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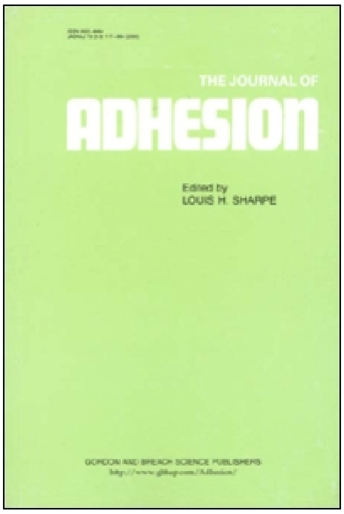

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Chain Conformation and Surface Characteristics of Polymers

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Films of styrene-butyl acrylate copolymers when pre-conditioned in polar or non-polar media, have been used for measurements of critical surface tension, for retention volume measurements by inverse gas chromatography, and as adhesives in joints with aluminium sheet. It has been shown that large variations in surface tension, and particularly in the non-dispersive force contribution, are generated by exposing the polymer to diverse media. Specific retention volumes indicate that the copolymer surface becomes enriched in polar groups when exposed to polar media including water and formamide. The peel strength of Al-polymer joints can be roughly doubled when the polymer surface is pre-conditioned in polar rather than in non-polar media. The magnitude of property variations diminishes with increasing content of the acrylic moiety in the polymer.

The results are interpreted as showing that the surface conformation of polymer chains is such as to diminish or enrich the surface concentration of polar moieties, depending on whether the polymer is in contact with polar or non-polar media. The proposed surface re-conformation appears to be reversible, and to proceed by diffusion-dependent rate processes. This evidence elaborates on the importance of attenuated responses in macromolecules to physico-chemical forces, and on the consequences of these responses to bulk as well as surface and interfacial properties of the polymer.

KEY WORDS Attenuated relaxation; chain conformation; critical surface tension; inverse gas chromatography; polymers; surface orientation.

Presented at the Eighth Annual Meeting of The Adhesion Society, Savannah, GA, U.S.A., February 24–27, 1985.

INTRODUCTION

Attenuated relaxation phenomena are a widely recognized feature of macromolecules. The consequences arising from long relaxation times generate much applied as well as fundamental interest. In bulk polymers, for example, it is possible to alter chain entanglement states by shearing or solution treatments,[1-3] the transient effect being sufficiently long-lived to affect the processability and mechanical properties of the polymers. Surface properties of film-forming polymers cast from solutions are also complicated by relaxation phenomena. Inverse phase gas chromatographic studies (IGC) on PMMA films cast from solutions have shown[4] that the polymer at the vapor phase interface can adopt various orientational states, depending on the thermodynamic quality of the solvent. Further, at any interface, the conformation of polar group containing macromolecules must respond to the nature of the medium with which the polymer is in contact. A film of such a polymer in simultaneous contact with polar and non-polar media can then become anisotropic, due to different chain orientations at the two interfaces. The phenomenon, and its influence on properties of the polymer as an adhesive have been discussed in recent articles.[5,6]

The work of Schultz and coworkers[7] provides additional insights into the conformational complexity of macromolecules. Working with graft copolymers of ethylene and acrylic acid, these workers have shown that the polar moiety in this polymer can orient either into the bulk or into the interface, depending on the contacting medium. The surface energetics of the polymer solidified in air arise quantitatively from dispersion forces, indicating an absence of acrylic groups. When immersed in water or other polar fluids, however, a gradual evolution is observed in the non-dispersive component of the surface energy, as the acrylic groups orient into the interface, thereby minimizing the interfacial tension. Expectedly, the bond strength of metal joints using the polymer in these distinct conformations as adhesive, differs greatly.[7]

The present paper extends the findings of Schultz and coworkers to styrene-acrylic block copolymers with limited content of the polar group moiety. Surface tension, IGC and peel strength results offer evidence for the reversibility of conformational states attainable by these polymers, and again show that profound changes in the polymer's adhesion characteristics can be attributed to these physico-chemical causes.

EXPERIMENTAL

i) **Materials**: Three styrene-butyl acrylate copolymers were used in this work. Their mole–% composition was:

$$\begin{aligned} \mathrm{S/BA} &= 97:3 \\ &= 95:5 \\ &= 85:15 \end{aligned}$$

All were experimental primer samples, obtained from commercial sources, and supplied as 45% solids in solutions of toluene/methyl–ethyl–ketone. The majority of results reported are based on the 97/3 copolymer. This material had a $Tg = 54°C$ (by DSC analysis, Perkin–Elmer DSC-2 instrument, scanning rate of $5°C\,min^{-1}$). The intrinsic viscosity of the polymer in dichloroethylene at 30°C was $0.74\,g\,dl^{-1}$, inferring an $M_v = 2.7 \times 10^4$.

ii) **Film preparation and surface energetics**: Films were prepared from solutions diluted to give an initial solids concentration of about 10%. Supported films were prepared on microscope slide glass, while free films could be prepared against clean PTFE plates. In both cases, draw-down techniques yielded 10 cm × 3 cm specimens, 0.008 cm in thickness. The standard drying procedure was air oven exposure at 140°C for 30 min. Certain of the films were used directly for analyses as described below, while others were immersed in water at 30°, 45°, and 60°C prior to use. Following any timed exposure to water, the samples were vacuum dried at 45°C for 3 h prior to further use. In a few instances formamide, and *n*-octane, were also used as immersing liquids to pre-condition polymer samples. In all these cases the above vacuum-drying procedure was followed prior to further use of the samples. Immersion periods in the conditioning fluids ranged to a maximum of about 35 days.

Freshly prepared and pre-conditioned films were used for determinations of the critical surface tension, γ_c, by the contact angle method using a Rame–Hart 100-07 Goniometer. The contacting fluids and their surface tensions were the following: water (72.3); glycerol (63.4); formamide (58.2); tricresyl phosphate (40.9); *n*-hexane (16.2); *n*-octane (21.3); and *n*-decane (25.2); bracketed figures being γ_L values in mJ m^{-2}. Values of γ_c were obtained from Zisman plots[8] of $\cos\theta$ *vs.* γ_L. The method of Schultz and coworkers[7,9] was followed to estimate the dispersive γ_c^D, and non-dispersive contribution, γ_c^{nD}, to the overall γ_c. This is obtained from contact angles of the alkanes against the polymer, and values of γ_L^D for the immersing liquids, using plots[7,9] of $\gamma_A - \gamma_L + \gamma_{AL}\cos\theta$ *vs*, $(\gamma_A)^{1/2} - (\gamma_L^D)^{1/2}$, where γ_A is the surface tension of alkane. For present purposes the following γ_L^D values were used:

$$\text{water} = 22.3 \text{ mJ m}^{-2}$$

$$\text{formamide} = 39.7 \text{ mJ m}^{-2}$$

iii) **Inverse gas chromatography**: The S/BA = 97/3 copolymer was used as the stationary phase in IGC experiments in which previously degreased and washed stainless steel columns housed the polymer. The polymer was deposited onto acid-washed, 40/60, mesh Chromosorb support, by evaporating the solvent under vacuum and then further vacuum drying the coated powder at 45°C for about 72 h. Standard ashing procedures[10] showed that in two columns prepared for this study, the percent weight of supported polymer was 10.7 (col. C-1) and 8.8 (col. C-2). Previously characterized columns[4] of polystyrene (PS) and polymethyl methacrylate (PMMA) also entered this phase of the work. Specific retention volumes, V_g^0, were measured for *n*-octane, *n*-butyl alcohol and *n*-butyl amine. The polar vapors are recognized as being a Lewis acid and base, respectively.[11] The ratio of V_g^0 data therefore can be used as an index of acid–base interaction for the stationary phase.[12,13] The interaction index, Ω, is defined by:

$$\Omega = (V_g^0)_{\text{acid}}/(V_g^0)_{\text{base}}$$

IGC experiments were conducted on the columns as freshly prepared, and following oven exposure to polar vapors. Column C-1 was conditioned in 85% R.H. air at 50°C for periods up to 30 days. Column C-2 received exposure at 50°C to formamide vapor, also for approximately 30 days. This was done in order to show whether or not orientational responses could also be detected in a thin layer of supported polymer in contact with polar vapor rather than immersed in bulk liquid. As is usual in IGC determinations, V_g^0 values were calculated from averaged retention times, the reproducibility in 3–5 separate determinations being within 3% of the mean.

iv) **Peel strength**: The performance of the copolymers as adhesives was rated on Al–polymer–Al joints using the free polymer films as adhesive. In control experiments, the polymer was used following drying against PTFE, as described above. Additional joints used the polymer after it had been immersed in water or octane; in these cases the immersion was at 30°C for 14 days. Test specimens were prepared by compression molding 10 cm × 3 cm polymer films between degreased washed and dried sheets of 0.005 cm thick aluminium at 140°C and 2000 p.s.i. platen pressure. The standard molding time was 1 min, but in certain experiments the dwell time in the hot mold was extended to a maximum of 15 min.

On removal from the mold, metal–polymer specimens were cooled to room temperature at a constant rate of about 10°C/min. Bond strengths were determined by peeling one of the Al sheets from the joint at 180°, using an Instron table model tester. The jaw separation speed was 0.5 cm min^{-1}. Certain of the test samples were annealed in dry N_2 at 80°C prior to peel strength determination.

RESULTS AND DISCUSSION

i) **Surface energetics**: Values of the critical surface tension and its non-dispersive component for the S–BA (97–3) copolymer are given in Table I. The data show the evolution of γ_c and γ_c^{nD} following increasing immersion periods in water. In contrast, immersion in *n*-octane produces no measurable changes in these surface properties. The slow evolution of γ_c^{nD} is particularly noteworthy, suggesting that over a period of approximately 14 days at 30°C, there is an increasing concentration of the acrylic moiety in the polymer surface region. The γ_c data follow a similar trend but the total change in this property is less pronounced than in γ_c^{nD}. As will be shown below, formamide, though less polar than water, produces a similar effect on surface tension parameters, so that the

TABLE I
Critical surface tension results

Specimen	γ_c mJ m^{-2}	γ_c^{nD} ($\pm$0.7)
Control S/BA (97/3)	32.9	0.7
Water immersed 1 h	32.8	0.6
@ 30°C— 1 d	34.0	2.4
— 3 d	35.4	6.2
— 7 d	37.5	9.9
—14 d	39.0	15.3
—20 d	38.9	17.9
—25 d	39.6	17.7
—30 d	39.4	18.0
n-octane immersed		
@ 30°C— 1 d	33.1	3.5
— 7 d	32.8	3.9
—14 d	32.4	3.2
—21 d	33.0	3.3

changes noted in Table I cannot be attributed to spurious causes, such as the ad- or absorption of water. Instead, in agreement with Schultz and coworkers,[7,9] we attribute the observations to molecular re-orientation in the surface region of the polymer, driven by thermodynamic demands to minimize the interfacial tension between polymer and a polar orienting liquid. No such drive exists, of course, when the polymer is immersed in octane. Consequently, the molecular orientation originally produced during the air drying step, is consistent with the thermodynamic requirements of this case.

It is apparent then, that the surface composition of the copolymer is inconsistent with its bulk stoichiometry. Comparing initial values of γ_c and γ_c^{nD} with the γ_c of polystyrene (see Table I) leads to the conclusion that the copolymer surface region is originally enriched in styrene groups, the γ_c values being essentially equal. In the steady-state against water, the surface region is again non-stoichiometric relative to the bulk; an exact calculation of the molar content of butyl acrylate groups in the surface would require the currently unavailable datum of γ_c^{nD} for pure polybutyl acrylate. Clearly, however, at ~18 mJ m^{-2}, that value is far in excess of expectations for the 97–3 mole ratio of this copolymer.

Finally, in connection with Table I, it is remarkable that the

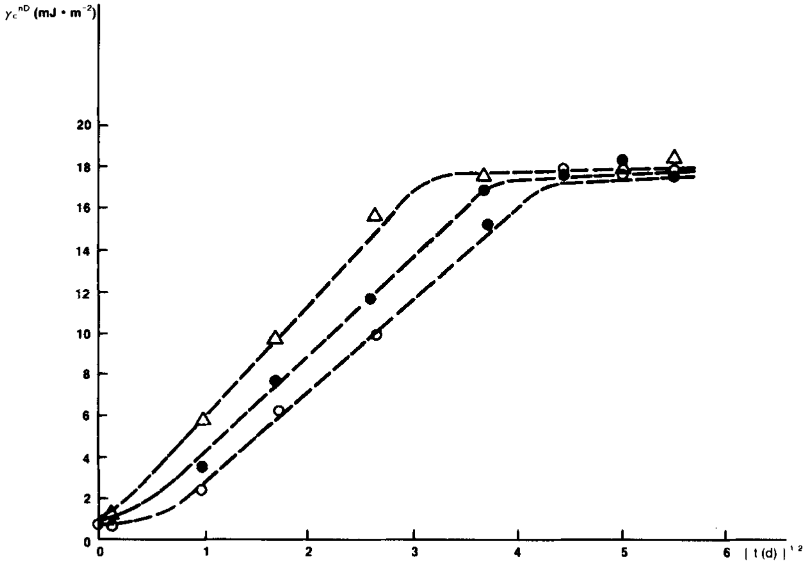

FIGURE 1 Evolution of γ_c^{nD} in S–BA copolymer due to water immersion. Immersion T: 30°C . . . ○; 45°C . . . ●; 60°C . . . △.

observed re-orientation occurs below the apparent polymer Tg, albeit at a slow rate. Speculatively, this may be due to a surface "plasticization" by water during the immersion period, lowering the effective Tg. A further view of the orientational kinetics is provided in Figure 1, which compares the evolution rate of γ_c^{nD} for water immersion at 30°, 45° and 60°C. In this comparison the polymer is above the nominal Tg at 60°C, and below the transition at the lower immersion temperatures. A slight increase in the process kinetics with rising T is evident, but no major increase occurs in going from 45°C to 60°C immersion. The surface plasticization concept therefore, may gain credibility. The root time abscissa was chosen for Figure 1 on the hypothesis that time dependent relaxation phenomena in polymers occur by segmental diffusion mechanisms.[1,2] The well-defined linear segments in Figure 1 are consistent with the concept. We note also that immersion temperature in water affects only the time for steady-state attainment, but not the final γ_c^{nD}. In each of the three cases, therefore, fully developed steady-state surface compositions appear to be attained.

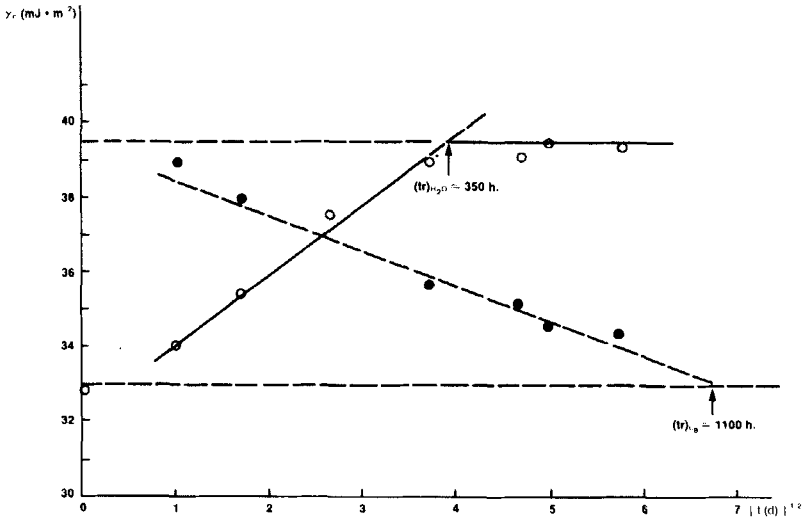

FIGURE 2 Orienting effect on γ_c of S–BA (97/3) copolymer: ○ Sample immersed in water, 30°C; ● Sample immersed in *n*-octane 30°C, following 21 days in water.

A point of obvious interest in whether the transition from a non-polar to an enriched polar surface state in the copolymer is reversible. The matter was investigated by allowing samples of the copolymer to attain their steady-state in water, and then re-immersing the dried film in *n*-octane. The results of the experiment are shown in Figure 2, in terms of γ_c. The effect, clearly, is reversible, showing similar diffusion dependent kinetics and apparently forcing the polar groups back into the bulk of the copolymer when the film is immersed in the non-polar liquid. The thermodynamic, or physico-chemical origins of the observation are thereby reinforced. The reversion in octane, however, proceeds at less than half the rate of the corresponding orientation in water. The attractive forces acting between the polar orienting liquid and the polar groups of the polymer apparently constitute more powerful driving forces than the repulsion produced by the mismatch of dispersive and non-dispersive forces in the re-immersion experiment. The subject is considered again in the next section.

ii) **IGC data**: The V_g^0 data obtained in this part of the study are presented in Table II. The freshly deposited copolymer freed of

TABLE II
IGC data for variously conditioned S/BA [V_g^0 results at 30°C; repeatability of ±3%]

V_g^0 for:	nC_8	but. amine	but. alcohol	Ω[a]
Conditioning:				
Nil	16.2	12.9	14.3	1.11
80% RH 50°C				
1 day	16.7	14.7	15.6	1.06
7 days	14.0	13.9	15.3	1.10
14 days	12.3	14.3	17.6	1.23
23 days	11.9	14.6	19.1	1.31
30 days	10.6	14.6	19.9	1.36
PS	22.8	8.7	9.3	1.07
PMMA	17.7	16.1	26.1	1.62

[a] $\Omega = (V_g^0)$ bu. alc./(V_g^0) bu. amine.
Butanol is acidic vapor probe; butyl amine is basic vapor probe.

solvent residues, has slightly higher retention of the acid than of the basic vapor probe, producing an $\Omega = 1.11$. The polymer surface therefore appears as slightly basic. In this regard, the Ω of pure PS falls well within the experimental error of the copolymer value. Both are clearly distinguishable from that for PMMA, which is here used as a qualitative reference point for acrylic group containing polymers. Conditioning the copolymer-containing column in humidified air leads to a systematic decrease in V_g^0 for octane, and a systematic increase in V_g^0 for butyl alcohol, the data for butyl amine remaining invariant. The resulting increase in Ω suggests that on exposure to water vapor the copolymer surface becomes increasingly basic, its capability for the retention of an acidic probe increasing at the expense of the retention for the non-polar vapor probe. We suggest that these observations are due to orienting effects in the copolymer deposited on the chromatographic support, which are entirely analogous to those responsible for the surface energy effects discussed above. The copolymer, clearly, becomes increasingly similar to PMMA in its retention properties, indicating surface enrichment in acrylate groupings. Unlike the bulk water immersion experiment, however, there is no evidence that a steady-state is attained after a 30-day conditioning of the column. Evidently liquid/solid contact produces a more powerful orienting effect than does vapor/solid contact.

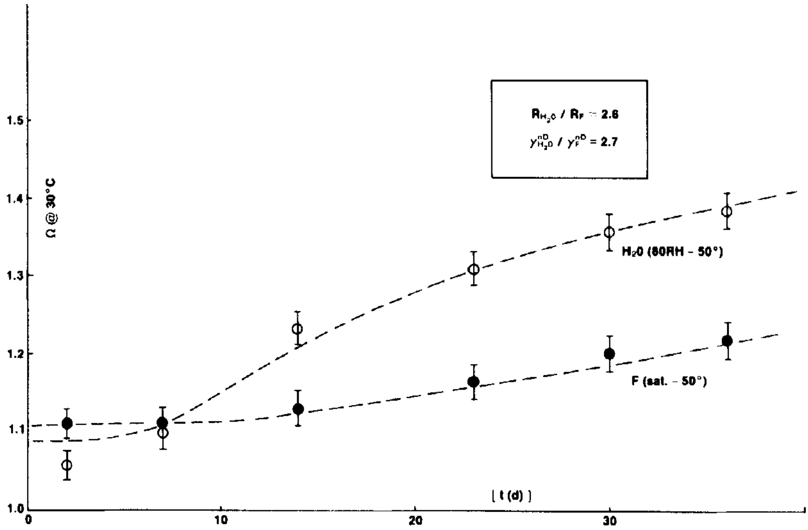

FIGURE 3 Showing change in Ω for copolymer exposed to vapors of water and formamide.

Column C-2, as noted already, was given saturated vapor exposure to formamide under time/temperature conditions identical to those involved in the case of water vapor. Again a significant, but slow, response was engendered. The changes in Ω when the copolymer is in contact with formamide and water vapors, (the latter reproducing data in Table II) are shown as Figure 3. Following what appear to be characteristic "induction" periods, nearly linear upward changes occur in Ω, the ratio of the slopes, $(d\Omega/dt = R)$, being

$$R_{H_2O}/R_F = 2.6 \pm 0.3$$

If we assume that the Ω shift is due to postulated chain conformational responses, then it would stand to reason that the response rate would depend on the relative values of non-dispersive forces in the orienting vapor media. Indeed,

$$(\gamma^{nD})_{H_2O} = 51 \text{ mJ m}^{-2}$$

and

$$(\gamma^{nD})_F = 18.5 \text{ mJ m}^{-2},$$

TABLE III
Peel strength for variously conditioned metal/polymer/metal joints

Peel strength ($N\,cm^{-2}$) for Polymer condition	Molded[a]	H_2O immersion[b]	nC_8 immersion[b]
Anneal $t(h)$ @ 80°C			
Nil	11.5	20.7	10.5
1	10.9	21.3	11.1
5	12.0	20.0	11.7
10	13.5	19.8	12.5
24	15.1	20.0	12.6
48	16.3	19.4	14.3
72	17.7	19.6	15.0
120	17.4	18.6	15.5

[a] Molding @ 140°C—2000 p.s.i.—1 min.

[b] Using polymer film which had been immersed 14 days @ 30°C in liquid as noted.

97/3 copolymer used in all cases.

Data are averages of 3–5 separate determinations with peel strength error of ±11‰.

so that

$$(\gamma^{nD})_{H_2O}/(\gamma^{nD})_F = 2.7$$

The correspondence may, of course, be fortuitous and additional systems need to be studied in order to verify the proposed hypothesis. We note that in the work of Schultz *et al.*,[7] ethylene–acrylic acid copolymers responded in a somewhat similar manner to immersion in water and formamide. The total increase in γ^{nD} for water immersion was $22\,mJ\,m^{-2}$, that for formamide immersion was $9\,mJ\,m^{-2}$, producing a ratio of 2.4, in reasonable agreement with the present IGC data.

iii) **Peel strength**: The performance of the 97/3 copolymer as adhesive is summarized in Table III. Each datum in the table is the average of at least 3, and in most cases of 5 separate evaluations. There is appreciable scatter of experimental results, but nontheless, significant trends are evident. In freshly prepared test specimens, the peel strength of joints using polymer as air dried, or following immersion in *n*-octane, is identical. On the other hand, roughly doubled adhesive strength is observed in joints using as adhesive polymer that had been conditioned in water. These results appear to be consistent with the concepts advanced above. The surface conformation of copolymer conditioned in air or in octane, is empoverished in polar groups in comparison with polymer conditioned in water. The aluminium metal used in this work has a significant γ_c^{nD} contribution of 16 mJ m^{-2}. Much higher bond strength can then be generated when polar group interactions between substrate and polymer take place.

The performance of joints annealed at 80°C—some 25°C above the nominal Tg—also follows expectations arising from the conformational effect hypothesis. Since the Al surface provides an orienting force similar to, though weaker than polar liquids like water, it is reasonable that characteristic surface conformations must be attained to establish steady-states of metal/polymer interaction. Thus, the surface concentration of acrylic moieties should increase in joints using air dried or octane-conditioned polymer, and decrease somewhat when the polymer was water conditioned. The peel strength data reflect these trends.

A surprising feature in Table III is the apparent inadequacy of the standard molding operation to produce steady-state conformations in the polymer, and therefore time-invariant bond properties. A similar problem had already been reported for the case of ethylene–acrylic acid graft copolymers.[7] The source may be the relatively weak non-dispersive driving forces represented by Al, a notion supported by data in Figure 4. Here peel strength variation is reported as a function of time in the mold at 160°C. Evidently, a major increase in bond strength takes place, the peel strength after 15 min molding being in the range of 22 N cm^{-2}. This seems some 15% higher than would be expected from the results in Table III, but we cannot exclude the possibility of mild, thermally-induced oxidation of the polymer during the lengthy molding procedure, and its positive contribution to the adhesive strength of the system.

iv) **Polymer composition**: A brief study on the generality of the phenomena presented here has involved the 95/5 and 85/15 S–BA copolymers, and has been limited, so far, to the response of γ_c to water immersion. Relevant data are shown in Figure 5.

The initial values of γ_c increase with acrylic content, and correspondingly, there is a significant decrease in the total change of γ_c upon water immersion. The steady-state γ_c ($\sim$39 m J m^{-2}) is common to all three copolymers. The results then confirm the

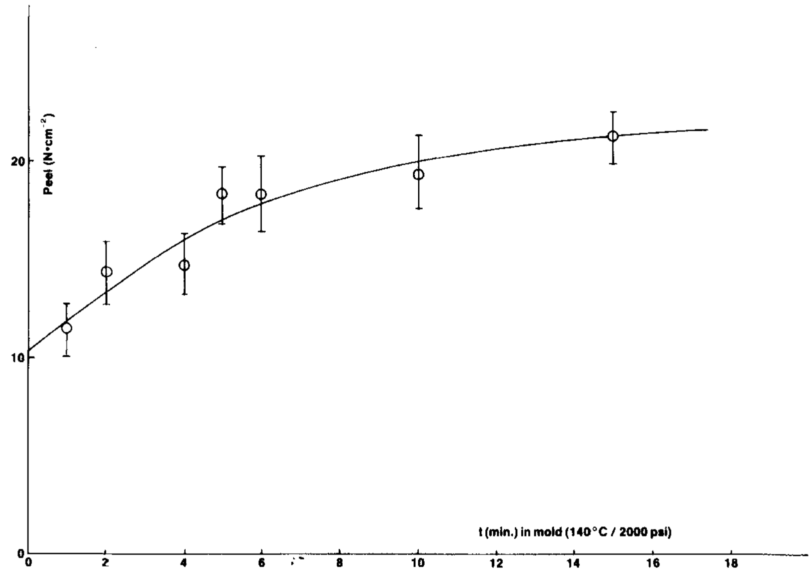

FIGURE 4 Variation in 180° peel strength of Al/S-BA/Al joints with molding time at 140°C.

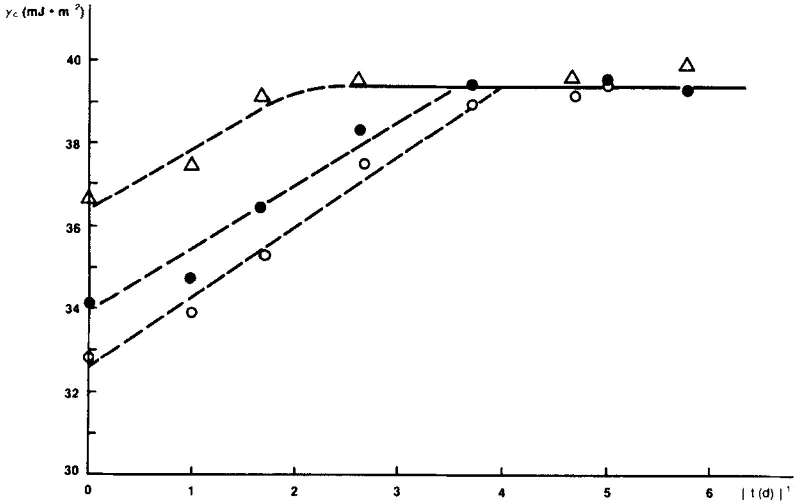

FIGURE 5 Effect of composition on evolution of γ_c for S–BA copolymer due to immersion in water at 30°C. ○ S/BA = 97/3; ● S/BA = 95/5; △ S/BA = 85/15.

general tendency of polar group containing macromolecules to alter surface conformations in response to their thermodynamic environments, but also suggest the importance of steric factors in this connection. Evidently it is not possible to eliminate effectively the polar groups from the surface when these are present at high concentration (*i.e.* in the neighborhood of 85/15 in this case). Such copolymers will then be in thermodynamic equilibrium when in contact with polar media, but there should be a tendency to increases in surface strains when these materials are in contact with non-polar media. This may influence the durability of interfacial properties, such as adhesion. The subject clearly warrants additional study.

Acknowledgment

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