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Materials and Design



journal homepage: www.elsevier.com/locate/matdes

The role of carbon fibers and silica nanoparticles on friction and wear reduction of an advanced polymer matrix composite



W. Österle^{a,*}, A.I. Dmitriev^{b,c}, B. Wetzel^d, G. Zhang^{d,e}, I. Häusler^a, B.C. Jim^d

^a BAM Bundesanstalt für Materialforschung und -prüfung, 12200 Berlin, Germany

^b ISPMS Institute of Strength Physics and Materials Science, 634050 Tomsk, Russia

^c TSU Tomsk State University, 634050 Tomsk, Russia

^d IVW Institut für Verbundwerkstoffe, 67663 Kaiserslautern, Germany

^e State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China

ARTICLE INFO

Article history: Received 28 October 2015 Received in revised form 29 December 2015 Accepted 31 December 2015 Available online 4 January 2016

Keywords: Carbon fibers Silica nanoparticles Hybrid composite Tribological properties Tribofilm Sliding simulation

ABSTRACT

Excellent tribological properties of an advanced polymer matrix composite were obtained by a combination of micro- and nano-sized fillers. Surface features and the nanostructure of tribofilms were characterized by advanced microscopic techniques, and correlated with the macroscopic behavior in terms of wear rate and friction evolution. A model based on movable cellular automata was applied for obtaining a better understanding of the sliding behavior of the nanostructured tribofilms. The failure of the conventional composite without silica nanoparticles could be attributed to severe oxidational wear after degradation of an initially formed polymer transfer film. The hybrid composite preserves its antiwear and antifriction properties because flash temperatures at micron-sized carbon fibers, lead to polymer degradation and subsequent release of nanoparticles. It has been shown that the released particles are mixed with other wear products and form stable films at the disk surface thus preventing further severe oxidational wear. Furthermore, the released wear product also is embedding carbon fibers at the composite surface thus preventing fiber fragmentation and subsequent third body abrasion. With nanoscale modeling we were able to show that low friction and wear can be expected if the nanostructured silica films contain at least 10 vol% of a soft ingredient.

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1. Introduction

Compared to metals or ceramics, polymer materials show some special features in tribological applications due to their viscoelastic properties [1,2]. Furthermore, polymers are easily transferred to counterbodies during moderate sliding conditions [3–8]. Bahadur pointed out that certain fillers of polymer matrix composites (PMCs) affect the development of transfer films and can reduce the wear rate drastically [7,8]. Carbon fibers and silica nanoparticles (SNPs) are widely used in all kinds of PMCs either reclusively or in combination. Compared to unfilled polymers, fiber-reinforced PMCs provide higher strength and wear resistance [9]. On the other hand, a number of interesting material properties were achieved by adding SNPs to polymer materials [10–13]. Special applications of silica nanofiller are: polymer coatings for corrosion protection [14–18], usage as modifier of the binder phase in concrete [19,20] and improved elastomers [21]. Considering tribological properties, previous studies 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 [22–32]. Especially SNPs are very effective in this respect, and the authors could show that only 0.05 vol.% SNPs was enough to exert a measurable effect on friction evolution [33]. In the following, the composite containing micro- and nanofillers will be termed a hybrid and its counterpart without nanoparticles will be termed a conventional composite. In the meantime, the conditions under which the conventional composite fails, while the hybrid material still shows good performance, were studied comprehensively. The results will be presented later. Nevertheless, it is still kind of a mystery, why the two materials behave so differently under severe stressing conditions. Finding an explanation for this was the main objective of the present study.

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 [34]. 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 [35]. Sawyer and al. pointed out that high wear rates are correlated with thick, patchy and non-uniform tribofilms, whereas low wear rates can only be expected if the films are thin, continuous and uniform [36]. The tribofilms formed from polymers by transfer to steel disks are usually 100 nm thick, but also may become thicker, depending e.g. on disk topography

^{*} Corresponding author.

[7]. For polytetrafluorethylene (PTFE) a film thickness of 400 nm was reported [6]. According to Jacobson et al. beneficial tribofilms from inorganic third bodies are only 10-50 nm thick and consist of a nanocrystalline or amorphous structure [35]. This is too thin for standard Finite Element Modeling (FEM). Therefore, particle-based models have been developed for simulating the friction and wear behavior of third body films and loose wear particles [37]. A model developed in Tomsk combines features of FEM and Discrete Element Modeling (DEM) [38]. The so-called method of Movable Cellular Automata (MCA) has proven to be very suitable for visualizing sliding mechanisms on the nanometer scale. We have already applied this method successfully for sliding simulations of tribofilms formed during automotive braking [39], to graphite films with hard nanoinclusions [40] and to a polymer film filled with SNPs [41]. Furthermore, it was shown that a soft film with hard inclusions exerts a similar effect as a hard film with soft inclusions. In all our previous papers the approach was firstly to identify the nanostructure of the tribofilm, and secondly to get a better understanding of tribofilm sliding behavior by modeling.

We used the same approach in the present study for obtaining a better understanding of beneficial and inferior performance properties of the hybrid and conventional composite, respectively. The envisaged application is using advanced polymer matrix composites for raceways of sliding bearings or bushings. For this application both, wear and friction had to be minimized. Furthermore, it was necessary to ensure low friction and wear under mild as well as under severe stressing conditions. Therefore the different types of films forming from the two materials under different stressing conditions had to be considered. Although some new modeling results will be discussed as well, the focus of the present work is on the characterization of tribofilms and identification of the micro-mechanisms leading to film formation and improved wear resistance.

2. Materials and methodology

2.1. Materials

Although our recent paper has shown that graphite is not needed as a filler of the hybrid composite [33], the materials considered in the following always contained 8 vol.% graphite (G) and 10 vol.% short carbon fibers (SCF) in an epoxy matrix (EP). This was necessary for better comparison with the standard composition of the conventional material in previous studies [30,42]. In the following, all compositions throughout this paper will be given as volume fractions in %. The standard hybrid material was prepared by adding nominally 5% silica nanoparticles (mean diameter 20 nm) to the conventional composite. The technology of compounding was described comprehensively in [30]. The main features of the microstructure are the SCFs embedded in EP as shown by Light optical Microscopy (LM) in Fig. 1a, and, three orders of magnitude smaller, the SNPs also embedded in EP, revealed by Scanning Transmission Electron Microscopy (STEM) of a thin slice cut from the neat EP + 5% SNP composite by ultra-microtomy (Fig. 1b). The latter image was taken as a template for modeling of the stress-strain and sliding behavior of polymer-based transfer films, as described in [41].

2.2. Tribological testing

The same pin-on-disk tribometer as described in previous studies [30] was used for the continuous determination of the coefficient of friction (COF) and wear rate of the two pin materials during sliding against 100Cr6 steel disks (German standard DIN 616). Standard testing parameters were applied, such as: $4 \times 4 \text{ mm}^2$ nominal contact area, 33 mm mean wear scar diameter, 0.3 µm average surface roughness of the disk and 20 h test duration at ambient temperature and humidity. The applied friction power as described by the product of normal pressure (p) and sliding velocity (v) was varied in a wide range between 0.1 and 24 MPa m/s. The higher value is far beyond the limits defined by Friedrich et al. as application range for neat polymers and PMCs with traditional fillers (without nanoparticles) [23].

2.3. Tribofilm characterization

The wear scars on the disk surfaces were examined by optical inspection, Light optical Microscopy (LM) and Scanning Electron Microscopy (SEM) in combination with Energy Dispersive x-ray Spectroscopy (EDS). After identification of regions of interest, sites were marked by the deposition of platinum bars $10 \times 2 \times 2 \ \mu m^3$ with the aid of a Focused Ion Beam (FIB) and a Chemical Vapor Deposition (CVD) unit. Furthermore, FIB was used to prepare micronsized cross-sections below the platinum bars and, in a second step, also thin lamellae for further Transmission Electron Microscopy (TEM) or Scanning Transmission Electron Microscopy (STEM). For FIB, SEM and EDS a DualBeam instrument of type FEI Quanta 3D was used, whereas an analytical TEM of type JEOL 2200FS was used for TEM/STEM/EDS-investigations.

2.4. Nanoscale modeling of tribofilm sliding behavior

The most important features of the model are shown in Fig. 2 and will be explained in the following.

The structure of first bodies and adhering tribofilms is built as two dimensional networks of linked particles, as shown in Fig. 2a. Links to neighboring particles are displayed by lines. If we define a particles



Fig. 1. a) LM of micro constituent (SCF), b) STEM of nano constituent (SNP).

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