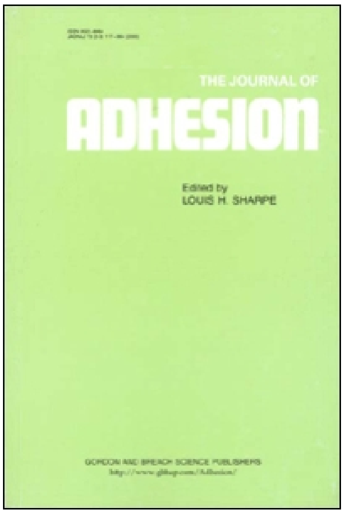

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The Interaction Parameter and the Strength of Adhesive Joints†

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A "blister test" technique has been used to determine the fracture surface energy of a range of adhesive joints formed using a polyurethane adhesive and a range of solid substrates. For each adhesive pair examined the work of adhesion was calculated from the contact angles formed by liquids for which the polar and dispersion force components of the surface tension are known. For each adhesive pair, the solubility parameter of adhesive and substrate were determined by swelling measurements in a range of liquids. Although cohesive failure of the joints was observed for some of the pairs for which the solubility parameters were matched, this was not true for all such pairs and an explanation of this behaviour has been sought in a new calculation of the volume interaction component of the molecular interaction parameters.

KEY WORDS Adhesive fracture surface energy; adhesive joint strength; blister test; interaction parameter; solubility parameter; work of adhesion.

INTRODUCTION

Since the Adhesive Fracture Surface Energy of an adhesive joint is controlled by the molecular interactions across the interface, it must be a function of the Work of Adhesion.[1] The problems of measuring the interfacial energy for the interface between two solid materials are considerable and many approaches to the problem are

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based upon the Girifalco and Good[2] expression for the work of adhesion

$$\omega_a = 2\phi(\gamma_a\gamma_s)^{1/2} \tag{1}$$

where γ_a and γ_s are the surface energies of the adhesive and substrate respectively and ϕ is the so-called "interaction parameter". The interaction parameter is[3] the product of the molecular attraction parameter ϕ_I and the volume interaction parameter ϕ_V. The former may be written as the ratio of the geometric mean of the attractive constants for the individual phases to the attractive constant for the two-phase system. The latter can be calculated assuming a specific form for the intermolecular potential energy function and a specific form for the combining relationships between the attractive and repulsive constants. Good[4] has suggested that the molecular attraction parameter is approximately unity whenever the intermolecular forces in the two phases are of the same type and has shown that when the intermolecular forces in the two phases are dissimilar then it can fall to values as low as 0.5. Gardon[5] has similarly shown that the volume interaction parameter when calculated on the assumption that the intermolecular distance across the interface is the arithmetic mean of the intermolecular distances in the bulk materials of the two phases, does not differ significantly from unity and that a ratio of 5 to 1 in the molecular volumes will only reduce the volume interaction parameter to 0.93.

Although the relationship between adhesive fracture surface energy and the work of adhesion was demonstrated by Andrews and Kinloch[6] they had to use the method of Owens and Wendt[7] to calculate the work of adhesion. In so doing they used a value for the interaction parameter which remained constant with a value of approximately unity for all the adhesive substrate pairs used. The relationship between the fracture surface energy and the work of adhesion apparently broke down when cohesive failure took place due to covalent bonding across the interface and it also broke down when the surface energy of the substrate was less than that of the adhesive.

Equation (1) suggests that if the interaction parameter is constant, then for a given substrate there will be an increase in the adhesive joint strength with surface tension of the adhesive. However the wetting criterion for the formation of an adhesive joint put forward by Zisman[8] leads to the conclusion that such a relationship between work of adhesion and fracture surface energy can only apply when the surface tension of the adhesive is less than the critical surface tension of the substrate. This is because under those conditions when the adhesive surface tension is greater than that of the substrate, the joint strength must be weakened by the flaws at the interface introduced by poor wetting. The combination of the two effects therefore suggests a peak in the relationship between Adhesive Fracture Energy and the Adhesive Surface Tension. Such a peak can be inferred from the results of Iyengar and Erikson.[9]

The peak in the relationship between the adhesive fracture surface energy and the surface tension of the adhesive has been advanced by some workers as evidence that the adhesive fracture surface energy is controlled by the interfacial energy for the system. An examination of the factors controlling the interfacial free energy has led these workers to postulate that the maximum adhesive fracture surface energy should be attained when the solubility parameters of adhesive and substrate are matched. This hypothesis, sometimes known as the mutual solubility approach to adhesive bonding was originally based upon the work of Hansen[10] and has been justified by the results of Harrison.[11]

The relationship between the surface tension and the solubility parameter may be expressed in the form[12]

$$\gamma = K\delta^2 V^{1/3} \tag{2}$$

where δ is the solubility parameter, V is the molar volume and K a constant. The peak in the curve relating joint strength to solubility parameter[6] would therefore not be predicted by the combination of Eqs (1) and (2). If it is assumed that variations in the molar volume between different adhesives are unlikely, when reduced to the one-third power, to make a material difference to the proportionality between the surface tension and the square of the solubility parameter then the work of adhesion would increase monotonically with the surface tension of the adhesive. However, variations in the molar volume may also affect the volume interaction component of the interaction parameter, therefore one objective of the present work is to examine the dependence of joint strength on adhesive surface tension at the same time as examining values of the interaction parameter, in order to see whether the changes in the different components of the interaction parameter are capable of explaining the variation of joint strength.

EXPERIMENTAL AND RESULTS

A suitable experimental system for the examination of the interaction parameter and its influence on the failure of an adhesive joint was designed as follows. A number of joints were constructed with the same adhesive and a range of substrates (each substrate had a different surface energy or solubility parameter). To avoid the complicating effects of compositional changes and hence possible changes in the surface energy of the adhesive, a solvent-free, castable polyurethane elastomer was used. The use of the castable polyurethane elastomer and sheets of commercially produced polymers produced a joint ideally suited to the blister test method for measuring the fracture surface energy.

Measurement of fracture surface energy

The blister test was developed by Williams[13] to measure the fracture surface energy between an elastic adhesive and a rigid substrate. During the blister test a pressurised fluid (which may be gas or liquid) is applied through a hole in the substrate, to the underside of a Teflon® disc. Since the disc is located at the interface between the adhesive and the substrate, the pressurized fluid forms a blister. The pressure is then increased until failure occurs (Figure 1). The fracture surface energy is calculated from a knowledge of the pressure at which the crack propagates, the geometry of the specimen and the modulus of the adhesive. The blister test has been used in many diverse applications such as the adhesion between rocket liners and propellants[14] and the adhesion of molluscs and dental adhesives.[15]

The relationship between the fracture surface energy and the experimental variables can be written in a general form (Equation 3),

$$R = P_{cr}/[E \times Q(h/a)] \tag{3}$$

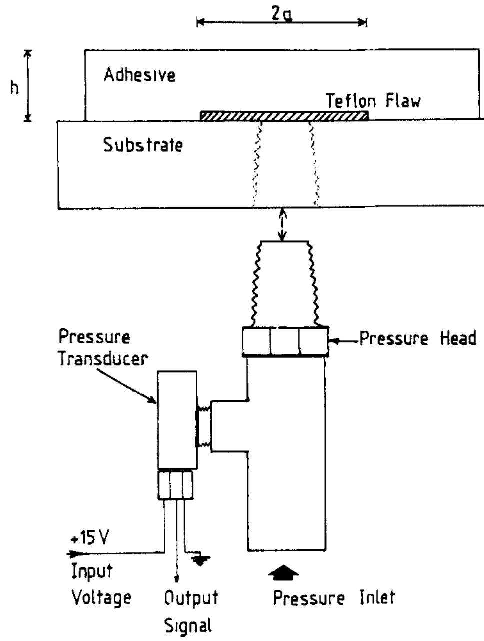

FIGURE 1 Blister test specimen.

here "$Q(h/a)$" is a geometry factor which accounts for the variation of the fracture surface energy with the geometry of the joint. Andrews and Stevenson[16] have derived an analytical expression for the geometry factors. P_{cr} is the pressure at which the flaw propagates, a is the radius of the flaw, h is the height of the adhesive and E is the modulus of the adhesive.

Two different blister test rigs were built, a low-pressure source test rig and a high-pressure source test rig. Each relies on a different method of producing and also controlling the pressure applied to the interface of the specimen. The specimen in the low-pressure rig is part of a closed volume system which allows the pressure to be increased by reducing the volume of the system using a piston and cylinder arrangement. The second type of rig which is capable of higher pressures uses a regulated air supply. With both test rigs the specimen was attached to the pressure head, by screwing a 1/8 B.S.P. tapered male fitting into the bottom of the substrate.

Characterisation of the adhesive and substrate

Both the surface energy as measured according to the method of Owens and Wendt[7] and the solubility parameters of the adhesive and substrate were determined.

The solubility parameters of the adhesive and the substrates used in the experimental programme were determined by measuring the swelling of each polymer in a range of organic solvents. The swelling was measured using the percentage mass increase of the polymer as a function of immersion time in the solvent.[17] The swelling measurements were taken at different time intervals to obtain the equilibrium swelling, as some solvents were found to approach equilibrium faster than others. The equilibrium swelling values were then plotted against the solubility parameter of the solvents, and the solubility parameter of the polymer was taken to be that of the solvent which produced the largest equilibrium swelling. The results are shown in Table I.

The contact angles of methylene iodide and water were measured

TABLE I

Substrate	Contact angle measurements				Solubility parameter
	θ_1	θ_2	γ_s^d mJ/m^2	γ_s^p mJ/m^2	
H.M.W.P.E.	56	103	31.4	0.1	8.6
Polypropylene	62	98	26.4	1.0	8.6
Polystyrene	38	83	38.3	2.8	9.2
P.M.M.A.	33	70	38.3	7.7	9.5
Rigid P.V.C.	40	86	37.9	1.9	9.7
Acetal resin	36	79	38.6	4.0	9.3
Epoxy resin	41	78	35.6	5.0	9.3–9.5
COO4 urethane	32	84	41.5	2.0	10.2
Polycarbonate	37	83	38.7	2.6	10.6
P.E.T.	26	76	42.8	4.1	10.9
Nylon 6-6	34	70	37.5	8.2	14.5
Nylon 6	39	61	33.1	14.2	15.0
Polyurethane Adhesive	68	94	22.1	2.4	9.3

θ_1 refers to the contact angle of methylene iodide.
θ_2 refers to the contact angle of water.
γ_s^d refers to the dispersion component of the surface energy.
γ_s^p refers to the polar component of the surface energy.

on the adhesive and the substrates used in the blister tests. According to Owens and Wendt[7] this allows the calculation of the components of the surface energy of the adhesive and the substrate. The contact angles were measured using a contact angle analyzer (manufactured by IMass of the USA). The results are also shown in Table I.

The fracture surface energy measured in the blister test versus the solubility parameter of the substrate is presented in Figure 2. The maximum fracture surface energy is associated with a change of the failure mode from interfacial failure to cohesive failure. The maximum occurs for some substrates when the difference between the solubility parameters of the adhesive and the substrate is small. This indicates that the toughness of the interface for these joints

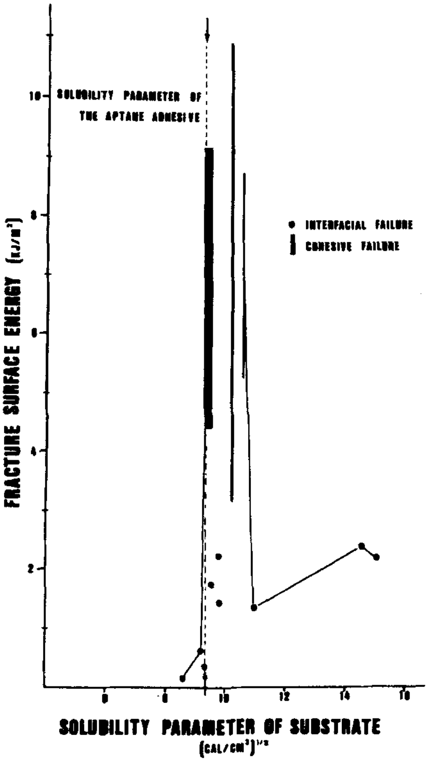

FIGURE 2 Blister test results.

goes through a maximum as the differences between the solubility parameter decreases. However, a close examination of the blister test results shows that significant differences exist between the results of the blister test experiments and the results obtained by Iyengar and Erickson. The experimental results of Iyengar and Erickson suggest a matching of the solubility parameters maximises the fracture surface energy. However, it can be seen that this is not always the case as some joints with the same solubility parameter for the adhesive and the substrate failed interfacially. It has been suggested earlier that variations in the interaction parameter may be responsible for such effects and consequently this is now examined more closely.

DISCUSSION

The value of the work of adhesion was calculated by the method of Owens and Wendt[7] and this is shown in Table II. For a system in which the adhesive is a constant for all joints, the dissipative energy losses should be nearly the same for all joints and hence the work of adhesion should vary linearly with the fracture surface energy. The ratio of the work of adhesion to the fracture surface energy is shown in Table II and it can be seen that this is far from constant and, in fact falls into three groups. There is a group of substrates including HMWPE, PP, PS and PMMA for which the calculated work of

TABLE II

Substrate	R J/m^2	ω_A mJ/m^2	R/ω_A $\times 10^3$	γ_c mJ/m^2
H.M.W.P.E.	142	50.6	2.8	26.0
Polypropylene	128	51.3	2.5	25.6
Polystyrene	629	63.3	9.9	31.6
Acetal resin	336	64.6	3.5	32.3
P.M.M.A.	1,770	66.7	5.0	33.4
Rigid P.V.C.	2,267	62.1	28	31.1
Epoxy resin	9,165	63.0	145	31.5
COO4 urethane	10,908	64.9	168	32.5
Polycarbonate	8,732	63.4	137	31.7
P.E.T.	1,375	65.4	21	33.9
Nylon 6-6	2,284	66.5	34	33.2
Nylon 6	2,417	65.7	36	32.9

adhesion appears to be high, and a group of substrates for which (because the failure is cohesive) the calculated work of adhesion is apparently low. The reason for this is not clear.

The epoxy resin, the polycarbonate and the polyurethane substrates all yielded a cohesive failure with a large cohesive work of fracture. The wetting approach to bonding would suggest that cohesive fracture would always occur when the surface tension of the adhesive is less than the critical surface tension of the substrate. The appropriate critical surface tension is, however, that which would be found if it were determined using a range of liquids which have the same polarity (ratio of the polar to the dispersion components of the surface energy) as the substrate. This may be calculated for the adhesive used as follows. On the basis of the Owens and Wendt formulation then since

$$\gamma_a(1+\cos\theta) = 2(\gamma_s^d\gamma_a^d)^{1/2} + 2(\gamma_s^p\gamma_a^p)^{1/2} \tag{4}$$

and $\cos\theta = 1$ when $\gamma_A = \gamma_c$

$$\gamma_c = (\gamma_s^d\gamma_a^d)^{1/2} + (\gamma_s^p\gamma_a^p)^{1/2} \tag{5}$$

or for the adhesive used

$$\gamma_c = 4.70(\gamma_s^d)^{1/2} + 1.55(\gamma_s^p)^{1/2} \tag{6}$$

The calculated value of the critical surface tension for each substrate which is appropriate to a liquid of the polarity of the adhesive is shown in Table II. This reveals that the adhesive has a lower surface tension than the critical surface tension of any of the substrates and hence that the failure should have been cohesive in all cases.

The mutual solubility approach to adhesive bonding has some success in predicting the joint strength in that there is a maximum in the strength and the failure becomes cohesive when the cohesive energy densities of substrate and adhesive are matched. The approach is less successful in predicting the strength in the case of polystyrene, acetal, Perspex and rigid PVC for which the failure was adhesive.

If, following Gardon,[5] the volume interaction parameter is put approximately equal to unity then the interaction parameter is a function only of the molecular attraction parameter and can be calculated from equation (1) expressed in terms of the fractional polarities.

$$\phi_A = (p_a p_s)^{1/2} + (d_a d_s)^{1/2} \tag{7}$$

The values of the molecular attraction parameter were calculated for each of the blister test pairs using equation (7) and it can be seen from Table III that it does not deviate significantly from unity.

The small deviation of the molecular attraction parameter values in Table III from unity would suggest that the interaction parameter is not a significant variable. However, the small variation is difficult to reconcile with the fact that for water/organic liquid systems the measured values of the interaction parameter range from 0.55 to 1.13.[2] The lower values are typical of non-polar liquids such as the hydrocarbon liquids in contact with water. Furthermore, Good[4] has shown that the molecular attraction parameter reduces to one only when dispersion forces predominate on both sides and across the interface. This is in direct conflict with the treatment proposed by Owens and Wendt. Calculations based on Owens and Wendt treatment for substrates with large polar components such as Perspex, the epoxy resin, and nylon 6-6 all yield interaction parameter values of 0.99 according to equation (7) and similar results are obtained with reported surface energy components for such unlikely combinations as P.V.C./Polyethylene, P.V.C./Nylon 6-6, Epoxy/P.M.M.A. and Epoxy/Polyethylene.

Since the molecular attraction parameters calculated and shown in Table III do not reveal the reason for the observed relationship

TABLE III

Substrate	d	p	ϕ_i	ϕ_u
H.M.W.P.E.	0.9975	0.0025	0.9646	0.7938
Polypropylene	0.9510	0.0037	0.9510	0.8731
Polystyrene	0.9310	0.0690	0.9987	0.9740
P.M.M.A.	0.8320	0.1680	0.9944	0.9629
Rigid P.V.C.	0.9520	0.0480	0.9954	0.8726
Acetal resin	0.8766	0.1234	0.9991	1.0442
Epoxy resin	0.8766	0.1234	0.9991	1.0442
COO4 urethane	0.9534	0.0466	0.9951	0.9999
Polycarbonate	0.9369	0.0631	0.9980	0.9940
P.E.T.	0.9125	0.0875	0.9998	0.9985
Nylon 6-6	0.8196	0.1804	0.9925	1.0690
Nylon 6	0.6994	0.3006	0.9654	0.9930

between the fracture surface energy and the properties of the adhesive and substrate, an examination of the volume interaction parameter was attempted.

If a Lennard-Jones potential energy function is used to describe the intermolecular attraction between the two phases then the volume interaction parameter can be calculated by assuming the appropriate combining relationships between the function constants for the interfacial interactions and those for the intermolecular interactions in the individual phases. Girifalco and Good[2] used a geometric mean relationship for both attractive and repulsive constants. Kong, however,[18] has developed a more rigorous method for the calculation of the repulsive constant which yields

$$B_{12} = (B_{11}/2^{13})[1 + (B_{22}/B_{11})^{1/13}]^{13}$$

where B_{11}, B_{22} and B_{12} are the Lennard-Jones repulsive constants for the interactions between molecules within one phase and across the interface. If this combining relationship is used then the volume interaction parameter can be calculated from an expression of the form

$$\phi_v = \left(\frac{V_{22}}{V_{11}}\right)^{5/6}\left(\frac{\delta_{22}}{\delta_{11}}\right)^{1/3}\left[\frac{2}{1 + ((\delta_{22}/\delta_{11})^2(V_{22}/V_{11})^5)^{1/3}}\right]^{13/3} \tag{8}$$

The results of such calculations are shown in Table III.

From Table III it can be seen that all the systems which failed cohesively had a high value for the volume interaction parameter. Although the P.E.T. and nylon joints appear to be exceptions to this, it is suggested that the molcular interaction parameter may be smaller in this case than is indicated by the Owens and Wendt calculation.

CONCLUSIONS

Interfacial failure is possible even with systems in which the adhesive is capable of wetting the substrate. Although the fracture surface energy of the joint (which measures the work of adhesion) demonstrates a general increase as the surface energy of the substrate increases, this relationship is perturbed within the region where cohesive failure occurs. The cohesive failure occurs when the solubility parameters of adhesive and substrate approach one another but only if the volume interaction parameters of the system are high.

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