

Molecular dynamics study of the relative sliding mechanisms in amorphous silica

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Abstract

In the paper simulation of the treatment of two crystals with amorphous interlayer was carried out using the method of molecular dynamics. We studied a α -silica (quartz) sample with amorphous interlayer. The simulation result revealed several processes realized in the contact area as a result of shear loading. Depending on the temperature of the sample we observed deformation of an amorphous layer and formation of wear particles. It has been found that a necessary condition for the formation of wear particles is the presence of free volume in the interface. We compare the time dependencies of resistance forces for all samples. Results of simulation allows us to explain the low friction properties of silica tribofilm and also to say about silica amorphous layer as a solid lubricant.

1 Introduction

Carbon fibers and silica nanoparticles (SNPs) are widely used in all kinds of polymer matrix composites (PMCs) either reclusively or in combination. Compared to unfilled polymers, fiber-reinforced PMCs provide higher strength and wear resistance [1]. On the other hand, a number of interesting material properties were achieved by adding silica nano-particles (SNPs) to polymer materials [2]. Considering tribological properties, studies described in [3, 4] have shown that the application field of PMCs with micron-sized functional fillers can be extended by additionally incorporating a small fraction of inorganic nanoparticles. Especially SNPs are very effective in this respect, and it was shown that only 0.05 vol.% SNPs was enough to exert a measurable effect on friction evolution [5]. In the following, the composite containing micro- and nanofillers will be termed as hybrid composite whereas its counterpart without nanoparticles will be termed conventional composite.

The key for obtaining a better understanding of dry sliding properties of a tribological couple is a thorough investigation of the third body films, also termed tribofilms, forming at the tribological interface. The concept of a third body layer being responsible for load transfer and velocity accommodation between the first bodies of a tribological couple was first introduced by Godet [6]. Especially, antifriction and antiwear properties, i.e. a low coefficient of friction and wear rate, usually can be attributed to the formation of stable tribofilms [7]. During our own previous studies

we have shown that effective tribofilms, formed during automotive braking, consist of structural features on the nanometer scale [8]. Furthermore, we could simulate the sliding behavior of such films by nanoscale modeling. Since silica-based tribofilms are most crucial for providing wear protection and low friction, it was of great interest to simulate their sliding behavior. So the objective of this paper was to study the sliding behavior of silica tribofilm in order to understand the low friction properties of hybrid composites.

2 Materials

The raw materials used for preparation of the EP + 5% SiO₂ composite were: a standard diglycidil ether of bisphenol A (DBEBA) offered by DOW as DER331, a cycloaliphatic amine hardener HY 2954 from Huntsman and a colloidal silica masterbatch with a concentration of 40 mass% and a nominal particle diameter of 20 nm in DGBEBA offered as Nanopox F400 from Evonik. A thin slice was prepared from the EP + 5% SiO₂ composite by microtomy and investigated in a Scanning Transmission Electron Microscope (STEM) of type JEOL 2200FS.

3 Experimental Data

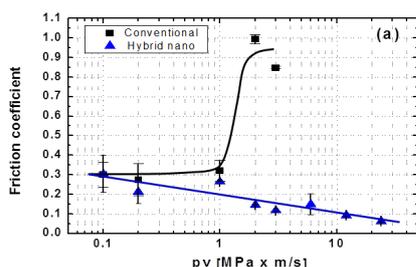


Figure 1: Friction coefficient as function of pv for composites with 5% silica nanoparticles (hybrid) and for the conventional composite without SNPs.

composite [4].

Striking differences were observed between the tribological performance of conventional and hybrid composites at certain stressing conditions, as shown in Fig. 1. Friction is almost the same at pv -values lower than 1 MPa m/s. Then a steep increase is observed for the conventional composite. It should be mentioned here that the beneficial effect of the SNPs is only observed in combination with the carbon fibers. Composites consisting solely of EP and SNP do not provide low friction at high pv , and furthermore, wear is not reduced to the same extent as for the hybrid

4 An overview of previous results

Details of modelling of tribofilm sliding behavior have been described in our recent paper [9]. The size of modelling elements was adjusted to 10 nm which is close to the size of the nanofiller of the polymer matrix composite (20 nm) and also is well suited for sliding simulations of 100 nm thick tribofilms, as demonstrated in previous studies [8, 10]. The method of Movable Cellular Automata (MCA) was used for sliding simulations [9]. It was expected that the results of these simulations may enable us to understand the very low friction coefficient observed for the hybrid

composite at $p v = 24$ MPa m/s. Unfortunately, this was not the case. Despite of a very well developed mechanically mixed layer and smooth sliding simulation the friction coefficient of tribofilms did not drop below 0.2 [10], whereas 0.06 was measured for the hybrid composite at $p v = 24$ MPa m/s.

The result shown in Fig. 2 is only one example of a comprehensive parameter study of the silica-graphite system. Briefly, the following trends were observed during this study: decreasing the graphite content to 6% increases the COF fluctuations significantly and the mean COF slightly. The same effect was observed for the structure with 10% graphite if the normal pressure was reduced from 130 to 70 MPa. On the other hand, an increase from 130 to 150 MPa made no difference. In order to find conditions of smooth sliding we identified the parameters given in Fig. 2 as an optimum for the silica film with 10% graphite inclusions.

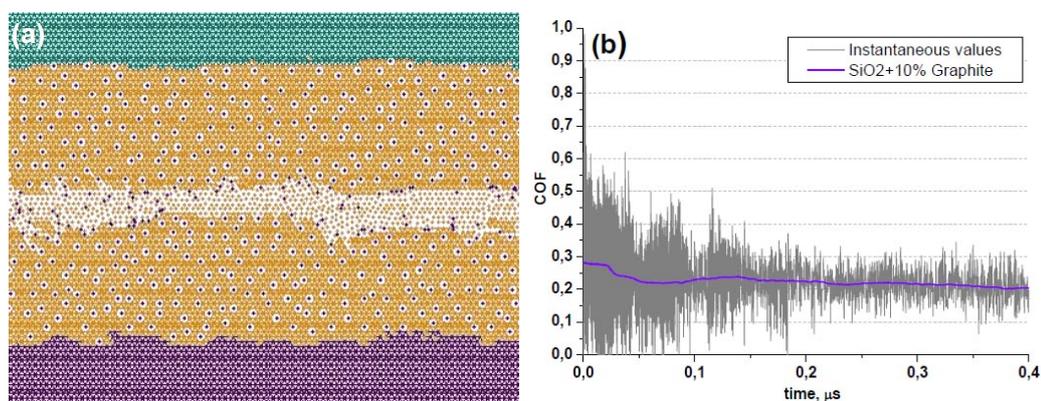


Figure 2: a) Structure formation and b) friction evolution during sliding simulation of a tribofilm consisting of 10% graphite (black) and 90% silica (orange) supported by carbon fiber (violet) and steel (green). External parameters: $p = 130$ MPa, $v = 10$ m/s.

A possible explanation of this very low friction coefficient could be assigned with silica transition to amorphous state. Another study even suggests amorphization of graphite being responsible for friction reduction [11]. Since we have found no means for considering such mechanisms in our model, the observed superlubricity effect could not be explained by the MCA method. Effort of finding explanation by Molecular Dynamics (MD) simulation was done in this work.

5 A model description

Since amorphous silicon oxide played a crucial role in the present study, we made an attempt to study its sliding behavior. The first step comprised of building a sample by linking SiO_4 tetrahedrons to form the appropriate crystal structure. Then an intermediate layer of this crystal sample was transformed to the amorphous state by virtual heating beyond the melting temperature and subsequent quenching. Next, the sliding behavior of the samples was studied while tangential and normal forces and a sliding velocity were applied to the rigid substrates comprising of crystalline SiO_2 .

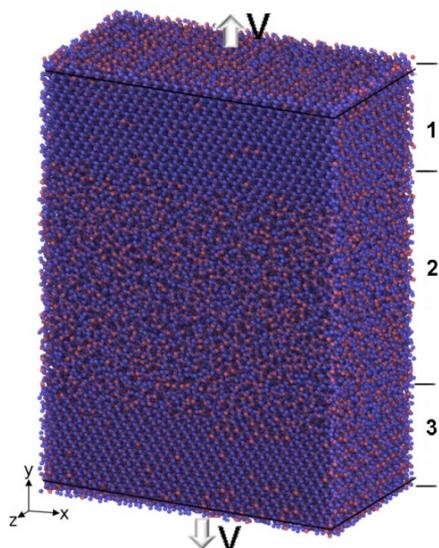


Figure 3: Initial structure of the modeled sample and a loaded scheme.

A modeled sample with two crystalline parts (on the top (block 1) and on the bottom (block 3)) and one amorphous centered layer with the initial thickness of about 8 nm (block 2) was designed as shown in Fig. 3. The total geometry of the sample was $14.3 \times 42.9 \times 8.58$ nm in $X \times Y \times Z$ axis respectively. Atoms located on top of the block 1 and on bottom of the block 3 within thickness of about 0.87 nm were subjected to external loading. Loading was applied through the constant velocity oriented along X axis and was equal to $V = 15$ m/s. Loading to top and bottom layer was applied in opposite direction, so totally the modeled sample was subjected to shear deformation with relative velocity of 30 m/s. Additionally a compression was applied to the loading layers through the constant force along Y direction. Taking into account the square of the loaded area this was equivalent to the loading with about 2 GPa on

top and on bottom layers.

The amorphous layer in the central part was created through instantly heating of the block 2 up to 6000 K and then quenching to the desired temperature. To study the behavior of silica sample the tree-body interatomic interaction suggested by Tersoff was used [12].

6 Results of simulation

As it was described above the sample was subjected simultaneously to sliding with the constant velocity and compression loading. The behavior of sample was investigated when quenched temperature was equal to 300 K (room temperature) and 1100 K (flash temperature easily reached during friction sliding with single contact).

6.1 Sliding at room temperature

According to the results of simulation the sliding behavior of silica sample at room temperature is very sensitive to the loading conditions and to the configuration of amorphous interlayer. By following we will try to systemize these features.

1. Sliding simulation of silica sample with amorphous layer under external compression.

The amorphous layer was created by heating and quenching as was described above. The thickness of that layer was about 20% of the whole sample size along Y direction. In case of shear loading applied simultaneously with compression the intensive deformation of the sample was observed without relative sliding of two blocks 1 and 3. Decreasing of loading pressure twice (from 4 GPa to 2 GPa) didn't change the behavior as shown in Fig. 4.

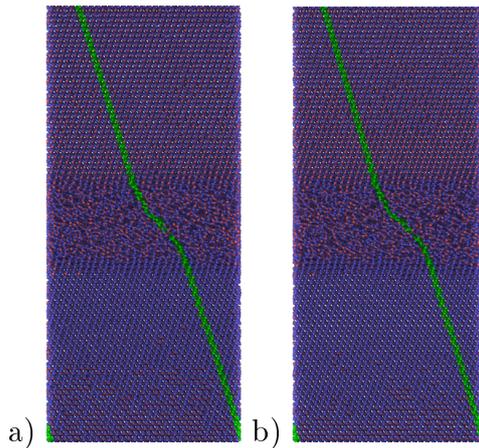


Figure 4: The resulting structure of the central fragment of the modeled sample after 0.5 ns with pressure (a) 4 GPa and (b) 2 GPa. The shear deformation corresponds to $\sim 34\%$.

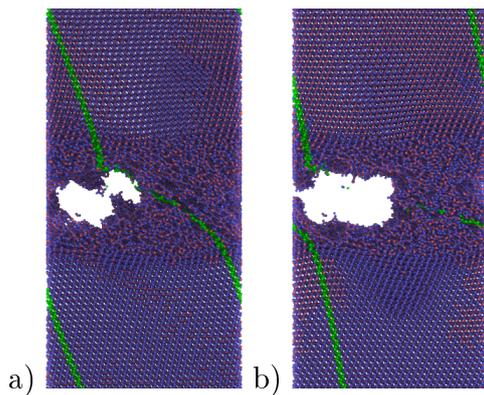


Figure 5: The resulting structure of the central fragment of the modeled sample after (a) 0.745 ns and (b) 0.750 ns without external pressure.

blocks through rolling of the formed lump of atoms. This sliding regime is characterized by very low resistance force.

3. Sliding simulation of silica sample under compression with pore inside amorphous layer.

Within the next step of our study we use the structure shown in the Fig. 5b as an initial structure for the sliding simulation under same loading condition as was used in case of tasks shown in Fig. 4a. This means that external pressure equivalent to 4 GPa was apply through loaded layers. In this case the pore still presents and relative sliding or two blocks is accompanied by rolling of atoms inside early formed lump. Fig. 6 shows the evolution of the modeled silica sample during relative sliding. Time dependencies of resistance forces (force acting on loaded atoms of block 1 in X direction) for the sample with pore inside the amorphous layer is shown in Fig. 7a.

Further shear loading until relative deformation of about 46% leads to total destruction of the silica sample. Probably this can be explained by relatively high compression and high initial density of amorphous interlayer.

2. Sliding simulation of silica sample with amorphous layer without external loading.

In order to check the previous assumption the sliding simulation of silica sample with amorphous interlayer without external pressure was implemented. The position of atoms in loaded layers along Y direction was fixed while X coordinates were linearly changed according to sliding velocity. This kind of loading provides discontinuity formation within amorphous layer after ~ 0.75 ns. This time corresponds to relative shear deformation of about 50%.

The analysis of structure gives us a certain explanation of this process. During shear deformation with fixed vertical positions of loaded atoms, both crystalline silica blocks (1 and 3) become intensively extended along the diagonal. As a result after reaching of a critical value the strength of amorphous layer is lower than tension forces and there is a separation of two blocks with discontinuity or pore formation inside the amorphous interlayer. Fig. 5 demonstrates the evolution of silica sample at two consistent moments of time corresponding to formation of inner pore inside block 2. Further shear loading leads to relative sliding of two

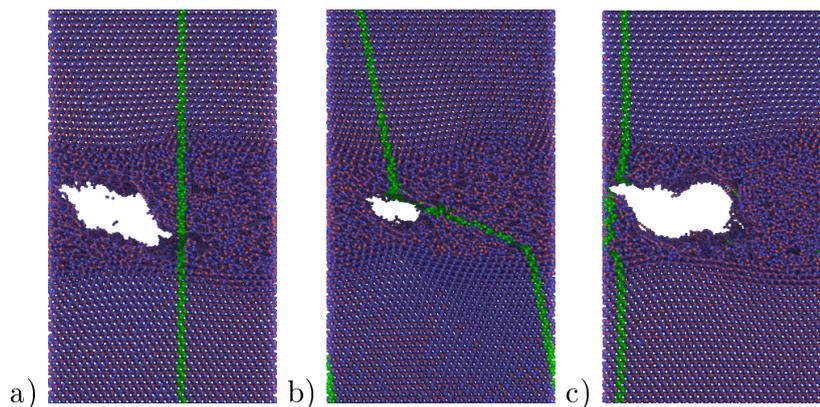


Figure 6: Evolution of the central fragment of the modeled silica sample. The structure at different moments of time: a) $t = 0$ ns, b) $t = 0.5$ ns and c) $t = 2.5$ ns.

According to Fig. 7a we can observe small stick-slip oscillations at the beginning of sliding connected with rolling of lamb of silica atoms. In spite of such oscillations the mean value of resistance force is very low. This result allows us to explain the low friction properties of silica tribofilm. Nevertheless, it is necessary to keep in mind that the sliding mechanisms of amorphous silica layer are very sensitive at room temperature to the loading conditions and layer structure.

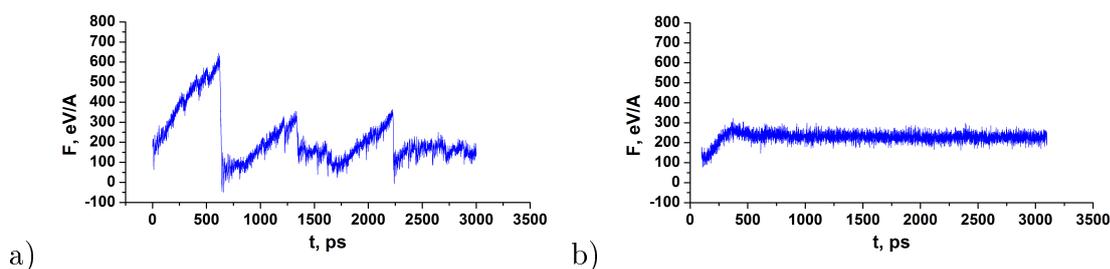


Figure 7: Time dependencies of resistance forces for the sample with pore inside amorphous interlayer at (a) 300 K and (b) 1100 K.

6.2 Effect of flash temperature

To study the features of silica sample sliding at elevated temperature the structure similar to one shown in Fig. 5 was taken as an initial structure for further shear deformation. The algorithm of the sample preparation was identical to the sample, shown in Fig. 6. First the dynamically equilibrium structure with amorphous interlayer in the central part of the silica sample was created by heating and quenching procedure of atoms from block 2. The next step includes deformation with constant velocity and fixed position of loaded atoms in vertical direction until micro-pore formation in the amorphous layer. Then simultaneously with shear deformation the compression with pressure equal to 4 GPa was applied. The evolution of the silica sample under combination of shear and normal loading at 1100 K is shown in Fig. 8. In comparison with similar sample behavior under room temperature here we can observe smooth sliding within amorphous interlayer.

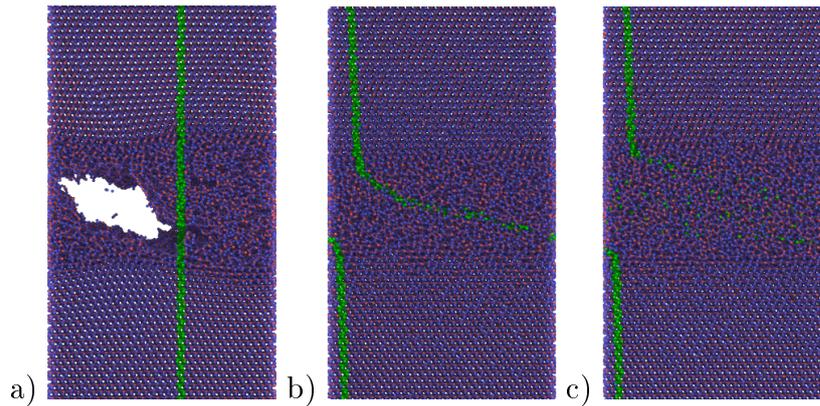


Figure 8: Evolution of the central fragment of the modeled silica sample. The structure at different moments of time: a) $t = 0$ ns, b) $t = 0.5$ ns and c) $t = 2.5$ ns.

Time dependence of resistance force is shown in Fig. 7b. The silica sample demonstrates low resistance force (about 250 eV/Å (4.0×10^{-7} N)). Thus not only amorphous carbon interlayer can represent solid lubricant with very low friction characteristics but amorphous silica layer as well.

7 Conclusion

As was described above the low COF of the silica-based tribofilm was partly confirmed by MCA modelling results, provided that an amount of 10 – 20 % soft inclusions was assumed. Furthermore, this result was verified by pin-on-disc tests with ball-milled powder blends, showing high friction (0.75) for pure silica, but a reduction to 0.2 for a blend of silica with 15% graphite and 10% Fe_2O_3 . Of course, we should not forget that modelling relies on many assumptions and simplifications and therefore cannot be considered as a reliable method for predicting tribological properties. We rather used modelling as an instrument for understanding what micro-mechanisms might be activated at sliding interfaces, and how variations of input parameters change the ongoing mechanisms. The stabilization of the wear rate up to the highest pv-values is attributed to the self-healing capability of the hybrid composite providing increasingly higher amounts of silica particles at more severe stressing conditions at the primary contact sites, the carbon fibers. As long as enough particles are available for cushioning the fibers and the films are thick enough to withstand complete removal before new layers are formed, the tribological system will function in the mild wear and low friction regime. It is very likely that the increase of carbon species with increasing pv will be responsible for the decrease of friction, although this could not be explained by MCA-modelling. MD-modelling of amorphous silica helps us to clear this point. Good correlation between tribological testing and modelling results indicates that sliding of thin surface films at asperity contacts can explain the observed antifriction and antiwear properties of the hybrid composite with hierarchical micro/nano-structure.

Acknowledgements

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