

A sulfonated modification of PEEK for ultralow friction

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Received: 21 December 2021 / Revised: 22 February 2022 / Accepted: 15 March 2022

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Abstract: Polyether ether ketone (PEEK) is a widely used material for friction pairs due to its excellent mechanical strength, good wear resistance, and chemical inertness. However, some modifications are necessary when PEEK is used as a water-lubricated friction pair. In this study, a novel sulfonation method was developed to design a water-lubricated friction pair with ultralow friction, good wear resistance, and high loading capacity. PEEK powders were sulfonated using ClSO_3H and sintered to form bulk plastic. The sulfonated PEEK (SPEEK) plastic exhibited good tribological properties. At a low sliding speed, the friction coefficient was smaller than 0.02 when a 3 wt% NaCl solution was used as the lubricant. The order of magnitude of the wear rate was as low as $10^{-8} \text{ mm}^3/(\text{N}\cdot\text{m})$. The mechanism of friction reduction was mainly hydration lubrication. The negatively charged $-\text{SO}_3^-$ groups on the friction pair can adsorb hydrated Na^+ cations by electrostatic interactions. These hydrated Na^+ cations have a high load capacity and low shearing resistance. The ultralow wear mechanism observed in this study is possibly due to ultralow friction properties of the friction pairs prepared through the proposed sulfonation and thermoforming procedures.

Keywords: polyether ether ketone (PEEK); sulfonation; hydration lubrication; friction; wear

1 Introduction

Water-based lubrication and water-based superlubricity have been studied extensively over the last decades. The lubrication mechanisms at the macro- and micro-scale have already been elucidated [1–6]. Currently, the application of water-based lubricants [7–9] and soft friction pairs [10–13], such as polyol solutions, synovial fluids, and hydrogels, are often studied. There still are few studies related to friction pairs with high load capacity. However, an appropriate friction pair with high load capacity is more essential for the industrial applications. In some conditions, lubricants cannot be substituted, like knee joint and water lubricated bearing. And the aqueous lubricants are typically corrosive to mechanical systems made of steel and alloys. Furthermore, the poor load capacity of soft materials limits their performance in industrial application. In our previous work, a method for

designing friction pairs with negative charges was proposed. The negatively charged friction pairs exhibited outstanding tribological properties when lubricated with a NaCl solution [14]. However, the mechanical strength of the epoxy resin matrix was not sufficient. Therefore, a more negatively charged material with better mechanical strength should be used to further improve the performance of the water-lubricated bearing.

Polyether ether ketone (PEEK) is widely used material for friction pair due to its excellent mechanical strength, good wear resistance, and chemical inertness [15–17]. It has been used for underwater [18–20] and biological [21–23] tribological applications. However, some modifications are still necessary when using PEEK as a water-lubricated friction pair, particularly when the sliding speed between two friction pairs is too low to form a sufficiently thick water film. As a potential material of stern tube bearings in ships, the

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tribological performances of PEEK on boundary lubrication and mixed lubrication need to be improved. Friction and wear of stern tube bearing can influence the service life and energy consumption of propulsion system. More importantly, noise of stern tube bearing can influence the stealth and safety of ships. The modification of PEEK based on hydration lubrication is beneficial to design new material for stern tube bearing and beneficial to overcome these problems. Sulfonation using H_2SO_4 or ClSO_3H is a common method employed to modify PEEK. Traditional sulfonation procedures alter the external surface of bulk PEEK [17, 21, 24, 25]. However, surface-modified bulk PEEK is not suitable as a friction pair because its modified layer wears off easily. To address this, the surface of PEEK powders can be modified. Then, the altered powders can be thermoformed to fabricate a bulk material. However, the traditional sulfonation procedure may not be suitable for modifying PEEK powders because the powders dissolve and precipitate out in concentrated and diluted H_2SO_4 solutions, respectively (Fig. S1 in the Electronic Supplementary Material (ESM)). Moreover, smashing and grinding the precipitate into micro-powders, and neutralizing the internal sulfonic acid ($-\text{SO}_3\text{H}$) groups are difficult. $-\text{SO}_3\text{H}$ groups decompose below the thermoforming temperature, lowering the mechanical strength and

deteriorating the tribological properties of the sulfonated PEEK. In addition, a solvent with better dispersibility is necessary when the PEEK powders are sulfonated using ClSO_3H . Therefore, designing an appropriate sulfonation procedure is imperative for preparing friction pairs suitable for stern tube bearing.

In this study, a novel sulfonation procedure for PEEK powders with excellent tribological properties is proposed. In this method, the PEEK powders were sulfonated using ClSO_3H in a dimethylformamide (DMF) solution (Fig. 1). The powders were dispersed well in the solution due to the strong polarity of the DMF molecules, without dissolution and agglomeration. After the sulfonation, the DMF solution was diluted with anhydrous ethanol. Then the sulfonated powders were rinsed with anhydrous ethanol, NaOH, and distilled water and next filtered and dried. The sulfonate ($-\text{SO}_3^-$) groups on the powders did not decompose during the sintering process, which comprised two constant-temperature stages (Fig. 1(g)). In the first stage, the sulfonated PEEK powders were sintered at 330°C to produce a bulk material without cracks and pores. In the second stage performed at 250°C , the crystallization of the bulk PEEK occurred. Then, the bulk PEEK sample was polished for the friction tests. The samples were prepared using different sulfonation

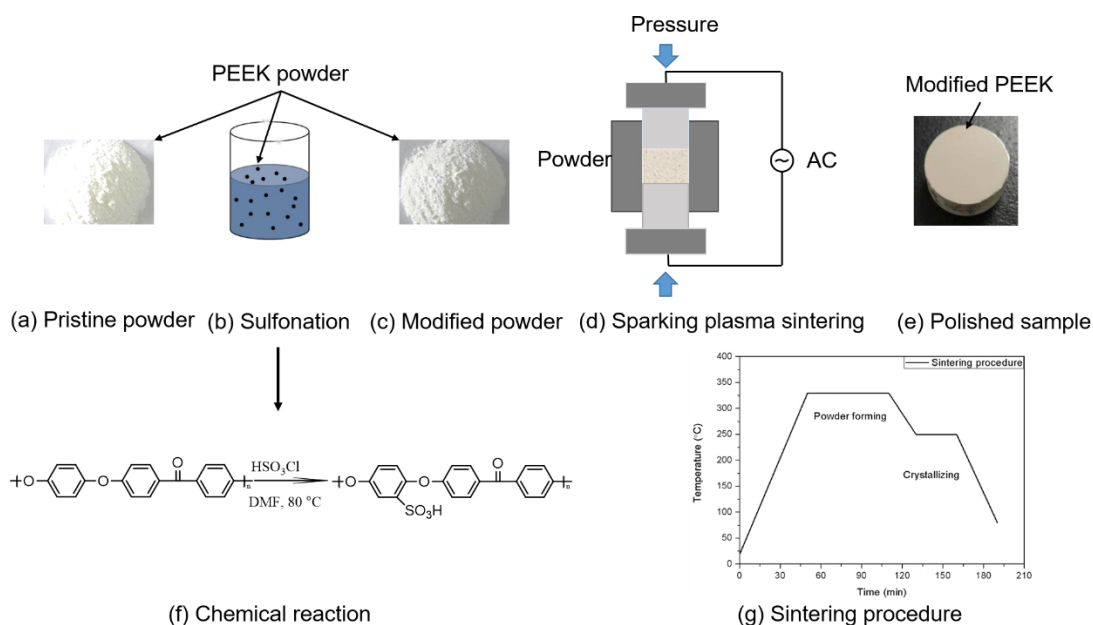


Fig. 1 Preparation of the sulfonated PEEK samples. (a–c, f) Sulfonation procedure of the PEEK powders and (d, e, g) sintering procedure for the SPEEK powders.

parameters. Herein, the unmodified powders are labelled as pristine PEEK. On the other hand, the sulfonated powders are denoted as SPEEK-3%-11-80. Here, 3%, 11, and 80 represents the concentration of the ClSO_3H in the DMF solution, the reaction time (h), and the reaction temperature ($^\circ\text{C}$), respectively.

2 Experimental

2.1 Materials

PEEK powders (Vicatex, UK) with an average diameter of approximately 13 μm were used in this study. ClSO_3H (Aladdin, AR) is a sulfonating agent that can graft $-\text{SO}_3\text{H}$ groups on the benzene rings of PEEK. Dimethylformamide (DMF, Aladdin, AR), dimethyl sulfoxide (DMSO, Aladdin, AR), CH_3COCH_3 (Aladdin, AR), CCl_4 (Aladdin, AR), and CH_2Cl_2 (Aladdin, AR) were used to disperse the PEEK powders during the sulfonation. Anhydrous ethanol (Aladdin, AR) was used to react with the residual ClSO_3H . NaOH (Aladdin, AR) was used to neutralize the $-\text{SO}_3\text{H}$ groups. NaCl (Aladdin, AR) was the main component of the lubricant. Distilled water was used to rinse the sulfonated PEEK powders.

2.2 Sulfonation of the PEEK powders

First, the appropriate solvent to produce the solution for the sulfonation of the PEEK powders (Fig. 1(a)) was determined. In previous studies, CCl_4 and CH_2Cl_2 have been used as solvents for ClSO_3H to sulfonate bulk PEEK [26–29]. However, these solvents were unsuitable for modifying PEEK powders. As shown in Fig. S1 in the ESM, the PEEK powders agglomerated when CCl_4 and CH_2Cl_2 were used. After some attempts, DMF was selected as the solvent for ClSO_3H to disperse the PEEK powders.

For the sulfonation of PEEK, ClSO_3H (10 mL) was added dropwise to DMF (100 mL) under magnetic stirring to ensure the homogenous mixing of the solute and the solvent (Fig. 1(b)). Then, PEEK powder (20 g) was added to the resulting solution. The temperature was maintained at 80 $^\circ\text{C}$ for 8 h to promote the chemical reaction between ClSO_3H and the PEEK powders. Thereafter, the solution was cooled down to room temperature (~ 23 $^\circ\text{C}$), which

was maintained for 15 h to increase the swelling of the PEEK powders. The temperature of the solution was increased again to 80 $^\circ\text{C}$ and was maintained for another 3 h. During these processes, the reaction container was sealed, and the solution was stirred continuously. Then, anhydrous ethanol was added to dilute the solution and to rinse the sulfonated PEEK powders. After that, the powders were rinsed with NaOH and distilled water. Finally, the sulfonated PEEK powder was dried at 130 $^\circ\text{C}$ for 3 h. The sample prepared through these procedures was denoted as SPEEK-10%-11-80, where 10% is the concentration of ClSO_3H , 11 is the reaction time in h, and 80 is the reaction temperature in $^\circ\text{C}$.

2.3 Sintering procedure

To form the bulk sulfonated PEEK plastic, the sulfonated PEEK (SPEEK) powders were sintered through sparking plasma sintering (SPS, Sinter Land, Japan). The SPEEK powders (Fig. 1(c)) were put into a graphite mold, where they were slightly compacted at 10 MPa (Fig. 1(d)). Then, the compacted SPEEK samples were heated through a five-step procedure (Fig. 1(g)). First, the temperature was increased from 20 to 330 $^\circ\text{C}$ within 50 min. Then, it was maintained at 330 $^\circ\text{C}$ for 60 min. In this step, the powders softened and agglomerated due to the application of high temperature and pressure. Third, the temperature was lowered to 250 $^\circ\text{C}$ within 20 min. Then, the samples were maintained at 250 $^\circ\text{C}$ for 30 min. During this step, the PEEK bulk samples crystallized quickly, improving the mechanical strengths of the samples. Finally, the samples were cooled from 250 $^\circ\text{C}$ to room temperature (~ 23 $^\circ\text{C}$) within 30 min. The bulk PEEK samples were polished for the subsequent characterization tests (Fig. 1(e)).

3 Characterization of the sulfonated PEEK powders

3.1 X-ray photoelectron spectroscopy (XPS) analysis

The pristine and sulfonated PEEK powders at different sulfonation conditions were characterized through XPS (PHI Quantera II, Ulvac-PHI, Japan) to validate if the $-\text{SO}_3^-$ groups were grafted to the molecular

chains of PEEK. Only C and O peaks were apparent in the full XPS spectra of the pristine PEEK (Fig. 2(a)) and SPEEK-3%-11-80 (Fig. 2(d)) powders. No S peak was recorded in the S 2p core-level region of the pristine sample (Fig. 2(c)). In contrast, S was detected in that of SPEEK-3%-11-80 (Fig. 2(f)). On the other hand, C, O, and S peaks were clearly visible in the XPS spectrum of SPEEK-10%-11-80 (Fig. 2(g)). The peak observed at 168.5 eV in the S 2p core-level region can be attributed to the presence of more $-\text{SO}_3^-$ groups (Fig. 2(i)). As such, more sulfonic acid groups were grafted onto the PEEK powders with increasing ClSO_3H concentration. However, the prepared solutions with ClSO_3H concentrations as high as 40% and 100% were not suitable for the sulfonation of the PEEK powders. At a ClSO_3H concentration of 40%, some PEEK powders floated on the liquid surface, negatively affecting the sulfonation process. On the other hand,

at a ClSO_3H concentration of 100%, the PEEK powders agglomerated. This makes the grinding of the sample into micro-powders, and the neutralization of the internal $-\text{SO}_3\text{H}$ groups difficult.

3.2 Thermogravimetric analysis

The melting point of pristine PEEK is approximately 334 °C. Its thermal decomposition occurs at temperatures higher than 500 °C [15]. The thermal stability of the SPEEK powders is crucial for the thermoforming process. This property was evaluated through thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) using a NETZSCH X70 thermal analyzer (NETZSCH, Germany). The temperature of the samples was raised to 400 °C at a heating rate of 10 °C/min and then held constant for 30 min. At 330 and 400 °C, the mass ratios of the pristine PEEK powder were 99.79% and 99.36%, respectively

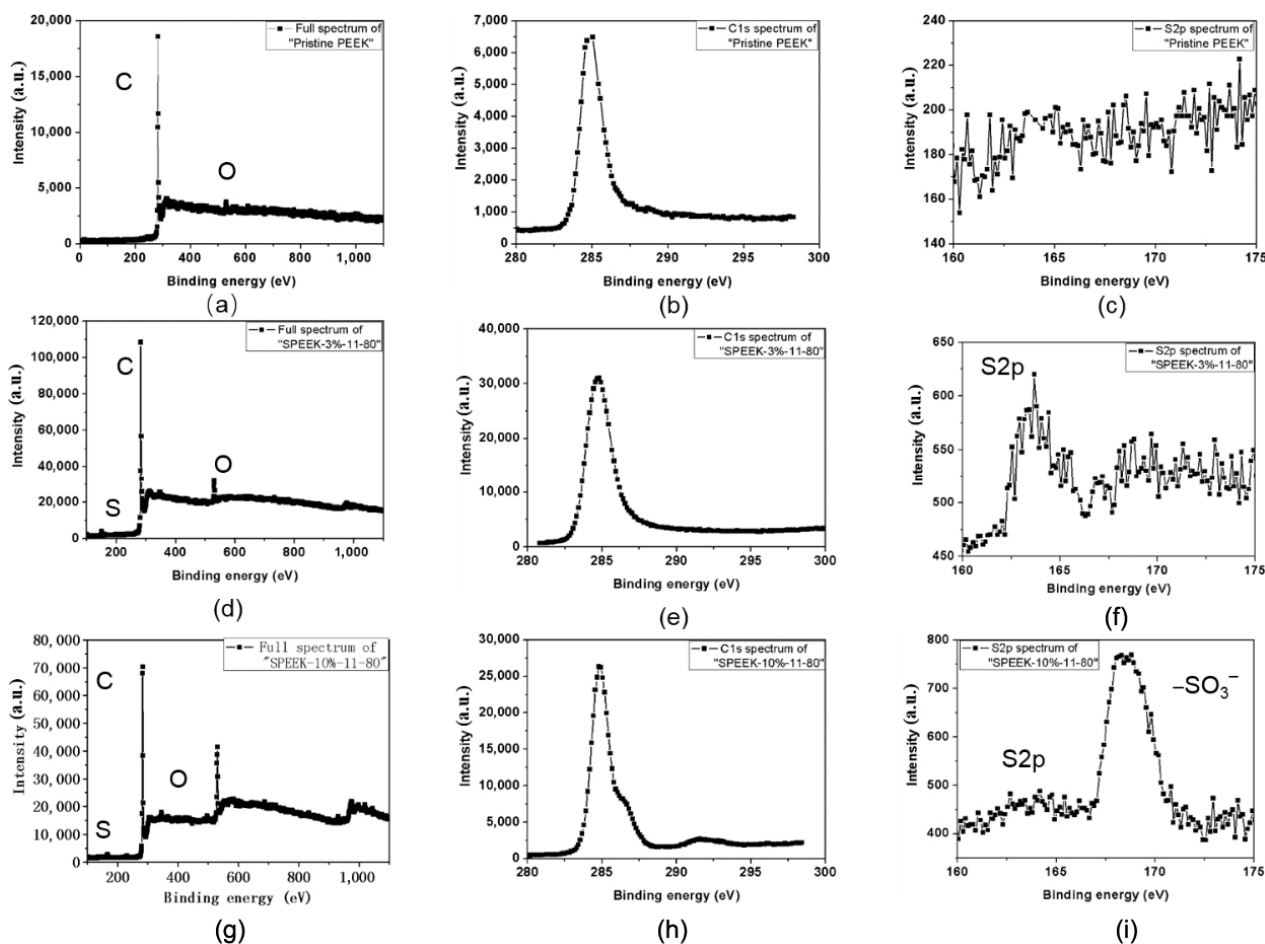


Fig. 2 Full XPS, C 1s, and S 2p spectra of (a–c) pristine PEEK, (d–f) SPEEK-3%-11-80, and (g–i) SPEEK-3%-11-80 powders. C and O peaks were detected in the pristine PEEK powder. In addition to these peaks, S peaks were recorded in the sulfonated PEEK powders.

(Fig. 3(a)). The SPEEK-10%-11-80 powders recorded approximately similar mass ratios. At 330 and 400 °C, the corresponding values for this sample were 99.50% and 99.34%, respectively (Fig. 3(c)). The temperatures employed for most PEEK thermoforming processes were lower than 400 °C and were usually in the range of 370–390 °C [30, 31]. The TGA results indicate that the SPEEK powders prepared through the method proposed in this work had good thermal stability. As such, these powders can be used for the thermoforming processes in industrial applications. Herein, the maximum temperature during SPS was set to 330 °C to restrain the flow of the PEEK powder. As shown in the DTA curves in Figs. 3(b) and 3(d), the absolute value of the heat flow increased after the sulfonation procedure. This implies that the molecular structure of the PEEK powders possibly changed after the sulfonation.

4 Tribological analysis of the sulfonated PEEK samples

4.1 Tribological analysis of the sulfonated PEEK samples

In this study, friction coefficient is used to evaluate the tribological properties of the sulfonated PEEK

samples. This parameter was determined using a ball-on-disk setup with a UMT-5 tribometer (Bruker, USA) (Fig. 5(a)). In this setup, Si₃N₄ balls (radius = 5 mm) and polished PEEK or SPEEK discs were used. Si₃N₄ is typically used as a friction pair in tribological research and industrial applications because of its good tribological properties [32, 33]. Besides, the zeta potential and isoelectric point (IEP) of silicon nitride are close to those of sulfonated PEEK. Therefore, Si₃N₄ ball and sulfonated PEEK both have negative surface charged, which is beneficial to hydration lubrication. The surface roughness of the Si₃N₄ balls and of the polished PEEK or SPEEK discs were approximately 20 [3] and 10 nm, respectively (Fig. S5 in the ESM). During the test, the ball was fixed to a force sensor, and the disc was rotated by a motor. Accordingly, a relative sliding motion was generated between the Si₃N₄ ball and the PEEK (or SPEEK) disc. A normal load of 15 N was applied to the Si₃N₄ ball and the tangential friction force was measured from which the friction coefficient was calculated. Herein, the average contact pressure was close to compressive strength of PEEK, which was beneficial to analyze load capacity of SPEEK plastic and hydration lubrication. During the friction test, a 3 wt% NaCl solution (volume: 1–3 mL), which had a concentration close to that of seawater, was used as the lubricant.

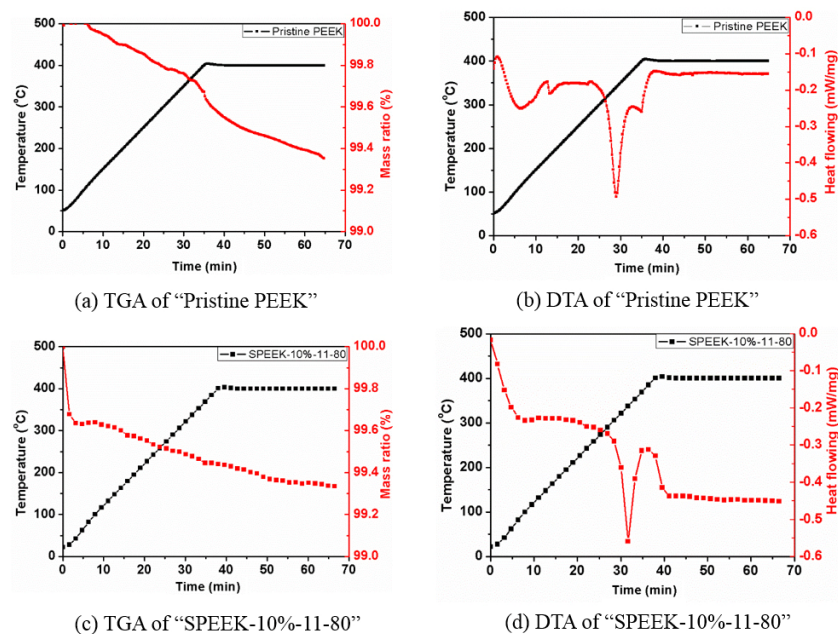


Fig. 3 TGA and DTA profiles of (a, b) pristine PEEK and (c, d) SPEEK-10%-11-80 powders. The sulfonated PEEK powders had good thermal stability and were suitable for the sintering procedure.

In addition, to better illustrate the friction reduction was mainly due to hydration lubrication, lower sliding speeds were set.

The friction coefficient between the Si_3N_4 ball and the pristine PEEK disc at a sliding speed of 12.5, 25, and 50 mm/s were approximately 0.08, 0.07, and 0.06, respectively (Fig. 4(a)). These values are lower than those in previous reports (approximately 0.1) [34–36] possibly due to the better thermoforming properties and lower surface roughness of the pristine PEEK sample. The observed fluctuation in the values of the friction coefficient is possibly due to the wearing off of the pristine PEEK disc. On the other hand, the friction coefficient between the Si_3N_4 ball and the SPEEK disc was considerably lower. Furthermore, the fluctuations of the values at different sliding speeds were also smaller. The friction coefficient between the Si_3N_4 ball and the SPEEK-3%-3-80 disc at a sliding speed of 12.5, 25, and 50 mm/s were approximately 0.03, 0.02, and 0.02, respectively (Fig. 4(b)). Correspondingly, the friction coefficient between the Si_3N_4 ball and the SPEEK-3%-11-80 disc were 0.025, 0.018, and 0.022 (Fig. 4(c)). Lastly, the friction coefficient between the Si_3N_4 ball and the SPEEK-10%-11-80 disc was approximately at 0.023 at a sliding speed of 12.5, 25,

and 50 mm/s (Fig. 4(d)). The friction coefficients obtained using the SPEEK-10%-11-80 disc (Fig. 4(d)) were slightly larger than those calculated when the SPEEK-3%-11-80 disc (Fig. 4(c)) was used. The excessive $-\text{SO}_3\text{H}$ groups possibly hampered the thermoforming of the SPEEK powders and, in turn, on the tribological properties of the bulk SPEEK samples. Figure S4 in the ESM shows the results of the replicates and the corresponding error bars of the measurements.

In our previous work, the mechanism of the reduction of friction on a negatively charged bulk material was analyzed systematically [14]. As shown in the lubrication model in Fig. 5(c), the negatively charged groups on the sulfonated PEEK sample adsorbs the hydrated Na^+ cations through electrostatic interactions. The shear strength between these hydrated cations is very small because of the fast exchange of the water molecules. In addition, it is challenging to completely remove the water molecules from the hydrated cations [1]. In other words, hydrated cations can effectively separate the surface asperities of the two friction pairs and generate a very small sliding resistance. This friction reduction mechanism is called hydration lubrication [1, 37].

To assess the density of the negatively charged

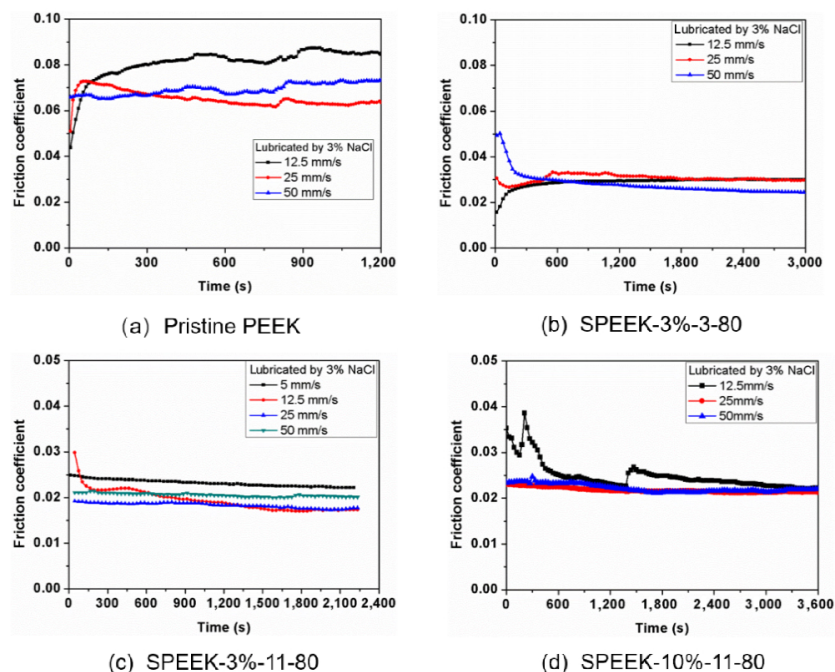


Fig. 4 Tribological characteristics of the pristine PEEK and sulfonated PEEK samples. Friction coefficients between Si_3N_4 ball and (a) pristine PEEK, (b) SPEEK-3%-3-80, (c) SPEEK-3%-11-80 discs. The friction coefficients decreased after the sulfonation of the PEEK powder precursors.

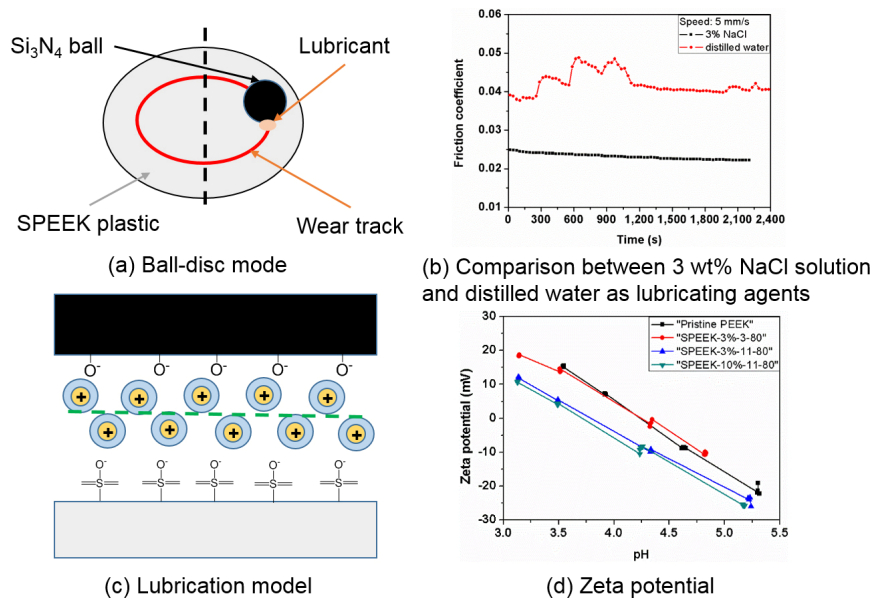


Fig. 5 Surface charges of SPEEK and their influence on friction. (a) Schematic of the friction test setup; (b) friction coefficients between Si_3N_4 ball and sulfonated PEEK disc obtained using distilled water and 3 wt% NaCl solution; (c) model of the hydration lubrication; and (d) zeta potential of the pristine PEEK and SPEEK discs at different pH. The negatively charged groups on the SPEEK sample adsorb hydrated Na^+ cations to separate the asperities of the two friction pairs.

groups, which are mainly $-\text{SO}_3^-$ groups, the zeta potentials of the pristine PEEK and SPEEK samples were measured. The zeta potential is an important parameter that describes the charge behavior of the solid–liquid interface in the electrical double layer model. In this work, this parameter was measured and its dependence on pH was investigated using Surpass 3 (Anton Paar, Austria). Prior to the measurements, all the samples were immersed and rinsed with distilled water and then rinsed with a KCl solution. The pH was adjusted using KOH and HCl solutions. More details on the zeta potential and the procedure for its measurement have been introduced in our previous work [14]. With decreasing pH, the absolute value of the negative zeta potential initially decreased and then became zero (Fig. 5(d)). Thereafter, the zeta potential became positive, and its value increased. At a zeta potential of 0 mV, the surface charges are completely neutralized. The value of the pH at this zero-charge state is called the isoelectric point (IEP), which is usually used to evaluate the density of the acidic groups, such as the $-\text{SO}_3^-$ groups; low IEP values indicate high densities of the sulfonate groups. The IEP of the SPEEK-3%-3-80 sample was close to that of the pristine PEEK sample (4.3). On the other hand, the IEP of the SPEEK-

3%-11-80 sample was almost similar to that of the SPEEK-10%-11-80 (3.6). These findings correspond well to the XPS results, which revealed that some $-\text{SO}_3^-$ groups were grafted onto the benzene ring of the PEEK structure after the sulfonation procedure and confirmed that the sulfonation of PEEK powders was successful.

At a sliding speed of 5 mm/s, the friction coefficient between the Si_3N_4 ball and the SPEEK-3%-11-80 sample when lubricated with distilled water was approximately 0.04 (Fig. 5(b)). At the same sliding speed, the obtained friction coefficient was approximately 0.025 when 3 wt% NaCl solution was used as the lubricating agent instead of distilled water. These results reveal that the hydrated Na^+ cations played an important role in friction reduction. Moreover, it can be inferred from Figs. 4(b) and 4(c) that more negatively charged $-\text{SO}_3^-$ groups were more effective in reducing the friction when they had a little effect on the thermoforming characteristics of the bulk SPEEK.

As shown in Fig. S5(a) in the ESM, the surface roughness of the SPEEK-3%-11-80 plastic was approximately 10–20 nm. After the friction test performed for 3 h, the depth of the wear track was approximately equal to the surface roughness. These results indicate that the SPEEK sample exhibited

good tribological properties, i.e., good friction and wear characteristics.

To evaluate further the wear resistance of the sulfonated PEEK, reciprocating friction tests were performed (Fig. S6(d) in the ESM). In this testing mode, the Si_3N_4 ball is initially slid forward and then slid backward. Consequently, the sliding track was a straight line. The sliding speed and direction were varied during the friction tests. Compared to those encountered in the rotative mode, the friction and wear in the reciprocating mode were more severe due to the difficulty of forming a sufficiently thick lubricating film. Therefore, reciprocating friction tests suit friction pairs with ultrahigh wear resistance. The friction coefficients of a commercial Thordon SXL (Thordon, Canada) bearing and of the pristine PEEK

and SPEEK-10%-11-80 samples were measured at different sliding frequencies (Figs. S6(a)–S6(c) in the ESM). In these tests, the counter face and the lubricant were Si_3N_4 ball (radius = 5 mm) and 3 wt% NaCl solution, respectively. The applied load was 15 N, and the reciprocating stroke was 5 mm. Lastly, the average sliding speeds were 10, 30, and 50 mm/s. At all reciprocating frequencies, the SPEEK-10%-11-80 sample registered the lowest friction coefficient (approximately 0.04); the SPEEK plastic exhibited outstanding tribological properties even in the reciprocating mode. After the friction tests performed for 3 h, the wear tracks of the samples were measured using a 3D optical profilometer (Keyence, Japan). Figure 6 shows the cross-sectional wear tracks of the friction pairs at different sliding frequencies.

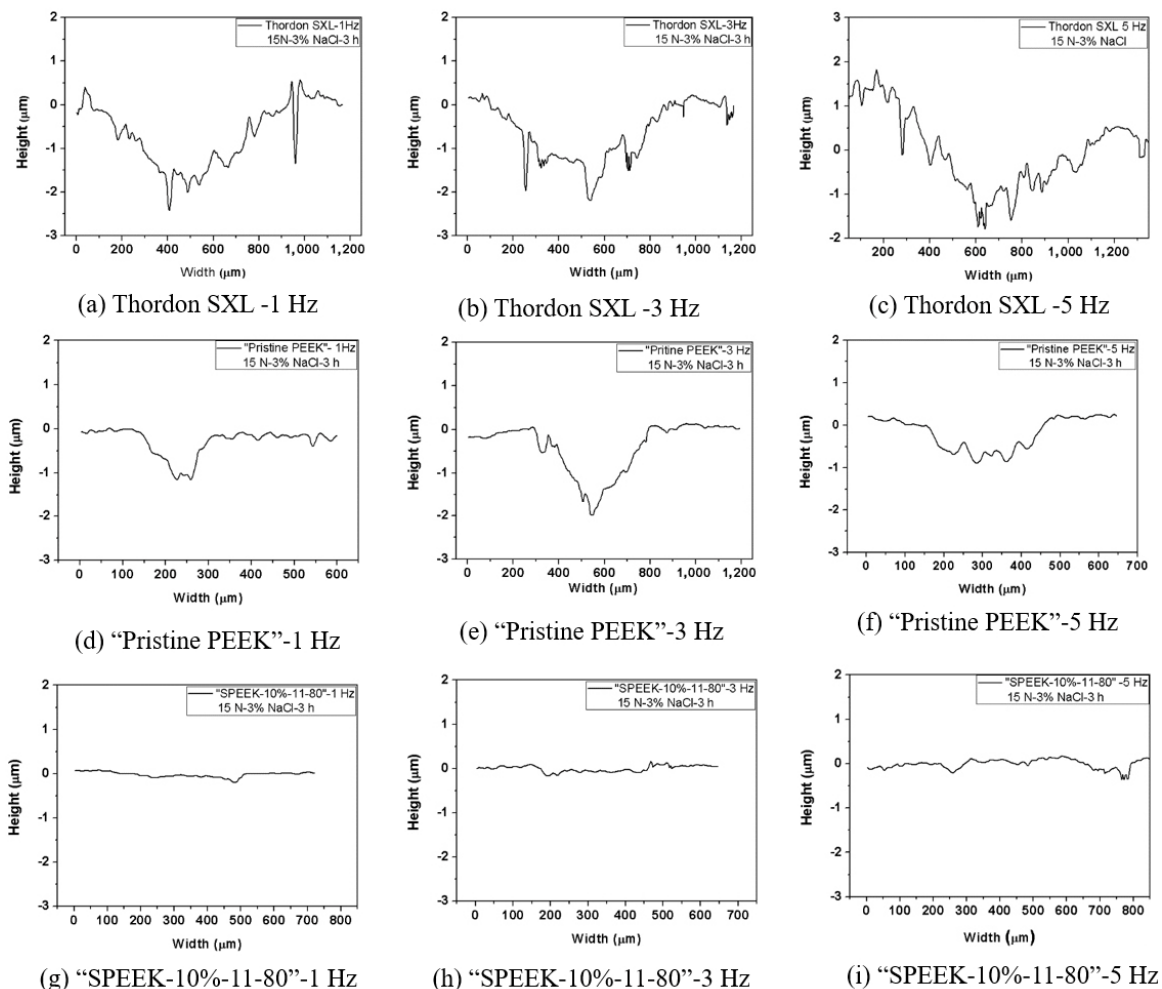


Fig. 6 Cross-section of the wear tracks at 1, 3, and 5 Hz of (a–c) Thordon SXL bearing, (d–f) pristine PEEK, and (g–i) SPEEK-10%-11-80 plastics. The test was performed for 3 h. The average wear rate of the SPEEK-10%-11-80 sample was smaller than those of the Thordon SXL bearing and the pristine PEEK plastic.

The curvature of the profiles was concave because of wearing during the friction tests. Correspondingly, the wear rate (γ) of each friction pair was calculated using the formula, $\gamma = (A \times S) / (F_n \times L)$. Here, A , S , F_n and L represent the cross-sectional area, the reciprocating stroke (5 mm), the normal load (15 N), and the sliding distance, respectively. In addition, L can be calculated using the formula, $L = 2S \times f \times t$, where f is the reciprocating frequency (1, 3, and 5 Hz), and t is the test duration. On the other hand, A can be calculated using the profiles of the sample. First, a baseline was fitted as the pristine surface of the friction pair. Then, the height difference was integrated with the width to calculate A . Table S1 in the ESM summarizes the calculated values of A and γ of the friction pairs at different frequencies. The values of γ of the Thordon SXL bearing were 4.9×10^{-6} , 6.7×10^{-6} , and 2.1×10^{-7} mm³/(N·m) at a reciprocating frequency of 1, 3, and 5 Hz, respectively. Correspondingly, the values of γ of the pristine PEEK sample were 5.0×10^{-7} , 6.7×10^{-7} , and 2.1×10^{-7} mm³/(N·m). However, the measurement of the cross-sectional areas of the wear tracks of the SPEEK-10%-11-80 plastic in Figs. 6(g)–6(i) was difficult. The average value of γ of the SPEEK-10%-11-80 sample was smaller than those of the

Thordon SXL bearing and the pristine PEEK plastic.

To further evaluate the wear resistance of SPEEK sample, reciprocating friction tests were performed for 8 h. The setup of the friction tests was the same as the previous friction test. The friction coefficient was approximately 0.04, which is consistent with the value calculated from the preceding friction test. The wear track was measured. Then, the corresponding values of A and γ were calculated. The values of γ of the SPEEK-10%-11-80 sample at 1, 3, and 5 Hz were 1.4×10^{-7} , 6.7×10^{-8} , and 6.1×10^{-8} mm³/(N·m), respectively. The wear rate γ of the SPEEK-10%-11-80 sample was smaller by one and two orders of magnitude relative to those of the pristine PEEK plastic and the Thordon SXL bearing, respectively. These results confirm further the outstanding wear resistance of the sulfonated PEEK sample. Besides, the width shown in Fig. 6 corresponds to wear region, and the width shown in Fig. S7 in the ESM corresponds to contact region. The wear region is smaller than the contact region, because some elastic deformation can recover after the friction test. It indicated that wear occurred severe in central region of wear track, where the real contact pressure was larger. The discrepancy of wear scar Fig. 7(d) was related to the deformation of cantilever in force sensor.

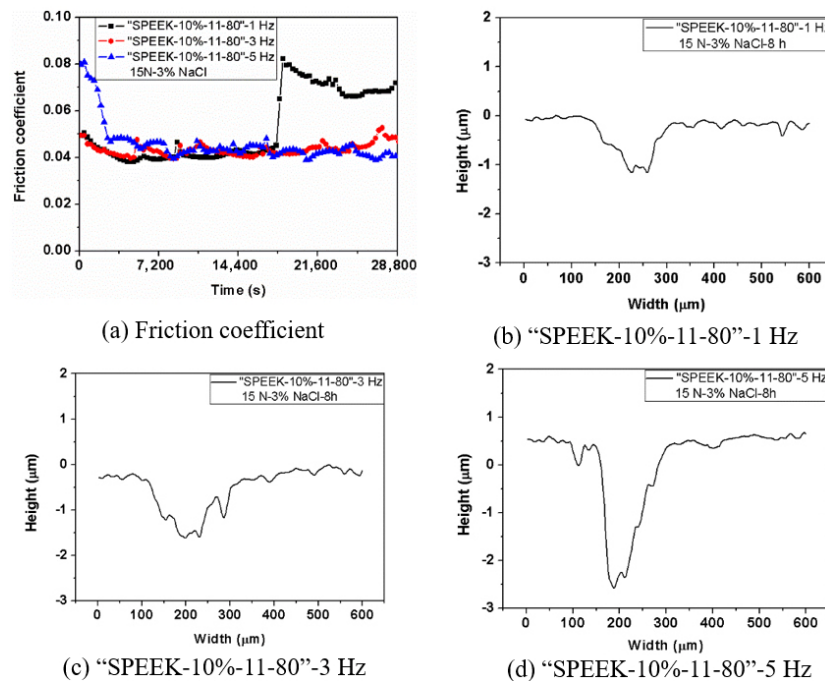


Fig. 7 (a) Friction coefficient and cross section of the wear tracks at (b) 1, (c) 3, and (d) 5 Hz of the SPEEK-10%-11-80 plastic. The reciprocating friction test was performed for 8 h. The sulfonated PEEK plastic showed outstanding wear resistance.

At a high load of the sensor and with a large wear height of the sample, the load may be not vertical to the sulfonated PEEK disc.

5 Discussion

Chemical and thermal stability ensure that PEEK can be used in extreme working conditions, such as in highly corrosive environments and high-temperature settings. However, attaining these characteristics limits the modification of PEEK to achieve exceptional properties, such as ultralow friction and biocompatibility. This work focused on the design of negatively charged friction pairs in aqueous solutions. PEEK powders dissolve in anhydrous H_2SO_4 , thereby making the smashing and grinding processes required to produce PEEK micro-powders difficult. To prevent powder dissolution and agglomeration during the sulfonations, many solutions have been tested. The PEEK powders agglomerated when ClSO_3H was added to CCl_4 and CH_2Cl_2 solvents. This caused the same problems encountered when anhydrous H_2SO_4 was used to sulfonate PEEK powders. Acetone disperses PEEK powders well at room temperature ($\sim 23^\circ\text{C}$); however, it volatilizes quickly and cannot be heated at a relatively high temperature. These issues were not encountered when DMF and DMSO were used as solvents. However, it was difficult to add ClSO_3H into DMSO safely. After these attempts, DMF was selected as the solvent for ClSO_3H to disperse the PEEK powder (Fig. S1 in the ESM). The resulting ClSO_3H -DMF solution was heated at a relatively high temperature to promote the chemical reactions.

After the sulfonation process, a S peak was detected in the XPS spectrum of the SPEEK powder (Fig. 2). However, this S peak was not recorded in the XPS spectrum of the PEEK powders after the immersion in ClSO_3H with no heating. These results indicate that the $-\text{SO}_3\text{H}$ groups were successfully grafted onto the PEEK powders. The $-\text{SO}_3\text{H}$ groups substituted the hydrogen atoms in the benzene rings of PEEK (Fig. 1(f)). Additionally, the SPEEK powders prepared using this method can be sintered at a temperature as high as 330°C (Fig. 1(g)), which was close to the melting point (approximately 334°C) of PEEK. The crystallization temperature was set to 250°C due to the high crystallization rate [30, 38, 39]. A high degree

of crystallinity enhances the mechanical strength and wear resistance of bulk PEEK. In addition, different sintering temperature (310 and 320°C), different sintering duration (20 , 40 , and 120 min), different sintering pressure (1 and 5 MPa) were tried, the resulting friction coefficients were larger. At a low sintering temperature and low compacted pressure, the performances of PEEK and sulfonated PEEK were undesired. Sintering procedure introduced in this work was optimized. The sintered SPEEK sample was polished well without pores or cracks. Its surface roughness was as low as approximately 10 nm (Fig. S4 in the ESM). Correspondingly, as shown in Fig. S3 in the ESM, the friction coefficients between the Si_3N_4 ball and the SPEEK discs were smaller than that between the Si_3N_4 ball and the PEEK–Na polystyrene sulfonate (NaPS) composite discs; the friction coefficient between the Si_3N_4 ball and the PEEK–NaPS composite disc with 10 wt% and 20 wt% NaPS were approximately 0.05 and 0.07 , respectively. Correspondingly, these values were almost similar and larger those between the Si_3N_4 ball and the pristine PEEK plastic. Additionally, with 20 wt% NaPS, the recorded friction coefficients fluctuated considerably. These results indicate the significance of the chemical modification to physical mixing. It was difficult to homogenize the composite at the micro- and nanoscales, which accounted for much of the friction reduction.

After the sulfonation, the friction coefficients were smaller than 0.02 at a low sliding speed. At a sliding speed of 12.5 mm/s, the friction coefficient was reduced from 0.08 (pristine PEEK) to 0.018 (SPEEK-3%-11-80). These results further confirm the success of the sulfonation process and support the rationale of designing negatively charged friction pairs. For water based lubrication, hydrodynamic pressure and surface force can reduce the direct contact of surface asperities and reduce friction. In this work, the sliding speeds are relatively low to hydrodynamic pressure, and the surface force is dominant. The surface force includes hydration repulsive force, electrical double layer force and van der Waals attractive force. In the condition of this work, the amplitude of hydration repulsive force is much larger than that of electrical double layer force [6, 43]. In a word, reinforced hydration repulsive force can bear more load and van der Waals attractive force. As a result, friction can be

reduced. In detail, when lubricated by NaCl solution, the hydrated Na^+ cations separate the two friction pairs with an ultralow shearing strength. In addition, as shown in Fig. S6 in the ESM, the width of the wear track of the SPEEK-10%-11-80 plastic was approximately 407 μm . From the ratio of the normal load to the contact area, the average contact pressure during the friction test was calculated to be 115 MPa. The average contact pressure on the SPEEK plastic was far greater than that on soft hydrogels [40–42]. This indicates that the proposed modification method in this study has potential for other engineering applications. Moreover, these results also reveal that the bearing capacity of the hydrated Na^+ cations was greater than 100 MPa.

The SPEEK sample exhibited excellent wear resistance in the rotative friction tests. From Fig. S5(b) in the ESM, the measurement of the wear volume was difficult. To better evaluate the wear resistance of the SPEEK plastic, friction tests in reciprocating mode were performed. When the friction test was performed for 3 h, the A and wear volume were measured, and the γ was calculated. The value of γ of the Thordon SXL bearing and pristine PEEK plastic were at a level of 10^{-6} and 10^{-7} $\text{mm}^3/(\text{N}\cdot\text{m})$ (Table S1 in the ESM). As shown in Fig. 6, the wear volume of the SPEEK-10%-11-80 plastic was smaller than those of the Thordon SXL bearing and the pristine PEEK sample. Therefore, the γ of the SPEEK-10%-11-80 sample was lower than 10^{-7} $\text{mm}^3/(\text{N}\cdot\text{m})$. At a longer test time (8 h), the wear volume of the SPEEK-10%-11-80 plastic was measured, and the value of γ was at a level of 10^{-8} $\text{mm}^3/(\text{N}\cdot\text{m})$. These results indicate that the thermoformed SPEEK plastic produced in this study showed excellent wear resistance.

6 Conclusions

In this study, a sulfonation method for inhibiting the decomposition of the $-\text{SO}_3\text{H}$ during the thermoforming process was reported. Herein, ClSO_3H was used to sulfonated PEEK (SPEEK) powders, and the $-\text{SO}_3\text{H}$ groups were neutralized to improve their thermal stability. Then the powders were sintered by sparking plasma sintering (SPS) to form bulk plastic. After the sulfonation, the isoelectric point (IEP) of SPEEK plastic decreased from $\text{pH} = 4.3\text{--}3.6$, revealing that

the plastic possessed more negative charges in aqueous solution.

Moreover, the thermoformed SPEEK plastic exhibited excellent tribological properties. At a low sliding speed of 12.5 mm/s, the friction coefficient of the SPEEK plastic (3%-11-80) was as low as 0.018 when 3 wt% NaCl solution was used as the lubricant. These results indicate that the $-\text{SO}_3^-$ were successfully grafted onto the PEEK powders. These negatively charged groups reduce friction through the hydration lubrication. The results of this work also indicated that the hydration lubrication was effective even when the average contact pressure was greater than 100 MPa. In addition, the SPEEK plastic showed excellent wear resistance. Its wear rate was at a level of 10^{-8} $\text{mm}^3/(\text{N}\cdot\text{m})$, far lower than that of pristine PEEK.

In a word, a friction pair that can be used as water-lubricated bearing was fabricated, with high load capacity, ultralow friction coefficient, and ultralow wear rate.

Acknowledgements

This study was financially supported by the National Natural Science Foundation of China (Grant No. 51925506).

Electronic Supplementary Material: Supplementary material is available in the online version of this article at <https://doi.org/10.1007/s40544-022-0625-6>.

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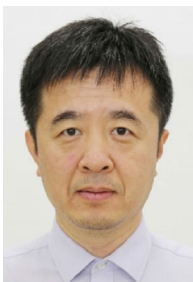
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