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RESEARCH ARTICLE

Tribological properties of PTFE-based fabric composites at cryogenic temperature

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Abstract: Fabric composites are widely employed in self-lubricating bearing liners as solid lubrication materials. Although the tribological behaviors of fabric composites have been extensively studied, the cryogenic tribological properties and mechanisms have been scarcely reported and are largely unclear to instruct material design for aerospace and other high-tech applications. Herein, the tribological properties of polytetrafluoroethylene (PTFE)-based hybrid-fabric composites were investigated at cryogenic and ambient temperatures in the form of pin-on-disk friction under heavy loads. The results suggest that the friction coefficients of the hybrid-fabric composites obviously increase with a decrease in wear when the temperature drops from 25 to −150 °C. Moreover, thermoplastic polyetherimide (PEI), as an adhesive for fabric composites, has better cryogenic lubrication performance than thermosetting phenol formaldehyde (PF) resin, which can be attributed to the flexible chemical structure of PEI. The excellent lubrication performance of hybrid-fabric composites is attributed to the transfer film formed by PTFE fibers on the surface of fabrics.

Keywords: cryogenic temperatures; fabric composites; friction and wear; transfer film

1 Introduction

With the rapid advancement of science and technology, human beings are exploring the universe more deeply [1]. The applications of spacecraft [2, 3], liquid propelled rockets [4], and large cryogenic wind tunnels [5] have posed great challenges to low-temperature lubrication. For example, spherical plain bearings for driving and supporting flexible steel plates in wind tunnel nozzles will work properly in nitrogen gas with a temperature lower than −150 °C. However, traditional lubricating oils/greases tend to freeze or become too viscous to lubricate at such cryogenic temperatures [6]. Self-lubricating polymeric materials, such as polyetheretherketone (PEEK), polyimide (PI), and polytetrafluoroethylene (PTFE) and their composites in particular have shown excellent mechanical and lubrication properties at cryogenic temperatures [7–10]. Therefore, the tribological behaviors of polymeric composites at cryogenic temperatures have been widely investigated for their cryogenic tribological applications. McCook et al. [11] indicated that the friction coefficient of PTFE increased with the decreasing temperature under a dry nitrogen atmosphere in the range of −100 to 44 °C. This trend was consistent with the characteristics of thermally activated friction. They used the improved Arrhenius equation to give a theoretical model of the friction coefficient changing with the temperature. Theiler and Gradt [12] found that the friction and wear mechanism of PIs under low-temperature conditions with gaseous and liquid hydrogen was related to the

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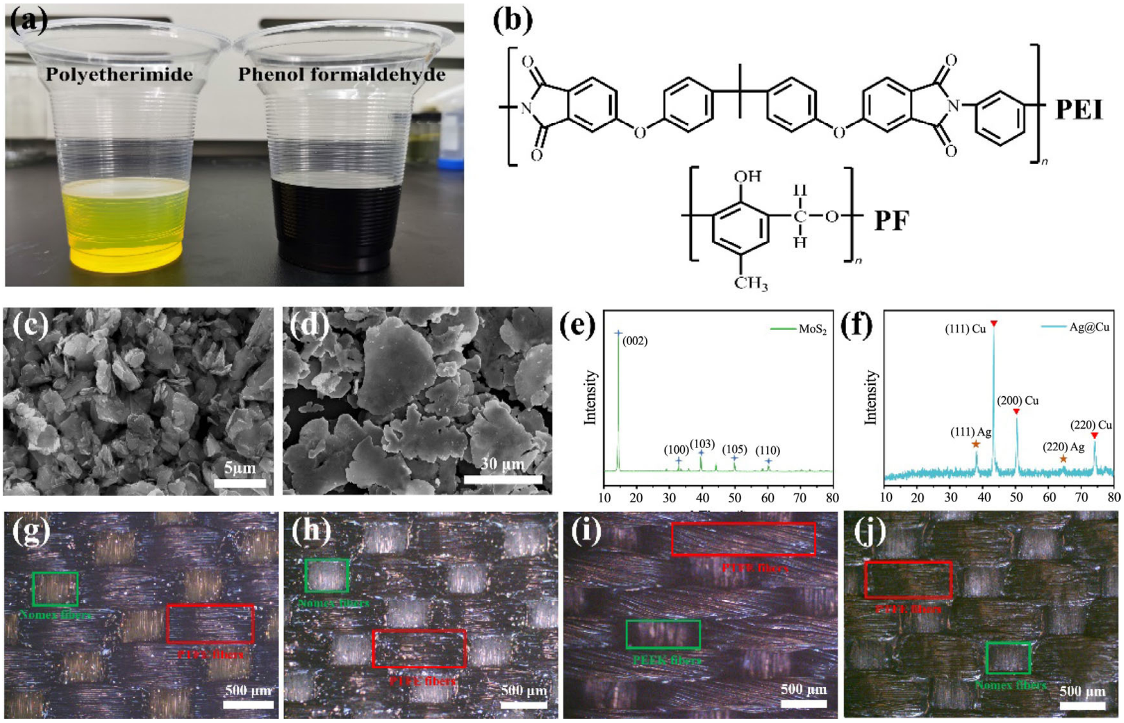


Fig. 1 (a) PEI resin and PF resin; (b) molecular structures of PEI and PF; scanning election microscopy (SEM) images of (c) MoS_2 and (d) Ag@Cu; X-ray diffraction (XRD) patterns of (e) MoS_2 and (f) Ag@Cu; and optical micrographs of (g) NP–PF–AC fabric, (h) NP–PEI–AC fabric, (i) PP–PEI–MoS_2 fabric, and (j) NP–PEI–MoS_2 fabric. Note: (1) PTFE/Nomex hybrid-fabric composites with PF adhesive and addition of Ag@Cu are abbreviated as NP–PF–AC; (2) PTFE/Nomex hybrid-fabric composites with PEI adhesive and addition of Ag@Cu are abbreviated as NP–PEI–AC; (3) PTFE/PEEK hybrid-fabric composites with PEI adhesive and addition of MoS_2 are abbreviated as PP–PEI–MoS_2; and (4) PTFE/Nomex hybrid-fabric composites with PEI adhesive and addition of MoS_2 are abbreviated as NP–PEI–MoS_2.

chemical structure and the formation or inhibition of the transfer films. Moreover, Wang et al. [13] indicated that the real contact area between the steel ball and polymers determined the friction coefficient instead of the formation and adhesion of the transfer film by studying the tribological properties of pure PI, PEEK, and PTFE in a cryogenic vacuum environment. Furthermore, the tribological properties of polymers can be greatly improved at cryogenic temperatures by incorporating molybdenum disulfide (MoS_2), graphite, and short carbon fibers in the polymer matrix [12, 14, 15].

At the same time, PTFE fabric composites, which are woven by PTFE fibers and other reinforcing fibers (aramid fibers [16, 17], PI fibers [18], PEEK fibers [19], etc.), have been widely investigated in the field of tribology because they possess the merits of both good lubricity of PTFE fibers and excellent mechanical properties of the reinforcing fibers [20]. Wang et al. [21] proposed the theory of the double-layer transfer film structure of PTFE/Kevlar hybrid fabrics under heavy loads by investigating the tribological behavior of PTFE/Kevlar hybrid-fabric composites with a heavy load liner tester. Yuan et al. [22] used the polymerization reaction of dopamine and polyethyleneimine to deposit carbon nanotubes on the surface of PTFE and Nomex fibers, which effectively improved the thermal stability and tribological properties of the PTFE/Nomex hybrid fabrics. Cui et al. [5] studied the tribological properties of spherical plain bearings with Nomex/PTFE fabric in a nitrogen environment at −160 °C and found that the transfer film formed on the outer surface of the bearing's inner ring was the main factor leading to the low-temperature lubrication performance. Although the tribological properties of hybrid-fabric composites have been well investigated under ambient- and high-temperature conditions [23–26], there is little research on the tribological properties of PTFE-based fabric composites at cryogenic temperatures; in particular, the mechanism of transfer film formation at cryogenic temperatures remains basically unknown [2, 5].

In this work, the tribological behavior and mechanism of PTFE/Nomex and PTFE/PEEK hybrid-fabric composites were investigated under a −150 °C nitrogen atmosphere and a 25 °C ambient atmosphere. The formation mechanism of the transfer film and its effect on the lubricating performance were discussed in detail. This work is expected to instruct the design and formulation of hybrid-fabric composites used at cryogenic temperatures and lay the foundation for their practical applications.

2 Experimental

2.1 Materials and reagents

In this work, low-friction PTFE fibers and high-performance Nomex and PEEK fibers (Deyang Zhengjia Chemical Technology Co., Ltd.) were woven into PTFE/Nomex fabric (twill 1/2 weave structure, area mass = 270 g/m^2) and PTFE/PEEK fabric (plain weave structure, area mass = 400 g/m^2). Polyetherimide (PEI) resin was purchased from Shanghai Synthetic Resin Institute, and phenol formaldehyde (PF) resin was provided by Xingguang Chemical Reagent Factory (Fig. 1(a)). The molecular structures of PEI and PF, as adhesives in the preparation of fabric composites, are shown in Fig. 1(b). Lamellar silver-coated copper (Ag@Cu) and MoS_2 were provided by Beijing Deke Daojin Science and Technology Co., Ltd. The shape of Ag@Cu is irregular flakes, and its main dimensions range from 10–20 μm. MoS_2 is in the shape of irregular flakes with main dimensions of 1–3 μm. Their morphologies and X-ray diffraction (XRD) patterns can be seen in Figs. 1(c)–1(f). Moreover, petroleum ether, acetone, ethanol, ethyl acetate, and N,N-dimethylformamide (DMF) were provided by Li'an Long Bohua Medicinal Chemical Co., Ltd. All reagents can be used directly.

2.2 Fabrication of hybrid-fabric composites

The original Nomex/PTFE and PEEK/PTFE hybrid fabrics were first placed in a Soxhlet extractor to wash with ethanol and petroleum ether for 12 h to remove the oil and impurities adhered to the surface of the fabric, and then dried in an oven at 100 °C for 2 h. Subsequently, the PEI adhesive was configured as follows: PEI resin and DMF were blended in a flask at a mass ratio of 15 wt%, and then mechanically stirred in an oil bath at 80 °C for 6 h. PF adhesive was prepared by mixing PF resin with ethyl acetate at a mass ratio of 1:2. The solid content of PF adhesive is 20 wt%. Subsequently, MoS_2 and lamella Ag@Cu were added to the PEI or PF adhesive at a mass ratio of pure resin:filler = 10:1, and then the fillers were dispersed more uniformly by mechanical stirring for 30 min and ultrasonic dispersion for 30 min. Finally, the prepared hybrid fabrics after drying were put into PEI or PF adhesive containing fillers, repeatedly dipped, squeezed, and dried until the mass fraction of resin adhesive in the resin–fabric composite reaches approximately 20%. The formulations of the hybrid-fabric composites are listed in Table 1. The optical microscopy surface morphologies of the hybrid-fabric composites are shown in Figs. 1(g)–1(j). The obtained composites were cut into a suitable shape, glued to a pin with PF resin, and cured for 4 h at 150 °C with a pressure of 0.1 MPa. The friction samples were obtained after natural cooling.

2.3 Tribological testing and characterization

To meet the special applications for spherical plain bearing support at heavy loads and low speeds, a pin-on-disk tribometer (MDZ-05GL) equipped with a liquid nitrogen cooling device was applied to investigate the tribological properties of hybrid-fabric composites (Fig. 2). The tribometer was provided by Jinan Yihua Tribology Testing Technology Co., Ltd. The friction and wear tests were performed in an air atmosphere at 25 °C and in nitrogen gas at −150 °C. A stationary GCr15 steel pin (7 mm in diameter) cylindrical in shape was stuck with a series of different hybrid fabric composite specimens in a pin-on-disk tribometer. During the tests, the stationary pin contacted the flat

Table 1 Formulations of fabric composites.

Fabric composite	Composition (wt%)		
	Fabric (78%)	Adhesive (20%)	Filler (2%)
NP–PF–AC	Nomex/PTFE	PF	Ag@Cu
NP–PEI–AC	Nomex/PTFE	PEI	Ag@Cu
PP–PEI–MoS_2	PEEK/PTFE	PEI	MoS_2
NP–PEI–MoS_2	Nomex/PTFE	PEI	MoS_2

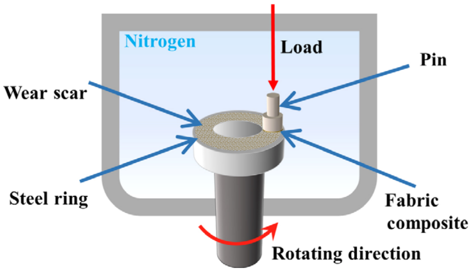


Fig. 2 Schematic diagram of pin-on-disk wear testing.

S03 ring (022Cr12Ni10MoTi, roughness = 112±12 nm), rotating with a radius of 11.5 mm at a speed of 10 r/min (12 mm/s). The contact load was gradually increased to 700 N within 16 min, and the theoretical plane–plane contact pressure was calculated to be 18.19 MPa. Prior to the test, the flat S03 rings were plated by Cr to increase the hardness of the material, and then sequentially cleaned with acetone and ethanol. All tribology tests were repeated three times, and the average values were taken for error reduction.

The surface texture structures of the hybrid-fabric composites and transfer films were determined by the optical microscopy. The crystal structures of the fillers were characterized by the XRD (X′Pert Pro, Philips). The storage moduli of adhesives and hybrid-fabric composites were characterized by the dynamic mechanical analysis (DMA; DMA 242 E, Netzsch Instruments) when heated from −150 to 25 °C at a rate of 5 °C/min and a frequency of 1 Hz. The surface roughness and three-dimensional (3D) topography of the specimens were characterized by a 3D white light interferometry surface topography instrument (NexView, ZYGO). The wear morphologies of the hybrid-fabric composites and their counterpart steel rings were tested by an SEM (Quanta 200 FEG, FEI) equipped with an energy dispersive X-ray spectroscopy (EDS) analyzer. The Fourier transform infrared (FT-IR) spectra of the transfer film on the rings were obtained by an FT-IR spectrometer (V70, Bruker) with a microscope.

3 Results and discussion

3.1 Friction coefficient analysis

The friction coefficients of different hybrid-fabric composites were obtained at −150 and 25 °C with a load of 700 N. As shown in Figs. 3(a) and 3(b), the load was applied gradually to 700 N in 16 min, and there was an unstable run-in period during the first 16 min of sliding. In the run-in period, the PEI and PF resins adhering to the surface of the PTFE fibers were worn firstly, which resulted in a high initial friction coefficient. PTFE fibers were exposed as the load increased, so the counterpart and PTFE fibers were worn against each other, which reduced the friction coefficient. Therefore, the friction curve fluctuated up and down under the combined action of the adhesive resin and the PTFE fibers during the run-in period. With the increasing time and load, the polymer transfer film on the counterpart surface was continuously formed, and the friction coefficient tended to be stable. Figure 3(a) indicates that the friction coefficient of the hybrid-fabric composites tended to be stable and fluctuated little after reaching the target load at 25 °C. The friction coefficient of PP–PEI–MoS_2 had a slow downward trend, and the friction coefficient was close to 0.10 at 25 °C. The friction coefficient of NP–PF–AC was high at 25 °C, and the friction curve fluctuates greatly. The friction coefficient of NP–PF–AC was finally stable at 0.12 at 25 °C. In a nitrogen atmosphere at −150 °C, the friction coefficients of different hybrid-fabric composites were quite different (Fig. 3(b)). The average friction coefficient of NP–PF–AC was still the highest at both 25 and −150 °C (Fig. 3(c)). The fluctuation of the friction coefficient at 25 °C was smaller than that at −150 °C, so the stability of the friction coefficient at ambient temperature was better than that at cryogenic temperature. The PTFE was easily sheared and deformed due to its low hardness and high mobility of molecular chains at 25 °C, so a transfer film can be quickly formed to promote the friction coefficient stability [27, 28]. However, the hardness and mobility of molecular chains of the PTFE increased rapidly as the temperature dropped from 25 to −150 °C, and it was difficult to quickly form a stable transfer film on the steel counterpart, which led to large fluctuations in the friction coefficient. Under cryogenic conditions, the friction coefficient of PP–PEI–MoS_2 with the lowest friction coefficient increased first, and then stabilized at approximately 0.15. The friction coefficient

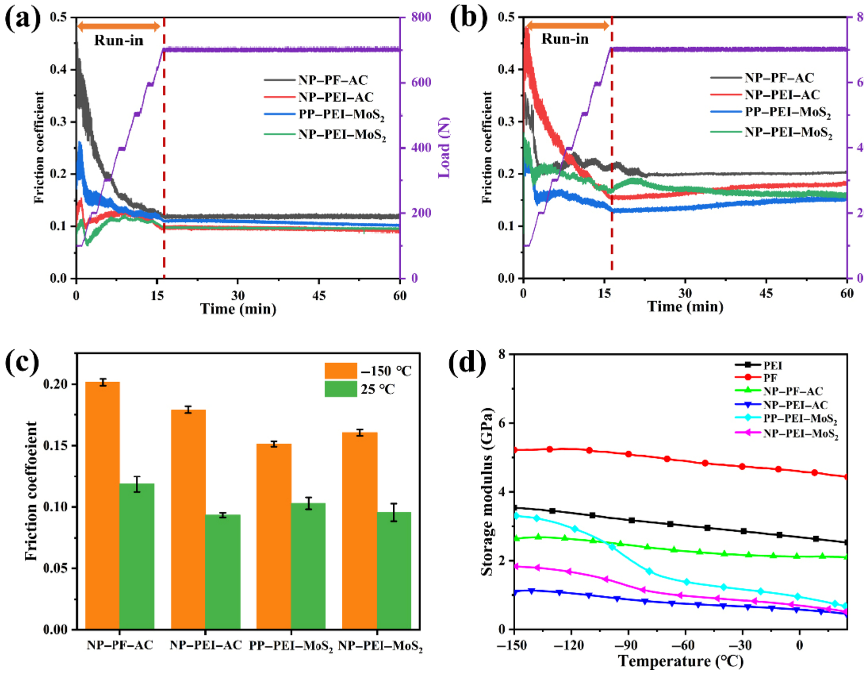


Fig. 3 Friction curves of hybrid fabric composites at (a) 25 °C and (b) −150 °C; (c) average friction coefficients of fabric composites at different temperatures; and (d) DMA curves of resins and fabric composites.

of NP–PEI–MoS_2 showed a trend of first decreasing and then stabilizing at 0.16 at cryogenic temperature. The friction coefficients of the four hybrid-fabric composites at 25 °C were relatively lower than those at −150 °C.

The mechanical properties of materials play an important role in friction and wear, and temperature is an important factor affecting the mechanical properties of polymers [29–31]. The DMA curves show that the modulus of the hybrid-fabric composites decreased with the increasing temperature (Fig. 3(d)). The storage moduli of the NP–PF–AC with PF adhesive decreased slowly with the increasing temperature because high temperatures make the molecular chains move more vigorously, and the deformation increases. At the same time, the storage moduli of pure PF resin were very high at cryogenic temperatures and slowly decreased as the temperature increased. However, the storage moduli of pure PEI resin were much lower than those of PF resin and decreased rapidly as the temperature increased. Therefore, the storage moduli of the NP–PF–AC fabric composite were higher than those of the PEI-impregnated fabric composites. Due to the cross-links or macromolecular entanglement between the molecular chains of thermosetting PF, the fluidity of polymer chains was not sensitive to temperature [32]. In contrast, thermoplastic PEI resin had higher toughness than thermoset PF resin at cryogenic temperatures due to its flexible linear molecular chains [33], so NP–PEI–AC and NP–PEI–MoS_2 had low storage moduli at cryogenic temperatures. PP–PEI–MoS_2 had higher storage moduli than the NP–PEI–MoS_2 composite at cryogenic temperatures because the PEEK fibers possessed better mechanical properties than the Nomex fibers [19].

3.2 Surface topography analysis

The wear of hybrid-fabric composites was qualitatively analyzed through the 3D topography of the fabric surface. Figures 4(a)–4(h) depict the morphologies of the wear surface of various hybrid-fabric composites at different temperatures, and the 3D topography of unworn hybrid-fabric composites is shown in Figs. 4(i)–4(l). Different degrees of abrasion occurred on the surface of the fabric composites, and the wear was significantly higher at 25 °C than that at −150 °C. Plastic deformation was difficult for polymer materials at low temperatures because the cryogenic temperature restricts the mobility of molecular chains, while the ductility of polymers was the result of molecular mobility [34]. Moreover, the hardness of PTFE increased

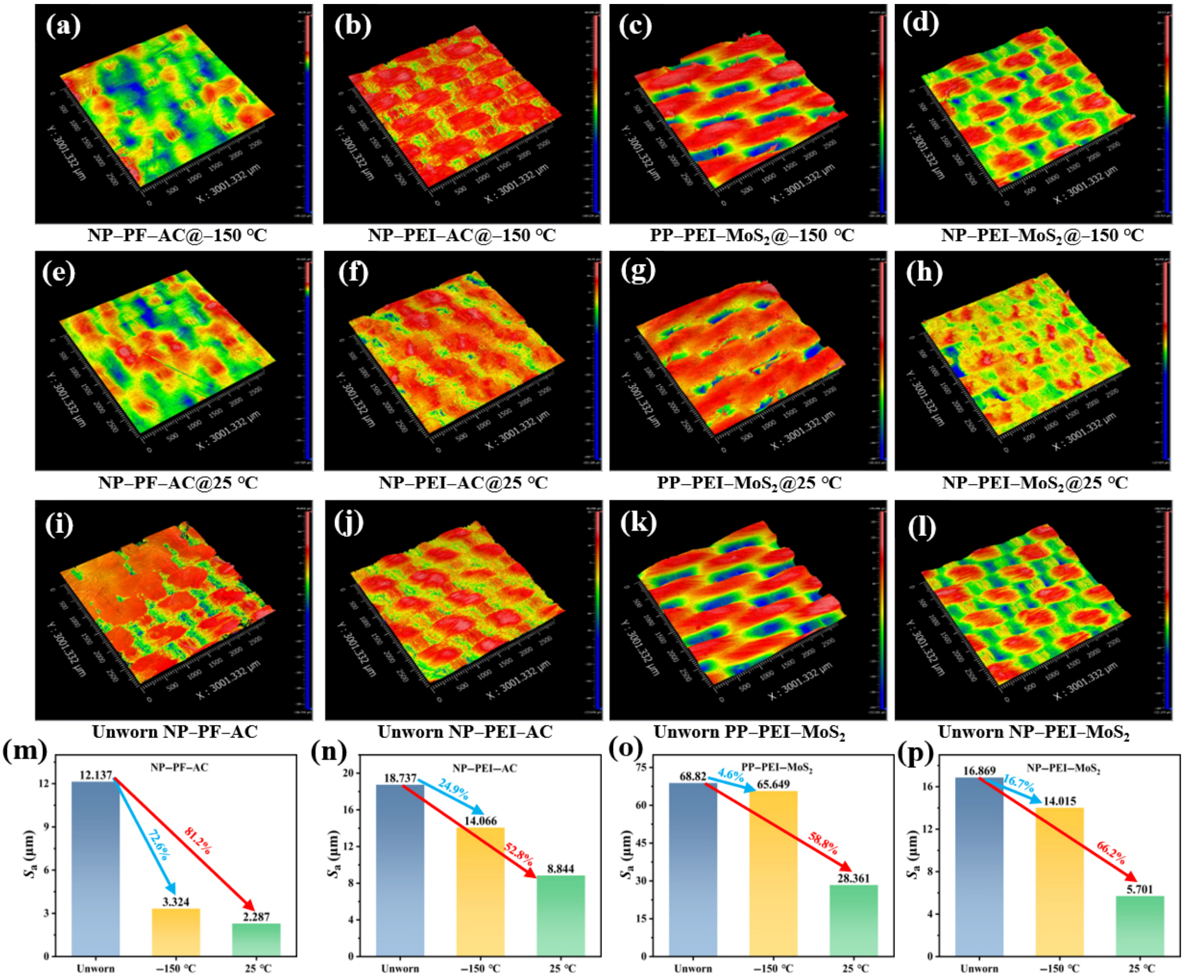


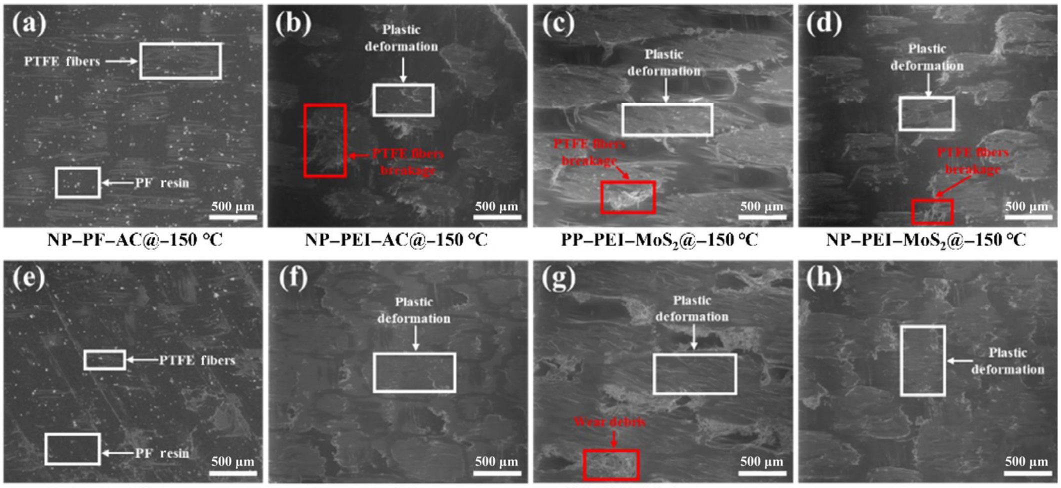
Fig. 4 3D morphology images of hybrid-fabric composites after tribometer at (a–d) −150 °C and (e–h) 25 °C; (i–l) unworn hybrid-fabric composites; and (m–p) surface roughness (S_a) of unworn and worn hybrid-fabric composites.

with the decreasing of temperature [13]. Therefore, the fabric composites had better wear resistance at low temperatures. PF resin will produce irregularly shaped PF microparticles during the friction process at low temperatures. Under the action of a high load, the PF microparticles generated local high pressures on the surface of the NP–PF–AC composite, and the PF resin and PTFE fibers on the surface of the NP–PF–AC were worn away during the friction process. Therefore, the NP–PF–AC composite exhibited abrasive wear behavior at −150 °C. As depicted in Fig 4(a), the PF resin on the surface of the NP–PF–AC composite was worn by abrasive particles, so the PTFE fibers were exposed. However, the PTFE fibers on the surface did not undergo severe plastic deformation, which indicates that the PTFE fibers do not completely touch the surface of the counterpart.

Figure 4 indicates that the wear of the composites was relatively low at −150 °C compared to that at 25 °C because polymer chains are trapped in a frozen state at low temperatures, making the polymer difficult to wear [13]. At 25 °C, the PTFE fibers of the NP–PEI–MoS_2 composite were severely worn off, and the hybrid-fabric composite lost the original warp and weft interweaving morphology of the fabric surface. The PTFE fiber bundles on the surface of NP–PEI–AC and PP–PEI–MoS_2 composites underwent plastic deformation under the action of stress and shearing force, which increased the actual contact area between the fabric composite and the counterpart. However, the contact area was not the root cause affecting the friction coefficient at 25 °C. PTFE has low intermolecular cohesion and easily forms a thin transfer film on the surface of its counterpart at room temperature, which reduces the friction force. Theoretically, the friction coefficient of fabric composites should decrease at low temperatures because the contact area between the friction pair decreases due to the increased storage modulus and hardness of the fabric composites at −150 °C. In fact, however, the friction coefficient of fabric composites at −150 °C was higher than that at 25 °C. The high friction coefficient at −150 °C was mainly because the molecular mobility of PTFE was obviously suppressed at −150 °C, and the molecular chains of PTFE became more entangled and were difficult to move, which obstructed the formation of PTFE transfer films [27].

The changes in the arithmetic mean height (S_a) of the fabric composites surfaces were used to characterize the degree of wear. The S_a of the hybrid-fabric composites before and after abrasion are shown in Figs. 4(m)–4(p). For different hybrid-fabric composites, the roughness at 25 °C is always smaller than that at −150 °C, meaning that the fabric composites underwent relatively obvious plastic deformation at room temperature, which indicates that hybrid-fabric composites possess higher wear resistance at −150 °C than that at 25 °C. In comparison to those of unworn hybrid-fabric composites, the worn surface roughness of NP–PF–AC was reduced by 72.6% (at −150 °C) and 81.2% (at 25 °C), while the worn surface roughness of NP–PEI–AC was reduced by 24.9% (at −150 °C) and 52.8% (at 25 °C). This suggested that PEI resin was more wear-resistant than PF resin both at 25 and −150 °C among the hybrid-fabric composites. In terms of wear performance, PEI resin has good toughness and is prone to plastic deformation to reduce the wear of PTFE fibers over a wide range of temperatures. However, PF resin was more likely to produce hard particles due to its high modulus and hardness, and the hard particles can easily lead to abrasive wear. PF resin, a thermosetting resin with a 3D network structure, will become brittle and hard at cryogenic temperatures, which is the origin of PF resin increasing the wear of hybrid-fabric composites. In contrast, PEI resin, a thermoplastic resin with a linear molecular structure, showed good toughness even at cryogenic temperatures and was difficult to wear away as abrasion debris during the friction process. Therefore, PEI resin was more suitable than PF resin for the use of adhesives for hybrid-fabric composites over a wide temperature range. In addition, Figs. 4(o) and 4(p) exhibit that the PEEK/PTFE hybrid fabric showed better wear resistance than the Nomex/PTFE hybrid fabric at both −150 and 25 °C, which is attributed to the higher mechanical strength and stress transmission ability of the PEEK fiber than the Nomex fiber.

The wear morphologies of the hybrid-fabric composites were further characterized by the SEM to comprehend the effect of different temperatures on the tribological performance of the hybrid-fabric composites, as illustrated in Fig. 5. The PTFE fibers of the NP–PEI–AC, PP–PEI–MoS_2, and NP–PEI–MoS_2 composites impregnated with PEI resin underwent plastic deformation at both −150 and 25 °C, as shown in Figs. 5(b)–5(d) and Figs. 5(f)–5(h), respectively.



NP–PF–AC@–150 °C NP–PEI–AC@–150 °C PP–PEI–MoS_2@–150 °C NP–PEI–MoS_2@–150 °C

NP–PF–AC@25 °C NP–PEI–AC@25 °C PP–PEI–MoS_2@25 °C NP–PEI–MoS_2@25 °C

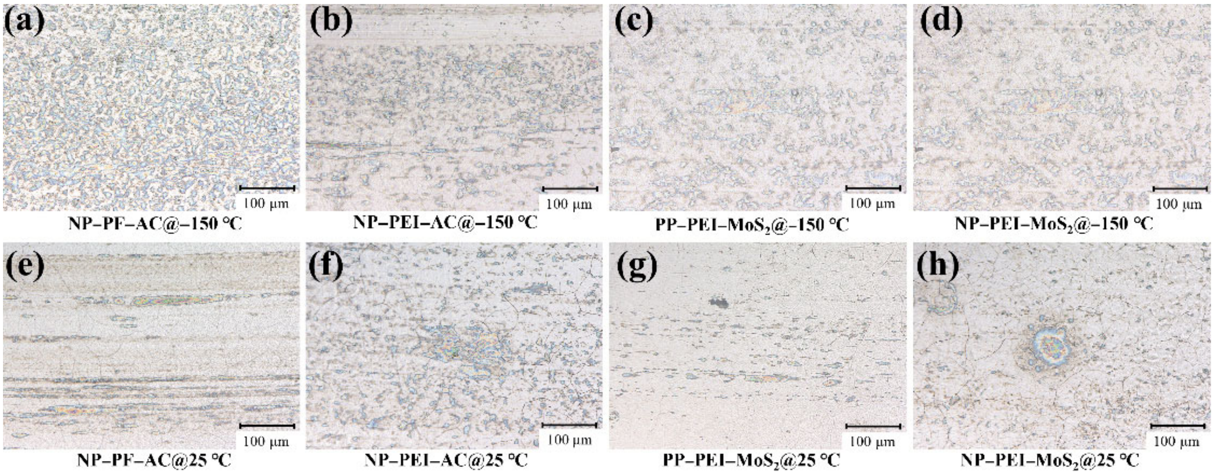
Fig. 5 SEM micrographs of worn surfaces for hybrid-fabric composites at different temperatures.

Simultaneously, PTFE fibers mixed with PEI resin will undergo adhesive wear and transfer to the counter face and form a polymeric transfer film (Fig. 6). Furthermore, the PTFE fibers were directly exposed on the surface of the steel counterpart, and the PTFE fibers at the edges were drawn out from the matrix due to the low interfacial force between the PTFE fibers and PEI resin. The peeled PTFE fibers were broken under the action of shear force and stress at cryogenic temperatures. Only plastic deformation occurred due to the low hardness of PTFE fibers and PEI resins at 25 °C. However, there was a stack of wear debris in the gaps on the surface of the PP–PEI–MoS$_2$ composite at 25 °C because of severe wear (Fig. 5(g)). The PF resin did not undergo plastic deformation, and only a small number of PTFE fibers were exposed on the surface of NP–PF–AC (Fig. 5(a)). Because the modulus and hardness of PF were higher at cryogenic temperatures, the PF resin-wrapped PTFE fibers further hindered the lubrication performance of PTFE. The worn PF caused abrasive wear of the material (Figs. 4(e) and 5(e)), so the friction coefficient of NP–PF–AC was high.

The morphologies of the transfer films formed at −150 and 25 °C were observed by the optical microscopy, as shown in Fig. 6. There was a weak van der Waals force between PTFE molecular chains, so PTFE can easily form a PTFE layer under a low shear force, which makes it an excellent self-lubricating polymeric material with a low friction coefficient [16]. During the friction process, the PTFE fibers easily deformed and slid, and then diffused and filled the gaps on the surface of the fabric to form a thin film under the shearing action of the friction force. PTFE was transferred to the surface of the metal counterpart and adhered to it to form a thin and uniform polymer layer, which is generally referred to as a transfer film [35]. The tribological properties of the polymeric composites were closely related to the quality of the transfer films. In this work, the transfer films formed at −150 °C were more uniform, large, and dense, while those formed at 25 °C were uneven and sparse. Notably, the transfer films on the ring against the NP–PF–AC composite tested at −150 °C were relatively uniform and dense, but the friction coefficient was the highest. Since PF was a thermosetting resin, the worn PF particles lacked the interaction force and cannot adhere to each other. Therefore, island-like transfer films were formed on the surface of the steel counterpart. PEI resin adhered to the surface of PTFE fibers to protect the PTFE fibers and reduce the wear of PTFE fibers. However, the PEI resin and PTFE fibers were plastically deformed under the action of shearing force, and then jointly transferred to the surface of the metal disk to form a high-quality transfer film, which can be confirmed in the subsequent FT-IR and EDS characterization.

3.3 Transfer film analysis

The chemical compositions of the transfer films tested at cryogenic and ambient temperatures were determined by the FT-IR, and the results are displayed in Fig. 7. Obviously, the IR spectra of transfer films formed by fabric composites of NP–PEI–AC,



NP–PF–AC@–150 °C
NP–PEI–AC@–150 °C
PP–PEI–MoS$_2$@–150 °C
NP–PEI–MoS$_2$@–150 °C
NP–PF–AC@25 °C
NP–PEI–AC@25 °C
PP–PEI–MoS$_2$@25 °C
NP–PEI–MoS$_2$@25 °C

Fig. 6 Optical microscopy images of counterpart ring sliding against hybrid-fabric composites at different temperatures.

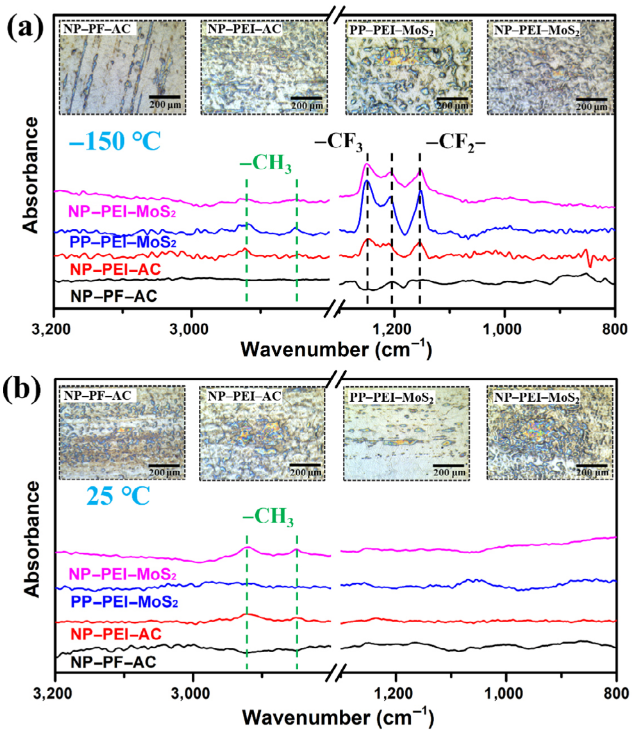


Fig. 7 FT-IR spectra of transfer films at (a) −150 °C and (b) 25 °C.

PP–PEI–MoS_2, and NP–PEI–MoS_2 tested at cryogenic temperature (Fig. 7(a)) have three main characteristic absorption peaks of PTFE, 1,149, 1,205, and 1,250 cm^{-1} corresponding to the symmetric and asymmetric stretching vibrations of difluoromethylene (–CF_2–) and asymmetric stretching vibrations of trifluoromethyl (–CF_3), respectively [36, 37]. However, the transfer films formed by all composites tested at 25 °C had no obvious PTFE peaks in the range of 1,000–1,300 cm^{-1} (Fig. 7(b)). This may be because the PTFE contents of these transfer films were too low to be detected by the FT-IR at 25 °C, which can be further confirmed in Fig. 8. Moreover, the double peaks at 2,910 and 2,846 cm^{-1} corresponding to the C–H stretching vibrations of methyl (–CH_3) from PEI molecules could be seen in the IR spectra of transfer films formed by fabric composites of NP–PEI–AC and NP–PEI–MoS_2, tested both at 25 and −150 °C [38].

The transfer film formed by the NP–PF–AC composite was the densest and most uniform among all transfer films formed at cryogenic temperature, but it had no obvious characteristic absorption peaks of PTFE, not similar to the three other composites (Fig. 7). A thermoset material, PF resin, will inhibit the lubricating property of PTFE and the formation of a transfer film containing PTFE once it has covered the fibers. Similarly, the IR spectra of the transfer film formed by composite NP–PF–AC tested at 25 °C did not display significant characteristic peaks of PTFE. It may be that the weak signals from traces of PTFE were not detected by the IR spectroscopy. However, the EDS results (Fig. 8(d)) illustrate that the counterpart surface still contained a small amount of F, which indicates that the transfer film contains a small amount of PTFE at 25 °C. The NP–PF–AC composite exhibited poor lubricating properties and had the highest friction coefficients at both −150 and 25 °C. Although the absorption peaks occurred with a similar wavenumber in the IR spectra of transfer films formed by composites of NP–PEI–AC, PP–PEI–MoS_2, and NP–PEI–MoS_2 tested at cryogenic temperature (Fig. 7(a)), the characteristic peak (–CF_3 and –CF_2–) intensities of PTFE are quite different. According to the Lambert–Beer law, the peak intensity of the IR spectrum was related to the concentration of the absorbing substance [31]. As shown in Fig. 7(a), the peak intensities of –CF_2– and –CF_3 in the IR spectroscopy curves of PP–PEI–MoS_2 and NP–PEI–MoS_2 were much higher than those in NP–PEI–AC, which means that the transfer films in Figs. 6(c) and 6(d) have more PTFE. The friction coefficients of composites PP–PEI–MoS_2 and NP–PEI–MoS_2 tested at cryogenic temperature were also lower than that of NP–PEI–AC, which illustrates that PTFE in the transfer film is beneficial to reducing the friction coefficient.

Normally, the transfer film is taken as a consequence of tribological behaviors; it can reflect the tribological properties of composites and even promote friction reduction in the material system. To further investigate the morphologies and compositions of the transfer films, Fig. 8 depicts the SEM images of counterpart rings sliding against different fabric composites at cryogenic temperature (Fig. 8(a)) and ambient temperature (Fig. 8(b)) and the EDS results of the transfer film (Figs. 8(c) and 8(d)). Due to a layer of Cr plated on the surface of flat S03, the hardness of the ring surface was improved, and there were no scratches or furrows on the ring after friction testing.

As depicted in Figs. 8(a) and 8(b), the transfer films formed at low temperatures were indeed denser than those formed at 25 °C. The contents of C, O, F, and Cr

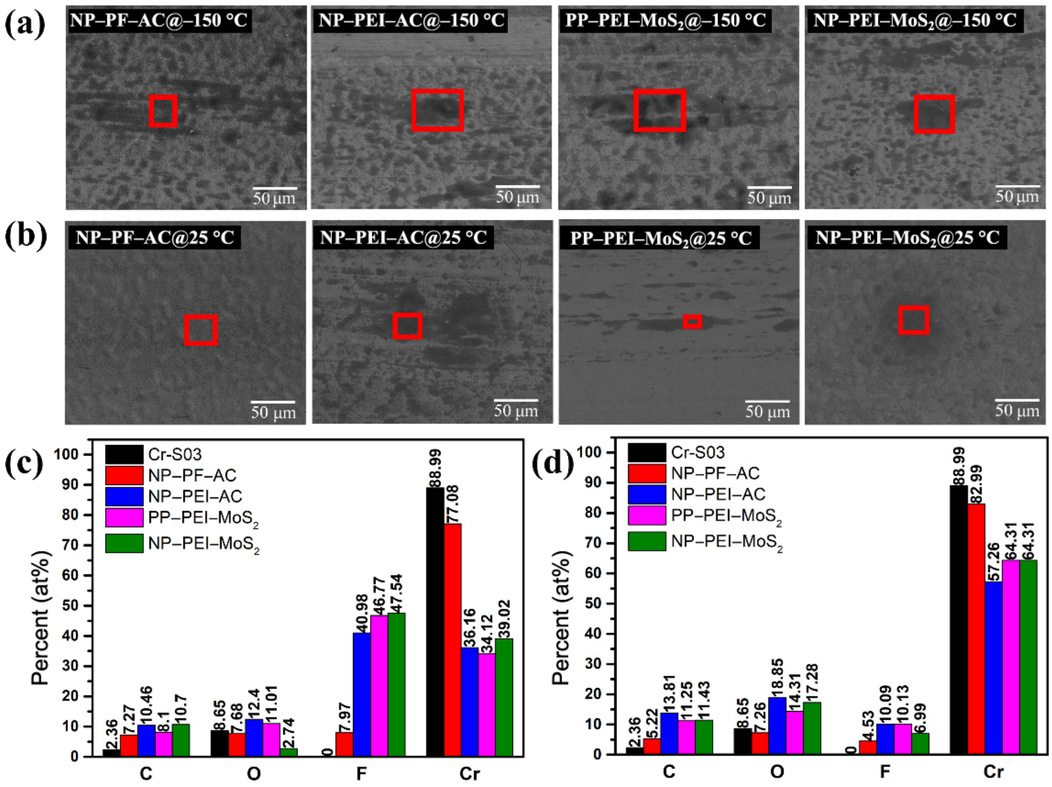


Fig. 8 SEM images of transfer films for counterpart rings sliding against fabric composites at (a) −150 °C and (b) 25 °C; (c, d) corresponding EDS results of the red regions in (a, b), respectively.

in the transfer film can be clearly seen in Figs. 8(c) and 8(d). Moreover, the content of F in the transfer film formed at cryogenic temperatures was much higher than that formed at 25 °C. Here, F could be distinguished from Fe since the Cr-plated S03 steel surfaces did not show Fe/F peaks, as shown in Fig. 8. The transfer film, which is formed by PTFE and PEI resins and adheres to the counterpart surface at cryogenic temperature, was thicker than that at 25 °C and was hard to wear due to the poor mobility of polymeric molecules at cryogenic temperature. From the results of elemental analysis on the surface of the transfer film (Figs. 8(c) and 8(d)), it can be seen that the F element contents in the transfer film formed by the NP–PEI–AC, PP–PEI–MoS_2, and NP–PEI–MoS_2 composites at cryogenic temperature were above 40%, which indicates that the main component of the transfer film is PTFE. The local shear force was more likely to cut the rigid PTFE fibers into pieces, obtaining peeled wear debris. Under the action of extrusion, transfer films with high concentrations of PTFE were formed. The PTFE fibers underwent plastic flow under the action of shear force at 25 °C, forming wear debris and being discharged out of the friction interface, which resulted in a lower PTFE content in the transfer film on the counterpart surface. Since the hardness of PTFE increases with the decrease of temperature [13], the PTFE had better plastic deformation ability at room temperature than that at cryogenic temperatures, which indicates that the transfer film is easier to form at 25 °C than that at −150 °C. However, there was a large difference among the transfer films of the fabric composites due to the difference in adhesives. At low temperatures, the hardness of the PF resin increased significantly. The phenolic resin covered the surface of the PTFE fiber and inhibited the PTFE fiber from participating in the interfacial friction, resulting in very little PTFE contents in the transfer film formed by NP–PF–AC and the highest friction coefficient. Fabric composites impregnated with PEI adhesives mainly suffered from adhesive wear at cryogenic temperatures because thermoplastic PEI resin still had a certain degree of toughness.

4 Conclusions

In this study, the tribological properties of Nomex/PTFE and PEEK/PTFE fabric composites were studied at −150 and 25 °C. The effects of thermosetting PF resin and thermoplastic PEI resin as fabric adhesives and lamellar Ag@Cu and MoS_2 as fillers on their friction and wear properties were explored. The following conclusions were drawn.

1) For PTFE/Nomex and PTFE/PEEK hybrid-fabric composites, the friction coefficients at −150 °C were higher than those at 25 °C. On the other hand, due to the low mobility of PTFE molecular chains and increase in the hardness of polymer itself at −150 °C, the destruction of the PTFE fibers was impeded, which prevents the hybrid-fabric composites from wearing out, and thus the wear at −150 °C was lower than that at 25 °C

2) In terms of adhesives for hybrid-fabric composites, PEI resin showed better cryogenic tribological properties than PF resins. Compared with layered silver materials, two-dimensional MoS_2 was more suitable as a filler for fabric composites at low temperatures. A high-quality PTFE-based transfer film was beneficial to reducing the friction coefficient.

3) The tribological performance of the PTFE/PEEK hybrid-fabric composite was better than that of the PTFE/Nomex fabric composites, mainly due to the abundant PTFE fibers on the surface and the excellent mechanical properties of the PEEK fibers, which can play the role of load-bearing and stress transmission.

4) For the same hybrid-fabric composites, the transfer film was the main factor affecting the tribological properties. Although the transfer film formed at −150 °C had a higher PTFE content than that at 25 °C, the molecular chains of PTFE were frozen and difficult to slip at cryogenic temperatures, resulting in a high friction coefficient.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

References

[1] Koerner C, Kampf D, Poglitsch A, Schubert J, Ruppert U, Schoele M. Development of cryogenic filter wheels for the HERSCHEL photodetector array camera & spectrometer (PACS). In: Proceedings of the 42nd Aerospace Mechanism Symposium, Greenbelt, USA, 2014: 19–30.

[2] Yu C G, Chen W H, Liang B, Wang T M, Cui W Y, Ma B, Zhao W H, Tao L M, Ma T B. Study on the tribological properties of a self-lubricating spherical plain bearing at a cryogenic and wide temperature range. *Scientia Sinica Technologica* **50**(6): 775–785 (2020) (in Chinese)

[3] Park S Y, Choi H S, Choi W J, Kwon H. Effect of vacuum thermal cyclic exposures on unidirectional carbon fiber/epoxy composites for low earth orbit space applications. *Compos Part B-Eng* **43**(2): 726–738 (2012)

[4] Nosaka M, Kikuchi M, Oike M, Kawai N. Tribo-characteristics of cryogenic hybrid ceramic ball bearings for rocket turbopumps: Bearing wear and transfer film©. *Tribol Trans* **42**(1): 106–115 (1999)

[5] Cui W Y, Raza K, Zhao Z J, Yu C G, Tao L M, Zhao W H, Chen W H, Peng S G, Xu Q, Ma L R, et al. Role of transfer

film formation on the tribological properties of polymeric composite materials and spherical plain bearing at low temperatures. *Tribol Int* **152**: 106569 (2020)

[6] Voevodin A A, Zabinski J S. Nanocomposite and nanostructured tribological materials for space applications. *Compos Sci Technol* **65**(5): 741–748 (2005)

[7] John M, Menezes P L. Self-lubricating materials for extreme condition applications. *Materials* **14**(19): 5588 (2021)

[8] Theiler G, Gradt T. Friction and wear of polymer materials at cryogenic temperatures. In: *Polymers at Cryogenic Temperatures*. Kalia S, Fu S Y, Eds. Berlin, Germany: Springer Berlin Heidelberg, 2013: 41–58.

[9] Kumar R, Antonov M. Self-lubricating materials for extreme temperature tribo-applications. *Mater Today* **44**: 4583–4589 (2021)

[10] Meng Y G, Xu J, Jin Z M, Prakash B, Hu Y Z. A review of recent advances in tribology. *Friction* **8**(2): 221–300 (2020)

[11] McCook N L, Burris D L, Dickrell P L, Sawyer W G. Cryogenic friction behavior of PTFE based solid lubricant composites. *Tribol Lett* **20**(2): 109–113 (2005)

[12] Theiler G, Gradt T. Friction and wear behaviour of polymers in liquid hydrogen. *Cryogenics* **93**: 1–6 (2018)

[13] Wang Q H, Zheng F, Wang T M. Tribological properties of polymers PI, PTFE and PEEK at cryogenic temperature in vacuum. *Cryogenics* **75**: 19–25 (2016)

[14] Theiler G, Gradt T. Friction and wear of PEEK composites in vacuum environment. *Wear* **269**(3–4): 278–284 (2010)

[15] Oyamada T, Ono M, Miura H, Kuwano T. Effect of gas environment on friction behavior and tribofilm formation of PEEK/carbon fiber composite. *Tribol Trans* **56**(4): 607–614 (2013)

[16] Sun W B, Gu Y Z, Yang Z J, Li M, Wang S K, Zhang Z G. Enhanced tribological performance of hybrid polytetrafluoroethylene/Kevlar fabric composite filled with milled pitch-based carbon fibers. *J Appl Polym Sci* **135**(19): 46269 (2018)

[17] Qiu M, Yang Z P, Lu J J, Li Y C, Zhou D W. Influence of step load on tribological properties of self-lubricating radial spherical plain bearings with PTFE fabric liner. *Tribol Int* **113**: 344–353 (2017)

[18] Su M, Liang L, Ren F, Yao W G, Yu M M, Ren M S, Sun J L. Influence of reinforcing fiber on the dry sliding wear behavior of hybrid fabric/benzoxazine composites. *Text Res J* **89**(23–24): 5153–5164 (2019)

[19] Wang C L, Luan J S, Xu Z P, Zhao W Y, Zhang M. Preparation and properties of a novel, high-performance polyether ether ketone fabric. *High Perform Polym* **30**(7): 794–802 (2018)

[20] Yang M M, Zhang Z Z, Yuan J Y, Wu L F, Zhao X, Guo F, Men X H, Liu W M. Fabrication of PTFE/Nomex fabric/phenolic composites using a layer-by-layer self-assembly method for tribology field application. *Friction* **8**(2): 335–342 (2020)

[21] Wang H, Qi X W, Zhang W L, Dong Y, Fan B L, Zhang Y. Tribological properties of PTFE/Kevlar fabric composites under heavy loading. *Tribol Int* **151**: 106507 (2020)

[22] Yuan J Y, Zhang Z Z, Yang M M, Guo F, Men X H, Liu W M. Carbon nanotubes coated hybrid-fabric composites with enhanced mechanical and thermal properties for tribological applications. *Compos Part A-Appl S* **102**: 243–252 (2017)

[23] Yuan J Y, Zhang Z Z, Yang M M, Guo F, Men X H, Liu W M. TiB_2 reinforced hybrid-fabric composites with enhanced thermal and mechanical properties for high-temperature tribological applications. *Tribol Int* **115**: 8–17 (2017)

[24] Li P L, Zhang Z Z, Yang M M, Yuan J Y, Jiang W. MoS_2-decorated talc hybrid for improving the tribological property of Nomex/PTFE fabric composites. *Polym Compos* **42**(11): 5839–5849 (2021)

[25] Yuan J Y, Zhang Z Z, Yang M M, Wang W J, Men X H, Liu W M. POSS grafted hybrid-fabric composites with a biomimic middle layer for simultaneously improved UV resistance and tribological properties. *Compos Sci Technol* **160**: 69–78 (2018)

[26] Yuan J Y, Zhang Z Z, Yang M M, Zhao X, Wu L F, Li P L, Jiang W, Men X H, Liu W M. Combined effects of interface modification and micro-filler reinforcements on the thermal and tribological performances of fabric composites. *Friction* **9**(5): 1110–1126 (2021)

[27] Xu Q A, Zhang J E, Li X, van Duin D M, Hu Y Z, van Duin A C T, Ma T B. How polytetrafluoroethylene lubricates iron: An atomistic view by reactive molecular dynamics. *ACS Appl Mater Interfaces* **14**(4): 6239–6250 (2022)

[28] Sápi Z, Butler R. Properties of cryogenic and low temperature composite materials—A review. *Cryogenics* **111**: 103190 (2020)

[29] Burton J C, Taborek P, Rutledge J E. Temperature dependence of friction under cryogenic conditions in vacuum. *Tribol Lett* **23**(2): 131–137 (2006)

[30] Babuska T F, Pitenis A A, Jones M R, Nation B L, Sawyer W G, Argibay N. Temperature-dependent friction and wear behavior of PTFE and MoS_2. *Tribol Lett* **63**(2): 15 (2016)

[31] Barry P R, Chiu P Y, Perry S S, Sawyer W G, Sinnott S B, Phillpot S R. Effect of temperature on the friction and wear of PTFE by atomic-level simulation. *Tribol Lett* **58**(3): 50 (2015)

[32] Qu J J, Zhang Y H, Tian X, Li J B. Wear behavior of filled polymers for ultrasonic motor in vacuum environments. *Wear* **322–323**: 108–116 (2015)

[33] He Y X, Li Q, Kuila T, Kim N H, Jiang T W, Lau K T, Lee J H. Micro-crack behavior of carbon fiber reinforced

thermoplastic modified epoxy composites for cryogenic applications. *Compos Part B-Eng* **44**(1): 533–539 (2013)

[34] Chen D, Li J Z, Yuan Y H, Gao C, Cui Y G, Li S C, Liu X, Wang H Y, Peng C, Wu Z J. A review of the polymer for cryogenic application: Methods, mechanisms and perspectives. *Polymers* **13**(3): 320 (2021)

[35] Ye J, Khare H S, Burris D L. Transfer film evolution and its role in promoting ultra-low wear of a PTFE nanocomposite. *Wear* **297**(1–2): 1095–1102 (2013)

[36] Gu Y Q, Wang Z D, Peng S G, Ma T B, Luo J B. Quantitative measurement of transfer film thickness of PTFE based composites by infrared spectroscopy. *Tribol Int* **153**: 106593 (2021)

[37] Mazhar S I, Shafi H Z, Shah A, Asma M, Gul S, Raffi M. Synthesis of surface modified hydrophobic PTFE–ZnO electrospun nanofibrous mats for removal of volatile organic compounds (VOCs) from air. *J Polym Res* **27**(8): 222 (2020)

[38] Tong W S, Zhang Y H, Zhang Q, Luan X L, Duan Y, Pan S F, Lv F Z, An Q. Achieving significantly enhanced dielectric performance of reduced graphene oxide/polymer composite by covalent modification of graphene oxide surface. *Carbon* **94**: 590–598 (2015)

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