Composition dependence of the glass transition temperature of polymer–diluent systems: 1. Experimental evidence of a dual behaviour in plasticized PVC

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The glass transitions of six PVC–diluent systems have been studied using differential scanning calorimetry (d.s.c.). The diluents were: di-(methyl, ethyl, n-propyl, n-butyl)-phthalate, n-butylacetate and tritolylphosphate. A large number of compositions have been examined over the whole concentration range, from pure polymer to pure diluent. For all systems but PVC–butylacetate, the T_g/concentration dependence shows a 'cusp' in the vicinity of 40% diluent content. The width of the glass transition increases in the concentration range of the 'cusp' reaching values as high as 50°C. PVC–butylacetate mixtures show two glass transitions, both decreasing with increasing diluent content, in a narrow composition range. For all systems two T_g/concentration dependencies can be identified: the fast decrease of the polymer T_g caused by plasticizer addition and the much slower increase of the diluent T_g due to the presence of the dissolved polymer molecules. Also the specific heat increment at $T_g(\Delta C_p)$ shows a dual concentration dependence, suggesting that it is the component present 'in excess' that dictates the ΔC_p/composition behaviour.

(Keywords: poly(vinyl chloride); glass transition; plasticizers; binary mixtures; differential scanning calorimetry)

INTRODUCTION

The decrease in the glass transition temperature of polymers (T_g) brought about by the presence of low molecular weight substances has been studied mainly in the low to moderate diluent content range, i.e., the range of interest of the plasticization process[1]. The compositional dependence of T_g has been commonly described by more or less empirical equations that predict a regular decrease of the glass transition temperature of the polymer–diluent mixtures from the polymer T_{g2} to the diluent T_{g1}. Such relationships are usually considered to fit satisfactorily the experimental T_g data; it has to be pointed out, however, that often the T_g value of the pure diluent is unknown and only a narrow composition range is experimentally explored.

A few scattered studies[2-4] have reported evidence of an apparent 'anomaly' in the T_g/concentration dependence, that seems to be composed of two monotonically decreasing sections rather than of a single regularly decreasing curve connecting the pure components' T_g's. Recent papers by the present authors[5-7] concerning a number of poly(vinyl chloride)–diluent systems have shown that the above-mentioned 'anomaly', i.e., a change of curvature in the central composition region of the T_g/concentration dependence, seems to be a common feature of the systems examined.

The present paper reports and compares experimental results relative to six PVC–diluent systems, focussing on the glass transition of the mixtures examined over the whole concentration range, from pure polymer to pure diluent.

EXPERIMENTAL

Di-methylphthalate (DMP), di-ethylphthalate (DEP), di-n-propylphthalate (DPP) and di-n-butylphthalate (DBP) (purity >99%), were synthesized and characterized as previously reported[5]. Tritolylphosphate (TTP) and n-butylacetate (BuAc) were purchased from Fluka. Commercial poly(vinyl chloride) (PVC), suspension polymerized at 60°C, was mixed at 90°C for 30 min with different amounts of diluent. This procedure was applied to all diluents but BuAc, due to the extremely high volatility of this substance. The PVC–BuAc mixtures were prepared directly in the aluminium d.s.c. pans, by adding appropriate amounts of BuAc to weighed amounts of PVC, sealing and weighing the sealed pans. After heat treatment, to ensure polymer–diluent mixing (10 min at 90°C in the calorimeter were found to be sufficient), the pans were reweighed to check for possible weight loss.

The temperature dependence of the heat capacity of the pure components and mixtures was determiend by means of a Differential Scanning Calorimeter DSC-2 equipped with a scanning autozero for baseline linearization and a liquid nitrogen subambient accessory. The d.s.c. curves were recorded at a scanning rate of 20 K/min, over a temperature range from 100 to 400 K. In the first scan, each mixture was heated to 50°C above its glass transition temperature and then rapidly cooled to a low temperature. At least three samples (four scans each) were examined for all mixtures. Excellent reproducibility of the second and subsequent scans was obtained. Owing to the width of the range explored, the temperature was

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calibrated with four different high purity standards: lauric acid, benzene, n-octane and n-heptane. The glass transition was quantitatively described by means of three parameters: (1) the glass transition temperature T_g, determined as the intercept between the extrapolation of the baseline preceding the transition and the steepest tangent to the step; (2) the glass transition width on the temperature scale ΔT_g, as defined by Fried[8]; (3) the specific heat increment at T_g, ΔC_p.

As regards the pure diluents, whereas DMP and BuAc easily vitrify on cooling but are able to crystallize and melt when heated above their respective T_g's, the other diluents examined do not crystallize and melt in similar conditions. When present in the mixtures, DMP and BuAc did not crystallize on heating except if the glass transition of the mixture was lower than the pertinent crystallization/melting range. The parameters of the glass transition of the pure components are collected in *Table 1*. Throughout the paper, subscripts 1 and 2 refer to diluent and polymer respectively and w_1 is the diluent weight fraction. Dynamic mechanical measurements were performed with a Dynamic Mechanical Thermal Analyser (Polymer Laboratories Ltd.) at a frequency of 1 Hz and a heating rate of 2°C/min on PVC–DBP mixtures. While most of the samples employed were cut from sheets calendered at 150°C, a strip of glass fibre filter paper (Whatman GF/C) was used as an impregnating support for pure DBP and the highly diluted $w_1 = 0.9$ PVC–DBP mixture.

RESULTS AND DISCUSSION

As an example representative of most of the systems examined, *Figure 1* shows the calorimetric curves for PVC–DBP mixtures at increasing diluent content. It is clearly seen that the specific heat increment that characterizes the polymer glass transition is shifted to lower temperatures by increasing amounts of diluent and that the transition broadens in the central composition range. Interestingly, the glass transition of the pure diluent shows the so-called enthalpy relaxation peak, a well known phenomenon connected with the thermal history of the sample[9]. Phase separation of pure diluent at high diluent contents ($w_1 > 0.7$) is peculiar to two of the systems investigated, PVC–DMP and PVC–TTP. Over the composition range of complete miscibility, a thermal behaviour analogous to that shown in *Figure 1*, i.e., a single glass transition whose temperature decreases with increasing diluent content is observed for all the systems examined but PVC–BuAc, this latter system showing two glass transitions in a narrow range of intermediate concentrations.

The calorimetric curves of selected PVC–BuAc mixtures are shown in *Figures 2* and *3*; two glass transitions are clearly observed for the 27, 32 and 37% BuAc samples. In order to identify these transitions, the one at higher temperature will be indicated as T_g^u (upper), the lower one as T_g^l (lower). At diluent contents $\geq 46\%$, crystallization of some BuAc during the heating scan at $T > T_g^l$ prevents the detection, if present, of T_g^u.

Table 1 Glass transition parameters of PVC and diluents

Substance	T_g (K)	ΔC_p (J/g K)	ΔT_g (K)
PVC	355	0.27	12
Tritolylphosphate (TTP)	216	0.41	4
Dimethylphthalate (DMP)	194	0.50	5
Diethylphthalate (DEP)	183	0.52	4
Di-n-propylphthalate (DPP)	180	0.52	5
Di-n-butylphthalate (DBP)	178	0.54	4
n-Butylacetate (BuAc)	118	0.84	2

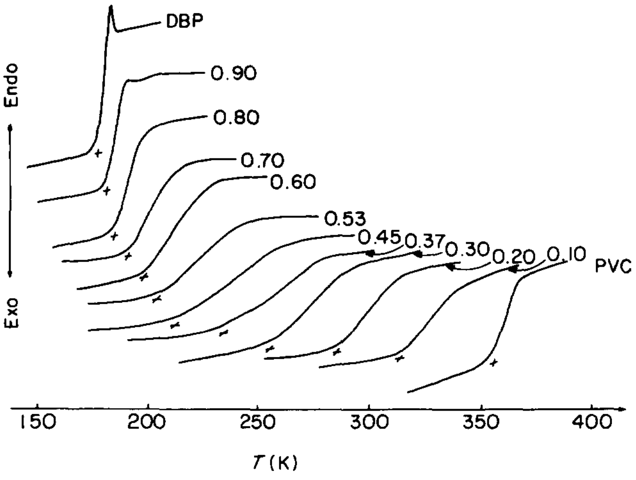

Figure 1 Calorimetric curves for PVC–DBP mixtures with different DBP weight fractions

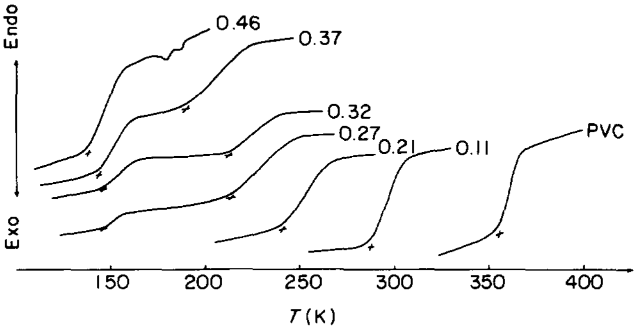

Figure 2 Calorimetric curves for PVC–BuAc mixtures with BuAc weight fraction ≤ 0.46

The concentration dependence of the glass transition temperature for the systems PVC–DBP and PVC–BuAc is shown in *Figure 4*. The plot of T_g vs. w_1 for PVC–DBP evidences a feature that was not immediately apparent from the calorimetric curves of *Figure 1*: an unexpected fast decrease of T_g appears in the intermediate concentration range, followed by a much slower temperature decrease towards the diluent T_{g1}. This behaviour is common to all systems where a single glass transition is found and corresponds to the previously reported 'cusp' in the T_g/concentration dependence[2,3]. In order to visualize this feature, the experimental T_g data are compared in *Figure 4* with the predictions of the following equation (solid curves):

$$\ln(T_g/T_{g2}) = [\ln(T_{g1}/T_{g2})]/[1 + (kw_2/w_1)] \qquad (1)$$

where k is an adjustable parameter responsible of the curvature of the T_g/composition dependence, chosen to give the best fit to the experimental T_g data in the composition range of polymer-rich mixtures.

It is interesting to note that, in the case of PVC–BuAc, equation (1) satisfactorily fits not only the experimental T_g values in the range of low diluent concentrations where a single glass transition is observed, but also the values of

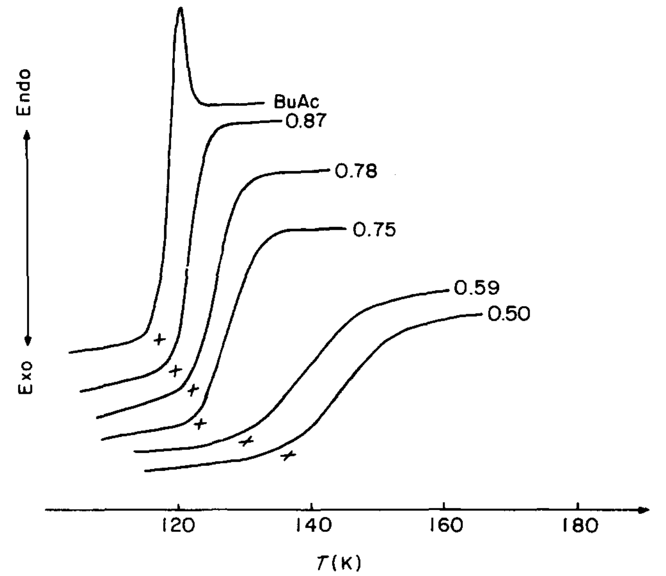

Figure 3 Calorimetric curves for PVC–BuAc mixtures with BuAc weight fraction $\geqslant 0.50$

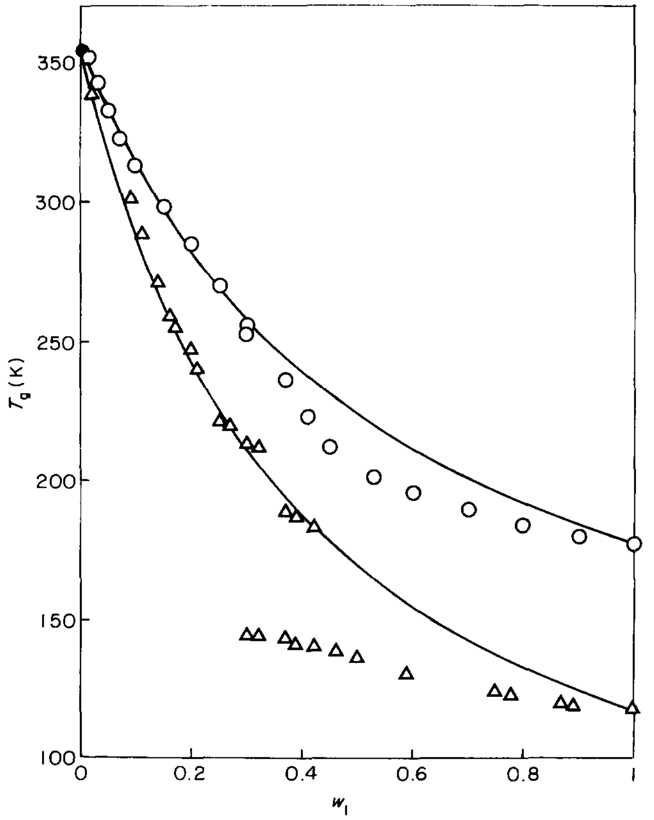

Figure 4 Composition dependence of the glass transition of the systems: (△) PVC–BuAc; (○) PVC–DBP. Curves: equation (1)

the upper transition, when two T_g's are revealed. Conversely, the lower glass transition follows a totally different concentration dependence, showing a much less steep approach to the glass transition of pure BuAc with increasing w_1.

In the intermediate concentration range ($0.3 < w_1 < 0.6$) the glass transition of all single T_g systems very much broadens (see *Figure 1*), reaching ΔT_g values as high as 50°C (see *Table 1* for ΔT_g's of the pure components). Interestingly, when two glass transitions are found in PVC–BuAc mixtures, the sum of ΔT_g^u and ΔT_g^l equals the maximum ΔT_g for the other systems.

The dual dependence of T_g on composition, relative to mixtures either rich in polymer or in diluent, is parallelled by an analogous dual behaviour of the specific heat increment at the transition (ΔC_p), as shown in *Figure 5*. In the upper part of *Figure 5* ΔC_p is plotted as a function of concentration for all six PVC–diluent systems examined. Some ΔC_p data for PVC–BuAc are omitted due to poor definition of the specific heat increment when two glass transitions are present. Though the evaluation of ΔC_p is inevitably affected by uncertainties due to graphical extrapolation, especially for broad transitions, the data reported in *Figure 5* clearly show a common trend. In the range of low w_1, the common polymeric component seems to determine the ΔC_p of the mixture, rather independently of the nature of the low molecular weight component. On the contrary, in the composition range of diluent-rich mixtures, the ΔC_p values seem to tend individually to ΔC_p of the corresponding pure diluent. It is quite clear that all systems show negative deviations from a simple additivity rule such as $\Delta C_{p,mix} = w_1 \Delta C_{p,1} + w_2 \Delta C_{p,2}$, the largest deviations appearing in the composition range where the T_g values change their dependence on concentration.

The lower part of *Figure 5* shows a ΔC_p vs. composition plot for three binary systems having a common diluent (TTP) and different high T_g components: PVC, polystyrene[10] and phenolphthalein (a low molecular weight substance with a high glass transition temperature[6]). Interestingly enough, the ΔC_p vs. w_1

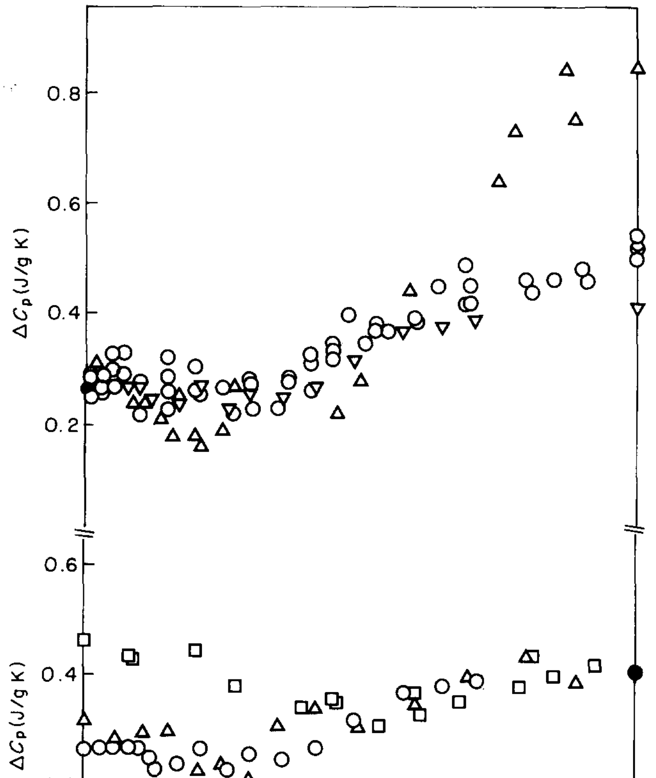

Figure 5 Specific heat increment (ΔC_p) as a function of composition. Upper section: mixtures of PVC with (○) phthalates, (▽) TTP, (△) BuAc. Lower section: mixtures of TTP with: (△) polystyrene, (○) PVC, (□) phenolphthalein

behaviour of these systems is quite similar in the range of diluent-rich mixtures, irrespective of the nature of the high T_g component. It appears therefore that the compositional dependence of ΔC_p is dictated by the component present 'in excess' in the mixture (i.e., component 2 when $0<w_1<0.4$ and component 1 when $0.6<w_1<1$).

In the light of these considerations it can be suggested that the upper decreasing section of the T_g/w_1 curves of *Figure 4* represents the decrease of the polymer glass transition temperature caused by plasticizer addition, while the lower section reflects the changes of the glass transition of the diluent due to the presence of dissolved polymer molecules.

As already pointed out, only the PVC–BuAc system is presently found to show a true discontinuity in the T_g/concentration dependence, possibly due to the extremely large difference between the T_g's of polymer and diluent (237 K). Analogously, it might be inferred that in the remaining PVC–diluent systems the very broad glass transition at intermediate concentration could be due to two overlapping phenomena quite close on the temperature scale, as recently demonstrated by these authors for the system polystyrene–TTP[10]. For this latter system the presence of heterogeneities such as phase separation was ruled out, since both upper and lower transitions follow their own concentration dependence; the same argumentation applies to the present PVC–diluent systems.

In the study of polystyrene–TTP mixtures the dynamic mechanical technique was found to be a useful integration to calorimetry. Application of the dynamic mechanical technique to one of our systems, PVC–DBP, yields the curves shown in *Figure 6*. Unlike the PS–TTP system[10], each PVC–DBP mixture shows a single and rather symmetrical absorption peak related to the glass transition, whose intensity and width varies with composition. Correspondingly, the dynamic storage modulus E' shows a drop of about three orders of magnitude whose steepness again depends on the composition of the mixture, being more abrupt for pure components than for mixtures. A relationship between modulus drop and width of the transition peak is found: the broader the absorption peak, the more gradual the modulus decrease. It is interesting to note that the maximum width of the relaxation peak is found in the concentration range where the calorimetic glass transition is broadest (*Figure 1*) and the system considered shows a change of curvature in the compositional dependence of T_g (*Figure 4*). Also the dependence on w_1 of the temperature of the dynamic mechanical tan δ peak shows a small but clear change of curvature in the composition range of the 'cusp'.

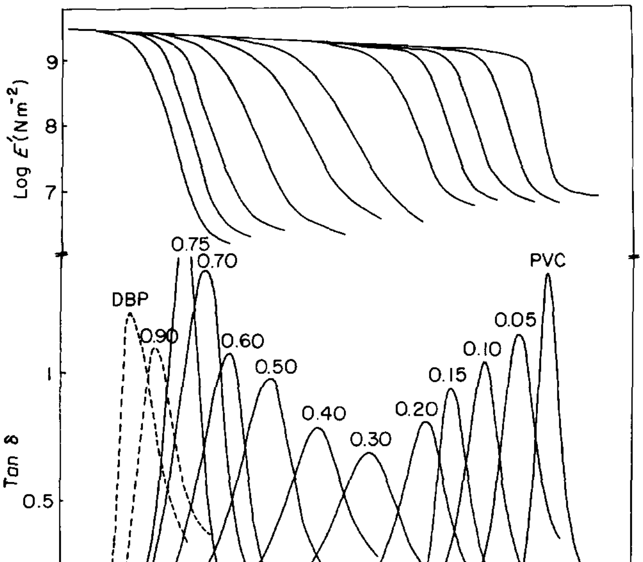

Figure 6 Dynamic mechanical spectra of PVC with different amounts of DBP (1 Hz, 2 deg/min). Broken lines: samples supported on glass fibre paper

Observation of the inability of the dynamic mechanical measurements to provide evidence for possible overlapping transitions in the present case suggests that, besides the rather obvious parameters $T_{g2}-T_{g1}$ (compare the two systems in *Figure 4*), additional characteristics of the polymer and/or the diluent are also important in the detection of two individual glass transitions. It is likely that one of the most relevant parameters is the width of the distribution of relaxation times of the polymer at the glass transition. In this connection we emphasize the rather different morphological characteristics of polystyrene and PVC, the former being a totally amorphous polymer, the latter a partially crystalline and morphologically complex one[11]. Due to the presence of microcrystallites, the relaxation peak of PVC appears to be rather broad when compared with that of polystyrene. When poly(vinyl chloride) is mixed with diluents this broadening of the distribution of relaxation times is likely to persist, yielding, as a consequence, less sharp transitions and therefore an inherent difficulty in detecting separately the mobilization of the diluent hindered by the presence of dissolved polymer and the cooperative mobilization of the polymer segments promoted by the presence of the diluent.

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