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TEMPERATURE DEPENDENCE OF POLYMER INTERACTION: RELEVANCE TO ADHESION

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Acid-base interaction parameters, obtained from inverse gas chromatographic data, have been studied as function of temperature for a series of homopolymers. Acid-base functionality varies inversely with temperature, permitting the identification of a critical temperature where acid-base interaction abates, leaving dispersion forces to act at the surface. Polymer assemblies, prepared at temperatures encompassing the critical values, display a discontinuity in lap-shear bond strength. In inherently incompatible pairs, the abatement of unfavorable acid-base forces enhanced bond strength. An adverse effect was noted in assemblies containing polymers with favorable acid-base interaction. Bond strengths of assemblies joined above critical temperatures display a time-dependent reversion to equilibrium values when exposed to lower temperatures.

Keywords: Acid-base forces; Temperature dependence; Critical temperatures; Lap-shear bond strength; Time-dependence

INTRODUCTION

The ascendancy of research directed at quantifying properties of polymer surfaces, interfaces and interphases has much to do with the quest for optimizing the properties of polymer systems. The control of interfacial and interphase properties through the use of coupling agents and the design of novel polymeric intermediaries may be cited as an important facet of the quest. The work of Hatsuo Ishida, to

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whom the present paper is dedicated, and of his associates, has made significant contributions to this field [1, 2]. A concern for polymer surfaces, interfaces, etc., inescapably leads to considerations of the kind and strength of interactions occurring at these sites. In particular, one may focus on the contribution of non-dispersion or, adopting the terminology of Fowkes [3, 4], of acid-base interactions to the properties displayed by a polymer system. It is to this theme that the present paper is directed. Specifically, we consider the temperature dependence of acid-base interactions in selected polymers, notably as this relates to the strength of adhesive bonds formed by them. In the process, a “window” for preferred processing temperatures of certain polymers seems to have been defined.

Oddly, the temperature dependence of polymer interactions has not been explored exhaustively. The statement applies more strictly to polar (*i.e.*, acid-base) than to dispersion, or Lifschitz/van der Waals (L/W) interactions, since the T -dependence of the latter may be inferred for non-polar polymers from the corresponding variation of the surface energy [5]. A strong contributor to this lack of reliable information has been the experimental difficulty of amassing acid-base interaction data over appreciable ranges of temperature. With the advent of inverse gas chromatographic (IGC) techniques [6], however, that difficulty has been much reduced. In the present work, IGC has been used to generate values of the acid-base interaction parameters, K_a and K_b , for a number of commodity polymers, including polycarbonate (PC), polystyrene (PS), Nylon 6 (PA), polymethyl methacrylate (PMMA) and polyvinyl chloride (PVC). The acid (K_a) and base (K_b) numbers are those originally defined by Papirer [7], and Schultz and coworkers [8]. In the relevant experiments, polymer stationary phases are first “probed” by vapors (*e.g.*, n -alkanes) able to interact with the polymers by L/W forces only. Subsequently, vapors are used with defined electron donor (acid) and acceptor (base) properties, as defined by the Gutmann acid-base theory [9]. Following well-established protocols [6–8], the retention data for the polar probes define an acid-base contribution to the free energy of adsorption, ΔG^{ab} . When this is measured over a limited T range (for example 20–30°C), conventional thermodynamic expressions are used to obtain the acid-base enthalpy of interaction, ΔH^{ab} , and this finally enters into the equation:

$$-\Delta H^{\text{ab}}/\text{AN} = K_a \text{DN}/\text{AN} - K_b \quad (1)$$

where the AN and DN are Gutmann’s acceptor and donor values [9] for the vapor probes involved in the experiment. The K_a and K_b so obtained are averaged values over the restricted T range in question. Of

course, since IGC can be performed over very broad temperature ranges, the method allows for a detailed examination of the $\partial K_a, K_b / \partial T$ functions. The cited capability notwithstanding, the warning must be issued that experimental K_a and K_b values (and, therefore, their derivatives) have a relative but not an absolute significance. In part, this is due to a need to choose an acid-base theory on which to base these parameters. There is as yet no general agreement on which of the contending theories best represents physical reality; the current selection of Gutmann's approach is made for reasons of convenience. Some of the procedures in IGC leading to K_a and K_b also merit mention. Notable is the descriptor selected to characterize properties of the vapor-phase probe. The area of cross-section (a) of the molecule is a frequent choice. This, however, introduces uncertainties particularly when non-spherical probe species are involved, for, then, the question of orientation of the probe to the adsorbing surface requires consideration. In this work, the difficulty has been circumvented by using the normal boiling point of the probe as the characterization datum. As was shown in earlier work, discussed in [13], this choice leads to property designation of the stationary phase in quantitative agreement with data obtained with a as the probe designator.

PROBABLE SHAPE OF K_a , K_b TEMPERATURE DEPENDENCE

No formal mathematical treatment is given here for the temperature variation of the interaction parameters. A qualitative evaluation, however, may be proposed. Evidently, in order for short-range acid-base interaction to occur between probe and polymer solid, the probe molecule must come within intimate contact of the solid, *e.g.*, ≤ 1 nm, and remain there for a finite period in an adsorbed state. At increasing temperatures, the kinetic mobility of both the polymer chains and especially of small probe molecules rises, inhibiting the adsorption process, and rendering more problematic the joint requirement of intimate contact/finite residence time for an effective acceptor/donor exchange to take place. It follows that at some critical temperature, T_c , acid-base functionality ceases, leaving only the long-range L/W forces to act between members of the system. The relationship between K_a , K_b and temperature, therefore, should be inverse, both parameters attaining a zero value at T_c . In the event that the loss of acid-base interchange is largely attributable to the probe molecule's excess thermal energy, then, as noted later in this article, the loss is illusory and not truly indicative of fundamental polymer properties. In this case T_c should be probe dependent, and

increase with the probe's molar mass. More importantly, inability to interact by short-range forces may also be due to the chain dynamics of the substrate, however. In that event, T_c should be functionally related to a chain mobility factor. Such a factor would be dependent (at least) on molar mass, steric hindrance effects and the inherent segmental mobility of the polymer.

Initial explorations of the matter were reported recently [10, 11]. Particularly in [11], IGC was used over appreciable T ranges in order to generate data suitable for correlating interfacial tensions between polymer pairs with their acid-base pair interaction parameters, I_{sp} [12], defined in Eqn. (3) of this paper. The posited inverse relationship between K_a , K_b and temperature, and the apparent existence of T_c limits, were indeed confirmed. The present paper extends the inquiry and broadens it by seeking relevance to adhesion and, thus, more directly to a range of mechanical properties in polymer systems.

EXPERIMENTAL SECTION

Materials

The following polymers were involved in this study: Polycarbonate (PC): This was a Lexan[®] 140 sample from General Electric Co., Schenectady, NY, described in an earlier communication [13]. A reference polystyrene (PS), from Dow Chemical Co., had a reported $M_w = 87,000$ and $M_w/M_n = 1.35$. In a limited experimental series additional PS samples, from the same source, were used. One of these had $M_w = 40,600$ and the second $M_w = 22,000$. The PA sample was from DuPont Chemical Co, and was described earlier [14]. The PMMA, also from the DuPont Co., had a viscosity-average molar mass of 43,500. PVC supplied by Synergistic Chemical Co., Canada, had a viscosity average molar mass of 66,000. It was used without additives.

In IGC experiments the vapor probes included the usual n-alkane series from nC6-nC9, and polar probes selected on the basis of the Gutmann theory [9]. These were the acids chloroform (CHL, AN = 23.1, DN = 0) and benzene (BZ, AN = 8.2, DN = 0.1), and the bases diethyl ether (DEE, AN = 3.9, DN = 19.2) and tetrahydrofuran (THF AN = 8.0, DN = 20.0).

Procedures

A Varian 3400 chromatograph, with hot wire and ionizing flame detectors, was used for IGC work. With the exception of PA, polymer stationary phases were prepared by coating the polymers from solution onto Chromosorb[®] AW 60/80 support. Toluene was used as solvent for

PS and PMMA, and methyl ethyl ketone for PC and PVC. Initial solution concentrations were in the vicinity of 1.5 wt%. Following solvent evaporation in a Rotovap[®] unit, the coated powders were vacuum dried, and samples taken from them were ashed, showing that the mass of retained polymer was 7.6 wt% for PS, 9.0 wt% for PC, 7.7 wt% for PMMA and 6.9 wt% for PVC. In all cases, this was adequate to ensure full multi-layer coverage of the available support surface. Coated support was packed in previously degreased, washed and dried stainless steel columns, between 90–130 cm in length. The relatively cumbersome length was necessitated by the requirement to generate adequately long retention times at the high temperatures involved in this work. The PA sample was ground under cryogenic conditions, and 2.77 g of the powder packed directly into a column 1.2 mm in diameter and 28 cm in length. All columns were conditioned in the chromatograph for 24 h, at 60°C under a flow of dry He, which was the carrier gas for the work. Triplicate determinations of retention times were then carried out at temperatures in the range from 50–300°C. Vapors were injected at extreme dilution into He carrier gas flowing at 8 ml/mm. Retention peaks were invariably symmetrical, allowing for the determination of retention times and volumes to an accuracy of better than 4%. A slightly higher uncertainty of 6–8% applies to the K_a and K_b values obtained from the retention results.

Specimens intended for bond strength evaluations were obtained by first compression molding the polymers in a modified Carver press. The polymers were placed onto a mechanically joined mold, 10 × 3 cm in dimension. A Teflon[™] sheet was placed on the bottom of the mold, so as to control the thickness of molded specimens at 1.5 mm. A steel piston, bolted to the top plate of the press, had dimensions marginally lower than the mold, allowing it to enter the mold and, thus, exert direct pressure on polymer samples placed therein. Polymer samples were covered with a Teflon[™] sheet and molded at 200 ± 10°C under an applied pressure of approximately 135 kg/cm². About 15 specimens of each polymer were produced in this manner. They were cooled and their surfaces thoroughly cleaned with warm ethanol and distilled water. They were then dried and stored in desiccators for further use.

The molded samples were used to form single lap-shear joints with a bonded area of 5 cm × 3 cm. This portion of the study was limited to the pairs PC/PS, PC/PA and PC/PVC. Bonding took place in the T range between 200 and 300°C. Bonded joints were quenched in running cold water, then carefully dried and conditioned at 25°C/50% RH for 24 h prior to evaluation. This utilized an Instron table model tester at a clamp separation speed of 5 mm/mm. At least 3 assemblies of each

pair were tested, with a reproducibility of not less than 8% about the average value.

RESULTS AND DISCUSSION

The present inquiry fully confirmed earlier indications [10] of an inverse relationship between the apparent acid-base functionality of polymers and temperature. Figures 1 and 2 illustrate the point for PS (Figure 1) and PC (Figure 2). The other polymers of this study displayed analogous behavior. A linear decrease of K_a and K_b in each case lead to an extrapolated value of T_c , the temperature at which acid-base functionality disappeared, leaving only L/W forces to act between probe and polymer. A curious point of behavior was the cross-over, in several cases, of the $\partial K_a/\partial T$ and $\partial K_b/\partial T$ lines, as shown in Figure 1 for PS. In relevant cases the dominant functionality appeared to be more T -sensitive than the lesser. Thus, the inherently basic PS appears to go through an acid-base inversion at about 240°C (Figure 1). The well-defined linearity of the K_a , K_b vs T relationships permitted the definition of T_c values from the analytic statement:

$$K_a \text{ (or } K_b) = \alpha + \beta t \quad (2)$$

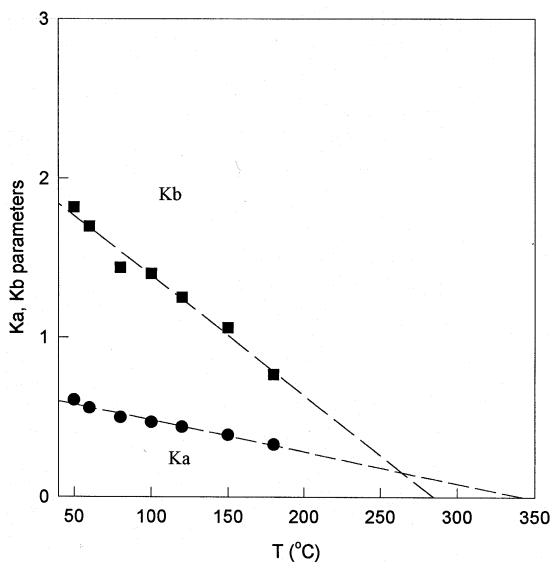


FIGURE 1 Temperature dependence of K_a and K_b for polystyrene.

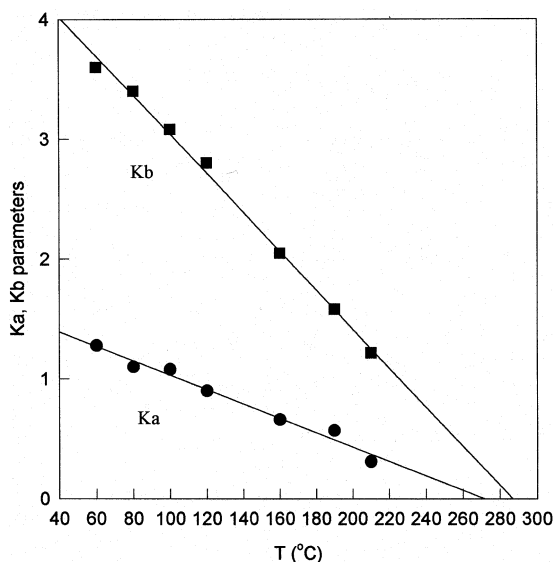


FIGURE 2 Temperature dependence of K_a and K_b for polycarbonate.

where t is expressed in °C. Table 1 displays values of T_c and of the empirical constants for the polymers of this work. Use of the α and β values allows for a computation of K_a and K_b over a very broad temperature range.

As noted earlier, the reported results do not resolve the question whether the loss of acid-base functionality is merely an artifact of increased molecular probe mobility or has more fundamental origins in the capability of the polymers to participate in an electron exchange

TABLE 1 Empirical Constants for Computing K_a and K_b and Critical Temperatures for Their Abatement

Polymer	PS	PC	PMMA	PA	PVC
For K_a :					
α	0.73	1.11	0.92	0.56	2.29
$\beta(\times 10^3)$	-2.00	-3.02	-3.30	-1.43	-8.22
$T_c(^{\circ}\text{C})$	340	270	280	360	270
For K_b :					
α	2.26	6.40	5.70	3.37	0.82
$\beta(\times 10^2)$	-0.73	-2.80	-2.33	-1.30	-0.27
$T_c(^{\circ}\text{C})$	280	290	250	260	300

sequence. A possible probe-dependence of T_c indicative of the former option, has not been scrutinized; the present results are averaged over the four probes used in the experiments. On the other hand, if the observed T -dependence of K_a and K_b were due solely to the dynamics of the probe molecule, then the temperature variation of K_a and K_b should be independent of the structural characteristics of the polymer. The T_c values in Table 1 do not support this notion. The point was examined further, using the three PS samples of differing molar mass as stationary phases. The results, restricted to K_b , are given in Figure 3. They clearly distinguish among the three polymers, the T -dependence of K_b becoming greater with increasing molar mass. The exact reason for this cannot be specified at this time, but the observed results support the argument that the abatement of acid-base functionality is at least partly attributable to changes in the inherent properties of the polymer.

Another indication of a polymer-dependent abatement of acid-base functionality is offered by Figure 4. Here is shown the temperature variation of the acid-base pair interaction parameter, I_{sp} , for three polymer pairs. The I_{sp} is computed from:

$$I_{sp} = (K_a)_1(K_b)_2 + (K_a)_2(K_b)_1 - (K_a)_1(K_a)_2 - (K_b)_1(K_b)_2 \quad (3)$$

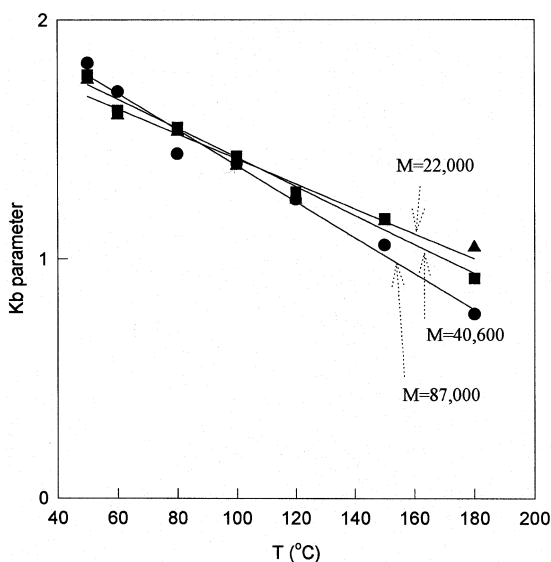


FIGURE 3 Effect of varying molar mass on temperature dependence of K_b for polystyrene.

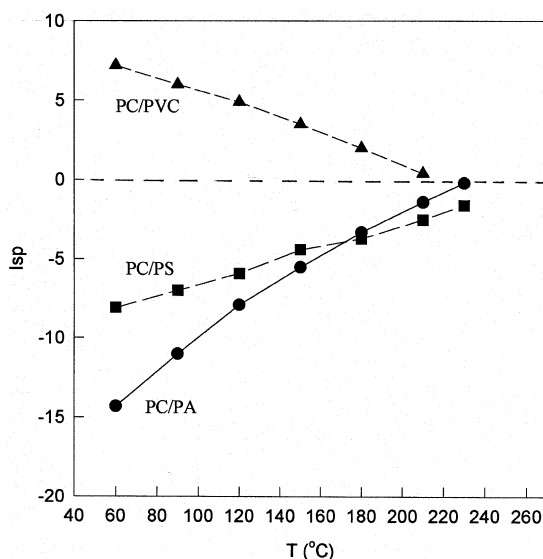


FIGURE 4 Temperature dependence of acid-base pair interaction parameter.

as stipulated in Ref. [12]. In each of the three cases, a polymer-characteristic temperature is attained designating the apparent cessation of acid-base interaction, leaving only L/W forces to act between the polymer pairs. Furthermore, in the predominantly basic pairs PS/PC and PC/PA, the slope of the functions is positive, in contrast to the PVC/PC case. In other words, the loss of acid-base functionality at higher temperatures appears to be favorable to the interaction between the inherently incompatible basic polymers, but deleterious to the PVC/PC case where favorable acid-base interaction exists at lower temperatures. The finding may have consequences on properties of these polymer combinations, when processed over the critical temperature interval. Adhesive bond strength, one important property, is examined in the next section.

The relevant lap-shear data are stated in Table 2; for convenience, the temperature for abatement of acid-base interaction, as inferred from the I_{sp} results, is included in the tabulation. In the pairs PC/PS and PC/PA a slight rise in lap-shear bond strength is noted when the assemblies are prepared at rising temperatures below their characteristic T_c . A discontinuity occurs in the vicinity of T_c . PC/PS assemblies joined above 260°C, and those of PC/PA prepared above 240°C, display considerable increments in lap-shear strength.

TABLE 2 Lap-shear Bond Strength of Polymer Joints as a Function of Bonding Temperature and Critical Temperature for Abatement of Acid-base Pair Interaction

System:	PC/PS	PC/PA	PC/PVC
I_{sp} @ 50°C	-8.1	-14.3	7.2
$(T_c)_{I_{sp}}$ (°C)	255	250	265
Bond Strength (MPa) for assembly at °C:			
200	1.3	1.1	4.5
220	1.6	1.3	4.8
240	1.9	1.6	4.8
260	2.1	2.7	3.0
280	3.6	3.1	-
300	4.0	3.4	-

The observation is consistent with an hypothesis arguing that the abatement of prevalent base-base forces in these cases, in favor of persisting L/W interactions, allows for more intimate contact between the polymers, thereby increasing the bond strength. In contrast, the gradual lowering of favorable acid-base forces with increasing joining temperature in the PC/PVC pairing is counterproductive to the generation of stronger interfacial bonds. The inherent thermal instability of PVC, unfortunately, curtailed the experimental work to the temperature range shown in the table.

The postulated account of the data in Table 2 suggests that a preferred temperature “window” of processing may be defined in specific cases, resulting in improved properties due to control over short-range, acid-base interactions. The process of rapidly quenching assemblies formed at the relevant high temperatures to below the respective glass transition temperatures, effectively freezes the polymers in unstable states, from which they must be expected to modify, if raised above the T_g value. In other words, quenched joints prepared at $T > T_c$, should show time-dependent changes in bond properties when annealed above their T_g values. The direction of change should depend on whether new equilibria re-establish favorable or unfavorable interfacial acid-base forces. The reality of time-dependence in lap-shear bond strength is shown for the system PC/PS in Figure 5. This traces the time-dependent variation of joints made at 280°C, and annealed at 220°C, above the T_g of the participating polymers. Comparison with data in Table 2 confirms that the pair re-attain the bond strength of about 1.6 Mpa following a gestation of some 20 h. The time involved is surprisingly large. It is not possible to offer a full account of the

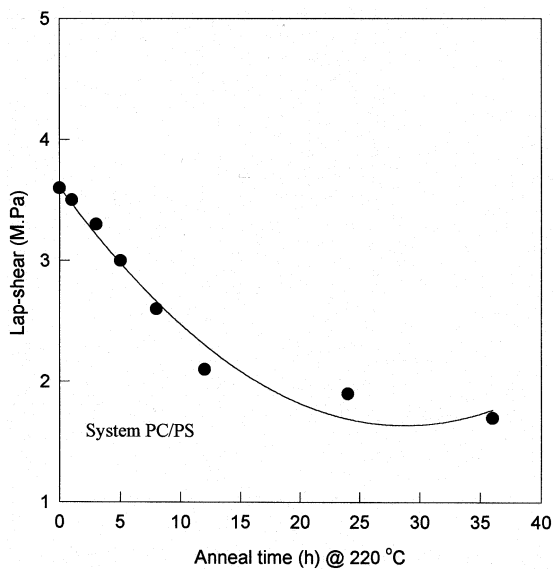


FIGURE 5 Time-dependent variation in bond strength for PC/PS bonded at 280°C and annealed at 220°C.

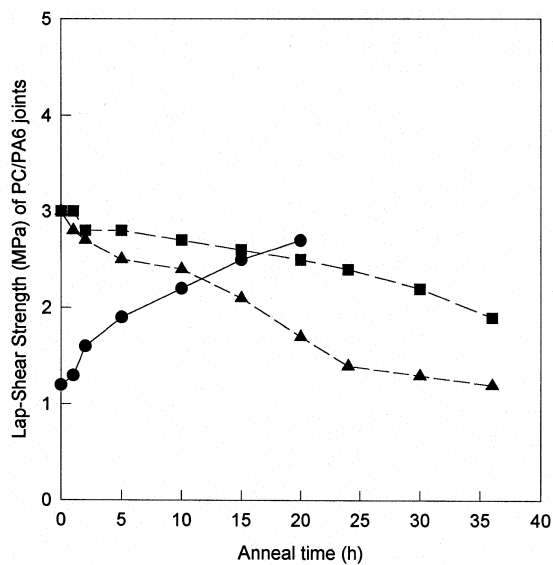


FIGURE 6 Time-dependent variation in bond strength for PC/PA assemblies: (●) bonded at 220°C, annealed at 270°C; (▲) bonded at 270°C, annealed at 220°C; (■) bonded at 270°C, annealed at 100°C.

mechanism responsible for the slow reversion. It is apparent, however, that it would be very rapid were it dependent only on the re-establishment of base-base interfacial forces. A more likely scenario involves a decoupling of polymer chains which, in the period dominated by L/W forces, interpenetrated to establish an interfacial network structure. The re-diffusion of interpenetrated chains would seem to require a period consistent with observation.

A second example supporting the proposed hypotheses involves the base/base coupling of PC/PA. Figure 6 shows the progression of lapshear bond strengths in assemblies prepared at 220°C, below the T_c of that pair, and at 270°C, above the critical temperature. The assemblies made above T_c report decreases in bond strength, the kinetics varying with the temperature of annealing. Thus, annealing at 100°C, near the T_g values of the polymers, is highly attenuated when compared with the effect of annealing at 220°C. On the other hand, the assemblies made below T_c and exposed to a temperature above T_g , actually show a time-dependent increase in bond characteristics. Once again, the length of time consumed in the variations suggests that some diffusion processes resulting in an interphase of interpenetrating chains may be taking place.

CONCLUSION

The acid-base interaction parameters for specific polymers have been shown to vary inversely with temperature.

The temperature dependence cannot be ascribed solely to increasing mobility of probe molecules, but appears to be an inherent property of the polymers.

A critical temperature, T_c , can be assigned to the polymers at and above which short-range acid-base interaction is abated, leaving longer-range dispersion forces dominant at the interface. This appears to offer a preferred processing window for inherently incompatible polymers.

The bond strengths of lap-shear joints of polymer pairs prepared over a temperature range encompassing T_c show a discontinuity in the vicinity of T_c . In base-base pairs (PC/PA and PC/PS), the abatement of acid-base forces above T_c produces joints with superior, but metastable, adhesive bonds. In the acid-base pair of PC/PVC, joint strength is reduced when only dispersion forces remain at the interface.

Assemblies prepared above T_c and then exposed to lower temperatures report a time-dependent reversion to equilibrium bond strength. The kinetics involved suggest that diffusion-dependent processes are taking place. In inherently incompatible pairings, the

reversion reduces the bond characteristics, but increases bond strength in pairings where favorable acid-base forces can function at the interface.

REFERENCES

- [1] Ishida, H., In: *The Interfacial Interactions in Polymer Composites*, Akovali, G., Ed., NATO ASI series 230 (Kluwer Academic Publishers, 1993), Chap. 8.
- [2] Xu, R., Schreiber, H. P., Huang, M. and Ishida, H., *J. Polym. Sci. Phys. Ed.* **36**, 1441 (1999).
- [3] Fowkes, F. M., *J. Adhesion Sci. Tech.* **1**, 7 (1987).
- [4] Fowkes, F. M., In: *Adhesion and Adsorption, Part A*, Lee, L. H. Ed. (Plenum Press, New York, 1980), p. 43.
- [5] Wu, S., *Polymer Interface and Adhesion* (Marcel Dekker Inc., New York, 1982), Chap 3.
- [6] Lloyd, D. R., Ward, T. C. and Schreiber, H. P., Eds., *Inverse Gas Chromatography*, ACS Symposium Series 391 (Amer. Chem. Soc., Washington, DC, 1989).
- [7] Saint Flour, C. and Papirer, E., *J. Colloid Interface Sci.* **91**, 63 (1983).
- [8] Schultz, J., Lavielle, L. and Martin, C., *J. Adhesion*, **23**, 45 (1987).
- [9] Gutmann, V., *The Donor-Acceptor Approach to Molecular Interactions* (Plenum Press, New York, 1978).
- [10] Liang, H., Xu, R., Favis, B. D. and Schreiber, H. P., *Polymer* **40**, 4419 (1999).
- [11] Liang, H., Xu, R., Favis, B. D. and Schreiber, H. P., *J. Polym. Sci. Phys. Ed.* **38**, 2096 (2000).
- [12] Kloubek, J. and Schreiber, H. P., *J. Adhesion* **42**, 87 (1993).
- [13] Panzer, U. and Schreiber, H. P., *Macromolecules* **25**, 3633 (1992).
- [14] Ulkem, I. and Schreiber, H. P., *J. Appl. Polym. Sci.* **52**, 1857 (1994).