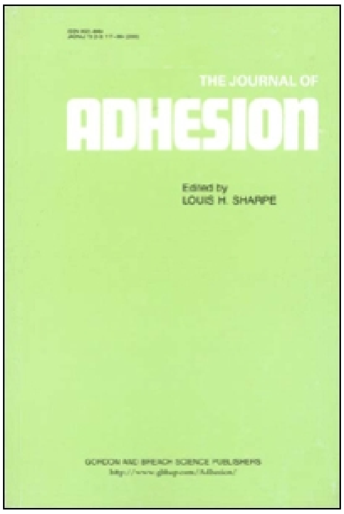

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Polymer diffusion and the evolution of adhesive bond strength

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POLYMER DIFFUSION AND THE EVOLUTION OF ADHESIVE BOND STRENGTH

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An attempt has been made to establish the role of diffusion across the polymer interface as a contributing factor to lap-shear bond strength. The assemblies studied were polypropylene/linear low-density polyethylene (PP/LLDPE); polystyrene/polyvinyl chloride (PS/PVC); polystyrene/polymethyl methacrylate (PS/PMMA); and polyvinyl chloride/polyvinylidene fluoride (PVC/PVDF). Initial bond strength measurements were followed by measurements on joints that had been annealed for up to 72 h at temperatures in the range of 60–160°C. Following induction times of tens of minutes where bond characteristics remained constant, substantial increments in bond strength were observed for PP/LLDPE and for PS/PVC but not for PS/PMMA or PVC/PVDF. Results point to a significant contribution to bond strength arising from diffusion when dispersion forces and favorable acid/base interactions act at the interface. The times required to establish the apparent diffusion effects far exceed normal bonding times and may account for the failure of diffusion to be recognized as a significant mechanism in the formation and maintenance of adhesive bonds.

Keywords: Diffusion; Interfaces; Annealing times; Dispersion forces; Acid-base interaction

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INTRODUCTION

Adhesion is a complex phenomenon; no single theory encompasses its various manifestations. Instead, several conceptual approaches have been proposed to account for experimental observations. These underscore the many disciplines which can affect the creation and maintenance of an adhesive bond including, inter alia, principles of rheology, of mechanical interlocking, of electron transfer, of electrostatics, and of the diffusion of chain elements across an interface. The last of these, the subject of this article, seems intuitively attractive since, when polymers above their glass transition temperatures are brought into intimate contact, entropic considerations should favor the transfer of chain elements across the interface, thereby strengthening the interface and the resulting bond [1]. Yet, in a recent succinct review of adhesion theory, Allen [2] has noted that, with the exception of rubber adhering to itself, there is little experimental evidence to support the diffusion concept. As a result, diffusion tends to be disregarded as a viable partner in the compendium of concepts explaining adhesion. This article offers results of experiments designed to question again the possible contribution of diffusion to the creation of adhesive bonds. The evidence presented herein is believed to point to a significant role played by diffusion across interfaces without, however, proving the matter unequivocally.

Various reasons may be offered for the apparent failure of diffusion to affect significantly the creation of adhesive bonds. While chain dynamics as described by the Rouse or the reptation models [3] would favor their transfer across an interface of contacting macromolecules, that transfer would be limited by chain entanglements in bulk polymers, hindering the free motion of surface-localized chains. Another barrier to chain transport would be the presence of crystalline morphology at interfaces. Moreover, the thermodynamic motivation for chain transfer, noted above, is reportedly weak [4] due largely to the very small entropy gains associated with the mixing of macromolecules. An additional reason may also be suggested: In most experimental disciplines of bond formation and evaluation, and particularly those associated with industrial practice, the polymers may spend only short times at temperatures and pressures favorable to chain mobility. The time requirement for effective diffusion of chain elements may not be met under these conditions, thereby subscribing to the notion that the diffusion effect is of little importance. Of course, the effect of contact time on bond characteristics is open to experimental scrutiny and constitutes one of the objectives of the present inquiry. Along similar lines, it may be necessary to distinguish between diffusion processes at interfaces involving nonpolar and polar polymers. An electron exchange at interfaces where an acidic and basic polymer are in contact should benefit the creation of a strong bond. However, as was shown in earlier inverse gas chromatographic (IGC) work [5], when a polymer surface can donate or accept an electron, then the adsorption of interacting polar vapors on that surface is enhanced. Their penetration into the polymer bulk is attenuated, however, even when the experiments are carried out under conditions favoring their absorption into the polymer bulk. In other words, diffusion is delayed by the presence of acid-base interactions at contacting surfaces, leading to the illusory impression of diffusion being inconsequential to the bond properties. Again, the posit is open to experimental study and represents an added objective for this work.

EXPERIMENTAL

Materials

Six polymers were chosen for the study. They were:

Linear low density polyethylene (LLDPE), a hexene copolymer supplied by AT Plastics, Canada, with a reported melt flow index of 2.2 and an Mw value of 140,000.
Polypropylene (PP) from the above supplier, with a reported melt flow index of 1.5.
Poly(methyl) methacrylate (PMMA) from DuPont Canada Ltd., with a reported Mw datum of 48,000.
Polystyrene (PS) from Dow Chemical Company, with an Mw value of 75,000.
Poly(vinyl)chloride (PVC) from Synergistic Chemicals, Canada.
Poly (vinyledene) fluoride (PVDF) from the above source.

No molar mass characteristics were available for the last two polymers.

All of the polymers were received in pellet form and were used as received, without the further addition of stabilizers. The choice of materials was made in the light of earlier IGC studies which defined the interaction potential of the polymers. The characterizing parameters of note here are the acid and base interaction potentials, Ka and Kb; these have been defined and discussed in many recent publications [6–8]. The relevant parameter values for the polymers, obtained experimentally by IGC as noted later on, are stated in Table 1. The data relate to the temperature range 40–80°C.

TABLE 1 Relevant Parameter Values for Polymers Used

	Ka	Kb	Kb/Ka
LLDPE	0.0	0.0	0
PP	0.1	0.0	0
PMMA	0.1	2.5	25
PS	0.2	1.6	8
PVC	2.0	0.5	0.25
PVDF	2.4	0.2	0.08

The olefinic polymers are capable of interacting through dispersion forces only. The minor acidic signal for PP falls within the experimental uncertainty of IGC determination and may be neglected. PMMA and PS are electron donors, with Kb/Ka ratios far exceeding unity. In contrast, the vinyl polymers are acids, PVDF more pronouncedly so. The findings are in agreement with many literature reports [8].

Procedures

From the polymers listed above, the following combinations were chosen for the formation of adhesive joints:

LLDPE/PP
PS/PVC
PS/PMMA
PVC/PVDF

Thus, only dispersion forces would be operative at the polyolefin interface, while “favorable” acid-base interactions would be in effect for PS/PVC. The base-base and acid-acid pairings were chosen so as to illustrate the effect of what may be termed “unfavorable” surface polarity.

The starting polymers were compression molded in a Carver press operating in the range 180–200°C, to form sheets 1.0 mm in thickness. The mold used was that described in an earlier report [9]. Rectangular sections, 22 × 12 cm in size, were cut from the molded sheets and were used to form single lap-shear joints. Again the Carver press was employed, with temperatures in the range 180–200°C and under applied loads of about 130 kg/cm^2. The bonded joints, 2.0 mm in thickness, were quenched to room temperature in cold running water immediately on removal from the press. The bonded overlap in these specimens was 6.0 cm, corresponding to an area of 72 cm^2. Following a gestation period of 24 h under ambient conditions, an initial bond strength datum was obtained by deforming the assemblies in an Instron Table Model tester at a jaw separation speed of 5.0 mm/min. At least 2 separate determinations were performed, and the average results reported here carry an uncertainty not exceeding ± 4%. In order to favor possible diffusion across the interfaces, additional specimens were aged in an oven swept with dry nitrogen and maintained in the temperature range of 130–160°C, well above the respective Tg values for the polymers. Ageing was extended to 72 h; preliminary experiments using the Perkin-Elmer DSC-4 showed that the thermal stability of these polymers was adequate to withstand the maximum annealing time. To enhance the putative diffusion mechanism in the course of annealing, the bonded areas were placed under a load of 2 kg. In the case of PS/PVC, several joints of this combination were aged at 60°C, beneath the glass transition temperatures of the polymers. At least duplicate determinations of lap-shear bond strength were carried out following specified times of gestation. The experimental uncertainty in these measurements was found to be ± 6% of the reported mean values.

The degree of specific interaction operative at the polymer interfaces was calculated from the Ka and Kb parameters listed above, using the pair interaction parameter, Isp, as defined in an earlier communication [9],

$$\mathrm{Isp} = (\mathrm{Ka})_1(\mathrm{Kb})_2 + (\mathrm{Ka})_2(\mathrm{Kb})_1 - (\mathrm{Ka})_1(\mathrm{Ka})_2 - (\mathrm{Kb})_1(\mathrm{Ka})_2. \quad (1)$$

For comparison we also measured $\chi_{2,3}$, which is the Flory-Huggins interaction parameter for the polymer pairs. Further in the interests of comparison, values of the solubility parameter, δ, for the individual polymers were taken from Barton's tabulation [10]. The Ka, Kb, and Flory-Huggins parameters were determined experimentally from IGC measurements. The acid-base values were obtained using the procedures accounted in Schultz et al., Lloyd et al., and Xu et al. [7–9]. Flory-Huggins parameters were determined using protocols first described by Patterson and coworkers [11], thus applying the expression

$$\chi_{1,2,3} = \phi_2\chi_{1,2} + \phi_3\chi_{1,3} - \phi_2\phi_3\chi_{2,3}. \quad (2)$$

Here the ϕ are volume fractions of polymers in the stationary phase of the IGC experiment, the subscripts 2 and 3 pertaining to the components of the stationary phase, while 1 pertains to the volatile probe. All IGC measurements were carried out with a Varian 3400 chromatograph, equipped with hot wire and ionization flame detectors. The temperature throughout the measurements was 50°C, well below the Tg values of the polar polymers, thereby avoiding potential difficulties due to the absorption of probes into the polymer bulk. The stated temperature is above the Tg of polyolefins, but by selecting a He carrier gas flow rate of 20 mL/min, excellent symmetry of elution peaks was secured, indicating that any bulk penetration was held to a minimum. The probe molecules were the n-alkanes from n-pentane to n-octane, all injected in triplicate at extreme dilution. For polar polymer work a lower flow rate of 12 mL/min was found to be convenient. Stationary phases of individual and of mixed polymers were prepared by conventional deposition techniques onto Chromosorb™ AW 60/80 support. Quantitative assays showed that the w%-supported polymer fell into the range 7.7–10.3. The nominal composition of mixed stationary phases was 1:1 although, as shown earlier [12], this does not necessarily correspond to the true surface composition, which may reflect changes caused by the requirement to minimize the surface energy of the deposited polymer layer. The individual and mixed polymer phases were housed in previously degreased, washed, and dried stainless steel columns, 60–75 cm in length. Symmetric retention time peaks were used to determine the retention volume, Vn, required to determine both the Ka and Kb parameters and to calculate the χ parameters of Equation (2). The values of Vn reported here were obtained from experimentally measured retention times, which were accurate to within ± 3%.

RESULTS AND DISCUSSION

Interaction Characteristics

Table 2 presents the various descriptors of interaction potential for the individual polymers and for the pairings used in the formation of bonded joints. Also shown are Tg values, as given in Barton [10]. Quite different inferences as to polymer compatibility may be drawn from the tabulated data. This may be due, in part, to the emphasis on surface interactions reported by Isp and on the closer relationship of δ and of χ to bulk interactions. In terms of δ, the close match of PP and LLDPE values would argue in favor of compatibility for this pair, a prediction contrary to practical experience. Compatibility also would be forecast for PVC/PVDF and possibly for pairings of either of these polymers with PMMA. In contrast, incompatibility is inferred for all mixtures involving PS. The Flory-Huggins parameters present a somewhat different picture. They again suggest compatibility for the polyolefin pairing and arguably for PS/PVC. The PS/PMMA and

TABLE 2 Summary of Relevant Polymer Characteristics

A: Individual polymers

	PP	LLDPE	PVC	PVDF	PS	PMMA
Tg (°C)*	≤ -40	≤ -40	92	108	98	102
δ(MPa)$^{1/2}$*	16.5	16.0	27.0	28.1	18.6	26.2

B: Polymer pairs

	PP/LLDPE	PS/PVC	PS/PMMA	PVC/PVDF
$\chi_{2,3}$ (at 50°C)	−0.6	0.08	1.3	2.7
Isp	0	2.1	−2.8	−3.3

*From Barton [10].

PVC/PVDF combinations, however, must be rated as incompatible. The Isp results are in general accord with the $\chi_{2,3}$ ratings. The positive index for PS/PVC indicates the presence of significant acid/base interaction at the polymer interface, a factor beneficial to compatibility. The acid/acid and base/base pairings produce negative Isp, indicative of weak interfaces. The Isp datum, of course, cannot shed any information on the polyolefin pairing. The ratings based on the Flory-Huggins and on the Isp parameters appear to be superior to those given by δ, which is given less credence. A principal reason for this is the large discrepancy between conditions for which δ is tabulated and those actually in effect. The stated values are based on experiments carried out near room temperatures with the polymers as the (very) minor phase [10]. More realistic δ values would require knowledge of the dependence of this parameter on temperature and on composition. The observed broad agreement between ratings by χ and Isp leaves the choice of descriptor a matter of convenience. In the following discussion further use will be made of the Isp ratings.

Bond Characteristics

The discussion to follow is based on the evidence presented in Figures 1 and 2 and Table 3. Figure 1 shows the variation of lap-shear bond strength in PP/LLDPE joints as a function of annealing time at temperatures in the range 130−160°C. The annealing procedure results in a substantial increment in bond strength following an induction period which varies from about 50 min at 160°C to 90 min at 130°C. A considerable portion of the plot in Figure 1 is linear in $t^{1/2}$,

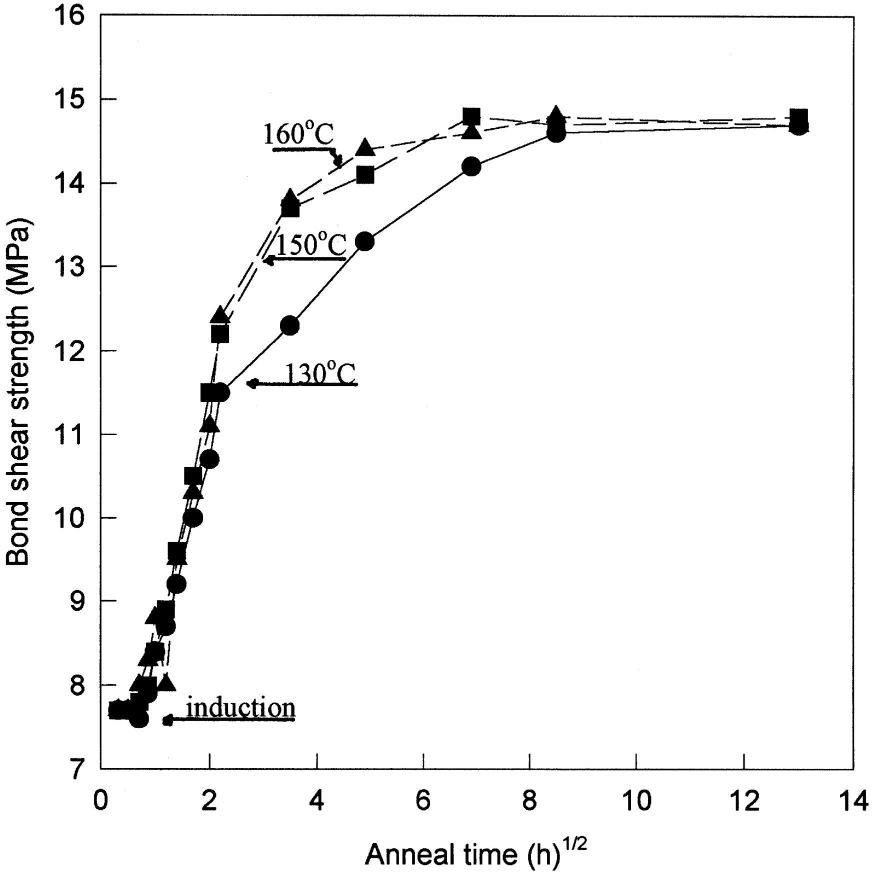

FIGURE 1 Bond lap-shear strength of PP/LLDPE joints as function of anneal-annealing time and temperature.

suggesting that the bond strength increment is related to a diffusion effect. The data yield an apparent activation energy of 5.5 Kcal/mol for the posited process, a value which is consistent with diffusion processes in polyolefins [13]. The induction period is noteworthy; the exact origins for it cannot be specified but logically it should be related to the molar mass of chains moving across the interface. Initially, one would expect low molar mass chains (weak boundary layer constituents) localized at the polymer surfaces to be involved in transport across the interface. These, however, would not contribute to a strengthening of the interface. That strengthening would arise only when chain segments anchored to longer, entangled chains in

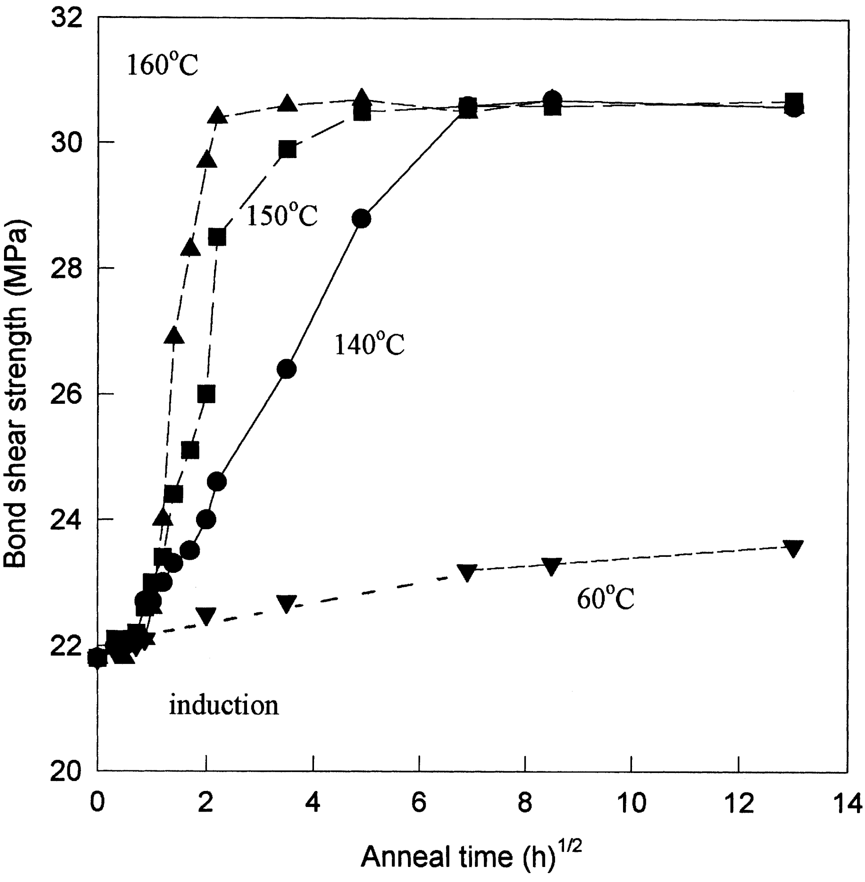

FIGURE 2 Bond lap-shear strength of PS/PVC joints as function of annealing time and temperature.

amorphous regions near the surface took part in the proposed diffusion process. The time requirement for this to occur clearly exceeds the time during which olefinic polymers of the type used here would be in intimate contact in industrial processes, such as heat sealing. As noted in our introductory remarks, the discrepancy between practical contact times and those reported here may account, at least in part, for the tendency to neglect diffusion as a significant factor in the establishment of adhesive bonds.

Figure 2 expands on the above considerations. Here are shown the responses to annealing of bond strength in PS/PVC assemblies. The substantial linearity in $t^{1/2}$ of much of the bond strength increment is

TABLE 3 Total Bond Strength Variation Resulting from Annealing

	PP/LLDPE	PS/PVC	PS/PMMA	PVC/PVDF
Initial bond (MPa)	7.7	22.8	19.3	19.7
Final bond (MPa)	14.7	30.4	21.4	20.3
Change (%)	90	33	11	3
Induction time (h)	1.2	4.0	—	—

Comparing initial bond strength with that following 72 h exposure at mean T = 150°C.

repeated here, but only following more extended induction times which now fall in the range of about 1.5–4 h. Referring again to Mukhopadhyay and Schreiber [5], strong acid/base coupling of chain elements at the polymer surfaces should promote the formation of a stronger initial bond, as is indeed the case, but delay any significant penetration of chain elements across the interface into the interphase of the cohabiting polymer. Of course, an added element is the relative closeness in this case of the annealing temperatures to the polymer Tg. Accordingly, chain mobility would be lower than in the polyolefin pairing, further attenuating the onset of significant diffusion across the interface. The apparent activation energy computed for the PS/PVC case is 11 Kcal/mole, again consistent with diffusion involving polar group-containing chains [13]. Finally, lowering the annealing temperature below the polymer Tg effectively eliminates bond strength increments, the accumulated data at 60°C being within the experimental uncertainty of each other. In summary, there is persuasive evidence, if not proof, for the existence of diffusion-abetted adhesion, provided the physical conditions favoring diffusion are maintained over sufficiently long periods of time.

Table 3 summarizes the bond strength variations in each of the four assemblies studied. New here are the results for PS/PMMA and for PVC/PVDF. In both of these couplings, evidence of bond strength increment during the annealing periods is marginal and barely in the range of experimental significance. Either the induction times for bond strength change in these cases are greater than 72 h or, far more likely, the mismatch in electron exchange capabilities simply inhibits any effective transport of chain elements across the interface. Clearly implicated in these findings are the contributing roles to apparent diffusion played by acid-base interaction and by chain mobility. The former implication is elaborated in Figure 3. Here are shown the total changes in adhesive bond strength, following 72 h exposure at 150°C, as a function of the Isp values for the contacting pairs. The acid-base factor is strongly demonstrated by comparing the responses of

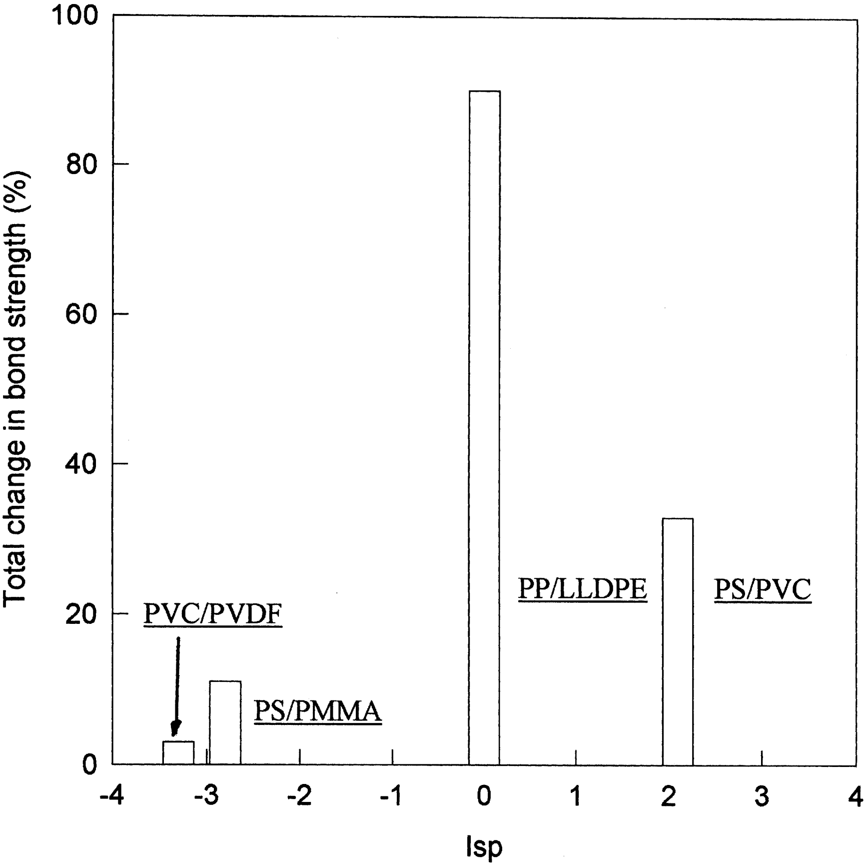

FIGURE 3 Apparent variation with acid-base interaction of total change in bond strength of polymer joints, annealed for 72 h at 150°C.

PS/PVC, PS/PMMA, and PVC/PVDF. The largest increment in bond strength, however, is in the polyolefin pairing. No acid-base factor can be attributed to this case. Instead, the focus of attention again falls on chain mobility. The ratio of annealing to glass transition temperatures is relevant to the point. Taking an average Tg for the polyolefins to be in the vicinity of 230°K, this places the ratio at about 1.7. Using the literature data for Tg given in Table 2, however, places the ratio for the polar polymer pairs near 1:1. In other words, these polymers would have to be annealed at prohibitively high temperatures in the 500°C range in order to bring their chain mobilities into closer proximity to those of the polyolefins.

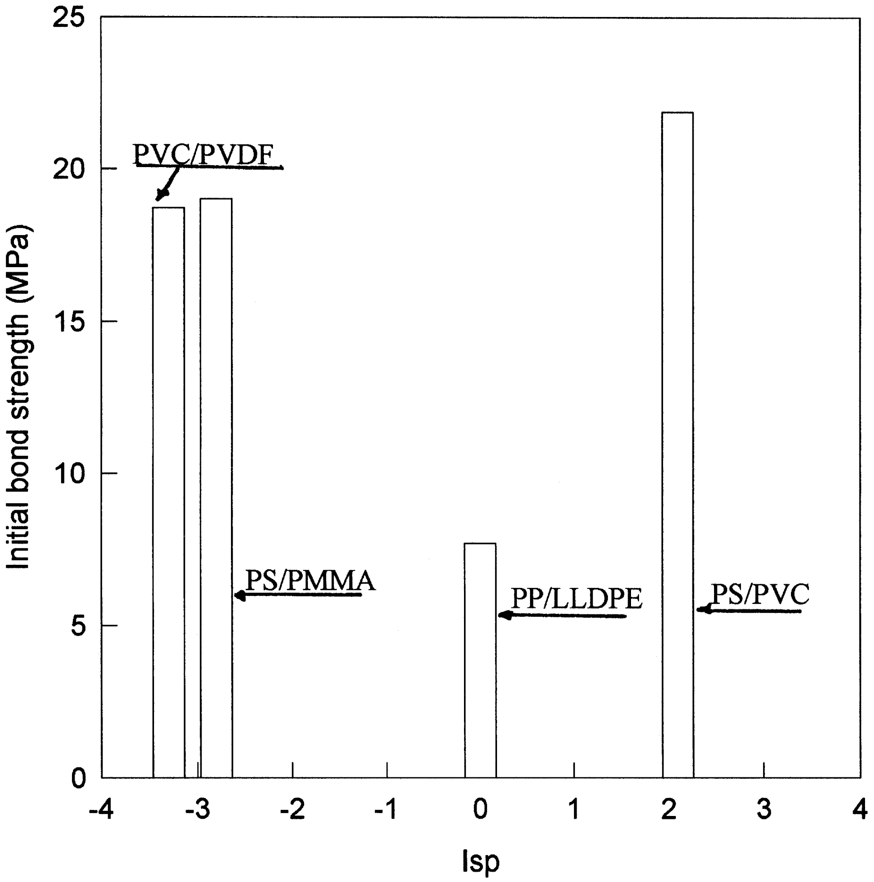

FIGURE 4 Initial lap-shear strength of polymer joints as a function of acid-base interaction.

Finally, the Isp number has been used to indicate the possible link between initial bond strengths and specific interaction at polymer contacts. The relevant information is given in Figure 4. The importance of acid-base interchanges is best demonstrated by comparing the data for PS/PMMA and PS/PVC. The difference of about 35% in favor of PS/PVC may be ascribed to the strong acceptor/donor exchange operative in this case. The initial bond strength of the polyolefin assembly is low. Among the materials selected for this study, the LLDPE and PP are the polymers most likely to form cohesively weak boundary layers at their surfaces. The bond created by the present compression molding procedure would be dominated by these moieties and improved only when adequate time had been allowed for a cohesively stronger interface to be established.

CONCLUSION

The following may be concluded:

- Increases in bond shear strength on annealing above Tg have been observed in assemblies pairing polymers which interact through dispersion forces and where favorable acid-base interaction can occur. Time-dependent changes in bond strength were minimal when interfaces combined acid-acid or base-base interactions.
- Induction times, kinetics of bond strength change, and apparent activation energies for the changes in bond strength are consistent with a mechanism of diffusion of polymer chains across the interface.
- The proposed diffusion process is abetted by favorable acid-base interaction and by high chain mobility, the latter represented by flexible polyolefin chains far above their Tg values.
- While diffusion across the interface presents a very reasonable explanation of the empirical findings reported here, the data do not represent unequivocal proof for the existence of diffusion processes.

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