

Contact Adhesion of Rubber: Influence of Humidity, Substrate History and Viscoelasticity

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An estimate of the surface energy of polymeric solids can be obtained by wetting measurements. An alternative, in the case of rubber, is to deduce the apparent surface energy by direct optical observations of solid-solid contact areas. This study reports contact observations for the adhesion of rubber hemispheres against glass and plastics substrates. The measurements suggest that the level of adhesion is sensitive to ambient humidity, substrate surface history and viscoelastic response of the rubber. Particular emphasis is placed upon the difference between the making and the breaking of contact. Analysis of the measurements indicates the important roles of surface energy and rubber hysteresis, an increase in either or both leading to higher apparent peel energies but lower adhering energies.

The strength of adhesion of rubber to a substrate depends on many factors such as interfacial surface energy and rubber hysteresis¹⁻³. The latter increases the total energy required to peel rubber off a substrate. The reversible work of adhesion, W_a , which has been related⁴ to the individual free surface energies of the contacting bodies, arises from several kinds of interactions that may be physical or chemical in nature. Physical thinking tends to be in terms of van der Waals' attractive forces⁵, originally advanced to explain the behaviour of dense gases. Some experiments⁶⁻⁸ suggest the adhesion of polymeric particles and films owes much to electrostatic attraction, but this does not appear to be significant for the self-generated charge associated with smooth surfaced rubber contacts⁹. Some recent results imply the importance of acid-base interactions¹⁰.

In this study we report physico-chemical measurements of rubber adhesion by investigating the *quasi*-static contact of rubber against glass and polymethylmethacrylate (PMMA). Vulcanised rubber hemispheres were brought into contact with glass and PMMA 'coverslips' and from contact observations the apparent

work of adhesion, W , was calculated. Adhesion was measured for different surface treatments of the glass and for the effect of ambient relative humidity. Supplementary sliding friction measurements were made on the effect of humidity. It will be shown that the level of adhesion clearly depends on these factors and the hysteretical properties of the rubber.

EXPERIMENTAL

Sample Preparation

Rubber samples employed had optically smooth surfaces produced by hot compression moulding to yield hemispheres. The usual hemisphere diameter was 37 millimetres. They were produced in a chrome-plated steel cavity mould possessing surfaces lapped to an optical finish. Formulation details of the rubbers used are given (Table 1). Rubber surfaces were washed with isopropylalcohol (IPA) and left to dry. Glass and PMMA coverslips were first cleaned in soapy water, rinsed in tap water, then abundantly rinsed with distilled water. In addition to the usual procedure³ of finishing

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TABLE 1. RUBBER COMPOUND FORMULATIONS

Compound	Parts by weight				
	NR	IR	CR	SiR	NBR
NR (SMR-L)	100				
Polychloroprene (Neoprene WRT)			100		
Polyisoprene (Cariflex 305)		100			
Acrylonitrile butadiene (Krynac 801)					100
Silicone rubber (GE RTV 602)				100	
Dicumyl peroxide (Di-Cup R)		2			2
Stearic acid	2		0.5		
Zinc oxide	5		5		
N-isopropyl-N-phenyl- p-phenylenediamine (Nonox ZA)	1		1		
Sulphur	2.5				
N-tert-butylbenzothiazole-2-sulphenamide	0.5				
Magnesium oxide (Maglite D)			4		
Ethylene thiourea (NA-22)			0.5		
Catalyst (organic amines)				0.5	
Cure time/temp. (min/°C)	40/140	60/160	30/150	30/20	50/160
Hardness (IRHD)	40	40	50	15	51
Young's modulus (MPa)	1.5	1.5	2.4	0.4	2.5
Glass transition temperature (T_g)	-69	-67	-45	-133	-25

by washing the glass or PMMA with IPA, sometimes the glass was treated with aqueous 2M HCl or aqueous 2M NaOH to render its surface either acidic or basic¹⁰. In these cases, the glass was dried at 22°C or 400°C for 30 min after a final rinse with distilled water.

Adhesion Measurements

Static contact adhesion energies, W , can be derived from experiments according to the general expression¹

$$W = \frac{1}{6\pi Ka^3} \left(\frac{Ka^3}{R} - P \right)^2 \quad \dots 1$$

where a is the observed radius of the circle of contact between the touching spherical surfaces of reduced elastic modulus $K = \frac{4}{3\pi(k_1 + k_2)}$

where $k = \frac{1 - \nu^2}{\pi E}$. Each surface has a Young's modulus E and a Poisson's ratio ν . The applied load is P and the reduced radius of curvature is $R = \frac{R_1 R_2}{R_1 + R_2}$, R_1 and R_2 being the radii of curvature of the two materials in contact. For the case of contact between a hemisphere of radius R and $\nu = 0.5$, and a rigid plane this analysis gives:

$$W = \frac{3}{32\pi Ea^3} \left(\frac{16Ea^3}{9R} - P \right)^2 \quad \dots 2$$

where E is the Young's modulus of the rubber. One may note that at equilibrium W , denoted W_0 , corresponds to what is termed in fracture mechanics the strain energy release rate, written as G^{11} .

Measurements of contact diameter were made with the vernier eyepiece of a low power microscope (*Figure 1a*). For touch-on tests (the making of contact) solid substrates were brought very gently into contact with rubber hemispheres. To ensure gentle contact a coverslip was supported on two fine nylon wires and the rubber hemisphere raised slowly by the fine control of the microscope stage. The increase in contact diameter with time was measured as surfaces adhered together and corresponding values of W_a were calculated.

Measurements were done differently for peel tests (the breaking of contact). Coverslips were pressed onto hemispheres under a load of 0.5 N, held there under load for 15 s and then the load was removed whereupon the shrinking of the contact radius with time was recorded. Contact radius values were used to calculate W_p from *Equation 2*. It is noted that the externally applied load P , corresponding to the weight of the coverslip, was small (0.001 N) and this makes for a more sensitive measurement of W .

To change the ambient relative humidity, the rubber hemisphere was placed in a glass crystallising dish (*Figure 1b*) covered with a thin polymer sheet (clingwrap). In this dish was placed either water or silica gel, depending on whether a high or low humidity was required. A calibrated hair hygrometer was employed to give a measure of the humidity in the dish. The room humidity was measured with the hygrometer and was found to be typically $50\% \pm 10\%$ RH for the period of the experiments.

All adhesion measurements were carried out at $22^\circ\text{C} \pm 1^\circ\text{C}$.

Contact Angle Measurements

In an attempt to correlate adhesion measurements with the surface properties of rubber and adhering substrates, contact angles with water were measured at 22°C . The method consisted in measuring the radius of calibrated drops ($1\ \mu\text{l}$ or $2\ \mu\text{l}$ volume) assuming a spherical profile¹². This was done using the same microscope set up (*Figure 1*).

Friction Measurements

To further understanding of interfacial events, simple apparatus was constructed to allow measurements of the sliding force between a rubber hemisphere and glass or another rigid substrate such as PMMA (*Figure 2*). The contact area was observed in reflected light under a low power microscope. The interfacial average shear strength, τ , was taken to be the friction force divided by the contact area. The measurements were made at a constant sliding speed of $0.2\ \text{mm s}^{-1}$ at room temperature ($21^\circ\text{C} \pm 2^\circ\text{C}$). The ambient humidity was varied by enclosing the major portion of the apparatus in a polythene sheet under which the humidity was raised with water or lowered with silica gel. The relative humidity was measured with a hair hygrometer placed close to the contacting surfaces. The test surfaces were allowed to equilibrate at a given humidity for 1 h before bringing them into contact.

RESULTS

Wettability

Study of liquid/solid interactions by contact angle measurements have been undertaken by Zisman¹³. The work of adhesion of a liquid on a solid W_{SL} , can be estimated from its contact angle, Θ , using the well-known Young-Durpe relationship:

$$W_{SL} = T(1 + \cos \Theta) + \pi_e \quad \dots 3$$

where T is the surface tension of the liquid and π_e the spreading pressure of the liquid on the solid surface. For water on freshly crushed¹⁴ soda glass $\pi_e = 230 \pm 20\ \text{mJ m}^{-2}$, but for polymers¹⁵ π_e is approximately zero.

Contact angles of water on rubber and glass substrates have been measured by the method described above. The results are reported in *Table 2*. The polytetrafluorethylene (PTFE) and PMMA were used as reference surfaces to check the method. The corresponding values of water contact angles are in good agreement with those usually obtained¹³.

It can be seen that the wettability of glass is closely dependent on its surface treatment

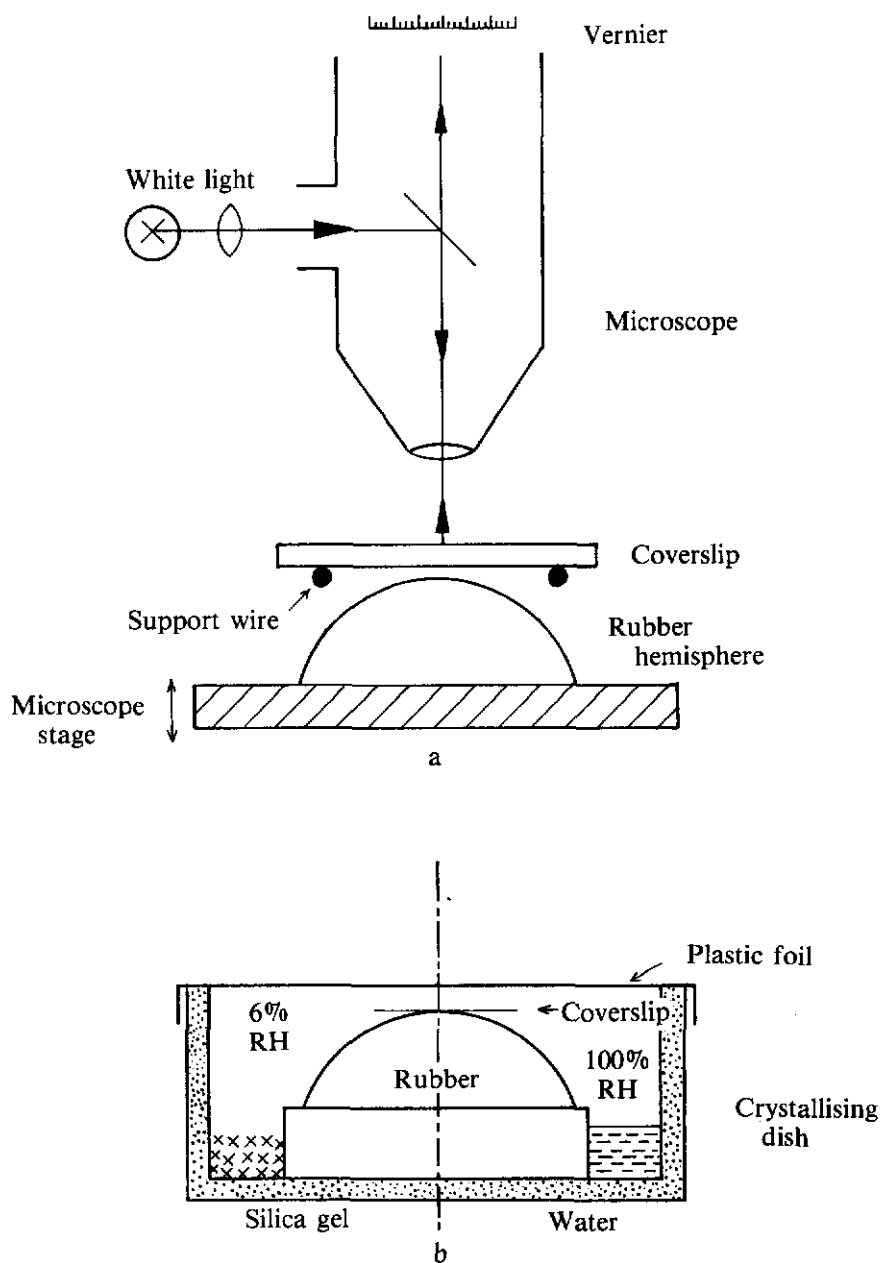


Figure 1. (a) Method for observing the contact area between rubber and hard substrate (coverslip). (b) Arrangement for varying the relative humidity.

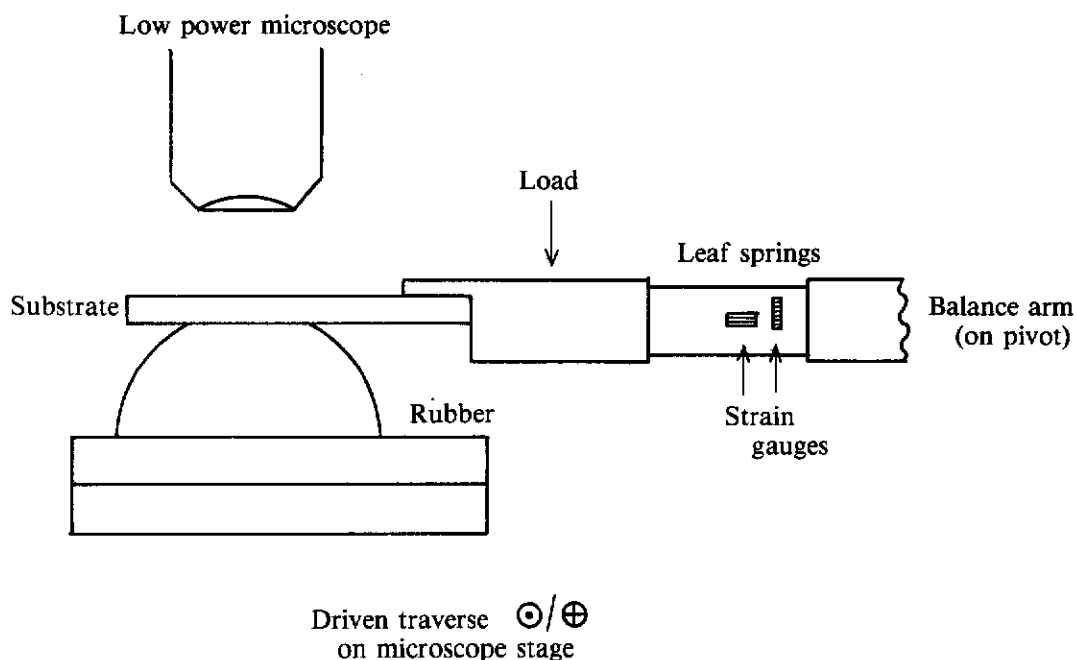


Figure 2. Apparatus for measuring interfacial shear strength.

TABLE 2. CONTACT ANGLE OF WATER ON GLASS AND POLYMERS

Substrate	Θ (degree)	$W_{SL}(\text{mJm}^{-2})$
IPA washed glass	43.5	≥ 125
Dried glass at 400°C	0	≥ 146
NR	76.5	90
IR	100.5	59
CR	77	89
NBR	82.5	82
SiR	110.5	47
PTFE	119	37
PMMA	74.5	92

Measurements made at room temperature (20°C–22°C).

W_{SL} is the reversible work of adhesion with water (using Equation 3).

history. The glass is more hydrophilic after drying at 400°C for 30 minutes.

Rubbers are poorly wettable by water, especially the silicone rubber. If one supposes that the spreading pressure can be neglected on

low surface energy solids such as polymers¹⁵, water/rubber interactions can be calculated from Equation 3. For high energy surfaces, such as glass, only a lower limit has been given (Table 2). However, it is clearly shown that glass dried at 400°C is highly hydrophilic.

Acid-base Interactions

A large number of experiments were performed with rubbers of different chemical structures. Some, such as NR can be considered to be basic because of the electron-donating character of olefinic groups. Others such as polychloroprene (CR) may be acidic because of the presence of chlorine groups, and possibly free HCl. Silicone rubber (SiR-1) may tend to be neutral; it is non-polar.

Figure 3 shows the variation with time of the apparent work of adhesion, W , calculated from Equation 2 for the making and the breaking of the rubber/glass interface. First of all, there appears to be a large difference between the adhering and peeling energies, W_p being always greater than W_a at any time. More energy is required to separate surfaces than is gained when they adhere. This can be attributed to the greater dissipation of energy incurred when rubber is peeled away from the glass.

This dissipation, in part, relates to a visco-elastic effect as the peel front moves^{2,3}. When a *quasi*-stable contact diameter is reached after some hours an energy difference exists between W_p and W_a and this remained constant to the longest times studied (ten days). An explanation of this phenomenon may be attributable to the elastic energy stored in the macromolecular chains to be broken¹⁶. Taking into account this phenomenon in the peeling process, it has been proposed¹⁷ that

$$W_p = W_o \times g \times f(V, T) \quad \dots 4$$

where the product $W_o \times g$ stands for the limiting value of W_p in the absence of visco-elastic losses. The parameter g is related to the length of the stretched molecular chains of the rubber^{16,17} and $f(V, T)$ is the macroscopic dissipation factor varying with the rate V , and the temperature, T , of peeling. On the other hand, for the formation of the rubber/glass interface, the apparent work of

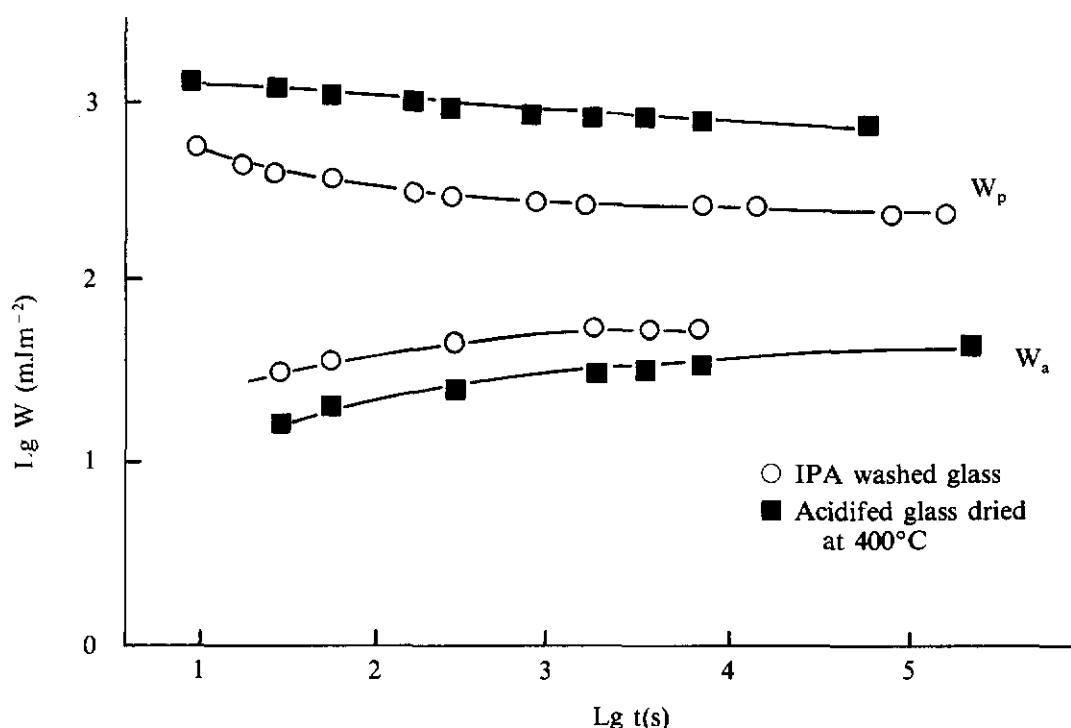


Figure 3. Variation in contact energies with time for NR against glass.

adhesion is small ($20\text{--}50\text{ mJm}^{-2}$) but of the order of magnitude of values obtained by wetting methods ($\sim 50\text{ mJm}^{-2}$). Thus the impression gained is that the adhesion experiments lead approximately to the W_o values when the *quasi*-equilibrium contact radii, a , are attained.

Secondly, the experiments showed that the adhesion was dependent upon the method of cleaning of the glass surfaces, with the possible exception of silicone rubber. This may be due to its non-polar-character (high wetting angle, see *Table 2*). When NR was peeled (*Figure 3*), the separation energy was highest against glass treated with acid (1 h soak in $2M$ HCl), particularly if the glass had been dried at 400°C , but intermediate or least when the glass was simply cleaned with IPA or treated with alkali (1 h soak in $2M$ NaOH). This observation implies that NR exhibits a nett basic character.

The highest values of W_o resulted when NR was brought into contact with glass cleaned with IPA. On the other hand, W_o was lowest at short contact times when contact was made with acidified glass dried at 400°C . There appears to be a change in the kinetics of interface formation that leads to an opposite ranking in adhering energies (albeit at a lower level) compared with peeling. Interface formation is slower on acidic glass. Heating of the glass at 400°C accentuates this tendency.

By heating coverslips at 400°C , the surface energy of the glass is increased due to the elimination of adsorbed compounds from its surface, especially water¹⁴. This is well-confirmed by the peel experiments with NR that show correspondingly high levels of adhesion. It may be inferred that the 'atmosphere layer' present on the glass, mainly water, plays an important role in the kinetics of the rubber/glass adhering process and in the level of interactions across the interface. This led us to study in more detail the effect of humidity upon rubber/glass adhesion.

Effect of Humidity

Peeling and adhering experiments were performed at three relative humidities: 6%,

55% and 100%. The glass coverslips were dried for 30 min at 400°C and, after a delay of 30 s for cooling to room temperature, brought into contact with clean rubber hemispheres.

Heating makes the glass highly hydrophilic (see water contact angles, *Table 2*) and adsorption of water reduces considerably its surface free energy^{14,18}. As a consequence, a reduction of rubber/glass adhesion with increasing humidity can be foreseen. The peel experiments (*Figure 4*) illustrate well the sensitivity of rubber/glass systems to humidity.

The peeling energy, W_p , for NR is four to five times lower at 100% than at 6% humidity. A reduction in the reversible work of adhesion W_o due to the presence of water vapour is a suitable explanation for this effect. Given that the spreading pressure of liquid is usually small on polymer surfaces¹⁵, the reduction of W_o can be mainly related to the spreading pressure, π , of water vapour on glass.

The action of humidity in peel experiments can be imagined as shown in *Figure 5a*. Water reduces the surface free energy of the glass without altering the rubber/glass interface.

In the foregoing peel experiments it is emphasised that rubber and glass interfaces were initially dry, and brought into contact in that state. Once contact had been established the adhering surfaces were placed in either a low or high humidity environment. Peeling was then carried out in that environment. An alternative to this procedure was to bring contact surfaces together in a high humidity environment ($\sim 100\%$ RH). This contact system was easily unpeeled (low W_p values), as shown by the so-called 'wet' glass results of *Figure 4*. It is believed that the water layers present on surfaces before contact is made (*Figure 5b*) explain why the peel adhesion is so low. This is not to be confused with the way in which water vapour, condensed in the crack of adhered dry surfaces, helps the crack opening (*Figure 5a*).

Adhering experiments were carried out in which initially dry glass and rubber surfaces were gently touched together. They were then

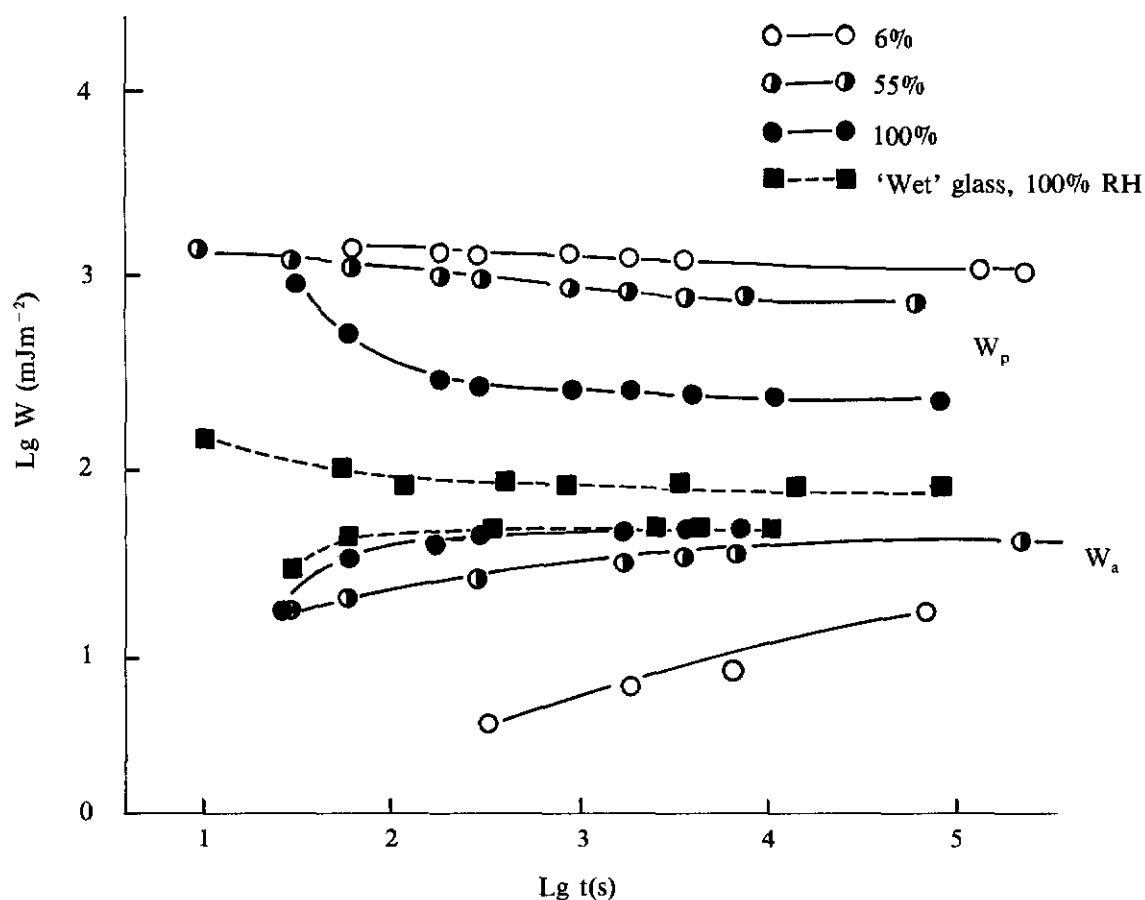
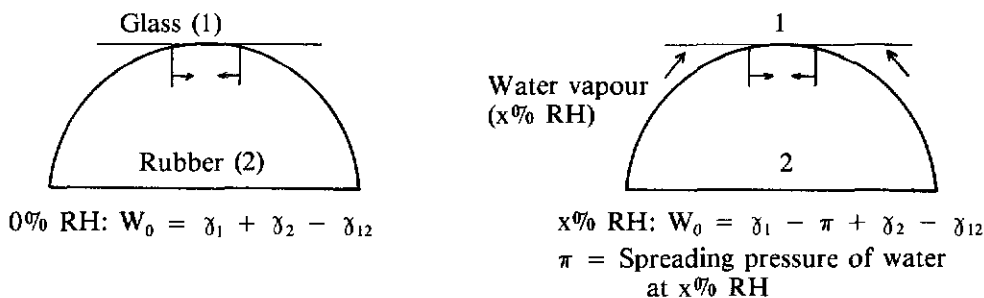


Figure 4. Influence of relative humidity on contact energies of NR against glass.

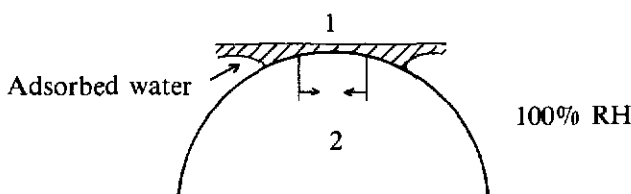
transferred to an environment of higher humidity. Surprisingly, it was found that the highest apparent adhering energy, W_a , was obtained at 100% RH (Figure 4) and the least at 6% RH. The unexpected result may mean that condensed water vapour at the contact periphery is helping to bring surfaces into an extended contact due to the effect of liquid surface tension. This is reminiscent of earlier work by McFarlane and Tabor¹⁹ and Isrealachvili *et al.*²⁰ concerning the influence of liquid films on the adhesion between solid surfaces. They found, for example, that glass surfaces adhered better as the relative humidity was increased above 80%. In the case of rubber/glass contact, suppose the condensed water

vapour forms a meniscus having a radius of curvature r . The capillary pressure, P , created by this meniscus is T/r , where T is the surface tension of water, and $r < A$ and a . The corresponding capillary force, F , 'drawing' the glass coverslip against the rubber hemisphere is $P\pi(A^2 - a^2)$, where A is the radius of the edge of the circular meniscus where it touches the glass and a is the radius of the Hertz contact circle. Given that water fully wets the dried glass (Table 2), the following expression can be deduced from simple geometric considerations.

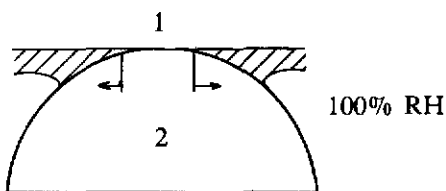
$$F = 2\pi TR (1 + \cos \Theta) \quad \dots 5$$



a. Action of water vapour in the separation of rubber from dry glass.



b. Peeling of rubber from 'wet' glass at 100% RH.



c. Formation of contact at 100% RH.

Figure 5. Intervention of humidity in the breaking and making of the rubber/glass interface.

Thus, it appears that F is independent of the meniscus radius r , that is, of the amount of liquid condensed in the contact periphery, but directly proportional to the rubber hemisphere radius R . Similar conclusions were established by McFarlane and Tabor¹⁹, Isrealachvili et al.²⁰ and O'Brien and Herman²¹.

F can be considered as an additional load that increases the contact radius a . This capillary effect leads to an overestimation of the

actual value of the reversible energy of adhesion, W_{ow} , between glass and rubber in the presence of water. The water of W_{ow} may be estimated from JKR¹ theory by the following expression

$$W_{ow} = \frac{3}{32\pi a^3} \left[\frac{16Ea^3}{9R} - (F + P) \right]^2 \quad \dots 6$$

From Equations 5 and 6, the reversible energy of adhesion W_{ow} has been calculated from the

equilibrium contact radius obtained at 100% RH for a range of rubbers (*Table 3*). It is clearly demonstrated that water reduces the Dupre work of adhesion in the rubber/glass contact. Thus the surface tension effect can explain to some extent the unexpected results obtained from the adhering experiments.

In support of the notion that condensed water vapour can extend the 'touch-on' contact area, a series of contact observations were made as follows. Dried glass was brought into touch-on contact with dried NR. The contact area observed was rather small (*Figure 6a*) though it grew a little with increasing dwell time. However, when the surrounding air was saturated with water vapour the contact began to grow quite quickly towards a larger size (*Figure 6b*). This demonstrated in a readily visible way the effect of condensed water in drawing the rubber into an enlarged contact with the glass. The effect was photographed both for sulphur (*Figure 6*) and peroxide cured NR. Similar results were obtained with chloroprene rubber, so it can be foreseen that the role of water in the formation of the rubber/glass contact is not a phenomenon particular to a given rubber.

Influence of Rubber Properties

It is generally agreed that the separation process involves dissipation phenomena (elastic

and viscoelastic) that increase considerably the work necessary to peel apart adhering rubber-like solids^{2,3,17}. This point is illustrated by the data presented in *Figure 7* for a range of rubber types. The higher the glass transition temperature, T_g , of a particular rubber, the higher its level of peel energy and the slower its separation kinetics. The same figure also shows that the higher the T_g , the slower a rubber makes contact. In addition, the higher the T_g the greater the difference in levels of adhering and peeling energies. Clearly, T_g has a direct influence upon the amplitude of the apparent hysteresis between the making and the breaking of contact. The more elastic a rubber, the less is the hysteresis.

Hydrophobic Surfaces

The contact phenomena were re-examined for a *cis*-polyisoprene rubber hemisphere against a coverslip of PMMA ('Perspex'). Both attract less water than NR and glass, respectively. Adhesion levels were found to be less sensitive to ambient humidity (*Figure 8*), but even so there was a ranking that showed the same pattern of behaviour as previously. In particular, the drier the surroundings (and presumably the higher the free surface energies) the higher the level of peel energy but the lower the adhering energy.

TABLE 3. APPARENT AND CORRECTED VALUES OF W_{ow} AT 100% RH

Rubber	Θ (degree)	F (N)	$W_a(\text{mJm}^{-2})$	$W_{ow}(\text{mJm}^{-2})$
NR	76.5	0.0104	48.4	7.2
CR	77	0.0103	36	2
NBR	82.5	0.0095	52	12.2
SiR	110.5	0.016	29	6.4

F calculated from *Equation 7*

Θ by direct measurement of water drop on rubber surface

$$W_{ow} = \gamma_{1w} + \gamma_{2w} - \gamma_{12}$$

1 = glass

2 = rubber

W = water

γ_{iw} = interfacial free energy between solid and water ($i = 1$ or 2)

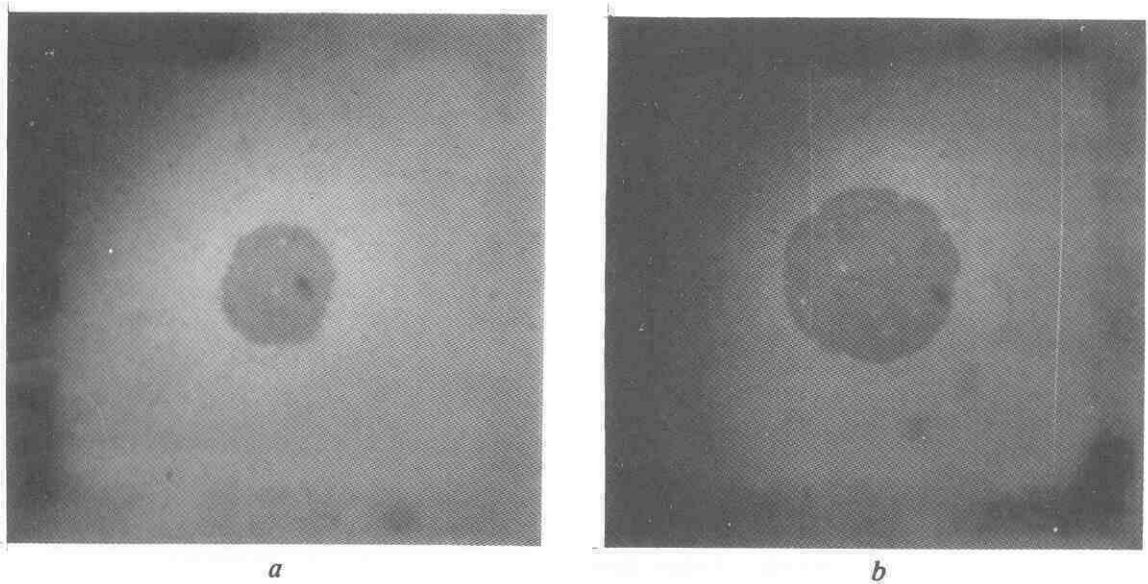


Figure 6. (a) Natural rubber in adhering contact with dried glass after 1.25 h dwell time, 6% RH ($2a = 0.623$ mm, $W_a = 8$ mJm⁻²). (b) The same contact pair after 1 h exposure to 100% RH, showing how the contact area has grown in size ($2a = 0.943$ mm, $W_a = 38$ mJm⁻²).

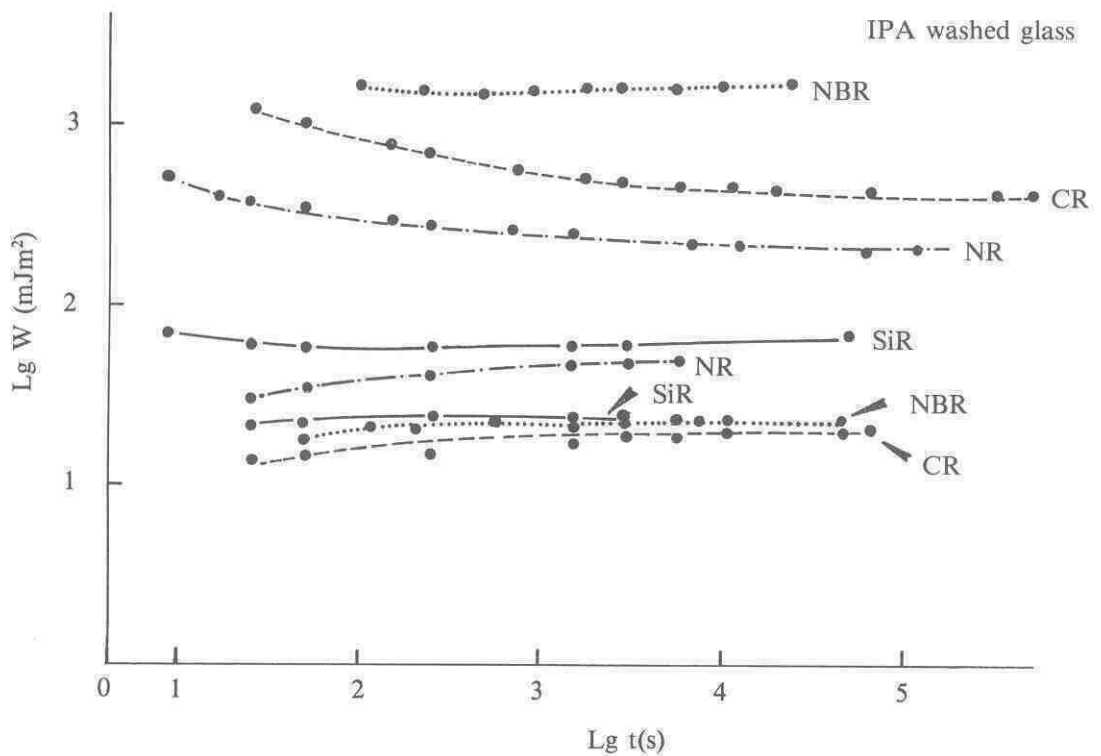


Figure 7. Influence of hysteresis properties on contact energies of different rubbers against glass.

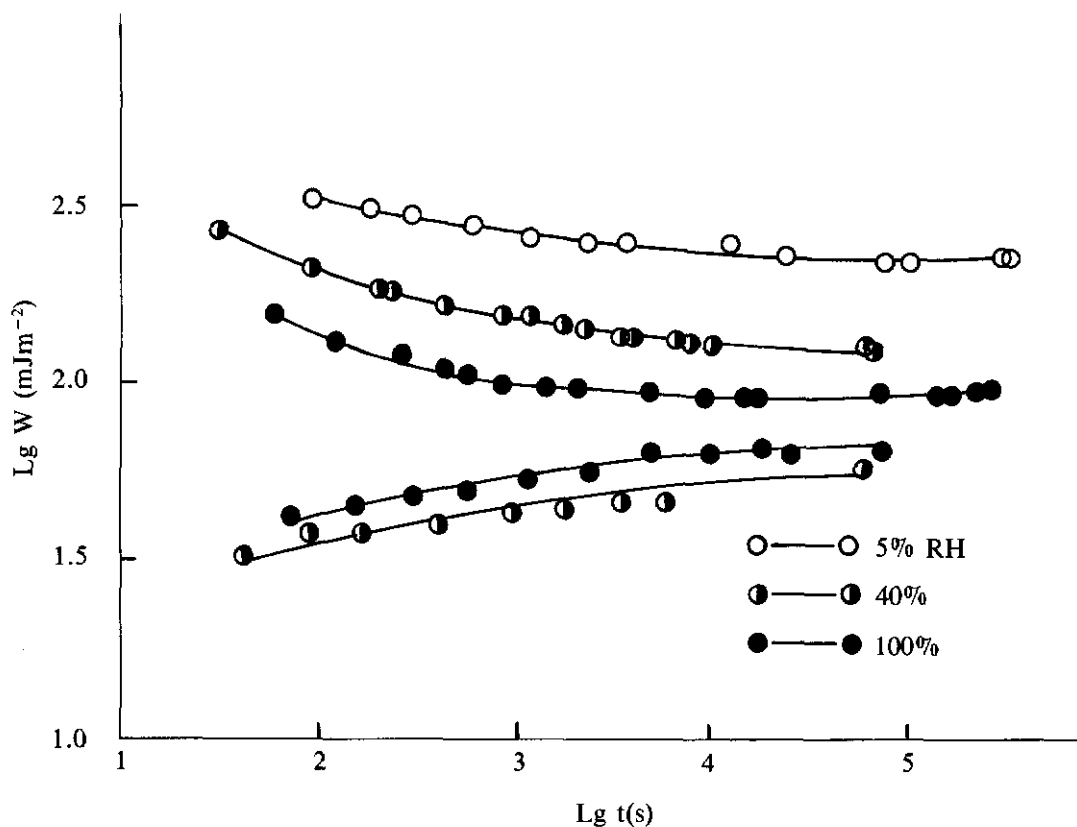


Figure 8. Influence of relative humidity on contact energies of isoprene rubber against PMMA.

Interfacial Shear Strength

Measurements were made for the sliding of a NR hemisphere against glass, PMMA and polyethylene (PE) as a function of the ambient relative humidity (Figure 9). Only friction on the glass showed sensitivity to humidity. This observation may relate to the touch-on adhesion of rubber to glass, if it is assumed that there is some small degree of interfacial microslip²². When surfaces are dry the friction at the advancing contact periphery may be high and therefore hinder the advance. It was often seen that when glass surfaces were contaminated with hydrocarbon residues, or water layers were present at high humidity, then contact areas in touch-on contact rapidly advanced towards their equilibrium value. This suggests thin film lubricant action.

DISCUSSION

In the original elastic contact adhesion experiments¹, measurements were made for rubber against rubber (polyisoprene) and this yielded a value of $71 \pm 4 \text{ mJm}^{-2}$ for the contact pair, corresponding to an energy of 35 mJm^{-2} for each dry surface assuming the γ_{12} term to be zero. This is a reasonable value for a hydrocarbon surface. Subsequently, it became apparent that energy values for rubber/glass contact were smaller than for rubber/rubber, this being so for a range of rubbery polymers¹⁰. This study shows that by treating substrate glass surfaces, either chemically or physically, the level of adhesion can be changed to a large extent. Acid-base interactions may be inferred. Adsorbed water films, mainly associated with the glass surface, appear

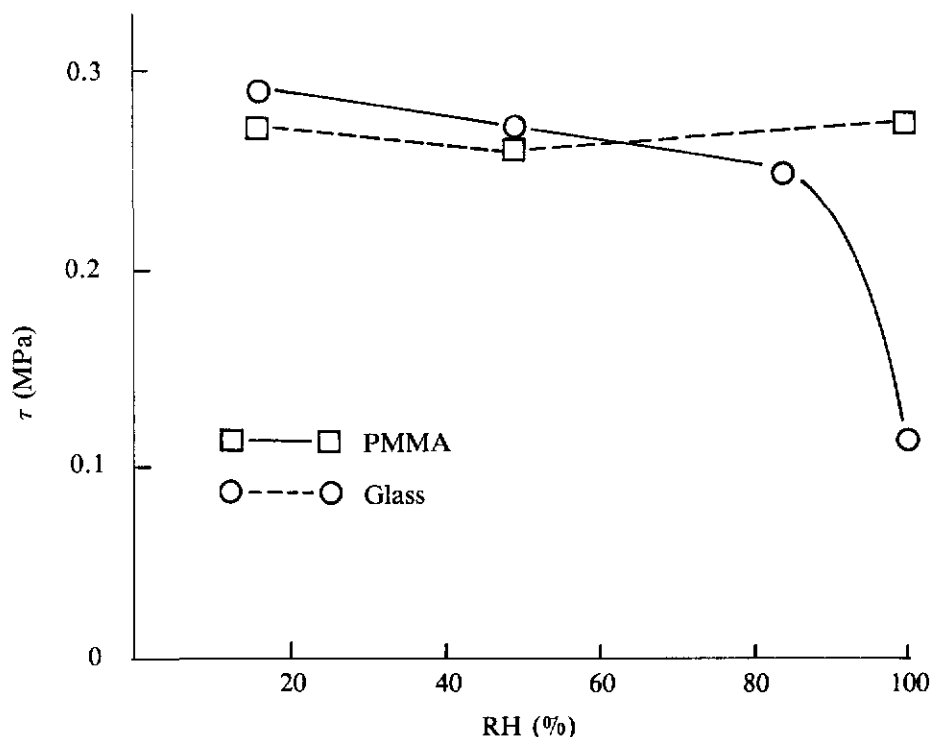


Figure 9. Variation in shear strength with humidity for NR hemisphere sliding on flat substrate under a mean contact pressure of 0.1 MPa.

capable of pulling rubber and glass surfaces together by capillary action. Measurement of the touch-on contact area formed at high humidity leads to a high value of apparent free surface energy, as had incidentally been observed for rubber against ice²³. However, when surfaces were peeled apart under high humidity, the associated energy was low. Dry surfaces, on the other hand, may exhibit only a small touch-on contact area (low RH) but require considerably more energy to separate. Thus it appears that adsorbed water films can complicate the interpretation of touch-on surface energy measurements, a falsely high energy being deduced from the observed contact radius due to capillary action. An allowance can be made for this action, whereupon 'true' solid-solid contact energies in the presence of water might be derived.

The overall pattern of adhesion results quite definitely suggest that with increasing free

surface energy W_o and increasing 'lossiness' of a rubber (as indicated by a high value of T_g) the level of peel energy W_p increases, whereas the adhering energy W_a decreases. This may offer clues as to the adhesion mechanism. One may ask whether rate-dependency in the different cases of peeling and adhering are the same.

In the case of making contact one may write

$$W_o - G = W_o \alpha (V, T) \quad \dots 7$$

where G is the instantaneous value of W_o and $\alpha (V, T)$ is a dissipation factor, so that visco-elastic losses rise as W_o increases. At equilibrium $G = W_o$, which means that $\alpha \leq 1$.

In the case of peeling to break contact one may write:

$$G - W_o = W_o \cdot \phi (V, T) \quad \dots 8$$

where G is the instantaneous value of W_p and $\phi(V, T)$ is a dissipation factor, noting that $\phi \geq 0$. To investigate matters the variation of ϕ and α with rate was examined using the experimental data for the making and breaking of contact. This was done by plotting ϕ and α against the average rate of movement at the contact periphery given by $\Delta t/\Delta a$, noting that $\alpha = 1 - (W_o/W_o)$ and $\phi = (W_p/W_o) - 1$. A value for W_o was taken from the *quasi*-stable touch-on contact diameter. Using the IPA washed glass data of Figure 3, the results for NR are shown in Figure 10, plotted as a function of reduced rate $a_T V$ where $V = \Delta t/\Delta a$ and a_T is the WLF shift factor²⁴. Data for two other rubbers, polychloroprene and silicone (Figure 7), are also plotted in the same way onto Figure 10. Gradients, m , of lines through the points are indicated. It is clear that ϕ and α are of different magnitude. Further, although this is an $a_T V$ plot which takes account of different rubber glass transition temperatures, the peel data do not form a continuous line — and that is in spite of normalising the peel energy by the equilibrium energy, *i.e.* (W_p/W_o) . It implies that W_o and $\phi(V, T)$ may not be separable, contrary to Equation 8.

The experimental observations for NR in contact with acidified glass dried at 400°C (Figure 3) were also examined in terms of ϕ and α . Unfortunately, it is not clear from the touch-on data what to take for a value of W_o . As the glass was baked it seems not unreasonable to suppose a higher equilibrium contact energy than for the IPA washed glass and so, conservatively, a value of 100 mJm⁻² was assumed. The results of these calculations are also plotted in Figure 10. Looking first at the adhering values of α , although the results for all rubbers against IPA washed glass do approximately form a continuous line, there is an upward jump for baked glass. Looking next at the peel values of ϕ , a similar jump is seen for baked glass. Once again, an inference is that α and ϕ may not be separable from W_o .

Thus, the general impression given by the results of Figure 10 is that energy losses, as indicated by α or ϕ , increase with surface energy and with glass transition temperature.

Precisely how this comes about must await further analysis. However, it may be anticipated that differences in geometry at the crack tip when making or breaking contact will have an effect. The curvature of the crack will be different, and most importantly, the crack tip strain will be greater when breaking contact making the strain fields for peeling and adhering scale differently with surface energy. If it is assumed that losses are proportional to the energy stored in the strain field, then dissipation of energy will be greater during peeling. Although the strains are different in the two cases, the rate-dependency is likely to be similar. This would lead to parallel plots of ϕ and α against V , but displaced due to different strains (see Figure 10).

There remains the question of what is the value of the reversible interfacial energy of contact, in the absence of bulk polymer losses. Our optical contact experiments indicate (Figure 7) that the touch-on 'equilibrium' energy value of W_o for polychloroprene is 25 mJm⁻² and for NR 63 mJm⁻². Yet the wetting angles of water against these two rubbers are virtually the same, 77° and 76.5° respectively (Table 2). The suspicion is that the optical touch-on values of surface energy are affected by viscoelasticity; that neither the value for polychloroprene, nor NR, are truly reversible values, but underestimates. This prompts us to hypothesise as follows.

Suppose the optical contact experiments amount in effect to the wetting of rubber by water, because glass at normal room humidity and temperature is covered by several molecular layers of water. Then it may be considered that the reversible contact energy is given by the Young-Dupre relation (Equation 3). Such values for different rubbers are given as W_{SL} in Table 2, and lie between the minimum of W_p and the maximum of W_a found from the optical contact experiments (Figure 7). Note that the low level of energy values for silicone rubber are satisfactorily accounted for. Even so, there is a considerable difference in energy level between the minimum of W_p and W_{SL} , and that between W_{SL} and the maximum of W_a is not negligible.

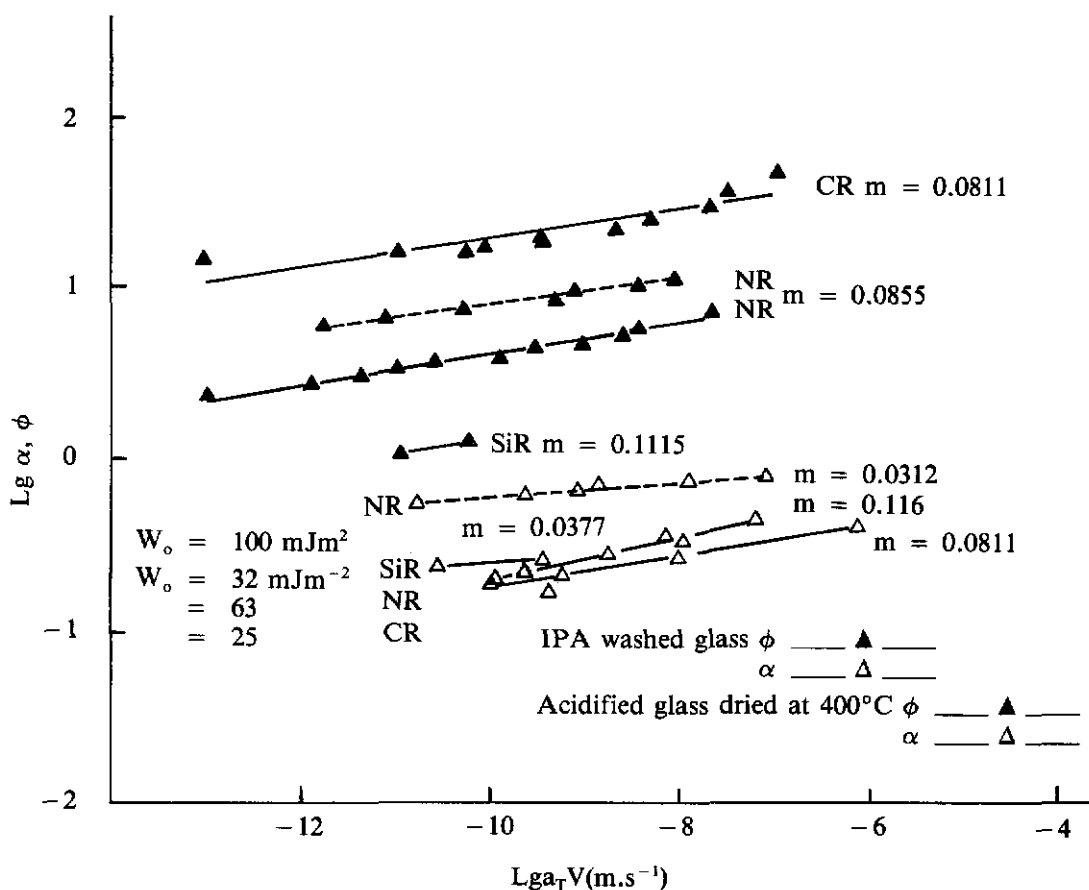


Figure 10. α and ϕ as a function of reduced rate $a_T V$.

With regard to the peel energy values (Figure 7) it may be argued that W_p (min)/ W_{SL} represents the parameter g of Equation 4. For the rubbers studied one then finds g values of 5.1 (polychloroprene), 2.6 (NR), 1.7 (silicone rubber) and 24 (acrylonitrilebutadiene). In their study, Lake and Thomas¹⁶ found values of g up to 10. However, it could be that the long-term constancy of W_p (min) may be due to some other effect, such as for example, the well-known dwell time effect whereby the interface adhesion rises with the time of contact. Another possible reason for a value of W_p (min) greater than W_o may be due to bulk stress relaxation of the rubber hemisphere, so removing the driving force (stored elastic energy) that unpeels surfaces. In particular,

stress relaxation may account for the high W_p (min) of acrylonitrilebutadiene rubber.

Concerning adhering energy values, W_a , found from the optical experiments (Figure 7) it is seen that they are all in differing amounts less than W_{SL} . The more viscoelastic a rubber, the lower is W_a . This may be due to viscoelastic delay.

It was noted in an earlier investigation¹⁰ that the adhesion of NR to PMMA is larger than to glass. One may ask why. Natural rubber is hardly polar, so London dispersion forces are likely to predominate in its adhesion against PMMA and glass. The contribution these forces make to the contact adhesion energy can be calculated¹⁵ according to the expression

$$W_o \approx 2 (\gamma_1 D \gamma_2 D)^{1/2} \quad \dots 9$$

where $\gamma_1 D$ and $\gamma_2 D$ represent the dispersion components of the free surface energies of the rubber and the other solid. For PMMA $\gamma_2 D = 43 \text{ mJm}^{-2}$ ²⁵. If one considers that the glass is completely covered by a film of water, one can accept that $\gamma_2 D \approx D_{\text{water}} = 21.6 \text{ mJm}^{-2}$ ²⁶. Suppose that for NR $\gamma_1 D \approx 30 \text{ mJm}^{-2}$, as most non-polar rubbers, then Equation 9 leads to:

$$W_o(\text{NR/PMMA}) = 2(30 \times 43)^{1/2} = 72 \text{ mJm}^{-2}$$

$$W_o(\text{NR/glass}) = 2(30 \times 21.6)^{1/2} = 51 \text{ mJm}^{-2}$$

Even if one does not know $\gamma_1 D$, the ratio $W_o(\text{NR/PMMA})/W_o(\text{NR/glass})$ is $(43/21.6)^{1/2} = 1.4$.

Thus it may be expected that the adhesion of rubber to PMMA will be greater than to glass. In the earlier investigation¹⁰ static contact energies were about 20% greater, and peel energies 50%–90% greater against PMMA depending on peel rate.

A general point is that there is an experimental difficulty in measuring W because of its insensitivity to contact radius ($W \propto a^{1/2}$). This can lead to uncertainty as to whether a constant energy value has genuinely been reached.

Turning now to practical matters, it is observed with windscreen wiper blades that the highest friction occurs in operation just as the windscreen is becoming dry. The implication is that capillary forces at this moment are sufficiently powerful to pull the rubber blade lip into maximum contact with the glass. On finally drying out real contact is diminished and the friction falls. Similar effects may arise with rubber gloves. These are generally easier to pull on when dry, rather than when slightly moist. The practical implications of the present study are numerous.

CONCLUSION

Measurements of rubber/glass and rubber/plastics adhesion reveal the importance of surface preparation in determining the level of adhesion. Adhesion for NR is increased by acid treatment of glass substrates or by heating them

to 400°C. It is reduced by adsorbed water films, despite larger apparent radii of contact. Details of mechanisms associated with the different levels of adhesion came from simple experimental observations of the change in contact radius with time. A way of analysing the observations was to plot apparent energy dissipation factors in peeling and adhering as a function of the rate of movement of the contact periphery. Peel dissipation increased with rate and always resulted in energy values greater than that of the reversible interfacial energy as estimated by wetting measurements. The source of the peel dissipation may be both elastic and viscoelastic in nature. Adhere dissipation also increased with rate, but acted to diminish the reversible energy and appears to be viscoelastic in nature.

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