INTERFACE PREDICTION:
INVERSE GAS CHROMATOGRAPHY (IGC) AND ITS POTENTIAL APPLICATION TO FIBRE-MATRIX ADHESION PROBLEMS

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SUMMARY: The purpose of this work is to show how the use of Inverse Gas Chromatography technique can be employed for predicting fibre-matrix adhesion in composites. This technique allows to determine different physical-chemical properties of the solid surfaces which can be combined for knowing the interaction that exists between fibres and matrices in composites. This technique can be employed in the zero coverage region and in the finite coverage region and also the distribution of active sites existing on the solid surface can be determined. Different values of the physical-chemical properties are given for different materials, and finally we show a good correlation between these properties and some mechanical properties of composites. However further work must be carried out in this subject in order to achieve a more complete knowledge of any type of material used for obtaining composites.

KEYWORDS: Interface, Surface free energy, Adhesion, Inverse Gas Chromatography, Fibre-Matrix Characteristics, Distribution of Active Sites.

INTRODUCTION

The control of the interaction at the interface is of key relevance when designing any

type of Composite Material ″1› . This means a deep knowledge of the surface of the reinforcement, in terms of free energy, and its potential attraction or repulsion when the

matrix material comes close to the surface and interpenetrates the solid surface ″2›.

Among the manufacturers of composites, very often, the *tray and test*, is the philosophy to obtain optimum characteristics of adhesion at the interface. Much effort can be avoided if there could be found, accessible before-hand, useful information, about the *capability of interaction* of those materials, that will, potentially, form part of the finished composite.

In the last forty years, a great deal of quite sophisticated techniques have been developed in order to study the surfaces and the *active groups* in them, such as IRRS, XRF, XPS, AES, RBS, SIMS, SCANIIR, SEM, TEM, CPXS, etc. Mostly these techniques result in the identification of any surface atoms or surface groups, but little is learned about their *potential interactivity* with the external environment.

Inverse Gas Chromatography (IGC) has proved to be a suitable tool to study solid surfaces and their interaction capability. There is a growing interest in the application of this technique to the solution of all kind of adhesion problems. Much literature has been published recently on this topic [1-3]. Now we will show what information can be obtained from IGC to characterize interfaces in composite materials.

INVERSE GAS CHROMATOGRAPHY

Gas chromatography (GC) is a separation technique widely used for analytical purposes. In this technique different unknown solutes that travel the chromatographic column are separated, identified according their retention times, and finally quantified in respect their peak area. On the other hand, IGC uses well-known solutes or probes which travel the chromatographic column packed with the solid to be characterized. Fibres, fillers and any kind of polymer matrix can be used for packing chromatographic columns and then their surface can be characterized. Finally, knowing these surface characteristics the interface of the composite material can be described in terms of adhesion energy [4,5].

IGC is also a versatile technique which permits to obtain information about surface properties in different aspects. When very low probe concentrations are employed IGC is at infinite dilution or zero coverage and surface energies such as dispersive components, acid-base components, hydroxyl contributions, etc., can be obtained for the solid surface. On the other hand, high probe concentrations can be used and then IGC is at finite dilution, obtaining in this way the surface distribution of active sites on the solid surface.

Now we will discuss the potential information which can be obtained by means of IGC to resolve adhesion problems of composite materials.

IGC AT INFINITE DILUTION OR IN THE ZERO COVERAGE REGION

IGC at infinite dilution is achieved when very small amounts (less than 0.01 µl) of probes are injected into the chromatographic column. At these concentrations the adsorption of the probe is in accordance with the Henry´s law and then the free energy of adsorption, ΔG_A, (interaction of the probe on the solid surface) is related with the retention volume, V_R, of the probe in the column:

$$\Delta G_A = -R\ T\ Ln\ V_R + C \qquad (1)$$

being R the gas constant, T the experimental temperature and C a constant.

According to Fowkes [6]. the interaction energy between a gas and a solid can be expressed as

$$\Delta G_A = \Delta G_A^D + \Delta G_A^{SP} \qquad (2)$$

where the symbols D and SP correspond to dispersive and specific interactions respectively.

Equation (2) permits to obtain the D and SP energies of any surface of each material used for preparing composites. These surface energies are employed for evaluating the interface adhesion of different materials.

Dispersive interactions. Dispersive Energy of the Solid Surface: γ_S^D

When alkane probes are used in IGC only dispersive interactions take place. Therefore equation (2) is reduced to:

$$\Delta G_A = \Delta G_A^D \qquad (3)$$

Two methods are proposed for obtaining the D interactions of any solid surface, and

both methods give similar results [7]. Plotting ΔG_A versus the number of carbon atoms or versus $a(\gamma_L^d)$ of the n-alkane molecule, the slope of the line gives the dispersive energy of the solid surface γ_S^D. Figure 1 shows such plot for carbon fibres. Table 1 gives results of dispersive energies of fibres and matrices used in composites.
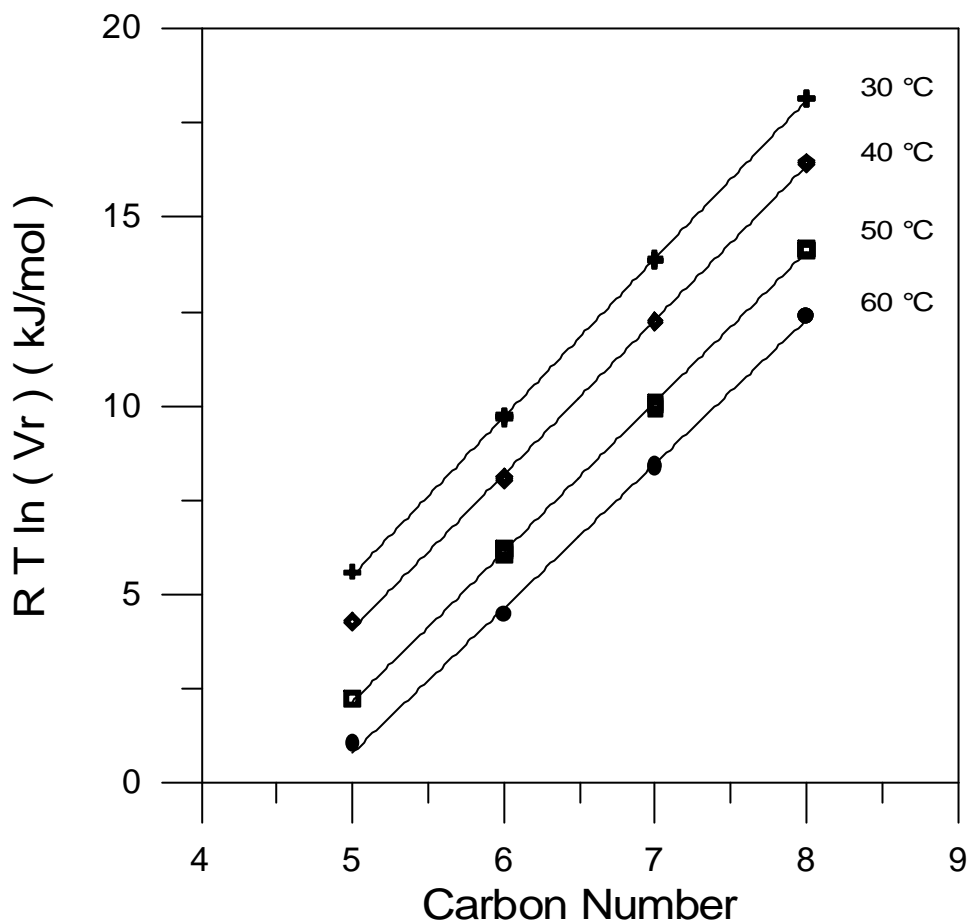

Fig. 1.- Adsorption free energy of n-alkanes vs number of C atoms.

Specific Interactions: Acid-Base (k_A, k_B), Hydroxyl (k_{OH}) and Functional Groups (k_{FG})
Acid-Base Interactions.
Equation (2) allows the estimation of the specific interaction energy ΔG_A^{SP} of any solid surface by means of determining the adsorption energy of organic probes which have the capability of interacting specifically with the solid surface. Because specific organic probes have both dispersive and specific interaction capabilities it is necessary to develop a method which permits separate such both interactions. Several methos have been proposed during the last fifteen years and all of them consist on plotting ΔG_A for neutral (n-alkanes)and specific

probes as a function of a characteristic molecule property [3,7,8].: saturation pressure (P_O), molecular area (a), polarizability (P_D), boiling temperature (T_B), topography index (P), etc. In such plot n-alkanes fall on a straight line because such molecules only change dispersive interactions with the solid surface (according to equation (3)), however specific probes fall above a given distance of the n-alkane line and such distance is considered as the specific interaction energy with respect to the solid surface.

More recently Gutierrez et al. [7]. have proposed a new method for obtaining the specific contribution of the solid surface. This method calculates the specific interactions through the measurement of I_{CH2} , *the shift of CH2 index*, of polar probes. The significance of I_{CH2} is well-defined in other paper of this ICCM.

In all of these methos it is necessary to use several organic probes with different acid-base characteristics. Then, probes with acid, amphoteric and base characters are used. Normally benzene, chloroform, ethyl acetate, diethyl ether, methylene chloride, acetone, tetrahydrofuran, are used, and all of them are characterized by their base and acid character according to their donor number (DN) and acceptor number (AN) respectively. Figure 2 shows a characteristic plot used for obtaining $) G_A^{SP}$ of carbon fibres.
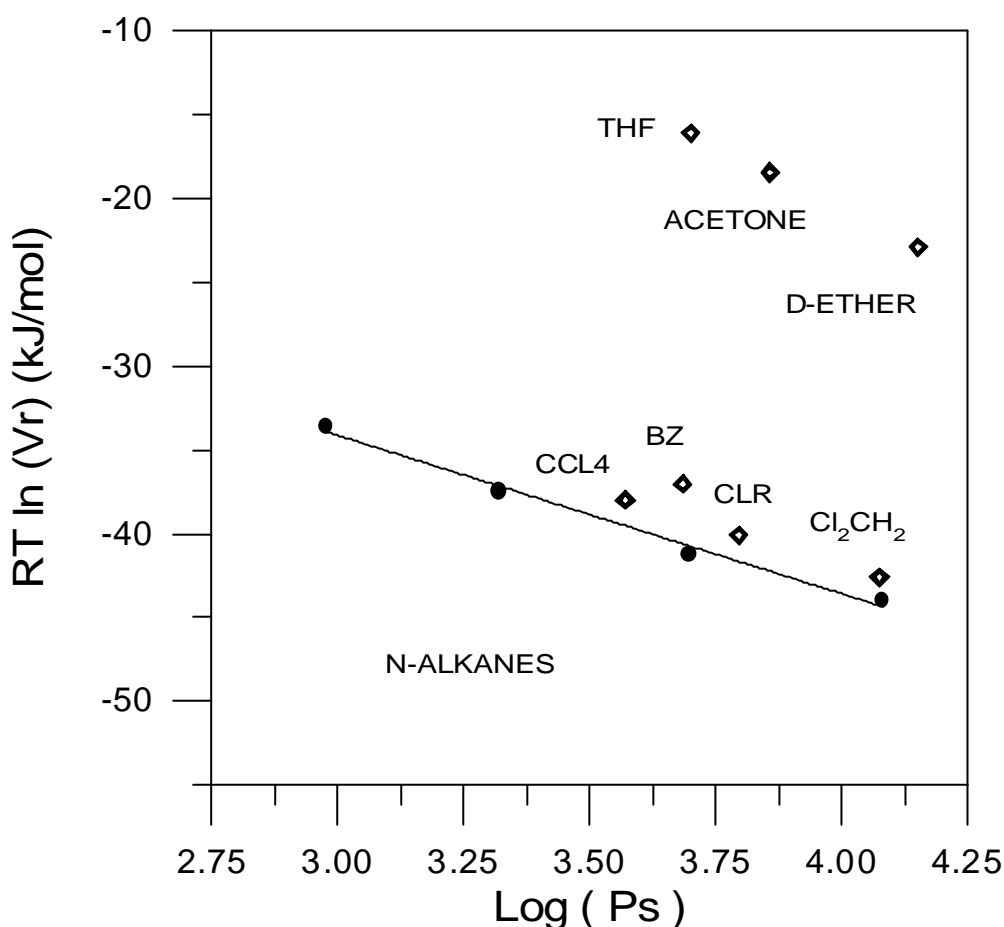

Fig. 2.- Adsorption free energy of polar probes vs log(Ps).

When $) G_A^{SP}$ is obtained by means of any of these above mentioned methos then the acid, k_A, and the base, k_B, characters of the solid surface are obtained according to the following equation:

$$) G_A^{SP} = k_A \, DN + k_B \, AN \qquad (4)$$

In this equation it is assumed that the acidic part of the probe interacts mainly with the base

part of the solid surface, and the base part of the probe interacts with the acidic part of the solid surface. This equation is a straight line where ΔG_A^{SP}, DN and AN are known, and therefore k_A and k_B can be determined. Figure 3 shows such plot for carbon fibres. Table 1 gives also k_A and k_B values for different materials used in composites.

Table 1.- Surface Properties of different materials.

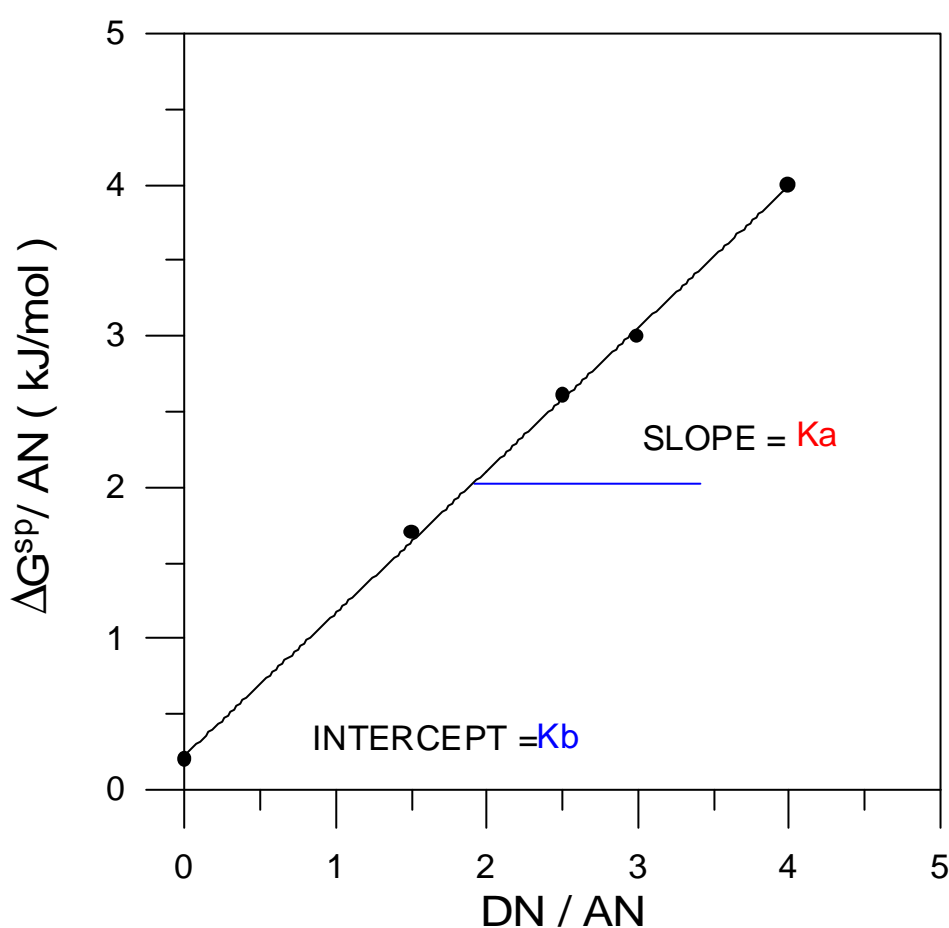|	Carbon Fibre	Glass Fibre	Silica particles	Epoxy resin	Polyethylene
γ_S^D	59	32	82	68	28
k_A	7.4	2.5	14.8	6.7	-
k_B	15.3	2.6	2.2	17.5	-

Fig. 3.- Determination of acid and base characteristics of the surface.

Hydroxyl and functional interactions.

It is well-known that in the just commented definition of acid-base interactions are included all possible type of specific interactions such as electron donor or electron acceptor,

hydrogen bonding, dipole-dipole, dipole-quadrupole, etc. However IGC allows to separate these interactions from the acid-base classification. This can be carried out by using organic

molecules of homologous series. "9). For example if we tray to determine the hydroxyl contribution of the solid surface then it is necessary to employ alcohols with different radical length such as methanol, ethanol, propanol, butanol, etc. Plotting the interaction energy of these molecules on the solid surface as a function of the radical length and also plotting the respective interactions of the same parent n-alkane molecules, then it will be observed that both curves approach when increase the radical length, and will be zero at high number of carbon atoms in the molecule. Extrapolation at zero radical length only the hydroxyl contribution will be obtained, i. e. k_{OH} . Obviously surfaces of high concentration of hydroxyls (glass fibres, oxidized carbon fibres, etc) give high values of k_{OH} .

This same analysis can be carried out with different functional groups such as: alcohol, amine, imine, nitrile, sulfide, chloride, B bonds, etc., and finally we will obtain a complete description of the physical-chemistry nature of the solid surface. Figure 4 shows this plot for the interaction of alcohols and benzene derivates on carbon fibres.

In summary, IGC at infinite dilution allows to determine different properties of any solid surface. These properties are: $(_S^D, k_A, k_B, k_{OH}, k_N, k_{Cl}, kB$, etc., and all of them can be determined for fibres, fillers and matrices widely used in preparing composite materials. This information will be used for predicting adhesion in composites as will show at the end of this work.
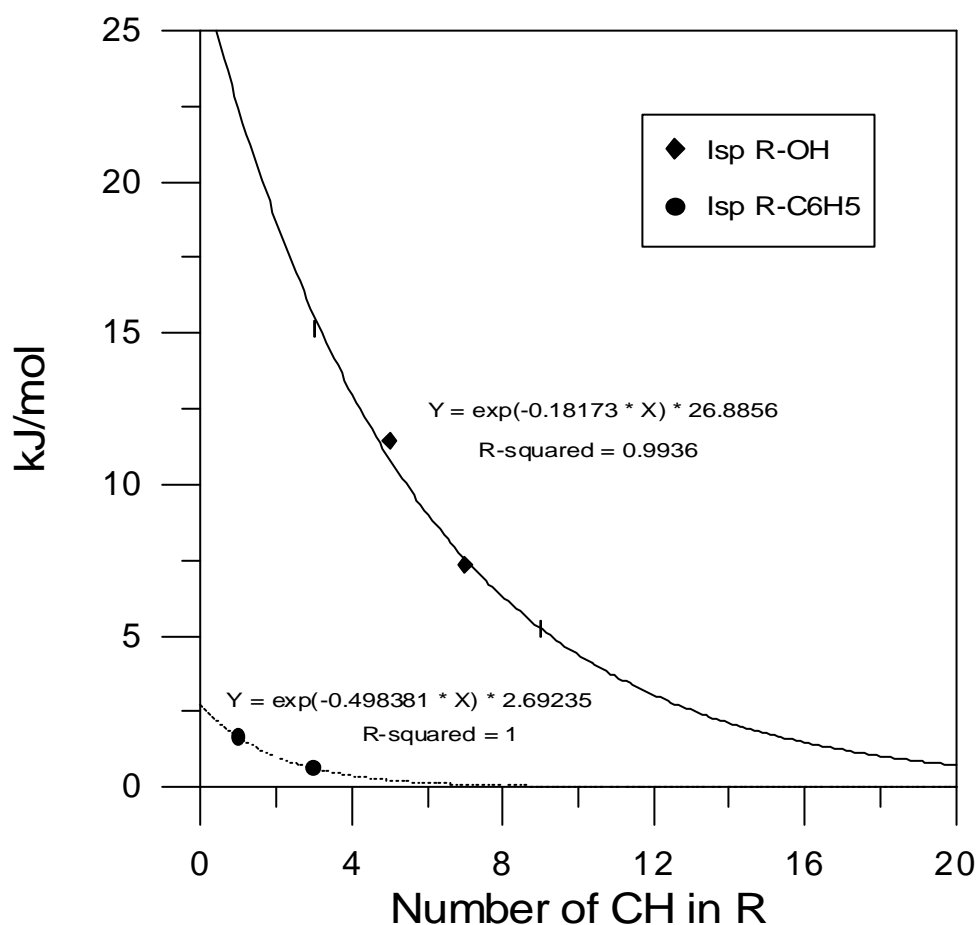

Fig. 4.- *Specific Interactions of homologous groups.*

IGC AT FINITE DILUTION

When high solute (probe) concentrations are used the IGC is the region of finite dilution. Here the solid surface can be covered by a monolayer or by multilayers of probe molecules obtaining the corresponding adsorption isotherms. By analysing isotherms obtained at different temperatures isosteric heats of adsorption, free energies and entropies of adsorption can be obtained. However these physic-chemical variables are of low interest by comparing them with the above mentioned obtained by IGC at zero coverage, i.e. ($_s^D$, k_A, k_B, k_{OH}, etc.

A very important information which can be obtained from adsorption isotherms is the surface energy distribution function F(U). This function corresponds to a picture of the different active sites or energy sites existing on the solid surface. F(U) is obtained from the adsorption isotherm by solving the integral adsorption equation:

$$V_N (p,T) = \textbf{m} v(p,T,U) F(U) dU \qquad (5)$$

where $V_N (p,T)$ is the experimental isotherm, $v(p,T,U)$ is the local isotherm and U the energy.

Several methos have been proposed for solving equation (5) and all of them are now

well-established ″10»... Any type of organic probe can be used for obtaining adsorption isotherms and their corresponding energy distribution function, thus by using n-alkanes only the distribution of dispersive sites will be obtained, and by using any specific probe distribution of acidic, base, hydroxyls, etc., will be also obtained. Figures 5 and 6 show different distributions of active sites of carbon fibres.
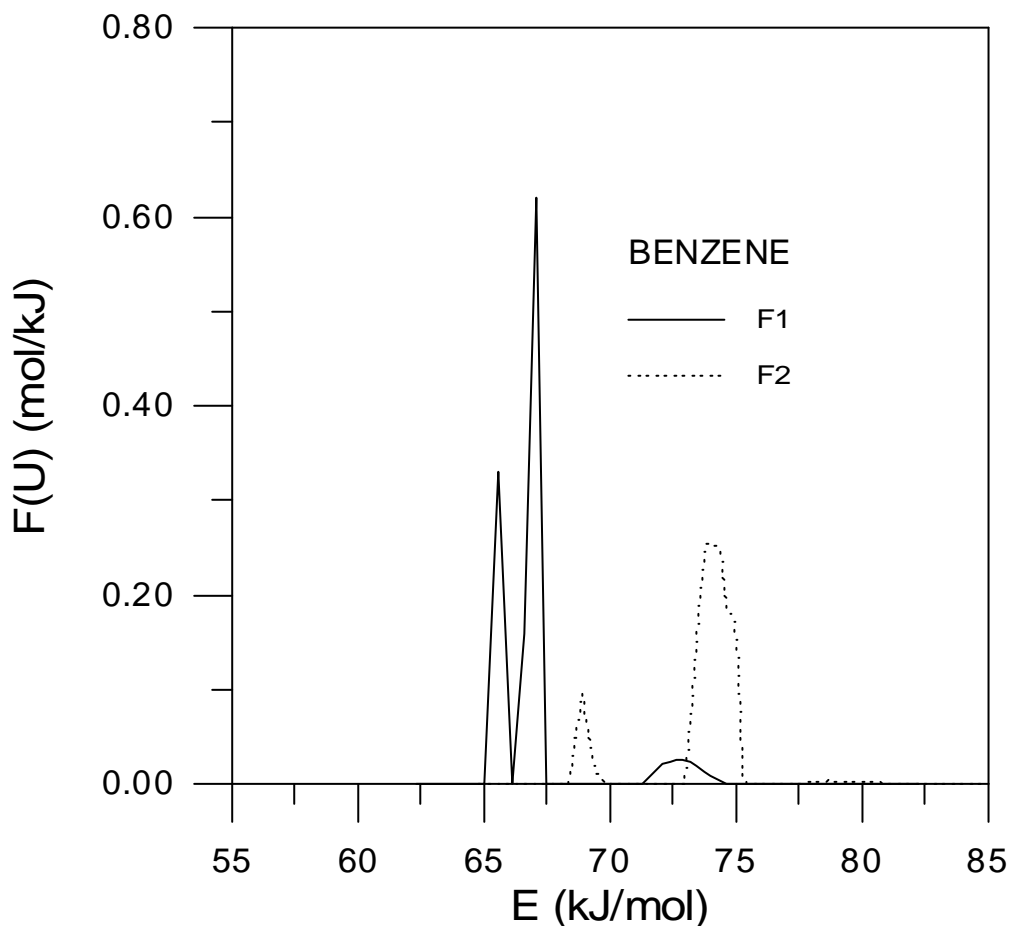

Fig. 5.- *Energy distribution functions of n-hexane on different carbon fibres.*
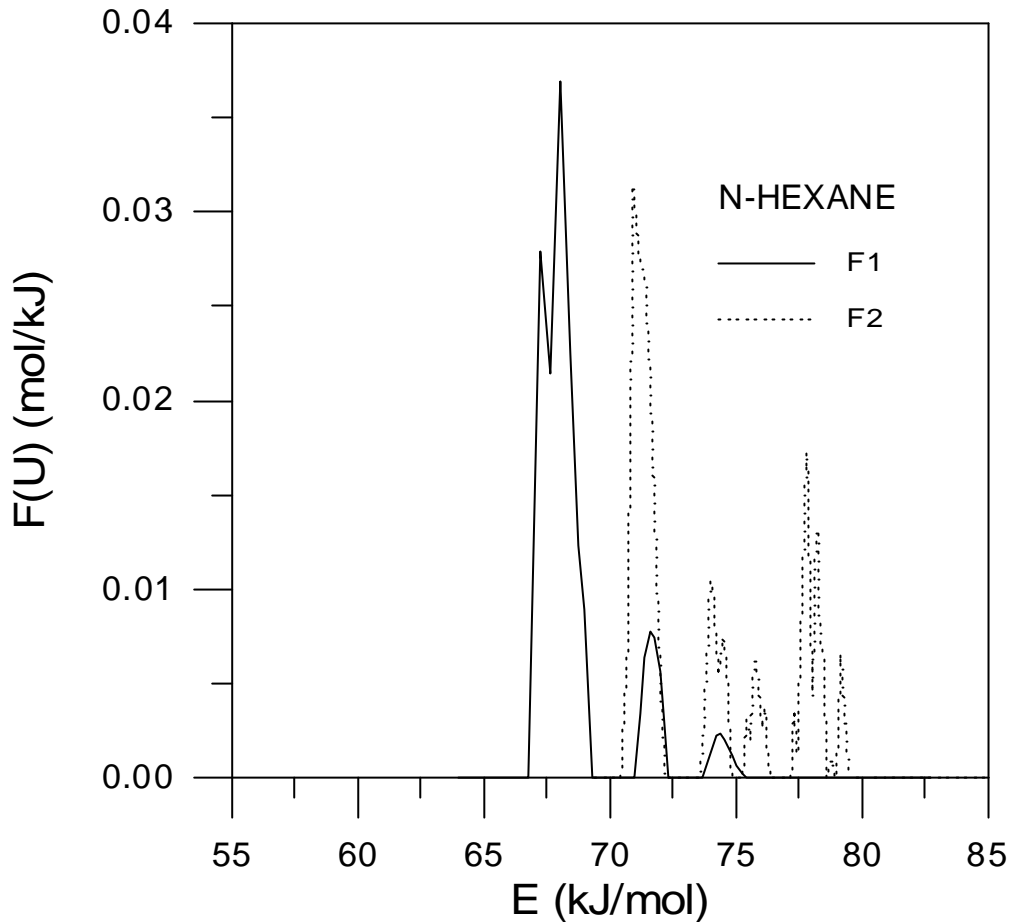
Fig. 6.- Energy distribution functions of benzene on different carbon fibres.

The distribution functions of active sites usually give different peaks each of them corresponding to a different active site existing on the solid surface. By numerical integration of these peaks it can be calculated the number of molecules which interact with each peak. If a given treatment is carried out then it is possible to follow the evolution of the active sites by analysing the energy distribution function.

APPLICATION OF IGC TO FIBRE-MATRIX ADHESION PROBLEMS

The IGC technique can be used for predicting fibre-matrix adhesion in composites. When a reinforcing fibre is mixed with a polymer matrix a given process take places where non-specific and specific active sites of both fibre and matrix interact continuously until an equilibrium is obtained. At the end of this process the adhesion between fibre and matrix will depend on the strong intensity of such interactions. It must be taken into account that different active sites with different character, acid, base, etc., can exist on both fibre and matrix, and therefore attraction and repulsion forces are possible to be developed during adhesion.

If no chemical reaction occurs between fibre and matrix during fabrication of composites, then only physical adhesion exists in the interface. This physical adhesion is expressed in the same for as equation (2), then the final work of adhesion, W_A, will be:

$$W_A = W_A{}^D + W_A{}^{SP} \qquad\qquad (6)$$

where A, D and SD represent adhesion, dispersive and specific respectively. Developing this equation for the interaction between a fibre and a matrix we obtain:

$$W_A = W_A{}^D{}_{fibre} * W_A{}^D{}_{matrix} + W_A{}^{SP}{}_{fibre} * W_A{}^{SP}{}_{matrix} \qquad\qquad (7)$$

If we assume that specific interactions are only characterized as acid-base, then equation (7) can finally be expressed as:

$$W_A = ((_{fibre}{}^D . (_{matrix}{}^D) + (k_{A,fibre}.k_{B,matrix} + k_{B,fibre}.k_{A,matrix}) \qquad\qquad (8)$$

Table 2 gives the results obtained for different fibre-matrix combinations in respect to their work of adhesion and mechanical properties of respective composites. All fibres are high strength carbon fibres, and matrices are of epoxy type "5›..

Table 2.- Relation between surface and mechanical properties of composites.

Composite	Dispersive Energy	Acid-Base Energy	Work of Adhesion	Interlaminar Shear Strength
F1 - R1	126.7	2.3	129.0	37 ± 3
F2 - R2	126.7	2.3	129.0	33 ± 5
F3 - R2	148.0	1.2	149.2	98 ± 4
F3 - R3	127.3	0.9	128.2	91 ± 5

According to these results it may be observed a good correlation between the fibre-matrix work of adhesion and the interlaminar shear strength of composites. In other works presented by our group "9,11›. at the ICCM-12 can be observed how IGC results also give good correlations with other composite properties.

CONCLUSIONS

We have tried to show in this paper how IGC can be used for a previous analysis of the interactions between fibres and matrices used in composites. Different physical-chemical properties can be obtained which characterize the surface of fibres and matrices. If these properties are known adhesion problems in composites can be further analysed. However more effort must be carried out in this respect and future work will show interesting results in the field of composite interfaces.

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