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THE ROLE OF MOLECULAR DIFFUSION IN THE ADHESION OF EDPM
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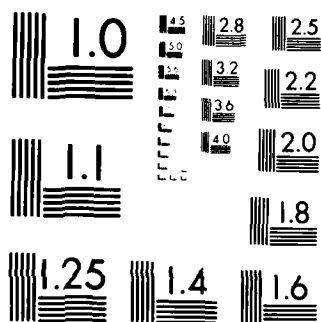
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THE ROLE OF MOLECULAR DIFFUSION IN THE ADHESION
OF EPDM AND EPR ELASTOMERS

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Adhesion of lightly crosslinked sheets of EPDM (ethylene-propylene-diene terpolymer) to themselves and to a Mylar substrate has been investigated over wide ranges of peel rate and test temperature. The effect of incorporating ethylene-propylene copolymer (EPR) before crosslinking, to yield a loose macromolecular network containing dissolved linear EPR macromolecules, was also studied. The self-adhesion of these materials was found to be much		

greater than their adhesion to Mylar, over a wide range of effective peel rates. This is attributed to interdiffusion of EPR and EPDM molecular strands. At extremely low peel rates the enhancement of adhesion was smaller, probably because of back-diffusion, and at high rates, the strength of adhesion became high in all cases. These results are compared to those obtained previously for polyisobutylene-co-isoprene networks containing linear polyisobutylene molecules. The enhancement of self-adhesion at intermediate rates of peel was considerably greater for the EPDM based materials, probably because of a lower degree of crosslinking and a greater tendency to form molecular entanglements.

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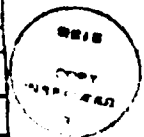
Introduction

Studies of the strength of adhesion of a simple elastomeric system have already been reported (1). The system consisted of crosslinked butyl rubber (polyisobutylene-co-isoprene) containing a proportion of uncrosslinked linear polyisobutylene. In such a system, the dissolved linear molecules can presumably diffuse readily across an interface into any compatible material. It was found that the strength of adhesion to an incompatible rigid material, polyethylene terephthalate (Mylar 300A, E.I. du Pont de Nemours and Co.), was relatively low and much the same whether linear polyisobutylene molecules of high molecular weight were present or not. On the other hand, the strength of self-adhesion of the crosslinked butyl rubber was considerably greater, as much as 5X, when high-molecular-weight polyisobutylene was present. This effect seems clear evidence for a direct contribution to self-adhesion from interdiffusing macromolecules.

However, some of the observed changes in the strength of adhesion with composition, or with the effective rate of peeling, might have arisen from stress-induced crystallization (2). Results over a wide range of temperature were found to obey reasonably well the rate-temperature equivalence proposed by Williams, Landel and Ferry for simple amorphous viscoelastic substances (3), and this suggests that effects due to crystallization, if any, were relatively small. Nevertheless, it seems worthwhile to examine an analogous system which does not exhibit stress-induced crystallization, and to explore again the effect upon the strength of adhesion of incorporating high-molecular-weight linear molecules into a macromolecular network.

Mixtures of polyethylene-co-propylene (EPR) have therefore been made with a crosslinkable compatible terpolymer of ethylene, propylene and a few per cent of a diene comonomer (EPDM). The small-strain viscoelastic properties of such materials, when the EPDM fraction is crosslinked and the EPR fraction is present in solution in the resulting network, have been studied by Ferry and coworkers (4). They were found to behave in a similar way to corresponding materials made with butyl rubber and polyisobutylene (5). Measurements of the strength of adhesion of such materials to a rigid substrate, Mylar, and to themselves, are reported here and compared with those obtained previously for mixtures of butyl rubber and polyisobutylene (1).

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2. Experimental details

(a) Materials

Mixtures of EPDM (Vistalon 4608, Exxon Chemical Company) and EPR (Vistalon 404, $\overline{M}_v = 2 \times 10^5$ g/mole, Exxon Chemical Company) in various proportions were prepared on an open two-roll mill. It proved extremely difficult to find a vulcanization recipe for the EPDM fraction that yielded crosslinked sheets free from surface contamination by additives or by-products of the vulcanization reaction. The recipe finally chosen was the following, in parts by weight: EPDM (Vistalon 4608), 100; EPR (Vistalon 404), 0 to 100; zinc oxide, 1.5; tetramethylthiuram disulfide, 1.5; zinc-2-ethyl hexanoate, 1.5. Crosslinking was effected by heating for 4 h at 150°C in a press. The equilibrium volume swelling ratio in hexane of the EPDM material containing no EPR was quite large, 6.7X, indicating a rather low degree of crosslinking. Sheets were prepared about 1.5 mm thick with a thin cotton cloth backing adhering to one surface and the other molded against a polished Ferrotype chrome-on-steel plate (Apollo Metals Inc., Chicago) to yield a smooth surface.

(b) Test methods

The procedures used to measure the strength of self-adhesion, adhesion to a rigid (Mylar) substrate, and tear strength were the same as before (1). For self-adhesion, test strips were first washed with petroleum ether to remove surface contaminants, dried, and then pressed into contact for 48 h at 60°C.

under a pressure of about 1.5 MPa. Longer contact times or higher pressures did not result in any significant increase in the force required to peel strips apart subsequently. The results are expressed in terms of the work $\underline{G}_a$ required to separate unit area of interface, given by

$$\underline{G}_a = 2F/w \quad (1)$$

where $\underline{F}$ is the average peel force and $\underline{w}$ is the width of the interface, generally 10-20 mm.

The test procedure for determining the work $\underline{G}_a$ of detachment from a Mylar substrate was essentially the same, the Mylar film being held flat by bonding it to a metal plate and the elastomer layer being peeled back from it at an angle of 180°. Values of fracture energy $\underline{G}_c$ for tearing a sheet were determined in a similar way, the tear force $\underline{F}$ being employed in equation 1 with the test-piece width $\underline{w}$ replaced by the torn thickness $\underline{t}$, generally about 1.5 mm. Two cloth sheets were adhered to each surface of the elastomer layer and straight cuts made in them along the center line before tearing. In this way the tear was constrained to follow a straight path and ductile flow of the elastomer was limited to a region around the tear tip.

(c) Data reduction

Measurements of the work of separation $\underline{G_a}$ or of fracture $\underline{G_c}$ were made at various rates $\underline{R}$ of propagation of the line of separation or of the tear tip and at various temperatures $\underline{T}$. They were reduced to an effective rate $\underline{Ra_T}$ at a reference temperature $\underline{T_s}$ of 25°C by means of the WLF rate-temperature equivalence factor $\underline{a_T}$, where:

$$\log_{10} a_T = C_1 (T - T_s) / (C_2 + T - T_s). \quad (2)$$

Values were assigned to $\underline{C_1}$ of 6.6 and to $\underline{C_2}$ of 137°C, in accordance with the "Universal" form of the WLF relation, taking the glass temperature of EPR and EPDM to be -60°C (3,6). Measurements at different temperatures are denoted by different symbols in the figures given later. They were in reasonable accord in all cases with single relations between the work of separation or fracture and the effective rate of separation or fracture $\underline{Ra_T}$. Thus, the observed temperature dependence of the adhesive and cohesive strengths of the present materials appear to arise solely from their viscoelastic character.

3. Results and discussion

(a) Adhesion to Mylar

Measurements of the work G_a required to separate a layer of the uncrosslinked ethylene-propylene copolymer EPR from a Mylar substrate are plotted in Figure 1 against the effective rate R_{aT} of peeling at 25°C. These measurements were made over a wide temperature range; -40°C to + 100°C; they superimpose reasonably well using the WLF rate-temperature equivalence, equation 2. Measurements of the work G_c required to tear in two a layer of the EPR material are also plotted in Figure 1 against the effective rate of tear propagation.

The tear strength increased continuously over the entire range of tear rate. The strength of adhesion to Mylar, however, was found to undergo a rather broad transition. At low peel rates, it was comparable to, but somewhat lower than, the tear strength and increased with the rate of separation in a similar way. In the transition region, it was quite erratic, varying by large factors, and failure proceeded in a "stick-slip" fashion. Then, at high rates of peel the strength of adhesion - now two orders of magnitude smaller than the tear strength - increased smoothly again with increasing rate of peel.

Similar behavior was shown by the crosslinked EPDM material and by the crosslinked EPDM material containing EPR molecules in solution, Figure 2. For the crosslinked EPDM material, the strength of adhesion at low rates was considerably smaller and the transition was less obvious, but at high rates the adhesion strength became indistinguishable

from that for EPR and EPDM plus EPR. Thus, linear EPR, crosslinked EPDM, and a mixture of both, show greater adhesion at low rates of peel than would be expected from a simple extrapolation of results obtained at high rates, represented by the broken curves of Figures 1 and 2. This extrapolation was made by comparison with results for butyl rubber and mixtures of butyl rubber and polyisobutylene, which did not exhibit a similar transition in their adhesion to Mylar (1).

A transition in adhesive strength with increasing peel rate was observed previously for a simple uncrosslinked elastomer, a copolymer of styrene and butadiene (7). At low peel rates the material split apart, leaving a thin layer on the Mylar substrate, and the measured strength represented the cohesive (tear) strength. Then, at a well-defined peel rate a sharp transition took place to interfacial failure at much lower forces.

The transition was attributed to a change in the physical character of the adhering material. At low rates it flowed apart under the imposed peeling stresses, like a viscous fluid, whereas at high rates molecular entanglements did not slip free so that it behaved like a loosely-crosslinked layer and pulled away cleanly.

A similar explanation is proposed for the present results. The relation between nominal tensile stress $\underline{\sigma}$ and tensile strain $\underline{\epsilon}$ for the EPDM-EPR material is strongly dependent upon the rate of strain $\dot{\underline{\epsilon}}$, as shown in Figure 3. At high effective rates $\dot{\underline{\epsilon}}_T$, this material is relatively stiff and elastic. At low effective rates, however, it becomes highly extensible and shows semi-ductile behavior, even though it is lightly crosslinked. Apparently, molecular entanglements

account for much of the observed stiffness at high rates of deformation, and, when the rate of deformation is sufficiently slow, they rearrange and allow extensive deformation to occur.

The onset of strain hardening at large deformations takes place at strain rates of $1 - 100\text{s}^{-1}$, Figure 3. This corresponds to a range of peel rates of about $1 - 100\text{ mm/s}$ for an adhering layer 1 mm thick, if it is assumed that the whole layer is subjected to a tensile deformation at the peel tip.

The transitions in adhesive strength shown in Figures 1 and 2 do, indeed, occur at peel rates in this general range. They are therefore attributed to changes in the rheological response of the adhering layers, from highly-extensible semi-solids at low rates of deformation to rubberlike elastic materials at high rates, when the molecular entanglements are fully effective.

No comparable effect was found in the adhesion of butyl-rubber-based materials to Mylar, probably because they were crosslinked to a somewhat higher degree than the present materials and also because the density of molecular entanglements is considerably lower.

(b) Self-adhesion

Measurements of the work G_a required to separate two layers of a crosslinked EPDM material containing EPR dissolved within it are plotted against the effective peel rate Ra_T in Figure 4. For comparison, the strength of adhesion to Mylar is shown again, from Figure 2. The two measures of adhesion are approximately equal at low rates, when ductile processes within the adhering layer appear to account for most of the work expended in detachment. At higher peel rates, however, the strength of self-adhesion is much larger than the adhesion to Mylar, by a factor of up to 100X. This marked increase is attributed to interdiffusion.

Molecular strands which have diffused across the interface and become entangled in the adjoining layer cannot readily disentangle at high peel rates. Moreover, ethylene-propylene copolymers are known to entangle densely (8). Thus, a major contribution to self-adhesion from interdiffused and entangled molecules would be expected for these materials at high peel rates.

A small discontinuity was noted in the strength of self-adhesion at an effective peel rate of about 100 mm/s at 25°C. Above this rate, the strength appeared to decrease to a value about one-half to one-third as large. A similar transition was seen before in the self-adhesion of butyl rubber materials containing polyisobutylene, and attributed to a change from pull-out to fracture of interdiffused molecules (1). For the present materials, the transition takes place at about the same peel rate as that at which contributions to the strength of adhesion to Mylar from ductile processes finally disappear, Figures 2 and 4.

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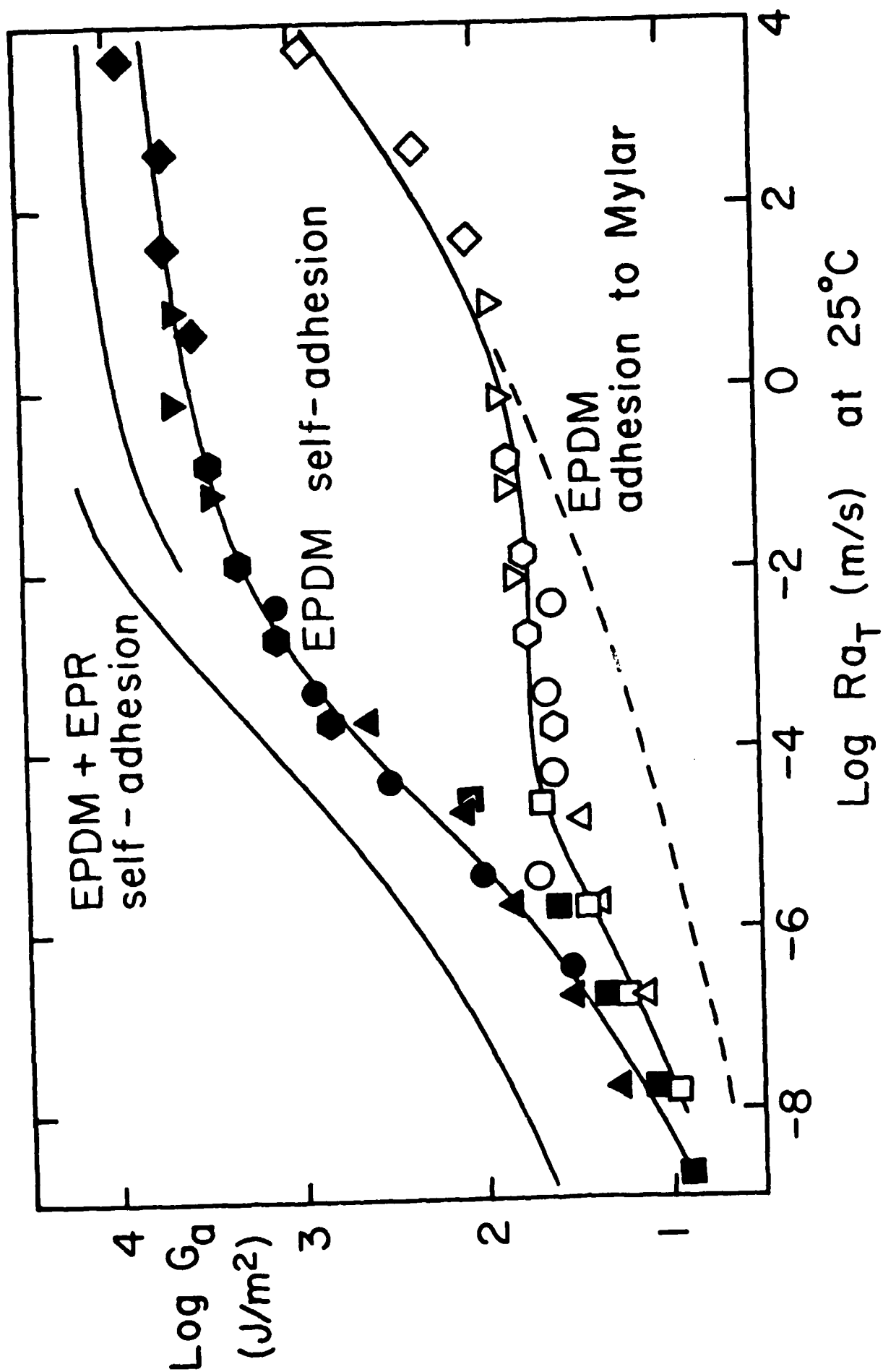


Figure 5

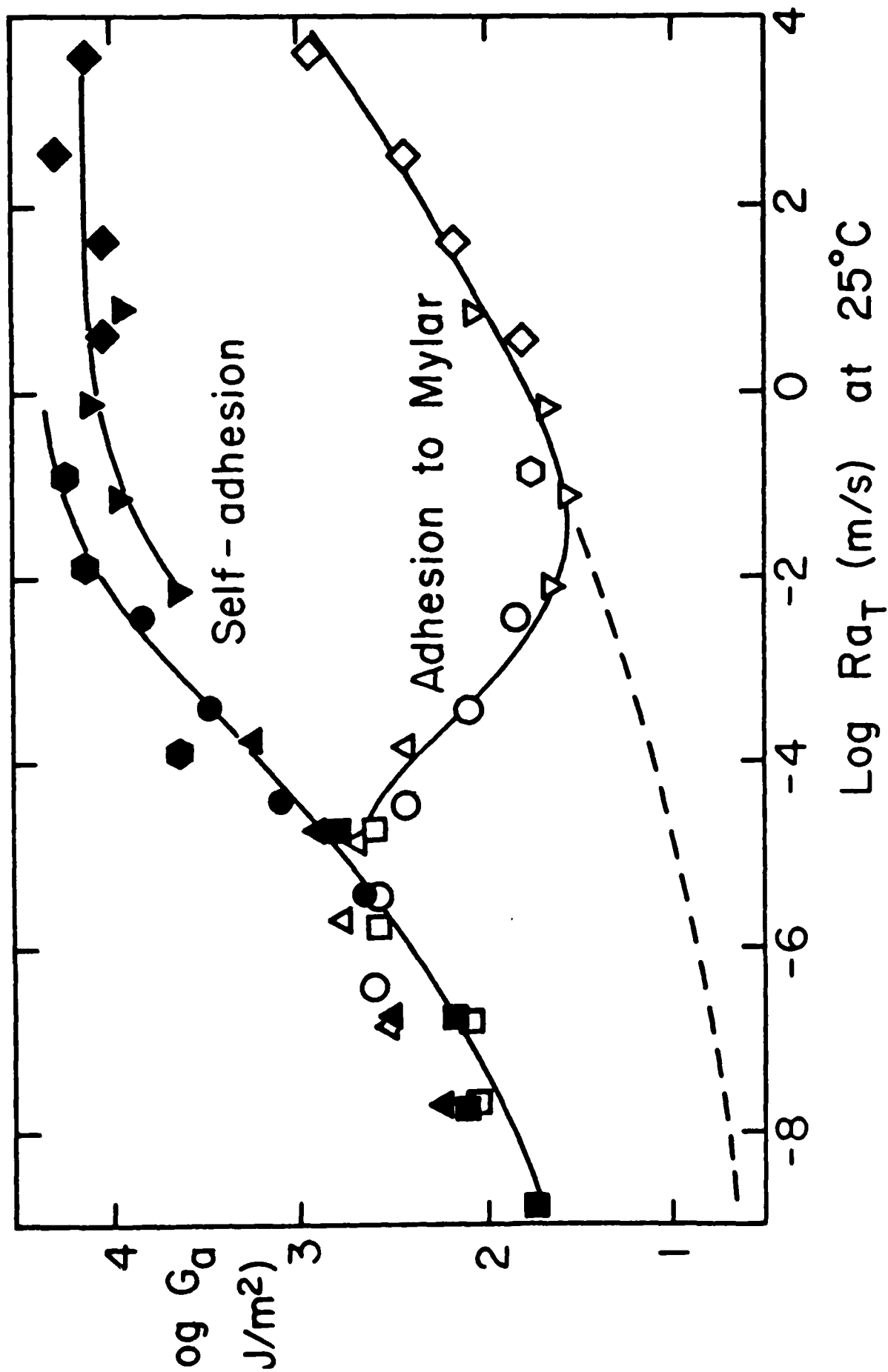


Figure 4

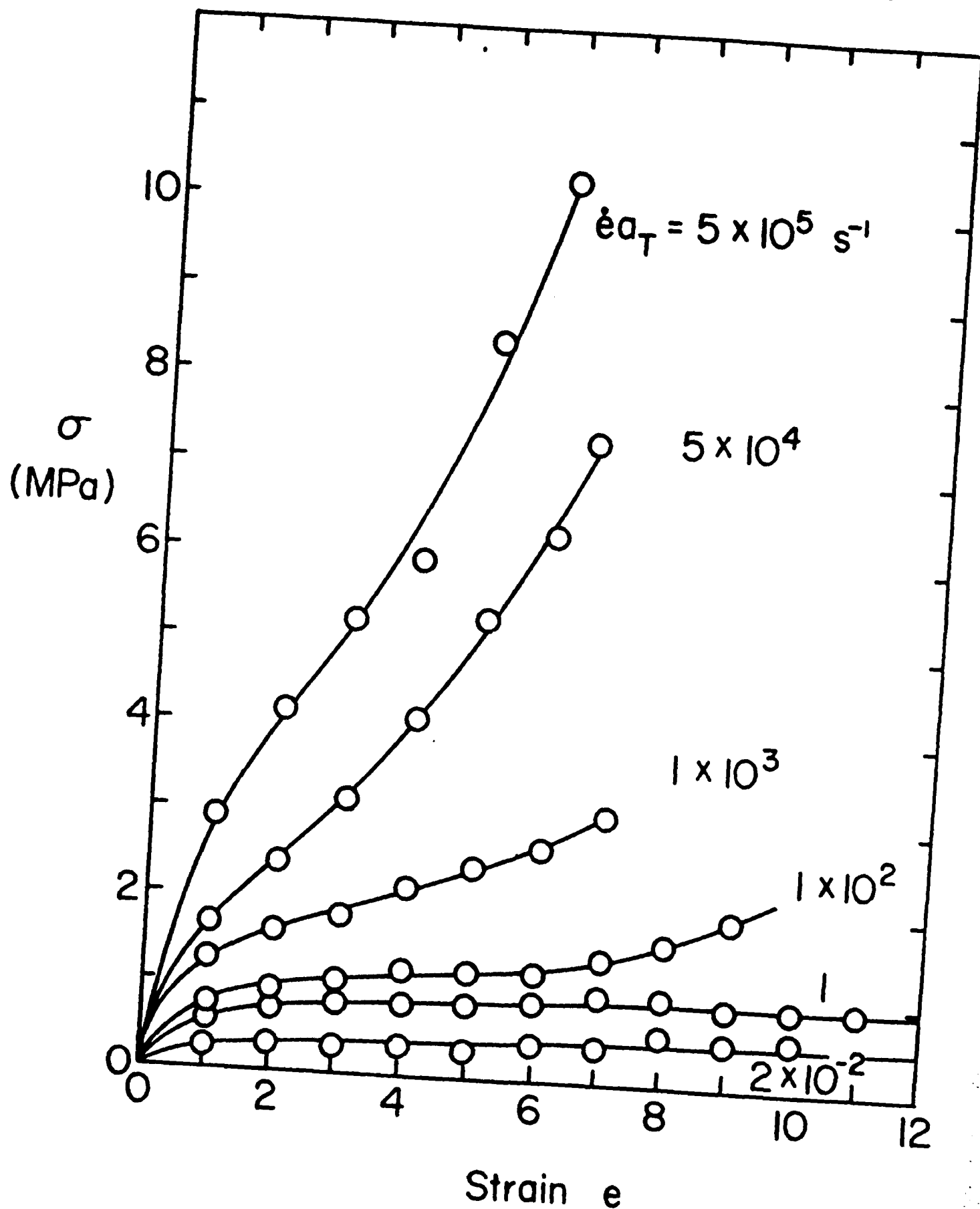


Figure 3

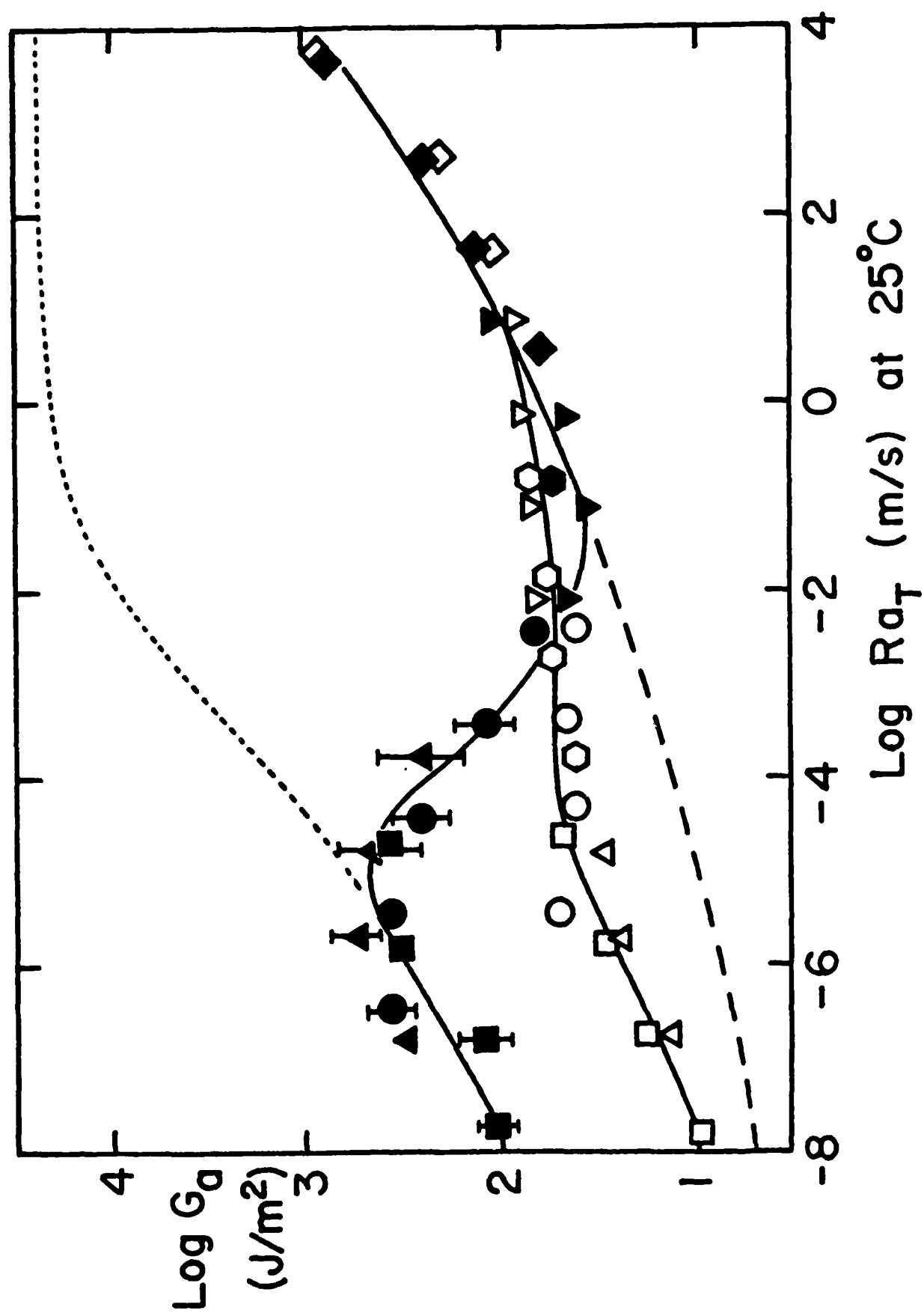
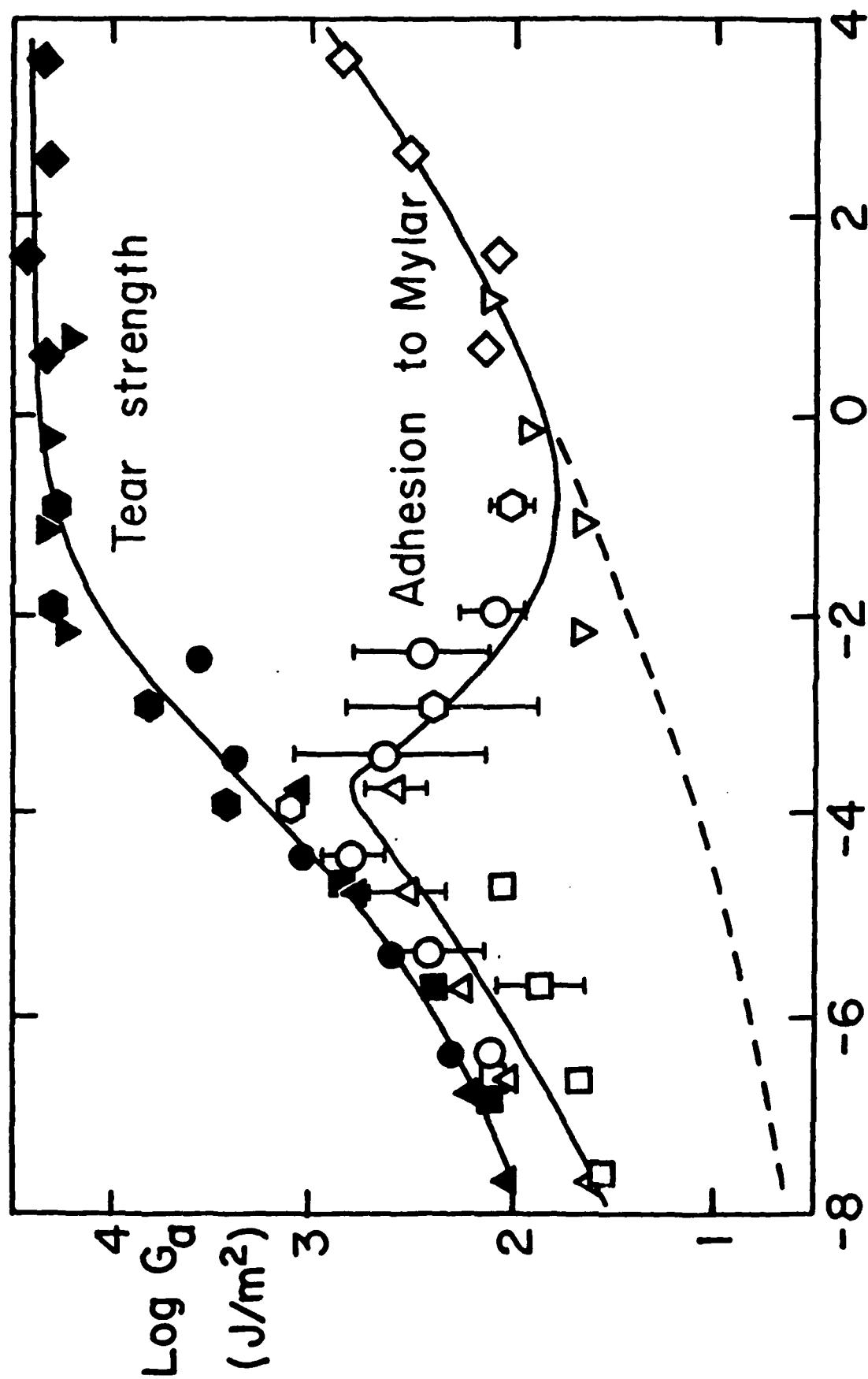


Figure 2



Log Ra_T (m/s) at 25°C

Figure 1

Figure Captions

- Figure 1. Adhesion to Mylar and tear strength of EPR 404, plotted against the effective rate of peeling or tearing at 25°C. Temperature of measurement: -40°C, $\diamond, \blacklozenge$; -20°C, $\nabla, \blacktriangledown$; 0°C, $\circ, \bullet$; 25°C, $\circ, \bullet$; 60°C, $\triangle, \blacktriangle$; 100°C, $\square, \blacksquare$.
- Figure 2. Adhesion to Mylar of crosslinked EPDM 4608 (open points) and crosslinked EPDM 4608 containing an equal amount of EPR 404 (filled-in points) plotted against the effective peel rate at 25°C. The temperature of measurement is represented by the same symbols as in Figure 1. The upper dotted curve represents the tear strength of EPR 404 as a function of the rate of tearing, taken from Figure 1.
- Figure 3. Tensile stress-strain relations at different effective rates of strain at 25°C for crosslinked EPDM 4608 containing an equal amount of EPR 404.
- Figure 4. Self-adhesion (filled-in points) and adhesion to Mylar (open points) for crosslinked EPDM 4608 containing an equal amount of EPR 404, plotted against the effective peel rate at 25°C. The temperature of measurement is denoted by the same symbols as in Figure 1.
- Figure 5. Self-adhesion (filled-in points) and adhesion to Mylar (open points) for crosslinked EPDM 4608, plotted against the effective peel rate at 25°C. The temperature of measurement is denoted by the same symbols as in Figure 1. The upper full curves for EPDM + EPR are taken from Figure 4.

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of such interdiffused molecules is noted, when the (high) strength of self-adhesion undergoes a small reduction at a peel rate of about 100 mm/s.

The effect of interdiffused species on self-adhesion seems to be more pronounced for the present materials than in previous studies with butyl rubber networks containing linear polyisobutylene molecules (1). This is probably due to a somewhat lower degree of crosslinking in the present EPDM system, and to the tendency of ethylene-propylene polymers to entangle more densely (10).

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4. Conclusions

The strength of adhesion of a layer of uncrosslinked EPR to a Mylar substrate undergoes a marked transition at effective peel rates in the range 100 $\mu\text{m/s}$ - 100 mm/s at 25°C. Below this range, adhesion is relatively strong, close to the tear strength of the polymer. Above this range of rates, the adhesion is weaker although it increases markedly at higher peel rates as the material approaches the glassy state.

The transition is attributed to a cessation of entanglement slipping as the rate of imposed deformation increases. In consequence, the EPR material changes from a highly-extensible soft solid to a stiffer elastic substance. Apparently, ductile flow processes are associated with a major part of the work of separation at low peel rates.

A similar, but smaller, transition is seen in lightly-crosslinked EPDM, and a quite-comparable one in crosslinked EPDM containing EPR. Such materials also appear to be softer and more extensible when the rate of deformation is low and entanglement slippage is possible. The peel strength is correspondingly enhanced. However, at high peel rates when no entanglement slippage occurs, all of these materials show a similar, and rather low, level of adhesion to a Mylar substrate.

In contrast, the level of self-adhesion of these materials is much higher at high peel rates, as much as 100X higher. This remarkable enhancement is attributed to the presence of inter-diffused molecular strands, especially when linear EPR molecules are present, which are unable to disentangle at high peel rates. Indeed, some evidence for a transition from forced flow to fracture

It may be concluded that entanglements within the polymer layer no longer slip free at this peel rate. In the case of self-adhesion, the interdiffused molecules must then break, rather than disentangle. There is apparently somewhat less work expended in rupture of molecules crossing the interface rather than in pull-out, so that the peel force then becomes smaller.

Even the crosslinked EPDM material with no added EPR showed a remarkably high level of self-adhesion at high rates of peeling, Figure 5. Experimental values at an effective peel rate of 1 m/s were some 30X greater than for adhesion to Mylar, approaching one-half of those obtained for the EPDM-EPR mixture. It may be inferred that a considerable amount of interdiffusion and entanglement of network strands takes place between two layers of this lightly-crosslinked material.

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