Conferring Polytetrafluoroethylene Micropowders with Hydrophilicity Using Dopamine Chemistry and the Application as Water-Based Lubricant Additive

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ABSTRACT: The hydrophilicity of polytetrafluoroethylene (PTFE) micropowders was easily achieved by modifying the surface with thin polydopamine(Pdop) layer deposited through spontaneous oxidative polymerization of dopamine. Compared with the pure PTFE, the Pdop modified PTFE(PTFE@Pdop) possesses excellent hydrophilic property such as low active ratio, and good dispersivity in water. The quantity of coating and the surface amphiphilic properties were readily controlled by adjusting the deposition time. The tribological properties of the as-prepared PTFE@Pdop micropowders as additives in water were evaluated. The results confirmed that the PTFE@Pdop exhibited good antiwear and friction reduction properties even under low concentration in water. The simplicity of the method makes large-scale production of hydrophilic PTFE possible and may be extended as a powerful route for modification of other organic solid lubricating materials that can be exploited as water-based lubricant additives. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 3145–3151, 2011

Key words: PTFE micropowders; hydrophilicity; polydopamine; water-based lubricant additive

INTRODUCTION

Polytetrafluoroethylene (PTFE) has a number of attractive properties such as high thermal stability, high chemical resistance, low surface energy, low dielectric constant, potential biocompatibility, etc. It has been widely used in electronics, chemical, medical, energy industries, etc.[1–4] PTFE is also widely used as friction-reducing material due to its unique low intermolecular interaction (low shear strength). For real applications, PTFE micropowders are commonly blended with other materials or dispersed in lubricating base oils.[5–9] However, the best known property of low surface energy makes it unable to wet almost any kind of liquids and incompatible with solids as well.[10] The extreme hydrophobicity and poor adhesive properties of PTFE limit its compatibility and dispersion in matrices, and then restrict the performance of composites made of it. To solve this, much effort has been made to improve its hydrophilicity and compatibility with other materials,[11,12] including the chemical etching with sodium naphthalene,[12] shining with UV-laser,[13,14] electron and ion beam irradiation,[2,15–17] 60Co γ-ray irradiation and plasma modification.[11,12,18–24] Among these methods, plasma treatments including plasma polymerization and plasma induced grafting polymerization, are attractive for their high efficiency.[21–24] However, both approaches require complicated processes and specially made instruments.[25] The complicated steps of plasma grafting polymerization process in vacuum system are the knotty problem in industrial production.[11] What's more, the plasma cannot be used to treat micropowders of PTFE because of the treatment process can be carried out only under vacuum.

Recently, Lee et al. reported a simple, yet effective method to coat substrates with polydopamine layer through oxidative polymerization of dopamine monomer.[26–28] The polydopamine layer can strongly adhere to a wide range of inorganic and organic materials, including noble metals, oxides, polymers, semiconductors, and ceramics, providing an efficient approach to surface modification. In this article, the spontaneous oxidative polymerization of dopamine was used to modify PTFE micropowders. The surface properties and the dispersivity of the polydopamine-modified PTFE micropowders in the water

were systematically investigated. The tribological properties of PTFE micropowders in pure water lubrication system were also studied.

EXPERIMENTAL

Materials

The micropowder of PTFE with the average diameter of 1 μm was purchased from Shanghai 3F New Materials Company Limited (Shanghai, China). Analytical grade dopamine(2-(3,4-dihydroxyphenyl) ethylamine) and 2-amino-2-hydroxymethylpropane-1,3-diol were purchased from Aldrich. All materials were used as provided without further purification.

Surface modification

The surface-modified polytetrafluoroethylene, PTFE@Pdop, was prepared with the following procedures: 1.21 g 2-amino-2-hydroxymethylpropane-1,3-diol were added into 1000 mL distilled water, and the pH of the solution were adjusted by hydrochloric solution until pH = 8.5, which was called the Tris-HCl and before use. A typical procedure was described by following: 30 mg Dopamine (1 mg/mL) was dissolved in 300 mL aforementioned buffer solution, and then 420 mg PTFE micropowder were added. Selection of dopamine concentration is to ensure there is no visible Pdop precipitate in bulk solution.[29] This mixture was vigorously stirred at room temperature (20°C) for different periods. The final products PTFE@Pdop were filtered, washed with water for several times, and then dried at room temperature.

Characterization and test of PTFE@Pdop

Fourier transform infrared (FTIR) transmission spectra were recorded on IFS 66 v/S FTIR spectrometer (Bruker, Germany) in the 4000 cm^{-1} to 400 cm^{-1} range. The PTFE@Pdop was taken for FTIR analysis after treatment with 36 h. According to standard technique, all of the samples were ground to a powder pressed into KBr substrates. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a PHI-5702 multifunctional spectrometer with pass energy of 29.35 eV and employing a Al Kα(1476.6 eV) X-ray source. The binding energy of C1s (284.8 eV) was used as a reference. Elemental analysis (EA) of C, N, and H was performed on Elementar Vario EL instrument. Thermal gravimetric analyses (TGA) were made with a Perkin–Elmer TGA-7 instrument under nitrogen at a heating rate of 20°C/min. Scanning electron microscopy (SEM) images were examined using a JEM-1200EX (JEOL, Japan) microscope.

The effect of surface modification of PTFE was evaluated by the active ratio test. The surface wettability property and dispersion character of PTFE and PTFE@Pdop in water were assessed by following method: The PTFE or PTFE@Pdop micropowder was dispersed in water and placed in vial, respectively, and then photograph were taken using ordinary digital camera. These properties were also characterized by optical microscope images of the sample dispersed in water. Powder (0.1 g) and 20 mL of water were put into a test tube. After being dispersed, the suspension were dropped onto a crystal flake and observed using a CFM-330 numeral optical microscope.

The test of friction and wear properties in water lubrication environment were conducted on a four-ball friction and wear tester (made in Jinan Testing Machine Factory of China). All wear experiments were conducted at room temperature at a rotating rate of 1450 rpm and loads of 147, 196, 245, and 294N, for test duration of 30 min. The balls (diameter 12.7 mm, HRc 59-61) were made of GCr15 bearing steel (AISI-51,200). At the end of each test, the average wear scar diameter (WSD) on the three lower balls was determined using optical microscopy to an accuracy of 0.01 mm.

RESULTS AND DISCUSSION

Surface modification of PTFE micropowder

The FTIR spectra of pure PTFE, PTFE@Pdop, polydopamine, and dopamine monomer are shown in Figure 1. Pure dopamine show many narrow peaks; while polydopamine (synthesized at the same condition for PTFE@Pdop) presented only a few intense absorptions at around 1620 cm^{-1} from aromatic rings and a large broad band at around 3420 cm^{-1} from catechol ─OH groups. The IR absorption peaks
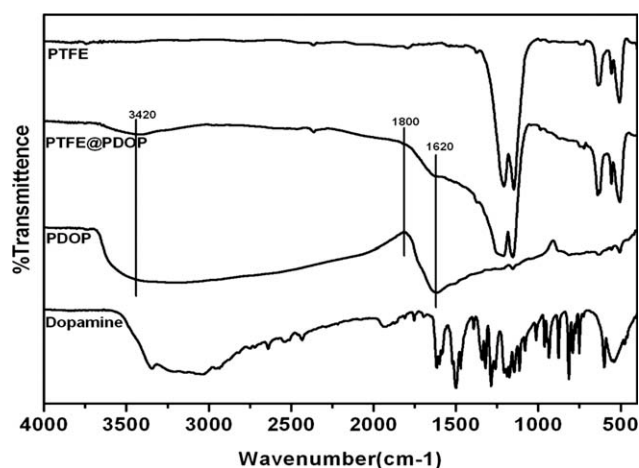

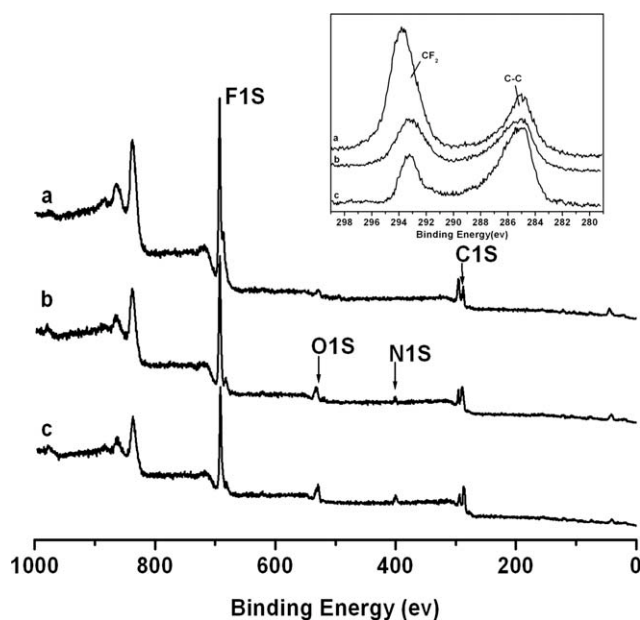**Figure 1** FTIR spectra of PTFE, PTFE@Pdop, polydopamine, and mono-dopamine.

Figure 2 XPS spectra of PTFE micropowder: (a) pure, (b) after treatment with 8 h, and (c) after treatment with 36 h. The inset is C1s spectra.

Figure 3 The effects of the treatment time on the C% and the CR%.

of pure PTFE observed at 1146 and 1202 cm^{-1} correspond to CF$_2$ symmetric and asymmetric stretches, and the absorption peaks at 640 cm^{-1}, 555 cm^{-1}, and 512 cm^{-1} characterize the IR spectrum of crystalline PTFE. The spectrum of PTFE@Pdop showed broad bands at the positions of 1620 and 3420 cm^{-1}, which were ascribed to the Pdop aromatic rings and catechol —OH groups. These structural features supported the wrapping of PTFE by Pdop. However, the characteristic bands of PTFE and its crystalline characteristic bands in the spectra between PTFE and PTFE@Pdop were similar. This indicated that polydopamine coating did not ruin the intrinsic structure of PTFE micropowder.

XPS was used to verify the surface chemical compositions of the PTFE and PTFE@Pdop. Figure 2(a–c)
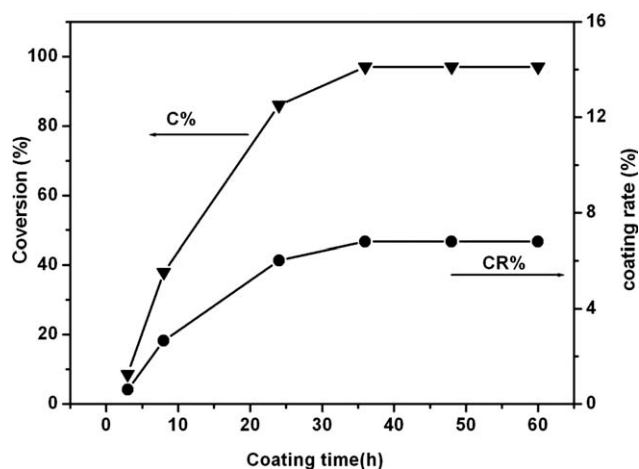
showed Survey-wide scans of the original PTFE micropowder, PTFE coated by Pdop with different deposition time, 8 h and 36 h, respectively. The spectrum of the original PTFE micropowder [Fig. 2(a)] showed the peak around 690 eV of F1s. The peak around 290 eV from the signal of C1s is clearly shown, which corresponds to the well known chemical shift associated to the C—F bond. In addition, a small peak between 520 and 540 eV were ascribed to absorbed oxygen in the sample. Figure 2(b) showed the XPS survey of PTFE@Pdop micropowder for 8 h deposition. The successful coating of Pdop on the surface of PTFE was verified by the appearance of the peak of N1s at 400 eV. This observation was confirmed by sharp decrease in F1s peak and the dramatic increase in the O1s peak. Figure 2(c) corresponds to the Pdop coated PTFE micropowder for 36 h. It is seen that the intensity of the peak at 690 eV (F1s) further decreased, at the same time the intensity of the peak at 400 ev (N1s) and 530 ev (O1s) further increased because of the increment of Pdop thickness and the uniform coverage on PTFE
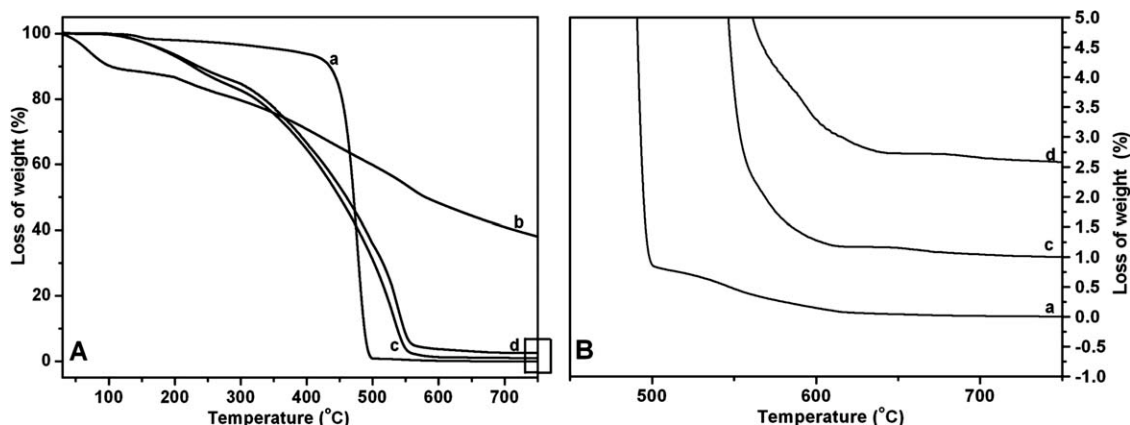

Figure 4 A: TG curves of pure PTFE (a), pure Pdop (b), PTFE@Pdop coating with 8 (c), and 36 (d) h. B: Magnification of square section in (A).
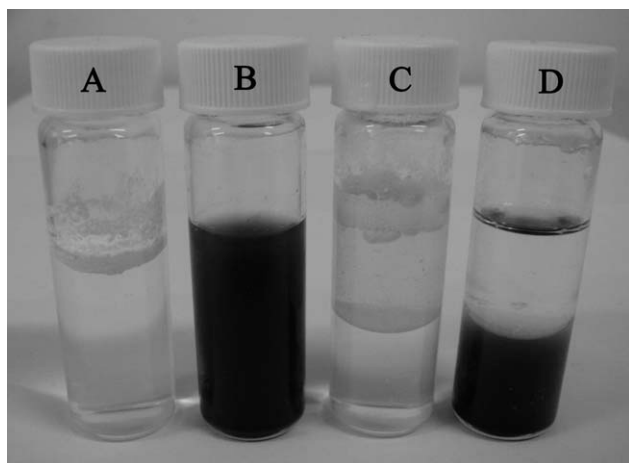
Figure 5 Digital photos: (a) pure PTFE in water, (b) PTFE@Pdop in water (c) and (d) PTFE and PTFE@Pdop in water and toluene system, respectively.

surface. The inset C1s spectra in Figure 2 showed that the intensity of the peak of CF_2 decreased and the one of C—C increased with the treatment time.

Because there was no nitrogen element in PTFE, it was possible to calculate the conversion of the pure dopamine (C%) and the coating rate (CR%) from the results of element analysis. The C% and the CR% were calculated according to the following relationships:

$$C\% = \frac{Pdop(g)}{Mono-dop\ used(g)} \times 100\%$$

$$CR\% = \frac{Pdop(g)}{PTFE\ charged(g)} \times 100\%$$

The effects of the treatment time on the C% and the CR% are investigated and the results shown in Figure 3. It was found that the C% and CR% increased with the increase of coating time and reached almost 100 and 7% after the treatment time of 36 h, respectively. There are two possible locations for Pdop aggregation: heterogeneous nucleation at PTFE surfaces or self-nucleation in aqueous solution. According the feeding ratio, the C% and the CR% there is no homopolymer during the coating process.
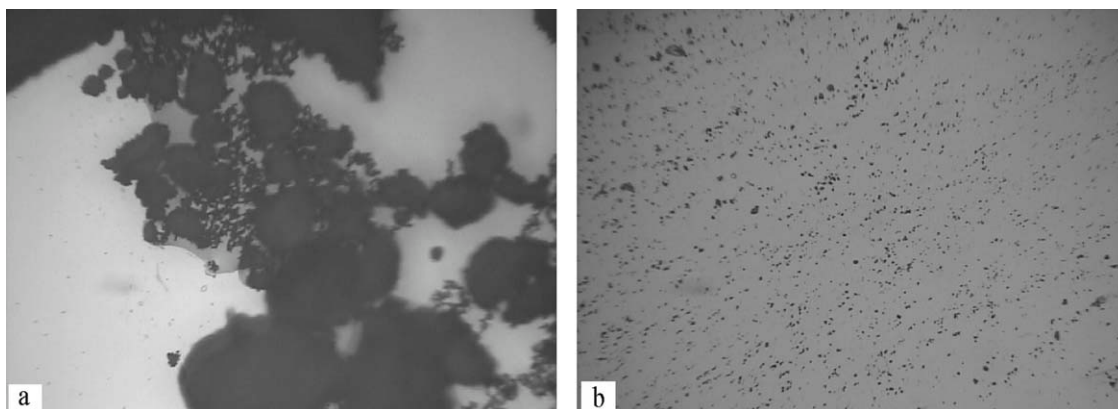

Figure 6 The dispersion character pictures of sample in water (the objects have been photographed at a magnification of 400): (a) pure PTFE and (b) PTFE@Pdop.
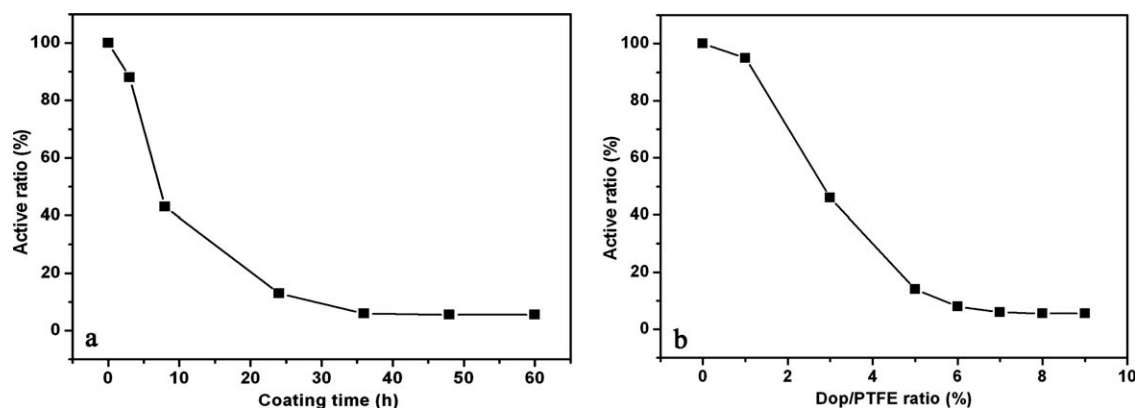

Figure 7 a: Influence of treatment time on the active ratio of micropowder products. (Dop/PTFE ratio: 7.0 wt %). b: Influence of Dop/PTFE ratio on the active ratio of micropowder products. (Treatment time: 36 h).
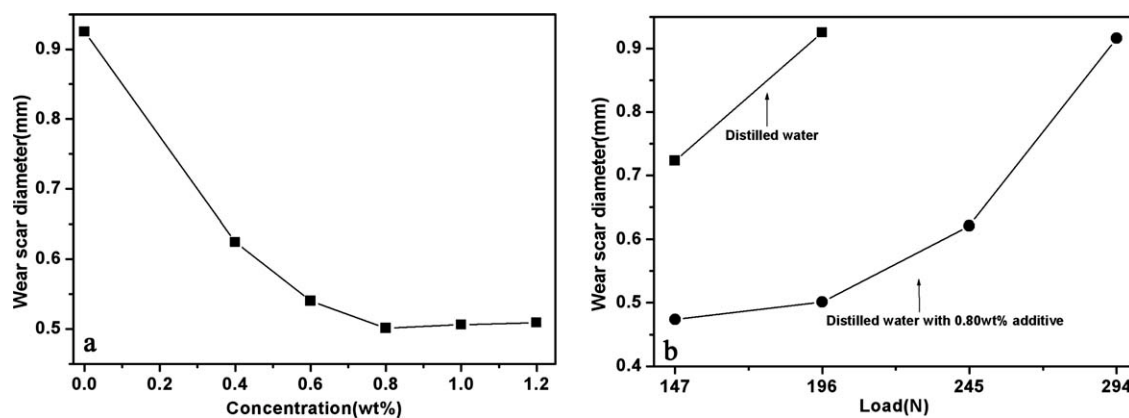
Figure 8 a: Variations of the wear-scar diameter with PTFE@Pdop concentration (room temperature, 196N, 30 min, 1450 rpm). b: Variations of the wear-scar diameter with applied load for with or without PTFE@Pdop water lubricating systems (room temperature, 30 min, 1450 rpm).

The results of elemental analysis are in good agreement with the gravimetric measurement, as shown in Figure 4. It can be seen that the thermodecomposition temperature of the pure PTFE was about 415°C [Fig. 4A(a)], whereas the pure Pdop started to lose weight early from 200°C [Fig. 4A(b)]. The pure PTFE have no residue at the end of degradation, whereas the pure Pdop have 38% residue at the end of degradation [Fig. 4A(a,b)]. Therefore, the C% and CR% of the PTFE@Pdop are calculated as 38% and 2.66% respectively, coating with 8 h as shown in Figure 4B(c). In the similar manner, the C% and CR% reached 98 and 7% after the treatment time of 36 h as shown in Figure 4B(d).

Dispersion character of PTFE@Pdop in water

Dispersion of pure PTFE into aqueous solution was very difficult even with assistance of sonication. However, dispersion of PTFE@Pdop into aqueous solution was very easy. Figure 5 gives the digital photos of pure PTFE and PTFE@Pdop in water. It is clear that pure PTFE is unable to disperse in water and is actually floating on water as shown in Figure 5(a). However, PTFE@Pdop dispersed very well in water, forming homogeneous dispersion system, and little floated product is observed as shown in Figure 5(b). Figure 5(c,d) display that the PTFE and PTFE@Pdop dispersed in water and toluene double layered system. The pure PTFE inhabited in upper toluene phase [Fig. 5(c)], whereas the PTFE@Pdop dispersed well in water phase [Fig. 5(d)].

The surface wettability property and dispersion images of pure PTFE and PTFE@Pdop in water are also shown in Figure 6(a,b), respectively, which were prepared by spreading a drop of PTFE solution onto slides. The Figure 6(a) showed the pure PTFE presented very large agglomerates. On the contrary, the PTFE@Pdop dispersed very well in water as

shown in Figure 6(b). All of the evidence revealed that the surface of PTFE@Pdop turned to hydrophilic noticeably.

The surface modification was also evaluated by the floating test, which measures the active ratio of the weight of the floated product to the overall weight of the sample after it is mixed in water and stirred vigorously. Since the pure PTFE is hydrophobic, a lower ratio represents a better surface modification. Figure 7(a) illustrates the active ratio of the samples obtained at different coating time from 3 to 60 h. When the coating time was 3 h, the active ratio was as high as 88%. From 3 to 36 h, the active ratio decreases quickly to 6%. After 36 h, the active ratio decreases slowly from 6% to 5.5%. The fact revealed that 36 h was the appropriate time to achieve almost maximum active ratio. Figure 7(b) shows the effect of the dopamine/PTFE (varied from 1.0 wt % to 7.0 wt %) on the active ratio of samples (36 h deposition time). When the weight ratio was 1.0 wt %, the active ratio
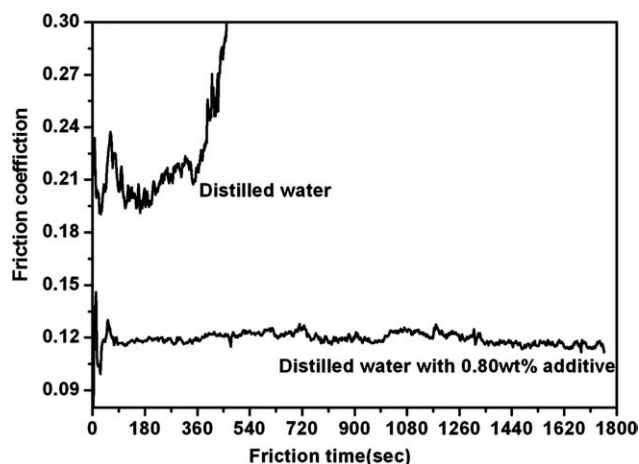

Figure 9 The effect of PTFE@Pdop on the friction coefficient of the distilled water and distilled water with additive (room temperature, 30 min, 196N, 1450 rpm).
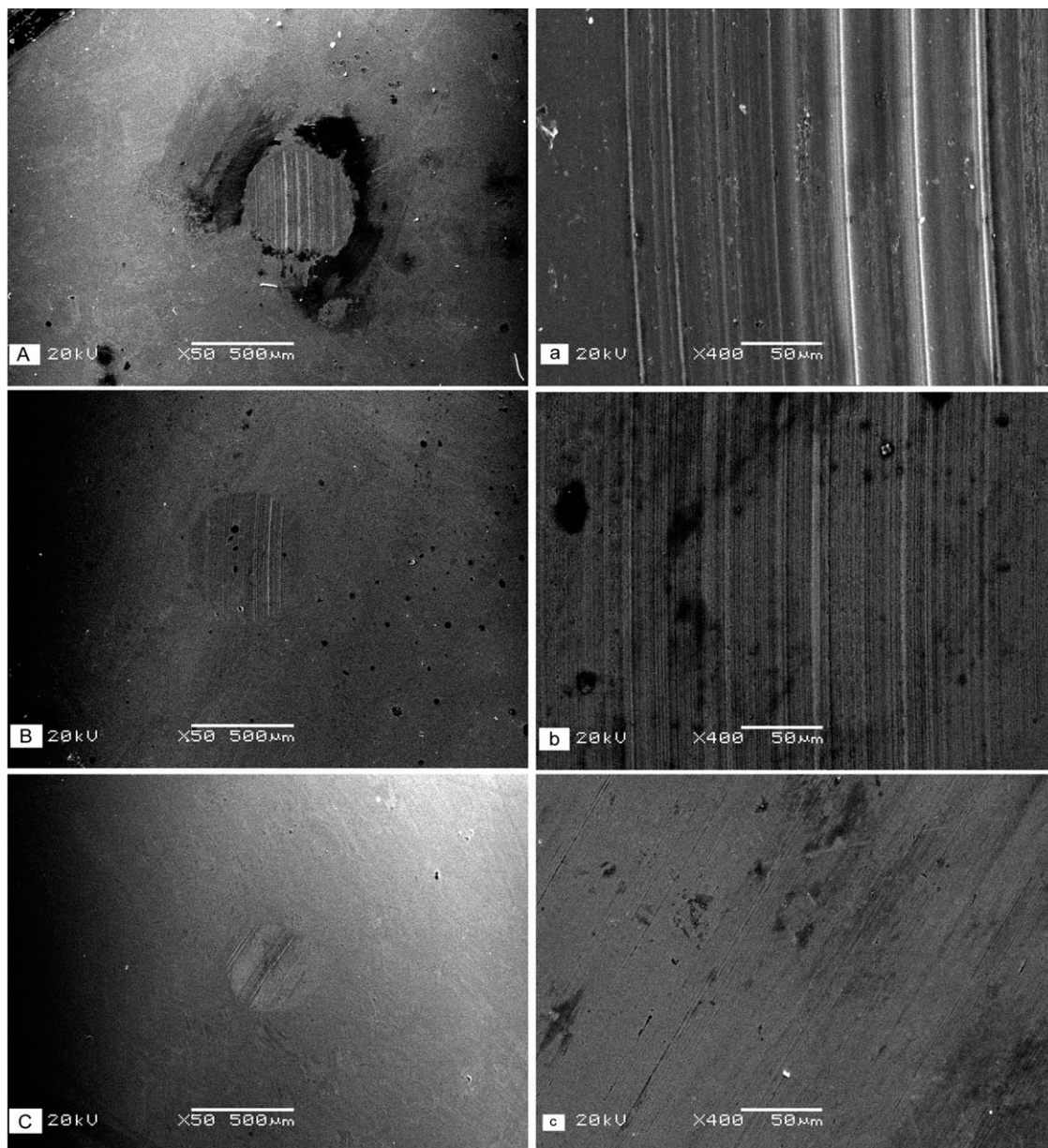
Figure 10 Morphology of the wear scar lubricated by: (A) Distilled water at 147*N*; (B) 0.8 wt% PTFE@Pdop/distilled water at 196*N*; (C) 0.8 wt% PTFE@Pdop/distilled water at 147*N*; (a, b, c) magnification of (A, B, C), respectively. (Room temperature, 30 min, 1450 rpm).

was 95%, and it quickly decreased to 6% as the weight ratio increased to 7.0 wt %. This indicated that the hydrophilic property of PTFE micropowder increases with the increase of Dop/PTFE weight ratio and the 7.0 wt % was optimal.

Tribological properties in water lubrication environment

To investigate the tribological properties of the PTFE@Pdop, distilled water was chosen as the base stock and PTFE@Pdop as the water soluble additives. To clearly compare the contribution from PTFE@Pdop, no other additives were added to water

(Note: normally a number of additives are present in any water based lubricants, of which the anticorrosion additive is the most important.). The relationship between the concentration of PTFE@Pdop and wear scar diameter (WSD) under 196*N* for 30 min is shown in Figure 8(a). It can be seen that the addition of PTFE@Pdop can decrease the WSD of distilled water considerably. With the increase of additive content from 0 wt % (distilled water) to 0.80 wt %, the wear-scar diameter (WSD) dropped strikingly from 0.93 mm to 0.50 mm. The lowest wear-scar diameter was found when the content was 0.80 wt %. Higher concentrations of the additive resulted in a slightly increased WSD and were not helpful to

improve the antiwear property any more. The optimum concentration of the additive at 0.80 wt % was suitable for the water lubrication condition.

Figure 8(b) showed the WSD of distilled water and of distilled water with 0.80 wt % of PTFE@Pdop. It can be seen that under the testing loads (147N and 196N), the WSD of distilled water with 0.80 wt % PTFE@Pdop were smaller than that with pure water. At the applied load above 245N, the test for distilled water had to be stopped right away because of the too high friction and excessive noise. However, distilled water with 0.80 wt % additive ran smoothly at all testing loads and gave relatively low wear-scar diameters. This means PTFE@Pdop as an additive can improve the antiwear property of the water lubrication environment.

The evolution of friction coefficient with time when lubricated with pure water and water plus 0.80 wt % PTFE@Pdop is shown in Figure 9. It can be seen that under the applied load of 196N, the tribological property of distilled water after 6 min friction became unstable and the friction coefficient turned very large. For comparison, the distilled water with 0.80 wt % additive gives a more stable and smaller friction coefficient and remained stable throughout all the test time.

The wear-scar morphologies of balls in four-ball machine test lubricated with pure water and the water containing 0.80 wt % PTFE@Pdop were given in Figure 10. It can be seen that severe wear scar with sharp tracks and obvious scuffing were clearly observed when lubricated with pure distilled water at the applied load 147N. However, the worn surface lubricated with pure water plus 0.80 wt % PTFE@Pdop was obviously much weaker and exhibited mild scratches at 147N or 196N. The dark regions were the transferred film of PTFE, which helps for lubrication and antiwear during sliding. This means PTFE@Pdop additive was helpful in protecting the friction surface from severe wear under the friction conditions. In other words, the PTFE@Pdop as water lubrication additive play a significant role of reducing friction coefficient and improving wear condition in water lubrication environment. Future work will be to develop effective water based lubricant formulation containing the synthesized composite together with other additives.

CONCLUSIONS

In this work, we have demonstrated a practical method of using spontaneous oxidative self-poly-

merization of dopamine to confer PTFE micropowders with hydrophilicity. The hydrophilic PTFE micropowders, PTFE@Pdop, can be very easily dispersed into aqueous solution and the active ratio in water decreased to 6%. The conversion of the pure dopamine and the coating rate increased with the treatment time and reached almost 100 and 7% after deposition time of 36 h, respectively. When the concentration of the PTFE@Pdop additive was 0.80 wt% in water-based lubrication condition, it could greatly reduce friction coefficient and showed outstanding antiwear ability. These results may be extended as a powerful route for modification of various solid lubricating materials that can be exploited as water-based lubricant additive.

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