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The Journal of Adhesion

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713453635>

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To cite this Article Migdal, A. and Schreiber, H. P.(1995) 'Specific Interactions, Initial and Equilibrium Bond Strength in Polymer/Polymer Assemblies', *The Journal of Adhesion*, 52: 1, 1 – 11

To link to this Article: DOI: 10.1080/00218469508015183

URL: <http://dx.doi.org/10.1080/00218469508015183>

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Specific Interactions, Initial and Equilibrium Bond Strength in Polymer/Polymer Assemblies*

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(Received January 19, 1994; in final form April 5, 1994)

This paper reports on bonding characteristics of assemblies using as substrates poly(vinyl chloride) (PVC), acrylonitrile-butadiene-styrene (ABS) and polypropylene (PP), and as melt adhesives an ethylene-vinyl acetate (EVA) copolymer, a polyurethane (PUr), and low density polyethylene (LDPE). Peel strength measurements on freshly assembled joints were compared with results for samples aged under inert and humid conditions. Significant time-dependent variations of bond strength were observed in all cases, but the direction of change varied among the assemblies. Those involving only dispersion-force materials displayed losses of bond strength, attributable to the gradual accumulation of cohesively weak layers at the substrate/adhesive interface. In assemblies involving materials able to interact by non-dispersion (acid/base) forces, as indicated by inverse gas chromatographic data, a variety of responses was obtained. These have been rationalized by the ability of the EVA and PUr adhesives to reorient when in contact with an appropriate polymer substrate. Reorientation, leading to bond strength increments, was associated with substrate/adhesive pairs (*e.g.*, PVC/EVA and ABS/PUr), in which significant acid/base interaction could take place

KEY WORDS polymer adhesives, surface restructuring, peel strength, acid/base effects; adhesion; adhesive joints; aging

INTRODUCTION

Surface properties play a vital role in establishing the usefulness of polymer materials in a wide range of applications. Detailed characterization of polymer surface properties is a high priority activity, and one that has increased our awareness of how subtle are the structural and morphological aspects of polymer surfaces, interfaces and interphases. The work of Drzal and his coworkers, notably as applied to the behavior of fiber-reinforced composites, has been prominent in this regard.^{1,2} Among the subtleties referred to is the dictum that the composition of polymer surfaces always differs from that of the bulk.^{3,4} Important reasons for this include the possible existence at surfaces of cohesively weak boundary layers,⁵ and the more recently documented evidence^{6,7} that some polymers undergo surface restructuring when in contact with

*One of a Collection of papers honoring Lawrence T. Drzal, the recipient in February 1994 of *The Adhesion Society Award for Excellence in Adhesion Science*. Sponsored by 3M.

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polar orienting media. It is the latter event in particular which provides a motive for the present work.

In preceding surface restructuring studies^{7,8} it was shown that when polymers such as two-component polyurethanes (PUr) and ethylene/vinyl acetate copolymers (EVA) are exposed to polar liquids, including water, formamide, etc., their non-dispersion surface energy, γ^{nd} , changes from an initial to a steady-state value over periods of several days. A reasonable question then arises whether or not similar restructuring may occur when a susceptible polymer, initially in equilibrium with ambient surroundings, is placed in contact with a polar solid, *e.g.*, a polymer with a significant γ^{nd} component. Direct experimental documentation of the event is difficult to envisage; however, indirect evidence may be attainable. Since adhesion is strongly dependent on non-dispersive interactions at interfaces, the adhesive bond between the materials in contact should change as steady-states of orientation are sought. This presupposes that when freshly prepared under normal bonding conditions, the orientation of susceptible polymers remains in a non-steady-state. The supposition appears to be reasonable when viewed from the very long time requirement for reorientation in liquid media.

The purpose of this work, then, is to question the possibility of time-dependent changes in the bond strength of assemblies in which the polymer adhesive is susceptible to surface restructuring. To this end the peel strengths of selected polymer assemblies have been studied as a function of controlled residence times in inert, and in humid, environments.

EXPERIMENTAL SECTION

Materials

Three commercially available polymers were selected as substrates. The PVC was obtained courtesy of Esso Canada, Inc. It was a medium molecular weight polymer (K 66 value); for ease of processing it was combined with 2 parts/100 parts PVC (by wt.) of Rohm & Haas Paraloid K 125 processing aid. The ABS was from Borg-Warner Corp. and the PP (melt flow index = 0.4) was supplied by Shell Canada Inc. Certain experiments made use of PP specimens previously surface modified by exposure to corona discharges at 15 mA, 12 kV, 30 sec. duration.

The adhesives were an EVA copolymer with 28 mol% VA, supplied by DuPont Canada, Inc., and an LDPE from the same supplier, with a melt flow index of 12, and $M_w = 85,000$ (from GPC determinations in trichlorobenzene at 130°C). The PUr adhesive was obtained from 3M Canada, Inc. It was a two-component product, based on an aromatic isocyanate with NCO/OH = 1.03, combined with a mixture of castor oil and a polycaprolactone-based triol. The adhesive contained 0.5 wt% of a silane adhesion modifier.

Bond Strength Evaluation

Peel tests were carried out on specimens in which two sheets of the substrate polymer were bonded by the adhesive. Substrates were compression molded to form sheets 0.13 mm thick, and from these were cut sections 12 × 2 cm in dimension. For EVA and

LDPE adhesives, 8×2 cm joints were assembled by compression molding at 150°C , for 90 sec. under a pressure of 1500 psi (10.3 MPa), 4 cm lengths of the substrates being left for attachment to the test instrument. In the molding operation outer surfaces of the assemblies were protected by a sheet of poly(tetrafluoro)ethylene. Following bonding, the assemblies were allowed to cool to room temperature over a period of about 5 min. Joints with PUr adhesive were prepared by coating both substrate surfaces with the adhesive, contacting the assembly and curing at RT/24 h., followed by 48 h/ 50°C , 50% RH. The adhesive thickness was 0.25 mm. Triplicate specimens of each system were evaluated within 24 hours of preparation, the averaged value being taken as the "initial" bond strength. Additional specimens were aged for up to 1200 h. to obtain an "equilibrium" value of the bond strength. In one set, aging was at 70°C under a flow of dry nitrogen. In a second set aging was at 70°C in air controlled at 85% RH. Aged samples were conditioned under ambient conditions for 24 h prior to testing. Throughout, triplicate determinations in 180° peel were made on an Instron table model tester, with a separation speed of 50 mm/min. Separated surfaces were examined by optical microscopy in an attempt to establish, if only qualitatively, the failure mechanism. Reported peel strengths have an uncertainty not exceeding 12% .

Surface Characterization

Contact angle determinations were used to establish the susceptibility of the polymers of this study to restructure. The data were acquired with a Rame-Hart Goniometer. Test liquids included *n*-heptane, *n*-decane, formamide, ethylene glycol, glycerol and pyridine. The protocol of Kaelble⁹ was used to compute values of γ^{nd} . Measurements were made on freshly prepared specimens, and on polymer samples following immersion in water at 60°C , for 120 h. This procedure was shown earlier⁷ to be effective in triggering changes in the surface conformation of polymers susceptible to the effect.

Inverse gas chromatography (IGC) was used to establish the acid/base interaction characteristics of polymer surfaces. Detailed discussions of the procedure leading to the information have appeared in recent literature.¹⁰⁻¹² Briefly, in IGC work the polymers formed the stationary phase, deposited from dilute solutions onto Chromosorb A/W, 60-100 mesh support. Standard ashing procedures showed the polymers to form from 7.2-10.4% of the total mass of solids. Vapor probes were injected at very high dilution, in triplicate, to determine retention times and volumes, again following well-established procedures.¹³ The vapors included the *n*-alkanes from C 7 to C 10, chloroform, benzene, diethyl ether and tetrahydrofuran. The alkanes were used as an alternative measure of the dispersion surface energy of the polymers, following the precedents of Refs. 10-12,

$$RT \ln V_n = 2N (\gamma_s^{\text{d}})^{1/2} \cdot a \cdot (\gamma_l^{\text{d}})^{1/2} + C. \quad (1)$$

where V_n is the retention volume, the γ are the dispersion surface energies of the solid (s) and vapor (l) phases, a is the cross-sectional area of the adsorbed vapor molecule, C is an integration constant and other symbols retain their usual meaning. The other vapors were selected from Gutmann's tabulation of acids and bases,¹³ chloroform and

benzene being representative acids, ether and THF the corresponding bases. The position of retention volumes for these vapors, relative to the reference line established by the alkane data, defines ΔG_{ab} , the contribution from acid/base forces to the free energy of adsorption of the vapors.^{10,11} Empirically, these values may then be used as a measure of the electron donor and/or acceptor potential of the polymer stationary phases; the parameters are labelled DN and AN, respectively.

All IGC determinations were made with a Varian 3400 Chromatograph, using a thermal conductivity detector. The carrier gas was Helium at a constant flow rate of 15 mL/min, and all measurements were at 30°C. Values of the retention volumes used in this work were reproduced to better than 4%.

RESULTS AND DISCUSSION

A first concern in this work was to establish the surface reorientation potential of the polymers. The contact angle data, and specifically the non-dispersion contributions to the surface free energy calculated from them, are used as relevant indicators. The data are summarized in Table I. The capability of EVA and PUr surfaces to restructure when moved from an air environment to water is indicated by the substantial increases in their γ^{nd} values. These increases are far above levels of experimental error, and follow patterns previously documented for bicomponent polyurethanes.¹⁴ As in previous discussions of restructuring, we assume that the thermodynamic drive to minimize the interfacial tension between the polymer and its polar, aqueous environment, leads to diffusion-dependent rearrangements which raise the polarity of the polymer surface. None of the other polymers in this series exhibits a similar effect. None would be expected in the polyolefins, these being dispersion-force solids. In part, the failure of PVC and ABS to respond may reside in the exposure to an orienting medium having taken place below the glass transition temperature of the materials. However, on the basis of their γ^{nd} , both polymers may be viewed as representing orienting surfaces for EVA and PUr. Consequently, if the adhesives reorient in assemblies of these polymers, then corresponding variations in the bond strengths may be of considerable practical importance.

TABLE I
Apparent restructuring tendency of polymers

Polymer	$(\gamma^{nd})_i^*$	$(\gamma^{nd})_f^{**}$
	(mJ/m ²)	
EVA	0.8	3.7
PUr	1.3	5.2
LDPE	0	0
PVC	3.3	3.7
ABS	9.7	10.6
PP	0.4	0

* Surface energy of freshly prepared film.

** Following exposure to water, 60°C, 120 h.

Peel Strengths

The bond characteristics of the polymer joints were found to vary substantially over the aging periods to which they were exposed. Illustrations of the variations are given in Figures 1, 2 and 3. Figure 1 displays the time-dependence of peel strength in PVC, ABS and PP joints bonded by LDPE. The illustration is for aging under inert conditions. Without exception, in these cases, failure appeared to be adhesive, with interfacial separation of substrates and adhesive. There is broad similarity in the three curves; in each case there is a significant decrease in peel strength over the first 10–15 h. of aging, whereupon the bond strengths remain essentially constant. The property loss is less pronounced for ABS substrates, which also generate the highest initial peel strength. The apparent constancy of data following extended conditioning under the stated conditions allows for the definition of an initial and an apparent "equilibrium" peel strength. Ratios of these values are given in Table II, which also reports similar data for samples aged under the more aggressive humid-air conditions. Clearly, the loss of peel strength in the PE-bonded joints cannot be attributed to reorientation phenomena. The accretion at the LDPE/substrate interfaces of cohesively weak boundary layers⁵ may be a plausible cause. Recently, the existence of such layers has been questioned,¹⁵ and suggestions made that low molecular weight chains of polymers like LDPE become absorbed in the underlying matrix. LDPE, however, is not readily miscible with PVC or ABS, so that an absorption mechanism in these cases does not seem too credible. With PP as matrix, the creation by segmental interdiffusion of a cohesively

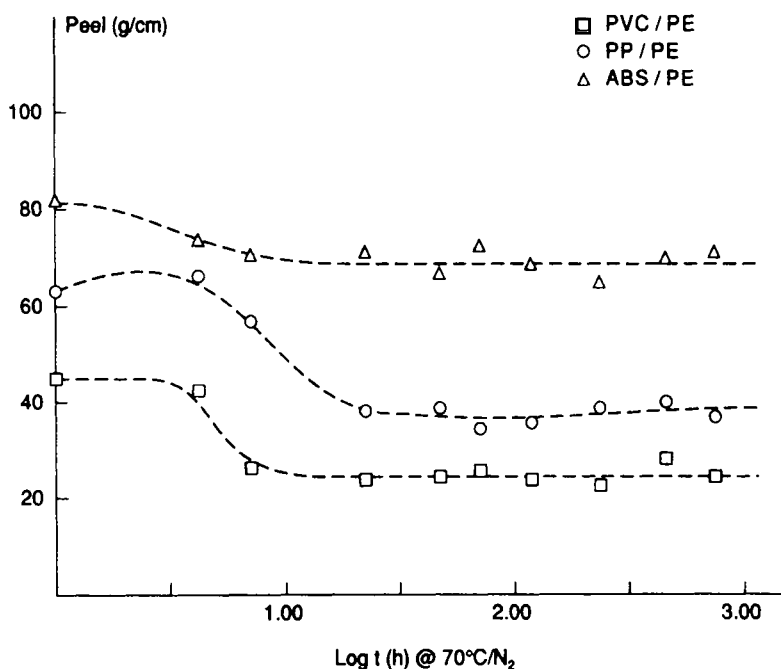


FIGURE 1 Peel strength variation of joints bonded by low density polyethylene as a result of aging under dry nitrogen. Peel test at 30°C.

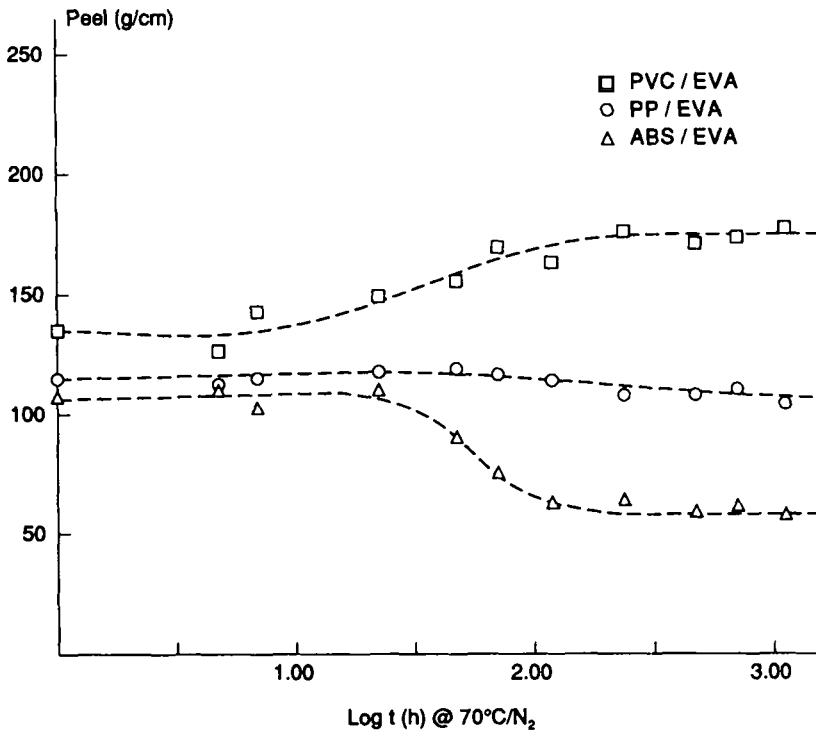


FIGURE 2 Peel strength variation of joints bonded by ethylene-vinyl acetate copolymer as a result of aging under dry nitrogen. Peel test at 30°C.

TABLE II
Summary of initial and equilibrium peel strengths

Aging	Peel (i)		Peel (eq)		Eq/In	
	[g/cm]					
	Dry	Wet	Dry	Wet	Dry	Wet
PVC/EVA	135	172	110		1.27	0.81
ABS/EVA	106	60	38		0.57	0.36
PP/EVA	115	108	77		0.94	0.67
PP*/EVA	130	127	92		0.98	0.71
PVC/PU _r	115	85	57		0.74	0.50
ABS/PU _r	162	190	150		1.17	0.93
PP/PU _r	42	35	18		0.83	0.42
PP*/PU _r	73	64	47		0.88	0.64
PVC/PE	45	24	27		0.53	0.60
ABS/PE	82	74	40		0.90	0.49
PP/PE	63	38	34		0.60	0.52
PP*/PE	68	44	35		0.65	0.51

PP* is corona-treated polymer.

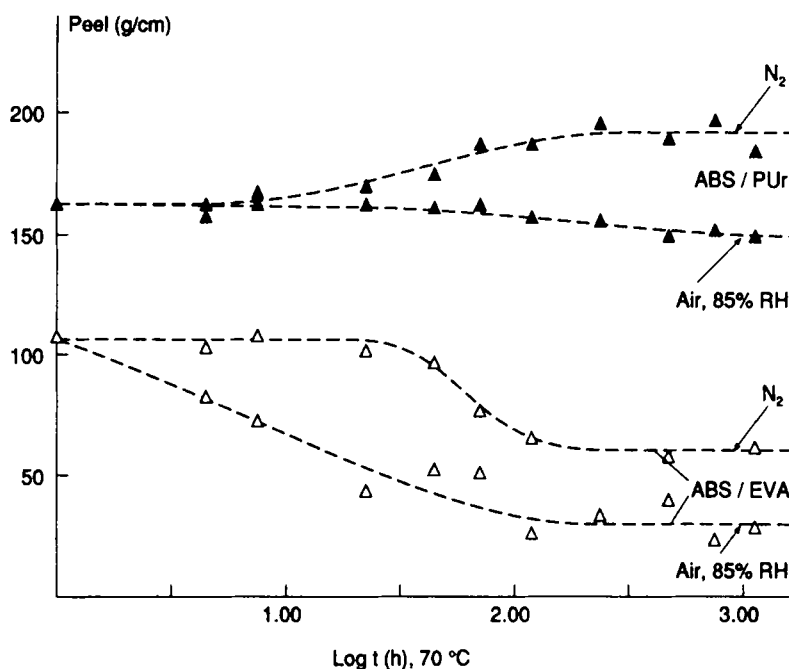


FIGURE 3 Comparing peel test variation in ABS joints bonded with EVA and polyurethane adhesives and aged under dry nitrogen and in humid air.

weak PP/LDPE interphase is more plausible. The reduced bond strength in this system may be argued on that basis; however, we shall return to this issue shortly.

The behavior of assemblies bonded by EVA and subjected to aging under dry nitrogen is shown in Figure 2. There are striking differences in the pattern of results when compared with those in Figure 1. For all practical purposes the PP/EVA system remains invariant over the time of study, and the failure mode appeared very similar to that observed in LDPE-bonded assemblies. In initially weak ABS joints, a sharp reduction in peel strength is observed on aging, however the major portion of the decrease occurs much later in the aging sequence than was the case with LDPE as adhesive. A similar delayed time-effect is observed for PVC/EVA, but the arresting feature is the direction of change, with the peel strength rising to an "equilibrium" value nearly 30% above the initial. Optical analyses showed that under the steady-state regime there was some evidence of material transfer across the interface in these systems. Quantitative documentation of changes in bond characteristics is given in Table II. Since the EVA surface layer is able to restructure it is tempting to ascribe the peel strength changes to this effect. The constancy of results for PP is then accounted for, as is the delay in the onset of bond strength changes. The diverse influence of PVC and ABS, however, the latter presumably the stronger orienting medium, requires rationalization.

A step in that direction may be obtained by examining the results in Figure 3. Here a comparison is made between the effects of dry and "wet" aging on the peel strengths of

ABS joints bonded by the EVA and PUr adhesives. Aging in humid air accelerates property loss in ABS/EVA and the total drop in peel strength becomes more severe. The system ABS/PUr, however, has many of the features of PVC/EVA, with a rise in peel strength under nitrogen of some 20%, again as reported in Table II. Failure in these rather strongly adhering joints was clearly cohesive but localized in the interfacial region and not within the bulk adhesive. In contrast, it is the PVC/PUr assembly which now displays trends entirely analogous to those of ABS/EVA. If restructuring minimizes interfacial tension between polymers in intimate contact, then, reasonably, bond strength should *increase* as the interface tends to a thermodynamic steady-state. The behavior of PVC/EVA and ABS/PUr under dry conditions is consistent with this concept. The behavior of the counterpart systems, again, needs further reflection. Aging under "wet" conditions offsets the benefit in PVC/EVA and ABS/PUr, ostensibly due to the damaging effects of water intrusion to the interface. Inspection of data in Table II shows, however, that the negative influence of wet aging is much less severe in these two systems than in the others under investigation. To conclude consideration of Table II we turn to the behavior of joints with corona-treated PP as substrate. Although the effects of corona treatment on surface properties of polyolefins, and notably on PP, remain a subject of discussion, there is substantial evidence^{16,17} for the introduction of oxygen linkages. The consequence is a rise in the total surface energy, accounted for by now significant contributions from γ^d . Literature reports¹⁷ then lead to the expectation of increased bond strengths with adhesives of the type used here. Indeed, the bond strength of PP*/EVA and PP*/PUr have been increased significantly, and the former of these systems is remarkably stable under dry aging conditions. Polar group interaction may be responsible. Increased surface energy in PP* should also lead to some improvement in the PP*/PE assembly, but no such effect is observed. The existence of a cohesively weak boundary layer at the LDPE surface could account for this; a general rejection of the effect for polyolefins¹⁵ should be viewed with some reservations.

The Evidence for Acid/Base Contributions

The disparate effects on bond characteristics introduced by the supposed surface restructuring of EVA and PUr adhesives when in contact with polymer orienting media require explanation. The IGC data summarized in Table III are useful in this regard. Given are the acceptor and donor numbers, AN and DN, for the various polymer solids, their dispersion surface energies as calculated from the alkane retention volume data (*viz.* eqn. 1), and an acid/base pair interaction parameter, P_{ad} . The latter expresses the magnitude of acid/base effects for stated combinations of substrate and adhesive. The definition of P_{ad} is empirical, its justification having been argued in an earlier publication¹⁸:

$$P_{ad} = [AN_1 \cdot DN_2 + AN_2 \cdot DN_1] - [AN_1 \cdot DN_1 + AN_2 \cdot DN_2]. \quad (2)$$

Viewed from the values of γ^d , the adhesives should spread readily on all substrates. The system PUr/PP, however, is a possible exception to this. The data in Table II

TABLE III
Surface energies, acid/base indices (all data from IGC experiments at 30°C)

Material	$(\gamma^s)^d$ (mJ/m ²)	AN	DN
PVC	43.8	7.3	3.6
ABS	38.0	4.6	8.0
PP	31.7	0	0
LDPE	28.8	0	0
EVA (28)	29.5	2.7	6.4
PUr	37.7	4.4	2.7

$$P_{ad} = [AN_1 DN_2 + AN_2 DN_1] - AN_1 AN_2 - DN_1 DN_2$$

for:

$$\begin{aligned} \text{PVC/EVA} &= 13.3 \\ \text{ABS/EVA} &= -12.2 \end{aligned}$$

$$\begin{aligned} \text{PVC/PUr} &= -6.3 \\ \text{ABS/PUr} &= 5.8 \end{aligned}$$

showed this pairing to produce the lowest overall peel strengths. Adequate wetting is a prerequisite for good adhesion, but it is an insufficient criterion. The findings in Table III clearly identify PVC as an acidic polymer, ABS as basic. Among the adhesives EVA is predominantly basic, the PUr being a mild acid. Assuming that the orienting potential of the substrate is given by the sum of its acceptor and donor tendencies, then, as already inferred by γ^{nd} values, ABS is the dominant orienting surface, with AN + DN being some 20% greater than that for PVC. Expectedly, PP has no orienting potential in the present context. Presumably, however, the orienting potential of the substrate will be realized only in those cases where no surface energy barrier hinders contact with the adhesive and where significant acid/base interaction can take place. A reinforcement of adhesive bonds through acid/base interaction should then be foreseen for the pairs PVC/EVA and ABS/PUr, as is indeed the case. In combinations of like pairs, represented by PVC/PUr and by ABS/EVA, acid/base coupling will be diminished, and this should be reflected in adhesion performance. These are the pairs, of course, which showed no enhancement of bond strength during inert aging. Values of P_{ad} are entirely consistent with this analysis. These show PVC/EVA to be the most strongly interactive pair. The ABS/PUr combination follows despite the superior orienting strength of ABS, a reflection of the relatively low interaction potential of the PUr used for this demonstration.

The above analyses suggest that a close relationship should exist between P_{ad} and the ratio of equilibrium to initial bond strengths in the various assemblies. The representation of Figure 4 confirms the expectation. Though non-linear in the selected coordinates, the relationship appears to be well established, and followed by specimens aged under both dry and the more aggressive humid conditions. As stated previously, the presence of moisture during aging reduces the benefits assigned to restructuring. The reduction seems to gain in importance where the peel strength ratio is large, that is where there are strong acid/base forces at the interface. According to Gutmann's classification,¹³ the AN and DN indexes for water exceed those of commodity polymers of the type used here. By this rationale water would then preferentially form an

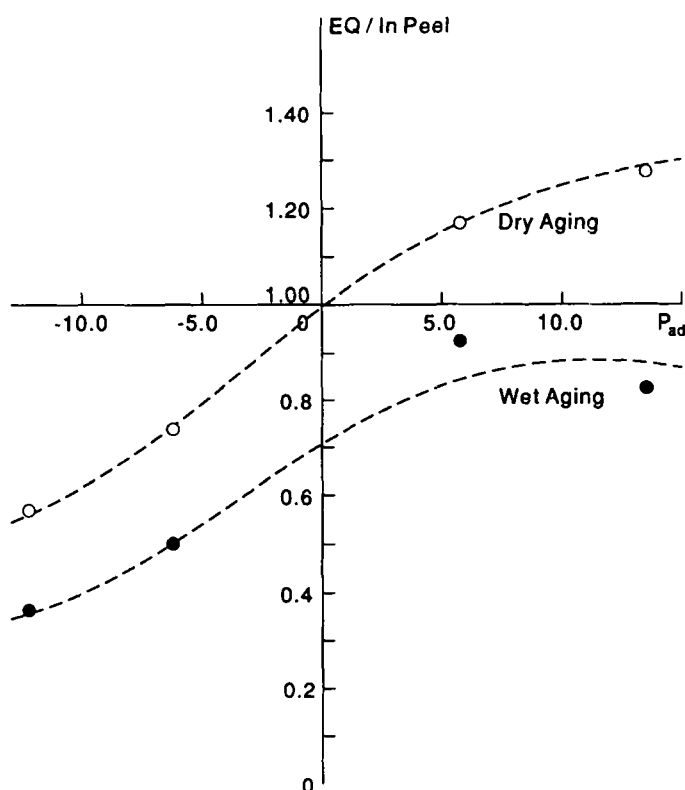


FIGURE 4 Ratio of equilibrium and initial peel strengths as a function of the acid/base pair interaction

interphase between substrate and adhesive, actually promoting the surface restructuring of a susceptible adhesive but, of course, adversely affecting bond strength.

CONCLUSIONS

- * When used as adhesives, polymers susceptible to surface restructuring, here exemplified by EVA and PUr, appear to do so when in contact with polar polymer substrates.
- * Restructuring of adhesive molecules at the substrate/adhesive interface has significant influence on bond characteristics, as indicated by a comparison of peel strengths for freshly formed joints and those aged in controlled atmospheres. Interfacial failure is observed, with a significant enhancement of bond characteristics in assemblies formed by acid/base pairs.
- * The magnitude of beneficial effects on bond strength arising from molecular rearrangements appear to be strongly related to the magnitude of acid/base interactions between adhesive and substrate, as measured by parameters calculated from IGC data.

- * Cohesively weak moieties at the surface of an LDPE adhesive play a dominant role in the peel strength of bonds formed with polar and non-polar substrates.

Acknowledgement

This work was supported by grants from the Natural Sciences and Engineering Research Council, Canada.

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