

The Origin of Residual Internal Stress in Solvent-Cast Thermoplastic Coatings

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Synopsis

Experiments on polystyrene and poly(isobutyl methacrylate) coatings cast from toluene have shown that residual internal stress is independent of dried coating thickness and initial solution concentration. A theory is presented that predicts the magnitude of the stress and shows that it has no dependence on thickness or initial solution concentration. Internal strain is calculated from the volume of solvent lost after the coating has solidified. This solidification point is identified with the solvent concentration that is sufficient to depress the glass transition of the polymer to the prevailing experimental temperature. A one-to-one correlation is confirmed between the volume of solvent lost from solution during drying and the volume change of the polymer film.

INTRODUCTION

Objects, whether for decorative or protective purposes, are frequently coated by brush, dip, or spray application of a polymer solution. As the coating dries, it loses solvent and must consequently shrink. Its thickness can contract, but the area is constrained by adhesion to the substrate. There is still some solvent 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.

Stresses may have an adverse effect on the adhesive and cohesive properties of the coating. A previous investigation¹ of stresses in a simple, air-dried acrylic lacquer has shown them to be significant relative to the strength of the coating. Results on polystyrene coatings presented in this paper show loss of adhesion owing to the effects of internal stress.

Because of the large quantities involved, considerable economic and raw material savings could be made by extending the service life of coatings. One way of doing this would be to reduce the internal stress. The purpose of this paper is to provide a basis for understanding the origins of internal stress in simple, physically drying, thermoplastic coatings and thereby identifying possible means of removing that stress.

To that end, experiments on polystyrene and poly(isobutyl methacrylate) (PIBM) coatings were carried out and compared successfully with a theory that predicts the final value of the internal stress. The theory identifies the internal strain, and thus stress, with the volume of solvent lost from the time that the film solidifies until the final "dry" state. It is assumed that the solidification point occurs when solvent loss is sufficient to raise the glass transition temperature of the coating solution to the ambient temperature.

THEORY

Calculation of Residual Internal Stress

The theory presented is concerned only with the equilibrium value of the internal stress, i.e., the residual stress. An algebraic description of the way in which the stress reaches its final value would be extremely complicated, involving diffusion through a polymer solution with great changes in concentration, evaporation of solvent from the surface, and the nonlinear viscoelastic properties of a drying polymer solution. It is assumed here that residual internal stress is due solely to the difference between the volume fraction of solvent at which the film solidifies, ϕ_s , and the volume fraction of retained solvent in the "dry" film, ϕ_r . Prior to solidification, the coating is mobile enough to flow and allow the volume change demanded by solvent evaporation. The area is constrained at its original size by adhesion to the substrate; thus, the volume change appears as a change in thickness. After solidification, the polymer can no longer flow, and further loss in solvent produces internal stress in the plane of the coating. The thickness is still unconstrained and can contract in response to the component of stress in that direction.

The volume of solvent lost is responsible for 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 stress measured experimentally. Because PIBM and polystyrene are amorphous solids, there will be no complications due to crystallization in the coating during drying.

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

$$\Delta V = \phi_s V - \phi_r (V - \Delta V) \quad (1)$$

where V = volume of coating at solidification and ϕ_r is measured in free, unstrained films. Equation (1) can be rewritten as

$$\Delta V/V = \phi_s - \phi_r (1 - \Delta V/V) \quad (2)$$

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

$$= 3\epsilon$$

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

Thus, the internal linear strain is given by

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

For a Hookean material in this biaxial, plane stress situation, the stress σ is given by

$$\sigma = \frac{E\epsilon}{1 - \nu} \quad (4)$$

where E = Young's modulus of the coating and ν = Poisson's ratio. Hence, the residual internal stress is given by

$$\sigma = \frac{E}{1 - \nu} \frac{\phi_s - \phi_r}{3(1 - \phi_r)} \quad (5)$$

Normally $\phi_r \ll 1$, and eq. (5) can be slightly simplified to give

$$\sigma = \frac{E}{1 - \nu} \frac{\phi_s - \phi_r}{3} \quad (6)$$

It can be seen that the residual internal stress, the endpoint, does not depend on the thickness of the coating because drying kinetics do not enter the calculation. There is also no dependence on the concentration of the initial coating solution because of the assumption that a stress is not induced until the coating has achieved the much higher concentration at solidification, ϕ_s .

A method to test the assumption that the volume of solvent lost is exactly the volume change of the coating, or the internal bulk strain, is presented in a later section.

In order to predict the internal stress σ from eq. (5), one needs to know the values of ϕ_s and ϕ_r as well as the mechanical properties of the dried coating, which, while non-Hookean, are readily obtained by conventional means. The measurement of ϕ_r , the retained solvent, can be easily obtained by a variety of means, gas chromatography being the method chosen here. One needs to identify, however, the solidification point in order to calculate ϕ_s .

Identification of Solidification Point

The solidification point ϕ_s occurs when the solution first behaves like a solid rather than a highly viscous liquid, i.e., when large-scale molecular motion ceases in the polymer. At this point, the solution has become sufficiently concentrated for the macromolecules to essentially 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 relative molecular motion is allowed; below, the polymer is frozen into a glassy state.

It is known that solvents or plasticizers incorporated into a polymer will lower T_g considerably, the depression increasing with solvent concentration. Thus, ϕ_s can be identified as the solvent concentration at which the glass transition of the polymer-solvent mixture coincides with ambient temperature. This transition is not due to changes in temperature but to changes in solvent concentration during drying. To determine ϕ_s , T_g is plotted as a function of solvent concentration and the concentration that corresponds to the room (or test) temperature is chosen.

Correlation of Film Shrinkage and Solvent Loss

By measuring the change in volume of a coating during drying and comparing it with the volume of solvent equivalent to its loss in weight, one can test whether the two volumes are identical and whether the calculation of internal strain given in the preceding section is reasonable. The results can be analyzed in the following way:

$$\begin{aligned} \text{weight of solvent in initial solution} &= V_i C_i \\ \text{weight of solvent in final film} &= V_r C_r \end{aligned}$$

Therefore,

$$\text{loss in weight of solvent} = V_i C_i - V_r C_r$$

equivalent to

$$\text{solvent volume} = (V_i C_i - V_r C_r) / \rho$$

where C_i = initial solvent concentration in solution (kg/m^3), C_r = retained solvent concentration in dried film (kg/m^3), V_i = volume of initial solution, V_r = volume of dried film, and ρ = density of solvent.

Assuming that the volume of solvent lost is equal to the change in volume during drying results in

$$V_i - V_r = (V_i C_i - V_r C_r) / \rho \quad (7)$$

and rearranging gives

$$\frac{V_i - V_r}{V_i} = \frac{\Delta V}{V_i} = \frac{C_i - C_r}{\rho - C_r} \quad (8)$$

which is the relative volume change.

Plotting $\Delta V/V_i$ against C_i should yield a straight line with the following properties: slope = $1/(\rho - C_r)$; intercept = $-C_r/(\rho - C_r)$; extrapolating to $\Delta V/V_i = 1$, $C_i = \rho$; and intercept on the C_i axis is C_r . A straight line satisfying the above conditions justifies the following assumptions: volume shrinkage in the film corresponds exactly to the volume of solvent lost; C_r is independent of C_i .

EXPERIMENTAL METHODS AND RESULTS

Internal Stress Measurements

Internal stress was measured by coating one side of a thin steel cantilever and measuring the bending induced by the in-plane internal stress set up in the coating as it dried. Experimental details and the data related to the PIBM coatings have been presented in another publication¹; the results are shown in Figure 1(a). The internal stress results for polystyrene coatings were measured in the same manner and are presented in Figure 1(b). The polystyrene was Dow Styron 685 cast from solution in reagent-grade toluene.

In both cases, provided that the film adhered completely to the substrate, the residual internal stress had no systematic dependence on dried coating thickness or the initial coating solution concentrations used. For PIBM coatings, the residual internal stress was 4.5 MPa (± 0.3 MPa standard deviation) and for polystyrene coatings, 14.3 MPa (± 0.7 MPa standard deviation).

In the case of polystyrene, it was impossible to prepare a dried coating of greater than 18 μm , approximately. Coatings anywhere thicker than this lost adhesion and became detached from the substrate, giving an anomalously low deflection. Apparently the internal stress provides enough energy to overcome adhesion above a certain coating thickness.

Correlation of Film Shrinkage and Solvent Loss

The difference in weight between a solution of known concentration and the dried film was obtained by weighing. The solution was weighed in a PTFE pan, 1 mm deep, from which the resultant film could easily be peeled intact after 24 hr for PIBM and 48 hr for polystyrene. The original volume of the solution was obtained from its weight and density that had been calculated assuming a linear law of mixing between polymer and solvent.

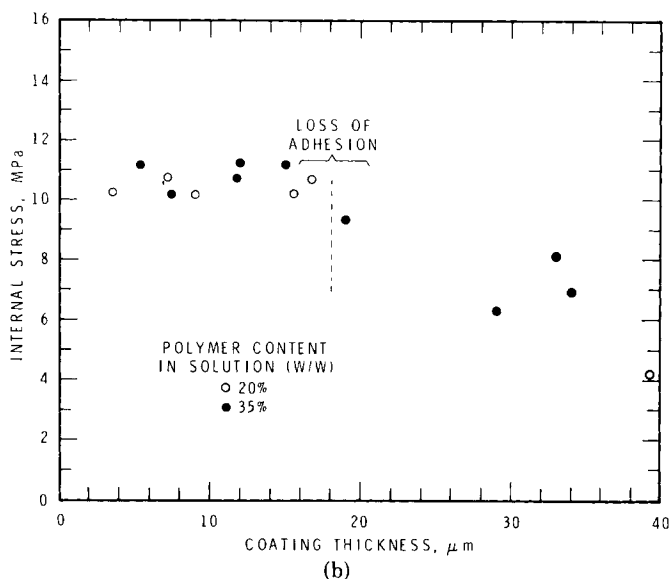
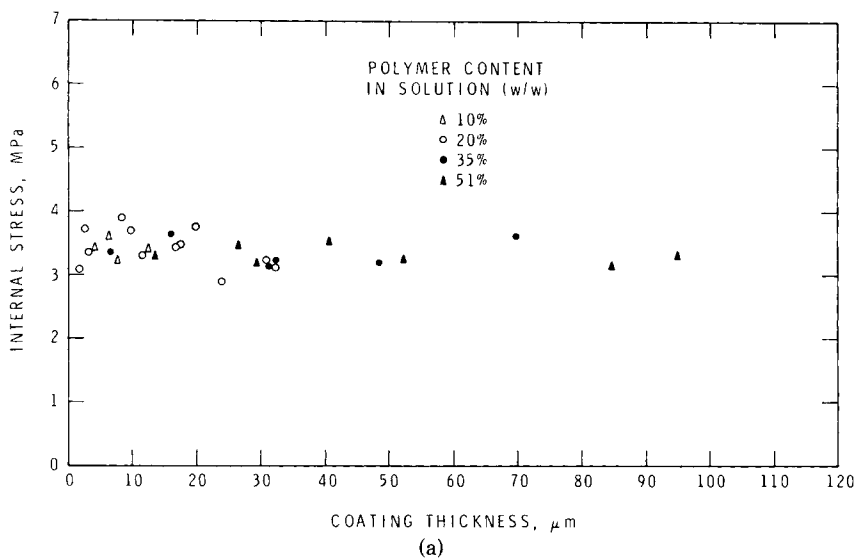


Fig. 1. (a) Dependence of internal stress on coating thickness and solution concentration, PIBM. (b) Dependence of internal stress on coating thickness and solution concentration, polystyrene.

The densities of the constituents were as follows: PIBM, 1050 kg/m^3 ; polystyrene, 1048 kg/m^3 ; toluene, 862.7 kg/m^3 . The resin densities were determined using the additive technique² in a Hubbard-Carmick pycnometer. In this work the added liquid was Bronoco odorless solvent, density 750.3 kg/m^3 , which has a very low solvent power.

Approximately 95% of the weight loss occurred in 24 hr, but the final weighing was delayed for about 13 weeks to ensure that the retained solvent had reached a constant level. The final volume of the film was measured, also using the specific gravity bottle and odorless solvent.

The relative volume change $\Delta V/V_i$ is plotted as a function of initial solution concentration C_i in Figures 2(a) (PIBM) and 2(b) (polystyrene). The results are as follows:

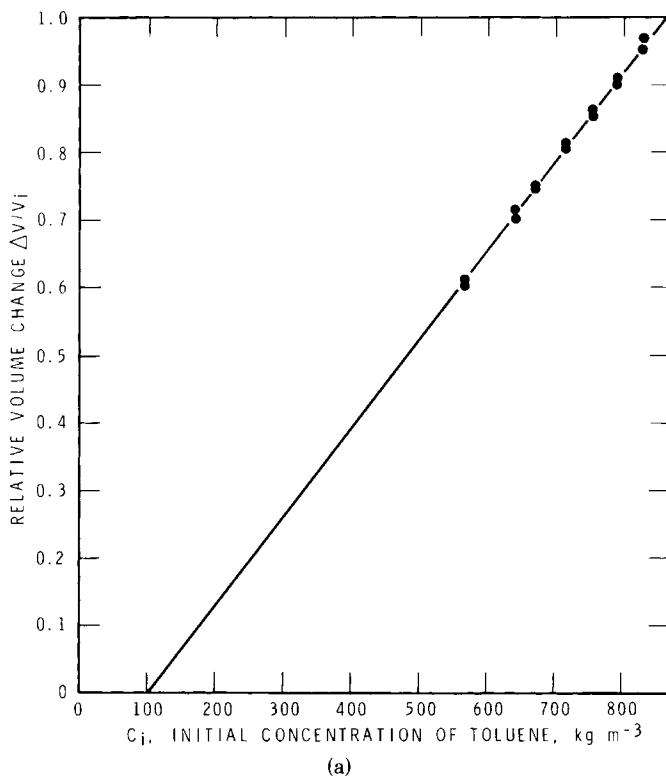


Fig. 2. (a) Correlation of coating volume change and volume of solvent lost, PIBM. (b) Correlation of coating volume change and volume of solvent lost, polystyrene.

PIBM. Slope = 1.32×10^{-3} (7×10^{-5} standard deviation), intercept = -1.39×10^{-1} (5×10^{-2} standard deviation), which give $C_r = 105 (\pm 44) \text{ kg/m}^3$, $\phi_r = 0.12 (\pm 0.05) \text{ v/v}$ (or 0.10 w/w), and $\rho = 863 (\pm 84) \text{ kg/m}^3$.

Polystyrene. Slope = 1.22×10^{-3} (8×10^{-5} standard deviation), intercept = -6.3×10^{-2} (5×10^{-2} standard deviation), which give $C_r = 51.5 (\pm 44) \text{ kg/m}^3$, $\phi_r = 0.06 (\pm 0.05) \text{ v/v}$ (or 0.05 w/w), and $\rho = 869 (\pm 98) \text{ kg/m}^3$.

Both graphs have good straight lines, and the extrapolation agrees well with the measured solvent density. However, there is considerable uncertainty in the intercept, which is a reflection of the large gap between the axes and the experimental points.

Films cast from different solutions started with approximately the same thickness when wet and dried to differing thicknesses of 0.1 to 0.35 mm. The results confirm the assumptions made in the construction of eq. (8) and indicate that $C_r(\phi_r)$ is independent of the film thickness. The results also show that the density of the original solutions was calculated properly from their solids content, i.e., there was no important volume change upon mixing. In these free films the volume of solvent lost and the change in volume of the film were shown to be equal. Thus, the method of calculating internal strain in coatings has been justified.

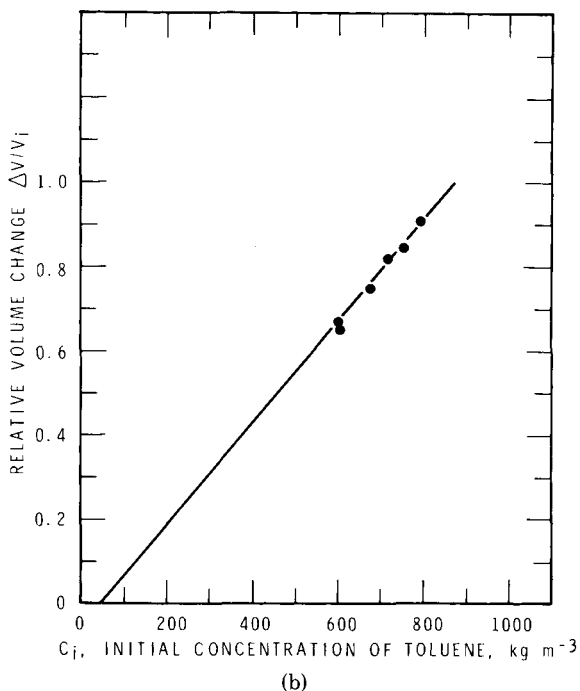


Fig. 2 (Continued from previous page.)

Depression of T_g by Included Solvent

Knowledge of the depression of T_g by solvent is necessary to calculate the value of the solvent concentration ϕ_s at which the mixture of polymer and toluene behaves like a solid.

The measurement of T_g was performed in a conventional differential scanning calorimeter over a range of heating rates of 0.2 to 20°K/min. The temperature at which the appropriate maximum occurred in the specific heat was plotted as a function of heating rate and extrapolated graphically to zero heating rate in order to obtain T_g . This procedure appears to be sufficiently accurate for the purposes of this investigation.

The effect of differing amounts of solvent on T_g is presented in Figures 3(a) (PIBM) and 3(b) (polystyrene). Higher degrees of solvent retention than that at room temperatures were achieved by drying solutions under varying degrees of refrigeration. The solvent retention was measured by weighing the dried film, knowing the original weight of the solution and its initial solids content. This simple gravimetric technique is justified in the light of the previous section. Data presented by Adachi, Fujihara, and Ishida³ on the depression of T_g in polystyrene by toluene agrees well with that presented in Figure 3(b).

It can be seen that at a test temperature of 23°C, T_g for PIBM occurs when the volume fraction of solvent is 0.162, i.e., $\phi_s = 0.162 (\pm 0.014)$. Similarly, for polystyrene, $\phi_s = 0.176 (\pm 0.014)$. The uncertainty in ϕ_s results from the $\pm 2^\circ\text{C}$ uncertainty in T_g measurements.

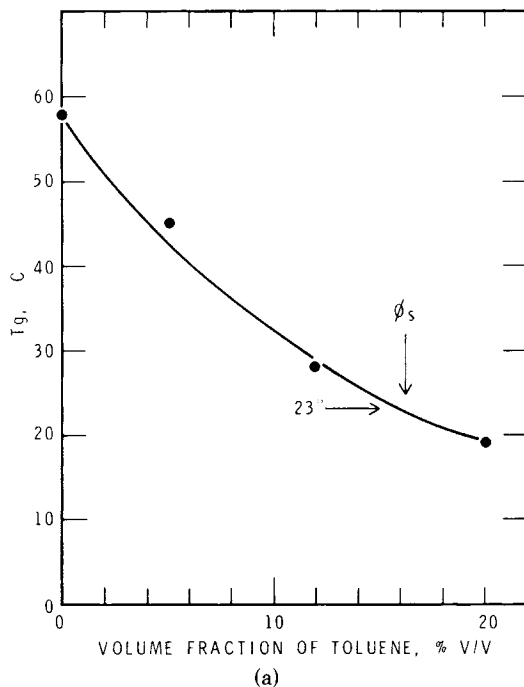


Fig. 3. (a) Depression of T_g in PIBM by retained solvent, toluene. (b) Depression of T_g in polystyrene by retained solvent, toluene.

Mechanical Properties of Dried Coatings

The stress-strain properties of the coating are necessary to predict a value of internal strain from eq. (5) and compare it with the experimental value. In order to compare theory and experiment, the stress-strain relationship must be determined after the stress has relaxed to its residual value.

Stress relaxation tests were carried out in a conventional tensile testing machine on strips of solvent-cast film $50 \times 4 \times 0.5$ mm. For both PIBM and polystyrene, the load relaxed to an approximately constant value after 8 hr. However, a gap of 48 hr was maintained between each increment in strain. The stress-strain curves are presented in Figures 4(a) (PIBM) and 4(b) (polystyrene) and are isochronous at 48 hr. The predicted internal strain is indicated in both cases.

Unfortunately, in contrast to the coatings, the polystyrene tensile specimens crazed considerably above approximately 1% strain and often broke before reaching the highest level of strain indicated. The PIBM species did not craze in the strain range tested. The spread of the stress-strain curves is probably a result of slightly varying amounts of solvent present in the test pieces.

Poisson's ratio ν was measured by casting thicker specimens (2 to 3 mm thick) and measuring the contraction in thickness and width in a stepped tensile experiment. The value obtained for PIBM, $0.4 (\pm 0.05$ standard deviation) seems reasonable for a plasticized acrylic, as does the value for polystyrene $0.39 (\pm 0.05$ standard deviation). Crazing of the polystyrene occurred in the measurement of Poisson's ratio in the same way as for relaxation measurements.

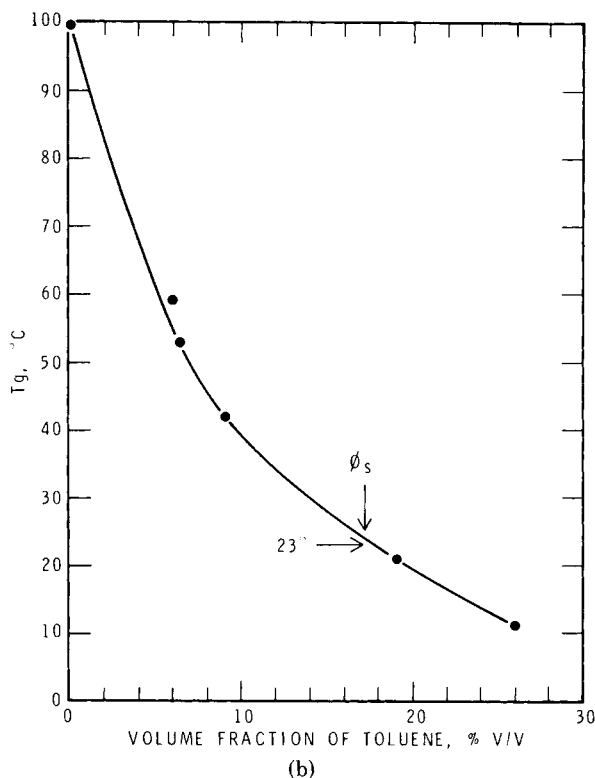


Fig. 3 (Continued from previous page.)

Retained Solvent Concentration

After drying for about 13 weeks, films of PIBM or polystyrene were redissolved in reagent-grade carbon tetrachloride. These solutions were then analyzed in a gas chromatograph using the thermal conductivity detector (ASTM E260 and D3271).

The initial concentration of polymer film in the carbon tetrachloride was known, and the ratio of carbon tetrachloride to toluene was determined from the ratio of the peak areas on the chromatogram. Thus, the proportion of toluene retained in the dried coating was easily calculated: $\phi_r = 0.078$ (0.005 standard deviation) for PIBM, $\phi_r = 0.096$ (0.01 standard deviation) for polystyrene. These are the values used in the calculation of internal strain from eq. (3).

DISCUSSION

In both the PIBM and polystyrene coatings, the residual internal stress is independent of coating thickness and initial solution concentration. It seems likely that the residual stress will behave thus in all such lacquers, which dry by evaporation of solvent. The independence of thickness suggests that the final value of the stress does not depend on the diffusion or evaporation behavior of the solvent.

In order to compare the theoretical and experimentally determined values of the residual internal stress, one must first calculate the strain from eq. (3).

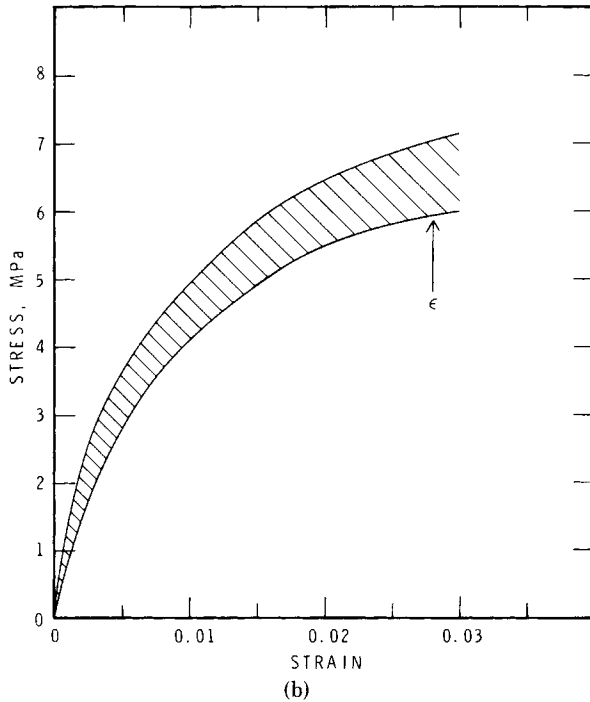
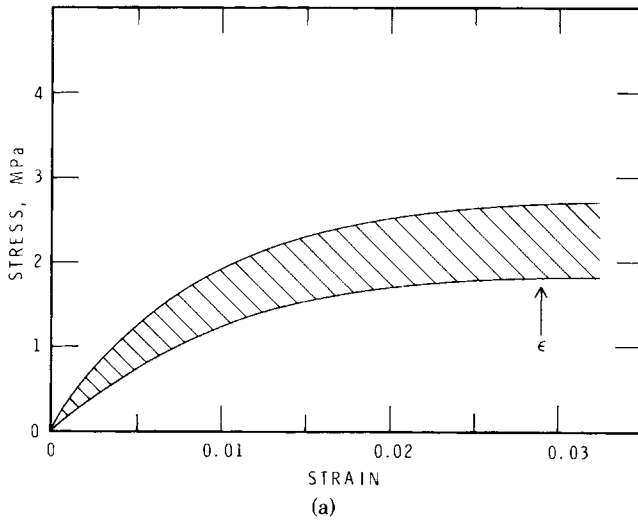


Fig. 4. (a) Isochronous stress-strain data at 48 hr, PIBM (dry film). (b) Isochronous stress-strain data at 48 hr, polystyrene (dry film).

Using the values of ϕ_s and ϕ_r obtained in previous sections, the results are $\epsilon = 0.030 (\pm 0.007)$ for PIBM, $\epsilon = 0.029 (\pm 0.008)$ for polystyrene. Using these values, the corresponding uniaxial stress can be obtained from Figures 4(a) or 4(b) and divided by $1 - \nu$ to obtain the equivalent biaxial stress corresponding to the internal stress. The results of this calculation are $\sigma = 3.8 (\pm 0.9)$ MPa for PIBM, $\sigma = 10.8 (\pm 1.7)$ MPa for polystyrene. The numbers in brackets are the spread due to the uncertainty in the stress-strain curves, ϕ_s and ϕ_r .

The experimentally determined values are 4.5 MPa for PIBM and 14.3 MPa for polystyrene; agreement is reasonably good although a little low. The success of the calculations lends weight to the ideas behind them: first, that stress does not arise until the coating solidifies at a high solids content; second, that the final value of internal stress depends only on the difference between that solidification point and the dry coating, and not on the kinetics of drying; last, that the solidification point can be identified with the glass transition of the drying polymer solution. Although the glass transition is not a sharp one, the central point, T_g , does provide a parameter to describe the solidification, which intuitively seems very reasonable. Because the glass transition is not sharp, there is some molecular motion allowed at temperatures below T_g . Thus, the calculation of internal strain may be an overestimate, and this could account for the difference between theory and experiment.

It was noted previously¹ that the experimental determination of the internal stress was very sensitive to small changes in temperature. This is now readily explained since the coating dries through its glass transition, and it is well known that the properties of polymers undergo considerable changes in the transition. The dried coating is still close to the transition region and can be influenced greatly by small temperature changes.

A major virtue in measuring the internal stress by the cantilever technique is that the deflection of the cantilever is dominated by the steel substrate, and thus one does not require the mechanical properties of the coating to calculate its internal stress. Unfortunately, those mechanical properties are needed to compare physical fact with theory, which essentially calculates the internal strain. Ideally one would measure the internal strain directly and compare that with the theory, particularly since the mechanical properties of the coatings are such that the stress is not particularly sensitive to changes in strain after a certain point.

A greater degree of sophistication might be attempted by calculating ϕ_s from a theory of the depression of T_g by solvent, e.g., that of DiMarzio and Gibbs.⁴ Unfortunately, no corresponding theory appears to exist for calculating ϕ_r (see the review by Newman and Nunn⁵). One might speculate that perhaps ϕ_s and ϕ_r are in some way related.

If the internal stress is thought to menace the effectiveness or life of a coating, then the theory suggests that the coating system be chosen such that ϕ_s and ϕ_r are close together, i.e., large-scale molecular motion is retained for as long as possible during the drying process.⁶ This would mean that the coating would be closer to its glass transition and thus would be softer, more flexible, and more permeable. These may not always be desirable coating properties, however.

CONCLUSIONS

Residual internal stress is independent of dried coating thickness and initial solution concentration in both PIBM and polystyrene coatings cast from solution in toluene. It seems reasonable to expect this with all thermoplastic coatings that dry from solution in a single solvent. This behavior suggests that the residual stress results from the quantity of solvent that evaporates after solidification and not the transport phenomena that govern the rate at which it is removed.

A simple theory has been put forward which incorporates these ideas and

calculates the internal strain from the difference in solvent content at solidification and that in the "dry" coating. Knowing the mechanical properties of the coating, a comparison can be made with the measurements of internal stress. The agreement between theory and experiment is fairly good.

One of the features of the theory is that it identifies the point at which the solution solidifies as that point when the glass transition of the drying solution has reached the testing temperature.

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