Supporting Information: Ageing of polymer frictional interfaces: the role of quantity and quality of contact

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1 Methods

1.1 Coverslips silanization

Glass coverslips were washed in a teflon rack in 3% Hellmanex III solution by sonication for 30 minutes at 40 °C. Then they were sonicated in deionized water (Milli-Q, Millipore, Bedford, MA, USA) for 10 minutes and in 99% EtOH for 20 minutes. Afterwards each coverslip was dried with a nitrogen stream and further cleaned in the rack in an ozone photoreactor for 2 hours. Coverslips were silanized with 2% (volume) (3-aminopropyl)triethoxysilane (APTES) in 96% EtOH in which 2% (by volume) of H2O was added. The pH of this solution was adjusted to 6 by addition of acetic acid. Right after the ozone treatment a teflon rack with 4 coverslips was inserted into the reaction mixture for 30 minutes while stirring. The rack can contain 8 coverslips, the choice of 4 coverslips was made in order to have an empty space between coverslips large enough in order to have a uniform liquid flow for both sides of each coverslip within the rack. The coverslips afterwards were sonicated in EtOH for 30 minutes, dried with a nitrogen stream and kept in an oven for 24 hours at 110 °C.

1.2 Immobilization of DCDHF on glass coverslips

DCDHF dye (2-(1-(4-(4-cyano-5-(dicyanomethylene)-2,2-dimethyl-2,5-dihydrofuran-3-yl)phenyl)-piperidin-4-yl) acetic acid (10 mg, 0.03 mmol, 1 eq) together with 1-[bis(dimethylamino)-methylene]-1H-1,2,3-triazolo[4,5-b]pyridinium 3-oxid hexafluorophosphate (HATU) (45.6 mg, 0.12 mmol, 4 eq), and diisopropylethylamine (64 μl, 0.37 mmol, 12 eq) were added to the 4 silanized coverslips in dry N,N-dimethylformamide (80 mL). The reaction mixture was stirred for 2 hours at room temperature. The coverslips were removed from the reaction mixture, rinsed with dichloromethane, acetone and EtOH and sonicated in EtOH for 30 minutes.

1.3 Setup

Fluorescence lifetime images were measured with an inverted confocal lifetime microscope MicroTime 200 (PicoQuant GmbH) on top of which a rheometer (Anton Paar DSR 301) was mounted. A coverslip chemically modified with DCDHF dye was inserted in the sample holder. A polystyrene or PMMA bead was glued to the rheometer plate. The bead was pressed with a controlled normal force against the modified coverslip on which a droplet of Formamide was deposited. For excitation, an NKT SuperK Extreme pulsed (9 MHz) white-light continuum laser with the SuperK Select acousto-optical tunable filter (AOTF) operating at a repetition rate of 9 MHz was used. Time-correlated single photon counting (TCSPC) histograms in each of the pixels were recorded using on average $3 \cdot 10^6$ photons. Total decay curves were double-exponentially fitted for each measurement using a Maximum Likelihood Estimation method, and deconvolution with a calculated Gaussian instrument response function (IRF) was applied. The full width at half maximum of the IRF was 200 ps.

The visualization experiments were performed using an Olympus IX71 microscope at the Tokyo Institute of Technology. A coverslip chemically modified with DCDHF as described above was inserted in the sample holder. A polystyrene bead with a roughened surface (preparation is given below) was pressed with a controlled normal force against the modified coverslip soaked in formamide. For excitation an argon-ion laser at 488 nm was used. A 100x 1.3NA UplanFLN objective was used.

TCSPC traces of the DCDHF dye in PMMA were measured using a home-built setup. A Ti:sapphire laser (Coherent Chameleon Ultra) was used as an excitation source. The repetition rate of the laser was decreased from the fundamental frequency of 80 MHz to 8 MHz using a pulse picker (PulseSelect, APE). A second-harmonic generator (SHG) was used to produce the required excitation wavelength (488 nm). The excitation light was guided towards the sample and the "reference" light was guided through a delay line towards the fast photodiode (PD). Fluorescence from the sample was gathered under magic angle conditions and focused towards the multichannel plate photomultiplier tube (MCP, Hamamatsu R3809U-51) through a single-grating monochromator (Newport Cornerstone 260, f = 250 mm, grating 300 lines/mm, blaze wavelength 422 nm, or grating 300 lines/m, blaze 750 nm). The instrument response function (IRF) was obtained by measuring a dilute scattering solution (Ludox). In order to maximize the photon collecting efficiency of the instrument, the emitted photon was used as a "start" signal for voltage ramp build-up in the time-to-amplitude converter (TAC). The voltage was built up until a "reference" photon reached the PD, which produced the "stop" signal. The produced voltage was then converted to a corresponding arrival time by a multi-channel analyzer (MCA) and added to the decay histogram in the computer.

1.4 Materials

Smooth PS spheres were purchased from Cospheric (radius 600 μm). Smooth PMMA spheres were purchased from Cospheric (radius 1 mm). Glass coverslips were purchased from MARIENFELD high precision thickness 1.5H. Spheres were shaken for 24 hours, using a vortex shaker, in a container with 240-grit sandpaper walls in order to obtain rough surfaces.

2 Additional measurements

2.1 Static friction force PMMA/glass

We measure the static friction force at PMMA / glass contacts both for dry coverslips (that is, no solvent added, under ambient conditions) and contacts immersed in formamide. In both cases the relative increase in static friction is larger than that in the area of real contact, measured using diffraction-limited fluorescence microscopy (see Figure S1). However, we do find that the dry PMMA-on-glass friction coefficient is larger ($\mu \approx 0.6$) than the wet one. This difference may be due to swelling of the PMMA surface in the presence of formamide.

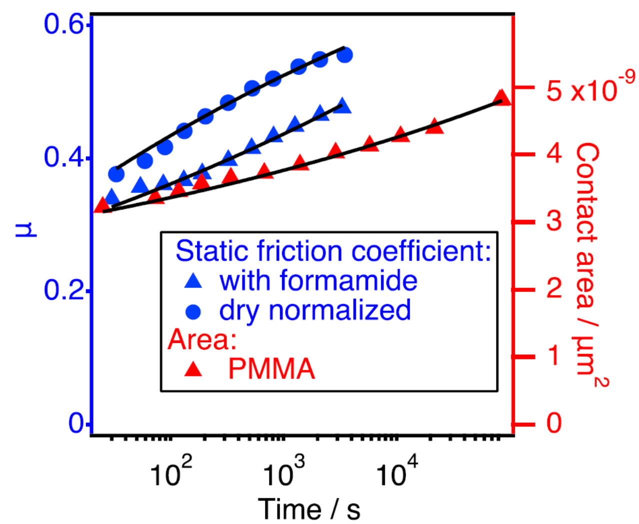

Figure S1: Ageing of the static friction force for PMMA on glass (in blue). All data sets show pronounced ageing: the static friction force increases logarithmically over the duration of the experiment. The black lines are semilogarithmic fits to the data. Red data points depict the growth of the PMMA-on-glass contact area with time as determined from molecular-probe fluorescence images taken during a static ageing experiment, in which the contact is only loaded in the normal direction.