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INTERNAL STRAIN IN
SOLVENT-CAST COATINGS

by S. G. Croll

SOMMAIRE

Après amalgamation de leurs substrats composés de feuilles de fer-blanc, la contraction des revêtements en période de séchage physique est mesurée et comparée à la contrainte interne desdits revêtements. Celle-ci découle de la perte de solvant qui se produit entre le point de solidification du revêtement et son état final, soit l'état "sec". Les mesures n'ont indiqué aucune variation de la contrainte interne, que ce soit en fonction de l'épaisseur du revêtement ou de la concentration initiale de la solution. Un modèle permet d'expliquer clairement les résultats. Il se base sur l'hypothèse que le point de solidification est fonction de la concentration du solvant qui abaisse à la température ambiante la transition du polymère à l'état de verre.

Internal Strain
In Solvent-Cast Coatings

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After mercury amalgamation of their tinplate substrates, the shrinkage of physically drying coatings was measured and identified with their internal strain. This strain arose from the solvent lost between the solidification point of the coating and its final "dry" state. The measurements showed no variation of internal strain with coating thickness or initial solution concentration.

A model is presented which explains the results quite successfully. It is based on the assumption that the solidification point can be identified with the solvent concentration which depresses the glass transition of the polymer to the ambient temperature.

INTRODUCTION

Coatings, for decorative or protective purposes, are commonly produced by brush, dip, or spray application of a polymer solution. The coating must shrink as it dries because the solvent evaporates. However, whereas the thickness can contract, the area is constrained by adhesion to the substrate. Further solvent is lost after solidification, but the coating can no longer flow to satisfy the change in volume. Because of this constraint internal stress arises in the plane of the coating.

Previous investigations[1,2] have measured the stress in solvent-cast coatings and found it to be independent of dried coating thickness and initial solution concentration. The stress also proved to be sufficiently large to endanger the cohesive and adhesive qualities of the coating. Thus, reduction in internal stress may extend the service life of a coating. A greater understanding of this problem is required. This paper presents the results of measurements of strain corresponding to the internal stress. They confirm previous measurements of internal stress and the theory developed to explain them.[2]

In the present experiments, the shrinkage of coatings released from tinplate substrates was measured. This shrinkage was assumed to be identical with the strain

corresponding to the internal stress and, as such, was compared with the predictions of the theory. The experiments were conducted on the same coatings as used before, polystyrene and polyisobutyl methacrylate.

THEORY

Calculation of Internal Strain

The theory is concerned only with the equilibrium value of the internal stress or the potential shrinkage, i.e., internal strain. An exact description of how it arises as the coating solidifies would be extremely complicated and probably unedifying.

It is assumed that the residual internal stress is due solely to the difference between the volume fraction of solvent present in the film at solidification, ϕ_s, and the volume fraction retained in the "dry" film, ϕ_r. Before solidification, the coating can flow to accommodate the volume change demanded by the solvent evaporation. The area is constrained at its original wet size by adhesion to the substrate so the volume change appears as a change in thickness. After solidification the polymer can no longer flow and further solvent evaporation produces internal stress in the plane of the coating. The dry polymer film has been formed in such a way that the polymer molecules are not at their equilibrium position with respect to one another and, thus, are in a strained state. The thickness is not constrained and can still contract in response to the component of stress in that direction.

The volume of solvent lost produces internal bulk strain within the coating, equivalent to an isotropic linear strain field. The two components of strain remaining in the plane of the coating give rise to the internal stress. In this work the internal strain is measured as the shrinkage in coating length after it has been removed from its substrate.

The volume of solvent lost from the coating after solidification, ΔV, is given by

$$\Delta V = \phi_s V - \phi_r (V - \Delta_z V) \qquad (1)$$

where V = volume of coating at solidification; ϕ_r is measured in free, unstrained films.

Equation (1) can be rewritten as

$$\frac{\Delta V}{V} = \phi_s - \phi_r (1 - \frac{\Delta V}{V}) \qquad (2)$$

= internal bulk strain, assuming an exact correspondence with the volume of solvent lost

$$= 3\epsilon \qquad (3)$$

where ϵ = isotropic linear strain, which is equivalent to the internal bulk strain.

In fact, the bulk strain does correspond to the solvent loss, for the coatings used here, as demonstrated previously.[2]

From equations (2) and (3), the internal linear strain is given by

$$\epsilon = \frac{\phi_s - \phi_r}{3(1 - \phi_r)} \qquad (4)$$

It is this result that will be compared with the experimentally determined values of shrinkage. Previously, the internal stress was measured and compared with an equation for the stress derived from equation (4) as follows.

For a plane stress situation the stress, σ, is given by

$$\sigma = \frac{E(\sigma) \cdot \epsilon}{1 - \nu} \qquad (5)$$

where $E(\sigma)$ = Non-linear modulus of the material
ν = Poisson's ratio.

Thus, the internal stress could be predicted from equations (4) and (5). Measurements of ϕ_s, ϕ_r, ν, and $E(\sigma)$ produced predictions that agreed well with the independently measured internal stress (*Table* 1). However, $E(\sigma)$ is difficult to measure accurately for thin coatings and is, in any case, insensitive to differences in strain. A more stringent test of this theory would be to compare equation (4) with experimental values of shrinkage, as is done in this paper. The previous published values of internal stress differ due to a miscalculation of substrate modules, but the error does not affect any conclusions.

Identification of Solidification Point

The solidification concentration, ϕ_s, occurs when the wet coating first behaves like a solid rather than a viscous liquid, i.e., when large-scale molecular motion ceases in the polymer. At this point, the solution is highly concentrated and the macromolecules retain their positions relative to each other. Solidification of a polymer solution thus resembles the glass-rubber transition in solid polymers: above the transition temperature, T_g, large-scale molecular motion is allowed; below, the polymer is "frozen" into a glassy state. A somewhat different discussion along the same lines can be found in reference (3).

A solvent or plasticizer incorporated in a polymer will lower T_g greatly, the depression increasing with solvent concentration. Thus, ϕ_s might be identified as the solvent concentration at which T_g of the polymer solution coincides with ambient temperature. This transition is not due to temperature changes but to the changing of solvent concentration during drying. In previous work ϕ_s was determined by plotting T_g as a function of solvent concentration and choosing ϕ_s as the concentration that corresponded to the ambient temperature. The glass transition, however, is rather diffuse and molecular motion does not cease altogether at the transition temperature.

EXPERIMENTAL

The polyisobutyl methacrylate (PIBM) used was Du Pont Elvacite® 2045, and the polystyrene (PS) was Dow Styron® 685; both were dissolved in reagent grade toluene. The materials came from the same batches as used before.[2] All experiments took place at 23°C ($\pm0.25°$). Both of these materials produce amorphous coatings from solution so there are no complications due to crystallization.

Tinplate was chosen as the most reliable substrate on which to prepare coatings that were to be detached subsequently.[4] The substrates were masked to a convenient length, 60 mm, and width, 12 mm and coated using a variety of doctor blades. Drying was monitored by weighing to 0.1 mg and when there was no further systematic loss in weight the coating was considered dry. A typical coating weight was 15 mg. After a coating was completely dry (3 to 4 weeks) its length was found using a travelling microscope capable of measuring to 25 μm. The coating was then freed by amalgamating the tin with mercury, in a fume chamber. The length of the now free film was measured periodically until it stabilized, approximately two weeks for PIBM and two to three days for PS. Internal strain was calculated as the change in length divided by the original dried coating length.

free film and using a calibration of weight/length versus the film thickness obtained previously. It proved difficult to obtain consistent measurements from either coating material at thicknesses less than 15 μm; it seems that they were too delicate to withstand the handling necessary in this process.

There were two added complications with the PS coatings. Firstly, crazing and cracking were very prevalent. No measurements taken from crazed or cracked samples were used in the final results. Secondly, many of the thicker films spontaneously peeled from the substrate. However, provided these films had not crazed, they gave shrinkage results consistent with those that retained their adhesion.
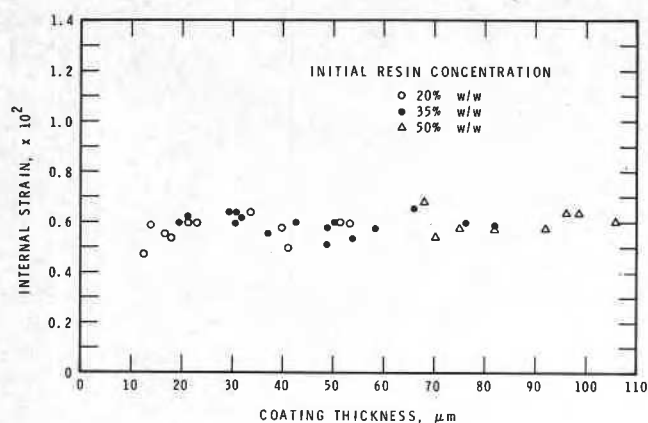
Table 1—Comparison of the Values for Internal Stress (MPa) Measured and Predicted from Equation (4)

	PIBM	PS
Experimental	4.5 (±0.30)	14.3 (±0.7)
Predicted	3.9 (±0.9)	10.8 (±1.7)

Figure 1a—Internal strain in PIBM coatings

Figure 1b—Internal strain in PS coatings

Tinfoil substrates were also tried. They have two disadvantages. One is that being wholly tin they require more mercury to free the coating. The second is that tin is very soft and allows the coating to contract whilst adhering to the substrate. Consequently, it was necessary to use the "masked" length to calculate internal strain, not the dried coating length. On tinplate these two lengths were identical. The PS coatings adhered better to tinfoil than to tinplate, presumably because the foil allowed some relaxation of the internal stress.

All the results presented here were taken from coatings formed on tinplate.

RESULTS AND DISCUSSION

Shrinkage Measurements

In *Figures* 1a and 1b measurements of internal strain for PIBM and PS are plotted against thickness for various initial solution concentrations. One can see that there is no systematic dependence on dried coating thickness or solution concentration, which confirms the previous results on internal stress.[1,2]

For PIBM:
Average internal strain = 5.8×10^{-3}
standard deviation = 4.4×10^{-4} (31 values)

For PS:
Average internal strain = 1.75×10^{-2}
standard deviation = 9.9×10^{-4} (11 values)

A least squares fit to the PIBM data gives:
Slope = 2.7×10^{-6} (std. dev. 1.7×10^{-5})
Intercept = 5.7×10^{-3} (std. dev. 9×10^{-4})

i.e., there is no significant slope to the data.

The relative decrease in length of those PS specimens which crazed was typically 5×10^{-3}. Obviously, much of the internal stress had been relieved by crazing or cracking. If this small scale damage is tolerable it might be regarded as a practical means of internal stress relief.[6]

Those PS samples which completely peeled off spontaneously did not craze or crack often, because there was no constraint on them and they could shrink freely. The spontaneous detachment from the substrate should have only a negligible effect on the shrinkage value because the coating will not detach until the stress builds up and overcomes adhesion, i.e., the coating is almost completely dry. Thus, the endpoint is practically the same as in the regular procedure.

Comparison with Theory

The theory presented here does not take into account transport phenomena within the drying coating; in other
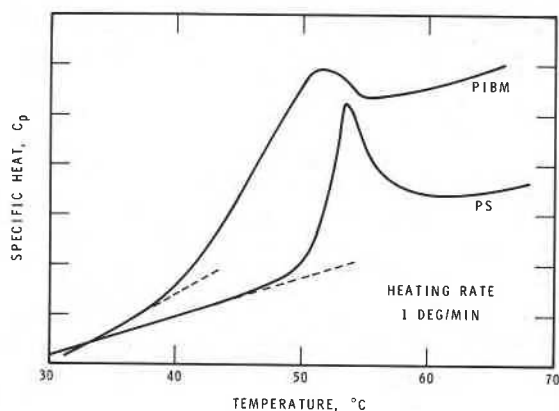

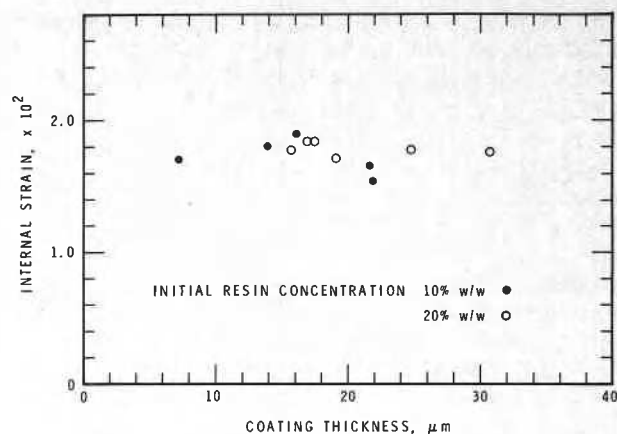Figure 2a—Specific heat of dried coating material (vertical scale is arbitrary, to aid comparison of the curves)
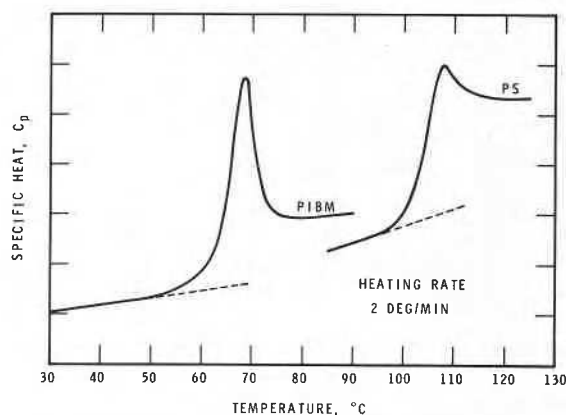

Figure 2b—Specific heat of polymer resin, as received (vertical scale is arbitrary, to aid comparison of the curves)

words, it does not allow any dependence on thickness or coating solution concentration. Qualitatively, the results agree with this assumption. They also permit a sensitive test of the quantitative predictions of the theory.

Values of ϕ_s and ϕ_r measured previously are presented in *Table* 2, together with the resultant prediction for internal strain, ϵ. The measured values of ϵ were 5.8×10^{-3} and 1.75×10^{-2} for PIBM and PS, respectively. Although the agreement is not good, it is at least within an order of magnitude and the discrepancy is easily accounted for.

Solidification was assumed to occur when the glass transition temperature, T_g, coincided with ambient temperature. No allowance was made for the fact that it is not a sharp transition and some molecular motion takes place below T_g, i.e., at solvent concentrations less than ϕ_s. An illustration of this point is seen in *Figure* 2a for dried coatings and in *Figure* 2b for the original resins. These are graphs of specific heat against temperature obtained from conventional Differential Scanning calorimetry. The vertical scales are arbitrary. It can be seen that the peaks in specific heat, which give a measure of molecular motion, are not at all sharp. In fact, it is possible to obtain thermally induced changes in the structure of solid polymers at temperatures below T_g,[5] which again indicates significant molecular motion below T_g.

Assuming that equation (4) is correct, a better estimate of ϕ_s is necessary. This requires knowledge of exactly at what point in the transition molecular motion freezes. This knowledge, however, does not seem to be available at present, either experimentally or theoretically. The shape and size of the transition are a function of the particular polymer involved, its flexibility, molecular weight and distribution, plasticizer content, etc.

Insight into this problem might be gained by approaching it from another direction. Using the experimental values of internal strain and ϕ_r, a new value of the solidification point, ϕ_s', can be calculated using equation (4), with the following results:

$$\text{PIBM}, \phi_s' = 0.094$$

$$\text{PS}, \phi_s' = 0.143$$

These new values correspond to glass transition temperatures of 33°C (PIBM) and 28°C (PS) derived from *Figures* 3a and 3b, which show the relationship between T_g and solvent volume fraction, ϕ, determined previously.[2] The differences, ΔT, between the foregoing values and ambient temperature are 10°C (PIBM)
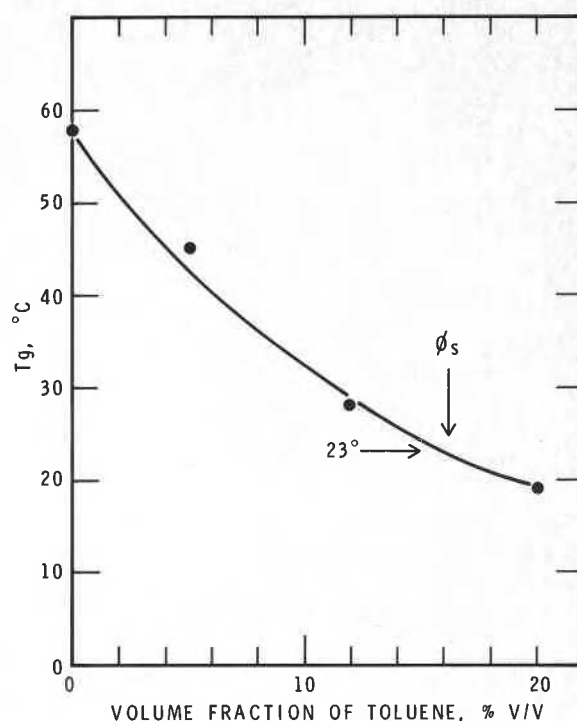

Figure 3a—Depression of T_g in PIBM by retained solvent, toluene

Figure 3b—Depression of T_g in polystyrene by retained solvent, toluene

Table 2—Previously Measured Values Of ϕ_s and ϕ_r

	PIBM	PS
ϕ_s V/V	0.162	0.176
ϕ_r V/V	0.078	0.096
ϵ	0.030	0.029

and 5°C (PS), which might be construed as measures of the effective width of the two glass transitions. The ΔT are more correctly a reflection of the steepness of the curves in *Figures* 3a and 3b, which represent the internal kinetics of the polymer-solvent system.

Inspection of *Figures* 2a and 2b does, indeed, reveal that the transition in PIBM is a few degrees wider than that for PS and that these ΔT do still fall within the transition widths.

Consequently, it remains reasonable to associate the solidification of a physically drying coating with the glass transition, but in a rather more complex way than before which is, as yet, impossible to describe accurately.

CONCLUSIONS

Internal strain in physically drying PIBM and PS coatings has been determined by measuring their shrinkage upon release from tinplate substrates, by mercury amalgamation. This method is simple, direct and, with care, non-toxic.

The results confirm conclusions drawn earlier from measurements of the internal stress in the same systems, i.e., that the stress depends neither on dried coating thickness nor initial solution concentration.

It seems reasonable to expect this behavior in all physically drying coating systems where the residual internal stress/strain results from the volume of solvent lost after solidification, rather than the kinetics that govern the rate at which it is removed.

A theory has been presented that accounts for the lack of variation of the internal stress/strain with coating thickness or initial solution concentration. It does overestimate the internal strain, however. This was not apparent in previous measurements of the internal stress because the stress/strain curve of the coating is insensitive to changes in strain above a certain point. The overestimation may be due to the assumption that the solidification point of a coating is the solvent concentration which depresses the T_g of the polymer-solvent mixture to the ambient temperature. One must make allowance for the diffuse nature of the glass transition, which permits significant molecular motion at temperatures (or solvent concentrations) lower than T_g. At present it is impossible to predict the width of the glass transition or the exact point at which solidification occurs.

In PS coatings the internal strain, or stress, is large enough to provoke cohesive and adhesive failure. However, the cohesive failure is on a small scale and may be tolerable and, thus, a means of stress relief.

ACKNOWLEDGMENT

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