{rcp}} \]  

where $\phi_{\mu} \equiv \phi_J(a = 0, f = 1)$, $\phi_{\text{alp}} \equiv \phi_J(a = 1, f = 1)$, $\phi_{\text{acp}} \equiv \phi_J(a = 1, f = 0)$, and $\phi_{\text{rcp}} \equiv \phi_J(a = 0, f = 0)$ are the onset packing fraction for shear jamming of frictional particles in the absence of adhesion, the adhesive loose packing fraction, adhesive close packing fraction $\phi_{\text{acp}} \equiv \phi_J(a = 1, f = 0)$, and random close packing for hard spheres, respectively. $\phi_{\text{rcp}} = 0.64$ was fixed, and the other parameters were used to fit both the shear-thinning and -thickening regimes of the measured rheology curve. Using the fitting parameter, yield stress of each suspension was estimated by setting $\phi_J = \phi$ where $\eta_r \to \infty$. Errors were estimated from fits with varied fitting ranges.
Supplementary References


