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Polymer-Aluminium Adhesion. III. Effect of a Liquid Environment

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Polymer-Aluminium Adhesion. III. Effect of a Liquid Environment

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Quantitative relationships have been established between the properties of the solids in contact and the separation strength of aluminium/elastomer assemblies, in particular in a liquid environment.

These relationships allow us to predict the modification induced by the liquid by taking into account the surface properties of the liquid and the surface and bulk properties of the assembled solids.

INTRODUCTION

In the first part of this study, we have shown how to determine the surface energy of a series of aluminium substrates as a function of the surface treatment of the aluminium.¹

In a second part, the separation of aluminium/elastomer model assemblies has been studied.² A novel theory of the adhesion of visco-elastic materials has been tentatively established. According to this

theory, the energy of separation, \mathcal{W} , as measured by a peel test, can be expressed as a product of three terms:

$$\mathcal{W} = W_o \times g(M_c) \times f(R)$$

where W_o is the reversible energy of adhesion (or cohesion) and $g(M_c)$ and $f(R)$ are respectively molecular and macroscopic dissipation factors.

In this part, we shall tackle the quantitative interpretation of the variations of the energy of separation of aluminium/elastomer assemblies in several liquid media. This study is devoted to the thermodynamic aspect of the separation taking into account the surface properties of the solids determined previously.¹

The failure strength of aluminium/elastomer assemblies has been measured in different media by using a 180° peel test.

The action of a liquid on an adhesive assembly can be very different. In a liquid which does not display any chemical reactivity towards the materials, the liquid can affect:

- the bulk properties of the adherends, for instance by swelling the elastomer and thus altering its viscoelastic properties,
- and/or the interfacial properties, in particular by modifying the reversible energy of detachment.

It is only towards the change of the interface properties that we have directed by our study by using liquids which have no appreciable action on the viscoelastic properties of the elastomers considered.

MATERIALS

Among the most current surface treatments of aluminium, we have chosen two treatments resulting in two distinctly different surface energies, but both maintaining a very slight roughness at the metal surface.¹ These are:

- anodization followed by sealing,
- and conversion by amorphous phosphatization.

SBR and NBR elastomers² were chosen as model adhesives on account of their well known rheological properties.

The aluminium/elastomer assemblies were realized by using the method described previously.²

Peel experiments were conducted at 20°C for a large range of separation rates from $4.2 \cdot 10^{-6}$ to $4.2 \cdot 10^{-3}$ m.s.⁻¹ (*i.e.* 0.25 to 250 mm.

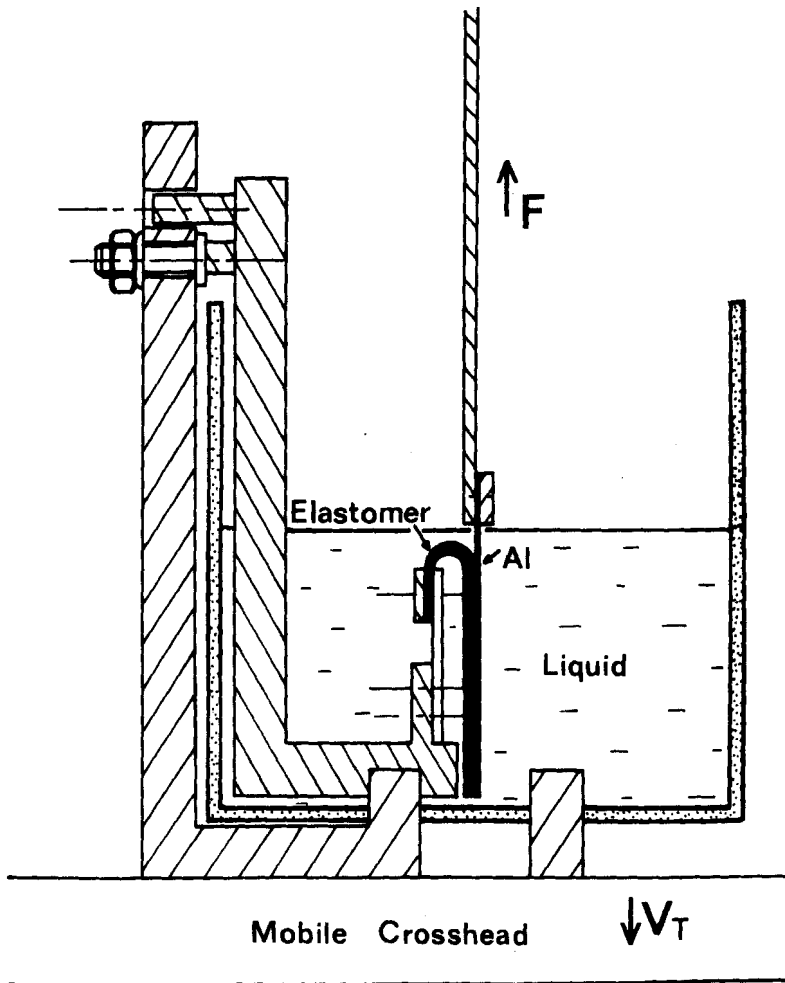


FIGURE 1 Schematic diagram of the experimental set-up.

min^{-1}). A special device adapted on the dynamometer allowed us to perform the peel test in a liquid environment (Figure 1).

The surface characteristics of the solids and the liquids, γ_s and γ_L , are given in the Appendix.

PRINCIPLE OF THE METHOD

First, we shall recall that the energy of separation measured by a peel test, \mathcal{W} , is in fact composed of two principal terms; the reversible energy of adhesion (or cohesion) W_o , necessary to create reversibly a new unit of interfacial area, and the energy irreversibly expended in the elastomer during the failure process. The theory developed by Gent and Schultz^{3,4} and modified by Carre and Schultz² expresses the relation between the measured energy of separation and the reversible energy as:

$$\mathcal{W} = W_o \times g(M_c) \times f(R) \quad (1)$$

$f(R)$ being a factor of viscoelastic dissipation which depends, at constant temperature and test geometry, only on the rheological properties of the elastomer, and thus on the propagation rate, R , of the failure front and $g(M_c)$ being a molecular dissipation factor equal to the number of C-C bonds between crosslinks contained in chains crossing or attaining the fracture plane.

In a liquid medium, and if the chosen liquid does not modify by swelling or reaction the bulk characteristics of the elastomer, the dissipation function $f(R)$ does not vary and the failure energy \mathcal{W}_L is given by:

$$\mathcal{W}_L = W_{oL} \times g(M_c) \times f(R) \quad (2)$$

Now, if we consider the failure energies, \mathcal{W} and \mathcal{W}_L , determined in air and in a liquid medium at a given peel rate, the ratio of equation (1) and (2) leads to:

$$\frac{\mathcal{W}_L}{\mathcal{W}} = \frac{W_{oL}}{W_o} \quad (3)$$

Given that the dissipation factors cancel, changes in the interfacial or cohesive properties can be predicted directly from peel properties.

The ratios of equation (3) can be determined directly, either experimentally or by calculation.

The term $\mathcal{W}_L/\mathcal{W}$ can be obtained by peeling both in air and in a liquid medium.

The calculation of the term W_{oL}/W_o depends on whether the failure is interfacial or cohesive within the elastomer.

As will be seen in the experimental part of this work, in the case of an interfacial failure W_{oL}/W_o is calculated from the surface characteristics

of the solids in contact and of the liquid, whereas in the case of a cohesive failure the breakage of chemical bonds is also taken into account.

RESULTS AND DISCUSSION

Let us first consider the two distinct types of failure, adhesive and cohesive, observed with our assemblies. For sake of clarity it must be recalled that with the sealed anodized aluminium substrate the failure is always interfacial (index a) and with the phosphated aluminium substrate the failure is always cohesive within elastomer (index c).²

a) Adhesive failure

The reversible energy of adhesion in an inert medium, denoted W_o^a , is given by the DUPRE's relationship:

$$W_o^a = \gamma_{S_1} + \gamma_{S_2} - \gamma_{S_1S_2} \quad (4)$$

where γ_{S_1} and γ_{S_2} are the surface free energies of the two solids and $\gamma_{S_1S_2}$ the interfacial free energy between the two solids.

The reversible energy of adhesion in a liquid medium, W_{oL}^a , is equal to^{3,4}:

$$W_{oL}^a = \gamma_{S_1L} + \gamma_{S_2L} - \gamma_{S_1S_2} \quad (5)$$

γ_{S_1L} and γ_{S_2L} being now the interfacial free energies between the two solids and the liquid. Thus, we can easily show that:

$$W_{oL}^a = W_o^a + \Delta W_o^a \quad (6)$$

with

$$\Delta W_o^a = 2\gamma_L - W_{S_1L} - W_{S_2L}$$

W_{SL} represents the liquid/solid adhesion energy and is given by the relationship of Owens and Wendt⁵:

$$W_{SL} = 2(\gamma_S^D \gamma_L^D)^{1/2} + 2(\gamma_S^P \gamma_L^P)^{1/2} \quad (7)$$

Although there is no generally accepted theoretical relationship describing the polar interaction, we have adopted the geometric mean equation as representing a first approximation.

Using the surface characteristics of the solids and of the liquid, W_o^a and ΔW_o^a are finally expressed as:

$$W_o^a = 2(\gamma_{S_1}^D \gamma_{S_2}^D)^{1/2} + 2(\gamma_{S_1}^P \gamma_{S_2}^P)^{1/2} \quad (8)$$

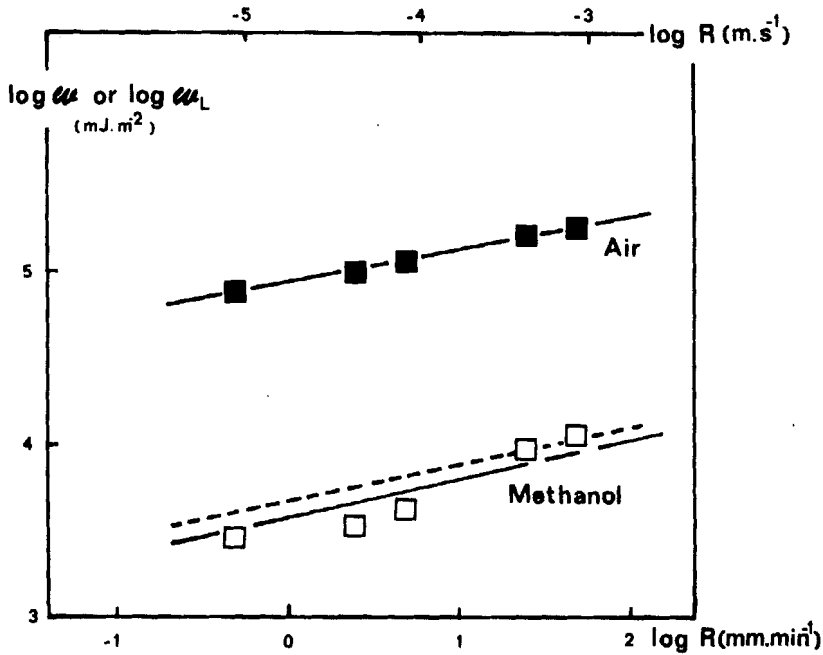


FIGURE 2 Influence of a liquid medium on the failure of sealed anodized aluminium/SBR assembly. Experimental and theoretical (---) results.

$$\Delta W_0^a = 2\gamma_L - 2(\gamma_L^D)^{1/2}[(\gamma_{S_1}^D)^{1/2} + (\gamma_{S_2}^D)^{1/2}] - 2(\gamma_L^P)^{1/2}[(\gamma_{S_1}^P)^{1/2} + (\gamma_{S_2}^P)^{1/2}] \quad (9)$$

All these calculations suppose that:

- only physical interactions take place during the solid/solid and solid/liquid contact,
- the potential rate of penetration of the liquid to the fracture front is higher than the propagation rate of the fracture, *i.e.*, that the liquid is always present at the fracture tip.

A series of experiments has been carried out with the sealed anodized aluminium/SBR or NBR assemblies for which the locus of failure is clearly interfacial.² As an example, Figure 2 shows the behaviour of the SBR based assembly, the separation being effected in air and in methanol, respectively. By examining the variation of the failure energy, \mathcal{W} and \mathcal{W}_L , with the peel rate, R , the following observations can be made:

—the curve in air and in methanol are parallel on a logarithmic scale, verifying that the ratio $\mathcal{W}_L/\mathcal{W}$ (equation [3]) is constant and independent of the peel rate R , *i.e.* that the product $g(M_c) \times f(R)$ is not modified by the presence of the liquid,

—the dotted curve shows the theoretical values of \mathcal{W}_L calculated by using equation (3) as follows:

$$\mathcal{W}_L = \mathcal{W} \times \frac{W_{oL}^a}{W_o^a} \quad (10)$$

W_o^a and W_{oL}^a being calculated from the surface properties of the solids and of the liquid according to equations (8), (6) and (9).

A good agreement between the experimental data and the curves calculated with relation (10) can be seen.

Other liquids wetting completely both elastomer (SBR and NBR) and aluminium have been used. Table I gives the experimental and theoretical relative variations, $\Delta \mathcal{W}/\mathcal{W}$ and $\Delta W_o^a/W_o^a$, expressed by:

$$\frac{\Delta \mathcal{W}}{\mathcal{W}} = \frac{\mathcal{W}_L - \mathcal{W}}{\mathcal{W}} \quad (11)$$

and

$$\frac{\Delta W_o^a}{W_o^a} = \frac{W_{oL}^a - W_o^a}{W_o^a} \quad (12)$$

TABLE I

Comparison of the experimental and theoretical variations of adhesion for sealed anodized aluminium/elastomer assemblies.

Assemblies	$W_o^a(2)$ (mJ.m ⁻²)	Liquids	$\frac{\Delta \mathcal{W}}{\mathcal{W}}$ exp.(%)	$\frac{\Delta W_o^a}{W_o^a}$ th.(%)
Al/SBR	76	Methanol	-97	-95
	76	Ethanol	-92	-97
	76	Butanol	-92	-98.5
Al/NBR	88	Methanol	-96	-93
	88	Ethanol	-91.5	-92.5
	88	Butanol	-92	-88

It is seen that the residual adhesion in the presence of alcohols is less than 10% of the original value in air. The loss of adhesion is therefore very close to 100% which would correspond to spontaneous separation.

The good agreement between the theoretical and experimental reductions allows us to confirm that:

—only physical interactions of dispersive and polar type take place at the sealed anodized aluminium/elastomer interfaces,

—the failure propagates only at the interface.

Thus it has been verified that the modification of the energy of separation induced by a liquid medium can be quantitatively predicted from the surface properties of the assembled solids and of the liquid, in the case of a purely adhesive failure.

b) Cohesive failure

In the case of cohesive failure in the elastomer, we have proposed² to replace the reversible energy of adhesion by the reversible energy of cohesion, denoted W_o^c .

The reversible energy of cohesion, W_o^c , of the elastomer is considered as the sum of the respective contributions of the physical interactions, $W_{o\text{phys}}^c$, and of the chemical interactions, $W_{o\text{chem}}^c$:

$$W_o^c = W_{o\text{phys}}^c + W_{o\text{chem}}^c \quad (13)$$

It should be noted the breakdown of entanglements may contribute to $W_{o\text{chem}}^c$. The term "reversible" may be confusing when applied to the irreversible breakage of chemical bonds. It simply means that this value is considered in the total absence of either molecular or viscoelastic dissipation.

The contribution of physical interactions being equal to twice the surface energy of the elastomer, equation (13) can be written:

$$W_o^c = 2\gamma_S + W_{o\text{chem}}^c \quad (14)$$

Supposing now that the presence of the liquid modifies only the physical and not the chemical interactions, the reversible energy of cohesion in a liquid medium, W_{oL}^c , is given by:

$$W_{oL}^c = 2\gamma_{SL} + W_{o\text{chem}}^c \quad (15)$$

which can be written:

$$\left. \begin{aligned} W_{oL}^c &= W_o^c + \Delta W_o^c \\ \text{with } \Delta W_o^c &= 2\gamma_L - 2W_{SL} \end{aligned} \right\} \quad (16)$$

where W_{SL} is the elastomer/liquid adhesion energy.

However, if γ_S can be obtained from contact angle measurements, the chemical contribution to the cohesion energy, $W_{o\text{chem}}^c$, which depends on the number of chemical bonds broken in the

fracture zone, is not easily measurable experimentally. Nevertheless, our experiments and our analysis allow us to calculate the total reversible energy of cohesion, W_o^c , from the values of the peel energy on one hand, and on the other hand from the surface properties of the rubber and of the liquid as shown below:

—In the case of a cohesive failure in the elastomer, equation (3) can be written:

$$\frac{\mathcal{W}_L}{\mathcal{W}} = \frac{W_{oL}^c}{W_o^c} = \frac{W_o^c + \Delta W_o^c}{W_o^c}$$

then,

$$W_o^c = \frac{\Delta W_o^c}{\frac{\mathcal{W}_L}{\mathcal{W}} - 1} = 2\gamma_s + W_{ochem}^c \quad (17)$$

In order to determine the precise value of the cohesion energy, the failure energies of phosphated aluminium/elastomer assemblies, \mathcal{W} and \mathcal{W}_L , have been measured in air and in a liquid taken as a reference, ethanol (Figure 3). From equation (17), the total cohesion energies W_o^c in the fracture zone have been calculated and are given in Table II, ΔW_{oth}^c being determined using equations (16) and (7)

TABLE II
Determination of cohesive properties of elastomer SBR and NBR in the fracture zone from peeling experiments.

Elastomers	$\mathcal{W}_L/\mathcal{W}$ exp. in ethanol	ΔW_{oth}^c ($\text{mJ}\cdot\text{m}^{-2}$)	W_o^c ($\text{mJ}\cdot\text{m}^{-2}$)	$W_{ophys}^c = 2\gamma_s$ ($\text{mJ}\cdot\text{m}^{-2}$)	W_{ochem}^c ($\text{mJ}\cdot\text{m}^{-2}$)
SBR	0.44	-52	93	60	33
NBR	0.18	-69	84	72	12

The contribution of the chemical bonds to the reversible energy of cohesion of SBR and NBR near the interface represents only about 35% and 14% of the total cohesion energy respectively for SBR and NBR. These W_{ochem}^c values are in fairly good agreement with the calculation made in the previous paper² based on the number ν of C-C bonds broken using different network models as shown in Table III. Let us recall that:

$$W_{ochem}^c = \nu \times u \quad (18)$$

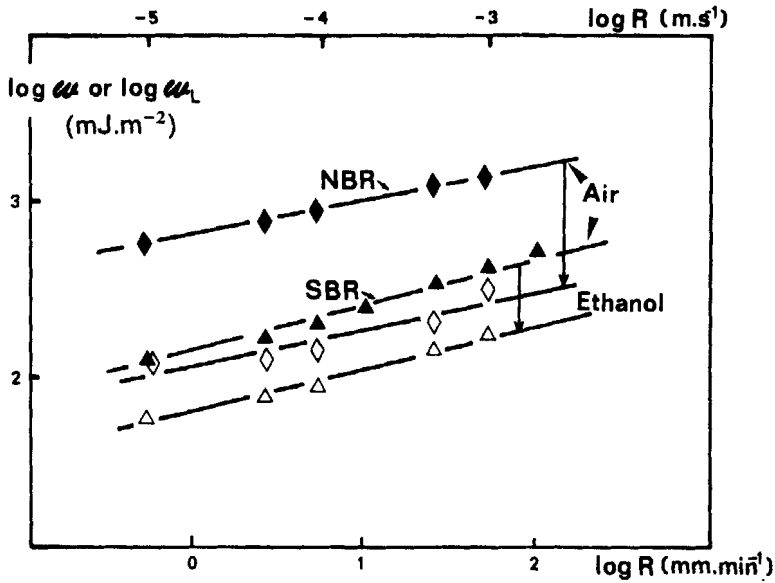


FIGURE 3 Failure of phosphated aluminium/elastomer assemblies. Experimental results in air and in ethanol.

where u is the energy of dissociation of an elementary C-C bond of the elastomer chain.

TABLE III

Chemical contribution to the reversible energy of cohesion, W_{ochem}^c (mJ.m^{-2}), calculated using different network models.

Elastomer	Model of Lake and Thomas ⁶	Model of Bueche ⁷	Model of Flory and Rehner ⁸
SBR	50	33	42
NBR	35	22	29

In a second step, using different liquid media, the values obtained have been verified by comparison of the relative variations of the failure energy obtained experimentally with the ones obtained by calculation, taking into account the experimental values of W_{ochem}^c (Table IV). As an example, Figure 4 gives the theoretical and experimental curves of failure in butanol.

It can also be noted that the presence of water increases the

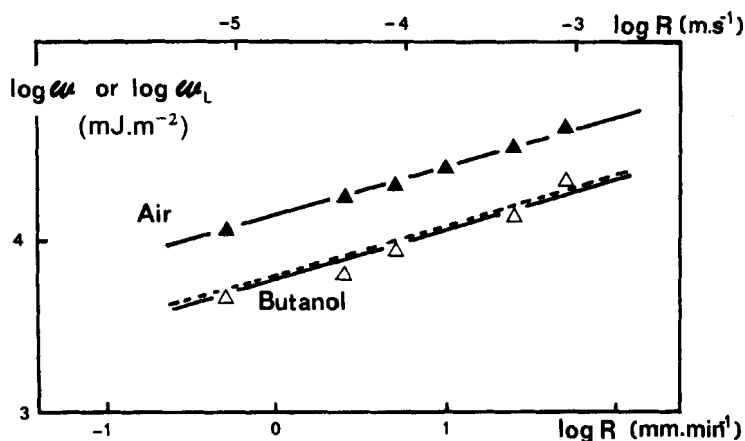


FIGURE 4 Influence of a liquid medium on the failure of phosphated aluminium/SBR assembly. Experimental and theoretical (---) results.

work of separation for the phosphated aluminium/SBR assembly. This results from the positive value of ΔW_c^c in equation (16). This term is negative for wetting liquids and positive for poorly wetting liquids such as water.³

The observed agreement justifies the interpretation of a failure propagating cohesively in a layer of elastomer in which the contribution of the chemical bonds to the reversible cohesion energy is respectively 35% for SBR and 14% for NBR. Thus, the contribution of the

TABLE IV
Influence of various liquids on the failure energy of phosphated aluminium/elastomer assemblies.

Assemblies	Liquid	$\frac{\Delta W_c^c}{W_c^c}$ (experimental) (%)	$\frac{\Delta W_c^c}{W_c^c}$ (calculated) (%)
Al/SBR	Butanol	-60	-61
	PDMS* 1.7 cP	-63	-61
	PDMS* 970 cP	-57	-62
	H ₂ O	+27	+31
Al/NBR	Methanol	-79.5	-82
	Butanol	-70	-75
	H ₂ O	-48	-47

*PDMS: polydimethylsiloxane (Rhône-Poulenc, 47V2 and 47V1000).

chemical bonds and/or entanglements to the reversible energies of cohesion are small as clearly demonstrated before.²

Thus it is clearly shown that this method of separation in a liquid medium allows us to determine the respective part of chemical and physical interactions in the fracture zone. In addition, this analysis has been successfully extended in recent work to the case of an interfacial separation demonstrating the creation of chemical links at the interface.

CONCLUSION

The thermodynamic aspect of the separation of model adhesive assemblies in liquid media has been studied.

In the case of an adhesive failure, the decrease of the adhesive strength due to the presence of a liquid environment can be quantitatively predicted by taking into account the surface characteristics of the solids and of the liquid.

In the case of a cohesive failure in the elastomer, the contributions of both physical and chemical interactions to the cohesion energy of the crosslinked elastomer have been considered. Assuming that the liquid affects only the physical interactions, the method of peeling in a liquid medium allows one to calculate the reversible energy of cohesion of the elastomer and in particular its chemical contribution. The values obtained are in good agreement with those calculated using network models.

APPENDIX

For the liquids used the total surface energy γ_L has been determined by tensiometry using the Wilhelmy method.

Surface properties of solids and liquids used

Surface	γ (mJ.m ⁻²)	γ^D (mJ.m ⁻²)	γ^F (mJ.m ⁻²)
SBR	30	29.5	0.5
NBR	36	26.5	9.5
Sealed anodized aluminium	56	41	15
Phosphated aluminium	151.6	150	1.6
Methanol	22.6	15.2	7.4
Ethanol	22.8	17	5.8
Butanol	24.6	23.8	1
PDMS 1.7 cP	18.7	18.7	0
PDMS 970 cP	21.2	21.2	0
Water	72.6	21.6	51

The dispersive component of the surface energy γ_L^D of liquids have been obtained by measuring their contact angles, Θ , on polytetrafluoroethylene (PTFE) ($\gamma_S = 19 \text{ mJ.m}^{-2}$) and by using the following well known relationship:

$$W_{SL} = \gamma_L (1 + \cos \Theta)$$

W_{SL} being the solid/liquid energy of adhesion.

With the apolar PTFE, W_{SL} results only from dispersive interactions and can therefore be expressed, according to Fowkes⁹ by:

$$W_{SL} = 2 (\gamma_L^D \gamma_S)^{1/2}$$

Thus:

$$\gamma_L^D = \frac{[\gamma_L (1 + \cos \Theta)]^2}{4 \gamma_S}$$

The polar component γ_L^P is readily determined from:

$$\gamma_L^P = \gamma_L - \gamma_L^D$$

The data listed above are in good agreement with commonly accepted values.

The determination of the surface energy components of the solids has been described previously.¹

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