

# Surface Tension Measurements on Film-Forming Polymers: Thermal Aging Effects

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## Synopsis

The surface property changes caused by exposure to specific time/temperature regimes have been followed by critical surface tension data ( $\gamma_c$ ) in a series of styrene-acrylic polymers frequently used as film-formers. A simple, experimental method for  $\gamma_c$  evaluation, previously described, proved useful for present purposes. Surface tensions change more rapidly when polymers age above their characteristic  $T_g$ . In the polymers studied, increases in  $\gamma_c$  indicate an apparent enrichment in the acrylic content of the surface, the rates apparently dominated by diffusion-controlled processes. The importance of the effect increases with overall acrylic content in the polymer and with molecular weight.

## INTRODUCTION

In previously published papers,<sup>1,2</sup> a thermal gradient bar (tgb) has been described and its use documented for critical surface tension measurements  $\gamma_c$ , of low-surface-energy polymers used as film-formers. We have been espousing the tgb route to  $\gamma_c$  evaluations because the experimental method is relatively simple, the apparatus is rugged enough to be suitable for routine industrial uses, and because it offers the possibility of measuring  $\gamma_c$  and its temperature variation  $d\gamma_c/dT$  in the same experimental operation. Furthermore, there is no need for a direct measurement of contact angles, a procedure associated with both experimental and conceptual limitations.<sup>3-6</sup>

We have been particularly interested recently in the use of  $\gamma_c$  as an analytic parameter describing the surface condition of polymer films. In particular, the changes occurring in these surfaces as a result of aging at selected temperatures have been targets for study. Understanding the nature of such changes has both basic and applied value and should help in more selectively tailoring the polymer structure to meet desired performance properties. In this paper we present  $\gamma_c$  data for typical film-formers based on styrene (S), butyl acrylate (BA), and methacrylic acid (MAA) and analyze the variation of  $\gamma_c$  following exposure of the films to selected temperature/time regimes.

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## EXPERIMENTAL

### Materials

Six polymers were used in this work. Four of these have a comonomer weight ratio of S/BA/MAA = 80/15/5; the others have the comonomer ratios shown in Table I but an apparent molecular weight similar to sample 3, based on nearly equal values of the reduced viscosity. The 80/15/5 materials have already been studied extensively,<sup>7</sup> and their characteristics are given in Table I. As noted elsewhere,<sup>7</sup> the molecular weight parameters, calculated from gel-permeation elution spectra, are intended for comparison purposes and are not reported as absolute values. Glass transition temperatures of the polymers were measured by differential scanning calorimetry using the Perkin-Elmer DSC-2 and linear temperature variations of 2.5°C/min. All materials were synthesized and donated by the Paint Research Laboratory, Canadian Industries Ltd, Toronto; they were supplied as dry, free-flowing powders and were used without further purification.

### Procedures

The design and operation of the tgb has been discussed previously.<sup>1,2</sup> In the present work the instrument was operated isothermally at  $30.0 \pm 0.5^\circ\text{C}$  in a laboratory space maintained at that temperature. In one experimental series, a linear thermal gradient was established on the metal bar, with the cold end at  $30^\circ\text{C}$  and the hot end at  $82^\circ\text{C}$ . Details of operation were those described in the earlier papers. Polymer samples were prepared by compression molding the powders against a "Bonderite" panel ( $15 \times 5 \times 0.4$  cm) in a press set at  $185 \pm 5^\circ\text{C}$ . A copper foil was used as the top molding "plate," and following molding, this was removed by amalgamation with freshly distilled Hg. The free polymer surface was then degreased by washing with lint-free paper saturated in pure  $\text{CHCl}_3$  and finally air dried at  $30^\circ\text{C}$  for 24 hr. A number of test panels were aged at  $60^\circ\text{C}$  and others at  $90^\circ\text{C}$  by storing in ovens which were maintained under a nitrogen atmosphere so as to eliminate the possibility of oxidative changes on the polymer surfaces. The absence of these was confirmed by repetition of intrinsic viscosity measurements, which reproduced initial values to  $\pm 5\%$ . Following oven exposure, these aged samples were used to follow  $\gamma_c$  changes, again at the reference temperature of  $30^\circ\text{C}$ .

TABLE I  
Characterization of Polymers Used in Study

Sample	Composition S/BA/MAA, wt. %	Reduced viscosity, <sup>a</sup> dl/g	$M_n$ , <sup>b</sup> $\times 10^{-4}$	$M_w$ , <sup>b</sup> $\times 10^{-4}$	$T_g$ , °C
1	80/15/5	0.12	1.20	1.77	62
2	80/15/5	0.23	1.96	4.52	62
3	80/15/5	0.38	3.31	15.1	62
4	80/15/5	0.49	3.36	17.3	62
5	84/15/1	0.39	—	—	67
6	70/25/5	0.42	—	—	53

<sup>a</sup> Reduced viscosities measured at  $25^\circ\text{C}$  in 95/5 (v/v) ethylene dichloride/ethanol mixtures; polymer concentration, 0.5% (w/v).

<sup>b</sup> Polystyrene-equivalent molecular weights, see Ref. 7.

In earlier tgb work,<sup>1,2</sup> the areas of constant-volume droplets needed for  $\gamma_c$  evaluations were estimated by planimetry. Greater reproducibility is possible by the variation used in this case, as outlined below. A microsyringe of 10  $\mu\text{l}$  capacity was used to place droplets of standard wetting liquids onto the polymer substrate. The standard fluids, all solutions of purified propionic acid in distilled water, had known  $\gamma_{LV}$  values, as determined by du Nuoy ring tensiometry and recorded in Table II.

Preliminary experiments showed that at 30°C these solutions interacted slowly with the polymer films, significant spreading of droplets being detectable after 10–15 min of contact. The interaction may be due to either or both components of the test solution; in the present context, it was desirable to eliminate its effects. Consequently a photograph of deposited droplets was taken at 1-min intervals up to a maximum contact time of 5 min. Prints of the photographs were then used to make photocopies on standard graph paper. Droplet shapes were carefully cut out and weighed, at least two weight determinations being used for each contact time, and an average value  $\bar{W}$  for each of the test fluids at zero contact time was then calculated from  $\sim 10$  data points. Values of  $\bar{W}$  normalized to a constant enlargement factor of 5:1 were found to be reproducible to within  $\pm 3\%$ . An illustration of five droplets on a S/BA/MAA = 80/15/5 substrate (5-min contact time) is shown in Figure 1. As in previous work,<sup>1,2</sup>  $\bar{W}$  was plotted against

TABLE II  
Composition and  $\gamma_{LV}$  of Test Fluids

Fluid	Propionic acid, g/100 ml	$\gamma_{LV}$ , dyn cm <sup>-1</sup>
1	1.910	60.2
2	5.838	49.2
3	9.804	44.0
4	13.002	40.9
5	21.705	35.8
6	30.115	33.5
7	50.001	31.5

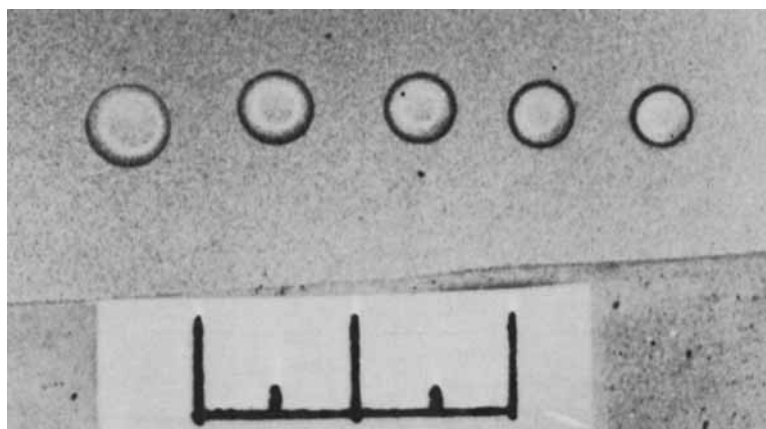


Fig. 1. Droplets of propionic acid solutions on S/BA/MAA polymer film at 30°C; note 2-cm scale marking.

$\gamma_{LV}$ , producing well-defined linear relationships (Fig. 2). The key to determining  $\gamma_c$  is the construction of a horizontal line representing  $W_{lim}$ , the limiting weight of a circle produced by a liquid having  $0^\circ$  contact angle with the substrate. Theoretically,  $W_{lim}$  would be defined by the circle corresponding to a droplet forming a monolayer on the solid; that is,  $\bar{W}$  must increase nonlinearly as this condition is approached. Empirically, however, we have found that  $W_{lim}$  may be obtained to within an error of  $\pm 3\%$  by applying droplets of the test fluids to calibrated standard substrates, the values for which were measured by the Zisman contact angle method. These solids were as follows:

Linear polyethylene:  $\gamma_c = 30.7 \pm 0.5 \text{ dyn cm}^{-1}$

Polystyrene:  $\gamma_c = 34.5 \pm 0.5 \text{ dyn cm}^{-1}$

"Mylar":  $\gamma_c = 42.2 \pm 0.5 \text{ dyn cm}^{-1}$

Each of these polymers defined the same limiting value,  $W_{lim} = 0.514 \text{ (g)} \pm 0.008$ . Adopting this parameter in further analysis, values of  $\gamma_c$  for the experimental polymers were determined with a precision of about 3%, as shown in Figure 2 for samples 3 and 6 of Table I. The reference values of  $\gamma_c$  (that is, prior

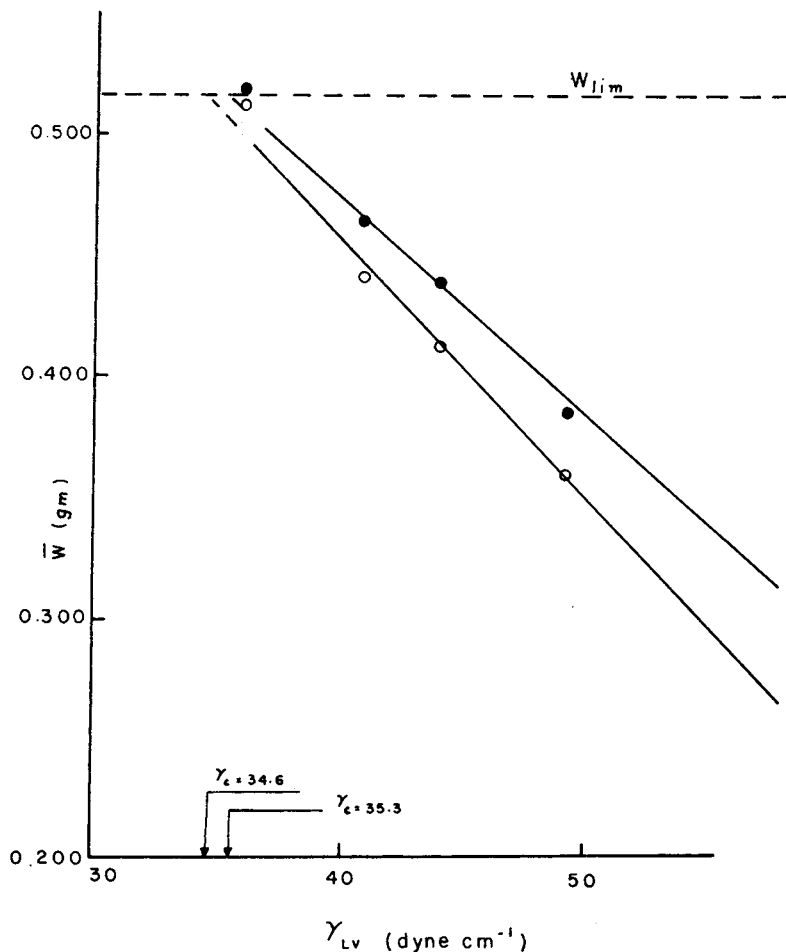


Fig. 2. Illustration of  $\gamma_c$  determination from droplet weight measurements: ●, 70/25/5 polymer (sample 6); ○, 80/15/5 polymer (sample 3).

to high-temperature aging of the samples) are as follows:

$$80/15/5 \text{ series} = 34.5 (\pm 0.7) \text{ dyn cm}^{-1}$$

$$70/25/5 \text{ series} = 35.3 (\pm 0.7) \text{ dyn cm}^{-1}$$

$$84/15/1 \text{ series} = 33.8 (\pm 0.8) \text{ dyn cm}^{-1}$$

Since the  $\gamma_c$  values for samples 1–4 were within the 3% experimental error, only one datum is used to represent this series of polymers. The datum is in very good agreement with previous evaluations,<sup>2</sup> in which planimetric measurements of droplet surface area were used to estimate the surface tension. It is evident that the  $\gamma_c$  values of these polymers are dominated by the low-surface-energy component of the material. Indeed, in the case of samples 1–5, the  $\gamma_c$  values are essentially those of polystyrene, the contribution of the acrylic component—expected<sup>8</sup> to be in the range 40–44 dyn cm<sup>-1</sup>—becoming evident only in sample 6, though to a lesser extent than expected on the basis of stoichiometry.

### RESULTS AND DISCUSSION

In this section emphasis is placed on the use of  $\gamma_c$  data as an analytic tool for the detection of surface changes due to high-temperature exposure of the test films. The suitability of this experimental approach is clearly demonstrated in Figure 3, in which  $\gamma_c$  variations for the 80/15/5 polymer series resulting from aging at 60 and 90°C is documented. Only one set of data points is given for 60°C exposure, no detectable difference having been found among samples 1–4. Thus while an experimentally significant rise in  $\gamma_c$  toward 36.5 dyn cm<sup>-1</sup> is observed within the maximum exposure time of ~500 hr, this increase seems not to depend on the molecular weight of the materials. Aging at 90°C—some 30°C in excess of the  $T_g$  for the polymers—produces not only an accelerated and sharper rise in  $\gamma_c$ , but one which is now distinctly more pronounced at higher molecular weights.

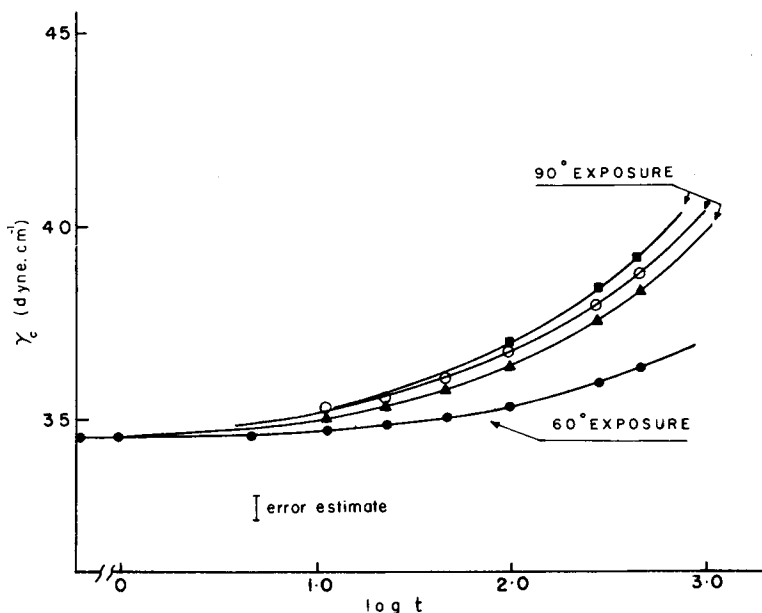


Fig. 3. Time/temperature effect on  $\gamma_c$  of 80/15/5 polymers. Code for 90°C exposure: ■, sample 4; O, sample 3; ▲, sample 1.

A comparison of the surface property changes in the three polymer structures represented in this work is given in Figure 4. Here samples 3, 5, and 6, all at approximately constant inherent viscosity (i.e., apparent molecular weight), are involved. Again, aging up to  $\sim 500$  hr at  $90^\circ\text{C}$  produces significant increases in  $\gamma_c$ , these being particularly evident in the polymers with high acrylic content. The  $\gamma_c$  change for sample 5 ( $\sim 1.5$  dyn  $\text{cm}^{-1}$ ) is much less pronounced but still significant. The high-temperature aging effect is therefore promoted by higher molecular weight and by the increased content of the acrylic components.

The inference in the given results, i.e., that surface property changes occur more rapidly at  $T > T_g$  of the polymers, is confirmed by the results in Figure 5. Samples 1, 3, 5, and 6 represent the three polymer groups, and the data were obtained from tgb experiments in the temperature range  $35\text{--}82^\circ\text{C}$ . Samples were aged on the gradient bar for several hours,  $\gamma_c$  of the polymers being determined systematically at  $30^\circ\text{C}$  following fixed aging times at the indicated temperatures. The data in Figure 5, typical of the results obtained, display the change in critical surface tension after 8-hr aging; the parameter  $\Delta\gamma_c$  is defined as  $\Delta\gamma = (\gamma_t - \gamma_0)$ , where  $\gamma_t$  is the surface tension after the polymer was aged for time  $t$  and  $\gamma_0$  is the initial value of  $\gamma_c$ . Clearly, significant increases in  $\gamma_c$  occur in each case when aging occurs at  $T > T_g$ . For the 70/25/5 series (sample 6) this occurs above  $\sim 50^\circ\text{C}$ , consistent with the  $T_g$  of this material (see Table I). At the other extreme, sample 5, representing the 84/15/1 series, shows significant  $\Delta\gamma_c$  above  $\sim 65^\circ\text{C}$ , again consistent with its higher  $T_g$  value. The inferences of these data are to the effect that a diffusion-controlled mechanism produces an apparent enrichment of acrylic content in the surfaces of these polymers, the importance of this enrichment effect varying directly with overall acrylic content in the polymer and with molecular weight.

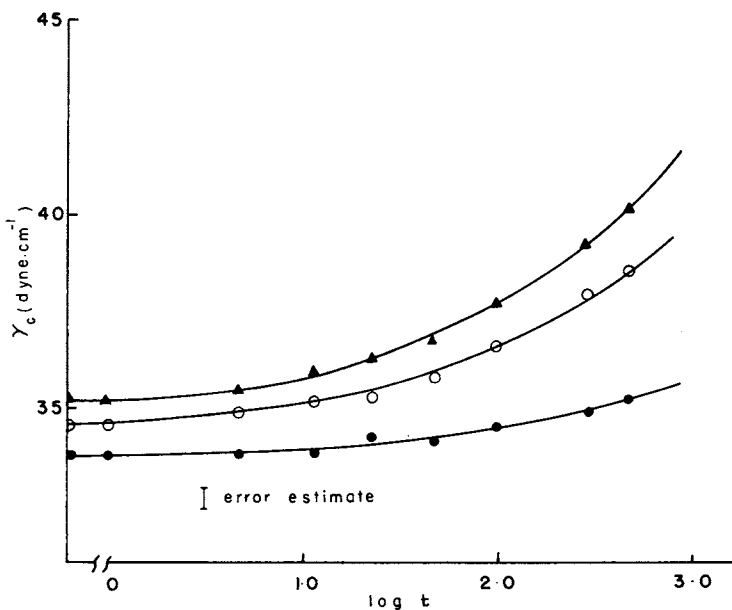


Fig. 4. Comparison of  $\gamma_c$  changes due to exposure at  $90^\circ\text{C}$ : ▲, 70/25/5 polymer; ○, 80/15/5; ●, 84/15/1.

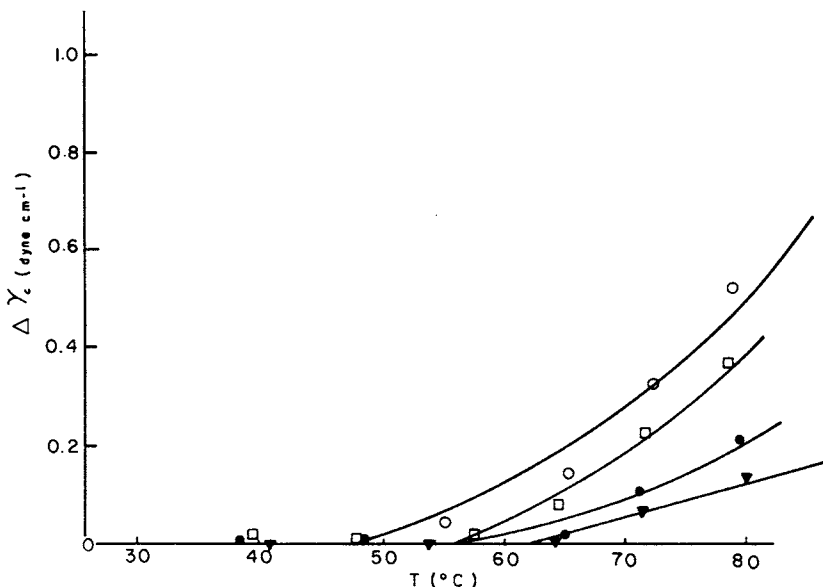


Fig. 5.  $\Delta\gamma_c$  due to isochronous aging at temperatures to 80°C: ○, 70/25/5 polymer; □, 80/15/5 polymer, sample 3; ●, 90/15/5 polymer, sample 1; ▼, 84/15/1 polymer.

### NATURE OF AGING EFFECT

The data in hand do not permit a resolution of the mechanism(s) responsible for the observed aging effects. Thermal instability may be ruled out, earlier work with the 80/15/5 series having shown these polymers to be stable for many hours at temperatures well above those involved here.<sup>7</sup> An increase in  $\gamma_c$  toward some equilibrium value higher than the initial measurement is not consistent with the thermodynamic behavior of miscible systems. It is likely therefore that the present polymer systems are multiconstituent in nature and that included in them are immiscible moieties, richer in acrylic content. These may gradually migrate to the interfaces, the increase in  $\gamma_c$  at the air interface being offset by the overall decrease in the bulk free energy of the system on demixing. The known, broad molecular weight distribution in these polymers<sup>7</sup> is qualitatively consistent with this suggestion. Further, the polymers were prepared by a proprietary process in which it is probable that the methacrylic acid serves as a particle stabilizer. It may, therefore, be sorbed by the polymer particles, remain there as a low-molecular-weight moiety and thus be the species alluded to above. An alternative suggestion consistent with the observations is based on recently published results of gas chromatographic experiments,<sup>9</sup> which showed that the initial chain orientation of poly(methyl methacrylate) at solid-gas interfaces depended strongly on the solvent from which the polymer film was formed and changed slowly on subsequent thermal aging of the polymer. These conclusions were drawn from the behavior of specific retention volumes for various probe gases in contact with the polymer surfaces; analogously, it may be argued that thermally induced chain orientation effects in the present acrylic copolymers favor an apparent surface enrichment of the polar groups, giving the overall impression of nonisotropy. Additional experiments will be required to discuss this matter more fully.

In any event, the practical consequences of these surface property changes

should be important, since presumably, such characteristics of coatings produced from the polymers as intercoat adhesion, wettability, etc., should respond to aging effects in a manner consistent with the structural changes attributed to it. Indeed, experimentally significant temperature and time-dependent changes in the bond strength of joints using these polymers as adhesives have been observed, and they will be discussed in a separate publication.

The allegation of diffusion-dominated mechanisms for surface property changes, made above, is more readily tested through an application of the theory for diffusion mechanisms. If migrating acrylic-rich polymer chains are regarded as solvents in the overall polymer structure, then well-known theory<sup>10-12</sup> may be applied to the set of  $\gamma_c$ ,  $T$ , and  $t$  data. Thus if  $\gamma_0$  is the initial surface tension datum, characterizing some starting apparent concentration of acrylic moieties in the surface, then  $(\Delta\gamma_c)_t$  is associated with a finite increase in that effective concentration at time  $t$ . Following standard procedures,<sup>10-12</sup> we then write:

$$(\Delta\gamma_c)_t = (\Delta\gamma_c)_\infty \frac{2}{l} \left[ \left( \frac{Dt^{1/2}}{\pi} \right) \right] \quad (1)$$

where  $(\Delta\gamma_c)_\infty$  is the final steady-state value,  $l$  is the half-thickness of the polymer film, and  $D$  is the diffusion coefficient for the process, which has a value in the range  $10^{-8}$ - $10^{-9}$   $\text{cm}^2 \text{sec}^{-1}$ . In accordance with eq. (2), a plot of  $(\Delta\gamma_c)_t$  versus  $t^{1/2}$  should be linear and pass through the origin. Figures 6 and 7 represent a test of this concept, the former giving data at  $60^\circ\text{C}$ , the latter at  $90^\circ\text{C}$ . In both cases substantial linear segments support the diffusion mechanism, though only the 84/15/1 specimens satisfy the condition of linearity passing through the origin. The polymers with greater acrylic content appear to have "induction times," these being of the order of 20 hr at  $60^\circ\text{C}$  and about 2-5 hr at  $90^\circ\text{C}$ . As before,

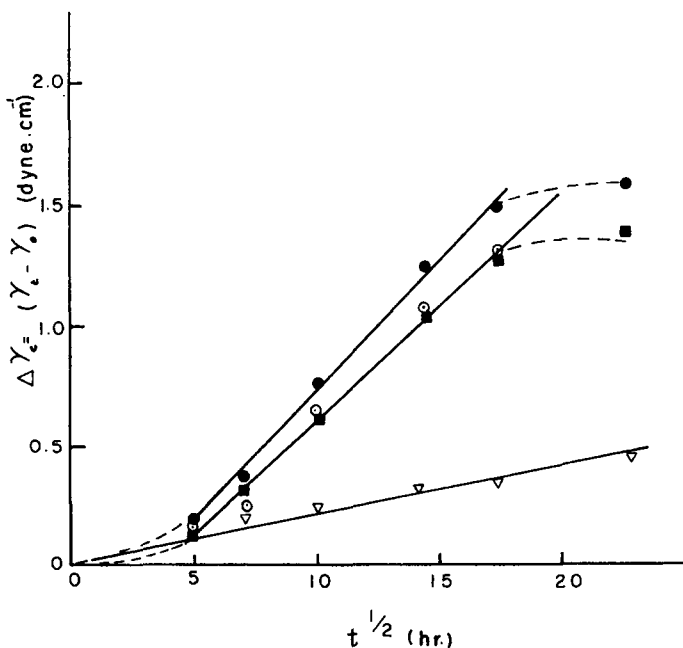


Fig. 6. Time dependence of  $\gamma_c$  for  $60^\circ\text{C}$  exposure: ●, 70/25/5 polymer; ■, 80/15/5 polymer, sample 3; ○, 80/15/5 polymer, sample 1; ▽, 84/15/1 polymer.



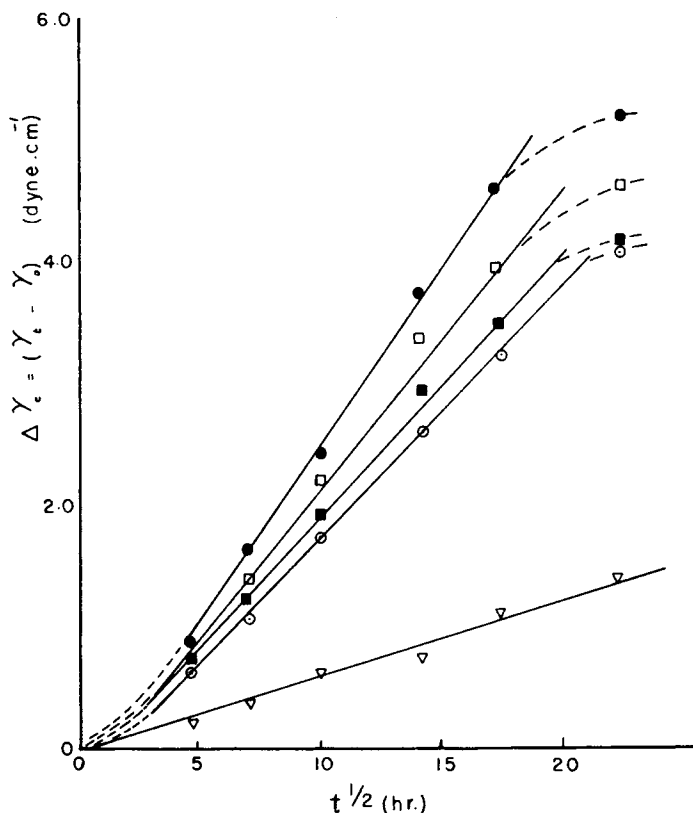


Fig. 7. Time dependence of  $\gamma_c$  for 90°C exposure: ●, 70/25/5 polymer; □, 80/15/5 polymer, sample 4; ■, 80/15/5 polymer, sample 3; ○, 80/15/5 polymer, sample 1; ▽, 84/15/1 polymer.

at 60°C no molecular weight effect is to be seen in the 80/15/5 sequence, the matter being different at the higher temperature. At both temperatures, deviation from linearity occurs as expected at long times. Presumably this indicates a close approach to or attainment of equilibrium surface conditions. Qualitatively the present diffusion-controlled changes in the surface states ( $\gamma_c$ ) of these polymers are consistent with the findings of Lee<sup>13</sup>; the high value of the diffusion coefficient favors the idea that the diffusing species are oligomeric, the diffusion coefficients for many polymers being several orders of magnitude smaller.<sup>13</sup> Present  $\gamma_c$  data also follow patterns similar to those reported recently by Chang and Gray<sup>14</sup> for hydroxypropyl cellulose. In the latter case, time-dependent nucleation and crystallization phenomena were responsible for major surface tension variations. As already noted, the data available to us do not permit a resolution of the possibilities offered above; their fundamental and practical inferences, however, indicate the need for further analysis of the root causes for the phenomena discussed here.

## CONCLUSIONS

The present paper gives initial evidence that monitoring critical surface tension data is an informative guide to surface property changes induced by time/temperature cycles in a series of styrene-acrylic film-forming polymers. A thermal

gradient bar is a particularly convenient tool for such monitoring procedures. A diffusion-controlled mechanism (or mechanisms) seems to be responsible for an effective increase in the surface concentration of acrylic content, leading to a systematic rise in the critical surface tension of the polymers from initial values in the range 34–35 dyn cm<sup>-1</sup>, typical of styrene polymers, to values in the 38–40 dyn cm<sup>-1</sup> range, which is consistent with the surface tensions of predominantly acrylic polymers. The effect, suggesting the migration of immiscible moieties to the interface, is of increasing importance in polymers with high overall acrylic content and is also accentuated at higher molecular weight. Further study is in progress to clarify the processes involved and to outline their practical consequences in the performance of these polymers as coatings or adhesives.

We thank the Paints Division, Canadian Industries Ltd., Toronto for their support of this work. Financial aid from the National Research Council of Canada is gratefully acknowledged.

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Received April 25, 1979

Revised June 4, 1979