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Thickness of Aqueous Boundary Films in Static Rubber/Glass and Rubber/ Rubber Contacts

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The thickness of equilibrium water films sandwiched in rubber contacts has been measured by optical interferometry. In particular, the effect of pH has been observed. It is found that stable. equilibrium films can form when an aqueous solution is squeezed between rubber/glass and rubber/rubber contacts. The separating film thickness depends on pH. The thickest, most stable films were associated with natural rubber and the thinnest, least stable, with its synthetic equivalent. The presence of naturally occurring substances other than rubber hydrocarbon may be responsible for the thicker films found with natural rubber.

Optical interferometry has been used previously in the study of squeeze-films between rubber and glass[1]. Various aqueous liquids, including surfactant solutions, salt solutions, and biological fluids have been examined[1-14]. In these studies, the presence of stable equilibrium films was attributed to two mechanisms. For surfactant solutions, the mechanism was thought to be electric repulsion arising from adsorbed surfactant molecules on the contacting surfaces. The mechanism of film support for biological fluids was considered to be a combination of electric repulsion and stearic hindrance.

Glass, containing a large proportion of silicon dioxide, forms silanol groups at its surface in an aqueous environment[15]. If it is assumed that the dissociation of the silanol group is

Silanol group: $-O_3$-Si-OH<--->$SiO^- + H^+$

similar to that of silicic acid[16], then the glass surface will behave as a weak acid and acquire a negative charge on its surface. This charge continues to be associated with the positively charged counterion in the surrounding aqueous liquid.

The attachment of SDS (sodium dodecyl sulphate) molecules to surfaces of both rubber and glass has been shown to occur[7]. It was suggested that the negatively charged glass surface would prevent adsorption by anionic materials such as SDS. This led to the suggestion that adsorption of the SDS would occur *via* the carbon chain. The adsorption of SDS to the largely hydrophobic rubber surface was also thought to occur *via* the carbon chain, with attachments at one or more sites.

Work carried out to find the surface charge density on various materials provides data which would suggest a different picture for the

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adsorption of SDS to glass than that given above. It was found[17] that a clay (with a surface of similar character to that of glass) had a surface charge of 0.12 Cm^{-2}. This means that each charged site, on average, occupies an area of about 1.30 nm^2, which is an area likely to contain some tens of molecules. It is therefore apparent that charged species on the surface are widely spaced on an atomic scale. A model for the structure of the adsorbed species, leading to the production of an electric double layer, is given in *Figure 1*.

For a specified type of glass (powdered, type 519/604), the surface charge, measured as a 'zeta potential', has been found as a function of the concentration of SDS solution[7]. It was 50-100 mV, depending on concentration. The zeta potential of both polyisoprene rubber, and glass, was found[7] as a function of the pH of an electrolyte solution in contact with the surfaces. More recently, the zeta potential of three different types of rubber (HA latex, *Natsyn* and DPNR) were found as a function of the pH of the liquid. It was seen that the results for each rubber were basically the same[18]. Data are plotted for polyisoprene rubber and for glass in *Figure 2*. The zeta potential at pH 10 is around –80 mV for the *Natsyn*, whereas a value of around –20 mV was given for the *Cariflex*. It is not clear why the earlier results[7] are of much lower potential. What is clear from all the results is that the pH of the electrolyte greatly influences the magnitude of the zeta potential. This will be shown later to be of consequence with respect to film thickness results.

An appreciation of the zeta potential at the surface of particles in colloidal systems has led to theories describing the balance of forces which prevent flocculation[19,20]. A development of these theories, for charged planes in close proximity, has led to relationships between the separation of electrically charged surfaces, as a function of the pressure exerted on the surfaces[6,7]. This pressure is counterbalanced by the repulsive electrical forces to give an equilibrium film. The form of this repulsive force, as a function of film thickness for various surface charges can be calculated.

The previous work on equilibrium films between rubber and glass gave data which agreed reasonably with theory. The aim of the present investigation of equilibrium films in rubber/glass and rubber/rubber contacts is a better understanding of the mechanisms involved. Measurements using rubber/rubber contacts potentially assist interpretation due to symmetry.

The use of solutions at various pH without surfactant was a follow-up to observations made on wet sliding friction[21]. The very low friction found for some of the solutions of higher pH was similar to values with SDS solutions[22]. This suggested the possibility of equilibrium films with liquids of high pH in these contacts. Measurements on such films would perhaps reveal further aspects of film support.

EXPERIMENTAL

The rubber compounds used for the measurements of film thickness were natural rubber (NR) and *Cariflex 305* (IR), as given in *Table 1*. All contact surfaces were optically smooth. Rubber surfaces of this quality were made by hot compression moulding against polished glass or metal formers[23]. In this work, a hemispherical rubber surface was achieved by clamping a glass-moulded 2 mm thick rubber sheet over a supporting rubber hemisphere of radius 18.5 mm. Peroxide cured rubber was sufficiently transparent for the measurements, although light scatter was a limitation.

Procedure for Taking a Measurement of Film Thickness

The following procedure was adopted, after some trials, because it gave the most

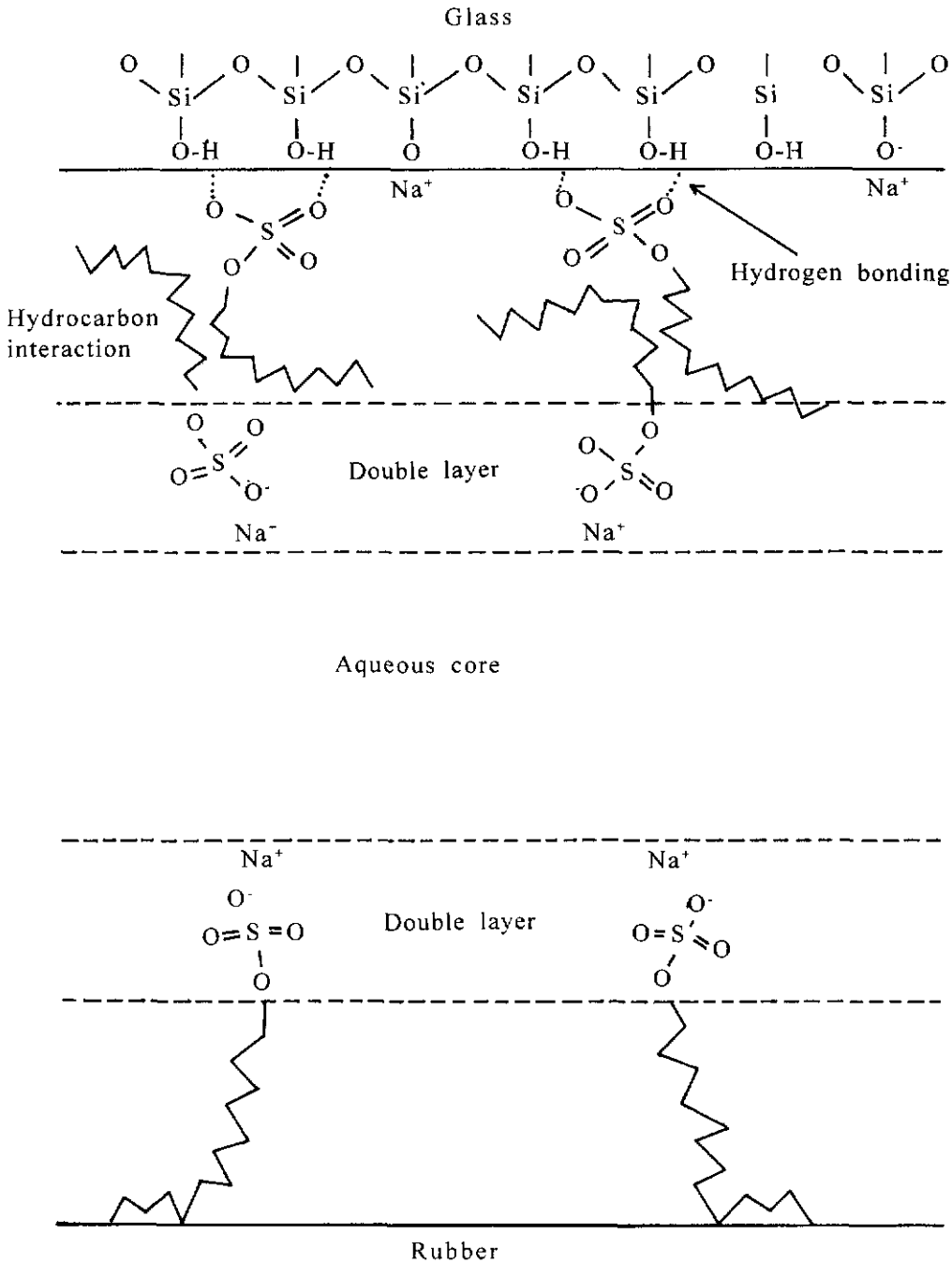


Figure 1. Model for adsorption of SDS molecules to rubber and glass surfaces.

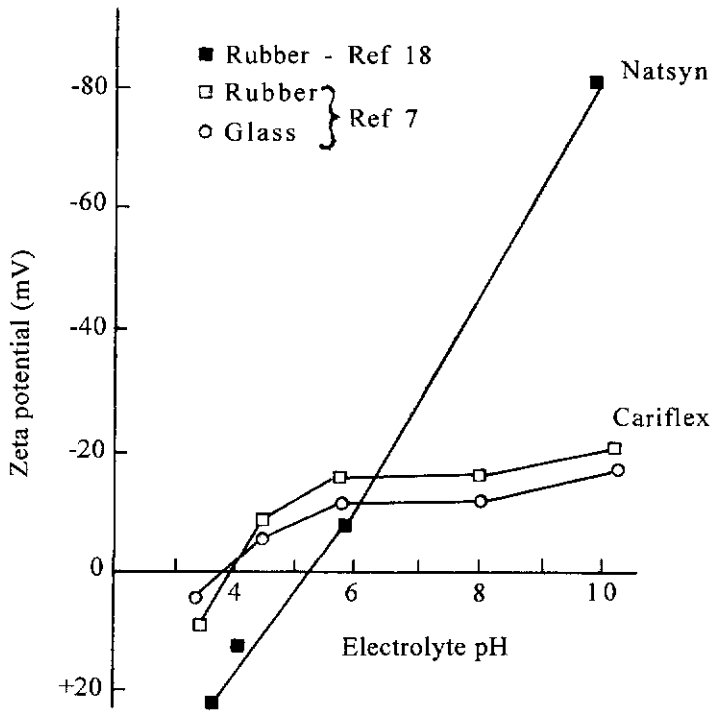


Figure 2. Zeta potential variation with electrolyte pH for polyisoprene rubber and glass.

TABLE 1. FORMULATIONS OF RUBBER COMPOUNDS (PARTS BY WEIGHT)

Compound	Formulation NR	NR
Standard Malaysian Rubber. Grade L	100	
IR : *Cariflex 305*		100
Dicumyl peroxide (*Dicup R*)	2	2
Cure time/temp (min/°C)	50/160	60/160
Vulcanisate hardness (IRHD)	41±2	39±2

reproducible results. Firstly, the surfaces were cleaned. A glass surface was cleaned by swabbing with cotton wool soaked with acetone, followed by swabbing with cotton wool soaked with distilled water. The glass was then dried with clean, dry, cotton wool. Rubber was cleaned by swabbing with cotton wool soaked with distilled water, then with cotton wool soaked with acetone. The rubber was then left to dry for at least 2–3 min before commencing measurements. The procedure was thought suitable for removing both organic and inorganic contaminants. Care was taken that pieces of cotton wool did not remain behind on surfaces, and that the surfaces remained dust-free after cleaning. The lower rubber surface was cleaned with the test piece clamped in place ready for testing.

To find the thickness of liquid films in rubber/glass and rubber/rubber contacts an optical interferometric method was used as previously[3]. In addition to using a two-part beamsplitter to direct illumination into the contact *(Figure 3a)*, an alternative 30° prism was also tried *(Figure 3b)*. The optical contrast of the two-part beamsplitter was insufficient for film thickness values less than 10 nm, due to the presence of scattered light in the rubber bulk. By using a simple 30° glass prism in place of the beamsplitter the illuminating beam is at non-normal incidence to the contact area, so the amount of scattered light received by the detector is reduced. By tilting the base of the prism an externally illuminating horizontal light beam can be made to give a vertical output signal beam that enters the microscope objective.

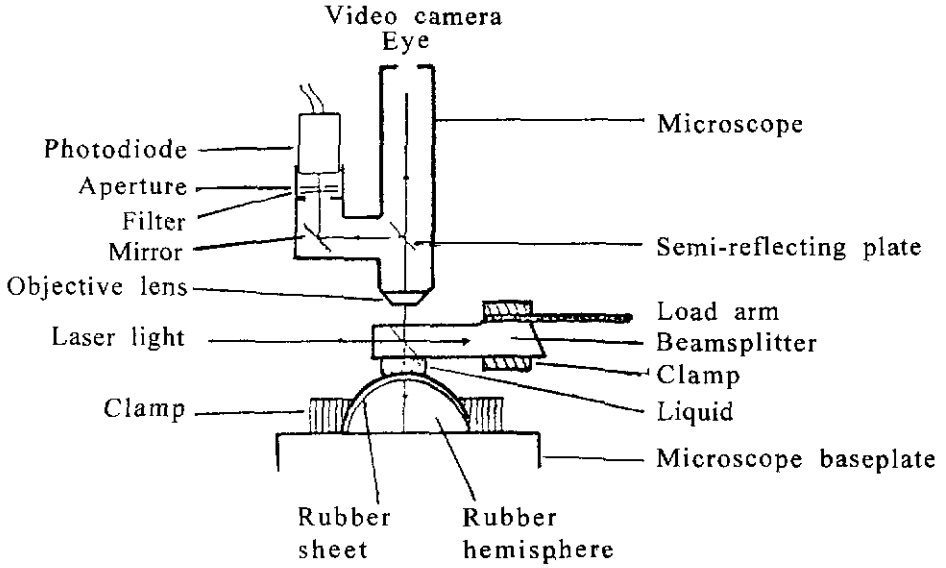
The load-arm was levelled, using fine balance weights, to give maximum laser light intensity at the detector. The intensity received at the detector will be referred to as I_{AIR}. The rubber surface was then raised, using the microscope stageplate vertical adjustment, until contact occurred between the two surfaces. The light intensity then received at the detector will be referred to as I_{DRY}.

By following these steps for cleaning and alignment, the system was at its optimum. Measurements of film thickness were obtained by inserting the test liquid into the contact area with a dropping pipette, applying the required load, breaking the contact by gently lifting the load-arm manually, then releasing it carefully. The maximum signal intensity in the subsèquent film-thinning (squeezing) is an internal standardising intensity, I_{max}, to be used along with the intensity at any other time in determining the film thickness.

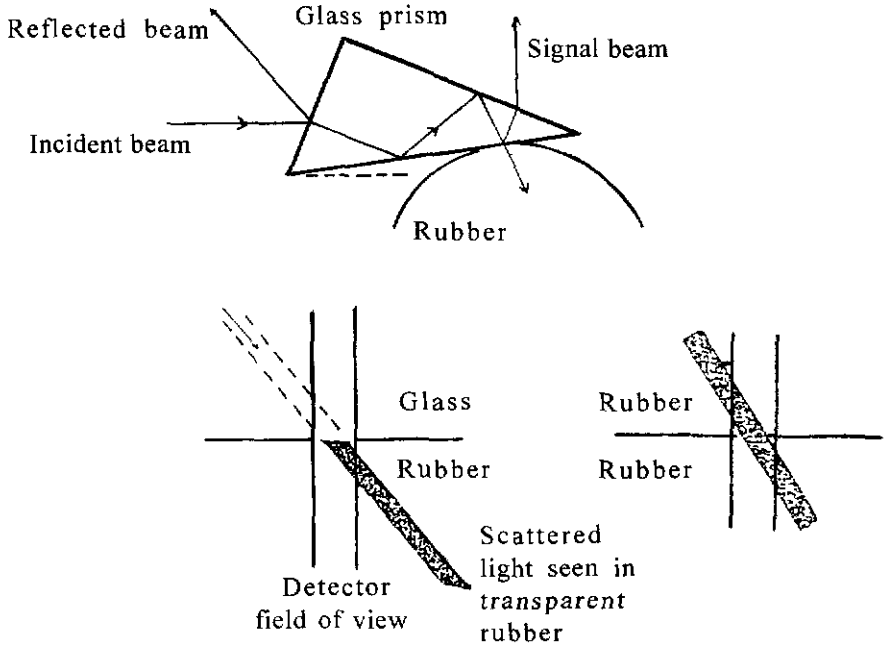
Factors Affecting the Minimum Light Intensity Detected During Measurements of Film Thickness

When working with the beamsplitter *(Figure 3a)* effort was made to understand sources of 'noise' in the optical system. Noise meant that zero reflected light intensity, as would be expected in the contact of rubber and glass of equal refractive index, was never attained. It was thought that the semi-reflecting coating in the beamsplitter was a cause of scattered light entering the detector. However, it became clear from tests using the newly-developed 30° prism arrangement *(Figure 3b)* that a seemingly unavoidable signal results from scatter of light in the bulk of the rubber.

Non-normal incident light highlights the passage of the laser beam through the rubber. The scatter intensity from a rubber/glass contact would be expected to be half that for rubber/rubber contact, since the volume of material causing scatter is halved. The diameter of the circle from which light is detected is about 0.3 mm *(Figure 3)*. Therefore the depth of rubber from which scattered light is detected, with an angle of incidence of 15°, is around



(a) Interferometric film thickness apparatus



(b) Top: schematic diagram of the path of a light beam through the 30° prism. Bottom: the scatter of laser light in rubber.

Figure 3 A two-part beamsplitter to direct illumination

0.8 mm. However, the scatter intensity found in a rubber/glass contact was always more than half of that for rubber/rubber, leading to a range of detector output voltages of 1.0–2.0 mV, rather than 0.4–0.85 mV. No amount of cleaning would serve to reduce this value, so it seemed to be a permanent feature of the glass surface. It is known that the surface of glass will have water molecules adsorbed on it and it has been found that under certain conditions a film of up to 530 Å can be present[24]. Under normal atmospheric conditions it is unlikely that there would be films of more than a few molecules thick[25]. A typical detector output value of I_{DRY} in rubber/glass contact is 1.3 mV which, with the 0.4 mV scatter correction, gives a residual intensity of 0.9 mV. A typical value for I_{MAX} is 5600 mV. Using these values gives a theoretical film thickness of around 8.5 Å (see *Appendix I*). A monolayer of water is about 3 Å thick; the experimental data therefore suggest that the layer adsorbed to the glass is 3 molecules thick. For a glass surface exposed to laboratory air, at a relative humidity of 45%–60%, this is a reasonable thickness of adsorbed water[25]. Given the necessarily rather inexact method of assigning a value to the scatter intensity, film thickness resolution is limited to approximately 5 Å.

Determination of the Contact Pressure

The average pressure over the contact area, P', is

$$P' = \frac{W}{\pi a^2} \quad ...1$$

where W is the normal load and a is the radius of the contact area. The centre of contact was the point at which most measurements of film thickness were made. At this point the pressure, P, is given by[26]:

$$P = 1.5P' \quad ...2$$

In some circumstances the contact radius may not be measurable. However, it can be calculated from the expression[26]:

$$a^3 = \frac{3WR_1R_2}{4(R_1 + R_2)} \left(\frac{1 - \sigma^2_1}{E_1} + \frac{1 - \sigma^2_2}{E_2} \right) \quad ...3$$

where R is the surface radius, E is the Young's modulus, and σ is the Poisson's ratio. The suffixes 1 and 2 refer to the two contacting surfaces.

Film Thickness Measurements Using Aqueous Buffer Solutions in Rubber/Glass and Rubber/Rubber Contacts

Measurements of film thickness were made in rubber/glass and rubber/rubber contact. The buffer solutions used had pH values of 4.85 to 12.25 *(Table 2)*. Unless otherwise specified, 15 min conditioning was allowed, with the solution between the contact surfaces, but the surfaces not touching each other, before a measurement was made.

Experimentally determined values of light intensity were converted to values of film thickness using the calibration curves for aqueous liquids (see *Appendix I*).

During the course of these experiments, it became clear that the glass prism was affected by prolonged contact with the buffer solutions. This showed as a large value of the received light intensity for dry contact between the surfaces. It was generally found that use of a solution at high pH caused this intensity to rise, whereas a solution of low pH caused it to fall. Film thickness values were calculated by assuming that the increased intensity at dry contact was due to an increase in the 'adsorbed water layer' on the glass. A series of film thickness values was calculated using this method, then further measurements were taken

TABLE 2 LIQUIDS TESTED AS LUBRICANTS

Concentration (M)	Buffer	pH
0.2	Sodium acetate + acetic acid	4.85
0 05	Potassium dihydrogen phosphate + NaOH	6.0
0.05	Potassium dihydrogen phosphate + NaOH	7 0
0 05	tris(hydroxymethyl) aminomethane + HCl	8.0
0.05	Borate + NaOH (0.1*M* in KCl)	9.0
0.05	Glycine + NaOH	10.3
0.051	Glycine + NaOH (0.051*M* in NaCl)	11.0
0.046	Glycine + NaOH (0 046*M* in NaCl)	12.25

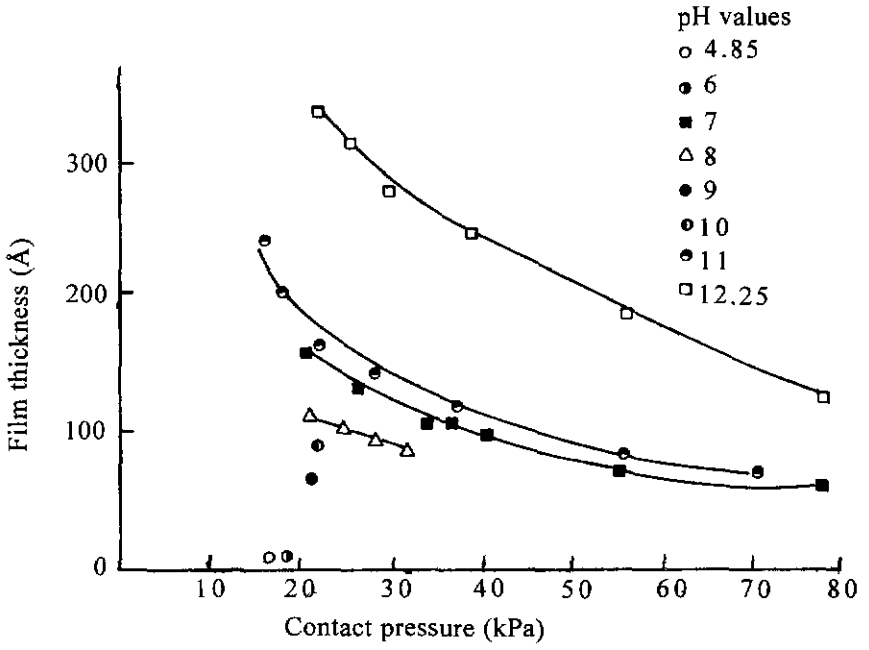


Figure 4 Film thickness in IR/glass contact lubricated with buffer solutions.

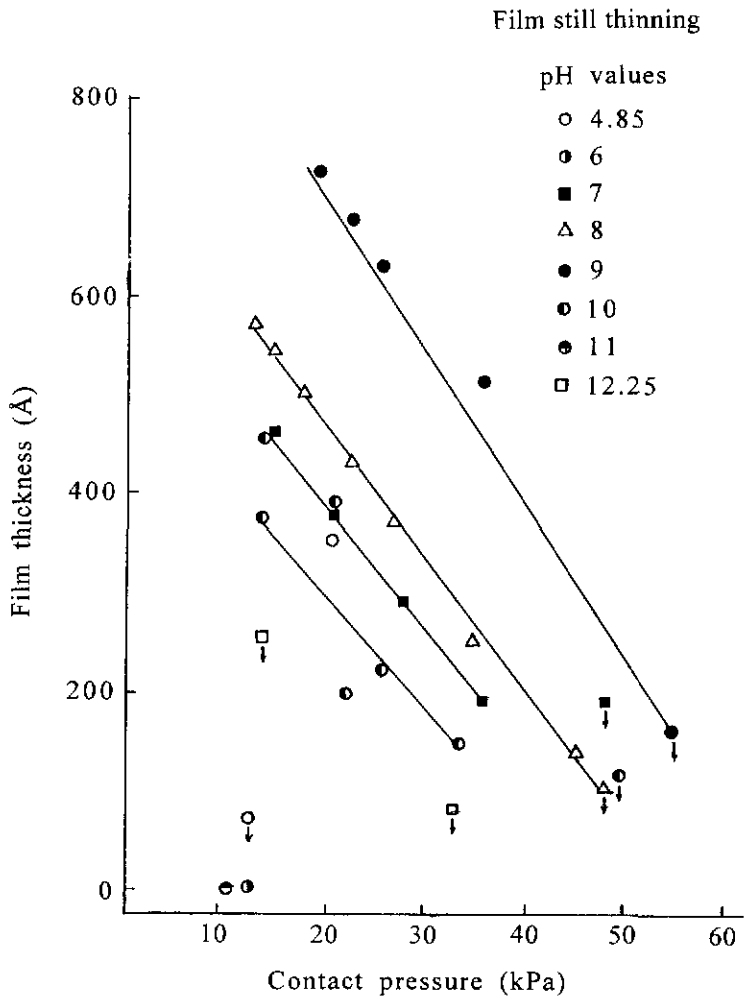


Figure 5 Film thickness in NR/glass contact lubricated with buffer solutions.

using a new 30° glass prism with the same buffer solution. Both sets of film thickness values were almost the same, so the intensity adjustment procedure was adopted for all subsequent work.

RESULTS

Film Thickness in Rubber/Glass Contact

In both IR/glass and NR/glass contact some of the solutions of different pH gave equilibrium films, whereas others gave a contact which could not be distinguished from dry contact. When a stable film was given at a low contact pressure (around 20 kPa), further loads were added in an attempt to find any pressure dependence of the film thickness. The results for IR/glass and NR/glass are shown in *Figures 4* and *5*, respectively. On these figures, a down-pointing arrow under a data point indicates that when observations were terminated, the liquid film was still thinning very slowly.

Film Thickness in Rubber/Rubber Contact

The results for both NR/NR contact and IR/IR contact are shown in *Figure 6*. In NR/NR contact, equilibrium films were only given with solutions at pH 8.0 and pH 9.0. The pressure which these films will support is limited, up to about 20 kPa at pH 8.0 and 40 kPa at pH 9.0.

In IR/IR contact, the only buffer solution which gave equilibrium films was at pH 12.25. The thickness of these films is shown as a shaded region in *Figure 6*. Repeat tests gave values anywhere in this region and no two sets of data were the same.

Film Thickness After Soaking NR Samples in Buffer Solutions at pH 6 and pH 11

In a study[21] of wet rubber friction, it was found that the friction of two NR surfaces in contact depended upon the pH of the lubricant liquid. However, soaking NR in a buffer solution at pH 11 for two weeks removed this effect.

Film thickness measurements were made using NR samples which had been soaked in buffer solutions at pH 6 and pH 11 for two weeks, and dried in a vacuum desiccator for a week over concentrated sulphuric acid.

Film thickness values were taken for rubber/glass contact at a contact pressure of 20 kPa using a solution at pH 9. For the sample which had been soaked at pH 6 the film thickness was 560 Å which may be compared to the value of 700 Å given in *Figure 5*. However, the sample soaked at pH 11 gave a film thickness of only 40 Å. It is interesting to note the value of 40 Å is about that expected for IR/glass contact at 20 kPa lubricated with a solution at pH 9 (see *Figure 4*).

DISCUSSION

The film thickness data for IR/glass contact lubricated with buffer solutions *(Figure 4)* may be explained as follows.

From *Figure 2*, it is seen that above about pH 5 the surface charge on rubber and glass will increase with increasing pH. Thus it is expected that an increase in solution pH above pH 5 will lead to an increase in the equilibrium film thickness. In essence this is the trend in *Figure 4* as shown more clearly at constant pressure by the plot given in *Figure 7*. Possible conditioning effects of the solutions on the glass may lead to film thickness values, at pH 7.0 and pH 8.0, which do not fit the trend (dotted line) of increasing film thickness with pH.

The film thickness values for NR/glass contact lubricated with buffer solutions were the highest seen in this investigation. They are

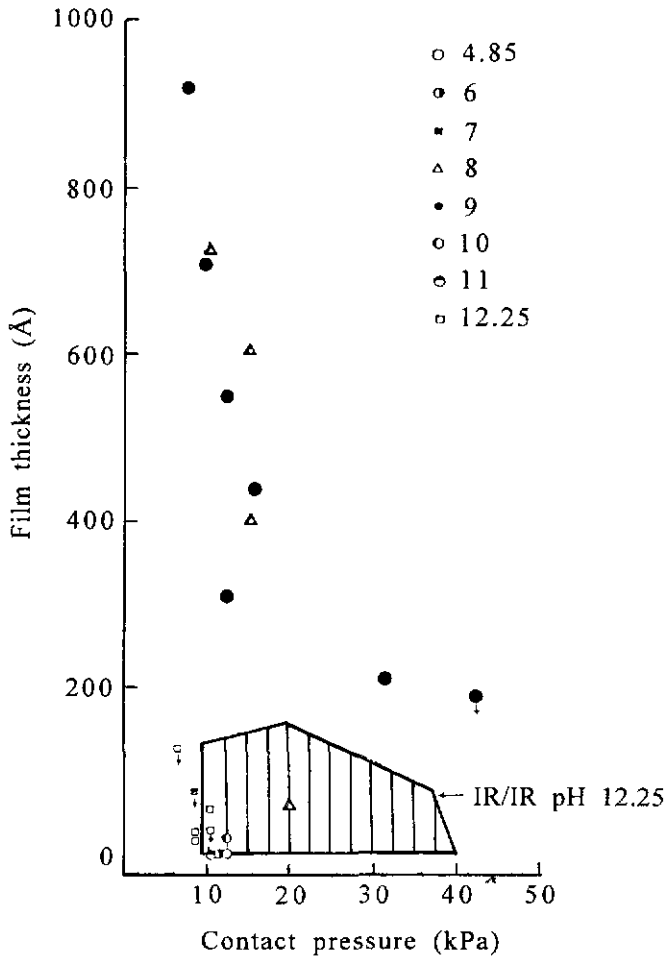


Figure 6. Film thickness in rubber/rubber contact lubricated with buffer solutions.

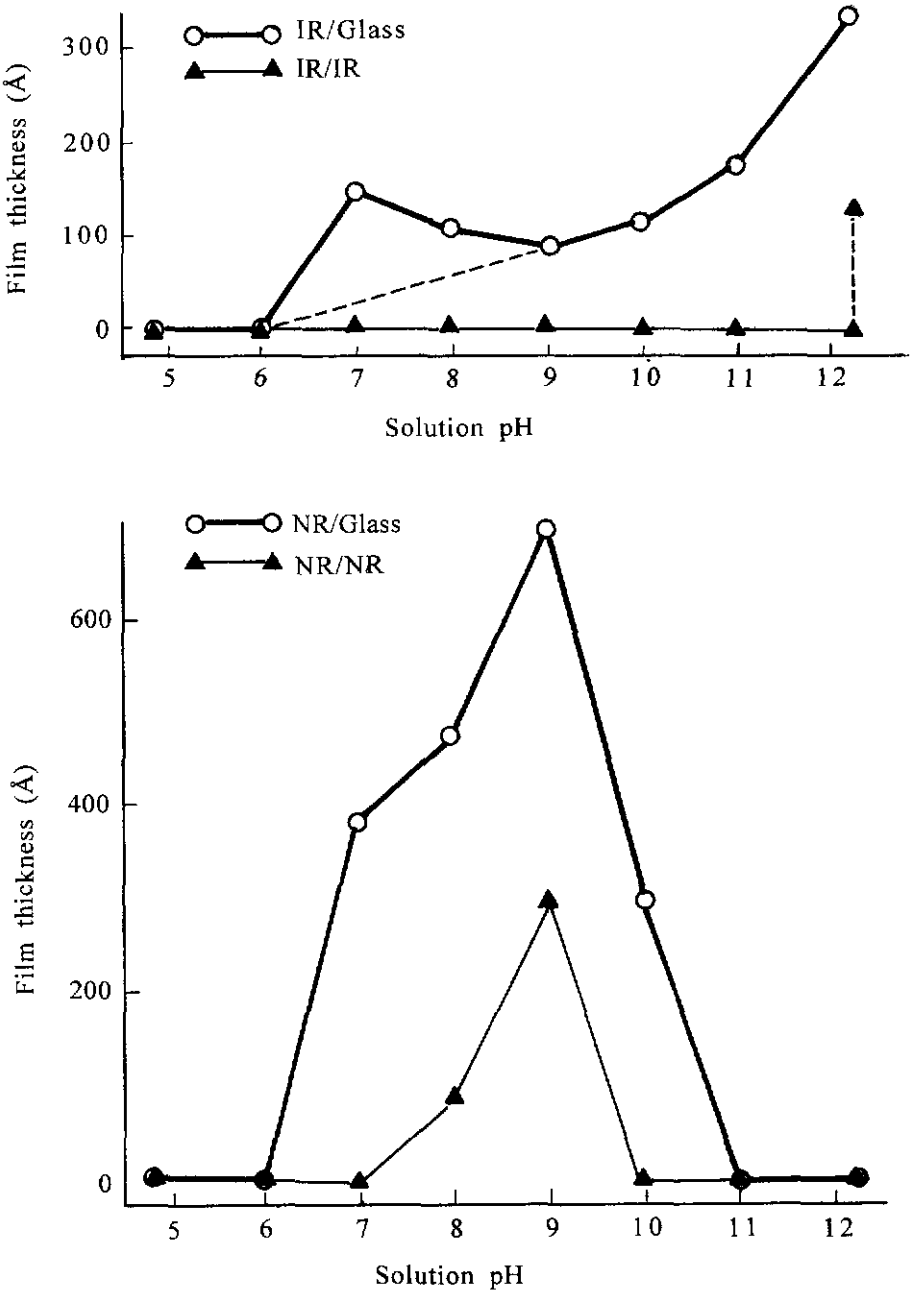


Figure 7. Film thickness as a function of solution pH at a contact pressure of 20 kPa.

replotted at constant pressure in *Figure 7*. It is recalled[21] that when NR is in contact with buffer solutions at pH 9.0 and above, fatty acids are leached from the rubber into the surrounding liquid. The rate at which this occurs increases as the pH rises. The fatty acids will be increasingly ionised as the solution pH is increased. At pH 4.85 and 6.0 there is not much surface charging (see *Figure 2*) and the fatty acids in the NR surface are only partially ionised. At a solution pH of 7 to 9, surface charging becomes significant, and this is augmented by the ionised fatty acid molecules near to the surface. These molecules are drawn out of the surface by a solution at pH 9.0, so it is reasonable to assume that at pH 8.0 more molecules are very close to the surface than at pH 7.0, and that at pH 7.0 more molecules are closer to the surface than at pH 6.0. This leads to an increase in the observed film thickness from pH 7.0 through to pH 9.0.

At pH 10.0 the number of ionised fatty acid molecules in solution is presumably sufficient to reduce the effective surface potential by charge screening, leading to a thinner equilibrium film than at pH 9.0. For solutions at pH 11.0 and pH 12.25, the concentration of ionised fatty acid molecules in solution is possibly so great that all surface charge is screened, and so no equilibrium films are formed. This effect has been reported in other work, when a reduction in film thickness was seen on the addition of sodium chloride in solutions of SDS[6,7].

This interpretation may explain the likely effect of fatty acid concentration on the electric double layer repulsion force, but the magnitude of equilibrium films in NR contacts calls for comment. Why are the equilibrium films so thick in NR/glass contacts? A possible explanation is as follows.

When fatty acids are in solution, as soaps, they form different phases. The phase in any system is determined by the concentration of the fatty acid[27]. The amount of fatty acid in solution increases with pH, so at different solution pH there will be different phases present. In a very broad sense these phases can be thought of as containing globular or lamellar structures. The globular phases extend isotropically whereas the lamellar phases are layered. A globular phase would be the more likely one with which to create an equilibrium film whereas the lamellar phase would be squeezed out of the contact. After soaking NR in the range of buffer solutions during friction measurements[21] the solutions remaining after the first week of soaking seemed to indicate the presence of globular phases at pH 9 and pH 10, since the liquid was uniformly misty in appearance. The solutions remaining at pH 11 and pH 12.25 became doubly-refracting when stirred, which is an indication that the particles were lamellar[27].

Most of the observed trends in film thickness have been explained in terms of surface charging and the presence of fatty acids in the rubber. A major feature throughout all the results presented is the difference of film thickness between rubber/glass contact and rubber/rubber contact. Apart from a few results, all at very low contact pressure, the film thickness in rubber/glass contact is greater than that in rubber/rubber contact, for the same lubricant and contact pressure. The data shown in *Figure 7* for IR/glass contact, seem to confirm the importance of surface charging in the formation of an equilibrium liquid film thickness between two surfaces. However, the data for IR/IR suggest that the charge on a rubber surface is not the same as that on a glass surface. It would appear that charging of a rubber surface is either not as great, or not as persistent, as that of a glass surface.

Relevance to Future Applications

The experiments undertaken in this work were concerned with the film thickness values obtained using idealised systems, in which the surfaces were optically smooth and the liquids were simple. Even so, the results suggest a possible use for natural rubber as a material in an area which hitherto has been the domain of synthetics. Seals are used most commonly in oily environments. Due to the high degree of swelling which NR undergoes in oil, synthetics, such as nitrile rubber, are used in preference as seal material. Recently, for hydraulic systems which operate under conditions of high fire and explosion risk, there has been a trend towards aqueous-based fluids. The results of this work suggest that NR-based formulations may have potential as seal materials in water-based hydraulic systems.

CONCLUSION

The boundary lubrication of rubber by aqueous solutions is complicated by factors such as the interaction of the solution with the rubber and counterface, the action of electrostatic repulsion forces in solution and the possibility of support from fatty acid soaps. Solution viscosity alone is no indicator of likely lubricity.

This study has focused on the effect of solution pH. For rubber/glass and rubber/rubber contacts stable equilibrium films of solution can form and so separate contact surfaces. Film thickness depends on pH. The thinnest, least stable films were found in IR/IR contacts and the thickest, most stable in NR/glass contacts. Fatty acid soaps may be responsible for the thicker films found in NR contacts. All equilibrium films measured in static contact were less than 100 nm thick, and most were in the range 10 nm–20 nm. Acid solutions gave 'zero' film thickness. Alkaline solutions gave stable films over the pH range 7 to 12, their precise thickness depending on pH and the particular surfaces in contact. The results have a bearing upon the action of water lubricated rubber articles.

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APPENDIX 1

Calibration curves for reflected intensity relative to maximum reflected intensity were produced from a theory for reflection from a multilayer film sandwiched between two transparent substates[29]. In the case of an aqueous lubricant layer the system is relatively simple, as shown in *Figure 8.*

The calibration curve for film thickness as a function of relative light intensity is shown in *Figure 9.*

Rubber n = 1.515	Glass n = 1.517
Aqueous film n = 1.333	Aqueous film n = 1.333
Rubber n = 1.515	Rubber n = 1.515

n = refractive index

Figure 8. Models for reflection from aqueous film.

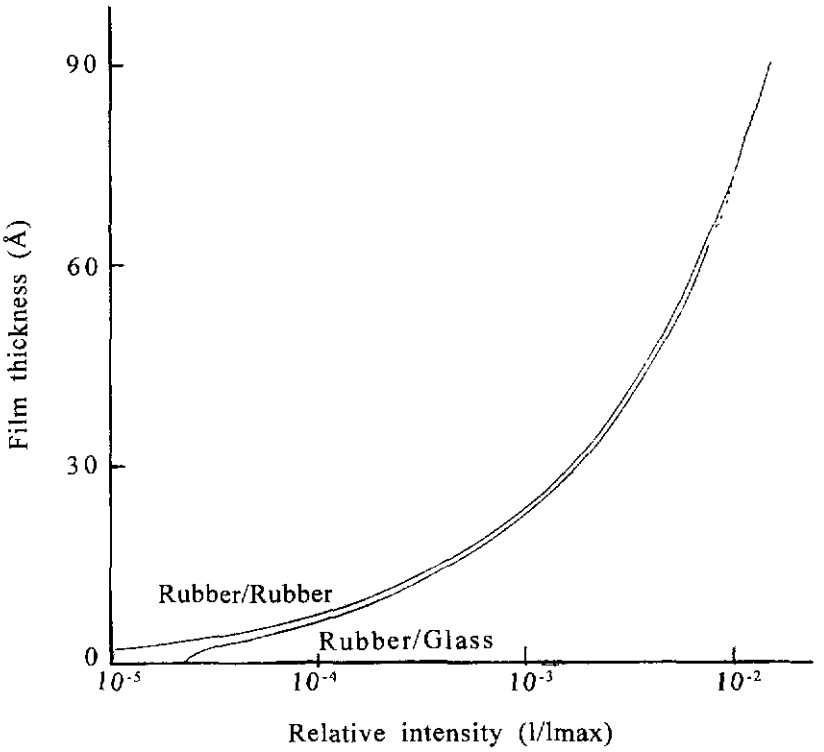

Figure 9. Theoretical relationship for relative intensity as a function of film thickness (0-90 Å) in rubber/rubber and rubber/glass contacts lubricated with aqueous solutions.