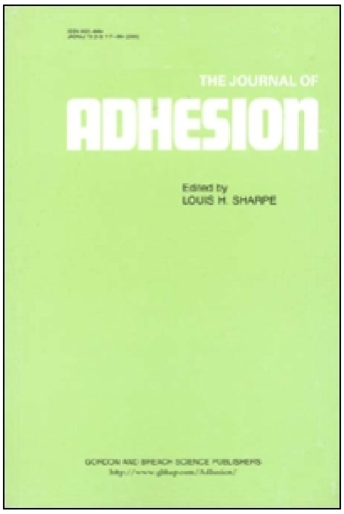

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On the Surface Tension and its Temperature Variation in Film-Forming Polymers†

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A thermal gradient bar has been used for convenient measurements of γ_c and $d\gamma_c/dT$ in complex polymers used as film-formers. The technique yields both γ_c and its temperature variation in one experimental sequence well suited for rapid, routine applications. Surface tension data have been obtained for a styrene–acrylic terpolymer, and these have also been used to characterize the compatibility of external plasticizers for the polymer. The surface tension approach has shown that glyceryl dibenzoate, though compatible with the polymer at temperatures above ~70°C becomes incompatible at use temperatures, and exudes to the polymer film surface. Measurements of moisture sensitivity in plasticized polymer samples have confirmed the incompatibility and illustrated one of the applications to which the gradient bar and its data generation potential may be put.

INTRODUCTION

The need to evaluate physical interactions among components of coating systems as a means for rationalizing important properties including intercoat adhesion, adhesion to substrates, permanence, etc. is well recognized. It is reflected in the widespread use of the solubility parameter[1] as a formulation guide. Among several shortcomings of the solubility parameter, however, is its inaccessibility to direct experimental evaluation for polymers. It is therefore ill suited for the detection of changes in the compatibility among components of a polymer system, as that system ages or becomes exposed to diverse environmental conditions of temperature, humidity, etc. For that

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reason time-dependent changes in product performance cannot generally be correlated with solubility parameter concepts. Alternative experimentally measured parameters of interaction states are required. The critical surface tension of a polymer,[2] γ_c, and $d\gamma_c/dT$ appear to be attractive. The thermodynamic significance of γ_c is admittedly ambiguous[3] but it reliably fingerprints the surface state of a polymer film; by repeating the determinations periodically, changes in surface condition caused by ageing or by exposure to unusual environmental conditions may be monitored and rationalized. The attractiveness of $d\gamma_c/dT$ as a surface characterization parameter resides in the suggested dependence of γ_c on polymer molar volume.[4, 5] For example, according to Roe,[4] γ_c is related to Sugden's Parachor,[5] polymer density and segment molecular weight, so that $d\gamma_c/dT$ should be a continuous, linear function which varies with the 3 or 4 power of density. Deviation from slow, linear variations should be indicative of phase transitions or of changes in component compatibility. These effects may forewarn of important changes in the performance of the polymer coating. The expected non-linearity in temperature variations of γ_c at phase transitions has been considered theoretically by Lee[7] and confirmed experimentally on several occasions.[8] The present paper espouses the view that γ_c and $d\gamma_c/dT$ are useful and valuable indices of component interaction in complex film-forming polymers. It presents a new, simple variant of the well known Zisman approach[2] to determining these values. The variant is particularly well suited for routine applications. Use of the new experimental approach is illustrated by γ_c and $d\gamma_c/dT$ data for a typical styrene/acrylic film-former. These data were also applied to describe interaction states of the polymer with external plasticizers and to account for the water sensitivity of polymer films.

EXPERIMENTAL

Apparatus

The intent of the present method is to make possible rapid and convenient measurement of γ_c and $d\gamma_c/dT$, preferably in a single operation. Neither the classical contact angle method of Zisman and co-workers, nor the ingenious capillary rise method of Neumann[8] is suitable for the envisaged routine purpose. Accordingly a thermal gradient bar (TGB), long familiar in protective coatings technology,[9] has been adapted for measurements of γ_c and $d\gamma_c/dT$. Details of the construction and operation of the TGB have been given elsewhere.[10] In summary, a linear temperature gradient is imposed on a massive, insulated metal block by controlling the heat flux created by heating one end of the block (300 W cartridge heater) while cooling the other end (cold water flow). Linear temperature gradients of 0° to about 60°C can be maintained for periods of several hours, with maximum attainable temperatures near 150°C. Polymer-bearing metal support panels are placed in thermal contact with the block *via* circular magnets recessed into the TGB. When steady-state temperature is reached (indicated by thermocouples along the length of the TGB), constant volumes of droplets of liquids with known γ_{LV} are dispensed onto the polymer surface from calibrated microsyringes; in the present case 50 μl volumes were involved. Droplets are placed in isothermal (vertical) arrays and at selected temperature intervals, as illustrated in Figure 1. Photographs are taken of the assembly with the camera mounted normal to the plane of the substrate. Magnified prints are used to measure the droplet areas and their variations with γ_{LV} and temperature. The procedure also allows for measurements of area versus contact time which may be

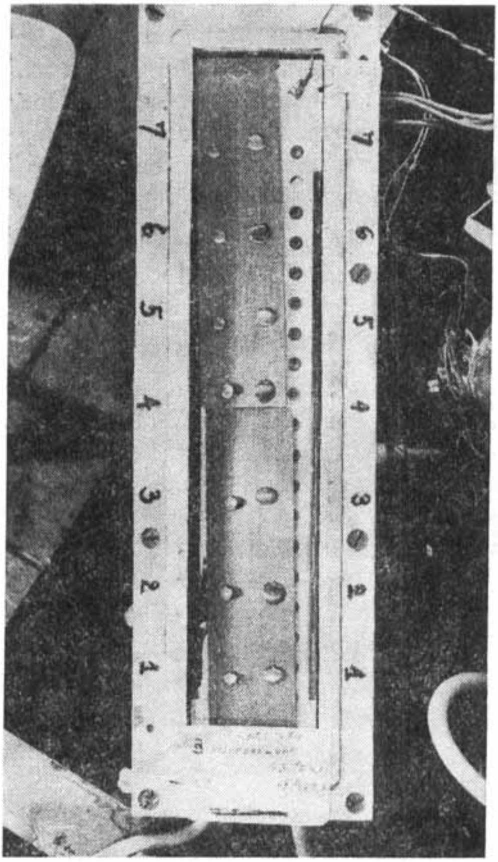

FIGURE 1 Thermal gradient bar, showing placement of droplets of wetting liquids. Numbers on bar refer to thermocouple stations.

extrapolated to zero contact time or used to evaluate the kinetics of the processes influencing the contact area.

The constancy of droplet volumes ensures the existence of a simple relationship between droplet area and contact angle (θ) at the liquid/solid/vapor interface. Minimum area corresponds to $\theta = 90°$, the droplets then being hemispherical with a radius r_0. Maximum droplet radius r_m corresponds to $\theta = 0°$, the two limits being related via

$$r_m = r_0(1+k\cos\theta) \tag{1}$$

Analogous to the Zisman method,[2] γ_c may be estimated by extrapolating the linear section of a plot of γ_{LV} versus droplet area, A, to the limiting area, A_{lim}, defined by

$$A_{\text{lim}} = \pi r_m^2 \tag{2}$$

To avoid coping with problems of surface irregularity, and allied experimental artefacts, in practice A_{lim} is obtained by calibrating the apparatus with polymers having well-defined γ_c values. In this work standard contact angle data[2, 11] were employed to obtain γ_c for polyethylene, polystyrene and polymethyl methacrylate, and these materials were then used to define A_{lim} for the pertinent experimental conditions of this work.

The data, already reported,[10] define A_{lim} (in cm^2) in the range 25–120°C as given by the expression:

$$(A)_{\text{lim}} = 1.72(\pm 0.01)+(T\text{-}25)\times 1.07\times 10^{-3} \tag{3}$$

Materials

The film-forming polymer used was a styrene/butyl methacrylate/methacrylic acid (S/BA/MAA) terpolymer with an overall mole-% composition of 80/15/5. The polymer was synthesized by Paint Research Laboratories, Canadian Industries Ltd., Toronto, and supplied as a dry powder. Butylbenzyl phthalate (BBP) and glyceryl dibenzoate (GDB) were used as external plasticizers in several experiments. Plasticizers were added to the host polymer by mixing in a Brabender Plasticorder at 60°C and 50 rpm until a steady torque response was obtained (generally 8–10 min). Contacting fluids and their γ_{LV} (at 25°C) are given in the following tabulation:

	γ_{LV}(25°C) (dyne-cm^{-1})
Chlorobenzene	33.2
1-2 propane diol	34.1
Nitrobenzene	41.5
Ethylene glycol	47.7
Thiodiglycol	53.6
Glycerol	63.4

Further details of experimentation are noted in relevant sections of the following discussion.

RESULTS AND DISCUSSION

The γ_c value for the S/BA/MAA polymer is determined from the plot given in Figure 2. The intersection of the rectilinear part of the line drawn through the data points with the area value of 1.72 cm^2 occurs at 34.0 dyne-cm^{-1}, and this is identified as γ_c.[12] The value is in good agreement with expectations for a primarily styrenic polymer.

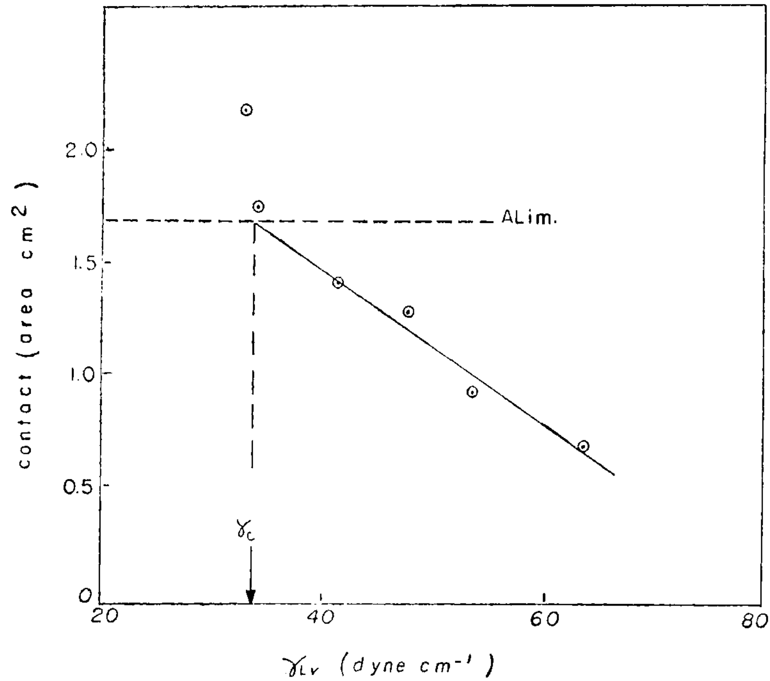

FIGURE 2 Contact area *vs.* γ_{LV} for S/BA/MAA terpolymer. Isothermal operation of TGB at 25°C.

The γ_c route was next followed to assess the effectiveness of the two competitive plasticizing fluids. These were added either singly or in combination, at up to 35 volume percent, to the host polymer. The room temperature γ_c values are entered in Table I, along with those for the pure polymer and plasticizers. One would not expect major differences in the plasticization effectiveness of GDB and BBP, if such an expectation were based on solubility parameter concepts, since both fluids have δ values in the 11 ± 1 $(\text{cal. cm}^3)^{-\frac{1}{2}}$ range.[1] The data in Table I, however, show that the fluids interact very differently with the host polymer. The presence of BBP produces first a slight

TABLE I

Critical surface tensions at 25°C for variously plasticized polymer films

Composition polymer	(%) BBP	(%) GDB	γ_c (dyne cm^{-1})
100	0	0	34.0
95	5	0	29.5
95	0	5	35.8
85	15	0	30.2
85	0	15	37.3
85	10	5	36.5
75	25	0	31.5
75	0	25	40.7
65	35	0	32.5
65	0	35	41.0
65	20	15	38.8
65	15	20	39.5
0	100	0	40.4
0	0	100	41.5

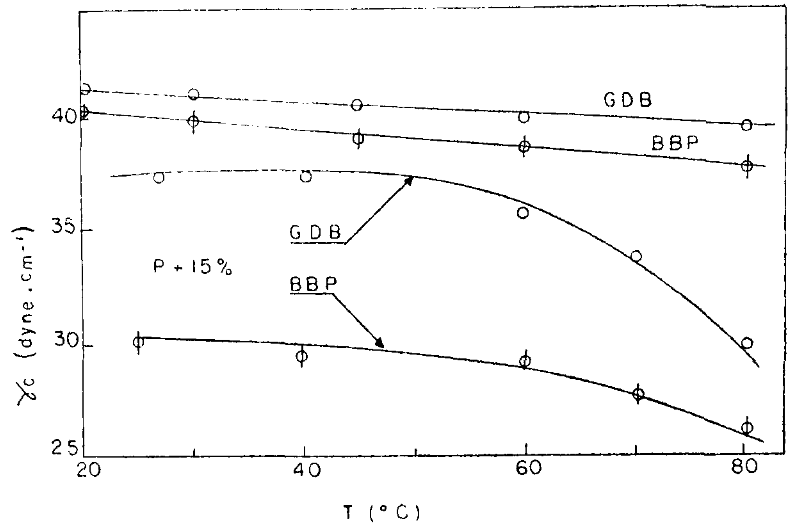

FIGURE 3 Temperature variation of γ_c for plasticized terpolymer and for pure plasticizing fluids. BBP is Butyl Benzyl Phthalate, GDB is Glyceryl Dibenzoate.

reduction in γ_c, then a systematic increase toward the γ_{LV} value of the fluid. The initial drop may signal a reduction in surface energy of the polymer due to the solvating effect of the compatible BBP. In contrast, addition of GDB produces sharp increases in γ_c, the value for the pure additive being attained (within experimental error) when it is present in amounts greater than *ca.* 20%. It may be postulated that the wetting liquids detect free GDB rather than polymer at the solid/air interface, and that therefore GDB is incompatible with the host polymer even at low volumes of addition. The supposition is borne out by the data for mixed GDB/BBP additions, γ_c invariably following the pattern of GDB additions: that is, GDB appears to be selectively exuded to the film surface and thus dominates the value of the apparent γ_c.

An interesting elaboration to this follows from Figure 3, which presents the γ_c *vs.* T relationship for 15 vol. % plasticization up to 90°C; the temperature dependence of γ_c for the pure plasticizers is also given. The latter and $d\gamma_c/dT$ of BBP plasticized polymer follow the expected behavior. The temperature variation of γ_c for the plasticizing fluids, at -0.04 dyne cm^{-1}

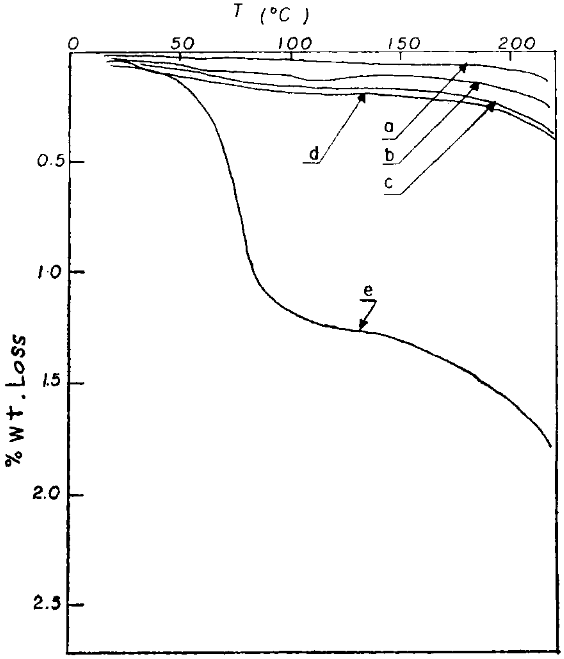

FIGURE 4 Weight-loss characteristics of polymer films due to loss of sorbed water.
a) Unplasticized terpolymer.
b) Polymer/5% Butyl Benzyl Phthalate.
c) Polymer/5% Glyceryl Dibenzoate.
d) System b following ageing, surface wash.
e) System c following ageing, surface wash.

$(^\circ C)^{-1}$, is in general agreement with data reported by Neumann[8] for various alkanes. The systematic decrease in γ_c with rising T for BBP plasticized samples also follows convention, but the pattern of data for the GDB containing sample is distinct. The high absolute values of γ_c at lower temperatures extend earlier suggestions of incompatibility; again exudation of GDB may be postulated to account for the observations. Evidently, however, the interaction balance for the contact of these materials changes radically in the range ~60 to ~75°C, and at temperatures above about 75°C little significant difference is seen in the surface tension characteristics of BBP and GDB—plasticized films.

The proposed shift in the interaction balance should produce significant effects in the glass transition temperature (Tg) of the compounds. Unfortunately, attempts to measure Tg of these compounds *via* scanning calorimetry, using a Mettler Thermoanalyser, proved inconclusive due to experimental difficulties inherent in the apparatus. A more detailed analysis of the interaction balance effect therefore is deferred to a later date; however, the practical implications of the findings in Figure 4 as to choice of effective diluent for this polymer, cannot be mistaken.

Water sensitivity of polymer films

Moisture resistance is one of the principal performance criteria for protective films, and in a final experimental sequence an attempt was made to show whether or not this performance criterion would reflect the compatibility effects attributed to the chosen plasticizers by the γ_c and $d\gamma_c/dT$ results. Films of the host polymer and of polymer containing 5% plasticizer were prepared by compression molding at 160°C. The films were chipped away from the support plate, powdered, and samples (~400 mg) placed into the Mettler Thermoanalyser for thermogravimetric analysis. In this, powdered specimens were first conditioned at 80°C under dry N_2 in the apparatus, then cooled to room temperature and exposed for about 2 hours to air conditioned at 75% relative humidity. Samples were then heated at a linear, programmed rate of 5°C/minute. Their weight loss characteristics up to about 200°C are given in curves a–c of Figure 4. A more complex preparation procedure was followed for samples generating curves d and e. Films of P/BBP and P/GDB were prepared as before, allowed to rest at room temperature for 24 hours and then wiped with lint-free tissue paper saturated with methyl ethyl ketone. The film was then dried by heating to 80°C for 15 minutes whereupon the ageing, surface washing and drying procedure was repeated. Films were then powdered and analyzed as in the cases described above. The curve d, Figure 4, gives the experimental response of the BBP—plasticized specimen, curve e that of the GDB—containing material.

The moisture sorption/loss properties of BBP and GDB—plasticized formulations are essentially the same (Figure 4, curves a, b, and c). If exudation of GDB does occur, the effect does not appear to influence the water vapor sorption properties of a freshly prepared film. The solvent wipe procedure may be viewed as a simulation of accelerated ageing, and this leads to the drastically different properties shown in curves d and e. Apparently only a slight increase in water sorption/loss occurs in the case of BBP plasticization. We may assume in contrast that significant fractions of GDB exude to the film surface during the ageing sequences and that these are removed by the surface wash, leaving behind a porous structure which has an increased capacity for water sorption and into which moisture penetrates more rapidly. We use the evidence of Figure 4 to stress the usefulness of γ_c and $d\gamma_c/dT$ data, as obtained by the TGB method. The results of Figure 3 differentiated clearly between two competitive plasticizers for the host polymer, inferring incompatibility in the case of GDB. In an internally consistent manner, moisture uptake properties of the films (important performance criteria for such materials) fulfill expectations based on the implied differences in plasticizer compatibility, thereby demonstrating the potential value of routine applications of the TGB method in the formulation and property control of film-forming polymer systems.

CONCLUSION

The ability of the thermal gradient bar to measure γ_c and $d\gamma_c/dT$ for complex film-forming polymers has been illustrated. The method was applied to study the compatibility performance of two plasticizers, with indications of unexpected shifts in the compatibility balance of polymer glyceryl dibenzoate systems near 70°C. Causes for this have not been established and the subject is one warranting further study. Measurements of moisture uptake/release involving non-plasticized as well as plasticized samples of the styrene/acrylic polymer have shown markedly higher moisture sensitivity in films involving GDB under conditions of suspected incompatibility. In this manner, the relatively simple, rapid measurement of surface tension data by the TGB method has been correlated with an important performance criterion. Further studies are underway, aimed at an exploration of the TGB method and at the definition of surface tension properties in a wider range of complex polymer systems.

Acknowledgments

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