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Comparative Study of Diluent Effects on the Glass Transition of Polyvinylchloride and Phenolphthalein

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Summary

Some binary polymer-diluent systems, previously studied by the Authors (SCANDOLA et al., 1982), showed an "unusual T_g-concentration dependence". In order to investigate the relevance of the polymeric nature of the high-T_g component in determining this "anomaly", two series of mixtures having the same diluent (di-n-Butylphthalate or Tricresylphosphate) and, as the high-T_g component, either a polymer (PVC) or a low-molecular weight substance (Phenolphthalein), have been examined. A discontinuity is found, as expected, in the "polymeric" systems PVC-di-n-Butylphthalate andPVC-Tricresylphosphate, as well as in Phenolphthalein-di-n-Butylphthalate mixtures where, however, the deviations from the calculated T_g-composition curve are much less marked. It is concluded that the presence of a polymer is not a necessary requirement for the occurrence of the above mentioned "anomaly".

Introduction

In a recent paper (SCANDOLA et al., 1982), concerning the dependence of the glass transition temperature T_g on concentration for plasticized Polyvinylchloride, evidence of a sudden change of curvature at a critical plasticizer concentration was reported. In other words, instead of a single regularly decreasing curve connecting the pure components T_g's, the compositional variation of the glass transition temperature seems to be made of two monotonically decreasing sections having different curvatures and whose intersection forms a cusp. Besides the systems PVC-di-Methylphthalate and PVC-di-n-Propylphthalate studied by the Authors (SCANDOLA et al., 1982), a few more polymer-diluent systems presenting a similar singularity have been reported in the literature (ADACHI et al., 1975; BRAUN and KOVACS, 1965; FRIED and LAI, 1982; RIANDE et al., 1975). In other binary systems the occurrence of such a peculiar behaviour is not easily revealed owing to the small amount of data commonly available over the entire composition range, i.e. from pure polymer to pure diluent.

No comprehensive interpretation of the complex T_g vs. composition behaviour has yet been given, apart from a free-volume treatment by BRAUN and KOVACS (1965), which however does not apply satisfactorily to the PVC-diluent systems recently examined by the present Authors. One of the important points to be investigated is the role played by the component whose glass transition temperature is depressed by addition of the diluent. Usually such a substance is a high polymer, whose long-chain molecules may be fully or partially responsible of the above mentioned peculiar behaviour. By substituting the polymer with a low molecular weight substance having a sufficiently high T_g, one can try to clarify the point. In this paper we compare the behaviour of binary systems having the same low-T_g component (di-n-Butylphthalate or Tricresylphosphate) and, as the high-T_g component in the mixture, either a polymer (Polyvinylchloride) or another low molecular weight substance (Phenolphthalein). Since the glass transition temperature of Phenolphthalein is very close to that of PVC, the selected systems provide a very attractive test of the occurrence of the change of curvature in the T_g-composition dependence in systems of widely different molecular dimensions.

Experimental

Di-n-Butylphthalate (DBP, purity>99%) was synthetized and characterized as previously reported (SCANDOLA et al.,1982). Phenolphthalein (purity>99%) was purchased from C. Erba and Tricresylphosphate (TCP, mixture of isomers) from Fluka. Commercial Polyvinylchloride (PVC, polymerized in suspension at 60°C) was mixed with different amounts of DBP or TCP at 90°C for 30 min. The low-diluent content mixtures, whenever necessary, were subjected to short treatments at a slightly higher temperature in order to insure complete mixing. The mixtures of Phenolphthalein with DBP or TCP were prepared as follows: the appropriate amounts of crystalline Phenolphthalein and DBP or TCP were sealed in the DSC pans and a first run in the calorimeter up to 20°C above the melting point of Phenolphthalein was carried out followed by rapid cooling to room temperature. This procedure - also used to vitrify pure Phenolphthalein - yielded homogeneous mixtures that vitrified on cooling and crystallized neither on storage at room temperature nor in the testing conditions employed.

The temperature dependence of the heat capacity of the pure components and mixtures was determined by means of a Differential Scanning Calorimeter DSC-2 equipped with a Scanning Autozero for baseline linearization and a Liquid Nitrogen Subambient Accessory. DSC curves were recorded over a temperature range from 100 to 390°K at a scanning rate of 20°K/min. Excellent reproducibility

TABLE 1

Calorimetric Parameters for the Components of the Mixtures

Substance	T_g (°K)	Δc_p (J/g°K)	ΔT_g (°K)	$T_g \cdot \Delta c_p$ (J/g)
PVC	355	0.27	12	96
Phenolphthalein	362	0.46	6	167
DBP	168	0.54	4	96
TCP	216	0.40	4	86

of the second and subsequent runs was obtained. Owing to the width of the range explored, the temperature was calibrated with three different high purity standards: lauric acid, benzene and n-octane. The glass transition was quantitatively described by means of three parameters: 1) the glass transition temperature T_g, determined by the method of the baseline deviation (unless otherwise specified); 2) the glass transition width on the temperature scale ΔT_g, as defined by FRIED et al.(1978); 3) the specific heat increment at T_g, Δc_p. The calorimetric data for the pure components are collected in TABLE 1. Throughout the paper, subscripts 1 and 2 refer to the low- and high-T_g component of the mixture respectively.

Results and Discussion

All the mixtures examined show a single glass transition at a temperature which decreases with increasing diluent content; no evidence of phase separation is found over the whole range of concentration.

Fig. 1 shows the experimental results for the PVC-DBP system, together with a calculated T_g vs. composition dependence. From the lower plot in the Figure, it is readily apparent that an abrupt change of curvature, quite similar to that previously found by the Authors (SCANDOLA et al.,1982) for other PVC-phthalate systems, occurs in the range $0.3<\phi_1<0.4$. The sudden increase of slope is evidenced by comparison with the drawn curve (solid line), calculated by means of the following equation:

$$T_g = \frac{\phi_1 T_{g1} + K\,\phi_2 T_{g2}}{\phi_1 + K\,\phi_2} \qquad (1)$$

where ϕ_1 and ϕ_2 are the volume fractions of the components at the glass transition temperature of the mixtures, calculated by assuming volume additivity.

The above equation is a generalized version of empirical equations commonly used to describe the variation of T_g with composition. In fact, depending on the concentration variable used (volume, weight or mole fraction) and on the particular significance attached to the parameter K (i.e. $K= \Delta\alpha_2/\Delta\alpha_1$ or $K= \Delta c_{p2}/\Delta c_{p1}$ or $K= T_{g1}/T_{g2}$), equation 1 corresponds to well known empirical relationships (KELLEY and BUECHE, 1961; GORDON et al., 1977; FOX, 1956). In the present paper, K has been used as an adjustable parameter to give the best fit to the experimental results in the range from the pure high-T_g component up to the critical concentration where the cusp singularity occurs.

It is well known that the width of the glass transition region on the temperature scale ΔT_g is larger for mixtures than for pure substances. An investigation of the variation of ΔT_g with composition may provide useful information on the glass transition of mixed systems. From Fig. 2, where the average values of ΔT_g and Δc_p for the PVC-DBP system are shown, it is readily apparent that ΔT_g for all mixtures is always larger than that of the pure components (12^oK and 4^oK for PVC and DBP respectively) and reaches a maximum value $\Delta T_g = 48^oK$ in the central concentration region.

As already mentioned in the experimental section, the values of T_g have been determined by the method of the baseline deviation, owing to the excellent reproducibility of the results obtained by this method over the whole range of concentration. Nevertheless, examination of the ΔT_g data for PVC-DBP may suggest that the alternative determination of T_g as "mid-step" or "inflection" temperature would probably yield values variously influenced by the broadness of the transition, i.e. not uniformly higher than the ones shown in the lower plot of Fig. 1. In order to ascertain whether the peculiar T_g vs. composition behaviour described above is a characteristic feature of the systems examined rather than an artifact connected with the graphical method employed, T_g values were also obtained by the "inflection point" method described by GRIFFITHS and MAISEY (1976). The results, plotted in the upper part of Fig. 1, show again a change of curvature in the dependence of T_g on concentration, thus confirming the existence of the cusp as a real feature of the PVC-DBP system.

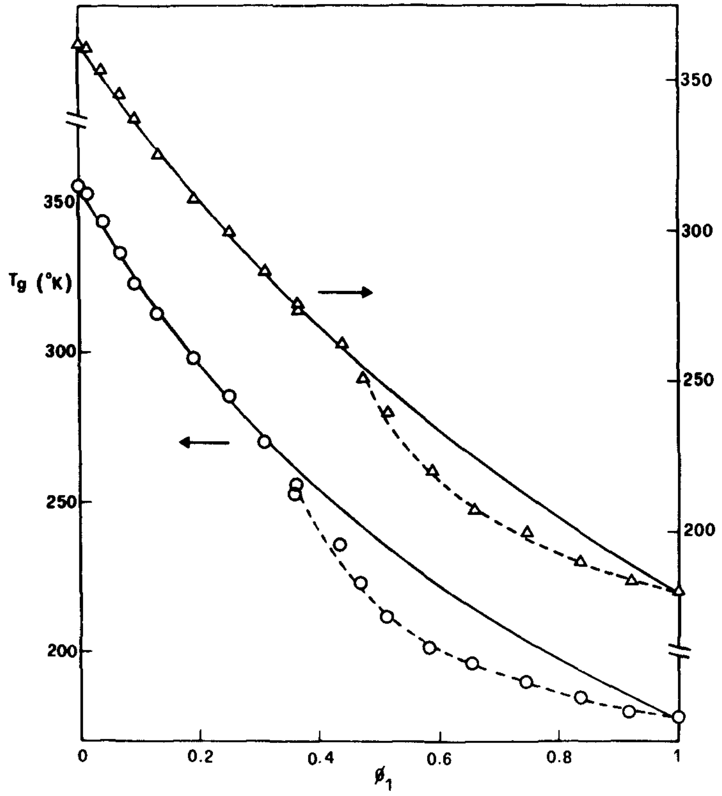

Fig. 1. Glass transition temperature of PVC-DBP mixtures as a function of the diluent volume fraction ϕ_1: ○:T_g from baseline deviation; △:T_g, "inflection point". ———: Equation 1; - - - - : drawn through the experimental points.

Both solid lines of Fig. 1 have been calculated by means of equation 1 by adjustement of the "curvature parameter" K for the best fit to the experimental results. The K values used are as follows: K= 0.500 for the "baseline deviation" T_g and K= 0.625

for the "inflection point" T_g. It is worthy of note that the former value exactly corresponds to the $\Delta c_{p2}/\Delta c_{p1}$ ratio for the system PVC-DBP, so that equation 1 becomes identical to the equation derived by GORDON et al. (1977) on the assumption that, near T_g, Δc_p= const./T. Inspection of the calorimetric values of Table 1 shows indeed that, for this particular system, $T_{g1}\cdot\Delta c_{p1}= T_{g2}\cdot\Delta c_{p2}$.

Turning now to Phenolphthalein-DBP, i.e. to the corresponding binary low molecular weight system, the glass transition temperatures of the mixtures are shown in Fig. 3. The solid curve drawn in the figure has been calculated by means of an equation formally identical to equation 1, but containing the composition variable appropriate to mixtures of low molecular weight substances:

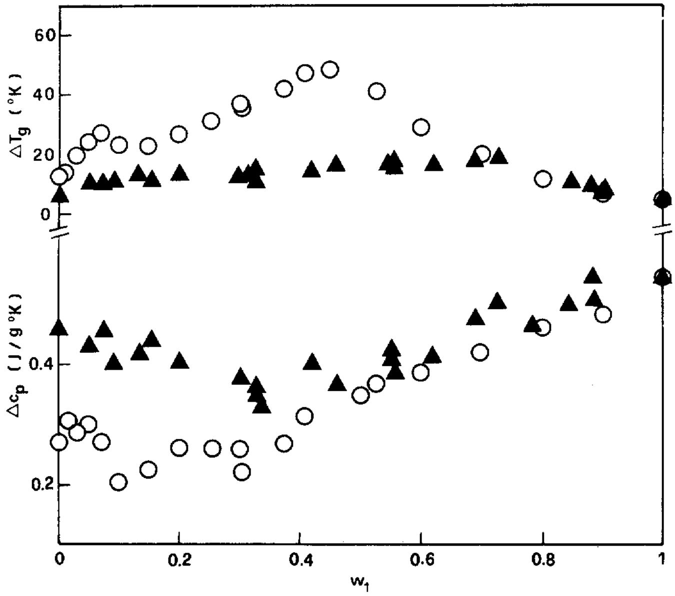

Fig. 2. Width of the glass transition region (ΔT_g) and specific heat increment at T_g (Δc_p), as a function of diluent weight fraction w_1 for the systems: ○: PVC-DBP and ▲ : Phenolphthalein-DBP.

$$T_g = \frac{x_1\, T_{g1} + K\, x_2\, T_{g2}}{x_1 + K\, x_2} \qquad (2)$$

where x_1 and x_2 are the molar fractions of DBP and Phenolphthalein respectively. In this instance, the value of the adjustable parameter (K= 0.540) has no correlation with the ratio of the specific heat increments of the pure components ($\Delta c_{p2}/\Delta c_{p1}$= 0.85). This is in keeping with the large difference in the $\Delta c_p\cdot T_g$ values reported in Table 1 for the two pure substances. The high value (167 J/g) of the product $\Delta c_p\cdot T_g$ for Phenolphthalein is not surprising, since increasing values with increasing T_g, up to

$\Delta c_p \cdot T_g$= 200 J/g for glucose, are reported in the literature (BOYER, 1973) for organic compounds containing hydroxyl groups.

The results of Fig. 3 show that, at high DBP contents, also the Phenolphthalein-DBP mixtures exhibit T_g values lower than the calculated ones. Though this deviation is less marked than that previously found for polymer-diluent systems, it has to be pointed out that no single curve in the form of equation 2 is able to fit the experimental data over the whole concentration range. The best fit is given by the solid curve and all the experimental data at high dilutions ($0.7<x_1<1$) lay below it. Even though the difference between experimental and calculated T_g values in this composition range is of the order of the scatter of the results at low x_1, the absence of any random scatter about the curve at high x_1 leads to the conclusion that the trend is significant. In other words, also for this particular system composed by two low molecular weight substances there is an indication of a curvature change in the dependence of the glass transition temperature on composition, at high dilutions.

As regards the glass transition parameters ΔT_g and Δc_p for Phenolphthalein-DBP mixtures, they can be directly compared in Fig. 2 with the same parameters for the system PVC-DBP. The most striking - though not surprising - feature is that the broadening of the glass transition region in the central composition range is strongly reduced ($\Delta T_g<20^oK$) when the high-T_g component is a low molecular weight substance instead of a polymer ($\Delta T_g \simeq 50^oK$). In addition, the largest ΔT_g values are reached in concentration regions which correspond in both cases to the composition range where the change of curvature in the T_g-composition dependence is found. Taking into account the Δc_p variations with composition, it has to be pointed out that in both systems Δc_p does not follow a linear additivity relationship such as: $\Delta c_{pmix} = w_1\Delta c_{p1} + w_2\Delta c_{p2}$, the heat capacity increments of the mixtures being always lower than those calculated by means of this equation. Moreover, from about 50% DBP up to the pure diluent, the Δc_p values increase towards the value of pure DBP in a very similar way. This observation suggests that the common low-T_g component - when present in excess - determines the Δc_p vs. composition behaviour irrespective of the polymeric or low molecular weight character of the high-T_g component.

On the basis of the above results it is reasonable to assume that the change of curvature in the dependence of T_g on composition is not an exclusive peculiarity of plasticized polymeric systems.

A further point to be investigated is the relevance of the difference between the pure components T_g's ($T_{g2} - T_{g1}$) in determining the deviation of the T_g values of some mixtures from the theoretical predictions. To this purpose, we have considered two different systems, having TCP (whose T_g is 40^oK higher than that of DBP) as the common low-T_g component and either PVC or Phenolphthalein as high-T_g component. These two systems differ from the previous ones by a reduced value of $T_{g2} - T_{g1}$ and they provide a useful means of evaluation of the influence of this parameter on the T_g vs. composition behaviour.

The experimental T_g data for Phenolphthalein-TCP are shown in Fig. 3, together with the results for Phenolphthalein-DBP previously discussed. The T_g of the mixtures monotonically decreases with increasing TCP content over the whole range of concentrations and, interestingly, no evidence of a change of

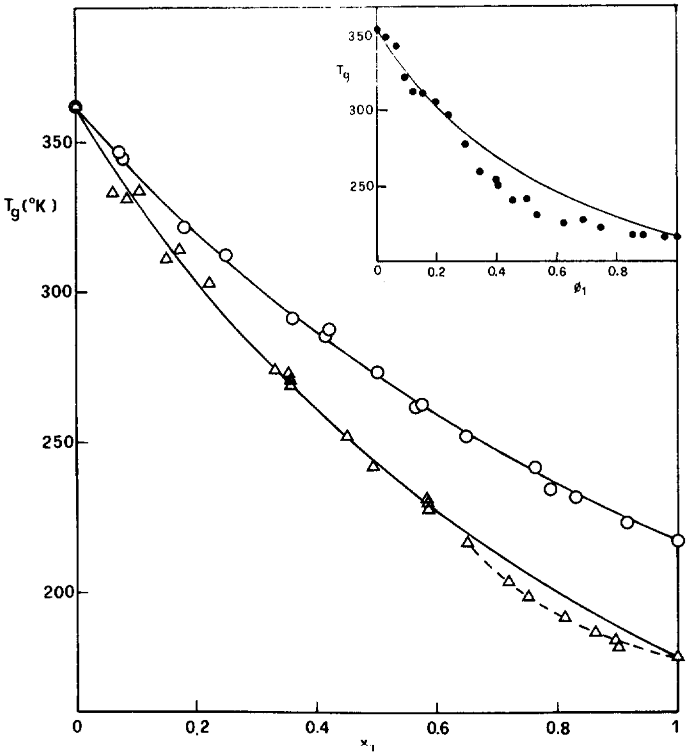

Fig. 3. Glass transition temperature as a function of diluent content for Phenolphthalein with: △ DBP and ○ TCP. ——— : equation 2; - - - -: drawn through the experimental points.
Insert: ● : experimental points; ——— : equation 1.

curvature is found. The results are satisfactorily fitted by the drawn curve, calculated according to equation 2 with a value of the "curvature parameter" K= 0.615. Again this value has no correlation with the $\Delta c_{p2}/\Delta c_{p1}$ ratio which is greater than one for Phenolphthalein-TCP and, if used in equation 2, would raise the calculated curve - by means of an inversion of curvature - above the straight line connecting T_{g2} and T_{g1}.

Finally, the glass transition temperatures of the PVC-TCP mixtures are plotted as a function of composition in the insert of Fig. 3. The drawn curve corresponds to equation 1 with a value of the "curvature parameter" K= 0.410 ($\Delta c_{p2}/\Delta c_{p1}$= 0.68). The PVC-TCP system shows an evident change of curvature in the T_g vs. composition dependence at about 0.3 diluent volume fraction. The above observations indicate that a decrease of 22% in the T_{g2}- T_{g1} difference, which apparently suppresses the T_g "anomaly" in mixtures of low molecular weight substances (Phenolphthalein-TCP), does not produce a similar effect on the plasticized polymer system PVC-TCP. On the other hand, even in the case of Phenolphthalein-DBP, where the difference T_{g2} - T_{g1} is quite large (184°K), the deviation is small indeed, in comparison with that of the plasticized polymer. It would be very interesting to investigate the effect of an increase of T_{g2} - T_{g1}; unfortunately it seems very difficult to find two such low molecular weight substances able to give glassy mixtures in all proportions.

The composition dependence of the glass transition parameters ΔT_g and Δc_p for the two systems containing TCP as the low-T_g component is quite similar to that previously found for the corresponding mixtures containing DBP, shown in Fig. 2. The width of the glass transition is narrow and remains fairly constant at a value of about 10°K for the low molecular weight mixtures of Phenolphthalein and TCP, while the polymer containing mixtures show ΔT_g values as high as 50°K at TCP contents lower than 50%. As regards Δc_p, both systems display a similar dependence on composition from diluent weight fraction $w_1 \approx 0.5$ up to pure TCP; on the contrary, at $w_1 < 0.5$, the data points diverge and tend to the Δc_p values of Phenolphthalein and PVC respectively, being practically superposed to the $0 < w_1 < 0.5$ region of the Δc_p vs. w_1 plots of Fig. 2. From a crossed comparison of the four systems examined, which in turn have a common component in their mixtures, it may be suggested that it is the component present in excess that determines the Δc_p-concentration dependence, i.e. component 2 at $w_1 < 0.5$ and component 1 at $w_1 > 0.5$.

Summing up the present results, it must be stressed that a change of curvature in the composition dependence of the glass transition temperature has been found not only for the PVC-plasticizer systems previously and presently studied by the Authors but also for a system constituted by two low molecular weight substances, Phenolphthalein and DBP. A number of points are raised for further consideration; in particular, a reexamination of the literature data for polymer-diluent systems is desirable, since T_g "anomalies" such as the ones presently described may be difficult to detect if an insufficient number of reliable experimental results is available. In most papers, the fit of the data by empirical relationships is usually considered satisfactory. Moreover, it has to be pointed out that - historically - the dependence of the glass transition temperature on composition has been studied to explain the problems connected with the plasticization of polymers, i.e. mainly referring to low diluent contents. Since it is the high w_1 region that shows the peculiar deviations from the calculated curves, it may be worth reconsidering the theoretical approaches in this composition range, in terms of changes to the glass transition of the diluent brought about by the addition of polymer. Finally, we believe that the use of different experimental techniques, such as mechanical or dielectric spectroscopy, will be very helpful to confirm and explain the observations presented in this work.

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