

Atomistic Understanding of Surface Wear Process of Sodium Silicate Glass in Dry versus Humid Environments

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Abstract

Understanding surface reactions of silicate glass under interfacial shear is critical as it can provide physical insights needed for rational design of more durable glasses. Here, we performed reactive molecular dynamics (MD) simulations with ReaxFF potentials to study the mechanochemical wear of sodium silicate glass rubbed with amorphous silica in the absence and presence of interfacial water molecules. The effect of water molecules on the shear-induced chemical reaction at the sliding interface was investigated. The dependence of wear on the number of interfacial water molecules in ReaxFF-MD simulations was in reasonable agreement with the experimental data. Confirming this, the ReaxFF-MD simulation was used to find further details of atomistic reaction dynamics that cannot be obtained from experimental investigations only. The simulation showed that the severe wear in the dry condition is due to the formation of interfacial $\text{Si}_{\text{substrate}}\text{-O-}\text{Si}_{\text{counter_surface}}$ bond that convey the interfacial shear stress to the subsurface and the presence of interfacial water reduces the interfacial bridging bond formation. The leachable sodium ions facilitate surface reactions with water producing hydroxyl groups and their key role in the hydrolysis reaction is discussed.

1. Introduction

Silicate-based glasses are one of the most versatile materials in terms of technological perspective with wide ranges of industrial applications including windows, windshields, display panels, fiber optics, bioglasses, etc.^{1,2} In most applications, glass products are exposed to various aqueous environments (either humid air or liquid water) and subject to physical contacts with foreign objects, which leads to deterioration of chemical and mechanical properties of glass surfaces. The physisorption and chemisorption of water are closely coupled with the type (geminal, vicinal, isolated, H-bonded) of silanol groups (SiOH) at the silicate glass surface as well as their areal densities. Therefore, understanding their interactions with adsorbed interfacial water molecules is critical to explain many surface properties of the glass.³⁻⁵

It has been reported from previous investigations that soda lime silica (SLS, sodium calcium silicate) glasses exhibit enhanced wear resistance with increasing relative humidity (RH).^{6,7} If one speculate that wear behaviors would follow the conventional stress corrosion theory,⁸⁻¹⁰ it would be anticipated that a sliding contact between the two silicate materials would cause more wear in a humid condition than the dry condition; but the observed result is opposite. It is intriguing to note that fused quartz, borosilicate, sodium-aluminosilicate and Na⁺/K⁺-exchanged aluminosilicate glasses show an increase in wear as RH increases from 20% to 90%.^{7,11,12} These glasses do not have readily leachable sodium ions in aqueous environments at room temperature, while SLS has easily leachable Na⁺ ions associated with non-bridging oxygen (NBO) atoms of the silicate glass network. This comparison led to a hypothesis that the interplay of Na⁺ ions attached to NBO groups and interfacial water molecules may have a critical role. Supporting this hypothesis, it was found that the sodium-depleted surface of SLS shows more wear upon the increase in humidity, while sodium-enriched surface exhibits less wear at high

RH.^{12,13} However, molecular details associated with this hypothesis could not be elucidated from macro-scale experimental studies.

Molecular dynamics (MD) simulations can provide atomistic details needed to understand experimentally observed wear behaviors. Prior MD simulations on mechanochemical wear had mostly focused on amorphous silica (a-SiO₂) substrates.¹⁴⁻¹⁷ However, the surface reactivity of a-SiO₂ is very different from that of silicate glasses with modifier ions; thus, there is a critical need that such studies to be conducted with additional force fields for modifier ions. Because mechanical stress applied during the sliding contact can distort the silicate network and alters the reaction barriers of the Si-O-Si hydrolysis,¹⁸ and such distortion would be a function of glass composition, it is important to simulate dynamic responses of glass network with modifier ions relevant to experimental conditions. Such studies are now possible for a sodium silicate glass since the ReaxFF reactive force field^{19,20} for Na⁺ ions compatible with the Si/O/H force field has recently been developed,²¹ allowing MD simulations of reactive events in sodium silicate glass.

In this work, we carried out reactive MD simulations with Si/O/H/Na ReaxFF reactive force field²¹ to investigate the effect of water on mechanochemical reactions occurring at the interface of a-SiO₂ and sodium silicate glasses. To the best of our knowledge, ReaxFF is the most comprehensive reactive potential parameter set, compared to other reactive force field models currently available, for the silicate glass system of our interest. Using ReaxFF-MD simulations, we investigated how the interfacial shear process distorts the glass network during the wear process in the absence and presence of interfacial water molecules. The role of water molecules and sodium ions at the sliding interface and its effect on the subsurface deformation is elucidated in this work.

2. Methods

2.1 ReaxFF-MD Simulations

Mechanochemical wear processes involving an amorphous silica slab sliding on a sodium silicate glass were simulated within the ReaxFF-MD framework. ReaxFF is a general bond-order dependent potential which has been extensively applied – but is not limited to – the mechanochemistry domain.^{14–17,22,23} Prior studies with ReaxFF reactive force field have proved its versatility in modeling of silicate glass materials as well as describing dynamic reaction steps involved in mechanochemistry.^{24–27} The ReaxFF parameterization used in this current work is described in an earlier publication,²¹ and had been developed by fitting against quantum-mechanical (QM) data relevant to the surface chemistry of silicates with the presence of sodium ions and water molecules. Details of the ReaxFF reactive force field method and development of the parameter set used herein can be found elsewhere.^{19–21}

A model system for MD simulations was constructed in the following way. An amorphous sodium silicate slab was generated through the melt-and-quench approach (melting at 4000 K and then cooling to 300 K) with an initial composition of $\text{SiO}_2:\text{Na}_2\text{O} = 70:30$ mol %. Separately, amorphous silica (a- SiO_2) was modeled with the same procedure. Since sodium silicate glass was used as a substrate in this study, the dimensionality of contacting surface (in xy -plane) was kept the same for the construction of amorphous silica slab. After equilibrating and relaxing the contact surfaces of each sample, we integrated two materials into a simulation box size of $34.43 \times 34.43 \times 90 \text{ \AA}^3$. Details of the glass preparation and surface construction procedures are further elaborated in the Supporting Information. A more detailed atomic structural analysis on the ReaxFF modeling of sodium silicate glass can also be found in ref. [28].

Figure 1 provides an overview of the MD simulation steps that we employed for the mechanochemical reaction at the contacting interface. We have followed the same simulation protocols reported in previous MD studies with the slab-on-slab geometry^{17,22} which mimics the contact geometry of a ball-on-flat tribometer. As shown in Figure 1, our simulation consists of three steps. First, we applied a normal load to the substrate by vertical compression of the counter-surface (silica). When contact is made between the two surfaces, we equilibrated the system at 300 K to relax the contacting configuration and prevent any unrealistic interaction at the interface. After the system is equilibrated with the normal stress applied, we applied forces to the rigid body region of the counter-surface so that sliding contact is made at the interface. Finally, the counter-surface is separated and equilibrated to reproduce the wear amount.

To investigate the effect of interfacial water on the mechanochemical wear, we added 25, 50 and 100 water molecules between two slabs and compared the simulation results with the case of a dry condition. These numbers of water molecules correspond to areal densities of 0.02, 0.04 and 0.08 H₂O per Å², which are comparable with the monolayer coverage determined in a previous adsorption isotherm study.⁴ In order to produce the results with reasonable statistics, we carried out MD runs in triplicate with different random positions of water molecules in the interfacial layer. All simulations were performed using ReaxFF implementation in the LAMMPS package.²⁹ A timestep of 0.25 fs was used with the Verlet algorithm to integrate the Newton's equation of motion. Mechanochemical simulations were carried out under NVT ensemble with Nosé-Hoover thermostat at 300K with a temperature damping constant of 100 fs. Further details of the modeling procedure can be found in the Supporting Information.

2.2 Experimental ball-on-flat wear test in controlled humidity environment

To test and confirm that the ReaxFF-MD simulation result is realistic, experimental wear testing was conducted with a custom-built ball-on-flat tribometer. The details of the experimental system can be found in earlier publications.^{30,31} The glass substrate tested in this study is a sodium silicate glass ($\text{SiO}_2:\text{Na}_2\text{O}:\text{Al}_2\text{O}_3=76.7:21.3:2.0$ mol %), which were prepared in-house by melting raw materials of sodium carbonate, calcined alumina (Almatis), and silica (Berkeley fine sand, US Silica) at 1650 °C. The Pyrex glass balls (McMaster-Carr, OD 2.4mm) were used as a counter surface. In order to remove organic contaminants, both substrate and ball surfaces were rinsed with ethanol and blow-dried with nitrogen gas. The sample was then put in UV/O₃ chamber for 20 minutes prior to mechanochemical wear tests. The wear test was performed at RH of ~0%, 20%, and 60%. For all cases, a contact load of 0.2 N was applied to the Pyrex ball and a sliding speed was kept at 6 mm/s. After the wear test at controlled RHs, the samples were analyzed with optical profilometry (Zygo NV7300) to obtain the line profiles of the wear tracks on sodium silicate glass and Pyrex ball surfaces.

3. Results and Discussion

3.1 Comparison of ReaxFF-MD simulations with experimental observations

Figure 2 shows the snapshots from ReaxFF-MD simulations during the separation process after sliding for 344 ps at a contact pressure of ~1.0 GPa. The simulation shows that mechanochemical wear occurs mostly in the sodium silicate surface. The glass network connectivity of sodium silicate is less than that of silica due to the presence of Na⁺ modifier ions and thus, mass transfer is speculated to occur more readily from the sodium silicate surface to the silica surface as in the form of adhesion. Further details are discussed in Section 3.3. In the dry condition (Figure 2a-d), the sodium silicate glass substrate shows severe wear.³² In the presence

of water molecules at the sliding interface, the simulation results show that the silicate wear is significantly suppressed (Figure 2e).

In order to check whether ReaxFF-MD simulation results are reasonable, the ball-on-flat tribo-test was conducted in controlled RH conditions. Figure 3 displays the line profiles of the Pyrex ball and sodium silicate glass substrate after sliding at a nominal Hertzian contact pressure of 280 MPa for 200 reciprocating cycles. The experimental results confirm that the wear occurs in the sodium silicate substrate side. In the dry condition ($RH \approx 0\%$), the silicate glass surface wears badly, leaving about 30 μm deep scratch (Figure 3b). The wear debris particles are mostly piled up around the wear track; mechanical abrasion during the sliding might have pushed the weakly adhered particles out of the sliding track. When RH is increased to 20%, then the wear depth on the silicate surface is reduced to ~ 400 nm, orders of magnitude smaller than the dry case. When RH is further increased to 60% to ensure that the surface is fully covered with adsorbed water molecules, then the wear depth is only ~ 200 nm. In the humid condition, no debris particles are found on the substrate; all mechanochemical wear products are adhered and accumulated at the ball counter-surface (Figure 3a).

Figure 4 compares the wear amount calculated in ReaxFF-MD simulations and with the wear depth observed in ball-on-flat tribo-tests. In simulations, the local wear track cannot be defined because the slab-on-slab geometry and periodic boundary conditions are used; instead, the wear amount is calculated based on the atomic mixing during the sliding and transfer from one surface to the other after the vertical separation of two surfaces.¹⁷ For this reason, a quantitative comparison with experimental wear volumes may not be feasible within the scalability of our simulations; nonetheless, the overall qualitative trends are quite comparable to each other.^{12,32} This agreement with experiment validates that ReaxFF-MD simulation results for the sodium silicate

of this study can provide an insight into the role of interfacial water in wear reduction of SLS at high humidity conditions. It should be noted that the experimental conditions of contact load and sliding speed are different from that of MD simulations, especially simulation sliding speed being several orders of magnitude higher due to the computational limitations. Nonetheless, the congruency in the qualitative dependence on interfacial water molecules in simulations and experiments, as shown in Figure 4, suggests that despite such discrepancies in two methodologies, MD simulations could provide atomistic understanding of how the hydrolysis reactions are triggered by mechanical shear stress.

Hereafter, mechanochemical simulations of the silica/sodium silicate interface with 100 water molecules ($0.08 \text{ per } \text{\AA}^2$) will be considered as a representative sample of humidity conditions in which a monolayer of water can be adsorbed on the glass surface and compared with the dry sliding case. Although only the surface coverage of up to a monolayer water adsorption was investigated in this study, it is worth commenting that the thickness of interfacial water layer could reveal more details of tribochemical wear process as excessive water layer could play a role as a lubricant, leading to the reduction of surface wear.^{6,7,17,33} Follow-up simulations as a future work can focus on these aspects along with a variety of surface morphologies.

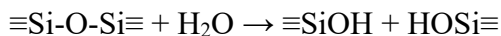
3.2 Structural change during mechanochemical reactions in the sliding interface region

Local mechanical stress can facilitate chemical reactions that typically do not occur in ambient conditions by lowering the effective activation barriers.^{22,23,34,35} The reaction pathway enabled by frictional shear stress depends on the reactant availability at the sliding interface.^{35,36} The reduction in wear of sodium silicate with interfacial water (Figures 2–4) is the consequence of differences in mechanically-activated reaction pathways occurring at the sliding interface in the

absence and presence of water molecules. To evaluate this, the oxygen speciation was examined from the MD trajectories before and after the sliding contact (Figure 5a-c).

The system is first equilibrated with the normal stress only applied to the substrate. During the equilibration stage (prior to shear), interfacial Si-O-Si bonds are formed¹⁷ between the amorphous silica counter-surface and the sodium silicate substrate surface. In Figures 5b and 5c, it is noted that, before sliding, the number density of BO in the interface region is slightly higher in the dry condition (43.3/nm³), compared to the humid condition (40.7/nm³). This implies that in the presence of interfacial water molecules, the formation of the Si_{silica}-O-Si_{silicate} bond is suppressed. Among the BOs counted in Figures 5b and 5c, the fraction of interfacial Si_{silica}-O-Si_{silicate} bonds is 3.4% in the dry case and 1.3% in the $n[\text{H}_2\text{O}] = 100$ case (Table 1). In the presence of water, the number density of NBOs is also slightly lower (as shown in Figures 5b and 5c) because, even before sliding, some NBOs react with water and are converted to SiOH groups (3.2/nm³ in Figure 5c).

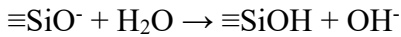
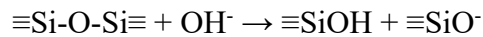
While the primary role of interfacial water molecules at the interface is NBO hydroxylation to prevent the formation of Si_{silica}-O-Si_{silicate} bonds prior to the sliding, the situation changes once the sliding begins and shear stress is applied. The presence of water facilitates shear-induced hydrolysis of Si-O-Si bonds, leading to the decrease in BO which is accompanied by the increase in Si-OH. The increase in SiOH is about twice the decrease in BO (Figure 5c), as expected from the stoichiometry of hydrolysis reaction:^{8,37}



In the absence of water, the shear of two solid surfaces connected via Si_{silica}-O-Si_{silicate} interfacial bonds requires the dissociation of such bonds; however, the dissociated bond pairs can re-form similar interfacial bonds with different pairs. Overall, the fraction of Si_{silica}-O-Si_{silicate} bonds in the

interfacial region increases from 3.4% to 8.1% in the dry case (Table 1). This implies that not just the interfacial bonds, but also some BOs of the original glass substrate are also dissociated and then participated in the formation of interfacial $\text{Si}_{\text{silica}}\text{-O-Si}_{\text{silicate}}$ bridge bonds. In the presence of water molecules at the sliding interface, the increase in $\text{Si}_{\text{silica}}\text{-O-Si}_{\text{silicate}}$ bonds bridging two surfaces is less (from 1.3% to 3.4%); some of this increase would come from reactions between Si-OH groups whose number density is increasing during the sliding (Figure 5c).

A slight reduction of NBO is noticed after sliding in the presence of interfacial water molecules (Figure 5c), while the NBO concentration change is negligible in the dry case (Figure 5b). This means that some of Na^+ ions are separated from their original NBO sites in the humid case; after which they can induce dissociation of water molecules, forming $\text{Na}^+\cdots\text{OH}^-$ species.²⁶ To show this reaction path, we tracked the oxygen atoms of water molecules and their conversions to different species during the sliding in ReaxFF-MD simulation. Figure 6 shows the mass balance in the conversion of oxygen species of water molecules as a function of the sliding time. The simulation shows that there are a small but steady amount of OH^- residing at the interface during the sliding process. Those OH^- groups can further facilitate the hydrolysis of BO via an autocatalytic process:^{38,39}



The oxygen speciation analysis shows how the presence of interfacial water molecules alter chemical reaction pathways (Figures 5 and 6) leading to reduction of wear (Figures 2 and 4); the main effect can be summarized as the prevention of re-formation of interfacial bridging bonds by the dissociated Si-O-Si BO pairs (Figure 5c). However, it is known that the activation barrier (E_a) for the Si-O-Si hydrolysis is very high. For example, density functional theory (DFT) calculations

for the hydrolysis of a $\text{H}_6\text{Si}_2\text{O}_7$ dimer at the B3LYP/6-311++G(d,p) level estimate the activation barrier (E_a) to be ~ 30 kcal/mol.⁴⁰ With this high E_a , the Si-O-Si hydrolysis rate would be extremely low (essentially zero) in static conditions at moderate temperatures. Considering that our simulation has been carried out at 300 K, it can be suggested that the interfacial shear stress must lower E_a substantially. It is well known that strained Si-O-Si bonds are more reactive than non-strained Si-O-Si bonds, with a hydrolysis reaction barrier as low as ~ 4.5 kcal/mol to ~ 25 kcal/mol depending on the level of theory and model cluster used in calculations.^{37,38,40-43} Based on this concept, we have analyzed the silicate glass network structure and calculated the Si-O-Si bond angle distribution and the O-O radial distribution function (RDF) within the interfacial region defined in Figure 5a during the sliding.

The Si-O-Si bond angle distribution (Figure 7a) suggests that regardless of the environmental condition, the mechanical stress results in the decrease in Si-O-Si bond angles of the glass network. In the same manner, the O-O RDF (Figure 7b) also suggests substantial deviation of the glass network from the stress-free structure. This could be due to the compression of the interfacial region, which would increase the local density.⁴⁴ The difference between the dry and humid cases is small but discernable. In the dry case, there are slightly higher populations in the lower and higher bond angle sides ($102-112^\circ$ and $138-142^\circ$, respectively) and less population in the most probable angle region ($125-133^\circ$), implying more distortion of Si-O-Si bonds compared to the humid case. The deformation of the glass network consequently facilitates hydrolysis reaction.³⁸

The Si-O bond dissociation would be more sensitive to the Si-O bond length. Figures 7c and 7d compare that Si-O bond length ($d_{\text{Si-O}}$) distributions during the sliding in dry and humid conditions with those of the stress-free condition. At the beginning of sliding, the $d_{\text{Si-O}}$ distribution

shifts to the lower length side in both dry and humid conditions (first 5 Å plots in Figures 7c and 7d). However, at the end of sliding, a significant fraction of the Si-O bonds is highly elongated in the dry condition, while the d_{Si-O} distribution is almost fully recovered to the stress-free state in the humid condition (see last 5 Å plots in Figures 7c and 7d). This implies that the Si-O bonds in the glass network are more strained during the interfacial shear in the dry condition compared to the humid condition. This also explains the large wear of the silicate glass in the absence of interfacial water molecules and reduction of wear in the presence of adsorbed water molecules at the sliding interface (Figures 2–4).

3.3 Subsurface deformation upon frictional shear

The primary reason for the dry condition to exhibit larger wear after the sliding contact would be the interfacial bonds that are formed between the two solids. Through these Si_{silica}-O-Si_{silicate} bridges, the interfacial shear action can be relayed deep into the subsurface region. To investigate the subsurface damage during the interfacial shear, we analyzed the BO and NBO contents of the subsurface region within the sodium silicate glass. Here, the subsurface is defined as a rectangular region with the periodicity maintained in the xy -plane from $z=12.5$ Å to $z=25.0$ Å, where there is no penetration of protons or water molecules from the interface. The number of BO and NBO per nm³ within this region calculated from the trajectories of MD simulations is plotted in Figure 8.

The structural integrity can be judged from the change in the number density of BO and NBO. In the absence of interfacial water molecules, a larger decrease of BO and a larger increase of NBO are observed in the subsurface region after the sliding (Figure 8). The magnitude of BO decrease is even larger in the subsurface region (~ 1.6 per nm³, Figure 8) than in the interface region

(~ 0.7 per nm^3 , Figure 5b). This confirms that a significant fraction of frictional shear stress is transferred from the interface to the subsurface through the chains of covalent Si-O-Si bonds.

In contrast, only a minute change is observed in the number of BO and NBO in the subsurface region when there are water molecules at the sliding interface (Figure 8). This must be the consequence of suppressing direct interfacial $\text{Si}_{\text{silica}}\text{-O-Si}_{\text{silicate}}$ bonds by hydroxylation of both silica and sodium silicate surfaces through reactions with water molecules. During the sliding contact in humid conditions, the condensation reaction of SiOH groups between two surfaces could facilitate the Si-O-Si bridge bonds (Table 1). However, the OH^- ions and water molecules at the interface (Figure 6) will also significantly enhance the hydrolysis of these strained bridging bonds. Thus, most of mechanical shear energy is consumed at the sliding interface through chemical reactions and the subsurface damage could be minimized effectively. This could be manifested as the reduction of chain transfer (wear) from the substrate to the counter-surface (Figure 2e).

To further confirm that interfacial water molecules can protect the subsurface region from friction-induced damage, we calculated and plotted the local von Mises shear strain in Figure 9a-h. The frames in Figure 9 show that significant shear strain develops in the subsurface region in the dry case, while the strain is confined mostly in the interface region in the wet case. This explains the reason that there is a significant material transfer from the sodium silicate substrate to the counter-surface in the dry condition (Figure 2d), while the material transfer is relatively insignificant in the wet condition (Figure 2e).

The reason why the chain transfer starts from the sodium silicate substrate, not from the silica counter-surface, during the vertical separation process after sliding in the dry condition (Figure 2d) can also be explained by the subsurface damage. In Figure 9d, it can be seen that the subsurface region of silica is structure-wise less affected than that of sodium silicate glass. This is

because silica contains all Q^4 species (where Q^n notation denotes a SiO_4 tetrahedron with n number of bridging oxygens)⁴⁵ in the bulk. Sodium silicate, on the other hand, contains low silica fraction and sodium ions introduces Q^3 species in the glass network, lowering the network connectivity. The more highly-connected glass network would be more resistant to structural damage than the less-connected network.

Conclusions

The dynamic roles of interfacial water in mechanochemical reactions leading to glass wear under frictional shear stress were studied using molecular dynamics (MD) simulations with a ReaxFF reactive force field for the silica/sodium silicate interface. These ReaxFF-MD simulations provided molecular-level insights that explained why mechanochemical wear occurs mostly in the sodium silicate surface and how the presence of interfacial water molecules suppresses mechanochemical wear. The primary role of water molecules is to hydroxylate the silica and sodium silicate surface and suppress the formation of direct $Si_{\text{silica}}-O-Si_{\text{silicate}}$ interfacial bonds. The presence of sodium ions in the interface region results in production of OH^- species in the interfacial region containing water molecules, which facilitates the hydrolysis and dissociation of Si-O-Si bonds and thus reduces the possibility of transferring frictional shear stress from the interfacial region to the subsurface region. These insights explain the humidity dependence of mechanochemical wear behavior observed in experiments.

Supporting Information

Modeling procedures of the sodium silicate glass and amorphous silica surfaces, initial configuration set-up procedures for ReaxFF mechanochemical wear MD simulations.

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Figure Captions:

Figure 1. ReaxFF-MD simulation of a sodium silicate glass surface rubbed with an amorphous silica ($a\text{-SiO}_2$) slab.

Figure 2. Snapshots during the vertical separation of the amorphous silica counter-surface after sliding against the sodium silicate glass substrate. The contact pressure is 1.0 GPa and the sliding time is 344 ps. In the dry condition (a-d), a significant amount of material transfer from the substrate to the counter-surface is observed, whereas the material transfer is suppressed in the presence of interfacial water molecules (e). Note that the color legend for oxygen and hydrogen atoms of water molecules are intentionally omitted in (e).

Figure 3. Line profiles of (a) Pyrex ball and (b) sodium silicate glass substrate surfaces after sliding in 0%, 20 %, and 60 % RH conditions. Note that in (a) the original ball surface is represented with black-colored dashed lines.

Figure 4. Effect of the amount of interfacial water molecules on mechanochemical wear amount of the sodium silicate glass from ReaxFF-MD simulations. Note that for the simulation results, atomic mass transferred from the substrate to the counter-surface has been quantified as the wear amount obtained from the last trajectory after the vertical separation process.

Figure 5. Changes in oxygen speciation (BO, NBO, SiOH) in the interfacial region during the sliding in (b) dry and (c) humid conditions. In (a), the dashed box in the illustration denotes the interface contact region used to investigate the oxygen speciation. Note that all the oxygen atoms in the dashed region were examined without distinguishing whether they are part of silica or sodium silicate.

Figure 6. Changes in the oxygen species during the sliding. Only the oxygens of molecular water at the beginning of sliding simulation were tracked in this plot to depict the disproportionation of water molecules during the sliding.

Figure 7. Structural analysis of silicate network during the sliding. (a) Si-O-Si bond angle distribution, (b) O-O radial distribution function (RDF), (c,d) normalized RDF of the Si-O length during the shear load in (c) dry and (d) humid conditions. In (c) and (d), the distribution is calculated separately for the first and last 50 ps (sliding distance = 5Å) of the sliding.

Figure 8. Oxygen speciation in the *subsurface* region of sodium silicate substrate.

Figure 9. Local von Mises shear strain during the mechanical shear load applied in dry and humid conditions.

Table 1. Contribution of interfacial bond ($\text{Si}_{\text{silica}}\text{-O-Si}_{\text{silicate}}$) before and after the sliding.

BO contribution (%)	Dry	$n[\text{H}_2\text{O}]=100$
Before sliding	3.4	1.3
After sliding	8.1	3.4