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A criterion for optimum adhesion applied to fibre reinforced composites

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The effects of physical adhesion on the mechanical properties of a composite structure are examined in this work. A criterion for optimum adhesion between matrix and reinforcing fibres is proposed based on maximizing the wetting tension. It is shown that the maximum wetting tension criterion best fulfils two important requirements for a strong interface:(i) the physical interactions at the molecular level between the resin and the fibres must be maximized, and (ii) the liquid resin must spontaneously wet the fibre surface in order to minimize the flow density at the interface. The conditions on the surface energy of the various phases leading to maximum wetting tension are analysed considering three mixing rules: two based on dispersive–polar interactions, and a third one based on acid–base interactions. The optimum adherend for a given adhesive, and the optimum adhesive for a given adherend, are examined. The analysis shows that maximum wetting tension is obtained when the substrate and adhesive surface energies are very high and equal, so that their polar and dispersive components are equal when the polar–dispersive mixing rule is used, and e.g. their Lifshitz–van der Waals' components are equal and the acid component of one phase is equal to the basic component of the other phase when the acid–base approach is considered. It is shown using data from the literature that interfacial strength correlates with the wetting tension for fibre reinforced composites. Additional observations show that under poor wetting conditions the voids tend to concentrate at the fibre–resin interface, whereas under favourable wetting conditions they tend to coalesce in regions away from the fibre surface.

1. Introduction

It is generally recognized that mechanical properties of composite materials can be greatly affected by the bond strength at the fibre–resin interface. When a composite structure is loaded, the load is transferred from the matrix to the fibres mainly through shear stresses at the fibre–matrix interface. Load transfer increases with strong bonds, thus improving the composite strength. Extensive work on the study of the influence of the shear strength at the fibre–resin interface on mechanical properties of composites is reported in the literature [1–7]. Shear strength, which depends on the quality of adhesion at the interface, has often been measured on single fibre model systems embedded in a resin [8–10]. Gent and coworkers [11, 12] propose that the measured adhesive strength is a product of two terms: an equilibrium term of detachment given by thermodynamic considerations, and a numerical factor representing the inelastic contribution of fracture. The latter term can be very large, and is strain dependent in the case of viscoelastic materials. This suggests that, with a given inelastic contribution, there is a strong correlation between interfacial strength and thermodynamic adhesion.

Physical interactions between resin and fibres (e.g. van der Waals' forces and hydrogen bonds) are always present at the interface and their relative contributions to adhesion between the two phases depend on whether chemical bonds (e.g. covalent bonds) can be formed or not. When the latter kind of interactions are neglected, and only physical interactions are present, then the interfacial strength of a composite part can be related to the surface energies of the two phases. Numerous attempts to correlate the bond strength to different thermodynamic *wetting parameters* can be found in the literature. Today, the choice of a criterion for optimum adhesion is still actively debated. Bond strength was alternately compared to the work of adhesion, W_a [13], spreading coefficient, λ [14], wetting tension, ΔF_i, and interfacial energy per unit area, γ_{sl}, respectively [15–17].

Adhesive interactions can be achieved only if a sufficient intimate contact at the interface is established between the two phases. This is particularly critical for

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fibres reinforced composites because their processing involves the flow of a liquid resin, often highly viscous, into an assembly of closely spaced fibres of the order of 10 μm in size. The liquid resin must flow through narrow and often tortuous channels and wet a large surface area (e.g. in order to impregnate a 1 cm side cube half-filled with 10 μm diameter fibres fully, the liquid resin must form a 1 m^2 interface with the fibres). The analysis of the capillary forces present in a composite part during fibre impregnation shows that spontaneous impregnation is enhanced by a small contact angle, and can occur only if it is smaller than $\pi/2$ [18]. If the contact angle is large, the system will show poor wetting properties resulting in the presence of flaws at the interface. Flaw concentration can be considerably reduced at a macroscopic level by applying high pressures during the impregnation process, thus forcing the resin to wet the fibre surface. At a microscopic level, however, it is nearly impossible to eliminate all the voids present at the interface by the sole action of externally applied mechanical pressure. Spontaneous wetting is therefore a necessary condition to improve the interfacial strength of a fibre reinforced composite.

The objectives of this work are first, to analyse the principal factors controlling physical adhesion between two phases, leading to a definition of the thermodynamic criterion for optimum adhesion, and second, to determine the surface energies of the materials fulfilling this criterion. Four criteria for optimum adhesion, found in the literature are reviewed and discussed. The wetting parameters related to adhesion are first presented, followed by an algebraical analysis that leads to their optimization. This is done by considering two cases separately: (i) for a given adhesive what surface properties of substrate yield maximum adhesion, and (ii) for a given substrate, which is the optimum adhesive. It is proposed in this paper that the criterion for optimum adhesion must best fulfil two requirements that are not always compatible: (i) the physical interactions at the molecular level between the resin and the fibres must be maximized, and (ii) the liquid resin must wet the fibre surface spontaneously in order to minimize the flaw density at the interface. Experimental results from the literature on both flat interfaces and fibre reinforced composites are compared with the theory presented herein.

2. Background

2.1. Wetting parameters

Four wetting parameters are presented here, which are considered in the literature as characteristic of the quality of the physical adhesion between two phases. These are, the work of adhesion W_a, the spreading coefficient, λ, the wetting tension, ΔF_i, and the interfacial energy per unit area, γ_{sl}.

2.1.1. *Work of adhesion*

The work of adhesion, W_a, is the work required to disjoin a unit area of the solid–liquid interface, thereby creating a unit area of liquid–vacuum and solid–vacuum interface [21]; this situation is illustrated in Fig. 1a. It is expressed by Dupré equation [22]

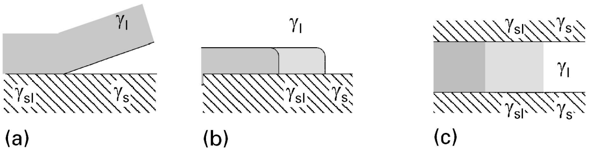

Figure 1 Physical representation of the wetting parameters: (a) work of adhesion, $W_a = \gamma_s + \gamma_l - \gamma_{sl}$; (b) spreading coefficient, $\lambda = \gamma_s - \gamma_l - \gamma_{sl}$; and (c) wetting tension, $\Delta F_i = \gamma_s - \gamma_{sl}$.

$$W_a = \gamma_l + \gamma_s - \gamma_{sl} \tag{1}$$

where γ_l is the liquid surface tension, and γ_s is the solid surface energy per unit area. Using Young's equation [23]

$$\cos\theta = \frac{\gamma_s - \gamma_{sl}}{\gamma_l} \tag{2}$$

that relates the finite equilibrium contact angle, θ, to the surface and interfacial energies, allows the thermodynamic work of adhesion (Equation 1) to be expressed as

$$W_a = \gamma_l(1 + \cos\theta) \tag{3}$$

that permits direct determination of the work of adhesion from surface tension and contact angle measurements. Equations 2 and 3 are written in forms that neglect the adsorption of vapours from the resin liquid onto the solid surface, a good practical assumption when the liquid is non-volatile.

Several workers have shown that the thermodynamic work of adhesion correlates well with adhesive bond strength of a flat interface [24–26] and with composite strength [27]. Although it is intuitively easy to accept that there is a correlation between work of adhesion and adhesive strength, it must be kept in mind that the former is a thermodynamic quantity referring to the reversible work needed to create two new surfaces from a defect free interface, while the latter is a mechanical quantity also affected by irreversible processes like inelastic deformations, and the presence of voids at the interface. The work of adhesion is thus not sufficient to characterize the interfacial strength. Wu [28] calculated the theoretical bond strength of a flaw free interface typical of a polymer–polymer bond, and obtained a value of about two orders of magnitude greater than what was experimentally observed with real interfaces. De Bruyne [29] proposed that voids located at the interface, the size of which he related to the contact angle between adhesive and adherend, could act as nuclei for crack propagation. Wu [28] related the void size to the spreading coefficient, λ.

2.1.2. *Spreading coefficient*

The spreading coefficient can be defined as the work required to expose a unit area of solid–vacuum interface while destroying corresponding amounts of solid–liquid and liquid–vacuum interfaces [21]

$$\lambda = \gamma_s - \gamma_l - \gamma_{sl} \tag{4}$$

A negative value of λ results in a finite equilibrium contact angle θ. In that case, Equation 4 together with Young's Equation 2 can be expressed as

$$\lambda = \gamma_l(\cos\theta - 1) \tag{5}$$

A positive value of λ corresponds to instantaneous spreading. This situation is illustrated in Fig. 1b. Wu [28] suggests that the interfacial strength, σ_f, can be related to the spreading coefficient as

$$\sigma_f = \frac{K_m}{(1 - (\lambda/\gamma_s))} \tag{6}$$

where K_m is a mechanical parameter characteristic of the system. According to Equation 6, it is clear that the interfacial strength is maximum at maximum spreading coefficient.

2.1.3. Wetting tension

Various authors [16, 17, 30, 31] have proposed that maximum adhesive strength is obtained at maximum *wetting tension* (or *adhesive tension*), ΔF_i. The wetting tension can be defined as the work done in eliminating a unit area of the solid–liquid interface while exposing a unit area of the solid–vacuum interface [21]

$$\Delta F_i = \gamma_s - \gamma_{sl} \tag{7}$$

that is actually the arithmetic mean of the work of adhesion and the spreading coefficient. This approach thus gives equal weight to the influence of the work of adhesion and the presence of flaws at the interface. This situation is illustrated in Fig. 1c. It can be seen that this situation is the most representative of a resin impregnating a fibre bed, because in a fibre reinforced composite the liquid–vacuum interface area can be neglected compared to the fibre–vacuum and fibre–resin interface areas.

2.1.4. Interfacial energy

Finally, it was proposed [16, 17, 30, 32] that minimizing the interfacial energy, γ_{sl}, would yield a more stable system and hence increase the adhesive strength. Various expressions were proposed for the interfacial energy. Four definitions are presented: the Sell–Neumann expression, the Good–Girifalco equation for dipolar interactions with two different definitions of the interaction parameter, ϕ, and finally an expression based on acid–base interactions.

The Sell–Neumann relationship [33, 34] expresses the interfacial energy in terms of the surface energies of the adhesive and adherend only

$$\gamma_{sl} = \frac{[(\gamma_s)^{1/2} - (\gamma_l)^{1/2}]^2}{1 - 0.015(\gamma_s\gamma_l)^{1/2}} \tag{8}$$

The validity of this equation is contested, however, and will not be used in this study. Good and Girifalco [35–38] introduced an interaction parameter, ϕ, into their definition of interfacial energy

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\phi(\gamma_s\gamma_l)^{1/2} \tag{9}$$

It was first assumed that the surface energy of a phase *i* could be expressed in terms of a dispersive and a polar component, such that

$$\gamma_i = \gamma_i^d + \gamma_i^p \tag{10}$$

where d and p refer to dispersive and polar, respectively. Following the dispersive–polar theory, Wu [28] proposed that the interaction parameter, ϕ, between a low and a high energy material, is well described by the geometric mean equation, ϕ_G

$$\phi_G = (x_s^d x_l^d)^{1/2} + (x_s^p x_l^p)^{1/2} \tag{11}$$

and the harmonic–mean equation, ϕ_H, is preferred for interaction between a polymer and a low energy material

$$\phi_H = 2\left\{\frac{x_s^d x_l^d}{[(\gamma_l/\gamma_s)^{1/2} x_l^d] + [(\gamma_s/\gamma_l)^{1/2} x_s^d]} + \frac{x_s^p x_l^p}{[(\gamma_l/\gamma_s)^{1/2} x_l^p] + [(\gamma_s/\gamma_l)^{1/2} x_s^p]}\right\} \tag{12}$$

where $x_i^k = \gamma_i^k/\gamma_i$, ($i$ = s and l and k = d and p). The sum of the polar and dispersive components of the surface energy is unity

$$x_i^d + x_i^p = 1 \tag{13}$$

It was argued in the literature [39] that while the geometric mean and the harmonic mean equally well describe the dispersive component of the interaction parameter, neither combining rule can be applied satisfactorily to the polar component. A more recent approach considers the acid–base interaction between molecules and expresses the surface energy of a compound in terms of the Lifshitz–van der Waals' component, γ^{LW}, and the acid–base component, γ^{AB}, as

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB} = \gamma_i^{LW} + 2(\gamma_i^A\gamma_i^B)^{1/2} \tag{14}$$

where γ^A and γ^B are the (Lewis) acid and base parameters of the surface free energy, respectively. The interfacial energy is defined as

$$\gamma_{sl} = \gamma_s^{LW} + \gamma_l^{LW} + 2[(\gamma_s^A\gamma_s^B)^{1/2} + (\gamma_l^A\gamma_l^B)^{1/2} - (\gamma_s^{LW}\gamma_l^{LW})^{1/2} - (\gamma_s^A\gamma_l^B)^{1/2} - (\gamma_s^B\gamma_l^A)^{1/2}] \tag{15}$$

Note that a molecule can be both a Lewis acid (electron acceptor) and a Lewis base (electron donor); such a substance is called bipolar, as for example water. A substance is apolar if neither that acid nor the basic properties are appreciable. If only one of the properties is appreciable, it is termed as monopolar substance. More details on the acid–base approach can be found in a review by Good on wetting and adhesion science [39].

It can be shown that the acid–base interaction, Equation 15, can be expressed in terms of the Good–Girifalco Equation 9 by defining the acid–base interaction parameter, ϕ_{AB}, as

$$\phi_{AB} = (x_i^{LW} x_j^{LW})^{1/2} + (x_i^A x_j^B)^{1/2} + (x_i^B x_j^A)^{1/2} \tag{16}$$

where, as for the dispersive–polar theory, $x^k{}_i = \gamma_i^k/\gamma_i$, with

$$x_i^{\mathrm{LW}} + x_i^{\mathrm{A}} + x_i^{\mathrm{B}} = 1 \tag{17}$$

so that ϕ_{AB} can be characterized by two parameters: x_i^{LW} and x_i^{A}.

Four wetting parameters, work of adhesion, spreading coefficient, wetting tension and interfacial energy, have been presented above. In the following, the optimization of these parameters to maximize interfacial strength will be performed.

3. Adhesion optimization

Four wetting parameters have been considered alternately by various authors as criteria for optimum adhesion: maximum work of adhesion, W_{a}, spreading coefficient, λ, and wetting tension, ΔF_{i}, respectively, and a minimum interfacial energy, γ_{sl}. In this section, the conditions required to optimize these parameters will be analysed individually. Then, the question as to what criterion is more representative of adhesion will be addressed. Finally, the validity of the selected criterion will be tested by applying it to experimental data from the literature.

3.1. Extremes of the wetting parameters

In this case phase j is kept constant, the four wetting parameters, W_{a}, λ, ΔF_{i}, and γ_{sl}, referred to by the symbol, χ, depend on the surface energy of phase i, γ_i, and on its polar component, x_i^{p}, for the polar–dispersive theory (Equations 11 and 12) and the LW- and acid-components, x_i^{LW} and x_i^{A}, respectively for the acid–base theory (Equations 15 and 17). The maximum possible work of adhesion, W_{a}, spreading coefficient, λ, and wetting tension, ΔF_{i}, respectively (assuring maxima exist), and minimum of interface energy, γ_{sl}, as a function of phase i can thus be found by setting equal to zero the variations of Equations 1, 4, 7 and 9 upon an arbitrary variation in the i-surface energy, γ_i, and its k-component, x_i^k, (k = p or LW and A, depending on the theory under consideration) at constant γ_j

$$\mathrm{d}\chi = \frac{\partial\chi}{\partial\gamma_i}\mathrm{d}\gamma_i + \sum_k \frac{\partial\chi}{\partial x_i^k}\mathrm{d}x_i^k = 0 \tag{18a}$$

Supposing that we can vary all γ_i and x_i^k independently, Equation 18 is satisfied when each term on the high-hand side vanishes, i.e.

$$\frac{\partial\chi}{\partial\gamma_i} = 0 \tag{18b}$$

and

$$\frac{\partial\chi}{\partial x_i^k} = 0 \tag{18c}$$

Two cases need to be considered separately: (i) for a given adhesive what surface property of the substrate will optimize adhesion, and (ii) what adhesive will adhere optimally to a given substrate.

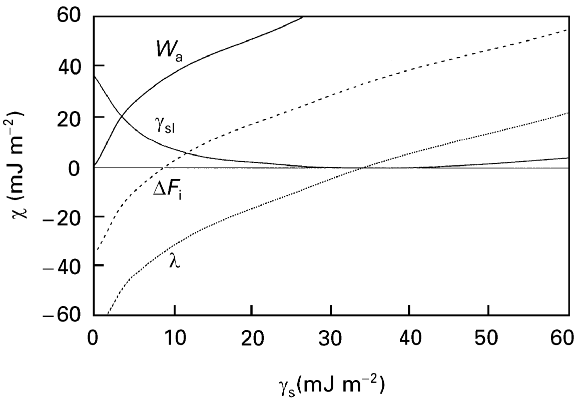

Figure 2 Wetting parameters, W_{a}, λ, ΔF_{i} and γ_{sl} as a function of the surface energy of the substrate using Equations 1, 4, 7 and 9, respectively, with $\phi = 1$ and $\gamma_{\mathrm{l}} = 35\ \mathrm{mJ\,m^{-2}}$.

3.1.1. Optimum surface properties of the substrate for a given adhesive

Work of adhesion, spreading coefficient, wetting tension and interface energy are plotted in Fig. 2 as a function of the surface energy of the substrate. It can be seen that, for a given adhesive, the first three wetting parameters follow parallel curves when plotted as functions of γ_{s}. Thus maximizing W_{a} is equivalent to maximizing the next two parameters.

For a given adhesive, the subscript i, refers to the substrate, and j to the adhesive. Differentiating Equations 4, 7 and 9 with respect to γ_{s} and x_{s}^k gives

$$\frac{\partial W_{\mathrm{a}}}{\partial\gamma_{\mathrm{s}}} = \frac{\partial\lambda}{\partial\gamma_{\mathrm{s}}} = \frac{\partial\Delta F_i}{\partial\gamma_{\mathrm{s}}} = 1 - \frac{\partial\gamma_{\mathrm{sl}}}{\partial\gamma_{\mathrm{s}}} \tag{19a}$$

and

$$\frac{\partial W_{\mathrm{a}}}{\partial x_{\mathrm{s}}^k} = \frac{\partial\lambda}{\partial x_{\mathrm{s}}^k} = \frac{\partial\Delta F_i}{\partial x_{\mathrm{s}}^k} = -\frac{\partial\gamma_{\mathrm{sl}}}{\partial x_{\mathrm{s}}^k} = 2(\gamma_{\mathrm{s}}\gamma_{\mathrm{l}})^{1/2}\frac{\partial\phi}{\partial x_{\mathrm{s}}^k} \tag{19b}$$

Hence Equation 18b and c yields two alternative criteria for $\partial\gamma_{\mathrm{sl}}/\partial\gamma_{\mathrm{s}}$ and a single criterion for $\partial\gamma_{\mathrm{sl}}/\partial x_{\mathrm{s}}^k$

$$\frac{\partial\gamma_{\mathrm{sl}}}{\partial\gamma_{\mathrm{s}}} = 1 \tag{20a}$$

or

$$\frac{\partial\gamma_{\mathrm{sl}}}{\partial\gamma_{\mathrm{s}}} = 0 \tag{20b}$$

and

$$\frac{\partial\gamma_{\mathrm{sl}}}{\partial x_{\mathrm{s}}^k} = 0 \tag{20c}$$

The criterion based on maximum W_{a}, λ and ΔF_{i} (Equation 20a), however, is in contradiction with the criterion of minimum interfacial energy (Equation 20b). The validity of minimum interfacial energy as a criterion for optimum adhesion is, however, arguable because interfacial energy is only one component of the total surface energy of the system. A valid criterion should consider the total surface energy and not one of its components only. For this reason, we suggest that for a given adhesive, optimum adhesion is obtained when W_{a}, λ and ΔF_{i} are maximum, i.e. when Equation 20a and c is satisfied.

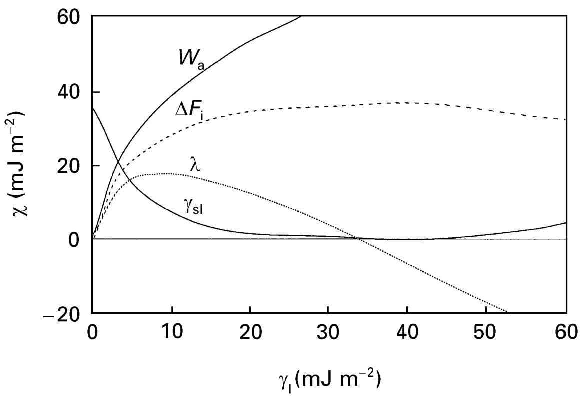

Figure 3 Wetting parameters, W_a, λ, ΔF_i and γ_{sl} as a function of adhesive surface tension, using Equations 1, 4, 7 and 9, respectively, with $\phi = 1$ and $\gamma_s = 35$ mJ m^{-2}.

3.1.2. Optimum adhesive for a given substrate.

Fig. 3 shows a plot of the wetting parameters as a function of the adhesive surface energy, with a constant adherend surface energy. This situation corresponds to testing various adhesives on a given substrate.

For a given substrate, the subscript *i*, refers to the adhesive, and *j* to the substrate. Again, differentiating the various parameters represented by ϕ gives

$$\frac{\partial W_a}{\partial \gamma_l} = 1 - \frac{\partial \gamma_{sl}}{\partial \gamma_l} \tag{21a}$$

$$\frac{\partial \lambda}{\partial \gamma_l} = -1 - \frac{\partial \gamma_{sl}}{\partial \gamma_l} \tag{21b}$$

$$\frac{\partial \Delta F_i}{\partial \gamma_l} = -\frac{\partial \gamma_{sl}}{\partial \gamma_l} \tag{21c}$$

and

$$\frac{\partial W_a}{\partial x_l^k} = \frac{\partial \lambda}{\partial x_l^k} = \frac{\partial \Delta F_i}{\partial x_l^k} = -\frac{\partial \gamma_{sl}}{\partial x_l^k} = 2(\gamma_s\gamma_l)^{1/2}\frac{\partial \phi}{\partial x_l^k} \tag{21d}$$

With Equation 18b and c we obtain three alternative criteria for $\partial\gamma_{sl}/\partial\gamma_l$ and a single one for $\partial\gamma_{sl}/\partial x_l^k$

$$\frac{\partial \gamma_{sl}}{\partial \gamma_l} = 1, \ -1 \quad \text{or} \quad 0 \tag{22a–c}$$

and

$$\frac{\partial \gamma_{sl}}{\partial x_l^k} = 0 \tag{22d}$$

It can be seen from Equation 22a–c that all three parameters cannot be maximized simultaneously, and Equation 21c shows that the maximum of the wetting tension corresponds to the minimum of the interfacial energy. Maximizing the work of adhesion ($\gamma_l \to \infty$) yields a negative value of the spreading coefficient, hence a high flaw density at the interface might be expected; whereas the maximum spreading coefficient corresponds to a low value of the work of adhesion. As pointed out by Wu [28], the optimum conditions must be a compromise between these two antagonistic mechanisms. The optimum condition should correspond to the situation where the work of adhesion is maximum within the region where spontaneous wetting occurs, i.e $\lambda \geqslant 0$; these two conditions are fulfilled when the wetting tension is maximum.

Maximum wetting tension can thus be used as a criterion for optimizing adhesion in both situation of a given adhesive, i.e. $\partial\gamma_{sl}/\partial\gamma_s = 1$ and $\partial\gamma_{sl}/\partial x_s^k = 0$ (Equation 20a and c), and a given substrate, i.e. $\partial\gamma_{sl}/\partial\gamma_l = \partial\gamma_{sl}/\partial x_l^k = 0$ (Equation 22c and d), respectively. Conditions required to maximize the wetting tension are studied in the following section.

3.2. Maximum wetting tension

Conditions leading to maximum wetting tension can be found by solving Equation 20a and c if the substrate is being optimized for a given adhesive, and Equation 22c and d if it is the adhesive that is to be optimized. The solutions to both sets of equations depend on the definition of the interfacial energy selected. The Good–Girifalco Equation 9 will be examined here using three different mixing rule theories for ϕ: the geometric mean definition, Equation 11; the harmonic mean, Equation 12; and the acid–base, Equation 16; respectively. All Equations 9–12 and 16 are symmetric with respect to γ_l and γ_s, so henceforth the subscripts *i* and *j* will be used instead of s and l.

According to the Good–Girifalco Equation 9, the derivative of the interface energy with respect to the *i*-surface energy is defined as

$$\frac{\partial \gamma_{sl}}{\partial \gamma_i} = 1 - \phi\frac{\gamma_j^{1/2}}{\gamma_i^{1/2}} - 2(\gamma_i\gamma_j)^{1/2}\frac{\partial \phi}{\partial \gamma_i} \tag{23}$$

As all three Equations 20, 22 and 23 depend on the interaction parameter, ϕ, it is now necessary to examine its different definitions separately.

3.2.1. Geometric mean equation

In the case of the geometric mean, Equation 11 is used; it can be shown that the solutions to Equations 20c and 22d, i.e. $\partial\phi_G/\partial x_i^k = 0$ are given by

$$x_s^p = x_l^p \tag{24}$$

As the geometric mean definition, Equation 11, is independent of γ_i, the last term on the right-hand side of Equation 23 is zero. The optimum substrate energy for a given adhesive is thus found by solving Equation 20a, i.e. by setting

$$\frac{\partial \gamma_{sl}}{\partial \gamma_s} = 1 - \phi_G\frac{\gamma_l^{1/2}}{\gamma_s^{1/2}} = 1 \tag{25}$$

which yields the solution

$$\gamma_s \to \infty \tag{26}$$

The optimum adhesive surface energy for a given substrate is found by solving Equation 22c, i.e., by setting

$$\frac{\partial \gamma_{sl}}{\partial \gamma_l} = 1 - \phi_G\frac{\gamma_s^{1/2}}{\gamma_l^{1/2}} = 0 \tag{27}$$

which yields the solution

$$\gamma_l = \gamma_s\phi_G^2 \tag{28}$$

It must be noted that when Equation 24 is fulfilled, then $\phi_G = 1$ and the condition in Equation 28 simplifies to $\gamma_l = \gamma_s$.

It can thus be concluded, according to the Good–Girifalco equation (Equation 9), and using the geometric mean mixing rule for ϕ, that the maximum wetting tension between an adhesive and a substrate is obtained when the surface energy of the substrate is as high as possible (cf. Equation 26), and when the two phases have the same polarities (cf. Equation 24) and surface energies (cf. Equation 28).

3.2.2. Harmonic mean equation

In case the harmonic mean Equation 12 is used, it can be shown that Equations 20c and 22d yield the same solution as Equation 24 as with the geometric mean mixing rule, i.e.

$$x_s^p = x_l^p$$

The optimum surface energy of the substrate for a given adhesive can be found by solving Equation 20a, which also yields the same solution as Equation 26 as with the geometric mean mixing rule, i.e.

$$\gamma_s \to \infty$$

Equation 22d, however, which defines the optimum adhesive surface energy for a given adherend, cannot be solved analytically and a numerical solution is required, because the last term in Equation 23, $\partial\phi_H/\partial\gamma_i \neq 0$. Fig. 4 describes γ_l/γ_s and γ_{sl}/γ_s ratios yielding maximum wetting tension as a function of the polarity of the adhesive for an adherend polarity of, $x_s^d = 0.2$. The solutions using the two mixing rules, geometric and harmonic, are compared. It can be seen that the geometric solution (Equation 28) is very similar to the harmonic solution found numerically; particularly when the polarity of the two phases are similar.

It can be concluded that, according to the Good–Girifalco equation, using the harmonic mean mixing rule, ϕ_H, the same criterion for optimum adhesion of a given adhesive on various substrates as with the geometric mean mixing rules (Equations 24 and 26) can be used. When various adhesives are tested on a given substrate, the geometric and harmonic solutions are very similar. Equation 28 can thus be used to approximate the harmonic solution.

3.2.3. Acid–base interaction equation

In case the acid–base interaction theory is used, it can easily be shown that $\sum_k \partial\phi_{AB}/\partial x_i^k = 0$ (k = LW, A and B) when

$$x_i^{LW} = x_j^{LW} \tag{29a}$$

$$x_i^{A} = x_j^{B} \tag{29b}$$

$$x_i^{B} = x_j^{A} \tag{29c}$$

As the acid–base interaction parameter, ϕ_{AB}, is independent of γ_i, the last term on the right-hand side of Equation 23 is zero. The optimum surface energy of the substrate for a given adhesive is thus easily found by solving Equation 20a, which, as for the geometric mean mixing rule, yields the solution, Equation 26,

$$\gamma_s \to \infty$$

The optimum adhesive surface energy is found by solving Equation 22c, which yields the solution

$$\gamma_l = \gamma_s\phi_{AB}^2 \tag{30}$$

Again when Equation 29 is fulfilled, $\phi_{AB} = 1$, and Equation 30 simplifies to $\gamma_l = \gamma_s$.

It can now be concluded that according to acid–base interaction theory, maximum adhesive tension is obtained when the surface energy of the substrate is as high as possible (cf. Equation 26), and when the two phases have the same surface energies (cf. Equation 29) such as their Lifshitz–van der Waals' components are equal (cf. Equation 29a), and the acid component of one phase is equal to the basic component of the other (cf. Equation 29b and c).

Table I summarizes the solutions to the criterion of maximum wetting tension found using the Good–Girifalco Equation 9 with the geometric mean, harmonic mean and an "acid–base" mixing rule defined by Equations 11, 12 and 16, respectively.

A relationship between wetting tension and adhesive strength is examined in the next section for a number of examples from the literature.

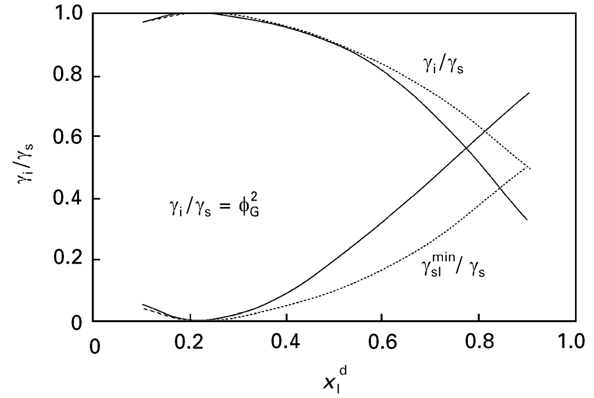

Figure 4 γ_{sl}/γ_s and γ_l/γ_s ratios yielding maximum wetting tension as a function of x_l^d, with $x_s^d = 0.2$. The harmonic solution to Equation 22c (—) found numerically is compared to the geometric solution $\gamma_l = \gamma_s\phi_G^2$ (---).

TABLE I Solution to maximum wetting tension for various mixing rules

Mixing rule ϕ	Fixed adhesive (γ_l = constant)	Fixed substrate (γ_s = constant)
Geometric mean, ϕ_G (Equation 11)	$\gamma_s \to \infty$ $x_s^p = x_l^p$	$\gamma_l = \gamma_s\phi_G^{2\,a}$ $x_s^p = x_l^p$
Harmonic mean, ϕ_H (Equation 12)	$\gamma_s \to \infty$ $x_s^p = x_l^p$	$\gamma_l \cong \gamma_s\phi_G^{2\,a}$ $x_s^p = x_l^p$
Acid–base, ϕ_{AB} (Equation 16)	$\gamma_s \to \infty$ $x_s^{LW} = x_l^{LW}$ $x_s^A = x_l^B$ $x_s^B = x_l^A$	$\gamma_l = \gamma_s\phi_{AB}^{2\,a}$ $x_s^{LW} = x_l^{LW}$ $x_s^A = x_l^B$ $x_s^B = x_l^A$

[a] Note that if the respective x_i^k terms are equal, the $\phi = 1$, and $\gamma_l = \gamma_s$.

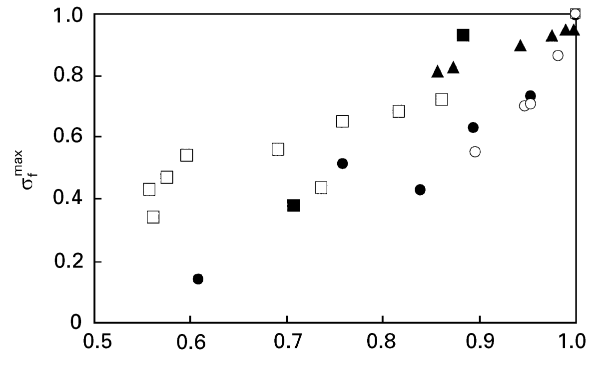

Figure 5 Normalized interface strength as a function of normalized wetting tension of flat interfaces [28]: (■) shear strength of different polymer pairs (Table 11.1), (●) butt strength for a given epoxy adhesive on various substrates (Table 11.2), (□) peel strength for a rubber adhesive on various adherends (Table 11.3), (○) shear strength of an epoxy adhesive on surface-treated polyethylene (Table 11.4), and (▲) shear strength of an epoxy adhesive on surface-treated aluminium (Table 11.4).

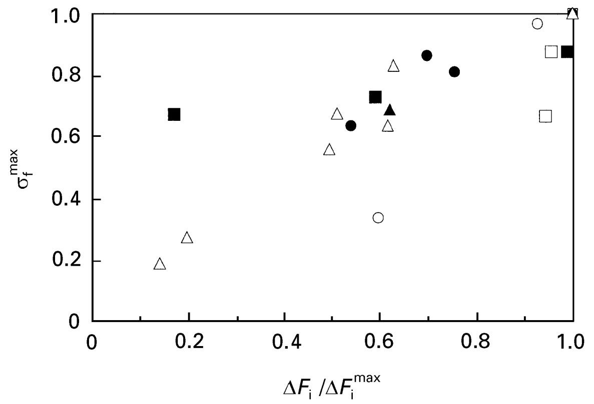

Figure 6 Normalized interface strength as a function of normalized wetting tension of unidirectional fibre reinforced composites: (■) transverse flexural strength of surface treated carbon fibre reinforced PEEK [40]; (●) shear strength (fragmentation test) of surface-treated carbon fibre reinforced epoxy LY [41]; (□) transverse flexural strength of different types of carbon fibre reinforced PEKK [42]; (○) transverse flexural strength of surface-treated carbon fibre reinforced PEEK [43]; (▲) transverse tensile properties of different types of carbon fibre reinforced PEEK [44]; and (△) shear strength (fragmentation test) of surface-treated carbon fibre reinforced epoxy D [41].

4. Discussion

Mechanical properties of flat interfaces and fibre reinforced composites are plotted as a function of the wetting tension in Figs 5 and 6, to verify the validity of the criterion for optimum adhesion presented above. Different mechanical tests were applied to determine the mechanical properties of the various series of samples. For this reason, normalized values of the interfacial strength and wetting tension are reported for each set of data on Figs 5 and 6.

As proposed earlier, it can be seen that adhesive strength increases monotonically with wetting tension for both flat interfaces and fibre reinforced composites. It must be noted that each set of data has to be considered independently and can have a different slope, because each series refers to different systems and mechanical tests. This is particularly true in Fig. 6, which reports mechanical properties of composite systems with different fibre types and contents, measured by different techniques such as transverse flexural strength and the fibre fragmentation test. In composite systems (cf. Fig. 6), only studies in which the influence of the fibre surface energy on the mechanical properties for a given matrix have been found in the literature. Consequently, comparing the interfacial strength to the wetting tension of such systems is equivalent to comparing it to either the work of adhesion or the spreading coefficient, because the three wetting parameters vary similarly when the adhesive (matrix) is kept constant and only the adherend surface energy (fibres) is varied (cf. Fig. 2). In Fig. 5, however, results for flat interfaces of different adhesive–adherend combinations are reported from Wu (Table 11.1 in [28]). It is interesting to note that in this case, no correlation can be found between interfacial strength and work of adhesion, while the former increases monotonically with wetting tension (black squares in Fig. 5). This supports the assumption of using wetting tension as a criterion for optimum adhesion, instead of the work of adhesion.

Bucher and Hinkley [42] studied the carbon fibre reinforced poly(ether-ketone-ketone) (PEKK) system (white squares in Fig. 6). It must be noted, however, that they allowed a variation in interfacial area by using different fibre diameters, ranging from 6.2 to 7.9 μm. This corresponds to a variation of 50% in interfacial area at constant fibre volume fraction, a change expected to have profound effects on mechanical properties. Connor *et al.* [40], Nardin *et al.* [44] and Hodge *et al.* [43] studied the influence of various fibre surface treatments on carbon fibre–reinforced poly(ether-ether-ketone) (PEEK). Asloun [41] reports results for carbon fibre epoxy systems.

As discussed earlier, maximum wetting tension corresponds to the situation where the work of adhesion is maximum within the region where spontaneous wetting occurs, so as to minimize flaw density at the fibre–matrix interface. The influence of the contact angle between fibre and resin on the void density at the interface of the surface-treated carbon fibre reinforced–PEEK composite laminates is illustrated in Fig. 7 [40]. During composite manufacturing, a finite quantity of air will always be trapped and will remain in the part after processing. Under favourable wetting conditions, i.e. small contact angle, the area of the solid–air interface will be minimized and any entrapped air will tend to coalesce in regions away from the fibres (cf. Fig. 7a and b). Under poor wetting conditions, the large contact angle provides no mechanism to expel the air from the surface and the void space will be concentrated at the fibre–resin interface (cf. Fig. 7c and d). The interfacial strength of the former system characterized by a low void density at the interface was about 30% higher than that of the latter system (cf. the black squares in Fig. 6 at $\Delta F_i / F_i^{max} = 1$ and 0.17, respectively).

The additive effect of the two mechanisms, molecular interaction across the interface (which is a function of the work of adhesion, W_a) and the presence of a flaw

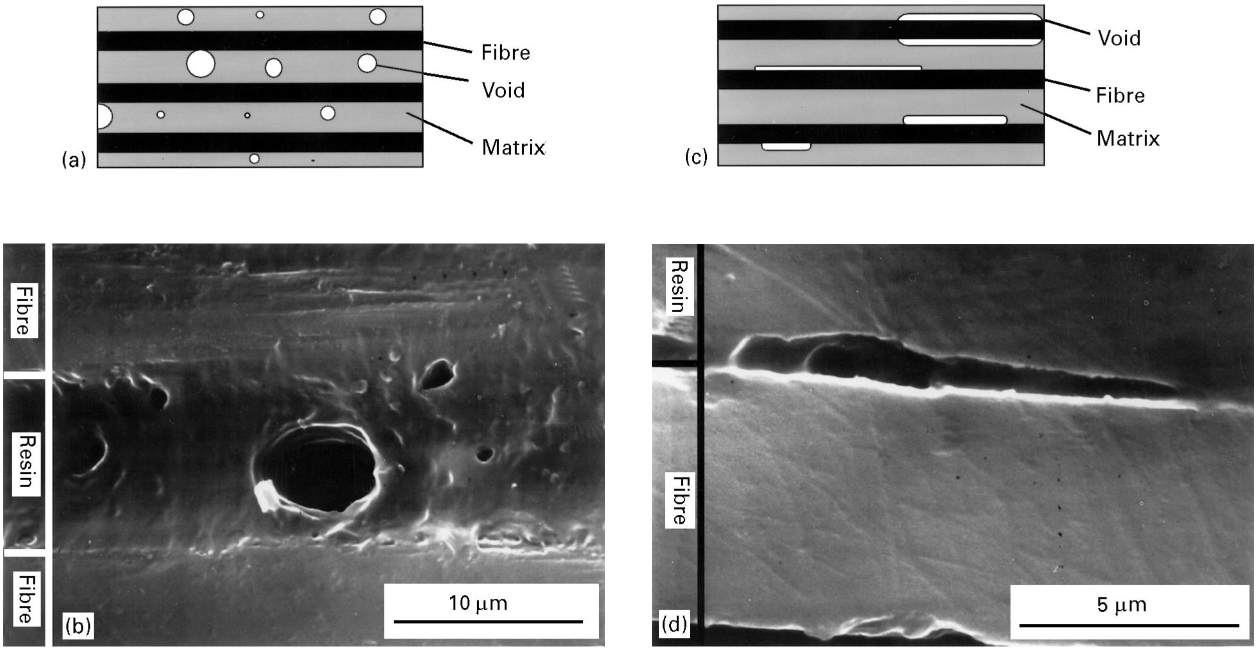

Figure 7 Micrographs (b, d) and corresponding schematic drawings (a, c) of void morphology (a, c) as a function of contact angle of surface treated carbon fibre–PEEK composite laminates [40]: (b) $\theta = 1^\circ$, $\Delta F_i/\Delta F_i^{max}$; and (d) $\theta = 80^\circ$, $\Delta F_i/\Delta F_i^{max} = 0.17$.

at the interface (which is a function of the spreading coefficient, λ), supports the choice made in this study of maximizing the wetting tension as a criterion for the characterization of interfacial adhesion. Because the wetting tension is the arithmetic mean of the work of adhesion and the spreading coefficient, it takes both effects into account.

5. Conclusions

This work provides an understanding of how the properties of the various phases of a composite must be modified to improve its mechanical properties. It has been shown that the adhesive–adherend surface energy combinations will yield maximum bond strength at the interface of a two phase system (e.g. fibre reinforced composite). A criterion for optimum adhesion between two phases has been proposed based on maximizing the wetting tension. This situation corresponds to maximum work of adhesion under the condition of positive or null spreading coefficient. The optimum adherent for a given adhesive, and the optimum adhesive for a given adherend have successively been examined. It has been shown that, in the former case, maximizing the wetting tension was equivalent to maximizing the work of adhesion and the spreading coefficient. For this reason, the same correlation can be found between interfacial strength and either of these three wetting parameters. This is not the case when the adherend is kept unchanged and the adhesive is varied. In this case, maximizing the wetting tension is equivalent to minimizing the interfacial energy.

The conditions on the surface energies of the various phases yielding maximum wetting tension have been analysed using the Good–Girifalco equation with three different mixing rules: the polar–dispersive geometric and harmonic means, and acid–base geometric mean interaction parameter. It has been shown that maximum wetting tension is obtained when the substrate and adhesive surface energies are very high and equal, such as their polar and dispersive components are equal when the polar–dispersive mixing rule is used, and such as their Lifshitz–van der Waals' components are equal and and acid component of one phase is equal to the basic component of the other phase when the acid–base approach is considered.

Experimental data from the literature show that interfacial strength increases monotonically with increasing wetting tension for both flat interfaces and fibre reinforced composite structures. These results support our assumption that wetting tension can be used as a criterion for optimum adhesion. The mechanical properties of a composite part strongly correlate with the wetting tension, which controls on the one hand, the physical adhesion between fibre and resin and on the other hand, the morphology of the voids present in the structure.

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