



Influence of wet contact conditions on the multidirectional fretting behavior of Polyetheretherketone and composites



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ABSTRACT

Polyetheretherketone (PEEK) polymers are increasingly used in tribological applications where fretting damage occurs. Fretting wear results from the repeated sticking and slipping of mutually loaded contacts. In this study, a custom built multi-axis tribometer is used to replicate fretting of filled and unfilled PEEK in a pin-on-flat configuration in both dry and wet conditions. The performance of the PEEK based polymers is shown to depend on the shear stresses generated when adhesive contacts are broken during slip. Unfilled PEEK experiences frictional heating that leads to softening of the wear surface. The softened material can be easily sheared from the bulk and leads to cratering and fracture of the samples. The extent of damage depended strongly on MW. The buildup of heat is prevented when water lubrication is used and wear is also reduced. Lubricating fillers such as PTFE and graphite lower the frictional forces and reduce the tractive shear stresses. Filled samples however were susceptible to softening from water that exacerbated fretting damage. The fretting performance appears strongly tied to the static friction response on the material. Static friction measurement along with FEA analysis was conducted to better understand the observed phenomena. A stop-go experiment was used to capture the friction response due to the shearing of adhesive contacts.

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1. Introduction

Polymers are increasingly used in tribological applications. Often, it is necessary for such polymeric material to function across a broad range of environments. Design challenges frequently occur since a material may offer outstanding wear resistance in one application or environmental condition but suffer in another. Polyetheretherketone (PEEK) polymers are an attractive material for use in such varied environments. These semicrystalline polymers are resistant to most solvents and possess a high glass transition temperature (T_g) around 150 °C and melting temperature (T_m) near 350 °C [1]. Such properties coupled with their inherent wear resistance make PEEK a popular choice for use in extreme environments. The tribological behavior of PEEK has been studied in both the unfilled virgin state and with the incorporation of various fillers [2–4]. Wear resistance has been attributed to transfer films that protect against abrasion from counterface asperities [5]. A

number of studies have focused on the relationship between counterface roughness and sliding wear rate [6–9]. Ovaert observed that there exists an optimal surface roughness that minimizes wear [8,10]. With increasing surface roughness the wear rate was mostly invariant due to the presence of transfer films [10]. Bahadur believed that these films form when debris becomes physically entrapped between asperities [11]. However, the exact role of transfer films in determining PEEK wear behavior is not fully known. Fillers are often incorporated into PEEK to enhance desirable properties. Commonly, low friction additives such as PTFE, graphite, and MoS₂ are used to reduce friction [12]. Although PEEK has high wear resistance in its unfilled state, the coefficient of friction is higher than desired. Fillers have been identified that assist in the formation and functionality of the transfer films. Inorganic fillers like Al₂O₃, CuF, and CuS have been found to enhance polymer transfer film adhesion and thereby mitigate wear [13–15]. The incorporation of PTFE alone can even form films that achieve ultra low friction and wear behavior [16]. However, the addition of fillers into the PEEK matrix may come with a loss in mechanical integrity. A wide selection of fillers and loadings can be used depending on the specific application. However, fill ratios of

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10% PTFE, 10% graphite, 10% carbon fiber has been a popular formulation for PEEK based tribo-composites [17].

The use of polymer based bearing material in wet environments creates a number of challenges [18]. Polymers may be plasticized in the presence of solvents. Evans studied the effect of various fluids on the wear rate of polymethylmethacrylate (PMMA) and polyphenylene oxide (PPO). It was observed that wear increased when the solubility parameters of the polymer and liquid closely match [19]. In this instance, it was noted that the solvent could penetrate the polymer surface and promote stress cracking that accelerates the formation of debris. Such conditions are also said to promote adhesive-fatigue over abrasive wear. Omar suggested that plasticizers promote subsurface crack propagation resulting in the formation of large plate-like debris [20]. The deleterious effects of lubricants on polymer wear performance can also be accelerated under conditions with high contact pressures. For some polymer with lubricant pairs, plasticization of the polymer surface can occur leading to a rapid increase in friction. Briscoe termed this behavior scuffing and studied this phenomenon in PEEK at length [21–23]. Briscoe observed that the high pressures found in boundary lubrication can accelerate this scuffing failure [23]. Furthermore, frictional heating elevates the contact temperature and plasticizes more of the bulk. Recently, Berer observed that the hydrostatic pressure resulting from oil lubricants can exacerbate the propagation of subsurface cracks in unfilled PEEK on PEEK rollers [24]. Even though PEEK is resistant to most solvents, it can be plasticized in a number of environments [25,26]. Nanoindentation and scratch studies have shown that even water can significantly soften the surface of PEEK-based materials [25]. The effects of water lubrication on the sliding wear behavior of PEEK and its composites have also been reported. For pin on disc sliding, water lubrication generally lowers the coefficient of friction [27]. However, for most PEEK samples studied, wear rates increase significantly [27–29]. The increase in wear volume is believed to depend on the penetration of water below the PEEK surface. The high contact stress and frictional heating that occur during sliding is believed to promote this process. Yamamoto for instance observed plasticization of unfilled PEEK samples after sliding that did not occur after immersion alone [28]. The selection of filler type will also affect the performance. Glass fibers for instance are found to suffer from stress corrosion cracking in water [30]. Carbon fiber based fillers were found to offer some improved performance, but generally all PEEK samples suffer in wet conditions. Unfortunately, only a small number of studies have been done regarding the wear of PEEK in wet conditions so any conclusion remains speculative. Jacobs asserted that water lubricated wear rates depend primarily on counterface tribochemistry [30]. The presence of water was said to induce a hydrolysis like degradation of the PEEK. In their work they proposed that chemically inert diamond like coatings and Al_2O_3 counterfaces should be used in place of steel for aqueous environments. It is suggested that water lubrication may also wash away transfer films that reduce wear in dry sliding tests. Yamamoto observed that compared to PEEK, samples of polyphenylsulfide (PPS) were still capable of forming transfer films in wet conditions [28,29]. This behavior has been attributed to the bonding between sulfur compounds in PPS with iron in the steel counterface. Although PPS does not perform considerably better in wet sliding, transfer films are thought to protect against abrasion. Water is a seemingly innocuous fluid, but it can have a substantial affect on PEEK polymers in tribological applications.

Fretting is often characterized by conditions with high contact pressures and nominally small displacements. Damage occurs when adhesively bonded asperity contacts repeatedly become unstuck and slip. The static friction that results from sticking and slipping can induce surface cracks that may propagate

catastrophically. Typically, fretting damage can be related to the degree of slip. The well-established Mindlin criterion for slip allows for some prediction of fretting based on contact mechanics [31,32]. However, a lot of the theories surrounding fretting cannot be applied for polymers due to their viscoelastic nature. Typical fretting experiments are done using unidirectional reciprocation in a ball on flat configuration. However, polymers may develop anisotropic orientation in the direction of wear. The polymer surface may also prevent slip from occurring through a mechanism termed velocity accommodation [33]. Laux recently demonstrated that for unfilled polyaryletherketones (PAEKs), intermittent and random slip trajectories can produce fretting damage not observed in unidirectional reciprocation [34]. Surface cratering or fracture occurred in samples depending on their fracture toughness and crack growth parameters. It is unclear though how changes in the contact conditions might affect this fretting response. The introduction of lubricating fillers will result in lower frictional forces and can increase the likelihood of slip. Some fillers may potentially reduce fracture toughness, which can increase the severity of fretting damage. Wet conditions can plasticize the PEEK surface but may also serve as a lubricant reducing the buildup of heat and expelling entrapped debris. The aim of this work is to study the influence of both filler and environmental conditions on the fretting behavior of PEEK. The PEEK material will be selected from a range of molecular weights M_w as this can influence relevant mechanical properties. The selected fillers and ratios used will be 10% PTFE, 10% graphite, and 10% carbon fiber, as this composition is commercially relevant and commonly applied across a broad range of application spaces in energy sector markets. It is impossible to study every combination of fillers, so we have chosen a popular material that exhibits a balance of lubrication and reinforcement. The resulting analysis will then help with understanding how changes in contact conditions impact the material response to fretting.

2. Materials and methods

2.1. Materials

A total of eight different samples of PEEK based material were used in this work. Four of the samples are neat unfilled PEEK and labeled based on their weight average molecular weight M_w . Within this selection two samples are termed low molecular weight, labeled L1 and L2, while the high molecular weight samples are H1 and H2. Gel permeation chromatography (GPC) was used to differentiate the sample molecular weights M_w and values are listed in Table 1. Additionally, relevant material properties are included in Table 1. All neat unfilled test specimens were injection molded under controlled conditions described in previous work [35]. Tensile tests were performed in accordance with ASTM standard D638 using type V tensile specimens. Wear samples were made from injection molded rods of approximately 14 mm diameter that are machined into pins that are 6.35 mm in diameter and 20 mm long. As the data shows, lower M_w PEEK typically achieves higher degrees of crystallinity compared to higher M_w PEEK under the same conditions. Mechanically, the unfilled samples are similar with the exception of the elongation at break. Although fracture testing was not performed, it is expected that such properties differ between samples. Typically, lower M_w PEEK forms larger spherulites and suffers from decreased fracture toughness K_{1C} [36]. Additionally, lower tie chain density will lead to less stable fatigue crack growth [37].

It is expected that these differences will occur in the filled samples as well. The same four grades were also used to make compression-molded samples containing 10%PTFE, 10% carbon

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