

Electropolymerized films for low friction microactuator bearings

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Abstract

The application of thin films in low friction bearings is well known but conventional materials (e.g., PTFE or graphite) suffer from poor processability, susceptibility to chemical attack or thermal runaway. In contrast, electrochemically grown conducting polymer films can be readily deposited onto complex surfaces with good thermal properties. The tribological properties of electropolymerized films can also be selected as desired, i.e., a low friction coefficient and a low wear rate, this makes them a promising choice for bearing material in microactuators or other sliding systems.

Introduction

Thin films of low shear strength, such as lead, graphite or molybdenum disulfide, are commonly used as lubricants. Although these materials are attractive as they have little effect upon the stiffness of a bearing system, they are difficult to deposit evenly onto complex surfaces and are susceptible to chemical attack in hostile environments. Thin polymer films of a PTFE/lead composite in a bronze matrix show greater advantage and have already been shown useful in low friction bearings of nanometric precision [1, 2]. This system has the advantage that the bronze matrix improves upon the low thermal conductivity of PTFE and reduces wear. Yet PTFE is difficult to process and any application is restricted to planar macrosystems in which the polymer can be keyed into a porous matrix.

Recent advances in molecular engineering have led to a new range of organic compounds, the so-called conducting polymers. Thin films can be readily deposited using conventional electrochemical techniques to polymerize the monomer from an aqueous or organic solvent. Moreover, the physical properties of polymer films (e.g., electrical and thermal conductivities) can be controlled through an appropriate choice of the monomer, counter-ion, solvent and deposition conditions. Applications of conducting polymer films in nanotechnology look promising [3], with processing techniques compatible with microelectronic devices [4].

We report here on the measurement of the tribological properties of some conducting polymers with various film thicknesses 50 nm to 5 μm . Results were obtained

using a pin-on disc apparatus with a moderate load. Friction coefficients spanned a range of 0.7 down to less than 0.07 and specific values could be achieved through an appropriate choice of the polymer system and the deposition conditions. Wear coefficients also showed considerable variation with very low values of less than 10 nm mm^{-1} observed in some cases. We believe that these materials have enormous potential in the fields of micromechanics and nanotechnology.

Friction-measuring apparatus

The frictional properties of the polymer films were measured using a test rig similar to that described by Eldridge and Tabor [5]. The specimen under test consists of a fused glass plano-convex lens of surface roughness $R_a \sim 10 \text{ nm}$ onto which a 100 nm thick circular gold electrode (10 mm diameter) had been thermally evaporated and a conducting polymer electrochemically grown. This is glued onto one end of the pivot arm which is pressed against an optically flat glass disc with a load (0.1 to 2 N) determined by a sliding counter weight (Fig. 1). The contact point is 15 mm from the rotational axis with sliding speeds of 0.1 to 100 mm s^{-1} available. An LVDT transducer is used to measure the deflection of a linear spring caused by the tractional force between the rotating disc and the bearing. Tractional forces can be measured in the range of 40 mN to 10 N with a calibration accuracy of about 2% and resolution of 5 mN. All experiments were carried out in air at constant ambient temperature of $(20 \pm 2)^\circ\text{C}$ and 40% relative humidity.

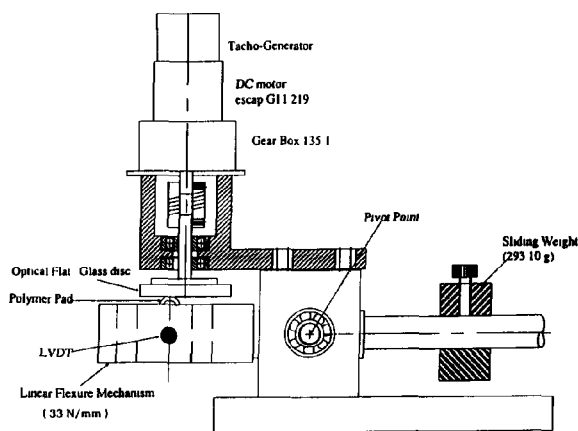


Fig 1 Experimental apparatus to measure the friction and wear properties of thin polymer films

Thin polymer films

The plano-convex lens (radius of 51 mm, thickness 3 mm) with its thermally evaporated 100 nm gold electrode was washed in acetone to degrease, followed by rinsing in deionized water. The gold electrode was placed in a conventional three-electrode electrochemical cell to form the working electrode. Commercially available monomers of pyrrole, *N*-methylpyrrole and 5-carboxyindole were further purified, whereas aniline was used as received. Electropolymerization was carried out by either cyclic voltammetry or potential stepping. In all cases charge was monitored during growth to determine an estimate of the film thickness. The details of the polymer systems and deposition are summarized in Table 1. Further details of the growth conditions may be found elsewhere [6].

TABLE 1 Details of electrochemically deposited thin polymer bearings

| Monomer (0.1 mol dm ⁻¹) | Counter-ion/ solvent ^a (0.1 mol dm ⁻³) | Growth potential (V) vs SCE | Oxidation state | Number of samples | Thickness range |
|--|---|-----------------------------------|--------------------|----------------------|--------------------|
| Pyrrole | DBSA/H ₂ O | 0.80 | oxidized | 6 | 30 nm–0.1 μm |
| Pyrrole | TSA/H ₂ O | 0.80 | oxidized | 19 | 0.23–3.78 μm |
| Pyrrole | TSA/H ₂ O | 0.80 | reduced | 9 | 0.26–3.47 μm |
| <i>N</i> -Methylpyrrole | DBSA/H ₂ O | 0.79 | oxidized | 30 | 90 nm–2.65 μm |
| <i>N</i> -Methylpyrrole | DBSA/H ₂ O | 0.79 | reduced | 12 | 80 nm–0.73 μm |
| <i>N</i> -Methylpyrrole | DBSA/H ₂ O/MeCN | 0.85 | oxidized | 4 | 0.34–0.49 μm |
| Aniline | NaHSO ₄ /H ₂ O | 0.90 | oxidized | 6 | |
| 5-Carboxyindole | TEATFB/MeCN | 1.40 | oxidized | 4 | 12–53 nm |
| Copolymer ^b | TSA/H ₂ O | 0.80 | oxidized | 3 | 0.22–4.16 μm |
| Bilayer ^b | TSA/H ₂ O | 0.80, 0.79 | oxidized | 4 | 0.92–3.34 μm |

^aAbbreviations: dodecylbenzene sulfonic acid (DBSA), toluene sulfonic acid (TSA), tetraethylammonium tetrafluoroborate (TEATFB), acetonitrile (MeCN). ^bPyrrole/*N*-methylpyrrole.

Theoretical considerations

The frictional traction F_t between two sliding surfaces is generally believed to arise from the shearing of the softer material over a contact area A

$$F_t = A\sigma_s \quad (1)$$

where σ_s is the shear stress of the contact. The contact area A can be related to the applied load W through a power law with an exponent varying from 2/3 (elastic behaviour) to 1.0 (plastic behaviour). For our polymer films, it seems likely that the interface will be nearly plastic due to the low yield stress of the film and the high substrate elastic modulus. Consequently, we suggest that the contact area A has a radius given by the Hertzian distortion of the substrate and a small correction due to the film. Thus, the apparent area A is given by

$$A = \pi a^2 \approx \pi \left[r \frac{W_{app}}{k} \right]^{2/3} \quad (2)$$

where r is the radius of the spherical contact (i.e. 51 mm), k the combined elastic constant of the polymer bearing and interface [6], and W_{app} the apparent Hertzian load related to the true load W_0 (which lies in the range of 0.1 to 2 N) by [7]

$$W_{app} = W_0 + 3\gamma\pi r + [6\gamma\pi r W_0 + (3\gamma\pi r)^2]^{1/2} \quad (3)$$

with γ the surface energy per unit area. In practice, the elasticity of the interface will vary with increasing load from that of the polymer to that of the substrate at high loads. In our models this is represented by an exponential function from polymer to glass substrate. As the coefficient of friction μ is defined by the ratio of traction F_t to applied load W_0 , we can predict two mechanistic regions from our model. At relatively high loads, the surface energy γ may be neglected and the

friction coefficient μ_h is determined by the apparent load and the shear stress, while at low loads the friction coefficient μ_l is determined by the surface energy γ . Thus, the choice of magnitude of the load will determine the behaviour of the friction coefficient

Results and conclusions

The variation of friction coefficient μ with applied load W_0 was measured over the range 0.12 to 2.0 N. Figure 2 shows the typical behaviour of a conducting polymer film. The friction coefficient μ falls continuously from a high value to a low slowly varying value as the load steadily increases. A good theoretical fit is obtained when the shear stress and surface energy are estimated as 0.65 MPa and 0.04 J m⁻², respectively, for the 2.48 μ m copolymer bearing. The theoretical curve for high loads from eqns (1), (2) and (3) is $\mu_h \propto W_0^{-1/3}$. As the friction coefficient becomes slowly varying above an applied load of 1 N, all subsequent measurements were made at a load of 2 N.

The static and dynamic friction coefficients of each conducting polymer were measured using the rig shown in Fig 1 with a load of 2 N and a sliding speed of 7.7 mm s⁻¹. The values observed for polymers are compared to that for a standard PTFE bearing (Glacier Metals Ltd). Figure 3 shows the dynamic frictional characteristics of a 0.11 μ m polypyrrole film. There is some evidence of a stick-slip mechanism but the mean dynamic friction coefficient μ_d of 0.085 is similar to that observed for PTFE. The full range of achievable friction coefficients is shown in Fig 4. The spread of points for each polymer system is determined by the different counter-ion, solvent and film thicknesses listed in Table 1. Polypyrrole exhibits the largest observed

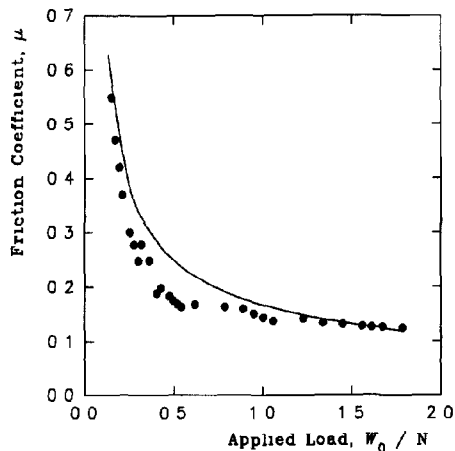


Fig 2 Comparison of observed variation in friction coefficient of a copolymer film (●) with our theoretical model (—)

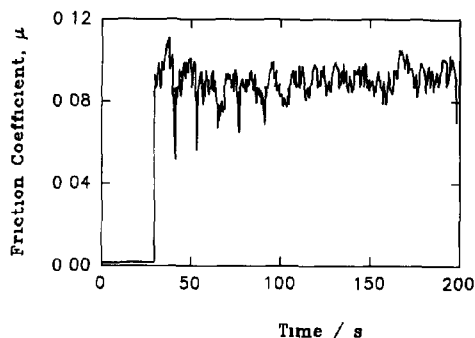


Fig 3 Typical dynamic characterization of a thin polypyrrole bearing. Note that the friction measurement starts after a period of about 30 s for equilibration of the apparatus

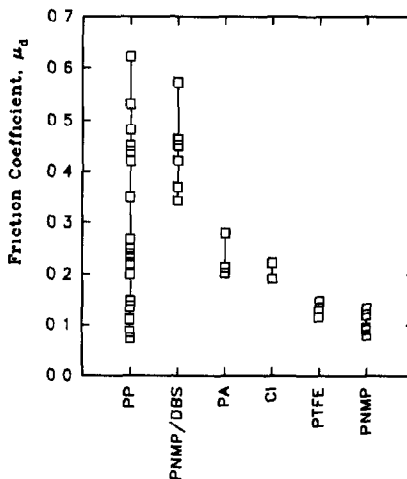


Fig 4 Full range of achievable friction coefficients measured. Note that the observed friction coefficients of PTFE are higher than some polypyrrole and all poly(*N*-methylpyrrole) values. Key: PP = polypyrrole, PNMP/DBS = poly(*N*-methylpyrrole) DBSA, PA = polyaniline, CI = poly(5-carboxyindole), PNMP = poly(*N*-methylpyrrole)

range of coefficient from a value of 0.07 to 0.62. Low values of the friction coefficient correspond to the thin polymer films (~ 100 nm) but a steady increase is observed to ~ 0.6 at film thicknesses of ~ 4 μ m. As can be seen, the other polymer systems together span the entire range from poly(*N*-methylpyrrole) (DBSA) (0.6 to 0.35) down to poly(5-carboxyindole) (~ 0.1). It appears that the choice of film thickness and the counter-ion are more important than the film structure. Polyaniline has a fibrillar microstructure, poly(*N*-methylpyrrole) is microspheroidal and poly(5-carboxyindole) is smooth on the microscopic level, yet they all have similar coefficients.

Finally, Fig 5 shows the considerable variation in wear rate of polypyrrole with film thickness. The thinnest films tend to have the lowest friction coefficient and

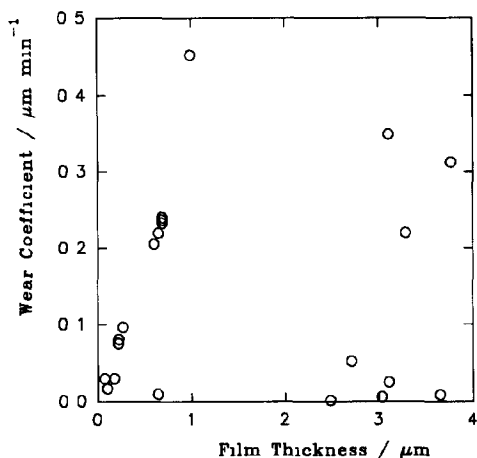


Fig 5 Variation in wear rate of typical polypyrrole with film thickness. The sample of $2.5 \mu\text{m}$ showed no wear during the test period and has been recorded as zero.

wear rate ($< 0.03 \mu\text{m min}^{-1}$), although very low values are also observed for thicker films. The exact relationship is difficult to assess due to scatter but we can conclude that very low wear rates are achievable in thin polymer films. It is well known that the microscopic structure of very thin conducting polymer films is different to that of much thicker films, so the variation observed here may well reflect those changes. Nevertheless the results presented here have important implications in the design of bearings that are durable as well as low friction.

The unique combination of the tribological properties of conducting polymers coupled with the ability to deposit them electrochemically in a controlled manner should produce a new generation of low friction microactuator bearings as well as improved macroactuators [8].

References

- 1 K Lindsey, S T Smith and C J Robbie, Sub-nanometre surface texture and profile measurement with Nanosurf 2, *Ann CIRP*, 37 (1988) 519-522
- 2 S T Smith, S Harb and D G Chetwynd, Tribological properties of polymeric bearings at the nanometre level, *J Phys D Appl Phys*, 25 (1992) 240-248
- 3 J W Gardner and P N Bartlett, Potential applications of electropolymerised thin organic films in nanotechnology, *Nanotechnology*, 2 (1991) 19-32
- 4 E W Paul, A J Ricco and M S Wrighton, Resistance of poly(aniline) films as a function of electrochemical potential and the fabrication of poly(aniline)-based microelectronic devices, *J Phys Chem*, 89 (1985) 1441
- 5 K.R Eldridge and D Tabor, The mechanism of rolling friction I The plastic range, *Proc R. Soc London, Ser A*, 229 (1955) 181-198
- 6 S T Smith, S Harb, V Eastwick-Field, Z Q Zao, P N Bartlett, D G Chetwynd and J W Gardner, Tribological properties of electroactive polymeric thin film bearings, *Wear*, 169 (1993) 43-57
- 7 K L Johnson, K Kendall and A D Roberts, Surface energy and the contact of elastic solids, *Proc R. Soc London, Ser A*, 324 (1971) 301-314
- 8 P N Bartlett, D G Chetwynd, J W Gardner and S T Smith, Tunable low friction bearings, *UK Patent Applic No 136129* (Sept 1, 1993)