

An evaluation of the properties of enteric coating polymers: measurement of glass transition temperature

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When submitted to X-ray crystallography, two enteric coating polymers, cellulose acetate phthalate and polyvinyl acetate phthalate, were found to be essentially amorphous in structure. Values for the glass transition temperature, T_g , of each polymer have been obtained using both a surface microindentation technique and differential scanning calorimetry. The effect on this parameter of an increasing concentration of a plasticizer, diethyl phthalate, has also been determined. Measured values for T_g have been compared with predicted values obtained using a suitable mixture-rule model: the surface microindentation technique values were closer to the predicted.

When the temperature is reduced to a sufficiently low level, all amorphous polymers assume the characteristics of a glass, particularly hardness, stiffness and brittleness. The temperature at which this occurs is called the glass transition temperature, T_g .

The dramatic change in physical properties is due mainly to the fact that in the glassy state, molecular movement other than bond vibration is very limited. Above the transition temperature, the molecule has more energy and movement of molecular segments becomes possible. The glass transition does not involve a change in state, since the glass retains the amorphous structure of a liquid rather than the regular structure of a crystal.

Pierce (1969) considered that a polymer film is at its toughest in the vicinity of the glass transition temperature, the toughness declining rapidly as the temperature is increased and, depending upon the polymer structure, giving rise to a material which is often soft and rubbery. The fact that polymer properties change significantly at or around the glass transition temperature can be used in determining its value.

The available methods include measuring the volume expansion coefficient by dilatometry, the heat content by differential scanning calorimetry, and the mechanical properties by stiffness and hardness measurements. Other methods are based upon the examination of molecular motion, and include the measurement of internal friction, dielectric loss in polar polymers, and the use of n.m.r. spectroscopy.

Knowledge of the glass transition temperature of a polymer used for tablet coating can be very useful, since it will determine the behaviour of that coating under ambient conditions. Entwistle & Rowe (1979) have suggested that a knowledge of the effect of plasticizers on the glass transition temperature can be equally useful since it can be used to assess plasticizer efficiency.

Additionally, in describing some of the factors that can lead to problems in any tablet coating formulation, Rowe (1981) has indicated that a major cause for concern is the development of internal stress in the coating as it dries, which can result in bridging of intagliations and cracking of the coating. Plasticizers can be used effectively in reducing this stress by reducing both the modulus of elasticity and the glass transition temperature of the polymer, with the magnitude of the effect being dependent on the degree of interaction between the polymer and the plasticizer.

In the present work, the glass transition temperatures of two polymers, cellulose acetate phthalate and polyvinyl acetate phthalate, have been determined as a function of the concentration of a plasticizer, diethyl phthalate, by differential scanning calorimetry and by indentation hardness measurements.

MATERIALS AND METHODS

Materials

The polymers used were cellulose acetate phthalate (Wako Pure Chemicals Industries Ltd, Osaka, Japan) and polyvinyl acetate phthalate (Colorcon, Inc., West Point, PA, U.S.A.). The plasticizer was diethyl phthalate (Koch Light Laboratories, U.K.).

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Methods

Since glass transition is a characteristic of an essentially amorphous material, with any increasing degree of crystallinity tending to cloud any results obtained, it was essential to know beforehand something of the nature of the polymers. This was achieved by submitting them to X-ray diffraction analysis. For this purpose, free films of each polymer containing 0, 9.1, 16.7 and 33.3% w/w of total solids as plasticizer, were cast from 20% w/w solutions in a 50:50 by weight mixture of dichloromethane and methanol onto vinyl-coated cards. The films were air dried under ambient conditions for 7 days, and were subsequently stored in a desiccator before testing.

X-ray diffraction analysis was carried out using a Nominus MK.2 self-focusing Guinier diffractometer utilizing nickel-filtered copper radiation as the source.

The glass transition temperature for each polymer, containing the requisite level of plasticizer, was initially determined using a Perkin-Elmer D.S.C. IB differential scanning calorimeter, which had been calibrated using indium (melting point 156 °C) as a reference standard. Samples for evaluation were prepared by transferring solutions of polymer and plasticizer (containing 5% w/w total solids in 50:50 by weight dichloromethane and methanol) a drop at a time to small crucibles, allowing each drop to dry before the next was added. Once prepared, the crucibles, containing small film block samples, were stored in a desiccator for two weeks before testing.

Each sample was tested over a temperature range of -30 °C to +50 °C, using a scan speed of 8° min⁻¹. Five replicate determinations were made for each formulation.

A second method for determining glass transition temperature, involving an evaluation of the effect of temperature on the Brinell hardness of the polymer, was also utilized.

For this, measurements were made using an ICI pneumatic microindentation tester (Research Equipment Ltd, London), as described by Ridgway et al (1970), which monitors the penetration, under load, of a spherical indenter into the surface of the material under test. Values for Brinell hardness number, BHN, were calculated using equation (1).

$$\text{BHN} = \frac{W}{\pi D h_1} \quad (1)$$

where *W* is the applied load (g), *D* is the diameter of the indenter (in this case 1.55 mm) and *h*₁ is the depth (μm) of the indentation produced after 75 seconds.

For the purpose of examining the temperature effect on the film samples, the normal stage platform was replaced by a thermoelectric controlled cooling and heating plate (T.E.C.H.), which operated by the Peltier effect. The sample under test could thus either be cooled or heated.

Test films for each polymer (incorporating various levels of plasticizer as shown earlier) were cast from 20% w/w solids solutions in a 50:50 by weight mixture of dichloromethane and methanol solvent mixture onto 2.5 cm square stainless steel plates. The films were air dried under ambient conditions for 7 days, and kept in a desiccator before testing. During the testing procedure, samples were fixed to the platform of the T.E.C.H. unit by means of a pair of toolmaker's clamps. The entire indentation tester and samples were placed in a Perspex glove box together with trays of silica gel desiccant. The glove box and its contents were allowed to equilibrate for 24 h before testing of the samples began.

For each sample, a range of temperatures from approximately -20 ° to +40 °C was used, five individual measurements of indentation being taken at 4 °C intervals, with the temperature being allowed to stabilize at each level for 20 min before readings were taken.

RESULTS AND DISCUSSION

The results for the examination of films of each polymer by X-ray crystallography indicated an apparent absence of any crystallinity; i.e. both were completely amorphous, indicating they should have readily-determinable glass transition temperatures.

Unfortunately, some difficulty was encountered in accurately measuring the glass transition temperature using differential scanning calorimetry, particularly where the samples contained plasticizer, a problem which was also encountered by Entwistle & Rowe (1979). Generally, the specific heat changes involved were very small, and this, coupled with the fact that the base-line tended to drift, somewhat obscured the transition point.

Lee & Knight (1965) have discussed the reasons for the inconsistencies that occur in glass transition measurements, and concluded that the main factors are failure to establish near-equilibrium conditions during measurement, and secondly, the use of too great a rate of temperature change, faster than the changes in molecular arrangement. The first problem is difficult to overcome, but the second may be significantly reduced by employing very low rates of temperature change, in the region of 1 °C h⁻¹, which is impractical unless the approximate transition zone

is known beforehand to enable final determinations to be made over very narrow temperature ranges. An additional cause of error is impurities in the sample, which typically include unreacted monomer, residual solvents used in sample preparation, and water, any of which may shift the transition temperature by as much as 40–50 °C. Despite the difficulties, the results obtained, shown in Table 1, illustrate the trends that occur when a plasticizer is added in increasing proportions.

Using the microindentation method, it was possible to obtain a more discernible transition point when evaluating the temperature effect on Brinell hardness number, as can be seen in Fig. 1 for polyvinyl acetate phthalate and Fig. 2 for cellulose acetate phthalate. Again, the effect of increasing plasticizer concentration is readily evident, with the exception of the two cellulose acetate phthalate formulations containing the highest levels of plasticizer, where all indications were that the transitions either occurred outside the range of the instrument (the lowest temperature attainable being –20 °C) or

so close to the lower limit that insufficient determinations were possible below the transition temperature.

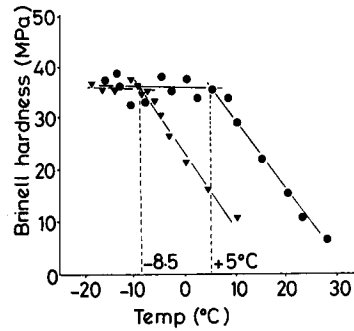


FIG. 2. Effect of temperature on the Brinell hardness of cellulose acetate phthalate (C.A.P.) films (points represent a mean of 5 replicates). ● C.A.P. ▼ C.A.P. + plasticizer (volume fraction 0.11).

Table 1. Values for the glass transition temperatures, T_g , of polyvinyl acetate phthalate (P.V.A.P.) and cellulose acetate phthalate (C.A.P.) determined by differential scanning calorimetry.

P.V.A.P. formulations		C.A.P. formulations	
Volume fraction of plasticizer	T_g	Volume fraction of plasticizer	T_g
0	42.5 ± 1.0	0	18.5 ± 0.5
0.10	39.0 ± 1.5	0.11	-4.0 ± 1.0
0.18	32.0 ± 2.0	0.20	-20.5 ± 1.0
0.35	23.5 ± 1.5	—	—

Bondi & Tobolsky (1971), in considering the importance of the polymer-plasticizer mixture as a factor in glass transition determinations, have described the relevance of mixture-rule models. In such models, assuming the mixture to be ideal, the contribution of the individual components to the observed T_g is dominated by that of the component with more free volume, whether it be that with the lowest molecular weight or greatest internal molecular mobility. Non-ideal mixtures produce values of mixture T_g somewhat different from the ideal, depending on the degree of compatibility between the components.

A simple form of mixture rule is

$$T_{g(1,2)} = \frac{\phi_1 \Delta \alpha_1 T_g^{(1)} + \phi_2 \Delta \alpha_2 T_g^{(2)} + K \phi_1 \phi_2}{\phi_1 \Delta \alpha_1 + \phi_2 \Delta \alpha_2} \quad (2)$$

where ϕ_1 and ϕ_2 are the volume fractions of components¹ and², $\Delta \alpha_1$ and $\Delta \alpha_2$ are the differences in thermal expansion, for the same components, between liquid and glass at T_g , and K represents the interaction between components at or near T_g , which for many polymer-plasticizer systems (Bondi 1968), has a value of -0.04.

A simplification of this rule, proposed by Kelley & Bueche (1961) and shown in equation (3), has been used by Entwistle & Rowe (1979) to calculate the glass transition temperatures of plasticized ethyl cellulose and hydroxypropyl methylcellulose.

$$T_g = \frac{(\alpha_p v_p T_{gp} + \alpha_d v_d T_{gd})}{\alpha_p v_p + \alpha_d v_d} \quad (3)$$

where T_g is the glass transition temperature of the

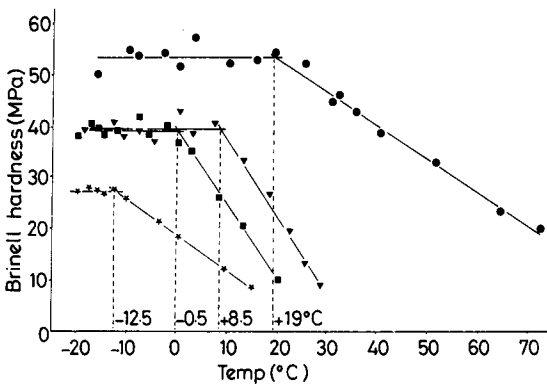


FIG. 1. Effect of temperature on the Brinell hardness of polyvinyl acetate phthalate (P.V.A.P.) films (points represent a mean of 5 replicates). ● P.V.A.P. ▼ P.V.A.P. + plasticizer (volume fraction 0.10). ■ P.V.A.P. + plasticizer (volume fraction 0.18). ◆ P.V.A.P. + plasticizer (volume fraction 0.35).

mixture, T_{gp} and T_{gd} are those of the polymer and plasticizer respectively, α_p and α_d are the respective coefficients of volumetric expansion, whilst v_p is the volume fraction of the polymer in the mixture and v_d is that of the plasticizer.

This equation has been used in the present work to predict the glass transition temperatures of plasticized cellulose acetate phthalate and polyvinyl acetate phthalate. For this purpose, the value for the coefficient of thermal expansion has been taken, as in the case of Entwistle & Rowe (1979), to be $4.8 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$. The values of T_{gd} and α_d used for diethyl phthalate were those given by Kelley & Bueche (1961), namely $-65 \text{ }^\circ\text{C}$ and $1 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ respectively.

In each case, calculations have been based on experimental values of T_g for each unplasticized polymer; obtained using both techniques previously described. These calculated values, along with those determined experimentally, are shown in Figs 3 and 4.

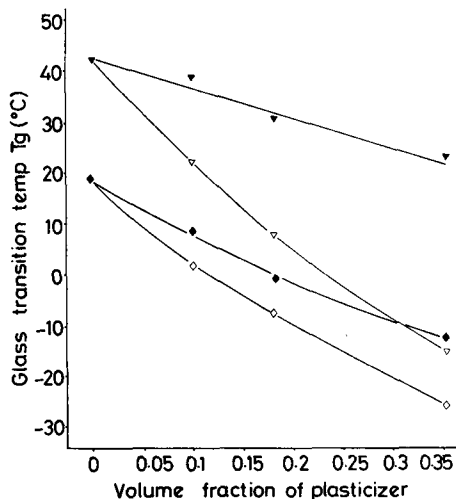


Fig. 3. Effect of plasticizer volume fraction on the T_g of polyvinyl acetate phthalate (P.V.A.P.) films. Differential scanning calorimetry method: \blacktriangledown Measured values. ∇ Calculated values. Evaluation of Brinell hardness method: \blacklozenge Measured values. \diamond Calculated values.

The calculated values can be seen to show reasonable correlation with those obtained experimentally, particularly in the case of cellulose acetate phthalate. The main disparities are found where the experimental values have been obtained by differential scanning calorimetry, particularly for polyvinyl acetate

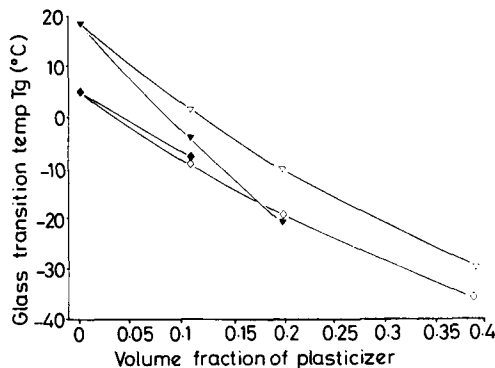


Fig. 4. Effect of plasticizer volume fraction on the T_g of cellulose acetate phthalate films. Differential scanning calorimetry method: \blacktriangledown Measured values. ∇ Calculated values. Evaluation of Brinell hardness method: \blacklozenge Measured values. \diamond Calculated values.

phthalate, which is not so surprising when one considers the difficulty encountered in determining the transition point for plasticized samples with this technique.

In conclusion, although difficulties arose in using the differential scanning calorimetric technique for determining values for the glass transition temperatures of the various formulations, the pneumatic microindentation hardness tester proved to be a most useful tool, yielding values which correlated closely with those predicted by a simple mixture-rule model. Obviously, the technique has its limitations, owing to the limited temperature range permitted by the apparatus, and thus would be unsuitable for determinations on, for example, hydroxypropyl methylcellulose, which has been shown by Entwistle & Rowe (1979) to have a T_g value of $177 \pm 1 \text{ }^\circ\text{C}$.

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