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Characterization of Acid-Base Properties of a Polyetherimide and Two Liquid Crystalline Polymers by Inverse Gas Chromatography

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Inverse gas chromatography has been used to examine the dispersive and acid-base forces contributing to the potential work of adhesion of three commercial polymers: the polyetherimide Ultem-1000 and the liquid crystal polymers Rodrun-LC 5000 and Vectra B-950. Acid-base interaction enthalpies of each polymer with different low-molecular-weight probes have been determined. In this analysis, dispersion and specific interactions are considered to contribute independently to the adsorption of probe molecules at the adsorbent surface. Following the approach of Gutmann, these enthalpies were correlated with donor and new acceptor numbers of the probes, both in thermodynamically consistent units. From this approach, parameters expressing the polymer ability to accept or donate electrons were obtained. The polymers may be described as being amphoteric, Ultem 1000 having a predominant basicity.

KEY WORDS Inverse gas chromatography, polyetherimide, liquid crystal polymers, acid-base properties

INTRODUCTION

In fields of polymer science such as composites, blends and adhesives, interfacial interactions may play a significant role in determining material properties. The surface properties of polymeric materials are of critical importance. Many methods are used for surface characterization, ranging from modern surface-specific spectroscopic methods for chemical analysis, such as the various electron spectroscopies, to simple empirical tests of wettability. The adsorption of vapors is a classical method for investigating surfaces. Unlike other conventional gas adsorption techniques, inverse gas chromatography (IGC) measures adsorption down to extremely low gas or vapor concentrations corresponding to nearly zero surface coverage.

The magnitude of the interfacial forces ranges from strong covalent or ionic chemical bonds to comparatively weak van der Waals interactions. When no chemical bonds are

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involved, thermodynamic functions such as the work of adhesion W_A between the components of a multiphase system are due to physical forces only. Fowkes [1] has proposed a quantitative description of polymer interfaces based on acceptor-donor interactions. An important magnitude in this theory is the acid-base interaction heat at the polymer interface, ΔH^{ab} .

Calorimetry [2,3], infrared [4–6] and NMR spectroscopic methods used for determining the heats of mixing of organic liquids can also be used for the determination of the heats of acid-base interactions of polymers. There have also been several efforts to determine heats of acid-base interaction of polymers with organic solvents by inverse gas chromatography [7]. The IGC method can provide a related parameter, namely, the adsorption heat in the “infinite” dilution region ΔH . It is suggested that ΔH^{ab} can be calculated from ΔH , and thus IGC data can be used to examine the surface properties of polymers.

This work examines the acid-base characteristics of three commercial polymers: the polyetherimide Ultem-1000 and the liquid crystal polymers Rodrun-LC 5000 and Vectra B-950 which can be blended to prepare in situ composites. The interest of this type of in situ composites has grown in recent years primarily due to the possibility of their having a variety of processing options and relatively high mechanical performance. As pointed out by Baird *et al.* [8], the morphology and properties of in situ composites should be affected by the interactions between the liquid crystal polymer and the matrix. In order to understand and predict the mechanical behavior of the composite, it is necessary to gain better knowledge of the nature and level of interactions likely to be exchanged at the interface.

Theory

In inverse gas chromatography the solid adsorbent to be characterized is the stationary phase, while a volatile probe of known characteristics is passed through the column via an inert gas. Simple thermodynamic assumptions applied to IGC at infinite dilution lead us to the equation

$$\Delta G_D^0 = -\Delta G_A^0 = N \cdot a \cdot W_A \quad (1)$$

where ΔG_D^0 is the free energy of desorption, ΔG_A^0 the free energy of adsorption per mole of solute, and W_A the work of adhesion per unit area between the probe (solute) molecule and the solid. N is the Avogadro's number and a the surface area of an adsorbed probe molecule. Here we consider that only physical interactions take place and therefore adsorption is reversible.

At infinite dilution all thermodynamic parameters derived from the experimental retention volume V_n exclusively reflect the interaction between adsorbent and adsorbate.

The free energy of adsorption per mole of solute ΔG_A^0 is given by

$$\Delta G_A^0 = -RT \ln V_n + \text{const.} \quad (2)$$

where R is the gas constant and T the temperature, the constant depending on the chosen reference state [9]. Dispersion and specific interactions are considered to contribute independently to the adsorption of probe molecules at the adsorbent surface. An evaluation of the role and size of specific interactions requires a separation of the contributions from dispersion and nondispersion forces. The magnitude of dispersion effects is usually quan-

tified by using n-alkanes, which are supposed to interact with the polymeric stationary phase exclusively throughout dispersive interactions.

Fowkes [1] applied the Lewis acid-base theory to problems in the field of surface chemistry and adhesion. The acid-base contribution to the work of adhesion can be determined from the change in enthalpy ΔH^{ab} due to electron donor-acceptor interactions and the number of acid-basic pairs.

The two most frequently used theories to quantify these acid-base interactions are due to Drago and Gutmann. Drago et al. [2,10], from studies of the heats of mixing of acids and bases in a neutral (i.e., weakly solvating) solvent, introduced the empirical four-parameter equation

$$-\Delta H^{ab} = E_a \cdot E_D + C_a \cdot C_D \quad (3)$$

E_a and E_D were originally interpreted as the susceptibility of the acid and base, respectively, to undergo electrostatic interaction and C_a and C_D as the susceptibility of the acid and base, respectively, to form covalent bonds. The experiments are done with low concentrations of an acid in an excess of base, resulting in partial molar heats of interactions for the acid species. Equation (3) generally predicts heats of mixing within $\approx 5\%$ of experimental results. According to Drago, a molecule is considered to be either an acid or a base. This statement does not agree with the amphoteric character of most molecules.

According to Gutmann's acid-base concept [11], a Lewis base is an electron-pair donor characterized by the donor number DN. It is the actual heat of mixing of the basic liquid with antimony pentachloride in 1,2-dichloroethane. A Lewis acid is an electron-pair acceptor characterized by the acceptor number AN. It is calculated from the ^{31}P NMR chemical shift of triethyl phosphine oxide upon mixing with the investigated acid. The AN values are arbitrarily scaled by assigning a zero value to the shift induced by hexane and a value of 100 to the shift induced when only antimony pentachloride is in a dilute solution of 1,2-dichloroethane. The NMR measurements are made without solvent, so the resulting acceptor numbers include an appreciable contribution from the van der Waals interactions. In the Gutmann's approach it is possible to consider a liquid or a solid to be both an acid and a base.

The enthalpy of acid-base interactions may be correlated with the so-called acceptor number (AN, nondimensional units) and donor number (DN in $\text{kcal}\cdot\text{mol}^{-1}$) of the testing solutes, as expressed in the semi-empirical Gutmann scale, by means of

$$-\Delta H^{ab} = K_A \cdot \text{DN} + K_D \cdot \text{AN} \quad (4)$$

where K_A and K_D represent the ability of a given polymer to interact as, respectively, electron acceptor or electron donor. The literature contains much more information on the AN and DN values of the solutes than is available for Drago's parameters. Because of that and because Gutmann's approach recognizes amphoteric molecules, we have selected Gutmann's method to examine the surface properties of our polymers.

However, the arbitrary scaling of the AN values and the asymmetry of AN and DN units relate these descriptors of acidity and basicity only subjectively. Recently, Riddle and Fowkes [12], have shown that the ^{31}P NMR shift of triethyl phosphine oxide dissolved in acidic solvents is made up of two additive contributions: a dispersion contribution $\Delta\delta^D$ and a Lewis acid-base contribution $\Delta\delta^{ab}$. Consequently, AN values have to be corrected for these dispersion effects. In many cases, the correction is quite substantial. These authors have also

found that the acid-base contributions $\Delta\delta^{ab}$ are directly proportional to the enthalpies of acid-base interaction between triethyl phosphine oxide and acidic liquids, $AN^* = -\Delta H_{\text{acid-Et}_3\text{PO}}$. This results in new acceptor numbers AN^* , having the same units as DN. Riddle and Fowkes [12] further link AN^* with the original AN numbers by the equation.

$$AN^* = 0.288(AN - AN^d) \quad (5)$$

where AN^d is the dispersion contribution reported by these authors. DN numbers are free of dispersion force effects [12]. We will determine ΔH^{ab} as well as K_A and K_D by using Gutmann's DN values [11] and AN^* values modified and expressed in kcal·mol⁻¹ according to Riddle and Fowkes [12].

EXPERIMENTAL

Materials

The polyetherimide Ultem-1000 is an amorphous thermoplastic resin recently developed by General Electric Co. (General Electric Co., Plastics Operations, Pittsfield, MA, USA). It is considered as an engineering plastic with excellent processing characteristics, transparency and broad chemical resistance. Its glass-transition temperature is 215°C. The liquid crystal polymer Rodrun LC-5000 is a random copolyester of p-hydroxybenzoic acid (PHB) and polyethylene terephthalate (PET) and was provided by Unitika (Unitika LTD, Chuo-Ku, Osaka, Japan). It has a melting temperature of 260°C measured by DSC without any other transition temperature. The Vectra B-950 is a thermotropic liquid crystal polymer manufactured by Hoescht Celanese (Hoechst Aktiengesellschaft, 6230 Frankfurt, Gein). It is a copolyesteramide with a composition of 60 mol % 6-hydroxy-2-naphthoic acid, 20 mol % terephthalic acid and a 20 mol % p-aminophenol. It has a glass-transition temperature of 140°C and a melting temperature of 282°C measured by DSC.

The solutes were: n-octane, n-nonane, n-decane, n-dodecane, n-tetradecane, THF, ethyl acetate, 1,2-dichloroethane, chloroform, acetone, methanol and ethanol. They were chromatographic quality or reagent grade and were used without further purification.

Apparatus and Procedures

The columns were prepared in the usual manner [13]. The polyetherimide Ultem-1000 was coated from a chloroform solution onto Chromosorb G (AW-DMCS treated, 80/100 mesh). The Rodrun LC-5000 LCP was coated from a 1,1,1,3,3,3-hexafluoro-2-propanol solution. After drying in a vacuum oven for ca. 48h. at 373 K, the coated support was packed into a 1/4-in o.d. stainless-steel column by applying vacuum to the end. The Vectra B-950 was crushed mechanically due to its insolubility and packed into a 1/4-in o.d. stainless-steel column by applying vacuum to the end. Its surface area, determined by N_2 adsorption, was found to be 1.3 m²·g⁻¹.

Glass-wool was used to block the ends of the columns. The relative concentration of the polymer in the blends was assumed to be identical to that in the original solution prior to the deposition on the inert support. A description of the columns is given in Table I.

TABLE I

Stationary phase and column parameters			
Polymer	Loading (%w/w)	Wt. polymer W_t (g)	Column length
Ultem-1000	9.09	0.497	1m
Rodrun LC-5000	8.34	0.451	1m
Vectra B-950	—	2.859	1m

Measurements were taken on a modified Sigma 300 Perkin Elmer Gas Chromatograph equipped with a flame ionization detector. Nitrogen was used as the carrier gas. Methane, as a noninteracting marker was used to correct the dead volume in the column and the retention time was directly measured with the aid of an Olivetti M-24 micro-computer, provided with a CHROM+ card and appropriate software. A minimum of four measurements were taken for every molecular probe and for each temperature in all columns.

Pressures at the inlet and outlet of the column, read from a mercury manometer, were used to compute corrected retention volumes by the usual procedures. Flow rates were measured at the end of the column with a bubble flowmeter, and its value was 6–7 mL/min. The columns were conditioned at 100°C for ca. 48 h prior to use while N_2 was flushed through the column in order to achieve equilibrium. The oven temperature was measured within $\pm 0,1^\circ\text{C}$ in the whole temperature range. All IGC measurements were made below the glass transitions in a range of temperatures between 80–155°C for Ultem-1000 and for Rodrun LC-5000, and between 60–85°C for Vectra B-950. Hence, surface adsorption was the dominant mechanism, and adsorption of probe molecules into the bulk of the deposited polymer could be neglected. The molecular probes, including a small amount of methane marker, were manually injected with a 10 μl Hamilton syringe (< 0.01 mL).

In cases where support was used (Ultem and Rodrun), we have not done any correction due to the support contribution to the adsorption. Previous measurements in our Department [14] have shown that in the temperature range we are using, the support does not contribute to the retention volume.

On the other hand, previous experiences in our Department [15] have shown that the crushing of the Vectra B polymer does not produce any change in the polymer properties unless it is processed several times at elevated temperatures.

Computations

Retention volumes were calculated using

$$V_n = \Delta t \cdot F \cdot \left(\frac{P_o \cdot 273.16}{760 \cdot T_r} \right) \cdot \left(\frac{3 \cdot \left(\frac{P_i}{P_o} \right)^2 - 1}{2 \cdot \left(\frac{P_i}{P_o} \right)^3 - 1} \right) \quad (6)$$

where $\Delta t = t_p - t_m$ is the difference between the retention times of the probe and the marker, F is the flow rate of the carrier gas at room temperature T_r , and P_i and P_o are the inlet and outlet pressures, respectively, in mm Hg.

RESULTS AND DISCUSSION

According to Fowkes [16] the thermodynamic work of adhesion between a solid (S) and a liquid (L), when only dispersion interactions take place, is given by

$$W_A = 2(\gamma_S^D \cdot \gamma_L^D)^{1/2} \quad (7)$$

where γ_S^D and γ_L^D are the dispersion components of the surface free energies of the solid and the liquid, respectively. Combining Equations (1), (2) and (7) leads to

$$RT \ln V_n = 2 \cdot N \cdot (\gamma_S^D)^{1/2} \cdot a \cdot (\gamma_L^D)^{1/2} + \text{const.} \quad (8)$$

Therefore plotting $RT \ln V_n$ vs $a \cdot (\gamma_L^D)^{1/2}$ should give a straight line. From the slope, the dispersion component of the solid surface free energy γ_S^D can be calculated.

In order to test the validity of Equation (8) and to quantify the dispersive character of the polymer surfaces by the dispersive component of surface free energy γ_S^D , $RT \ln V_n$ for the n-alkanes vs $a \cdot (\gamma_L^D)^{1/2}$ has been plotted in Figure 1.

The area a occupied by the adsorbed molecules is difficult to quantify, given the possibility of different configurations at the adsorbent-adsorbate contact. It is possible to determine the molecular area experimentally by means of adsorption measurements, but these results also depend on the choice of adsorbing surface. In this work the n-alkanes molecular areas a were calculated by Bondi's radii [17], to avoid the possible experimental uncertainties.

The dispersion component of the surface free energy of the liquid γ_L^D for n-alkanes was obtained in refs 18 and 19. The dispersive components of surface free energy for the n-alkanes have a small dependence with the temperature, but we have not taken it into

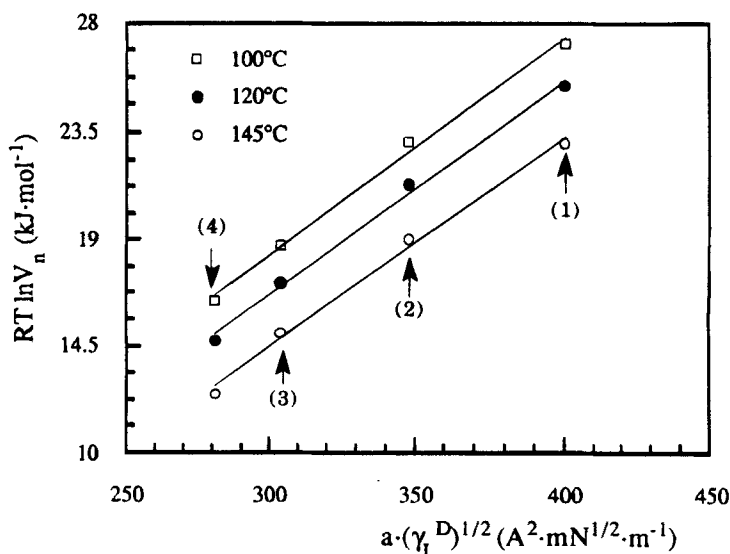


FIGURE 1 $RT \ln V_n$ versus $a \cdot (\gamma_L^D)^{1/2}$ plot for the adsorption of n-alkanes on: (a) Ultem-1000, (b) Rodrun-LC 5000, (c) Vectra B-950 at different temperatures. Solvents: (1) n-octane, (2) n-nonane, (3) n-decane, (4) n-dodecane and (5) n-tetradecane.

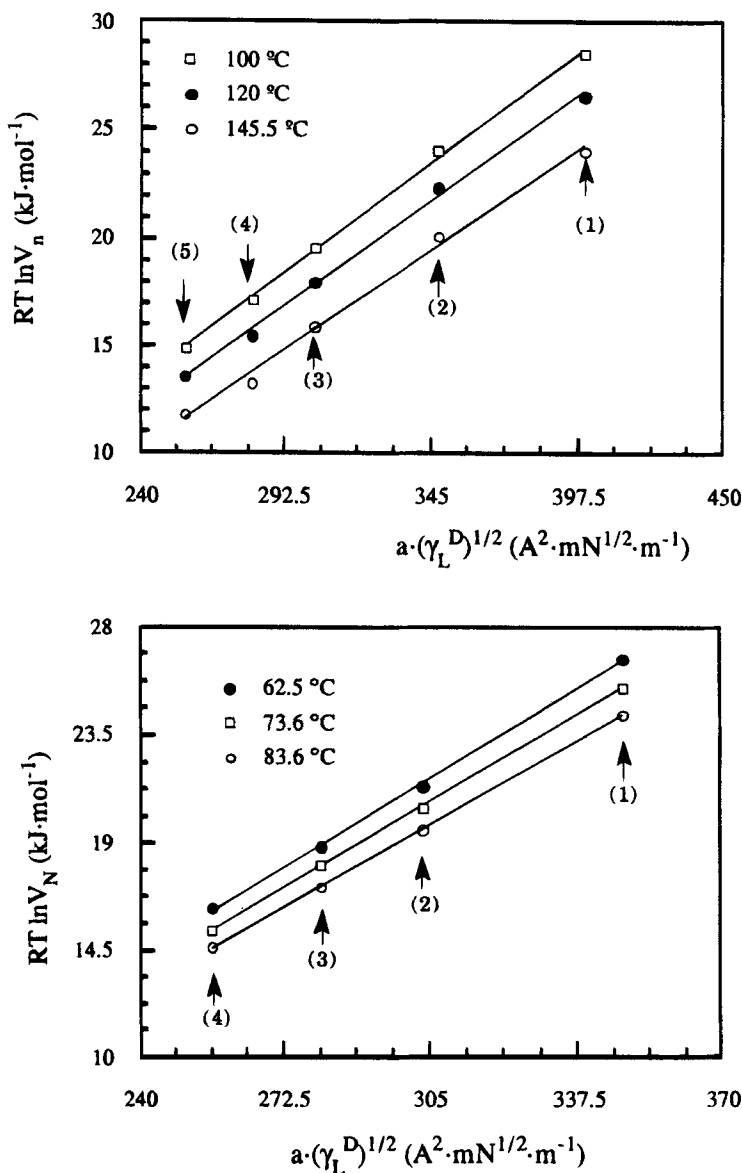


FIGURE 1 (Continued)

account because the purpose of our measurements was more qualitative than quantitative. Moreover, it was not possible to find this dependence for all the probes.

The excellent linearity of each isotherm confirms the applicability of this equation to polymeric stationary phases. The values of γ_s^D obtained for Ultem, Rodrun and for Vectra B are listed in Table II at different temperatures. The values obtained are in good agreement with those obtained by Bolvari and Ward [20] for the polyetherimide ($\gamma_s^D = 45.5 \text{ mJ/m}^2$ below the glass transition).

TABLE II
Dispersive component of surface free energies

T (°C)	γ_S^D (mJ/m ²) Ultem-1000	T (°C)	γ_S^D (mJ/m ²) Rodrun-LC	T (°C)	γ_S^D (mJ/m ²) Vectra B-950
81.1	59.26	81.4	67.71	62.8	72.91
100.5	56.48	86.1	66.62	65.9	72.64
119.8	53.78	91.0	65.50	67.8	72.49
124.8	53.08	95.7	64.43	71.8	72.16
129.6	52.43	100.6	63.33	73.7	71.99
134.4	51.78	105.8	62.17	77.5	71.68
140.2	51.0	110.4	61.15	80.6	71.41
145.0	50.35	115.0	60.14	83.6	71.18
		120.0	59.05		
		124.8	58.47		
		134.5	56.38		
		144.5	54.60		

In view of the extreme dilution of the probe molecules, it is probable that they will adsorb preferentially on high-energy sites within the solid's site energy distribution. The γ_S^D obtained by this experiment may therefore be greater than values obtained from macroscopic sampling of the surface, for example, from contact angle measurements.

Mukhopadhyay and Schreiber [21] found a linear relation of γ_S^D with temperature below the T_g of the polymer, but the established trend was interrupted above the glass transition where the slopes of the n-alkane function increase significantly. The shape of the diagram obtained from the variation of γ_S^D with the temperature through the T_g is similar to those obtained for the retention diagram in IGC for polymers through T_g . This is taken as an evidence of the penetration of the vapor probes into the bulk polymer, a process which perturbs the chromatographic retention data and, consequently, compromises the value of the information as an indicator of surface properties. In our case, we have not reached temperatures above the T_g , avoiding such type of problems.

If the adsorbent is capable of specific as well as of dispersion interactions, then the adsorption of polar solutes gives rise to an interaction term, leading to higher net retention volumes when compared with the occurrence of dispersion interactions alone.

In order to determine quantitatively these specific interactions, we consider, as a first approximation, that the specific interactions are simply added to the dispersive interactions previously defined. Therefore, the experimental point corresponding to a probe capable of specific interaction always lies above the reference straight line of $RT \ln V_n$ vs $a \cdot (\gamma_L^D)^{1/2}$ corresponding to the n-alkanes. At a given value of $a \cdot (\gamma_L^D)^{1/2}$, the difference of ordinates between the point corresponding to the specific probe and the reference line leads to the value of the free energy of adsorption corresponding to specific interactions ΔG_A^{sp} .

$$\Delta G_A^{sp} = RT \ln V_n - RT \ln(V_n)_{ref}. \quad (9)$$

where the reference subscript designates the term of dispersive interactions evaluated by the retention of n-alkanes.

As in the case of n-alkanes, the surface free energies γ_L^D for polar solutes are generally available but the area a occupied by the adsorbed molecules presents additional difficulties. Presently, we rely on an experimental approach by taking as a variable not the

quantity ($a \cdot (\gamma_L^D)^{1/2}$), but the boiling temperature of the solutes. The choice of the boiling temperature is based on the fact that it is a macroscopic reflection of the various forces which assure the cohesion of the solute. Panzer and Schreiber [22] have compared the values obtained for the specific contributions to the free energy of adsorption by three different approaches plotting $RT \ln V_n$ vs:

1. $a \cdot (\gamma_L^D)^{1/2}$
2. the logarithm of vapor pressures $\log P_0$.
3. boiling points T_b of the solutes.

The differences were not relevant and do not identify any one method of data representation as being superior to the others. We decided to use the boiling temperature because of its experimental convenience. The boiling temperatures of most widely-used solutes are readily available and the difficulties in determining exact values of the molecular area a and of the dispersion component γ_L^D are avoided.

The differences between the measured retention volumes and the reference line given by the n-alkanes are used to compute the specific interaction contributions ΔG_A^{sp} to the free energy of adsorption. Figure 2 shows, as examples, the data at 120°C for the Ultem-1000, at 100°C for the Rodrun and at 80.5°C for the Vectra B. The pertinent data are listed in Table III.

The extra adsorption of the polar probes shows that Ultem is the more active and polar of the polymers we studied. The liquid crystal polymers, Rodrun and Vectra B, show a higher chemical resistance with less adsorption. In the case of Vectra B, its well-known insolubility is on the origin of its restricted adsorption compared with the other samples.

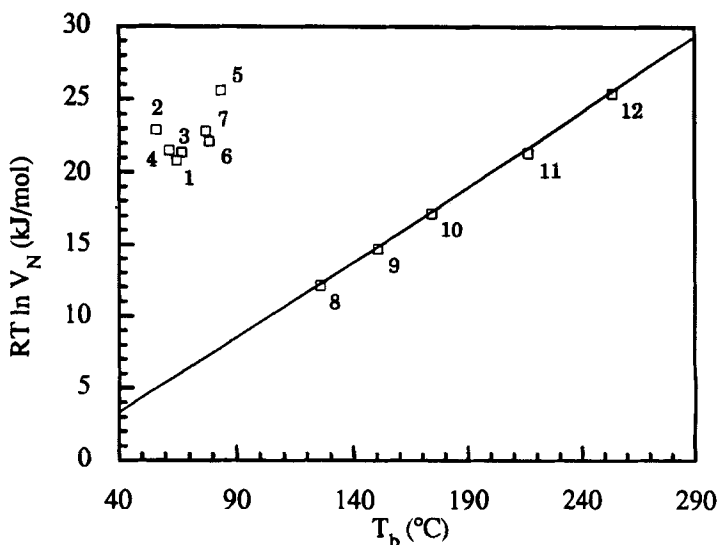


FIGURE 2 Determination of the specific contributions to the free energy of adsorption from IGC data by plotting $RT \ln V_n$ versus T_b at: (a) 120°C for the Ultem-1000, (b) 100°C for the Rodrun-LC 5000, (c) 80.5°C for the Vectra B-950. Solvents: (1) methanol, (2) acetone, (3) THF, (4) chloroform, (5) 1,2 dichloroethane, (6) ethanol, (7) ethyl acetate, (8) n-octane, (9) n-nonane, (10) n-decane, (11) n-dodecane and (12) n-tetradecane.

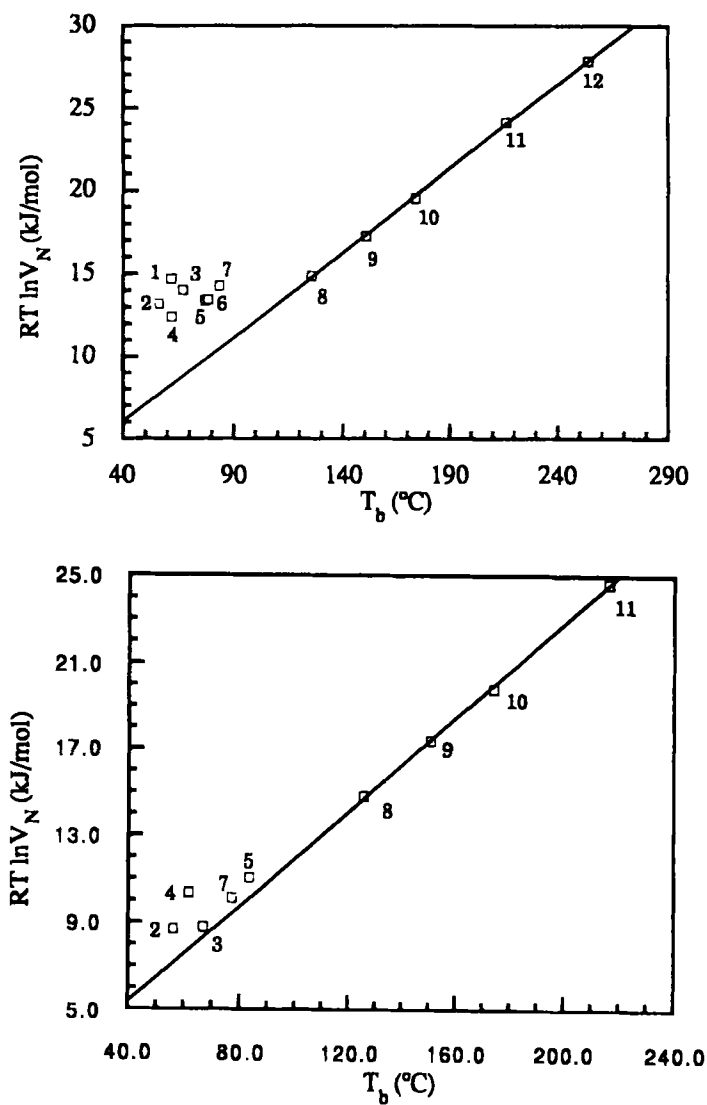


FIGURE 2 (Continued)

TABLE III

Specific components ΔG_A^{sp} of the free energy of adsorption of solutes

Solute	ΔG_A^{sp} (kJ/mol) Rodrun (100°C)	ΔG_A^{sp} (kJ/mol) Ultem (120°C)	ΔG_A^{sp} (kJ/mol) Vectra (80°C)
THF	5.27	15.31	0.46
Ethyl acetate	3.63	15.75	0.62
1,2 dichloroethane	3.85	17.84	0.89
Acetone	5.56	17.99	1.48
Chloroform	4.21	16.00	2.56
Methanol	6.13	14.96	—
Ethanol	3.53	14.91	—

From these data we have calculated the values of the specific contributions ΔH_A^{sp} to the enthalpy of adsorption. These have been calculated from the variation of ΔG_A^{sp} with temperature (Figure 3). Given that

$$\Delta G_A^{sp} = \Delta H_A^{sp} - T \cdot \Delta S_A^{sp} \quad (10)$$

where ΔS_A^{sp} is the specific contribution to the change in entropy due to adsorption per mole of adsorbate, the slope of a plot of $\Delta G_A^{sp}/T$ vs $1/T$ is equated to ΔH_A^{sp} .

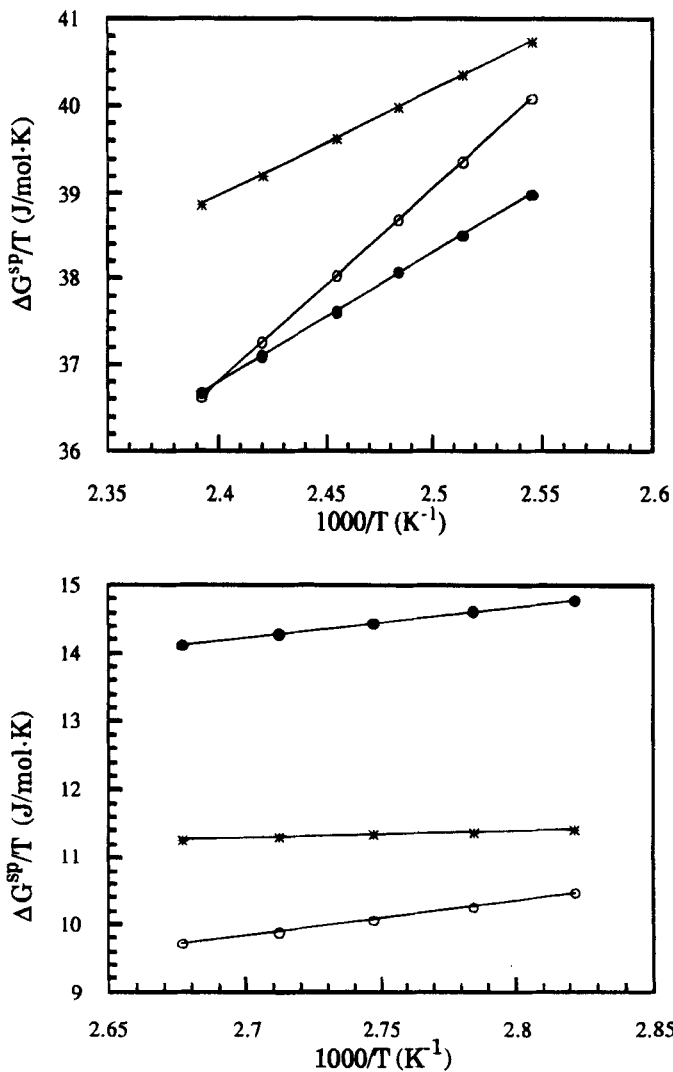


FIGURE 3 Evaluation of specific enthalpies of adsorption according to Equation (10) by plotting $\Delta G^{sp}/T$ versus $1/T$: (●) THF, (○) ethyl acetate and (*) chloroform on: (a) Ultem-1000, (b) Rodrun-LC 5000 and (c) Vectra B-950.

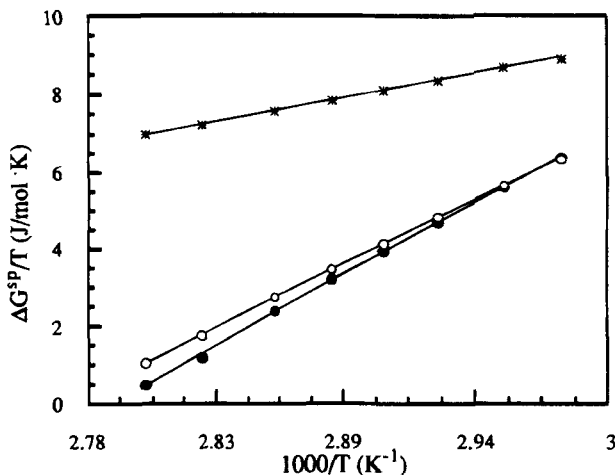


FIGURE 3 (Continued)

If we assume that the specific interactions are in fact Lewis acid-base interactions, ΔH_A^{sp} determined by IGC and the acid-base properties of solutes and the polymers are related as follows:

$$-\Delta H^{ab} = -\Delta H_A^{sp} = K_A \cdot DN + K_D \cdot AN^* \quad (11)$$

The specific enthalpy of adsorption and the Gutmann's numbers (DN and AN*) are listed in Table IV. Plotting $-\Delta H_A^{sp}/AN^*$ versus DN/AN* we obtained a straight line, with K_A and K_D evaluated from its slope and intercept. Figure 4 shows the plots for the polymers. The linear relation is not so good, and it is due to the impossibility of finding more probes with DN/AN* values intermediate between THF and the others, covering the whole range of values. However, we think that the Gutmann approach is applicable to these systems and that specific interactions referred to, may be taken as electron donor-acceptor interactions. Thus the polymers are characterized by means of two parameter describing its acidity (K_A) and basicity (K_D) listed in Table V.

The three polymers are amphoteric and considered as electron acceptors as well as an electron donors. However, in the case of the Ultem, the latter capacity is dominant and the polymer can be considered predominantly basic. This conclusion is in good agreement with its capacity to dissolve in acidic and halogenated solvents and with the previous results obtained by Bolvari and Ward [20].

The small values encountered for the Rodrun are consistent with its chemical resistance to solvents and acid and base aqueous solutions, which is also reflected in the low diffusion coefficient of different chemicals in Rodrun, as in other oriented LCP [23].

The Vectra B-950 is a thermotropic aromatic poly(esteramide) with a hydrogen bonding capability into the chain, reflected in a greater K_D value, which might result in some useful property improvements. The greater interchain interaction could result in increased fiber fatigue resistance, higher filament shear modulus (and tensile modulus), and improved fiber surface adhesion.

TABLE IV

Specific components ΔH_A^{sp} of the enthalpy of adsorption and acid-base characteristics (Gutmann's numbers) of solutes

Solute	AN* (kcal/mol)	DN (kcal/mol)	$-\Delta H_A^{sp}$ (kcal/mol) Rodrun	$-\Delta H_A^{sp}$ (kcal/mol) Ultem	$-\Delta H_A^{sp}$ (kcal/mol) Vectra
THF	0.5	20	1.10	3.62	8.05
Ethyl acetate	1.5	17.1	1.25	5.42	7.21
1,2-dichloroethane	1.8	0.0	0.55	2.93	1.84
Acetone	2.5	17.0	1.30	5.66	12.19
Chloroform	5.4	0.0	0.24	2.93	2.65
Methanol	12.0	19.0	2.80	2.60	—
Ethanol	10.3	20.0	3.50	5.40	—

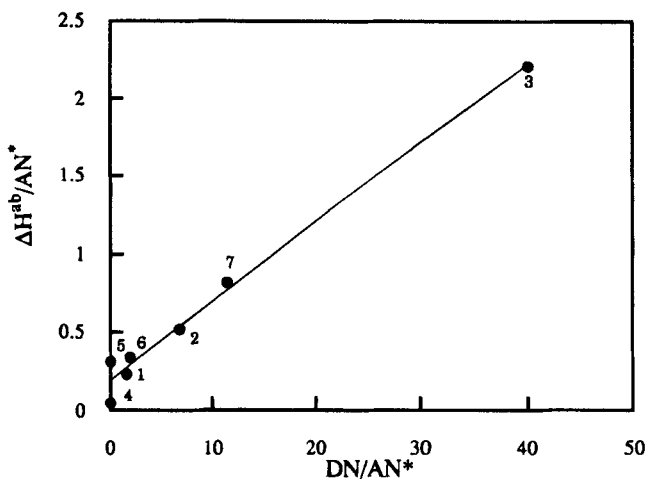
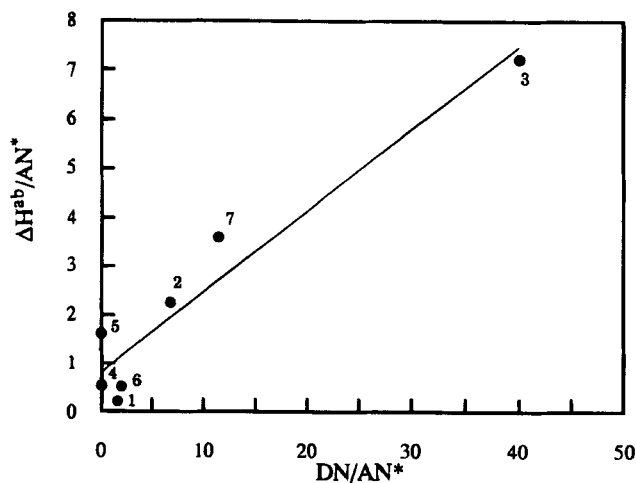


FIGURE 4 Correlation between specific enthalpies ΔH_A^{sp} of adsorption and the DN and AN* values of different solutes according to Equation (11). Data for: (a) Ultem-1000, (b) Rodrun LC-5000 and (c) Vectra B-950. Solutes: (1) methanol, (2) acetone, (3) THF, (4) chloroform, (5) 1,2 dichloroethane, (6) ethanol and (7) ethyl acetate.

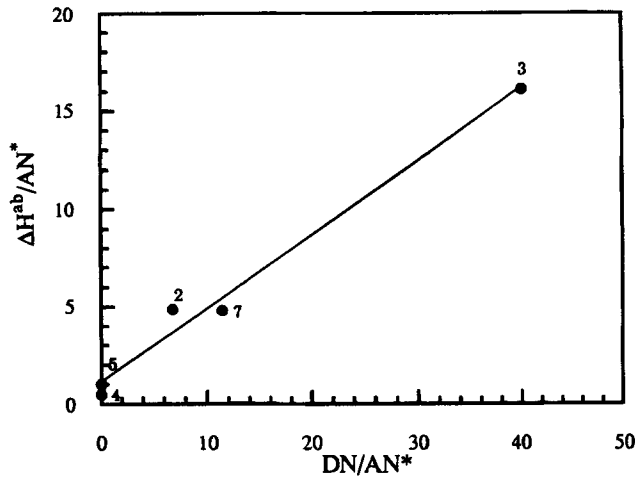


FIGURE 4 (Continued)

TABLE V
Surface parameters describing polymer acidity and basicity

Polymer	K_A	K_D	K_D/K_A
Ultem-1000	0.17	0.82	4.82
Rodrun LC-5000	0.05	0.19	3.8
Vectra B-950	0.38	1.07	2.82

Voelkel *et al.* [24] determined these parameters for two poly(dimethacrylate)s by inverse gas chromatography. The obtained values were of the same magnitude and appeared to be sufficiently sensitive to describe changes occurring on the surface during thermal treatment.

Schultz and Lavielle [18] have proposed to define a specific interaction parameter A describing the acid-base interaction between the components of a composite as:

$$A = K_{A(1)} \cdot K_{D(2)} + K_{A(2)} \cdot K_{D(1)} \quad (12)$$

by analogy with Equation (11). They obtained good correlation between the interfacial shear strength, a mechanical property, and the specific interaction parameter A , related to the acid-base interactions exchanged at the interface. They conclude that the A parameter obtained in this way can be used as a qualitative indication of the mechanical properties of a composite. The values obtained for the systems Ultem/Rodrun and Ultem/Vectra were $A = 0.073$ and $A = 0.493$, respectively. The values seem to be certainly low. However, it must be taken into account that acid-base interactions are not the only explanation for the adhesion. Many other mechanism and phenomena, such as formation of an interface, co-cross-linking, interdiffusion, mechanical anchoring, and interfacial shrinkage, could also participate.

Felix *et al.* [25, 26] propose an expression to calculate acid/base pair parameter from K_A and K_D values:

$$P_{ad} = (K_{A(1)} \cdot K_{D(2)})^{1/2} + (K_{A(2)} \cdot K_{D(1)})^{1/2} \quad (13)$$

The expression is to some extent arbitrary, other averaging methods being possible. They do not find, however, a general behavior of the mechanical properties with the acid/base pair parameter which varies substantially from matrix to matrix.

With this expression, the values obtained for the systems Ultem/Rodrun and Ultem/Vectra were $P_{ad} = 0.38$ and $P_{ad} = 0.98$, respectively, similar to those obtained by Felix et al. [26] for composites having PS or PCE as matrix.

We can conclude that IGC at infinite dilution appears to be a powerful tool for studying the surface properties of polymers and quantifying the acid/base interactions. These interactions play a role in the adhesion at the interface of composites although they are not exclusively responsible for improvements in mechanical properties.

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