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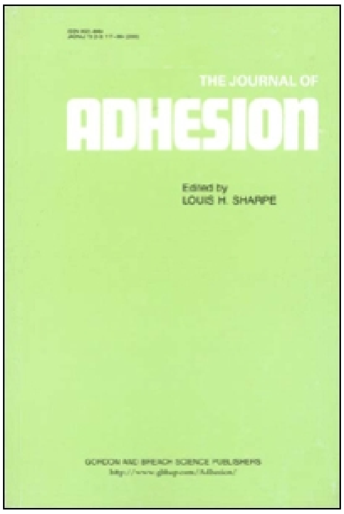

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The Role of the Interface in Carbon Fibre-Epoxy Composites

J. Schultz[a]; L. Lavielle[a]; C. Martin[b]
[a] Centre de Recherches sur la Physico-Chimie des Surfaces Solides, C.N.R.S., Mulhouse, France [b] Laboratoire de Recherches sur la Physico-Chimie, des Interfaces de l'Ecole Nationale Superieure de Chimie de Mulhouse 3, Mulhouse Cedex, France

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The Role of the Interface in Carbon Fibre–Epoxy Composites†

J. SCHULTZ, L. LAVIELLE and C. MARTIN

Centre de Recherches sur la Physico-Chimie des Surfaces Solides, C.N.R.S., 24, avenue du Président Kennedy, 68200 Mulhouse, France

and

Laboratoire de Recherches sur la Physico-Chimie des Interfaces de l'Ecole Nationale Supérieure de Chimie de Mulhouse 3, rue Alfred Werner, 68093 Mulhouse Cedex, France

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The final performance of a composite material depends strongly on the quality of the fibre-matrix interface. The interactions developed at the interface were studied using the acid-base or acceptor-donor concept.

The surface characteristics of the carbon fibres and the epoxy matrix were studied using a tensiometric method and the inverse gas chromatography technique. Acid-base surface characters could be determined allowing the interactions at the interface to be described by a specific interaction parameter.

It was shown that the shear strength of the interface, as measured by a fragmentation test, is strongly correlated to this specific interaction parameter, demonstrating the importance of acid-base interactions in the fibre-matrix adhesion.

KEY WORDS Acceptor-donor interactions; acid-base interactions; carbon-fibre/epoxy composite; fibre-matrix interface; inverse gas chromatography; wetting.

INTRODUCTION

It is generally accepted nowadays that the final performance of a composite material depends, to a large extent, on the adhesion of

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the polymer matrix to the reinforcing fibre and, therefore, on the quality of the interface which is formed between the two solids.

When interactions of physical origin are being exchanged at the interface, the reversible energy of adhesion can be determined from the surface energies of both the fibre and the matrix.

For many years, the surface energy γ_S of a solid has been described by a sum of two terms, the dispersive component γ_S^D and the polar component γ_S^P. However, more recently, it appears that the non-dispersive interactions may be better described in terms of the electron acceptor or -donor (acid-base) characters of the solids. Both polar and acceptor-donor aspects will be considered in this study.

The purpose of the present study is to examine the role of these specific interfacial interactions in the adhesion between carbon fibres and an epoxy matrix.

MATERIALS

Three high-strength PAN based carbon fibres corresponding to different stages of manufacturing have been used in this study:

- the untreated fibre ①,
- the untreated fibre having received a proprietary surface treatment designated oxidized fibre ②,
- the oxidized fibre having received a supplementary sizing treatment denoted coated fibre ③.

The fibres were handled as little as possible to prevent surface contamination or damage.

SURFACE PROPERTIES OF CARBON FIBRES

1 Wetting technique

The surface energy γ_S of solids, in particular their dispersive component γ_S^D and polar component γ_S^P, are usually determined through wetting experiments. The method consists of measuring contact angles of a series of liquids of known surface energy components on the solid surface. In the case of high surface energy solids however, virtually all liquids spread spontaneously on the surface. Moreover the spreading pressure can generally not be neglected. Therefore, for such solids, a two-phase liquid method has been developed.[1,2] Experimentally, as shown on Figure 1, the single fibre is attached to the arm of an electro-balance and immersed first in the non-polar liquid phase (hydrocarbon), and then in both the hydrocarbon and the non-miscible polar liquid (formamide)[3]. From the resulting weight increase, the contact angle of formamide on the fibre in the presence of hydrocarbon is determined. The same analysis as that used for flat surfaces[2], may be applied and allows us to determine the surface energy components of the carbon fibres. The results are presented on Table I.

It is observed that the untreated and oxidized fibres have a rather high dispersive term of the order of 50 mJ . m^{-2} whereas that of the coated fibre is only about 34 mJ . m^{-2}. On the contrary, the surface polarity of the untreated fibre is low, whereas that of the two other fibres is relatively high. These values are in rather good agreement with published data of surface energy of carbon fibres measured by a tensiometric method,[4,5] but are much lower than those obtained on graphite.[6,7]

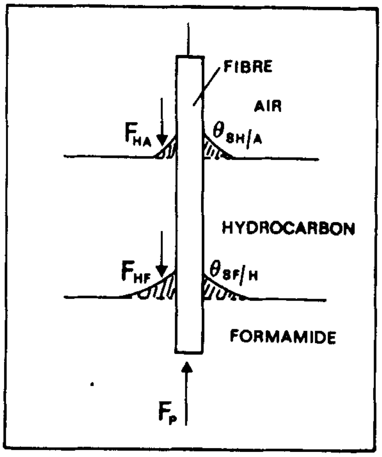

FIGURE 1 Representation of the two-liquid-phase technique applied to a carbon fibre.

TABLE I
Surface energy components of carbon fibres (Wettability technique) (in mJ . m^{-2})

Carbon fibre	γ_S^D	γ_S^P	γ_S
Untreated (1)	50 ± 8	7 ± 3	57
Oxidized (2)	48 ± 10	15 ± 4	63
Coated (3)	34 ± 6	13 ± 3	47

It must be noted that the tensiometric method gives good precision concerning the evaluation of γ_S^P, but is less reliable for γ_S^D. Moreover, given the small diameters of the fibres and the range of forces measured, the method requires a great deal of patience and painstaking effort.

2 Inverse gas chromatography at infinite dilution[8]

In the inverse gas chromatography (IGC) technique, the surface characteristics of the solid are determined by injection of probes of known properties into the column containing the solid. The retention times of these probes measured at "infinite" dilution or near zero surface coverage, allow us to determine the interactions between the probes and the solid in the absence of interactions between the probe molecules themselves.

Measurements were carried out with an Intersmat IGC DLF chromatograph equiped with a flame ionization detector of high sensitivity. The retention data were obtained with a stainless steel column of 0.6 m length and 4.4 mm internal diameter packed with 3 to 5 g of carbon fibres. The amount of each probe injected corresponds to the limit of sensitivity of the detector (10^{-4} to 10^{-3} ppm) in order to ensure practically zero surface coverage. Optimum working conditions allowed us to record quite symmetrical peaks obeying, in all cases, the laws of linearity and ideality required for interpretation.

The net retention volume V_N was calculated from:

$$V_N = jD(t_R - t_0) \tag{1}$$

where t_R is the retention time of the given probe, t_0, the zero retention reference time measured with a non adsorbing probe such as methane, D, the flow rate, and j, a correction factor taking into account the compressibility of the gas.

Simple thermodynamic considerations applied to the inverse gas chromatography technique at infinite dilution lead to the following general relationship:

$$\Delta G_D^0 = -\Delta G_A^0 = RT \ln \left(\frac{V_N P_0}{S.g\pi_0}\right) \tag{2}$$

where ΔG^0 is the free enthalpy of desorption (or adsorption) of 1 mole of solute from a reference adsorption state defined by the bidimensional spreading pressure π_0 of the adsorbed film to a reference gas phase state defined by the partial pressure P_0 of the solute, S is the specific surface area of the fibres and g is the weight of fibres in the column.

Two reference states are generally considered[8]:

–the reference states of Kemball and Rideal

where $P_0 = 1.013 \times 10^5$ Pa and $\pi_0 = 6.08 \times 10^{-5}$ Nm^{-1},

–the reference states of De Boer

where $P_0 = 1.013 \times 10^5$ Pa and $\pi_0 = 3.38 \times 10^{-4}$ Nm^{-1}.

ΔG^0 can therefore be written:

$$\Delta G^0 = RT \ln V_N + K \tag{3}$$

K being a constant depending on the chosen reference states.

To a first approximation, ΔG^0 is related to the energy of adhesion W_A between the probe and the solid, per unit surface area, by

$$\Delta G^0 = \mathcal{N} a W_A \tag{4}$$

$\mathcal{N}$ being Avogadro's number and a the surface area of the probe molecule.

a) *Dispersive interactions* According to Fowkes[9], the energy of adhesion W_A, in the case of dispersive interactions, for instance with n-alkanes probes, is given by:

$$W_A = 2(\gamma_S^D \gamma_L^D)^{1/2} \tag{5}$$

Therefore, combining Eqs. (3), (4) and (5) leads to:

$$RT \ln V_N = 2\mathcal{N}(\gamma_S^D)^{1/2} a (\gamma_L^D)^{1/2} + C' \tag{6}$$

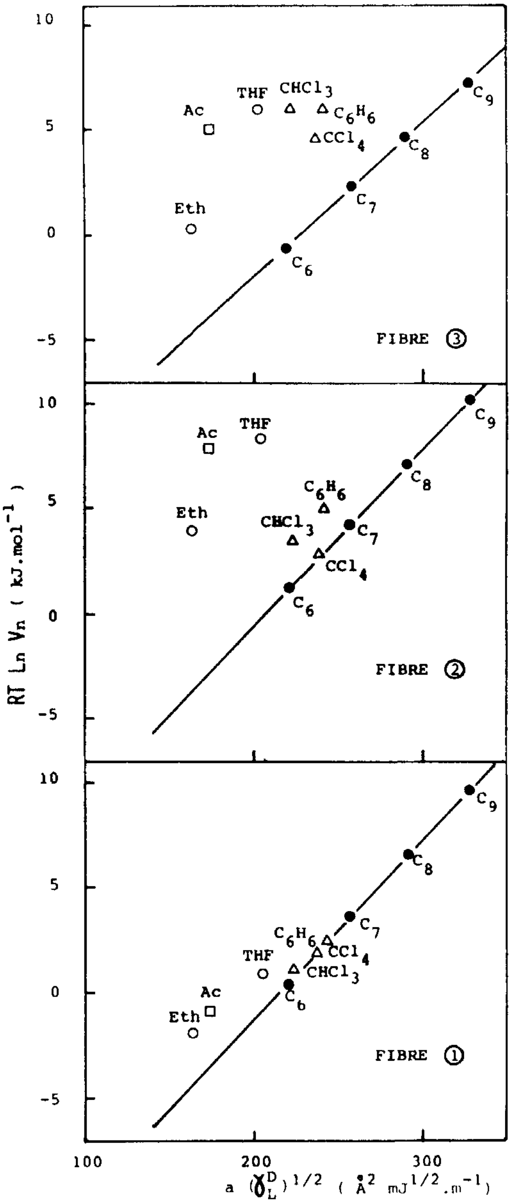

FIGURE 2 $RT \ln V_N$ *vs* $a(\gamma_L^D)^{1/2}$ diagram for the 3 carbon fibres.

This analysis is confirmed, on the examples shown in Figure 2, where it is observed that for a series of n-alkanes, $RT \ln V_N$ is a linear function of the quantity $a(\gamma_L^D)^{1/2}$. The slope of the straight line leads to the values of γ_S^D of the three carbon fibres listed on Table II.

Gray[10] uses a similar method for the determination of γ_S^D by considering the increment of ΔG^0 per methylene group in the n-alkanes series of general formula C_nH_{2n+2}. The increment $\Delta G^0_{(CH_2)}$ defined by $\Delta G^0_{(C_{n+1}H_{2n+4})} - \Delta G^0_{(C_nH_{2n+2})}$ leads to:

$$\gamma_S^D = \frac{\left[RT \ln \dfrac{V_N C_{n+1}H_{2n+4}}{V_n C_n H_{2n+2}}\right]^2}{4\mathcal{N}^2 a^2_{CH_2} \gamma_{CH_2}} \tag{7}$$

where a_{CH_2} is the surface area of a CH_2 group, *i.e.* 6 Å^2 and γ_{CH_2} the surface energy of a CH_2 group, *i.e.*, of a surface constituted of close packed CH_2 groups analogous to polyethylene and given by:

$$\gamma_{CH_2} = 35.6 + 0.058(20 - T), \text{ in mJ . m}^{-2}$$

The values of γ_S^D obtained by using Gray's method are also presented on Table II.

It must be noted that the chromatographic method leads to values of γ_S^D much more precise than the ones obtained by wetting, although they agree satisfactorily. The untreated and oxidized fibres have rather high values of γ_S^D whereas the coated fibre exhibits a somewhat lower value close to the one of a polymer.

b) *Specific interactions* Non-dispersive interactions have usually been referred to in terms of polar interactions. More recently, the works of Drago[11,12] Gutmann[13] and Fowkes[14,15] stress the fact that the non-dispersive or specific interactions are essentially Lewis

TABLE II
Dispersive component of the surface energy of carbon fibres (IGC method)

	γ_S^D (mJ . m^{-2})	
Carbon fibres	Our method	Gray's method
Untreated (1)	50 ± 4	48 ± 4
Oxidized (2)	49 ± 2	50 ± 4
Coated (3)	36 ± 3	33 ± 3

acid-base interactions or electron acceptor-donor interactions. According to this new concept, strong interactions develop only between an acid and a base. Materials of the same character, both acids or both bases, even with high surface polarities will exchange nearly zero specific interaction.

According to Gutmann[13] for instance, liquids can be characterized by donor or acceptor numbers:

- the donor number DN defining the basicity or electron-donor ability is the molar enthalpy value for the reaction of the electron-donor D with a reference acceptor $SbCl_5$.
- the acceptor number AN characterizing the acidity or electron acceptor ability is defined on a different basis. It is the NMR chemical shift of ^{31}P contained in $(C_2H_5)_3PO$ when reacting with the acceptor A.

In this study, several specific probes have been chosen, exhibiting either a strong donor (base) character or a strong acceptor (acid) character, or both characters (amphoteric).

Table III shows the main characteristics of some of the probes used in this work. The surface area *a* of the probe molecules has been determined by injecting the probes on neutral reference solids

TABLE III
Characteristics of some probes

	a (Å^2)	γ_L^D (mJ . m^{-2})	*DN*	*AN*	Specific character
C_6H_{14}	51.5	18.4			
C_7H_{16}	57.0	20.3	—	—	
C_8H_{18}	62.8	21.3			Neutral
C_9H_{20}	68.9	22.7			
THF	45	22.5	20.0	8.0	Base
Ether	47	15	19.2	3.9	
$CHCl_3$	44	25.9	0	23.1	
CCl_4	46	26.8	0	8.6	Acid
C_6H_6	46	26.7	0.1	8.2	
Acetone	42.5	16.5	17.0	12.5	Amphoteric
Ethyl-Acetate	48	19.6	17.1	9.3	

(PTFE, poly-ethylene, graphitized carbon black,...). The dispersive component γ_L^D has been measured by the contact angle method on reference solids. The values of DN and AN are taken from tables published by Gutmann[13].

In order to be able to determine quantitatively these specific interactions, we consider, to a first approximation, that the specific interactions are simply added to the dispersive interactions defined previously.

Therefore, the experimental point corresponding to a specific probe having an acid or base character will always lie well above the reference straight line of $RT \ln V_N$ *vs* $a\ (\gamma_L^D)^{1/2}$ corresponding to the *n*-alkanes as schematically illustrated in Figure 3.

At a given value of $a(\gamma_L^D)^{1/2}$, the difference of ordinates between the point corresponding to the specific probe and the reference line leads to the value of the free *enthalpy* of *desorption* ΔG_{sp}^0 corresponding to specific acid-base interactions.

$$RT \ln \frac{V_N}{V_N^{ref}} = \Delta G_{sp}^0 \tag{8}$$

Such experiments have been carried out on the three carbon fibres at various temperatures. An illustration of the $RT \ln V_N$ *vs* $a(\gamma_L^D)^{1/2}$ diagrams obtained at 40°C are presented in Figure 2.

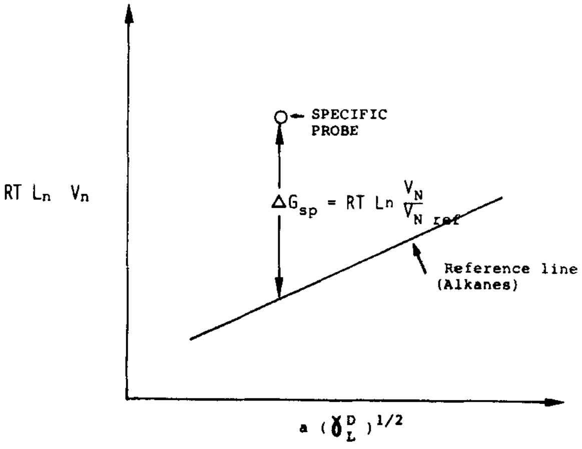

FIGURE 3 Schematic representation of a general $RT \ln V_N$ *vs* $a(\gamma_L^D)^{1/2}$ diagram.

It can easily be concluded, on a qualitative basis, that:

–the untreated fibre (1) has an average acid or acceptor character and practically no base or donor character,

–the oxidized fibre (2) has a strong acid character and a rather low base character,

–the coated fibre (3) could be called "amphoteric" since it exhibits a strong acid character together with a high base character.

In order to get at least a semi-quantitative estimate of the acid-base surface properties of the carbon fibres, the enthalpy of desorption ΔH^0_{sp} corresponding to the specific interactions has been determined by the intercept at the origin of the variation of ΔG^0 with temperature T according to

$$\Delta G_{sp} = \Delta H_{sp} - T\,\Delta S_{sp} \tag{9}$$

An example is presented in Figure 4. Following Papirer's approach[16], we assume that:

$$\Delta H_{sp} = K_A\,.\,DN + K_B\,.\,AN \tag{10}$$

where DN and AN are Gutmann's numbers for the probes and K_A and K_B are numbers describing the acid and base characters of the fibres.

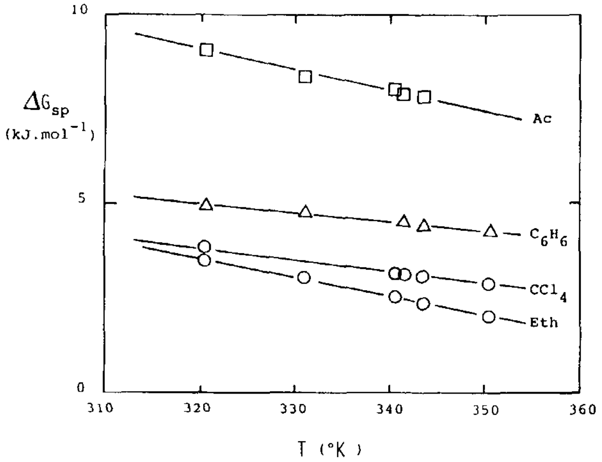

FIGURE 4 The variation of the free energy of desorption, ΔG_{sp}, with temperature.

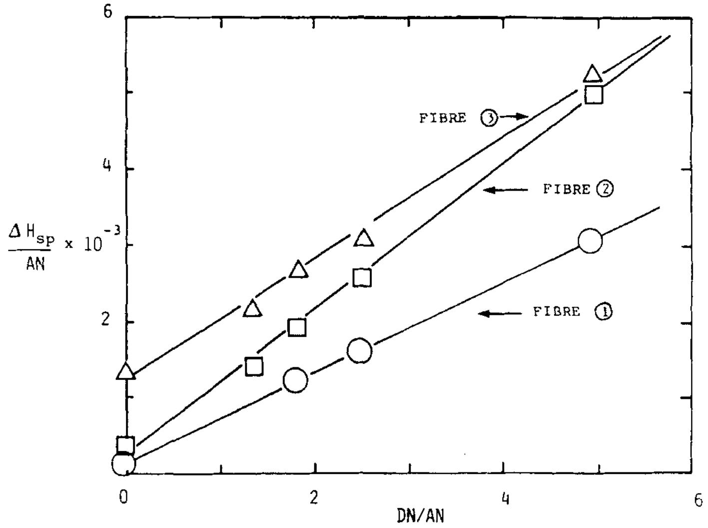

FIGURE 5 $\frac{\Delta H_{sp}}{AN}$ *vs* $\frac{DN}{AN}$ diagram.

Equation (10) can be written:

$$\frac{\Delta H_{sp}}{AN} = K_A \frac{DN}{AN} + K_B \tag{11}$$

It is shown in Figure 5 that a plot of $\Delta H_{sp}/AN$ *vs* DN/AN is actually linear. Therefore K_A and K_B can be determined from the slope and intercept at the origin of this straight line.

Table IV gives the values of K_A and K_B found for the three carbon fibres. We are aware that, given the approximations used in the chromatographic analysis, K_A and K_B can only be considered as semi-quantitative values of the surface acidity and basicity of the

TABLE IV
Acceptor-donor (acid-base) character of the carbon fibres (arbitrary units)

Carbon fibres	K_A	K_B
Untreated (1)	6.5	1.5
Oxidized (2)	10.0	3.2
Coated (3)	8.6	13.0

TABLE V
Surface properties of the epoxy matrix

γ_S^D	γ_S^P	γ_S^D	K_A	K_B
(Wettability)			(IGC)	
40	4	40	7.6	6.2

TABLE VI
Specific interaction parameter A between carbon fibres and epoxy resin (in arbitrary units)

Carbon fibres	A
Untreated (1)	52
Oxidized (2)	86
Coated (3)	152
Coated (4)	127

fibres, allowing comparison to be made. This semi-quantitative approach leads to the same conclusions as the ones drawn from the qualitative examination.

The same type of study has been effected on an epoxy matrix (DGEBA–DDS) after grinding at low temperature in an inert atmosphere. Its surface properties are shown in Table V.

Knowing the K_A and K_B values for the fibres and matrix and by analogy with relation (10), it is now possible to define a "specific interaction parameter" A describing the acid-base interaction between the fibre (f) and the matrix (m) by:

$$A = K_A^f K_B^m + K_A^m K_B^f \qquad (12)$$

The calculated values of A for the three fibres, together with the one for a commercial fibre of different characteristics (Coated Fibre ④), are shown in Table VI. It is seen that the specific interaction increases when going from the untreated to the coated fibre. As expected the amphoteric coated fibre 3 leads to the highest acid-base interaction with the amphoteric epoxy matrix.

FIBRE–MATRIX ADHESION

The fibre–matrix adhesion has been evaluated by using the fragmentation method[17,18].

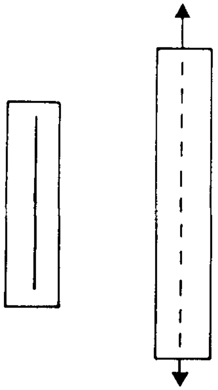

FIGURE 6 Schematic representation of the fragmentation technique.

As shown schematically in Figure 6, the elementary carbon fibre is embedded in the epoxy matrix and the parallelepipedic test piece is submitted to an uniaxial tensile stress in the direction of the fibre. The fibre-matrix adhesion, *i.e.*, the capacity of the interface to transfer the stress from the matrix to the fibre, is evaluated from the shear resistance τ of the interface. By applying a tensile force, the single fibre is broken into small fragments until the shear strength of the interface is reached. τ can, therefore, be calculated from the average length of the fragments and the tensile strength of the fibre at this average length. Weibull statistics have been used to determine both parameters.

The values of τ given in Table VII have been calculated assuming that the shear strength is maximum at the extremities of the fibre fragments.[19,20] The adhesion of the coated fibre 3 is roughly 30% higher than the adhesion of the untreated fibre 1.

TABLE VII
Fibre/matrix adhesion

	τ (MPa)	A (a.u.)	$I^D + I^P$ (mJ . m^{-2})
Untreated fibre 1	101	52	101
Oxidized fibre 2	113	86	105
Coated fibre 3	135	152	87
Coated fibre 4	128	127	—

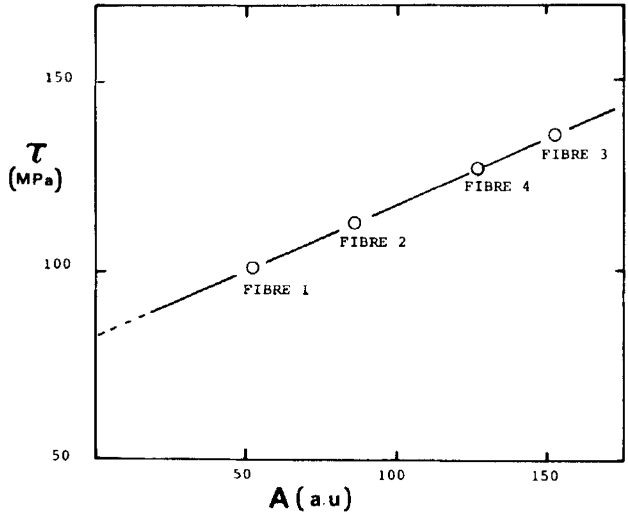

FIGURE 7 Interfacial shear resistance τ *vs* specific interaction parameter A.

As shown on Table VII, the increase of adhesion obtained by the oxidation treatment and by the coating cannot be explained by assuming that the interactions at the interface are the result of dispersive and polar forces. There is no correlation between τ and the sum $(I^D + I^P)$.

However, as shown on Figure 7, there is a very strong correlation between τ and the specific interaction parameter A. This could mean that the interfacial adhesion principally results from acid-base or acceptor-donor interactions between the fibre and the matrix, assuming that the dispersive interactions are of the same order of magnitude. The meaning of the value of τ obtained by the intercept at the origin of the straight line, of the order of 80 MPa, is not clear yet; this value could be considered, to a first approximation, as being the contribution of the dispersive interactions to the shear resistance of the interface.

CONCLUSIONS

Tensiometric and chromatographic methods for the study of the surface of carbon fibres have been developed. The inverse gas chromatography technique appears to be a very powerful tool for the characterization of solids in terms of the dispersive component of the surface energy and of the acid-base or acceptor-donor character.

The concept of acid-base interactions constitutes an interesting, if not universal, approach to a better understanding of the interfacial properties of composite materials and could constitute a basis for a better choice for the surface treatments of the fibres.

However, we do now claim that acid-base specific interaction is the only explanation for the increased adhesion of the coated fibre, since other mechanisms could intervene such as interdiffusion or co-cross-linking.[21,22]

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