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# **The Tribological Behaviour of Carbon Fibre Reinforced Polyaryletherketones (PAEKs) through their Glass Transitions**

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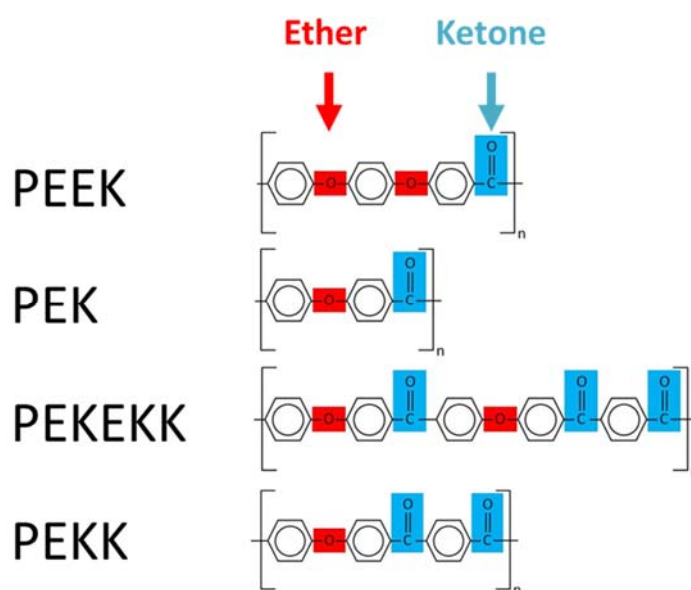
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## **Abstract**

Advanced engineering polymers of the Polyaryletherketone (PAEK) family with carbon fibre reinforcement are finding application in engineering systems as tribological bearing surfaces under severe operating conditions that cyclically move the polymer into and beyond the glass transition temperature region. To support such an application, the friction in high speed and low load PAEK-steel sliding contacts was investigated both unlubricated and lubricated with a tri-nonyl trimellitate ester, a base fluid for high temperature industrial lubricants. Four polymers in the PAEK family, PEEK, PEK, PEKEKK and PEKK, with 30%wt of carbon fibre whiskers were tested against an AISI 4140 steel disc. When unlubricated, low friction depended upon the formation of a PAEK transfer film on the steel disc and when this became unstable in the glass transition region the friction increased to much higher levels with associated polymer surface damage. Frictional heating due to the high sliding speed dominated the differences in glass transition behaviour between the four PAEKs. When lubricated, the lubricant film controlled friction and there was no significant effect of the glass transition of any of the PAEKs. The irreversible nature of the glass transition in PAEKs in such tribological applications, due to high surface damage at high temperature, means that it is essential to ensure effective lubrication in both fluid film and boundary lubrication.

## 1 Introduction

Polyaryletherketones (PAEKs) are semi-crystalline thermoplastic polymers that are finding increasing use across industry. PEEK is the most commonly used of the PAEK family. However, efforts to develop the performance of these materials have resulted in the use of other polymers in the family. PAEK polymers are made by polymerising phenolic and benzaldehyde ring molecules in different proportions to give a family of materials whose structural unit consists of aromatic rings that are connected by ether and ketone linkages in varying proportions, Figure 1. The properties that differentiate their performance from other polymers are that they have high mechanical strength and are extremely resistant to most chemicals. The melting points of PAEKs are also higher than many other engineering polymers and so PAEKs are often employed in systems at elevated temperatures.



**Figure 1: Example Monomers of Polyaryletherketones**

The main variation in properties between the various PAEKs is in their thermal behaviour. By varying the proportions of ether and ketone in the polymer, the melting point,  $T_m$ , and glass transition temperature,  $T_g$ , can be varied. The lower the ether to ketone ratio, the higher the  $T_g$  and  $T_m$ , Table 1. The glass transition is the temperature range through which the amorphous regions in the polymer increase sufficiently in energy to change the properties of the polymer from a brittle glass at low temperature to a softer, rubbery solid at high temperature. This change manifests itself as a change in many mechanical properties such as the storage modulus (elastic modulus under shear) [1, 2], the Young's modulus (elastic modulus under extension) [3], yield stress [4] and the thermal expansion coefficient [4]. The glass transition has both thermodynamic and kinematic aspects and can occur over a range of approximately 50°C, the mid-point of which is termed the glass transition temperature,  $T_g$ . Whilst the transition in most of the properties is gradual, a more precise glass transition temperature can be established by measuring the viscoelastic response of the polymer. This can be achieved by Dynamic Mechanical Analysis (DMA) using ASTM D7028-07e1 [5] and ASTM E1640-13 [6], where the glass transition is marked by a clear peak in the Mechanical Loss Factor ( $\tan \delta$ ) [1, 2].

PAEK	Ether : Ketone	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)
PEEK [4]	2	143	343
PEK [4]	1	157	374
PEKEKK [4]	0.67	162	387
PEKK [7]	0.5	165	357

**Table 1: Glass Transition Temperatures and Melting Points for Various PAEKs**

PAEKs are finding use in an increasing number of tribological systems as metal substitutes. Their high mechanical strength, high melting temperatures, low density (relative to metals) and chemical resistance make them suitable for systems where these properties are not achievable using other thermoplastics, particularly in high temperature systems. In almost all tribological applications, PAEKs are used with fibre reinforcement to reduce friction and wear. Glaesser reported that a 30%wt fill of carbon fibres is optimal for this purpose under typical conditions [8]. Glass fibres are also found to be effective in reducing wear rates [9] whereas carbon fibres are more suitable for reducing friction [10] and wear [9-11] under some conditions. In many systems, PAEKs are used without a liquid lubricant and in such cases a solid lubricant is also often added to the polymer to further reduce friction e.g. graphite [11-17], PTFE [11-14, 16-21], molybdenum disulphide [16, 22], or a combination [11, 12, 17]. Some systems are also liquid lubricated [23-25] and, as may be expected, solid lubricants are not typically used in these situations.

Typical tribological conditions where PAEKs find the most common use are low speed (0.1 – 1 ms<sup>-1</sup>) and low contact pressure (0.25 – 2 MPa). However, some systems use PAEKs in more extreme conditions, such as high speeds of up to 10ms<sup>-1</sup>, which normally require liquid lubrication to function reliably.

Some authors have reported that there is a significant difference in tribological behaviour below and above the glass transition temperature, T<sub>g</sub>, of the particular PAEK used [11, 26-28]. As can be seen in Table 2, the nature of these changes depends upon the contact geometry and reinforcement of the PAEK matrix. Under all reported conditions, the wear rate increases above T<sub>g</sub> and in most cases the friction coefficient decreases. These changes are attributed to the increased abrasive wear and reduced shear strength of the PEEK as it softens above T<sub>g</sub>. Using an indenter, Briscoe et al [3] reported that the interfacial shear strength between PEEK and the counterface reduces significantly above T<sub>g</sub>. The work of Friedrich et al, using a PEEK pin sliding on a steel disc [11, 29], is representative of the typically encountered tribological mechanisms. He observed adhesion, abrasion and surface melting, that the friction coefficient was lower above T<sub>g</sub> and that the wear rate was higher because of the lower shear strength of the PEEK above T<sub>g</sub>. Under these conditions, unreinforced PEEK, especially with solid lubricants added, had a lower wear rate. The influence of solid lubricants in this study may have been the cause of this apparently counterintuitive result. Under most conditions, however, when shear strength has a significant influence, fibre reinforcement reduces wear rate significantly.

In comparison, Hanchi and Eiss [27] used a steel ball on a PEEK disc and the wear rate below T<sub>g</sub> was lower when carbon fibre reinforcement was used. However, above T<sub>g</sub>, the friction coefficient for unreinforced PEEK was approximately a factor of 3 higher than below T<sub>g</sub>. However, the friction coefficient above T<sub>g</sub> was a factor of approximately 2.5 lower for carbon fibre reinforced PEEK than below T<sub>g</sub>. Under these conditions, the ball ‘ploughed’ the PEEK disc surface,

using the terminology of Hanchi and Eiss. Thus, above  $T_g$ , as the polymer softened and the shear strength reduced, the energy required to plough the reinforced disc surface decreased. Conversely, the increased wear depth of the unreinforced polymer increased the contact area between the ball and disc and, though the shear strength of the polymer had reduced, the greater contact area increased the work rate required to plough the disc, increasing the resistance to motion. These results are supported by those of Zhang et al [28], who considered unreinforced PEEK only.

Reinforcement	Material	Contact Geometry	Performance Above $T_g$ versus Below		Source
			Friction Coefficient	Wear Rate	
Carbon Fibres	PEEK and PEK with PTFE, Graphite	PAEK Block on Steel Disc	Lower	Higher	Friedrich et al [11]
Carbon Fibres	PEEK	Steel Ball on PEEK Disc	Lower	Higher	Hanchi and Eiss [27]
Unreinforced	PEEK with PTFE and Graphite	PEEK Block on Steel Disc	Lower	Higher	Friedrich et al [11]
Unreinforced	PEEK	Steel Ball on PEEK and PEEK coated Disc	Higher	Higher	Hanchi and Eiss [26] [27], Zhang et al [28]

**Table 2: Relative Tribological Performance of PAEKs Above and Below Glass Transition**

In a separate study, Briscoe et al, using a 6.5mm steel blade/wedge sliding on a PEEK disc at  $0.45 \times 10^{-3} \text{ ms}^{-1}$  and 10N normal load, examined the variation of friction coefficient with gradually increasing system temperature [23]. A blade was chosen to reduce the effect of ploughing on the friction force, the authors having identified this as a factor when using a 6.5mm diameter steel ball. A decrease in friction coefficient at lower temperatures was observed and a large increase from 170 to 280°C. However, as it was the steel temperature which was measured, it was not possible to definitively correlate this behaviour with a specific thermal transition in the polymer. When a model lubricant was used, a reduction in friction coefficient was seen under some conditions. However, other conditions and lubricants produced an increase in the coefficient of friction.

In many reported studies of unlubricated PAEKs, transfer films of PAEK on typically steel counterfaces were shown to have a large effect on the friction and wear behaviour of the system [13, 30-32]. A stable transfer film can undoubtedly reduce friction and control wear [33] and is most effectively formed in unidirectional sliding as the polymer is predominantly transferred to one flank of the counterface asperities. Reciprocating sliding, on the other hand, does not produce such a thick transfer film [15]. Transfer film material is often highly aligned, which influences their friction and wear reduction [33, 34]. The presence of a liquid lubricant can inhibit the adhesion of wear particles to the counterface, preventing transfer film formation [24, 33] and yielding extremely high wear rates, particularly at higher loads [20, 25].

Some industrial systems use PAEKs at typical temperatures of 130 to 180°C and there is concern about the variation in tribological properties in the glass transition region itself, as well as above and below it. This study, therefore, considered the changes in the tribological properties of PAEKs in as well as around the glass transition region, including both lubricated and unlubricated conditions to identify any differences in frictional behaviour that may occur.

## 2 Experimental Method

The principal aim of the investigation was to observe and characterise the changes in the frictional response that occurred from an initially stable tribological system, representative of high speed and high temperature industrial applications, as the system temperature was increased through the glass transition region. A pin-on-disc tribometer, Figure 2, was used with a 10mm diameter, flat faced PAEK pin loaded against an AISI 4140 steel disc with a controlled initial surface roughness of  $0.6\mu\text{m R}_A$ . PEEK, PEK, PEKEKK and PEKK were evaluated, all with 30%wt of carbon fibre whiskers approximately  $200\mu\text{m}$  long were evaluated. Two features of this apparatus were designed to simulate a typical industrial system that uses PAEKs under such conditions. First, the system temperature was controlled by heating the air in an insulated enclosure around the pin-on-disc contact. Second, when lubricated, the contact was not flooded but instead lubricant was fed onto the leading edge of the pin using a syringe pump at 0.20 ml/hr. Because of the low flow rate, the lubricant was reasonably assumed to be supplied to the contact at the enclosure air temperature without the need to heat it externally.

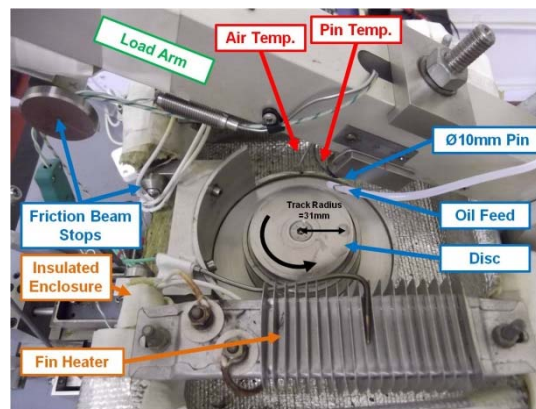
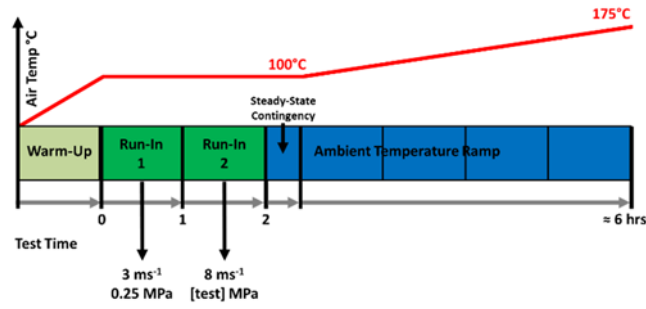
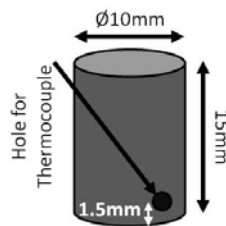


Figure 2: Pin-on-Disc Tribometer

The standard test procedure followed is shown schematically in Figure 3. The stationary machine was warmed up for an hour to allow the enclosure to reach 100°C. Then the lubricant feed (if used) and the disc drive motor were started, running in the samples for an hour at low sliding speed ( $3\text{ms}^{-1}$  at the pin centre) and low contact pressure (0.25MPa) so that a stable friction coefficient was reached. The speed was then increased to  $8\text{ms}^{-1}$  and the contact pressure to the test value. After an hour or after the friction and component temperatures had reached a steady-state, whichever was later, the enclosure temperature was set on a programmed linear ramp from 100 to 175°C over a 4 hour period. During this time, no other parameters were changed.



**Figure 3: Schematic of Test Procedure**



**Figure 4: PAEK Test Pin Geometry**

The friction, the enclosure air temperature and the pin temperature were recorded throughout each test. The pin temperature was measured using a thermocouple in a hole drilled to the centre of the pin 1.5mm from the running face, Figure 4, giving a near-contact region temperature. The temperature of the disc was not recorded during this work as the most thermally critical component in this system was the polymer. Also, the wear of the pin and the disc were not quantified. As previously discussed, the wear rates of PAEKs vary significantly above and below  $T_g$  and a test duration average would therefore have little meaning in these particular experiments. Also the formation of polymer transfer films on the disc complicates the quantification of wear.

#### **Trinonyl Trimellitate Ester**

Kinematic Viscosity @40°C (cSt)	<b>91.9</b>
Kinematic Viscosity @100°C (cSt)	<b>10.2</b>
Viscosity Index	<b>90</b>
Density @20°C (g/cm <sup>3</sup> )	<b>0.983</b>
TGA Onset of Oxidation (@10°C/min) (°C)	<b>258</b>

**Table 3: Test Lubricant Data**

The lubricant used was a trinonyl trimellitate ester and the key data for this synthetic lubricant base fluid are shown in Table 3. This type of fluid is typically used in formulated products for high temperature industrial systems. In order to eliminate the effect of chemically or physically formed additive films on the surfaces, the base fluid alone was used. Because of the low but continuous supply of lubricant to the contact, there was no observed failure of the lubricant even though some decomposition of the lubricant in the contact was inevitable.

### 3 Results

#### 3.1 Full Test Sequence

A typical test sequence result for an unlubricated test is shown in Figure 5, in this case for PEK at 0.5 MPa. There are four distinct phases evident in the results:

**Phase 1.** This period exhibited the typical behaviour expected of running-in in any engineering system, with an initially high coefficient of friction that quickly decreased as early life wear progressed and then stabilised.

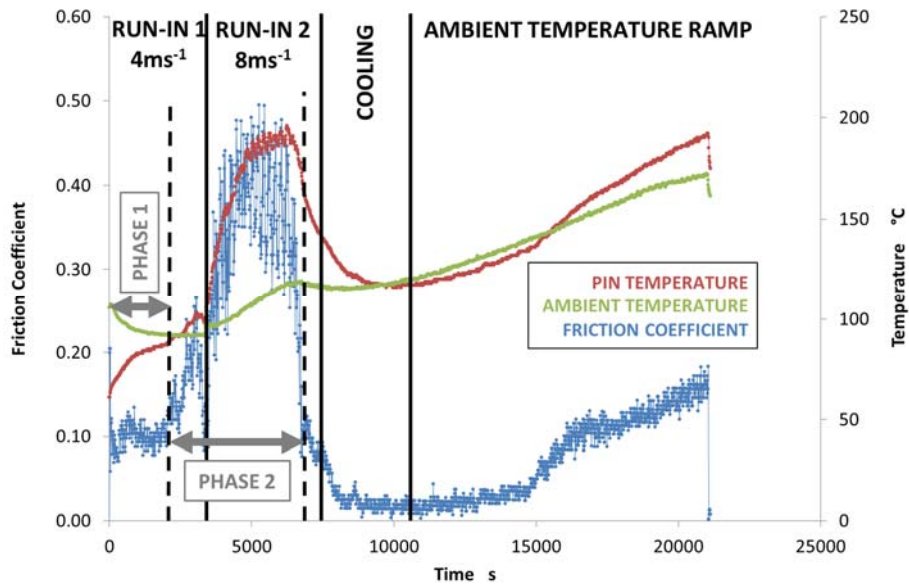
**Phase 2.** Subsequently the friction coefficient increased dramatically along with the pin temperature. This period of high friction persisted typically for one hour. In many tests, repeated sudden friction rises and subsequent falls were observed, each lasting around 20 to 60 seconds.

So in effect there were two distinct stages of running-in behaviour, Phase 1 and 2. However, their occurrence did not correlate with the two running-in sets of operating conditions shown in Figure 3, Run-in 1 and 2, as can be seen in Figure 5. Furthermore, estimation of the energy dissipation through the contact area based on the measured friction did not identify a critical frictional energy for the onset of Phase 2 behaviour. To investigate further, an experiment was stopped a few minutes into this phase and the pin and disc surfaces are shown in Figure 6 and Figure 7. They show that a thin transfer film has formed across much of the wear track on the disc and there is also a large smear of polymer across a portion of the wear track. The pin surface shows a large quantity of pulled out fibres and an uneven surface that indicates uncontrolled large-scale removal of material from the surface, which has then been smeared on to the counterface. This suggests the transfer film formation described by Stachowiak [35] as the wear mechanism occurring 'at temperatures slightly below the transition to continuous melting wear', Figure 8. In this, the accumulation of frictional heat at the PAEK surface leads to accumulation of an increasingly large molten layer on the pin surface. This layer then fails under shear and is smeared onto the disc surface, as witnessed in Figure 6. This smear is then spread evenly across the wear track area by repeated passes of the pin. In short, this process, when repeated, is how the stable polymer transfer layers in these tests were formed. In a transfer film, an interface of molten polymer provides a low shear strength layer that provides effective lubrication between the surfaces. A stable transfer film is, therefore, a film of sufficient thickness that the molten layer does not form an interface with the steel surface, such that a polymer-polymer interface results.

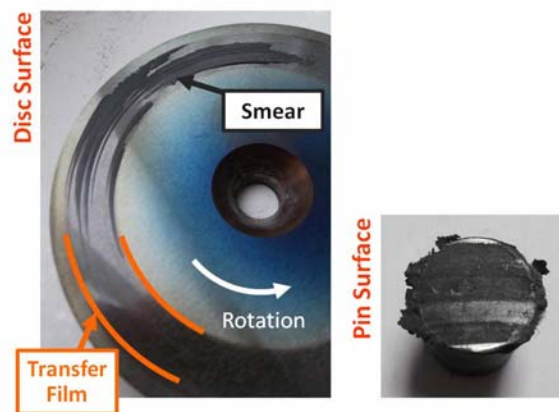
**Cooling.** When a stable transfer film had formed, the friction coefficient reduced dramatically and the cyclic large-scale wear described above apparently ceased. As the frictional energy generated reduced, the pin cooled until thermal and tribological equilibrium was again achieved.



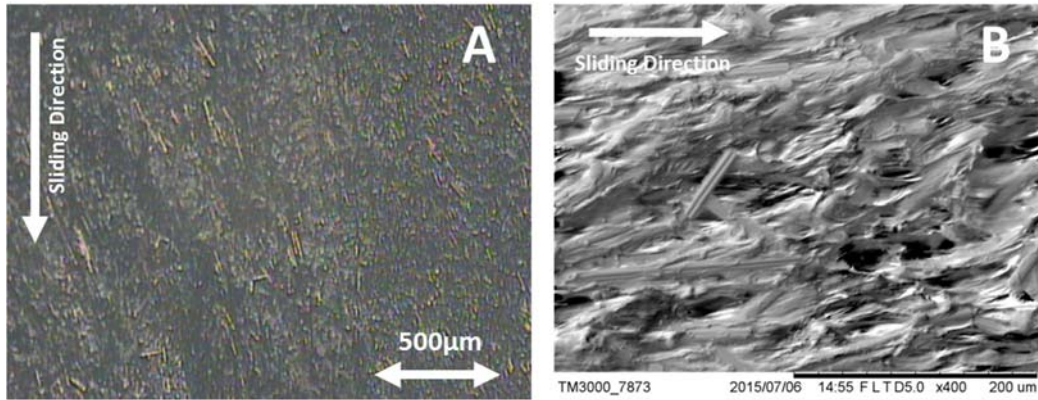
**Ambient Temperature Ramp.** When equilibrium was reached, the enclosure temperature ramp was begun. During this phase, in the unlubricated case of Figure 5, the increase in enclosure and pin temperature resulted in an increase in friction coefficient.



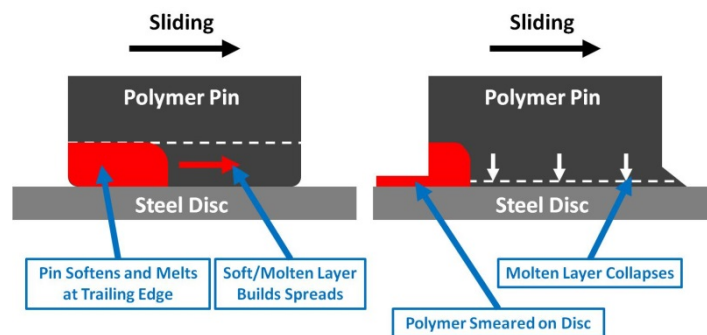
**Figure 5: Full Test Sequence Result for Unlubricated PEK at  $8\text{ms}^{-1}$  and  $0.5\text{ MPa}$**



**Figure 6: PEKEKK Steel Disc and Pin Surfaces for Unlubricated Sequence Halted during Phase 2**



**Figure 7: Detailed PEKEKK Pin Surface for Unlubricated Sequence Halted during Phase 2:  
A) Optical Microscope; B) Scanning Electron Microscope (SEM)**



**Figure 8: Mechanism of PAEK Wear and Transfer Film Formation, after Stachowiak [35]**

The nature of the friction and temperature rise in Phase 2 is not one that is tolerable, advisable or feasible in an industrial application. The formation of a stable transfer film would have to occur at lower load and speed over a longer duration. However, in the context of this work, this phenomenon was tolerated as it shortened the duration of the tests and was generally repeatable for the unlubricated tests.



**Figure 9: PEEK Pin after Failure During Phase 2 at 1MPa**

The exception to this pattern was the test for unlubricated PEEK at 1MPa, where under these conditions the wear during Phase 2 was catastrophic, Figure 9. This reflects the fact that the decrease in ether to ketone ratio decreases the melting point of the polymer and, by inference, the maximum frictional energy that can be dissipated through the PAEK before gross melting. Thus, considering that PEEK has the lowest melting temperature of the PAEKs here, it is clear that, under these conditions, the temperature of the pin was sufficient to cause a critically large molten region around the con-

tact, leading to a catastrophic wear rate. The frictional energy dissipated was therefore sufficient for PEEK to reach the regime of ‘continuous melting wear’ described by Stachowiak [35] but sufficiently low that the other PAEKs were kept in the discontinuous melting regime described above. As the frictional energy dissipation in Phase 2 was calculated to be approximately similar in all tests, this indicates that there is a significant difference in the maximum operating temperature and maximum friction energy dissipation tolerable between the PAEKs tested.

A typical lubricated test sequence, for PEKK at 1 MPa, is shown in Figure 10. Several differences are apparent between the profile of the lubricated test and the unlubricated equivalent, Figure 5. First, the dramatic Phase 2 of running-in is not present suggesting no transfer film was produced on the steel counterface. This was confirmed by the post-test condition of the pin and the disc shown in Figure 11. Thus, the run-in process simply constitutes the removal of the highest asperities from each surface until greater conformance and lower abrasive wear occurs, Phase 1 as described in the lubricated tests. Second, there is little variation in the friction coefficient as temperature increases during the ambient temperature ramp. The Scanning Electron Microscope (SEM) image in Figure 11 shows some evidence of plastic flow, indicating that local regions in contact with the steel surface initially flow plastically under the action of shear and heat. This yields a relatively uniform and stable polymer surface which allows an effective lubricant film to form, reducing the subsequent rate of PEKK deformation and wear.

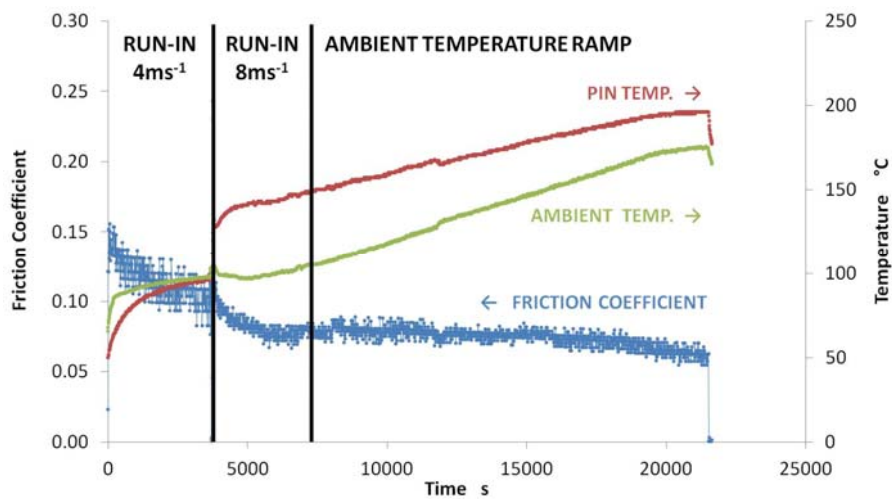


Figure 10: Full Test Sequence Result for Lubricated PEKK at  $8\text{ms}^{-1}$  and 1 MPa

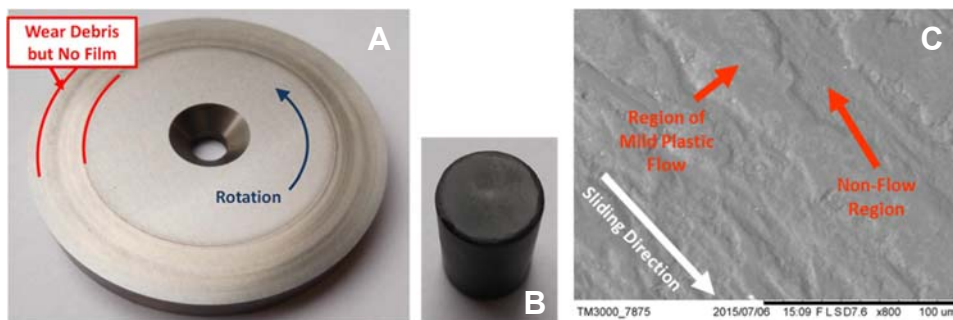
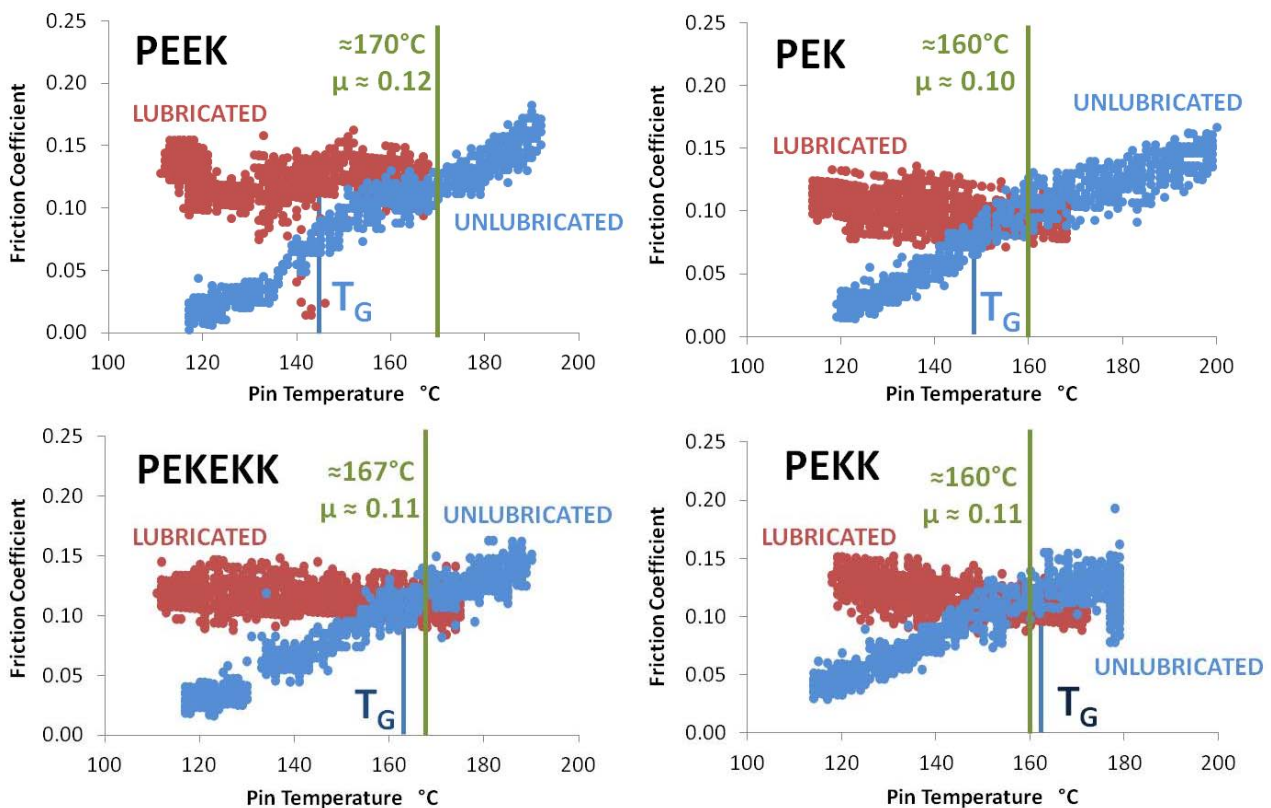


Figure 11: Example Steel Disc (A) and PEKK Pin Surface, Optical (B) and SEM (C), after a Lubricated Test

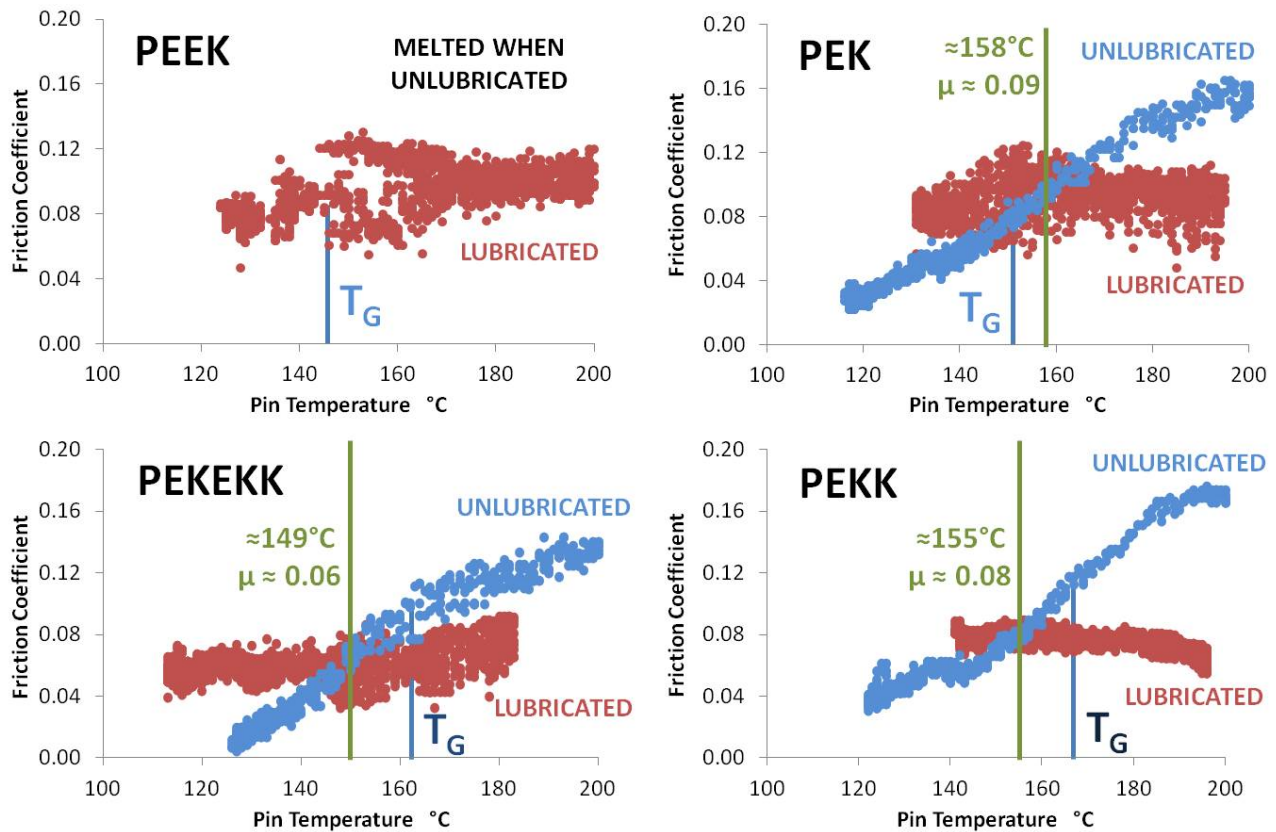
### 3.2 Variation in Friction Coefficient with Temperature

During the ambient temperature ramp phase of the test sequence, all operating conditions except temperature were kept constant, so the relationship between friction and temperature can be examined directly for the different PAEKs. The resulting variations in friction coefficient with pin temperature for four lubricated and unlubricated PAEKs are shown in Figure 12 and Figure 13 at 0.5 MPa and 1 MPa respectively.

In the unlubricated cases, there is a clear increase in friction coefficient as pin temperature increases and, above some upper critical temperature, the increase in friction coefficient either ceases or the rate of increase reduces. In several cases, below a lower critical temperature, a lower variation in friction coefficient with temperature was observed. Comparing these two regions of lower variation, the friction coefficient in the high temperature region is much greater than in the lower temperature region. Taking the example of PEK at 1 MPa, there is a factor of 5.3 difference in friction coefficient between these regions (120-200°C). The variation in friction coefficient between these regions is a largely linear increase with pin temperature and in all cases the  $T_g$  of the PAEK in question falls generally in the central region of this linear increase, as indicated in Figures 12 and 13. It therefore appears that this increase in friction coefficient with pin temperature results from the glass transition of the PAEK. Interestingly, the reduction in yield stress of a PAEK through the glass transition follows a similar but inverse trend to the variation in friction [4].



**Figure 12: Friction for Lubricated and Unlubricated PAEKs at 8ms<sup>-1</sup> and 0.5 MPa (green lines indicate the crossover point of the two curves and the corresponding conditions at this point)**



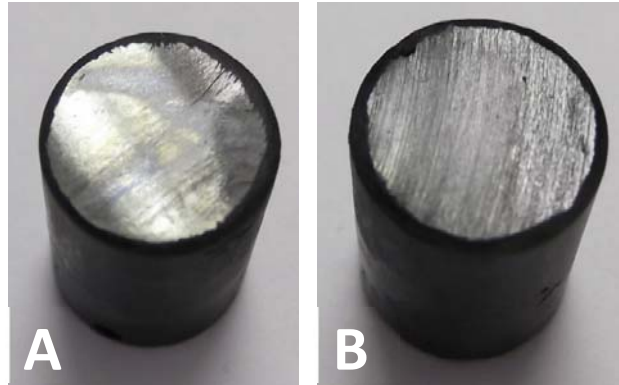
**Figure 13: Friction for Lubricated and Unlubricated PAEKs at  $8\text{ms}^{-1}$  and 1 MPa.**

**(green lines indicate the crossover point of the two curves and the corresponding conditions at this point)**

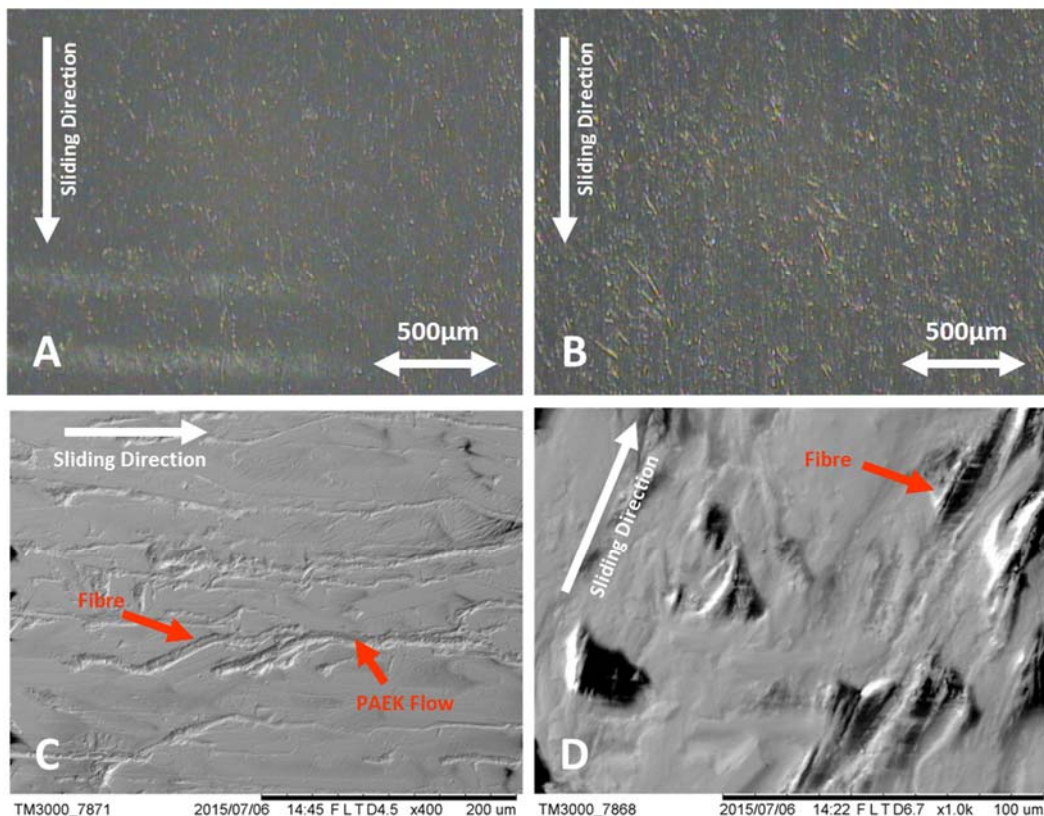
To explore the mechanisms that cause this transition more closely, two unlubricated tests were performed on PEK at a less severe  $4\text{ms}^{-1}$  and 0.25MPa using the same test sequence as before. In one, instead of imposing the ambient temperature ramp after the cooling phase, the enclosure temperature was retained at 100°C. In the other, the temperature ramp proceeded as normal from 100 to 175°C. The pin surfaces at the end of these tests are shown in Figure 14, with higher resolution images in Figure 15.

The fixed temperature condition produced a highly polished surface with highly aligned fibres. The fibres were largely intact, aligned with the sliding direction and located parallel with the surface. The SEM image (C) of Figure 15 shows some fibres that have not been aligned in the sliding direction with evidence of surface PAEK flow around their edges. A large quantity of polymer matrix is present at the surface, yielding a smooth finish. This indicates that, under these stable transfer film conditions, there was little interaction between the polymer and steel surface. Instead, a molten layer of polymer between the transfer film on the disc and the pin surface provided a low shear strength interface. The contact under these conditions is, therefore, a polymer-on-polymer system which produced an extremely low coefficient of friction, typically 0.02 - 0.04. The aligned fibres at the surface resist the flow of molten and softened polymer under shear, which prevents catastrophic flow and wear. This allows the transfer film to remain stable under more extreme conditions than would be achievable with unreinforced PEK, where the flow of molten polymer is not resisted by the

fibres [36]. Also, when reinforcement is present, frictional heat dissipation is increased compared to unreinforced PAEKs due to the increased thermal conductivity of carbon-fibre-reinforced composites [4], which reduces the build-up of heat at the interface and, thus, reduces the interfacial softening and melting of the PAEK for an equivalent thermal energy generation.



**Figure 14: Pin Surfaces of PEK at  $4\text{ms}^{-1}$  and  $0.25\text{ MPa}$  when A) Ambient Temperature Held at  $100^\circ\text{C}$  and B) Ambient Temperature Increased as per Figure 3**



**Figure 15: Detailed Pin Surfaces of PEK at  $4\text{ms}^{-1}$  and  $0.25\text{ MPa}$  when Ambient Temperature Held at  $100^\circ\text{C}$  (Optical Microscope (A) and SEM (C)) and Ambient Temperature Increased (Optical Microscope (B) and SEM (D)) as Figure 3**

Under the high temperature condition of the ambient temperature ramp, the pin surface shows a high degree of abrasion and melting of the polymer, Figure 14. The fibres are more extensively pulled out and there is more evidence of plastic flow of the PAEK at the sliding interface, Figure 15. This indicates that a stable transfer film was not formed at the higher temperatures and so there was a higher degree of interaction between the steel disc and the polymer pin surfaces with abrasive wear. Thus, at the high temperature condition, it is apparent that the molten or softened layer between the transfer film and pin surface had grown in size such that it is caused the whole transfer film on the disc surface to be molten or softened, producing a sliding interface between the steel disc and the PAEK. Thus, the more extensive flow of PAEK produced a polymer-on-steel contact. A PAEK-steel interface has a higher friction coefficient than a PAEK-PAEK interface, hence the higher friction coefficients observed at high temperature.

Several published mechanisms have been offered to explain thermal transitions in friction in this type of polymer. Briscoe et al [3, 23, 33] explained the increase in friction above a critical load or temperature as junction growth above the  $T_g$ . In this mechanism, as the near-contact area softens at high temperature, the polymer hardness decreases and the contact area increases. Thus, although the softening of the polymer surface reduces its shear strength, the contact area increase dominates and the friction force increases. This explanation was based upon lubricated tests and transfer film formation may not have been as extensive as the unlubricated tests in this study. The impact of the junction growth relies on an initially low contact area and, therefore, low adhesive friction. The stable transfer films observed under the low temperature condition here indicate a relatively high contact area and a molten interface. Thus, it is proposed that the increase in frictional energy dissipation observed cannot be related to a significant increase in contact area through the glass transition. The research of Briscoe et al appears to correlate the thermal transition in friction with the breakdown of a boundary lubricant film. Therefore, whilst the phenomena observed here are linked to near-contact glass transition, this transition appears to correlate with a transition to PAEK-steel contact rather than an increase in contact area. The junction growth phenomenon is probably more indicative of the spikes in friction and temperature and the wear seen in Phase 2 of running-in.

Rhee and Ludema tested a variety of polymers sliding on steel [37] and hypothesised that the a high polymer wear rate region was initiated when the cooling of the molten layer on the surface of the transfer film exiting the contact was insufficient to bring the temperature below the polymer melting/softening temperature before re-entering the contact. Under these conditions, the frictional energy causes melting of the pin surface only because the transfer film is already molten, producing a high wear rate. On the other hand, a stable transfer film occurs when the transfer film entering contact with the pin is sufficiently below the melting temperature and the frictional energy dissipated is sufficiently low that complete melting of the transfer film is not possible. It is important to note that the wear rate observed above the thermal transition by Rhee and Ludema was catastrophic [37]. Whilst the wear rate was not measured in this study, it is clear that wear was not catastrophic, except in one case for PEEK. The mechanism Rhee and Ludema described was based on melting rather than softening in the glass transition. Thus, whilst there are similarities with their work in terms of the thermal behaviour of the transfer film, the mechanism observed here is not based on melting of the near-contact region. The mechanism they describe is more indicative of the wear transition seen in exceptional case of the run-in failure of PEEK under the high load condition, as described earlier.

The transitions in friction coefficient with temperature in this study correlate best with the glass transition region rather than the melting temperature. This suggests that the transition observed here, whilst similar in outcome in some ways to Rhee and Ludema [37], is based on glass transition in the near contact region rather than melting. Calculating the frictional energy dissipated into the contact using the measured friction and imposed sliding velocity, the interface temperature can be estimated using the approach of Bhushan [38] under the ‘high contact stress’ condition. The theoretical interface temperature in these tests does not give a good correlation between the thermal transitions in friction and either the glass transition temperature or the melting temperature of the polymer. For example, the transition from low to high friction for PEKEKK at 1MPa and 8ms<sup>-1</sup> occurs between predicted interface temperatures of 120 and 260°C, a range that does not correlate with T<sub>g</sub> or T<sub>m</sub> regions. Thus, this phenomenon appears to be governed by near-contact phenomena rather than interface behaviour.

So whilst the mechanism involves transfer films, where the relative extent of melting/softening and plastic shear/flow are uncertain, the melting temperature of the PAEKs do not correlate with the frictional transition phenomena observed here. Also, the temperature range of the friction variation through the glass transition is greater than the glass transition temperature range for the corresponding PAEK. This can be explained by considering the frictional change as the progression of a PAEK glass transition spatially through the near-contact region.

Drawing on these observations, an alternative hypothesis is offered. Due to frictional heating there is a temperature gradient from the interface through the near-contact region to the bulk of the pin and, similarly, through the transfer film on the steel counterface. So a gradual increase in system temperature will cause an increasingly larger volume of the PAEK to soften during its glass transition. As the extent of softening in the near-contact region grows, the shear strength of the transfer film, in particular, will reduce significantly and plastic shear and flow of PAEK in the transfer film will occur within a greater volume of the transfer film. It is proposed that this will increase the likelihood of slip at the PAEK-steel interface and, therefore, the extent of PAEK-steel sliding in the interface. Therefore, the transition in this system, in particular the near-contact region, through the glass transition is defined by a transition from a polymer-on-polymer contact to a greater extent of polymer-on-steel contact with a consequent increase in friction.

This hypothesis helps explain why even though there are clear differences between the glass transition temperatures of the PAEKs tested, there is no significant difference between any of the friction coefficient versus pin temperature traces under the same given test conditions. As discussed, the reported glass transition temperatures of each of the PAEKs falls generally in the central region of the linear increase in friction coefficient. However, the significant fact seems to be that the glass transition temperature is greatly exceeded in all cases due to the high sliding speed in the contact and it is the friction generated as a result which dominates all these experiments, much more than subtle property differences between the PAEKs. Experiments at lower speeds may perhaps differentiate the PAEKs to a greater extent but this study was focused specifically on performance in industrial systems with high sliding speeds and low contact pressures.



### 3.3 Variation in Tribological Behaviour in Lubricated and Unlubricated Systems

The variations in friction coefficient with pin temperature, the near contact temperature, for the lubricated tests and their equivalent unlubricated tests are also shown in Figure 12 and Figure 13. The first and key observation is that there is no significant variation in friction coefficient with pin temperature for any of the PAEKs in lubricated tests under the same operating conditions. This implies stable tribological conditions and that the changes that transform the polymer through glass transition do not affect the friction coefficient as the near-contact temperature is increased. Therefore, at a given set of tribological conditions, the friction response is controlled by the action of the lubricant and the effectiveness of the lubricant film. As a logical extension to this, it would also appear that the variations in PAEK properties through the glass transition do not affect the lubricant nor the lubricant film significantly.

The lack of significant variation in the coefficient of friction with temperature indicates that there is no substantial degradation of the lubricant under these conditions, with a maximum ambient temperature of 170°C. This is as expected for a trinonyl trimellitate ester with a stated temperature for the onset of oxidation of 258°C, Table 3. More importantly, the lack of variation in friction coefficient with near contact temperature implies that variation in the viscosity of the lubricant is not a significant parameter. This along with the observed polishing of pin surfaces and lack of transfer films on the metal disc during these lubricated tests indicates that the contact was operating in the mixed lubrication regime. The friction coefficients for the lubricated tests in Figures 12 and 13 are consistent with mixed lubrication at the high sliding speed of these tests.

That the presence of lubricant has suppressed the friction coefficient increase with rising temperature when the system is operating in the glass transition region has significant implications for industrial systems operating under such conditions. This is in stark contrast to the unlubricated contact, where the friction coefficient increase with rising near-contact temperature due to the softening of the PAEK could produce thermal and tribological instability in dry and even marginally lubricated machinery. Small variations in system temperature could then be expected to cause significant changes in friction power loss, wear, and frictional energy dissipation as heat. The worst case would occur if thermal management of a system was insufficient and a feedback loop was created whereby increases in friction result in further increases in temperature, which further increases friction. Tribological conditions in such systems could rapidly become unmanageable and potentially dangerous.

When comparing the lubricated and unlubricated tests for different PAEKs under same conditions, there are several observations that can be made. Under low temperature conditions, when a stable transfer film was formed in the unlubricated contact, the friction coefficient of the unlubricated contact was lower than that of the lubricated contact. In contrast under high temperature conditions, when there was no stable transfer film in the unlubricated contact, the friction coefficient of the unlubricated contact was greater than that of the lubricated contact. Due to the nature of the trends with temperature, Figures 12 and 13, there is a point in the glass transition when the friction coefficients of both the unlubricated and lubricated systems are equal at a distinct crossover. The crossover temperature and the magnitude of the friction coefficient at this point are compared for each PAEK in Table 4, noting that unlubricated PEEK failed catastrophically at 1 MPa and so there is no crossover data for this case. There is generally no significant difference in either of these parameters for any of the PAEKs tested here at the same speed and load, with the possible exception of

PEKEKK at 1 MPa. This insensitivity to the precise PAEK is consistent with the previously discussed controlling influence of the high sliding speed in the unlubricated tests and the lubricant film in the lubricated tests.

PAEK	Sliding Speed (ms <sup>-1</sup> )	Contact Pressure (MPa)	Crossover			
			Pin Temperature (°C)	Standard Deviation (°C)	Friction Coefficient	Standard Deviation
PEEK	8	0.5	170	± 7	0.12	± 0.01
PEK			160	± 8	0.10	± 0.01
PEKEKK			167	± 5	0.11	± 0.01
PEKK			160	± 11	0.11	± 0.01
PEK	8	1.0	158	± 2	0.09	± 0.01
PEKEKK			149	± 2	0.06	± 0.01
PEKK			155	± 1	0.08	± 0.01

**Table 4: Temperature and Friction Crossovers for Lubricated and Unlubricated Tests**

It is evident from Figure 11 that when the contact was lubricated a PAEK transfer film was not formed. As described, a transfer film is formed by the melting and then physical and mechanical adhesion of PAEK to the steel surface. When a polar lubricant such as the ester in this study is present, it will physically adhere to the steel surface and inhibit the adhesion of PAEK as melt or wear particles to the steel surface. So in this instance generated wear particles should be entrained in the lubricant flow through and around the contact. The presence of polymer wear particles in the lubricant that drained from the contact in these experiments, Figure 16, supports this argument. Some authors report that, under such lubricated conditions, wear rates of PAEKs can be impractically high [23, 25]. However, this was observed particularly when the lubricant film broke down and was unable to prevent high wear [23, 25]. This was not the case in this study because the lubricant proved very effective in reducing friction. Other studies have observed similar beneficial tribological behaviour with suitable lubricants [23].



**Figure 16: Steel Disc after a Test but before Cleaning (PEK at 8ms<sup>-1</sup> and 1MPa) showing Wear Debris removed from the Contact Area**

## 5 Consequences for Polymer Applications in Tribology

Industrial systems utilise lubricated PAEK-steel sliding contacts where there is unavoidably boundary lubrication between the component surfaces in normal operation, for example during start-up or shut-down, or in the case of the breakdown of the fluid lubricant film, due to degradation or starvation. Under these conditions, the increase in friction, wear and temperature will be lower and less catastrophic with a PAEK-steel interface than for example with a steel-steel interface.

However, the frictional increase evident in an unlubricated PAEK-steel contact as the polymer passes through its glass transition and the protective transfer film is lost, will limit the effectiveness of this type of design as system performance demands increase, unless satisfactory lubrication can be assured.

Furthermore, generally the glass transition of a polymer is considered a reversible process where the material can alternate between a brittle glass at low temperature and a soft rubbery solid at high temperature. However, in tribology the damage that occurs to the surface at high temperature is retained at lower temperatures and so the behaviour can no longer be considered reversible, Figures 14 and 15.

So the industrial challenge is optimise the polymer properties and the lubricant to minimise the impact of operation at temperatures into the glass transition of the polymer, even with the PAEK family of advanced engineering polymers that are generally considered appropriate for high temperature applications.

## 5 Conclusions

The tribology of various PAEK polymers, with 30%wt of carbon fibre whiskers, sliding against steel has been evaluated under high speed and low load conditions as they passed through their glass transition temperature region, both with and without an ester base fluid as a model lubricant. This was to simulate a specific industrial application but has broader generic interest and implications.

- Without additional lubrication at temperatures below the glass transition, a stable transfer film of PAEK on the steel counterface was formed for all the polymers, yielding a PAEK-PAEK contact with low coefficients of friction.
- Without additional lubrication at temperatures into the glass transition region, the transfer film formed at lower temperatures became unstable and resulted in a larger degree of steel-PAEK contact and damage to the polymer surface. In this region the friction increased linearly with temperature, with friction coefficients at high temperature up to 5.3 times greater than those seen at low temperature with a stable transfer film. Frictional heating due to the high sliding speed dominated the small differences in glass transition behaviour between the four PAEKs.

- When the contact was lubricated with an ester base fluid, the lubricant film prevented the adherence of PAEK to the steel disc surface and no discernible PAEK transfer film was observed. The lubricant film was therefore dominant in defining the frictional response of the system and there was no significant variation in friction coefficient with near-contact PAEK temperature. The system response was characteristic of an interface operating in the mixed lubrication regime.
- In tribology, the glass transition of a polymer is not a reversible process due to the surface damage that can occur at higher temperatures if lubrication is not effective. The polymer and lubricant properties need to be optimised to ensure surface protection in fluid film and boundary lubrication in industrial systems that utilise such materials.

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