Thermal Analysis of the Glass Transition of Plasticized Poly(vinyl Chloride)

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Synopsis

Earlier studies by differential scanning calorimetry showed anomalous behavior of T_g with varying amounts of dioctyl phthalate, while by dynamic mechanical analysis 2 T_g's were found over a limited concentration range. In this study, two adjacent T_g's were found over the complete range of concentrations of dioctyl phthalate or dioctyl adipate, changing in relative contributions over the range. The results are shown to be consistent with the earlier work and to fit the Couchman model more closely than other models tested.

INTRODUCTION

Since the early 1950s, numerous equations have been proposed to relate the glass transition temperatures of homogeneous blends of a polymer with a second component to pure component properties.[1-6] These equations have ranged from totally empirical formulae to predictive theoretical treatments. The two most successful of the predictive equations have been proposed by Fox[2] and by Couchman.[5] Couchman's thermodynamic assessment of glass transitions, which relies on the continuity of mixture entropy at the glass transition (T_g), leads to the relationship:

$$\ln(T_g) = \frac{w_1 \Delta C_{p1} \ln(T_{g1}) + w_2 \Delta C_{p2} \ln(T_{g2})}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \tag{1}$$

where the ΔC_p terms represent the incremental changes in heat capacity which occur at the pure component glass transitions. w_1 and w_2 are the weight fractions of diluent and polymer, respectively. If the assumptions that $T_{g1}/T_{g2} \approx 1$ and $\Delta C_{p1} T_{g1} \approx \Delta C_{p2} T_{g2}$ hold, then the above equation reduces to the Fox equation or inverse rule of mixtures:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{2}$$

Equations (1) and (2) have been evaluated experimentally[5,7] and have been successful in predicting T_g's for both polymer/polymer and polymer/plasticizer blends.

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Recently Chow,[6] based on statistical mechanics and classical thermo-dynamics, has shown that

$$\ln(T_g/T_{g2}) = \beta[(1 - \theta) \ln(1 - \theta) + \theta \ln \theta] \qquad (3)$$

where β and θ are dimensionless parameters given by

$$\beta = zR/(M_m \Delta C_{p1}) \qquad (4)$$

$$\theta = M_m w_2/[zM_d(1 - w_2)] \qquad (5)$$

In eqs. (4) and (5), z is the lattice coordination number, R is the ideal gas constant, M_m is the molecular weight of the polymer repeating unit, and M_d is the molecular weight of the plasticizer. A value of $z = 2$ was used to predict T_g's from the Chow equation in this paper. Little experimental testing of the Chow equation has been reported.[6,8]

The experimental techniques which have been used to measure glass transition temperatures include volume dilatometry,[3] dynamic mechanical analysis,[9] differential thermal analysis, thermal optical analysis,[10] and differential scanning calorimetry (DSC). Recent improvements in DSC technology, especially through computerization, have made this technique more versatile than in the past.

While many investigators have reported a regular decrease in T_g with increasing diluent concentration[7,11] as predicted by eqs. (1)–(3), experimental data which do not follow this pattern exist. Blends exhibiting multiple glass transitions are common. Bair and Warren[12] have postulated that the two T_g's which they observed by DSC in poly(vinyl chloride) (PVC)/diisodecyl phthalate, PVC/tricresyl phosphate, and PVC/dioctyl azelate blends are attributable to two distinct glassy phases. The higher T_g is assigned to noncrystalline syndiotactic PVC sequences, whereas the lower temperature transition is assigned to the more easily solvated atactic chain segments. Bair and Warren also detected an unsolvated syndiotactic crystalline PVC phase from its crystalline vibrational spectrum. Their findings agree with those of Tabb and Koenig,[13] who confirmed by Fourier transform infrared spectroscopy that, in PVC/di(2-ethylhexyl) phthalate (DOP) systems, crystalline regions are unsolvated by plasticizer.

In other polymer blends, investigators have reported a single transition which exhibits an unusual sigmoidal dependence on composition.[8,9,14-17] Instead of a single, monotonically decreasing curve, the T_g vs. w_1 dependence appears to be composed of two sections which have different curvatures and intersect at a cusp. In their recent investigation of PVC/dimethylphthalate and PVC/di-n-propylphthalate blends, Scandola et al.[8] located a discontinuity in the T_g vs. w_1 curves of both systems near $w_1 = 0.4$. Fried et al.,[9] using the DSC technique, reported a similar sigmoidal dependence for PVC/di(2-ethylhexyl) adipate (DOA) and PVC/tri(2-ethylhexyl) trimellitate (TOTM) systems as well as suggesting that data reported by Brennan[18] showed a similar pattern for PVC/DOP blends. Dynamic mechanical analysis (DMA) of the Fried samples indicated that the apparently single, broad glass transitions observed from the DSC scans are the result of two separate

glass transitions ocurring in the same temperature range. The apparent sigmoidal dependence of the PVC/DOA and PVC/TOTM T_g vs. w_1 curves reflects the changes in the relative sizes and positions of the two overlapping transitions.

The purpose of this study is to investigate further the nature of glass transitions in blends of PVC with DOP and DOA by differential scanning calorimetry. Experimental values of T_g are compared with those predicted from eqs. (1)–(3) and with experimental findings from previous studies.

EXPERIMENTAL

Materials

The PVC resin used was GEON 121 supplied by the B.F. Goodrich Chemical Co. Commerical grades of DOP and DOA were obtained from Imperial Oil Ltd. and BASF Canada, respectively. Thermolite 340, a sulfur-containing organotin stabilizer, was obtained from M & T Chemicals, Inc.

Quantities of PVC in the order of 10 g and plasticizer were weighed to the nearest 0.1 g and were blended together. Approximately 10 mg of sample, weighed to the nearest 0.1 mg, was then encapsulated in Perkin-Elmer aluminum sample pans. Several samples were prepared both with and without Thermolite heat stabilizer in concentrations of 2 phr (parts per hundred resin). It was found that thermal degradation effects on the glass transitions were negligible at experimental conditions, so that the results reported are those of unstabilized samples.

Samples were conditioned by heating to 150°C in the Perkin-Elmer DSC under a helium purge, and annealing for 5 min to ensure fusion and intimate mixing of PVC and plasticizer. To erase any thermal history effects, the sample was then cooled below its glass transition region at 40°C/min, reheated to 150°C, and recooled below the T_g, both at 40°C/min.

Measurements

After conditioning, the DSC scans were performed at 40°C/min, starting at least 50°C below the transition onset and continuing well past the transition region. The temperature was calibrated at a point, using high purity n-octane with a fusion onset temperature of −57.6°C. Enthalpy was calibrated using the automatic ordinate calibration method outlined in the Perkin-Elmer manual.[19] The scanning auto zero accessory was used to optimize baseline linearity. Differential power vs. temperature plots were generated and rescaled using a Perkin-Elmer software package on the 3600 data station. This package also performed T_g and ΔC_p calculations.

RESULTS

Experimental values of ΔC_p were determined to be 0.266 J/g K for PVC, 0.672 J/g K for DOP, and 0.792 J/g K for DOA. These results are in reasonably close agreement with ΔC_p values of 0.309 J/g K for PVC, 0.607 J/g K for DOP, and 0.645 J/g K for DOA reported by Fried et al.[9]

Eleven PVC/DOP blends ranging from 5 parts plasticizer per hundred resin (phr) to 500 phr were examined. The glass transition temperatures for these blends and the pure components are plotted as a function of plasticizer weight fraction in Figure 1. Given as well in Figure 1 are the corresponding Couchman,[5] Fox,[2] and Chow[6] predictive curves.

As shown in Figure 1, T_g decreased with increasing weight fraction of DOP. Unlike the narrow glass transition ranges typical of pure components, the blend glass transition regions observed on the DSC scans were very broad, especially for the samples between 30 and 150 phr DOP. The 70 phr sample had the largest transition range, of about 80° C, between −60 and 20°C. As the concentration of DOP increased to 100 phr, it became apparent that this large transition region was the result of two overlapping glass transitions. While evidence of two glass transitions is present even in the 5 phr scan shown in Figure 2, the best evidence of two transitions can be seen in the 150 phr scan of Figure 3. The lower of the two glass transition temperatures for the 150 phr sample occurs near −60°C, while the higher T_g is near −10°C. When analyzed as a single transition, however, a value of −55.26°C is obtained. This is the value plotted in Figure 1.

Ten PVC/DOA blends, ranging from 5 to 400 phr DOA, were investigated. On each DSC scan, there was evidence of two glass transitions. The overlap between the two T_g's, however, made exact measurement of their individual locations difficult in most instances. As a result, midpoint temperature values for the region containing the two transitions were measured. These values are plotted in Figure 4 as a function of plasticizer weight fraction. DSC scans for the 5 and 150 phr samples are given in Figures 5 and 6, respectively, in order to show the presence of the two T_g's even at the extremes of the concentration ranges.
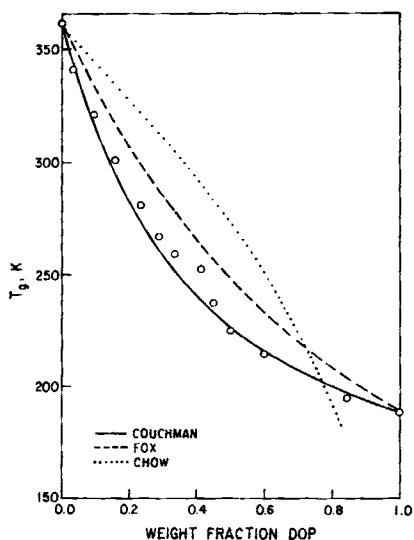

Fig. 1. Overall glass transition temperatures of poly(vinyl chloride) plasticized with dioctyl phthalate of various weight fractions. The curves represent the mathematical models of Couchman[5] (—), Fox[2] (- - -), and Chow[6] (···).
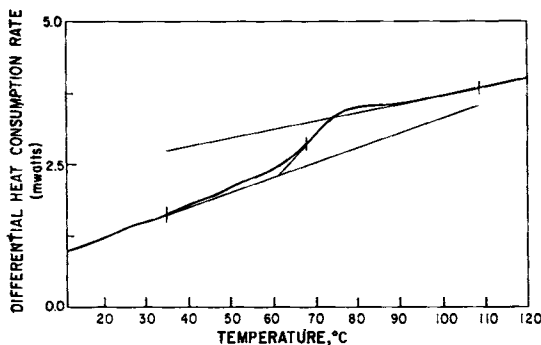
Fig. 2. Thermogram of poly(vinyl chloride) containing 5 parts (phr) dioctyl phthalate. Scanning rate is 40°C/min.

DISCUSSION OF RESULTS

The results for the PVC/DOP blends investigated are similar to those reported by Brennan.[18] Slight differences in T_g values may be attributed to an uncertainty of approximately 2°C in the transitions having a broad range. As well, the difference in the T_g's of the pure PVC resins suggests that a different molecular weight polymer may have been used in the Brennan study. Two distinct glass transitions were not, however, reported by Brennan for samples between 80 and 200 phr. Instead, one broad transition had been noted. It is reasonable to conclude that two glass transitions may well have occurred in the PVC/DOP blends investigated. A smaller transition could easily be obscured by a nearby larger transition. Dynamic mechanical analysis or thermal optical analysis should be used to investigate these apparently single T_g's.

From Figure 1 it is evident that, of the three predictive equations shown, the Couchman curve provides the best fit of the data. The Fox curve T_g is consistently above the actual value and the Chow curve is concave downward, whereas the experimental data follow a concave upward curve. The reason for the deviation of the data from the Fox curve is that the two pure component T_g's differ by over 100 K. Even the Couchman curve, however, does not predict the cusp exhibited by the data near 40 wt % plasticizer.
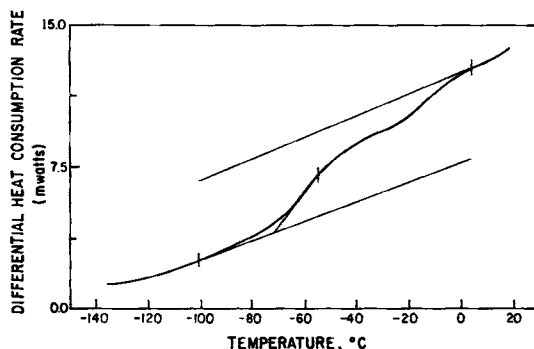

Fig. 3. Thermogram of poly(vinyl chloride) containing 150 parts (phr) dioctylphthalate. Scanning rate is 40°C/min.
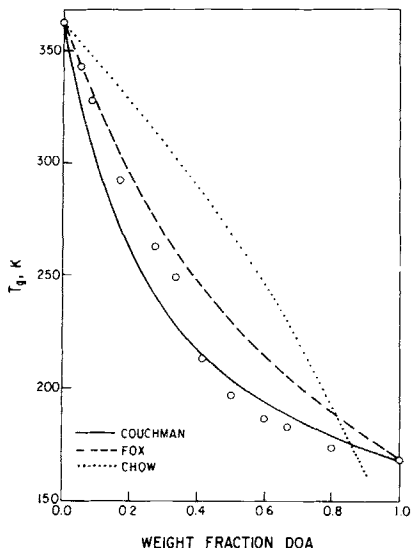
Fig. 4. Overall glass transition temperatures of poly(vinyl chloride) plasticized with dioctyl adipate of various weight fractions. The curves represent the mathematical models of Couchman[5] (—), Fox[2] (- - -), and Chow[6] (···).

The results obtained for the PVC/DOA blends differ from those reported by Fried et al. in that only one T_g was previously indicated by DSC scans. The midpoint T_g values of Figure 4, however, agree with the Fried findings, within experimental error. Both sets of data show a sigmoidal dependence of the midpoint T_g on the composition. Fried et al. attributed this sigmoidal dependence to the measurement of two overlapping glass transitions which could not be differentiated by DSC, but which were observed by DMA. The two glass transitions observed by DSC in the present study support this hypothesis. Fried reasoned that, from 0 to 40% plasticizer, the upper T_g was dominant and that, from 40 to 100 DOA, the lower T_g was dominant. As a result, samples containing less than 40% plasticizer exhibited T_g's higher than predicted by Couchman, and samples containing higher concentrations of DOA gave T_g's lower than predicted.

The probable reason that two T_g's were observed in the present study is that the present system allows for improved temperature control and au-
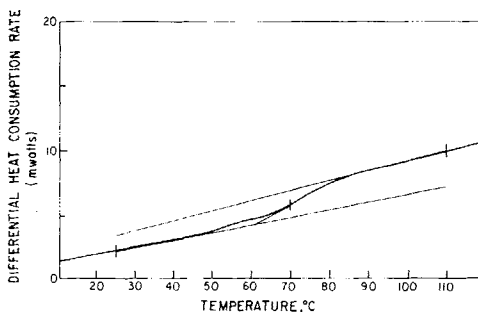

Fig. 5. Thermogram of poly(vinyl chloride) containing 5 parts (phr) dioctyl adipate. Scanning rate is 40°C/min.
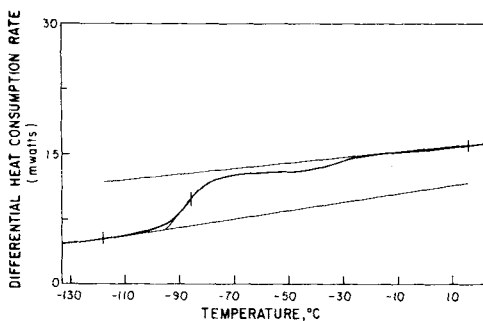
Fig. 6. Thermogram of poly(vinyl chloride) containing 150 parts (phr) dioctyl adipate. Scanning rate is 40°C/min.

tomatic data rescaling not possible with earlier analysis systems. These improvements enhanced the separation between the two transitions.

The occurrence of two glass transitions in PVC/DOP and PVC/DOA blends suggests that two glassy phases have been formed. Bair and Warren have attributed similar behavior in other PVC/plasticizer systems to syndiotactic·and atactic regions in the polymer matrix, which accept plasticizer to different degrees. This postulate would explain the two transitions observed in the blends investigated in this study.

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