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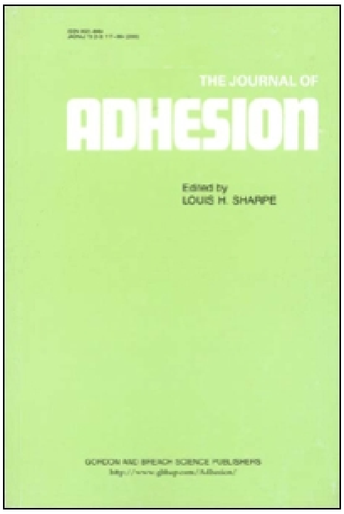

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Orientation Phenomena at Polyurethane Surfaces*

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The surface energies of soft-segment polyurethanes (SPU) have been evaluated by contact angle measurements. These showed that when solidified in air, the surface energies of the polymers were due almost entirely to dispersion forces. When immersed in liquids including formamide, water and saline solutions, surface rearrangements took place, gradually elevating the non-dispersive surface energy component. Equilibrium values varied with the corresponding non-dispersive surface energy of the contacting liquid. XPS analyses confirmed that compositional variations were responsible for changes in the surface energy. The surface restructuring was shown to affect the bond strengths of SPU/adhesive tape joints. The observations are relevant to property control in this important group of macromolecules.

KEY WORDS surface restructuring; contact angles; surface energies; adhesion; polymers; bond strength; interphase.

1 INTRODUCTION

Polymer surfaces represent a particularly interesting aspect of macromolecular science. Even chemically simple polymers, such as polyethylene, display complex surface properties, transcrystallinity and weak boundary layers[1,2] differentiating them from bulk properties. The influence of these morphological features on specific use properties of polyethylene, such as its adhesion to metals and other substrates, has long been recognized.[3] In more complex polymers, containing both polar and non-polar structural groups, more complex surface phenomena have been reported. For example, the surface characteristics of polymethyl methacrylate (PMMA), as sensed by inverse gas chromatography, were found to be dependent on the solvent from which the polymer was cast, and to change slowly when the polymer was maintained above its glass transition temperature.[4] More generally, as noted by Lipatov among others,[5] the composition of polymer surfaces differs from that of the polymer bulk, due to thermodynamic drives which will enrich the surface region

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with low surface energy components. Further complications arise from the ability of certain polymers to restructure at surfaces, when these are brought into contact with specific orienting media.[6,7,8] Surface structure then becomes a function of the medium in contact with the polymer. This is a matter of fundamental importance, and one that has repercussions on applied interfacial phenomena, including that of polymer adhesion.[6] Recent reports[8] have shown that polyurethanes also are subject to surface restructuring. The present work deals with soft-segment polyurethanes with different molecular weights of the soft segment, a polymer category of value in bioengineering uses. Our objective is to establish the degree to which these polymers display surface restructuring, and to help establish mechanisms for the effect.

2 EXPERIMENTAL

Materials

The study utilized a group of 3 soft-segment urethane polymers, labelled SPU1, SPU2 and SPU3. The structural characteristics of the hard and soft segments, and of the extender in this group, are given in Table I. The table also reports the molecular weights of the soft segment (S), which vary from 1100 to 4165 in the series. Molecular weights of the hard (H) and extender (E) segments were invariant, as were the mole ratios of H/S/E in the group. Intrinsic viscosities of the polymers were measured in dimethyl formamide (DMF) solutions at 30°C, using calibrated Ubbelohde viscometers. They, and the bulk N/O ratios are entered in Table I as further means of characterization.

Procedures

For surface energy measurements, free films of the SPU's were prepared by casting from dilute solutions (1–2 wt%) in DMF onto previously degreased, washed and dried sheets of PTFE. Films were vacuum dried for 24 h at 25°C, then placed in desiccators prior to further use. Initial evaluations of surface energy were made by measuring contact angles with a Rame-Hart goniometer (25°C), using the following contacting liquids: Water ($\gamma^d = 21.8$, and $\gamma^{nd} = 51$ mJ/m^2), Formamide (32 and 26.2 mJ/m^2), Ethylene glycol (29.3 and 19 mJ/m^2), Tricresyl phosphate (39.2 and 1.7 mJ/m^2) and linear alkanes from n-heptane to dodecane, all with zero values of γ^{nd}. The procedure of Kaelble[9] was applied to obtain values of dispersive and non-dispersive surface energies for the solids, γ_s^d and γ_s^{nd}. In these measurements, experimental uncertainties in contact angles were of the order of 3°, with a consequent uncertainty of about 3% in values of the surface energy parameters.

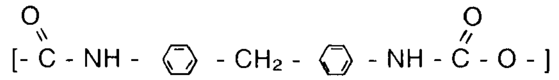
To establish the potential of SPU surfaces to restructure, film samples were immersed for controlled times in the following orienting fluids, their orienting strengths being indicated by the pertinent non-dispersive γ_l values: Formamide and water (see listing in preceding paragraph), and 1% and 5% salt solutions, with $\gamma^{nd} = 51.3$ and 52.6 mJ/m^2, respectively. Immersion was carried out at controlled

TABLE I

SOFT-SEGMENT PU RESINS

STRUCTURAL MOIETIES

HARD SEGMENT (H):



SOFT SEGMENT (S):

$CH_2-CH_2-CH_2-CH_2-(-0-CH_2-CH_2-CH_2-CH_2)_N-OH$

EXTENDER: (E):

$-CH_2-CH_2-CH_2-CH_2-0-$

GENERAL STRUCTURE:

$CH_3-0-(-H-E-H-E-H-S)_M-OH$

PROPERTY:	SPU-1	SPU-2	SPU-3
Mol. Ratio H/S/E	3/1/2	3/1/2	3/1/2
Mol. Wt. S	1100	2955	4165
Bulk N/O	0.228	0.115	0.087
$[\eta]$ * dl.g^{-1}	0.421	0.496	0.325

* DMF sol., 30 °C

temperatures of 30, 50, and 70°C. Following immersion, samples were dried as above, and their surface energies re-evaluated.

XPS analyses were carried out on SPU samples prepared as noted above. Spectra were obtained using the Vacuum Generators ESCAlab 2 apparatus, with Mg source and 0.7 eV resolution. In view of the structure of H and S segments, particular attention was given to the N/O ratio, which would differentiate strongly between these members of the SPU series. The N_{1s} and O_{1s} peaks in XPS spectra were used for this purpose. As shown in Figure 1, these features were very well defined. Analyses were performed on control samples as in Fig. 1, and also on specimens following immersion in orienting fluids. Variations in take-off angles allowed esti-

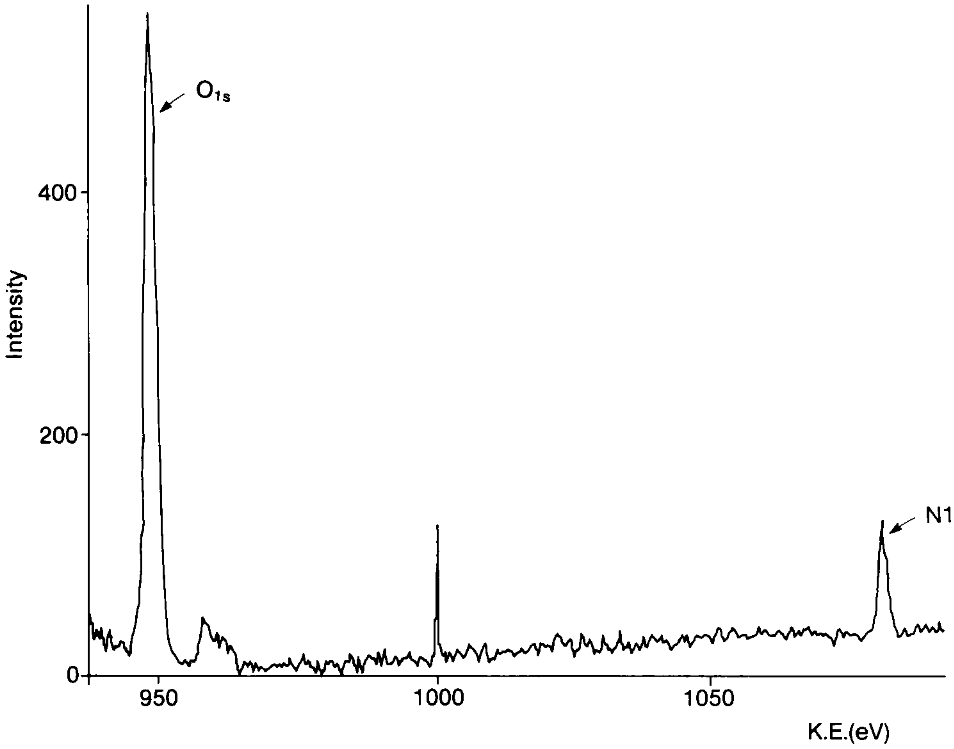


FIGURE 1 XPS spectrum for control specimen of SPU1, showing N_{1s} and O_{1s} signals.

mates to be made of N/O ratios in the surface and near-surface regions to depths in the vicinity of 100 A°, thus obtaining some indication on the persistence of postulated restructuring effects.

The performance of SPU polymers in adhesively bonded joints was assessed by constructing test materials in the following manner: The SPU's were cast from solution and drawn down onto degreased, washed and dried strips of aluminium, 15 cm × 3 cm in dimension, which were masked so as to leave a 5 × 3 cm strip uncoated. The thickness of SPU films was 0.75 mm. The coated strips were dried by the procedures given above. Some of these were retained as "controls", while others were exposed to the orienting fluids for 10 days at 50°C. Following exposure, these strips were vacuum-dried as usual. The SPU surfaces with different conditioning histories were then overcoated with industrial masking tape, cut to the same dimensions as the aluminium. The composite joints were kept under a compressive force of 44 N/cm^2 for 20 min prior to further use. Adhesion was evaluated by 180° peel tests, in which the adhesive tape was removed from the SPU/aluminium composite. Peel tests made use of the Instron tester, with a jaw separation speed of 10 cm/min. Initial calibration experiments showed this setting to be preferred for reducing sample-to-sample variations. Averages of 3–5 separate determinations are reported here. The reproducibility was ±12%.

3 RESULTS AND DISCUSSION

Surface Restructuring

Each of the SPU samples of this work was found to be capable of displaying a characteristic range of surface properties, depending on the medium of contact. The change in surface properties is most evident in γ^{nd} following water immersion, as shown in Figure 2 for SPU1. The pattern displayed in Figure 2 was followed closely by the other polymers in each of the immersion media. It is evident that the surface energy of the vaccum-dried polymer, found to be 41.5 mJ/m^2, is largely due to dispersive-force contributions, since γ^{nd} contributes only about 2.5 mJ/m^2 to that total. If the hard segments were randomly dispersed in the soft-segment matrix, as postulated in recent models,[10] then a higher non-dispersive component would have to be observed. The SPU's in their initial states thus appear to have surface compositions enriched in the S segments. In each of the curves of Fig. 2, and in other cases studied in this research, an "induction" period was observed, during which the surface energy parameter changed relatively little. Subsequently, however, the γ^{nd} began to rise appreciably. In the present context, that increase may be attributed

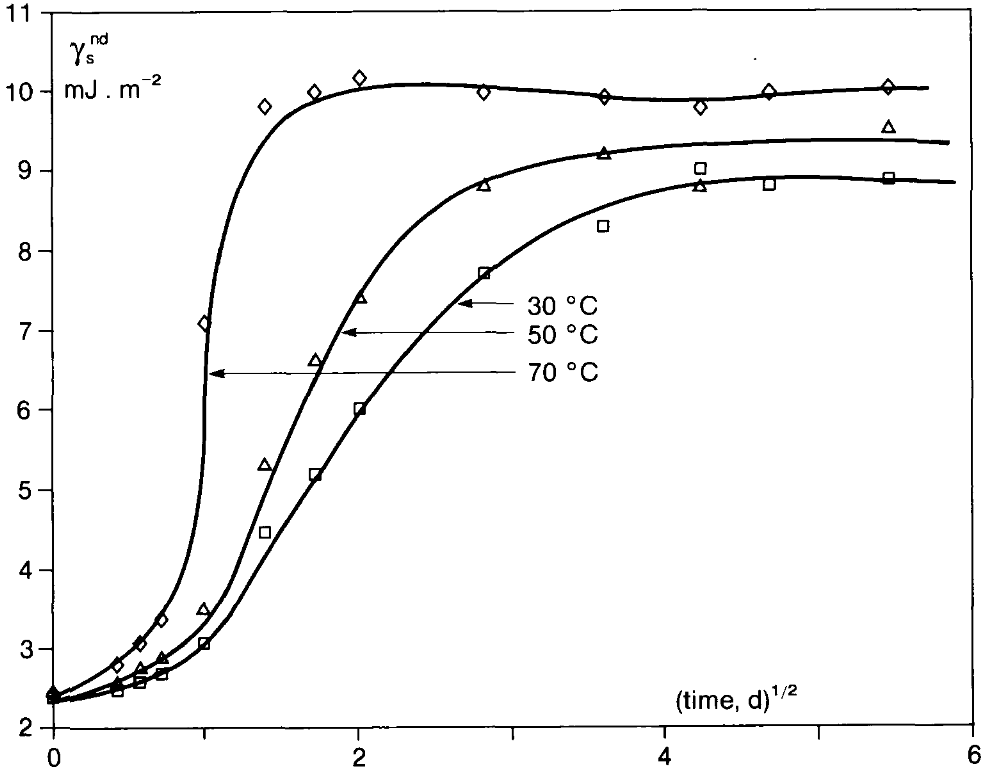


FIGURE 2 Response of γ_S^{nd} for SPU1 to immersion in water.

TABLE II
Initial and equilibrium values of non-dispersive surface energy of SPU: dependence on orienting medium

Immersion fluid		Formamide	Water	1% saline sol.	5% saline sol.
SPU1:	$(\gamma^{nd})_i^*$	2.4	2.4	2.4	2.4
	$(\gamma^{nd})_{eq}$	6.5	9.5	10.0	10.7
SPU2:	$(\gamma^{nd})_i$	1.7	1.7	1.7	1.7
	$(\gamma^{nd})_{eq}$	5.4	8.5	8.8	9.3
SPU3:	$(\gamma^{nd})_i$	1.2	1.2	1.2	1.2
	$(\gamma^{nd})_{eq}$	4.6	6.8	7.0	7.5

*All surface energy data in mJ/m^2.

to a continuing enrichment of the surface region in H segments, driven by the need to minimize the interfacial tension between the SPU and its contact medium. Clearly, the process is dynamic, responding to immersion temperature. In the case shown in Fig. 2, equilibria are reached within about 3 days at 70°C, some 9 days at 50°C and in more than 16 days at 30°C. There appears to be a slight increase in $(\gamma^{nd})_{eq}$ with increasing temperature, but the effect is minor and not to be found at all with SPU2 and SPU3.

Initial and equilibrium surface energy data are summarized in Table II for the three polymer samples immersed in each of the 4 orienting fluids. The magnitude of change in γ^{nd} for immersion in all of the fluids decreases as the molecular weight of the soft segment increases. This may be due to a reduction in the free volume through which the hard segment must diffuse in order to increase the non-dispersive surface energy value. The sequence of events shown in Fig. 2 suggests that immersion in water, and in other orienting media, first leads to a swelling of the surface region. This accelerates the diffusion of H segments into the surface, thereby satisfying the thermodynamic demands of the situation. The available results lend themselves to Arrhernius-type representations of equilibrium times *vs.* T^{-1} (°K), resulting in the following apparent activation energy values:

SPU1 ..	4.9 Kcal/mol
SPU2 ..	4.4 Kcal/mol
SPU3 ..	6.5 Kcal/mol

Values in this range seem to be consistent with activation energies for diffusion phenomena in polyurethane rubbers, as reported by Stannett and coworkers.[11] In summary, the restructuring mechanism seems to involve the diffusion of hard segments through a swollen surface region in which, initially, the S segment is the dominant constituent.

Perhaps the most striking feature of results in Table II, however, is the strong dependence of changes in γ^{nd} on the orienting medium. The polymer's response is related to the medium's "orienting power". Figure 3 has been constructed on the assumption that this orienting tendency may be expressed by the liquid's γ^{nd}. The result is a satisfactory correlation for each of the three polymer samples. The degree of restructuring demanded by the need to diminish the interfacial energy between

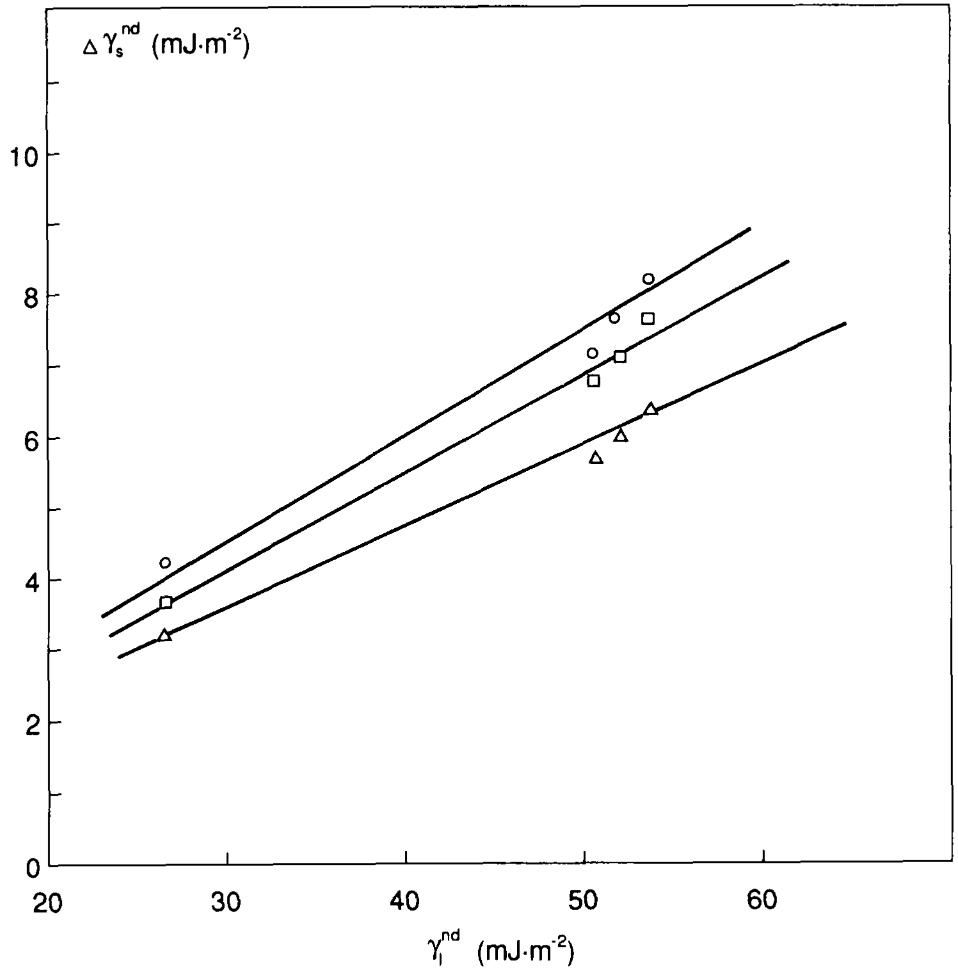


FIGURE 3 Showing the increase in non-dispersion surface energy of SPU as a function of the medium orienting strength.
SPU1 = ○ ; SPU2 = □ ; SPU3 = Δ

polymer and liquid clearly depends on the non-dispersive character of the immersion fluid. As already noted above, the rate at which SPU's respond and the degree to which the restructuration can take place depend on the polymer architecture, the molecular weight of the soft segment being the principal variant in this instance.

Independent confirmation of surface structural changes brought about by immersion of the SPU polymers is offered by XPS data. The most comprehensive work was carried out on SPU1, for which N/O ratios at the surface are given in Table III. Results for surface-modified specimens are for immersion at 50°C.

The sequence closely follows patterns set by changes in γ^{nd}. The N/O ratio for the vacuum-dried material is much lower than called for by the bulk composition, again inferring an excessive presence of S segments in the surface layer. The surface

TABLE III
Response of surface structure to immersion of SPU polymers
(N/O ratios determined from XPS spectra)

Immersion fluid (50°C)	N/O
Bulk polymer	0.228*
Nil, vac. dried control	0.088
Formamide	0.117
Water	0.129
1% saline solution	0.131
5% saline solution	0.139

*Calculated value.

composition obviously responds to immersion, and the extent to which the population of hard segments in the surface layer is enriched again increases with the γ^{nd}. Once more this supports the conclusion that surface composition, and non-dispersive surface energies in SPU polymers are highly dependent on the environment in contact with the polymer. In confirmation of recently published evidence,[8] it also follows that SPU's belong to a group of polymers which are anisotropic, due to the existence of significant differences between surface and bulk compositions. An interesting question relates to the depth to which compositional anisotropy can persist.

A partial answer to the above query is given by XPS spectra taken at different take-off angles. The procedure integrates the signals of interest over the sensing depth. The results are illustrated in Figure 4 for the three polymers as dried by the standard procedure. In each case the surface N/O ratio is much below the calculated bulk value (see Table I). The concentration of H segments increases into the bulk, but at a depth of 100 A° the composition remains skewed in favor of the soft segment. It is therefore justified to consider the surface region of the SPU specimens as representing an interphase with a compositional gradient linking the surface layer to the bulk. The depth to which the non-stoichiometry persists, however, suggests that more may contribute to its existence than a simple preferential orientation of the S (or H) segments. Since these constituents are chemically linked, then deviations from the stoichiometric N/O value should be restricted to depths in the order of the gyration radius of the polyurethane molecule. This would be of the same order as the 100 A° range investigated by the XPS data. No definitive explanation can be offered at this time for the apparent anomaly. One possibility is that the extender of this polyurethane formulation is incompletely incorporated in the macromolecular structure. The extender is essentially an oligomeric version of the S segment, and under this assumption unreacted moieties of the E segment would be able to accumulate at the polymer surface, thus extending the range of the interphase region.

Adhesion to SPU Surfaces

It seems reasonable to suppose that the bond strength of joints involving the polyurethanes would vary with the proportion of soft and hard segments populating the

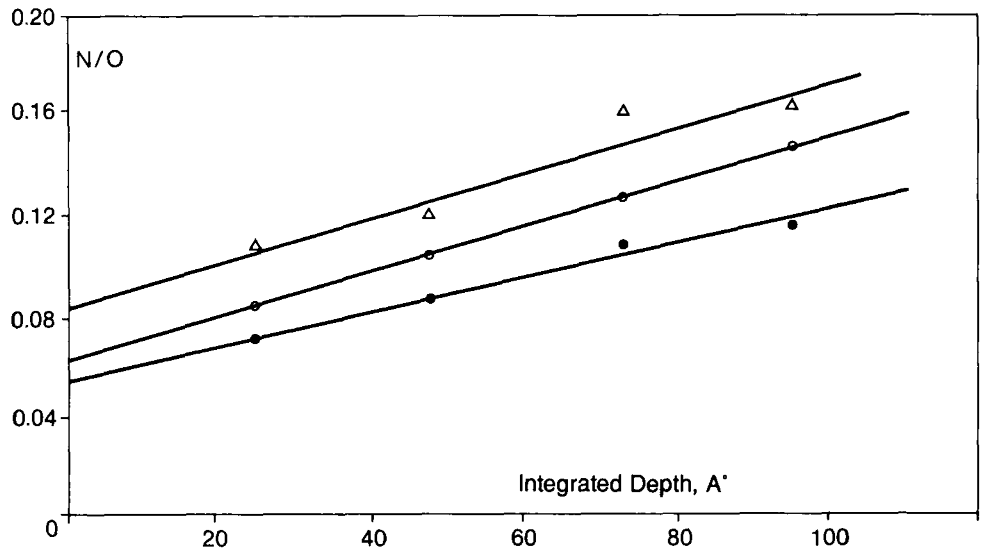


FIGURE 4 Compositional variation in the surface interphase of SPU polymers. SPU1 = △ ; SPU2 = ○ ; SPU3 = ●

surface interphase. The expectation is met, as shown by the peel strength data of Table IV. The peel strength increases uniformly in going from joints with control, vacuum-dried SPU to polymer substrates which had been conditioned in the immersion media. Further, there are significant decreases in the bond strength with increasing molecular weight of the soft segment. The peel strength appears to correlate strongly with the γ^{nd} of the SPU surfaces. This is evident from the representation in Figure 5. Here the bond strength, obtained from the peel test measurements, is plotted against the equilibrium values of γ^{nd} for the SPU surfaces. The procedure assumes, of course, that during immersion the surface energies of the SPU coatings attained the same values as given earlier in this paper, with the aluminium substrate not affecting the reading. The assumptions seem to be reasonable in light of the good correlations shown in Figure 5. Interestingly, though well-defined linear plots are generated, these are placed very differently in the y-axis for each of the SPU's. Molecular weight differences of S again seem to influence the issue. In part, differ-

TABLE IV
Peel strengths of SPU/adhesive tape joints

(Peel strengths in N/m are averages from 3-5 determinations with uncertainty of ±6%)

SPU immersion	Control	F*	W*	1% saline sol.	5% saline sol.
Material:					
SPU1	18.5	20.1	22.7	22.3	23.5
SPU2	12.2	15.3	17.0	17.2	17.8
SPU3	9.4	10.6	11.7	11.8	12.2

*F is formamide, W is water.

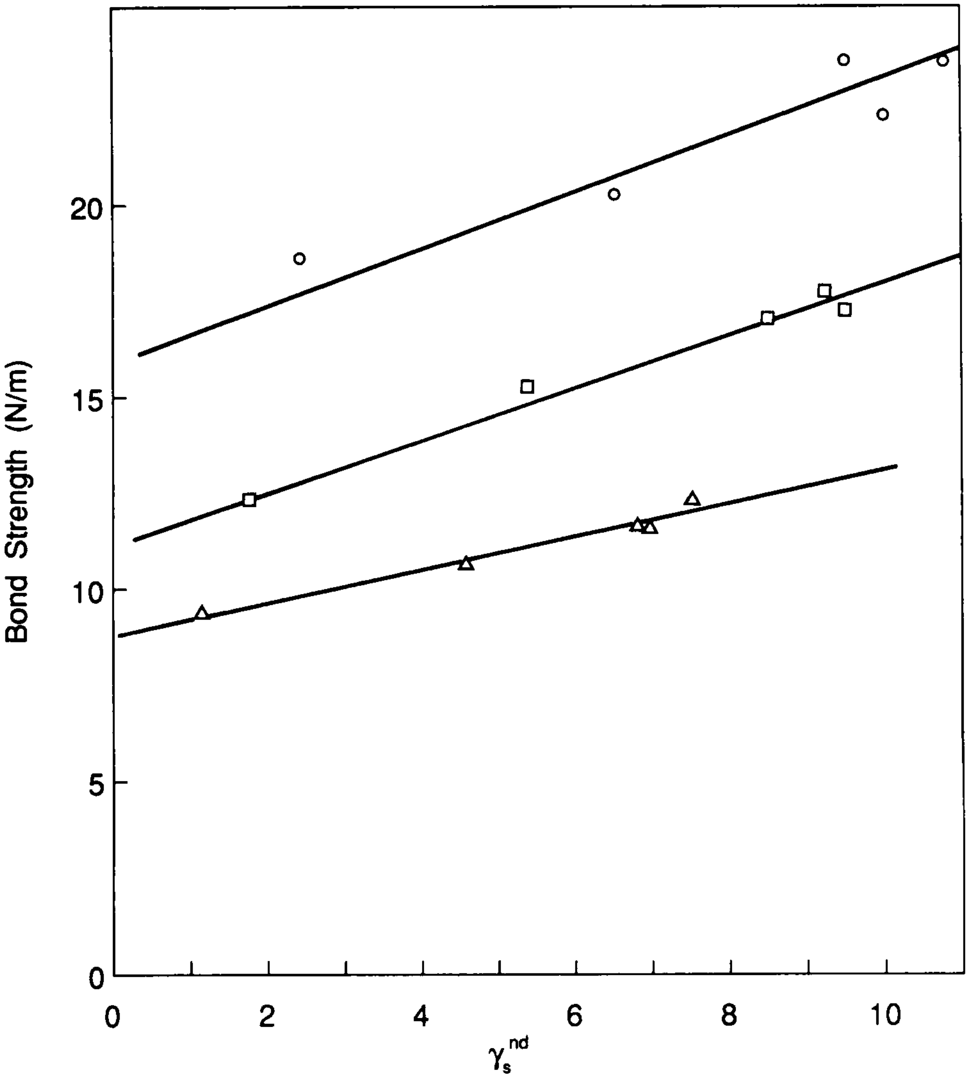


FIGURE 5 Variation of bond strength for SPU/tape joints with the non-dispersive surface energy of SPU.
SPU1 = ○ ;SPU2 = □ ; SPU3 = Δ

ences in viscoelastic properties of the SPU's may contribute to the observations. Further in this connection however, it can be argued that in control samples, where S segments dominate the surface, the peel strength would be determined mainly by the dispersion forces exerted by the largely hydrocarbon-like polyether, with subordinate contributions from the terminal OH groups of this constituent. Since the effective number of OH groups would vary inversely with the molecular weight, their contribution to peel strength would decrease, consistent with the observations in Table IV. Persistence of the peel strength trends in joints with restructured SPU surfaces again corroborates the diagnostic data presented earlier, and suggests that the migration of H segments is inhibited by the molecular weight of the polymer's S constituent. An additional factor not taken into consideration in the adhesion data, is the ability of the SPU surfaces to respond to the "orienting strength" of the masking tape applied to them. Given the long times needed to effect surface restructuring, it is assumed that the SPU surface orientations produced by the various conditioning procedures were retained in the tested joints. The reported data then are non-steady-state responses, however, since over a sufficiently long period of time, the SPU chain molecules in contact with the adhesive would restructure to minimize that interfacial tension, and thus alter the bond characteristics. Extrapolating this argument, it may be suggested that in certain industrial bond formation procedures, where stress must be laid on operational economics, the bonds produced leave the constituents in transient states of surface orientation. As a result, a thermodynamic drive toward "aging" of the structures may be built into them inadvertently.

4 CONCLUSIONS

The surfaces of soft-segment polyurethanes were shown to be capable of restructuring when placed in contact with orienting liquids. The orienting power of the media was defined conveniently by their non-dispersive surface energies, the degree of polymer restructuring was found to depend on the orienting strength of the medium, and the kinetics of restructuring were found to be temperature dependent. Polyurethane surfaces dried against non-orienting media have surface compositions enriched in the relatively non-interactive soft segment. Contact with specifically interactive liquids leads to the diffusion of hard segments into the surface region. The polyurethanes were shown to have non-isotropic surface interphases extending more than 100 A° into the polymer bulk. The bond strength of adhesive tape/polyurethane joints, measured by peel testing, was found to be strongly dependent on the surface structure of the polymer. Results suggest that transient states of polymer orientation may exist in many industrially produced adhesive joints, with the consequence of time dependent changes in the bond characteristics of such structures.

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