Supporting Information

Liposomes Tethered to a Biopolymer Film through the Hydrophobic Effect Create a Highly Effective Lubricating Surface

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Synthesis of hm-chitosan

4 g of chitosan was dissolved in 220 mL of 1% (v/v) acetic acid, and then 150 mL ethanol was added to allow the aldehyde used in the alkylation step to be in a solvating medium. The pH was adjusted to 5.1 by the addition of sodium hydroxide, and then a solution of dodecyl aldehyde in ethanol was added at a concentration that 2.5% of the monomer concentration. This is followed by the addition of an excess of sodium cyanoborohydride (3 mol/mol sodium cyanoborohydride/chitosan-monomer). The mixture was stirred for 24 hours at room temperature and the final product was first precipitated with ethanol and sodium hydroxide solution, and then was washed with ethanol and deionized (DI) water three times. The molecular structure of hm-chitosan was characterized through ^{1}H NMR spectroscopy to verify the attachment of the hydrophobes. The experiments were conducted in deuterium oxide using a Bruker Avance 500 MHz NMR spectrometer.

[1]H NMR Spectroscopy of hm-chitosan:

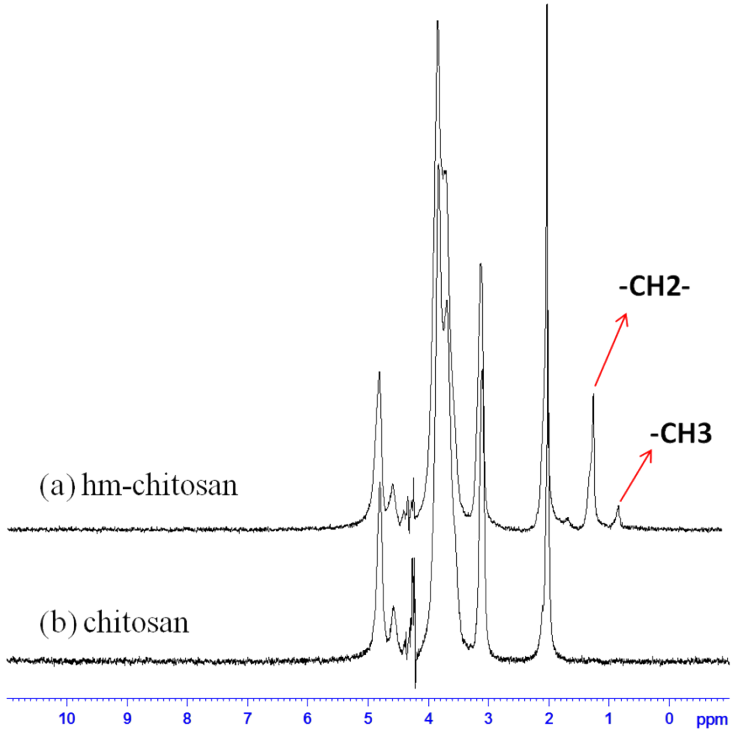

Figure S1. [1]H NMR spectroscopy of 0.50% (a) hydrophobically modified chitosan (hm-chitosan) and (b) chitosan samples indicates the successful addition of alkyl groups to the chitosan backbone.

Contact Angles of Water Droplet on hm-chitosan Film:

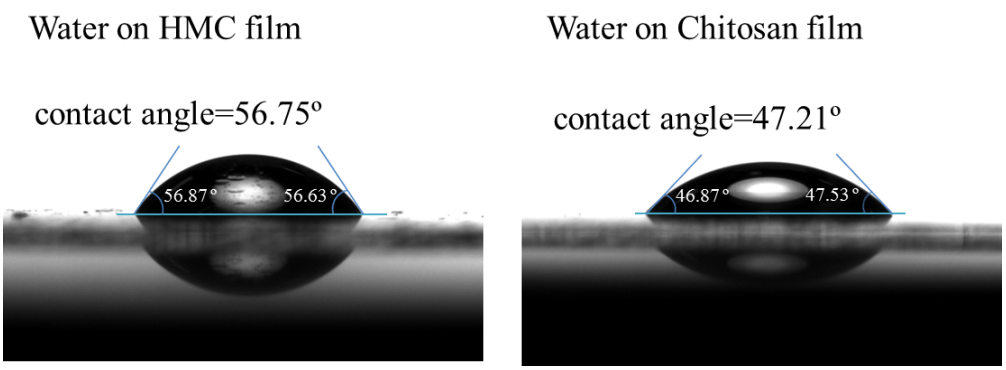

Figure S2. The contact angles of a water droplet on (a) hm-chitosan film and (b) chitosan film. The increase in contact angle with hm-chitosan is representative of the increase in hydrophobicity with exposure of alkyl groups.

Cryo-TEM Image of DPPC Liposomes:

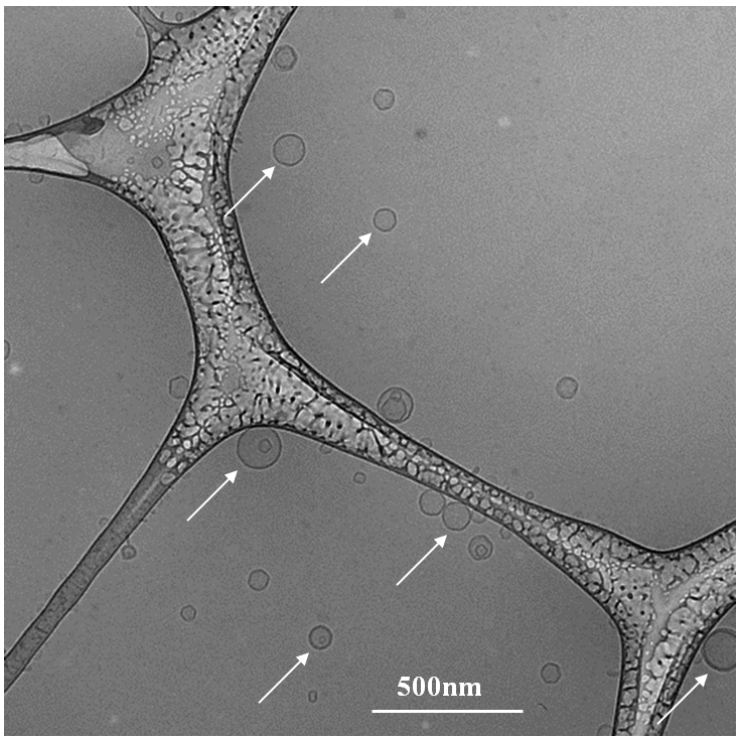

Figure S3. Cryogenic transmission electron microscopy (cryo-TEM) image of prepared DPPC liposomes.

Friction Measurements:

The experiments were performed with a cover glass (Fisherfinest Premium Cover Glass, Fisher Scientific), chitosan/liposome film and hm-chitosan/liposome film as the bottom shearing surfaces and a curved optically polished glass surface (radius of curvature = 3 cm, Anchor Optics, Barrington, NJ) as the probe (top surface). The glass surface was cleaned by sonication in ethanol for 5 min, followed by rinsing with DI water and a subsequent plasma-cleaning step (Harrick Plasma, Ithaca, NY). In a typical experiment, the bottom surface, either a cover glass or a prepared film, was glued onto a holder and a drop (~50 μL) of the DPPC liposome (2%, wt/v) suspension or PBS buffer solution was placed between the bottom surface and the probe. The probe, attached to a force sensor (DFM-0.5, CETR, Campbell, CA) with a cantilever (spring constant k_{DFM} = 4113 N/m), was then brought into contact with the bottom surface at a predetermined preload. A universal materials tester (CETR, Campbell, CA) was used to measure the friction force between the shearing surfaces as the load was either held constant or increased stepwise with each shear cycle. The COF was determined by taking the slope of the average friction force versus the average load for each shear cycle.

Complete Data of the Coefficient of Friction Measurement:

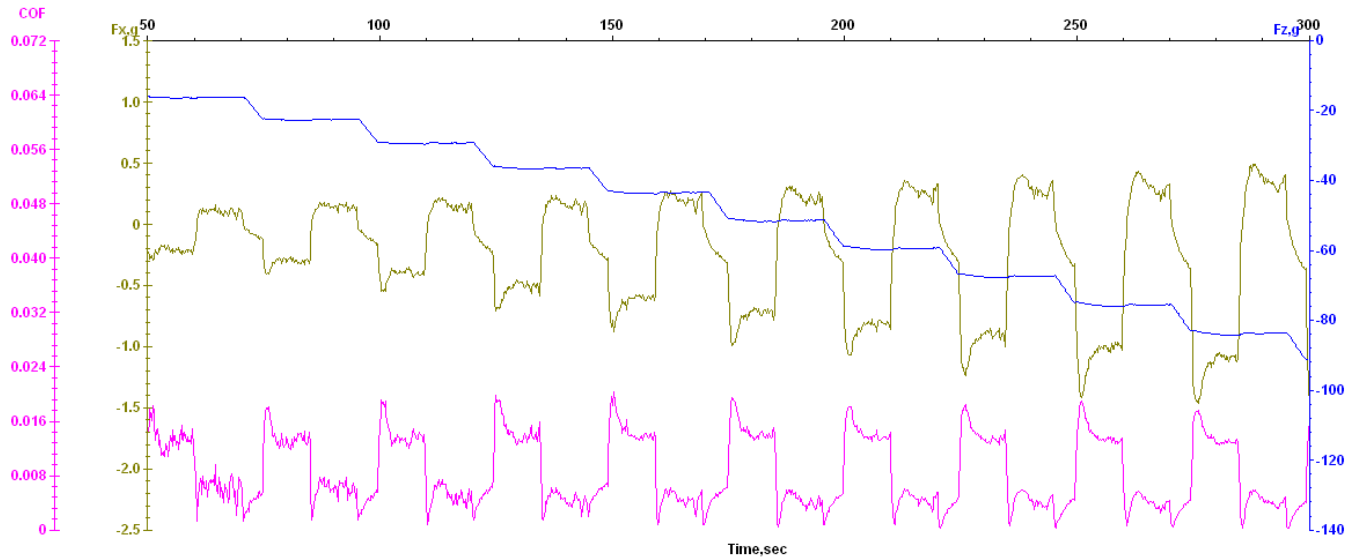

Figure S4. Complete data from the universal materials tester (tribometer) showing the friction force (gold), and the COF (pink) as a function of increasing load (blue). The measurements were performed with a stepwise increasing load from 196 mN (20 g) to 784 mN (80g), a sliding velocity of 1mm/s, and a dwell time of 5s. The specific measurement shown is for the system of hm-chitosan film containing tethered liposomes in contact with a glass probe. We note that the COF remains constant at 0.0076.

Coefficient of Friction Between hm-chitosan/liposome Film and Glass Probe in 2% DPPC Liposome Solution:

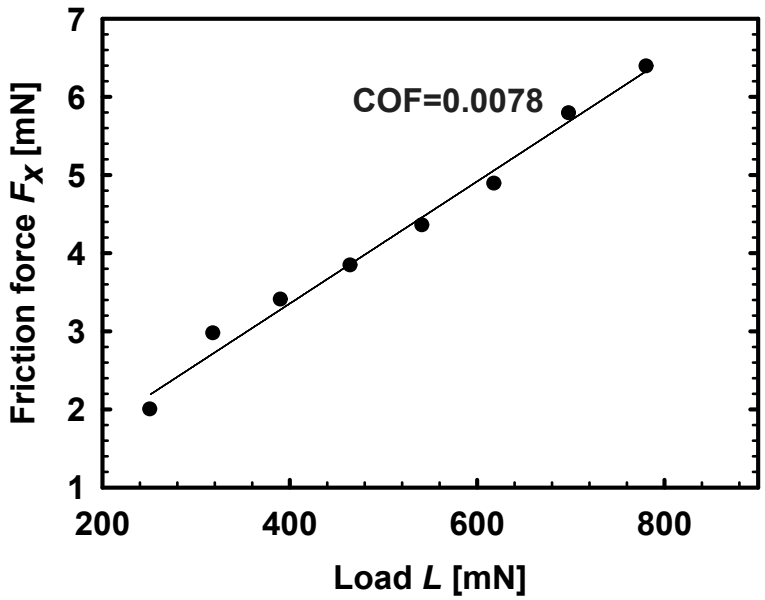

Figure S5. The plot of the friction force $\mathbf{F_x}$ versus the applied load **L** while shearing a spherical glass probe versus hm-chitosan/liposome film in 2 % (wt/v) DPPC liposome solution. The measurements were performed with an increasing load from 196 mN (20 g) to 784 mN (80g), sliding velocity of 1mm/s, and dwell time of 5s. The data indicates that the addition of liposomes in solution does not affect the lubrication properties of the film.

Complete Data of the Wear Test:

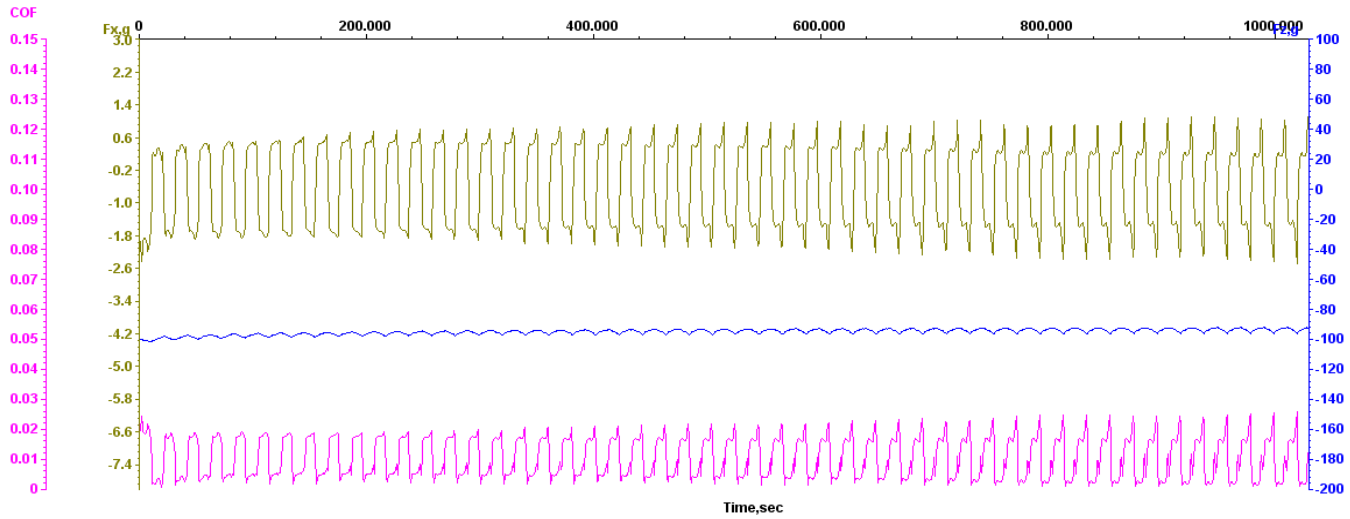

Figure S6. Complete data from the universal materials tester (tribometer) showing the friction force (gold, F_x, g), and the COF (pink) as a function of increasing load (blue, F_z, g). The measurements were performed with a constant load of 980 mN (100g), a sliding velocity of 1 mm/s. The specific measurement shown is for the system of hm-chitosan film containing tethered liposomes in contact with a glass probe. The COF value remains stable during the test.