

INTERFACE ADHESION IN COMPOSITES. CORRELATION BETWEEN IGC MEASUREMENTS AND MECHANICAL TESTING RESULTS.

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SUMMARY: The main role of the interface in a CFRP is to transfer the load from the *stiff* carbon fibres to the *soft* matrix material. The good interaction between both components of the composite governs the efficiency of this transference process. This adhesion is the result of many phenomena: mechanical gripping and physicochemical adsorption, principally. This adhesion relies on the free groups in the surface of the fibres, and the chemical composition of the resins. The strength of the interface is of vital importance in the behaviour of the composite. The deep knowledge of these surface groups and the quantification of the interface interaction has been the subject of much research effort.

Inverse Gas Chromatography (IGC) has proved to be one of the most valuable and available tools for evaluation of the characteristics of solid surfaces that cannot be easily studied by other methods, like powders and fibres. There are several methods described in the literature for the evaluation of the *non-polar character*, and the *acid and basic character* of the free surface energy by IGC, we have recently proposed a new method for the evaluation of the polar part or *specific component* of the free energy of a solid surface and its application to CFRP.

The ILSS test or determination of the apparent interlaminar shear strength, in principle, gives information about the matrix-fibre interface.

Keywords: Interface, Inverse Gas Chromatography, Apparent Interlaminar Shear Strength, Carbon Fibres, Epoxy Resin, Cyanate Ester Resin, Surface Characteristics, Matrix Characteristics.

INTRODUCTION

The relevance of the interface in CFRP composite materials it is due to the fact that adhesion forces between fibre and matrix govern the load transfer from the “rigid” reinforcement to the “soft” materials of the matrix. The evaluation and quantification of these forces has been for long, a problem, and many tentative and much effort has been devoted to its solution.

One of the mechanical tests that best show the interface interaction, is the determination of the apparent interlaminar shear strength (ILSS). That consists of the resistance to

delamination under shear forces parallel to the layers of the laminate. For this determination, a specimen of rectangular cross section is tested in flexure on two supports. This test gives information about the quality of the fibre-resin relation [1].

Owing to the inherent structural weakness of carbon-fibre/matrix composite laminates, delamination has been one of the main issues in current composites application and technology. This premature fracture can lead to a substantial reduction in stiffness and strength, and eventually to the final failure of a composite laminates is closely related to their delamination toughness which in turn is related to the material strengths under tension conditions. Because of the significance of delamination toughness, analyses of the delamination behaviour of composite laminates have been extensively pursued by means of various fracture-mechanics methods [1].

On the other hand, Inverse Gas Chromatography (IGC), has proved to be one of the best tools for the characterisation of solid surfaces, specially of those materials like powders or fibres which can not be easily studied by other techniques.

In this paper two carbon fibres are evaluated by IGC at infinite dilution. By similar technique, three resins are characterised as well. Coupling the obtained characteristics, some calculated interactions are given, in terms of energy by surface unit.

Unidirectional laminates are prepared with an unsized medium modulus carbon fibre of and two different epoxy resins, and with a high modulus carbon fibre and an epoxy and a cyanate ester resin, using in all cases commercially available prepregs. The apparent interlaminar shear strength is determined of all four laminates, according to the standard method BS EN 2563: 1997. Correlation is made of testing results and interface strength predictions calculated with measurements by IGC.

THEORY

Inverse Gas Chromatography

Gas Chromatography is an easy technique of separation and/or identification of solutes in a mixture, based on the fact that, each solute, has a *particular* interaction with the stationary phase, and therefore, the different solutes travel through the column, carried by an inert gas, at different rates. The solutes come out of the column separately and the retention volume, V_R , of each solute, depends on different parameters, among others, the nature of the stationary phase and the nature of the solute.

IGC takes advantage of this fact, by using a series of solutes (probes), of well known physicochemical characteristics. Introducing them into the column, and measuring their V_R , valuable information of the nature of the column can be obtained. The column is built with the fibre or the resin to be studied. When adsorption takes place at infinite dilution, only interactions between probes and the surface of the stationary phase occur, Henry's law can be applied, and V_R is practically independent of the probe concentration [1][2]. Fowkes [1] proposes to split the interaction energy between a gas and a solid surface in two terms

$$W_A = W_A^D + W_A^{SP} \quad (1)$$

W_A^D including the weak dispersive interactions and W_A^{SP} including the other types of interactions mainly polar, like acid-base, hydrogen bonding, π bonding etc.

The free energy of adsorption, $-\Delta G_A$, as a first approximation, can be linked with the work of adhesion W_A as follows

$$-\Delta G_A = NaW_A \quad (2)$$

where N is Avogadro's number and a is the area of the probe. Also the free energy of adsorption is related to the Ln of the retention volume accordingly to

$$\Delta G_A = -RTL \ln V_R + K \quad (3)$$

When n-alkanes are employed as probes, the work of adhesion is dominated by dispersive interactions at the interface, equation (1) is reduced to $W_A = W_A^D$, and according to Fowkes's expression ¹

$$W_A = 2\sqrt{\gamma_s^d \gamma_L^d} \quad (4)$$

where γ_L^d is the dispersive component of the free energy of the adsorbate and in the case of n-alkanes, the free energy and γ_s^d is the London component of the solid surface free energy.

The retention volumes of n-alkanes will give information about the capability of the solid surface of interacting with non-polar material. Two methods are described in the literature to access to the γ_s^d value of the solid stationary phase: The method of Dorris and Gray², and Shultz's[3]. Both methods use the areas of n-alkanes given by Avgul et al.³. The values obtained by these methods are fairly concordant. In this paper we use the method of Gray, corrected according to Gutierrez et al.[5] where γ_{CH_2} , is calculated by plotting $a\sqrt{\gamma_L^d}$ versus number of carbon atoms of the series of n-alkanes. The slope of the line gives us a value of 36.71 mJ/m² for γ_{CH_2} .

When polar molecules are injected in the column interactions other than the dispersive ones take place between the polar molecules (probes) and the material in the column. The total V_R obtained for each polar probe comes from two types of interactions with the solid surface, as seen in equation (3). ΔG_A must be split in two terms, one including the *dispersive interaction* and the other with the *specific interaction*.

In this paper the method of Gutierrez et al. [10] is used for the splitting of the total adsorption energy of the polar probes and the estimation of the *specific interaction*. In order to compare with one of the most used methods described in the literature, also some results are given obtained by Schultz et al. [8]. According to the former method, the specific interaction is calculated through the measurements of the *shift of CH₂ indexes*, $I(CH_2)$, of the polar probes, where

$$I(CH_2) = \frac{I(Kóvats) + 100}{100} \quad (5)$$

The chosen polar probes for the evaluation of the acid or basic character of the solid stationary phase are volatile molecules like: benzene, chloroform, acetone, ethyl acetate, diethyl ether, methylene chloride, tetrahydrofuran etc. Their electronic donor and acceptor character is found in the literature [4] as DN values and AN values. DN values, measure the energy of a coordinate bond between a donor atom and the Sb of $SbCl_5$, its value is expressed in kcal/mol. AN is derived from relative [3] P NMR chemical shifts in Et_3PO , when dissolved in the acid species being evaluated, and is a dimensionless

number. Riddle and Fowkes [4], made corrections of Gutmann's original AN values. But if AN and DN values are not normalised to the same scale, the results of acid-base interactions would turn out to be meaningless. This is done according to Mukhopadhyay [4] through the DN value of Et_3PO (the AN reference molecule) that is 40 kcal/mol. DN values can be recalculated in a dimensionless scale, or AN values in kcal/mol. The acid-base interaction, in most papers, and also in this one, use the expression

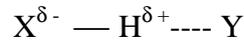
$$Isp = (K_{as})DN_{probe} + (K_{bs})AN_{probe} \quad (6)$$

where K_{as} and K_{bs} are related to the acid or basic character of the solid stationary phase. These constants can be obtained plotting Isp/AN of each polar probe, versus DN/AN . The slope is K_{as} , and K_{bs} the intercept. The dispersive fibre-resin adhesion (W_A^D) is calculated with Fowkes expression eq. (4). The acid-base fibre-resin adhesion (W_A^{SP}) between the fibre and resin is also calculated with a linear expression like equation (6):

$$W_A = (K_{afibre})(K_{bresin}) + (K_{bfibre})(K_{aresin}) \quad (7)$$

Interaction of the surfaces with OH groups: Hydrogen bonding.

The hydrogen bond (H bond) is the term given to the relatively weak secondary interaction between a hydrogen atom bound to an electronegative atom and another atom, generally also electronegative, which has one or more lone pairs and can thus act as a base. The generalised representation of it can be



The main proton donors are N-H, O-H and F-H. The acceptor atoms can be N, O, F, Cl, Br, I, S or P, but carbon never acts as an acceptor other than in certain π systems. The H bonding can be considered as part of W_A^{SP} of eq. (1). Injecting a series of 1 alcohols (R-OH) as probes, the specific interaction can be calculated, and as the difference between the members of the series is $n CH_2$, a line is obtained when plotting this interaction versus the number of C-H bonds in the group R, in Fig 1 an example is given of the evaluation of the -OH group interaction in a cyanate ester resin cured over the surface of glass beads. From the intercept of this line, the interaction of an -OH group with the column material can be obtained. The units given in this paper are kJ/mol-OH. This magnitude can give us information about the abundance of *electronegative donors* in the surface.

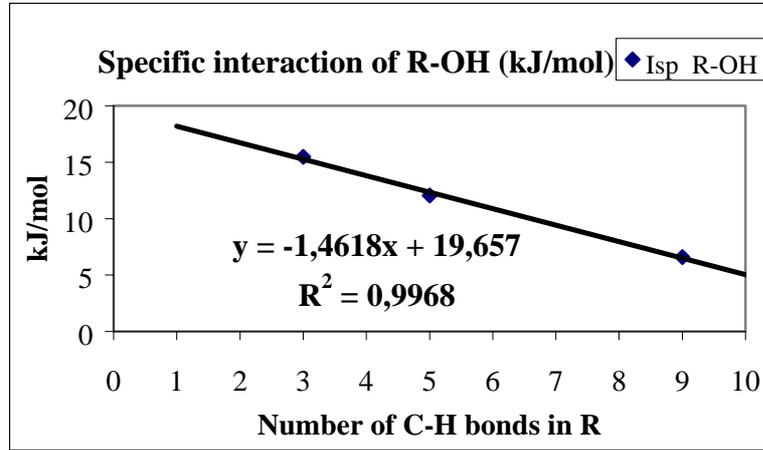


Fig.1. Specific interaction of methanol, ethanol and butanol on a cyanate ester resin.

Interlaminar Shear Strength test

Apparent interlaminar shear strength: it is the maximum shear stress calculated at half thickness of the specimen at the moment of first failure.

The apparent interlaminar shear strength can be calculated as follows:

$$\tau = \frac{3P_R}{4bh} \quad (8)$$

where:

- τ is the apparent interlaminar shear strength, in megapascal;
- P_R is the maximum load at the moment of first failure, in newtons;
- b is the width of specimen, in millimetres;
- h is the thickness of specimen, in millimetres.

EXPERIMENTAL

IGC

The instrument used is a Perkin Elmer Autosystem with flame ionisation detector in the highest sensitivity scale. The amount of probes injected is 0.01 to 0.05 μl of gas of the headspace of the vessels to be sure of the infinite dilution condition. After the column has been conditioned several probe molecules with known properties are injected into it and carried through by helium. The key parameter to be measured is the net retention volume V_R of each probe.

Mechanical Test

ILLS of plied laminates have been measured at INTA with an Instron 4204 Universal machine. The standard test applied is the BS EN 2563: 1997.

Materials

Resins:

R-8552: epoxy resin with no curing agent or accelerator (Hexcel)

R-3501-6: formulated epoxy resin obtained by liquid extraction of commercial prepregs (Hexcel).

R-954-2A: formulated cyanate ester resin obtained by liquid extraction of commercial prepregs (Fiberite).

Glass beads are impregnated with the resin solutions and put into teflon tubing by the “slurry” method. The beads are dried inside the 2 m. long, and 1/4” diameter tubing, and cured at 150°C for 6 h.

Fibres:

F-IM7: High modulus carbon fibre (Hexcel).

F-AS4: Medium modulus carbon fibre (Hexcel).

The fibres are introduced into 1–2 m. long and 1/4” diameter teflon tubing for their characterisation by IGC.

Laminates: All specimens were prepared with a commercial available preregs. Unidirectional plied laminates were cured in autoclave with six bars overpressure at 180°C for a period of four hours.

RESULTS AND DISCUSSION

Non-polar interaction in the fibre-matrix interface

The London component of the free surface energy of the two fibres and the three resins obtained by the method described by Schultz (ref. 8) and the method of Gray corrected as indicated before (ref. 10) are included in Table I.

Table I. London component of fibres and resins surfaces in mJ/m^2 .

Fibre or resin	Method (ref. 10)	Method (ref. 8)
Fibre IM7	32.3	34.3
Fibre AS4-12k	38.5	40.9
Epoxy resin 8552	34.5	36.7
Epoxy resin 3501-6	33.6	35.7
Cyanate ester resin 954-2A	37.7	40.0

With these values, and accepting Fowkes expression (eq. 4), the non-polar calculated interaction between the following fibre-matrix couples is:

Table II. Non-polar interaction in mJ/m^2 .

Fibre/Matrix	Method (ref. 10)	Method (ref. 8)
AS4/8552	73	77
AS4/3501-6	72	76
IM7/8552	67	71
IM7/954-2A	71	75

Acid and basic character of the fibres and resins studied.

In Table III we can see the acid character K_a , and the basic character K_b , of the surfaces of fibres and cured resins studied, calculated in mJ/m^2 by the methods of ref.10 and ref.8.

Table III. Acid and basic character of the fibres and resins surfaces in mJ/m^2 .

Fibre or resin	Method (ref. 10)		Method (ref. 8)	
	K_a	K_b	K_a	K_b
Fibre IM7	-0.11	0.38	0.24	1.28
Fibre AS4-12k	0.04	0.13	0.28	0.72
Epoxy resin 8552	0.01	1.11	0.32	1.87
Epoxy resin 3501-6	0.11	1.29	0.43	2.11
Cyanate ester resin 954-2A	0.04	2.22	0.27	2.70

According to these values, the acid-base calculated interaction between the following fibre-matrix couples is:

Table IV. Acid-base interaction in mJ/m^2 .

Fibre/Matrix	Method (ref. 10)	Method (ref. 8)
AS4/8552	0.04	0.74
AS4/3501-6	0.29	1.24
IM7/8552	-0.12	0.84
IM7/954-2A	-0.23	0.98

Interaction with –OH groups of the fibres and resins studied.

In Table V, the values of specific interaction with –OH groups of the different materials are given:

Table V. Interaction of the samples with –OH group in kJ/mol .

Fibre or resin	-OH group interaction
Fibre IM7	4
Fibre AS4-12k	2
Epoxy resin 8552	6
Epoxy resin 3501-6	7
Cyanate ester resin 954-2A	20

Interlaminar shear strength test results (ILSS).

The mechanical test results are included in Table VI.

Table VI. ILSS test results

Fibre/Matrix	Maximum load at the moment of first failure (KN)	Apparent interlaminar shear strength (MPa)	Failure type
AS4/8552	3.8	97.8	Single interlaminar shear
AS4/3501-6	3.6	91.0	Single interlaminar shear
IM7/8552	2.5	94.2	Plastic deformation
IM7/954-2A	2.3	80.2	Plastic deformation

If a specimen fails in shear approximately at the neutral axis (see figure 2), the interlaminar shear strength is calculated in accordance with the formula (8).

If a specimen fails in flexure or by plastic deformation (see figure 2), the results obtained by the formula (8) do not mean a true stress at failure.

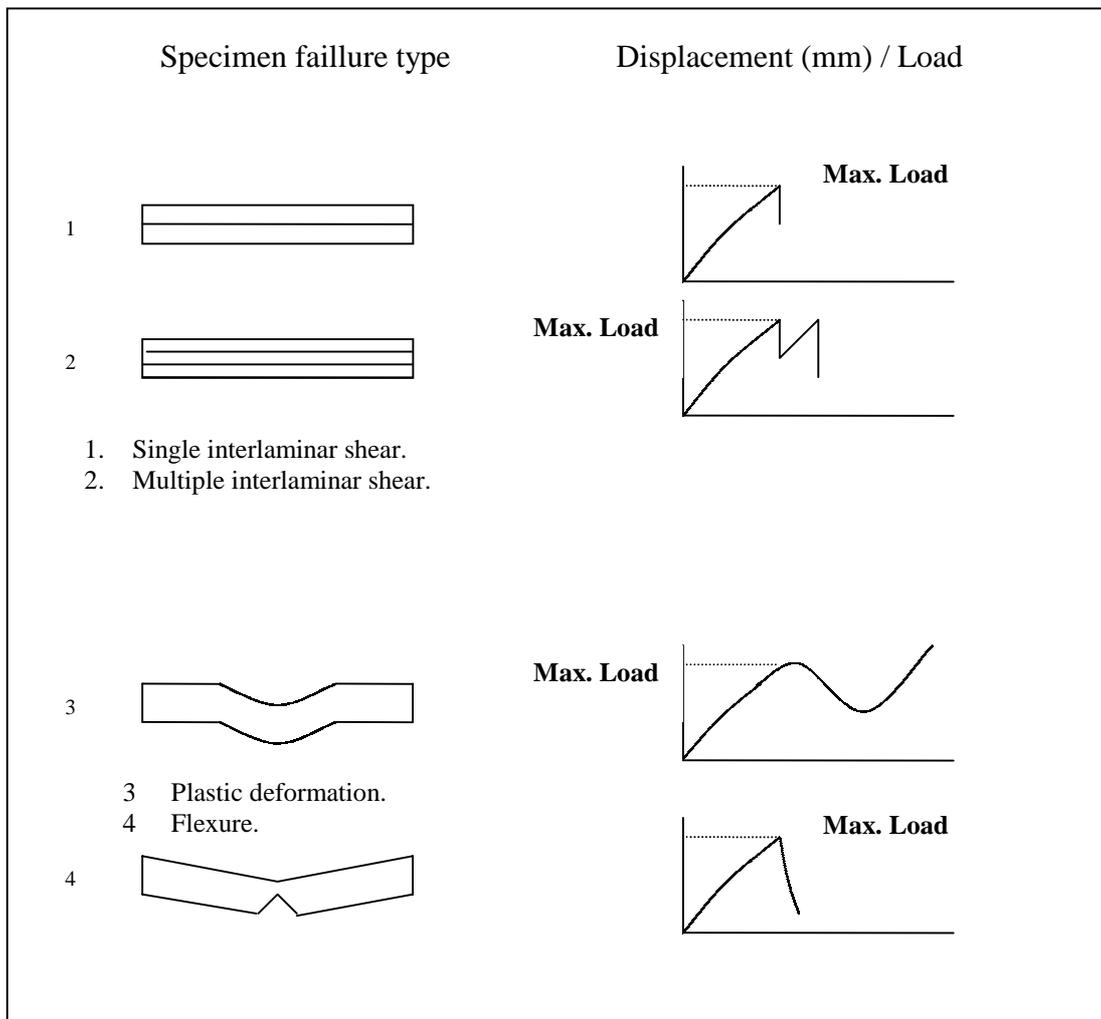


Fig. 2. Failure patterns in ILSS test.

Discussion

With the values obtained by IGC regarding the physicochemical characteristics of fibres' surfaces and the solid resins' ones, we calculate the hypothetical interaction in the interfaces. Four specimens of unidirectional plied laminates were prepared with the commercial available preregs in autoclave. The mechanical testing results should correlate with the calculated values by IGC measurements

In table VII the calculated interface interactions evaluated by IGC are given in mJ/m^2 , both non-polar interaction and the acid-base interaction for each laminate. The results obtained from the ILSS test are also given in the same table.

Table VII. Calculated interactions in mJ/m^2 , and mechanical testing results in MPa

N°	System	Calculated interface interaction in mJ/m^2			Mechanical properties
		Non-polar interaction	Acid-base interaction	Total interaction	ILSS (Mpa)
1	AS4/8552	73	0,04	73,36	97.8
2	AS4/3501-6	72	0,29	71,32	91.0
3	IM7/8552	67	-0,12	66,71	94.2
4	IM7/954-2A	71	-0,23	69,62	80.2

In Fig. 3 the total calculated interaction and the ILSS results are shown. Systems 1 and 2 belong to the laminates built with AS4, and systems 3 and 4 two those built with IM7.

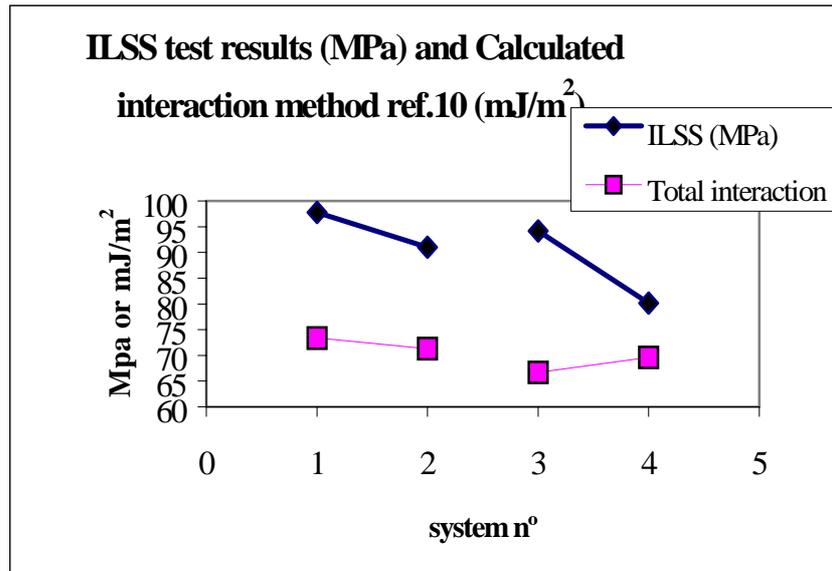


Fig. 3. Correlation between ILSS test results (MPa) and calculations by IGC in mJ/m^2

From the data given in table VII. we can find a good correlation between the calculated interface interaction values and mechanical testing results in the two laminates derived from AS4 carbon fibre: resin 8552 interacts mainly with weak non-polar forces with the fibre and this interaction is higher than that of resin 3501-6. The acid base interaction has an opposite trend, but the contribution of this polar term is obviously very small and the non-polar forces dominate the total calculated interaction. ILSS max. load at failure shows also a slightly higher interaction of resin 8552 than 3501-6 with AS4 carbon fibre. This is in agreement with the data of tables III and V. AS4 has very low K_a and K_b values, and its interaction with $-\text{OH}$ groups is very low as well, so the adhesion must be controlled by weak non-polar dispersive forces.

In the case of IM7, the max. load at “failure” shows completely opposite trend than the calculated interface interactions, but in this case the type of failure is plastic deformation and the data do not reflect the interface. Besides, The provided fibre and measured by IGC, is a sized fibre. The prepreg was manufactured (as we learned later on) with unsized fibre. The sizing affects very much the surface characteristics of the fibre as it covers the active polar groups. Therefore the predictions have been made with a *different* fibre than the one used in the prepreps when manufactured. But useful conclusions can be drawn from the data found by IGC: resin 8552 is clearly more basic than acid and should interact more with a fibre with acid groups in the surface. This happens also with resin 954-2 A , but in this case the basic character is outstanding, more than twice the value than resin 8552 (table III). The polar contribution of this resin should be more significant provided that the fibre has a minimum of acid centres. At the same time the also the data of table V mean that this resin has a much greater interaction with $-\text{OH}$ groups, or a good great number of *basic electronegative centres*. An oxidised fibre should provide a good substratum for this resin.

CONCLUSIONS

1. Good correlation is found in the mechanical test results and the calculated interface interaction values in the two systems formed with AS4 unsized fibres and two epoxy resins.
2. ILSS test cannot be used as a checking criterion for evaluation of the interface in a laminate because plastic deformation masks the real interaction forces.
3. Measurements of interaction of solid samples with –OH groups by IGC are in agreement with the data obtained with before described methods to evaluate the acidic or basic character of a surface.

ACKNOWLEDGEMENTS

We gratefully thank to HEXCEL COMPOSITES S.A. and FIBERITE S.A. for providing us with the material. Also we thank to E.A. Romero and J.L. G^a Bueno for their experimental work, and the staff in the processing laboratory that prepared the laminates.

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