Effect of titania pigment on the residual strain, glass transition and mechanical properties of a PMMA coating

S. G. Croll
Materials Section, Division of Building Research, National Research Council of Canada, Ottawa, Canada K1A 0R6

(Received 23 April 1979)

INTRODUCTION

Polymeric coatings such as paints, varnishes and inks tend to shrink as they dry. This is true whether the coating dries due to chemical change or purely physical change, e.g., solvent evaporation. The area of a coating is constrained to remain at its original wet size by adhesion to a normally rigid substrate so volume changes are accommodated by a change in thickness accompanied by fluid flow. After the coating solidifies and can no longer flow, however, subsequent chemical change or solvent loss produces an internal strain in the plane of the coating as it proceeds to its final dry state. Unfortunately, this internal strain, or stress, seldom disappears completely after the normal viscoelastic relaxation in the polymer but remains to threaten the cohesive and adhesive properties of the system. Because reduction in residual stress may extend the service life of a coating and bring about considerable financial and raw materials saving, greater understanding of this phenomenon is required.

This paper is concerned with the effect of pigment on the residual strain, modulus and glass transition temperature (T_g) of a PMMA lacquer.

Previous work[1] on clear, unpigmented lacquers, which dry only by evaporation of the solvent, has shown that the residual stress, or strain, is independent of dry coating thickness or initial solution concentration. In these systems the solidification point has been identified as that point at which the T_g of the polymer solvent mixture coincides with ambient temperature.

The literature on residual stresses[2,3] is mainly concerned with chemically cured, convertible coatings. There is information, however, on an aluminium powder-filled polystyrene lacquer[4] for which the internal stress decreases with increasing filler content.

One might expect the filler (pigment) simply to reduce the residual strain by dilution, but data are presented here which show that the situation can become more complicated when polymer, solvent and pigment interact and the coating thickness varies. It is possible for the modulus of a coating to increase or decrease with increasing pigment content depending on the interaction between the constituents and the size and shape of the pigment particles. In the system studied here, the modulus increased.

In the current experiments residual strain was measured as the relative shrinkage of dry coatings upon release from a tinplate substrate. The polymer used was polymethylmethacrylate, the solvent was toluene and the pigment was rutile titanium dioxide, a very common white pigment.

THEORY

A phenomenological theory has previously been proposed to explain the residual strain in clear lacquers. In this section it is extended in a simple way to account for the effect of pigment.

This investigation is concerned only with the final, equilibrium value of the internal strain. A complete study of how it arises as the coating solidifies would be a much more complicated undertaking.

It is assumed the residual strain is due only to the difference between the volume fraction of solvent present in the coating when it solidifies, ϕ_s, and the volume fraction retained in the 'dry' film, ϕ_r. Prior to solidification the coating mixture can flow to accommodate the volume change under the constraint of constant area. When the coating solidifies, however, further loss of solvent volume results in an internal strain in the plane of the coating because the area cannot change due to adhesion to the substrate, whereas the thickness dimension is always free to contract. It is assumed that the coating would contract isotropically, if free, and that loss of solvent produces an internal bulk strain within the coating, equivalent to an isotropic linear strain field.

Residual strain and solvent loss

In this subsection an expression is derived for the residual strain in terms of the volume of solvent lost after the coating solidifies.

The volume fraction of solvent is expressed as a fraction of the volume of the polymer and solvent combined, as it would be in a free clear film. Hence, at the solidification point

$$\phi_s = \frac{\text{vol of solvent}}{V + \text{vol of solvent}}$$

$$\therefore \text{vol of solvent} = \frac{\phi_s V}{1 - \phi_s}$$

where V = volume of polymer present.

0032–3861/79/111423–08$02.00

Similarly in the dry film

$$\text{vol of solvent} = \frac{\phi_r V}{1 - \phi_r}$$

V remains constant in the calculation because ϕ_r is measured for free unstrained films.

Thus the loss in volume of solvent after solidification, ΔV, is

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

The pigment volume fraction, ϕ_p, is expressed as the fraction of pigment with respect to polymer + pigment. Hence the volume of pigment in a film, which remains unchanged, is given by

$$\text{pigment volume} = \frac{\phi_p V}{1 - \phi_p}$$

Then the total volume of the film at solidification, V_T, is given by

$$V_T = V \left(1 + \frac{\phi_s}{1 - \phi_s} + \frac{\phi_p}{1 - \phi_p} \right) \qquad (2)$$

The bulk strain, $\Delta V / V_T$, is equivalent to an isotropic linear strain, ϵ, in the usual manner

$$\epsilon = \frac{1}{3} \frac{\Delta V}{V_T} \qquad (3)$$

which can be expressed using equations (2) and (3) as

$$\epsilon = \frac{1}{3} \left(\frac{\phi_s}{1 - \phi_s} - \frac{\phi_r}{1 - \phi_r} \right) \Bigg/ \left(1 + \frac{\phi_s}{1 - \phi_s} + \frac{\phi_p}{1 - \phi_p} \right) \qquad (4)$$

To calculate the residual strain, ϵ, values of ϕ_s, ϕ_r and ϕ_p are necessary. Direct measurements of ϕ_r and ϕ_p are possible, as explained in the experimental results section. To obtain a value of ϕ_s, one must first identify the solidification conditions.

Coating solidification

Solidification 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. It resembles the glass-rubber transition in solid polymers: above the transition temperature, T_g, large-scale molecular motion is allowed; below, the polymer 'solidifies' into a more rigid structure.

Incorporating a solvent into a polymer will lower T_g considerably, the depression increasing with solvent concentration. The depression can be readily measured and for this work ϕ_s is chosen as the solvent concentration that depresses T_g to the ambient temperature. As will be seen later, it is necessary to allow for the diffuse nature of the glass transition in an, as yet, empirical fashion.

The addition of pigment (filler) frequently increases the value of T_g. In this case ϕ_s will increase because in order to bring the value of T_g back to coincide with ambient requires a greater concentration of solvent in the mixture. Since the solvent retained in the dry film does not alter significantly upon addition of pigment, the increased shrinkage observed in some pigmented films, compared with the corresponding clear film, may be attributable to the greater difference in solvent concentration between the solidification point and the final dry state.

If the pigment does not affect the glass transition of the polymer, then the concentration of solvent in the polymer at solidification will not be changed either. Thus one might expect a decrease in the over-all residual strain as the pigment is merely diluting the mixture.

In order to test these ideas the depression of T_g by solvent was measured not only in clear coatings but in a pigmented formulation.

EXPERIMENTAL RESULTS

The coatings were made using polymethylmethacrylate, PMMA (duPont Elvacite 2010) dissolved in reagent grade toluene. A commonly used pigment, rutile titanium dioxide, was chosen; the grade used was Titanox RA (97 per cent pure). An examination by scanning electron microscope showed that the pigment particles were spherical and that a representative diameter was 0.3 μm, which is typical for this type of pigment.

All measurements were performed at 23(±0.5)°C and 50(±2) per cent R.H.

Residual strain measurements

This type of measurement has been described before[1]. An area is masked off on a tinplate substrate (60 x 10 mm) and the coating applied using a drawdown blade. After the coating is completely dry, checked by weighing, it is released from the substrate by mercury amalgamation. Subsequent contraction in its length is monitored using a travelling microscope until it reaches a final steady value. The original length of the coating on the substrate is used to calculate the relative shrinkage, or residual strain.

This is a simpler procedure than measuring the residual stress and can be readily carried out on many samples at

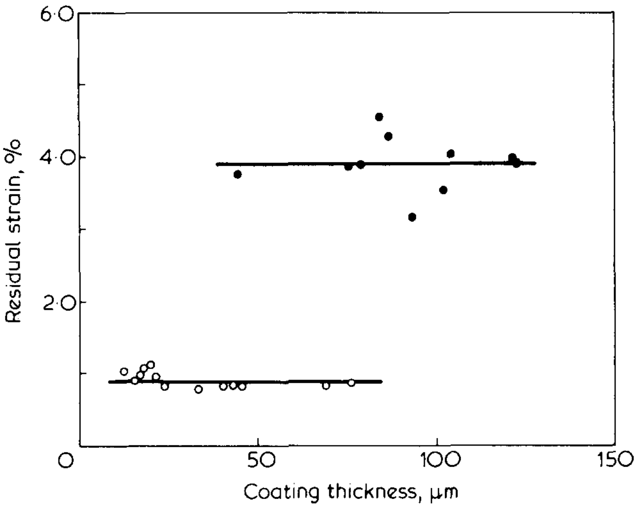

Figure 1(a) Extreme examples of the effect of coating thickness on residual strain (shrinkage). Line represents mean value. ○, 5% pigment all adhered; ●, 49% pigment all detached

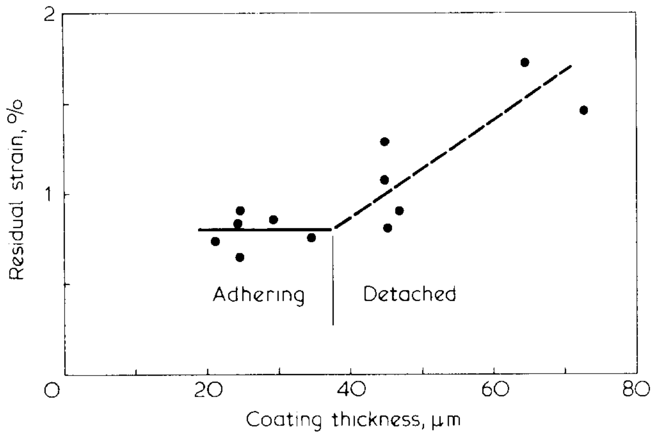

Figure 1(b) Effect of coating thickness on residual strain for an intermediate 20% pigment content. Solid line represents mean value for adhering coatings

once. Measuring the residual strain is also a more direct test of the theory than measuring the equivalent stress (see Ref 1).

Examples of the results obtained are presented in *Figures 1(a)* and *(b)*. Those coatings which remained adhered to the substrate when dry gave one value of residual strain, independent of coating thickness, as found previously for clear lacquers[1]. Those which spontaneously detached gave a larger value. At low pigment concentrations, ⩽20%, thin coatings adhered and gave the low strain result; thicker coatings detached and gave a higher result which became constant for very thick coatings. It was noted that the thickest coatings were the first to detach. For pigment content >20%, all the coatings detached. Some of them broke into many pieces, particularly at high pigment concentrations. If only two or three breaks occurred then a value of residual strain was observed that was consistent with that obtained from whole specimens. Generally, if a specimen broke into three pieces or more it was discarded.

Figure 2 displays the variation of residual strain with pigment concentration for both the attached and detached type of specimen with the bars representing one standard deviation. At 68% pigment concentration all the coatings detached, but still gave only a very low value of shrinkage.

Effect of solvent and pigment on T_g

It is necessary to know the effect solvent and pigment have on the glass transition of the polymer in order to calculate ϕ_s, the solvent concentration at which the coating mixture solidifies.

A Differential Scanning Calorimeter (DSC), duPont 990, was used conventionally to measure T_g over a range of heating rates 0.2 to 20K/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. The results are presented in *Figure 3*. This procedure appeared to be sufficiently accurate and consistent for the purposes of this investigation.

Differing concentrations of solvent were obtained by drying specimens from solution at various elevated (70°C) and depressed temperatures (room temperature to −70°C).

The glass temperature of only one pigmented mixture, 30% by volume, was measured. At lower concentrations of pigment the effect on T_g was too small to give a reliable difference between pigmented and clear mixtures. At greater concentrations the peak in specific heat became rather indistinct because of the low proportion of polymer. Even 30% by volume pf pigment represents over 60% by weight because of large differences in density between PMMA, 1196 kg/m^3, and rutile TiO_2, 4200 kg/m^3.

A peak in specific heat was found at 50 to 60°C which was due to the titania pigment. The phase diagram for titanium dioxide is quite complicated, but there is a change consistent with the experimental finding. Generally the peaks due to polymer and pigment could be distinguished.

A wide range of moulding temperature and pressure was used in an attempt to obtain a solventless mixture of PMMA and titanium dioxide pigment by compression moulding. It was found impossible to combine more than about 10% by volume of pigment. When tested in the DSC the compression moulded sample showed no perceptible difference in T_g from the original resin.

Measurement of solvent content

In order to measure the toluene content of a film, clear or pigmented, it was first redissolved in reagent grade carbon tetrachloride. The resulting solution was then analysed in a gas chromatograph using the thermal conductivity detector (ASTM E260 and D3271). The initial concentration of the coating with respect to 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. The retained solvent volume is expressed in this paper as a fraction of the solvent-polymer total. The solvent concentration in the mixtures used in the T_g measurements was also measured in this manner.

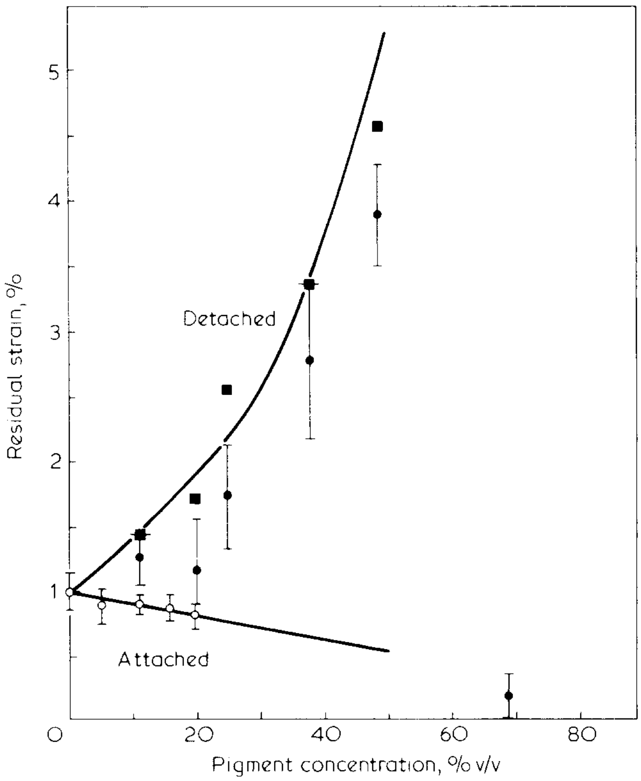

Figure 2 Residual strain as a function of pigment concentration ●, mean value (±1 std. dev.); ■, highest value; ———, predicted value

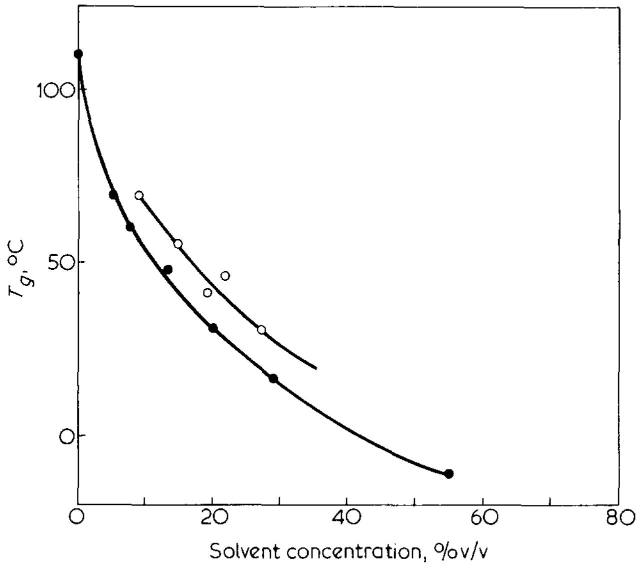

Figure 3 Variation of T_g with solvent concentration ●, clear films; ○, 30% pigmented films

In *Figure 4* the variation of retained solvent as a function of pigment volume concentration is presented. There appears to be a small increase with pigment concentration. When fitted to a straight line by a least squares analysis it gives the following results:

slope = 4.2×10^{-2} (std. error 5.5×10^{-3})

intercept = 7.4×10^{-2} (std. error 1.5×10^{-3})

The samples used in the measurement were of a variety of thicknesses and had been drying for about 12 weeks. They were, in fact, the same specimens used to measure internal strain.

Measurement of pigment volume concentration

The proportion of pigment was determined by ashing a known weight of freed coating in an oven at 480°C for two hours. At this temperature solvent and polymer either evaporated or decomposed into gaseous products leaving the titanium dioxide pigment as a residue; it was then weighed.

Knowing the solvent content and the densities of the various constituents allowed the calculation of the pigment volume concentration as a fraction of the pigment–polymer total.

Effect of pigment on the mechanical properties of the coating

To decide whether a particular residual strain endangers the integrity of a coating requires knowledge of its breaking strain. Free films, the same size as the residual strain specimens, were tested in tension on a conventional testing machine at a strain rate of 2×10^{-4} s^{-1}.

For unpigmented films, the breaking strain ranged between 1.2 and 1.8% for those that failed within the gauge length. For pigmented films the value reduced to between 0.5 and 0.7% with no discernible trend with pigment concentration.

In the case of the pigmented films, it was possible to obtain a value for the initial slope of the stress–strain curve, i.e., Young's modulus. This is plotted as a function of pigment volume concentration in *Figure 5*. Fitting a least squares straight line to the data up to 25% v/v pigment gives the solid line on the graph.

slope = 2.19 (std. error 0.26)

intercept = 1.96 (std. error 0.043)

DISCUSSION

The mechanical properties and the glass transition are discussed first because these results aid the understanding of the residual strain measurements.

Mechanical properties

As one might expect, the inclusion of an inorganic pigment in the polymer made it more brittle, the breaking strain was reduced to 0.6% from 1.5% for the clear coating. There was no crazing visible in the clear coating prior to breaking.

As the volume concentration of titania increased so did the modulus of the composite, see *Figure 5*. There are several theories[5] which predict this increase and these results are compared with two of the more recent ones.

Firstly, that of Chow[6] relates the modulus of a composite to that of its components, assuming perfect adhesion between the two and that the pigment particles interact with each other. This theory generates the dashed curve in *Figure 5*. The parameter values used to generated the theoretical curves are as follows:

Modulus of polymer = 1.96 GPa (least squares intercept)
Poisson's ratio polymer = 0.4 (assumed)
Modulus of rutile titania = 328 GPa
Poisson's ratio rutile titania = 0.21

The last two values are the average of the Reuss and Voigt estimates for homogeneous particles of a tetragonal material. The elastic constants were obtained from the literature[7]. It can be seen that the curve does not describe the data.

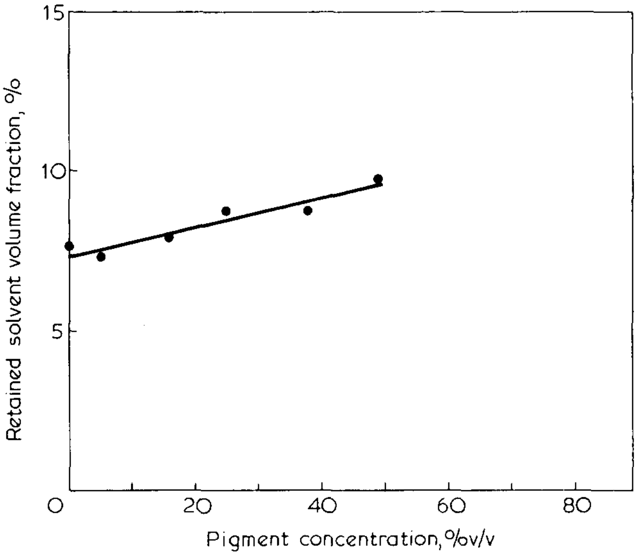

Figure 4 Variation of toluene retained in the PMMA-toluene matrix as a function of the volume fraction of rutile pigment

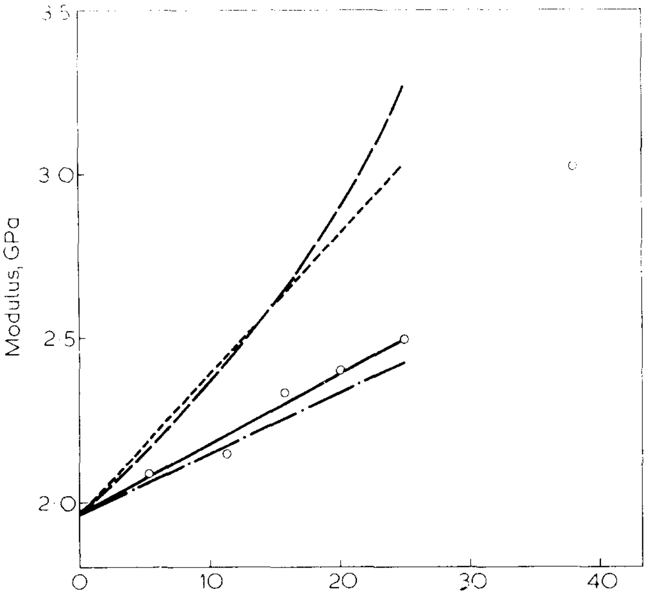

Figure 5 Variation of modulus with pigment content ○, experimental values; ——— interacting particles + adhesion; - - - - non-interacting particles + adhesion; —·— non-interacting particles + slipping

Secondly, the theory of Takahashi *et al.*[8] predicts the composite modulus assuming that the pigment particles are spherical and do not interact with each other. The lower dashed line, *Figure 5*, represents the prediction if free slipping, i.e., no adhesion, is allowed between pigment and polymer. The upper dashed line is the prediction for perfect adhesion between the two. It is obvious that the case where the pigment and polymer slip with respect to one another fits the experimental data closely. The other dashed line for perfect adhesion is consistent with the dashed curve at low values of pigment concentration where the interaction between pigment particles would be slight.

The rather high experimental value for the modulus at 38% pigment volume concentration likely indicates a degree of interaction between particles at this level of pigmentation.

Comparison with the various theories of composite modulus indicate that in this case the pigment particles do not interact up to 25% pigment concentration and that when the composite is stressed there is a complete loss of adhesion between pigment and polymer.

Glass transition temperature

There is indeed an increase in the glass transition of PMMA when rutile titania is added, but only it seems in the presence of a solvent, toluene. It proved very difficult to compression mould PMMA and this pigment, and the resultant mixture showed no appreciable increase in T_g. This must mean that there is no interaction between the two unless the polymer is dissolved in a solvent that allows it to wet the pigment surface and thus adhere. Conclusions drawn from the previous section on mechanical properties are consistent with this.

The degree of compatibility between components of a mixture might be expressed by their respective solubility parameters[9]. Since these properties for PMMA, an organic polymer, and titania, a metallic oxide, are widely different the two are unlikely to adhere or interact much.

Possibly a pigment influences the glass transition only if it is wetted by the polymer. Otherwise it may be necessary to aid interaction by using a suitable solvent as a wetting agent. Any surface treatment of the pigment during manufacture will also be significant in this respect.

It is interesting to note in *Figure 3* that there is an approximately constant difference in T_g between the two curves, independent of solvent concentration.

Solvent retained in the polymer

Figure 4 shows that the concentration of toluene retained by the film increases slightly with pigment concentration when expressed as a fraction of the total polymer-solvent volume. It may be that the pigment surface adsorbs solvent and no change occurs in the polymer matrix. The graph may not truly be linear, but these changes are so slight that they will have little effect on subsequent calculations.

Residual strain

Detached coatings. The upper branch of the data presented in *Figure 2* represents the shrinkage in those films that spontaneously peeled off the substrate as they dried. In these coatings the internal strain (stress) is large enough to initiate failure of the adhesive bond and there is sufficient strain energy to overcome the work of adhesion and create new surface area, thus the coating detaches.

Adhesion of coatings with pigment concentrations of greater than about 20% is poor and all the coatings detached sooner or later. It seems that the polymer does not wet the pigment well, thus pigment particles may come into direct contact with the substrate. Hence, with high pigment loading there may be comparatively little polymer in contact with the substrate to provide adhesion. Spontaneous peeling does mean that the coatings are not constrained and can shrink as they will. Consequently, the possibility of internal damage is much reduced and the polymer and pigment can adhere and interact.

In *Figure 2*, the values of internal strain from the coatings that detached quickest (in general, the thickest coatings) are displayed. They are the largest values and are probably more typical of this type of behaviour. Those points with the one-standard deviation bars represent the average value recorded for all those films which eventually detached. Because most coatings have dried partially under internal stress, there is a considerable chance of internal damage which will tend to reduce the value of shrinkage measured.

The value of strain at 68% pigment by volume is very low, in contrast to the ever increasing values up to 48% shown. The pigment is much stiffer than the matrix and at a concentration such that there is a significant chance of many pigment particles touching, the over-all strain should diminish considerably. In a perfectly dispersed system of spheres, such as the pigment particles, the particles will touch when the spheres (diameter = $2r$) have only the minimum cubic space (side = $2r$) to occupy. The packing in this case is equivalent to a simple cubic lattice. A more complete treatment of pigment packing is given by Bierwagen[10].

The volume fraction of pigment, ϕ_p, at this initial touching concentration is given by

$$\phi_p = \frac{4}{3}\pi r^3 \Big/ (2r)^3$$

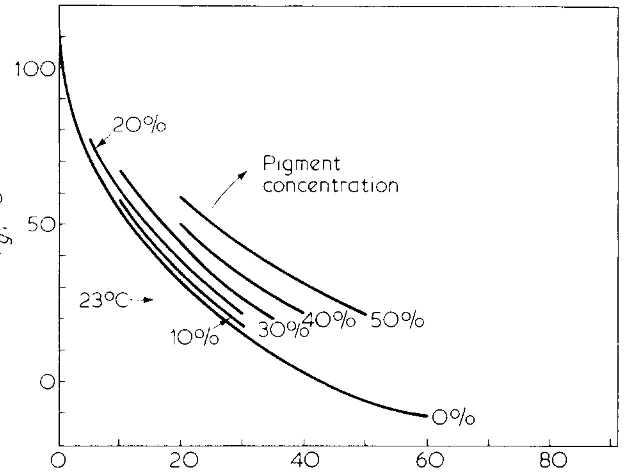

Figure 6 Determination of solidification point from variation of T_g with solvent and pigment content

$$= \frac{\pi}{6} = 0.52$$

In other words for ϕ_p above 52% the shrinkage of the films should diminish greatly because a significant part of their linear dimensions will comprise touching pigment particles. This effect may also depress the values of shrinkage recorded at ϕ_p below 52%.

The densest form of packing for spheres is face-centered cubic or hexagonal close packed which amounts to a ϕ_p of 74% so it is hardly surprising that the shrinkage of films with 68% pigment volume is so small.

The data in *Figures 3* and *4* can be used in equation (4) to predict the internal strain in the detached pigment coatings.

For the clear film

$$\epsilon = 0.01, \phi_r = 0.073$$

and ϕ_s can be deduced from equation (4), setting ϕ_p equal to zero, which gives

$$\phi_s = 0.101$$

But the value of solvent content, which reduces the T_g to room temperature (23°C), ϕ_{23}, is 0.247. Thus $\Delta\phi$, which represents the width of the glass transition, can be found

$$\Delta\phi = \phi_{23} - \phi_s = 0.146$$

In this calculation ϕ_s, via $\Delta\phi$, has been used as an adjustable parameter.

Now for the 30% pigmented film, it can be seen from the graphs that

$$\phi_{23} = 0.325$$

and

$$\phi_r = 0.087$$

Using $\Delta\phi$ obtained from the clear film above we have

$$\phi_s = 0.179$$

which gives from equation (4) a value for the residual strain

$$\epsilon = 2.5\%$$

This is in very good agreement with the experimental result, as can be seen in *Figure 2*.

It seems that equation (4), which predicts the value of the residual strain from the effect pigment has on the glass transition, is successful at 30% pigment concentration.

The next part of this section extends the data to cover the full range of pigment concentration.

Calculation of T_g *and* ϵ *over complete* ϕ_p *range*

There is an equation which has been used to model the influence of filler on T_g in polymers[11]. Its form is essentially

$$\Delta T_g = K \frac{\phi_p}{1 - \phi_p} \tag{5}$$

where

ΔT_g = increase in glass transition
ϕ_p = pigment volume fraction
$1 - \phi_p$ = polymer volume fraction
K = constant for a particular polymer–pigment system.

There is some detail in K, but it is unnecessary for the purposes of this treatment.

Although equation (5) does not appear to have been used previously for systems containing significant amounts of solvent it will be used to construct further T_g-solvent fraction curves for different pigment concentrations. Thus ϕ_{23} and ϕ_s can be deduced for other values of ϕ_p and hence values for ϵ obtained using equation (4).

First a value of K can be deduced from the experimental data on clear and 30% pigmented films. As noted before there is a remarkably constant difference between the two T_g-solvent fraction curves of some 12°C, which means that the value of K obtained is approximately independent of solvent concentration. Over the experimental range of solvent concentration, K varies from 27.3 to 30.1, an average value being 28.4 (ΔT_g = 12.2°C).

Curves of T_g versus solvent content can be interpolated for ϕ_p of 10 and 20%, and extrapolated for ϕ_p of 40 and 50%. Where extrapolation outside the experimental range of solvent content was necessary, the average value of K was used, within that range there was a particular value of K for each concentration of solvent. The constructed curves are shown in *Figure 6*, along with the experimental curves of *Figure 3*. Values of ϕ_{23} can be deduced from these curves, and reduced to ϕ_s, assuming that $\Delta\phi$ obtained from clear films remains applicable. ϕ_r is, of course, obtained from *Figure 4*. *Table 1* gives these values for each value of ϕ_p, together with the prediction for ϵ using equation (4).

The upper full line in *Figure 2* shows the prediction which is in very close agreement with the experimental points. It not only demonstrates that the theory proposed for residual strain is successful but that equation (5) can be extended to cover the variation in T_g in systems containing pigment and solvent. It is worth noting that the same value of $\Delta\phi$ was used in all pigment concentrations, which is essentially assuming that the glass transition has the same effective width independent of pigment content.

Table 1 Predicted values of residual strain, ϵ, and solidification point, ϕ_s, as a function of pigment fraction, ϕ_p

ϕ_p	ϕ_{23}	ϕ_s	ϕ_r	ϵ
0	0.247	0.101	0.073	0.01 (exptal)
0.1	0.265	0.119	0.078	0.015
0.2	0.291	0.145	0.082	0.019
0.3	0.325	0.179	0.087	0.25
0.4	0.39	0.244	0.091	0.37
0.5	0.48	0.334	0.095	0.53

Disparity between the predicted and experimental values at high values of ϕ_p can easily be accounted for. It may be that the touching of pigment particles reduces the measured shrinkage from the ideal value, even below 52% pigment content. Any error in the experimental curves for T_g ϕ_s would be magnified with extrapolation. It may well be that $\Delta\phi$ is not a constant or that K is not constant over such a wide range. Bearing all this in mind, the combination of extrapolation and assumption provides a very good description of the data.

Adhering coatings. This branch of the strain versus pigment concentration graph represents the situation wherein the coating remains adhered to the substrate.

The thinner coatings that remained attached to the tinplate substrates as they dried displayed a slight decrease in residual strain compared with that of the clear coating. In this case the coating is always constrained by adhesion to the substrate, and thus under stress, so if there is a potentially large internal strain, as in the detached samples, it must be relieved in some way.

One possible explanation is that the pigment particles or agglomerates thereof, produce stress concentrations promoting local crazing in the polymer, which relieves the over-all strain in the coating. No crazes or cracks could be detected, however, using either the optical or scanning electron microscope and only very few imperfections could be found using an electrical breakdown method (ASTM D1670). However, the microscopy did reveal Bénard cells (*Figure 7*) and strain relief may occur at their boundaries.

There is an alternative explanation. In thin coatings, the total internal strain energy developed as the pigmented polymer solidifies is insufficient to overcome the adhesion to the substrate. If the cohesive strength of the polymer prevents cracking then the coating will be under stress and the interface between polymer and pigment may fail. This is consistent with the results of the previous section which showed that the modulus (measured under stress) of the polymer pigment composite was best modelled if there was no adhesion between pigment and binder. In this case, there will be no interaction between polymer and pigment, no change in glass transition, and the polymer will not solidify until the lower solvent concentration of an unpigmented, clear, film is reached.

Using equation (4) to predict the residual strain in pigmented coatings, while retaining the values of ϕ_s and ϕ_r obtained for an unpigmented coating gives the lower solid line in *Figure 2*, which gives excellent agreement with the experimental results. Essentially, the over-all residual strain of the coating is decreased by the presence of pigment.

For this particular coating formulation one is led to believe the second explanation because of the agreement between theory and experiment and in the absence of strain relieving damage to the coating. It seems that this is a case of adhesive failure between pigment and polymer. Although the reidual strain is comparatively small in this branch of the data, it is still significant compared with the breaking strain of even the clear coating (~1.5%) and must be regarded as detrimental in practical usage.

The explanation probably depends on the particular formulation. Among the factors that should be taken into consideration are adhesion to the substrate, adhesion between polymer and pigment, pigment particle size and shape.

CONCLUSIONS

(1) Residual strain measurements have been made on a PMMA lacquer pigmented with titania. There appears to be two regimes. One of increasing strain with pigment concentration in thick and highly pigmented coatings that detach from the substrate; the second is of decreasing residual strain in thin, adhering coatings. Both types are modelled well by a theory that relates the residual strain to the difference between the solvent concentration present at solidification and that in the final 'dry' coating. The idea central to this theory is that the solvent concentration present at the point when the coating solidifies is essentially the amount of solvent necessary to depress the glass transition of the pigmented polymer to ambient temperature.

(2) In thicker coatings, particularly at high pigment content, the residual internal strain is high and the adhesion between coating and substrate fails, i.e., the coating spontaneously peels off. It is then free to shrink. The theory presented describes the observations well in this case if the solidifica-

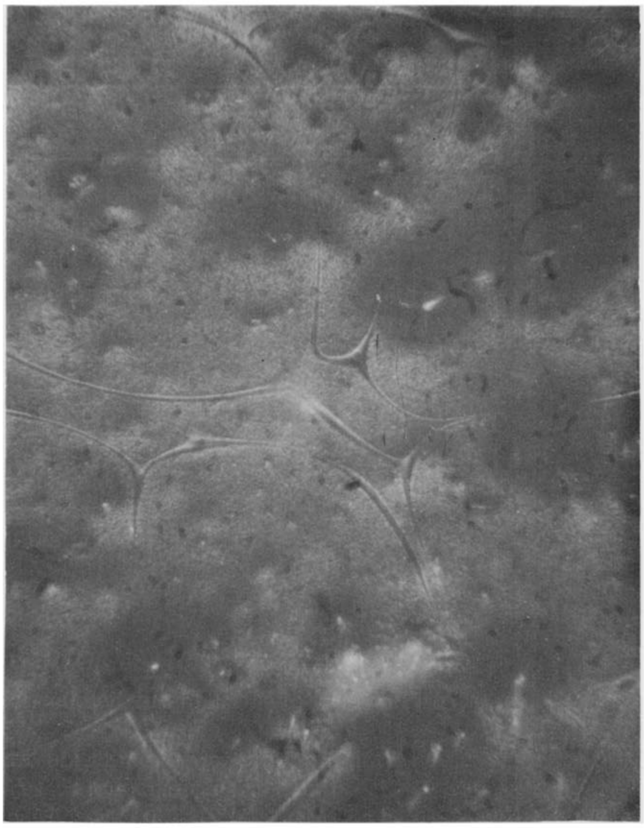

Figure 7 Surface of attached pigmented coating (x67 optical microscope) showing Bénard cells and some pigment agglomeration

tion point (glass transition) is allowed to change with pigment content.

(3) For thinner coatings, at low pigment concentrations, (⩽20%), the residual strain decreases slowly with pigment content but remains a large fraction of the strain to break. In this case, there seems to be insufficient strain energy to promote adhesive failure with the substrate, instead the strain appears to cause the polymer-pigment bond to break. Consequently, the polymer solidifies as it does in a clear coating, unaffected by the presence of pigment. This produces a lower level of residual strain compared with the thicker coatings. Again this behaviour is modelled well by the theory.

(4) Data are presented on the effect of both pigment and solvent on the glass transition of the polymer. It appears that there is a constant difference in T_g, independent of solvent concentration between the pigmented and clear films for this system at least.

(5) Equation 5, which relates the change in T_g with pigment concentration, used in conjunction with the theory predicting internal strain, equation 4, successfully extended the range of the predictions, even in the presence of solvent.

(6) The assumption that the width of the glass transition (expressed in terms of solvent content) is independent of pigment concentration appears to hold.

(7) The effect of the titania on the T_g of the PMMA was only a few degrees. Indeed, the presence of solvent seemed necessary to aid the interaction since compression moulding pigment into the polymer resin had no noticeable effect.

(8) Stresses introduced in making the polymer-pigment composite may cause the bond between the two to fail and thus prevent interaction and a change in T_g. Further, for an interaction to occur between polymer and pigment one might expect that they should be compatible, expressed by their solubility parameters, for example.

(9) The increase in modulus with pigment content was modelled well by a theory which assumes there is no interaction between pigment particles and no adhesion between the pigment and matrix.

(10) Measuring residual stress in coatings requires adhesion between coating and substrate in all cases, which means that considerable information about the coatings that detach, and thus the whole system, would not have been gathered, whereas, measuring the residual strain by shrinkage does embrace the whole spectrum of results.

ACKNOWLEDGEMENTS

The author would like to thank Mr. R. E. Myers for performing much of the experimental work. This paper is a contribution from the Division of Building Research, National Research Council of Canada, and is published with the approval of the Director of the Division.

REFERENCES

1 Croll, S. G. *J. Paint Tech.* 1979, **51**, 648, 64–68
2 Prosser, J. L. *Paint Res. Assn. (U.K.) Tech. Rep. TR/8/72* 1972
3 Zubov, P. I. and Sukhareva, L. A. *Colloid J. USSR*, 1977, **38**, 4, 587–598
4 Lewis, A. F. and Forrestal, L. J. 'Treatise on Coatings', (Ed. R. R. Myers and J. S. Lang), Dekker, New York, 1969, **2**, Ch. 3
5 Sato, K. *Prog. Org. Coat.*, 1976, **4**, 4, 271–302
6 Chow, T. S. *J. Polym. Sci., Polym. Phys. Edn.*, 1978, **16**, 6, 959–965
7 Handbook of Physical Constants. Rev. Edn, (Ed. S. P. Clark, Jnr), Geol. Soc. Am. 1966
8 Takahasi, K., Ikeda, M., Harakawa, K., Tanaka, K. and Sakai, T. *J. Polym. Sci., Polym. Phys. Edn.*, 1978, **16**, 3, 415–425
9 Hansen, C. M. *J. Paint. Tech.*, 1967, **39**, 511, 505–510
10 Bierwagen, G. P. *J. Paint Tech.*, 1972, **44**, 574, 46–55
11 de Ruvo, A. and Alfthan, E. *Polymer*, 1978, **19**, 8, 872–874