

Supporting Information

Mechanochemistry at solid surfaces: Polymerization of adsorbed molecules by mechanical shear at tribological interfaces

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I. Wear prevention by adsorption of allyl alcohol vapor and tribopolymer formation

The wear of the substrate after friction tests (Figure S-1a) was analyzed with optical profilometry. In dry N₂, the surface was always worn severely, even at the lowest load (0.25 GPa) tested in this experiment (Figure S-1b). The friction coefficient was low, likely because wear debris particles made third-body rolling contact conditions.¹⁻³ In the presence of allyl alcohol vapor with $p/p_{\text{sat}} \geq 10\%$, the substrate did not wear; after removing tribo-polymer products with ethanol rinse, there was no discernable wear mark within the resolution limit of the optical profilometer used in this study (Figure S-1c).

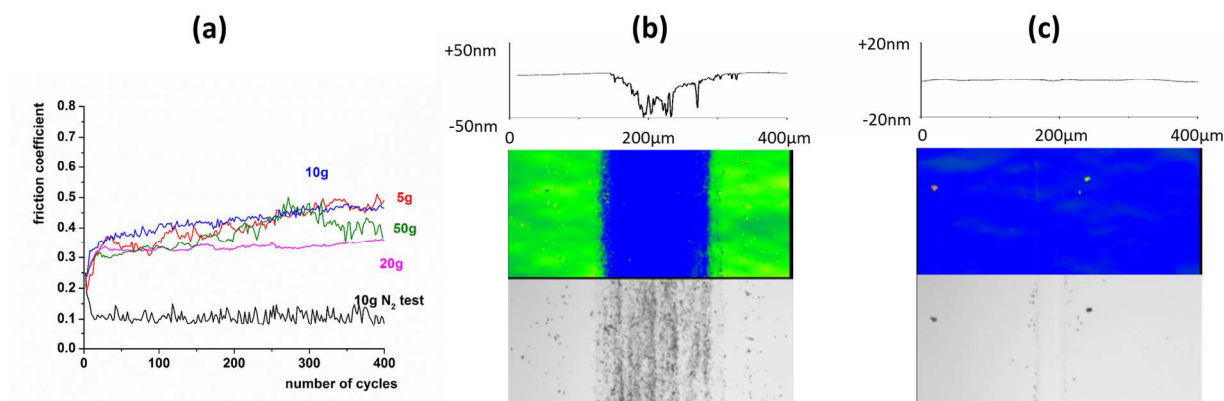


Figure S-1. (a) Friction coefficients measured in dry N₂ and allyl alcohol vapor ($p/p_{\text{sat}} = 40\%$). Optical profilometry line profile and optical image of (b) wear track after tribo-test in dry N₂ and (c) slide track after tribo-test in allyl alcohol vapor and removal of tribo-polymers by rinsing with ethanol.

II. Calculation of flash temperature due to frictional energy dissipation

During the sliding process, the frictional energy could be dissipated as heat. The local temperature due to frictional heat is often called flash temperature.⁴ Various numerical models

have been developed to estimate the average flash temperature rise, ΔT_f . If the model proposed by M.F. Ashby et al is used, then ΔT_f can be estimated as:⁴

$$\Delta T_f = 0.5 \mu P v \frac{l_f}{k} \approx 3.9 \text{ } ^\circ\text{C}$$

where μ is friction coefficient (see Figure 1a), P normal contact pressure (0.4 GPa), v sliding speed (4 mm/s), l_f linear diffusion length ($= \frac{a\sqrt{\pi}}{2} = 14 \text{ } \mu\text{m}$; where a is the radius of the Hertzian contact area $= 16 \text{ } \mu\text{m}$ at a contact pressure of 0.4 GPa), and k thermal conductivity of silicon oxide (1.2 W/(m·K)).

Alternatively, the average temperature increase, ΔT_{avg} , can be estimated using the model developed by J.F Archard et al.⁵ In this model, the Peclet (Pe) number is used to determine if the heat dissipation is dominated by advection or diffusion:

$$Pe = \frac{v a}{2 \kappa}$$

where a is the radius of the Hertzian contact area (16 μm), κ the thermal diffusivity ($8.7 \times 10^{-7} \text{ m}^2/\text{s}$), and v the sliding speed (4 mm/s). The Pe number calculated for our system is less than 0.04, meaning that the frictional heat will be dissipated quickly to the substrate through the diffusive transport. Then, assuming the steady state heat conduction, ΔT_{avg} is estimated to be:

$$\Delta T_{avg} = \frac{Q}{4 a k} \approx 4.6 \text{ } ^\circ\text{C}$$

where Q is the total rate of heat generation (420 μW) calculated from the work of friction, and k is the thermal conductivity of silicon dioxide (1.2 W/(K·m)).

In the Archard model, the maximum flash temperature increase, $\Delta T_{f,max}$, can be estimated assuming that when the total applied load is absorbed by plastic deformation at a single area:⁵

$$\Delta T_{f,max} = 0.25 \frac{\mu \cdot g \cdot \pi \cdot Y}{\rho \cdot c} \frac{F^{0.5} \cdot v}{\kappa (\pi \cdot Y)^{0.5}} \approx 12 \text{ }^{\circ}\text{C}$$

where g is the gravitational acceleration (9.8 m/s), Y the yield pressure (155 MPa), ρ the density (2.65 kg/m³), c the specific heat (730 J/(kg·K)), and F the applied normal load (0.22 N). This value can be taken as the upper limit of the flash temperature increase.

III. XPS analysis of tribo-polymer product

Tribo-polymers piled up at the end of the slide track were analyzed with XPS. The XPS analysis spot size was less than 50 μm in diameter and the tribo-polymer area was larger than that. Figure S-2 shows the high-resolution XPS spectra of the O1s, C1s, and Si2p photoelectron regions. Four slide tracks were analyzed and the average atomic ratio of C/O was calculated (Table S-1). By fitting the C1s spectra with a Voigt line profile function, the relative concentrations of carbon species with different oxidation states were obtained (Table S-1).

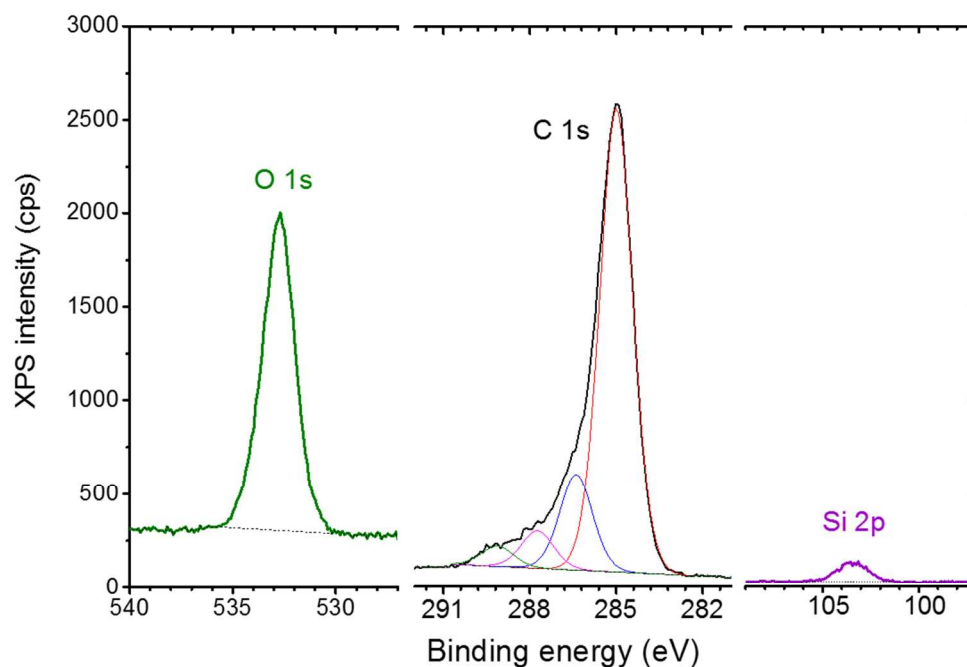


Figure S-2. XPS spectrum of tribo-polymer film piled at the end of sliding tracks. Tribo-polymers were synthesized by sliding a glass bead on a thermal oxide film on a silicon wafer at 0.4 GPa for 600 reciprocating cycles in 30% p/psat allyl alcohol vapor.

Table S-1. Chemical composition of tribo-polymer film produced from allyl alcohol at the sliding interface of silicon oxide.

Chemical species	C/O atomic ratio	C 1s high resolution fit			
		C-C/C=C	C-O	C=O	O-C=O
Tribo-polymer [*]	$3.7 \pm 0.2^{\#}$	$74.8 \pm 1.4 \%$	$15.6 \pm 0.5 \%$	$7.0 \pm 0.5 \%$	$3.4 \pm 0.5 \%$
Allyl alcohol ⁺	3	66.7 %	33.3 %	-	-

^{*} From XPS analysis; ⁺ From molecular structure; [#] The contribution from the substrate was removed based on the Si 2p intensity and the O:Si ratio of the substrate measured outside the tribo-tested region.

IV. Details of ReaxFF MD simulation process

The ReaxFF force field was chosen to simulate the tribochemical reactions under shearing conditions in atomic scale.^{6,7} ReaxFF is one of the reactive empirical force field methods, which is based on bond order – bond distance relationship. This allows the ReaxFF force field to calculate not only short distance covalent bonds, but also the transient state of bond formation or dissociation and long range interaction, with comparable accuracy to DFT. The ReaxFF potential parameters applied in this study were originally developed for PTFE and PDMS interactions.⁸ In this force field, parameters for Si/O/H/C/F interactions are combined together for hydrocarbon and fluoro-carbon systems. The original C/H/O and Si/C interaction parameters were developed by Chenoweth et al.,^{9,10} and then the carbon parameters were updated by Srinivasan et al. using DFT.¹¹ Based on this force field, parameters to describe the C-O, C-C-O and C-O-C angles, and the C-O-C-O and C-C-O-C dihedrals were updated to realistically simulate the behavior of carbon-oxide chain and bulk system, producing a comparable match with DFT.

To check the validity of the ReaxFF force field used in this study, the energy curves for hypothetical reactions of allyl alcohol molecules were calculated and compared with the DFT calculation results for the same reactions. All DFT calculations were performed with B3LYP, 6-311G++ G(d,p) basis sets. Figure S-3 shows the energy profile of two association pathways of allyl alcohol molecules. The first reaction energy curve, depicted in Figure S-3a, was simulated for the reaction between two C=C bond bonds. The second case, shown in Figure S-3b, was for the reaction between Oa and C2 atoms, and donating hydrogen from alcoholic hydroxyl (Oa) to the surface oxygen (Os). In both cases, the agreement between ReaxFF and DFT calculation

results was good. These results indicate that the ReaxFF force field used in this study will be able to simulate the reactions of allyl alcohol with an accuracy comparable with DFT.

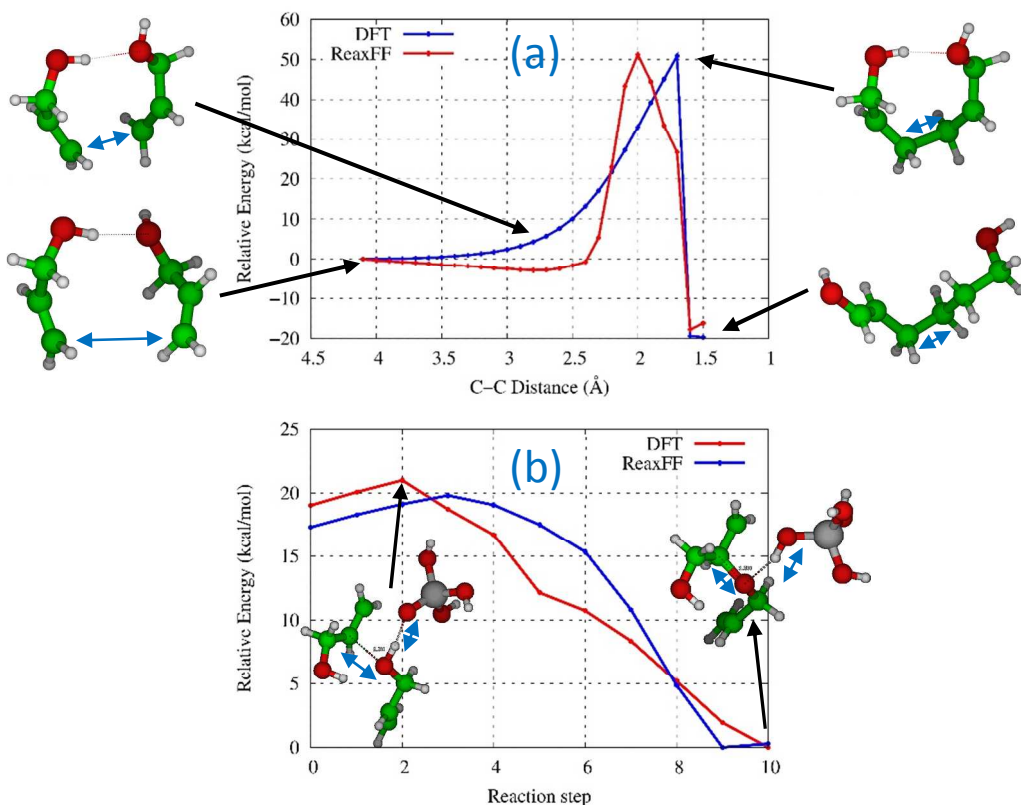


Figure S-3. Comparison of ReaxFF MD and DFT simulation results for reactions forming (a) the single bond between the carbon atoms of two C=C double bonds and (b) the covalent bond between hydroxyl oxygen (Oa) and one of the carbons in the C=C double bond with proton donation from Oa to the surface oxygen atom (Os).

V. Reaction rates and intermediate species from ReaxFF MD simulations

Figure S-4 displays the temporal profiles of all species during the sliding for 1 nm at various contact pressures. One critical caveat of VPL is that the intermediates with high vapor pressures would be lost to the vapor during the tribotest. For this reason, we ignored the molecules

containing less than 3 carbons observed in MD simulations (Figure S-4) when we compared the results with the experimental data. By fitting the temporal profiles of products with the number of carbons (x) larger than three with an exponential function approaching a plateau value ($y(t) = A(1 - e^{-r_p t})$), the rate constant (r_p) at a given contact pressure (P) can be obtained. Then, from the slope of the semi-log plot of r_p versus P shown in Figure 1b, the critical activation volume can be estimated.

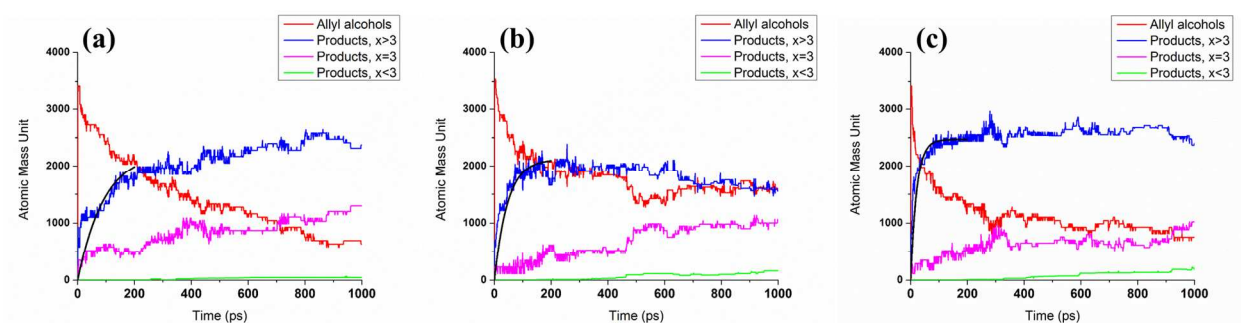


Figure S-4. Temporal profile of reactants, association products ($x > 3$), chemisorbed or partially dissociated species ($x=3$ or $x<3$) at a contact pressure of (a) 0.5 GPa, (b) 1 GPa, and (c) 2 GPa. The black line is the result from fitting with a $(1 - e^{-r_p t})$ function. Here, x is the number of carbon atoms in the molecule or intermediate species.

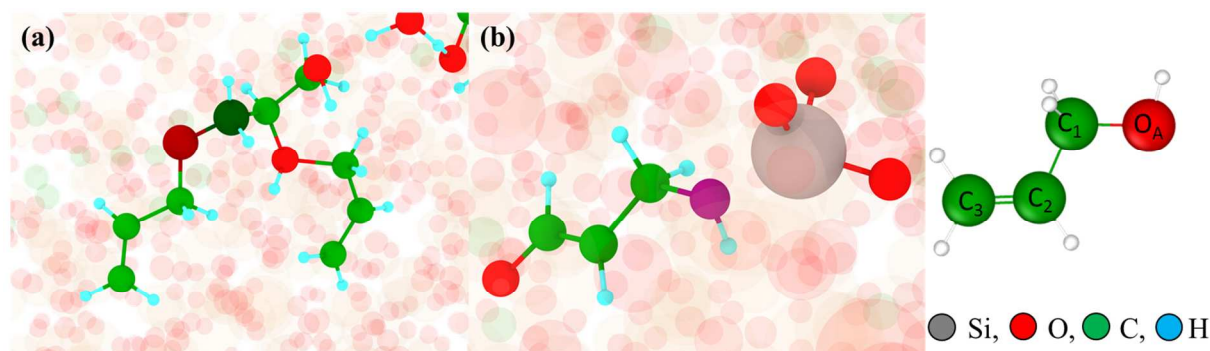


Figure S-5. Snapshot images of (a) an intermediate with the C3 (dark green) and Oa (dark red) atoms at 1.47 Å from each other and (b) an intermediate with the Oa atom (purple) positioned at 2.1 Å from the under-coordinated Si atom (large gray).

In the RDF between C3 and Oa (Figure 4c), there is a sharp peak at 1.47 Å in the case of 300K without sliding. Figure S-5a shows the snapshot of an intermediate with a distance of 1.47 Å between the C3 and Oa atoms of two molecules. This bond formation between C3 and Oa appears to follow the hydrogen donation from Oa to a surrounding atom. Thus, it is speculated that the C3-Oa reaction at 300K is the consequence of the strong hydrogen bonding interaction between Oa-Oa (Figure 4i) or Oa-Os pairs; this may facilitate the hydrogen abstraction from the Oa atom and the formation of the C3-Oa covalent bond. The population of the 1.47 Å peak in the C3-Oa RDF decreases when the system temperature is increased to 900 K where hydrogen bonding interactions are insignificant due to high thermal energy (Figure 4i). The C3-Oa bond formation path is relatively rare in the sliding simulations (Figure 4c). Instead, the Oa-C2 bond formation is dominant during the sliding (Figure 4b). In contrast, the Oa-C2 bond formation appears to be insignificant in thermal reaction conditions (Figure 4b).

Figure S-5b shows the Oa atom of an intact hydroxyl (OaH) interacting with the under-coordinated silicon (u-Si) atom, which is responsible for the 2.1 Å peak in the Si-Oa RDF in Figure 4j. Such long-range interactions between the OaH group and the u-Si atom were frequently observed during the sliding condition where the u-Si species are more abundant, compared to the thermal reaction conditions at 300 K and 900 K without sliding (Figure 4j). This state is an unstable intermediate state; the covalent bond between Oa and u-Si is not possible until the hydrogen atom of the OaH is donated to another oxygen atom nearby.

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