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SURFACE CHARACTERISATION OF ELECTRO-ACTIVE THIN POLYMERIC FILM BEARINGS

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SUMMARY

We report the results of a recent study of tribological properties of electropolymerised thin film bearings. Poly(pyrrole) films of different thickness and incorporating different counter ions have been grown onto gold electrodes on glass lens substrates and tested under a pin-on-disk apparatus. The topography of the films has been studied in order to set up correlation between surface parameters and the tribological functions, which is in turn to identify crucial parameters in the film processes for an optimum surface performance. Based upon this study, roughness distribution parameter, skewness and kurtosis are playing an important role in controlling friction. Film surfaces with positive skewness and high kurtosis values are favourable for low friction bearings. © 1998 Elsevier Science Ltd

1.0 INTRODUCTION

Thin film lubrication has been widely used in precision translations [1], high density memory drives [2] and integrated silicon micromechanisms such as micromotors and actuators [3] to improve performance through the reduction of friction and wear at the contact surfaces. Coatings are generally very thin layers of soft metals (Au, In, Pb), laminar solids (MoS_2) or polymers (PTFE, polymide composites). In recent years the electrodeposition of conductive polymers onto well defined surfaces has attracted more attention in microenginnering and nanotechnology. A distinctive advantage of this technique is that the deposition process is well-controlled and works on irregular surfaces. The choice of monomer, counter-ion, solvent, and growth potential determines the film morphology and can lead to smooth, fibrillar or spherical microstructures which may enable the optimisation of a polymer coating to a particular tribological requirement. Earlier research on conductive polymers like poly(N-methypyrrole), poly(aniline), poly (5-carboxyindole) and poly(pyrrole) showed that poly(pyrrole) films give the most promising results in terms of friction coefficient and wear resistance [4]. A systematic study on poly(pyrrole) films has been concentrated in optimising the polymerisation processes for better tribological properties [5,6]. In certain cases, a pyrrole-based film can have a friction coefficient comparable to or even better than that of PTFE. However, it has been found that films produced under nominally the same conditions sometimes give variable performance in friction, which adds complexity in data interpretation and the control of the film production. Off-line AFM measurement of the films shows that the film morphology varies in size, shape and the distribution of features and this is likely to affect the mechanical and tribological properties. Efforts have been made to measure and characterise the polymer films by using a range of surface analysis techniques in order to identify essential parameters of a surface and the statistical relations between the parameters and the tribological performances, so that a good feedback loop covering the film design, processing and performance could be developed.

Results reported here are focused on the characterisation of surface topography and tribological properties such as frictional coefficient and wear of the poly(pyrrole) specimens.

2.0 EXPERIMENTATION

2.1 Polymer films

Electrically conducting films based on poly(pyrrole) can be easily prepared electrochemically. The poly(pyrrole) films incorporating various counter ions were prepared using pyrrole (0.1 mol dm^{-3}) from an aqueous solution containing 0.1 mol dm^{-3} of the corresponding counter ion. Polymerisation reactions were performed under potential control using a commercial potentiostat and a three electrode cell. Five counter-ions of toluene sulfonic acid sodium salt (TSA) and dodecylbenzene sulfonic acid from Lancaster, and methane phosphonic acid (MPA) and n-decane phosphonic acid (DPA) from Aldrich were used and the growth conditions were adjusted for a variety of film properties. The bearing specimen consist of a plano-convex glass lens of 13 mm in diameter and 3 mm in thickness with a curvature radius of 21 mm and four heart shaped electrodes about 4 × 4 mm^2 each were vacuum deposited with 20 nm chromium then 200 nm gold films. The gold pads were then individually connected so that a polymer film could be grown separately on each. The use of a set of four film pads on a single bearing lens offers flexibility to control the batch process variability and is also cost effective for a large number of specimens. All films were grown under potential control by either stepping the potential between the working and reference electrodes to a value corresponding to polymerisation current density (typically 0.6 to 0.65 V *vs* saturated calomel electrode) or a double potential step which first steps the potential to a higher value for a short period of time to create a large number of nucleation sites then steps to a lower value to continue the growth. All specimens used in this work were produced at University of Southampton as a part of an EPSRC research project.

2.2 Measurements of friction and wear

A pin-on-disk configuration of a special test-rig has been designed and used in all experiments shown in Fig. 1. It consists of a rotating optically-flat glass disk, a sample assembly holding both a specimen under test, a vertical probe for monitoring the height variation which therefore measures the wear of the polymer film, and a spring flexure for the friction measurements via high precision capacitive micrometry.

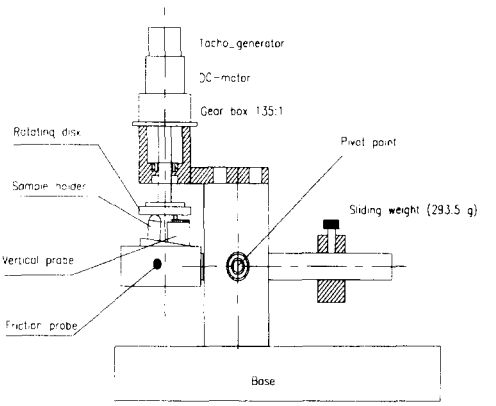


Fig. 1 Schematic of the friction test rig.

The sample assembly is attached tightly to the moving platform of the spring flexure which is a notch-hinge linear mechanism and is centrally pivoted with a graduated rod on the other side. A counter mass of 293.5 grams can be moved along the rod to give a required loading force. The sample assembly has a holder which allows the lens to be turned so that one of the polymer pads comes in contact with the disk counterface. Detailed discussion on instrumentation for friction and wear measurements is given elsewhere [4,5]. The friction test-rig can be operated at a constant speed from 0.1 to 120 mm s^{-1} with an adjustable normal loading from 0.1 to 5 N. In this paper, friction tests were run under a normal loading force of 2 N with a sliding speed of 5 mm s^{-1}. All the experiments have been performed in a temperature-controlled laboratory, normally at 20 ± 2°C.

2.3 Measurement of film topography

The topographies of polymer films were measured by an atomic force microscope (AFM, Burleigh) and a home-built scanning probe microscope [7] which is conceptually similar to an AFM but uses a contact force about 20 times larger for engineering applications. The latter SPM has a metrological scanning stage which enables the probe to measure an area repeatedly

Table 1 Details of specimens produced.

Polymer film	Growth potential V *vs* SCE	Film thickness (μm)	Friction coefficient min	max	Avg ± std	Wear rate (nm mm^{-1}) min	max	Avg	Number of Samples
PP/TSA	0.60 - 0.8	0.06 - 1.5	0.058	0.575	0.164 ± 0.08	0.03	8.7	1.2	84
PP/MPA	0.63	0.05 - 5.2	0.076	0.235	0.154 ± 0.04	0.2	3.8	0.8	80
PP/DPA	0.60 - 0.8	0.06 - 0.91	0.075	0.192	0.131 ± 0.04	0.1	2.2	0.7	16
PP/DBSA	0.5 - 0.7	0.06 - 0.74	0.159	0.8	0.326 ± 0.20	0.01	1.6	0.4	16
PP/BPA	0.65	0.06 - 0.35	0.193	0.45	0.264 ± 0.12	0.1	2.0	0.9	4
PTFE	—	—	0.05	0.12				0.2	1

to lateral resolution of better than a few nanometres and the successive measurements show no significant distortion on the film even at a contact force about 100 nN. This indicates that the films have considerable toughness. Specimens were also examined under a scanning electron microscope (SEM) but only for thicker films as the thin films are too smooth for our SEM to resolve any detailed features. The topography measurements provide information about the formation of polymer surface such as size an distribution of polymer molecules which could correlate to their tribological behaviours.

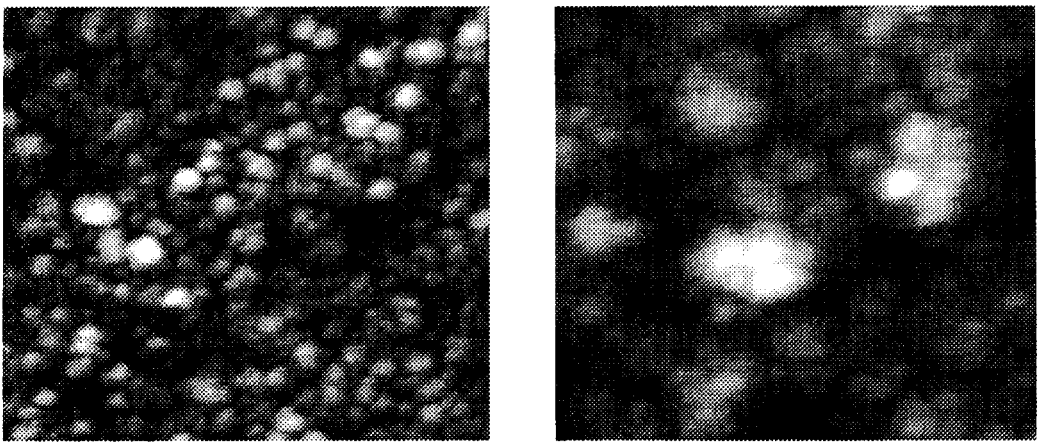
3.0 RESULTS

A range of polymer films were produced with various growth conditions such as counter ions, potential steps, film thickness, and different temperature treatment, and tested on the friction apparatus. The details of the samples and the their tribological properties are listed in Table 1 with a PTFE bearing (Glacier Metals Ltd) for comparison. Each sample was evaluated by continuously monitoring its frictional force and wear and then mean values of dynamic friction coefficient and wear rare were computed. The table gives an averaged friction coefficient and its standard deviation over all samples of the same type of polymer. Poly(pyrrole) films grown with MPA, DPA and TSA usually have friction coefficients less than 0.2 while those with DBSA and BPA have much higher values. With an appropriate thickness, films of PP/TSA, PP/MPA and PP/DPA can give a friction coefficient comparable to PTFE ($\mu < 0.1$), and the lowest friction coefficient of 0.058 was obtained from PP/TSA with a film thickness 0.16 μm. The wear rates of all films were no more than a few nanometre per millimetre sliding, with mean values generally below 1 nm mm^{-1} and some being better than that of PTFE.

4.0 SURFACE ANALYSIS

4.1 Film topography

Poly(pyrrole) films grown with the five counter ions are smooth and shiny, and vary in colour from greeny (MPA and DPA) or purple (DBSA) to black with increasing film thickness. In general, AFM measurements show that those poly(pyrrole) films have surface topography of typical spherulitic or granular patterns, with the size of spheres ranging from 0.03 to 5 μm depending on film thickness, counter ion and quality of electrode. Poly(pyrrole) films grown from MPA, DPA and TSA usually have small, evenly packed spheres which tend to clumped together to form large agglomerations as the film thickness increases. Fig 2 shows two typical AFM images taken from PP/MPA films with a thickness of 0.11 and 1.4 μm. The scan size is 1.36×1.36 μm^2 with 256×256 data points for both images. It can be seen that the thin film



(a) (b)

Fig 2. AFM images of PP/MPA with a film thickness (a) 0.11 μm and (b) 1.4 μm, and height variations of 21 and 97 nm respectively.

has an average size of polymer spheres of about 50 nm. The other has a major structure of about 400 nm accumulated from smaller spheres of around 100 nm. With the same thickness, the grain size generally increases with film type in the order of, from small to large, PP/DPA, then PP/MPA, PP/TSA, PP/BPA and PP/DBSA. The large size of polymer features of PP/BPA and PP/DBSA could be a reason for their high friction coefficients, as the bonding force within molecules is high. The quality of electrode also makes contribution on film smoothness, as it has been found that whenever the gold substrate was scratched, less uniform films were produced. The scratches seemed to be favourable sites for nucleation leading to isolated mounds of polymer.

4.2 Film thickness effect

It is known for thin film bearings that film thickness plays an important role in controlling friction. Fig. 3 shows the dependence of friction coefficient on film thickness with three types of polymers, PP/TSA, PP/MPA and PP/DPA. There exists a general trend that friction coefficient is high for very thin films < 0.1 μm, decreases sharply to a minimum at a thickness around 0.14~0.16 μm, then increases steadily and finally stabilises at thicker films. The fluctuation in friction coefficient within specimens is higher for thin films than thick films, and higher for PP/TSA than PP/DPA and PP/MPA. Here the film thickness is estimated from the nominal area of deposition and the total charge transferred during the growth or background cycling. However, in practice there are a number of factors influencing film thickness such as potential distribution, contaminants on the electrode and the topography of substrate, which makes the

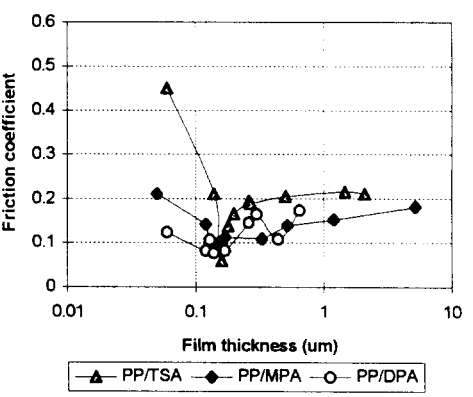
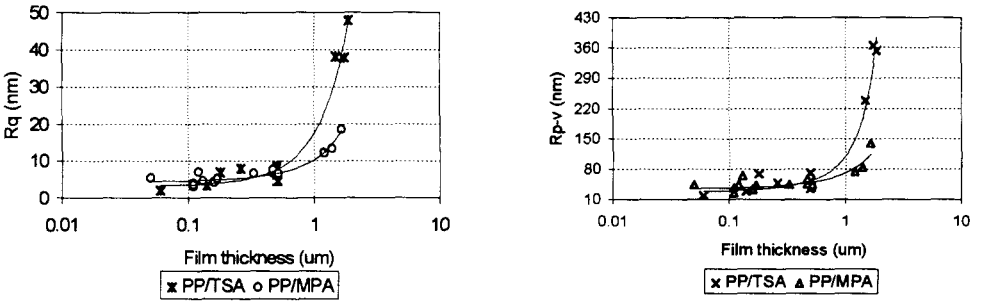


Fig. 3 Effect of film thickness on friction.

growth process less predictable and leads to variation in friction coefficient. Thus it is necessary to combine film topography with the average film thickness to give a good estimation of the uniformity of a polymer surface.

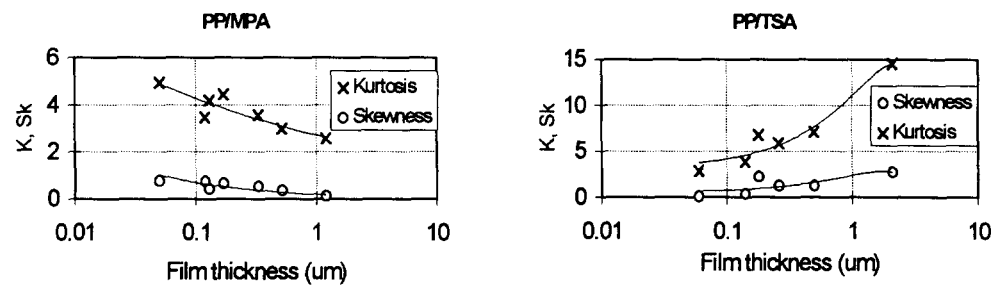


(a) (b)

Fig. 4 Dependence of surface roughness on film thickness with (a) for PP/STA and (b)PP/MPA.

4.3 Surface evaluation

Extensive study on surface topography was made on two main polymer films of PP/MPA and PP/TSA. Specimens were characterised under AFM and evaluated by area surface roughness parameters, R_q (standard deviation) and $R_{p\text{-}v}$ (peak to valley), and height distribution parameters of skewness and kurtosis in order to set up any correlation between these parameters and frictional behaviours. The polymer specimens were normally sampled by 1.36×1.36 μm^2 or 6.8×6.8 μm^2 consisting of 256×256 data points. In general, surface roughness parameters, R_q and $R_{p\text{-}v}$, remain fairly stable, for both type of polymer films, around 5~10 nm in R_q and 10~80 nm in $R_{p\text{-}v}$, when the film thickness is less than 0.6 μm, but increase rapidly afterwards, in Fig. 4 (a, b). PP/TSA films are about twice rough as PP/MPA for films thicker than 1 μm. The two graphs have a similar trend which indicates a good linear relationship between the root-mean-squares roughness, R_q, and the peak-valley magnitude, $R_{p\text{-}v}$. The consistency of graphs for R_q and $R_{p\text{-}v}$ suggests that there are no major change of topographic structure with film thickness. The reason that thin films have more or less the same roughness value is probably due to the finite or basic size of polymer molecular spheres which is about 20~50 nm. For very thin films the substrate may not be fully covered, which leads to high friction. Therefore roughness distribution parameters of skewness and kurtosis were calculated. Skewness is a measure of the asymmetric spread of surface height and the kurtosis represents the peakedness of the distribution. A Gaussian surface has a skewness of zero and a kurtosis of 3 with an equal number of peaks and valleys at a certain height. The skewness and kurtosis of PP/TSA and PP/MPA at different film thickness are plotted in Fig. 5, which interestingly show different trends with film thickness. The skewness and kurtosis of PP/MPA decrease with increasing film thickness while PP/TSA shows the opposite trend.



(a) (b)

Fig. 5 Roughness distribution of (a) PP/MPA and (b) PP/MPA with different film thickness.

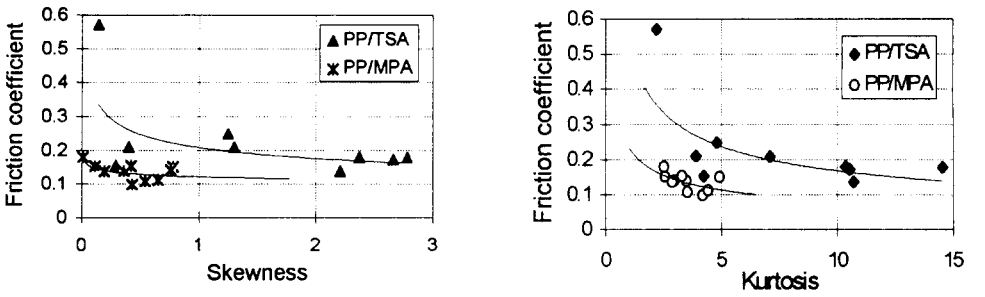


Fig. 6 Effects of (a) skewness and (b) kurtosis on friction coefficient of PP/MPA and PP/TSA.

The PP/TSA films have larger kurtosis than PP/MPA. Most of polymer films have positive skewness values and a kurtosis larger than 3, and these surfaces are generally flat but with isolated lumpy sites. If a surface has some deep valleys or uncoated sites, its skewness tends to be a negative value and the kurtosis is low (less than 3) as well. The effect of roughness distribution on friction coefficient is shown in Fig. 6. The graphs show clear clusters between the two types of polymer films. A skewness larger than 0.2 and a kurtosis larger than 3.0 result in low friction coefficient. Lower values in skewness and kurtosis result in higher friction coefficients.

It is worth to note that all trendy lines are drawn from best fitting generated by Excel spread sheet.

4.4 Effect of heat treatment

Some specimens were baked in an oven over night in a hope of improving film durability. The study shows that, statistically, there is a slight improvement in the wear resistance but an increase in friction as well. The effect of the high temperature treatment could be the result

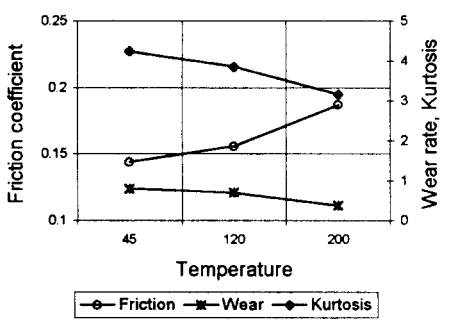


Fig. 7 Effect of heat treatment for PP/MPA.

of the rearrangement of surface topography, leading to of the a smoother surface with stronger bonding force between polymer spheres or to a change in film thickness after baking. The film thickness may vary from one part to another after baking at a temperature of 200°C due to the curved substrates used. A colour change from dark blue to yellow/gold has been observed in some specimens of PP/MPA with thickness up to 0.5 μm. The topography study shows a reduction in kurtosis and but no significant change in other parameters. Fig. 7 gives a typical result of the heat treatment for PP/MPA films with a thickness 0.5 μm, where both kurtosis and wear rate values decrease while the friction coefficient increases as the temperature increases.

5.0 Conclusion

Correlations have been demonstrated between the surface topography and tribological properties of the polymeric film bearings. The film thickness, film roughness and micro/nano structure distribution play an important role in controlling friction. A film surface with positive skewness value and kurtosis larger than 3 is preferred for a low friction bearing. Heat treatment can improve film wear resistance but leads to a higher friction coefficient and no significant change in surface topography. Work is continuing to characterise film surfaces laterally, better to quantify the sizes of submicron spheres and their distribution.

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