

Supplementary Material

Material characterization of the fibre-reinforced thermoset

In order to study the microstructure and composition of the fibre-reinforced thermoset bearing material, characterization was carried out using X-ray microtomography (XMT) and elemental analysis.

X-ray microtomography (XMT) was used in order to study the microstructure of the fibre-reinforced thermoset using a Zeiss Xradia 510 Versa (Carl Zeiss X-ray Microscopy, Pleasanton, CA, USA). The full geometry of the $4 \times 4 \times 4 \text{ mm}^3$ polymer sample was initially scanned using a $4\times$ objective with a field of view (FOV) of 6.02 mm and a spatial resolution of $5.96 \mu\text{m}$. The low-resolution scan was carried out using an X-ray tube voltage of 50.4 kV and an output effect of 4 W. During the imaging, 1601 projections were acquired with an exposure time of 4 s each.

In order to study microscale features, a region of interest (ROI) was selected based on the results from the initial scan (low resolution) and scanned at a higher resolution using a $20\times$ objective with a FOV of 0.55 mm and a spatial resolution of $0.56 \mu\text{m}$. This scan was carried out using an X-ray tube voltage of 60.4 kV and an output effect of 5 W. During the imaging 2201 projections were acquired with an exposure time of 11 s each.

Both scans were carried out without X-ray filters. The 3D visualization and quantitative analysis of the microstructure of the fibre-reinforced thermoset were obtained using Dragonfly Pro software (object research systems (ORSs), Montreal, QC, Canada). A standard threshold procedure was used to segment the different phases in the material in order to estimate volume fraction of the internal phases and pore size distribution. More details about the XMT system and the method are presented in [20].

In order to determine the composition of the identified phases in the fibre-reinforced thermoset, an unworn polymer pin was examined using a JEOL JSM-IT300 LV (Peabody, MA, USA) scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectrometer (EDS). The polymer pin was sputtered with a 15.3 nm layer of platinum (Pt) to reduce the charging effect in the SEM.

Inductively coupled plasma sector field mass spectrometry (ICP-SFMS) ELEMENT XR (Thermo Scientific, Bremen, Germany) was used to determine the chemical composition of the fibre-reinforced thermoset with respect to the inorganic elements. The method used for sample preparation and measurements is described in [20]. Four measurements (including separate microwave-assisted acid digestions) were performed for the material.

The microstructure of the fibre-reinforced thermoset material, from reconstruction of the XMT imaging using the $4\times$ and $20\times$ objectives, is presented in Figure S2 in grey scale and the volume fractions of the quantified internal phases are summarized in Table S2. The grey scale reflects the relative density of the features, where white corresponds to the highest density and black to the lowest. The contact surface, i.e., the surface that will be sliding against the stainless steel during the tribological tests, is visible in the figures.

Similar to the fabric-reinforced thermoset, the structure of the fibre-reinforced thermoset is more complex compared to the homogeneous thermoplastic [20]. The microstructure of the fibre-reinforced thermoset can be seen in more detail in the animation of the 3D visualization obtained using the $20\times$ objective (Video S1). From the reconstruction of the XMT imaging using the $20\times$ objective, four phases can be distinguished in the cross-sections of the full tomographic reconstruction (Figure S2 (a) and (b)). The first phase corresponds to the pores in the material, seen as black features in the XMT images due to their low density. The second identified phase displayed as light grey features was determined using EDS analysis of an unworn polymer pin surface (Figure S9) to be PTFE particles that are spun in to the polyester filaments. Since PTFE has a higher density compared to the epoxy resin and polyester filaments, it is therefore of a lighter grey colour. The third phase corresponds to impurities in the material, seen as white/bright features in the XMT images due to their higher relative density. The fourth phase is shown as darker grey features, with the highest volume fraction of the material (Table S2) and a lower relative density compared to the PTFE particles. This phase corresponds to both the polyester filaments and epoxy resin matrix containing graphite. The obtained XMT results show that the constituents of this phase have similar relative density and are hence hard to separate when considering the grey scale information.

It should be mentioned that it was hard to properly segment the PTFE particles from the epoxy resin and polyester filaments in the image using the standard threshold procedure. The PTFE particles were slightly under-segmented in order to avoid that part of the epoxy/polyester filament matrix included in the image segmentation, which occurred when all regions corresponding to PTFE particles were included. This means that the volume fraction of the PTFE particles (Table S2) is slightly higher in reality, while the volume fraction of the epoxy/polyester filament phase is lower, especially for the higher-resolution scan.

The higher-resolution scan (20×) reveals channel-like pores (Figure S2 (c)) in the fibre-reinforced thermoset. These pores are located in the phase containing epoxy resin and polyester filaments and follow similar curvature pattern (Video S2) as the PTFE particles in the material (Video S3). Cross-sections of the full tomographic reconstruction (Figure S2 (a) and (b)) shows that some thinner pores are located in the boundary between the PTFE particles and the epoxy/polyester filament phase. This means that the resin matrix does not perfectly adhere to the PTFE particles. There is also the presence of smaller pores, randomly distributed in the structure of the material. The pore size distribution (Figure S5) shows that the majority of the pores have a volume less than $1.5 \times 10^4 \mu\text{m}^3$, with only single pores having a volume up to $10 \times 10^4 \mu\text{m}^3$. The majority of the higher density particles (impurities) in the material have a volume below $1515 \mu\text{m}^3$, with few having larger volumes up to $1.06 \times 10^4 \mu\text{m}^3$ (Figure S6). Quantification of the internal phases in the material scanned using 20× objective showed that the volume fraction of pores is 1.25 vol.% and 0.07 vol.% for impurities (Table S2). The volume fraction of pores and size is lower for the thermoplastic (0.36 vol.% with volumes up to $166 \mu\text{m}^3$) and similar for fabric-reinforced thermoset (1.20 vol.% with volumes up to $9.2 \times 10^4 \mu\text{m}^3$) [20] compared to the fibre-reinforced thermoset, using the same resolution (20×) objective.

In Figure S2 (d), 3D visualization of the material from the tomographic scans of the whole polymer pin ($4 \times 4 \times 4 \text{ mm}^3$), using low-resolution (4×) objective, is presented with segmented pores and part of the whole structure visible. The macrostructure of the pin can be seen in more detail in the animation of the 3D visualization obtained using the 4× objective (Video S4). It is clear from the video that the reinforcement fibres have a layered structure. This is attributed to the winding process of the material using a rotating winding mandrel. This process involves winding filaments, i.e., reinforcement fibres, under tension over the mandrel. The fibres are impregnated with epoxy resin containing graphite by passing through a bath as they are wound onto the mandrel. The mandrel rotates while a carriage traverses horizontally back and forth along the axis of the mandrel, laying down fibres in a given angle to the rotational axis. This orientation angle is less than 90° for the fibre-reinforced thermoset. Hence, the continuous fibres are not parallel to the sliding direction in the tribological tests and will therefore form layers with positive and negative orientation angle on top of each other. The exact orientation angle is not disclosed for proprietary reason. This also means that the cross-sections of the of the full tomographic reconstruction using 20× objective (Figure S2 (a) and (b)) are not parallel and perpendicular to the reinforcement fibres but to the sliding direction in the tribological tests.

The low-resolution scan reveal uneven distribution of the segmented pores in the material, similar to the fabric-reinforced thermoset [20]. The pores are concentrated in regions between the layers of reinforcement fibres with a positive and negative orientation angle, forming a cross (Figure S2 (d)). These locations can be considered as weak points in the material due to the presence of pores which indicate insufficient adhesion between the layers. The majority of the pores are located between the PTFE particles and the epoxy resin/polyester filament phase, but some are also located within the latter (Figure S3). From the pore size distribution (Figure S7), it can be seen that the majority of the pores have a volume less than $2.3 \times 10^6 \mu\text{m}^3$, but some have larger volumes up to $10 \times 10^6 \mu\text{m}^3$. Quantification of the internal phases in the material scanned using 4× objective showed that the volume fraction of pores is 0.22 vol.% (Table S2), which is more than five times lower compared to the higher-resolution scan (20×). The deviation is mainly attributed to the differences in spatial resolution between the two objectives, $5.96 \mu\text{m}$ for the 4× objective compared to $0.56 \mu\text{m}$ for the 20× objective. Therefore, many of the pores visible in the higher-resolution scan are too small to be resolved in the low-resolution scan. Another explanation for the deviation in volume fraction of the pores between the two scans is the structural heterogeneity of the material. As seen in Figure S2 (d), several larger pores are situated on different locations and the pores are not distributed uniformly. Hence, the location of the higher-resolution scan will influence the obtained volume fractions of the internal phases. Nevertheless, as

there is presence of smaller pores in the material, the higher-resolution scan gives a better estimation of the volume fraction of the pores compared to the low-resolution scan due to better spatial resolution. Compared to the fabric-reinforced thermoset, containing 0.36 vol.% pores with a volume up to $19 \times 10^6 \mu\text{m}^3$ [20], the volume fraction of pores (Table S2) is less in the fibre-reinforced material and the pores are also smaller.

Quantification of the internal phases in the fibre-reinforced thermoset, scanned using the 4 \times objective, showed that the volume fraction of higher density particles (impurities) is 0.08 vol.% (Table S2), which is similar to the obtained results using a higher-resolution (20 \times) scan. The segmented higher density particles from the 4 \times scan are visible in Figure S4. The majority of these particles (impurities) have a volume below $1.17 \times 10^6 \mu\text{m}^3$, with single ones having larger volumes up to $9.28 \times 10^6 \mu\text{m}^3$ (Figure S8). These volumes are several magnitudes higher compared to the ones obtained from the higher-resolution scan. This means that the size of the particles varies between different locations; therefore, the location of the higher-resolution scan will influence the obtained volume fractions as well as the volume distribution of the impurities.

Average concentrations of inorganic constituents in the fibre-reinforced thermoset, measured by ICP-SFMS, are presented in Table S3. It should be noted that only elements with measured concentrations above 0.001 wt.% are included in the table, with a sum of 0.57 wt.%. The reproducibility between the four measurements is good with a relative standard deviation (RSD) below 7 % for all elements except copper (Cu) and titanium (Ti), with RSD around 10 %. This indicates high homogeneity of spatial distribution of inorganic constituents in the material. The total average sum of inorganic compounds (including those not shown in Table S3) is 0.61 wt.%, meaning that the fibre-reinforced thermoset is mostly an organic polymer. The thermoplastic has an even lower concentration of inorganic constituents (below 0.5 wt.%); meanwhile, the fabric-reinforced thermoset has several times higher concentration due to the addition of MoS_2 as a solid lubricant and CaCO_3 as a filler in the material [20].

Results show that the fibre-reinforced thermoset contains sulphur (S), which is potentially used as a curing agent of the epoxy resin [32]. Others have reported phosphorus/sulphur-based curing agents of epoxy resin [33-34]. Hence, the detected phosphor (P) in the material could also be used as a curing agent of the epoxy resin. Silicon (Si) was one of the detected elements in the material with a concentration of 0.03 wt.%, similar to the fabric-reinforced thermoset [20]. The elemental analysis does not provide information on structure or bonds of the component containing silicon in the material. It is possible that silica (SiO_2) is added to the material in order to enhance the mechanical properties, as it is a common filler in thermoset composites [35-38]. It is also possible that polysiloxane is added to the epoxy resin to improve its toughness [38-39]. Antimony trioxide (Sb_2O_3), used as a flame retardant in polymers, has previously been reported in [40-41], which could explain the detected antimony (Sb).

Lancaster [42] reported that small amounts of impurities are almost inevitably present in graphites that are used as fillers in polymers. These impurities can be abrasive towards the metal counter surface, especially in dry bearing design [42], and can also affect the properties of the graphite even at trace levels, such as iron (Fe), magnesium (Mg), and manganese (Mn) [43]. Hence, it is of interest to investigate presence and concentrations of impurities in a self-lubricating polymer-bearing material to aid the interpretation of the tribological results. Compared to the fabric-reinforced thermoset (11) and the thermoplastic (6) [20], the fibre-reinforced thermoset shows the highest number of traced inorganic elements (12) with concentrations above 0.001 wt.% (Table S3), especially in comparison to the latter. The majority of these elements are consistent with the reported metallic impurities found in graphite using similar measurements technique, such as aluminium (Al), Mg, Ti, Fe, Sb, Cu, and Mn [44-48]. The presence of impurities in the fibre-reinforced thermoset is also confirmed by XMT analysis (Figure S2), where impurities in the material are visible following EDS analysis (Figure S9).

However, it is also possible that some of the detected elements originate from external contamination during machining of the polymer pins. For the fibre-reinforced thermoset and the thermoplastic, Fe, Mg, Mn, and Ti were attributed to potential contamination during the preparation of the polymer pins [20]. However, these pins were machined in a different workshop; hence, the level of introduced contaminations can differ. Concentrations of Fe, Mg, and Ti are several times higher for the fibre-reinforced thermoset compared to the fabric-reinforced thermoset and the thermoplastic. This can be explained by impurities from graphite and/or a higher ability for the impurities to stick to the surfaces of the fibre-reinforced thermoset. According to the manufacturer of the fibre-reinforced thermoset, the

finished sliding layer, as well as the reinforcement fibres, are generally roughened or fibrous [18]. This, explains why a higher concentration of contaminations during machining of the polymer pins can stick to the surface even after the ultrasonic cleaning.

Approximately 78 % of the detected concentrations of inorganic constituents presented in Table S3 are potentially originated from impurities in graphite or contaminations during the sample preparation. Meanwhile, significantly lower concentrations are detected in the thermoplastic (15 %) and even lower in the fabric-reinforced thermoset [20]. This is mainly attributed to the addition of graphite in the epoxy resin of the fibre-reinforced thermoset.