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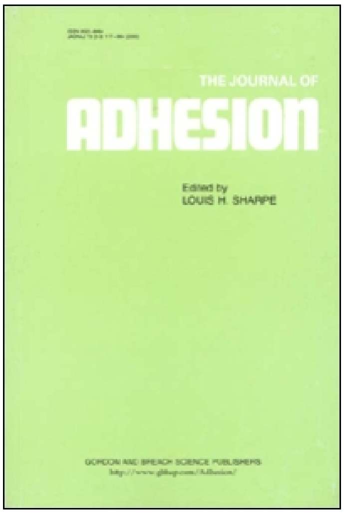

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Thermodynamic Criteria for the Maximum and Minimum Strength of Fibre-Reinforced Composite Materials†

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The overall performance and reliability of composite materials are, in most cases, dependent upon the behaviour of the reinforcement-matrix interface, particularly upon its ability to transfer stress.

A theory for predicting thermodynamic conditions for the maximum and zero-adhesion at the reinforcement-matrix interface is tested in this paper, based on experimental data. Proposed is a model of the relationship between mechanical properties of composite materials (tensile strength, flexural strength, Young's modulus and impact resistance) and energetic properties of matrix and reinforcement expressed by the energy ratio $a = \gamma_1/\gamma_2$.

KEY WORDS Adhesion; Composite materials; Flexural strength; Impact strength; Interfacial energy; Work of adhesion.

INTRODUCTION

The use of composite materials in aerospace, automotive and construction industries, instead of traditionally-used monolithic materials, *e.g.* metals, ceramics and plastics, is rapidly increasing. The principles of designing with composites are based on a

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knowledge of mechanical properties of bulk materials, *e.g.* matrix and reinforcement under expected service conditions and their properties in a composite. However, the overall performance and reliability of composite materials are, in most cases, dependent upon the behaviour of the reinforcement-matrix interface, particularly upon its ability to transfer stress. Therefore, there is a need for an understanding of interactions in this particular region in order to predict (a) conditions for maximum strength, (b) conditions under which the bond at the reinforcement-matrix interface fails, and (c) possibilities of adjustment of surface properties of the reinforcement and/or matrix material to maximise the strength and durability of the composite.

This becomes possible if the bond at the matrix-reinforcement interface is considered as a thermodynamic system whose properties are described in terms of relevant thermodynamic parameters, *e.g.* surface energies, enthalpies or solubility parameters and wettability characteristics of the components.

This paper has two purposes: firstly, to outline the theory of thermodynamic criteria for the maximum and zero-strength of adhesion between matrix and reinforcement, and secondly, to analyse the experimental data regarding fibre-reinforced composite materials to justify the theory.

THEORY

A theory of thermodynamic criteria for the maximum and zero-strength of an adhesive bond has been presented elsewhere.[1] In this paper, this theory is applied for predicting the performance of composite materials, assuming that the terms adhesive and substrate used previously can equally be regarded as matrix and reinforcement in the present case.

Criteria for the maximum strength

In accordance with the second law of thermodynamics, the system exhibits a maximum stability when its free energy is minimum.

It has been shown elsewhere[1-5] that the minimum of the above free energy, considered as minimum interfacial energy, gives conditions for a maximum adhesion between the substrate and adhesive, *e.g.* reinforcement and matrix.

From reference to the work,[1] interfacial free energy at the reinforcement-matrix interface can be estimated using the following expressions (see Nomenclature for explanations of the terms used):

$$\gamma_{12}=\begin{cases}\gamma_1-\gamma_2(1+m_1)+m_1\dfrac{\gamma_2^2}{\gamma_{C(1)}} & \text{for}\quad \gamma_2\geqslant\gamma_{C(1)} \qquad (1)\\ \gamma_1-\gamma_2 & \text{for}\quad \gamma_2\leqslant\gamma_{C(1)}, \qquad (2)\end{cases}$$

or alternatively

$$\frac{\gamma_{12}}{\gamma_1}=\begin{cases}1+\dfrac{m_1}{a^2\Phi_{0(1)}^2}-\dfrac{(1+m_1)}{a} & \text{for}\quad 0<a\leqslant a_s \qquad (3)\\ 1-\dfrac{1}{a} & \text{for}\quad a\geqslant a_s, \qquad (4)\end{cases}$$

where

$$\Phi_{0(1)}=[\gamma_{C(1)}/\gamma_1]^{1/2}, \tag{5}$$

and

$$a=\gamma_1/\gamma_2. \tag{6}$$

Accordingly, the minimum interfacial energy which corresponds to the conditions for the maximum strength is achieved at the energy ratio

$$a_{\mathrm{MIN}}=\frac{2m_1}{(1+m_1)\Phi_{0(1)}^2}. \tag{7}$$

Criteria for zero-strength

Conditions for zero-strength of adhesive bond at the reinforcement-matrix interface were found[1] from the analysis of expressions for thermodynamic work of adhesion, assuming that there is no net force across the interface when $W_A=0$. It follows that the strength is zero for any energy ratio:

$$a\leqslant a_1^{\mathrm{CRIT}}=\frac{m_1}{[2+m_1+(\pi_{e(1)}/\gamma_2)]\Phi_{0(1)}^2}. \tag{8}$$

It has been shown elsewhere[1] by the present author that apart from condition (8), there is another critical point at which $W_A=0$ and this relates to the complete thermodynamic wetting of the substrate (reinforcement) by matrix material. Accordingly, this is achieved for any energy ratio:

$$a \geqslant a_2^{\text{CRIT}} = \frac{[2 + m_2 + (\pi_{e(2)}/\gamma_1)]}{m_2} \cdot \Phi_{0(2)}^2. \tag{9}$$

in which

$$\Phi_{0(2)} = [\gamma_{C(2)}/\gamma_2^C]^{1/2}. \tag{10}$$

Further, we provide experimental evidence of existence of a_1^{CRIT} and a_2^{CRIT} indicating conditions for zero-strength of adhesive bond.

EXPERIMENTAL CONFIRMATION OF THE THEORY

General

Theoretical criteria developed in paper[1] have been evaluated based on experimental data. Thermodynamic parameters necessary for analysis were calculated using the following equations: (a) interfacial energy: Eqs. (1) to (4), (b) specific bonding efficiency factor: Eqs. (5) and (10), and (c) critical energy ratios: Eqs. (8) and (9).

Basic experimental data for analysis include: (a) surface energies of the reinforcement material, γ_1, and matrix in its cured state, *i.e.* γ_2^C, and (b) wettability characteristics of the reinforcement and matrix in terms of the parameters m and γ_C.

It is assumed as a first approximation that: (a) $m = 1$ and $\Phi_0 = 1$ when the wettability characteristics are unknown, and (b) equilibrium spreading pressure is negligible, *i.e.* $\pi_e \cong 0$.

Fibre reinforced composites

Polyester matrix. Evaluation of the theoretical criteria has been carried out using strength data from Yip and Shorthall[6] on fibre-reinforced composites as well as the author's data on surface energies of E-glass fibres surface-modified with the same type of polymers as used by these authors. Fibres ($d_{50} \cong 30\,\mu$m) were heat cleaned and water sprayed, followed by treatment with selected chemicals prior to fabrication of composites.

TABLE I
Data for construction of strength characteristic of polyester-glass fibre system

No.	Treatment of *E*-glass	γ_1 (mJ/m^2)	a[a]	γ_{12}/γ_1	Interfacial shear strength[b] (MPa)
1	heat + rinsed in H_2O	63.0	1.56	0.36	34.5
2	0.3% silane A-174	42.9	1.06	0.06	52.3
3	0.3% silane A-153	33.2	0.82	0.05	22.2
4	silicone resin	15.8	0.39	2.45	0
5	5% PVA resin	35.1	0.87	0.02	37.1

[a] calculated using $\gamma_2^C = 40.4$ mJ/m^2.
[b] strength data from Ref. 6 for single fibre pull-out tests.

Relevant data on strength and surface energies, listed in Table I, were used for calculation of interfacial energies; the strength characteristic diagram of the series of composites was constructed in coordinates; strength *v.* γ_{12}/γ_1 and is given in Figure 1a.

Figure 1a shows that the maximum strength is achieved when the surface energy of modified fibre (as achieved by treatment with silane A-174, Union Carbide) is closest to the surface energy of the

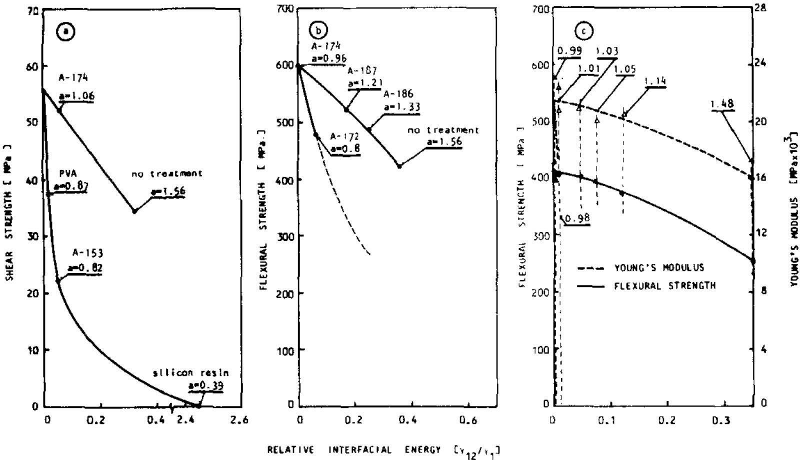

FIGURE 1 Relationship between strength and relative interfacial energy for *E*-glass/polyester composite material (a) single fibre pull-out, (b) laminate, and (c) dependence of the Young's modulus and flexural strength upon relative interfacial energy.

TABLE II
Data for construction of strength characteristic of polyester-glass cloth composite

No.	Treatment of *E*-glass	γ_1 (mJ/m^2)	a[a]	γ_{12}/γ_1	Flexural strength[b] (MPa)
1	No treatment	63.0	1.56	0.36	420.6
2	Silane A-172	32.3	0.80	0.06	475.7
3	Silane A-174	38.7	0.96	0.002	599.8
4	Silane A-187	48.8	1.21	0.17	524.0
5	Silane A-186	53.7	1.33	0.25	489.5

[a] calculated using $\gamma_2^C = 40.4$ mJ/m^2.
[b] strength data from Ref. 7.

cured matrix material. Treatment with another silane (A-153, Union Carbide) provides lower fibre surface energy than treatment with PVA, resulting in correspondingly lower strength. Treatment with the silicone resin leads to the energy ratio $a = 0.39$, which is close to $a_1^{\mathrm{CRIT}} \cong 0.333$ corresponding to zero-strength.

A similar strength characteristic diagram has been drawn from reinterpreted data of Broutman[7] who investigated composite materials of cloth treated with different silanes and a polyester matrix. Surface energies of cloth treated with silanes used in the experiment and the calculated resultant interfacial energies have been determined (see Table II) in order to construct the strength characteristic diagram illustrated in Figure 1b.

Again, the maximum strength is achieved when the energy ratio is close to $a_{\mathrm{MIN}} = 1.0$, as obtained after treatment with methacrylate-silane A-174. It can be argued at this stage that the organofunctionality of the A-174 silane, as being designed for polyester-based composites, is responsible for the maximum strength of this system. However, we provide further data which support an hypothesis that the minimum interfacial energy, resulting from equilibrium of energies of substrate and matrix, plays a primary role in enhancement of adhesion. It is the author's opinion that organofunctionality of the adhesion promoter (in this case the silane) plays only a secondary role.

It becomes apparent from Figures 1a and 1b that there are two branches on the strength characteristic diagram: strength *vs.* γ_{12}/γ_1: (a) a lower, steep branch for energy ratios $a \leq a_s$, and (b) an upper,

TABLE III

Data for construction of strength characteristic of polyester-glass cloth composite

No.	Concentration (%) of γ-MPS	γ_l (mJ/m^2)	a^a	γ_{12}/γ_l	Young's modulus^b (MPa $\times$ 10^3)	Flexural strength^b (MPa)
1	0	63.0	1.56	0.36	16.0	252
2	0.1	46.0	1.14	0.12	20.35	375
3	0.3	42.3	1.05	0.048	20.85	404
4	0.5	40.8	1.01	0.0099	21.20	406
5	0.8	39.5	0.98	0.0004	20.40	396
6	1.1	40.0	0.99	0.0001	20.50	412
7	1.5	40.8	1.01	0.0099	21.60	409
8	2.0	43.7	1.03	0.0750	20.05	396

[a] calculated using $\gamma_2^C = 40.4$ mJ/m^2

[b] calculated as average from data in Ref. 8.

shallow branch for $a \geqslant a_s$, which is relevant to thermodynamic wetting of a filament by matrix material.

An interesting study has been presented by Graf, Koenig and Ishida[8] who investigated the influence of γ-methacryloxypropyltrimethoxy (γ-MPS) silane on the structure of adsorbed silane layers and the flexural strength and the Young's modulus of E-glass-polyester composite materials. Our data on surface energies of γ-MPS modified E-glass, resultant interfacial energies and the strength data of Graf *et al.*,[8] are presented in Table III. It is necessary to note that we have calculated the flexural strength and Young's modulus (see Table III) as an average from Graf's dry and wet conditioning data because, in our view, 80°C water immersion for 40 hours (considered as wet conditioning[8]) is not sufficient to hydrolise Si—O—Si bonds to Si—OH.

The strength characteristic diagram in Figure 1c indicates an excellent agreement with our previous approach[1,5] emphasising the role of energy equilibrium at the interface on adhesion enhancement. Modulus of elasticity of the composites investigated (see Figure 1c), depends upon interfacial energy in the same manner as strength, as expected.

Epoxy matrix Adhesion of E-glass fibres to epoxy resin was investigated by Berger and Eckstein.[9,10] Glass fibres were treated with A-1100 and A-174 silanes diluted in water to the required concentrations. Epoxy resin DER 331 (Dow Chemical) was used as

TABLE IV
Data for construction of strength characteristic of epoxy-glass fibre system

No.	Treatment of *E*-glass	γ_1 (mJ/m^2)	a[a]	γ_{12}/γ_1	Flexural strength[b] (MPa)
1	No treatment	35.4	0.90	0.012	9.1
2	A-1100 0.2	31.35	0.80	0.062	6.8
3	0.5	34.63	0.88	0.018	7.1
4	1.0	36.19	0.92	0.008	8.7
5	2.5	44.07	1.12	0.107	5.4
6	A-174 0.2	40.31	1.02	0.024	12.2
7	1.0	42.1	1.07	0.065	8.2
8	2.5	41.0	1.04	0.038	7.1

[a] calculated using $\gamma_2^C = 39.33$ mJ/m^2 (data from Ref. 9)
[b] single fibre pull-out test; data from Refs. 9, 10.

a matrix. Data necessary for calculation of interfacial energies and strength of the systems investigated are listed in Table IV, as given by the original authors. The pattern of the relationship: strength *vs.* γ_{12}/γ_1, as Figure 2a shows, confirms the earlier approach.

It is apparent from data presented that the maximum strength (at the energy ratio $a \cong 1.0$), is achieved by treatment with a 0.2% solution of γ-MPS silane, which theoretically should give a lower strength than the amino-silane A-1100. However, the amino-silane, designed to provide more favourable conditions for chemical interaction with the epoxy resin matrix, has not been used at the optimum concentration to yield the energy ratio close to a_{MIN}.

It is seen that the surface energy of the substrate (treated by a silane) is crucial in regard to maximum adhesion. A similar conclusion can be drawn from analysis of the strength characteristic in Figure 2b, constructed from Plueddemann's data.[11] Also in this case, the glass fibre-epoxy composites were fabricated using fabric pretreated with different silanes, as described in Figure 2b. It is apparent that the maximum strength is achieved with the silane providing the energy ratio close to 1.0, *i.e.* styrylamine silane Z-6032 (Dow Corning).

Epoxy silane (Z-6040) yields the same strength of the composite as chloroalkyl-(Z-6076) and mercapto- (Z-6062) functional silanes, all Dow Corning materials, whilst theoretically the optimal (within the scope of the experiment) diamino-silane (Z-6020) results in even lower strength.

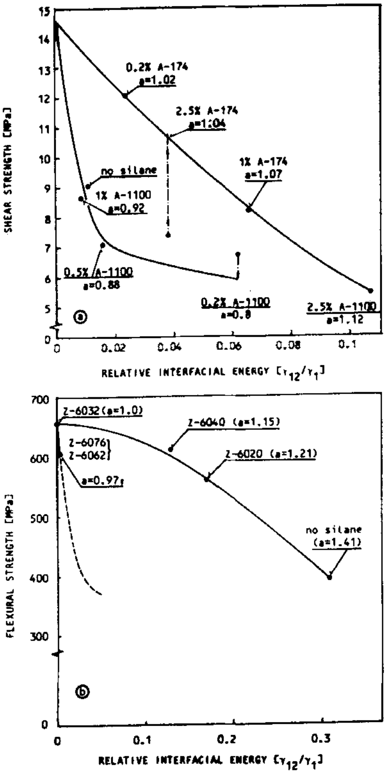

FIGURE 2 Relationship between strength and relative interfacial energy for *E*-glass/epoxy composite material (a) single fibre pull-out, and (b) laminate.

EXPERIMENTAL EVIDENCE OF THE EXISTENCE OF TWO CRITICAL REGIONS FOR ZERO-INTERFACIAL SHEAR STRENGTH IN COMPOSITES

As noted earlier, there are two theoretical boundaries relevant to zero-interfacial shear strength, as given by Eqs. (8) and (9). To a first approximation, these can be simplified to

$$a_1^{\mathrm{CRIT}} \cong 0.333, \quad \text{and} \tag{8}$$

$$a_2^{\mathrm{CRIT}} \cong 3.0. \tag{9}$$

In order to observe the trends in the relationship between the strength and the energy ratio of the system, we have analysed literature data on the strength of adhesive bonds (lap-shear specimens)[1–4,12,13]. These have been reinterpreted to give graphs of strength *vs*, a, illustrated in Figure 3a. The pattern of this relationship is the same for all the systems analysed, despite the type of substrates and adhesives.

It is apparent from the graphs that apart from the maximum at $a \cong 1.0$, there is a significant decrease in bond strength which can be deduced to approach a minimum at two different regions, *e.g.* for $a = 0.3$ to 0.5 and $a > 1.8$. (for non-metallic substrates this minimum corresponds to zero-strength, whilst for metals there is some

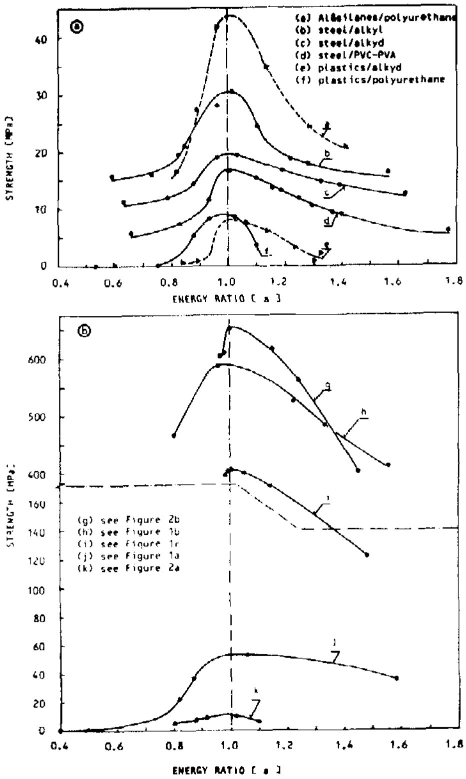

FIGURE 3 Experimental data on the relationship between strength and energy ratio (a) lap-shear adhesive joints, and (b) composite materials.

residual strength). In Figure 3b we have plotted a similar graph for the fibre-reinforced plastics analysed in this paper. The pattern of the relationship is similar to that exhibited by the lap-shear adhesive bonds. However, to apply the approach to composite materials we have to distinguish a substantial difference between the load-bearing capacity of classic adhesive bonds and composite materials, arising from the critical criteria of Eqs. (8) and (9), namely:

a) When the properties of the materials yield an energy ratio relevant to conditions (8) and (9) then, for an adhesive bond either the existing bond fails catastrophically, or attempts to produce an adhesive bond, using the given substrates and adhesive cannot be successful. In both cases the overall load-bearing capacity of the system is zero.

b) When conditions (8) and (9) are applicable in a fibre-reinforced composite, then similarly, there is no net attractive force across the interface (*i.e.* no adhesion between phases). However, the matrix itself provides inherent load-bearing capacity. This is further increased by a contribution from a friction bond created by

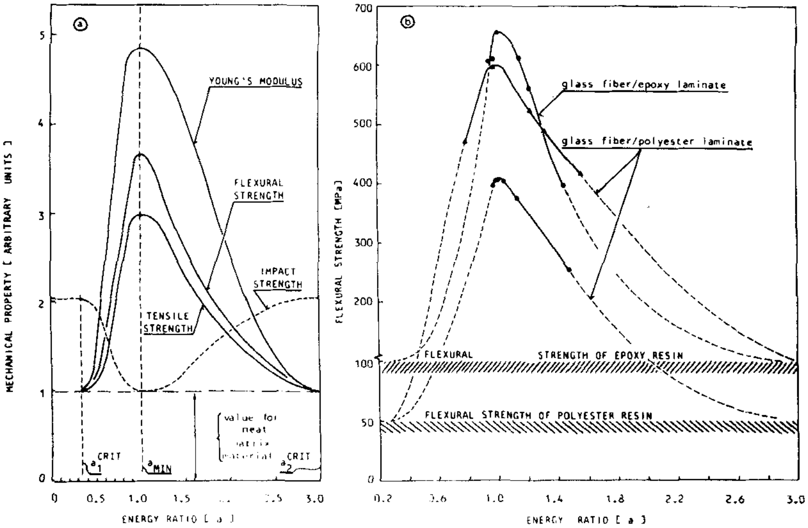

FIGURE 4 The model of the relationship between mechanical properties of composite materials (flexural strength, tensile strength, impact strength) and energy ratio in composite materials (a) proposed model, and (b) experimental evidence for polyester- and epoxy-based composites.

a radial compressive stress resulting from matrix shrinkage during cure. We propose that the critical criteria (8) and (9) applied to composite materials can be interpreted as Figure 4a illustrates.

Experimental points relating flexural strength and the energy ratio for polyester- and epoxy-based composite materials, as analysed in this paper, are shown in Figure 4b, as well as the average value of the flexural strength of neat polyester and epoxy resins.

If the model proposed in Figure 4a is followed (based on data from Figure 3) then we can deduce that it can be applied to composite materials. However, further experimental evidence must be given to locate strength *vs.* *a* graphs for those energy moduli which have not yet been fully investigated (*e.g.* '*a*' ranges from 1.5 to 3.0 and 0.4 to 0.6).

NOMENCLATURE

γ_1, γ_2	total surface energy of phase 1 or 2
γ_C	critical surface tension for wetting
γ_{12}	interfacial energy
W_A	thermodynamic work of adhesion
m	parameter dependent upon the slope of the wettability characteristic
γ_{12}/γ_2	relative interfacial energy
$a = \gamma_1/\gamma_2$	energy ratio of the system
$a_s = 1/\Phi_0^2$	threshold energy ratio for self-spreading
a^{CRIT}	critical energy ratio for $W_A = 0$, corresponding to zero-strength
a_{MIN}	optimum energy ratio for $\gamma_{12}^{\mathrm{MIN}}$ and $[\gamma_{12}/\gamma_1]_{\mathrm{MIN}}$, corresponding to the maximum strength
Φ_0	specific bonding efficiency factor

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