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Surface activity of perfluoropolyalkylether *N,N*-diphenylamide (PFPEA)

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Abstract A functional derivative of perfluoropolyalkylether, perfluoropolyalkylether *N,N*-diphenylamide (PFPEA) was synthesized and characterized by FT-IR, ^{1}H and ^{19}F NMR, and the thermo stability was determined by TG analysis. The surface activity of PFPEA was characterized by the determination of surface tension of organic solvents and the adsorption behavior on the surfaces of solids such as Fe, Al, Cu plates. PFPEA reduced the surface tension of organic solvents greatly such as benzene, toluene, hexane, and cyclohexane. PFPEA was adsorbed on surfaces of solids to form molecular thin films through the end groups. Surface properties of thin films of PFPEA formed by adsorption in organic solutions were characterized using contact angle measurements and X-ray Photoelectron Spectrum (XPS) analysis. The anti-wear performances of adsorbed thin films of PFPEA were determined on a four-ball tribo-tester under the lubrication of liquid lubricants. Films preadsorbed on the substrate surfaces could improve the anti-wear properties of liquid lubricants.

Introduction

Perfluoropolyethers (PFPE) are known for their valuable operation characteristics, wide temperature ranges, high viscosity indices, as well as chemical and heat-oxidation resistance [1–4], and are widely used as special lubricants in various fields such as aeronautical industry, nucleus industry and in nano-technology and micro/nano-electro-mechanical systems (MEMS/NEMS) in recent years [5–8]. But under severe conditions, PFPE based lubricants could be decomposed because of high temperature [9] and metal catalysis [10]. Anti-oxidation and anti-corrosion additives are essential to the requirement of stability. For their wonderful anti-oxidation and anti-corrosion properties, *N*-substituted perfluoropolyalkylether phenylamides have drawn the attention of scientists [11, 12].

PFPE derivatives with functional end groups may be used as oil soluble surfactants and surface modifying reagents [13]. Thin films derived from PFPE derivatives have very low surface free energy and are both hydrophobic and oilphobic, which makes it useful as an anti-corrosion protective coatings and lubricant films [14]. Perfluoropolyalkylether *N,N*-diphenylamide (PFPEA) has wonderful properties of anti-oxidation and anti-corrosion in PFPE based oils. However, the surface activity of PFPEA in organic solvents and the thin films formed on metal substrates had not been reported so far.

In this paper, organic solvent soluble PFPEA with a number average molecular weight of about 2,200 was synthesized, the molecular structure has been confirmed by FT-IR, ^{1}H and ^{19}F NMR analysis. Surface activities of PFPEA were investigated by measurements of surface tension of solutions of PFPEA in different organic solvents, and the surface properties of thin films of PFPEA formed by adsorption in organic solutions. The anti-wear behaviors

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of thin films of PFPEA were also determined on a MMW-1 four-ball tribo-tester using paraffin liquid and Mobile 1# (SW/30) synthesized lubricants as the lubricant, respectively.

Experimental section

Synthesis and characterization of PFPEA

PFPEA was synthesized using perfluoropolyetheroyl fluoride to react with diphenylamine in trichlorotrifluoroethane (F_{113}) with triethylamine as the catalyst. The perfluoropolyetheroyl fluoride was synthesized through the ring opening polymerization of hexafluoropropylene oxide (HFPO) according to the literature [15], having a number average molecular weight about 2,200 (n = 10–12). The chemical structure of PFPEA was shown in Fig. 1.

The chemical structure of PFPEA was characterized by FT-IR, ^{1}H and ^{19}F NMR. FT-IR spectra were recorded on an AVATAR3600 FT-IR (C.E.S.P) infrared spectrometric analyzer. ^{1}H and ^{19}F NMR were recorded on an AV400 nuclear magnetic resonance detector. To evaluate the heat stability, thermogravimetric analysis was carried out on an EXSTAR 6000 (Seiko Instrument Inc.) thermoanalyzer, under N_2 atmosphere with a heat rising rate 10 °C/min.

Surface tension isotherms

PFPEA was dissolved in different organic solvents with different concentrations. Surface tensions are determined using the falling meniscus method, based on the principle that the height of a liquid in a tube is dependent only on the radius of the capillary opening at the meniscus position. A tube is lowered into bulk solution until a meniscus is formed at the small capillary orifice at the top of the tube. The bulk solution is then lowered until a critical height, h_0, marked by the rupture of the meniscus. The relationship to surface tension is:

$$\gamma = \frac{\rho g r}{2}\left(h0 - \frac{2r}{3}\right) \tag{1}$$

where γ is the surface tension, ρ is the density of solvents, g is the weight unit, r is capillary radius, h_0 is height of meniscus break above bulk solutions.

In this paper, an Ostwald's Viscometer was used to make a simple instrument (shown in Fig. 2) to measure the surface tensions [16]. Before each measurement, the instrument was thoroughly cleaned by acid pickling with a solution of $K_2Cr_2O_7$ (5 g), H_2O (10 mL) and H_2SO_4 (100 mL), then rinsed with deionized water.

According to Eq. 1, when enough liquid A flowed from P to B, and reached to an equilibrium, if one liquid height at left (B) was h_{01}, and the height at right (Q) was h_1, then the height difference of left and right was $\Delta h_1 = h_{01} - h_1$. For the capillary radius r is so small compared with that of Δh_1, the surface tension of the liquid could be calculated as the following equation,

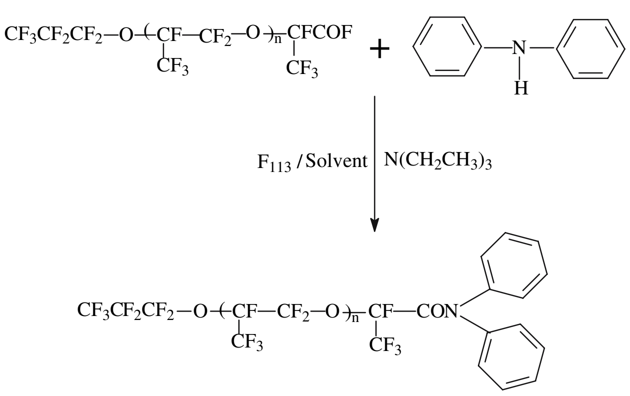
$$\gamma_1 = \rho_1 g r \Delta h_1/2 \tag{2}$$

and if the height difference of another liquid is Δh_2, it's surface tension is,

$$\gamma_2 = \rho_2 g r \Delta h_2/2 \tag{3}$$

if we have known the value of γ_1 and ρ_1, and ρ_2, then we could get the surface tension of γ_2, only need to get Δh_1 and Δh_2, using the following equation,

$$\gamma_2 = \frac{\rho_2 \Delta h_2}{\rho_1 \Delta h_1}\gamma_1 \tag{4}$$



(PFPEA)

Fig. 1 Schematics of synthesis of PFPEA

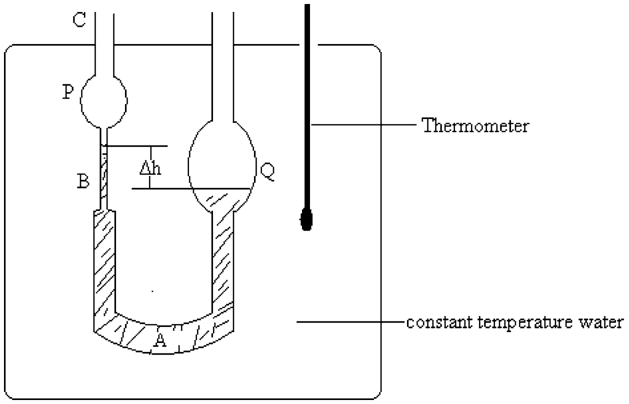


Fig. 2 A simple instrument based on a Ostwald's Viscometer for surface tension measurement

In this paper, deionized water was used as a criterion liquid, and the surface tension of pure water is 72.88 mN/m, and the density of water ρ is 0.99805 g/mL at 20 °C. To evaluate the validity of the proposed instrument for surface tension measurement, surface tensions of benzene, ethanol, and toluene were measured using deionized water as a standard liquid, and the results were listed in Table 1.

All values measured with the simple instrument proposed were so close to theoretic values. This means that the surface tensions measured by this simple instrument are credible. Thus, the surface tensions of PFPEA solutions were measured at 20 °C and calculated according to Eq. 4 in this article.

Adsorbed thin films of PFPEA on surfaces of metal plates

PFPEA adsorbed molecular thin films on metal plates were prepared as the following procedure. Aluminum plates, copper plates, iron plates (20 × 10 × 2 mm) and steel balls (φ12.7 mm) were thoroughly cleaned by ultrasonic washing in acetone, then dried in a 60 °C drying oven. The cleaned and dried substrates were immediately immerged into PFPEA (1 wt.%) solution of 1,1,2-trifluoro-trichloroethane and kept at 60 °C for 30 min. The substrates were dried at room temperature for several minutes, and then heated at 120 °C for 1 h to enhance the adsorption of PFPEA molecules on the surfaces.

Contact angle measurements

Wetting phenomenon is normally described as a contact angle (θ) of the specific surface, i.e., $\theta > 90°$ for hydrophobic behavior, $\theta < 90°$ for hydrophilic behavior. Contact angles of de-ionized water drops on the prepared surfaces were determined using an optical contact angle meter (Dataphysics, Model OCA40). The liquid droplet (3 μL) was dropped onto the sample surfaces by a syringe automatically. To achieve an equilibrium state, the measurement of contact angles should begin at the 5th minute of contact. Five drops of each liquid were placed at different locations on a horizontal surface, and five reading of contact angle were taken, and the average value of the five readings was taken as the contact angle of the sample surface.

Table 1 Surface tensions of some solvents measured with the simple instruments proposed, temperature 20 °C

Liquid	Surface tension (mN/m)	
	Theoretic values	Measured values
Water	72.88	
Benzene	28.9	28.8
Toluene	28.5	28.4
Ethanol	22.8	22.3

XPS analysis

To confirm the exist of PFPEA films on treated substrates, the chemical composition and structure of PFPEA treated Iron was analyzed using an Axis Ultra multi-technique electron spectrometer (Kratos, UK) with an AlKα X-ray source and a pass energy of 40 eV. The Al anode voltage was 15 keV and the filament current was 20 mA. The pressure in the spectrometer during analysis was typically in the 10^{-9} Torr range. XPS spectra were recorded automatically. Using a least-square curve fitting program installed in the spectrometer, the C_{1s} for the PFPEA thin films surface was split into several sub-peaks of functional groups.

Anti-wear performance

A MMW-1A model four-ball tribo-tester was used to estimate the tribological performance of the thin films of PFPEA at ambient conditions (RH: 40–45%). The balls (diameter 12.7 mm) used in the test are made of GCr15 bearing steel (composition: 0.95–1.05%; C, 0.15–0.35%; Si, 0.20–0.40%; Mn, <0.027%; P, <0.02%; S, 1.30–1.67%; Cr, <0.30%; Ni, and <0.025%; Cu) with HRC 61–64. The GGr15 ϕ12.7 mm steel ball was treated as the procedure above to form PFPEA thin films on the surface of the balls. Paraffin liquid was used as lubricant, which has a boiling point above 300 °C, density 0.835–0.89 g/cm^3, kinematic viscosity 10.28 mm^2/s (at 50 °C). And a commercially available lubricant Mobile 1# was also used as lubricant. The chemical components on the surface of steel balls before and after tribo-tests were characterized by XPS analysis.

Results and discussion

Synthesis and characterization of PFPEA

Perfluoropolyetheroyl fluoride reacted with a little excess diphenylamine at room temperature for several hours, using dry *1,1,2*-trifluoro-trichloroethane as a solvent and triethylamine as a catalyst. After the reaction was finished, excess insoluble diphenylamine was separated from soluble PFPEA. Then *1,1,2*-trifluorotrichloroethane was removed using a rotatory evaporator. The crude products were washed thoroughly with water, and dried under vacuum. The pure product was a yellowish sticky liquid, yield 86%.

FT-IR: the peak at 1,885 cm^{-1} due to C=O of –C=O(F) groups in perfluoropolyetheroyl fluoride and peaks at near 3,300 cm^{-1} of –NH in diphenylamine disappeared in the spectrum of PFPEA. Instead, a peak near 1,694 cm^{-1} appeared which is due to C=O in PFPEA molecules.

The ^{19}F NMR of PFPEA was recorded using Methanol-D_4 as solvent: δ –84.21 to –81.36 (–CF_3), –131.67 (–CF), –146.02 to –146.42 (–CF_2).

^1H NMR of PFPEA was recorded using trifluoroacetic acid—D_1 as solvent: δ 7.44–7.16 (–C_6H_5).

Thermogravimetric analysis

Thermogravimetric analysis of PFPEA was carried out under N_2 atmosphere with a heat rising rate of 10 °C/min. The TG/DTG curves of PFPEA were shown in Fig. 3. From which, below 150 °C, only about 5% weight loss was found, from the DTG curve, this loss occurred at about 120 °C, this may be the loss of solvent dissolved in the PFPEA as prepared. From 120 to 200 °C, the weight loss rate kept almost the same, this may be explained by the evaporation of PFPEA molecules, which was similar to L. Li's reports [17]. After that, from about 217.7 °C, the weight loss rate greatly increased with the temperature increased, and the most dramatically weight loss rate occurred at about 275.8 °C, this may be described as the heat decomposition of PFPEA molecules.

Surface tension isotherms

Surface activities of PFPEA were studied by surface tension isotherm measurement in different organic solvents. As shown in Fig. 4, small amounts of PFPEA was added to organic solvents, surface tensions were reduced dramatically. For toluene, the concentration of PFPEA was 0.5 g/L, surface tension was reduced from 28.3 to 13.8 mN/m. For benzene, the surface tension descended greatly with the rising of concentration of PFPEA, when the concentration of PFPEA was only 0.12 g/L, the surface tension of the solution was reduced from 28.8 to 16.6 mN/m, the lowest surface tension around 14.7 mN/m could be obtained when the concentration of PFPEA was 2.0 g/L. For hexane, the lowest surface tension reached to 14.9 mN/m, with the concentration of PFPEA was about 0.2 g/L. And for cyclohexane, surface tension of 14.7 mN/m could be achieved when concentration of PFPEA was 2.6 g/L. Interestingly, surface tensions of all the four solvents could be reduced to about 15 mN/m, although the concentrations of PFPEA needed were different. This may be due to the difference of solubilities of PFPEA in different organic solvents. For typical organic soluble fluoro-surfactants derived from oligo(hexafluoropropylene oxide) reduced surface tensions of organic solvents not so much compared with PFPEA. For example, $(HFPO)_4CONHC_6H_5$ could reduced the surface tension of toluene from 28.3 to 21.7 mN/m, and cyclohexane from 23.5 to 20.9 mN/m [18]. A possible explanation for the unusual surface activity is afforded by examination of the architecture of PFPEA. There are longer $(HFPO)_{10–12}$ chains in FPPEA molecules than in molecules of organic soluble fluoro-surfactants in literature [18], longer $(HFPO)_n$ chains would induce much more surface activities [18].

PFPEA adsorbed thin films on surfaces of metal plates

Contact angle measurement

Contact angles (CA) were measured at room temperature with a horizontal microscope with a protractor eyepiece. Droplets were placed at five different positions on one

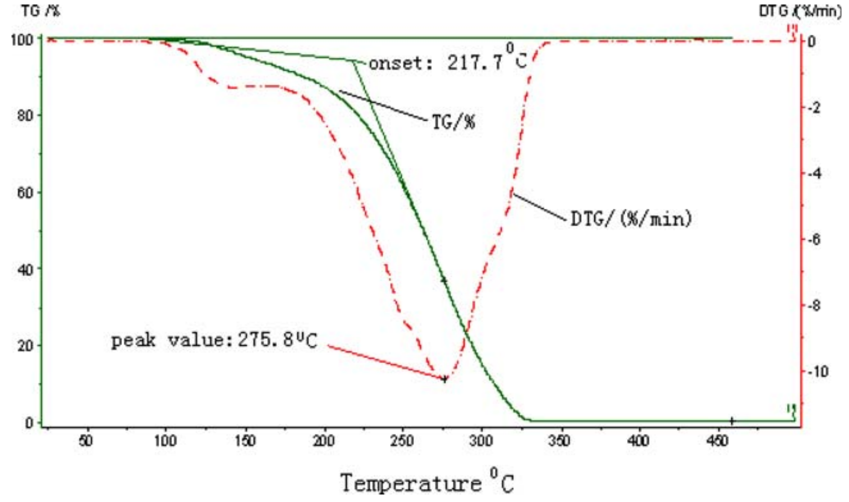


Fig. 3 TG/DTG curves of PFPEA, N_2 atmosphere, temperature rising rate 10 °C/min

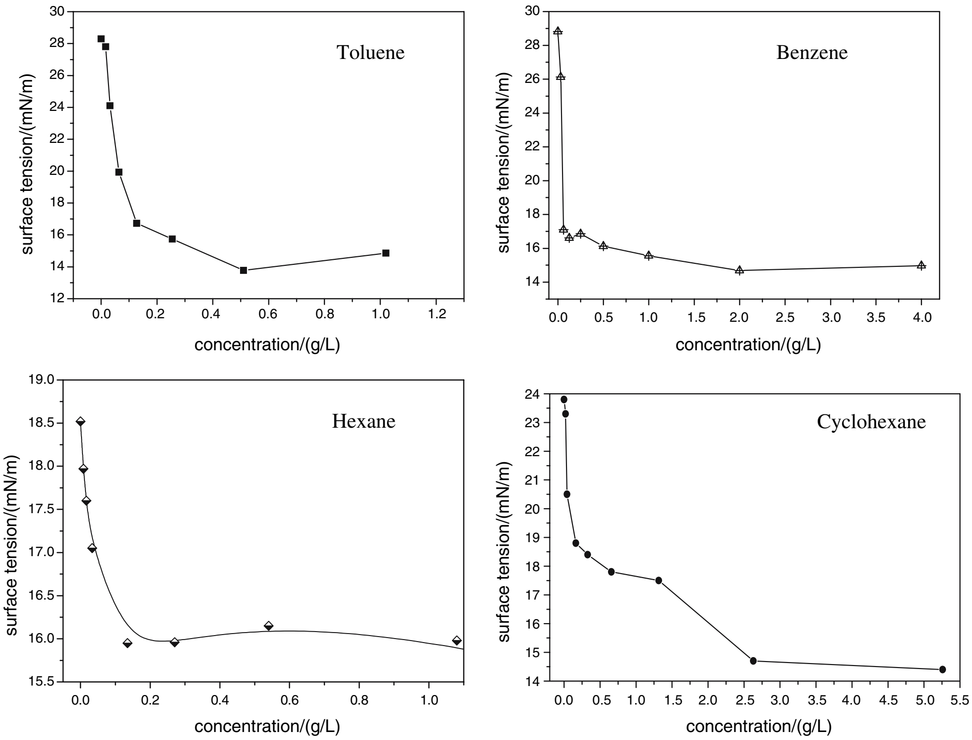


Fig. 4 Surface tension isotherm for different organic solvent: Toluene, Benzene, Hexane, and Cyclohexane at 21 °C

sample and the average value was adopted as the contact angle. Contact angles of PFPEA adsorbed thin molecular films on different substrates were listed in Table 2.

PFPEA treated substrates showed higher contact angles than bare substrates. For aluminum oxide plates, contact angle of water rose to 91° from 46°. For iron plates and copper plates, after treated with PFPEA, contact angles rose to 122° and 123°, respectively. PFPEA treated iron and copper plates showed more hydrophobic than aluminum oxide plates, this was suggested that PFPEA was much more surface active on iron and copper surfaces than on aluminum oxide surfaces. This means that PFPEA could be adsorbed easier on iron and copper surfaces than on aluminum oxide surface.

XPS analysis

To confirm the exist of PFPEA thin films on treated substrates, the chemical composition and structure of PFPEA treated Iron plate was analyzed using an Axis Ultra multi-technique electron spectrometer (Kratos, UK) with an AlKα X-ray source and a pass energy of 40 eV. The Al anode voltage was 15 keV and the filament current was 20 mA. The pressure in the spectrometer during analysis was typically in the 10^{-9} Torr range. XPS spectra were recorded automatically. Using a least-square curve fitting program installed in the spectrometer, the C_{1s} for the PFPEA thin films surface was split into several sub-peaks of functional groups.

Table 2 Contact angles for water on different substrates

Substrates	Contact angles/degree	
	Cleaned bare substrates	PFPEA thin films
Aluminum oxide plate	46	91
Iron plate	<30	122
Copper plate	<10	123

A typical splitting of the spectrum of C_{1s} was shown in Fig. 5a. The peaks in the spectra could be ascribed to groups as follows, CF_3 at 293.4 eV, CF_2 and CF at 291.0 eV, CO(N–) at 287.7 eV, C at 284.8 eV to hydrocarbon end groups. The C_{1s} and F1s (shown in Fig. 5b) XPS spectra indicated the formation of PFPEA film on the surface of substrates.

Anti-wear performance

Reducing friction and wear is one of the most important requirements in many technological devices. Various kinds of lubricants have been developed for attaining low friction and wear. To enhance the tribological performances, additives should be added into liquid lubricants. Molecules of some additives adsorbed onto surfaces of the friction counterparts to form a molecular thin film, acted as a protective thin films with friction reducing and anti-wear properties. Some times, this protective thin films were formed during the rubbing through a process called

Tribo-chemical reactions. This kind of adsorbed molecular thin film is very important in friction reducing and anti-wear throughout the lubrication, especially at the beginning and ending edges of rubbing. Fluorocarbon materials with certain molecular structure and functional groups, which attaches the molecules to the substrate surfaces either chemically or physically, form boundary lubricating films, to lower friction and wear. Since the molecules of PFPEA could be easily adsorbed on the metal surfaces, formed continuous films. What effect of such preformed thin films would do during the friction under the lubrication of a liquid lubricant? Did it play the role of a boundary lubricating film and reducing the friction and wear? The tribological properties of PFPEA adsorbed thin films were investigated in this paper. To evaluate the tribological performance of PFPEA thin films under lubrication of liquid lubricants. A MMW-1A model four-ball tribo-tester were used to estimate the tribological performance of thin films of PFPEA. PFPEA coated GGr15 φ12.7 mm steel balls and liquid paraffin and a commercial available lubricant branded Mobile 1# /3W/40 were used in this article.

Wear scar diameters (WSD) were measured at room temperature, under a load of 392 N, rotation speed of 1,450 r/min and duration of 30 min. The average WSD of bare steel balls under the lubrication of liquid paraffin and Mobile 1# lubricants were about 0.72 and 0.41 mm. However, steel balls pretreated with PFPEA showed smaller WSD, the average WSD under lubrication of liquid paraffin and Mobile 1# were about 0.689 and 0.391 mm, respectively. This suggested that molecular thin films of PFPEA preformed on surfaces of steel balls might protect the substrates under severe friction and enhanced the anti-wear of liquid lubricants.

According to Weimin Liu's report [19], organic fluorine containing compounds may be decomposed under boundary lubrication through tribo-chemical reactions to form metal fluorides such as FeF_2 and FeF_3 which are anti-scratch components, known as solid lubricant films. The chemical component changes of PFPEA thin films before and after tribo-tests were determined by XPS analysis. The typical F1s XPS spectrum of FPFEA film surface and worn surface were shown in Fig. 6. The F1s peak of PFPEA film was at 688.83 eV, which ascribed to C–F in PFPEA. And

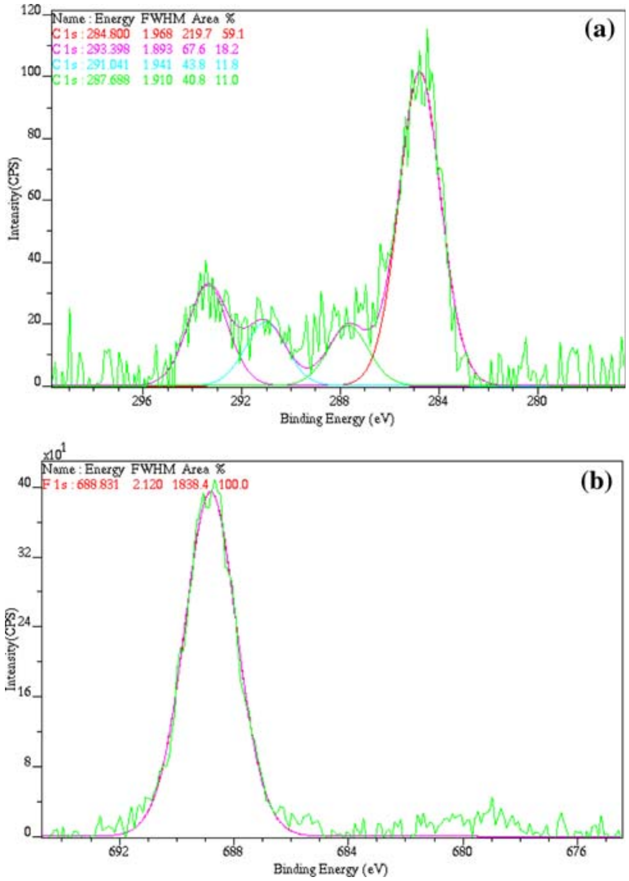


Fig. 5 XPS spectrum of C1s (**a**) and F1s (**b**) for PFPEA thin films adsorbed on iron surface

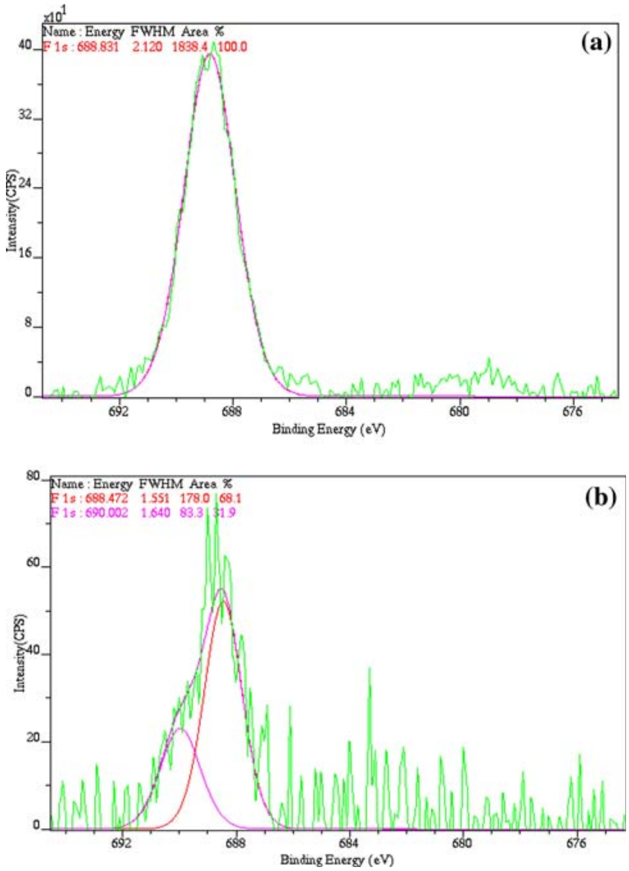


Fig. 6 XPS spectra of F1s of PFPEA coated steel ball surface (**a**), and worn surface (**b**)

the F1s spectrum of the worn surface was at 688.47 eV (68.1%) and 690.00 eV (31.9%), which were corresponded to C–F and FeF_2, respectively. This suggested that iron fluorides were formed during the friction. Thus PFPEA adsorbed thin films may work as an effective boundary lubrication film under severe friction conditions, the main chain of PFPEA would decompose to form fluorides to reduce friction and wear, which was confirmed by the XPS spectra on the worn surfaces (Fig. 6a and b).

Conclusions

Perfluoropolyalkylether *N,N*-diphenylamide (PFPEA) could reduce surface tensions of organic solvents dramatically even at low concentrations. PFPEA adsorbed onto metal surfaces to form a molecular thin films, which had similar surface properties to polytetrafluoroethylene (PTFE) such as low surface free energies and hydrophobicity. These properties of PFPEA may be useful in organic soluble surfactants and surface protection of metals. The adsorbed thin films of PFPEA may be acted as a boundary lubrication film and reduced the wear under lubrication of liquid lubricants. This may be useful in a variety applications.

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