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Impact of counterface topography on the formation mechanisms of nanostructured tribofilm of PEEK hybrid nanocomposites

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ABSTRACT

The effect of steel counterface topography on the formation mechanisms of nanostructured tribofilms of polyetheretherketone (PEEK) hybrid nanocomposites was studied. Three types of surface finishes with mean roughness R_a ranging from nano- to micro-scale were investigated. Tribo-sintering of nanoparticles, oxidation of counterface steel and compaction of wear debris are identified to be competing factors dominating the formation and function of the tribofilms. Counterface topography played an important role on the competing factors, and thereby influenced significantly the final structure, the load-carrying capability and the lubrication performance of the tribofilms. It was disclosed that a thin tribofilm, which mainly consists of silica nanoparticles and which forms on the counterface with a submicron roughness, benefits best the tribological performance of the composites.

1. Introduction

Numerous studies [1–5] have demonstrated that the formation of a tribofilm, or namely transfer film, on metallic counterbody surface is of essential importance for the tribological performance of polymer materials under dry sliding conditions. Rhee et al. [3] supposed that when some polymer wear debris became attached to metal counterface such that shearing friction force seldom dislodges polymer attached to the substrate, then a polymer tribofilm began to form. Lancaster [4] claimed that transfer from a ductile thermoplastic to a metal counterface usually occurred via adhesive interactions and reduced the magnitude of the wear rate. It is a general opinion that a “good” polymeric tribofilm benefited the tribological performance by reducing the direct contact between the polymer bulk material and the metal.

It is well known that layer-structured solid lubricants, e.g. graphite and MoS_2 etc., in polymer matrix readily transfer to the metallic counterface and thus form a “self-lubricating” transfer film. The transfer of the solid lubricants is well understood nowadays in terms of easy shear planes of certain crystal structures.

Besides solid lubricants and ductile thermoplastics, it was manifested that inorganic nanoparticles enhanced the tribological properties of polymer matrix [6–9]. Moreover, nanoparticles improve significantly the mechanical properties of the polymer matrix [10,11]. The enhancement of the tribological properties were explained by improved “quality” of the tribofilm, in terms of uniformity, cohesion and interfacial adhesion properties, which are considered to be important factors providing an efficient and stable lubrication impact. These works are of great importance for understanding the tribological mechanisms of polymer nanocomposites and for developing high-performance materials as well. Nevertheless, the nanofillers used in the previous works are not known as typical solid lubricants, and it is not understood yet how the mechanisms of friction reduction works.

The incorporation of nanoparticles into conventional composites, e.g. polymer matrix filled with short carbon fibers (SCF) and solid lubricants, leads to striking effects on tribological properties [12–17]. In view of applications under severe conditions, such hybrid nanocomposite formulations have a great potential. It was disclosed in our previous work that the interesting tribological properties of epoxy hybrid nanocomposites result from the formation of an extremely thin tribofilm, which built from the initial roughness [13]. The positive action of tribofilm was evidenced in our previous work, i.e. the removal of the thin tribofilm caused an immediate increase of friction and wear of the material [17]. Although the dependency of tribological properties on the formation of the thin tribofilm could be identified, a sound understanding on structure and performance of the tribofilm is still lacking. When the multiple fillers are added into the polymer

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matrix, material transfer can occur either from the fillers, the polymer matrix, or both. In addition, tribo-chemical actions can be also an important factor influencing the formation and function of tribofilms. Regarding the hybrid nanocomposite system, the tribofilm formation is complicated since the multiple fillers can interact in a very complex way by material transfer and tribochemical reactions.

Counterface topography influences directly the contact interface in terms of localized asperity stresses and flash temperatures. Moreover, counterface topography plays a role on the compaction of polymer wear debris [18,19]. Therefore, it can be reasonably expected that the counterface topography exerts an important influence on the tribofilm structure of the hybrid nanocomposite system. On the other hand, a deep investigation on the topographic effect of counterface can lead to a better understanding on the tribological mechanisms of the hybrid nanocomposite system.

Polyetheretherketone (PEEK) is regarded as one of the best matrix materials for formulating high-performance tribomaterials subjected to extremely severe conditions, e.g. very high *pv* factors (pressure $\times$ velocity), high environment temperatures and strong corrosion mediums etc. Our previous work [13,20] showed that the addition of only small fractions of silica nanoparticles reduces substantially the friction and wear of a conventional PEEK composite filled with SCF/graphite/PTFE (polytetrafluoroethylene). Although it was noticed that the occurrence of a minimum friction and wear is related to formation of a homogeneous tribofilm, the tribological mechanisms were still not deeply understood. In this regard, the impacts of solid lubricant, nanoparticle fraction and *pv* factor on the tribofilm structure of the PEEK hybrid nanocomposites are still unknown. Moreover, the tribological behavior of PEEK filled only with SCF and nanoparticles (without solid lubricants) were never studied. From the viewpoint of material development, it is of practical interest to clarify whether solid lubricants are still necessarily required in the PEEK hybrid system.

The present work focuses on topographic effect of steel counterface on the tribofilm structure and tribological mechanisms of PEEK hybrid nanocomposites, i.e. PEEK filled with nanoparticles/SCF and PEEK filled with nanoparticles/SCF/graphite/PTFE. The mean roughness R_a of the counterface concerned varies from nano- to micro-scale. The effects of nanoparticles and solid lubricants on the structure and tribological performance of the tribofilm was investigated. An attempt was made to reveal the topographic effect on the tribological behaviors of PEEK composites, and to disclose the structure–performance relationship of the tribofilm.

2. Experimental

2.1. Material preparation

Fumed silica particles (Aerosil R7200, Evonik, Germany) with an average diameter of 13 nm were used as nanofillers. The nanoparticles were used as-received with a methacrylsilane surface treatment. Two conventional composites were used as control materials, i.e. PEEK filled with SCF and PEEK filled with SCF/graphite/PTFE. The first conventional composite, hereafter designated as CC1, was compounded via mixing 10 vol% PAN-based carbon fibers (Tenax 385, Germany) into PEEK matrix (4000G, Evonik, Germany) using a laboratory-scale melting mixer (Brabender® mixer 30/50, Germany) at 410 °C and with a screw rotation speed of 60 min^{-1}. The second conventional composite, hereafter referenced as CC2 was compounded at Evonik.

Silica nanoparticles were dispersed into the conventional composites by using the Brabender mixer. Three hybrid nanocomposites were compounded and designated as $1SiO_2+CC1$, $4SiO_2+CC1$, $1SiO_2+CC2$, respectively. The $1SiO_2+CC1$ refers to a PEEK composite filled with 1 vol% nano-SiO_2 together with 10 vol% SCF. The volume fraction of nano-SiO_2 particles in $4SiO_2+CC1$ was 4%. The $1SiO_2+CC2$ refers to a PEEK composite obtained by dispersing 1 vol% nano-SiO_2 into the CC2 composite. Table 1 listed the designations and compositions of the composites studied in this work. More details regarding the preparation process, structure and thermo-mechanical properties of bulk CC2 and $1SiO_2+CC2$ are available in [13,20]. After mixing, all PEEK composites were compression molded at 410 °C into plates with a dimension of $100 \times 80 \times 4$ mm^3.

Table 1
Compositions of composites studied.

Material codes	Compositions				
	Nano-SiO_2 (vol%)	SCF (vol%)	Graphite (vol%)	PTFE (vol%)	PEEK (vol%)
CC1	0	10	0	0	90
CC2	0	8.4	6.5	6.7	78.4
$1SiO_2+CC1$	1	10	0	0	89
$4SiO_2+CC1$	4	10	0	0	86
$1SiO_2+CC2$	1	8.3	6.4	6.6	77.7

2.2. Tribology tests

Tribology tests were performed at room temperature using a Pin-On-Disc test rig (POD, Wazau, Germany). Polymer pins were cut from the compression molded plates, with a contact surface of the pins of 4×4 mm^2 and a length of 12 mm. During the tests, a rotating polymer pin probe was pressed against a stationary 100Cr6 steel (DIN 616) disc. The diameter of the wear track was 33 mm.

The 100Cr6 discs were supplied by INA (Schaeffler group, Germany) and the mean surface roughness R_a of the as-received discs was 0.30 μm, which was finished by a standard industry grinding process. In order to study the topographic effect of the counterface, besides the ground disc as-received (R_a=0.30 μm), the polymer probe also slid against a mirror-polished disc with R_a=0.01 μm and a sandblasted disc with R_a=1.45 μm. Prior to friction tests, the sandblasted surface was cleaned in an ultrasonic bath to detach the loosened particles from the surface.

The surface topographies of the counterfaces were characterized by using a white light profilometer (FRT, Germany). The 3-D surface topographies of the ground (original), mirror-polished, and sandblasted discs are displayed in Fig. 1a–c, respectively. It is seen that randomly distributed roughness grooves exist on the original disc (Fig. 1a). Almost all the roughness grooves were removed after mirror-polishing (Fig. 1b). After sandblasting, the surface was obviously roughened and moreover the surface shows a distinctly different micro-topography from those of the two other surface finishes. Numerous pits and cavities are noticed at the sandblasted counterface (Fig. 1c). Such topographic features are expected to exert an influence on the formation process and the final structure of the tribofilms.

Pressures were applied on the sliding pair by applying dead weights and were controlled at 1 MPa and 3 MPa. The sliding velocities were kept constant at 1.0 m/s and the testing time was 20 h, which was long enough allowing the system to reach a steady friction and wear process. The friction coefficients were measured online by a torque sensor. The height of the polymer probe was measured online by a linear displacement sensor instrumented onto the test rig and thus the linear wear rate was obtained. In addition, the weight loss of the polymer probes was calculated by measuring the beginning and final weights after 20 h