Adhesion of Model Elastomers to Glass: Effects of Surface Treatment of Glass *

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The strength of adhesion of various elastomers, crosslinked in situ by a free-radical process, to Pyrex and quartz substrates was studied. The joint strength obtained depends on the etching agent employed to clean the glass plate after use. Scanning electron micrographs of etched glass plates suggested surface contamination by residual rubber but not surface roughness of the substrate as the cause of the difference in peel strength. Treatment of clean glass with allyl isocyanate, n-propyl isocyanate, vinyldimethylethoxysilane but not trimethylmethoxysilane gave up to a four-fold improvement in the strength of adhesion of suitable elastomers to glass. Similar wettability obtained for untreated and treated glass suggested interfacial chemical bonding as a possible cause of the enhancement of joint strength observed.

In adhesives technology, two common bonding techniques practised are:

- The surface of each adherend is roughened to obtain a stronger joint.
- Adhesives or coupling agents capable of forming chemical bonds with the adherends are used to obtain a more durable joint especially under exposure to high temperature or to a corrosive environment.

Careful and systematic experiments, however, have shown that the influence of surface roughness on adhesive joint strength is not unambiguous, ranging from either a strengthening[1-3] or a weakening[3] effect to no effect[4,5]. Likewise, opinions on the formation of chemical bonds at the interface range from those convinced[6-10] to those doubtful[11-13] of its occurrence or importance. Indeed, the necessity for interfacial chemical bonding is questioned and it is argued that complete wetting leading to physical adsorption of the adhesive by the adherend is more than sufficient to form joints which are stronger than the cohesive strength of existing adhesives[14].

This paper discusses the quantitative comparison of the effects of treating glass plates with several commonly used etching agents on the strength of elastomer-glass adhesion. A qualitative comparison of the surface roughness and cleanliness of the etched plates with the aid of scanning electron microscopy would provide an insight into the relationship between surface roughness or surface contamination and the measured joint strength. This paper also compares quantitatively the effects of treating glass plates with model isocyanate and silane coupling agents on the strength of elastomer-glass adhesion.

EXPERIMENTAL

Sample Preparation

The borosilicate (7740 Pyrex, Corning Glassworks) and quartz (TO 8 fused quartz, Amersil Inc.) glass plates (12.70 × 2.54 × 0.64 cm) were cleaned by immersing in a given etching agent for 16 h at 95°C. Rinsing of the etched plates was effected by extraction with distilled water for 24 h in a Soxhlet apparatus. These etched and rinsed glass plates were dried either under ambient conditions for 24 h or in a vacuum oven for 16 h at 80°C. For silane or isocyanate

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treatment, chromic acid-etched Pyrex and quartz plates were evacuated in a stainless steel cell (20.3 cm long, 8.9 cm diameter and 6.4 cm internal diameter) at 400°C or 530°C for 5 h under 10^{-4}–10^{-5} torr pressure. After cooling to room temperature, the evacuated plates were exposed to the vapour of the coupling agent at 33°C for 3 h or 6 h. This was followed by overnight evacuation (*ca.* 10 h) of the treated plates at room or slightly elevated temperatures. The treated plates were used within 1 h of disassembling the reaction cell. A schematic diagram of the vacuum system used for evacuating and treating the glass plates is shown in *Figure 1.*

Mixing of the crosslinking agent into the elastomer was effected on a two-roll mill, without preheating the rolls. To obtain a *cloth-backed elastomeric layer,* a sheet of cloth was pressed against a prepressed sheet of the milled elastomer in a hydraulic press for 1 h at 60°C for polybutadiene (PB: Diene 35 NFA, Firestone Synthetic Rubber and Latex Co.), or 80°C for ethylene-propylene copolymer (EPR: Vistalon 404, Exxon Chemical Co.) and ethylene-propylene-diene terpolymers (EPDM: Vistalon 4608 and 6505, containing 3.2 and 9.0 weight per cent diene respectively, Exxon Chemical Co.).

The glass plates were placed on the cloth-backed elastomer layer in a metal mould frame, between two steel backing plates, and the mould was heated for 2 h in the hydraulic press at 150°C for PB, or 160°C for EPR and EPDM (6505 and 4608). The crosslinked elastomeric layer (0.03 $\pm$0.01 mm thick) was then trimmed with a sharp razor blade to remove the excess portion at the edges of the plate, giving an elastomeric layer width of about 2 centimetres.

Peel Tests

The 180° peel test *(Figure 2)* was used to determine the strength of elastomer-glass adhesion by means of the Instron Tensile Tester. For each test-piece, the elastomer layer was peeled off the glass substrate at several constant peel rates; five or more test-pieces for each elastomer-glass combination were usually tested to obtain an average value of the peel strength of the joint at each peel rate. Peel measurements were generally made at 20°C, but several test were also made at 80°C to obtain near-
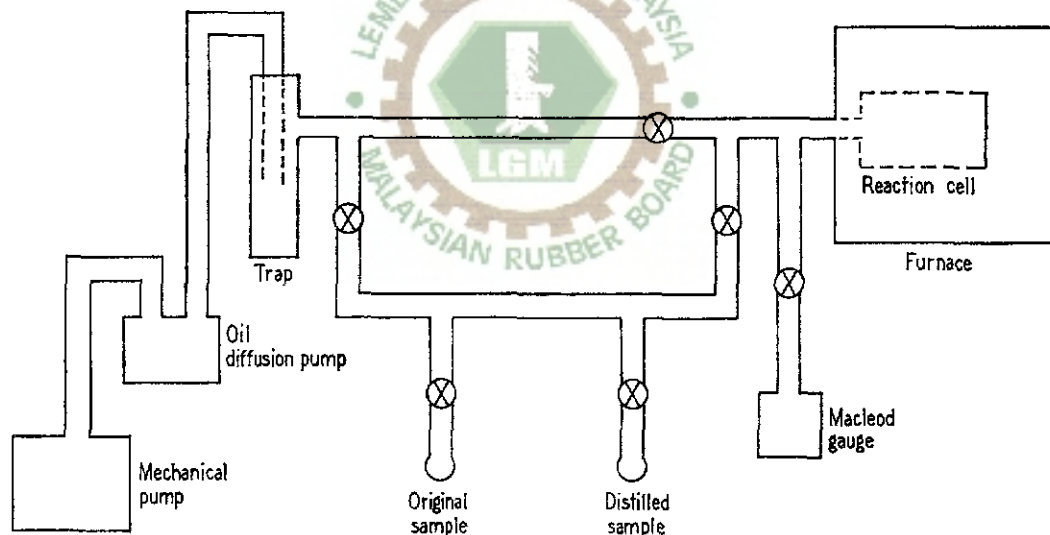

Figure 1. Schematic diagram of vacuum system.

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zero rate strength of adhesion values. In addition, several peel tests were conducted in the presence of distilled water at 20°C and 80°C over a range of peel rates.
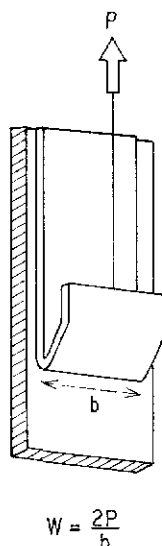

$$W = \frac{2P}{b}$$

Figure 2. Schematic representation of 180° peel configuration.

Scanning Electron Microscopy

A scanning electron microscope was used to examine the surface roughness and contamination of the glass substrate. Each glass plate to be examined was coated with a thin layer of gold in a vacuum evaporator (JEOL JEE 4C) after having evacuated the sample chamber to better than 10^{-5} torr pressure. The coating of gold was to prevent charging of the glass plate (an insulator) when irradiated by a beam of electrons in the scanning electron microscope (JEOL JSM-U3). For examination of the glass surface, the specimen chamber of the electron microscope was evacuated and an accelerating voltage of 25 kV was used to generate the electron beam impinging on the glass plate, which was tilted at 20° to the horizontal. From the scanning electron microscope image thus obtained, a representative area of the glass surface was selected and photographed under various magnifications.

Measurement of Contact Angles

A drop of liquid (*ca.* 1µlitre) was placed on the glass surface. To minimise evaporation of the liquid during the measurement, the entire system was enclosed with pans containing the same liquid in a closed box with transparent windows. The dimensions of the drop were determined from pictures taken of the drop at regular time intervals over a period of 10 minutes. By extrapolating the linear portions of the contact angle *versus* contact time plots back to zero time of contact, values of the effective contact angle in the absence of both spreading and evaporation were obtained, as recommended by Gent and Schultz[15].

RESULTS AND DISCUSSION

Effects of Relaxation Properties of Elastomer on Adhesion

The elastomers used were viscoelastic materials, and the measured strength of adhesion by mechanical separation of the elastomer from the rigid glass substrate was expected to depend on the Williams-Landel-Ferry (WLF) rate-temperature equivalent principle and the degree of crosslinking of the elastomer. An illustration of the dependence of the strength of elastomer-glass adhesion obtained in the present study on the viscoelastic response within the elastomer is given in *Figure 3:* a smooth curve was obtained when a plot of $(T_g/T)W$ against $\log_{10}Ra_T$ was made for each elastomer. The effective rates of detachment Ra_T at the glass temperature, T_g of the elastomer were calculated for each experimental rate R and test temperature T using the WLF relation:

$$\log_{10}Ra_T = \frac{-17.4\,(T-T_g)}{(51.6 + T - T_g)} \qquad \cdots (1)$$

For PB the T_g used was -90°C, while that for EPR was -60°C. The measured work of adhesion W was multiplied by a factor (T_g/T), according to convention. Ahagon
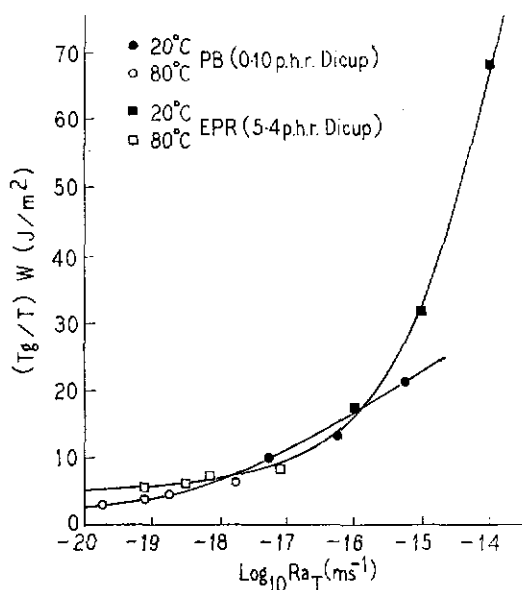
Figure 3. Work of adhesion W versus effective peel rate Ra_T at T_g for polybutadiene (0.10 p.h.r. Dicup) and ethylene-propylene copolymer (5.4 p.h.r. Dicup) adhering on chromic acid-etched quartz.

and Gent[9] have earlier reported that the strength of polybutadiene – Pyrex adhesion, measured as a function of peel rate at different temperatures, obeys the WLF rate-temperature superposition principle.

It is well known that the energy dissipation occurring within an elastomer in the region of rubbery response increases as the degree of crosslinking of the elastomer decreases. This increase in energy dissipation with decrease in crosslink density of the elastomer would be expected to influence the peel strength of elastomer-glass joints in a similar way *i.e.* for similar surface condition, the peel strength would increase with decrease in degree of crosslinking of the elastomer at a given peel rate. This effect appears to be borne out by the peel strength data shown in *Table 1* for PB and EPR adhering to chromic acid-etched Pyrex. Measurements of the strength of adhesion of PB and EPR to Pyrex and quartz, treated in various

etching agents, all indicated an increase in peel strength with a decrease in crosslink density of the elastomer. A similar observation that stronger adhesive joints were obtained with the less-crosslinked vulcanisates was made by Kendall[16], who eliminated shrinkage effect arising from crosslinking of the elastomer in preparing natural rubber-glass joints.

Effect of Surface Contamination of Glass on Adhesion

It was found that the strength of elastomer-glass adhesion obtained depended on the type of etching agent used to clean the glass plates after use. *Table 2* gives the peel strength data obtained for PB and EPR adhering to variously-etched Pyrex substrates. The peel strength values given by both chromic acid-etched and 1% HF-etched Pyrex were similar but were lower than those obtained with 1% and 85% H_3PO_4-etched Pyrex, both of which gave similar values of peel strength. It was observed, however, that new Pyrex plates treated in these etching agents all gave the same strength of adhesion for a given elastomer adhering on the differently-etched substrates; similar results were also obtained with new Pyrex cleaned only by Soxhlet extraction with distilled water *(Table 3)*. The similarity of peel strength values obtained with new Pyrex plates subjected to the different cleaning treatments suggests that the strength of elastomer-glass adhesion is unaffected by chemical changes at the surface of the glass caused by these different etching agents. Rather, a specific surface contamination effect is the likely cause of the different peel strength values obtained with the used plates after cleaning in the various etching agents.

A probable candidate would be rubber left on the glass substrates: many instances of microzones of cohesive failure have been reported in which apparent interfacial failure was observed by visual inspection[17,18]. In

TABLE 1. EFFECT OF DEGREE OF CROSSLINKING OF ELASTOMER ON STRENGTH OF ELASTOMER-PYREX (CHROMIC ACID-ETCHED) ADHESION AT 20°C

Elastomer	Work of adhesion, W (J/m^2)		
	0.42×10^{-5} (ms^{-1})	4.2×10^{-5} (ms^{-1})	42.0×10^{-5} (ms^{-1})
PB (0.07 p.h.r. Dicup)	37 ± 2	56 ± 7	92 ± 15
PB (0.10 p.h.r. Dicup)	24 ± 2	33 ± 6	43 ± 8
EPR (2.7 p.h.r. Dicup + 0.32 p.h.r. sulphur)	82 ± 8	162 ± 23	246 ± 6
EPR (5.4 p.h.r. Dicup + 0.64 p.h.r. sulphur)	24 ± 3	52 ± 8	118 ± 16

TABLE 2. EFFECT OF METHOD OF ETCHING OF PYREX ON STRENGTH OF ELASTOMER-PYREX ADHESION AT 20°C

Etching agent	Work of adhesion, W (J/m^2)		
	0.42×10^{-5} (ms^{-1})	4.2×10^{-5} (ms^{-1})	42.0×10^{-5} (ms^{-1})
PB (0.07 p.h.r. Dicup)-Pyrex			
Chromic acid	37 ± 2	56 ± 7	92 ± 15
1% HF	41 ± 9	55 ± 9	110 ± 8
1% H$_3$PO$_4$	57 ± 9	84 ± 14	151 ± 40
85% H$_3$PO$_4$	52 ± 4	75 ± 7	137 ± 33
EPR (5.4 p.h.r. Dicup + 0.64 p.h.r. sulphur)-Pyrex			
Chromic acid	24 ± 3	52 ± 8	118 ± 16
1% HF	25 ± 3	47 ± 7	113 ± 10
1% H$_3$PO$_4$	46 ± 6	90 ± 16	201 ± 37
85% H$_3$PO$_4$	50 ± 9	103 ± 21	210 ± 22

TABLE 3. EFFECT OF SURFACE CONTAMINATION BY RESIDUAL RUBBER UNREMOVED BY ETCHING TREATMENT ON STRENGTH OF ELASTOMER-PYREX ADHESION AT 20°C

Pyrex treatment	Work of adhesion, W (J/m^2)		
	0.42×10^{-5} (ms^{-1})	4.2×10^{-5} (ms^{-1})	42.0×10^{-5} (ms^{-1})
EPR (5.4 p.h.r. Dicup + 0.64 p.h.r. sulphur)-Pyrex			
New Pyrex etched in fresh 85% H$_3$PO$_4$	28 ± 4	52 ± 9	116 ± 20
Above Pyrex etched in 85% H$_3$PO$_4$ after peel tested once	43 ± 6	83 ± 10	177 ± 20
Used Pyrex etched in 85% H$_3$PO$_4$ followed by etching in chromic acid	26 ± 4	49 ± 7	103 ± 9
85% H$_3$PO$_4$-etched Pyrex heated at 530°C in air for 5 h	28 ± 6	52 ± 12	112 ± 17
Used Pyrex etched in chromic acid followed by etching in 85% H$_3$PO$_4$	23 ± 5	43 ± 13	92 ± 19
PB (0.10 p.h.r. Dicup)-Pyrex			
Chromic acid-etched	24 ± 2	33 ± 6	43 ± 8
New Pyrex extracted with distilled water for 24 h in Soxhlet apparatus	28 ± 4	36 ± 3	51 ± 6

the present study, evidence for the presence of gross surface contamination (presumably rubber patches) on the used glass plates was obtained using scanning electron microscopy. The scanning electron micrograph of a new Pyrex plate etched in 85% H_3PO_4 *(Figure 4)* shows no evidence of surface contamination, while that of a similar plate etched in 85% H_3PO_4 after being peel tested once *(Figure 4)* illustrates clearly the presence of patches of gross surface contamination. It was observed, however, that when the above contaminated plate was then etched in chromic acid, the resulting surface no longer showed gross contamination under the scanning electron microscope *(Figure 5)*. Etching in 1% H_3PO_4 was found to be similarly ineffective as 85% H_3PO_4 in removing rubber left on the glass after peel testing; heating such contaminated plates at 530°C in air for 5 h however, effectively removed the gross surface contamination *(Figure 5)*.

A comparison of the peel strength data given in *Tables 2* and *3* shows that new Pyrex plates etched in fresh 85% H_3PO_4 gave the same peel strength values as those obtained with used Pyrex plates after etching in chromic acid. However, these new Pyrex plates after being peel tested once, followed by etching again in 85% H_3PO_4, subsequently gave a higher level of peel strength characteristically obtained with used Pyrex etched in 1% and 85% H_3PO_4. *Table 3* also shows that for used Pyrex etched in 85% H_3PO_4, subsequent treatment by either etching in chromic acid or heating at 530°C in air for 5 h resulted in lowering of the peel strength obtained with these doubly-treated plates to values typical of those given by the new plates. It is further noted that the lower level of peel strength was also given by used Pyrex etched in chromic acid followed by etching in 85% H_3PO_4. Thus, the strength of elastomer-glass adhesion was significantly higher for glass surfaces con-

taining residual rubber not removed by the etching treatment, compared to that for etched glass free of such surface contamination.

The microregions of localised cohesive failure occurring during an apparent interfacial separation of the elastomer from the glass substrate probably arise from spots of inherent cohesive weakness of the surface structure of the elastomer as Kaelble[19] has suggested, or possibly are due to spots of inherently strong interfacial interactions. The possible reasons for the increase in peel strength caused by the presence of residual rubber not removed by the etching treatment are:

● The residual rubber was chemically modified by the etching agent resulting in stronger interactions with the fresh rubber during crosslinking of the latter.

● The residual rubber participated in further crosslinking with the fresh rubber causing a lowering of the degree of crosslinking of the elastomer in the interfacial region.

● A combination of the first and second reasons.

Effect of Surface Roughness of Glass on Adhesion

Apart from the cleaning effect of the etching agent, the etched glass surface was found to be roughened to different extents by the different etching agents. This is illustrated by the 85% H_3PO_4-etched new Pyrex surface in *Figure 4,* and by the used Pyrex after etching in chromic acid and 1% HF in *Figure 6.* The 1% HF-etched Pyrex surface consisted of a continuous network of craters of various sizes, while the chromic acid-etched Pyrex surface was relatively smooth except for a few isolated, small pits. The surface of the 85% H_3PO_4-
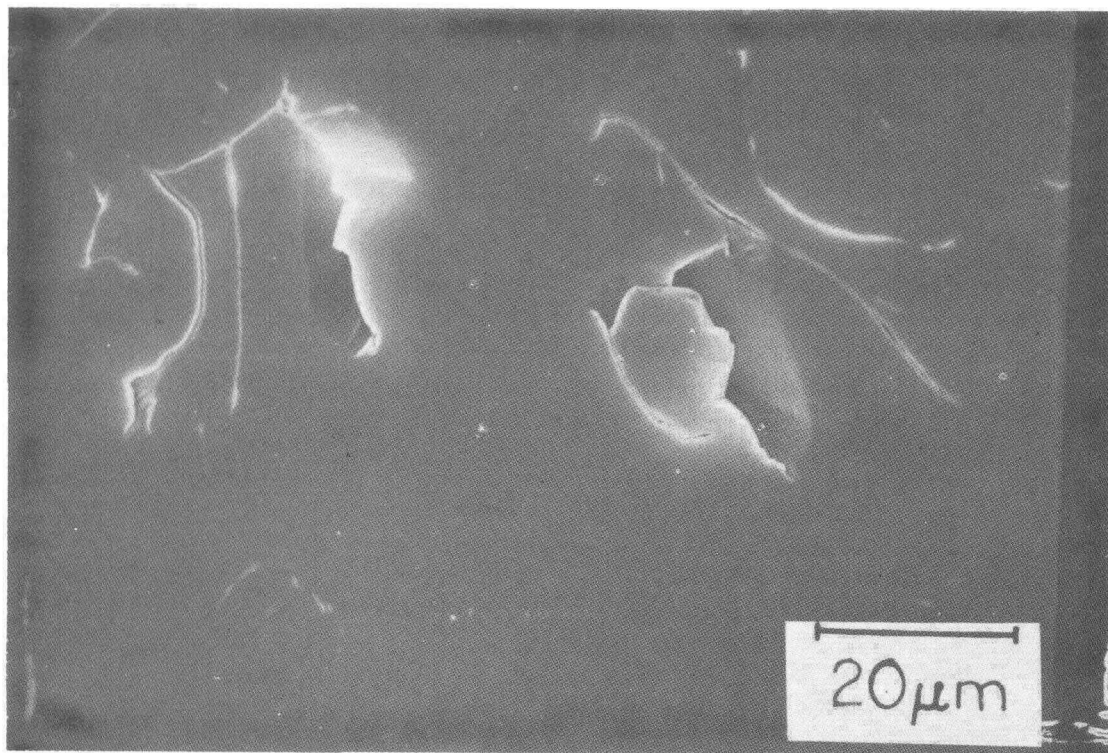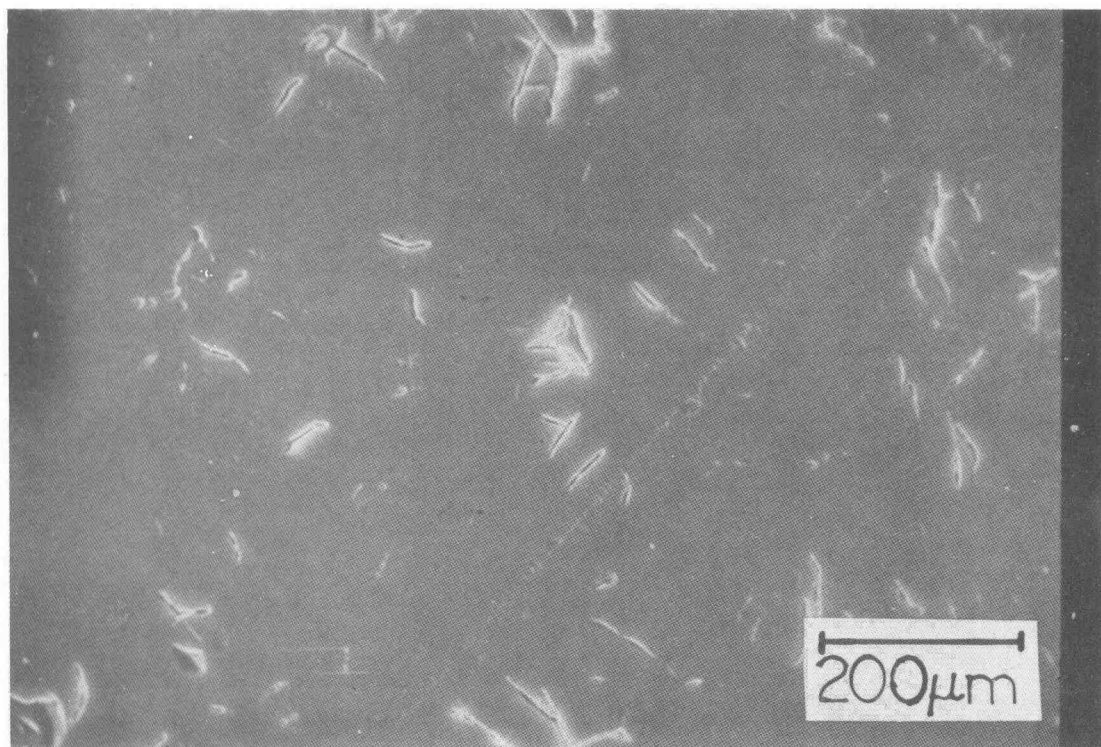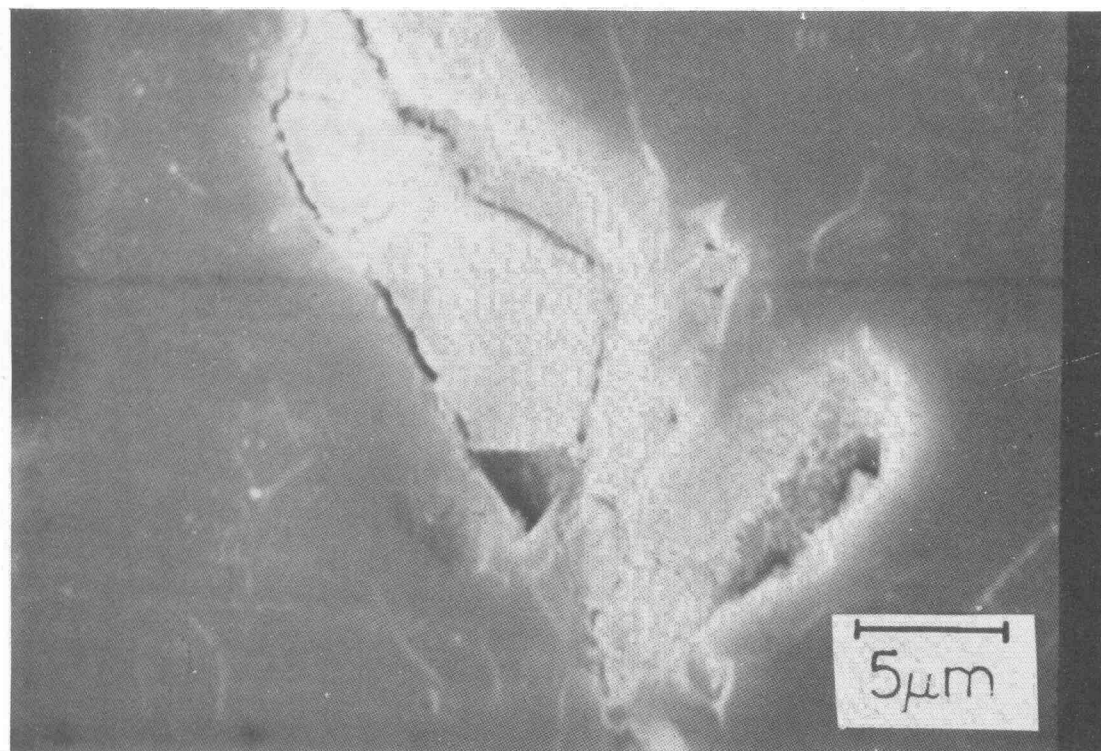
New Pyrex etched in 85% H₃PO₄ (×100)
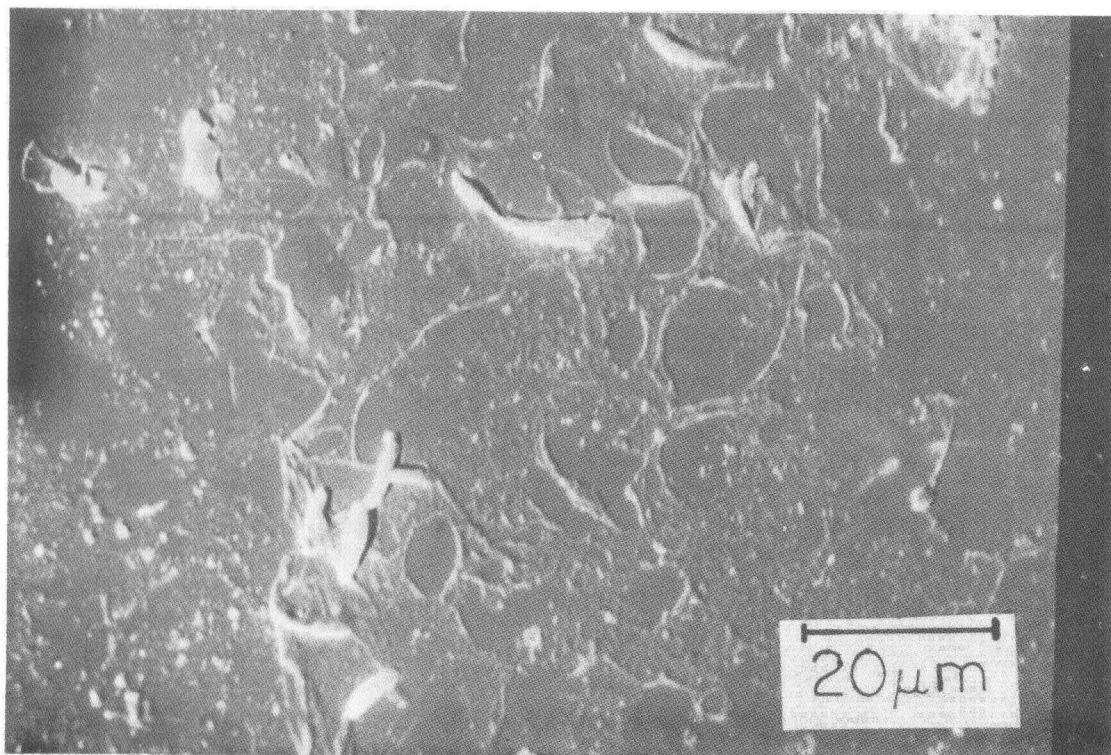
Pyrex etched in 85% H₃PO₄ after peel tested once (×1000)
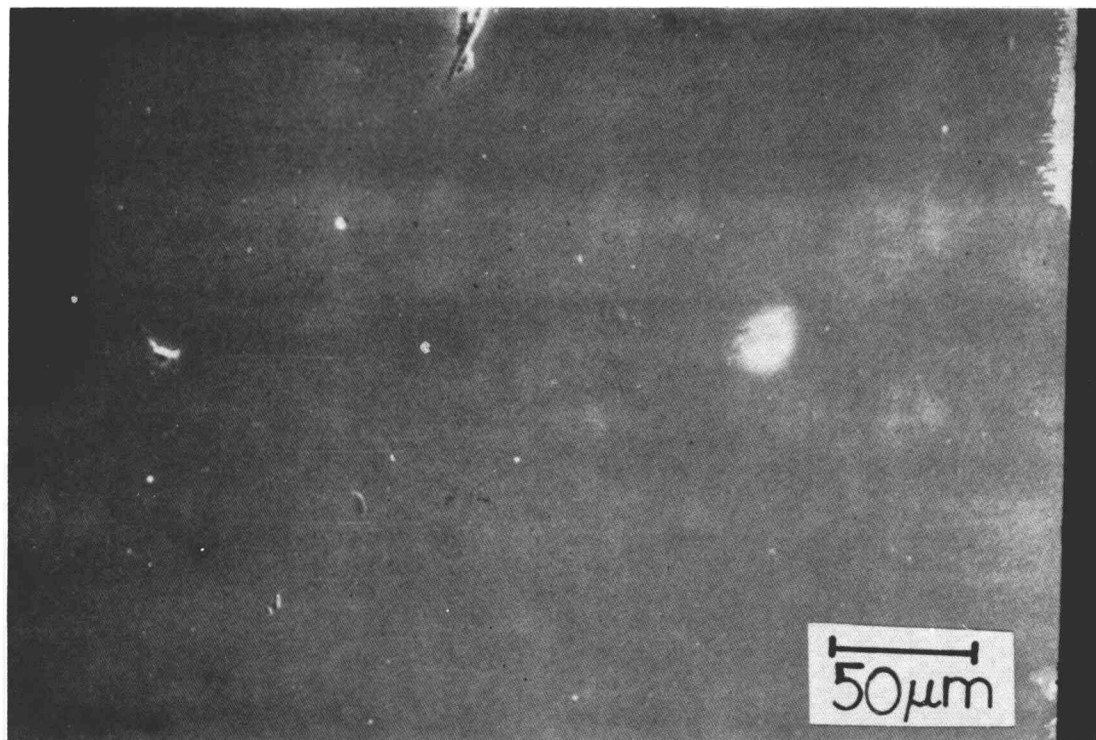
Figure 4.   Scanning electron micrographs.

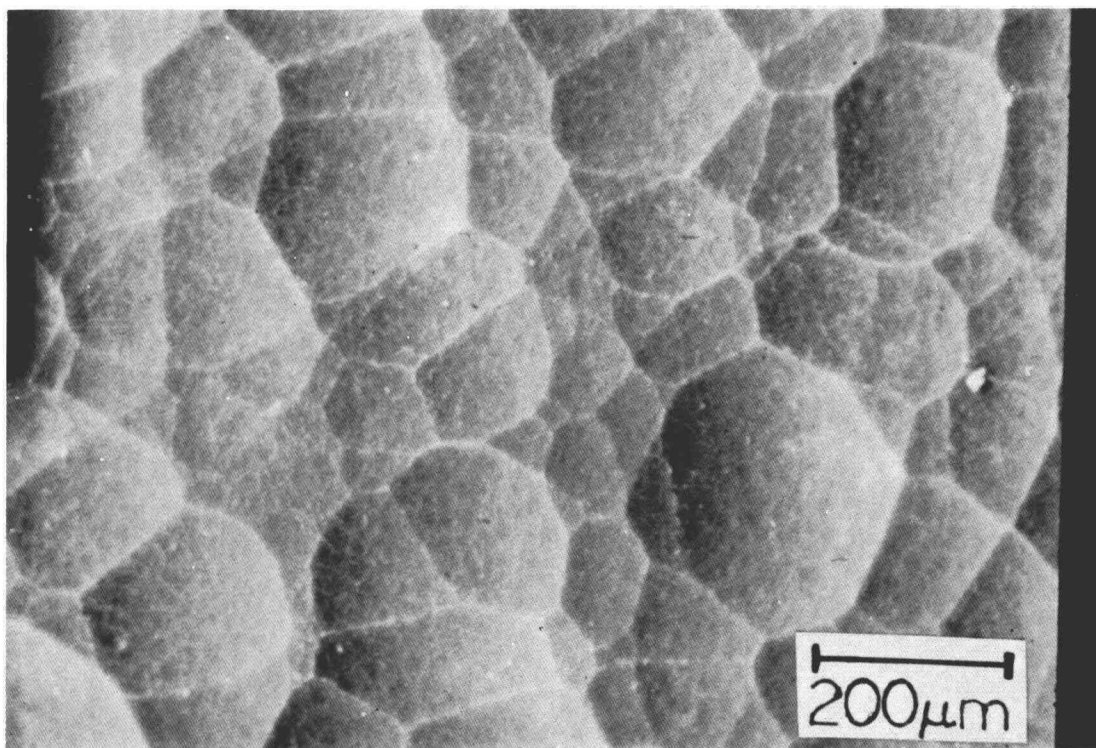*Pyrex (used) etched in 85% H₃PO₄ followed by etching in chromic acid (×100)*

Pyrex (used) etched in 1% H₃PO₄ and heated at 530°C in air for 5 h (×3000)

Figure 5.   Scanning electron micrographs.

*Pyrex (**used**) etched in chromic acid (×300)*

Pyrex (used) etched in 1% HF (×100)

Figure 6.   Scanning electron micrographs.

etched Pyrex differed from that produced by chromic acid etching in the greater number and size of the isolated pits it contained. In spite of the large difference between the surface topography of the chromic acid-etched Pyrex and that produced by etching Pyrex in 1% HF, the peel strength values given by both etched surfaces for a given elastomer were found to be similar under identical testing conditions. This can be seen from the peel strength data in *Tables 2* and *4* for PB and EPR adhering on Pyrex.

In the case of quartz, however, it was observed that etching of used plates in 1% HF resulted in surfaces which gave significantly higher peel strength than obtained with used quartz plates after etching in chromic acid *(Table 4)*. The lower level of peel strength given by chromic acid-etched quartz was obtained with used quartz etched in 1% HF followed by etching in chromic acid, as well as with new quartz etched in 1% HF. *Figure 7* shows the scanning electron micrograph of a used quartz plate etched in 1% HF, and the effect of subsequent treatment of the pre-

viously-etched quartz plate in chromic acid. In both cases the surface topography consisted of isolated, groove-like channels but with the difference that the surface of the used quartz plate etched only in 1% HF showed the presence of gross surface contamination (presumably residual rubber not removed by the etching treatment) especially in and at the edges of the groove, whereas the surface of the used quartz plate etched in 1% HF followed by etching in chromic acid was free of such surface contamination. *Figure 8* shows that the surface of a new quartz plate etched in 1% HF contained a fair number of randomly-distributed, groove-like channels, and that it was free of gross surface contamination; for comparison, a new quartz plate etched in chromic acid is also illustrated, which shows the etched surface to be planar.

It appears, therefore, that the higher peel strength values given by used quartz plates etched in 1% HF relative to those obtained with the used quartz plates after etching in chromic acid were attributable to residual rubber contaminating the 1% HF-etched quartz surface. Thus, for both the cases

TABLE 4. EFFECT OF SURFACE ROUGHNESS OF GLASS ON STRENGTH OF ELASTOMER-GLASS ADHESION AT 20°C

| Glass treatment	Work of adhesion, W (J/m²)		
	0.42×10^{-5} (ms⁻¹)	4.2×10^{-5} (ms⁻¹)	42.0×10^{-5} (ms⁻¹)
PB (0.10 p.h.r. Dicup)-Pyrex			
Chromic acid-etched	24 ± 2	33 ± 6	43 ± 8
1% HF-etched	25 ± 2	34 ± 5	50 ± 6
EPR (2.7 p.h.r. Dicup + 0.32 p.h.r. sulphur)-quartz			
Chromic acid-etched	52 ± 6	116 ± 11	210 ± 27
1% HF-etched (used plate)	98 ± 20	185 ± 35	333 ± 54
Used quartz etched in 1% HF followed by etching in chromic acid	68 ± 4	132 ± 10	205 ± 20
1% HF-etched (new plate)	58 ± 6	129 ± 6	235 ± 19
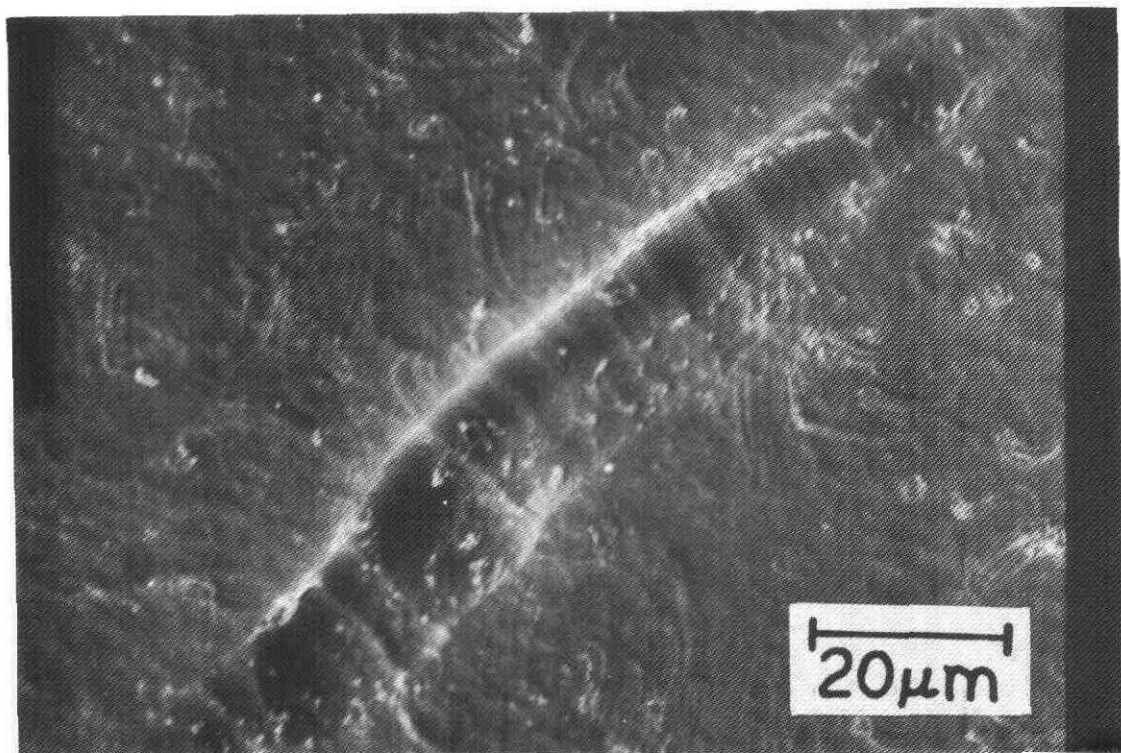
Quartz (used) etched in 1% HF (×1000)
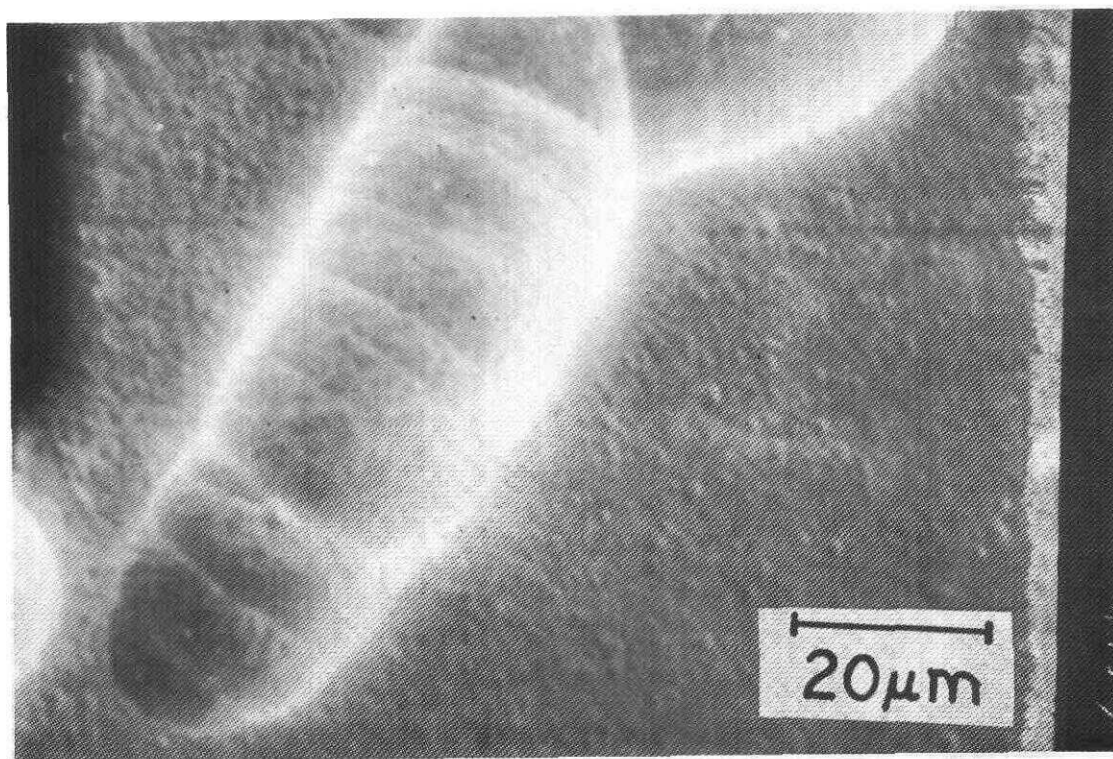
Quartz (used) etched in 1% HF followed by etching in chromic acid (×1000)

Figure 7. Scanning electron micrographs.
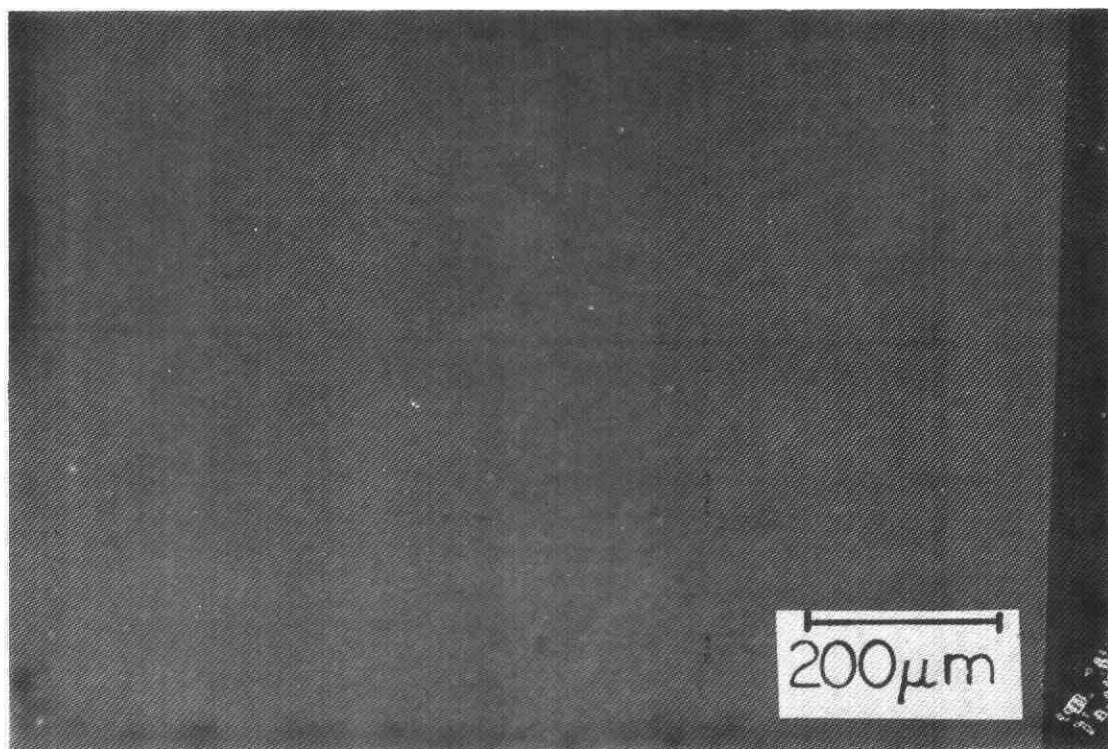
Chromic acid-etched new quartz (×100)
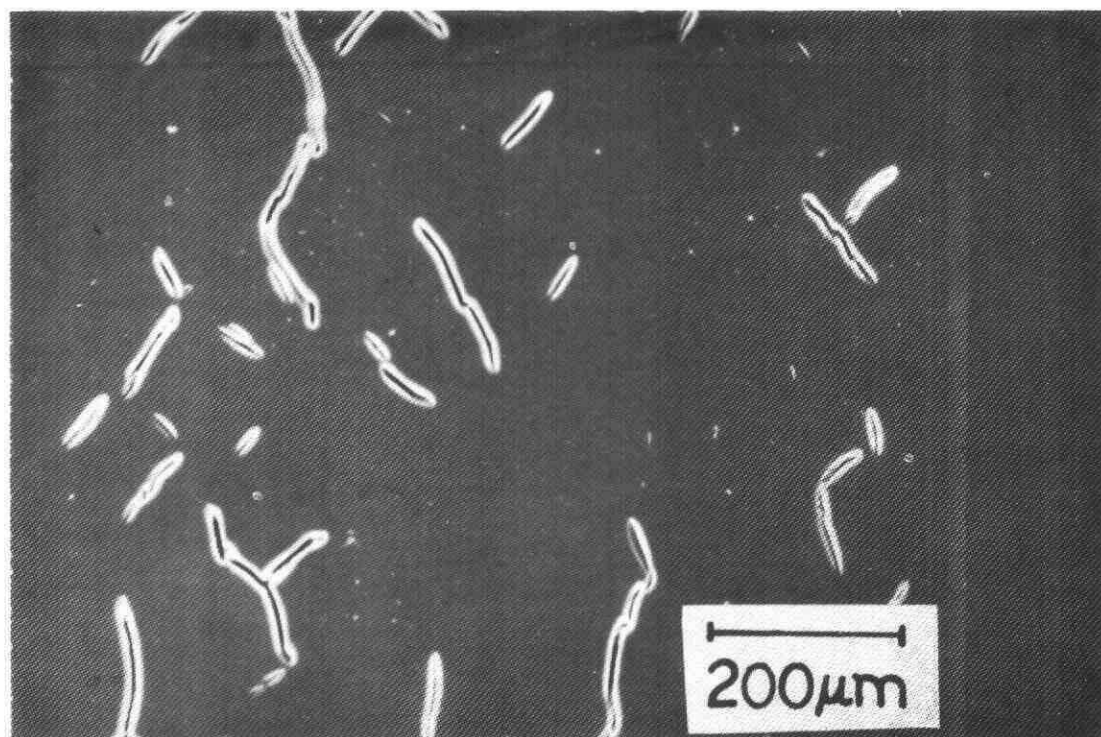
1% HF-etched new quartz (×100)

Figure 8.   Scanning electron micrographs.

of used Pyrex and new quartz etched in chromic acid or 1% HF where the etched surfaces were free of such gross contamination, the strength of elastomer-glass adhesion was independent of the etching treatment of the glass substrate, although the surface roughnesses produced by etching in chromic acid and 1% HF was very different. Consequently, it may be concluded that the strength of adhesion of elastomers to clean glass is unaffected by the surface roughness of the substrate.

To rationalise the above conclusion, surface roughness factors which have been considered to influence the strength of adhesion may now be discussed in relation to the experimental results obtained in this study. For the types of roughness produced on the etched glass surfaces in the present work, it is unlikely that mechanical interlocking between the elastomer and the roughened glass surface is a significant factor determining the elastomer-glass joint strength; 'mechanical adhesion' is usually considered only with regard to adherends which have fibrous or porous surfaces[20,21]. It also seems likely that entrapment of air or vapours is not an important effect in the present investigation, largely because under the bonding conditions used the trapped gases would have been squeezed out, or diffused into the elastomer. The increased actual contact area of the roughened glass surface would, however, be expected to enhance the strength of elastomer-glass adhesion. That this effect is not evident in this study suggests that probably only a small increase in actual surface area of the glass is produced by the etching treatment, and that the resultant minor improvement in joint strength is offset by a similarly minor effect of stress concentrations at surface asperities obtained with the relatively low-modulus elastomers used. The overall effect is then, at least for the types of surface topography obtained in the present study, a negligible influence of

surface roughness of the substrate on the strength of adhesion of elastomers to clean glass.

Effect of Isocyanate Treatment of Glass on Adhesion

Treatment of clean quartz with either allyl or n-propyl isocyanate was found to enhance the strength of adhesion of PB (0.10 p.h.r. Dicup) and EPDM 6505 (0.50 p.h.r. Dicup) to quartz two-fold and four-fold, respectively, but to effect no change in joint strength for EPDM 4608 (2.0 p.h.r. Dicup) and EPR (5.4 p.h.r. Dicup) adhering to quartz (Table 5). Measurement of contact angles of various liquids on both untreated and isocyanate-treated quartz indicated no difference in wettability of these surfaces. This suggests the possibility that, for PB (0.10 p.h.r. Dicup) and EPDM 6505 (0.50 p.h.r. Dicup) adhering to isocyanate-treated quartz, a significant amount of interfacial chemical bonding occurs during peroxide-initiated crosslinking of these elastomer systems, but not for EPDM 4608 (2.0 p.h.r. Dicup) and EPR (5.4 p.h.r. Dicup). In particular, the similar enhancement of peel strength obtained for both isocyanate treatments suggests interfacial bonding via free-radical abstraction of the hydrogen atom bonded to the nitrogen atom of the isocyanate group.

The strength of adhesion of PB (0.10 p.h.r. Dicup) to allyl isocyanate-treated quartz was found to be weaker in the presence of distilled water relative to that in air over the range of test temperatures and peel rates used, as illustrated in Figure 9. In comparison, the presence of distilled water does not appear to affect the strength of adhesion of PB (0.10 p.h.r. Dicup) to the untreated quartz substrate at 20°C. It can be further noted that the wet peel strength given by isocyanate-treated quartz at 20°C approached that given by untreated quartz with decreasing peel rate. At 80°C, however, the strength

TABLE 5. EFFECT OF ISOCYANATE TREATMENT OF QUARTZ ON
STRENGTH OF ELASTOMER-QUARTZ ADHESION AT 20°C

| Quartz treatment[a]	Work of adhesion, W (J/m^2)		
	0.42×10^{-5} (ms^{-1})	4.2×10^{-5} (ms^{-1})	42.0×10^{-5} (ms^{-1})
PB (0.10 p.h.r. Dicup)-Quartz			
Allyl isocyanate	33 ± 6	36 ± 7	74 ± 18
n-Propyl isocyanate	26 ± 7	34 ± 5	71 ± 14
Untreated	16 ± 3	21 ± 2	34 ± 9
EPDM 6505 (0.50 p.h.r. Dicup)-Quartz			
Allyl isocyanate	101 ± 26	173 ± 36	225 ± 54
Untreated	24 ± 2	49 ± 3	58 ± 1
EPDM 4608 (2.0 p.h.r. Dicup)-Quartz			
Allyl isocyanate	12 ± 4	18 ± 6	34 ± 13
Untreated	11 ± 1	16 ± 2	31 ± 3
EPR (5.4 p.h.r. Dicup)-Quartz			
Allyl isocyanate	19 ± 3	36 ± 8	95 ± 26
n-Propyl isocyanate	18 ± 3	35 ± 8	93 ± 24
Untreated	23 ± 4	43 ± 5	94 ± 15

[a]Quartz plates exposed to isocyanate vapour (40 mm Hg) for 3 h at 33°C.
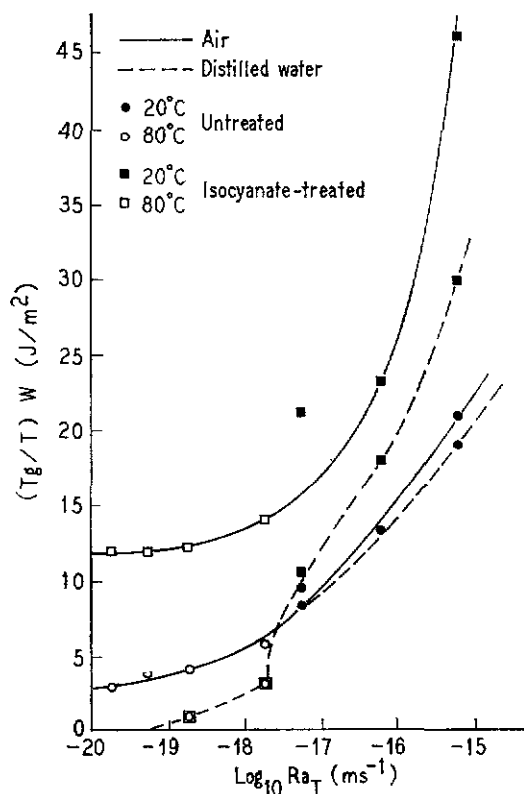
Figure 9. Effect of presence of water on the strength of adhesion of polybutadiene (0.10 p.h.r. Dicup) to allyl isocyanate-treated and untreated quartz substrates.

of adhesion of PB (0.10 p.h.r. Dicup) to either quartz substrate in distilled water decreased to a virtually negligible value. The observed apparent lack of effect of water on the strength of adhesion of PB (0.10 p.h.r. Dicup) to untreated quartz at 20°C suggests that there is a possibility of a specific but unknown type of interaction between the elastomer and the substrate. On the other hand, the observed weakening effect on the strength of adhesion of PB (0.10 p.h.r. Dicup) to allyl isocyanate-treated quartz caused by water is probably due to hydrolysis of interfacial chemical bonds. As for the drastic drop in the strength of adhesion of PB (0.10 p.h.r. Dicup) to both isocyanate-treated and untreated quartz caused by peeling in distilled water at 80°C, two possible reasons are: the interfacial bonds in both cases are almost completely destroyed; and corrosion of either quartz surface causing disintegration of the inter-facial region of the substrate.

Effect of Silane Treatment of Glass on Adhesion

The effect of silane treatment of glass on the strength of PB (0.10 p.h.r. Dicup)-glass

TABLE 6. EFFECT OF SILANE-TREATMENT OF GLASS ON
STRENGTH OF POLYBUTADIENE-GLASS ADHESION AT 20°C

Glass treatment[a]	Work of adhesion, W (J/m^2)		
	0.42×10^{-5} (ms^{-1})	4.2×10^{-5} (ms^{-1})	42.0×10^{-5} (ms^{-1})
PB (0.10 p.h.r. Dicup)-quartz			
Trimethylmethoxysilane	7 ± 1	11 ± 1	14 ± 1
Untreated	16 ± 3	21 ± 2	34 ± 9
PB (0.10 p.h.r. Dicup)-Pyrex			
Vinyldimethylethoxysilane	62 ± 3	100 ± 9	197 ± 16
Untreated	24 ± 2	33 ± 6	43 ± 8

[a]Chromic acid-etched glass plates evacuated at 530°C prior to exposure to trimethylmethoxysilane (100 mm Hg) or vinyldimethyl-etoxysilane (40 mm Hg) vapour for 3 h at 33°C.

adhesion is shown in *Table 6*. Treatment of quartz with trimethylmethoxysilane resulted in reduction by half in the strength of PB (0.10 p.h.r. Dicup)-quartz adhesion, whereas treating Pyrex with vinyldimethylethoxysilane caused up to four-fold enhancement of the strength of PB (0.10 p.h.r. Dicup)-Pyrex adhesion. A similar wettability for both the untreated and trimethylmethoxysilane-treated quartz surfaces was obtained. These results suggest the possibility of chemical bond formation between PB (0.10 p.h.r. Dicup) and vinyldimethylethoxysilane but not with trimethylmethoxysilane during crosslinking of PB. Evacuation of the silane-treated plates at 50°C prior to forming the elastomer-glass joints ensured that the observed reduction in joint strength obtained with trimethylmethoxysilane-treated quartz was not due to physically adsorbed trimethyl-methoxysilane. Rather, silane-treatment of glass probably resulted in a significant reduction in retardation of free-radical reactions by the glass surface[22], resulting consequently in a higher degree of cross-linking in the boundary region of the elastomer contacting the silane-treated quartz and hence the observed decrease in adhesion of PB (0.10 p.h.r. Dicup) to trimethyl-methoxysilane-treated quartz relative to un-treated quartz.

CONCLUSION

The strength of elastomer-glass adhesion was found to be consistent with the WLF rate-temperature equivalence principle, and to increase with decrease in the degree of crosslinking of the elastomer. The joint strength obtained was affected by the etching agent employed to clean the glass plate after use. Scanning electron micrographs of etched glass plates showed that the difference in peel strength observed was attributable to surface contamination by residual rubber but not to surface roughness of the substrate.

Treatment of clean glass with either allyl or n-propyl isocyanate gave up to four-fold enhancement of the strength of adhesion of PB (0.10 p.h.r. Dicup) and EPDM 6505 (0.50 p.h.r. Dicup) to quartz, but gave no change in joint strength for EPDM 4608 (2.0 p.h.r. Dicup) and EPR (5.4 p.h.r. Dicup) adhering to quartz. The presence of water, however, decreased the enhancement of joint strength given by isocyanate-treated quartz. A four-fold increase in PB (0.10 p.h.r. Dicup)-glass adhesion was also obtained with vinyldimethylethoxysilane-treated but not trimethylmethoxysilane-treated glass. A similar wettability for both untreated and

treated quartz surfaces was obtained, suggesting interfacial chemical bonding as a possible cause of the enhancement of joint strength obtained.

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