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Characterization and Tribological Behavior of Polystrene (PS)-TiO_2 Nano-spheres

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Abstract Polystrene (PS)-TiO_2 nano-spheres were chemically synthesized. The structure characterization of the prepared PS-TiO_2 nano-spheres was investigated by means of transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR). The thermal stability of PS-TiO_2 nano-spheres was identified using a thermal analyzer (DSC & TGA). The tribological behaviors of PS-TiO_2 nano-spheres as additives in paraffin oil were evaluated on a four-ball machine. The worn surfaces were analyzed with X-ray photoelectron spectroscopy (XPS) also. Experimental results indicate that the PS-TiO_2 nano-spheres, under a certain condition, have a good anti-wear performance and improve striking failure load. This is attributed to the formation of a chemical reaction boundary film consisting of TiO_2, Fe_2O_3 and organic fragments.

Key words Oil addititive, Nano-spheres, PS-TiO_2, XPS analysis

1 Introduction

Nano-spheres are quite different from those of bulk materials or individual molecules. Therefore, research on nano-spheres is gaining popularity in scientific and industrial communities[1]. Those nano-spheres are expected to being used as contact carrier, drug delivery aids, medical diagnostic tests, and many other areas[2]. In tribology study, some authors have recognized that those nano-spheres might roll like tiny ball bearing in sliding contact[3-5]. Now, a number of polymer nano-spheres have been synthesized and many of them have been studied in lubrication[6-8]. However, few of polymer/inorganic composite nano-spheres were used and studied as additives in oil lubrication.

The roughness of friction surfaces is often several micrometers thick, so that micron particles of certain hardness can result in abradant friction in lubricating oil[9]. Nanoparticles, however, can deposit in concave of rubbing surface[10-12]. It was anticipated that polymer/inorganic composite nano-spheres could exhibit innovative tribological properties. This paper deals with the synthesis of PS-TiO_2 nano-spheres, and the characterization of the prepared product with TEM, FTIR and DSC & TGA. The tribological behaviors of PS-TiO_2 nano-spheres as additives in paraffin oil were also studied.

2 Experiment

2.1 Preparation of PS-TiO_2 nano-spheres

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$Ti(O_4H_9)_4$ was chemical pure reagent and used without further treatment, styrene monomer was purified and distilled under reduced pressure. Sodium hydroxide, alcohol and potassium persulfate ($K_2S_2O_8$) were analytical grade. Cetyl pyridinium chloride was chemical pure reagent. The synthesis procedure and solubility in organic solvents of PS-TiO_2 nano-spheres have been described in our previous work[13].

2.2 Characterization

The TEM of the prepared TiO_2 seed and PS-TiO_2 nano-spheres were obtained on a JEM-1200 EX/S instrument, IR spectra of PS-TiO_2 nano-spheres was recorded with a Nicolet 10 DX-FTIR spectrometer and the differential scanning calorimetry (DSC) curve and thermogravimetric analysis (TGA) was measured under nitrogen on a Perkin Elmer 7 thermal analysis instrument at a heating rate of 10℃/min.

2.3 Tribological properties

The tribological properties of PS-TiO_2 nano-spheres were evaluated on a MRS-10A four-ball tester with a speed of 1450rpm. Each test was run with a new set of balls and a fresh sample of oil. A ball of 12.7mm diameter, with a composition of 0.95%1.05%C, 0.15%0.35%Si, 0.20%0.40%Mn, <0.027%P, <0.020%S, 1.30%1.65%Cr, <0.30%Ni and <0.25%Cu, and a hardness of HRc 64-66, was used. The base fluid was chemically pure paraffin oil with boiling point 300 ℃ and viscosity at 50℃ of 10.28mm^2/s. All additives were dispersed in paraffin oil with an ultrasonic vibrator before carrying out the tests.

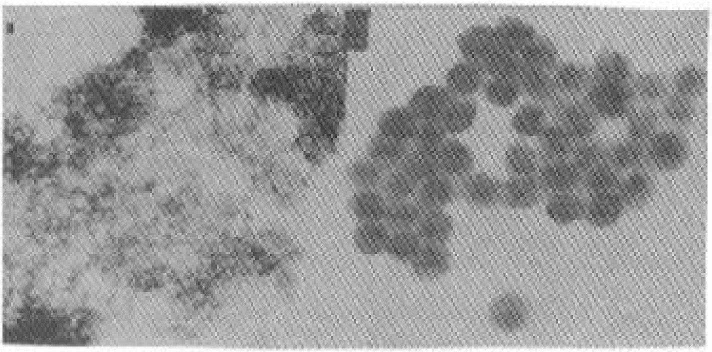
2.4 Analysis of the rubbed surface

After wear tests, the upper steel ball were rinsed with ultrasonic waves in petroleum ether (normal alkane with a boiling point of 6090℃) twice, and the chemical composition and chemical states of the elements on the worn surfaces were investigated through XPS. XPS analyses were carried out on a PHI-550 multi- technique spectrometer using pass energy of 30eV and the MgKα radiation as source, and the given binding energies used the reference binding energy of C1s at 284.6eV.

3 Results and discussion

3.1 Structure and property

TEM examination has shown that the size of the TiO_2 seed was about 10 nm, and the diameter of PS-TiO_2 nano-spheres was about 100nm (Fig.1). FTIR spectra, as indicated in Fig.2 the vibration absorption at low frequencies, such as at wavenumbers of 650 cm^{-1}, showed the existence of a Ti – O – Ti backbone, illustrating the existence of the nano-TiO_2 core. At the same time, the two strong absorption peaks at 2921 and 2850 cm^{-1} correspond to the long alkyl chain. The peaks at 30253100 cm^{-1} and 2000-1668 cm^{-1} correspond to the C – H of benzene. The absorption peaks at 1454, 1490 and 1598cm^{-1} corresponds to structure of benzene; the strong absorption peak at 1384 cm^{-1} corresponds to CH_2 structure. Thus, IR spectroscopy confirms that the samples contain



a. ×100000　　b. ×50000

Fig. 1　TEM of TiO_2 seed (a) and PS-TiO_2 nano-spheres (b)

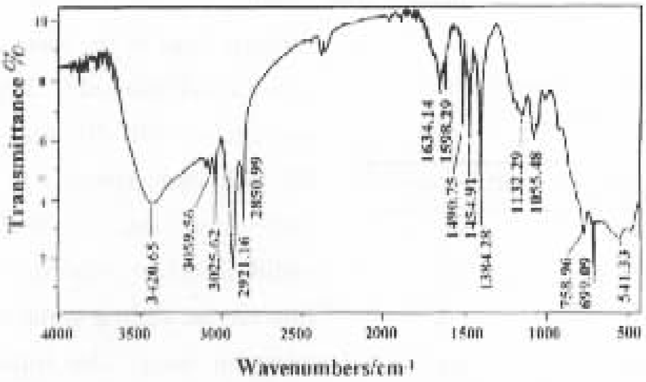


Fig. 2　The IR spectra of PS-TiO_2 composite nano-spheres

the structure of Ti – O – Ti and polystyrene. From the above analysis the structure of the PS-TiO_2 composite nano-spheres was suggested, as indicated in Fig.3.

The DSC and TGA of PS-TiO_2 composite nano-spheres were shown in Fig.4. A slow weak endothermic process at 25350℃ is observed in the DSC curve. Compared with the TGA curve, the endothermic process is caused by absorbed water and surfactant releasing, which is accompanied by weight losses of about 14%. Another endothermic process, from 350450℃, is caused by decomposition of PS layer, which corresponds to weight losses of about 61%. According to these results, we can conclude that the PS-TiO_2 nano-spheres have good thermal stability and are stable to a temperature of 350℃. This implies that the PS-TiO_2 composite nano-spheres may be used as lubricating additives at relatively higher temperature.

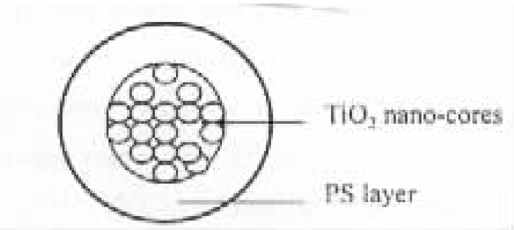


Fig. 3　The suggested structure of PS-TiO_2 nano-spheres

3.2　Tribological behavior of the PS-TiO_2 nano-spheres

Table 1 gives the maximum non-seizure load referred as the P_B value of PS-TiO_2 as an additive

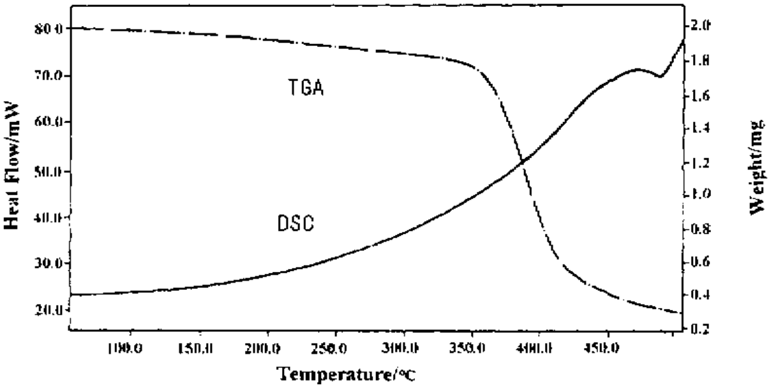


Fig. 4 DSC & TGA of $PS\text{-}TiO_2$ nano-spheres

in liquid paraffin at different concentrations . The results in table 1 show that the maximum non-seizure load of the base oil is only 392 N, and with the addition of 0.2% $PS\text{-}TiO_2$, the P_B value reaches 470 N, and when the addition of $PS\text{-}TiO_2$ nano-spheres is 0.5% the maximum non-seizure load is 598N. Since paraffin oil could absorb on the steel surface and form oil film on the sliding surfaces to protect the occurrence of wear, the liquid paraffin containing $PS\text{-}TiO_2$ might be different, the extreme pressure mechanism might be different, it not only forms lubricating film, but also might roll like tiny ball bearing in sliding contact [5,6].

Table 1 The maximum non-seizure load of $PS\text{-}TiO_2$ as an additive

Additive	Concentration %	P_B value/N
Base oil	100	392
$PS\text{-}TiO_2$	0.2	470
$PS\text{-}TiO_2$	0.3	510
$PS\text{-}TiO_2$	0.5	598
$PS\text{-}TiO_2$	1.0	598

Fig.5 shows the diameter of wear scar (DWS) as a function of additive concentration (quality per cent) of the $PS\text{-}TiO_2$ nano-spheres in liquid paraffin under a load of 300N. It is seen that the $PS\text{-}TiO_2$ nano-spheres as additives in liquid paraffin is effective for increasing the anti-wear ability even at a very low concentration and the optimum concentration of the $PS\text{-}TiO_2$ nano-spheres is 0.5%. The mechanism of the anti-wear of $PS\text{-}TiO_2$ dispersed in liquid paraffin can be proposed to be following. Under the boundary lubricating condition, the liquid paraffin containing $PS\text{-}TiO_2$ nano-spheres could not only form lubricating film, but also act as ball-bearing in sliding contact[5,6]. When the concentration of $PS\text{-}TiO_2$ is low (< 0.5%), the ball-bearing effect of $PS\text{-}TiO_2$ increases with increasing concentration of $PS\text{-}TiO_2$ dispersed in liquid paraffin. When the concentration of $PS\text{-}TiO_2$ is high (> 0.5%), the aggregating of $PS\text{-}TiO_2$ nano-spheres, which reduces the ball-bearing effect of PS-

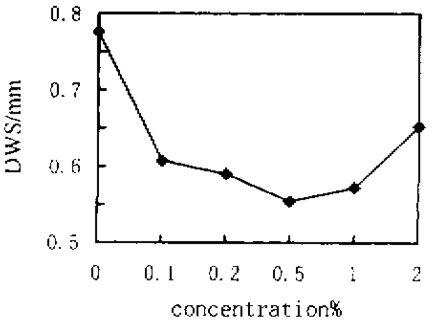


Fig. 5 Diameter of wear scar of $PS\text{-}TiO_2$ composite microsperes as a function of additive concentration 1450rpm, 300N, 30min

TiO_2, enhances with increasing concentration of PS-TiO_2, and the aggregate particles are too large to penetrate into the rubbing surfaces to reduce the friction, so these particles accumulate around the rubbing as a barrier which reduces the supply of oil available to the contact for boundary lubricating[4], hence there is an optimum concentration.

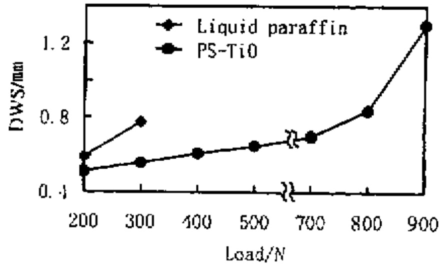


Fig. 6　Relationship between diameter of wear scar of PS-TiO_2 and liquid paraffin and applied load 1450rpm, 30min, 0.5%

Fig. 6 shows the variations of diameter of wear scar with applied load for base stock alone and for base stock containing 0.5% PS-TiO_2 composite nano-spheres. It is seen that the failure load of the liquid paraffin is only 400N, and the wear scar diameter of the liquid paraffin is 0.78mm at 300N. Contrary to the above, the wear scar diameter is smaller with liquid paraffin containing 0.5% PS-TiO_2 composite nano-spheres. In the latter case, the failure load increases to 800N, and the wear scar diameter is only 0.84mm even at a load of 800N, which almost equals the wear scar diameter of the liquid paraffin at 300N.

3.2 XPS analysis of the worn surfaces

Since XPS is very sensitive at investigating the chemical composition and chemical environment of the elements in a material, it was used to evaluate the chemical composition of the boundary film formed on the worn surfaces. Table 2 shows the binding energies of C1s, O1s and Ti2p on the worn surfaces after a four-ball test at 500N for 30min with the lubrication of a base stock containing 0.5% PS-TiO_2 composite nano-spheres.

Table 2　The binding energies of C1s, O1s, and Ti2p on the worn surfaces (eV)

Ti2p	C1s			O1s			
464.3	284.6	286.1	288.3	530.2	529.8	531.8	533.4

From the results in table 2, it is concluded that the boundary film on the rubbed surfaces is composed of TiO_2 (Ti2p: 464.3eV), Fe_2O_3 (O1s: 530.2eV), alkyl chain (C1s: 284.6eV), alkoxygroup (C1s: 286.1eV, O1s: 533.4eV) and carboxylate (C1s: 288.3eV, O1s: 531.8eV)[5,6]. Accordingly, we supposed that the excellent anti-wear capacity of PS-TiO_2 composite nano-spheres could be attributed to the formation of the boundary film on the steel surface.

4 Conclusions

The PS-TiO_2 composite nano-spheres could be well dispersed in some organic solvent and liquid paraffin base stock. The results of four-ball tests show that PS-TiO_2 nano-spheres as additives in oil could increase the anti-wear ability and failure load of the liquid paraffin effectively. The lowest wear scar diameter was observed , as the concentration of PS - TiO_2 nano - spheres in liquid paraffin was 0.5%. XPS analysis of the worn surface indicated the formation of a boundary film consisting of TiO_2, Fe_2O_3, alkyl chain, alkyl oxygen and carboxyl. This attributed to improving the anti-wear ability of the base stock.

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PS-TiO_2复合纳米微球的表征及摩擦学行为

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摘 要: 采用化学法合成了PS-TiO_2复合纳米微球,并对其进行了TEM、FTIR、TGA及DSC等分析表征。将这种微球用作润滑油添加剂,在四球试验机上研究了它的减摩抗磨性能,同时又对磨斑表面进行了X射线光电子能谱分析(XPS).研究表明:这种添加剂有良好的抗磨性能,并能在摩擦表面形成由TiO_2、Fe_2O_3以及有机碎片所组成的边界润滑膜。

关键词: 油性添加剂;纳米微球;PS-TiO_2;XPS分析

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