

## ***Influence of Proteinaceous Material on Rolling Friction of Rubber against Ice, Glass and PMMA***

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*Rolling resistance measurements were carried out to investigate the influence of non-rubbers (mainly proteinaceous components) on the strength of adhesion of rubber to various surfaces. A 'family' of cis-polyisoprene vulcanisates prepared with optically smooth surfaces were tested against polished ice at four different temperatures. These were also tested at room temperature against glass and PMMA at three levels of relative humidity. The results show that non-rubbers can have a marked influence on the rolling adhesion.*

It is well known that most grades of *Hevea* natural rubber (NR) contain non-rubber components such as proteins and phospholipids<sup>1</sup>. The protein macromolecules contain polar organic functional groups such as CO and NH which are capable of hydrogen-bonding interactions with ice. The subject of water-protein interactions is of fundamental importance in biological systems<sup>2</sup>.

The influence of non-rubbers (mainly proteinaceous material) on the rolling adhesion of predominantly *cis*-1,4-polyisoprene against pure ice has not been investigated in a systematic way. However, it is known that they do exert a marked influence not only on the mechanical behaviour<sup>3</sup> of raw NR but also on its subsequent vulcanisate properties<sup>4,5,6</sup> and that water absorption<sup>7-10</sup> also depends on the nitrogenous material present in NR.

The present study aims to assess the influence of non-rubber (nitrogenous) material on the rolling adhesion of *cis*-1,4-polyisoprene rubber against pure ice, glass and polymethyl methacrylate (PMMA). In particular the ranking, against ice, of gum vulcanisates containing various levels of proteinaceous material was examined at different temperatures.

### **Technique**

The energy,  $W_p$ , required to peel apart unit area of real contact provides a measure of the adhesion of smooth surfaces where adhesive hysteretic losses, inevitable during peeling of a rubber, are confined closely to the contact interface; in the absence of such losses, the peel energy is considered to be the equilibrium surface energy,  $W_0 = \gamma_1 + \gamma_2 - \gamma_{12}$  where  $\gamma_1$  and  $\gamma_2$  are the free surface energies of the contacting surfaces in air and  $\gamma_{12}$  is the interfacial energy term.

Many studies<sup>11-16</sup> over the years have suggested that the level of rolling friction of smooth rubber on a smooth substrate can be interpreted in terms of a rate-dependent peel energy,  $W_p$ . The latter depends upon both  $W_0$  and rate-dependent adhesive hysteresis losses accompanying the viscoelastic peeling process; these losses are considerable and depend upon the particular rubber and the prevailing test conditions. There is evidence<sup>17</sup> that the peel energy has the form  $W_p = W_0 f(H)$  where the function of hysteresis  $f(H)$  dominates.

For a smooth rubber cylinder of mass  $m$  and length  $l$  rolling down a smooth plane substrate (*Figure 1*), the rolling resistance

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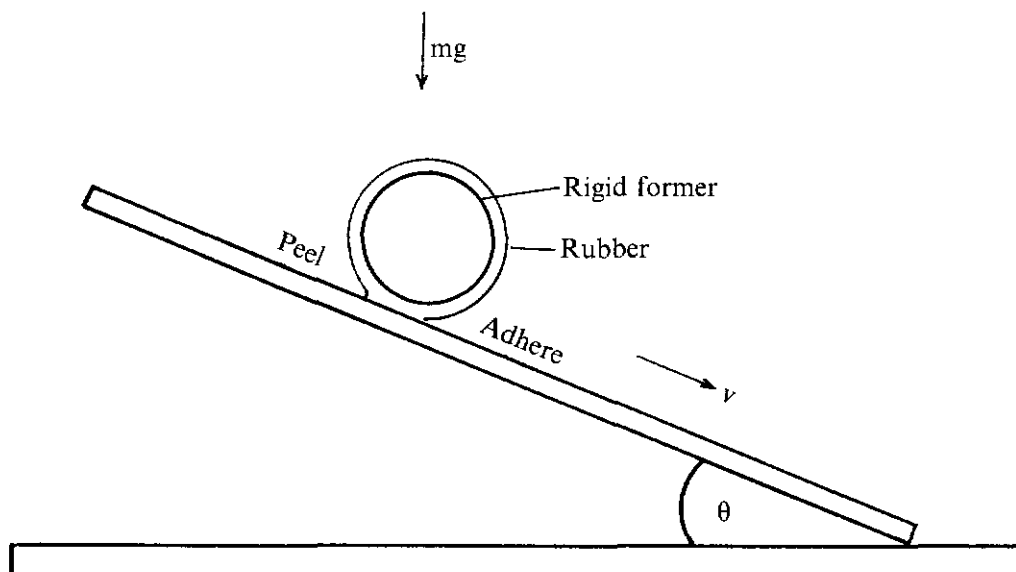


Figure 1. Smooth-surfaced rubber cylinder rolling on a rigid smooth-surfaced track.

can be expressed as an energy difference,  $\Delta W = W_p - W_a$  in peeling and adhering of the interface:

$$\Delta W = mg \sin \theta / l$$

where  $W_a$  is the adhering energy and appears to be almost rate-independent and identical with  $W_p$  (see Reference 1),  $\theta$  is the angle of inclination of the substrate to the horizontal and  $l$  is the axial length of the rubber cylinder. At high peel rates,  $W_p \gg W_a$  so that  $\Delta W \approx W_p$ . Expression 1 assumes that most of the mechanical potential energy goes towards peeling the real contact; the small bulk hysteresis loss is neglected.

It is implicitly assumed that the geometrical (apparent) area traversed by the roller is identical with the corresponding real area. The use of Expression 1 can only be justified if the following conditions are satisfied:

- Surface roughness is minimal so that intimate contact ensues.
- Surface contamination is almost absent.
- The rubber is sufficiently soft for intimate contact to ensue.

All three factors have a direct influence on the ratio of real to apparent (traversed) area. It is noted that the model vulcanisates and smooth-surfaced counterfaces satisfied these conditions, although skim rubber was slightly harder. The uncertainty due to the greater hardness of skim is considered unimportant because the rolling results on ice, glass and PMMA showed a genuine trend over all rubbers. In any case, skim showed a marked effect, too large to be accountable by a hardness effect alone.

## EXPERIMENTAL

### Rubber Samples

The sample vulcanisates used in this study were 2 – 3 mm thick sheets, all cured with 2% dicumyl peroxide by hot compression moulding against smooth glass plates at 100°C for 10 min followed by 160°C for 60 min. The polymers tested were synthetic isoprene rubber (IR), Standard Malaysian Rubber, latex grade (SMR L), the skim rubber obtained from the dilute latex that is separated during the concentration of natural rubber latex, and specially prepared

for us by the Rubber Research Institute of Malaysia, commercial skim, acetone extracted skim and bovine serum albumen (BSA) doped IR. Some of the physico-chemical properties of these materials are given in *Table 1*. These rubbers cover more than two orders of magnitude in nitrogen (and associated protein) content.

### Rolling Friction of Rubber on Smooth Ice

The ice track was made from de-ionised water of conductivity 0.05  $\mu\text{S}$ , levelled with a smooth metal plate and finally polished by skimming the surface with a clean sharp razor blade. During the rolling tests, the ice surface and its surrounding temperatures were monitored continuously using thermocouples and mercury contact thermometers.

Cylindrical rubber rollers were formed by wrapping optically smooth 3 mm thick gum vulcanisate sheets around weighted PMMA cylinder formers of external diameter 65 mm. The weight of the roller was 7.3 N and its axial length was 37.5 mm.

The smooth-surfaced rubber rollers were cleaned with propan-2-ol (analytical grade)-soaked cotton wool to remove any surface contamination and dirt. After the solvent had evaporated, the rubber rollers were placed in a temperature controlled and enclosed chest freezer (*Figure 2*) and allowed to cool to the required temperature. The rubber rollers were then sequentially allowed to roll under gravity over a fixed distance (usually 150–180 mm) of smooth-surfaced ice at a particular inclination, the descent time, and hence rolling speed, of each rubber type was measured with a digital stop-watch.

The random uncertainty in the dependent variable was estimated from independent repeated rollings, with and without re-cleaning of the rubber surfaces. The rubber and ice surfaces appeared, as judged visually and through a low power telescope, to be clean and free of ice crystals both before and after subsequent rolling; the peeling was interfacial.

TABLE 1. VULCANISATE PROPERTIES OF RUBBERS USED FOR ROLLING FRICTION MEASUREMENTS. ALL RUBBERS WERE GUM VULCANISATES (UNFILLED AND CURED WITH 2% DICUMYL PEROXIDE) WITH OPTICALLY SMOOTH SURFACES

Cis-1,4-polyisoprene vulcanisate	T <sub>g</sub> (°C)	Nitrogen (%)	Oxygen (%)	IRHD	E
IR	-67	0.01	0.6	42	1.6
DPNR	-70	0.08	1.4	40	1.5
SMR L	-70	0.38	2.5	42	1.6
Skim	-72	2.19	7.3	48	2.2
IR doped with aqueous BSA and vacuum-dried	-67	0.27	1.8	43	1.7
Acetone-extracted skim	-70	2.20 (2.02)	5.8	48	2.2

T<sub>g</sub> = Glass transition temperature ( $\pm 1^\circ\text{C}$ ) measured by differential scanning calorimetry and calibrated against a raw SMR L standard ( $-72^\circ\text{C}$ )

IRHD = International Rubber Hardness Degrees at  $21^\circ\text{C} \pm 1^\circ\text{C}$

E = Young's modulus ( $\text{MNm}^{-2}$ )

Figure within brackets denotes different commercial material

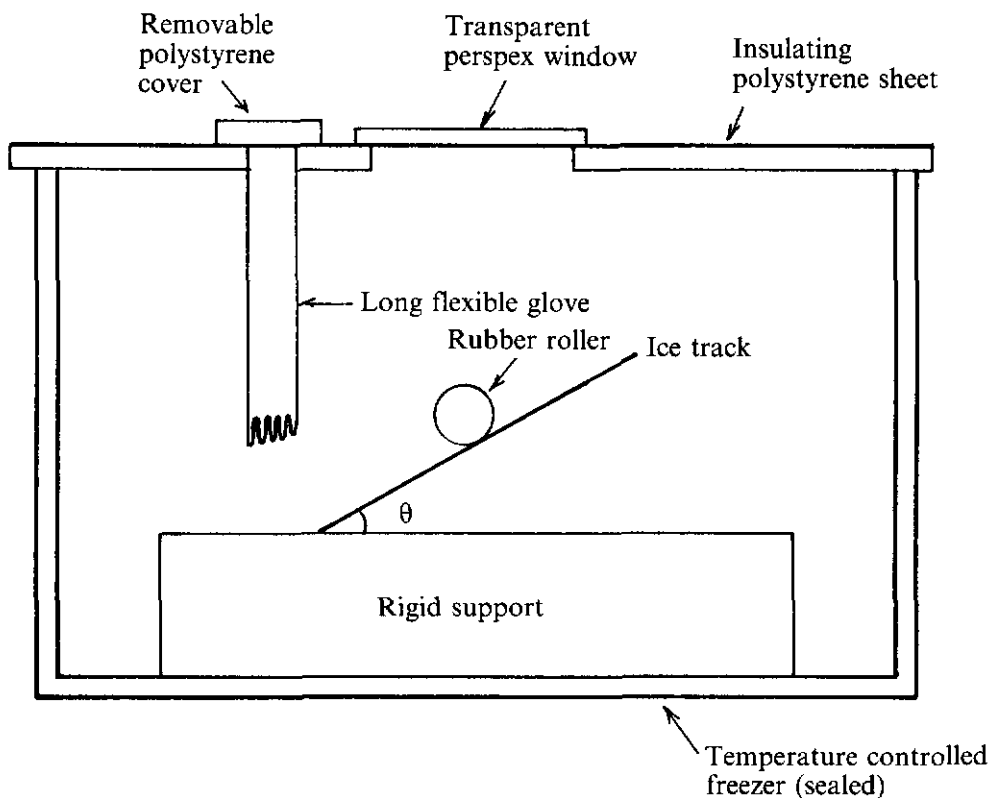


Figure 2. Experimental arrangement for rolling on ice track.

Precautions were taken to ensure that the temperature difference between ice and its environment did not exceed a maximum of about 0.5°C.

It was also found that the following three variations in the above experimental technique gave the same results:

- Before the sequential rolling of various rubber types at a particular inclination, the ice surface was made smooth by skimming it with a clean razor blade.
- Before *every* rolling, the ice surface was repolished.
- Before rolling measurements, the solvent-cleaned rubber rollers were dried in a vacuum oven at 25°C for 24 h and protected with clean Mylar film.

Generally, the rolling was steady as judged visually.

#### Rolling Friction of Rubber on Glass and PMMA Tracks

Using rubber rollers made as indicated above, rolling friction measurements were carried out on optically smooth glass and PMMA tracks at room temperature and humidity. The experimental method involved cleaning the rubber and glass surfaces with acetone and propan-2-ol soaked cotton wool before each rolling test and the rolling distance on the glass track was 170 – 180 mm.

#### Influence of Humidity on Rolling Friction

The influence of environmental relative humidity (RH) on rubber/glass and rubber/

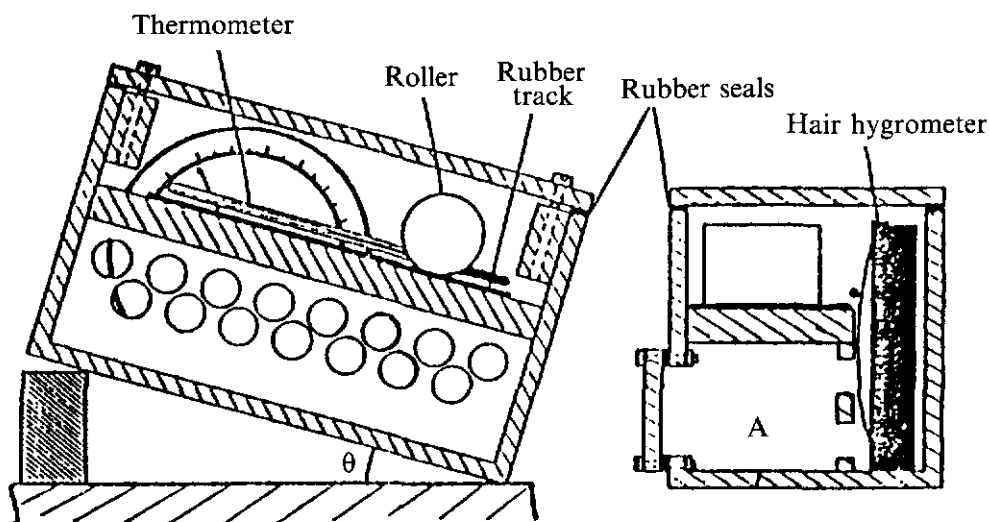


Figure 3. Rolling in a sealed 'Perspex' box, with desiccant placed in space A.

PMMA adhesion was investigated by rolling resistance measurements. The optically smooth rubber vulcanisates tested were IR, SMR L, skim, commercial skim, acetone-extracted skim and commercial skim, and BSA protein doped IR. All the rubbers were moulded with optically smooth surfaces.

The apparatus used to test the RH effect for rolling of glass on rubber consisted of a transparent enclosure<sup>10</sup> containing a thermometer, calibrated hair-hygrometer to give the RH, optically smooth glass cylinder (weight 0.18 N; diameter 18 mm; axial length 30 mm) and a smooth-surfaced 4 mm thick rubber track (Figure 3). The

relative humidity in the box was varied by using saturated salt solutions (Table 2) and silica gel/molecular sieve type 3A sachets (BDH Chemicals, Poole). Reproducibility of results was poor (erratic rolling) when loose silica gel was used, presumably due to surface contamination. The use of desiccant sachets improved reproducibility and the rolling was steady as judged visually. For rolling at high inclination angles ( $\theta$  close to  $90^\circ$ ), the saturated salt solution was replaced with water-soaked cotton wool.

The rolling friction measurements were carried out as follows:

TABLE 2. RELATIVE HUMIDITIES OBTAINED USING SATURATED SALT SOLUTIONS (SALTS IN WATER)

Saturated salt solution	Relative humidity (%)	
	20°C	25°C
Potassium sulphate	97	97
Sodium dichromate	55	54
Potassium carbonate	44	43

- a Before rolling tests, the rubber surface and glass roller were cleaned with propan-2-ol and the box was then sealed. The contents were undisturbed in a dark temperature-controlled room for three days to condition at a particular RH
- b. The rolling distance on the rubber flat was 100 mm

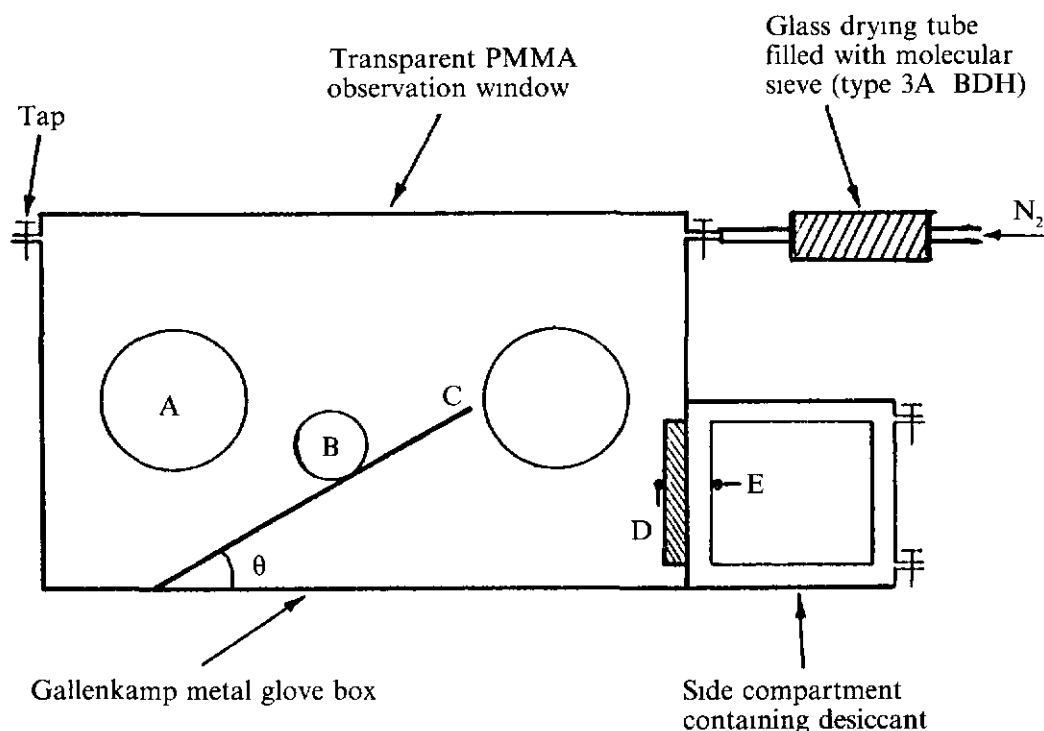
The apparatus used for rolling rubber on PMMA was a glove box (Gallenkamp, *Figure 4*), placed in a temperature-controlled room, containing mercury and digital thermometers, calibrated hair hygrometer, optically smooth transparent PMMA track (ICI, 'Perspex'), of centre line average roughness 0.005  $\mu\text{m}$ , and cylindrical rubber rollers (as above)

The relative humidity in the sealed glove box was varied by using saturated salt solutions (*Table 2*) and drying agents in an environment of dry nitrogen phosphorus pentoxide (BDH Chemicals Ltd, Poole) and molecular sieve, type 3A (as above).

### Experimental Errors

For rolling friction measurements on ice the estimated experimental error for  $\lg \Delta W < 0.5$  is 0.05, and for  $\lg \Delta W > 0.5$  is 0.02. The error for  $\lg v < -0.5$  is 0.05 and for  $\lg v > -0.5$  is 0.1. Some exceptions are indicated on the plots by error bars.

For measurements on glass and PMMA, the error for  $\lg \Delta W < 0.6$  is 0.05, and for  $\lg \Delta W > 0.6$  is 0.02. The error for  $\lg v < -0.5$  is 0.02, and  $\lg v > -0.5$  is 0.05.



*Figure 4. Rolling in a sealed glove box, A – Gloved port holes (sealed), B – Rubber roller, C – Perspex track, D – Internal door with rubber seal, E – External door with rubber seal.*

## RESULTS

## Rolling on Ice

The results of rolling friction measurements on a polished ice track at temperatures  $-4^{\circ}\text{C}$ ,  $-14^{\circ}\text{C}$ ,  $-17.5^{\circ}\text{C}$  and  $-32^{\circ}\text{C}$  are shown in *Figures 5* and *6*. It can be seen that the nitrogen content of the rubber has a marked influence on the observed rolling friction on 'cold' ice at  $-14^{\circ}\text{C}$  and lower. In particular, for a given peel rate, the peel energy decreases with increasing nitrogen content of the rubber.

However, the observed rolling resistance on ice at  $-4^{\circ}\text{C}$  appears to be generally independent of the nitrogen content. The results also show that while the rolling grip at  $-32^{\circ}\text{C}$  is high, it is drastically reduced at  $-4^{\circ}\text{C}$ , suggesting the presence of surface water on ice near its melting point. The complete set of rolling results at the four ice temperatures demonstrate that, for a given peel energy, the rolling rate increases progressively with rising temperature for all rubber types except skim whose peel rate appeared to be little affected by temperature change. Indeed, the  $-32^{\circ}\text{C}$  and  $-14^{\circ}\text{C}$  rolling friction curves of skim rubber almost coincide. This finding is surprising because the hysteresis loss and hence the peel energy is known to be strongly temperature dependent (the loss decreases with rising temperature); it strongly suggests a dominant surface effect.

The results of acetone-extracted skim and proteinaceous IR (doped with aqueous BSA protein and vacuum-dried) rolling on polished ice at  $-17.5^{\circ}\text{C}$  are displayed in *Figure 6*. A surprising observation is that the rolling friction of extracted skim is only slightly less than that of SMR L. Another interesting observation is that the rolling resistance of IR is much greater than that of proteinaceous IR (0.27% N) and the rolling friction of the latter is slightly greater than that of SMR L. That is, the rolling grip diminishes with increasing N-content of the rubber.

## Rolling on Glass

Rolling on smooth-surfaced glass and PMMA tracks demonstrated that with increasing nitrogen content the rolling friction decreased, as shown in *Figure 7*. The effect appeared to be more marked on glass. The results of rolling on glass at three levels of relative humidity (RH) are presented in *Figures 8* and *9*. From these the following trends are noted:

- For a particular rubber/glass contact pair, the rolling resistance decreases with increasing RH.
- At a particular RH level, the rolling resistance decreases with increasing N-content (or polarity) of the rubber. The only exception is that the rolling friction of extracted skim is almost equal to that of proteinaceous IR.
- The 3% – 97% (or 98%) RH difference in rolling resistance for a contact pair increases with increasing N-content of the rubber. The only exception is that the rolling friction difference of extracted skim is nearly equal to that of proteinaceous IR.

## Rolling on PMMA

The results of different vulcanisates rolled on smooth-surfaced PMMA at three levels of humidity are shown in *Figures 10* and *11*. The following trends may be discerned:

- For a particular rubber/PMMA contact pair, the observed rolling resistance decreases with increasing RH.
- At a particular RH level, the rolling resistance decreases with increasing N-content of rubber. The only exception is that the rolling friction of proteinaceous IR is slightly less than that of SMR L.
- The 2% – 97% RH difference in rolling resistance for a contact pair increases with increasing N-content of rubber.

## DISCUSSION

Various measurements (infra-red spectroscopic, water absorption, contact angle/

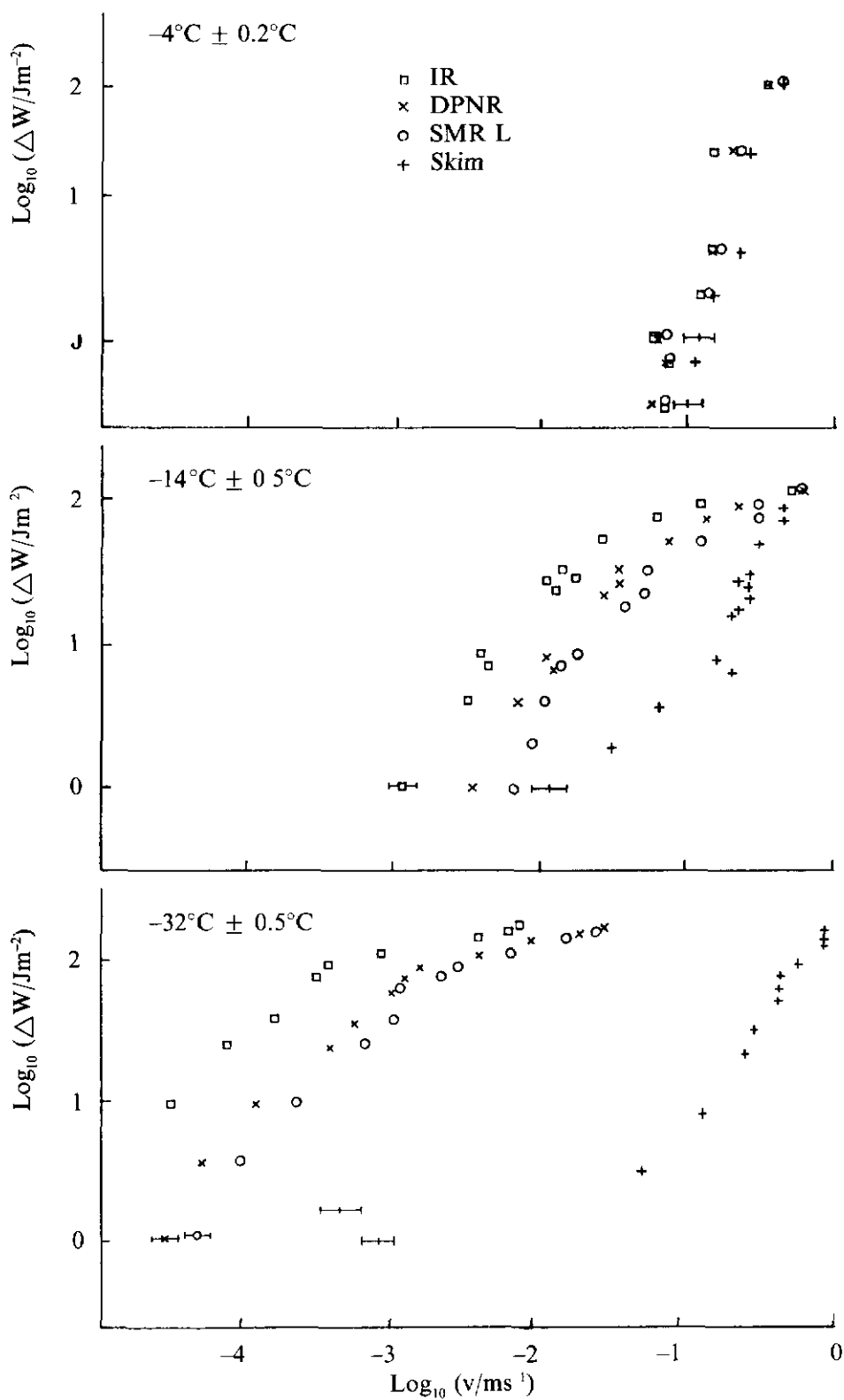


Figure 5. Rolling friction of rubber against polished ice track

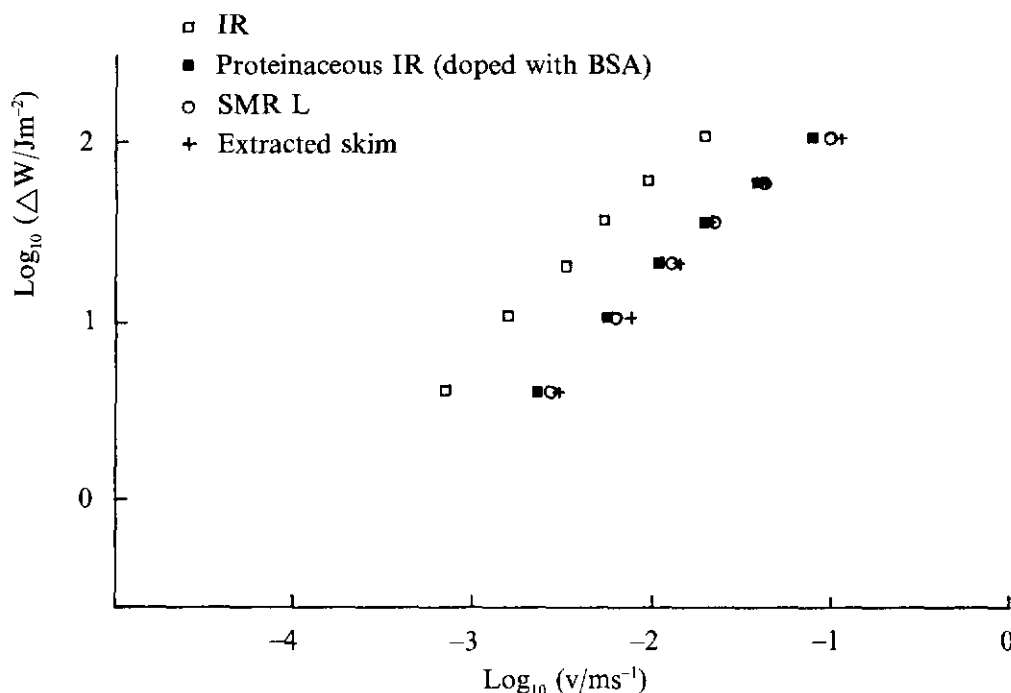


Figure 6. Rolling friction of rubber against polished ice track at  $-17.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ .

surface energy estimates and amino acid analysis) have shown<sup>18</sup> that proteinaceous skim rubber is highly hydrophilic (polar) as one might expect since proteins are known to strongly hydrogen-bond with water. It is generally accepted that some fraction of 'bound water' will behave differently to bulk water. Indeed, such bound fractions (of water) fail to freeze even when a proteinaceous system is cooled to temperatures well below  $-40^{\circ}\text{C}$ . This non-freezing bound water has been detected in many proteinaceous systems such as BSA, collagen and lysozyme. Even hydrophobic low energy surfaces such as polytetrafluoroethylene (PTFE) and polyethylene (PE) generally show some adsorption of water<sup>19</sup>. Furthermore, there is some evidence suggesting that the adsorbed water film on a polymer surface below  $0^{\circ}\text{C}$ , and especially below  $-10^{\circ}\text{C}$ , is more 'ice-like' than 'liquid-like'<sup>19</sup>. Any full explanation for the rolling results must take these observations into account.

There are two possible explanations of the present results depending on whether the bound water component acts as a gross surface contaminant reducing the real contact between the rubber and ice, or the bound water operates at a molecular level.

An adsorbed quasi-solid (or ice-like) film acting as a gross contaminant will reduce intimate contact so that real rubber/ice peeling occurs from an area smaller than the traversed apparent area, the ratio being dependent on the hydrophilicity (N-content) of the rubber. If the ratio markedly differs from one, which may be the case for skim rubber, then the use of *Expression 1* cannot be justified since the rolling contact will include ice-like film/ice substrate areas in addition to rubber/ice substrate interfaces. If this is so, the plotted data for skim rubber are not real rubber/ice peel energies, and this may explain the observed coincidence of the rolling friction curves.

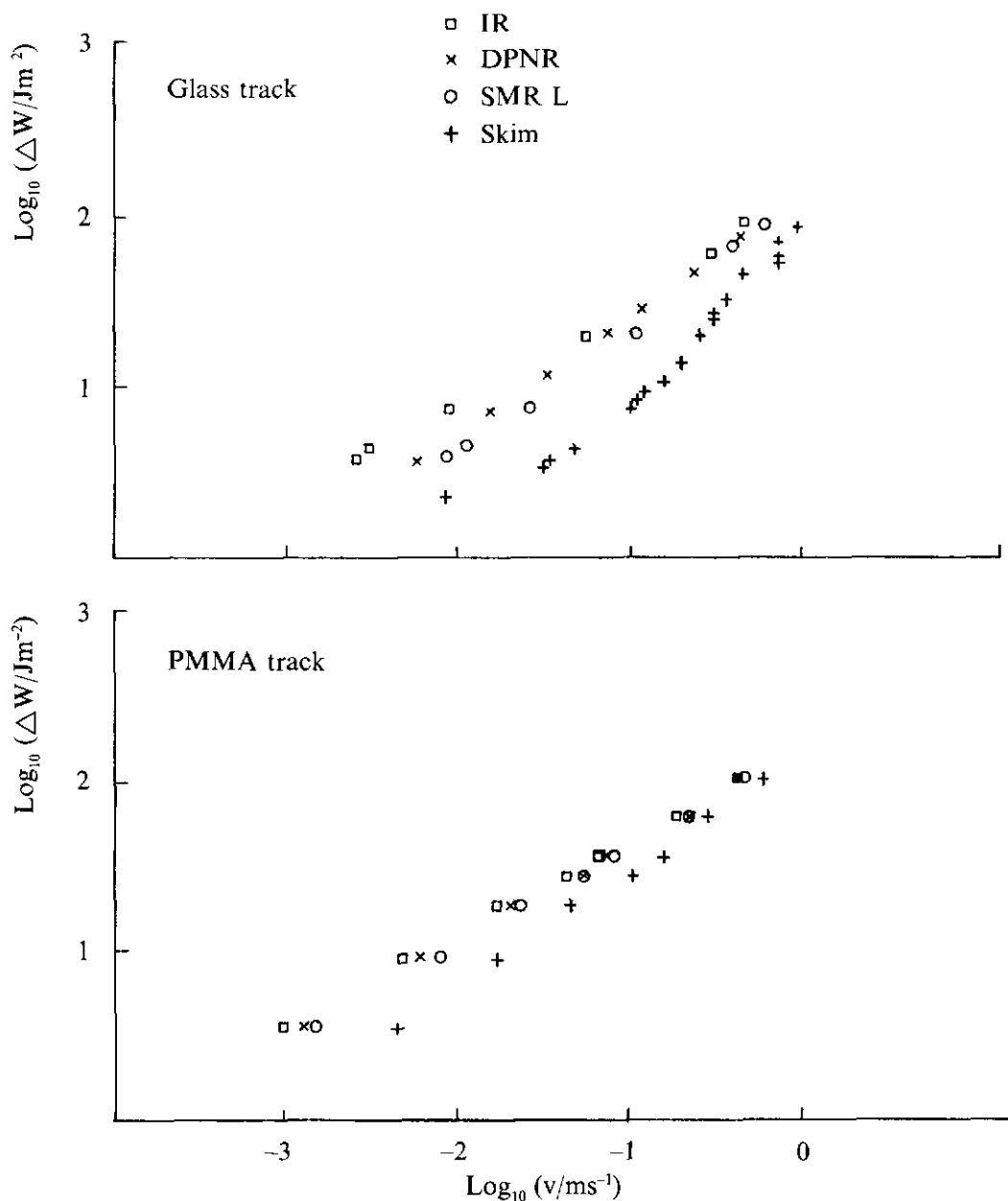


Figure 7. Rolling friction of rubber on smooth glass and PMMA tracks at  $22^{\circ}\text{C} \pm 1^{\circ}\text{C}$  and  $50\% \pm 10\% \text{ RH}$

A second explanation is that there is a bound water component of the proteinaceous rubber surface which operates at the molecular level reducing the rubber/ice

equilibrium surface energy,  $W_o$ . The following argument is based on the evidence that the peel energy  $W_p$  is of the form  $W_p = W_o f(H)$ , where the function of hysteresis

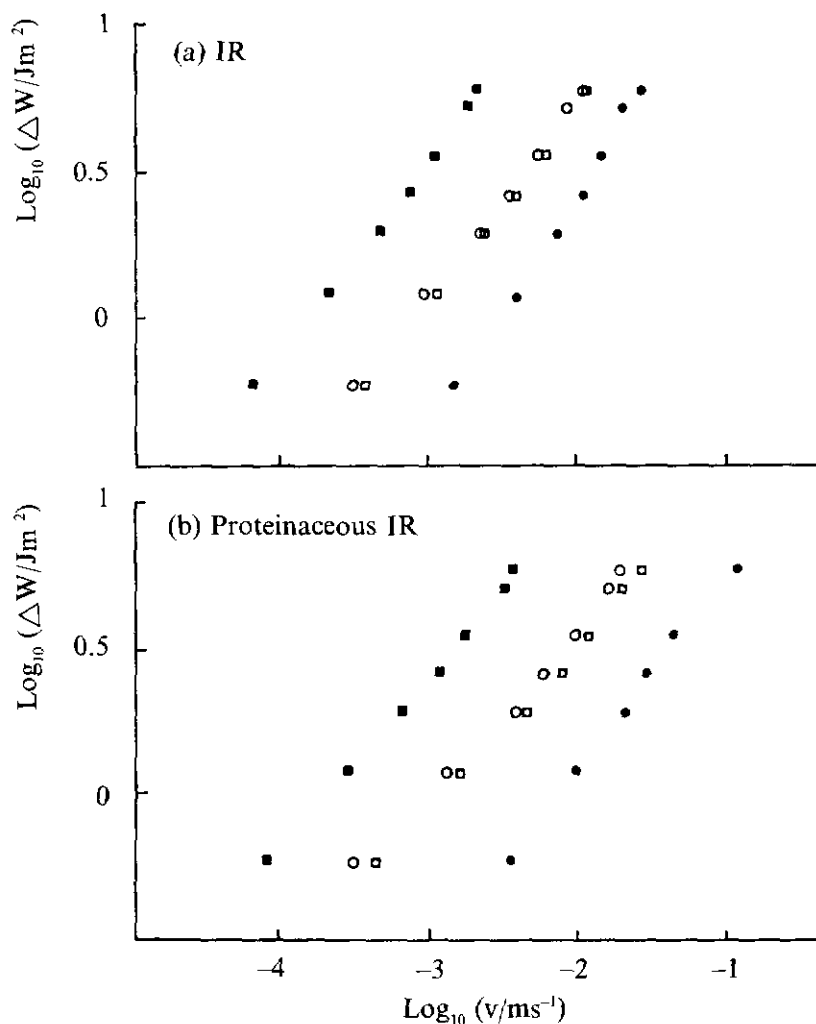


Figure 8. (a) Optically smooth glass rolling on smooth-surfaced IR track. To demonstrate reversible nature of humidity effect, the rolling experiments were carried out in the following sequence:

- 1)  $\square$   $21.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 44% RH; 3 days equilibrium
- 2)  $\bullet$   $21.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 98%  $\pm 1\%$  RH; 3 days equilibrium
- 3)  $\circ$   $21.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 3.5% RH; 3 days equilibrium
- 4)  $\bullet$   $21.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 98%  $\pm 1\%$  RH; 3 days equilibrium
- 5)  $\blacksquare$   $4.0^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 3% RH; initially 3 days at  $22^{\circ}\text{C}$  and then 1 day at  $4^{\circ}\text{C}$ . This low temperature rolling demonstrates the effect of temperature.

(b) Optically smooth glass rolling on smooth-surfaced track of proteinaceous IR (doped with BSA protein). Rolling experiments were carried out in the following sequence:

- 1)  $\square$   $21.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 44% RH; 3 days equilibrium
- 2)  $\bullet$   $21.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 98%  $\pm 1\%$ ; 3 days equilibrium
- 3)  $\circ$   $21.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 4% RH; 3 days equilibrium
- 4)  $\blacksquare$   $4.0^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 3% RH; 1 day equilibrium – this again demonstrates the effect of temperature.

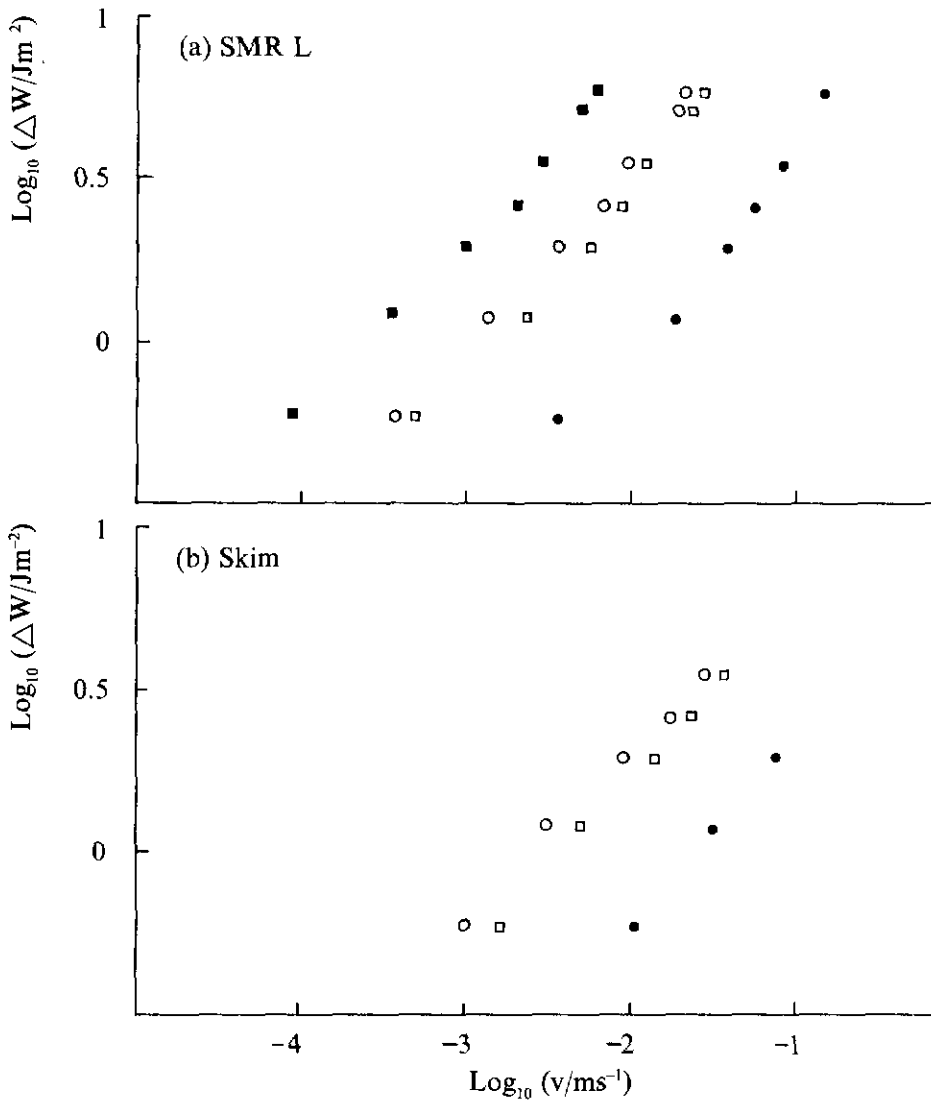


Figure 9. (a) Optically smooth glass rolling on smooth-surfaced SMR L track. To demonstrate reversible nature of humidity effect, the rolling experiments were carried out in the following sequence:

- 1)  $\square$   $21.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 44% RH; 3 days equilibrium
- 2)  $\bullet$   $21.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 97%  $\pm 1\%$  RH; 3 days equilibrium
- 3)  $\circ$   $21.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 3% RH; 3 days equilibrium
- 4)  $\bullet$   $21.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 97%  $\pm 1\%$  RH; 3 days equilibrium
- 5)  $\blacksquare$   $4.0^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 3% RH; initially 3 days at  $22^{\circ}\text{C}$  and then 1 day at  $4^{\circ}\text{C}$

(b) Optically smooth glass rolling on smooth-surfaced skim track. Rolling experiments were carried out in the following sequence:

- 1)  $\square$   $21.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 44% RH; 3 days equilibrium
- 2)  $\bullet$   $21.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 98%  $\pm 1\%$  RH; 3 days equilibrium
- 3)  $\circ$   $21.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 4% RH; 3 days equilibrium

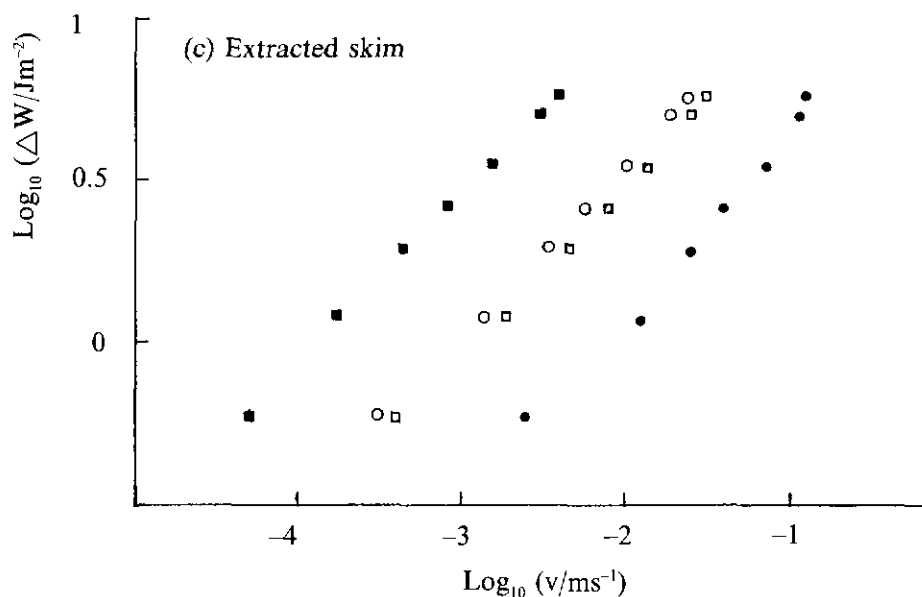


Figure 9. (c) Optically smooth glass rolling on smooth-surfaced track of extracted skim (or extracted commercial-skim which showed identical results). Rolling experiments were carried out in the following sequence:

- 1)  $\square$   $21.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 44% RH; 3 days equilibrium
  - 2)  $\bullet$   $21.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 98%  $\pm$  1% RH; 3 days equilibrium
  - 3)  $\circ$   $21.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 2% RH; 3 days equilibrium
  - 4)  $\blacksquare$   $21.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 1% RH; 1 day equilibrium
  - 5)  $\circ$   $21.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 2% RH; 1 day equilibrium
- $\rightleftharpoons$  3) i.e. thermal reversibility is demonstrated.

predominates<sup>17</sup>. It may be reasoned that the rubber/ice  $W_n$  decreases with increasing rubber polarity because of an increasing water content. To explain the observed coincidence of the skim rolling friction curves involves the assumption that the rubber/ice  $W_n$  at  $-32^{\circ}\text{C}$  is different from that at  $-14^{\circ}\text{C}$ . Upon temperature change from  $-32^{\circ}\text{C}$  to  $-14^{\circ}\text{C}$ , the  $W_n$  and the hysteretic factor,  $f(H)$ , act in opposite directions and change in such a way that their product remains independent of temperature. No macroscopic frosting of the rubber and ice surfaces were observed during the time scale of the rolling experiments; this would favour the second explanation.

It has already been established<sup>20,21</sup> by optical and rolling experiments that the measured peel energy is influenced by such factors as the rubber's glass transition temperature<sup>11</sup>, presence of filler<sup>20,22</sup>, cross-link density<sup>20</sup>, surface bloom<sup>23</sup>, contact dwell time<sup>20</sup> and surrounding humidity<sup>10</sup>. The first three factors have a direct influence on the magnitude of hysteresis losses and hence consequent peel energy. Table 1 indicates that the glass transition temperatures ( $T_g$ ) of various rubbers are nearly the same. Methersell<sup>6</sup> has shown that protein in a rubber vulcanisate acts as a filler making the rubber more hysteretic. Despite this, skim showed the lowest rolling friction

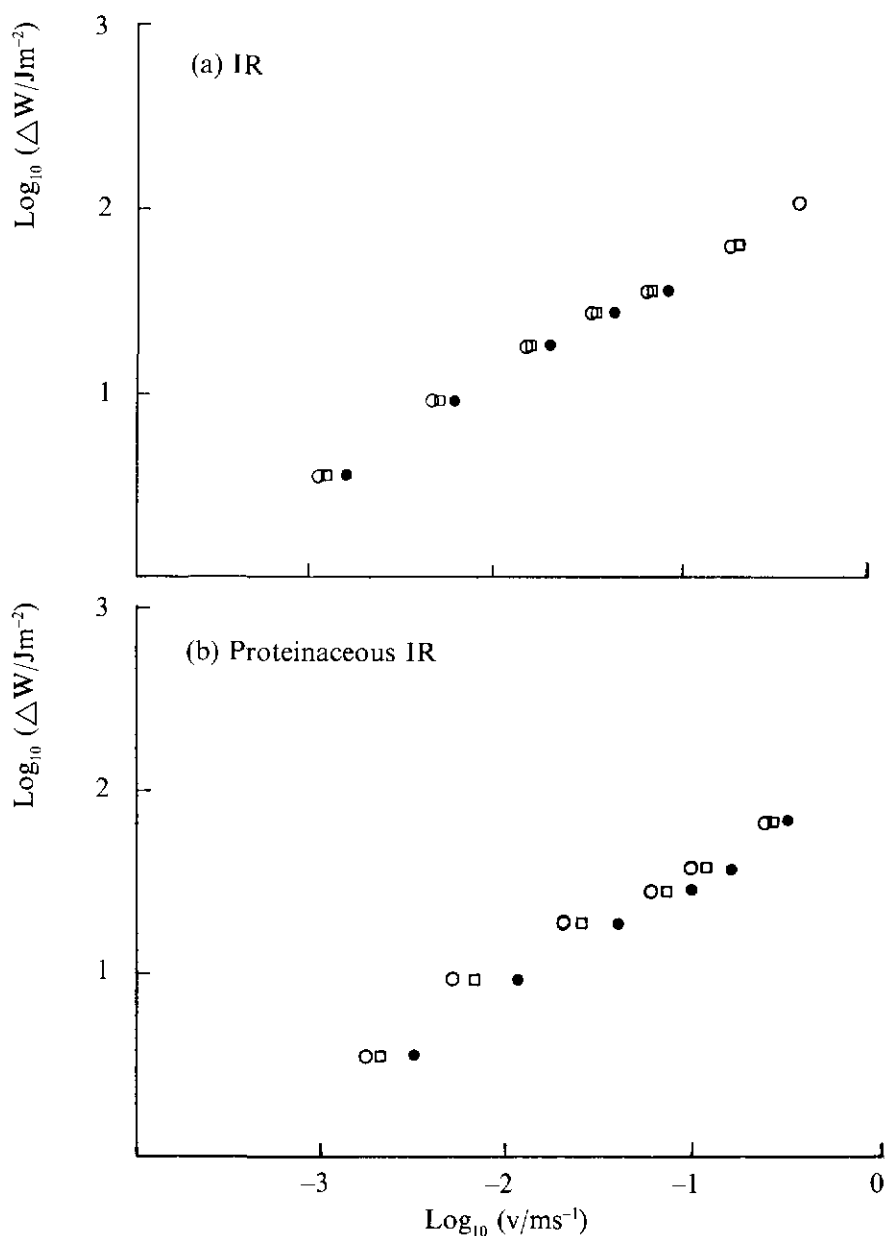


Figure 10. (a) Smooth-surfaced IR rolling on smooth Perspex track. To demonstrate reversible nature of humidity effect, the rolling experiments were carried out in the following sequence:

- 1)  $\square$   $22.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 44% RH; 3 days equilibrium
- 2)  $\bullet$   $22.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 97% RH; 3 days equilibrium
- 3)  $\circ$   $22.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 2% RH; 3 days equilibrium
- 4)  $\blacksquare$   $22.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 97% RH; 3 days equilibrium

(b) Smooth-surfaced proteinaceous IR (doped with BSA protein) rolling on smooth Perspex track. Rolling experiments were carried out in the following sequence:

- 1)  $\square$   $22.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 55% RH; 3 days equilibrium
- 2)  $\bullet$   $22.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 97% RH; 3 days equilibrium
- 3)  $\circ$   $22.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 3% RH; 3 days equilibrium

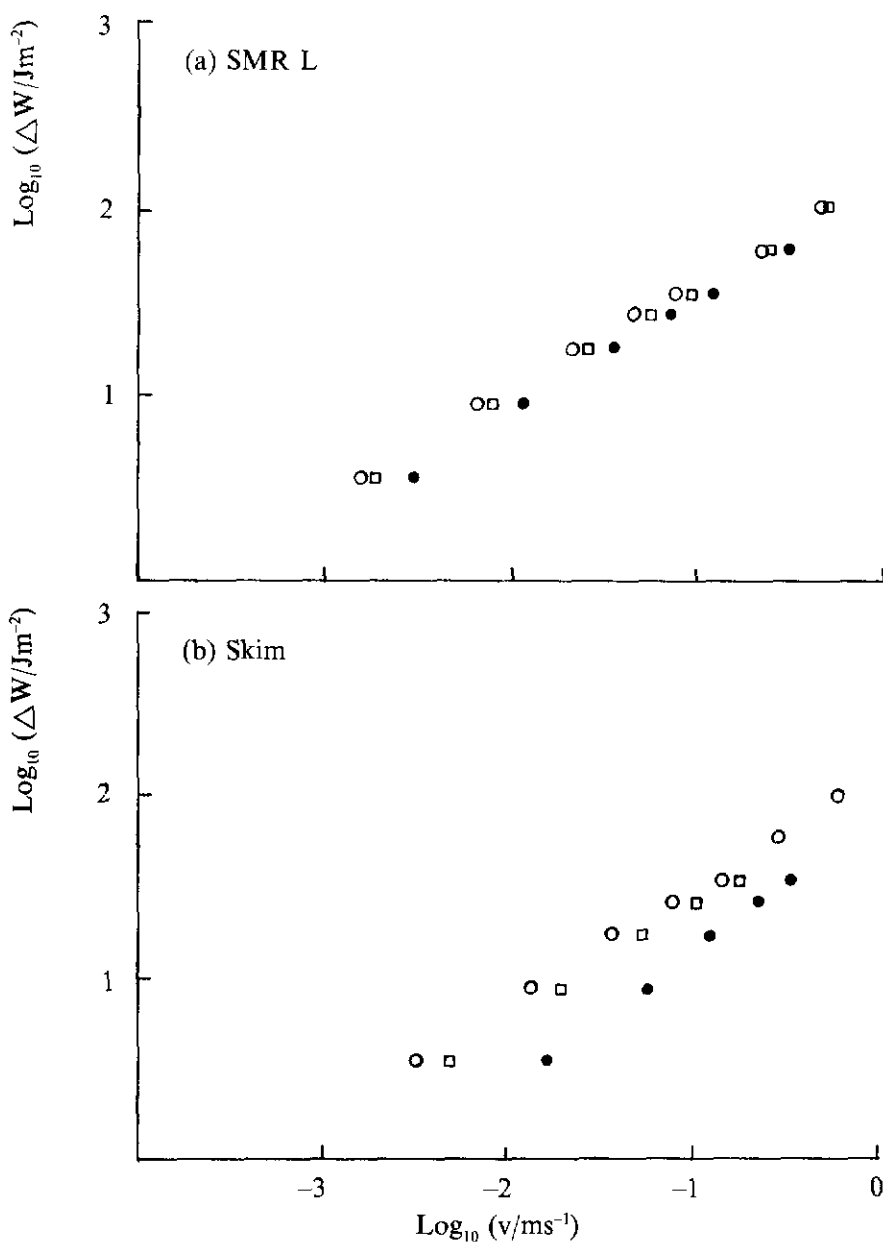


Figure 11. (a) Smooth-surfaced SMR L rolling on smooth Perspex track. To demonstrate reversible nature of humidity effect, the rolling experiments were carried out in the following sequence:

- 1)  $\square$   $22.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 55% RH; 3 days equilibrium
- 2)  $\bullet$   $22.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 97% RH; 3 days equilibrium
- 3)  $\circ$   $22.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 3% RH; 3 days equilibrium
- 4)  $\bullet$   $22.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 97% RH; 3 days equilibrium

(b) Smooth-surfaced skim rolling on smooth Perspex track. Rolling experiments were carried out in the following sequence:

- 1)  $\square$   $22.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 55% RH; 3 days equilibrium
- 2)  $\bullet$   $22.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 97% RH; 3 days equilibrium
- 3)  $\circ$   $22.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ ; 2% RH; 3 days equilibrium

against glass and PMMA tracks. This suggests that the equilibrium surface energy  $W$  decreases with increasing hydrophilicity (N-content) of the rubber, presumably due to an increasingly bound water film and this more than compensates for any increase in hysteretic losses.

The humidity effect on rubber glass rolling friction has been studied by Roberts and Parsons<sup>10</sup>. Their results showed that the rolling resistance decreased with rising humidity and that the effect is larger for more hydrophilic rubbers. They investigated a wide range of rubbers, two of which were 2% dicumyl peroxide cured IR and SMR L vulcanisates similar to those used in the present experiments, they found that while SMR L showed a noticeable humidity effect the synthetic material showed only a slight effect. Furthermore, their ball-rebound resilience measurements at various humidity levels showed only small changes in bulk hysteresis loss. In view of these findings, they suggested that the observed influence of humidity is predominately a surface effect, strongly dependent on the hydrophilicity of the rubber.

#### Comparison of Rubber/Glass and Rubber/PMMA

From the rolling experiments it was clear that

- At a particular RH level and for a particular rubber type, the rolling resistance of the PMMA rubber contact pair is greater than that of the glass/rubber interface
- For a particular rubber type, the 2% – 97% RH difference in rolling resistance for a glass rubber contact pair is greater than that of a PMMA rubber interface

These results are consistent with a more polar, hydrophilic glass surface, which possesses more adsorbed water relative to PMMA.

#### CONCLUSION

For rubber rolling on surface polished ice at temperatures below  $-14^{\circ}\text{C}$ , the rolling resistance decreases with increasing nitrogen content of the rubber test-piece. Rolling on smooth-surfaced glass and PMMA also showed the same effect at room temperature. For a particular contact pair made with glass or PMMA, the rolling resistance decreases with increasing relative humidity. This is presumed to be due to increased water adsorbed at hydrophilic sites on contact surfaces. Such water may be present as a so-called bound water component in the form of a quasi-solid film that will, to varying degrees, diminish the interface adhesion. The observed effect was particularly marked on glass and ice surfaces for proteinaceous rubber.

Although the effect can be marked on ice below  $-14^{\circ}\text{C}$ , on ice near to melting ( $-4^{\circ}\text{C}$ ), the measurements showed that the rolling resistance was low and, in general, independent of the nitrogen content of the rubber. The presence of a lubricating water film on the ice surface may explain these observations. It would appear that the properties of ice surfaces near the melting point are more important than those of vulcanisates in determining the level of rolling resistance.

Any future investigations might include incorporation of various pure proteins into rubber to establish the importance (if any) of *protein type*. Incorporation of pure protein into both rubber and ice surfaces might reveal any dynamic protein/protein interactions.

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