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Running-In Effects of Lubricated Polyether Ether Ketone on Steel for Different Spreading and Sorption Tendencies

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Abstract: Polyether ether ketone is a highly resilient thermoplastic that can withstand as an unfilled or filled polymer tribological high loads in high-temperature applications, as it has a high glass and melting temperature. Currently, it attracts interest as a lubricated material for drive systems to minimize noise, as a lightweight solution improving the CO_2 balance, or in combination with novel lubricants. We have produced friction and wear maps with pin-on-disk tests on steel axial bearing rings and investigated the interaction and running-in behavior with different lubricants, such as different polyalkylene glycols, polyalphaolefin, and various esters. In general, the behavior of polyether ether ketone is hardly influenced by the frictional heat when loaded at room temperature. It shows a lubricant-specific polymer transfer and surface softening. This running-in impact is enhanced if a loading strategy with initial high friction power is applied. The beneficial transfer forms on the track in mixed lubrication on the rough counterpart until an increasing adhesive contact limits this effect. The appearance of a minimal wear coefficient was found below the glass temperature with lubricants strongly sorbing in polyether ether ketones, such as polar polyalkylenglycol or trimellitic acid ester-based lubricants. Using the interfacial energy of the system to derive an energy term describing the tendency to form a stable transfer, systematic trends in the tribological behavior of polyether ether ketone and polyketone could be identified that can be projected on other systems.

Keywords: spreading; sorption; transfer; mixed lubrication; wear; polymer; run-in; surface hardness; lubricant substitution

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1. Introduction

Thermoplastic polymers are increasingly used in mechanical engineering for materials that experience tribological loads. As a result, lightweight and energy-efficient products or components with excellent performance in terms of noise, vibration and harshness are obtained. The use of lubricated polymers in tribological applications is complex [1] and remains an active area of research. The complexity arises in part from the interaction between the polymer, the lubricant, and the friction partner, steel. Observations of polymer transfer [2] and polymer "temperature hotspots" [3,4] during frictional loading in lubricated systems indicate that the adhesive coefficient of friction (COF, friction or μ) measured at static friction contributes to the tribology of polymers. In addition, physicochemical interactions between the friction partners, such as the sorption of the lubricant in the polymer and vice versa, must be considered.

As a result, a good insight into the complex polymer–lubricant interaction is a prerequisite for designing reliable lubricated drive elements with thermoplastic polymers. The analysis of the surface and interfacial energies and the thereof derived energies (e.g., spreading energy and "solving" energy) can be considered as a "screening tool" to obtain a first selection of promising polymer–lubricant combinations. The need for such a tool becomes more evident if the transition to a sustainable economy is considered: in order to use polymers of biological origin or biodegradable lubricants, a range of sustainable lubricants must be considered to find the optimum combination of lubricant and polymer. In addition to the rheological properties of the lubricant and the mechanical properties of the polymer, the instantaneous and long-term interactions between the lubricants and the polymers in contact must also be considered. The surface and interfacial energies [5] of the lubricant and tribological partners can provide initial insight into the performance of the tribological system and the "aging behavior" of the lubricant and polymer. The spreading tendency of the lubricant influences the adhesive contact of the friction partners and the polymer transfer and wear behavior. The interaction tendency of lubricant and polymer determines the dissolving, dissolution, adsorption, physical absorption and softening behavior [6] that influences polymer transfer, fatigue, abrasive and adhesive wear and friction. For example, the higher elastic deformability of a softened polymer surface reduces local stresses in tribological contact. However, an increased effective contact area can lead to increased friction and thermal overloading.

A thermoplastic, or thermosoftening plastic, is a plastic material, a polymer, that becomes pliable or moldable above a specific temperature and solidifies upon cooling. Samyn [7] showed for POM-H that for tribologic loading a softening region can be found in between mild wear and severe wear with melting phenomena. Supporting this, Clerico found a significantly decreased friction coefficient when POM was loaded above the polymer yield strength [8].

The investigated polyether ether ketone (PEEK) is a high-performance thermoplastic that is—both in its unfilled and filled state—very resistant to wear in extreme applications due to its high glass transition T_{glass} and melting temperatures T_{melt}. Depending on the cooling rate, different morphologies are created for PEEK such as Victrex 450. Victrex polymers are offered with different melt viscosities depending on thermoplastic process requirements that result in increased wear resistance at higher melt viscosities. Melt viscosity increases from the easy-flowing PEEK 90 polymer to the standard viscosity PEEK 450 to the highly ductile PEEK 650 polymer. The products are usually melt-filtered to unfilled granulate, ground to fine powder or compounded with various fillers. In the work of Harris et al. [9], the variation of the crystalline fractions of Victrex 450 was investigated, where a degree of crystallinity of 30–40% was usually detected. The crystalline forms are described as spherulitic and contain at least two different crystallization structures. The prepared samples post-crystallize when heated beyond the glass transition, e.g., at temperatures of ~170 °C [10]. Upon further temperature increase, the melting of crystals sets in above 300 °C until the melting temperature is reached at ~340 °C. All these effects have an influence on tribological behavior when higher mechanical and thermal conditions are applied.

For example, Zhang et al. investigated for neat PEEK the change in friction and wear rate at different normal forces and sliding velocities against 100Cr6. They found essentially an increase in the wear factor k ($\mathrm{mm^3/Nm}$) with increasing normal force F_N and velocity v [11]. The wear factor is already proportional to F_N and v, so Zhang inferred the contact temperature as an influencing variable. In later work, the contact temperature was therefore specifically adjusted. The wear factor showed a maximum just below the glass transition temperature T_{glass}, then formed a minimum above T_{glass}, at which point a maximum value of the friction μ was observed [12].

The behavior of PEEK depends on the composite strategy [13]. For example, CF-reinforced PEEK shows a lower scuffing resistance than neat PEEK, while its sliding and microwear resistance increases. This can be compensated by adding PTFE and graphite.

A review of friction and wear of PEEK has been presented by Mir et al. [13] and others. Lu et al. [14] investigated the friction and wear behavior of PEEK and composites with PTFE and C-fibers and found for low molecular weight PEEK with fillers an increasing wear factor k with temperatures up to 220 °C. He found for higher molecular weight PEEK 150 at 100–200 °C a decreasing wear factor k, and in the investigated PEEK composites an optimum C-fiber content of 10 vol.% and an optimum PTFE content of 10–20 vol.%. For application at higher temperatures, PTFE can be replaced by sulfide or graphite solid lubricants. For a sulfide-based PEEK composite, an optimum filling of 3 vol% nano-zinc sulfide was found with minimal wear rate in contact with steel by Knör et al. [15]. Although the stiffness was increased by the filling, the composite used retained its tensile strength and resistance to mild abrasive contact. Molybdenum disulfide (MoS_2) is a widely used solid lubricant [16] that can form several different possible structures (polytypes) and it can operate from temperatures below room temperature as well as high temperatures. According to Savan et al. [17] 200 °C can be withstood by MoS_2 without a reduction in shear stress. However, when loaded, the friction decreases with increasing contact pressure.

Pedroso et al. have investigated other materials besides PEEK for coating applications and observed superior performances of PEK in terms of friction, and PEKK in terms of wear [18].

A polymer transfer for dry contacts has been observed and discussed in the scientific literature for some time [19]. For PEEK in dry contact, the effect of asperite loading on the formation of transfer layers formation has been investigated [20]. In addition, the molecular weight and also the specific batch of PEEK have an influence on the wear and transfer behavior [21]. Optimally run-in dry systems were investigated for PEEK-PTFE composites [22]. A reduction in the wear rate by a factor of $>10^5$ was achieved.

In comparison, the evidence for polymer transfer in lubricated spreading systems is sparse. For PA46 against steel with PAO lubrication, the transfer for a spreading system could be proven via the transfer of radioactively marked nano-Fe fillers to the wear track, as well as via nitrogen enrichment in the transfer track [2]. In the current work, the polymer transfer of lubricated PEEK and the effect of the lubricant-induced surface softening of PEEK on the formation of a transfer layer is investigated.

- One hypothesis to be tested is whether the tendency to form a transfer layer can be affected by a specific loading strategy.
- Furthermore, it will be tested whether or not the time development of the build-up of a transfer layer depends on the local interaction between asperites and polymer and the already present transfer layer.
- The third hypothesis which will be tested is whether an altered wear behavior in the glass transition temperature region can be detected for lubricants that are strongly absorbed in PEEK.

For all the above-stated research questions it will be investigated whether interfacial- and surface energies and the subsequently derived energies such as the work of spreading, the work of solving and the energy term describing the tendency to form a transfer layer, can be used to obtain a first insight into trends of the frictional behavior of lubricated PEEK- and PK-systems.

2. Materials and Methods

Tribological experiments were conducted on a lubricated poly(ether ether ketone) (PEEK)– or polyketone (PK)–steel tribosystem. Unfilled PEEK 450sf (PEEK, T_{glass} at 160 °C) and filled PEEK MoS (10% MoS), PEEK TRM, X (10% graphite, 10% TiO_2, 10% ZnS) and PEEK TRM, XS (20% carbon fiber, 10% graphite, 1.5% MoS_2/WS_2) was obtained from Ensinger GmbH (Nufringen, Germany) and unfilled AKROTEK PK-VM natur 4774 (PK, T_{glass} at 15 °C) was obtained from AKRO-PLASTIC GmbH (Niederzissen, Germany). Pentaerythrite ester (PEEs), trimellitic acid ester (TSEs), polar and non-polar polyalkylenglycole (pPG and nPG) and synthetic base oil (PAO) were obtained from Klüber Lubrication München SE & Co. KG (München, Germany). The oils were chosen such that one group of liquids with comparable viscosity for high temperatures and one group of liquids with comparable viscosity for room temperatures were obtained. The PEEK and PK samples (see Figure 1) were prepared in the form of rectangular plates (6 mm × 3 mm × 15 mm) or pins, which were cut from tapered tensile test specimens (PEEK) or from molded plates (PK) (height 4 mm, diameter 5 mm).

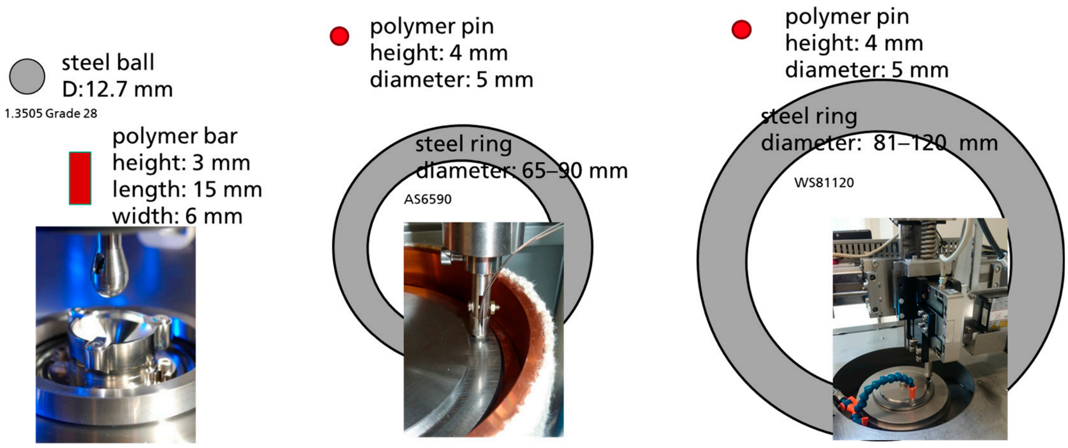


Figure 1. Tribological testing set-up: ball-on-plate and pin-on-disc experiments and polymer discs after cutting out of specimen (pins and bars).

The polymer specimens at the ball-on-plate test were in contact with a steel tribosystem with a 100Cr6 steel ball (diameter $\frac{1}{2}$ inch, R_a = 0.15 µm: R_z = 1.4 µm, R_{ku} = 3.85, R_{Pc} = 37/cm), which was integrated into the tribometer and used as a tribological partner. Wave washer INA WS81120 with technical roughness (diameter of track 110 mm, R_a = 0.23 µm, R_z = 1.86 µm, R_{ku} = 5.4, R_{Pc} = 131/cm) was used for contact with PEEK and axial bearing rings INA AS6590 with technical roughness (diameter of track 82 mm, R_a = 0.27 µm, R_z = 2.4 µm, R_{ku} = 4.0, R_{Pc} = 193/cm) were used for contact with PK and both were used as a tribological partner for pin-on-disc tests.

2.1. Tribological Experiments

Ball-plate tests (Figure 1) were used to perform oscillatory tribological tests. For this purpose, a rotational rheometer developed by Anton Paar GmbH, Ostfildern, Germany, was used by means of a tribological measuring unit. More detailed descriptions can be found in the preceding paper [23]. Conducting tests in this manner allows friction data to be recorded in the areas of static friction and boundary lubrication.

For this paper, only the results of continuous gliding mode tests (stribeck mode), are shown. For these tests, conventional unidirectional rotational experiments are conducted with steadily increasing gliding speeds ranging from 0.1 µm/s to 1.4 m/s. For a detailed description of the experimental set-up, we refer to the previous study [5].

Pin-on-disc tests for different sizes of steel bearings as the counterpart (Figure 1) were used to characterize the lubricated polymer contact. One tribometer can be used for high loads and medium temperatures and one for medium loads and high temperatures. Carrying out a continuous measurement of the pin height with an inductive displacement transducer, wear depths > 0.1 µm can be recorded.

Friction and wear maps were recorded to be able to choose a suitable loading scenario for the run-in condition. The 3-factor model (5) and (6) was chosen to describe the resulting dependence of the friction and wear coefficients (Table 1). Both factors had to be used to describe the transition behavior in mixed lubrication with respect to viscosity η and the mechanical interaction intensity with respect to surface hardness H for all combinations of p and v using λ. This is the ratio of the effective roughness of both partners R_a to the characteristic film height $h = \eta v/p$. If this ratio is 1, predominantly hydrodynamic lubrication is achieved [24]. The applicability of the product approach of a "minimal" 3-factor model was already tested in the preliminary study [5] and applied to the selected systems via the generation of the friction and wear maps. In this way, the running-in behavior can be visualized by systematic deviations.

Table 1. Table of equations.

Property	Equation	
Interfacial energy	$W_{13} = 2 \cdot \sqrt{\gamma_{11}^{p} \cdot \gamma_{33}^{p}} + 2 \cdot \sqrt{\gamma_{11}^{d} \cdot \gamma_{33}^{d}}$	(1)
Spreading energy of system	$W_{spreading} = W_{12} + W_{33} - W_{13} - W_{23}$	(2)
Solving energy of lubricated thermoplastic	$W_{solving} \leq \gamma_{13} = 1/2W_{11} + 1/2W_{33} - W_{13}$	(3)
Transfer energy of system	$W_{transfer} = 2W_{solving} - W_{spreading} = W_{23} + W_{11} - W_{13} - W_{12}$	(4)
Minimal isothermal 3-factor model for mixed lubricated friction	$\mu \sim \left[\frac{R_a}{h}\right]^m \sim \left[\frac{1}{\lambda}\right]^m \rightarrow \mu_{crit}\left[\frac{p}{H}\right]^n \left[\frac{R_a}{\frac{\eta v}{p}}\right]^m$	(5)
Minimal isothermal 3-factor model for mixed lubricated wear	$\frac{\dot{w}}{v} \sim \left[\frac{R_a}{h}\right]^s \sim \left[\frac{1}{\lambda}\right]^s \rightarrow k_{crit}\left[\frac{p}{H}\right]^r \left[\frac{R_a}{\frac{\eta v}{p}}\right]^s$	(6)

2.2. Indenter Measurements

The test was performed with a Vickers indenter using a Fischerscope H100C Xyp. At a load of 75 mN, indentations of several µm are achieved in engineering thermoplastics. Twenty indentations produce one measured value. Marten's hardness can be directly derived from the applied force F and the indentation depth h: HM = F/26.4 h^2 [25].

2.3. Contact Angle Measurements

Using a contact angle measurement device produced by Data Physics GmbH, Filderstadt, Germany, 2 µL sessing droplets were placed. Three standard liquids (water [26], ethylene glycol [26] and diiodomethane [27]) were used to characterize the unknown surface and interfacial energies. The droplet profile is recognized and recorded by the software of the instrument, and the contact angle is calculated automatically. All the calculations and interpolations were carried out according to Equations (1)–(4). A detailed description of the procedure was given by Wahed et al. [23].

3. Results and Discussion

Contact Angle Measurements and Interaction Energies

The results of the contact angle measurements can now be used to calculate surface- and interfacial energies ($W_{spreading}$ (2), $W_{solving}$ (3)). The procedure was described in detail by Wahed et al. [23], and the resulting energies are summarized in Table 2.

Table 2. Table of lubricant characteristics and interaction energies of neat thermoplasts and steel (e.g., hvPAO is of higher viscosity than PAO).

Lubricant or Body	**Viscosity**	**Cohesive or Surface Energy**		**PEEK**		**PK**	
	at 40 °C (mm^2/s)	**γ Polar (mN/m)**	**γ Dispersive (mN/m)**	**$W_{solving}$ (mN/m)**	**$W_{spreading}$ (mN/m)**	**$W_{solving}$ (mN/m)**	**$W_{spreading}$ (mN/m)**
PAO	30	0.6	31.5	-	-	6.4	9.8
PEE	23.5	0.7	31.6	-	-	6.0	9.0
nPG	30	0.27	30.1	-	-	7.6	11.7
pPG	30	1.4	34.7	-	-	4.8	7.1
hvPAO	66.1	6.5	30.9	4.1	−1.1	-	-
hvTSE	70.8	5.7	33.2	3.2	−1.6	-	-
hvPEE	52.7	5.7	32.3	3.3	−1.7	-	-
hvnPG	120.6	6.8	33.1	4.0	−1.0	-	-
hvpPG	97.8	2.4	38.9	0.74	−2.1	-	-
PEEK	-	0.5	40.5	-	-	-	-
PK	-	4.2	29.3	-	-	-	-
Steel	-	6.8	25.2	-	-	-	-

The sorption of lubricant in the polymer is determined by the matching of the disperse polar interactions and hydrogen bonds (which are usually neglected) between the molecules.

Solution and sorption are subject to the same driving forces. The corresponding interactions are expressed in terms of $W_{solving}$. An increasing value of $W_{spreading}$ indicates a reduced tendency to spread, so that separation of the adhesive solid contacts becomes more difficult, and friction increases. The hidden mechanisms in tribology can be described via their equilibrium behavior by rate processes [28] of the different energy states [29]. In the same way, the formation of a stable transfer film originating from the polymer and adhering to the steel frictional partner can be described. In the first step (Figure 2), $W_{solving}$ describes the tendency to dislodge polymer fragments from the polymeric frictional partner. If the polymer fragments adhere to steel, the stability of the transferred film is described in terms of $W_{spreading}$, in the same manner as for the original frictional contact between polymer and steel. A stable transfer film is thus obtained for a high solving tendency and a low spreading tendency. The corresponding "work" of the formation of a transfer film $W_{transfer}$ can be expressed with $W_{solving}$ and $W_{spreading}$ (4).

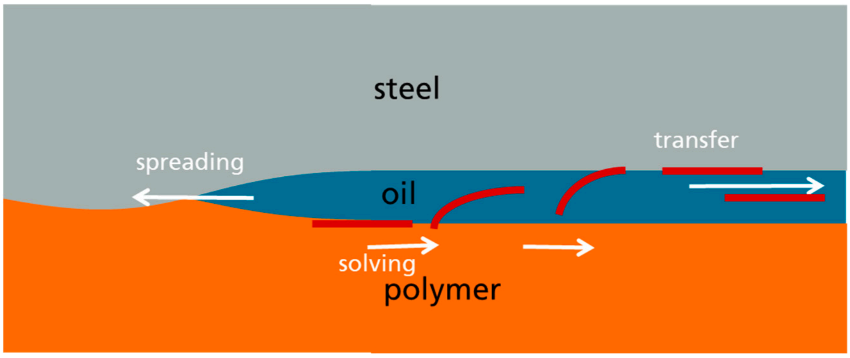
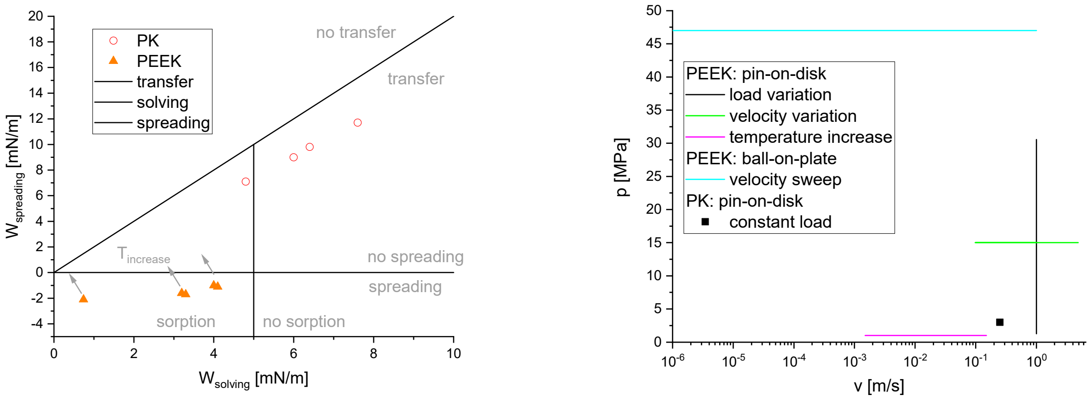


Figure 2. A schematic picture for adhesive even contact describing the formation of a stable transfer film.

For the interaction energies studied at room temperature (Figure 3a), the effects on the thermoplastics are different due to the different mobility of the amorphous phase, as their glass temperatures are different (T_{glass} (PEEK) = 160 °C, T_{glass} (PK) = 15 °C). The systems with PK should have a strong transfer tendency due to their low spreading tendency. However, according to our own experience, only the pPG oil has a sufficient solving and sorption tendency for PK ($W_{solving} < 5$ mN/m [6]). The systems with PEEK have a high solving tendency but the polymer chains are immobilized in the glassy state and protected by a lubricant film due to the good spreading tendency of the system. However, it is still possible to form a stable, mechanical enforced transfer film (which might be created at high contact pressures which lead to a "squeeze-out" of the lubricant).

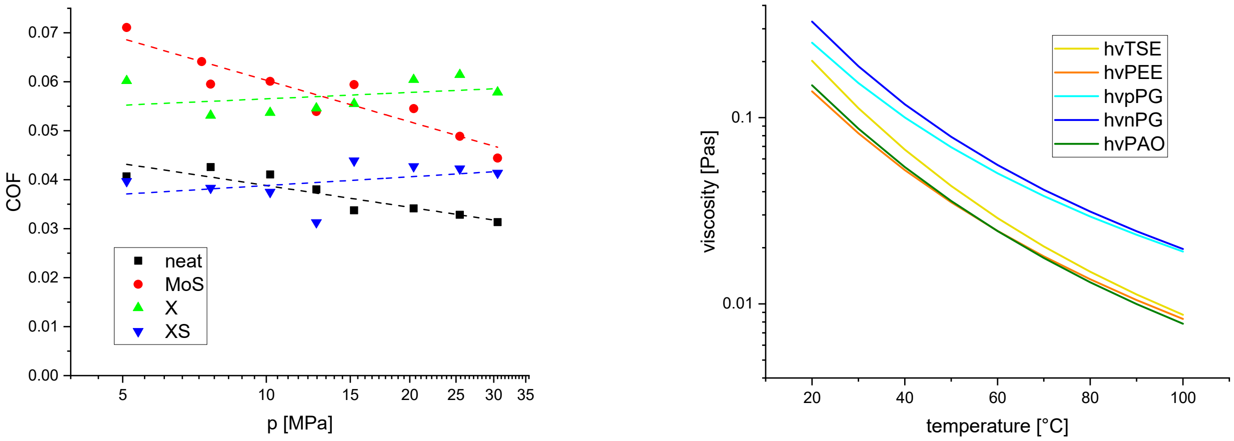
The systems are investigated at different loads depending on the focus of the investigation and the tribological method. An overview is given in Figure 3b.

The lubricant hvTSE was used as a "reference lubricant" since it has a wide application spectrum due to its higher viscosity and the wide temperature range it can be used in. hvTSE was also chosen to record wear and friction maps of the PEEK systems. To be able to evaluate them systematically, the proportions of the friction (5) and wear model (6) are factorized. The COF decreases with increasing pressure (Figure 4a) for PEEK systems without microfillers (as for neat and MoS) since with increasing pressure the possible shear stress in the bulk is limited by its strength. In contrast, the COF increases with increasing pressure for the PEEK systems with microfillers (as for XS with CF and X with TiO_2), due to the reinforcing effect in the bulk. The pressure dependence of the COF was determined by increasing the load at a gliding velocity v = 1 m/s and the load dependence was fitted according to the factor in (5). The resulting factor on contact pressure p was used to normalize the friction with an emphasis on the dependence in mixed friction (dependence on λ). Not only the pressure dependence but also the different viscosities and their temperature dependence must be considered. The viscosity data were provided by the lubricant supplier Klüber Lubrication München SE & Co. KG (Figure 4b).



(**a**) (**b**)

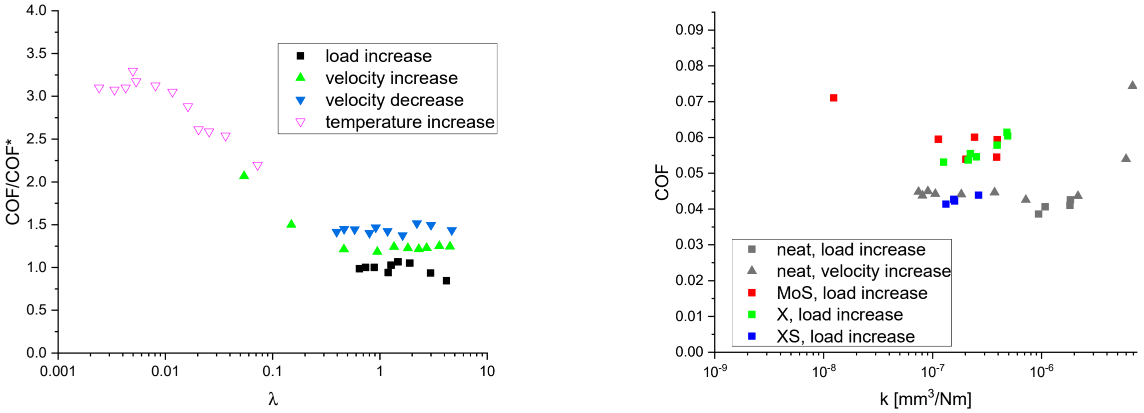
Figure 3. Schematic overview: (**a**) region of interaction energies of the lubricated systems at room temperature separated by lines and the arrows for PEEK indicate the extrapolation guess for increased temperatures, (**b**) loading regimes of increasing and decreasing series, sweeps and constant conditions of the applied tests in this paper.



(**a**) (**b**)

Figure 4. Load dependent parameter according to the tribologic model: (**a**) load dependence of friction of neat PEEK and composites on contact pressure when lubricated with hvTSE at v = 1 m/s by a load increase series and the polynomial fit (broken line), (**b**) temperature-dependent viscosity of oils with higher viscosity for calculations of the mixed lubricated condition.

Depending on the design of a sequence of load levels of pressure, speed or temperature, different running-in behavior is expected. To test the dependence of the tribological behavior in the mixed lubrication regime on the history of load application from low to high pressure, the already fitted pressure dependence (Figure 4a) must be used to normalize friction for all increasing and decreasing series (Figure 5a). The remaining differences after factorizing the results according to the factor model (5) can be attributed to the changed running-in behavior.

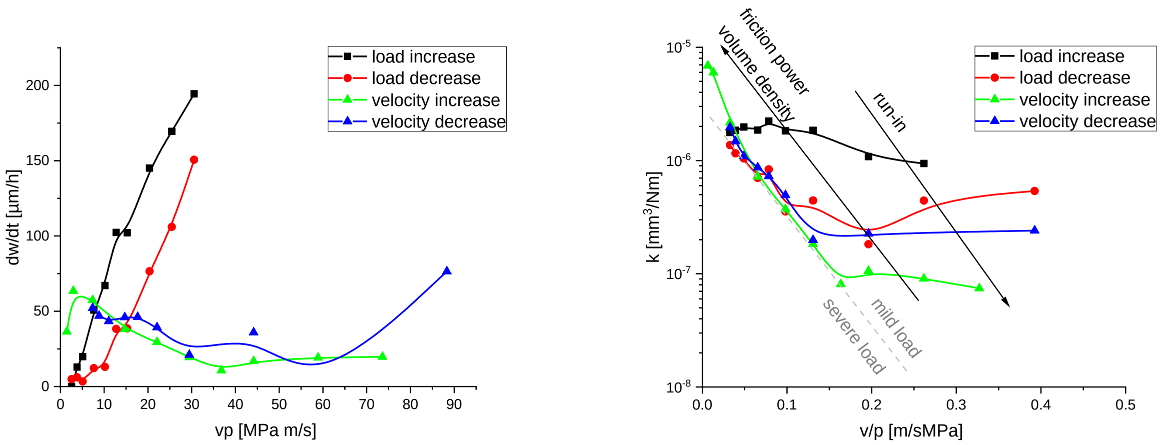


(**a**) (**b**)

Figure 5. Friction correlation: (**a**) friction factor of mixed lubrication (see Equation (5)) with hvTSE and neat PEEK at different series; (**b**) friction and wear coefficient correlation of neat PEEK and composites when lubricated with hvTSE at different running-in series.

This dominance in the friction behavior is similarly found in the wear behavior (Figure 5b). For neat, X, and XS PEEK systems, a predominant increase in the wear coefficient *k* with a coefficient of friction *μ* is observed. It is not surprising that there is no clear overload transition for PEEK which would result in a decreasing friction coefficient at high wear. Indicatively, this decrease was obtained for neat PEEK for steps of velocity increase. PEEK MoS shows such an overload behavior: the COF decreases with increasing wear factor. However, this behavior is expected: the surface active MoS component is mechanically overloaded on purpose and results in a reduction of the frictional forces as it is known for neat MoS_2 [17].

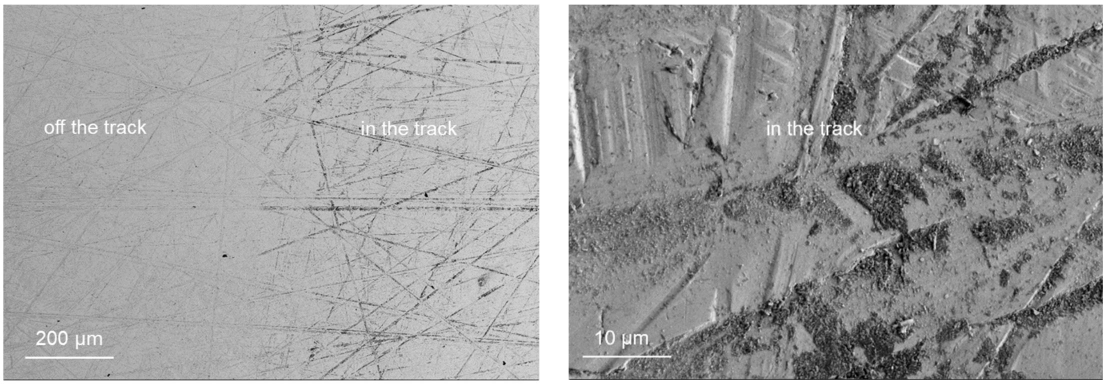
As was the case for friction behavior, the wear behavior was factorized into a product of an abrasive component (Figure 6a) and a mixed lubricated friction component. (Figure 6b) via the model that describes $1/v \times dw/dt = k \times p$ (5, 6). The series of the load variation is dominant for the first factor and that of the velocity variation for the second factor. In the depiction of the mixed friction dependence (Figure 6b), a positive running-in behavior with a velocity variation becomes clear, especially with increasing velocity and thus increasing film fraction. If a theoretical film formation *h* in the mixed friction and the tribological loading power *pv* are described as friction power volume density, then a decreasing friction power volume density *pv/h* is advantageous for the running-in behavior resulting in a lower wear coefficient. In other words, it is advantageous to rub with a higher friction power volume density at all or at the beginning and intensify the possible interactions such as polymer transfer or morphological changes. In this way, a condition is created in the contact that appears like a significantly reduced solid–solid contact in the mixed lubricated friction, similar to a reduced roughness. Above a certain severe boundary load (below a certain v/p ratio) a universal material-dependent tendency to wear seems to dominate. This boundary load should be equivalent to the boundary friction and absence of film formation or dominant solid–solid contact.



(**a**) (**b**)

Figure 6. Dominance of wear behavior for neat PEEK lubricated with hvTSE (**a**) pv-dependence of wear rate, (**b**) dependence of wear coefficient on mixed lubrication. Arrows indicate the impact of the expected run-in and friction power volume density.

After lubricated contact with PEEK, the steel surfaces clearly show polymer transfer into the surface structures of the ground surface (Figure 7). However, despite the good tendency to spread, the transfer takes place at the correspondingly high mixed friction load.

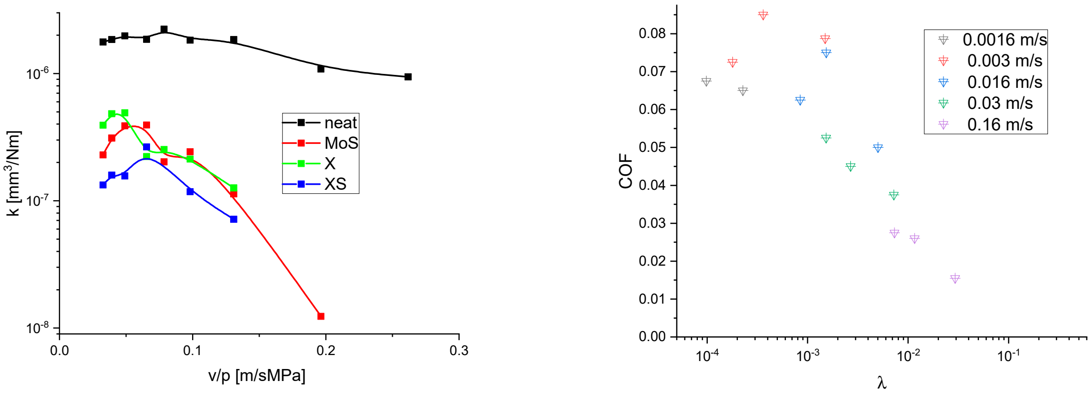


(**a**) (**b**)

Figure 7. Scanning electron microscope views of steel surface after running-in of neat PEEK with hvTSE (**a**) off and in the track and (**b**) high magnification view of polymer transfer in the track.

The wear coefficient of the different PEEK systems lubricated with hvTSE decreases at first glance if PEEK systems with fillers are tested. However, it is noticeable that a MoS-filled PEEK has as low a wear level as the composite X with TiO_2 as a microfiller (Figure 8a).

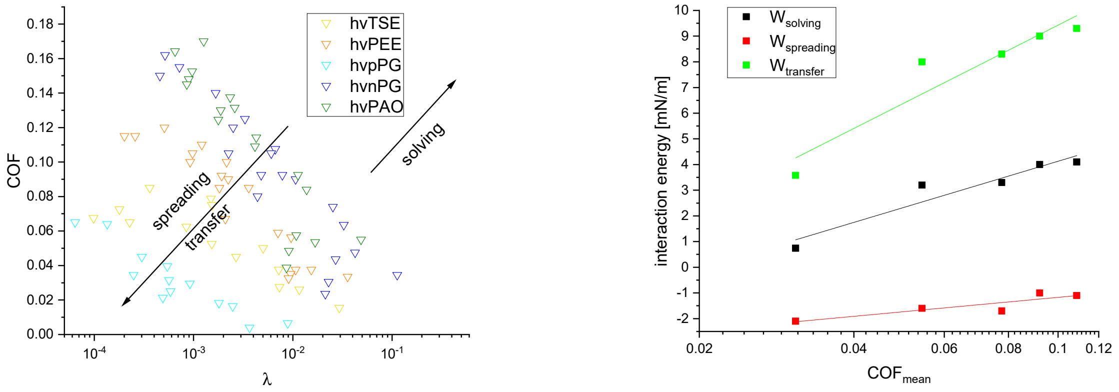
To efficiently test the friction behavior of the PEEK system for the mixed friction range with a single test strategy in a short time, a temperature-induced viscosity decrease (by increasing the temperature) was used to scan the mixed lubrication regime. Along with an increase in temperature to 140 °C, the same sequence of velocity variations was repeated. In this way, at a constant contact pressure of 1 MPa (Figure 8b), the different lubricants were efficiently tested.



(**a**) (**b**)

Figure 8. Maps for lubrication with hvTSE: (**a**) for dependence of wear coefficient on mixed lubrication for different PEEK systems; and (**b**) for viscosity dependence of mixed lubrication by temperature sweeps for velocity variation.

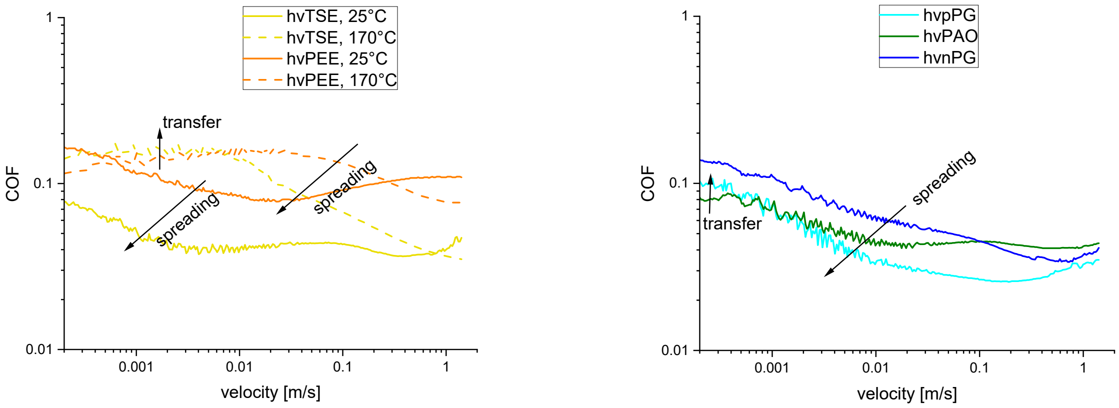
In this way, the running-in strategy of a velocity decrease is imitated, but the neat PEEK is also loaded from room temperature to temperatures just below its glass temperature, where particularly intensive running-in processes can be assumed. Indeed, for the lubrication with either the highest spreading or transfer tendency, reduced friction is found for hvpPG and hvTSE (Figure 9a). This systematic dependency on these energies is found for all lubricants (Figure 9b). A reduction in friction would be expected for increased spreading or transfer, but an increase in solving and sorption should increase friction—Figure 9b indicates therefore that transfer or spreading dominates the frictional behavior.



(**a**) (**b**)

Figure 9. Dependence of mixed lubrication by temperature and velocity variation for neat PEEK on steel (**a**) for each lubricant and (**b**) in correlation with interaction energies. Arrows indicate the impact of the expected interaction energy (solving, spreading, transfer).

To check whether spreading or transfer is dominant, the adhesion is tested for different temperature ranges with the ball-on-plate method. For this method, the "rough interaction" of the steel surface is very low based on previous experience with the method and the device. The high sensitivity of this method complements the energetic evaluation of the lubricated systems. For the ester oils, a comparison can be made at 25 °C and 170 °C due to their higher temperature stability (Figure 10a), whereas the other oils decompose at this high temperature.



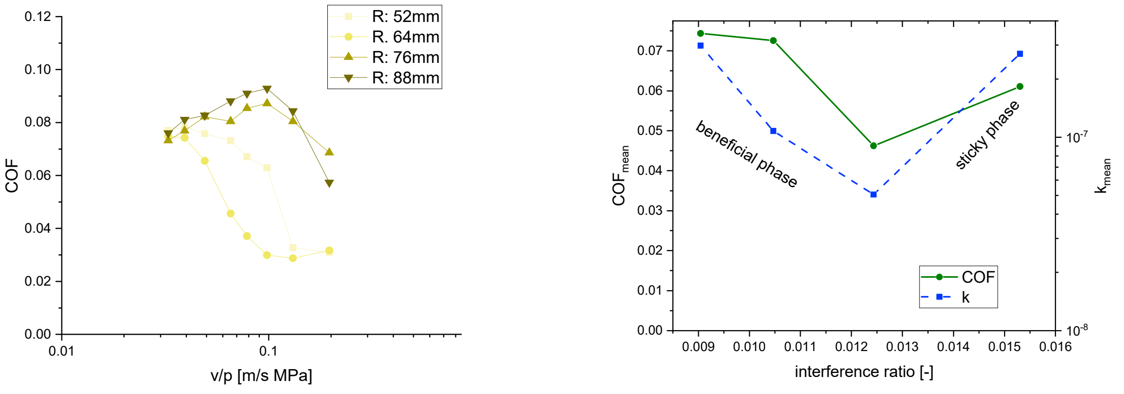
(**a**) (**b**)

Figure 10. Ball-on-plate test in stribeck mode for a PEEK on steel system (**a**) for ester-based oils, (**b**) for oils with less temperature stability at 25 °C. Arrows indicate the impact of the expected interaction energy (spreading, transfer).

The assumption that a better spreading tendency of hvTSE calculated for room temperature was confirmed by reduced friction compared to hvPEE. However, a reverse situation occurs at 170 °C when the friction of hvTSE exceeds that of hvPEE. At this temperature, increasing dominance of another mechanism can be assumed. The obvious assumption would be an increasing tendency for polymer transfer as the glass transition temperature was exceeded and the amorphous phases became mobile. For the oils hvpPG, hvPAO and hvnPG only the room temperature measurements could be considered, and accordingly for these one can confirm a friction reduction for lubricated systems with an increased tendency to spread (Figure 10b).

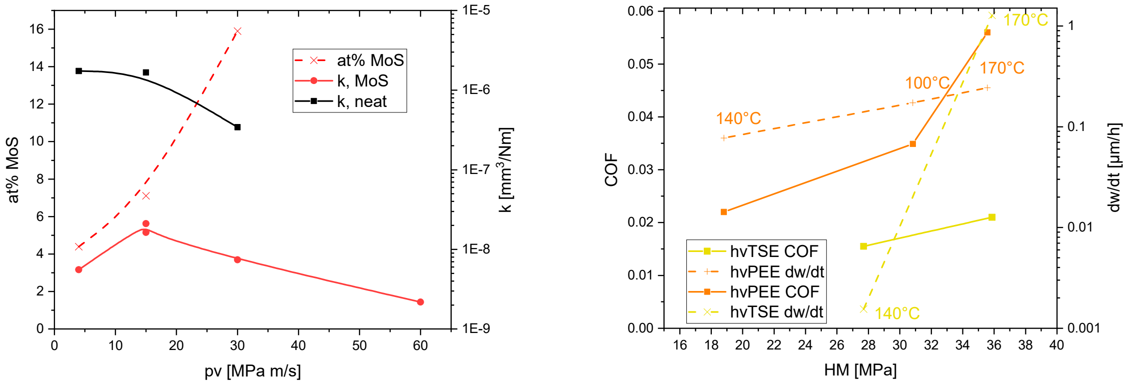
The effect of the run-in and the probable polymer transfer can also be checked by radius runs on a uniformly ground disc by changing the interference ratio of track length in contact. This is the ratio of pin diameter D and track length l (D/L). The tests were conducted at the same velocity, contact pressure and distance. A clear mixed friction dependence was found for all radii and a minimum friction value for a medium radius of 64 mm (Figure 11a). The reduced friction was also confirmed by averaging with a reduced wear coefficient. Such a minimum can only be explained by enhanced transfer behavior, which leads to increasing sliding distance to excessive adhesion and a further increase in friction and wear (Figure 11b).

The extent to which the transfer behavior depends on the applied power pv while keeping the gliding distances constant was examined for PEEK neat and PEEK MoS (Figure 12a). For MoS, it is possible to measure the transfer of MoS from the Mo signal by photoelectron spectroscopy (in at %) and even quantify it in comparison. Thus, an incipient reduction of the wear coefficient with an increasing transfer was confirmed.



(**a**) (**b**)

Figure 11. Radius runs on a uniformly ground disc: (**a**) mixed lubrication regime for neat PEEK with hvTSE, (**b**) mean friction and wear coefficient dependent on interference ratio.



(**a**) (**b**)

Figure 12. Running-in analyses by (**a**) dependence of wear coefficient at increased applied power for hvTSE lubricated systems; (**b**) by correlation to changes of surface hardness of neat PEEK.

If the running-in is not only a consequence of the polymer transfer but also of a change on the polymer surface, such changes can easily be determined by surface-sensitive indentations with depths of 5–10 µm via indentation with a Vickers indenter (Figure 12b). The Martens hardness is the directly measured quantity and decreases for loads just below the glass transition temperature. At the same time, friction and wear decrease. In this case, it can be hypothesized that the surface is toughened, in the sense that the interaction of the lubricant leads to uptake and necessary mobilization of the polymer phase which can better withstand the asperity interference by viscoelastic and not plastic deformation. A second possible explanation of the observed behavior is a reduced asperity interference caused by the formation of a transfer film. If the temperature is raised above the glass transition temperature to 170 °C, the surface hardness increases with friction and wear. It can be assumed that the usually not completely crystallized PEEK materials will crystallize at this load by a combination of mechanical and solving-induced mobilization. This behavior was repeatedly obtained for hvPEE. A similar increase at the transition to 170 °C was found for hvTSE.

If all lubricants, as well as PK and PEEK, are considered (Figure 13), the change from systems with low transfer tendency and spreading properties to those with increased transfer tendency and non-spreading properties becomes apparent. For the latter, the wear rate increases again, as excessive transfer behavior leads to an increase in adhesion, and thus increased friction and wear.

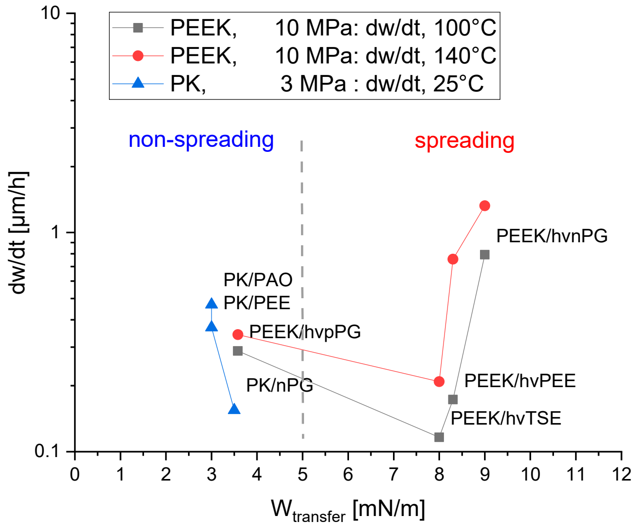


Figure 13. Overview for tendency to transfer for PEEK and PK neat systems.

4. Conclusions

Neat polyether ether ketone was found to be mechanically resistant even at loads up to 30 MPa contact pressure. This result is consistent with the scuffing strength and thermal resistance found in the literature. It is known that dry-loaded polyether ether ketone has a reduced tendency to wear at its glass transition temperature. Likewise, polyether ether ketone was known to form polymer transfer under dry tribological loading.

Since PEEK shows a good spreading tendency for the tested lubricants, a relevant transfer tendency at low loads is not likely. However, since PEEK can be subjected to very high pressures without thermally overloading, an adhesive contact can be forced under these conditions. As a result, a polymer transfer to steel was observed for all lubricants. The tendency to establish a stable transfer resulting in a significant change in the wear coefficient was examined for different running-in strategies. It was found that “high boundary friction loading,” i.e., high pressure and low velocity, was the most efficient loading scenario to achieve this goal. This significantly reduced wear tendency can be explained by the support of the lubricant film by the transfer. In addition, a favorable surface softening by the lubricant was observed. This favorable softening is unlike the typical softening-induced wear increase for other thermoplastics such as polyoxymethylene or polyamide. An even more pronounced reduction in wear was now observed for lubricated conditions directly below the glass transition temperature of PEEK when the amorphous phase obviously can be mobilized by rubbing in oil.

The calculation of transfer stability was performed for polyether ether ketones in comparison to polyketones. They have a similar chemical structure and the interaction energies of the tested set of lubricants show a similar trend. The relevant difference between the systems is, that for PK, the lubricants lie in the non-spreading regime, whereas they lie in the spreading regime for PEEK. As a result, a high tendency to form a transfer film is predicted for PK which explains the increasing wear tendency observed in the experiments.

Future testing of run-in strategies and pretreatment approaches for polyether ether ketone-based components will be of interest. Since a systematic change has already been obtained for polyketone, an extension of the understanding of other polyaryl ether ketone thermoplastics would be beneficial.

A beneficial use of molybdenum disulfide as a solid lubricant in polyether ether ketone was found that did not disturb the polymer transfer. Consequently, the wear reduction of the filling with molybdenum disulfide was on a comparable level as for PEEK composites based on hard microfillers.

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