Self-lubricating polymer composites
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Sample Preparation and Tribo-Tests

As aforementioned in Chapter 1, the objective of this work is to improve the tribological performance of particles or fibers reinforced self-lubricating composites, which are currently applied in dry sliding bearings. To carry out this study, apart from some materials supplied by SKF, other self-lubricating composites are produced via optimizing the composition, mixing process and curing process. Diamond-like coatings are deposited via reactive magnetron sputtering process. Characterization of their tribological performance is performed using a ball-on-disk tribometer. The details are discussed in the following sections.

2.1 Composites production

Epomet-PTFE composites

An epoxy- and SiO$_2$-containing powder, Epomet F, was purchased from Buehler GmbH. The powder is mainly composed of about 31±2 wt.% epoxy resin (tetrabromobisphenol-A epoxy, CAS: 26265-08-7) and 65±2 wt.% SiO$_2$ particles. It also contains 1-2 wt.% 2,4,6-tris(dimethylaminomethyl)phenol, ~1 wt.% antimony oxide (Sb$_2$O$_3$) particles (for flame retardant property) and less than 1 wt.% carbon black (pigment). The diameters of the SiO$_2$ particles range between 20 and 100 µm, and that of the Sb$_2$O$_3$ lies between 10 to 30 µm, as measured with light microscopy. The density of Epomet F powder is about 2.09 g/cm$^3$, according to the datasheet from the manufacturer. The PTFE powder, Zonyl MP 1000 fluoro-additive from DuPont, comprises of loose agglomerates with sizes up to 150 µm (the size of the primary particles is about 12 µm). The density of molded PTFE is around 2.2 g/cm$^3$, while the density of the loosely agglomerated PTFE particles is only about 0.5 g/cm$^3$. In order to minimize the agglomeration of the PTFE particles in the composite,
the PTFE powder was sieved through a 71 µm sieve with a sieve shaker (Retsch AS 200).

The two dry powders were mixed for 3 minutes in a clean glass container. Thereafter, the glass container with the pre-mixed powders was vibrated in a shaker for 40 min. The powder mixture was then transferred to a mounting press (Buehler Metaserv Pneumet II) for curing. It was cured at about 160 °C for 20 minutes under with a pressure of 4.1 bar and cooled down with water afterwards. The curing process was performed according to the recommendations of the powder manufacturer (Buehler). The molded samples, about 7 mm thick and ø30 mm in diameter, were then polished to about 6.5 mm thick with silicon carbide abrasive papers up to 4000 grade. The surface of the polished composite was rinsed with distilled water before tribo-tests.

The PTFE/SiO2/epoxy composite is referred as “Epomet-PTFE composite”, with the content of PTFE ranging from 0 to 30 wt.%. For conciseness, the Epomet-PTFE composites are named according to the content of PTFE as ‘Epomet-PTFE-xx’, where xx denotes the weight percentage of the PTFE powder. The measured Vickers hardness and compressive strength of the Epomet-PTFE composites are listed in Table 1. The mechanical properties of the composites are inversely proportional to the PTFE content.

**Epoxy 6078 composites**

Epoxy XB 6078 powder, supplied by Huntsman, is a one-component solid epoxy system. It can be cured by heating up to above 110 °C in several minutes. PTFE powder, purchased from Sigma-Aldrich (430943 Aldrich), has an average particle size about 12 µm, according to manufacturer’s datasheet. Hollow (partially hollow) glass micro-spheres (47Si, 37O, 8Na, 6Ca, 0.8Al, wt.%, measured with energy dispersive X-ray spectroscopy), from Sigma-Aldrich (440345 Aldrich), have average diameter around 8.4 µm as measured, which is a bit lower than the size 9-11 µm as indicated on the package.

After weighing, the epoxy and the PTFE powder together with 6.5 g water was ball milled (10 ø6 mm 100Cr6 steel balls) at 400 rpm for 7 minutes using a Fritsch Pulverisette planetary mill. The mixture and the balls are in one of the two steel cylinders as shown in Fig. 2.1b. Then, the hollow glass micro-spheres were added in and ball milled for another 2 minutes. The mixture was dried in an oven at 40°C overnight. The dried powder was then gently ground and transferred to a curing mold. According to SEM observations, the glass micro-spheres in the ground powder were not evidently fractured or broken.
The powder was cured at 8 bar pressure for 10 minutes in the curing mold which was placed in a hot press, Schwabenthan Polystat 100T. The curing temperature of the bottom heating plate and the top heating plate are 112°C and 245°C, respectively, due to the de-molding design of the curing mold so that the distance of curing composites is 56 mm to the top plate and 20 mm to the bottom plate. The curing process was optimized by the master student, Frank van Rijn, which is evaluated mainly by the hardness of the cured sample. The cured samples were cooled down with compressed air. After de-molding, the composite disks (around ø30 mm × 7.5 mm) were polished until 4000-grade polishing paper. The composites are named as Epoxy 6078 composites.

**Epoxy 25036 composites**

Solid epoxy resin, CAS No. 25036-25-3, Phenol, 4,4'-(1-methylenebridene)bis-, polymer with 2,2'(((1-methylethylidene)bis(4,1-phenyleneoxymethylene))bis[oxirane], was purchased from Hebei Duoke Chemical Technology Co., Ltd. The chemical structure is shown below:
A curing agent, dicyandiamide powder, was purchased from Sigma-Aldrich (D76609 Aldrich), while Epikure Curing Agent P-101 was used as an accelerator. The epoxy resin tends to agglomerate at room temperature. In order to effectively mix the different components, the epoxy is ground and subsequently sieved (<100 µm) and kept in a refrigerator. The harder and accelerator are also ground to break up major agglomerates. The fillers are (partially) hollow glass micro-spheres and PTFE powders, the same as those used in Epoxy 6078 composites.

After weighing the epoxy (epoxy: hardener : accelerator=92.2 : 6.5 : 1.5) and fillers, the method of mixing and drying is also the same as the one used in Epoxy 6078 composites. However, it is cured in a different hot-press, a THB 400 Table press. The top and bottom temperatures are set at respectively, 285°C and 162°C for curing, with a curing pressure around at 40 bar. The heating time is 60 minutes, thereafter the mold is left to cool in an ambient atmosphere until the temperature of the top plate has dropped to 180°C (± 70 min). Then, the hot-press is water-cooled until temperatures of both plates have dropped under 20°C (±10 min). Together with another master student Rogier J. Huls we optimized the curing process by also evaluating the hardness and porosity of the cured sample. After de-molding, the composite disks (around ø30 mm × 7 mm) were polished until 4000 grade polishing paper. The composites are named as Epoxy 25036 composites.

A short summary of the three different types of composites is presented in Table 2.1. Note that all the basic components are solid powders.

<table>
<thead>
<tr>
<th>Composites</th>
<th>Matrix</th>
<th>Solid lubricant</th>
<th>Reinforcer</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epomet-PTFE</td>
<td>epoxy 1</td>
<td>PTFE</td>
<td>SiO₂ particles</td>
<td>premixed epoxy/SiO₂ ratio fixed</td>
</tr>
<tr>
<td>Epoxy 6078</td>
<td>epoxy 2</td>
<td>PTFE</td>
<td>hollow glass spheres</td>
<td>one-component epoxy</td>
</tr>
<tr>
<td>Epoxy 25036</td>
<td>epoxy 3</td>
<td>PTFE</td>
<td>hollow glass spheres</td>
<td></td>
</tr>
</tbody>
</table>

2.2 DLC coating deposition

A hydrogenated diamond-like carbon (DLC) coating, TiC/a-C:H nanocomposite coating, was deposited on the honing patterned 100Cr6 steel balls and the smooth 100Cr6 steel balls in this study, which were ultrasonically cleaned with acetone and rinsed with ethanol, and further Ar-plasma etched before deposition. The surface roughness (Ra) of the honing
patterned 100Cr6 steel balls and the smooth 100Cr6 steel balls are around 170 nm and 50 nm, respectively. The coating was deposited by reactive magnetron sputtering in a TEER UDP400/4 closed-field unbalanced magnetron sputtering (CFUMS) system in an argon/acetylene atmosphere, as shown in Fig. 2.2. With this technology, a magnetic trap can be formed to prevent electrons to escape the plasma region towards the chamber walls, which increases the overall ionization of the discharge. Hence, the extent of ion bombardment on the targets and substrate and the reactivity of the reactive gases (mainly hydrocarbon gases) are enhanced, which is beneficial to have a compact deposited film and a high deposition rate.

**Fig. 2.2** (a) the Teer UDP-400/4 deposition system (b) a view of the inside of the deposition chamber (the front door is open), the magnetrons and the sample holder are visible. (courtesy by Damiano Galvan [1])

The system contains four targets in total. One Ti target (as seen in Fig 2.2b, embedded in the open front door) and one Cr target mounted face to face were used to deposit a TiCr intermediate layer, while other two Ti targets were used for reactive deposition of the top TiC/a-C:H nanocomposite coating. Before deposition, the chamber and the four targets were cleaned with argon sputtering. Then, an intermediate Cr-Ti layer (Cr % gradually decreases and Ti % gradually increases) is coated on the steel substrate to enhance the adhesion strength of the TiC/a-C:H coating. During the deposition of top TiC/a-C:H nanocomposite coating, the flow rate of argon and acetylene gases and the substrate bias voltage were 12 sccm, 8 sccm and 50 V, respectively. The thickness of the coating and the intermediate layer was measured to be 1.1 µm and 0.3-0.4 µm, respectively. A typical SEM image of
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the TiC/a-C:H coating on Si wafer is shown in Fig. 2.3. The surface roughness (Ra) of the TiC/a-C:H coating on the honing patterned steel balls and the smooth 100Cr6 steel balls are also around 165 nm and 50 nm. The hardness and modulus of the coating are estimated to be 15 GPa and 140 GPa, respectively. The effect of process parameters on the coating properties (i.e. hardness, composition, roughness, adhesion strength) have been investigated and presented in our previous publications [2]. Other detailed investigation of the nanocomposite can be found in [3, 4, 5].

Fig. 2.3 A SEM image of a TiC/a-C:H nanocomposite coating on Si wafer.

2.3 Tribo-tests

A systematic study of the friction and wear behavior of the self-lubricating composites was carried out using a ball-on-disk tribometer (CSM Instruments, Switzerland) under dry sliding conditions, as shown in Fig. 2.4. During tribological tests, the counterpart ball was stationary, while the sample disks were rotating anti-clockwise beneath the stationary ball. The normal load was transferred from a horizontal arm (where the ball holder is fixed) to the ball/sample contact interface. The normal load used in study ranges from 0.1 N to 60 N. The sliding speed ranges from 0.5 cm/s to 50 cm/s.
The total sliding distance is varied in different tests, while 1000 m distance is normally used for calculating wear rates.

The counterpart balls used in the tribo-tests were ø13 mm ball, including 100Cr6 bearing steel balls, Al₂O₃ balls, Si₃N₄ balls and TiC/a-C:H coated balls. Before the tribo-tests, the counterpart balls were cleaned with acetone and dried with clean compressed air. Most tests in this study – unless otherwise specified – were performed at room temperature (22 ± 2°C) and the relative humidity of 35 ± 2% maintained with feedback controlled flux of dry air or water vapor into the protection box, depending on the ambient humidity.

Fig. 2.4 (a) A photo of the CSM ball-on-disk tribometer; (b) a schematic drawing of the rotational sliding configuration of the ball-on-disk tribometer.

After the tribo-tests, the morphology of the worn surfaces of the composites and of the balls were observed using light microscopy and scanning electron microscopy (SEM, Philips XL-30 FEG ESEM). For SEM observations, a thin Au layer was applied on the surface of the Epomet-PTFE composites, Al₂O₃ and Si₃N₄ balls to avoid charging. Energy dispersive spectroscopy (EDS) was used to analyze the elemental composition on the worn surfaces. Confocal microscopy (Nanofocus µSurf) was used to measure the surface profile of the worn surfaces of the composites and the balls, for the assessment of the wear volume by a Matlab code with an error of ±5% for most cases and of ±30% for the balls having an average wear depth less than 1.5 µm.

XPS was performed to investigate the elemental composition and possible chemical bonding on the worn surfaces of the balls, using a Surface Science SSX-100 ESCA instrument with a monochromatic Al Kα X-ray source (hv = 1486.6 eV). During data acquisition, the pressure in the measurement
chamber was kept below $2 \times 10^{-9}$ mbar. The diameter of the analyzed area was 600 μm. Freshly prepared samples were used for all the measurements.

Other characterization techniques, including Raman, FT-IR, XRD, DSC and contact angle goniometer, were used in some chapters. The details of these techniques will be discussed in the following chapters.

References