



21st European Conference on Fracture, ECF21, 20-24 June 2016, Catania, Italy

Multiscale modeling of low friction sliding behavior of a hybrid epoxy-matrix nanocomposite

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Abstract

The method of movable cellular automata (MCA) and method of molecular dynamics (MD) were applied to simulate the friction and sliding behavior of model-tribofilms formed from a nanocomposite consisting of an epoxy matrix, 10 vol. % micron-sized carbon fibers and 5 vol. % silica nanoparticles. Whereas MCA considered the tribofilm as an agglomerate of silica nanoparticles released from the composite and mixed with graphite particles, MD simulated the sliding behavior of an amorphous silica layer supported by stiff crystalline substrates on both sides. The MCA model provided reasonable quantitative results which corroborate experimental findings at moderate stressing conditions. The very low coefficient of friction observed experimentally under severe stressing conditions was not explained by this model. This could be attributed to the lack of mechanical data at the high temperature expected under these conditions. Although based on a simpler assumption of the tribofilm composition, MD-modelling could be easily applied to the expected high flash temperature and was able to predict friction reduction and smooth sliding under these conditions.

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Peer-review under responsibility of the Scientific Committee of PCF 2016.

Keywords: Silica nanoparticles, Hybrid composite, Tribofilm, Tribological properties, Molecular dynamics, Movable cellular automata method;

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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 (Guo et al. 2009). Furthermore, a number of interesting material properties were achieved by adding silica nano-particles (SNPs) to polymer materials (Fereidoon et al. 2014). Considering tribological properties, studies described by Zhang (2010) 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 (Zhang et al. 2012). In the following, the composite containing micro- and nanofillers will be termed as hybrid nano-composite (HNC) 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 (1984). 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 (Jacobson and Hogmark 2010). During previous studies we have shown that effective tribofilms, forming during automotive braking, consist of structural features on the nanometer scale (Österle et al. 2014). 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. The objective was to study the sliding behavior of silica-based tribofilms in order to understand the low friction properties of hybrid composites. Application of a nano-scale discrete element model based on Movable Cellular Automata (MCA) could explain friction under mild and medium stressing conditions, but not the observed low friction under severe conditions (Österle et al. 2016). The latter behavior could be understood better by considering the sliding behavior of amorphous tribofilms by Molecular Dynamics (MD) modeling (Dmitriev et al. 2016). In the following a multilevel approach will be proposed in order to analyze possible sliding processes in detail. On the scale of a few microns the MCA-method will be used while for describing the sliding behavior of an amorphous silica film the MD-method will be applied. Both methods belong to the particle- based methods of discrete approach and use unique formalisms.

2. Experimental data

2.1. Materials

The manufacturing technology for conventional and hybrid composites was developed at IVW Kaiserslautern and was described e.g. by Zhang et al. (2012). The raw materials used for preparation of the epoxy based polymer (EP) + 5 vol. % SiO₂ composite were: a standard diglycidil ether of bisphenol A (DBEBA) offered by DOW as DER331, a

Nomenclature

SNP	silica nanoparticle
PMC	polymer matrix composite
HNC	hybrid nano-composite
MCA	movable cellular automata
MD	molecular dynamics
STEM	scanning transmission electron microscope
EP	epoxy based polymer
COF	coefficient of friction
pv	the pressure multiplied by the speed

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. For comparison, pure EP samples were prepared without mixing the DBEBA with the SNP containing master batch. 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. A STEM result is shown in figure 1a (Österle et al. 2016).

2.2. Friction test

Striking differences were observed between the tribological performance of conventional and hybrid composites at certain stressing conditions, as shown in Fig.1b (taken from Österle et al. (2016)). 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 extend as for the hybrid composite (Zhang et al. 2009).

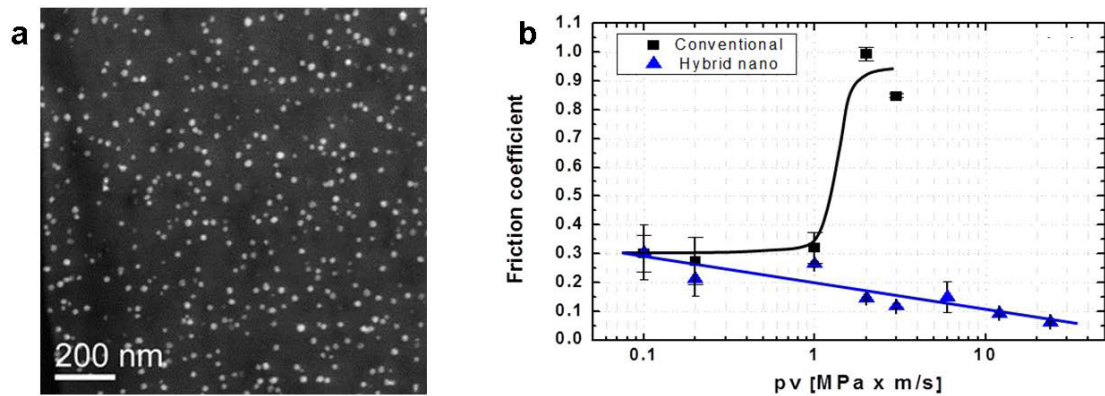


Fig. 1. (a) STEM dark field micrograph showing spherical silica nanoparticles in bright contrast embedded in epoxy matrix; (b) Friction coefficient as function of pv-factor for HNC with 5% silica nanoparticles and for the conventional composite without SNPs.

3. Principles and results of numerical modelling

3.1. MCA modelling

The MCA method is based on conventional concept of cellular automata (Psakhie et al. 1997, Dmitriev et al. 2015). It is an extension of cellular automaton approach achieved by incorporating some basic postulates and relations of particle-related methods. The movable cellular automaton is an object of finite size, possessing translational and rotational degrees of freedom. Interaction between automata is defined by normal (acting along the line connecting the mass centers) and tangential forces, each of which is the sum of the corresponding potential and the dissipative component. The principles of writing the equation of motion for a system of movable cellular automata and prescribing interactions between them are described by Dmitriev et al. (2015).

The modelling setup was designed as shown schematically in figure 2a. The automata size was adjusted to 10 nm according to the smallest size of silica nanoparticles, which are currently used experimentally for polymer matrix composites. A constant sliding velocity (V) equal to 10 m/s was applied on all automata of the top layers of the sample simultaneously with a normal pressure realized through the vertical forces. The automata of the bottom layer were fixed in both directions. Over the unmovable automata an additional dissipative layer was introduced in order to avoid the elastic wave's reflection. The geometry of the sample was: 1 μm along sliding direction and 0.8 μm in transvers direction. Thus, the loading conditions similar to shear + compression loading were reproduced for a small

fragment of the real sample. For the composite sample the concentration of silica inclusions embedded in epoxy was varied in the range between 5 and 27.5 vol. %. The distribution of silica inclusions in modeled setup was adjusted in a way to achieve best similarity with the real nanostructure shown in figure 1a. The total number of particles in the sample was more than 8000.

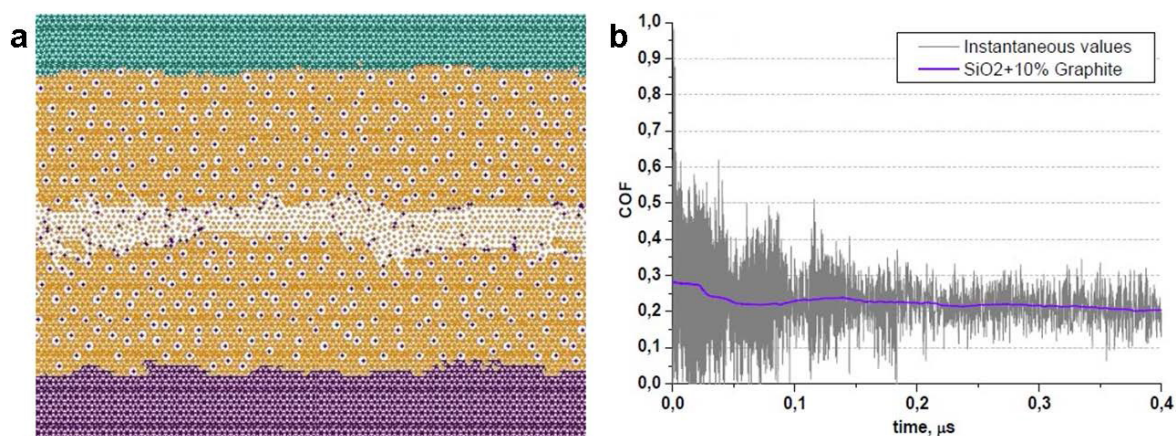


Fig. 2. (a) Structure formation and (b) friction evolution during sliding simulation of a tribofilm consisting of 10% graphite (black) and 90% silica (orange) supported by carbon fiber (violet) and steel (green). External parameters: $p = 130$ MPa, $v = 10$ m/s.

Details of MCA modelling of tribofilm sliding behavior have been described in our recent paper (Dmitriev et al. 2015). It was expected that the results of these simulations may enable us to understand the very low friction coefficient observed for the HCP at $pv = 24$ 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. This corresponds well to medium stressing conditions in the pv -range 1-3, but not to severe conditions at $pv = 24$, for which a COF as low as 0.06 was measured (Dmitriev et al. 2016). 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 figure 2 as an optimum for the silica film with 10% graphite inclusions.

A possible explanation of the very low friction coefficient observed for $pv = 24$ may be due to the amorphous structure of the silica-based tribofilm which is formed under these conditions. Another study suggests amorphization of graphite being responsible for friction reduction (Dmitriev et al. 2016). Since the MCA method could not explain this effect properly, we applied MD-modelling for sliding simulations of amorphous tribofilms consisting of either silica or carbon (Dmitriev et al. 2016).

3.2. Molecular dynamics study

According to our previous studies the amorphous silicon oxide can play a crucial role during sliding. To create a desired configuration the first step comprised of building a sample by linking SiO_4 tetrahedrons to form the crystal structure. The fragment of an ideal crystal structure is shown in figure 3a, where red and blue atoms correspond to Si and O respectively. Then an intermediate layer of this crystal sample was transformed in to the amorphous state by virtual heating beyond the melting temperature and subsequent quenching. The typical structure of amorphous layer is shown in figure 3b. 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 . A simulation ready sample with two crystalline parts (block 1 and 3) and amorphous centered interlayer (block 2) is shown in figure 3c.

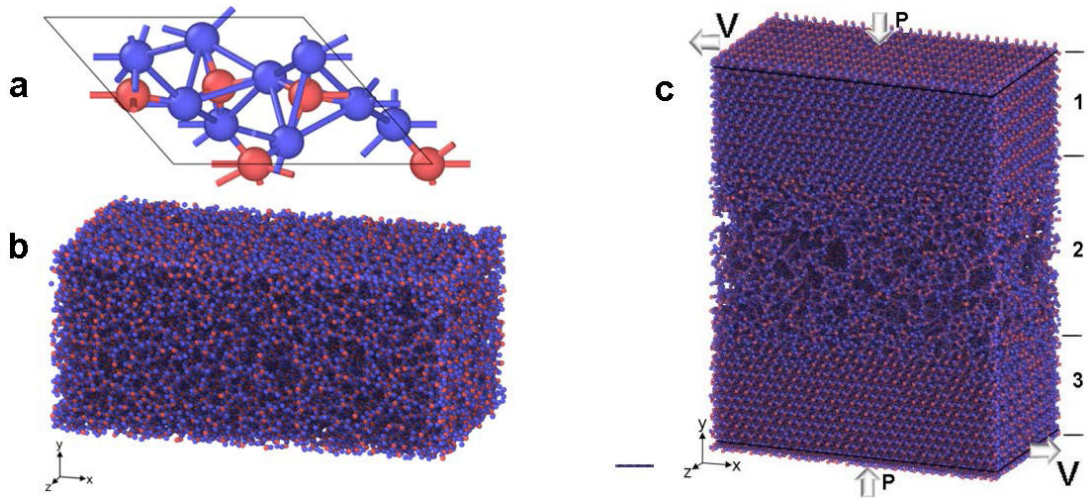


Fig. 3. (a) An arrangement of Si and oxygen atoms in the α -SiO₂ structure; (b) structure of amorphous layer; (c) resulting modelled sample and a loading scheme.

The total geometry of the sample was $14.3 \times 42.9 \times 8.58$ nm along 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 P with about 2 GPa on top and on bottom layers. The initial thickness of amorphous layer was about 8 nm. The two-body interatomic interaction suggested by Tersoff (1988) was used.

The behavior of specimen was analyzed when quenched temperature was equal to 300 K (room temperature) and 1100 K (flash temperature easily reached during friction sliding). According to the results of simulation the sliding behavior of silica sample at room temperature is very sensitive to the loading conditions. By following these features will be systemized.

3.2.1. Sliding at room temperature

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

In case of shear loading applied simultaneously with intensive compression of about 4 GPa the deformation of the specimen is taking place not only within the amorphous interlayer but inside both crystal blocks as well. The atoms marked by green color (see figure 4) allow one to visualize their relative displacement caused by shear deformation. The higher slope within amorphous interlayer indicates higher shear deformation in comparison with block 1 and 3 (see fig. 4b). Further shear loading until relative deformation of about 46% leads to destruction of the specimen.

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

In order to check the impact of loading the sliding of specimen without external pressure was studied. The position of atoms in loaded layers along Y direction was fixed while X coordinates were linearly changed according to sliding velocity. According to results of simulation 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 blocks (1 and 3) become extended along the diagonal. As a result after reaching of a critical value of tension forces there is a separation of two blocks with pore formation inside the amorphous interlayer. Figure 4c demonstrates the specimen structure after formation of pore inside block 2. Further shear loading leads to relative sliding of two blocks through rolling of the formed lump of atoms. This sliding regime is characterized by very low resistance force and stick-slip like character of COF time dependence.

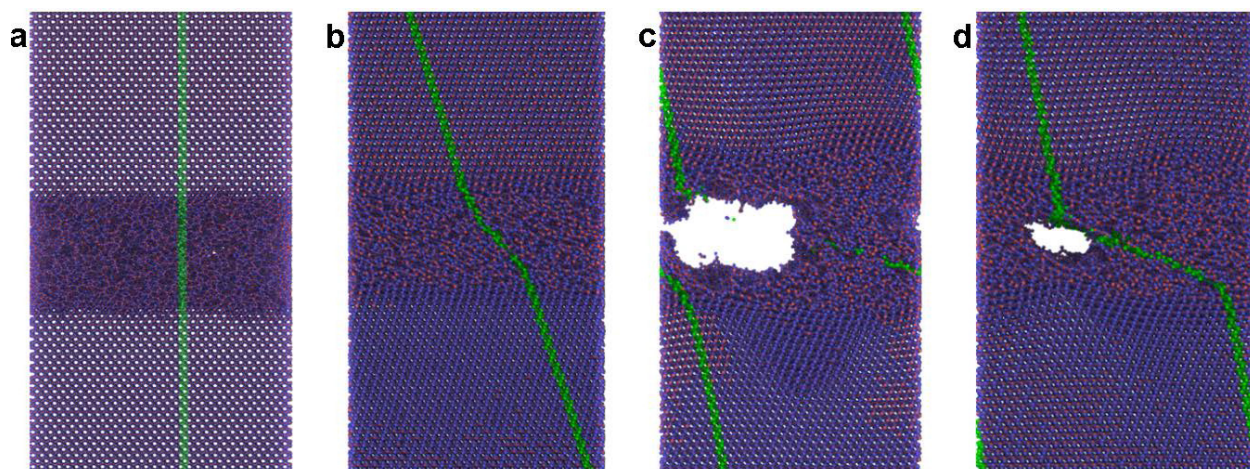


Fig. 4. (a) Initial structure of the central fragment of the modeled specimen. The resulting structure of the central fragment of the modeled silica sample after 0.5ns: (b) under total external compression 4GPa, (c) without pressure and (d) under pressure 4GPa when the configuration shown in figure (c) was used as an initial one. Here and further on projections of atoms on xy plane are used for the visualization.

c. 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 figure 4c as an initial structure for the sliding simulation under same loading condition as was used in case of tasks shown in figure 4b. This means that external pressure equivalent to 4GPa was applied through the loaded layers of atoms. In this case the pore is still present and relative sliding of the two blocks is accompanied by rolling of atoms inside early formed lump. Figure 4d shows the snapshot of the modeled specimen structure during relative sliding.

3.2.2. Effect of flash temperature

To study the influence of elevated temperature of features of silica specimen sliding the structure similar to one shown in figure 4c was taken as an initial structure for further shear deformation. According to this the algorithm of the sample preparation was the following. First the dynamic equilibrium structure with amorphous interlayer in the central part of the silica sample was created by heating and quenching procedure of atoms belonging initially to block 2. The next step includes shear 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 4GPa was applied. The evolution of the silica sample under combination of shear and normal loading at 1100K is shown in figure 5. In comparison with behavior of the similar sample under room temperature here we can observe smooth sliding within amorphous layer without any formation of pores or other defects.

3.2.3. Resistance force comparison

To analyze the frictional properties of amorphous interlayer at atomic scale the total resistance force (the sum of all forces acting on loaded atoms from block 1 or block 3) was calculated as a function of time. Two different tasks showed in figure 5 and 4d where compared. Thus, in both considered cases the initial configuration of the specimen where amorphous layer contains the pore inside was identical. Both tasks were calculated under external pressure 4GPa. According to the figure 6a we can observe small stick-slip oscillations at the beginning of sliding connected with rolling of lump 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. Time dependence of resistance force at flash temperature is shown in figure 6b. The silica sample demonstrates low resistance force with very stable mean value. Thus not only amorphous carbon interlayer can represent solid lubricant with very low friction characteristics but amorphous silica layer as well.

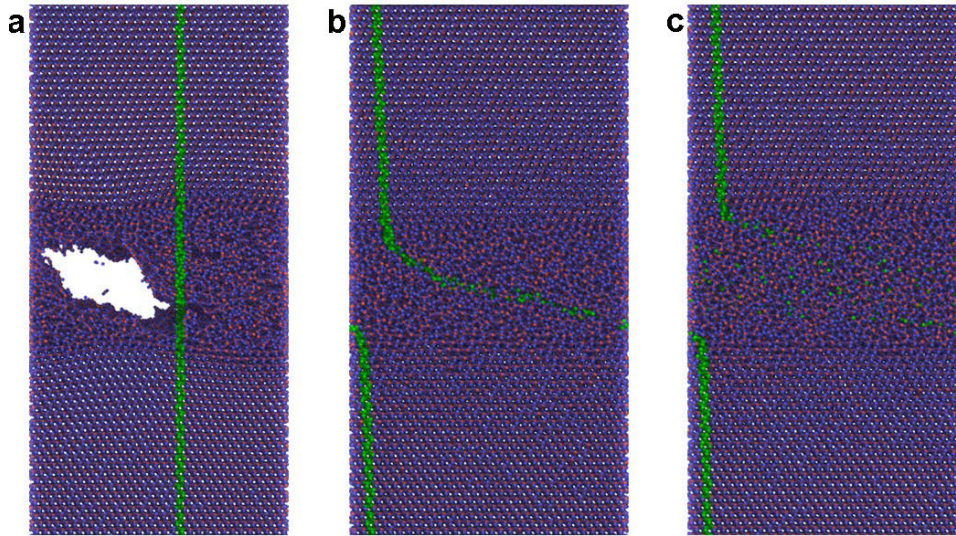


Fig. 5. Evolution of the central fragment of the modeled silica sample. The structure at different moments of time: (a) $t=0\text{ns}$, (b) $t=0.5\text{ns}$ and (c) $t=2.5\text{ns}$.

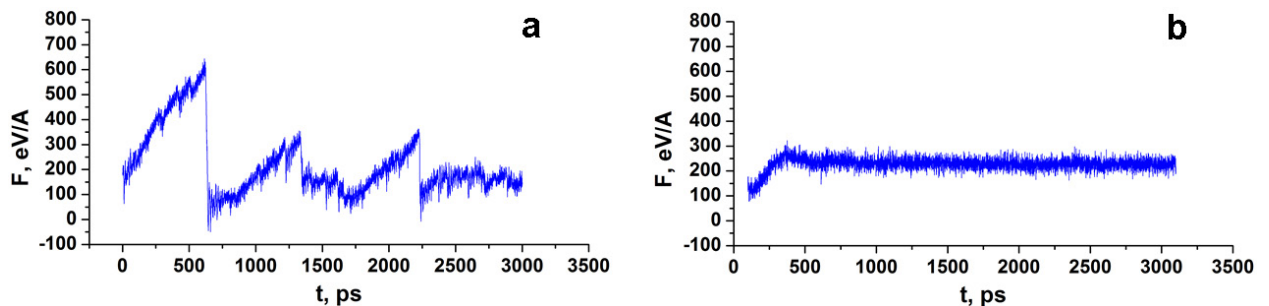


Fig. 6. Time dependencies of resistance force for the silica specimen under different temperatures: (a) 300K (b) 1100K.

4. Discussion and conclusions

MCA-modelling is a suitable tool for simulating the sliding behavior of tribofilms with multi-phase nanostructures. Unfortunately it is restricted to ambient temperatures, unless the mechanical properties of the different constituents are well known at elevated temperatures. In the considered case of a hybrid nanocomposite sliding against a steel disc, flash temperatures up to 1100 K have to be taken into account. Since no reliable data was available, MCA-modelling could only be applied to moderate stressing conditions, but not to severe stressing up to $p_v = 24 \text{ MPa m/s}$.

On the other hand, it was quite easy to perform MD-simulations at 1100 K, considering films consisting of pure amorphous silica obtained by virtual heating and subsequent quenching. Surprisingly, MD-simulations of the silica film provided low friction not only at 1100K, but also at 300K, although in the latter case a stick-slip phenomenon was observed. This could be attributed to the formation of pores and rolling of spherical lumps rolling along the interface in the center of the model structure.

Comparison with experimental results suggests that sliding in the medium p_v -range can be described best with the MCA-method while assuming only moderate temperature increase. On the other hand, the sliding behavior in the high p_v -range is simulated best by MD-modelling assuming an amorphous silica film slit at 1100 K. This high

temperature corresponds to the flash temperature developing at the carbon fibers of the hybrid polymer-matrix composite under severe stressing conditions.

Acknowledgements

The work was supported by RSF grant no. 14-19-0718. Results of MCA simulation was done within the Tomsk State University Academic D.I. Mendeleev Fund Program. It is also part of a cooperative research activity funded by the German Research Foundation (DFG) under contract numbers: OS 77/20-1 and ZG 352/3-1.

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