

## **VI. ANEXOS**



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## Fibres' Surface Mapping by Solvent Adsorption Methods

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### abstract

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## FIBRES' SURFACE MAPPING BY SOLVENT ADSORPTION METHODS

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### ABSTRACT

Inverse Gas Chromatography (IGC) has proved to be a suitable tool to study solid surfaces and their interaction capability. The solutes are *retained* in their way through the chromatographic column accordingly to their particular interaction with the stationary phase, which depends on the surface groups in the stationary phase and the solute nature. The retention volume,  $V_R$  is related to the free energy of adsorption and many thermodynamic parameters can be obtained from the experimental data.

Surface interactivity of fibers and fillers is of key importance in composite materials, particularly in CMCs. A new approach is proposed in this work, the main achievement being to bring acid-base characterisation of the surfaces to the same energetic scale than that of the London component of the free surface energy measured by the interaction of n-alkanes with the surface.

Traditionally, the main *reference set of probes* used in IGC at infinite dilution is the n-alkane series (R-H). The free energy of adsorption of the members of this series provides a significant value, *the free energy of adsorption of the CH<sub>2</sub> group*.

In this paper other homologous series are proposed as probes to obtain outstanding information of the surface characteristics, particularly the presence or not of potential hydrogen-bond sites. For this purpose n-alcohol series (R-OH), used as probes, can provide valuable information like *the free energy of adsorption of the OH group* with the surface that is clearly related to the acid-basic character of the surface.

In this paper we show a work carried out on different solid surfaces: polyethylene, clean glass fibre, sized glass fibre and carbon fibre where these magnitudes can be accurately evaluated and which allow to distinguish clearly different surfaces.

A new methodology is proposed which allows an *energetic surface mapping*.

The two homologous series here used as probes are n-alkanes (R-H) and n-alcohols (R-OH), as well as the widely acid-base solvent probes.

**KEYWORDS:** Surface Free Energy, Inverse Gas Chromatography, n-alkane series, n-alcohol series, surface mapping.

### INTRODUCTION

Reinforcing fibres, while able to carry only tensile load when in the form of non-impregnated strands, contribute most of the tensile, compressive, flexural and shear stiffness and strength of FRP laminates. The remarkable synergistic relationship between resin and reinforcement is highly dependent on the good adhesion at the interface between the fibre and the matrix. Reinforcement of marine FRP laminates is provided almost universally by glass fibres, especially E-glass fibres. Aircraft structures are mostly built with carbon fibre reinforced polymers. The deep knowledge of surface activity of commercial fibres will contribute to improve the choice of the manufacturing process parameters.

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, being in this case the column material to be investigated.

Injecting a minimum vapour amount of solutes, in the limit of FID detector sensitivity, allows assuming that no solute-solute interactions take place, only solid-solute interactions occur. In these conditions, Henry's law can be applied and the proportion of adsorbed solute, and therefore the retention volume  $V_R$ , is practically independent of the probe concentration.<sup>1-2</sup>

The retention volume ( $V_R$ ) of a solute is related to standard variation of the free energy of adsorption according to

$$-\Delta G_A = R T \ln V_R + C \quad (1)$$

where  $C$  is a constant that depends on the reference state<sup>3</sup>,  $R$  is the gas constant and  $T$  is the column temperature in °K

According to Fowkes<sup>4</sup>, the solid surface is a set of different accessible active sites of different nature and heterogeneous character. The surface energy,  $\gamma_s$ , is the sum of the free energy of all of those active sites. Generally,  $\gamma_s$  can be split in two components

$$\gamma_s = \gamma_s^d + \gamma_s^{sp} \quad (2)$$

where  $\gamma_s^d$ , or the London component of the free energy, is the sum of the free energy of those active sites non-polar, that can only interact with in-coming molecules, with dispersive interactions, and  $\gamma_s^{sp}$ , or the Specific component of the free energy, is the sum of surface free energy, of all other specific active sites of polar nature, with different character and intensity.

Van der Waals attractions are widely accepted to be three main types<sup>5</sup>:

- a) Keesom Interactions (dipole-dipole)
- b) Debye Interactions (dipole-induced dipole)
- c) London Dispersion (induced dipole-induced dipole)

When injecting n-alkane in a column  $X$ , we obtain  $\Delta G_{CH_2}$  (free energy of adsorption of a methylene group) from the slope of the line obtained when plotting  $\Delta G_A$ , versus number of carbon atoms. This work of adhesion lacks of Keesom type interactions but on heterogeneous surfaces, it encloses also the interaction of the methylene group with polar sites on the surface, so the following expression is traditionally used

$$W_{aCH_2} = W_{aCH_2 \text{ London}} = 2 (\gamma_{CH_2}^d * \gamma_X^d)^{1/2} \quad (3)$$

according to Fowkes's expression<sup>6</sup>, taking for  $\gamma_{CH_2}^d$  the surface energy of members of the n-alkane series<sup>7</sup>, or that of polyethylene. Therefore the value  $\gamma_X^d$  can be calculated.

This value however, encloses both types of interactions, London and Debye, when n-alkanes are retained by the solid surface. Up to date no method has been described to distinguish in the  $\gamma_X^d$  calculated value, the fraction of purely unspecific sites and that fraction which is originated by the Debye interaction of polar sites with n-alkanes. How to split these two terms of the London component is the main object of this work.



In this paper a method is proposed to obtain a specific/unspecific fractional distribution of the surface sites, and also an energetic distribution.

The study of the interaction of the series of n-alcohols can provide a good evidence of the presence or absence of potential hydrogen-bridge formers among the basic sites of the surface.

One of the problems found in the calculation of the specific components of surfaces described in the literature has the origin in the energy units used for the work of adsorption of the polar probes, their donor and acceptor numbers, and therefore the value of  $K_a$  and  $K_b$  calculated.

### TRADITIONAL CALCULATION OF $K_a$ AND $K_b$ OF A SURFACE THROUGH INJECTION OF POLAR PROBES

All methods described in the literature rely on the same philosophy. The free energy of adhesion is plotted versus a *chosen property* of the probes, which is likely to be in close relation with the *dispersive potential interactivity* of the molecule. The series of n-alkanes are included in this plot, which show a linear relation between the chosen property and the free energy of adhesion. The key point is to accept that, for a given polar probe, with a given value in the chosen characteristic, its dispersive work of interaction with the solid stationary phase, is the same, that the interaction of the hypothetical n-alkane with the same value in the chosen property. Among the chosen properties proposed by different authors are:  $\log P^{0.8}$ ,  $\alpha (\gamma_L^d)^{1/20}$ , boiling temperatures  $T_b^{10}$ , molecular refraction  $P_D^{11}$ , polarizability function<sup>12</sup>, a new topology index,  $\chi_T$ , is defined for this application<sup>13</sup>. We proposed a method<sup>14</sup> in the same line, where the chosen property was the Kóvats index of the probe on a non-polar column like polyethylene.  $K_a$  and  $K_b$  were calculated by plotting  $I_{sp}/AN$  of each polar probe, versus  $DN/AN$ . The slope being  $K_{a_s}$ , and  $K_{b_s}$  the intercept, assuming the equation

$$I_{sp} = K_{a_s} * DN_{probe} + K_{b_s} * AN_{probe} \quad (4)$$

We think that in most methods, too much free energy of adsorption is subtracted from the total interaction to find the specific fraction. With exception of J.B. Donnet et al.<sup>13</sup>, Vidal et al.<sup>15</sup>, and E. Brendlé et al.<sup>14</sup> approaches, all properties are greatly conditioned by, not only dispersive interactions between polar probes molecules but by also by molecule-molecule interactions of polar character.

Other important drawback of this methodology is that, although in principle  $DN/AN$  are meaningful figures provided that donor and acceptor numbers are normalised in the same scale, *Isp energy values are in a totally different scale than AN or DN values*. The consequence is that the plot of  $I_{sp}/AN$  versus  $DN/AN$  will produce  $K_a$  and  $K_b$  data in *arbitrary energy units* which only have a limited comparative value.

In this paper we propose new AN and DN numbers in *carbon index scales*, which is the same scale used to measure  $W_a$  of probes.

### EXPERIMENTAL

The instrument used is a Perkin Elmer Autosystem. The detector is flame ionisation (FID) in the highest sensitive range, in the limit of detection. The amount of probes injected is 0.01 to 50  $\mu$ l of gas, taken from the headspace of the vessels, to be sure of working at infinite dilution. The carrier gas is helium and the flow rates are in the range of 3 to 30 ml/min for each solid stationary phase studied.

Dead retention time,  $t_{M,}$ , is calculated by mathematical fitting of expression

$$(t_E - A) = \exp(B + Cn) \quad (5)$$

Therefore for  $n = 0$ ,

$$t_M = A + \exp B \quad (6)$$

which would be the retention time of an hypothetical n-alkane with 0 number of carbon atoms. The retention time of each member of the series of n- alkanes is

$$t_{Ri} = t_{Ei} - t_M \quad (7)$$

The fibres studied are

E-Glass fibre available in the laboratory with polyester sizing, and this same fibre solvent extracted.

Non-sized AS4 carbon fibre of Hexcel Composites.

The reference material is ground polyethylene (1- 5  $\mu\text{m}$  diameter grain size).

All materials were introduced in Teflon tubing of 1/4" or 1/8" outer diameter,  $V_R$  are *adjusted retention volumes*, calculated through

$$V_R = F_a (T_r/T_a) t_R \quad (8)$$

Where  $F_a$  is the carrier gas flow rate, measured at the column outlet at ambient pressure, and temperature ( $T_a$ ),  $T_r$  is the reference temperature 25°C.

All probes injected for are HPLC quality.

## RESULTS AND DISCUSSION

### POLYETHYLENE, PE, AS REFERENCE MATERIAL

The work of adsorption of any molecule can be expressed in different energy units. One of the most convenient is the before mentioned  $\text{CH}_2$  <sub>index</sub> ( $I_X$ ) which is a slight modification of the well known Kòvats's index which value is independent of many variables like flow rate, column size, dead volume, % stationary phase, contact area, etc.  $I_X$  is only dependent on the probe characteristics, the characteristics of the stationary phase, and the temperature<sup>16</sup>.

By definition, the  $I_X$  value for n-alkane series *in any column and temperature* is  $n$  for  $\text{C}_n \text{H}_{n+2}$

$I_X$  value, for any other molecule, is the work of adsorption of that molecule divided by the work of adsorption of the methylene group *in the same column and temperature*.

The polar probes in PE have a work of adsorption that result in different retention volumes and therefore different retention indexes. We observe that these indexes, on polyethylene are almost non-temperature dependent, as can be shown in tables 1 and 2.

**Table 1.  $I_X$  values of polar probes on PE**

Molecule	60°	70°	80°	85°	90°	Average
Chloroform	6.11	6.18	6.21	6.20	6.21	<b>6.18</b>
Acetone	4.82	4.67	4.87	4.82	4.70	<b>4.78</b>
Ethyl acetate	5.83	5.81	5.85	5.78	5.74	<b>5.80</b>
Diethyl oxide	5.08	4.98	5.11	5.02	4.94	<b>5.03</b>
Tetrahydrofuran	6.23	6.26	6.30	6.27	6.31	<b>6.27</b>
Acetonitrile	4.85	4.64	4.90	4.86	4.70	<b>4.79</b>
Methylene chloride	5.51	5.52	5.58	5.53	5.47	<b>5.53</b>
2-Propyl alcohol	4.71	4.69	4.73	4.72	4.61	<b>4.69</b>

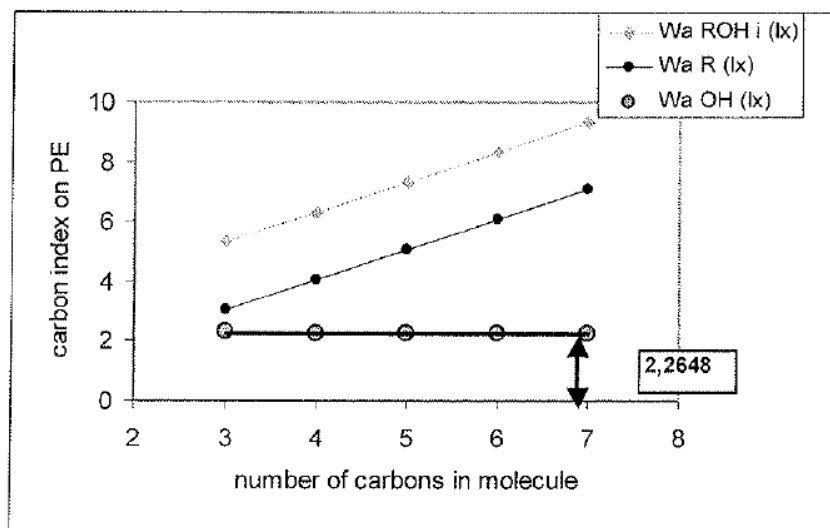
**Table 2. Ix values of n-alcohols on PE**

Molecule	60°	70°	80°	85°	90°	Average
Methanol	4.20	4.18	4.18	4.18	4.16	<b>4.18</b>
Ethanol	4.50	4.47	4.53	4.48	4.43	<b>4.48</b>
n-Propanol	5.28	5.33	5.36	5.34	5.26	<b>5.31</b>
n-Butyl alcohol	6.24	6.30	6.31	6.27	6.25	<b>6.28</b>
n-Pentyl alcohol	7.29	7.34	7.40	7.30	7.18	<b>7.30</b>
n-Hexyl alcohol	8.31	8.30	8.38	8.33	8.29	<b>8.32</b>
n-Heptyl alcohol	9.35	9.36	9.29	9.44	9.23	<b>9.34</b>
OH group	2.19	2.30	2.38	2.20	2.25	<b>2.26</b>

Ix of the hydroxyl group is obtained from the Ix of all members of the series of n-alcohols on PE. In fig.1 we see the Ix , average values, of ROH molecules on polyethylene versus number of CH<sub>2</sub> in the molecule. We obtain a line parallel to the n-alkane's where the *intercept* corresponds to Ix<sup>OH</sup> on PE. This value is

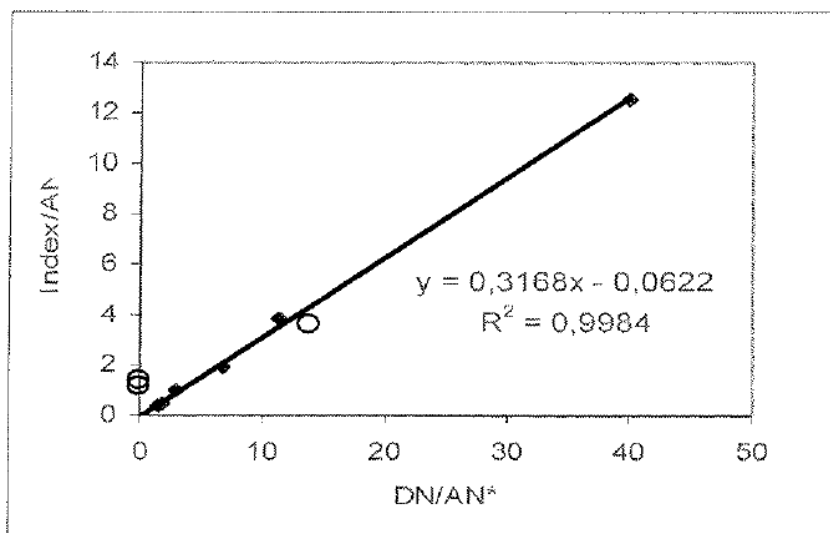
$$I_{x}^{OH} \text{ on PE} = 2.26 \pm 0.08 \quad (9)$$

The interaction of the polar probes with polyethylene surface is a two-term magnitude: one accounting the London interaction of the unspecific part of the probe molecule, and the other accounting Debye interactions with the polar part of the probe molecule. The expression governing these interactions is not known, but we find experimentally an approximately linear correlation when plotting DN/AN\* versus Ix/AN\* of acetone, ethyl acetate, tetrahydrofuran, acetonitrile, 2-propyl alcohol, methanol and ethanol on polyethylene as shown in fig.2. The outliers are chloroform, methylene chloride and ethyl ether.



**Fig.1. Carbon index of ROH homologous series on PE**





**Fig.2. Interaction of polar probes with PE**

DN and AN numbers used here are those given by V. Gutmann<sup>17</sup> F.L. Riddle Jr. and F.M. Fowkes<sup>18</sup> From the linear equation found we recalculate  $DN/AN^*$  values.

The linear relation shown in Fig.3 cannot be imputed to other than Debye interactions of polar probes with PE. Therefore we propose the following expression for these type of interactions

$$W_{\text{Debye}}(\text{probe L}) = \gamma_{\text{PE}} * \gamma_{\text{L}}^{\text{polar}} \quad (10)$$

and

$$\gamma_{\text{L}}^{\text{polar}} = (AN + DN)_{\text{L}} \quad (11)$$

With the  $DN/AN$  corrected values, and expressions 10 and 11 we calculate new AN and DN<sub>s</sub> for polar probes in index (on PE) energy units. These are shown in table 3

**Table 3. New values for  $AN^x$  and  $DN^x$  of polar probes, in index energy units on PE**

Probe	$DN/AN^{10,11}$	$DN/AN^*$ corrected	AN (index on PE)	DN (index on PE)
Chloroform	0	3.81	2.57	9.79
Acetone	6.80	6.23	1.32	8.23
Ethyl acetate	11.40	12.41	0.87	10.74
Diethyl ether	13.71	11.53	0.80	9.25
Tetrahydrofuran	40.00	39.80	0.31	12.24
Acetonitrile	3.00	3.41	2.17	7.41
Methylene chloride	0	4.67	1.95	9.10
Methanol	1.58	1.30	3.64	4.72
Ethanol	1.94	1.57	3.49	5.48
OH		1.01	2.25	2.28

### AN AND DN VALUES OF HYDROXYL GROUP, OH

In table 3 is also shown values for  $DN/AN$  and AN and DN numbers for the OH group. These are calculated in the following way.

Only three AN values of the series of n- alcohols are found in the literature: Methanol, Ethanol and Butanol. Methanol has enhanced OH polarity because of inductive effect of the  $CH_3-$  group. Ethanol shows the same effect but at a lesser extent because of the presence of the  $-CH_2-$  link. Butanol shows practically no inductive effect on the OH polarity. In the homologous series ROH. This inductive

effect decays exponentially with increasing number of carbon atoms in the series. The dipolar character of OH group tends to a constant value which we take as the dipole character of OH group. Experimentally we obtain this magnitude by adjusting AN values found in the literature for the n-alcohols series, to an exponential decay curve with increasing carbon number. The value obtained is

$$AN(OH) = 8.7449 \text{ kcal/mol in Riddel-Fowkes scale}^{19} \quad (12)$$

Introducing this value in the line of fig 2 we obtain DN/AN (OH), consequently we calculate AN and DN values of OH group in *carbon index units, on PE*, once we measure this magnitude from the carbon index numbers of the ROH series an extrapolate to number of carbons  $n = 0$ . This is shown in fig 4 and the value of  $Wa_{OH}$  in carbon index units on PE is found to be 2.2648

### ACID AND BASIC CHARACTER OF SEVERAL SOLID MATERIALS.

The plot of  $Wa/AN$  of several polar probes versus DN/AN values gives a line comprising the sum of two contributions: a) a line of interactions of polar probes with the fraction of unspecific active sites of the solid,  $S$ , and b) a line of interactions of polar probes with basic-acid sites of the solid surface,  $S$ . We disclose these two terms by splitting the  $Wa$  (probe L) /AN

$$Wa_{L, \text{ total}} / AN_L = Wa_{L, \text{ with specific sites of } S} / AN_L + Wa_{L, \text{ with unspecific sites of } S} / AN_L \quad (13)$$

where

$$Wa_{L, \text{ with specific sites of } S} = (AN_L * Kb_S + DN_L * Ka_S) + \gamma_L^d * (Ka_S + Kb_S) \quad (14)$$

$$Wa_{L, \text{ with unspecific sites of } S} = \gamma_S^d \text{ pure} (AN_L + DN_L) + 2 * (\gamma_S^d \text{ pure} * \gamma_L^d)^{1/2} \quad (15)$$

$$\gamma_S \text{ total} = Ka_S + Kb_S + \gamma_S^d \text{ pure} \quad (16)$$

In fig 3 we show the good correlations found in these plots on PE, non-sized carbon fibre, clean glass fibre and sized glass fibre. The four polar probes chosen are THF as basic, acetone and ethyl acetate as amphoteric and OH group as acid.

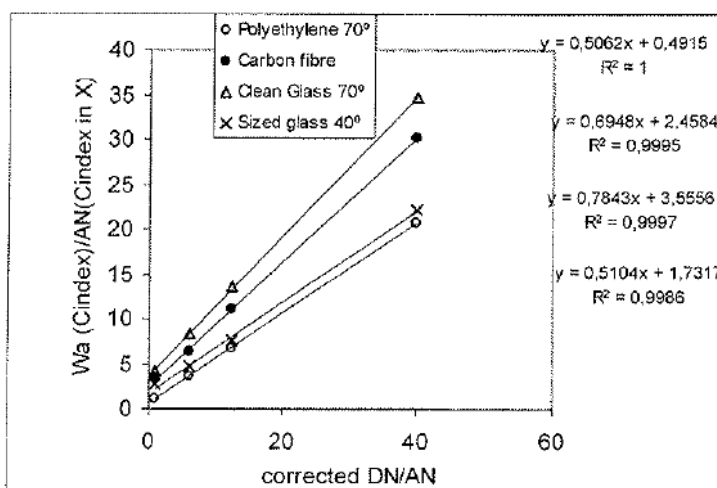
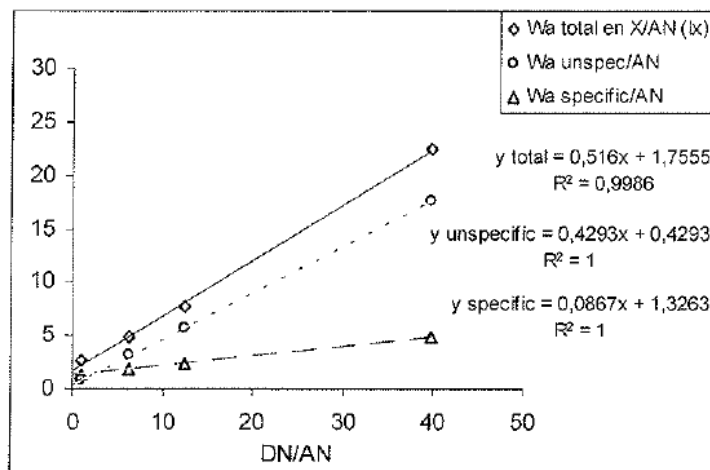


Fig.3.  $Wa_{L, \text{ total}} / AN_L$  versus  $(DN/AN)_L$  in specific carbon index units

We could obtain  $Ka_S$  and  $Kb_S$  with eqs. 14 and 15 if we knew  $\gamma_L^d$  of each probe and  $\gamma_S^d \text{ pure}$ . As a first approximation we take  $\gamma_S^d \text{ pure} \approx \gamma_S^d \text{ total}$ , and  $\gamma_L^d \approx 0$  for these four probes to split lines of fig.3 in two lines.

The application of expressions 13, 14 and 15 to the four chosen probes simultaneously (acetone, ethyl acetate, tetrahydrofuran, and the hydroxyl group), allows us by minimizing deviations of  $(Wa/AN)$

experimental values from the calculated ones through the expressions 13, 14 and 15 to split the total line  $(W_a/AN) = f(DN/AN)$  in two lines according with expression 13. The solution of this system provides us with optimum values for  $Ka_s$  and  $Kb_s$ , and therefore the fractional contribution of the non-specific sites to the total surface energy, which we give as an energetic map of the solid. As an example we show these splitting for the sized glass fibre in fig. 4.



**Fig.4. Total, specific and unspecific lines in the case of sized glass fibre.**

The slopes and intercepts obtained are used to evaluate the fractional energetic contributions to the total interaction, and the ratio slope/intercept of the *polar line*, as the  $(Ka_s / Kb_s)$  ratio.

The calculation of real  $Ka_s$  and  $Kb_s$  is done with  $W_a(OH)$  exclusively, where  $\gamma_L^d = 0$ , and therefore the second term in both expressions 14 and 15 are 0. We can thus obtain the three components of expression 16.

#### SURFACE MAPPING OF SEVERAL MATERIALS

Calculated  $\gamma_s^d$  pure,  $Ka$  and  $Kb$  of solid X we can map the surface as shown in table 4.

**Table 4. Surface map of several solid surfaces in kJ/mol. The total is  $\gamma_X^d + Ka_X + Kb_X$**

Material	Interaction energy fraction		London comp mJ/m <sup>2</sup>	Partial components in kJ/mol			kJ/mol
	%polar	%unspecific		Unspecific	Acid	Basic	
PE 70°C	0.01	0.99	40	1.4468	0.02	0.02	1.485
PE 80°C	-0.01	1.01	39	1.4063	-0.01	-0.01	1.388
Clean glass	0.79	0.21	33	1.1911	0.81	7.66	9.658
Sized glass	0.62	0.38	30	1.0788	0.28	4.21	5.568
Carbon fibre	0.61	0.39	61	2.2131	0.31	8.08	10.597

#### CONCLUSIONS

1. We can conclude from the results found that the *traditional total London component* of the surface is mainly an indication of the *concentration of active sites* giving no information of their energetic activity.
2. We propose new values of AN and DN for polar probes taking polyethylene as reference material and expressed in carbon number indexes.
3. We propose a method to evaluate AN number and DN number of hydroxyl group through the interaction of the n-alcohols with polyethylene.

4. We propose to use the work of adsorption of the hydroxyl group together with other three polar molecules to calculate unspecific, acid and basic components of the free surface energy of solids in the same energy units
5. We show, using this methodology an approximate surface map of the surface of polyethylene, clean glass fibre, sized glass fibre and carbon fibre.

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## Polymeric Resins and Their Potential Interactivity with Solid Reinforcements: The Hydrogen Bond

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### abstract

In reinforced polymers technology, the good adhesion between matrix resin and the reinforcement is of key importance. Both parts of the interface play a role and contribute to the adequate adhesion. In the side of the resin, or organic character, functional groups dominate the adhesion capability of the polymeric part to the reinforcement. Inverse gas chromatography (IGC) is a good tool to study surface sites of powders. In this paper, three cured resins of common use in composites are studied under the perspective of their surface activity.

### conference

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### terms

Solid Polymers  
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## POLYMERIC RESINS AND THEIR POTENTIAL INTERACTIVITY WITH SOLID REINFORCEMENTS: THE HYDROGEN BOND

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### ABSTRACT

In reinforced polymers technology it is of key importance the good adhesion between matrix resin and the reinforcement. Both parts of the interface play a role and contribute to the adequate adhesion. In the side of the resin, of organic character, functional groups dominate the adhesion capability of the polymeric part to the reinforcement.

Inverse Gas Chromatography, IGC, is a good tool to study surface sites of powders. In this paper three cured resins of common use in composites are studied under the perspective of their surface activity.

Traditionally, the main *reference set of probes* used in IGC at infinite dilution is the n-alkane series (R-H). The free energy of adsorption of the members of this series provides a significant value: *the free energy of adsorption of the CH<sub>2</sub> group*.

In this paper n-alcohol homologous series, ROH, are used as probes to obtain outstanding information of the surface characteristics.

The first result is *the free energy of adsorption of the OH group*, in close relation with the acid-basic character of the surface.

The second interesting result is the observation of the *anomalous free energy of adsorption of the lower members of the series*, which we think is closely related to the formation of hydrogen-bridge bonds.

Solid cured phenolic, furanic, cyanoester and PPS resins are studied, and their capability to form hydrogen-bridge bonds evaluated.

**KEYWORDS:** Solid polymers, Inverse Gas Chromatography, n-alcohol series, hydrogen-bridge bonding.

### INTRODUCTION

Among the most widely used resins are the phenolics. This family of thermosetting polymers have a complete name of polyphenolformaldehyde and acronym for these resins is PF. The main functional groups in the polymer network are *aromatic rings, OH groups and alkyl chains*.

Furanic resins are the linear condensation products of furfuryl alcohol or other self- or co-condensates containing furan rings. The acid-catalysed self-condensation reaction leads to the formation of linear oligomers containing mainly *methylene and methylene-ether linked to furan-ring groups*.

Cyanate ester resins are rapidly expanding in the aerospace industry. They are formed by the reaction of corresponding phenols with cyanogen halides. The functional groups always present in their network are *aromatic rings, -OCN groups and alkyl radicals*.

Poly (*p*-phenylene sulfide), PPS, is classified as an engineering thermoplastic because it possesses a favourable combination of mechanical, electrical, thermal and flame-resistant properties. They are formed by reaction of *p*-dihalogenbenzene and sodium sulfide. The functional groups present in the network are *aromatic rings, -S- and -S-S- groups*

The functional groups present in the polymer network are the anchorage tools to adhere properly on the reinforcement surface. In these polymers hydrogen-bridge bonding plays an important role. We pay

particular attention to this in the study presented here. We should study the resin character in a non-cured or perhaps B stage to go to the real situation when reinforcement and matrix form the interface, but as in those stages the polymeric systems are dynamic, we choose to study stable cured resin powders under the assumption that functional groups, in the polymer are the same than in the intermediate B stage, which is not always strictly true.

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, being in this case the column material to be investigated.

Injecting a minimum vapour amount of solutes, in the limit of FID detector sensitivity, allows assuming that no solute-solute interactions take place, only solid-solute interactions occur. In these conditions, Henry's law can be applied and the proportion of adsorbed solute, and therefore the retention volume  $V_R$ , is practically independent of the probe concentration.<sup>1-2</sup>

The retention volume ( $V_R$ ) of a solute is related to standard variation of the free energy of adsorption according to

$$-\Delta G_A = R T \ln V_R + C \quad (1)$$

where C is a constant that depends on the reference state<sup>3</sup>, R is the gas constant and T is the column temperature in °K.

According to Fowkes<sup>4</sup>, the solid surface is a set of different accessible active sites of different nature and heterogeneous character. The surface energy,  $\gamma_s$ , is the sum of the free energy of all of those active sites. Generally,  $\gamma_s$  can be split in two components

$$\gamma_s = \gamma_s^d + \gamma_s^{sp} \quad (2)$$

where  $\gamma_s^d$ , or the London component of the free energy, is the sum of the free energy of those active sites non-polar, that can only interact with in-coming molecules, with dispersive interactions, and  $\gamma_s^{sp}$ , or the Specific component of the free energy, is the sum of surface free energy, of all other specific active sites of polar nature, with different character and intensity.

When injecting n-alkane in a column S, we obtain  $\Delta G_{CH_2}$  (free energy of adsorption of a methylene group) from the slope of line obtained when plotting  $\Delta G_A$ , versus number of carbon atoms.

where according to Fowkes's expression<sup>5</sup>

$$W_{a_{CH_2 \text{ London}}} = 2 (\gamma_s^d \gamma_{CH_2}^d)^{1/2} \quad (3)$$

N-alcohols are, contrarily to hydrocarbons, *heterogeneous molecules*. The chain is of the same nature than hydrocarbons, and the hydroxyl group, a permanent dipole of amphoteric character.

We find that Voelkel et al.<sup>6</sup> relate directly the hydrogen bonding interactions ( $I_{12b}$ ) with the solubility parameters of n-alcohols compared with those of n-alkanes in some oligoethers, finding that these parameters decrease rapidly with the increasing length of the apolar hydrocarbon chain. The solubility parameters are determined by Voelkel et al.<sup>7</sup> by inverse gas chromatography.

Similarly we consider that the work of adsorption of the lower members of n-alcohols provides a similar evidence of the presence of hydrogen bridge bonds between the solute and the solid surface in the column. We, propose in this paper to distinguish the acid-base type interaction of the -OH group, as an amphoteric

radical, from the particular hydrogen bridge interaction with those solids, like some liquid resins with appropriate functional groups.

The hydrogen bond<sup>8</sup> is a term given to the secondary interaction between a hydrogen atom bound to an electronegative atom and another atom which is also generally electronegative and which has one or more lone pairs and can thus act as a base. A generalised representation of a hydrogen bond can be  $X^{\delta-} \cdots H^{\delta+} \cdots Y^{\delta-}$ . Main proton donors are N-H, O-H and F-H, and the most commonly encountered hydrogen bonds are  $O^{\delta-} \cdots H^{\delta+} \cdots O$  and  $N^{\delta-} \cdots H^{\delta+} \cdots N$ . 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  $\pi$ -systems like polarizable double bonds or aromatic ring systems. The energies of these bonds lie in the range 4-40 kJ/mol according to literature.

When injecting ROH series on columns filled with polymeric solids with functional groups such as those present in the resins that we study here, hydrogen-bridge bond interactions should be expected. We observe that the lower members of the series have an anomalous high retention and we propose in this paper that this effect is directly related to this type of bond.

### EXPERIMENTAL

The instrument used is a Perkin Elmer Autosystem. The detector is flame ionisation (FID) in the highest sensitive range, in the limit of detection. The amount of probes injected is 0.01 to 50  $\mu$ l of gas, taken from the headspace of the vessels, to be sure of working at infinite dilution. The carrier gas is helium and the flow rates are in the range of 3 to 30 ml/min for each solid stationary phase studied.

Dead retention time,  $t_{M,}$ , is calculated by mathematical fitting of expression

$$(t_E - A) = \exp(B + Cn) \quad (4)$$

Therefore for  $n = 0$ ,

$$t_M = A + \exp B \quad (5)$$

which would be the retention time of an hypothetical n-alkane with 0 number of carbon atoms. The retention time of each member of the series of n-alkanes is

$$t_{Ri} = t_{Ei} - t_M \quad (6)$$

Cured Furanic (Fuy) and cured phenolic (Fe-1) resins of Bakelite Iberica S.A, cured cyanoester resin extracted from a carbon fibre prepreg of Fiberite and cured PPS resin extracted from a carbon fibre semipreg of Tencate Advanced Composites were studied. The formers were introduced in the column as grinded powder, the later was solvent-extracted from a prepreg and glass beads were impregnated with the extract. The beads were heated until a complete curing is achieved. Grinded polyethylene (1- 5  $\mu$ m diameter grain size) was used as reference material.

All materials were introduced in Teflon tubing of 1/4" or 1/8" outer diameter,  $V_R$  are *adjusted retention volumes*, calculated through

$$V_R = F_a (T_r/T_a) t_R \quad (7)$$

Where  $F_a$  is the carrier gas flow rate, measured at the column outlet at ambient pressure, and temperature ( $T_a$ ),  $T_r$  is the reference temperature 25°C.

All probes injected for measurements are HPLC quality.

## RESULTS AND DISCUSSION

### POLYETHYLENE, PE, AS REFERENCE MATERIAL

The work of adsorption of any molecule can be expressed in different energy units. One of the most convenient is the before mentioned  $CH_2$  index, ( $I_x$ ) which is a slight modification of the well known Kovats's index which value is independent of many variables like flow rate, column size, dead volume, % stationary phase, contact area, etc.  $I_x$  is only dependent on the probe characteristics, the characteristics of the stationary phase, and the temperature<sup>9</sup>.

By definition, the  $I_x$  value for n-alkane series *in any column and temperature* is  $n$  for  $C_n H_{n+2}$

$I_x$  value, for any other molecule, is the work of adsorption of that molecule divided by the work of adsorption of the methylene group *in the same column and temperature*.

The polar probes in PE have a work of adsorption that result in different retention volumes and therefore different retention indexes. We observe that these indexes, on polyethylene are almost non-temperature dependant. The mean values measured experimentally are

**Table 1.  $I_x$  values of polar probes and n-alcohols on PE**

Molecule	Average	Molecule	Average
Chloroform	6.18	Methanol	4.18
Acetone	4.78	Ethanol	4.48
Ethyl acetate	5.80	n-Propanol	5.31
Diethyl oxide	5.03	n-Butyl alcohol	6.28
Tetrahydrofuran	6.27	n-Pentyl alcohol	7.30
Acetonitrile	4.79	n-Hexyl alcohol	8.32
Methylene chloride	5.53	n-Heptyl alcohol	9.34
2-Propyl alcohol	4.69	OH group	2.26

$I_x$  of the hydroxyl group is obtained from the  $I_x$  of all members of the series of n-alcohols on PE. In fig.1 we see the  $W_a$  of ROH molecules on polyethylene versus number of  $CH_2$  in the molecule. We obtain a line parallel to the n-alkane's where the *intercept* corresponds to  $W_a^{OH}$  on PE. This value expressed in  $I_x$  is

$$I_x^{OH} \text{ on PE} = 2.26 \pm 0.08 \quad (8)$$

The interaction of the polar probes with polyethylene surface is a two-term magnitude: one accounting the London interaction of the unspecific part of the probe molecule, and the other accounting Debye interactions with the polar part of the probe molecule. The expression governing these interactions is not known, but we find experimentally an approximately linear correlation when plotting  $DN/AN^*$  versus  $I_x/AN^*$  of acetone, ethyl acetate, tetrahydrofuran, acetonitrile, 2-propyl alcohol, methanol and ethanol on polyethylene.

$DN$  and  $AN$  numbers used here are those given by V. Gutmann<sup>10</sup> F.L. Riddle Jr. and F.M. Fowkes<sup>11</sup> From the linear equation found we recalculate  $DN/AN^*$  values.

The linear relation shown in Fig.3 cannot be imputed to other than Debye interactions of polar probes with PE. Therefore we propose the following expression for these type of interactions

$$W_{a,Debye}(\text{probe L}) = \gamma_{PE} * \gamma_L^{polar} \quad (9)$$

and 
$$\gamma_L^{polar} = (AN + DN)_L \quad (10)$$

With the  $DN/AN$  corrected values, and expressions 9 and 10 we calculate new  $AN$  and  $DN$ s for polar probes in index (on PE) energy units. These are shown in table 2



**Table 2. New values for AN<sup>x</sup> and DN<sup>x</sup> of polar probes, in index energy units on PE**

Probe	DN/AN <sup>10,11</sup>	DN/AN* corrected	AN (index on PE)	DN (index on PE)
Chloroform	0	3.81	2.57	9.79
Acetone	6.80	6.23	1.32	8.23
Ethyl acetate	11.40	12.41	0.87	10.74
Diethyl ether	13.71	11.53	0.80	9.25
Tetrahydrofuran	40.00	39.80	0.31	12.24
Acetonitrile	3.00	3.41	2.17	7.41
Methylene chloride	0	4.67	1.95	9.10
Methanol	1.58	1.30	3.64	4.72
Ethanol	1.94	1.57	3.49	5.48
OH		1.01	2.25	2.28

### HYDROGEN-BRIDGE BOND

Each alcohol will have, in contact with a heterogeneous surface, a complex mixture of works of interaction. The resulting is reflected in the retention volume  $V_{R,ROH_i}$ . We consider this work of adhesion  $W_{a,ROH_i}$  to be the result of adding the work of adhesion of the chain and the hydroxyl group, therefore

$$W_{a,ROH_i} = W_{a,R_i} + W_{a,OH_i} \quad (11)$$

The alkyl chain of n-alcohols behaves as the hydrocarbon chain and we obtain also a line when plotting  $R T \ln V_R$  of ROH<sub>i</sub> versus number of CH<sub>2</sub> groups. From the slope of this line on S we can obtain  $W_{a,CH_2ROH_i}$  and

$$W_{a,R_i} = n * (W_{a,CH_2ROH_i}) \quad (12)$$

where  $n$  is the number of CH<sub>2</sub> groups in -R.

Eqs. 11 and 12 allow to calculate  $W_{a,OH_i}$  for all members of ROH series.

The hydroxyl group, -OH, has no possibility of London-type interactions and its work of adsorption can be split in two terms

$$W_{a,OH_i} = W_{a,OH_i \text{ Debye}} + W_{a,OH_i \text{ Keesom}} \quad (13)$$

the first term enclosing the Debye interaction of the dipole -OH with the dispersive component of the solid surface according to Gutiérrez's proposal<sup>12</sup>

$$W_{a,OH \text{ Debye}} = \gamma_S^d (AN_{OH} + DN_{OH}) \quad (14)$$

and the second term enclosing the acid-base interaction of the -OH with the acid and basic sites of the solid surface. Accepting the simplest equation used in the literature<sup>13</sup>

$$W_{a,OH_i \text{ Keesom}} = K_{a_S} * DN_{OH} + K_{b_S} * AN_{OH} \quad (15)$$

When injecting ROH members in columns with solid resins we observe, as mentioned before, retention patterns like those shown in Fig. 1



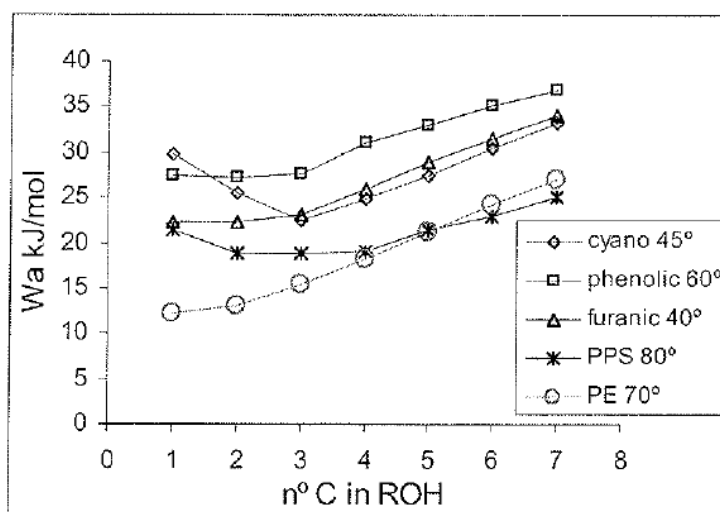


Fig. 1. Retention of ROH members on solid organic resins, in kJ/mol

In this figure we can compare the interaction of the *n*-alcohols with PE, as reference material, and the interaction of that homologous series with different solid resins.

We observe that the slope of the alkyl chain, compared with that of *n*-alkanes, is not the same in all the solid resins. In PE we know that is slightly higher than 1, while that of *n*-alkanes is by definition 1. The slope < 1 means a certain type of *orientation* of the molecules when travelling through the column. A higher affinity of the -OH group with the surface active sites will lead to a lower slope in the chain and at the same time a higher -OH interaction compared with the interaction of the CH<sub>2</sub> group. In a sense this is a measure of the polarity of the surface. We can observe that the phenolic and PPS resins are clearly more polar than the rest. In table 3 we show these slope values

Table 3. Wa CH<sub>2</sub> in Ix, of the alkyl chain of alkanes and alcohols on several resins

Wa CH <sub>2</sub> in Ix	Polyethylene	Cyano 45°	Furanic 40°	PPS 80°	Phenolic 60°
<i>n</i> -alkanes	1.00	1.00	1.00	1.00	1.00
<i>n</i> -alcohols	1.009	0.997	0.983	0.7405	0.7383

We also observe different adsorption patterns in the lower members of the ROH molecules.

We can say, that in polyethylene, where hydrogen-bridge bond is not possible, the *inductive effect* of the chain produces, in methanol, an increase of the -OH group adsorption of 0.90 Ix<sub>PE</sub> units caused by the higher AN\* value of this alcohol if compared with higher members of the series, in ethanol this increase is 0.20 Ix<sub>PE</sub> units, 0.02 Ix<sub>PE</sub> units in *n*-propanol and practically 0 in the rest of the members of the series.

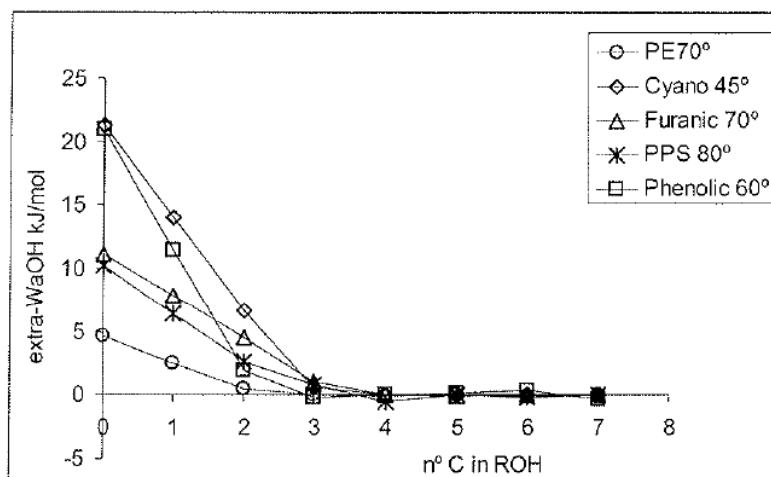
An alkyl chain, C<sub>3</sub>-C<sub>2</sub>-C<sub>1</sub>-X, linked to atom with higher electron affinity than C, will cause a shift of the σ electrons of the covalent bond towards the atom X, causing a slight positive charge in the C<sub>1</sub> atom, which in turn will attract to itself the σ electrons of the neighbouring C<sub>2</sub>-C<sub>1</sub> bond, effect that will propagate along the chain. This displacement of electrons is permanent and decreases drastically when increasing the distance to the focus. In practice can be neglected from the second carbon atom on<sup>14</sup>. This electron shift will weaken the O-H bond and consequently an increase in AN value of methanol should be observed while there is no reason for a change in DN value of the molecule. Values of AN and DN given in the literature for methanol, ethanol and butanol are in table 4 and are in agreement with this hypothesis.

**Table 4. AN and DN values of n-alcohols reported in the literature.**

Molecule	AN* <sup>15</sup> kcal/mol	DN <sup>16</sup> kcal/mol
Methanol	12.0	19.0
Ethanol	10.3	20.0
n-Butanol	9.1	
Water	15.1	18.0

The hydrogen bridge bond provokes the same electron shift in the O-H bond, but the origin is external to the alcohol molecule from certain basic sites of the solid surface. An extra-interaction of the type acid-base occurs and a way to measure the potentiality of a surface to form this type of bond is the consideration of this extra-interaction.

In fig. 2 we can observe the extra-retention of lower members of the series compared with the retention line that form the higher members of n-alcohol series. Extrapolation of these lines to  $n^{\circ}C=0$ , drawing a line ethanol-methanol, gives a new extra-Wa OH adsorption value that should reflect the potentiality of hydrogen bond interaction. As by definition polyethylene has no potentiality at all, the magnitude that we propose is the difference of these extra-WaOH values and the value found in PE.



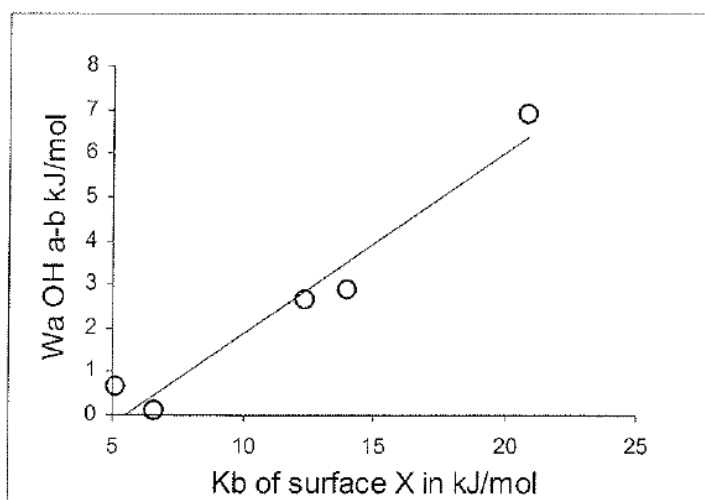
**Fig. 2. Extra-retention of ROH lower members on solid organic resins, in kJ/mol**

The Wa OH measured from the extrapolation to  $n^{\circ}$  of C = 0 in higher member of the ROH series is called OH a-b, and the Wa OH measured from extrapolation of methanol-ethanol line to  $n^{\circ}$  of C = 0, subtracted this value on polyethylene, is called OH h-bridge. In table 5 we show the measured data on several solid resins

**Table 5. Wa calculated for OH, for acid-base and hydrogen bridge interactions**

Material	OH a-b kJ/mol	OH h-bridge kJ/mol
Polyethylene 70°	6.55	0
Cyanoester 45°	13.51	16.70
Furanic 70°	12.43	6.54
PPS 80°	11.41	5.61
Phenolic 60°	23.22	16.32

As can be observed, these two Wa OH values have no relation, as Ka and Kb values of these solid surfaces have not necessarily direct relation with these extra-WaOH values which we think in relation with hydrogen bonding. On the contrary, Wa OH a-b values show a quite good correlation with calculated Kb values of the solid resins as shown in fig.3.



**Fig. 3. Correlation of Wa OH a-b values on cured organic resins and  $Kb_s$ , in kJ/mol**

Of the four cured resins studied we can say that

- a) Regarding acid-base surface activity the high-to-low order is

Phenolic > Cyanoester > Furanic > PPS

- b) Regarding hydrogen bonding surface activity the high-to-low order is

Cyanoester > Phenolic > Furanic > PPS

### CONCLUSION

1. We can *see* the presence of hydrogen-bridge bonding by injecting n-alcohols on the solid surface of resins with proton acceptor groups in their composition.
2. We propose a method to distinguish acid-base interaction of the amphoteric hydroxyl group from other specific interactions
3. We propose a method to estimate the potential interactivity of the cured solid resin with the hydroxyl group through hydrogen bridge bonding.
4. The projection of these results to choose the best processing resin in the manufacturing of reinforced composites is noted.

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## Solid surface mapping by inverse gas chromatography

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### Abstract

Inverse gas chromatography (IGC) at infinite dilution, is a technique for characterising solid surfaces. Current practice is the injection of *n*-alkane homologous series to obtain the free energy of adsorption of the CH<sub>2</sub> group, from which the London component of the solid surface free energy,  $\gamma_s^d$ , is calculated. A value around 40 mJ/m<sup>2</sup> is obtained for poly(ethylene), and 30 mJ/m<sup>2</sup> for a clean glass fibre, while the potential surface interactivity of a glass fibre is far greater than that of poly(ethylene). A specific component of the surface, in mJ/m<sup>2</sup>, should be calculated in order to obtain significant parameters. As applied up to date, when calculating the specific component of the surface energy, the fact that  $W_a^{sp}$  energy values are in a totally different scale than AN or DN values is a major drawback. Consequently, Ka and Kb values obtained are in arbitrary energy units, different from those of the London component measured by injecting the *n*-alkane series. This paper proposes a method to obtain Ka and Kb values of the surface in the same energetic scale than the London component. The method enables us to correct the traditional London component of a solid, obtaining a new value, where the amount of  $W_{aCH_2}$  accounting for Debye interactions with polar sites, is excluded. As a result, an approach to surface mapping is performed in several different substrate materials. We show results obtained on different solid surfaces: poly(ethylene), clean glass fibre, glass beads, chemically modified glass beads and carbon fibre.  
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**Keywords:** Surface free energy; Inverse gas chromatography; Surface mapping

### 1. Introduction

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 physicochemical properties of the stationary phase and of the solute itself.

Inverse gas chromatography (IGC) takes advantage of this fact, by using a series of solutes (probes), of well known physico-chemical characteristics. Information of the nature of the column can be obtained, from their measured  $V_N$  values.

Injecting a minimum vapour amount of solutes, allows us to assume that no solute–solute interaction takes place, only solid–solute interactions occur. In these conditions, Henry's law can be applied, and the proportion of adsorbed solute (and therefore the retention volume  $V_R$ ), is practically independent of the probe concentration [1]

#### 1.1. Theoretical background of IGC

The net retention volume,  $V_N$ , of a solute is related to the standard variation of the free energy of adsorption

$$-\Delta G_A = RT \ln V_N + C \quad (1)$$

where  $C$  is a constant that depends on the reference state [2],  $R$  is the gas constant and  $T$  is the column temperature in K.

According to Fowkes [3], the work of adhesion ( $W_a$ ) between two phases can be considered as the sum of dispersive and nondispersive (or specific) contributions, as the solid surface energy  $\gamma_s$  of any substance can be written as a

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sum of dispersive and nondispersive components [4]

$$\gamma_S = \gamma_S^d + \gamma_S^{sp} \quad (2)$$

where  $\gamma_S^d$ , or the London component of the free energy, is the sum of the free energy of those active non-polar sites, that can only interact with in-coming molecules, with dispersive interactions, and  $\gamma_S^{sp}$ , or the specific component of the free energy, is the sum of surface free energy, of all other specific active sites of polar nature, with different character and intensity.

### 1.1.1. Calculation of the London component, $\gamma_S^d$ , of the free surface energy

When injecting *n*-alkane in a column X, we obtain  $\Delta G_{CH_2}$  (free energy of adsorption of a methylene group) from the slope of the line obtained when plotting  $\Delta G_A$  versus number of carbon atoms. This work of adhesion, is dominated by dispersive interactions, so the following expression is traditionally used according to Fowkes's expression [4]

$$W_{aCH_2} = W_{aCH_2 \text{ London}} = 2(\gamma_{CH_2}^d \times \gamma_S^d)^{1/2} \quad (3)$$

where  $\gamma_{CH_2}^d$  is the surface energy of members of *n*-alkane series and  $\gamma_S^d$  is the London component of the solid surface. Taking for  $\gamma_{CH_2}^d$  the surface energy of members of the *n*-alkane series [5], or that of poly(ethylene), the value  $\gamma_S^d$  can be calculated.

### 1.1.2. Calculation of the specific component, $\gamma_S^{sp}$ , of the free surface energy

The attempts made up to now for the calculation of this component, have failed to give specific surface energy values in the same scale as  $\gamma_S^d$ . All methods described in the literature rely on the same philosophy. The free energy of adhesion is plotted versus a *chosen property* of the probes, which is likely to be closely linked to its *capability to interact in a non-specific manner*. The series of *n*-alkanes are included in this plot, which shows a linear relation between the chosen property and the free adhesion energy. The key point is to accept that, for a given polar probe (with a given value in the chosen property), its dispersive work of interaction with the solid stationary phase is the same, that the interaction of the hypothetical *n*-alkane that has the same value in the chosen property, and therefore, subtracting this work of adhesion from the total work of adhesion of each polar probe, a *specific work of adhesion*, *Isp*, is calculated for each probe. Among the chosen properties proposed by different authors are:  $\log P^0$  [6],  $a(\gamma_{CH_2}^d)1/2$  [5], boiling temperatures  $T_b$  [7], molecular refraction  $P_D$  [8], polarizability function [9]. A new topology index,  $\chi_T$ , is defined for this application [10]. We proposed a method [11] in the same line, where the chosen property was the Kóvats index of the probe on a non-polar column of poly(ethylene).

$Ka_S$  and  $Kb_S$ , acid and base "numbers" of the solid surface, were calculated by plotting *Isp/AN* of each polar probe,

versus *DN/AN*. The slope being  $Ka_S$ , and  $Kb_S$  the intercept, assuming the widely used equation

$$Isp = Ka_S \times DN_{probe} + Kb_S \times AN_{probe} \quad (4)$$

where *Isp* is the specific work of adhesion of each probe, and *AN* and *DN* the donor acceptor numbers as found in the literature [12,13]. We think that in most methods, too much free energy of adsorption is subtracted from the total interaction in order to find the specific fraction. With the exception of the approaches of Donnet et al. [9], Vidal et al. [14], and Brendlé and Papirer [10], all properties are greatly conditioned by not only dispersive interactions between molecules, but also by interactions of polar character.

Another important drawback of this methodology is that, although in principle *DN/AN* are meaningful figures, provided that donor and acceptor numbers are normalised in the same scale, *Isp energy values are in a totally different scale than AN or DN values*. The consequence is that the plot of *Isp/AN* versus *DN/AN* will produce *Ka* and *Kb* data in *arbitrary energy units* which have only a limited comparative value.

### 1.2. A novel approach proposed for surface energy splitting, by IGC

Van der Waals attractions are widely accepted to be of three main types [15]:

- Keesom interactions (dipole–dipole).
- Debye interactions (dipole-induced dipole).
- London dispersion (induced dipole-induced dipole).

Up to now, Debye interactions between probes and solid stationary phase have been ignored. Our proposal is based on the inclusion of these in all calculations.

If we separate electron donor and electron acceptor sites in a solid surface, Eq. (2) takes the form:

$$\gamma_S = \gamma_S^d + \gamma_S^A + \gamma_S^B \quad (5)$$

in which most other type of interactions are enclosed.

Probes also have, in most cases, both types of interactivity potential, represented by *R-X*, where *R* represents the non-polar part of the molecule, and *X* represents the active point/s.

The total work of adsorption of each probe *L*, with an heterogeneous solid surface *S*, will be the sum of the following terms:

$$\begin{aligned} W_{a \text{ Total}}(L - S) = & W_{a \text{ London}}(R - \gamma_S^d) \\ & + W_{a \text{ Debye}}(R - \gamma_S^{A \text{ and } B}) \\ & + W_{a \text{ Debye}}(X - \gamma_S^d) \\ & + W_{a \text{ Keesom}}(X - \gamma_S^{A \text{ and } B}) \end{aligned} \quad (6)$$

where  $W_{a \text{ London}}(R - \gamma_S^d)$  represents the work of interaction of the non-specific part of the probe molecule with the non-specific sites of the solid surface,  $W_{a \text{ Keesom}}$

$(X - \gamma_S^{A \text{ and } B})$  represents the acid base interaction between the probe molecule and the specific sites of the solid surface, and the other two terms account for the Debye interactions (dipole-induced dipole) between probes and solid.

For  $W_{a \text{ London}}(R - \gamma_S^d)$ , and  $W_{a \text{ Keesom}}(X - \gamma_S^{A \text{ and } B})$ , we apply analogous expressions to Eqs. (3) and (4). For  $W_{a \text{ Debye}}(R - \gamma_S^{A \text{ and } B})$  and  $W_{a \text{ Debye}}(X - \gamma_S^d)$  we apply simple expressions of the type shown in Eq. (9), therefore:

$$W_{a \text{ London}}(R - \gamma_S^d) = 2 \times (\gamma_L^d \times \gamma_S^d)^{1/2} \quad (7)$$

$$W_{a \text{ Keesom}}(X - \gamma_S^{A \text{ and } B}) = (\gamma_S^A \times DN_X) + (\gamma_S^B \times AN_X) \quad (8)$$

$$W_{a \text{ Debye}}(L - S) = \gamma_L^d \times (\gamma_S^A + \gamma_S^B) + \gamma_S^d \times (AN_X + DN_X) \quad (9)$$

This is done based on the experimental data obtained when polar probes interact with a non-polar solid surface, or reference solid, of poly(ethylene) (PE).

## 2. Experimental

The instrument used is a Perkin-Elmer Autosystem. Flame ionisation detection is used in the highest sensitive range. The amount of probes injected is  $10^{-5}$  to  $0.05 \text{ cm}^3$  of gas from the vessel's headspace, working at infinite dilution. Helium is used as carrier gas, and flow rates are in the range  $3\text{--}30 \text{ cm}^3/\text{min}$  for each solid stationary phase studied. Void retention time,  $t_0$ , is calculated by mathematical tailoring of expression:

$$(t_E - A) = \exp(B + Cn) \quad (10)$$

where  $t_E$  is the elution time, therefore for  $n = 0$ ,  $t_0 = A + \exp B$  which would be the retention time of an hypothetical  $n$ -alkane with 0 number of carbon atoms. The retention time of each member of the series of  $n$ -alkanes is then,  $t_{Ri} = t_{Ei} - t_0$ .

$V_N$  are net retention volumes at a reference temperature of  $25^\circ\text{C}$ , calculated through the carrier gas flow rate, measured at the column outlet at ambient pressure and room temperature, and corrected to  $25^\circ\text{C}$ .

Materials studied are:

The reference material is ground poly(ethylene) (1–5  $\mu\text{m}$  diameter grain size) provided by courtesy of Repsol YPF. E-Glass fibre solvent extracted, provided by Cristalera Española.

E-Glass beads solvent extracted, provided by Sovitec Ibérica, 600–800  $\mu\text{m}$  diameter.

These glass beads after in situ reaction, at  $120^\circ\text{C}$ , with aminopropyl-trimethoxysilane.

Non-sized AS4 carbon fibre of Hexcel Composites.

All solvents are from Merck-Schuchard, HPLC or zur Analysis.

All materials were introduced in PTFE tubing with 1/4 in. or 1/8 in. outer diameter.

## 3. Methods and applications

The proposed method deals with several non-solved problems in the following way.

### 3.1. The area problem

All terms of Eq. (6) have to be expressed in *work of adhesion per unit area*, and all free surface energy values have also to be expressed in *free surface energy per unit area*. An estimation of *contact areas* is then required.

Several area sets for  $n$ -alkanes and for polar probes are found in the literature, used by scientists for IGC calculations. Some are based on geometrical molecular models and others are based on experimental adsorption data. There is no clear correlation between them. In Fig. 1, we show some of these area sets for polar probes. We include those calculated by us as described below.

Recently Hamieh and Schultz [16] recalculated and reviewed various models in order to calculate the molecular areas of some non-polar and polar probes and proposed a chromatographic method to do it.

We think that in all cases, chromatographic methods provide higher molecular contact areas of polar molecules, because of the ignored Debye interactions.

We make an estimation of the area of all probes, both polar and non-polar. This is done with the help of atomic radii, and bond lengths of diatomic molecules found in the literature [17]. We use the generally accepted value for the  $\text{area}_{\text{CH}_2}$  of  $0.06 \text{ nm}^2$ . Another molecule, or a group of atoms, is supposed to occupy (when adsorbed on a solid surface) the sum of the areas of their constituting atoms. This approximation is likely to be valid in the case of simple molecules like those used as probes in IGC. The ratio ( $\text{area}_{\text{molecule}}/\text{area}_{\text{CH}_2}$ ) is calculated by building a scale with the *area of the circumferences*, as the *shadow on the plane* of atoms considered as spheres. These molecules are supposed to show a shadow by addition of the shadows of constituting atoms.

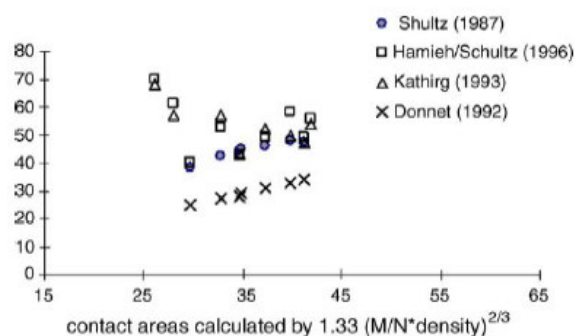


Fig. 1. Some sets of *area of interaction* of polar probes found in the literature,  $\times 10^2 \text{ nm}^2$ .

### 3.2. Units for AN and DN values

Polar probes often used for the evaluation of the acid or basic character of the solid stationary phase consist of volatile molecules like: chloroform, acetone, ethyl acetate, diethyl ether, methylene chloride, tetrahydrofuran, acetonitrile, alcohols, etc. Their electronic donor and acceptor character is given by Gutmann [12] as DN and AN values. The DN values measure the energy of a co-ordinate bond between a donor atom and the Sb of  $\text{SbCl}_5$ , its value is given in kcal/mol. AN is derived from relative  $^{31}\text{P}$  NMR chemical shifts in  $\text{Et}_3\text{PO}$ , when dissolved in the acid species being evaluated, and is a dimensionless number. Riddle and Fowkes [13], made corrections to Gutmann's original AN values for the Van der Waals contribution to the chemical shift, on the basis of the determination of the  $\gamma^d$  values yielded from measurement of the surface and interfacial tensions of the test liquids. Values of  $(\text{AN} - \text{AN}^d)$  are given, which we take as the corrected Gutmann's shift 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 and Schreiber [18] through the DN value of  $\text{Et}_3\text{PO}$  (the AN reference molecule) that is 40 kcal/mol. AN values can be recalculated in the same scale as DN original reported values.

DN and AN (Gutmann's scale) or  $\text{AN}^*$  (Riddle–Fowkes's scale), used in this work are given in Table 1.

Up to now, the values in Table 1 are used unmodified in most recent IGC studies [19–21].

AN and DN numbers are supposed to be in the same energy units, *but not in Isp energy units*. When we apply Eq. (4) for acid–base components of the solid surface, by IGC, only DN/AN data have physical meaning. Recalculation of AN and DN numbers, in the same energy units as the work of adsorption measured by chromatography, is needed, assuming that DN/AN reported values are correct.

This is done in this work by measuring adsorption energies of all polar probes on a reference column made of poly(ethylene), PE. Fortunately two experimental observations concur to fulfil our purpose:

- one is the fact that the adsorption of all probes on poly(ethylene), if expressed in  $W_{\text{aProbe}}/W_{\text{aCH}_2}$  (which we call  $\text{CH}_2$  index,  $I_x$ ) is non-temperature dependent.
- the other lucky fact is that on PE, (being unable to interact with Keesom forces) we obtain a line when plotting  $W_{\text{aProbe}}/\text{AN}$  versus DN/AN. We understand that Debye forces dominate these interactions, and are responsible for this phenomenon, thus Eqs. (9) and (6) are reduced to:

$$W_{\text{aDebye}}(\text{L} - \text{PE}) = \gamma_{\text{PE}}^d \times (\text{AN} + \text{DN}) \quad (11)$$

$$W_{\text{aTotal}}(\text{L} - \text{PE}) = 2 \times (\gamma_{\text{L}}^d \times \gamma_{\text{PE}}^d)^{1/2} + \gamma_{\text{PE}}^d \times (\text{AN} + \text{DN}) \quad (12)$$

Provided we can estimate  $\gamma_{\text{L}}^d$ , of each probe,  $(\text{AN} + \text{DN})$  in adsorption energy units, can be calculated.

With DN/AN values taken from the literature, AN and DN values derived from measured adsorption energies on PE can be recalculated.

### 3.3. Calculation methodology of partial surface energy contributions

Once AN and DN values of each probe are calculated from adsorption on PE, we are in a position to plot  $W_{\text{aKeesom}}/\text{AN}$  versus DN/AN in the same energy units, when studying an heterogeneous solid surface.

We have chosen those probes in which the splitting of the polar and non-polar part of the molecule are more obvious; these are acetone, ethyl acetate, tetrahydrofuran, acetonitrile, methanol and ethanol. We assume that  $\gamma_{\text{L}}^d$  of the non-polar part of the probe, *by unit area*, is the same as  $\gamma_{\text{L}}^d$  of *n*-alkanes and the same as  $\gamma_{\text{PE}}^d$ .

A system of six equations is established, one for each probe, with Eq. (6), using Eqs. (7)–(9). We optimise, to minimum quadratic,  $\sum(W_{\text{a exper.}} - W_{\text{a calc.}})$ , thus obtaining optimum values of  $\gamma_{\text{S}}^d$ ,  $\gamma_{\text{S}}^A$  and  $\gamma_{\text{S}}^B$ .

Table 1  
Donor and acceptor numbers of polar probes commonly used, according to Gutmann's [12], Fowkes' [13] normalised as Mukhopadhyay [18]

Polar probe	Gutmann		Fowkes	Gutmann	Fowkes
	AN n.u.	DN n.u.	$\text{AN}^*$ n.u.	DN/AN	DN/ $\text{AN}^*$
Chloroform	23.1	0	18.7	0.00	0
Acetone	12.5	42.5	8.7	3.40	4.89
Ethyl acetate	9.3	42.8	5.3	4.60	8.07
Ethyl ether	3.9	48.0	4.9	12.31	9.80
THF	8.0	50.0	1.9	6.25	26.32
Acetonitrile	19.3	35.3	16.3	1.83	2.16
Methylene chloride	20.4	0	13.5	0.00	0
Methanol	41.3	47.5	41.7	1.15	1.14
Ethanol	37.1	50.0	35.9	1.35	1.39
1-Butanol	36.8		31.7		



Table 2  
Calculated areas of polar molecules and radicals

Atom or group	Area of shadow $\times 10^2$ (nm <sup>2</sup> )	Area <sub>molecule</sub> /area <sub>CH<sub>2</sub></sub>	Calculated area $\times 10^2$ (nm <sup>2</sup> )	Non-polar fraction $\times 10^2$ (nm <sup>2</sup> )
CH <sub>2</sub> –	2.52	1.000	6.00	6.00
CH <sub>3</sub> –	2.86	1.133	6.80	6.80
Methane	3.19	1.266	7.59	7.59
Ethane	5.71	2.266	13.59	13.59
Propane	8.23	3.266	19.59	19.59
Butane	10.75	4.266	25.59	25.59
Pentane	13.27	5.266	31.59	31.59
Hexane	15.79	6.266	37.59	37.59
Heptane	18.31	7.266	43.59	43.59
Octane	20.83	8.266	49.59	49.59
Nonane	23.35	9.266	55.59	55.59
Decane	25.87	10.266	61.59	61.59
Undecane	28.39	11.266	67.59	67.59
Dodecane	30.91	12.266	73.59	73.59
Hexadecane	41.00	16.266	97.59	97.59
Chloroform	11.50	4.561	27.37	5.20
Acetone	8.26	3.279	19.67	13.59
Ethyl acetate	12.17	4.827	28.96	19.59
Ethyl ether	12.13	4.814	28.89	25.59
THF	11.46	4.549	27.29	24.00
Acetonitrile	5.34	2.120	12.72	6.80
Methylene chloride	8.73	3.463	20.78	6.00
2-Propanol	9.28	3.681	22.89	18.80
Methanol	4.57	1.814	10.89	6.80
Ethanol	7.09	2.814	16.89	12.80
1-Propanol	9.61	3.814	22.89	18.80
1-Butanol	12.13	4.814	28.89	24.80
1-Pentanol	14.65	5.814	34.89	30.80
1-Hexanol	17.17	6.814	40.89	36.80
1-Heptanol	19.70	7.814	46.89	42.80

## 4. Results and discussion

### 4.1. Areas of interaction of polar and non-polar probes

Bond lengths of covalent molecules are taken from literature [17] from which the approximate area of the atoms, groups or molecules are estimated. These are normalised to the generally accepted value of 0.06 nm<sup>2</sup> for the methylene group. The approximate area values calculated by us for *n*-alkanes and all polar probes used, are shown in Table 2.

Correlation between the calculated areas and those given by Dorris et al. [22] is fairly good, as Fig. 2 shows.

### 4.2. Interaction of polar probes with poly(ethylene)

The work of interaction  $W_a$  of a molecule of the *n*-alkane series with the surface of poly(ethylene) is obtained by Eq. (1). The plot of  $W_a$  of the series of *n*-alkanes, RH, versus the equivalent number of CH<sub>2</sub> = area<sub>molecule</sub>/area<sub>CH<sub>2</sub></sub> gives a line. The slope of this line is  $W_a$ CH<sub>2</sub>. Considering that the surface energy of both *n*-alkane molecules and poly(ethylene) are equal,  $\gamma_{PE} = \gamma_{RH}$ , we can calculate them with Eq. (3).

The work of interaction  $W_a$  of a polar molecule with the surface of poly(ethylene) is obtained with Eq. (1).  $W_a/W_a$ CH<sub>2</sub> is the work of adsorption expressed in an

equivalent CH<sub>2</sub> number, or index,  $I_{PE}$ . This value is quasi non-temperature dependant, as is shown in Fig. 3.

The interaction of these polar molecules with PE is dominated by Debye interactions. The plot of  $W_a/AN$  versus DN/AN gives a line for most polar molecules, as shown in Fig. 4.

We correct DN/AN with equations of these lines. We calculate, with Eq. (3),  $\gamma_L^d$  per 0.06 nm<sup>2</sup> of each of the six selected polar probes, assuming that the alkyl radical of each polar molecule has the same  $\gamma_L^d$  of the hypothetical *n*-alkane of the

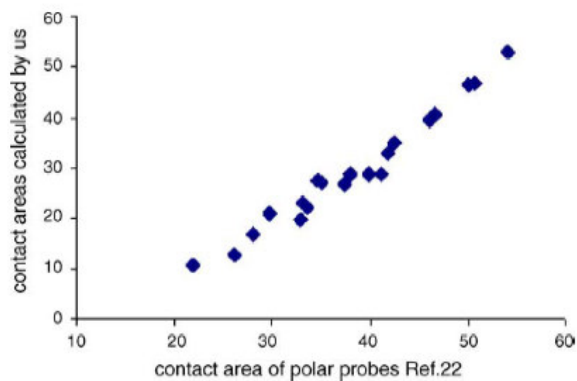


Fig. 2. Correlation of calculated areas with those of Ref. [22].

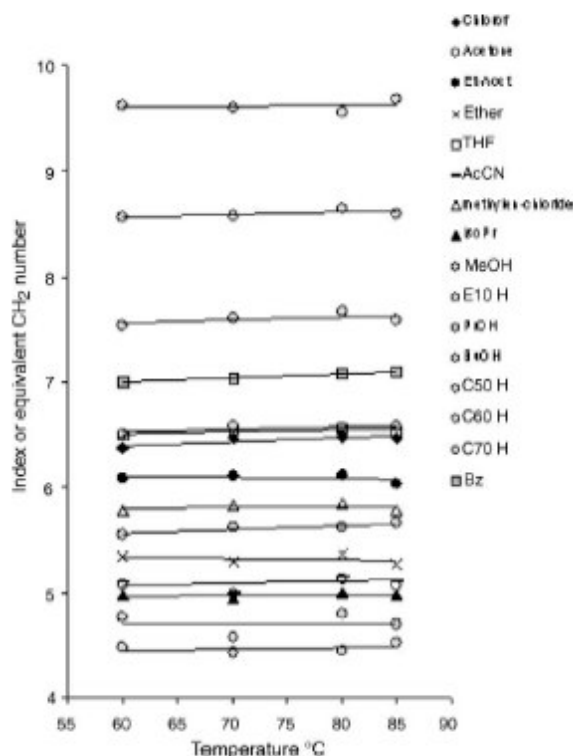


Fig. 3. Index, or equivalent  $\text{CH}_2$  number, of polar probes on poly(ethylene),  $I_{PE}$ .

same area. We divide this value by the calculated area of the probe and multiply this value by  $0.06 \text{ nm}^2$  (the area of the methylene group), thus obtaining for the six selected probes the following values shown in Table 3.

We calculate (AN+DN) of each polar probe in  $I_{PE}$  units/ $0.06 \text{ nm}^2$  with Eq. (12), where all magnitudes are given in those units. DN/AN values of the literature are used to calculate AN and DN values in this same energy scale. This values are given in Table 4.

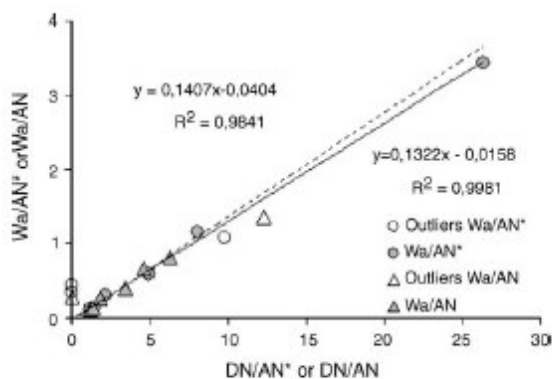


Fig. 4. Debye interaction of polar probes on PE using AN values of Refs. [12,13].

Table 3  
Calculated  $\gamma_L^d$  of polar molecules expressed in  $I_{PE}/0.06 \text{ nm}^2$

Atom or group	$\gamma_L^d$ in $I_{PE}$ units/ $0.06 \text{ nm}^2$
$\text{CH}_2$	0.500
Poly(ethylene)	0.500
Acetone	0.346
Ethyl acetate	0.338
THF	0.440
Acetonitrile	0.267
Methanol	0.312
Ethanol	0.379
Ethyl ether	0.443
2-Propanol	0.425

#### 4.3. Interaction of n-alkanes and polar probes with an heterogeneous surface X

$W_a$  molecule are experimentally obtained in kJ/mol from retention volumes. We obtain the index by dividing by  $W_a \text{CH}_2$  in kJ/mol. This index is exclusive of the column X ( $I_X$ ). To obtain the adsorption energy in  $I_X/0.06 \text{ nm}^2$ , we must consider the estimated areas in  $\text{nm}^2$ . To apply  $\gamma_L^d$ , AN and DN values of Tables 3 and 4, these must be converted to the same energy units,  $I_X/0.06 \text{ nm}^2$  using Eq. (13)

$$W_a(I_X) = W_a(I_{PE}) \times (W_a \text{CH}_2 \text{ in kJ/mol on PE} / W_a \text{CH}_2 \text{ in kJ/mol on X}) \quad (13)$$

We are able to establish six equations, one for each selected polar probe according to Eqs. (6)–(9). Optimum  $\gamma_S^d$ ,  $\gamma_S^A$  and  $\gamma_S^B$  are obtained in  $I_X$  units per  $0.06 \text{ nm}^2$ , easily convertible to kJ/mol and  $\text{mJ/m}^2$ . In Tables 5 and 6 we show the results obtained for several solid materials, together with the traditional London component value obtained exclusively from  $W_a \text{CH}_2$ , using AN values of Riddle–Fowkes' or Gutmann's scale respectively.

From Tables 5 and 6 we can see the non-polar character of PE, the polar character of clean glass material, and how acidic sites disappear when chemical reaction of the surface with aminopropyl ethoxysilane takes place. We can also appreciate the total value of the surface energy and establish that, energetically speaking:

C fibre > glass beads > glass fibre  
> modified glass beads > polyethylene

Which is not the order we would obtain from the traditional London component.

#### 4.4. Validation of the method

This method relies on of  $\gamma_L^d$ , AN and DN values derived from the interaction polar probes on PE. It is necessary to check if, in other materials, the experimental values and those derived from the proposed calculations above fit. In



Table 4  
Recalculated AN and DN values of polar molecules, in  $I_{PE}/0.06 \text{ nm}^2$

	AN <sup>*</sup> $I_{PE}$ units per $0.06 \text{ nm}^2$	DN <sup>*</sup> $I_{PE}$ units per $0.06 \text{ nm}^2$	AN $I_{PE}$ units per $0.06 \text{ nm}^2$	DN $I_{PE}$ units per $0.06 \text{ nm}^2$
Polyethylene	0	0	0	0
n-Alkane	0	0	0	0
Acetone	0.2570	1.1578	0.3405	1.0743
Ethyl acetate	0.0889	0.7807	0.1468	0.7228
THF	0.0368	0.9634	0.1409	0.8593
Acetonitrile	0.9564	2.3643	1.0529	2.2679
Methanol	1.7195	1.5888	1.6135	1.6947
Ethanol	0.7568	0.8392	0.7299	0.8661
Ethyl ether	0.0341	0.2827	0.0290	0.2878
2-Propanol	0.3656	0.4782	0.3610	0.4828

AN<sup>\*</sup> and DN<sup>\*</sup> are derived of Riddle–Fowkes' scale, AN and DN are derived of Gutmann's scale.

Table 5  
Calculated  $\gamma_s$  components of several solid materials studied, using new AN<sup>\*</sup> and DN<sup>\*</sup> values

Materials	Total $\gamma_s^d$ (mJ/m <sup>2</sup> )	New $\gamma_s^d$ (mJ/m <sup>2</sup> )	$\gamma_s^A$ (mJ/m <sup>2</sup> )	$\gamma_s^B$ (mJ/m <sup>2</sup> )	Total $\gamma_s$ (mJ/m <sup>2</sup> )
Polyethylene 90°	39	39	0	0	39
Glass fibre 90°	29	0	56	175	232
Glass beads 90°	29	0	67	182	248
Modified glass beads 90°	27	27	0	74	101
Unsize carbon fibre 90°	61	1	84	176	261

Table 6  
Calculated  $\gamma_s$  components of several solid materials studied, using new AN and DN values

Materials	Total $\gamma_s^d$ (mJ/m <sup>2</sup> )	New $\gamma_s^d$ (mJ/m <sup>2</sup> )	$\gamma_s^A$ (mJ/m <sup>2</sup> )	$\gamma_s^B$ (mJ/m <sup>2</sup> )	Total $\gamma_s$ (mJ/m <sup>2</sup> )
Polyethylene 90°	39	39	0	0	39
Glass fibre 90°	29	0	42	190	233
Glass beads 90°	29	1	43	201	246
Modified glass beads 90°	27	22	0	84	106
Unsize carbon fibre 90°	61	2	65	190	257

Table 7  
Reliability of the method using new AN<sup>\*</sup> and DN<sup>\*</sup> values

Materials adsorption, $I_x$	PE 90°		Glass fibre 90°		Glass b 90°		Modified glass beads		C fibre 90°	
	Exper.	Calc.	Exper.	Calc.	Exper.	Calc.	Exper.	Calc.	Exper.	Calc.
Acetone	5.04	5.05	12.08	10.67	14.19	11.85	8.16	7.79	7.22	6.60
Ethyl acetate	6.07	6.07	13.28	11.39	15.38	12.66	8.43	8.94	7.81	7.18
THF	6.54	6.55	12.28	12.65	13.63	14.12	8.33	9.56	7.52	8.05
Acetonitrile	5.07	5.08	12.92	13.15	13.70	14.53	8.82	8.68	7.71	7.85
Methanol	4.43	4.44	12.20	14.36	13.50	15.50	9.89	9.57	7.28	7.93
Ethanol	4.70	4.70	12.90	12.88	14.33	13.94	9.35	9.14	7.86	7.30
Ethyl ether <sup>a</sup>	5.29	5.30	8.92	10.25	10.45	11.20	6.26	8.49	5.65	6.23
2-Propanol <sup>a</sup>	4.95	4.95	12.80	11.93	14.96	12.94	8.49	9.00	8.11	6.90

<sup>a</sup> Not used in the equations system.

Table 8  
Reliability of the method using new AN and DN values

Materials adsorption, $I_x$	PE 90°		Glass fibre 90°		Glass beads 90°		Modified glass beads		C fibre 90°	
	Exper.	Calc.	Exper.	Calc.	Exper.	Calc.	Exper.	Calc.	Exper.	Calc.
Acetone	5.04	5.05	12.08	10.68	14.19	11.91	8.16	7.95	7.22	6.65
Ethyl acetate	6.07	6.07	13.28	11.38	15.38	12.82	8.43	9.04	7.81	7.28
THF	6.54	6.55	12.28	12.86	13.63	14.51	8.33	9.93	7.52	8.24
Acetonitrile	5.07	5.08	12.92	12.99	13.70	14.17	8.82	8.74	7.71	7.71
Methanol	4.43	4.44	12.20	14.00	13.50	15.24	9.89	9.31	7.28	7.84
Ethanol	4.70	4.70	12.90	12.69	14.33	14.01	9.35	9.01	7.86	7.35
Ethyl ether <sup>a</sup>	5.29	5.30	8.92	9.94	10.45	11.44	6.26	8.34	5.65	6.38
2-Propanol <sup>a</sup>	4.95	4.95	12.80	11.84	14.96	13.27	8.49	8.95	8.11	7.07

<sup>a</sup> Not used in the equations system.

Tables 7 and 8 we give  $W_{\text{probe calc.}}$  and  $W_{\text{probe exper.}}$ , to compare, by using Riddle–Fowkes and Gutmann scales.

## 5. Conclusions

- (1) We can conclude from the results found that the *traditional total London component* of the surface is mainly an indication of the *concentration of active sites* rather than real information of their energetic activity.
- (2) In all equations we use work of adhesion per unit area. Therefore we make an estimation of areas of polar probes based on bond lengths.
- (3) We propose new values of AN and DN for polar probes taking poly(ethylene) as reference material and expressed in index numbers.
- (4) Using this methodology, we show an approximate surface map of poly(ethylene), clean glass fibre, glass beads, modified glass beads and carbon fibre, and a ranking order in surface energy.

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## STUDY OF THE FREE SURFACE ENERGY IN ORGANIC MATRICES BY INVERSE GAS CHROMATOGRAPHY TO DEVELOPMENT OF COMPOSITES

**Composite materials** (or **composites**) are engineered materials made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct on a macroscopic level within the finished structure. Composites are made up of individual materials referred to as constituent materials. There are two categories of constituent materials: matrix and reinforcement. At least one portion of each type is required. The matrix material surrounds and supports the reinforcement materials by maintaining their relative positions. The reinforcements impart their special mechanical and physical properties to enhance the matrix properties.

Most commercially produced composites use a polymer matrix material often called a resin solution. There are many different polymers available depending upon the starting raw ingredients. The most common are known as polyester, vinyl ester, polyimide, polyamide, polypropylene, PEEK, and others. The reinforcement materials are often fibers but also commonly ground minerals or glass beads.

Composite materials have gained popularity (despite their generally high cost) in high-performance products that need to be lightweight, yet strong enough to take harsh loading conditions such as aerospace components<sup>1,2,3</sup> (tails, wings, fuselages, propellers), boat and scull hulls, bicycle frames and racing car bodies. Other uses include fishing rods, storage tanks, and baseball bats. The new Boeing 787 structure including the wings and fuselage is composed largely of composites. Composite materials are also becoming more common in the realm of orthopedic surgery.<sup>4,5</sup> Carbon composite is a key material in today's launch vehicles and spacecraft. It is widely used in solar panel substrates, antenna reflectors and yokes of spacecraft. It is also used in payload adapters, inter-stage structures and heat shields of launch vehicles.

A central goal of modern materials physics and nanoscience is the **control of materials and their interfaces** to atomic dimensions. In traditional semiconductors, this reconstruction is achieved by an atomic disordering and stoichiometry change at the interface. Shock, impact, or repeated cyclic stresses can cause the laminate to separate at the interface between two layers, a condition known as delamination. Individual fibers can separate from the matrix e.g. fiber pull-out.

We study the interface in composites using **Inverse gas chromatography** (IGC). IGC<sup>6</sup> has proved to be a suitable tool to study solid surfaces and their interaction capability. The solutes are retained in their way through the chromatographic column accordingly to their particular interaction with

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the stationary phase, which depends on the surface groups in the stationary phase and the solute nature. The principle of IGC is very simple<sup>7</sup>. A column is filled with the powder material under test and molecules with clearly identified features called probes are injected into the column. The retention time and peak elution profiles of the probes give information on their interactions with the surface of the solid and on the characteristics of both the surface of the solid and the probe. The complexity of these interactions depends on the amounts of probe injected. The retention volume,  $V_R$  is related to the free energy of adsorption and many thermodynamic parameters can be obtained from the experimental data. Surface interactivity of fibers and fillers is a crucial feature.

A new approach<sup>8</sup> is proposed in this work, the main achievement being to bring acid-base characterisation of the surfaces to the same energetic scale than the London component of the free surface energy measured by the interaction of the n-alkanes with the surface. Traditionally, the main reference set of probes used in the IGC at infinite dilution is the n-alkane series (RH). The free energy of adsorption of the members of this series provides a significant value, the free energy of adsorption of the CH<sub>2</sub> group. In this work other homologous series, ROH, are used as probes to obtain outstanding information of the surface characteristics.

A new methodology is proposed which allows an energetic surface mapping of the resins. The first result is quantification the free energy of adsorption of the OH group, in close relation with the acid-basic character of the surface.

The second interesting result is the observation of the anomalous free energy of adsorption of the lower members of the series, which we think is closely relate to the formation of hydrogen-bridge bonds. Solid cured phenolic, furanic, cyanoester and epoxy resins are studied, and their capability to form hydrogen-bridge bonds evaluated.

We can conclude from our results that the traditional total London component of the surface is mainly an indication of the concentration of active sites rather than real information of their energetic activity. In all equations we use work of adhesion per unit area. Up to now, Debye interactions between probes and solid stationary phase have been ignored. Our proposal is based on the inclusion of these in all calculations. Also, we make an estimation of areas of all probes, both polar and non-polar. This is done with the help of atomic radii, and bond lengths of diatomic molecules found in the literature.

We propose new values of AN (acceptor number) and DN (donor number) for polar probes using poly(ethylene), clean glass fiber, glass beads, modified glass beads and carbon fiber, and a ranking order in surface energy. We also propose a method to estimate the potential interactivity of the cured solid resin with the hydroxyl group through Hydrogen Bridge bonding. The projection of these results to choose the processing resins in the manufacturing of reinforced composites is noted.

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