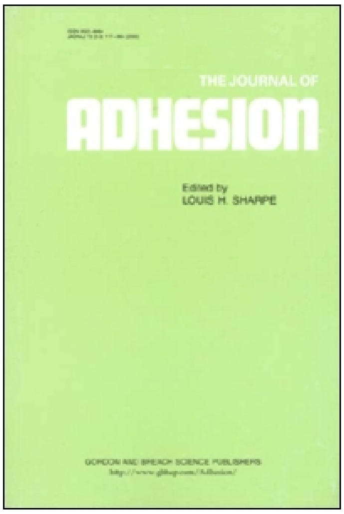

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# On Multi-valued Surface Properties of PMMA Films

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## NOTE

# On Multi-valued Surface Properties of PMMA Films

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An apparent link between the surface properties of polar group—containing polymers, such as PMMA and Styrene/Acrylic copolymers, and the thermodynamic quality of solvents used in solutions from which the polymers were cast, was described in earlier papers.[1,2] In these polymers, significant variations have been observed in critical surface tensions($\gamma_c$), and in the thermodynamic interaction parameters for selected vapor–polymer pairs, when the configuration of the polymer in solution was varied through the suitable selection of solvents of differing thermodynamic quality. The "solvent history" effect on surface properties of solid film was not detected however for non-polar polymers such as polystyrene (PS).[1,2] Apparently the distinct chain configurations adopted in solution by PMMA are carried over into the solid and result in different proportions of non-polar (backbone) and polar (side chain) moieties being located in the surface layer of the solid. Since only one surface state can correspond to a thermodynamic equilibrium, it may be expected that the film surface properties will change with time, as the thermodynamically preferred state is attained. As a consequence, use properties of these films should also display (initially) the "solvent history" effect, and should vary similarly with time. The present communication is concerned with these points.

## EXPERIMENTAL

The polymer involved is a commercial PMMA sample, $M_v = 80{,}000$.[1,2] The key data on which the premise of a "solvent-history" effect is based are

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excerpted from the earlier work in Table I. Here $V_g^\circ$ is the specific retention volume measured by an inverse gas chromatographic (IGC) experiment,[3,4] in which the polymer is the stationary phase and the indicated vapors "probe" the polymer surface (at 30°C, well below the polymer Tg, bulk sorption is assumed to be a negligible factor).[4] The $\gamma_c$ were measured by a recently developed method,[5] in which the area swept out by constant-volumes of calibration liquids is plotted against $\gamma_{LV}$ and an extrapolation is made to a previously defined reference line representing the area defined by a droplet which forms a monolayer (at $\gamma_c$). The intrinsic viscosities $[\eta]$, report on the polymer configuration in the indicated solutions. Chloroform is an excellent solvent for the polymer (P-5), systems P-2, P-3 are at the $\theta$-condition for the polymer and P-4 corresponds to a maximum in $[\eta]$ for PMMA solutions in toluene/butanol mixtures. The retention volume is directly related to the Flory–Huggins thermodynamic interaction parameter for each polymer-vapor pair;[3,4] although $\gamma_c$ is not a thermodynamic quantity in a strict sense,[6] it nevertheless provides independent support for the distinct nature of the five PMMA surfaces described in Table I.

Additional experiments were recently conducted with the five PMMA columns prepared for earlier work. During original column preparation, each of these was vacuum dried at 50°C to remove residual solvents. Subsequently, each column has been baked under nitrogen at 150°C (some 50°C above Tg) for up to 72 hour, whereupon the IGC procedure was repeated at 30°C using n-octane and propyl acetate vapors. Thermogravimetric and thermoanalytic analyses using a Mettler Thermoanalyser showed that the polymer was thermally stable under these experimental conditions, so that

TABLE I

Polymer/solvent systems, $V_g^\circ$ and $\gamma_c$ properties

| Code: | P-1 | P-2 | P-3 | P-4 | P-5 |
|---|---|---|---|---|---|
| Solvent | tol. | tol./hep. 80/20 | tol./but. 40/60 | tol./but 80/20 | Chloroform |
| $[\eta] dl\, g^{-1}$ | 0.298 | 0.165 | 0.165 | 0.350 | 0.535 |
| $V_g^\circ(ml\, g^{-1})^a$ at 30°C for: | | | | | |
| n-octane | 95.0 | 88.0 | 76.0 | 81.0 | 53.0 |
| toluene | 67.0 | 70.0 | 89.0 | 116.0 | 46.00 |
| p. dioxane | 63.0 | 70.5 | 150.0 | 135.0 | 56.0 |
| prop. acetate | 82.0 | 90.0 | 210.0 | 185.0 | 56.0 |
| $\gamma_c$(dyne $cm^{-1})^b$ at 30°C | 41.5 | 42.0 | 41.8 | 40.5 | 39.2 |

[a] Experimental error in $V_g^\circ = \pm 2\%$

[b] Experimental error in $\gamma_c = \pm 0.6$ dyne $cm^{-1}$.

any time dependent changes in $V_g^\circ$ would reflect changes in the surface condition of the polymer. Finally, five PMMA solutions defined in Table I were used to coat previously degreased washed and dried aluminium foils, cut to form 6 x 2 cm rectangular tabs. Following vacuum drying of the films (50°C, 48 hour), two coated tabs were overlapped to form a 2 x 2 cm contact, and these were compression molded for 3 minutes at 180°C to form joints suitable for seal-strength testing. The hot molds were cooled to room temperature at a rate of about 5°C/minute. An Instron tester (jaw separation speed = 0.5 cm $\text{min}^{-1}$) served to evaluate the adhesion properties of the PMMA films. In some cases joints were conditioned at 150°C, as in the IGC case, and comparisons made as to seal-strength performance.

## RESULTS AND DISCUSSION

The IGC results are presented in Figures 1 and 2 for n-octane and propyl acetate probes, respectively. In order to permit a simple comparison of time-dependent trends in $V_g^\circ$, the ordinates in Figures 1 and 2 have been normalized to the corresponding initial $V_g^\circ$ value given in Table I.

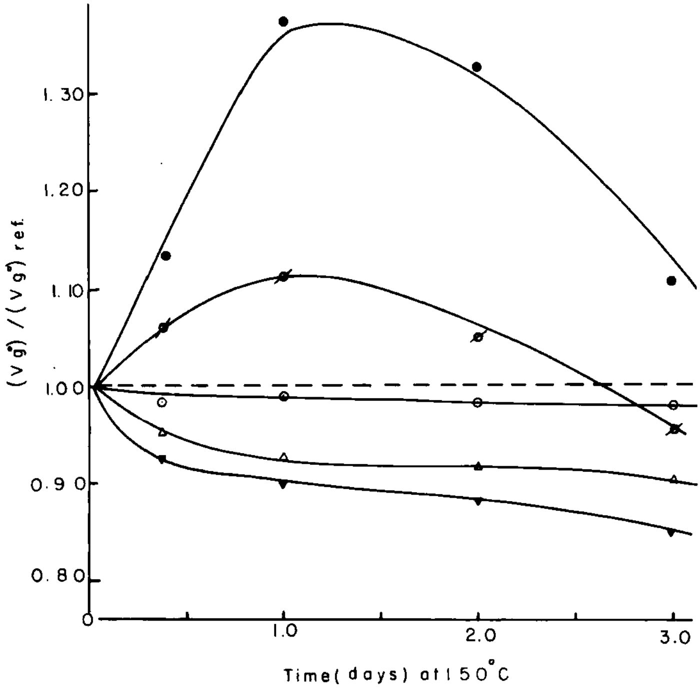

FIGURE 1 Effect of 150°C aging on $V_g^\circ$ for *n* C-8 interacting with: ▼P-1, △P-2, ●P-3, ∅P-4, ⊙P-5.

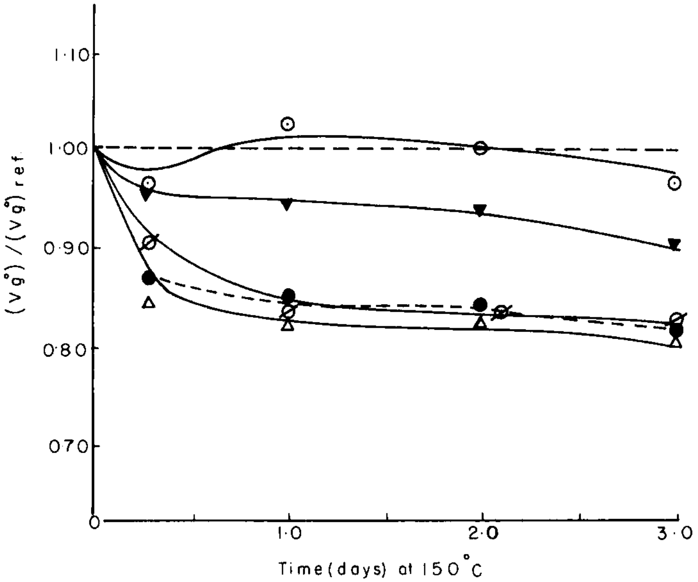

FIGURE 2 Effect of 150°C aging on $V_g^\circ$ for propyl acetate interacting with: ▼P-1, △P-2, ●P-3, ∅P-4, ⊙P-5.

The most apparent feature in these Figures is the significant time-dependence in $V_g^\circ$ for systems P-1 to P-4 and, in contrast, the near-constancy of this quantity for P-5. In terms of octane vapor, variations in $V_g^\circ$ for P-5 fall within the experimental error of determination, there is, however, a slight change in $V_g^\circ$ when propyl acetate is the vapor probe. The absolute $V_g^\circ$ and the $\gamma_c$ data in Table I already suggest that the polymers in P-5 is nearer to a thermodynamically favored state than in the other systems.

The near-stability of this surface state under extended exposure to a temperature well above the glass-transition, supports this concept. The time-dependent changes in $V_g^\circ$ for the other PMMA films argue in favor of gradual surface rearrangements tending towards a configuration similar to that originally present in the chloroform–cast film. Since the absolute $V_g^\circ$ values (Table I) for P-5 are the lowest in any given case of comparison, it should follow that all of the ordinate values in Figures 1 and 2 for systems P-1 to P-4 should fall below 1.0. This trend is followed where the polar probe is involved (Figure 2), and it may therefore be inferred that the extended exposure to elevated temperatures leads to a reduced concentration of polar groups in each of the film surfaces of samples P-1 to P-4. This is at once consistent with the proposed "solvent history" effect and a reassurance that the observations are not due to thermally-induced chemical changes in the polymer, which would have the opposite effects. A more complex pattern of variations is reported by the alkane probe (Figure 1). The toluene and toluene/heptane borne films again show a consistent tendency toward reduced absolute $V_g^c$ values. In films formed from butanol-containing solutions, however, $V_g^\circ$ passes through a maximum—particularly pronounced for the film formed at the $\theta$ conditions for this mixed solvent—prior to a sharp reduction in this parameter following longer bake times. The reason for this is not clear; it may be, however, that last traces of the high-boiling solvent were lost only during the prolonged 150°C exposure, in quantities not detected by thermogravimetric analysis but significant to the molecular probe experiment. This loss presumably introduces porosity into the film on a molecular level and this is detected by the n-alkane which now "penetrates" the microstructure with the result of attenuated retention times and volumes. Additional experimental clarification of this concept is planned.

The impact of these suggested changes in the surface configuration of PMMA chains on use properties of the polymer may be important, judging from the results of seal strength experiments shown in Figure 3. Each bar represents the mean value of seal strength determinations on three joints, the deviation about the mean being generally within 5%. Under the adopted sample preparation procedure, seal strength of PMMA-bonded metal

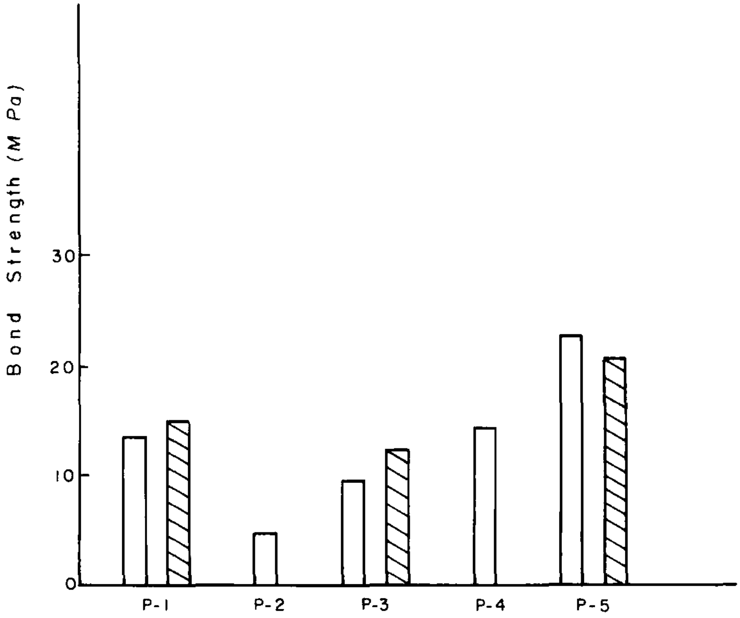

FIGURE 3 Bond strength of Al-PMMA joints. Open bars: immediately following preparation. Hatched bars: after aging 24 hour at 150°C.

joints varies from a high of near 23 MPa for the chloroform-borne polymer, to a low of ~4.5 MPa in system P-2. The failure of system P-5 is clearly cohesive, P-1 and P-4 apparently so, that in P-2 and P-3 apparently adhesive, although the films in these cases are extremely weak and a qualitative decision on the kind of failure occurring is not easily made. In the three cases where samples were aged for 24 hours at 150°C (hatched bars, Figure 3) there is some evidence for changes in seal strength. Presumably this is another manifestation of the time-dependent effects reported in Figures 1 and 2, this time in terms of a parameter more readily associated with practical applications of the polymer. The changes in bond strength are not as large as corresponding ones in $V_g^\circ$, nor is it clear whether the changes are due to configurational effects as suggested earlier. The slight decrease in seal strength in case P-5 (~9%) may be due to such causes as the gradual accumulation—by diffusion mechanisms—of cohesively weak boundary layers,[7] a feature common to polymers with an appreciably broad molecular weight distribution function. Such an occurrence would not necessarily be detected by either of the analytic methods used in other parts of this study.

We conclude that surface properties of solvent–cast PMMA films depend significantly on the thermodynamic quality of the solvent, and hence on the polymer chain configuration. Further, certain performance aspects of these polymers, such as lap-shear strength, appear also to depend on this variable. The existence of the reported effects offers some measure of control, by the user, over initial surface properties as well as over their variation during the use-life of the material.

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## References

1. M. D. Croucher and H. P. Schreiber, *J. Polym. Sci. Phys. Ed.* **17**, 1269 (1979).
2. H. P. Schreiber and M. D. Croucher, *J. Appl. Polym. Sci.*, in press.
3. D. Patterson, *et al. Macromolecules* **4**, 356 (1971).
4. J. M. Braun and J. E. Guillet, *Adv. in Polym. Sci.* **21**, 108 (1976).
5. H. P. Schreiber and F. Ewane-Ebele, *J. Adhesion* **9**, 125 (1978).
6. W. A. Zisman, *Adv. Chem. Series* **43**, 1 (1964).
7. H. Schonhorn and F. W. Ryan, *J. Poly. Sci.* **A-2**, 231 (1968).