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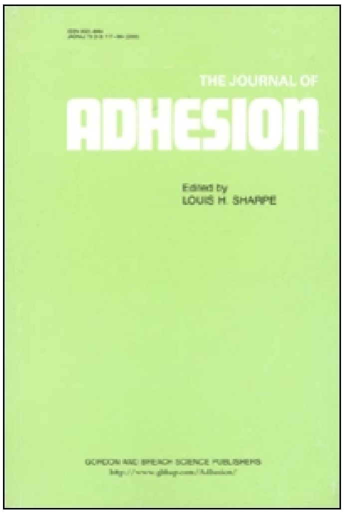

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Adhesion of elastomers: Dwell time effects

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ADHESION OF ELASTOMERS: DWELL TIME EFFECTS

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The strength of adhesion of elastomers to rigid substrates generally increases with time of contact. This effect has been studied for samples of butyl and chlorobutyl rubber adhering to some rigid substrates. The peel strength increased continuously over long periods of contact until in some cases failure became cohesive within the elastomer layer. At higher temperatures the strength increased more rapidly, consistent with the WLF relation governing molecular motions. It is postulated that slow molecular rearrangements occur at the interface and increase the bond strength. A criterion for the observed transition from interfacial to cohesive failure is suggested.

Keywords: Adhesion; Butyl Rubber; Dwell time; Elastomers; Failure; Interfaces; Peeling; Strength

INTRODUCTION

The mobility of molecular segments in butyl rubber increases with temperature at a much slower rate than for most elastomers [1]. As a result, even though the glass temperature is quite low, about –72°C, butyl rubber is less permeable and less resilient than other elastomers at room temperature. Also, it is relatively inert. It is, therefore, widely used in adhesives and sealants. From a scientific point of view, the low

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rate of molecular motion in butyl rubber and the chlorinated version, chlorobutyl rubber, makes them particularly attractive materials for studying the effect of contact time on adhesion. We have therefore examined the strength of adhesion of butyl rubber and chlorobutyl rubber to two rigid and relatively inert substrates—glass and Ferrotype plate—as a function of temperature and time of contact (dwell time). The results are reported here and compared with the strength of the materials themselves.

EXPERIMENTAL PROCEDURE

Rubber mixes were prepared using the recipes given in the Appendix. Vulcanized sheets, about 2.5 mm thick, were made by pressing the compounds in a sheet mold and simultaneously crosslinking them by heating the mold for 45 min at 160°C. Uncrosslinked sheets were prepared by molding the elastomer without additives for 10 min at 140°C; samples prepared in this way were found to be completely soluble, indicating that no crosslinking had occurred. A backing layer of thin cotton cloth was applied during molding to reinforce the uncrosslinked elastomer as it was torn or peeled away from the substrate. Before use, each substrate was washed with acetone and dried in an oven for 1 h at 80°C.

To study the effect of peel rate and temperature on the strength of adhesion, strips about 10 mm wide were cut from both vulcanized and unvulcanized sheets and pressed against the chosen substrate under a light pressure (about 10 kPa) for about 1 h before being peeled away at an angle of 180°. Values of fracture energy, $\mathbf{G_a}$, were obtained at peel rates ranging from 8 μm/s to 4 mm/s and at temperatures from −40°C to 100°C. $\mathbf{G_a}$ is given by

$$\mathbf{G_a} = \frac{\mathbf{2F}}{\mathbf{w}}, \tag{1}$$

where $\mathbf{F}$ is the peel force and $\mathbf{w}$ is the width of the adhering strip.

Effective peel rates at a reference temperature of 25°C were calculated by multiplying the actual rate by a shift factor, $\mathbf{a_T}$, to correct for changes in molecular mobility with temperature, where $\mathbf{a_T}$ is given by Ferry for polyisobutylene [1] as

$$\ln(\mathbf{a_T}) = \frac{-38(\mathbf{T} - \mathbf{T_g})}{(104 + \mathbf{T} - \mathbf{T_g})}. \tag{2}$$

The glass temperature, $\mathbf{T_g}$, was taken to be −70°C.

Similarly, measurements were made of the tear strength, $\mathbf{G_c}$, of the material at various rates and temperatures, by tearing through a layer of the material that was reinforced with a thin cotton cloth to prevent excessive deformation and flow. $\mathbf{G_c}$ was calculated using Equation (1), with $\mathbf{F}$ denoting the tear force and $\mathbf{w}$ the width of the tear path, given approximately by the thickness of the rubber layer.

As remarked later, the results were found not to conform well to Equation (2) relating the test temperature and rate of peel. Instead, other values for the numerical coefficients, 38 and 104°C, were found to give better superposition of results obtained at different temperatures. However, for consistency, all of the results reported here have been correlated using Equation (2).

To study dwell time effects, strips cut from the unvulcanized sheets were adhered to the chosen substrate by pressing them into contact under a moderate pressure of about 1 MPa and then storing them at temperatures between 25°C and 80°C for periods ranging from 10 min to 4 weeks. The strips were then peeled off at an angle of 180° at a peel rate of 170 μm/s at 25°C.

RESULTS AND DISCUSSION

Tear Strength and Peel Strength

The measured tear strength, $\mathbf{G_c}$, of unvulcanized butyl rubber is plotted against the rate of tear propagation in Figure 1, using logarithmic scales for both axes. The results are seen to increase markedly with tear rate and depend strongly on the test temperature, as is commonly observed for amorphous polymers. When replotted in Figure 2 as a function of the effective rate of tear at 25°C, using Equation (2) to correlate results at different test temperatures, they are seen to superpose fairly well to give a “master curve” of tear strength versus rate of tear.

Much better superposition was obtained using coefficients of 68 and 70°C in Equation (2), in place of 38 and 104°C. However, in view of the success of Equation (2) in simple viscoelastic studies [1] we have employed it here also, retaining the original coefficients. Note that the general form of the dependence of $\mathbf{G_a}$ and $\mathbf{G_c}$ on effective rate of peel or tear is maintained. Only the range of effective rates would be changed significantly by using the best-fit coefficients. [It is rather surprising that the best-fit coefficients, 68 and 70°C, are not the same as in viscoelastic studies of butyl rubber [1] because for other elastomers the same coefficients are found to describe both viscoelastic and fracture phenomena [1, 2].

A comparison is given in Figure 3 between the tear strength and the strength of adhesion to Ferrotype plate. At low rates the unvulcanized rubber layer could not be peeled away cleanly from the

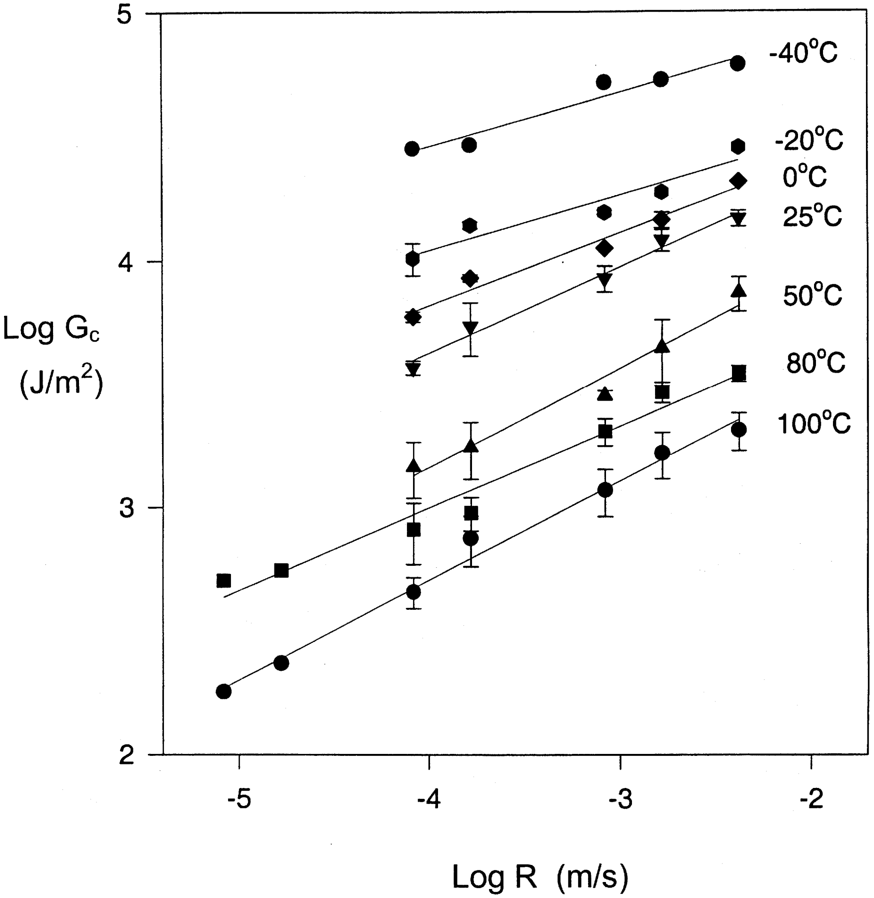

FIGURE 1 Tear strength, $\mathbf{G_c}$, of unvulcanized butyl rubber *versus* rate, **R**, of tearing.

substrate—instead it split apart, leaving rubber behind. This is termed "cohesive failure", where peel strength is the same as the tear strength. As the peel rate was increased, however, an abrupt transition occurred to interfacial failure at much lower peel forces, only about one-twentieth as high.

The transition is indicated in Figure 3 by a vertical broken line. It is attributed to failure of molecular entanglements to flow apart at a critical rate of peel [2]. The elastomer is then transformed abruptly from a viscous liquid to an elastic solid, and the work expended in detachment changes from viscous dissipation as the material flows apart to relatively small internal losses as the (now) elastic material is peeled away.

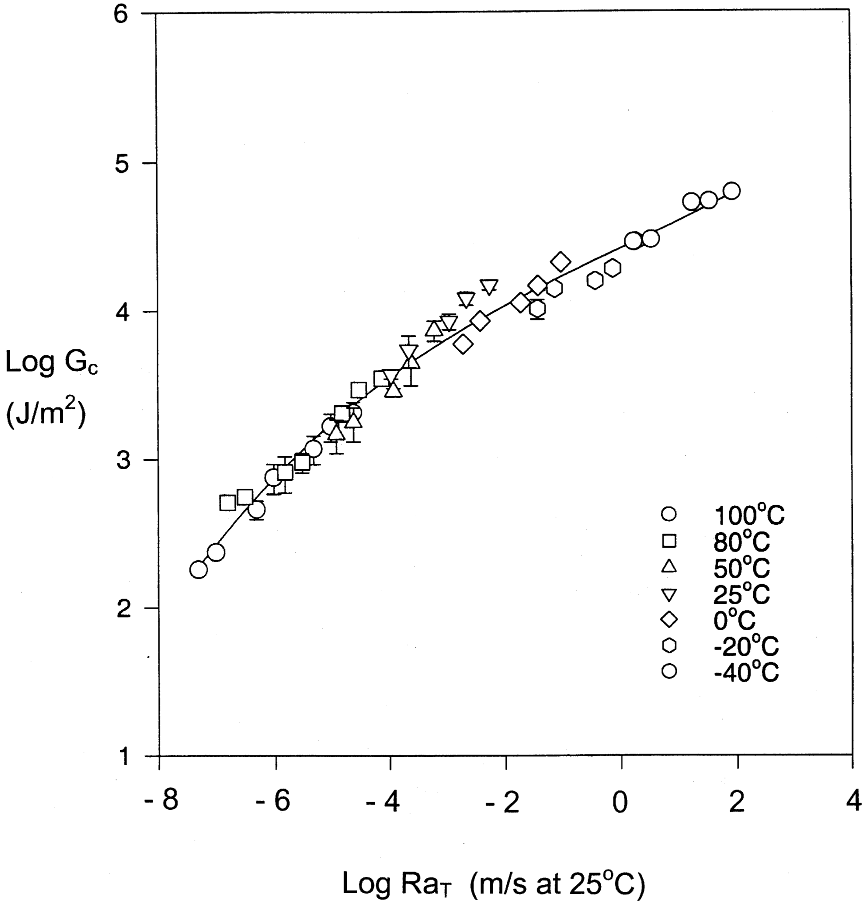

FIGURE 2 Tear strength, $\mathbf{G_c}$, from Figure 1 *versus* reduced rate, $\mathbf{Ra_T}$, of tearing at –25°C. Values of $\mathbf{a_T}$ were calculated from Equation (2).

After the transition, the peel strength again increased with peel rate, paralleling the cohesive strength of the polymer itself but now only about one-twentieth as high. This increase is attributed to increasing internal viscous losses as the elastomer approaches the glassy state.

Dwell Time Effect

Measurements were then made of the peel strength at room temperature and at one peel rate (about 200 μm/s) after various periods of contact with the countersurface at different storage temperatures. The

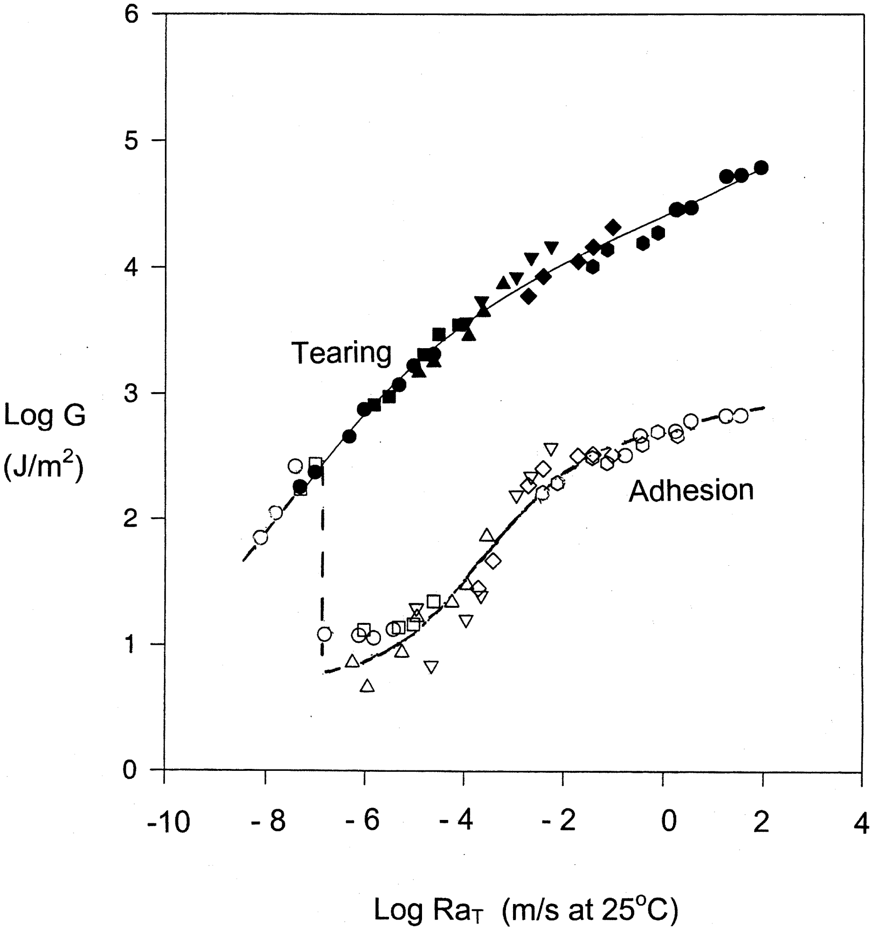

FIGURE 3 Strength, $\mathbf{G_a}$, of adhesion of unvulcanized butyl rubber to Ferrotype plate (open symbols) *versus* reduced rate, $\mathbf{Ra_T}$, of peeling. Tear strength, $\mathbf{G_c}$ (filled symbols), *versus* reduced rate, $\mathbf{Ra_T}$, of tearing, from Figure 2.

chosen peel rate is well above the transition rate at which failure becomes adhesive, about 100 nm/s for butyl rubber (Figure 3) and adhesive failures were, therefore, usually encountered. Typical results are shown in Figure 4. The strength of adhesion to glass was found to increase continuously with contact time (dwell time). After 1000 h of contact at 80°C it had become about ten times larger than the value measured after short contact times and still showed no signs of reaching an equilibrium level. Moreover, the strength increased more rapidly at higher temperatures (Figure 4). When the results were

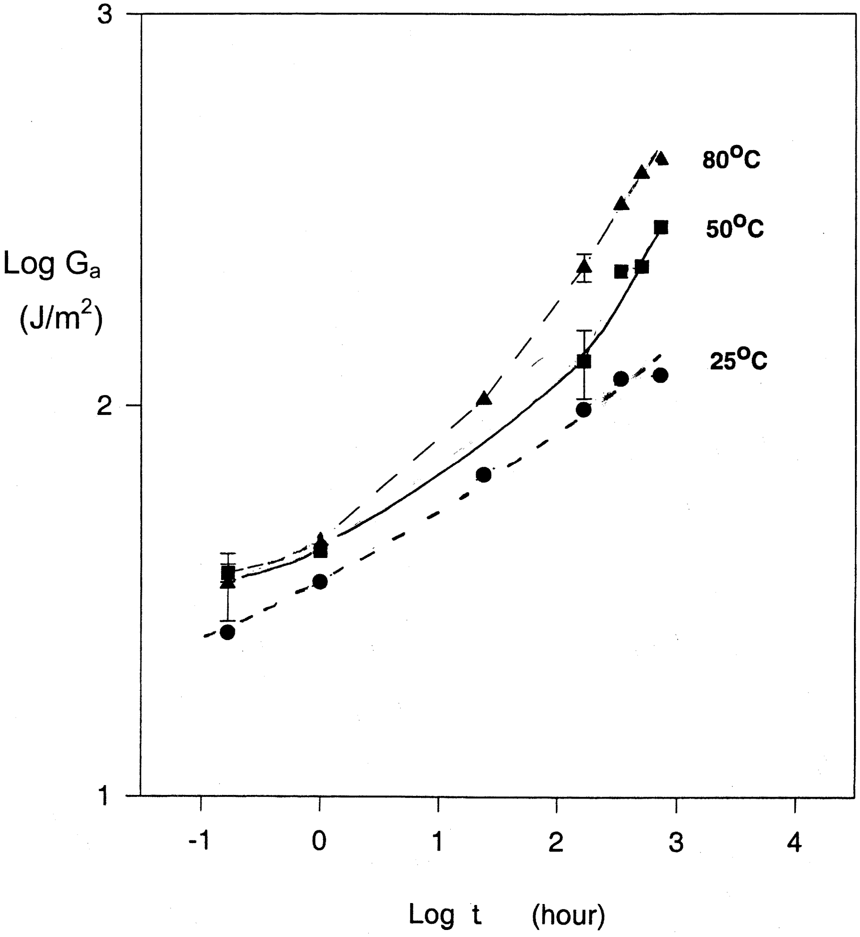

FIGURE 4 Strength, $\mathbf{G_a}$, of adhesion of unvulcanized butyl rubber to glass, measured at 25°C, *versus* dwell time, **t**, at various temperatures.

replotted as a function of a reduced dwell time, $\mathbf{t/a_T}$, where $\mathbf{a_T}$ is given by Equation (2), they formed a reasonably smooth master curve (Figure 5), suggesting that the effect of increased storage temperature is mainly to speed up the rate of molecular rearrangement and not to increase the rate of a specific bonding reaction at the interface.

Adhesion of vulcanized butyl rubber also increased with dwell time but at a lower rate (Figure 5). Again, the strength of adhesion showed no signs of reaching an equilibrium value, even after long periods of storage at 80°C.

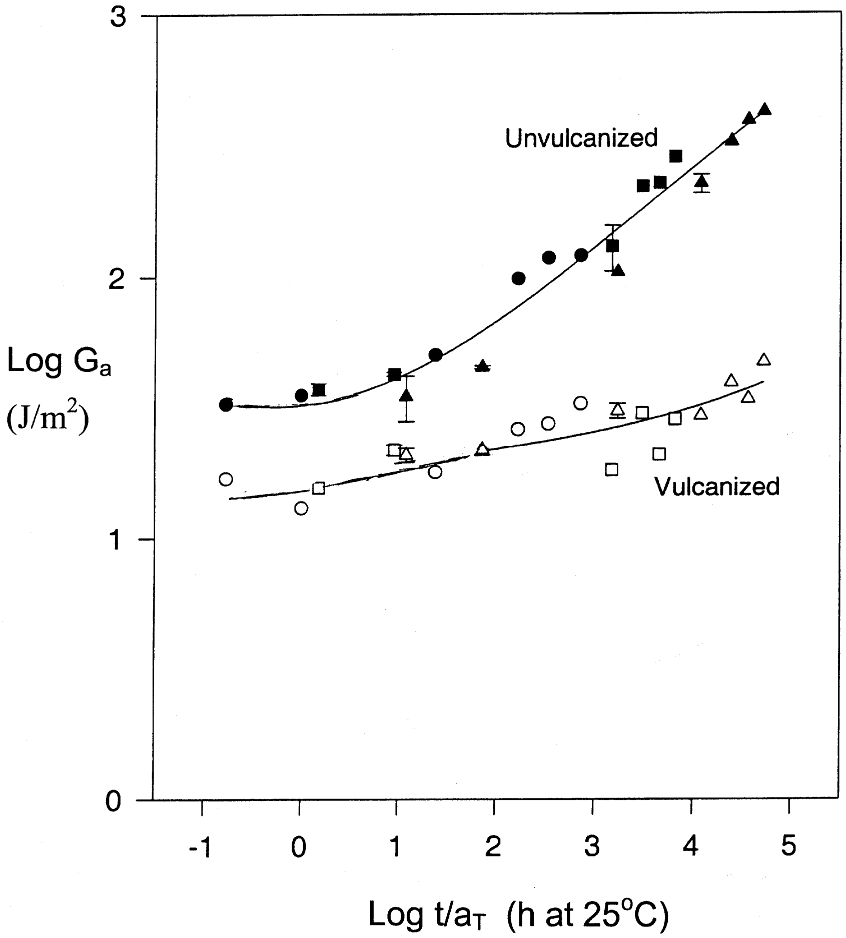

FIGURE 5 Strength, $\mathbf{G_a}$, of adhesion to glass of unvulcanized butyl rubber (filled symbols) and vulcanized butyl rubber (open symbols), measured at 25°C, *versus* reduced dwell time, $\mathbf{t/a_T}$, at various temperatures.

After long dwell times the adhesion of unvulcanized chlorobutyl rubber increased by more than ten times and became so high that the layer could not be detached cleanly. Instead it failed cohesively (Figure 6).

These large and surprisingly protracted increases in adhesion with dwell time are tentatively attributed to slow molecular rearrangements at the interface [3]. As shown schematically in Figure 7, the initial contact between elastomer and substrate will occur at single

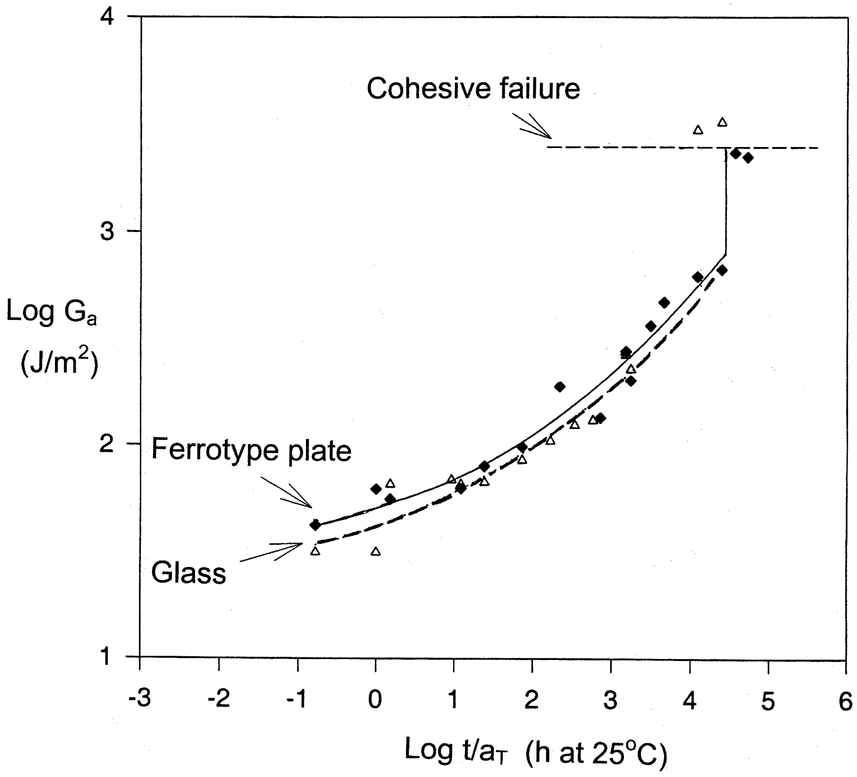

FIGURE 6 Strength, $\mathbf{G_a}$, of adhesion of unvulcanized chlorobutyl rubber to Ferrotype plate (filled symbols) and glass (open symbols), measured at 25°C, *versus* reduced dwell time, $\mathbf{t/a_T}$, at various temperatures.

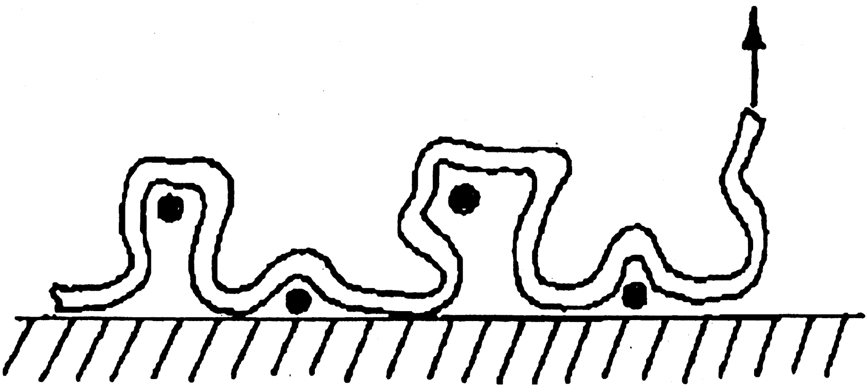

FIGURE 7 Sketch of an entangled molecule, partially absorbed on a substrate.

sites and comprise only short molecular sequences. As a result, detachment can be accomplished by breaking a few bonds at a time, by pulling on short molecular strands with a relatively small expenditure of energy. We suggest that, as time passes, the adsorbed molecules rearrange, bringing longer strands into contact with the substrate. The energy required to pull longer sequences away will be greater because desorption of several adsorbed units is involved. Moreover, the lengths of the molecular strands through which debonding forces are applied increase continuously during detachment. However, the process of molecular rearrangement that builds up stronger adsorption will be extremely protracted because cooperative desorption at several sites is needed for new configurations to form.

Another possible mechanism for the continuous increase in peel fracture energy would be the slow development of specific bonds between polymer molecules and substrate sites. However, this process is considered less likely to be the main cause of the observed increase in strength because the increase took place to a similar degree for both butyl rubber and chlorobutyl rubber, and against both glass and Ferrotype surfaces. Moreover, a similar but somewhat smaller increase in adhesion also occurred for vulcanized layers. Further work is needed to find the equilibrium level of adhesion in these systems. It is apparently reached only after extraordinarily long contact times.

Criterion for Detachment

As shown in Figure 6, when the strength of adhesion rises to about one-half of the tear strength, then failure changes abruptly to cohesive rupture of the adhering layer, at a force about twice as high. This transition is rather surprising, as no change occurs in the material itself (except possibly at the interface, as discussed above). It appears that detachment of a soft adhering layer from a rigid substrate requires more energy, about twice as much, as tearing through the layer. Some preliminary finite element calculations gave a similar result, that tearing is preferred to debonding by about the same ratio [4]. Thus, bonds that are only about one-half as strong as the adherends will appear to be as strong as or stronger than the tear strength. This conclusion accounts for the common and rather paradoxical observation that interfacial bonds often appear stronger than the adherends themselves.

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APPENDIX

Crosslinked sheets were prepared using the following mix formulation in parts by weight:

Elastomer, 100; stearic acid, 1; zinc oxide, 5; sulfur, 1; Altax (accelerator), 0.5; ethyl cadmate (accelerator), 2.

Crosslinking was effected by heating for 45 min at 160°C in a heated press.

The elastomer was either butyl rubber (Polysar Butyl 301, supplied by Akrochem Company, Akron, Ohio, USA, 1.75 mole% of isoprene, $M_w = 523$ kg/mole; $M_n = 183$ kg/mole) or chlorobutyl rubber (Chlorobutyl 1066, supplied by Exxon Chemical Company, Baytown, Texas, USA, 1.2 wt% of chlorine, $M_w = 443$ kg/mole; $M_n = 139$ kg/mole).