Surface Characteristics of Polymer/Small Molecule Blends

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SYNOPSIS

Inverse gas chromatographic data have been obtained for polystyrene, polycarbonate, and two substituted amines used as additives in the polymers. Surface energies have been determined and evaluations made of acid/base interaction parameters and Flory–Huggins χ values for the surface bounded interphase. It was shown that acid/base considerations are implicated in the miscibility of these polymer/additive systems. Surface energy analyses showed that surface and bulk compositions in blends differed whether or not the blend components were miscible. Composition differences were the result of thermodynamic drives to minimize surface free energy. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Two topics of current interest motivated the present research. One is the behavior of polymer matrices blended with small organic molecules. The other is the quantification of specific interactions between components of polymer systems. Both topics are of industrial concern: the former for its application to charge carrier generation layers and charge transport layers in xerographic technology,[1-4] the latter for contributions toward rationalizing concepts of miscibility in multicomponent polymer systems or its relevance to property development in these systems. Quantitative measurements of component interactions have risen in frequency since the development of the convenient inverse gas chromatographic method (IGC). When working above the glass-transition temperature, T_g, of the polymer, this has made it possible to evaluate thermodynamic interaction parameters (e.g. Flory–Huggins χ)[5,6] for polymer/solvent pairs, and also for mixed stationary phases combining two nonvolatile components of a system.[7,8] Recent applications of IGC at temperatures below the polymer T_g have focussed attention on properties of polymer surfaces and on surface-bounded interphases. This extension has made it possible to evaluate the dispersion surface energies

of polymers and to calculate acid/base interaction parameters for polymer surfaces and interphases.[9-11] The availability of acid/base indexes has helped measurably to clarify a variety of polymer system properties.[12]

In this work we have used the IGC method to obtain acid/base interaction numbers and thermodynamic interaction parameters for polymer/additive pairs relevant to xerographic applications. A polystyrene (PS) and a bisphenol-A polycarbonate (PC) were representative of matrix polymers; two complex diamines were used as small molecule additives. Measurements were made over a range of temperatures for various blend compositions, thereby providing some information on the importance of these variables to interaction phenomena at contacts between blend constituents.

EXPERIMENTAL

Materials

The PS used in this work was obtained from Dow Chemical Co. (Canada). Its molecular weights from GPC measurements were reported to be $M_n = 67{,}000$ and $M_w = 93{,}000$. The PC was from Bayer AG. GPC determinations in methylene chloride solutions showed $M_n = 83{,}000$ and $M_w = 163{,}000$.

Two substituted diamines were used as additives to the above polymers. That identified as additive

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A was N,N'-diphenyl-N,N'-bis(3 methylphenyl)-[1,1'-biphenyl]-4,4'-diamine.

Additive B was a more highly substituted analogue, 3,3'-dimethyl-N,N'-bis(4-ethylphenyl)-N,N'-bis-(4-methylphenyl)-1,1'-biphenyl-4,4'-diamine. Both of these chemicals were kindly supplied by Xerox Research Centre of Canada, and were used without further preparation.

Two component blends (PC/A, PC/B, PS/A, and PS/B) for use in preparing chromatographic columns were made in solution, using methylene chloride as solvent for PC-based combinations, and toluene for compounds with PS as matrix. Blend compositions were in the range from 5 to 50 wt % of the small molecule additive.

IGC Procedures

Stationary phases for IGC determinations were prepared by mixing solutions of the polymers or of polymer/additive combinations with Chromosorb G support (AW-DMCS treated diatomaceous earth from Chromatographic Specialties, Brockville, ON, Canada), and slowly evaporating the solvent in a Rotovap apparatus, operating near 50°C. Dry powders were vacuum dried to invariant weight, generally over a period from 60 to 84 h. Standard ashing procedures[12] showed that the weight fraction of solids supported on the Chromosorb varied between 0.082 and 0.11, in line with standard practice to ensure complete coverage of the support surface. The surface area of the support was found to be about 1.6 m^2/g. The surface/volume ratio in supported stationary phases therefore was about 1.5×10^6 cm^{-1}, favoring surface-localized events to dominate retention characteristics. It was assumed that the bulk composition of deposited blends was identical to that in the originating solutions. The surface compositions, however, are the subject of later discussion. Following sieving, coated powders were packed in previously degreased, washed, and dried stainless steel columns, about 1 m in length and 0.15 cm i.d. Columns were placed in a Perkin–Elmer Sigma-2 chromatograph equipped with a flame ionizing detector.

All columns were swept with He carrier gas at 70°C for at least 3 h prior to experimentation. Experimental runs were carried out in the temperature interval of 30–80°C, using the following vapor probes: n-alkanes from C_6 to C_9, diethyl ether (DEE), and chloroform (CHL). These were injected from 5-μL Hamilton syringes into He carrier gas flowing at 12 mL/min. The flow rate was selected for convenience after preliminary work, in which

flow rates were varied from 6 to 20 mL/min, showed that retention times were independent of this variable. Probe concentration was extremely low, attained by first filling the syringe with pure vapor, then pumping the syringe in air 10 times prior to injection. Symmetric peaks, obtained at least in triplicate, led to evaluations of retention times with a reproducibility not less than 3%. Standard procedures were then used to calculate retention volumes, V_n, and these in turn were used to calculate acid/base as well as Flory–Huggins χ values, as noted below.

Surface/Interphase Characteristics of Stationary Phases

The protocols relating V_n to the Flory–Huggins parameter of thermodynamic interaction between nonvolatile stationary and vapor phases, $\chi_{1,2}$, have been described frequently.[5,6,8] They lead to the statement

$$\chi_{1,2} = \ln(RTv_2/V_n p_1^0 V_1)$$
$$- 1 - p_1^0(B_{11} - V_1)/RT. \quad (1)$$

Here v_2 is the specific volume of the polymer, p_1^0 and V_1 are the probe saturation vapor pressure and molar volume, B_{11} is the second virial coefficient for the vapor probe, R is the gas constant, and T is the absolute temperature. Literature compilations[13,14] were used to obtain B_{11} and p_1^0 values.

The IGC procedure has been extended for use with mixed stationary phases,[7] leading to the determination of the interaction parameter for two nonvolatiles in the stationary phase $\chi'_{2,3}$, from:

$$\chi_{(1,23)} = \varphi_2 \chi_{1,2} + \varphi_3 \chi_{1,3} - \varphi_2 \varphi_3 \chi'_{23} \quad (2)$$

where the φ are volume fractions of the stationary phase materials, and the solid pair interaction parameter $\chi'_{2,3}$ has been corrected for differences in probe size by the procedure:

$$\chi'_{2,3} = V_1/V_2 \chi_{2,3}. \quad (3)$$

Formally, these expressions apply to situations where the probe molecule is in equilibrium with the bulk polymer, implying temperature conditions above the polymer T_g. Because, in this work, temperatures were below the T_g of host polymers, the IGC data characterize the properties of surfaces or of surface-localized interphases. Such interphases have been demonstrated[15] to have thicknesses in

the range of tens to hundreds of nanometers, with properties distinct from the bulk. We have assumed that eqs. (1)–(3) may be applied to the surface-bounded interphase, thereby reporting on the thermodynamic interaction parameters of this distinct region of the polymer. A frequent conundrum encountered in determinations of $X_{2,3}$ is its dependence on the choice of vapor molecule.[12] The problem has been discussed in some detail recently.[16] In this work the difficulty has been minimized by choosing chemically similar probes and limiting their number. Calculations of $X_{2,3}$ were based on data obtained with n-heptane and n-octane as the vapor probes. The reported parameter values are within 5% of each other and meet the reproducibility criterion stated above.

Values of V_n also may be used for estimations of surface energies and acid/base numbers for individual and blended stationary phases. The link between V_n and the solid's dispersion surface energy, $(\gamma_s)^d$, was developed through the arguments of Fowkes,[17] Papirer,[18] and Schultz.[19] At high dilution of the vapor phase, where Henry's law applies, it can be shown that:

$$\text{RT ln } V_n = 2Na[(\gamma_l)^d]^{1/2} \cdot [(\gamma_s)^d]^{1/2} + \text{const} \quad (4)$$

where a is the area of the adsorbed vapor molecule, and the subscripts l and s refer to the vapor and solid phases, respectively. When only dispersion forces are active, as is the case when n-alkane probes are used, then a linear plot of RT in V_n vs. the product $a(\gamma_l^d)^{1/2}$ leads to values of the solid's dispersion surface energy. We have used the procedure in this work knowing that it entails distinct limitations. One of these is the uncertainty relating to a. This is not necessarily equivalent to the area of the unadsorbed molecule, the latter being the datum used here. The difficulty can be avoided by alternate developments of IGC equations that replace a by the probe's vapor pressure or normal boiling point.[9,20] However, appreciable quantities of data in the literature now use the approach of eq. (4), motivating its retention in the present case.

A second particularity applies to surface energies obtained by this route, as noted by Wesson and Allred.[21] Because most solids have a broad spectrum of surface site energies and the quantity of vapor used in IGC is very small, IGC data tend to evaluate the $(\gamma_s)^d$ of high energy surface sites. Consequently agreement between IGC and contact angle determinations of $(\gamma_s)^d$ is not to be expected generally.

Finally, the IGC protocol is most convenient for the determination of nondispersive forces acting at solid surfaces. According to Fowkes,[22] these may be identified as acid/base forces. When an acid or base vapor of known a is used in the IGC experiment and the resulting V_n is plotted according to eq. (4), then any deviation from the straight line defined by the dispersion-force probes (e.g. n-alkanes) is a measure of the acid/base interaction between vapor and solid. Formally, the free energy change due to acid/base forces is written:

$$\Delta G_{ab} = \text{RT ln} (V_n/V_n^{ref}) \quad (5)$$

where V_n^{ref} is the net retention volume of a hypothetical alkane with the same dimension as the acidic or basic probe.

To make use of the concept a choice must be made of vapor probes and this also entails a choice of acid/base theory: that of Gutmann[23] has been applied in our laboratories. Gutmann defines organic vapors as electron donors (bases) or acceptors (acids) on the basis of calorimetric and NMR spectral data. Thus, the acid/base indicators, AN and DN respectively, have different units, making it difficult to define the net acidity or basicity of any given chemical. However, AN and DN may be compared for different materials leading to decisions on relative acid or base tendencies. (The units problem may be avoided by following procedures proposed by Riddle and Fowkes[24] and applied by Panzer and Schreiber.[11] The procedure, however, is laborious and was not followed in the present instance.)

The interaction characteristics of vapors used here are given in Table I. Expectedly, the alkanes are pure dispersion vapors, with AN = DN = 0. In Gutmann's terminology chloroform is a pure acid with DN = 0, while DEE is a strong bse, albeit with some acceptor potential. The position of the CHL and DEE probes in representations dictated by eq. (4) may then be used empirically to assign AN and DN numbers to the solid adsorbent. In other words, in terms of eq. (5), the position of the CHL datum

Table I Interaction Characteristics of Vapors Used in IGC

Vapor	Surface Area (Å^2)	γ_s^d (mJ/m^2)	AN	DN
n-Hexane	51.5	18.4	0	0
n-Heptane	57.0	20.3	0	0
n-Octane	62.8	21.3	0	0
n-Nonane	68.9	22.7	0	0
CHL	44.0	25.0	25.0	0
DEE	47.0	24.2	3.9	19.2

equates the ΔG_{ab} to the solid's DN, while the solid's AN is obtained from the position of the DEE datum.

RESULTS AND DISCUSSION

Individual Material Properties

A representation of IGC data in terms of eq. (4) is found in Figure 1. This shows results for the PS matrix at 30 and 50°C. Noteworthy are the well-defined straight line given by the alkane retention volumes and the positions of the CHL and DEE points. Values of the $(\gamma_s)^d$ are readily obtained from the slopes of linear portions in Figure 1. The PS, clearly, is a predominantly basic polymer. The position of the CHL data shows the polymer DN to be 5.17 and 4.83 (at 30 and 50°C, respectively). The AN numbers, although finite, are much lower at 2.77 and 2.50. Figure 1 is fully representative of the entire

set of IGC results, including those for the small molecules. Summaries of AN, DN, and surface energy parameters for the host polymers and for the additives are presented, respectively, in Tables II and III. The tables also list the ratio DN/AN, an indicator of the overall interaction tendency of each material at each temperature, but one which is viewed with the reservations noted in the preceding section.

Table II shows PS and PC to differ in their interaction behavior. The basicity of PS, as indicated by DN/AN > 1, is replaced in PC by amphoteric behavior, with the parameter ratio near unity at ambient temperatures. The present PC is similar to other bisphenol polycarbonates, also found to be amphoteric (11). Both polymers show a significant temperature variation of AN and DN. This is particularly notable in the PC, where the diminution with rising T of AN is proportionally greater than that of DN. As a result the polymer shifts toward
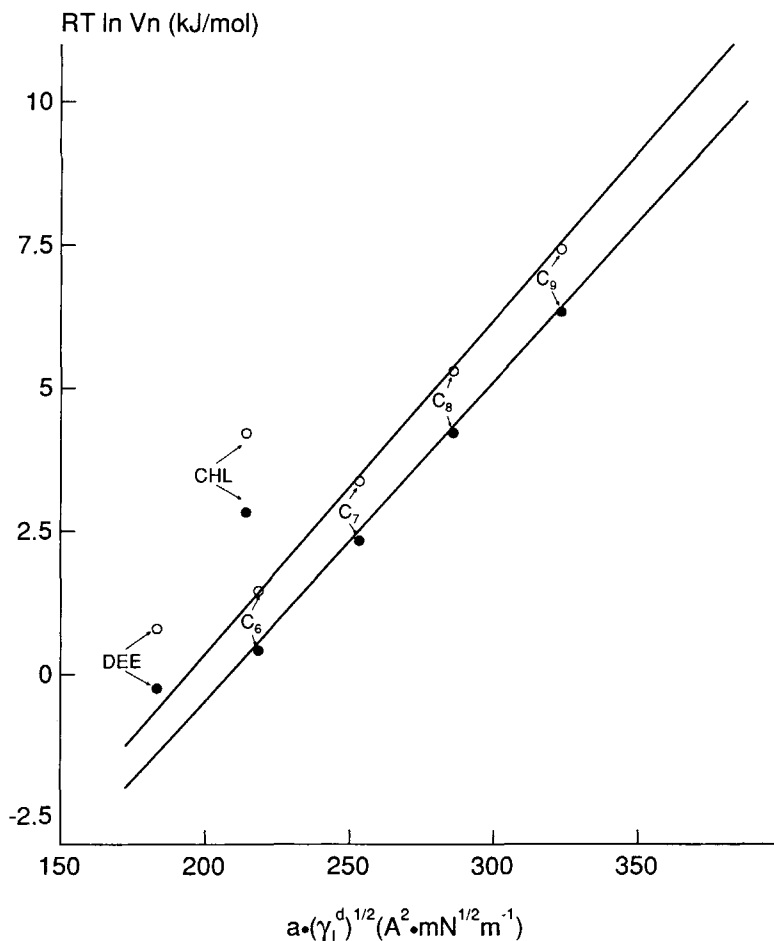
Figure 1   Representation of inverse gas chromatographic data for vapors retained by polystyrene: (O) 30°C; (●) 50°C.

Table II   Acid/Base Indices and Surface Energies for Polymers

	Temperature (°C)					
	30	40	50	60	70	80
PC						
AN[a]	12.9	12.7	11.7	10.0	8.9	8.0
DN[b]	14.3	14.1	13.3	12.0	11.1	10.6
DN/AN	1.11	1.14	1.14	1.20	1.25	1.33
γ_s^d (mJ/m²)	33.5	33.0	33.0	32.6	32.1	32.8
PS						
AN[a]	2.77	2.49	2.50	2.07	1.62	1.67
DN[b]	5.17	5.02	4.83	4.17	3.69	3.32
DN/AN	1.87	2.00	1.93	2.01	2.28	1.99
γ_s^d (mJ/m²)	30.4	29.6	29.0	28.6	27.9	27.2

[a] AN from retention of DEE.
[b] DN from retention of CHL.

basic behavior at temperatures above about 60°C. The inference may be drawn that the donor sites of PC are more energetic than acceptor sites. The variation with T of AN and DN in PS is roughly equivalent, leaving the ratio number near 2.0 throughout the investigated range. Of the two polymer hosts the PC may be the more interactive, with the numerical values of AN and DN greater than those for the PS.

Analysis of Table III establishes significant differences between the small additive molecules. Additive A seems more capable of specific interactions, its AN and DN numbers greater than those of B. Acceptor and donor sites are in balance for additive A, the ratio DN/AN remaining at unity throughout the temperature range studied. B is amphoteric at ambient temperatures, but in this more highly substituted diamine, the temperature dependence of AN and DN is considerably greater than in A, with ∂DN/

∂T particularly large. As a result, at temperatures above the 50–60°C range, the material seems to have net acid properties. However, the acid/base interaction indices are quite small suggesting a significant diminution in the importance of acid/base interactions at these more elevated temperatures. The dispersion surface energy of B is somewhat higher than of A, with similar temperature dependencies in the two cases.

Some Characteristics of Two-Component Systems

The availability of acid/base parameters for host and additive materials allows for the calculation of acid/base pair interaction numbers, P_{ab}. There are no firm theoretical guidelines for such a calculation, but as noted in a separate article,[25] a possible approach is found in the statement:

Table III   Acid/Base Indices and Surface Energies for Organic Additive Molecules

	Temperature (°C)					
	30	40	50	60	70	80
Additive A						
AN	7.7	7.3	7.3	5.8	6.1	5.2
DN	8.1	7.7	7.3	6.0	6.1	5.3
DN/AN	1.1	1.1	1.0	1.0	1.0	1.0
γ_s^d (mJ/m²)	37.5	37.5	37.0	36.6	36.1	36.0
Additive B						
AN	6.2	6.1	5.9	5.4	4.9	4.1
DN	6.0	5.9	5.0	3.7	2.0	1.8
DN/AN	0.9_7	0.9_6	0.8_5	0.6_9	0.4_1	0.4_2
γ_s^d (mJ/m²)	40.7	40.6	40.0	39.5	39.0	39.1

$$P_{ab} = [AN_1 \cdot DN_2] + [AN_2 \cdot DN_1]$$
$$- [AN_1 \cdot AN_2] - [DN_1 \cdot DN_2]. \quad (6)$$

Here the subscripts 1 and 2 stand for polymer and additive, respectively, and the computation defines a net specific attraction number for each pair at a given temperature. Because the AN and DN in eq. (6) apply to the pure components, P_{ab} is inherently unable to inform on possible variations of acid/base interaction with blend composition.

A tabulation of P_{ab} numbers is found in Table IV. No *a priori* decision can be made as to what absolute value of P_{ab} represents important acid/base effects. Obviously, however, such interactions would be identified by positive values of the index. Accordingly, acid/base interactions between polymers and additive A appear to be very slight, an exception being at 80°C for PS/A. The B additive tends to interact more strongly, notably at $T > 50$°C. At these temperatures P_{ab} numbers become sizeable, suggesting significant contributions from acid/base events to interactions with both PC and PS. A question of immediate concern is the possible contribution of acid/base interactions to the miscibility of a given polymer/additive pair. Using eq. (2), the retention volumes for polymer blends with 20 wt % additive have resulted in evaluations of χ'_{23}, to be used as indicators of miscibility, with relevant data given in Table V. We note, as earlier in this article, that this procedure estimates interactions between the additive molecules and the surface-bound polymer interphase. Different values of the parameter would be expected were IGC data to be collected well above the polymer T_g. The general conclusions drawn from an inspection of Table V are as follows:

1. Blends of PC/A are near the limiting value of the χ parameter for miscibility. One may

Table IV   Acid/Base Pair Interaction Parameter P_{ab}, for Polymer/Additive Systems

	System			
	PC/A	PC/B	PS/A	PS/B
T (°C)				
30	0.3	0.3	−1.0	0.5
40	−0.5	−0.2	−1.0	0.5
50	0	1.5	−0.4	2.2
60	−0.4	3.4	−0.4	3.7
70	0	6.4	0.4	6.0
80	−0.1	6.3	3.9	4.0

Table V   Thermodynamic Interaction Parameter, χ^1_{23}, for Polymer/Additive Systems

|	System			
	PC/A	PC/B	PS/A	PS/B
T (°C)				
30	0.27	0.13	0.37	0.36
40	0.24	−0.07	0.39	0.36
50	0.18	−0.17	0.44	0.40
60	0.22	−0.11	0.37	0.29
70	0.27	−0.30	0.19	0.25
80	0.30	−0.32	0.14	0.08

Additive concentration = 20 wt %.

surmise that very little thermodynamic driving force would be needed to phase separate these materials. The minute quantities of probe vapors used in the experiments are most unlikely to trigger measurable morphological changes.

2. PC/B appears to be a miscible pair, more particularly at increasing temperatures.

3. The pattern with PS as host is similar to the above for additive A. Again the miscibility is in question, except at $T > 70$°C; the pattern with molecule B is such as to suggest that PS/B is somewhat more miscible than PS/A. PC/B however remains the most obviously miscible pair in the group.

The attempt to link acid/base factors to the state of miscibility between additives A and B and the polymer surface layers has led to the representation of Figure 2. Each of the four systems (always at 20 wt % of the inclusion), at each of the temperatures, is shown in the figure. The data scatter is quite pronounced at P_{ab} values near 0 so that calculation of a correlation factor seems unwarranted. The existence of a correlation nevertheless is indicated when P_{ab} values fall in the range above about 2.0. The broad envelope into which the data fall at the lower end of the investigated P_{ab} range appears to narrow significantly at the higher end of the parameter scale. The conclusion is implied that acid/base interactions, when exceeding a yet to be defined lower limit, make important contributions to the miscibility of polymer/additive pairs, and that IGC experiments provide guidelines to this issue.

We have noted already that the IGC data characterize the surfaces of the present matrix polymers. Because polymers like PS and PC contain both dispersive and nondispersive constituents, it is very
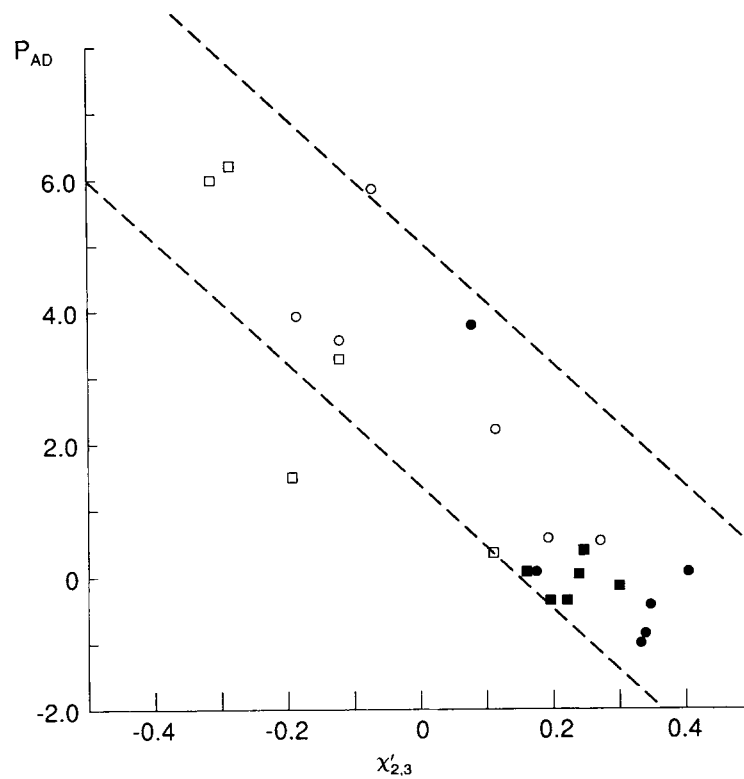
Figure 2 Possible relationship between acid/base interaction number P_{ab} and the Flory–Huggins $\chi'_{2,3}$. All experimental temperatures are represented for: (●) PS/A; (○) PS/B; (■) PC/A; (□) PC/B.
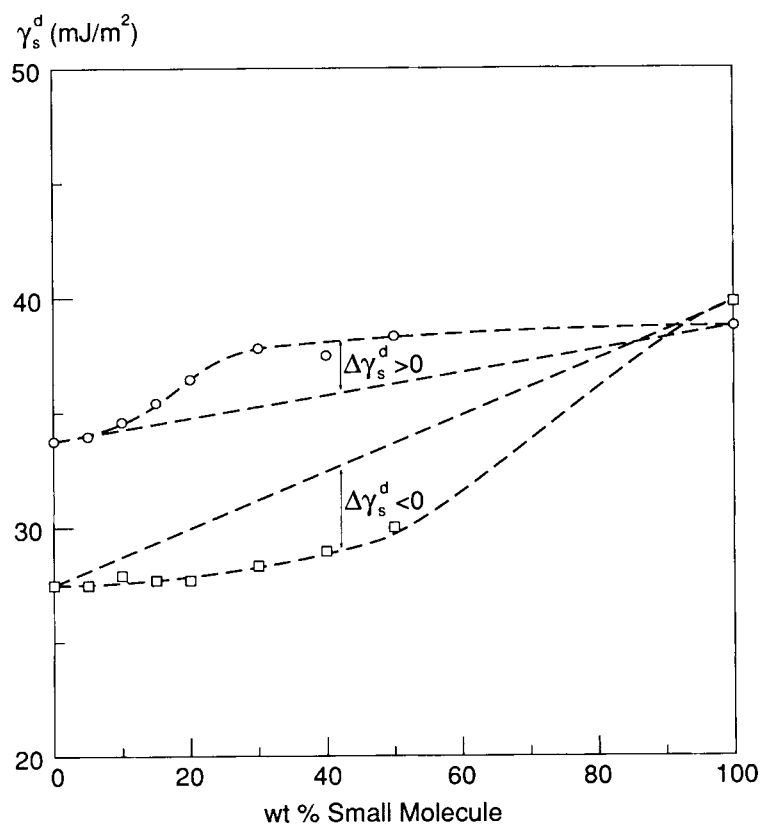
Figure 3 Dispersion surface energies for polymer/additive blends as a function of blend composition, illustrating deviation from combinatorial behavior: (○) PC/A at 30°C; (□) PS/B at 80°C.

likely that surface and bulk compositions differ, in keeping with thermodynamic demands to minimize surface free energy.[26] Thus, the acid/base properties of the bulk polymers also may differ from those attributed to their surfaces. The problem of differences in bulk and surface compositions becomes more emphatic in polymer blends. Even in miscible blends surface-to-bulk variations must be expected, in part due to the above-noted drive to minimize surface free energy that will tend to produce a surface excess of the component with minimum surface energy, and in part due to entropic considerations, as noted in contemporary work by Jones and Kramer.[27] Further inspection of Tables II and III shows that the dispersion surface energies of the additive molecules A and B differ, and that both tend to exceed those of the host polymers, particularly PS. Even though the total surface energies of all materials will exceed their $(\gamma_s)^d$, the contribution of nondispersion surface energies is slight with the exception of PC, the total γ_s of that polymer being near 44 mJ/m² at

room temperatures. It is possible therefore that the surface energy values may trigger substantial differences between surface and bulk compositions in at least some of the present blends.

One examination of the possibility is presented by way of Figure 3. The dispersion surface energies are plotted at various bulk compositions of systems PC/A at 30°C and of PS/B at 80°C. Clearly, neither system follows simple combinatorial rules: in the case of PC/A the $(\gamma_s)^d$ are rapidly skewed toward the higher datum of additive A, implying an excess surface concentration of the additive. The total surface energy of additive A, determined from contact angle measurements at 30°C, was found to be 40.5 mJ/m², some 4 mJ/m², lower than that of PC. Coupled with the tenuous miscibility indication in Table V, this is sufficient to promote a compositional gradient between surface and bulk.

In the case of PS/B the pattern is reversed, the data implying a surface excess of the host PS. The negative deviations displayed by this system, defined

Table VI   Apparent Surface Excess in Polymer/Additive Blends

Blend	Temperature (°C)					
	30	40	50	60	70	80
PC/A (bulk comp)						
90/10	5	3	9	3	2	5
80/20	60	45	50	46	26	21
70/30	53	60	55	57	40	33
60/40	40	51	42	50	22	32
50/50	35	30	28	42	15	15
PC/B						
90/10	−2	−4	0	0	−3	−3
80/20	−7	−8	0	0	−3	−8
70/30	−16	−5	−2	−3	−10	−14
60/40	−16	−11	−7	−15	−12	−11
50/50	−4	−4	−15	−10	−11	−7
PS/A						
90/10	−6	−10	−8	−5	−2	−6
80/20	−25	−18	−20	−8	−7	−3
70/30	−40	−46	−37	−11	−5	−11
60/40	−40	−42	−44	−16	−12	−12
50/50	−33	−25	−19	−10	−10	−7
PC/B						
90/10	−3	0	0	−4	0	−2
80/20	−3	−2	−4	−5	−11	−13
70/30	−8	−9	−7	−6	−16	−17
60/40	−12	−7	−14	−18	−20	−24
50/50	−13	−16	−13	−17	−28	−26

Surface excess expressed in wt % of small molecule: values > 0 denote excess of additive; values < 0 denote excess of polymer host.

as $\Delta\gamma^d < 0$ in Figure 3, were typical of all blends except the PC/A series where $\Delta\gamma^d$ was always positive. The excess PS in the PS/B system displayed is also consistent with the surface energy minimization hypothesis, the relevant datum for PS being some 12 mJ/m^2 lower than that for additive B (see Tables II and III). The surface enrichment here takes place in a blend whose components, with $\chi'_{2,3} = 0.08$, must be considered as miscible, confirming theory referred to above.[26,27]

An attempt was made to quantify the surface excesses using the surface energies of blends. The procedure was based on the construction in Figure 3, defining the quantity $\Delta\gamma_s^d$. We then equate the surface excess, in wt %, with the quotient:

$$[\Delta\gamma_s^d/(\gamma_s)_2^d - (\gamma_s)_1^d] \times 100,$$

with subscripts 2 and 1 referring to additive and polymer host. Thus, positive values signify an excess of the small molecule, and negative values a surface excess of the host polymer. Results of the estimation are presented in Table VI. These indicate the existence of surface excesses in the great majority of the current blends. The surface excess of the small molecule in PC/A persists at all compositions and all temperatures, rising to levels in the 50–60 wt % range. In PC/B, however, it is the host polymer that preferentially accumulates at the surface, although the effect is very small at lower concentration of the additive molecule. The systems based on PS always report an excess of the host polymer, although at 10 wt % additive A the results may not be significant.

CONCLUSIONS

1. An IGC study has been carried out on polymers and organic additive molecules useful in reprographic applications.
2. Surface energies and acid/base interaction parameters were obtained over a significant temperature interval and for polymer/additive blends as well as for individual components.
3. Flory–Huggins interaction parameters $\chi_{2,3}$ were calculated to characterize interactions between organic molecules and the surface-bound interphase of host polymers. Values of the interaction parameter tend to vary in relation with acid/base parameters for polymer/additive pairs, suggesting that acid/base forces contribute to miscibility criteria.

4. Surface energy data were used to infer the composition of blend surfaces. Surface excesses of either host polymer or additive were found in the great majority of cases. The driving force for these was the surface energy of blend constituents. Surface/bulk composition variations occurred regardless of whether blend constituents were miscible or immiscible.

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