SUPPORTING INFORMATION

SPREADING KINETICS OF ULTRA-THIN LIQUID FILMS USING MOLECULAR DYNAMICS

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Potential function interactions. Figure S1 (a) and (b) depict the potential function interactions for Zdol and Z molecules, respectively, using the corresponding equation numbers, and are similar to validated potentials and parameters used in previous research.[32,36-38] A truncated, shifted Lennard Jones potential U_{LJ} exists between all polymer beads, given by

$$U_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} - \left(\frac{\sigma}{r_c}\right)^{12} + \left(\frac{\sigma}{r_c}\right)^{6}\right], \quad (1)$$

where r is the distance between two beads, σ = 0.7 nm is the bead diameter, $r_c = 2.5\sigma$ is the cutoff distance within which interactions between neighboring beads are considered, and $\varepsilon = Tk_B$ is the potential well depth, where T = 300 K is the absolute temperature and k_B is the Boltzmann constant. A finitely extensible nonlinear elastic (FENE) potential U_{FENE} acts as a spring to bond neighboring beads of the same molecular chain, *i.e.*,

$$U_{FENE}(l) = -\frac{1}{2}kR_0^2 \ln\left[1 - \left(\frac{l - l_0}{R_0}\right)^2\right], \quad (2)$$

where l is the bond length, $l_0 = 1.3\sigma$ is the equilibrium bond length, $R_0 = 0.3\sigma$ indicates the maximum extensible range, and $k = 40\varepsilon/\sigma^2$ is the spring constant. The substrate interacts with the polymer molecules, and attracts polymer backbone beads via a dispersive van der Waals interaction $U_{bb\text{-}wall}$, described as

$$U_{bb-wall}(z) = 4\varepsilon\left[\frac{1}{2}\left(\frac{\sigma}{z}\right)^{9} - \frac{3}{2}\left(\frac{\sigma}{z}\right)^{3}\right], \quad (3)$$

where z is the distance between a substrate bead and a polymer bead. We use a short-range exponential potential $U_{eb\text{-}eb}$ to model the attraction of functional end beads to each other,

$$U_{eb-eb}(r) = -2\varepsilon \exp\left(-\frac{r - r_c}{d}\right), \tag{4}$$

where $r_c = 1.0\sigma$ is the cutoff distance and $d = 0.3\sigma$ is the decay length. Additionally, a fraction of the substrate beads is functional, and an attractive force exists between functional substrate and functional polymer beads, also modeled by a short-range exponential potential $U_{eb\text{-}wall}$,

$$U_{eb-wall}(z) = -2\varepsilon \exp\left(-\frac{z - z_c}{d}\right), \tag{5}$$

where $z_c = 1.165\sigma$ is the cutoff distance.

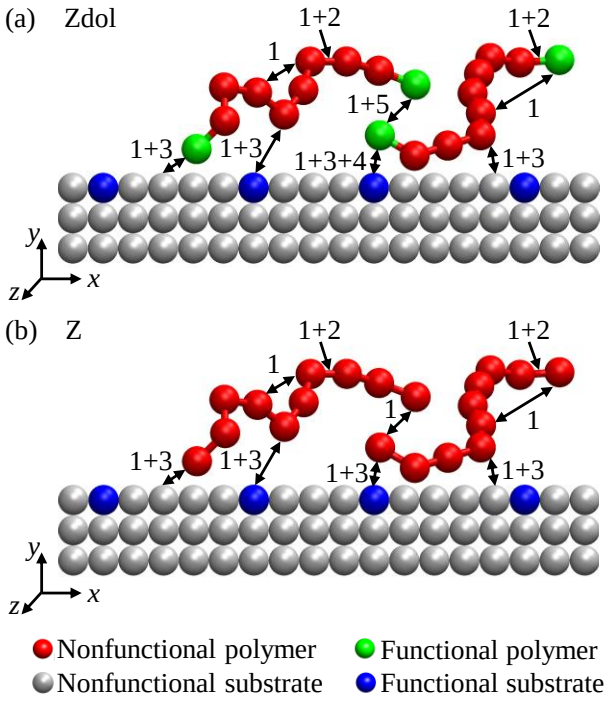

Figure S1. Schematic of potential function interactions for (a) Zdol and (b) Z polymer, with numbers referring to the corresponding equations.

Spreading exponents for all simulations. Table S1 shows the spreading exponents for Z lubricant with molecule length $10 \leq N \leq 400$ and lubricant quantity $5{,}000 \leq Q \leq 40{,}000$, supplementing the spreading exponent values reported in Fig. 2 and Fig. 3. We characterize spreading kinetics in some cases using one spreading exponent (v_1) whereas in other cases we use two spreading exponents that occur sequentially (v_1 followed by v_2). From Table S1, we observe pressure-driven flow (red) characterized by a single, fast spreading speed $v \approx 1/3$ for molecules $N < 50$, corresponding to Fig. 2. For molecules $N \geq 50$, we observe pressure-driven, entanglement inhibited flow (black) characterized by a transition in spreading speed from fast $v \approx 1/3$ when the central droplet is present, to slow $v \approx 1/10$ after the central droplet depletes, corresponding to Fig. 3. For some cases with $N \geq 50$ but small lubricant quantity (Q = 5,000), we only observe a slow spreading speed because the central droplet depletes almost instantaneously after spreading starts. For cases with $N \geq 50$ and large lubricant quantity (Q = 40,000), we only observe a fast mechanism because the droplet depletes near the end of the simulation (250 ns).

Table S1. Spreading exponents for Z lubricant

N	Q	v_1	v_2
10	5,000	0.27	-
	10,000	0.27	-
	20,000	0.32	-
	40,000	0.37	-
20	5,000	0.27	-
	10,000	0.29	-
	20,000	0.32	-
	40,000	0.36	-
50	5,000	0.16	-
	10,000	0.32	0.15
	20,000	0.34	0.13
	40,000	0.32	-
100	5,000	0.13	-
	10,000	0.28	0.14
	20,000	0.28	0.16
	40,000	0.38	-
200	5,000	0.29	0.10
	10,000	0.34	0.14
	20,000	0.30	0.15
	40,000	0.37	-
400	5,000	0.29	0.10
	10,000	0.33	0.12
	20,000	0.35	0.15
	40,000	0.38	-

Table S2 shows the spreading exponents for Zdol lubricant with functional substrate fraction S_f = 100%, molecule length $10 \leq N \leq 400$, and lubricant quantity $5{,}000 \leq Q \leq 40{,}000$. We characterize spreading kinetics in some cases using one spreading exponent (v_1) whereas in other cases we use two spreading exponents that occur sequentially (v_1 followed by v_2). From Table S2 we observe pressure-driven, chemically inhibited flow (blue), characterized by a single, slow spreading speed $v \approx 1/10$ for $N < 100$, corresponding to Fig. 4. For $N \geq 100$, we observe pressure-driven, entanglement inhibited flow (black) characterized by a transition in spreading speed from fast $v \approx 1/3$ to slow $v \approx 1/10$ after the central droplet depletes, corresponding to Fig. 3. For some cases with $N \geq 100$ but small lubricant quantity (Q = 5,000), we only observe a slow spreading speed because the central droplet depletes almost instantaneously after spreading starts. For cases with $N \geq 100$ and large lubricant quantity (Q = 40,000), we only observe a fast mechanism because the droplet depletes near the end of the simulation.

Table S2. Spreading exponents for Zdol lubricant with S_f = 100%

N	Q	v_1	v_2
10	5,000	0.12	-
	10,000	0.16	-
	20,000	0.15	-
	40,000	0.12	-
20	5,000	0.16	-
	10,000	0.16	-
	20,000	0.15	-
	40,000	0.16	-
50	5,000	0.15	-
	10,000	0.15	-
	20,000	0.13	-
	40,000	0.15	-
100	5,000	0.11	-
	10,000	0.16	-
	20,000	0.31	0.16
	40,000	0.30	0.16
200	5,000	0.27	0.10
	10,000	0.28	0.13
	20,000	0.29	0.12
	40,000	0.30	-
400	5,000	0.32	0.10
	10,000	0.34	0.11
	20,000	0.34	0.14
	40,000	0.35	-

Table S3 shows the spreading exponents for Zdol lubricant with functional substrate fraction S_f = 0%, molecule length $10 \leq N \leq 400$, and lubricant quantity $5{,}000 \leq Q \leq 40{,}000$. We characterize spreading kinetics in some cases using one spreading exponent (v_1) whereas in other cases we use two spreading exponents that occur sequentially (v_1 followed by v_2). From Table S3 we observe pressure-driven flow (red) characterized by a single, fast $v \approx 1/3$ spreading speed for $N < 50$, corresponding to Fig. 2. For molecules $N \geq 50$, we observe pressure-driven, entanglement inhibited flow (black) characterized by a transition in spreading speed from fast $v \approx 1/3$ to slow $v \approx 1/10$ after the central droplet depletes, corresponding to Fig. 3.

Table S3. Spreading exponents for Zdol lubricant with S_f = 0%

N	Q	v_1	v_2
10	5,000	0.29	-
	10,000	0.30	-
	20,000	0.33	-
	40,000	0.38	-
20	20,000	0.30	-
50	20,000	0.30	0.16
100	20,000	0.29	0.15
200	20,000	0.30	0.14
400	10,000	0.29	0.13
	20,000	0.35	0.16

Video supplements of spreading. We have included three videos of lubricant spreading to supplement Figures 2-4. Each video shows, as a function of time, the plot of droplet edge radius (top left), a side view of the lubricant droplet (bottom left), the entanglement map (top right), and the pressure map (bottom right, , the vertical scale is 10 times larger than the horizontal one, for clarity). We illustrate three specific cases. Video S1 shows pressure-driven flow of Z lubricant with molecule length N = 10 beads/molecule and lubricant quantity Q = 10,000 polymer beads, illustrating a case with only a fast spreading speed (v = 0.27) as no functional end groups attach to the substrate or molecule entanglement inhibits spreading. Video S2 shows pressure-driven, entanglement inhibited flow of Z lubricant with molecular chain length N = 400 beads/molecule and lubricant quantity Q = 10,000 polymer beads, illustrating a case in which the lubricant central droplet depletes, resulting in a transition in spreading speed

(initial fast spreading speed $v = 0.33$ followed by a slow spreading speed $v = 0.12$). Video S3 shows pressure driven, chemically inhibited flow of Zdol lubricant with functional substrate fraction $S_f = 100\%$, molecular chain length $N = 10$ beads/molecule, and lubricant quantity $Q = 10{,}000$ lubricant beads, illustrating a case with only a slow spreading speed ($v = 0.16$) caused by functional end bead pinning.