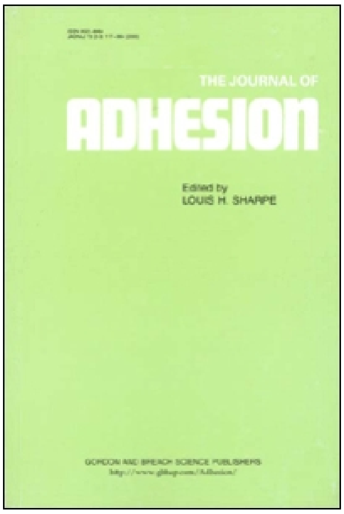

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# The Effectiveness of Silane Adhesion Promoters in the Performance of Polyurethane Adhesives

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A model polyurethane (PUr) adhesive has been modified by the addition of various silane adhesion promoters and used to bond PVC, ABS, a polyblend and glass. Inverse gas chromatography (IGC) data showed that epoxy silane substantially increased the surface reactivity of the adhesive while maintaining its amphoteric character. An aminosilane shifted the PUr surface to basicity, while vinyl, mercapto and chlorosilanes promoted surface acidity. Lap-shear data identified the amphoteric epoxy silane as the most successful adhesion promoter in all polymer and glass assemblies, increasing their initial bond strengths and also their residual bond strengths following accelerated aging. Elsewhere, the success of silane additives reflected the strength of interfacial acid/base interactions, the aminosilane being favored for bonding PVC, the others being preferred for the basic ABS and polyblend substrates. Correlations were developed between residual bond strength and initial bond properties of the assemblies and also between these system characteristics and an acid/base interaction parameter. The correlations may be useful as guidelines to the formulation of superior adhesives for bonding with substrates of known acid/base interaction potential.

*Keywords:* Polyurethane adhesives; silane modifiers; acid-base properties; initial bond strength; residual bond strength; accelerated aging; IGC

## INTRODUCTION

For many years now the formulation of multi-component polymer systems has made frequent use of silanes. These components are useful

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*Corresponding author.

as compatibilizers in immiscible or sparingly miscible polymer blends, as interphase modifiers in fiber-reinforced composites and, directly relevant to this paper, as adhesion promoters in the formulation of adhesives. Numerous publications have described aspects of silane chemistry and the forementioned applications thereof [1–4]. In many industrial formulations of adhesives, the most frequently used of the silane family are the primary amine and diamine versions, in good measure because of their relatively low cost. However, these do not necessarily produce optimum benefits in adhesion for all applications. Therefore, guidelines for the selection of silanes best suited for stated applications would be useful. These should be based on a fundamental understanding of the manner in which silane compounds affect the interface and interphase in adhesively-bonded systems. The present paper relates to that objective by describing the effect of various silanes on the adhesion performance of a model polyurethane as adhesive in joints involving selected polymers and glass. The adhesion and its retention under aggressive aging conditions is interpreted in terms of acid-base interactions at the adhesive/substrate interface. The interpretative basis appears suited for the selection of preferred silanes in the cases under study.

## EXPERIMENTAL SECTION

### 1. Materials

The adhesive used was a model semi-structural polyurethane (PUr), similar to one described in earlier work [5]. The two-part formulation was constituted of methylene bis-4-cyclohexyl isocyanate prepolymer and of trifunctional polyols with molecular masses in the range 500–900. A small amount of tin catalyst (Witco Chemicals UL-28) also was present. The PUr was used as control without additives and as modified by the following silanes:

APS – aminopropyl triethoxy silane
CS – chloropropyl trimethoxy silane
VS – vinyl trimethoxy silane
MS – mercaptobutyl trimethoxy silane
ES – epoxy trimethoxy silane

The silanes were obtained from Dow-Corning Corp. and were added at 0.5 wt% levels, an adequate concentration as demonstrated later in this section. All formulations were cured by a standard procedure of 1 hr @ 100°C, followed by 5 days @ 50°C and 50% relative humidity (RH).

The polymers to be bonded were polyvinyl chloride (PVC), acrylonitrile-butadiene-styrene (ABS), the thermoplastic polyester blend Xenoy$^{\mathrm{TM}}$(X) and microscope slide glass (G). Surfaces of these materials have been shown capable of widely differing acid-base interactions. The PVC was an unplasticized polymer with $Mw =$ 54,000 g/mol, obtained from Synergistic Chemicals, Inc. It contained 5 phr of Advastab TM-821SP thermal stabilizer. ABS (Cycolac AR 3501), was a molding grade commercial product of GE Plastics, Inc. The same source supplied the Xenoy blend; the exact composition of this material was not determined.

## 2. Procedures

The establishment of silane concentration in modified PUr adhesives was based on the tendency of PUr to restructure in response to the orienting strength of media in contact with the polymer [5, 6]. The process involves the diffusion-controlled accretion of polar moieties from the bulk to the surface layer of the polymer. Surface restructuring can be demonstrated by following the path of $\gamma^{\mathrm{nd}}$, the non-dispersive contribution to the polymer surface energy, when a film, initially dried in air, is immersed in a polar medium. This route was followed here. Static contact angles were measured for *n*-decane, methylene iodide and water, on a freshly prepared film specimen of pure PUr, and also on films of PUr containing up to 2 wt% APS and ES. The harmonic mean procedure [7] was used to compute $\gamma^{\mathrm{nd}}$. The measurements were repeated after each of the films had been exposed for 7 days to water at 90°C. Preliminary work showed that this was adequate to allow the PUr surface to equilibrate with respect to the aqueous environment. The difference between the equilibrium non-dispersive surface energies, $(\gamma)_e^{\mathrm{nd}}$ and the initial datum for the corresponding air-dried sample, $(\gamma)_i^{\mathrm{nd}}$, has been plotted against the silane content of the adhesive in Figure 1. Whilst the silane-free film restructures in water to increase $\gamma^{\mathrm{nd}}$ by about 5 mJ/m$^2$, the presence of silane sharply reduces the effect. The silane apparently anchors surface-localized moieties and restricts their ability to adopt new conformations. Figure 1 shows that ES is the more effective stabilizer of the PUr surface, but in both cases anchoring is essentially complete at 0.5 wt% silane addition. This was, therefore, chosen as the concentration level in subsequent work.

For testing bond properties, single lap-shear specimens were assembled from polymer and glass coupons cut following the practice outlined in Ref. [5]. The polymers were molded to a thickness of 1.5 mm and cut to 8 × 2.5 cm size. No mold release agents were used in molding operations. For convenience, the selected overlap area of

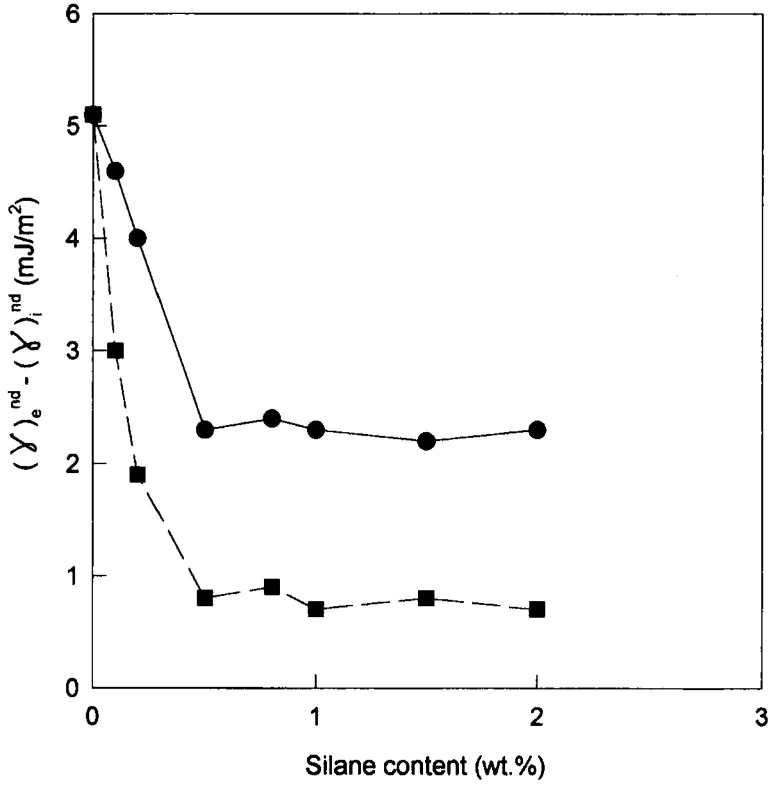

FIGURE 1 Restructuring potential of PUr adhesive as function of its silane content. ● = APS surface modifier; ■ = EP surface modifier.

4.5 $cm^2$ was bonded with adhesives drawn to a thickness of 0.4 mm. Following conditioning (24 hr, room temperature and RH), initial bond strengths were measured in triplicate with an Instron apparatus at a draw speed of 10 mm/min. To ascertain property retention, certain of the systems were exposed in air ovens to 60°C, 100% RH for up to 3 weeks under an applied stress. To generate stress, small holes were drilled near the ends of the lap-shear coupons, one of these being used to suspend the test pieces from a horizontal beam within the oven. Consistent with certain industrial procedures, stress was generated by a 200 g weight, suspended from the free end of the joint. Repeat evaluations of lap-shear bond strengths were carried out after various aging times.

Interfacial properties in assemblies were represented by acid-base interactions, as evaluated by methods of inverse gas chromatography (IGC) [8]. The polyurethanes and polymers represented stationary phases packed into previously degreased, washed and dried steel chromatographic columns. In each case the polymers were comminuted to fine powders by cryogenic grinding. Powdered glass beads were used as representative of the glass substrate. Following well-established procedures [8, 9], the solids were "probed" at infinite dilution with vapors including *n*-alkanes from $C_6$ to $C_{10}$, and with acidic and basic probes chosen on the basis of Gutmann's classification [10]. According to this, chloroform and benzene were the acids, diethyl ether and tetrahydrofuran the bases and acetone was used as an amphoteric substance. The temperature throughout IGC determinations was in the range 35–65°C. Net retention volumes, Vn, were obtained from at least triplicate vapor injections, generally with a reproducibility better than 4%.

The protocols leading to the determination of acid-base interaction potentials of the stationary phases have been fully described in recent publications [11–13]. They call for the establishment of a linear plot of log Vn *vs* the normal boiling point, $T_b$, of the alkane vapors [14], this representing the dispersion-force interactions between solid and vapor. The slope of the linear plot also may be used to evaluate the dispersion contribution to the solid's surface energy, $\gamma_s^d$. The position of Vn for the acid and base probes, at their respective $T_b$, defines the contribution of acid-base interactions to the free energy of adsorption, $\Delta G_{ab}$. When measured over the specified $T$ range, the corresponding enthalpy datum, $\Delta H_{ab}$, is also obtained. The enthalpy is then used to estimate the acid and base interaction parameters of the solid, $Ka$ and $Kb$, respectively, from the expression [11 – 13]

$$-\Delta H_{ab}/AN = KaDN/AN + Kb \tag{1}$$

Here $AN$ and $DN$ are Gutmann's values [10] for the acidity and basicity of the vapor probes. When $Ka$ and $Kb$ values for substrates and adhesives are known, an acid-base pair interaction value, $Isp$, is calculated from

$$Isp = (Ka)_1(Kb)_2 + (Ka)_2(Kb)_1 \tag{2}$$

where subscripts 1 and 2 refer to adhesive and polymer or glass substrate. In this work, $Isp$ values were primary tools for the generation of correlations between component interactions and the performance of the bonded systems. In so doing, we wish to establish the relevance to adhesion of a parameter related to the acid-base contribution to the enthalpy of component interaction.

## RESULTS AND DISCUSSION

The acid-base interaction potentials of polymer substrates and of the various adhesive formulations are given in Table IA. Table IB reports the relevant values of $Isp$. The IGC experiments show the model PUr to interact as both mild acid and base, with these tendencies well balanced. The presence of APS has no pronounced effect on the electron-acceptor capacity of the surface, but shifts the balance to basicity, presumably because of the surface localization of the silane's primary amine groups. Each of the CS, VS and MS additives produces the opposite trend, the adhesive surface now displaying stronger acidity, but without significant change in the basic interaction potential. Epoxy silane raises both the acid and base interaction potential with a predominance of basicity. Further, the total interaction potential, as given by the sum $Ka + Kb$, is most affected by the ES adhesion modifier. Expectedly, the PVC surface is strongly acidic, that of ABS is basic, and Xenoy is amphipatic with excellent balance between donor and acceptor capabilities. The glass surface is a

TABLE I Interaction constants and pair interaction parameters for PUr adhesives and substrates

*A: Acid-base interaction constants:*

| *Material* | *Ka* | *Kb* | *Ka + Kb* |
|---|---|---|---|
| PVC | 8.5 | 2.1 | 10.6 |
| ABS | 3.2 | 7.0 | 10.2 |
| Xenoy | 6.6 | 6.8 | 13.4 |
| Glass | 2.6 | 1.9 | 4.5 |
| PUr | 3.1 | 3.8 | 6.9 |
| + APS | 3.7 | 6.0 | 9.7 |
| + CS | 4.9 | 4.0 | 8.9 |
| + MS | 5.0 | 4.2 | 9.2 |
| + VS | 4.6 | 3.9 | 8.5 |
| + ES | 5.0 | 6.2 | 11.2 |

*B: Pair interactions:*

| *Isp for: and* | *PVC* | *ABS* | *Xenoy* | *Glass* |
|---|---|---|---|---|
| PUr | 39 | 34 | 46 | 16 |
| + APS | 59 | 45 | 65 | 23 |
| + CS | 44 | 47 | 60 | 20 |
| + MS | 46 | 48 | 62 | 20 |
| + VS | 41 | 45 | 57 | 19 |
| + ES | 64 | 55 | 74 | 26 |

weak acid. Noteworthy is the fact that as a result of choosing the Gutmann concept of acidity/basicity, all of the surfaces retain both acidic and basic interaction potentials.

The resulting *Isp* data in Table IB show ES and APS to be the most effective promoters of interaction between adhesives and PVC. The APS is not an effective interaction modifier for ABS substrates; here the acidic surface modifiers and ES exert a greater effect. Indeed, for each of the 4 substrates in this work ES produces the maximum increase of interaction, although for glass the interaction level with these adhesives remains low when compared with the polymeric substrates.

The effects of silane additives on the bond characteristics of assemblies is summarized in Table II. The initial bond strength, prior to accelerated aging, is reported. The contribution made by the silanes is variable, ranging from a few percentage points (e.g., PVC/PUr + MS) to a doubling of the bond strength (Glass/PUr + ES). The largest increment in bond strength is generated by ES. As seen in Table I, this confers the largest increase to the total interaction

TABLE II Initial bond strength of assemblies joined by PUr adhesive modified by silane additives. (All silanes at 0.5 wt%; see text for definition of silane codes)

| *Lap-shear bond* ($J/m^2$) *for:*<br>*Substrate:*<br>*and Adhesive:* | *PVC* | *ABS* | *Xenoy* | *Glass* |
|---|---|---|---|---|
| PUr no additive | 27 | 20 | 28 | 14 |
| + APS | 34 | 24 | 35 | 21 |
| + CS | 28 | 24 | 34 | 19 |
| + MS | 30 | 28 | 34 | 19 |
| + VS | 31 | 29 | 31 | 17 |
| + ES | 39 | 34 | 39 | 27 |

potential of the adhesive surface, while maintaining a balance between donor and acceptor characteristics. For the systems selected for study in this work, the epoxy silane is closest to a "universal" adhesion modifier. In other cases, the effects of acid/base functionality are evident. Thus, the acidic substrate (PVC) benefits from the presence of the basic APS modifier, but does not respond well to silanes which accentuate the acidity of the adhesive surface. ABS demonstrates the analogous effect of responding more strongly to the acidic modifiers than it does to APS. In joints based on Xenoy, a strongly amphoteric substrate, the choice of silanes is less critical, although ES maintains a slight advantage over the remainder. The strong performance of the epoxy silane notwithstanding, it seems doubtful whether a "universal" silane promoter can be identified for application to a wide range of substrates.

The critical question of interdependence between initial lap-shear bond strengths and the *Isp* parameters is addressed in Figure 2. Although each of the substrates tends to define a specific envelope of behavior (more particularly evident for glass), the first order regression line drawn through all of the points has a correlation coefficient of 0.915, sufficient to justify the claim of a true relationship. A more rigorous correlation is probably unrealistic, since no account is taken here of varying chemical interactions between the silanes and the substrates, nor of variations in the contributions to bonding made by longer range dispersion forces. Acid/base interactions at the adherent/adhint interface thus make important contributions to the initial lap-shear bond strength of these systems. The extrapolation to $Isp = 0$ suggests that dispersion forces make a net contribution of about 12

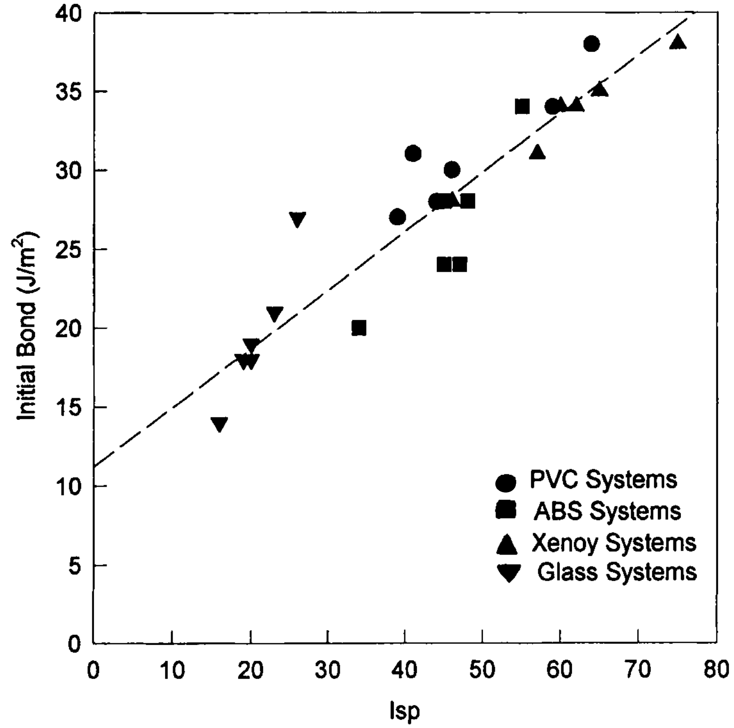

FIGURE 2 Initial lap-shear bond strength of assemblies joined by PUr adhesives as function of acid-base pair interaction.

J/m$^2$ to the bond property. Within experimental error this is the initial bond strength for glass joined by unmodified PUr, even though an *Isp* value of 16 is reported for this pair in Table IB. Evidently at this level of *Isp*, the strength of specific interactions is insufficient to influence the lap-shear bond strength as measured by the chosen procedure.

Of equal interest as the initial bond strength is the ability of the assembly to withstand aggressive aging, as represented by the regime chosen in this work. Joints using as adhesives the unmodified PUr and the PUr with 0.5 wt% APS, VS or ES adhesion promoters were subjected to the aging protocol of this work. Results of the procedure are presented in Table III. Aging periods are shown as (exposure hours)$^{1/2}$, in the expectation that property loss would be a diffusion-controlled process due to the intrusion to the interface of water. In the

TABLE III Effect of aging (60°C, 100% RH) on lap-shear bond strength. (*R* represents ratio of final to initial bond strength)

| *Age time* $(h)^{1/2}$: *Bond strength* $(J/m^2)$ *for:* | 0 | 1.3 | 3.5 | 6.9 | 11 | 22.4 | *R* |
|---|---|---|---|---|---|---|---|
| PVC/PUr | 27 | 22 | 17 | 14 | 14 | 9 | 0.33 |
| /+ APS | 34 | 33 | 30 | 27 | 24 | 22 | 0.65 |
| /+ VS | 31 | 28 | 23 | 21 | 17 | 14 | 0.45 |
| /+ ES | 38 | 37 | 37 | 33 | 30 | 28 | 0.74 |
| ABS/PUr | 20 | 18 | 16 | 12 | 8 | 7 | 0.35 |
| /+ APS | 24 | 21 | 21 | 16 | 17 | 13 | 0.54 |
| /+ VS | 28 | 25 | 24 | 22 | 20 | 19 | 0.68 |
| /+ ES | 34 | 34 | 30 | 29 | 27 | 26 | 0.76 |
| Xenoy/PUr | 28 | 23 | 19 | 16 | 16 | 12 | 0.43 |
| /+ APS | 35 | 35 | 32 | 28 | 28 | 25 | 0.71 |
| /+ VS | 31 | 29 | 27 | 24 | 19 | 17 | 0.55 |
| /+ ES | 38 | 36 | 35 | 32 | 32 | 29 | 0.77 |
| Glass/PUr | 14 | 12 | 7 | 0 | 0 | 0 | 0.00 |
| /+ APS | 21 | 20 | 16 | 11 | 11 | 7 | 0.33 |
| /+ VS | 18 | 17 | 12 | 9 | 7 | 4 | 0.22 |
| /+ ES | 27 | 25 | 25 | 20 | 17 | 13 | 0.48 |

Table, *R* is defined as

$$R = (\text{Bond Strength})_f/(\text{Bond Strength})_i$$

where the subscripts *f* and *i* represent the bond strength after 3 weeks of aging and the initial value, respectively. Each of the systems is adversely affected, but *R* varies significantly among the systems as well as within them. Qualitatively, a relationship between *R* and the initial bond strength becomes apparent on inspection of the data. The ES modified PUr, which has the strongest acid-base interaction with each of the substrates, producing the strongest initial bond, also produces the smallest property loss.

A clearer view of the apparent correlation is presented in Figure 3. This indicates that below initial bond strengths of about 13–14 $(J/m^2)$, corresponding to $Isp < 18-20$, the selected aging regime will totally destroy the bonded assembly. Best fit to the data in Figure 2 is obtained from the 2nd-order regression curve shown, with a coefficient of 0.932. However, a 1st-order linear fit to the data (not shown) with a coefficient of 0.917 is not much inferior and has the attraction of being extrapolatable to $R = 1.0$. If the linear fit is accepted as realistic, then

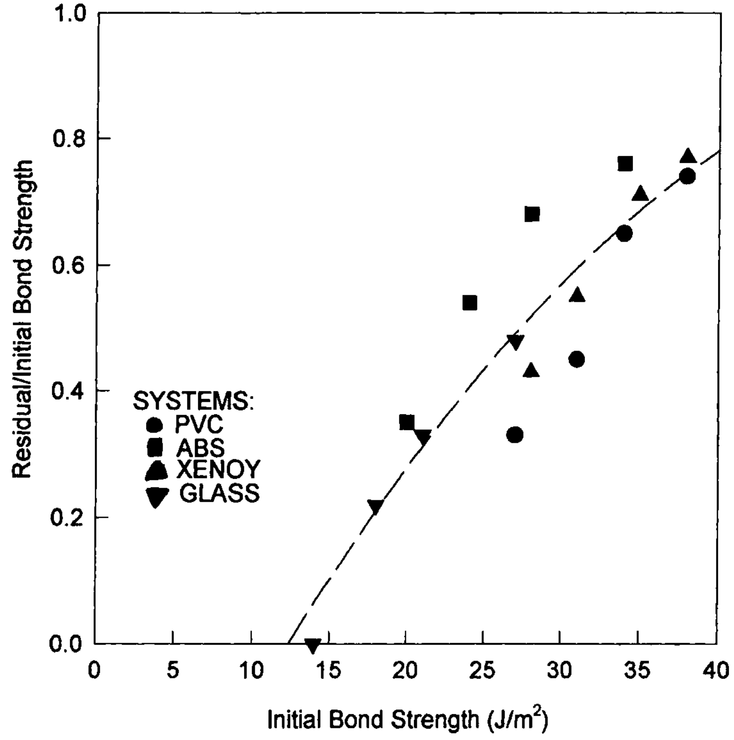

FIGURE 3 Residual lap-shear bond strength following 3 weeks @ 60°C, 100% RH, as function of the initial bond strength of assemblies joined by PUr adhesives.

the extrapolation predicts that an assembly with an initial lap-shear bond strength > 45 $J/m^2$ would withstand the chosen aging exposure indefinitely, without loss of bond strength. As the correlation in Figure 2 makes evident, the degree of acid/base interaction at the bonded interface also should correlate with the residual bond property. The matter is put to the test with results shown in Figure 4. The resulting linear fit to experimental data has a correlation coefficient of 0.938, with much of the scatter contributed by the glass joints, where acid/base interactions are feeble and most subject to uncertain determination. An extrapolation to $R = 1.0$ identifies $Isp \geq 85$ as the strength of acid-base interactions required to ensure long-term resistance to the selected aging procedure. The forecasts should be useful in optimizing the choice of silane (and other) adhesion promoters in the formulation

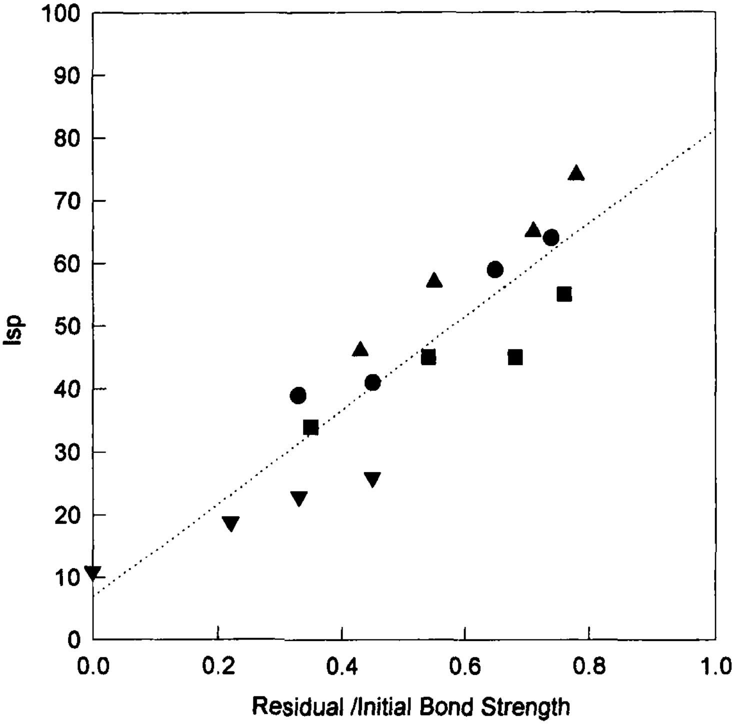

FIGURE 4 Correlation between acid/base interaction parameter and residual/initial bond strength ratio. Assemblies with PVC ●; ABS ■; Xenoy ▲; Glass ▼.

of adhesives such as the present PUr. However, the physico-chemical analyses on which these are based cannot specify the chemical approaches to be followed. Moreover, the general applicability of the physico-chemical analyses followed here calls for the study of a broader range of adhesive/additive/substrate systems.

## CONCLUSIONS

* A strong correlation has been shown to exist between initial bond strengths displayed by polymer and glass surfaces bonded by PUr adhesives containing a variety of silane adhesion promoters and the acid-base interaction at substrate/adhesive interfaces.

- * Silane additives change the surface interaction potential of PUr in distinct ways; APS accentuates surface basicity, while CS, MS and VS accentuate surface acidity. The addition of ES results in significant increases in both surface acidity and basicity.
- * Within the scope of the present work, ES was found to be the most effective adhesion promoter for each of the substrates. APS was particularly useful with the acidic PVC substrate, but the CS, MS and VS were preferred additives for the basic ABS substrate.
- * A correlation has been developed between the residual adhesion of bonded assemblies following accelerated aging and the magnitude of acid-base interfacial interactions. The strength of interactions needed to avoid property loss under the chosen aging conditions can be estimated. This capability represents a guideline to the selection of preferred silane additives for the adhesion of PUr adhesives to substrates with known acid-base interaction potentials.
- * IGC was shown to be a convenient and effective tool for an evaluation of acid-base interactions at substrate and adhesive surfaces.

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