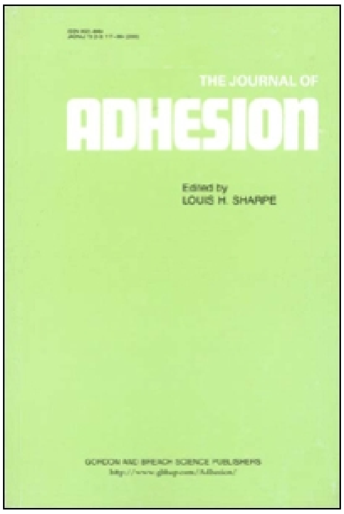

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Effect of Wetting Liquids on the Strength of Adhesion of Viscoelastic Material

A. N. Gent[a]; J. Schultz[ab]
[a] Institute of Polymer Science, The University of Akron, Akron, Ohio, U.S.A. [b] Le Centre de Recherches sur les Surfaces Solides, Mulhouse, France

To cite this Article Gent, A. N. and Schultz, J.(1972) 'Effect of Wetting Liquids on the Strength of Adhesion of Viscoelastic Material', The Journal of Adhesion, 3: 4, 281 — 294

To link to this Article: DOI: 10.1080/00218467208072199

URL: http://dx.doi.org/10.1080/00218467208072199

J. Adhesion, 1972, Vol. 3, pp. 281-294

Printed in Northern Ireland

Effect of Wetting Liquids on the Strength of Adhesion of Viscoelastic Materials[†]

A. N. GENT and J. SCHULTZ[‡]

Institute of Polymer Science
The University of Akron, Akron, Ohio 44304 U.S.A.

(*Received November* 8, 1971)

The effect of a variety of wetting liquids on the resistance to peeling separation for a lightly crosslinked rubbery adhesive in contact with a Mylar substrate has been studied over a wide range of peeling rates and at two temperatures. Although the magnitude of the peel strength is much greater than the thermodynamic work of detachment, it is reduced by alcohols and alcohol/water mixtures in good agreement with calculated reduction factors. It is concluded that the measured strength is a product of two terms: the thermodynamic work, and a numerical factor, generally large, denoting inefficiency. The latter term is strongly dependent on peel rate and temperature for viscoelastic adhesives. Two anomalies are pointed out: particularly low adhesion is observed at low rates of peel for certain liquids, attributed to swelling of the adhesive, and smaller effects are found for some other liquids than predicted.

INTRODUCTION

The observed strength of adhesion of simple viscoelastic adhesives to rigid substrates has been found to vary with the speed of detachment and with temperature in accordance with the well-known Williams, Landel and Ferry (WLF) rate-temperature equivalence governing the motion of molecular segments[1-5]. This observation proves that the strength of adhesion

---

[†] This paper was presented at the *Symposium on Recent Advances in Adhesion* during the 162nd National American Chemical Society Meeting, September, 1971.

[‡] On leave of absence from *Le Centre de Recherches sur les Surfaces Solides*, Mulhouse, France (1970/71).

depends on segmental mobility; that is, it depends on kinetic processes within the adhesive. The cohesive strength of simple viscoelastic materials has been found to depend on segmental mobility in the same way[6–9]. (Indeed, the tearing resistance of elastomers of quite different chemical structure appears to be substantially the same under conditions of equal segmental mobility[8].).

These effects bring into question the role of equilibrium thermodynamic properties, such as spreading coefficient, heat of wetting, etc., in determining the strength of adhesion under non-equilibrium conditions.

To examine the importance of both kinetic and thermodynamic factors an experimental study has been made of the peeling resistance of a model viscoelastic adhesive on an inert substrate, in the presence of a variety of wetting liquids. These measurements have been carried out over a wide range of peeling rate and at different temperatures. In addition, measurements have been made of contact angles in all cases, and the thermodynamic works of detachment have been calculated from them using known surface energies. The results obtained from both these procedures are described and compared below.

THEORETICAL CONSIDERATIONS

The reversible work of detachment under equilibrium conditions, denoted W_o, is given directly by the surface free energies of the various components as follows:

(i) For detachment in vacuo, or in an inert atmosphere,

$$W_o = \gamma_a + \gamma_s - \gamma_{as}, \tag{1}$$

where γ_a, γ_s, γ_{as}, are the surface free energies of the adhesive, substrate, and adhesive-substrate interface.

(ii) For detachment in the presence of a wetting liquid, indicated by the suffix l,

$$W_{ol} = \gamma_{al} + \gamma_{sl} - \gamma_{as}. \tag{2}$$

From equilibrium considerations the interfacial energies γ_{al} and γ_{sl} are related to the contact angles θ_{al} and θ_{sl} at liquid-adhesive and liquid-substrate boundaries by Young's equation:

$$\gamma_{al} = \gamma_a - \gamma_l \cos\theta_{al},$$

$$\gamma_{sl} = \gamma_s - \gamma_l \cos\theta_{sl}.$$

Substituting in equation 2 yields

$$W_{ol} = W_o - \Delta, \tag{3}$$

where $\Delta = \gamma_l(\cos\theta_{al} + \cos\theta_{sl})$.

The quantity Δ is the calculated reduction in the work of detachment in the presence of a liquid in comparison with that in its absence, expressed in terms of readily-measured properties of liquids. If Δ is greater than the work of detachment W_o in the absence of the liquid, then W_{ol} is negative and the adhesive and substrate will spontaneously separate when the liquid is present, as described by Owens[10]. The maximum value of Δ is $2\gamma_l$ when the liquid wets both the adhesive and the substrate completely, i.e., $\theta_{al} = \theta_{sl} = 0$. On the other hand, when the liquid is a sufficiently poorly wetting one, then Δ becomes negative and the work of detachment in the presence of the fluid is predicted to be greater than that in its absence, $W_{ol} > W_o$.

The physical significance of the contact angle θ and its relationship to other measures of the type and degree of interaction between media in contact have been given considerable attention by other workers[11-16]. These aspects of wetting are not considered here.

EXPERIMENTAL DETAILS

The material employed as a model viscoelastic adhesive was a rubbery copolymer of butadiene and styrene (60:40, Ameripol 1513) with a glass transition temperature T_g of −40°C. One per cent by weight of dicumyl peroxide and a similar amount of phenyl-2-naphthylamine were mixed into it on an open mill. The mixture was then pressed into a flat sheet about 0.6 mm thick between a film of polyethylene terephthalate (Type 300 A Mylar, E. I. du Pont de Nemours and Co.) and a sheet of finely-woven cotton cloth, and lightly crosslinked in this position by heating for 1 hr at 150°C.

Test strips about 2.5 cm wide and 15 cm long were cut from the cloth/polymer/Mylar sandwich. The cloth and Mylar layers at one end of the strip were separated, gripped in the clamps of a testing machine, and pulled apart at a controlled rate. Because the polymer had penetrated the cloth layer to some degree before crosslinking was effected, it adhered to this layer strongly and peeled cleanly away from the Mylar substrate. The experiments were conducted both with the sample immersed in various liquids and in the dry state. No effect was observed of the time of immersion before peeling apart, over the range 1 min to 24 hr.

The strength of adhesion is characterized below by the work of detachment W per unit area of growth of the cleavage plane, where W is obtained directly from the force P per unit width of the test strip:

$$W = 2P$$

for the present test arrangement.

The contact angle θ was measured directly by photomicrography and also calculated from the observed dimensions of a liquid drop assuming that the drop took up the shape of a spherical cap[17]. Good agreement was obtained between the two methods. To minimize gravitational effects a small drop size, about 0.5 μl, was employed.

EXPERIMENTAL RESULTS

(a) Contact angles

The angle of contact was found to depend on the time of contact, decreasing with increasing time as the result of two processes: rapid initial spreading of the drop, followed by slow evaporation without further spreading. Some typical results are shown in Figure 1. The initial spreading was generally completed in about 2 min; the subsequent decreases in angle took place linearly with time, at least over the next 6–8 min, at a rate of about 3° per min for water, higher rates for more volatile liquids (e.g., ethanol/water mixtures), and much smaller rates, about 0.1° per min, for relatively non-volatile liquids (e.g., glycol, glycerol and formamide). By extrapolating these linear relations back to zero time of contact, values of the effective contact angle in the absence of both spreading and evaporation were obtained. Denoted θ_o, they are given in Table I. (This procedure is assumed to be equivalent to measuring the advancing contact angle at zero rate.) Values of θ at the end of spreading were not greatly different from θ_o.

It was noticed that the Mylar substrate became slightly colored after the adhesive had been applied and peeled off. A corresponding change in contact angle was found to take place, the values measured after peeling being denoted θ_{os}' in Table I. Experiments using Ameripol 1513 purified in various ways revealed that the changes in contact angle and discoloration of the Mylar were eliminated either by extracting the Ameripol 1513 with hot butanol for three days before use or by washing the Mylar surface afterwards. We infer that the effect is due to a contamination of the Mylar surface by a butanol-soluble material present in Ameripol 1513. No significant changes in the wetting properties of the Ameripol 1513 were found to occur as a result of butanol extraction or washing.

Values of the surface tension γ_l were taken from published lists[18]; they are given in Table I, together with values of Δ calculated from them and the contact angles θ_{oa}, $\theta_{os'}$ by means of equation 3.

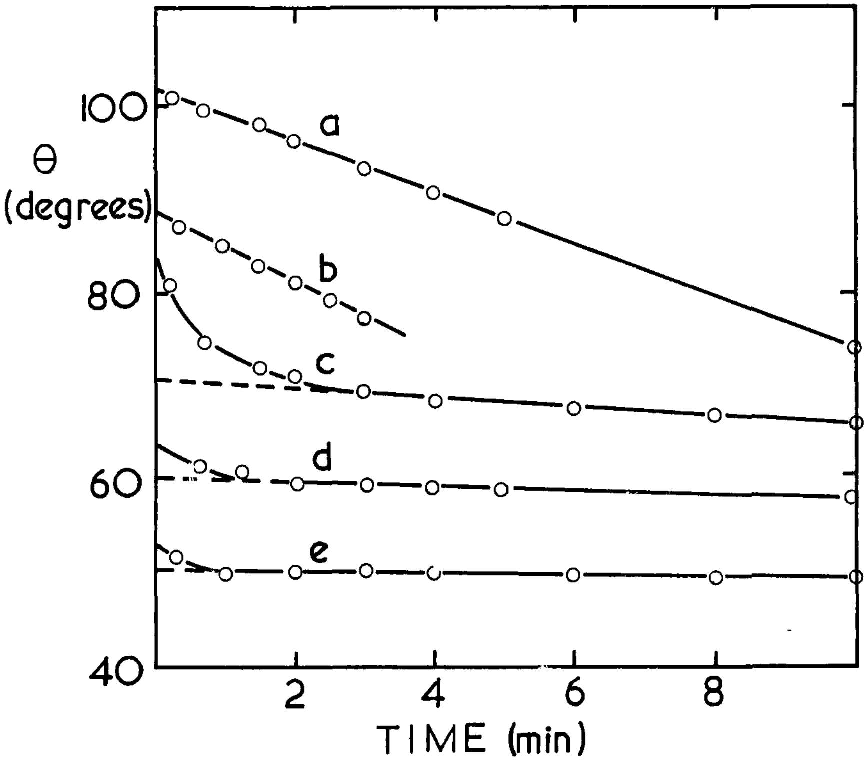

FIGURE 1 Contact angle *θ vs* contact time. a, Water on adhesive; b, 10% ethanol on adhesive; c, glycol on adhesive; d, glycerol on Mylar; e, glycol on Mylar.

(b) Work of detachment

Experimentally determined values of W are plotted in Figure 2 against the rate R of advance of the separation front. Logarithmic scales are used for both axes in view of the wide ranges. The results obtained in air agree closely with those obtained previously[3]. They depend strongly upon the rate of separation R and can be described satisfactorily by the empirical relationship:

$$W\,(\text{ergs/cm}^2) = 1 \times 10^5\,[R(\text{cm/sec})]^{0.42} + C \qquad (4)$$

over the entire range of rates, covering 4.5 orders of magnitude, where C is a small constant, lying between 50 and 500 ergs/cm². (Experiments at still

TABLE I

Wetting properties of various liquids on surfaces of Mylar (suffix *s*) and crosslinked Ameripol 1513 (suffix *a*).

Liquid	γ_l (ergs/cm^2)	θ_{os} (degrees)	θ'_{os} (degrees)	θ_{oa} (degrees)	Δ (ergs/cm^2)
Water	72.8	76	88	98	-7
Ethanol/water (10/90)	51	64	74	90	$+14$
Methanol/water (50/50)	35	54	55	60	35
Butanol	24.7	0	0	ca 10	49
Ethanol	22.7	0	0	ca 20	44
Glycerol	63.4	60	72	82	28
Formamide	58.2	56	68	72	39
Ethylene glycol	47.7	51	60	70	40

lower rates would be necessary to determine the value of C with any precision. It is provisionally attributed to the thermodynamic work of detachment W_0 under equilibrium conditions.)

In the presence of a wetting liquid two different effects are seen. First, the results tend to follow a parallel relation to that obtained in air. The ratio W_l/W, where W, W_l denote the values obtained for the work of detachment in air and in the liquid at a particular rate of separation, is thus a constant, characteristic of the liquid and independent of the rate of separation. The dependence of this ratio upon the wetting properties of the liquid is discussed below. Secondly, for some liquids the results ceased to follow a parallel relation at low rates of separation. Instead, the work of detachment at low rates was reduced to a greater extent than a parallel relation would have indicated. This anomalous behavior in some cases is attributed to local swelling; it is discussed in detail later.

In Figure 3 the experimentally—determined values of the ratio W_l/W, obtained from parallel linear relations such as those shown in Figure 2 at high rates of separation, are plotted against the calculated reduction Δ in the thermodynamic work of detachment for each liquid. For the series comprising water, alcohols, and mixtures of water and alcohols, the results fall substantially on a straight line in accordance with equation 3, extrapolating to zero work of detachment for a hypothetical fluid for which Δ is about 80 ergs/cm^2. This should be the thermodynamic work of detachment W_0 for the adhesive/substrate combination *in vacuo* or in an inert atmosphere, according to equation 3. It is indeed in good agreement with the maximum possible value of W_0 obtained by summing the reported surface energy of Mylar film, 47 ergs/cm^2 [10] and the value deduced for the butadiene-styrene copolymer, 36 ergs/cm^2, using the method of Owens and Wendt[19].

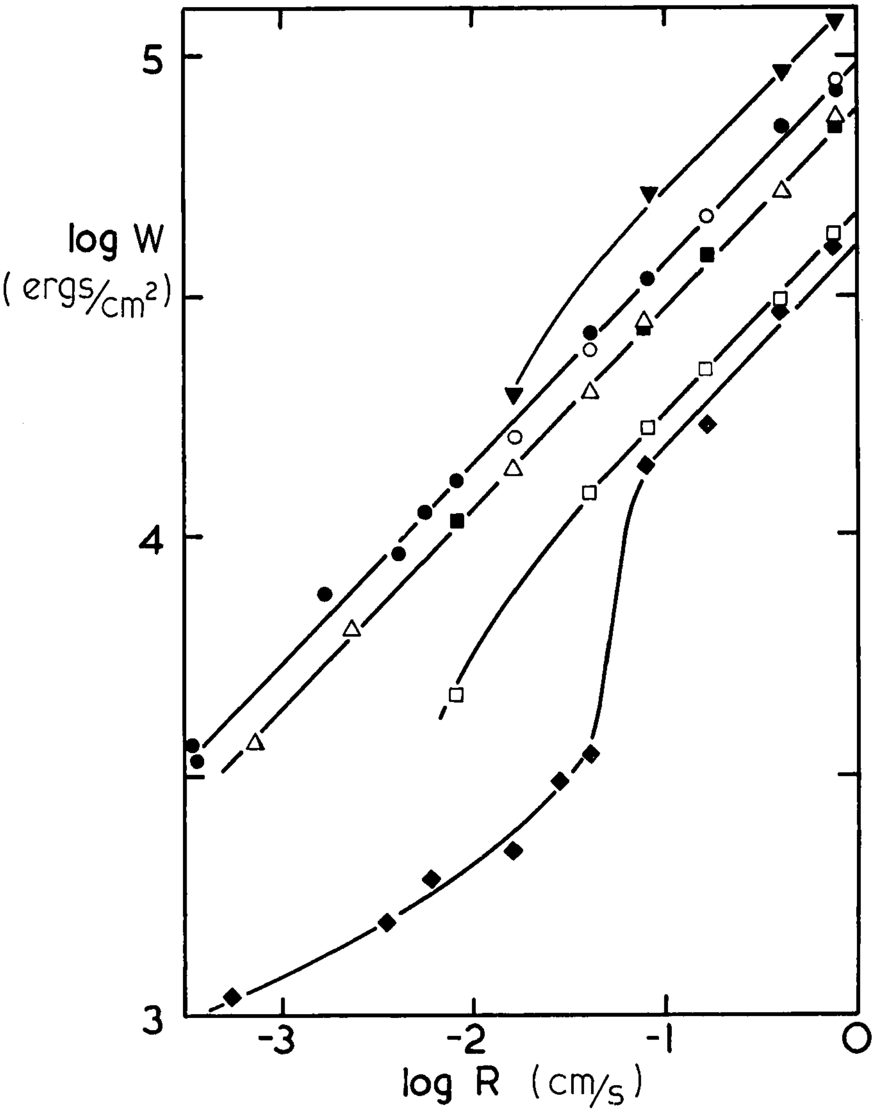

FIGURE 2 Peeling energy W *vs* rate of peel. ▼, Glycerol; ●, air; o, water; ■, ethanol/water 10/90; Δ, ethylene glycol; □, ethanol: ◆, l-butanol.

This agreement in both form and magnitude between the results shown in Figure 3 and the predictions of equation 3 is really rather surprising, because the actual values of the adhesion energies W and W_l are generally much larger than the equilibrium values W_o, W_{ol} (Figure 2). Apparently the ratio

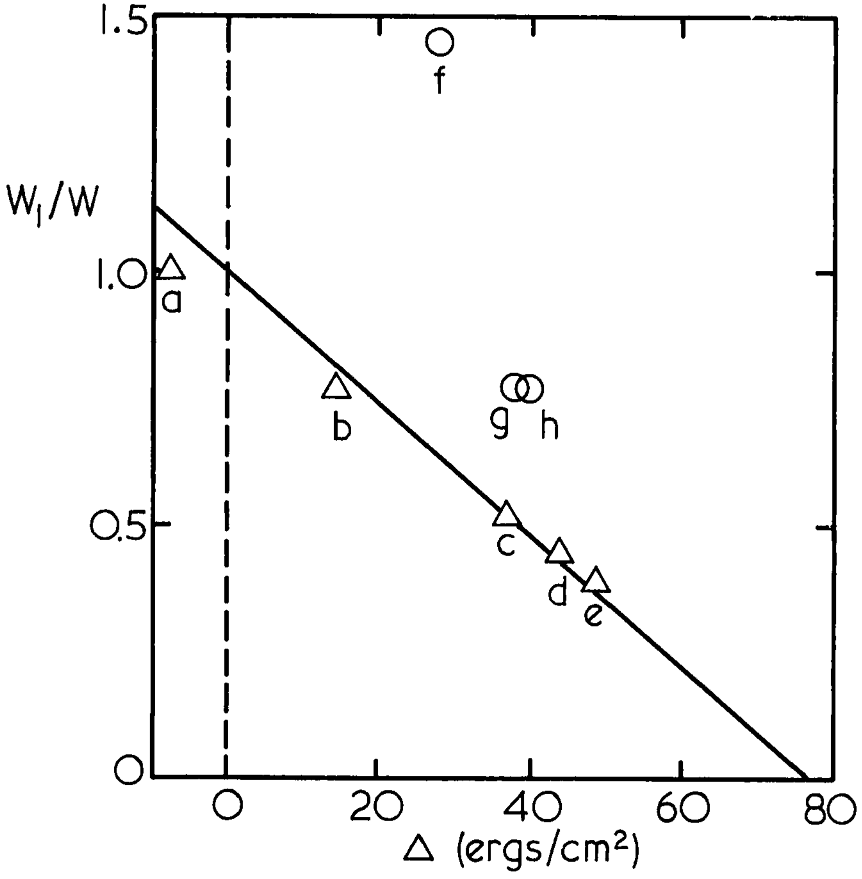

FIGURE 3 Peeling energy W_l in the presence of various liquids *vs* calculated reduction Δ. a, Water; b, 10% ethanol; c, 50% methanol; d, ethanol; e, butanol; f, glycerol; g, glycol; h, formamide.

is nevertheless equal to the equilibrium ratio and depends upon the wetting properties of the liquid accordingly.

We conclude that the observed adhesion energy W must be factorizable into two terms, one representing the equilibrium value W_0 and one, denoted $f(R)$, representing the magnification factor developed at a finite speed of separation R because energy is expended then in irreversible processes within the adhesive. Thus,

$$W/W_0 = W_l/W_{0l} = f(R). \tag{5}$$

From equation 4 the function $f(R)$ takes the empirical form

$$f(R) = 1.25 \times 10^3 \, [R(\text{cm/sec})]^{0.42} + 1,$$

assuming that C and W_0 take the value 80 ergs/cm². This relation, in conjuction with equations 3 and 5, describes the present results for a wide range of rates of separation and for a variety of liquids. (However, it will not apply at much larger rates than those used here when the adhesive fails to respond as a rubbery material and becomes glasslike[3].)

A second feature of the peeling resistance for samples immersed in wetting fluids is a change in behavior in some instances at low rates of peel. A particularly pronounced example was obtained using butanol, Figure 2; the peeling

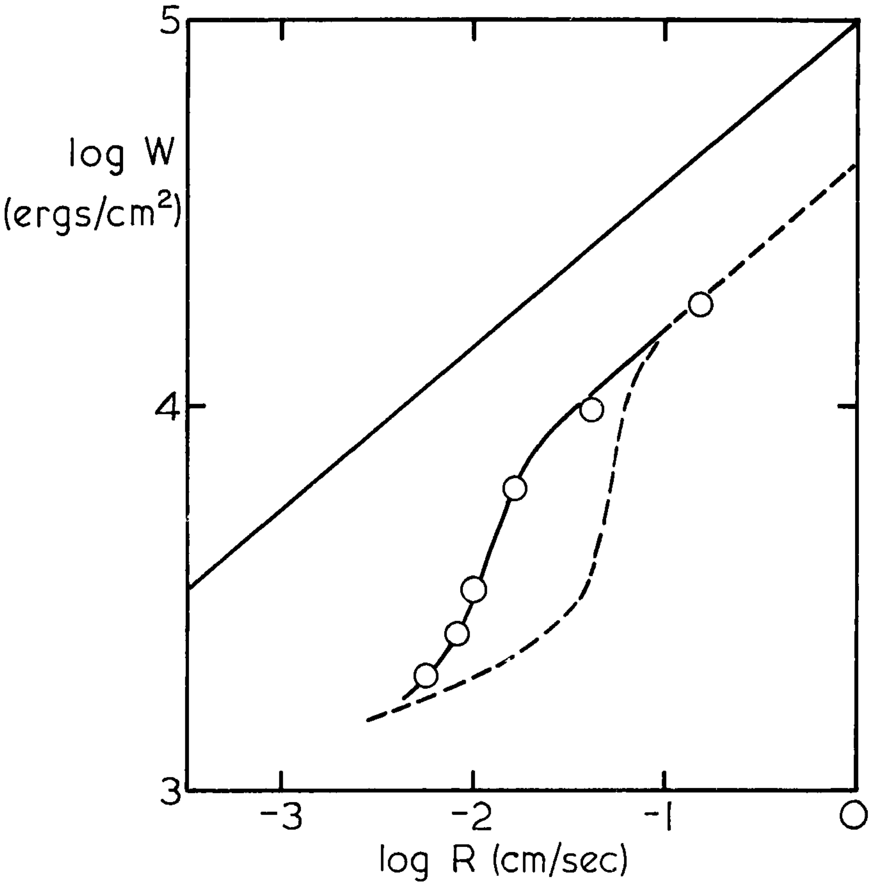

FIGURE 4 Peeling energy W *vs* rate of peel. Upper curve, in air; broken curve, in butanol; replotted from Figure 2. Circles, peeling results in butanol for testpieces made with butanol-extracted adhesive.

resistance at rates of less than about 5 cm/min became much smaller than would be expected on the basis of the results obtained at higher rates. This anomalous behavior was found to occur over the same general range of rates for methanol also, but to a somewhat smaller extent. Both of these liquids swell the rubbery adhesive significantly, butanol by about 3.5 per cent and methanol by about 1.5 per cent. It seems possible that the anomalous behavior at low rates of peel is due to a swelling action of the liquid on the adhesive in the peeling zone.

When the Ameripol 1513 was extracted with hot butanol for three days before use, the anomalous reduction in peel resistance at low rates of separation when immersed in butanol was still found to occur, but at lower rates of peel than before, Figure 4. The rate of swelling of the crosslinked material by butanol was also found to be significantly reduced by this prior extraction procedure, although the final degree of swelling was not altered appreciably. These observations suggest that slight swelling of the adhesive causes a severe reduction in peel strength. The effect might be due to swelling stresses set up in the contact region. It is restricted to low rates of peel presumably because the adhesive ahead of the separation front swells slowly. Although this hypothetical mechanism accounts for the observed rate effects in a qualitative way, and for the relative effects of different liquids, further experiments would be required to test it in a critical way.

Peeling results with some other liquids, for example ethylene glycol, glycerol, and formamide, gave energies of detachment appreciably higher than predicted by thermodynamic considerations, as shown in Figure 3. These liquids have been reported to differ in their wetting properties from the alcohol/water series[15]. Evidence of this is given in Figure 5 where the cosines of the measured contact angles on the rubbery adhesive and the Mylar film are plotted against the surface tension of the liquid, as suggested by Zisman[11]. A marked difference is clear in both cases between the relations for the ethanol/water series of liquids and the other liquids, corresponding to quite different values of the critical surface tension of the surface with the different types of liquid. These observations (and the much more extensive studies of Dann[15]) show that the contact angle is not related in a simple way to the interfacial energies. Indeed, the present observations raise the question whether the observed macroscopic contact angle for the aberrant liquids is really applicable to the interface on a molecular scale. It is noteworthy that the agreement between observed and predicted values of the peel strength in the presence of glycol, glycerol and formamide would be much improved if their contact angles were those for alcohols of the same surface energies, in place of the larger values observed here (and by others).

It should also be noted that the aberrant liquids are considerably more viscous than the alcohol/water series. Although the effect of liquid viscosity

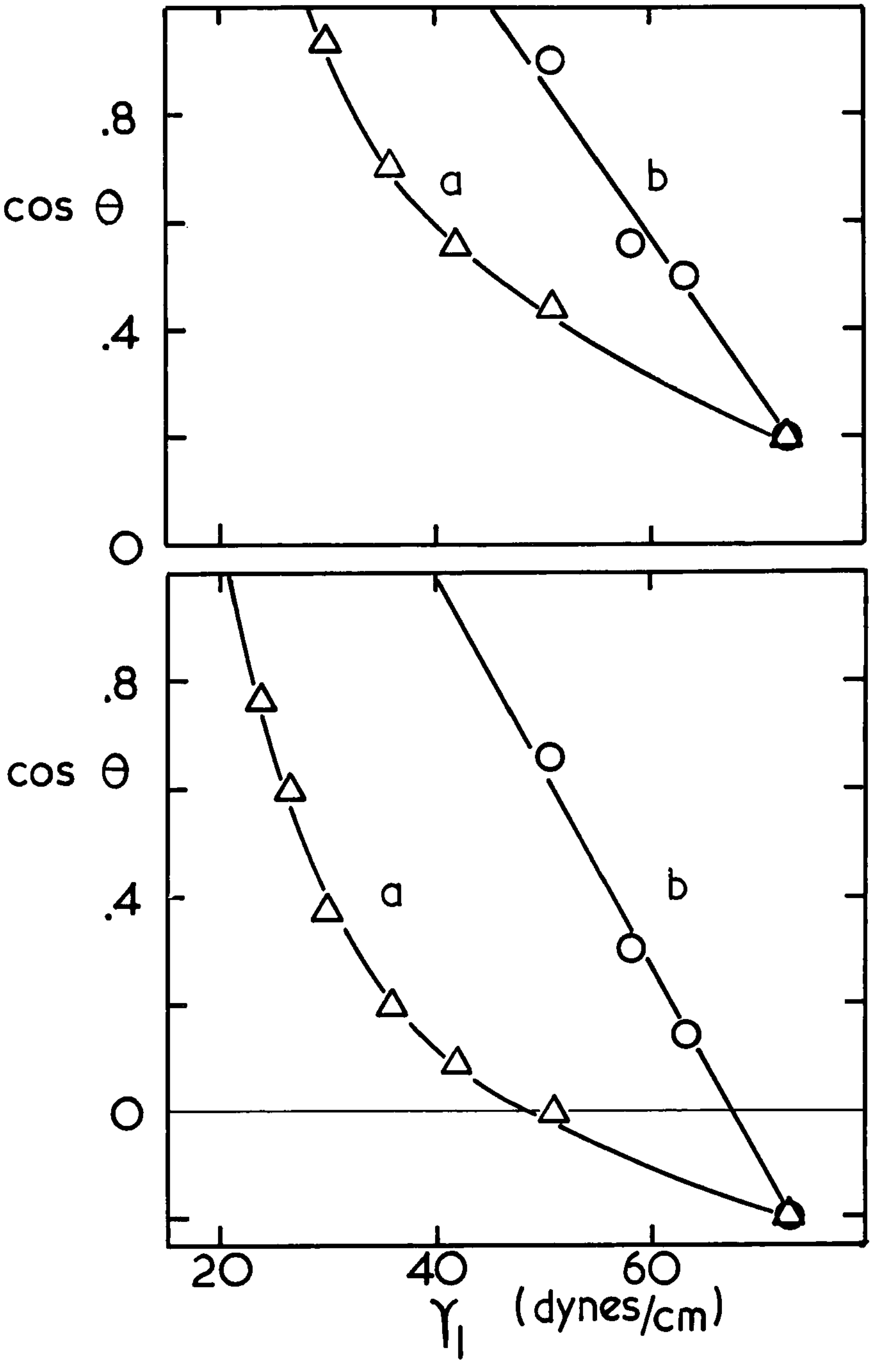

FIGURE 5 Zisman plots; upper curves for Mylar, lower curves for adhesive. a, Ethanol/water series; b, various other liquids.

has not been examined here, in extreme cases the viscous character would prevent direct wetting altogether[20] and the observed strength would then not reflect thermodynamic properties of the liquid at all.

Measurements were also made of the peel strength at lower temperatures, about 5°C. The strengths were higher in all cases; some typical results are shown in Figure 6. This enhancement in peel strength is mainly due to decreased segmental mobility of the adhesive molecules at the low temperature. As for other viscous and viscoelastic properties which depend upon segmental motion, the peel strength measured at a low temperature can be regarded as equal to that measured at an equivalent high rate of deformation (i.e., high rate of peel) at room temperature[1-5]. The equivalent rate of peel at room temperature may be calculated by means of the Williams, Landel and Ferry rate-temperature equivalence for simple glass-forming materials. When replotted in this way against the equivalent rate at room temperature (23°C), the peel strengths were generally found to agree reasonably well with the values measured directly at 23°C. The greatest discrepancy was found for butanol, Figure 6, where the WLF transformation seriously overcorrected for the effect of temperature. Some part if not all of this discrepancy is probably due to simultaneous changes in surface energies and contact angles with temperature; it became increasingly apparent with increasing effect of the wetting liquid, i.e., as the wetting properties became increasingly important.

CONCLUSIONS

The following conclusions are obtained:

(i) Although the work of detachment of a crosslinked rubber from Mylar depends strongly on the rate of peel, a variety of liquids reduce the work by factors independent of the rate. (For liquids which swell the rubber somewhat this is only true at high rates of peel.)

(ii) For the alcohol/water series of liquids the reduction factor is in good agreement with that predicted from simple thermodynamic considerations, even though the actual energies of detachment are larger by orders of magnitude than those predicted.

(iii) We deduce that the observed peel strength is the product of two terms: an equilibrium work of detachment given by thermodynamic considerations, and a numerical factor representing the enhancement of strength when the adhesive is imperfectly elastic. In the present instance the adhesive is viscoelastic and the second term is therefore both large and strongly dependent on the rate of peeling.

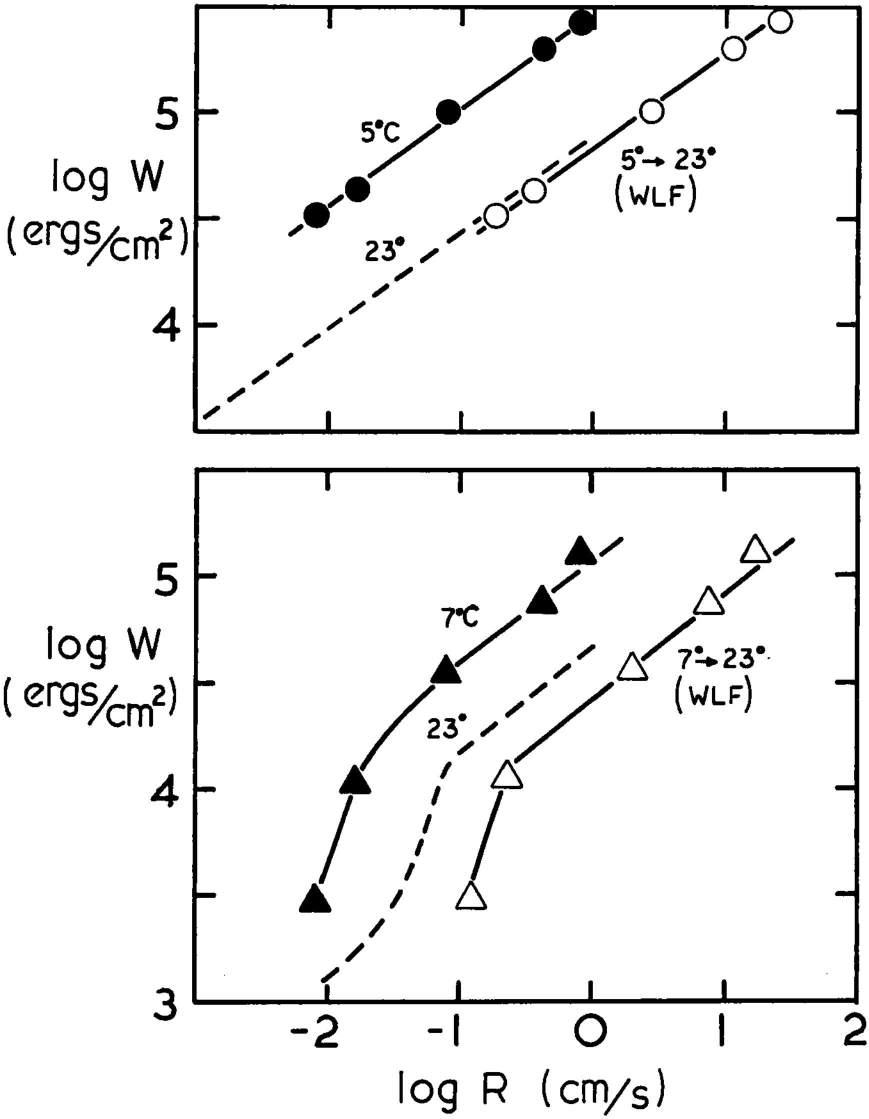

FIGURE 6 Peeling energy *vs* rate of peel at low temperatures. Upper curves, in glycol; lower curves, in butanol. Broken curves, relations obtained at 23 °C, replotted from Figure 2.

(iv) In agreement with this hypothesis the peel strength was found to increase at lower temperatures in reasonable accord with the WLF rate-temperature equivalence, even in the presence of wetting liquids. Other changes with temperature are tentatively attributed to changes in the wetting properties.

(v) Several liquids whose wetting properties are rather different from the alcohol/water series gave much poorer agreement between the observed reduction in peel strength and the calculated reduction in equilibrium strength. The reason for this difference is not known. It may reflect inadequacies in the determination of the true wetting properties of these liquids or it may arise from their significantly higher viscosities.

Acknowledgement

This work was supported by a research grant from the Engineering Division of the National Science Foundation.

References

1. D. H. Kaelble, *Adhesives Age* **3**, No. 5, 37 (1960).
2. D. H. Kaelble, *J. Adhesion* **1**, 102 (1969).
3. A. N. Gent and R. P. Petrich, *Proc. Roy. Soc. (London)* **A310**, 433 (1969).
4. A. N. Gent, *J. Polymer Sci. A*-2 **9**, 283 (1971).
5. A. N. Gent and A. J. Kinloch, *J. Polymer Sci. A*-2 **9**, 659 (1971).
6. F. Bueche, *J. Appl. Phys.* **26**, 1133 (1955).
7. T. L. Smith, *J. Polymer Sci.* **32**, 99 (1958).
8. L. Mullins, *Trans. Instn. Rubber Ind.* **35**, 213 (1959).
9. A. N. Gent and A. W. Henry, *Proc. Internatl. Rubber Conf., Brighton*, 1967 (Maclaren and Sons, London 1968), p. 193.
10. D. K. Owens, *J. Appl. Polymer Sci.* **14**, 1725 (1970).
11. W. A. Zisman, in *Adhesion and Cohesion*, P. Weiss, Ed. (Elsevier, Amsterdam, 1962), p. 176.
12. L. A. Girafalco and R. J. Good, *J. Phys. Chem.* **61**, 904 (1957).
13. R. J. Good and L. A. Girafalco, *J. Phys. Chem.* **64**, 561 (1960).
14. F. M. Fowkes, in *Treatise on Adhesion and Adhesives*, Vol. 1, R. L. Patrick, Ed. (Marcel Dekker, Inc., New York, 1967), Chap. 9.
15. J. R. Dann, *J. Coll. Interface Sci.* **32**, 302, 321 (1970).
16. D. H. Kaelble and E. H. Cirlin, *J. Polymer Sci. A*-2 **9**, 363 (1971).
17. H. Schonhorn, H. L. Frisch and T. K. Kwei, *J. Appl. Phys.* **37**, 4967 (1966).
18. *Handbook of Chemistry and Physics*, 51*st Edn.*, R. C. Weast, Ed., (Chemical Rubber Co., Cleveland, 1970), pp. F-28 to F-33.
19. D. K. Owens and R. C. Wendt, *J. Appl. Polymer Sci.* **13**, 1741 (1969).
20. G. Inverarity, *Brit. Polymer J.* **1**, 245 (1969).