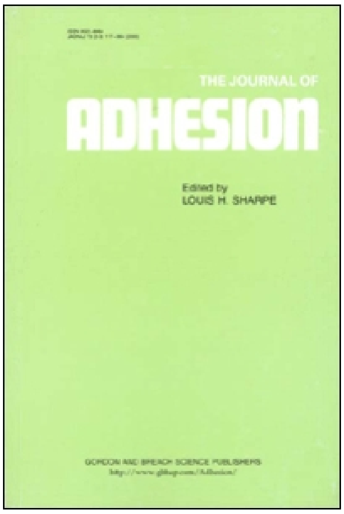

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Polymer—Aluminium Adhesion IV. Kinetic Aspect of the Effect of a Liquid Environment

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The effect of a liquid in the failure of an assembly depends strongly on the ability of the liquid to follow the fracture front. Thus, the existence of a critical rate of separation above which the liquid has no effect on the strength of the assembly, has been clearly demonstrated.

From a crack model, parameters determining the penetration rate of the liquid in the growing fracture have been established and are:

—the viscosity of the liquid,
—its surface energy,
—and the solid/liquid interactions.

This analysis also shows that the dimension of the crack opening is of the order of a micron.

INTRODUCTION

Separation in a liquid medium of an adhesive assembly is usually accompanied by a modification of the work of detachment. The changes resulting from the presence of the liquid can be quantitatively predicted by taking into account the surface characteristics of the liquid and the surface properties (adhesive failure) or the cohesive properties (cohesive failure) of the solids in contact.[1–4]

In a previous article,[4] we studied the thermodynamic aspect of the action of a liquid environment. According to the theory developed by Gent and Schultz[1] and modified by Schultz and Carré,[2] the failure energy, $\mathscr{W}$, in an inert medium is written:

$$\mathscr{W} = W_o \times g(M_c) \times f(R) \qquad [1]$$

where W_o is the reversible work of separation, $g(M_c)$ and $f(R)$, the molecular and macroscopic factors of energy dissipation in the elastomer.

In a liquid medium which does not modify appreciably by swelling the viscoelastic characteristics of the adhesive, the dissipation function $f(R)$ does not vary and the failure energy, $\mathscr{W}_L$, is given by:

$$\mathscr{W}_L = W_{oL} \times g(M_c) \times f(R) \qquad [2]$$

where W_{oL} is the reversible work of separation in the liquid medium.

One infers directly that, for given peel rate and temperature:

$$\frac{\mathscr{W}_L}{\mathscr{W}} = \frac{W_{oL}}{W_o} \qquad [3]$$

with $W_{oL} = W_o + \Delta W_o$,
ΔW_o being the variation of W_o resulting from the presence of the liquid.[1-4]

However, it appears that this theoretical approach is implicitly based on the hypothesis that the potential liquid penetration rate to the fracture front is greater than the actual fracture propagation rate. Equation [3] supposes that the liquid always stays in contact with the fracture front.

In this paper, we propose to determine the principal parameters which govern the penetration rate of a liquid to the separation front and which control the action of the liquid in the debonding phenomenon.

EXPERIMENTAL

Aluminium/elastomer assemblies were realised by pressing at 90°C under 5.10^6 Pa an SBR (styrene-butadiene copolymer) layer of 1 mm thickness between the aluminium substrate and a cotton fabric limiting the longitudinal elongation of the elastomer during the peel test. The elastomer was slightly crosslinked by incorporating 1.6% by weight of peroxide (1,1 di-t-butyl peroxy 3,3,5 trimethylcyclohexane) and maintaining the assembly at 150°C for 50 min. under the same pressure.

Before assembly, the aluminium was treated by an amorphous phosphatization.[2] This phosphatization treatment was chosen, since it leads, whatever the surrounding medium, air or liquid, to a cohesive failure within the elastomer near the interface, as described in detail in the two previous parts of this work.[3,4]

The fracture energies of assemblies were measured by a 180 degree peel test effected in air and in liquid media at different peel rates (from 0.25 to 250 mm min^{-1}) and at 20°C. A very simple device attached to the dynamometer allows the peeling to be done in a liquid environment.[4]

The liquids used were polydimethylsiloxane oils (PDMS) of viscosities ranging from 1.7 to 12,200 cP (Rhône-Poulenc, Rhodorsil 47V).

These liquids present the advantage of having very similar surface energies (Table I) and consequently the same thermodynamic effect on the failure energy, *i.e.*, a reduction $\frac{\Delta W_o}{W_o}$ of 60%.[4]

TABLE I
Viscosity and surface energy of PDMS (at 20°C)

PDMS	η (cP)	γ_L (mJ m^{-2})
47 V 2	1.7	18.7
47 V 50	48	20.8
47 V 350	340	21.1
47 V 500	490	21.1
47 V 1000	970	21.2
47 V 12500	12200	21.5

PROPOSED MODEL AND EXPERIMENTAL VERIFICATION

Figure 1 shows the kinetic phenomena observed in PDMS of three different viscosities (340, 970 and 12,200 cP). The dotted curve represents the theoretical energy of separation in PDMS calculated from equation [3].

When the potential penetration rate of the liquid to the separation front is higher than the peel rate, the experimental and the theoretical curves merge. When the penetration speed of the liquid is lower than the peel rate, the liquid is no longer in contact with the fracture front. We shall call this critical peel rate the "departure" rate, R_d; it corresponds to the peel rate at which the energy-peel rate curve in a liquid medium deviates towards the curve in air and leaves the theoretical curve. As

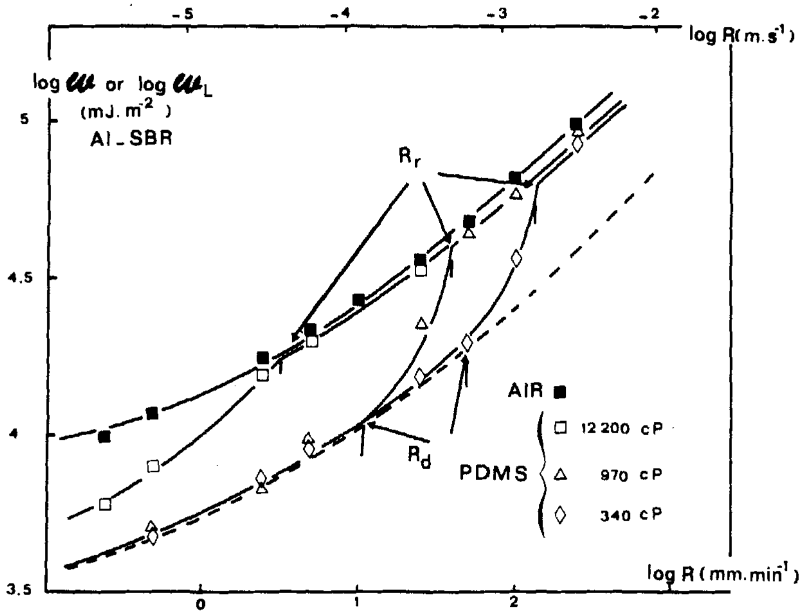

FIGURE 1 Failure energy *vs* peel rate in air and in PDMS oils of different viscosities.

an example, for the 970 cP PDMS, R_d is approximately equal to 10 mm min^{-1}.

In Figure 1, we can also see the peel rates at which the results in liquid and in air become superposable. These will be denoted "rejoining" rates, R_r. As an example, for the 970 cP PDMS, R_r is roughly equal to 36 mm min^{-1}. The range of separation rates between R_d and R_r, for a given liquid, corresponds to a partial effect of the liquid in the separation mechanism (transition range).

Based on work by Shanahan and Schultz[5] on the environmental stress cracking of polyethylene (ESC) and a study by Bikerman[6] concerning the kinetics of wetting of a solid by a liquid, we have developed a simple model for a crack allowing a quantitative explanation of the observed phenomena to be derived. The study concerns a cohesive failure near the interface in the elastomer.

We consider a wedge shaped crack of half angle α and width ω (Figure 2). Given the reduced dimensions of the crack, we suppose that the liquid meniscus has a constant mean curvature. Three effects determine the position of the meniscus in the fracture front:

—the viscous drag which is proportional to the liquid viscosity, η.

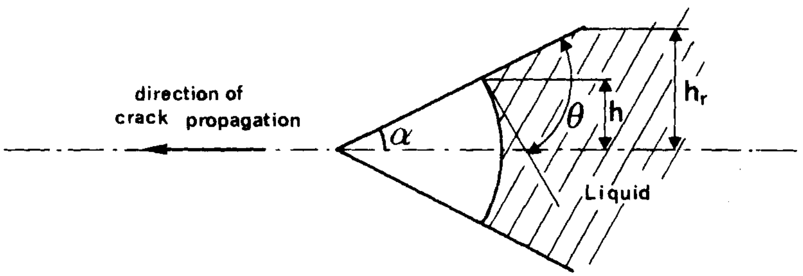

FIGURE 2 Model of crack.

In addition, simple dimensional analysis[7] shows that the drag is also proportional to the peel rate, R. We thus represent this effect by the force, F_v:

$$F_v = KR\eta\omega \qquad [4]$$

K being a dimensionless factor depending on the geometry of the crack.

—the capillary force, F_c, calculated from Laplace's law and equal to:

$$F_c = 2\omega\ \gamma_L \cos(\theta - \alpha) \qquad [5]$$

γ_L being the surface tension of the liquid and θ the liquid/solid contact angle.

—the force F_a, due to the hydrostatic pressure approximately equal to the atmospheric pressure, P_a. Its contribution is given by:

$$F_a = 2\omega\ h\ P_a \qquad [6]$$

h being the half height of the liquid front.

The two terms, F_c and F_a, propel the liquid within the crack.

When "dynamic equilibrium" is reached, we can consider that the three forces are balanced, so that:

$$F_v = F_c + F_a \qquad [7]$$

thus:

$$K\ R\ \eta = 2\ \gamma_L \cos(\theta - \alpha) + 2\ h\ P_a \qquad [8]$$

At the transition rate, R_r, for which the liquid is just at the limit of the fracture zone, we have:

$$K\ R_r\ \eta = 2\ P_a\ h_r + 2\ \gamma_L \cos(\theta - \alpha) \qquad [9]$$

h_r being the external half height of the fracture zone.

At the transition rate, R_d, the failure energy, $\mathcal{W}_L$, takes the theoretical value for the liquid medium. The liquid is in direct contact with the crack front. We shall suppose that $h = 0$, then:

$$K\ R_d\ \eta = 2\ \gamma_L \cos(\theta - \alpha) \qquad [10]$$

The extent of the transition range, $R_r - R_d$, can be obtained from [9] and [10]:

$$R_r - R_d = \frac{2\ P_a\ h_r}{K\ \eta} \qquad [11]$$

Relation [11] shows that the range of separation rates corresponding to the transition zone is inversely proportional to the viscosity of the liquid.

Approximate calculation of the crack dimensions

The failure energies of aluminium/SBR assemblies were measured in PDMS of different viscosities. From the energy *vs* peel rate curves obtained in air and PDMS, we determined the transition rate, R_d and R_r, for each PDMS. These values and the parameter $\frac{h_r}{\cos\alpha}$ defining the crack opening are given in Table II. The term $\frac{h_r}{\cos\alpha}$ has been calculated from relationship [9] and [10] using the fact that the contact angle of PDMS on SBR is zero. Then:

$$\frac{h_r}{\cos\alpha} = \frac{\gamma_L}{P_a}\left(\frac{R_r}{R_d} - 1\right) \qquad [12]$$

TABLE II

Transition rates R_d and R_r in PDMS. Calculated values of $\frac{h_r}{\cos\alpha}$

η (cP)	R_r (mm min^{-1})	R_d (mm min^{-1})	$\frac{h_r}{\cos\alpha}$ (μ m)
1.7	>1000	>1000	./.
48	650	160	0.64
340	160	50	0.46
490	80	16	0.85
970	36	10	0.55
12,200	3.5	<0.25	./.

It can be seen that the parameter $\frac{h_r}{\cos\alpha}$ determined from our model is of the same order of magnitude for the different liquids. In addition, if we suppose α sufficiently small ($\alpha < 25$ degrees) so that $\cos\alpha \approx 1$, then:

$$\frac{h_r}{\cos\alpha} \simeq h_r \qquad [13]$$

In such conditions, it can be considered that h_r is roughly equal to 0.6 μm. The crack opening 1.2 μm is of the same order of magnitude as values obtained by Williams who determined a crack opening displacement (COD) using fracture mechanics of about 2 μm for polymethylmethacrylate[8] and 1.7 μm for a high density polyethylene.[9] Shanahan and Schultz[10] found a value of 0.4 μm for a low density polyethylene.

Calculation of the reversible work of separation in the transition range ($R_d < R < R_r$)

In the transition range where the propagation rate of the fracture is between R_d and R_r, the liquid partially modifies the work of separation (Figure 1). We therefore propose to describe the reversible work of detachment W_{oL} by the relationship:

$$W_{oL} = W_o + \lambda\,\Delta W_o \qquad R_d < R < R_r \qquad [14]$$

with $\lambda = 0$ if $R = R_r$,
$\lambda = 1$ if $R = R_d$,

and ΔW_o being the variation of the thermodynamic work W_o when the liquid is present at the fracture front.[1,4]

We can consider quite simply that λ is equal to the fraction of the solid-liquid contact area in the fracture zone. By means of simple geometrical considerations and relationships [8], [9] and [14], it can be shown that W_{oL} can be expressed, in the transition range, by the relationship:

$$W_{oL} = W_o + \frac{R_r - R}{R_r - R_d}\Delta W_o \qquad \text{with } R_d < R < R_r \qquad [15]$$

The failure curve in a liquid medium can therefore be entirely calculated by taking into account both the kinetic and thermodynamic effects of the liquid on fracture energy.

To conclude, our results are capable of explaining the measured

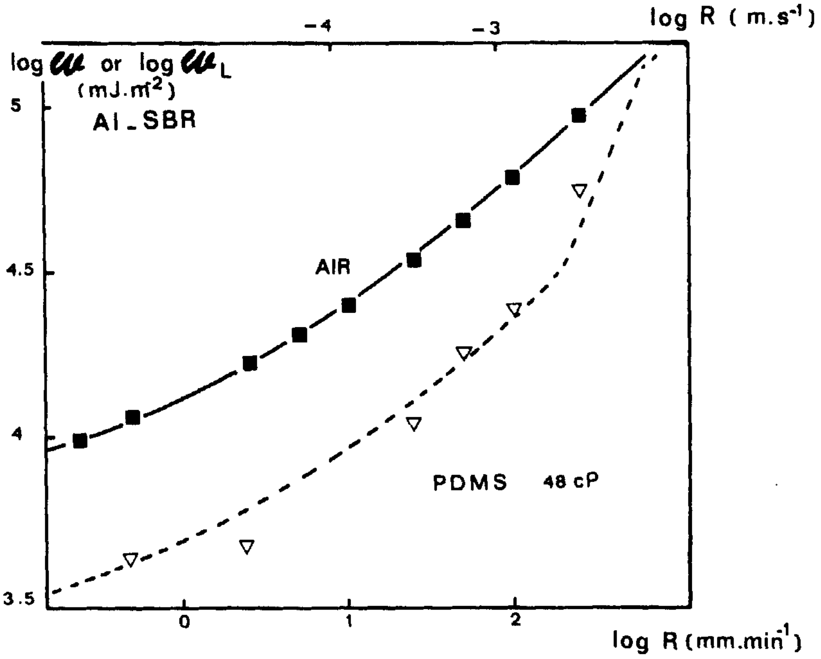

FIGURE 3 Failure energy *vs* peel rate.
---- Theoretical curve in 48 cP viscosity PDMS medium.
▽ Experimental points.

failure energy of an assembly as a function of the separation rate in a liquid medium. This is summarized by the following relations:

$$\mathcal{W}_L = (W_o + \Delta W_o) \times g(M_c) \times f(R) \text{ (maximum effect if } R < R_d\text{)}$$
$$\mathcal{W}_L = (W_o + \lambda\Delta W_o) \times g(M_c) \times f(R) \text{ (partial effect if } R_d < R < R_r\text{)}$$
$$\mathcal{W}_L = W_o \times g(M_c) \times f(R) \text{ (\textit{no effect if} } R_r < R\text{, then } \mathcal{W}_L = \mathcal{W}_{air}\text{).}$$

Figures 3 and 4 represent the curves of peel energy *vs* peel rate in air and in PDMS media. The theoretical curves (dotted lines) have been calculated from the proposed crack model. Excellent agreement is found between theoretical and experimental values.

CONCLUSION

The effect of a liquid on the failure energy of an assembly depends on the ability of the liquid to follow the fracture front. This kinetic aspect

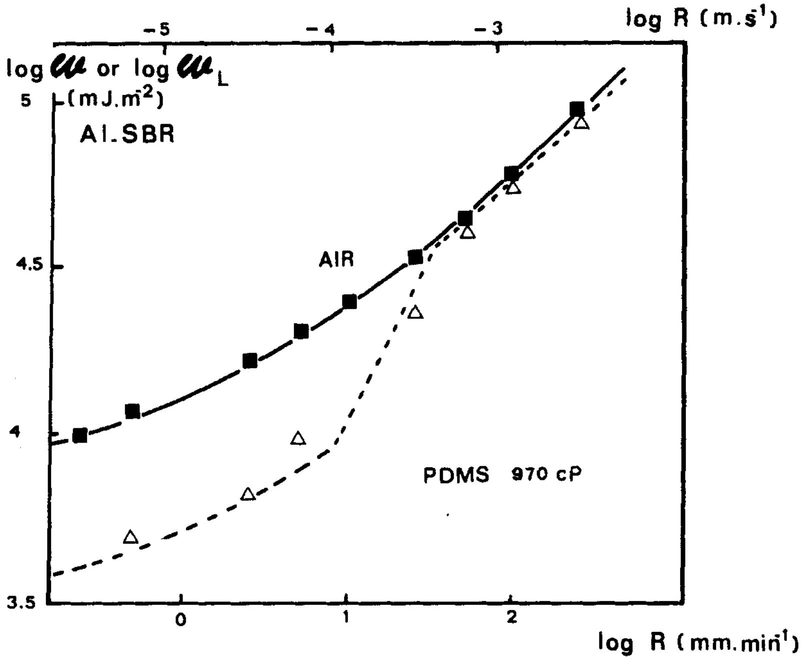

FIGURE 4 Failure energy *vs* peel rate.
---- Theoretical curve in 970 cP viscosity PDMS medium.
△ Experimental points.

of the effect of a liquid environment has been studied by developing a simple geometric crack model. This model has allowed us to demonstrate that the penetration rate of the liquid is determined by three effects:

—the viscous drag,
—the capillarity,
—and the hydrostatic pressure.

By taking into account both the thermodynamic and the kinetic aspects of the action of the liquid, it is now possible to explain quantitatively the change of peel energy in a liquid medium in the usual range of peel rates.

From this study the crack opening dimension has been calculated and is in good agreement with other values cited in the literature.

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