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Friction and adhesion of silica fibres in liquid media

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Contact adhesion and sliding friction between orthgonally configured silica fibres were measured in water, hexadecane, and cyclohexane. In the adhesion model of friction, the friction is interpreted in terms of shearing the junction and the shear strength (τ) can simply be represented by $\tau = F/A$ where F is frictional force and A is the real area of contact. While this model works well for the frictional behaviour of silica fibre in air, this was not the case in liquid media. The influence of liquid on the force required to break the adhesive junction cannot simply be interpreted in terms of the reduction in adhesional forces between two fibres; but the interpretations have to also include the nature of the liquids.

1. Introduction

Friction and adhesion properties of solid provide insight into the molecular forces of solid–solid interactions. Several studies have been made of the friction of polymers in liquid environments. Cohen and Tabor [1] investigated the influence of isopropyl alcohol–water mixtures on polyethylene terephthalate fibres and found that the greatest reduction in friction occurred when the surface tension of the mixture was less than the critical surface tension of the polymer. They attributed this effect to the formation of a weakly bound film of molecules from the liquid. Similar studies were made by Seiner and West [2] who extended the measurements to a large number of liquids with different wetting characteristics. It emerged that there was a general but somewhat variable reduction in the coefficient of friction with decreasing surface tension of the liquid medium. Adam and co-workers [3] did a more systematic study to establish a more quantitative framework for the general case of polymeric contacts in the presence of boundary lubricants. These studies investigated the frictional behaviour of polymeric materials (low surface energy) with the wettability of the liquid medium. A general conclusion drawn from these studies was that there is a marked discontinuity of frictional force at the critical surface tension of wetting liquid. When the fluid wets the polymer, the friction is low; when it does not wet the polymer, the friction is high. However, this general observation between the friction and the wettability can not be applied to a high energy surface such as silica fibres, unless the surfaces are properly modified to have a finite contact angle. Most liquids wet silica fibres, so the frictional behaviour in such a system cannot be interpreted in terms of their surface energetics. This is especially true when the liquid environments are nonpolar. One of the aims of this work is to investigate the friction and adhesion behaviour of silica fibres in liquids.

2. Experimental methods

2.1. Materials

Silica fibres having diameters in the range 25 to 35 μm were formed by drawing silica rods in an oxygen/natural gas flame at about the silica softening temperature (1300 °C). Care was taken to ensure that the rods were always placed in the same position in the flame.

Hexadecane was used as received without further purification (> 95%). Cyclohexane was purified by passing through a column containing florisil (60–100 mesh) which had been activated by heating at 200 °C for 2 h. The purified cyclohexane was used immediately. Deionized water was used with a conductivity of 10^{18} Mohm-cm or less. Freshly drawn fibres were immediately transferred to each liquid container. The sample containers were kept in a vacuum desiccator containing a molecular sieve for 6 h. The fibres were then slowly removed from the liquids using tweezers before testing.

2.2. Adhesion and friction measurements

The details of friction and adhesion measurements can be found elsewhere [4]. In these measurements contact adhesion and friction were measured for two fibres in an orthogonal configuration. The bending of one of the fibres is used as a means of applying a normal load and its deflection, produced by movement of the other fibre, is a measure of the frictional force. Since the curvature of the fibres is so acute the contact area is very small and hence the contact is likely to be between single asperities. Also, the magnitude of the applied normal loads are comparable to the surface

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forces, which is not usually possible in conventional friction measurements.

For the adhesion and friction measurements in liquid environments, the horizontal fibre-holding fixture was immersed in a glass container which had a flat window through which the fibre pair could be viewed. The container was filled with liquid so that the contact point between the two fibres was fully immersed. The solution was replaced for every measurement to avoid any cross-contamination between experiments. The sliding speed was 6.7 $\mu m\, s^{-1}$, which was slow enough to avoid hydrodynamic lubrication.

2.3. Contact angle measurements

The cleanliness of the fibres was examined by determining the contact angle of the water, hexadecane, and cyclohexane at room temperature (22 °C) on freshly drawn silica fibres using a Wilhelmy balance. For this technique, the fibre is suspended from the electrobalance and immersed in and emersed through the surface of the test liquid. The force exerted on such a fibre, F_w, is expressed by [5]

$$F_w = P\gamma_{lv} \cos\theta \qquad (1)$$

where P is the perimeter of the fibre along the three-phase boundary line, F_w is the force exerted on the fibre, γ_{lv}, the liquid surface tension and θ, the liquid contact angle. Calculation of θ requires an independently determined value for the liquid surface tension, γ_{lv}. In addition to the wetting force, any significant immersion of the fibre in the liquid will induce a buoyancy force F_b. However, this was not significant for small diameter fibres.

3. Results and discussion

The cleanliness of the fibres was examined by determining the θ of water ($\gamma_{lv} = 72.6\, mJ\, m^{-2}$), hexadecane ($\gamma_{lv} = 27.5\, mJ\, m^{-2}$), and cyclohexane ($\gamma_{lv} = 25.5\, mJ\, m^{-2}$) at room temperature (22 °C) on freshly drawn silica fibres. Table I summarizes these results. The contact angles of hexadecane and cyclohexane were close to zero. A finite contact angle of water, however, indicates some low level contamination which was probably introduced while mounting the fibre on the microbalance.

Friction and adhesion measurements of freshly drawn silica fibres were performed in deionized water. The effects of liquid media were also sought in the fibres equilibrated for 6 h in deionized water, hexadecane (> 99% purity) and cyclohexane. Table II summarizes the pull-off forces from orthogonally configured fibres. The pull-off force of silica fibres equilibrated in water and hexadecane was drastically reduced compared with those measured in air. In cyclohexane, the adhesion was very low and difficult to measure accurately.

Fig. 1 shows a comparision of frictional behaviour between freshly drawn fibre in air and in water. The good efficiency of the fibre/fibre lubrication in water was a little surprising despite its high surface tension. This is probably the result of a weakly bound film of water molecules adsorbed on the hydrophilic fibre surface. With the assumption that the mechanical properties of the fibre do not change significantly in water, the interfacial shear strength was calculated from the frictional force obtained from Fig. 1 and estimating the real area of contact from Hertzian analysis including an independently determined adhesional force. Fig. 2 shows the comparision of interfacial shear strength of the fresh fibre in air and in water as a function of contact pressure. It may be noted that the shear strength at zero contact pressure in deionized water is 27 MPa, which is lowered by 15 MPa than for the fresh fibres in air. Presumably, water reduces the adhesive component of the normal load and may also act as a boundary lubricant, which means that it provides a low friction coefficient at low sliding speeds where no hydrodynamic lift occurs. Fig. 3 shows the frictional behaviour of silica fibres

TABLE I Advancing and receding contact angles of fresh fibre to water, hexadecane and cyclohexane

	Advancing force (μN)	Receding force (μN)	Fibre diameter (μm)	θ(adv)	θ(rec)
Water	4.13	5.04	21.7	31.85	11.85
Hexadecane	2.39	2.46	27.6	3.27	0
Cyclohexane	2.29	2.32	28.4	5.57	2.78

TABLE II Pull-off forces measured in air and liquids

Test condition	Pull-off force (μN)	S.d. (μN)
In air	4.972	0.463
In water	1.697	–
In hexadecane	0.243	–
In cyclohexane	0.002	–

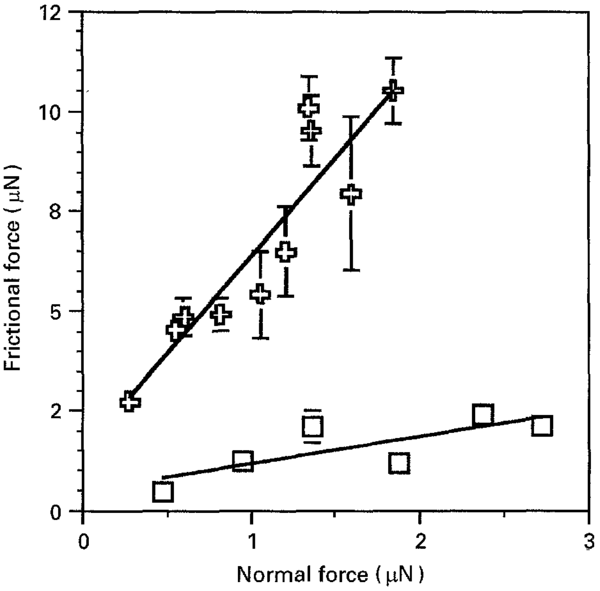

Figure 1 Comparison of frictional forces for fresh silica fibres in air (✚) and in deionised water (□).

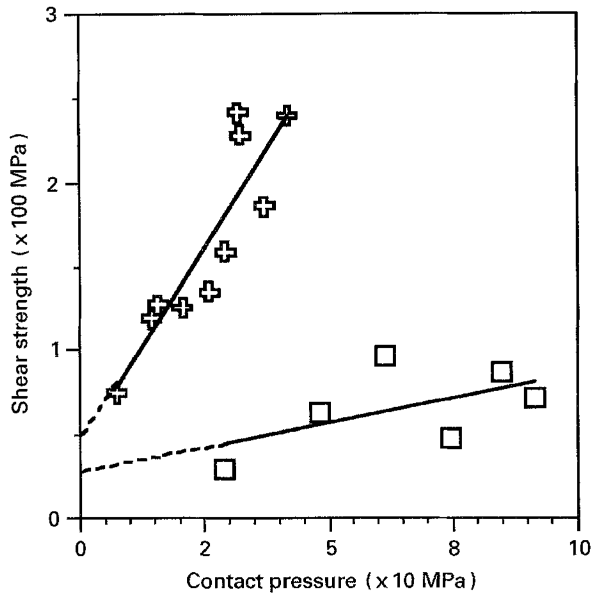

Figure 2 Pressure dependence of the shear strength for fresh silica fibers in air (✚) and in deionised water (□).

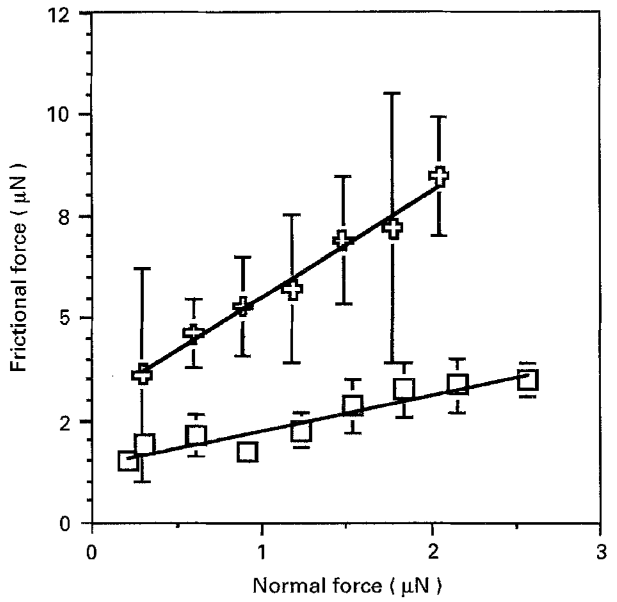

Figure 3 Frictional forces of silica fibres as a function of normal force for two hydration times. (✚) 10 days; □ 6 h.

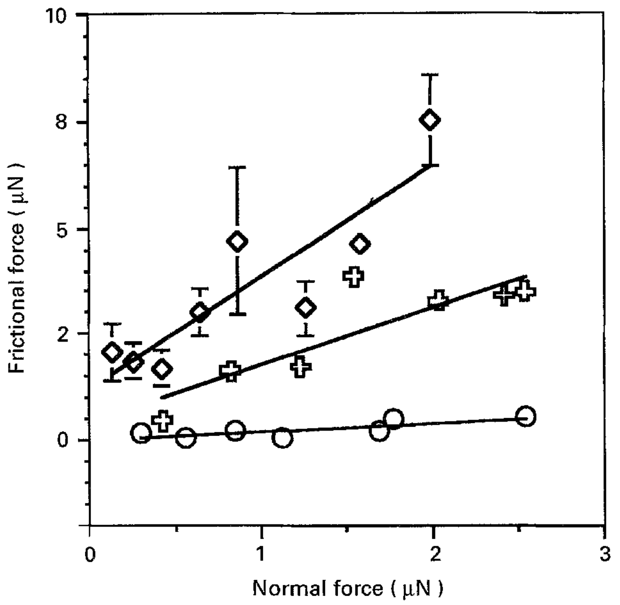

Figure 4 Frictional behaviour of silica fibres in water (✚) hexadecane (◇) and cyclohexane (○) after pre-equilibration with the liquids for 6 h.

hydrated for two different durations (six hours and 10 days) and tested in air. It was not possible to distinguish the frictional behaviour within short intervals of hydration time (1 to 6 h) due to the large scatter of the data. But it is obvious from the figure that after prolonged hydration (10 days) of the silica fibre, the frictional force increased significantly. This can probably be ascribed to surface degradation due to water attack resulting in a gel-like structure on the surface. If this occurs, the softening of the surface leads to an increase in area of contact and a consequent increase in friction.

Fig. 4 compares the frictional behaviour of silica fibres that were pre-equilibrated in water, hexadecane, and cyclohexane, and later tested in these liquids. The data indicate several phenomena. The most interesting are the observations in pure cyclohexane. From Table II, it was seen that the adhesional force was almost zero. Israelachvili and co-workers [6] observed that the force between two curved mica surfaces immersed in cyclohexane over a few nm (approximately 10 molecular diameter) is spatially oscillatory, and varies between attraction and repulsion, with a periodicity equal to the molecular size. These rapidly decaying oscillatory forces indicate that the molecules are layered near the surfaces, and this layering prevents the surfaces from coming into adhesive contact. This observation is consistent with our pull-off force results. Thus, the significantly reduced friction in cyclohexane can be ascribed to its capability of forming a stable film of liquid molecules on the fibre surface which acts as a boundary lubricating film.

Unlike cyclohexane, the friction in hexadecane was as high as in the dry friction. Clearly, hexadecane behaves differently when compared to cylohexane because it does not act as a boundary lubricant. This is in agreement with the lubrication of metals where pure paraffin does not provide a low friction coefficient at very low sliding velocities. Fisher and coworkers [7, 8] observed a high friction coefficient for 52100 steel in hexadecane, which was as high as for the dry materials. This comparison between silica and metals is reasonable because most metals have a thin oxide surface film.

It is interesting to estimate the Hamaker constants for silica fibres in different interacting media using the measured pull-off forces. The interacting force between two crossed cylinders is given by [9]

$$P = -\frac{AD}{12z^2} \qquad (2)$$

where P is the force (negative for attraction), D is the diameter of cylinder, z measures the gap between surfaces and A is the Hamaker constant for which it was assumed that the interaction is non-retarded and additive. However, the assumption of simple pairwise additivity, inherent in the above equation, and the definition of the Hamaker constant ignore the influence of neighbouring atoms on the interaction between any pair of atoms. In rarefied media these effects may be small, and the assumptions of additivity hold; but this is not the case for condensed media. In the Lifshitz- theory, the additivity problem is avoided, where the atomic structure is ignored and the forces between large bodies, now treated as continuous media, are derived in terms of bulk properties such as their dielectric constants and refractive indices. For two identical phases, both of which are labelled 1, within an interacting medium, labelled 3, the Hamaker constant is given by [9]

$$A = A_{\nu=0} + A_{\nu>0}$$

$$= \frac{3}{4}kT + \left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)^2 + \frac{3h\nu_e}{16\sqrt{2}}\frac{(n_1^2 - n_3^2)^2}{(n_1^2 + n_3^2)^{3/2}} \qquad (3)$$

where $A_{\nu=0}$ is the purely entropic zero-contribution, $A_{\nu>0}$ is the disperison energy contribution, K is the Boltzmann constant, h is Plancks constant, ε is the dielectric constant, n is the refractive index, and ν_e is electronic absorption frequency. From Equation 2, z is given a constant having a minimal value z_0 which is the distance between the outermost centres of polarization of two nearest atoms belonging to the two bodies. The value z_0 at 0.2 nm is a good approximation as discussed by Newman and colleagues [10]. Table III summarizes the Hamaker constants based on: (i) using Equation 2 with the experimentally determined adhesional forces; (ii) the calculated values from Equation 3 based on the constants given in Table IV, and (iii) the values from another source [9]. There is a good agreement between the Hamaker constants measured or calculated for air as the medium while this is not the cases in liquid media.

TABLE III Hamaker constants for silica fibres interacting in air, water, hexadecane and cyclohexane

Interacting media	A (Hamaker constant $\times 10^{-20}$ J)		Ref. 9
	Equation 1	Equation 2	
Air	6.28	6.30	5–6
Water	3.4	0.63	–
Hexadecane	0.3	0.03	–
Cyclohexane	0.07	0.03	–

TABLE IV Constants used in calculating Hamaker constant using Equation 3

Medium	Dielectric constant (ε)	Refractive constant (n)	Absorption frequency (10^{15} Hz)
Fused quartz	3.8	1.148	3.2
Water	80	1.333	3.0
Hexadecane	2.1	1.423	2.9
Cyclohexane	2.9	1.426	2.9

4. Conclusions

It was observed that the friction and adhesion behaviour of silica fibres in liquid environments were quite different from those in air. While adhesional pull-off forces were significantly reduced in all liquids compared to the result for the fresh fibres in air, they did not show any correspondence with the frictional forces at zero applied load in terms of their magnitude in reduction. These results imply that the influence of liquid media on the force required to break the adhesive junction cannot simply be interpreted in terms of the reduction in adhesional forces between two fibres; the interpretations have to also include the nature of the liquids.

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