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ORIGINAL PAPER

Preparation and characterization of poly(phthalazinone ether ketone)/SiO_2 hybrid composite thin films with low friction coefficient

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Abstract Organic–inorganic poly(phthalazinone ether ketone) (PPEK)/SiO_2 hybrid composite thin films were prepared by the dip-coating method on pre-cleaned glass substrates. The covalent bonds between organic and inorganic phases were introduced by an in-situ *O*-acylation reaction of isocyanatopropyltriethoxysilane (ICPTES) with the borohydride-reduced PPEK forming a polymer bearing triethoxysilyl groups. Theses groups were subsequently hydrolyzed with tetraethoxysilane (TEOS) and allowed to form a network via a sol–gel process. The polymer hybrid composite exhibited good thermal stability and a higher glass transition temperature as compared with the pure resin. Atomic force microscope, water contact angle measurement and scanning electron microscope were used to characterize the polymer hybrid thin films. The tribological experiment showed that the films have very low friction coefficient (about 0.1) and good anti-wear properties, without failure even after sliding for 18,000 s under modest loads. The improved tribological properties of the modified substrate were attributed to good adherence of PPEK/SiO_2 hybrid films on the substrate and synergy of both PPEK matrix and silica particles.

Keywords Thin films · High performance polymers · Polymer hybrid · Phthalazinone

1 Introduction

With the increasing interest in device miniaturization in fields such as biomedicine, telecommunication and mechanotronics, more and more attentions are being paid to the research in micro-electromechanical systems (MEMS) [1, 2]. However, the large surface-area-to-volume ratios raise serious adhesive and frictional problems for their operations [3–5]. In resolving the friction-related problems in MEMS, polymer thin films used as protecting and lubricating films have attracted increased attention in recent years [6–8].

The most popular system of polymer lubricative films is grafted polymer films, which can be graft polymerized onto substrate surfaces via free-radical initiators [9–12], cationic/anionic initiators [13–18], or by using a combination of a catalyst and an initiator [19–21] for controlled graft polymerization. Yet, each of these techniques relies on the presence of initiator sites covalently bound to the surface that act as anchoring sites for monomer grafting on inorganic oxide surfaces. The surface density of initiation sites is limited by the inherent availability of native surface hydroxyl groups for attaching the initiators to the substrate. Recently, investigations show that inorganic oxide particles and fullerene (C_{60}) possess higher mechanical stiffness and good load-carrying capacity. Since the combination of these inorganic materials, the wear-resistance of the modified polymer thin film is increased obviously [22–26]. Organic/inorganic polymer hybrid composites considered as innovative advanced materials can form a stable and dense film by virtue of the multiple functional groups strongly attached to the substrate [27]. In particular, combination of organic polymer matrices and inorganic particles, these materials possess unique properties like those of polymer systems but with improved mechanical,

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thermal and anti-wear properties. Therefore, a good alternative approach to preparing polymer film with good wear resistance and high surface density is formation of organic/inorganic polymer hybrid composite thin films [28–31].

The organic/inorganic polymer hybrid composites can be prepared by the incorporation of soluble polymers or monomers with organic metal alkoxides via a sol–gel process. In order to obtain homogeneous and transparent organic/inorganic polymer hybrids, it is necessary to increase the compatibility between organic polymer and inorganic phase. The introduction of covalent bonds between organic polymer and inorganic phases is effective in increasing the compatibility. Unsaturated monomers such as trimethoxysilyl propyl methacrylate or styrylethyltrimethoxysilane were homo- or copolymerized with methyl methacrylate [32–38], styrene [39–41], acrylonitrile [42] or other polyolefin. Novolac-type phenolic/SiO_2 [43, 44], novel epoxy/silica [45] and poly(methyl acrylate-co-itaconic anhydride)/SiO_2 [46] hybrid composite materials have been successfully prepared by using the alkoxysilane moieties modified organic polymers. However, few reports have been concerned with high performance thermoplastics as organic phase of the organic/inorganic polymer hybrid composites [27]. For the sake of enhancing the mechanical property for higher load-carrying ability and heat resistance due to the bonding and hermetic packaging at temperatures about 400 °C, there should be a great demand for alternative polymers that possessing the appropriate mechanical and physical properties.

Poly(phthalazinone ether ketone) (PPEK), one of poly(aryl ether ketone), is a high performance thermoplastic which shows excellent mechanical properties, outstanding thermal stability and well solubility in many organic solvents that makes it easer in processing as film and coating on the substrate.

In our research, we attempted to prepare PPEK/SiO_2 hybrid composite thin films on glass substrates by dip-coating method. In this work, organosilane modified PPEK resins were synthesized. Then PPEK/SiO_2 hybrid composite materials with covalent bonds between organic and inorganic phases were prepared with the use of isocyanatopropyltriethoxysilane (ICPTES).

2 Experimental sections

2.1 Materials

The PPEK was prepared according to the reported method [47]. Sodium borohydride ($NaBH_4$) was obtained from Shanghai Chemical Co., China. ICPTES was purchased from Beijing Entrepreneur Co., China. Tetraethoxysilane (TEOS) was supplied by Shenyang reagent factory, China. *N*-methyl-2-pyrrolidinone (NMP) was refluxed over toluene for 8 h. It was then refluxed in the presence of CaH_2 and freshly distilled before use. Pyridine (Py) was refluxed in an inert atmosphere in the presences of the KOH for 4 h and stored over 4 Å molecular sieves.

2.2 PPEK reduction

The reduction of PPEK was conducted according to the route shown as Scheme 1. NMP (600 mL) and $NaBH_4$ (6 g) were introduced in a three-neck flask equipped with a mechanical stirrer and a nitrogen inlet. The mixture was heated at 120 °C under stirring (dissolution occurred). PPEK (6 g, equivalent weight 416 g) was added into the reactive solution for 6 h at 120 °C. After cooling, the crude solution was slowly poured into 0.05 N HCl (1.2 L); a faint yellow solid was formed. After filtration and washing with water (three times), the solid “HPPEK” was dried under vacuum at 100 °C for 8 h.

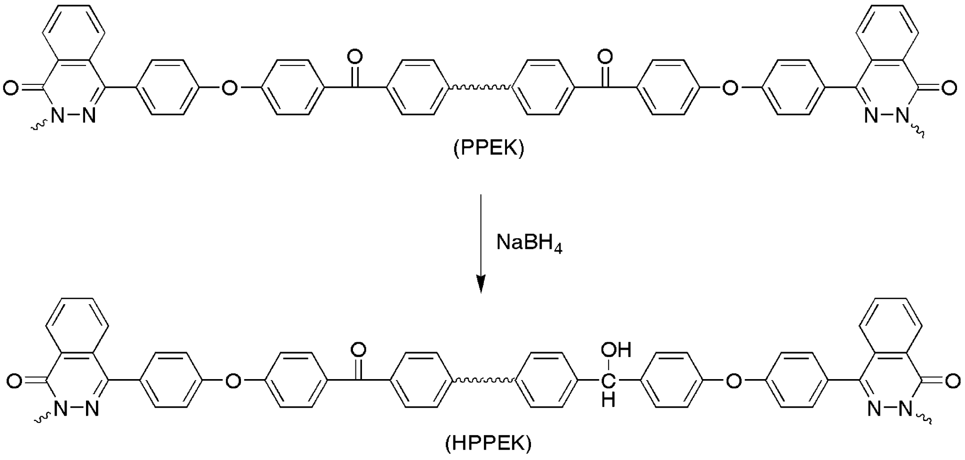
2.3 Preparation of PPEK/SiO_2 hybrid films

The organic–inorganic polymer hybrid thin films were fabricated by the dip-coating method on pre-cleaned glass slides (25.4 mm × 76.2 mm × 1 mm). The glass slides used as substrates for the reason of silicon is the most promising material for MEMS were hydroxylated by immersing in a piranha solution (a mixture of 7:3 (v/v) 98% H_2SO_4 and 30% H_2O_2) at 90 °C for 2 h.

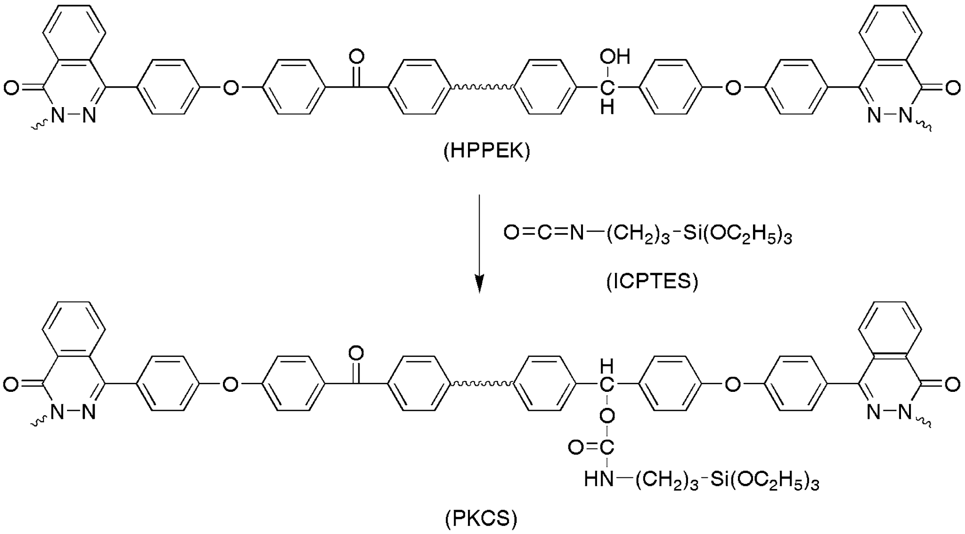
The precursor solutions were prepared by mixing two solutions, A and B. Solution A contains the triethoxysilyl-functionalized PPEK (designated as “PKCS”) as described in Scheme 2. Five grams of HPPEK (the reduction of PPEK was 45%) were dissolved in Py (125 mL). ICPTES (1 g, equivalent weight 247 g) was added slowly into the above solution. The mixture was stirred and refluxed at 100 °C for 12 h until the characteristic peak of the NCO group disappeared from the FTIR spectra. Solution B contained TEOS/H_2O with a molar ratio of 1:4. Diluted HCl was used as a catalyst for hydrolysis (pH 4). Then, the mixture of A and B was aged at room temperature for 5 h. After that the hydroxylated glass slides were dipped into the sol solution for 1 h and then dried at 120 °C for 1 h to obtain the polymer hybrid thin films.

2.4 Characterization

cThe FTIR spectra were recorded on a Thermo Nicolet Nexus 470 Fourier transform infrared spectrometer. PPEK and HPPEK samples were prepared using KBr pressed disc method. PKCS samples were prepared by the solution-casting method. UV–vis spectra (752PC, Shanghai Spectrum Instruments Corp., China) of samples



Scheme 1 The reduction of PPEK



Scheme 2 Synthesis of PKCS

dissolved in NMP were measured in the range of 300–500 nm. ^{1}H NMR spectra were measured in dimethyl sulphoxide (DMSO)-d6 solution with Varian INOVA 400 M NMR. Solid state ^{29}Si NMR spectra were performed by Varian INOVA 400 M NMR. Proton resonance frequencies were 400 MHz. The acquisition method was the cross-polarity/magic-angle spinning method. The contact time was 5 ms. The spin rate was 3,000 Hz. The pulse angle was 90°. The pulse width was 5 μs. The acquisition time was 1 s. The sample was treated at 180 °C for 2 h and then ground into fine powder.

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) were performed on a Netzsch 209 TGA instrument in a nitrogen atmosphere from 50 to 800 °C at a heating rate of 20 °C/min. The glass transition temperature (T_g) was determined with a Netzsch 204 differential scanning calorimetry (DSC) in flowing nitrogen at a heating rate of 10 °C/min. An NSIIIa SPM (DI Co., America) atomic force microscope (AFM) was employed to observe the film morphology using tapping scanning mode. The contact angles for water were measured on a Dataphysis OCA-200 model contact angle tester. Each contact angle was measured on five locations on all the samples. UMT-2 (CERT Co., America) model reciprocating friction tester was used to evaluate the tribological properties of the films at ambient conditions (RH: 40–45%). A stationary 5 mm diameter WC ball was used as the counterpart. The sliding velocity and stroke were 90 mm/min and 6 mm, respectively. The normal forces were selected from 50 to 400 mN. The coefficient of friction and sliding time were recorded automatically. It was assumed that lubrication failure of the film occurred as the friction coefficient rose sharply to a higher value similar to that of the glass substrate against the same counterpart (about 0.8). The sliding time at this point was recorded as the wear life of the film. Three replicate tests were carried out for each specimen. The morphology of worn surfaces of films was examined by KYKY-2800B scanning electron microscope (SEM).

3 Results and discussion

3.1 PPEK reduction

Functionalized polymers have caused great attentions for their improved properties and the achieved new application. Noiset et al. [48] have reported the surface reduction of amorphous poly(aryl ether ether ketone) (PEEK) film by wet chemistry technique using a solution of $NaBH_4$ in DMSO at 120 °C for 3 h. Because of their similar structures, the reduction of PPEK adopted the mild method to reduce some benzophenone motifs into the corresponding benzhydrol motifs leading to PPEK with well-defined hydroxyl groups, as shown in Scheme 1.

FTIR spectra for PPEK and HPPEK are shown in Fig. 1. HPPEK exhibited typical absorption bands in spectrum (b), including a strong peak at 3420 cm^{-1}, assigned to O–H, and small peak at 2872 cm^{-1} corresponding to C–H stretching vibration. The PPEK carbonyl band at 1663 cm^{-1} was no longer present in the FTIR spectrum of HPPEK due to the reduction. In contrast with PPEK, the characteristic absorption bands of aromatic ring at spectrum of HPPEK showed a significant diminution at 1600 cm^{-1} and a related increase at 1497 cm^{-1}. This is due to the variation of conjugated effect between benzene ring and carbonyl [49]. In the ^{1}H NMR spectra, recorded in DMSO, the C–H benzhydryl proton gave a resonance line at 5.8 ppm (Fig. 2b). The UV–vis spectra (Fig. 3) gave a strong absorption at 386 nm corresponding to the stabilized benzhydrylcation, while the native PPEK absorbed at 340 nm; a bathochromic effect of about 46 nm was observed because of the electron-donating property of the hydroxyl group. The figure showed the simultaneous change of characteristic peak of benzhydrylidene at 386 nm and the peak of benzophenone at 340 nm in various reaction products.

The percentages of reduction with respect to PPEK could be determined from the FTIR spectrum. Two typical bands were considered in the FTIR spectra of PPEK and HPPEK: the band at 1663 cm^{-1} due to the carbonyl and the band 1238 cm^{-1} due to the ether link. Their relatively intensity ratio of ${}_{v}1663$ cm^{-1}/${}_{v}1238$ cm^{-1} could determine the percentage of reduction approximately. As seen in Fig. 4, the ratio of reduced units with regard to HPPEK was around 33% in a short time (1 h) and the maximum percentage of reducing (about 81%) in this experiment was obtained at a reducing reaction time of 24 h.

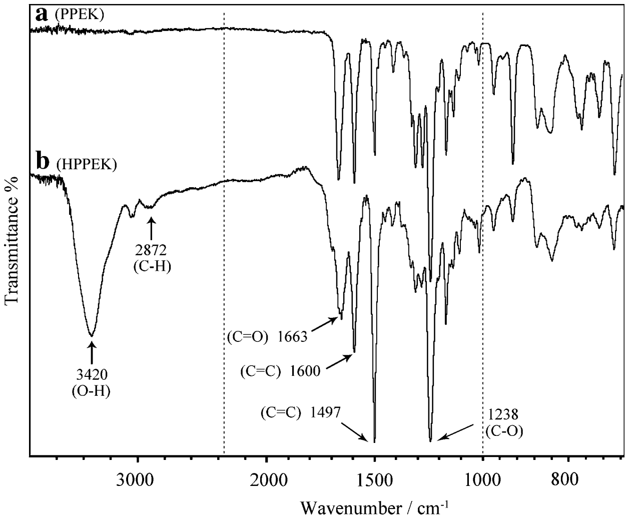


Fig. 1 FTIR spectra of PPEK (**a**) and HPPEK (**b**)

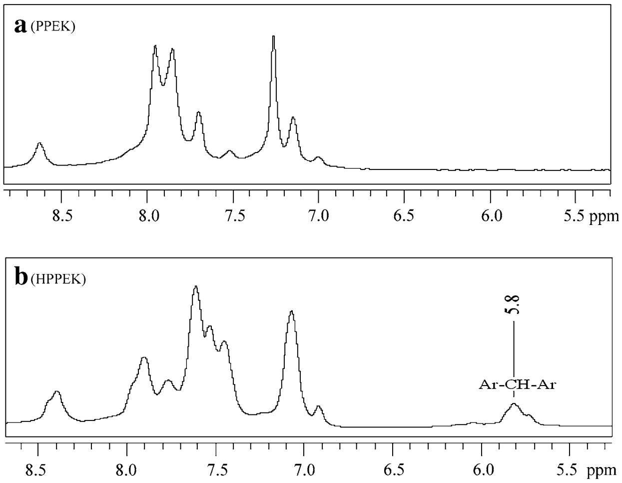


Fig. 2 ^{1}H NMR spectra of PPEK (**a**) and HPPEK (**b**)

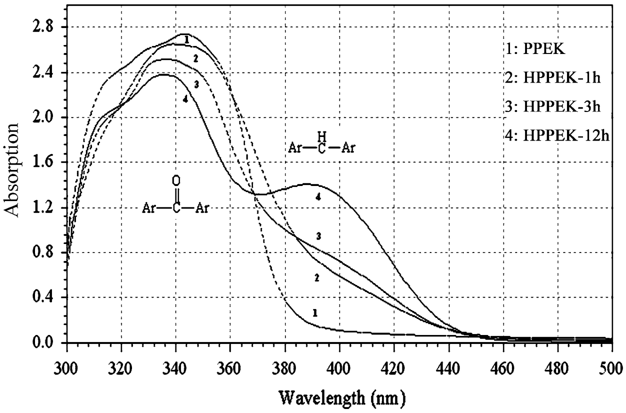


Fig. 3 UV–vis spectra of PPEK and HPPEK synthesized in various reaction time

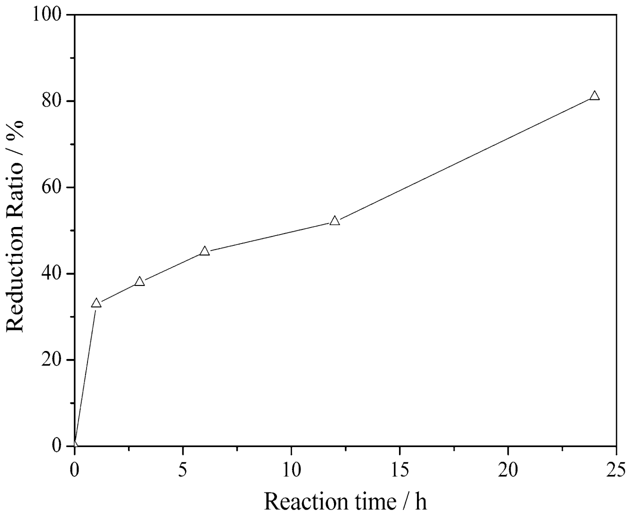


Fig. 4 The reduction ratio versus the hydroxylation time of PPEK

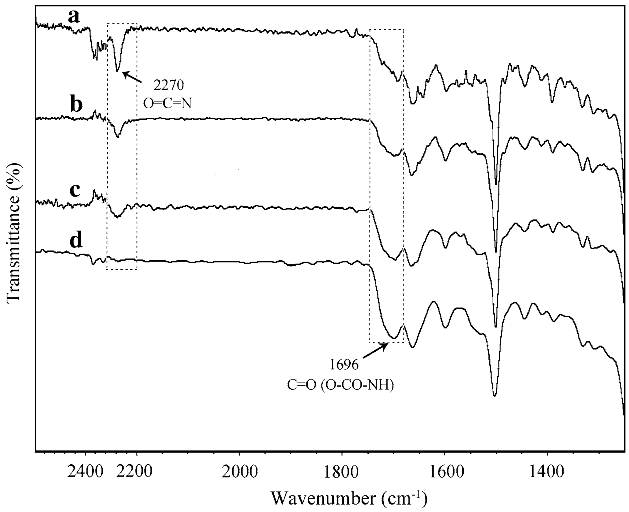


Fig. 5 FTIR spectra of the reaction between HPPEK and ICPTES

3.2 Preparation of PPEK/SiO$_2$ hybrids with covalent bonds between the organic and inorganic phases

A convenient way to introduce covalent bonds between organic and inorganic phases is to prepare the polymer bearing trialkoxysilyl groups along the backbone [32, 38, 50]. The trialkoxysilyl-functionalized polymers can be prepared by virtue of the reactions between the functional groups on the polymers and a suitable coupling agent. For example, these reactions can be the aminolysis of itaconic anhydride units with (3-aminopropyl)-triethoxysilane [46] and the ring-opening reaction of the bisphenol A epoxy resin with 3-glycidyloxypropyltrimehoxysilane [51]. In this way, the modified PPEK containing triethoxysilane moieties were prepared with an in-situ *O*-acylation reaction of HPPEK with ICPTES.

The reaction between HPPEK and ICPTES (Scheme 2) were monitored by IR spectrum analysis (Fig. 5). The figure shows the change of the characteristic peak of the NCO group of ICPTES at 2270 cm^{-1} and carbonyl of HN–COO group in PKCS at 1696 cm^{-1}. This result reveals that HPPEK reacted with ICPTES at various reaction times. The reaction between HPPEK and ICPTES was also further analyzed by solid-state ^{29}Si NMR spectrum, as shown in Fig. 6. The absolute signals due to T^1, T^2 and T^3 structures were observed at −50, −58 and −65 ppm for PKCS, respectively, indicating the presence of alkoxysilyl groups within the structure of the polymer. Since T^n indicates the siloxane unit structure, e.g., $RSi(OSi)_n(OR')_{3-n}$ [$n = 1(T^1)$, $2(T^2)$, and $3(T^3)$] [52], it can be concluded that the hydrolysis and condensation occurred among ethoxysilyl groups in atmosphere. This indicates that PKCS can be readily engaged in the sol–gel reaction with triethoxysilyl groups and therefore can be easily adsorbed onto any hydroxylated solid surfaces through chemical bonding. The higher ratio of T^3 to T^2 and T^1 in PKCS indicate that T^3 represents the major environment, i.e., it formed a network structure.

The ethoxysilyl groups contained in the polymer main chains subsequently were co-hydrolysis and co-condensation with TEOS in the sol–gel process. It can be seen from the structures (Scheme 3) that ICPTES plays a bridge role between organic and inorganic phases. A large network was formed of organic and inorganic phases that interpenetrate each other.

3.3 Characterization of the polymer hybrid materials

The thermal properties of polymer hybrid composite with 10 wt% TEOS were demonstrated in Fig. 7. The polymer hybrid composite showed a higher glass transition

(a: initial reaction, b: 3h, c: 7h, d: 12h.)

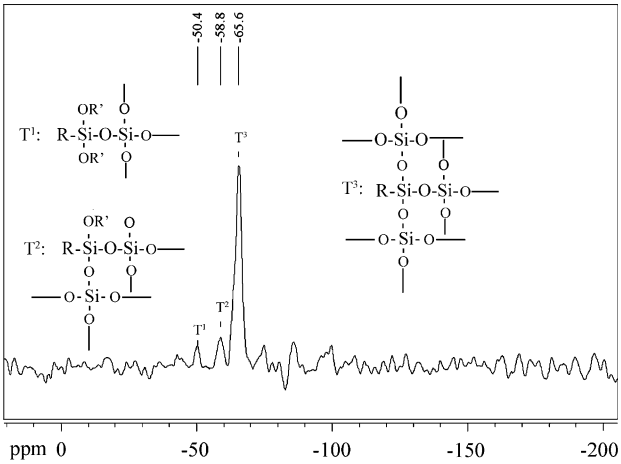
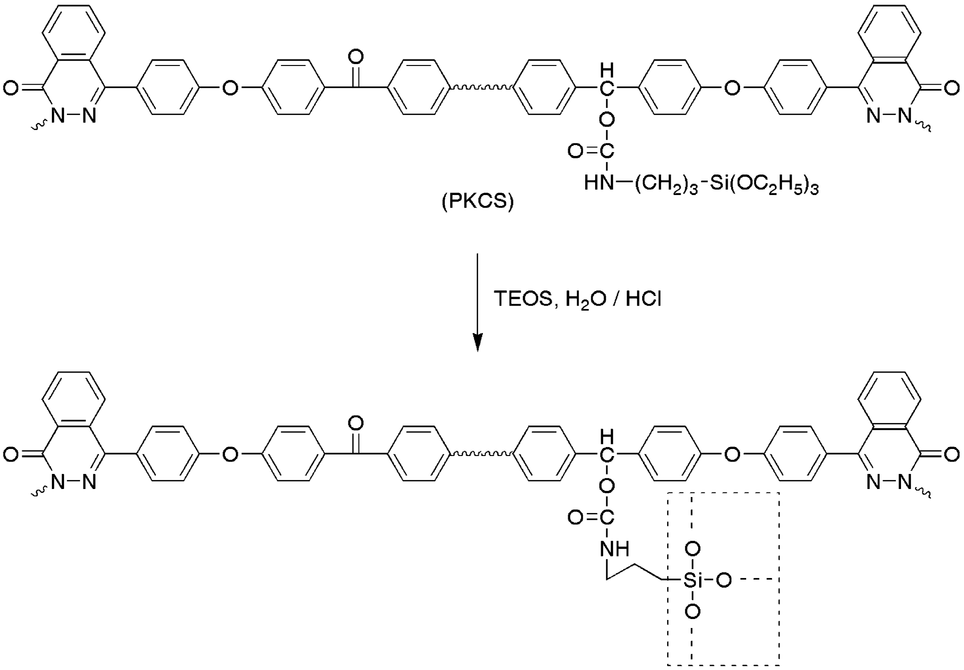


Fig. 6 The curve of solid-state ^{29}Si NMR spectrum of PKCS

Scheme 3 Preparation of PPEK/SiO_2 hybrid materials



temperature (T_g) than the pure resin as a result of the networks of inorganic components restricting the motions of the polymer chains. Besides, the curve of the polymer hybrid composite showed an indistinct glass transition temperature as compared with PPEK. This reveals that with the incorporation of ICPTES, the organic and inorganic phases were crosslinked into a network [46]. The polymer hybrid material was clearly found to experience a three-step weight loss procedure during the heat treatment from the curve of TG/DTG. The first degradation stage with onset temperature at about 94 °C was attributed to water loss resulted from the further condensation reaction between Si–OH during the thermal treatment. It indicates that the condensation reaction between the Si–OH could be completed by heat treating. The second degradation stage had a maximum decomposition rate at 315 °C which was due to the decomposition of the pendant aliphatic hydrocarbon. The weight loss above 392 °C was attributed to the thermal decomposition of the aromatic components in the main chains. These results indicate that PPEK/SiO_2 hybrid composite shows the better thermal stability than other aliphatic polymer hybrid composites with onset loss temperatures below 300 °C [30, 31].

The surface morphologies of the organic/inorganic polymer hybrid film and the glass substrate were observed using an AFM. The mean roughnesses (Ra) were 0.631 and 0.241 nm, respectively. It implies that the polymer hybrid composites were absorbed on the glass substrate. As shown in Fig. 8, the glass substrate surface exhibited irregular image of waviness. On the contrary, the PPEK/SiO_2 hybrid film showed continuous morphology over large surface area with fine grainy structure of silica nano-crystallite. It is considered that the polymer and silica components can exist in each domain, in which the chains of one component are intimately entwined with those of another through the covalent bonds [29].

Measurement of contact angle provides a sensitive probe of the chemical composition, order, and coverage of organic thin films on solid surface. Thus, the contact angles for water on the simple glass surface and the target polymer hybrid film were measured (Fig. 9). The water contact angle of simple glass (untreated) was 22° and that of the hydroxylated glass surface has a very small water contact angle about 4° [53]. After submerging the hydroxylated substrate into the PPEK/SiO_2 sol and keeping for 1 h, the contact angle of the obtained polymer hybrid film greatly increased to 65°, reflecting the successful formation of the hydrophobic polymer hybrid film on the hydrophilic substrate surface. The increase of contact angle suggests the decrease of the surface energy, and the low surface energy will certainly result in low friction coefficient during the wear test [53].

3.4 Friction and wear behavior

Figure 10 shows the variation of friction coefficient as a function of sliding time. The glass substrate without any coating had a very high friction coefficient value (about 0.8) after a rapid slide with steel ball. It was seen that the polymer hybrid films record relative-low initial friction coefficients (about 0.1–0.3). At the high loads of 200 and 400 mN, the polymer hybrid films failed after sliding for

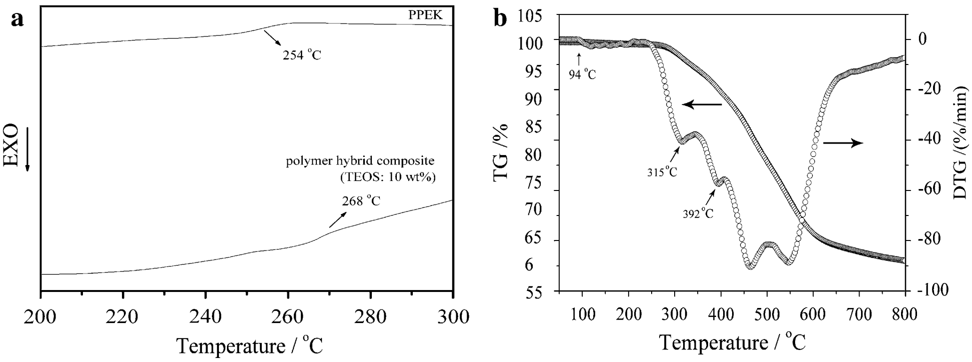


Fig. 7 Thermal properties of polymer hybrid composite. (**a**) DSC curves and (**b**) TG/DTG diagram

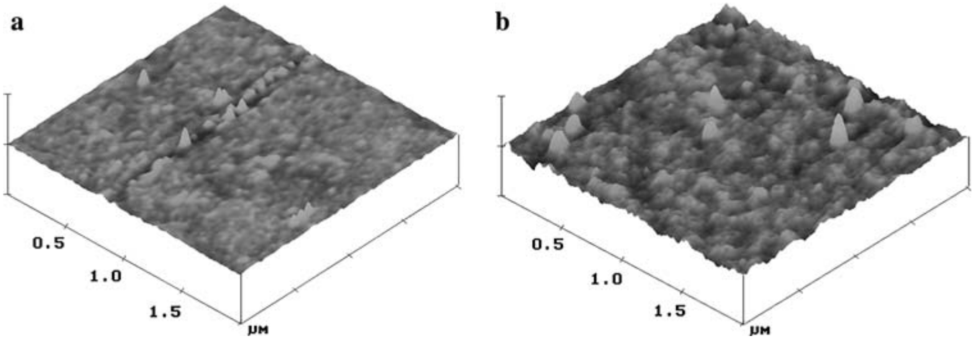


Fig. 8 AFM photographs of the glass substrate (**a**) and polymer hybrid film (**b**)

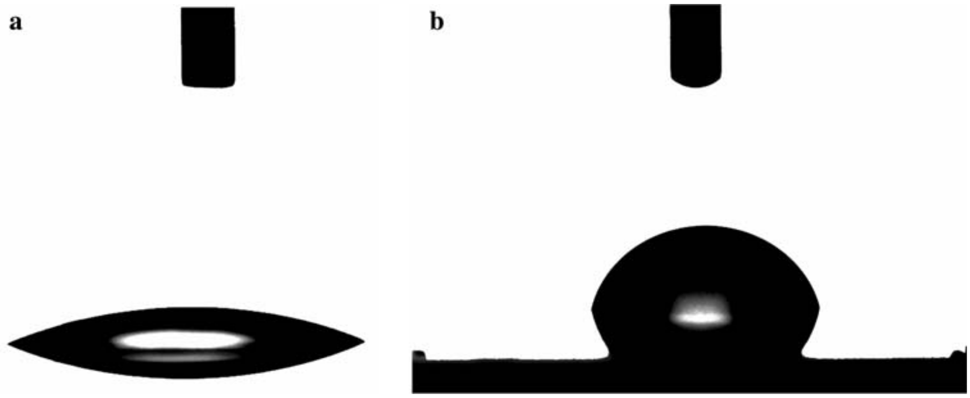


Fig. 9 The water contact angles of the glass substrate (**a**) and polymer hybrid film (**b**)

700 s approximately. A sharp increase in friction coefficient indicates the direct contact between the hard surfaces (steel–silicon). When the load decreased to 100 or 50 mN, the friction coefficients of the hybrid film samples had the similar stage including an initially sharp increase and subsequently steady state. The friction coefficient of the polymer hybrid films remained nearly unchanged at 0.1 −0.15 after sliding over 18,000 s. This indicates that the polymer hybrid films had excellent lubricating effect and relatively long wear life at corresponding normal loads of 50 and 100 mN.

The well lubricating property and wear resistance of the polymer hybrid films may be attributed to several factors. First, the polymer hybrids have densely distributed functional hydroxyl groups which are beneficial to the stable

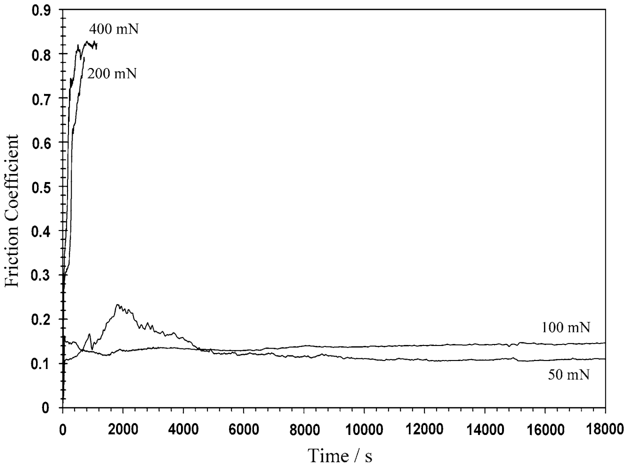


Fig. 10 Friction coefficient as a function of sliding time

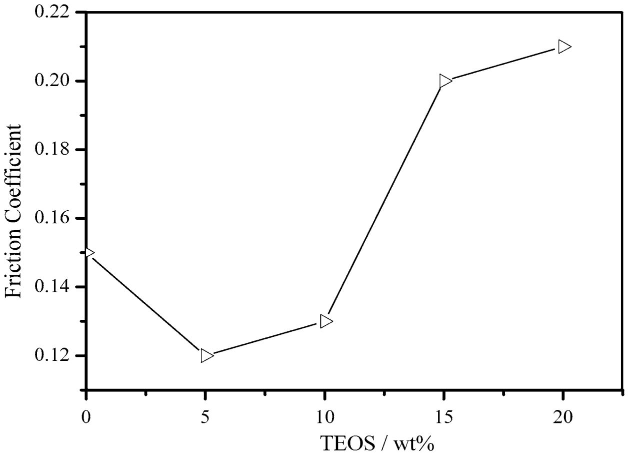


Fig. 11 The friction coefficient versus the silica content in the polymer hybrid films

attachment of the polymer hybrid films on the hydroxylated glass substrate. Second, Si–O–Si bond network exists between the organic and inorganic components, which could contribute to stabilize the polymer hybrid film. Third, PPEK as a high performance polymer shows excellent mechanical property and can endure high frictional heat as compared with general-purpose plastics. Thus, the polymer hybrid film in combination with the favorable lubricating effect of polymer and good anti-wear behavior of inorganic networks can avoid invalidation of the film. Moreover, owing to the poor wear-resistance of PPEK, it offers a good alternative method to improve the tribological properties of a polymer film by forming organic–inorganic polymer hybrid films. In this respect, the present work would be meaningful and important for the application of polymer film as protecting and lubricating films.

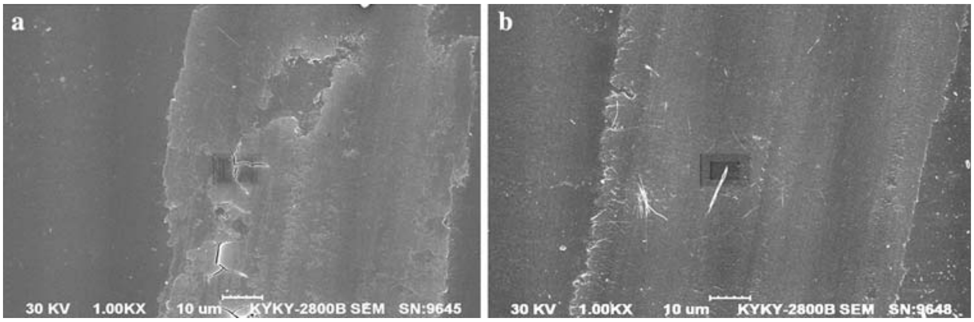
Figure 11 shows the effect of TEOS content on the friction coefficient of the polymer hybrid films when the normal load is 100 mN. It is obvious that the pure resin thin film or polymer hybrid thin films exhibited a decreased friction coefficient in comparison to the bare glass substrate (0.8). But the friction coefficients of the polymer hybrid films with TEOS content of 5 and 10 wt% were both smaller than that of pure resin. The lowest friction coefficient (0.12) of the polymer hybrid film in this experiment was obtained at a TEOS content of 5 wt%. Above 10 wt%, the friction coefficient was sharply increased with the increasing TEOS content, although it was still lower than the uncovered glass substrate. It is supposed that the excessive content of SiO_2 will cause the aggregates of the silica which lead to the increment of the surface roughness.

The mechanism of the rubbing process was analyzed according to the SEM pictures of the worn surfaces. As shown in Fig. 12, when the normal force was 400 mN, obvious cracks and pit appeared on the worn surface of the polymer hybrid film. The investigation [54] indicated that near the surface the largest deformation of material is propitious to the formation of cracks. The formed cracks will extend and intersect under the reciprocating friction force. The fatigue-process leads to the formation of wear debris (result in pit) and finally causes the invalidation of the film. Hence, it is suggested that fatigue wear dominate the wear mechanism of the film under higher loads. Different from the above, under the 100 mN normal force, there was no visible damage on the wear track.

4 Conclusions

PPEK/SiO_2 hybrid films with covalent bonds between the organic and inorganic phases were prepared in the presence of the coupling agent ICPTES using the dip-coating technique on glass substrate. The resulting composite films were of low processing temperature and high thermal stability. They exhibited a low friction coefficient of 0.1–0.15 and retained good friction-reducing behavior at sliding passes over 18,000 s. The failure of the film was mainly due to fatigue wear and the avoidance of the severe crack was partly responsible for the corresponding longer wear life of the polymer hybrid films. The superior friction reduction and long wear life of the thin film were mainly attributed to the special characteristic of the polymer hybrid composite with optimizing material combination and the chemical bonds between the film and the substrate.

Fig. 12 SEM micrographs of worn surface of polymer hybrid film. (**a**) 400 mN and (**b**) 100 mN



Thus, a good alternative method was presented to improve the tribological properties of polymer film by preparing organic/inorganic polymer hybrid composite in a sol–gel process. This makes it feasible for the high performance polymer to find promising application in resolving the tribological problems of MEMS.

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