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Shear properties of organic films adsorbed on silica fibres

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Contact adhesion and sliding friction of octadecylamine and silane molecules adsorbed on silica fibre were measured with orthogonally crossed silica fibres using an electronic microbalance. Interfacial shear strengths, τ, as a function of contact pressure, P, between organic films were deduced from the adhesional model of friction using the measured frictional force and the calculated real area of contact. The pressure dependence of the interfacial shear strength was then interpreted in terms of the molecular interaction of adsorbates with solvent and the surface energetics of molecules adsorbed on the silica fibre.

1. Introduction

When a solid is dipped into a solution consisting of a long-chain polar compound dissolved in a non-polar solvent, the excess liquid is found to retract from the surface of the solid as it is withdrawn. This effect is due to the presence of a layer of long-chain polar compound adsorbed on the solid surface from the solution. The polar ends of the molecules attach themselves to the substrate and the hydrocarbon chains extend outwards, presenting an outer space consisting largely of CH_3 groups. Recent review papers [1, 2] have described the surface properties of these adsorbed films.

Bowden and Tabor [3] described the ability of these adsorbed monolayers of long-chain compounds to reduce the coefficient of friction and wear between sliding surfaces. These films on solid surfaces act as lubricants for sliding or rolling by lowering the static and dynamic friction. Amines have been known for some time to self-assemble into monolayer films and there is currently a good understanding of these films in terms of surface energetics [4]. Another type of film-forming chemical is the group of *n*-alkyl silanes. At present, considerable information is available regarding the wettability of these adsorbed films. Despite the extensive work on these film-forming substances, the frictional behaviour of these films does not appear to have been examined extensively.

In order to investigate frictional shear behaviour of these adsorbed organic films, tests were conducted on silica fibres retracted from solutions of octadecylamine in hexadecane and cyclohexane and solutions of silanes in toluene.

2. Experimental procedure

2.1. Materials

The adsorbates used in this study were *n*-octadecylamine (ODA, Aldrich Chemical Co.), trimethyl monochlorosilane (TMCS, Petrach System Inc.) and *n*-octadecyl dimethyl monochlorosilane (DMODCS, Petrach System Inc.). They were used as obtained from the suppliers. The solvents from which ODA was adsorbed were hexadecane and cyclohexane, which proved to have a high enough surface tension to retract from the adsorbed monolayer. Toluene was used for the thin films of alkyl silane. All solvents (hexadecane, cyclohexane and toluene) were reagent grade materials ($>99\%$ purity). The cyclohexane and toluene were purified by passing through a column containing florisil (60–100 mesh) which was activated by heating at 200 °C for 2 h before use. Hexadecane was used as-received.

2.2. Film preparation

Solutions containing 0.1 wt% ODA were prepared in hexadecane and cyclohexane at 60 °C in a glass container. Freshly drawn silica fibres (≈ 15 μm diameter) were dipped in each solution and kept for 24 h over a molecular sieve desiccant. The fibres were then slowly retracted from the solutions using tweezers and placed in a glass jar to allow any solvent incorporated in the adsorbed films to evaporate.

Thin films of the alkyl silanes were prepared from solutions of TMCS (0.5 mol) and DMODCS (0.5 mol) dissolved in toluene. The freshly drawn fibres were immersed in the silanizing solution for 15 min and slowly retracted. A large amount of ethanol was

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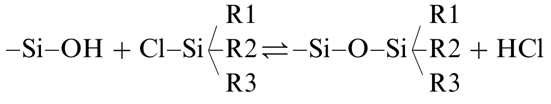
poured on to the fibre surface to remove any weakly adsorbed solute. The fibres were then placed in a preheated (70 °C) vacuum oven for 3 h under the gentle flow of nitrogen gas to remove residual HCl and ethanol. The conventionally accepted reaction of TMCS with the silica surface at room temperature is



$$-\mathrm{Si{-}OH} + \mathrm{Cl{-}Si}\begin{matrix}\mathrm{R1}\\ \mathrm{R2}\\ \mathrm{R3}\end{matrix} \rightleftharpoons -\mathrm{Si{-}O{-}Si}\begin{matrix}\mathrm{R1}\\ \mathrm{R2}\\ \mathrm{R3}\end{matrix} + \mathrm{HCl} \qquad (1)$$

2.3. Contact angle, friction and adhesion measurements

Contact angles of adsorbed films were determined for water, methylene iodide and α-bromonaphthalene on the films using the Wilhelmy balance method. Critical surface tensions, γ_C, were determined using the method of Zisman [5]: the value of γ_C was determined by extrapolating a linear regression analysis of the data to $\cos\theta = 1$.

The adhesional pull-off force and frictional force were measured for orthogonally configured surface-treated fibres using a Cahn balance and the experimental details are shown elsewhere [6].

3. Results and discussion

3.1. Wettability, friction and shear properties of octadecylamine

With hydrophilic silica fibre surfaces, amine molecules are oriented with their hydrophilic ends attached to the surfaces. It is anticipated that strong bonding will occur between the adsorbed molecular film and the surface of the fibre. For comparison with previous studies [5, 7] of the wettability of ODA films, the critical surface tension was determined for the films formed on the silica fibres that had been dried at room temperature (22 °C). Table I summarizes the critical surface tension and contact angle data for the ODA retracted from both hexadecane and cyclohexane. Hysteresis in the wetting force was manifested by different forces on immersion and emersion of a sample.

If amine molecules are densely packed and oriented with the hydrocarbon chains pointing away from the silica surface and exposing only a close-packed film of $-CH_3$ groups, a value of 22–24 $\mathrm{mJ\,m^{-2}}$ is expected [8]. Levine and Zisman [4] also reported 70° as the contact angles of methylene iodide on amine films retracted from the hexadecane and cyclohexane. The discrepancies in the values of the current work from the earlier works indicates that there is a possibility of the formation of mixed films of solvent and solutes, which, in the case of hexadecane, may not affect the contact angle compared to that for a solvent-free ODA monolayer. If the concentration of the polar solute is high enough, the film eventually becomes free of solvent as adsorption equilibrium is reached, and the retracted film is then free of solvent molecules. When the solute and solvent molecules are similar in shape or size, however, the intermolecular cohesion between them through London dispersion forces become a major factor for incorporation of the solvent in the adsorbed film. This would be especially true for the amine film retracted from hexadecane.

Fig. 1 compares frictional forces measured in air for the amine monolayer retracted from hexadecane and cyclohexane. The frictional force of the amine retracted from the hexadecane was an order of magnitude lower than that from the cyclohexane. The observed difference can be explained as follows: because the thin hydrocarbon chains of the hexadecane ($s^2 = 0.185\ \mathrm{nm}^2$, where s^2 is an area of a chain perpendicular to the surface) may fit in between the amine chains, one might expect lower friction from the amine retracted from the hexadecane, while the relatively larger molecular size ($s^2 = 0.36\ \mathrm{nm}^2$) of cyclohexane may not. Thus, presumably, the film adsorbed from cyclohexane may have a more open structure than the one retracted from the hexadecane. Furthermore, the loss of solvent is more effective in cyclohexane due to its higher vapour pressure.

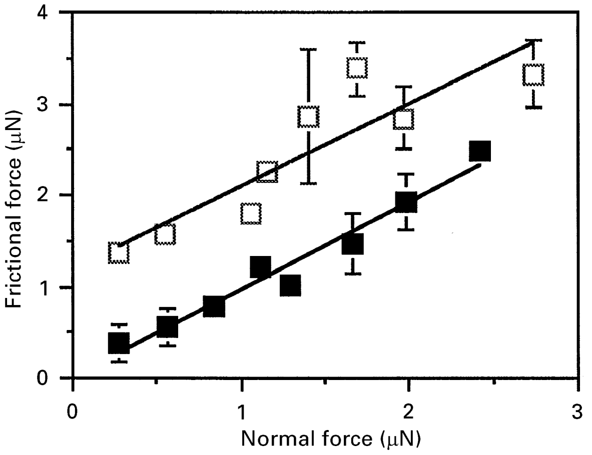


Figure 1 Comparison of frictional behaviour of octadecylamine retracted from (■) hexadecane and (□) cyclohexane.

TABLE I Contact angles and critical surface tensions, γ_C, of adsorbed octadecylamine (ODA) retracted from hexadecane and cyclohexane: adv = advancing, rec = receding

		θ (deg)					
		H_2O		CH_2I_2		α-bromonaphthalane	
	γ_C ($\mathrm{mJ\,m^{-2}}$)	Adv.	Rec.	Adv.	Rec.	Adv.	Rec.
Hexadecane	20.66	83.68	50.58	63.40	43.48	56.98	46.63
Cyclohexane	26.65	79.98	59.82	63.19	41.62	45.74	25.33

Adhesion is the result of attractive forces between two surfaces in close contact. When such surfaces are pulled apart, the strength of the adhesive junction can be determined by a balance between the surface attractive forces and bulk elastic forces opposing deformation. Two theories have been proposed to describe such a contact. The first is due to Derjaguin *et al.* [8] which was developed for hard materials. They suggested that, under the action of attractive forces, the solid is deformed according to the Hertzian equation for the elastic deformation of solid surfaces. The attractive force produces a finite area of contact and is balanced by the corresponding elastic forces in the contact zone. This is referred as the Derjaguin–Muller–Toporov (DMT) model. If an external load, N, is applied, the area of contact is increased. However, as all the deformations in this model are reversible, the area returns to its equilibrium value when N is removed. If a negative load or force is applied, the area of contact diminishes and the pull-off force, F_C, is given by

$$F_C = 4\pi R\gamma \qquad (2)$$

where R is the radius of curvature of the surfaces and γ is their surface energy. An alternative approach was proposed by Johnson *et al.* [10]. While the DMT analysis ignores modification of the Hertzian deformation by the surface forces, it postulates that for highly elastic solids, such modifications play a most important part in deformation and adhesional behaviour. It is found that, under the action of surface forces, the surfaces are drawn together and a finite area of contact is established for zero applied load. However, the shape is quite different from that associated with Hertzian deformation in having a small neck around the contact zone. According to the Johnson–Kendall–Roberts (JKR) model, the pull-off force, F_C is

$$F_C = 3\pi R\gamma \qquad (3)$$

The pull-off force is thus comparable with, but smaller than, that predicted by the DMT model. Table II summarizes the surface energies of silica fibre coated with amine, deduced from the two theories using the measured pull-off forces in this study. Zisman [11] reported γ_C in the range 22–24 mJ m^{-2} for the coated ODA film, assuming the surface exposes only close-packed $-CH_3$ groups. Table II shows that surface energies predicted by DMT theory seem to agree better with Zisman's theory. A slightly higher value in surface energy in this study, however, indicated that there are still significant amounts of hexadecane and cyclohexane which exposed some methylene groups at the surface.

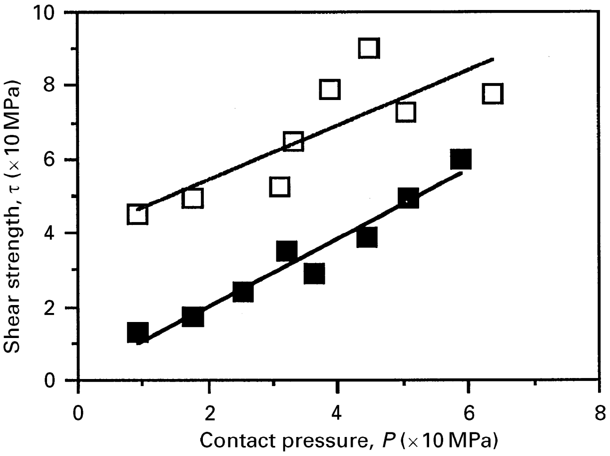


Figure 2 Pressure dependence of the shear strength of amines retracted from (■) hexadecane and (□) cyclohexane.

Assuming that the fibre properties are not significantly altered during film deposition, interfacial shear strength between two fibres in the presence of an adsorbed organic layer, can be deduced using the relationship

$$F = A\tau \qquad (4)$$

where F is frictional force, A is real area of contact, and τ is the shear strength. The real area of contact can be calculated from the Hertz equation by taking a normal load as a sum of an applied force and adhesional force [12]. Fig. 2 shows the calculated shear strength versus pressure for the ODA retracted from hexadecane and cyclohexane. It is found that τ is nearly linearly dependent on P and expressed in the approximate form

$$\tau = \tau_0 + \alpha P$$

where τ_0 is the shear strength under zero applied load and α is a constant. This relationship has been widely used in the past for a variety of systems. Despite the similarity in the adhesional pull-off forces, the shear strength of ODA retracted from cyclohexane appears to be much greater than that from hexadecane. One might speculate that ODA retracted from cyclohexane has a more open structure than ODA from hexadecane due to the different molecular size of the solvents.

3.2. Wettability, friction and shear properties of alkyl silanes

Although fatty acids and amines have been known for some time to self-assemble into monolayer films, film forming of organic silanes to various metal or silica surfaces has been recently developed. Considerable information is available regarding the wettability of

TABLE II Calculated surface energies of octadecylamine retracted from hexadecane and cyclohexane using DMT and JKR theories

			Calculated surface energy (mJ m^{-3})	
	Exposed surface group	Pull-off force (μN)	Eq. 1 $\gamma = F/4\pi R$	Eq. 2 $\gamma = F/3\pi R$
Hexadecane	$-CH_3$	3.4	26.3	35.1
Cyclohexane	$-CH_3$	3.2	25.5	34

TABLE III Contact angles and critical surface tensions, γ_C, of adsorbed TMCS and DMODCS

	γ_C(mJ m^{-2})	θ (deg)					
		H_2O		CH_2I_2		α-bromonaphthalane	
		Adv.	Rec.	Adv.	Rec.	Adv.	Rec.
TMCS	35.43	106	72	68	32	51	33
DMODCS	32.29	99	77	61	43	40	29

these surfaces [8, 13]. Organosilane reagents can be either monofunctional or multifunctional. Hair [8] studied the kinetics of the reactions of $Cl_nSi(CH_3)_{4-n}$ with silica ($n = 1$–4) and observed two different reactions with $Cl_2Si(CH_3)_2$ and only one type of reaction with $ClSi(CH_3)_3$. A similar observation was made by Hertl [14, 15] when alkoxy silanes were reacted with silica. Furthermore, multifunctional silanes tend to esterify in the presence of trace amounts of water. Thus, reaction of silica with multifunctional organosilanes results in highly heterogeneous surfaces. Better reproducibility and homogeneity is to be expected from reactions with monofunctional reagents which are therefore more suitable for the present work.

Table III summarizes the contact angle of thin layers of the TMCS ($n = 1$) and DMODCS ($n = 18$) adsorbed on silica fibres. Wolfman and Faust [16] reported 110° ± 2° and 88° ± 10° for the respective advancing and receding contact angles of a paraffinic surface containing only exposed methyl groups. Park and Andrade [1] measured the contact angles of water on *n*-alkyl derivatized borosilicate glass plates and found a strong dependence on the chain length and solution concentration. They reported the advancing angles (113° and 97°) and the receding angles (52° and 71°) for TMCS and DMODCS, respectively. The contact angles measured here are similar to those reported by Park and Andrade. Slightly higher angles of TMCS than DMODCS probably reflect a difference in the packing of the terminal groups exposed to the wetting liquids.

Fig. 3 shows the results of friction force measurements of TMCS and DMODCS. It appears that TMCS is much more effective in reducing frictional forces than DMODCS. This efficiency in reducing the frictional forces in TMCS is probably due to the bulky three methyl groups which are in a densely packed state.

Using the same assumptions made for amine, Fig. 4 shows the interfacial shear strength of TMCS and DMODCS as a function of pressure. Unlike octadecylamine, the pull-off forces for silanes were markedly large: 6.86 and 11.76 μN for TMCS and DMODCS, respectively. These large pull-off forces predicted the area of contact of the silica fibre coated with silane to be roughly twice that for the ODA. The values of τ_0 of TMCS and DMODCS are 20.18 and 9.85 MPa, respectively. While the τ_0 of DMODCS is a reasonably expected value when compared with ODA, a high τ_0 value of TMCS is assigned to contact between the fibres through the thin monolayer of TMCS.

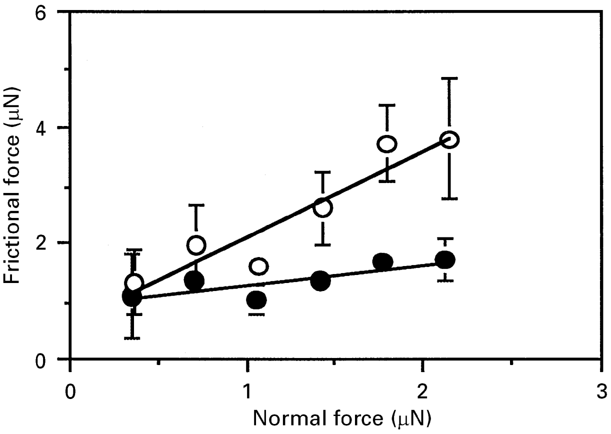


Figure 3 Comparison of the frictional behaviour of (●) TMCS and (○) DMODCS.

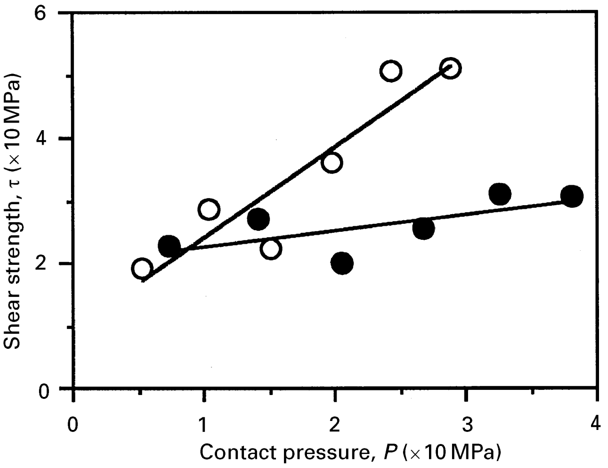


Figure 4 Pressure dependence of the shear strength of (●) TMCS and (○) DMODCS.

4. Conclusion

Friction studies have demonstrated that the presence of the ODA film retracted from hexadecane was more effective in reducing frictional forces than one retracted from the cyclohexane. TMCS appeared to be more effective in this reduction than DMODCS. Presumably, bulky methyl groups in TMCS can coat the fibre surface more effectively. The short chain length of TMCS, however, can be easily ruptured during sliding, and the underlying fibre surface can be exposed, resulting in high shear resistance. These observations are attributed to differences in vapour pressure, and size of molecules, which determines the closeness of packing of the adsorbed molecules. A detailed explanation in terms of intermolecular forces, chain entanglements, and side group interactions, must await further study. It was also observed that the increase in shear strength was approximately proportional to pressure for both octadecylamine and silanes when the adhesion model of friction was applied to film-forming molecules studied.

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