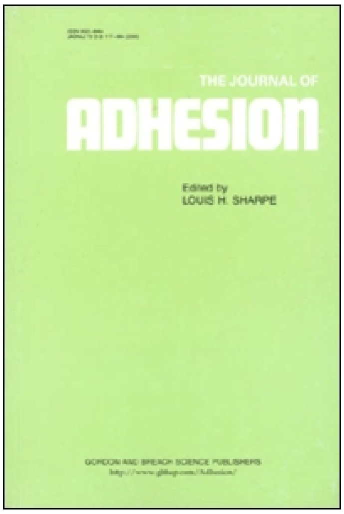

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Fibre Surface Energy Characterization

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A new technique has been developed to study the surface energy characteristics of small diameter fibres. This method is tensiometric and based on wetting properties in a two phase liquid system. Two types of carbon fibre have been investigated under both static and dynamic conditions in immersion and emersion.

The high strength fibre, which was found to have a polymeric coating, gave reproducible results consistent with typical values for a polymer. However, the high modulus fibre could not be characterized due to considerable scatter in the experimental results. It is suggested that the source of this phenomenon is the existence of surface energy gradients which leads to hysteresis effects.

INTRODUCTION

Composite materials consisting of a filamentary charge, such as glass or carbon fibres, embedded in a polymer matrix, are the subject of much interest and development at the present time. The fibres constitute the major load bearing element of the composite and it is the role of the polymer matrix both to distribute the internal stresses and to protect the fibres from the environment.

Clearly the overall mechanical properties of composites rely heavily on the strength of the interfacial zone filler/matrix. This resistance is a function of the number and type of bonds created at the interface during preparation of the material, or in other words, the interfacial adhesion. In turn, this adhesion

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is closely related to the free surface and interfacial energies of the system in question.

Now the values of free surface energy and related quantities can be obtained relatively easily for the matrix phase of a composite since macroscopically flat low energy surfaces can readily be obtained. Thus classical contact angle measurement techniques may be employed. However, in the case of fibres, small diameter cylindrical solids of potentially high energy are to be considered, and as a consequence, classical methods of measurement are unsuitable. It is the aim of the present paper to describe a novel technique which can be used to obtain surface energy data for fibres, and to report some values found for carbon fibres.

THEORY

It is supposed that the surface free energy, γ_S, of the fibre to be considered can be represented by the sum of its dispersive, or London, component, γ_S^D, and the polar component, γ_S^P. The method used to determine these characteristics is based on wetting properties, and depends on the immersion of the solid in a two phase liquid system in which the two liquids are immiscible. In the present case, carbon fibres have been studied in a formamide/hydrocarbon system. By applying the relationship of Young[1] and Fowkes[2] to the interface solid/formamide/hydrocarbon, the following equation can be deduced:[3]

$$\gamma_F - \gamma_H + \gamma_{HF} \cos \theta_{SF/H} = 2(\gamma_S^D)^{1/2} [(\gamma_F^D)^{1/2} - (\gamma_H)^{1/2}] + I_{SF}^P \qquad (1)$$

where γ_F, γ_F^D are the surface free energy of formamide and its dispersive component,
γ_H is the surface free energy of the hydrocarbon,
γ_{HF} is the interfacial energy formamide/hydrocarbon,
and I_{SF}^P is the polar interaction between the solid and formamide.

This last term is a function of the polar components of surface energy of the solid and formamide, γ_S^P and γ_F^P, but the exact function is in some doubt. However, I_{SF}^P gives an idea of the solid surface polarity. Thus by using a series of hydrocarbons of different surface free energies, γ_H, and determining corresponding contact angles $\theta_{SF/H}$, γ_S^D and I_{SF}^P can be determined respectively from the gradient and the intercept of Eq. (1).

Earlier work using this principle involved the direct measurement of the contact angle of one liquid in the presence of another on a flat solid surface.[3] However, in the present case, carbon fibres of small diameter (about 7 μm) are being considered and direct measurement would be extremely difficult. Therefore, a tensiometric method is more suitable. The fibre is suspended from

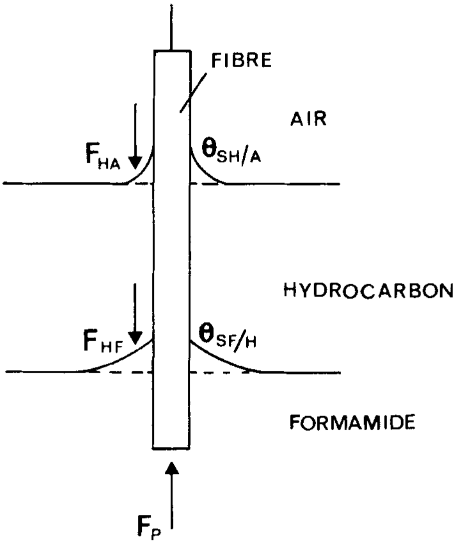

FIGURE 1 Fibre in two phase liquid system.

the arm of an electrobalance and during immersion and emersion cycles, the change in force, F, on the arm of the electrobalance due (essentially) to the menisci of liquid raised or lowered† at the two interfaces is recorded.

At equilibrium when the fibre is immersed in the two liquids, three contributions are responsible for this net force difference, F, : the apparent weight of liquid raised at the air/hydrocarbon/fibre interface, F_{HA}, the apparent weight of liquid raised at the hydrocarbon/formamide/fibre interface, F_{HF}, and the effect of buoyancy acting on the length of fibre immersed, F_P (Figure 1).

In the case of small diameter circularly cylindrical objects, the term F_P is negligible since $F_P/(F-F_P)$ is linear in r, the radius of the cylinder. For the present case, F_P is of the order of 10^{-8} N whilst the other contributions are of the order of 10^{-6} N.

F_{HA} can be shown to be given by:

$$F_{HA} = C\,\gamma_H \cos\theta_{SH/A} \qquad (2)$$

where C is the circumference of the fibre and $\theta_{SH/A}$ is the contact angle of the hydrocarbon on the fibre in air (or hydrocarbon vapour).[4] $\theta_{SH/A}$ is presumed to

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† The meniscus can either correspond to raised liquid in the case of a contact angle < 90° or, in the case of contact angle > 90°, the meniscus descends causing an apparent weight loss. For the following, the first case will be considered but clearly the second conformation can be treated in a similar manner.

be zero since the hydrocarbon is a low energy liquid and thus:

$$C = \frac{F_{HA}}{\gamma_H} \tag{3}$$

As a consequence, the circumference of the fibre can be determined by immersion in only the hydrocarbon phase. The contribution F_{HF} is given by an expression analogous to (2):

$$F_{HF} = C\ \gamma_{HF} \cos \theta_{SF/H} \tag{4a}$$

where $\theta_{SF/H}$ is the contact angle of formamide on the fibre in the presence of the hydrocarbon. A simplified derivation of the general case of Eq. (4a) is given in the Appendix.

Considering Eq. (1), it can be seen that the major variable on the left hand side is $\gamma_{HF} \cos \theta_{SF/H}$ and this will be defined as the tension of the adhesion, τ. Thus:

$$F_{HF} = C\ \tau \tag{4b}$$

and combining with Eq. (3):

$$\tau = \frac{F_{HF}}{F_{HA}} \cdot \gamma_H \tag{5}$$

As a consequence of Eq. (5), direct calculation of $\theta_{SF/H}$ is unnecessary when using the present tensiometric method.

With this two phase liquid method, there exists a potential problem. On immersion, the fibre must pass through the hydrocarbon phase before contacting the formamide. It must therefore be verified that the formamide in fact replaces the hydrocarbon on the solid surface, and that there does not remain a thin film of hydrocarbon acting as a barrier and preventing true formamide/fibre contact. Were this second eventuality to occur, the method would be invalid. Similarly, on emersion, the hydrocarbon must displace the formamide. This problem has been studied in detail and will appear in a separate article.[5] The essential may be summarized as follows. It is assumed that the solid surface is smooth and energetically homogeneous and that no time dependent sorption phenomena intervene. Under these circumstances, free interfacial energy changes may be calculated for the two eventualities—displacement and film formation. The case minimizing the overall free energy of the system will describe the final situation. It can be shown that the criterion to be fulfilled for the formamide to replace the hydrocarbon on immersion is given by:

$$I_{SF}^{P} > 2\left[(\gamma_S^D)^{1/2} - (\gamma_H)^{1/2}\right]\left[(\gamma_H)^{1/2} - (\gamma_F^D)^{1/2}\right] \tag{6}$$

Similarly, the hydrocarbon will displace the formamide on emersion if:

$$I_{SF}^{P} < 2\{\gamma_F^P - [(\gamma_S^D)^{1/2} - (\gamma_F^D)^{1/2}][(\gamma_F^D)^{1/2} - (\gamma_H)^{1/2}]\} \tag{7}$$

It can thus be ascertained for a given system whether or not the two phase liquid method is valid.

Experimental

In this study, two carbon fibres were considered: a high strength fibre, Toray T 300 and a high modulus fibre, also from Toray, the M 40.

The hydrocarbons employed as the apolar liquid phase were *n*-alkanes—the lowest member being hexane and the highest hexadecane—and decalin. These hydrocarbons are not totally immiscible with formamide, but it was established that any slight mutual dissolution did not affect values of surface and interfacial energies to any great extent, at least at the temperature considered.

The carbon fibre is attached by one end to the arm of the electrobalance and suspended above a beaker containing formamide and the hydrocarbon in question. By means of a motorized support, the beaker is raised until the fibre contacts the hydrocarbon. The difference in force corresponding to F_{HA} is recorded. Further raising of the beaker allows the lower end of the fibre to gain contact with the hydrocarbon/formamide interface leading to a value of $(F_{HA} + F_{HF})$. By lowering the beaker, equivalent emersion readings can be taken. All force measurements at the various stages of the immersion/emersion cycles are recorded continuously on a standard chart recorder. Thus both static and dynamic measurements are available.

All experiments were conducted at 20 ± 1°C.

RESULTS AND ANALYSIS

With respect to formamide, values of τ obtained from immersion measurements correspond to the advancing value of contact angle and values on emersion correspond to the receding contact angle. Both immersion and emersion values can be subdivided into static and dynamic. The former corresponds to a state of no relative movement between the liquid system and the fibre, and the latter to a measurement taken while the beaker containing the liquids is in motion. It would seem, in practice, that in this second case, the values recorded are not very sensitive to the speed of motion. Thus, in principle, four values exist for τ, and these will be denoted τ_{AD}, τ_{AS}, τ_{RS}, τ_{RD} where the suffices A, R, S and D refer respectively to advancing, receding, static and dynamic.

Static values

In the case of the fibre T 300, τ_{AS} and τ_{RS} values are similar indicating that static advancing and receding contact angles are close. Typical values in the case of the hydrocarbon being hexadecane are:

$$\tau_{AS} = 14.9 \pm 0.4 \text{ mJ} \cdot \text{m}^{-2}$$

$$\tau_{RS} = 16.1 \pm 0.9 \text{ mJ} \cdot \text{m}^{-2}$$

These values were found to be reproducible for each immersion/emersion cycle, including the first. This implies that no important modification of the fibre surface occurs due to adsorption of one or other of the liquids during contact, and that the fibre has a homogeneous surface not prone to showing hysteresis effects.

However, in the case of the fibre M 40, the situation was found to be different. Very large differences between values of τ_{AS} and τ_{RS} were observed and, in addition, each of these variables shows considerable variance. Values for the hexadecane/formamide system are:

$$\tau_{AS} = -6 \pm 2 \text{ mJ} \cdot \text{m}^{-2}$$

$$\tau_{RS} = +5 \pm 2 \text{ mJ} \cdot \text{m}^{-2}$$

The negative value of τ_{AS} indicates that in this case, the liquid/liquid meniscus is directed downwards, and corresponds to a contact angle greater than 90°.

Dynamic values

Typical values corresponding to dynamic readings for the fibre T 300 in the hexadecane system are:

$$\tau_{AD} = 10.9 \pm 0.9 \text{ mJ} \cdot \text{m}^{-2}$$

$$\tau_{RD} = 18.8 \pm 0.9 \text{ mJ} \cdot \text{m}^{-2}$$

It can be seen these values encompass the equivalent static values, as would be expected, but that the total range is however about 8 $\text{mJ} \cdot \text{m}^{-2}$.

However, for the fibre M 40, it was found that:

$$\tau_{AD} = -12 \pm 1 \text{ mJ} \cdot \text{m}^{-2}$$

$$\tau_{RD} = +12 \pm 2 \text{ mJ} \cdot \text{m}^{-2}$$

This corresponds then to a much greater hysteresis range of 24 $\text{mJ} \cdot \text{m}^{-2}$. Not only this, but it can also be seen that, with this fibre, immersion values correspond to a contact angle greater than 90° and emersion values to a contact angle less than 90°.

Analysis

It can be considered that the values of τ found for the fibre T 300 show that hysteresis effects are relatively unimportant. Static values of τ were used to calculate surface energy data, since these are closer to equilibrium values than are the dynamic data. Table I gives values of the parameters used in Eq. (1) in order to calculate γ_S^D and I_{SF}^P and Figure 2 shows graphically the relation

TABLE I

Surface free energy data, and tensions of adhesion for the two carbon fibres, T 300 and M 40 (units are mJ · m^{-2})

Hydrocarbon	γ_H	$(\gamma_F^D)^{1/2}-(\gamma_H)^{1/2}$	τ_{AS} (T 300)	$\gamma_F-\gamma_H+\tau_{AS}$ (T 300)	τ_{AS} (M 40)
Hexane	18.4	2.00	13.4 ± 0.4	53.2	—
Octane	21.3	1.67	13.1 ± 0.1	50.0	—
Decane	23.4	1.45	14.9 ± 0.5	49.7	-1 ± 2
Dodecane	25.4	1.25	15.1 ± 0.5	47.9	4 ± 2
Hexadecane	27.1	1.08	14.9 ± 0.4	46.0	-6 ± 2
Decalin	29.9	0.82	11.6 ± 0.4	39.9	-5 ± 1

$\gamma_F = 58.2$ $\gamma_F^D = 39.5$

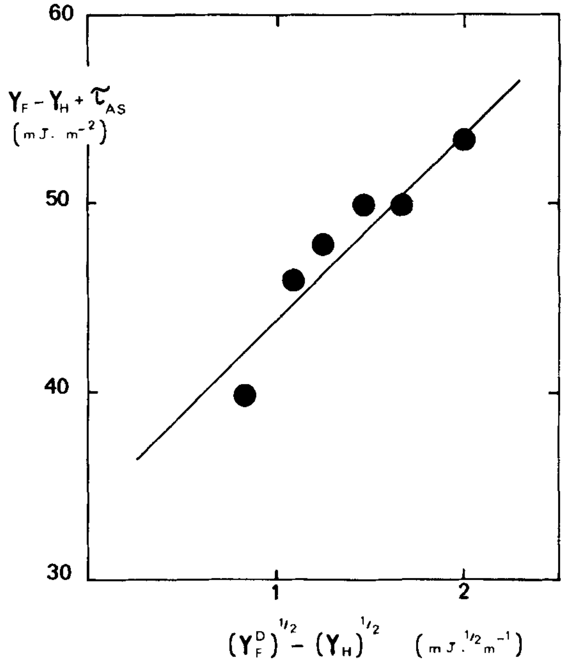

FIGURE 2 Determination of γ_S^D and I_{SF}^P for the carbon fibre T 300.

between $[\gamma_F - \gamma_H + \tau_{AS}]$ and $[(\gamma_F^D)^{1/2} - (\gamma_H)^{1/2}]$. Both refer to immersion data although emersion data are very similar.

The best straight line relationship was calculated by linear regression and the gradient and intercept obtained lead to the following values of γ_S^D and I_{SF}^P:

$$\gamma_S^D = 24 \pm 11 \text{ mJ} \cdot \text{m}^{-2}$$

$$I_{SF}^P = 34 \pm 3 \text{ mJ} \cdot \text{m}^{-2}$$

The equivalent emersion data lead to:

$$\gamma_S^D = 25 \pm 10 \text{ mJ} \cdot \text{m}^{-2}$$

$$I_{SF}^P = 34 \pm 3 \text{ mJ} \cdot \text{m}^{-2}$$

Thus it can be seen that advancing and receding contact angle results are in good agreement. If it is assumed that:

$$I_{SF}^P = 2\sqrt{\gamma_S^P \gamma_F^P}$$

in accordance with Owens and Wendt,[6] the above leads to a value of γ_S^P of approximately 16 mJ · m^{-2}. However, there is some doubt as to the validity of this expression.

Values of τ_{AS} obtained for the fibre M 40 are also given in Table I for comparison purposes. No results were obtained for the two lowest hydrocarbons since continuous adsorption of these liquids of high vapour pressure prevented equilibrium readings from being taken. An attempt was made to analyse these results as above. There was, however, far too much uncertainty involved and the relationship corresponding to Eq. (1) cannot be considered linear. This applies equally to results corresponding to τ_{AD}, τ_{RS} and τ_{RD}. The only systematic observation with this fibre was that in the case of all hydrocarbons employed,

$$\tau_{AD} < \tau_{AS} < \tau_{RS} < \tau_{RD}$$

which implies that the equivalent contact angles are such that:

$$\theta_{AD} > \theta_{AS} > \theta_{RS} > \theta_{RD}$$

DISCUSSION

Clearly, the two-phase liquid system works reasonably well with the fibre T 300. Substitution of the obtained values for γ_S^D and I_{SF}^P into relations (6) and (7) shows that the system is reversible for all the hydrocarbons employed and that the liquids employed are capable of mutual displacement.

There is however one slight discrepancy for this fibre. It is described in the theory section of this paper that the contact angle at the air/hydrocarbon/fibre interface is presumed zero since low energy liquids are involved. However, the obtained values of γ_S^D are slightly lower than the γ_H values for the higher hydrocarbons. This would imply that perfect wetting does not occur in these cases. Values of the fibre circumference, C, calculated by assuming perfect wetting by the hydrocarbon phase are nevertheless in very close agreement with direct electron microscope observation. This is the case for all of the hydrocarbons employed. It is therefore suggested that the true value of γ_S^D is slightly higher than calculated and greater than the γ_H value of 29.9 $\mathrm{mJ \cdot m^{-2}}$ for decalin. This is quite reasonable given the calculated error of about 10 $\mathrm{mJ \cdot m^{-2}}$ on γ_S^D.

The method gives good precision concerning the evaluation of I_{SF}^P but is less reliable for γ_S^D. This must be at least partially due to the fact that γ_S^D is obtained from a square root in Eq. (1) whereas I_{SF}^P is a linear term.

The values obtained for γ_S^D and I_{SF}^P indicate that this fibre can be considered to be a low energy surface. In fact, both values are fairly typical of certain polymers, which is in agreement with the known fact that this fibre has a polymeric surface layer.[7] Thus, the values obtained apply really to the surface coating rather than the fibre itself. However, this agreement supports the validity of the method in the present case.

The fibre M 40, in contrast to the T 300, gave very disappointing results which were unsuitable for analysis. As stated earlier, the only consistent observation was that $\theta_{AD} > \theta_{AS} > \theta_{RS} > \theta_{RD}$. An obvious interpretation of the above order for static and dynamic values would be the effect of viscous drag. However, approximate calculations of any viscous contribution showed this effect to be far too small to account for the observed differences. Therefore, the above order would suggest an inhomogeneous surface in agreement with Johnson and Dettre.[8,9] If the surface presents an inhomogeneous aspect, surface energy gradients will be apparent and this will lead to a spectrum of possible metastable contact angles. This inhomogeneity could well be due to local high energy sites capable of adsorbing one or other of the liquids to an appreciable degree. As stated earlier, with this fibre, it was found impossible to take any sensible equilibrium readings with the lower alkanes since a continual weight increase, due to adsorption of the vapour, was observed.

CONCLUSIONS

A tensiometric method for the study of surface energy characteristics of fibres has been developed in which a two phase liquid system is employed. Results for a polymer-coated carbon fibre were found to be reproducible and led to coherent values for the dispersive component of surface free energy, γ_S^D, and the polar interaction with formamide, I_{SF}^P. A second carbon fibre was also investigated but gave incoherent data. It is suggested that in this second case, surface inhomogeneities lead to preferential adsorption and surface energy gradients, which in turn allow a range of possible metastable liquid/solid configurations, to be observed. Further investigation into this second system is desirable.

APPENDIX

Figure A1 represents a vertical section of the meniscus of a liquid 1 against a flat solid surface, in the presence of a less dense immiscible liquid 2. The section is considered to have thickness, δw.

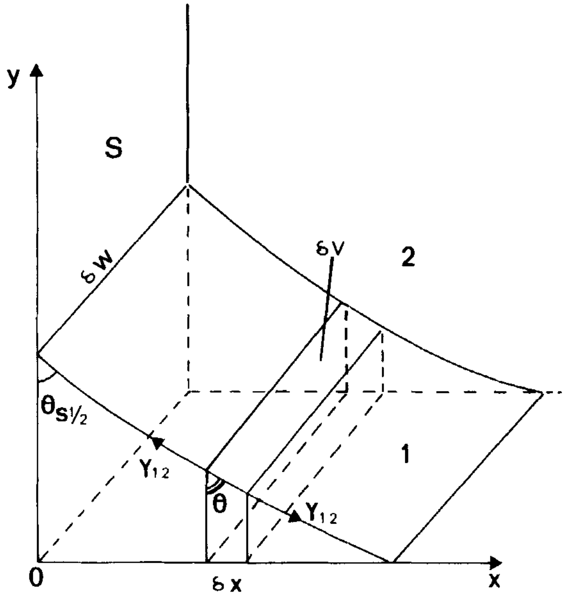

FIGURE A1 Representation of a vertical section of meniscus liquid 1/liquid 2.

Consider the element of volume, δV, of the meniscus as shown in the figure. The equation of equilibrium is:

$$P_1 - P_2 - P_3 = 0 \qquad \text{(A1)}$$

where P_1 represents the downward force due to the weight of liquid 1 in δV, P_2 represents the buoyancy term, and P_3 represents the net upward force due to the interfacial tension γ_{12}.

Using the coordinate system shown in Figure A1, it is readily seen that:

$$P_1 = \rho_1 g \delta w \delta x \left[\frac{y(x)+y(x+\delta x)}{2}\right] \quad \text{(A2)}$$

$$P_2 = \rho_2 g \delta w \delta x \left[\frac{y(x)+y(x+\delta x)}{2}\right] \quad \text{(A3)}$$

$$P_3 = \gamma_{12} \delta w [\cos \theta(x) - \cos \theta(x+\delta x)] \quad \text{(A4)}$$

where ρ_1 and ρ_2 are the densities of the two liquids, θ represents the angle of the interface liquid 1/liquid 2 with respect to the vertical axis, and g is the acceleration due to gravity.

Substitution into Eq. (A1) and taking the limit as $\delta x \rightarrow 0$ leads to the differential equation:

$$\gamma_{12} \sin \theta(x) \cdot \frac{d\theta}{dx} = (\rho_1 - \rho_2) g y(x) \quad \text{(A5)}$$

Now the total apparent weight of liquid 1 raised in the meniscus is given by:

$$P = (\rho_1 - \rho_2) g \delta w \int_0^\infty y(x) \cdot dx \quad \text{(A6)}$$

Combination of Eqs (A5) and (A6), followed by integration gives:

$$P = \delta w \gamma_{12} \cos \theta_{S1/2} \quad \text{(A7)}$$

where $\theta_{S1/2}$ is the contact angle of liquid 1 at the triple interface as shown in the figure.

Thus the apparent weight of liquid 1 raised, or force increase, is equal to $\gamma_{12} \cos \theta_{S1/2}$ per unit thickness of section.

Similar but slightly more complicated derivations obtain the same final expression for the apparent weight of liquid 1 raised when the solid is convex or concave with respect to the vertical axis. These, however, are not presented here for brevity.

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