

The Role of Thermodynamics in the Glass Transition of Poly (Vinyl Chloride)-Tributylphosphate Mixtures

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Abstract : The glass transition temperature and the interaction parameter, χ , for poly (vinyl chloride) plasticized with tributylphosphate have been determined over a wide concentration range. The classical iso-free volume theory of the glass transition fails to explain the experimental results. Consideration of Kovacs' modified iso-free volume theory with the addition to the free volume of an excess volume of mixing based on the χ parameter suitably rationalizes the experimental values.

Introduction

Rarely does a commercial polymer find application in industry in its pure state. By virtue of an additive, some modification of one or more polymer properties is usually required to meet an industrial need. In the case of poly(vinyl chloride), PVC, a common modification has been the addition of plasticizers. Addition of these low vapour pressure compounds, such as dioctylphthalate (DOP), causes the glass transition (T_g) and the viscosity to decrease. The polymer mixture thus obtained finds application in many forms, including flexible wire insulation, floor covering, automobile interiors, etc.

The technology involved in plasticization has

advanced only slowly over the past four decades, being limited by the lack in understanding the nature of the interaction between the polymer and plasticizer and the effect of the specific interaction on the various properties of the ensuing mixtures. As early as 1947, Boyer and Spencer¹ reviewed previous efforts to define the polymer-plasticizer interaction in terms of heats of mixing* of the two components and the relationship between that value and diminution in the T_g of PVC at given volume fraction of plasticizer. This review, which is summarized in Fig.1, raises a number of questions.

The non-linearity of the T_g shift with changing χ defies explanation although it may indicate that at higher values of χ a suspension of

*For the enthalpy of mixing the authors use the Flory-Huggins interaction parameter χ .

polymer in plasticizer, rather than a true solution, exists. A second point of contention relates to the utilization of the same value of χ irrespective of the volume fraction of the two components. The usual shift in χ with concentration was ignored¹.

The present paper is an attempt to shed light on this question. The T_g for PVC plasticized with tributylphosphate (TBP) has been determined over a wide concentration range and an effort made to rationalize the T_g shift in terms of the χ .

Experimental

Materials. Commercial PVC (Esso 366 resin, $\bar{M}_n=4.6 \times 10^4$, $\bar{M}_v=6.5 \times 10^4$ in THF at 25°C) was thermally stabilized by addition of 1wt. % free-flowing, non-plasticizing sulfur containing T-35 organotin stabilizer (M&T Chemicals). X-ray studies did not detect any crystallinity.

TBP (Monsanto Chemicals) was used as the plasticizer.

Procedure. Measurements of T_g were made by differential scanning calorimetry with a Per-

kin_Elmer_DSC-2C. The plasticized PVC samples were solution-cast from THF and dried under vacuum at 62–65°C.

The interaction parameters χ , were measured by Gas-Liquid chromatography (GLC). The instrument used in the present experiment has been described previously². The usual procedures were followed in the preparation of column materials and in their packing. Only the χ versus volume fraction of TBP data are presented here. A detailed description of the experimental procedures and the data from which the χ values were calculated are contained in the thesis of S.K. Roy³.

Results and Discussion

Fig. 2 shows the depression in the T_g of PVC plasticized with increasing volume fraction of TBP. Two factors are evident from the Figure. First, the change in T_g is nonlinear with volume fraction of plasticizer. Secondly, there is a cusp (T_c) at about 25 volume percent plasticizer. The dotted line compares the theoretical treatment of Kovacs⁴ to the experimental

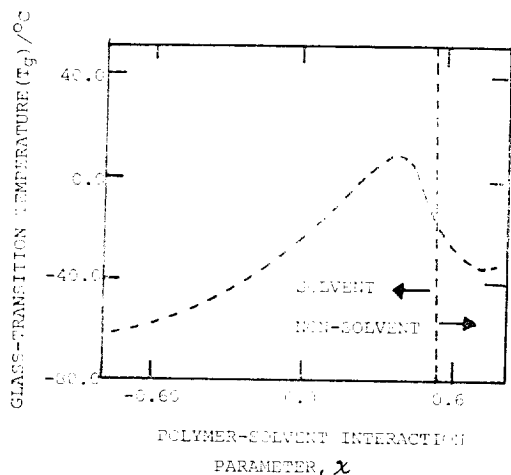


Fig. 1. Glass transition temperature (T_g) as a function of polymer-solvent interaction parameter (χ) at 30 volume % plasticizer¹.

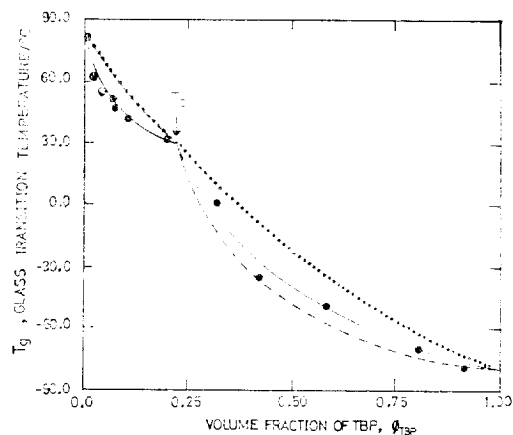


Fig. 2. Glass transition temperature (T_g) of polyvinyl chloride-tributyl phosphate (PVC-TBP) mixtures as a function of TBP volume fraction, ϕ_{TBP} (legend: iso-free volume theory; ---- Kovacs⁴; — present work)

results, solid line.

The equations from whence Kovacs derives his relationship are the following. He assumes that the free volume fractions of polymer and plasticizer, f_p and f_d respectively, are always greater than or equal to zero, i.e.,

$$f_p = f_{g,p} + \Delta\alpha_p(T - T_{g,p}) \geq 0 \quad (1)$$

$$f_d = f_{g,d} + \alpha_{g,d}(T - T_{g,d}) \geq 0 \quad (2)$$

where the subscripts p and d denote polymer and plasticizer respectively. The f_g are the free volume fractions at the respective T_g temperatures of the pure components. $\Delta\alpha_p$ represents the difference in expansivity between the polymeric liquid and glass ($\Delta\alpha_p = \alpha_{l,p} - \alpha_{g,p}$) and $\alpha_{l,d}$ is the expansivity of the liquid plasticizer.

At ϕ_p , volume fraction of polymer, the molar volume of the mixture may be written as:

$$V = \phi_p V_p + \phi_d V_d + V^E \quad (3)$$

where V^E is the excess volume of mixing. However, the excess volume fraction of mixing is V^E/V and, assuming it to be a contributory factor to the free volume, then the total free volume fraction, f , of the mixture may be written as:

$$f = \phi_p f_p + \phi_d f_d + \frac{V^E}{V} \quad (4)$$

Kovacs, to simplify his approach, assumed V^E/V to be zero. Eq. (4) then reduces to that of the hypothesis of the iso-free volume theory in which the free volume fraction of the mixture is simply the sum of the free volume fractions of the components, i.e.

$$f = \phi_p f_p + \phi_d f_d \quad (4a)$$

$$\text{or, } f = \phi_p [f_{g,p} + \Delta\alpha_p(T - T_{g,p})] + \phi_d [f_{g,d} + \alpha_{l,d}(T - T_{g,d})] \quad (5)$$

$$= \phi_p f_{g,p} + \phi_d f_{g,d} + [\phi_p \Delta\alpha_p(T - T_{g,p}) + \phi_d \alpha_{l,d}(T - T_{g,d})] \quad (5a)$$

According to the iso-free volume theory, at $T = T_g$, $f = 0.025$ ($\phi_p f_{g,p} + \phi_d f_{g,d}$) and the term in the square bracket of eq. (5a) equals to zero. Replacing T of eq. (5a) by T_g of the mixture

and subsequent rearranging gives eq. (6) which describes the iso-free volume theory for the compositional variation of T_g .

$$T_g = \frac{\phi_p \Delta\alpha_p T_{g,p} + \phi_d \alpha_{l,d} T_{g,d}}{\phi_p \Delta\alpha_p + \phi_d \alpha_{l,d}} \quad (6)$$

However, as Kovacs pointed out, examination of eq. (1) reveals that with $T_{g,p} > T_{g,d}$ then, for temperatures lower than $T_{g,p}$, the second term on the right-hand side signifies a diminishing contribution to the free volume. At a critical temperature, T_c , f_p becomes zero and T_c is given by

$$T_c = T_{g,p} - \frac{f_{g,p}}{\Delta\alpha_p} \quad (7)$$

The critical concentration of plasticizer, $\phi_{d,c}$ corresponding to T_c is obtained by substituting T_c of eq. (7) into eq. (6) and after rearranging it may be written as

$$\phi_{d,c} = \frac{f_{g,p}}{\alpha_{l,d}(T_{g,p} - T_{g,d}) + f_{g,p} \left(1 - \frac{\alpha_{l,d}}{\Delta\alpha_p}\right)} \quad (8)$$

For the plasticizer concentration $\phi_d > \phi_{d,c}$ eq. (6) no longer applies because at these temperature the polymer would add 'negative' free volume which is an absurd concept. The T_g variation from the critical point, T_c , is then given by eq. (9)

$$T_g = T_{g,d} + \frac{f_{g,p}}{\alpha_{l,d}} \frac{\phi_p}{\phi_d} \quad (9)$$

Returning to Fig. 2, it is evident that the agreement with Kovacs' treatment is excellent beyond the cusp (T_c). However, to the left of that point the experimental data fall considerably below the predicted values. This is thought to be due to the fact that Kovacs simplified his original approach by putting aside the excess volume of mixing which is a function of the enthalpy of mixing (ΔH^M or H^E) and assumed the mixing to be athermal⁵. The value of the excess volume of mixing, V^E , has been found by Eichinger and Flory⁶, using the Hildebrand-Scott approach⁵, to be about one-tenth of one

percent for the system natural rubber-benzene. While this value appears small at first glance, it represents a considerable fraction of the total free volume, 2.5%, which the iso-free volume theory defines as being necessary for the transition from a glass to a liquid.

To determine the magnitude of the V^E for PVC-TBP, assuming that the mixing is not athermal, the χ values for the mixing were measured over the total concentration range, as described in the experimental section. The results are shown in Fig.3.

It is evident from these data that below 0.35 volume fraction plasticizer the χ values exceed the critical value of 0.61, indicating an endothermic heat of mixing. The χ_{critical} is calculated from the Flory-Huggins relationship⁷ where $\chi_{\text{crit}} = \frac{1}{2}[1 + \gamma^{-1}]^2$, the quantity γ being the ratio of the molar volumes of polymer to plasticizer. In the case of the polymer used in the current work, $\bar{M}_n = 4.6 \times 10^4$, the solution to this equation yields $\chi = 0.61$. This value occurs at a concentration of 0.35 volume fraction plasticizer. For any plasticizer concentration below this value, the polymers will precipitate from solu-

tion. In such a case the V^E would be positive⁸, and it would be expected that the free volume in the mixture would be increased by the amount of V^E and result in a T_g below that predicted for an athermal mixture. The data in fig. 2 are consistent with these premises since the T_g to the left of the maximum is lower than value predicted on the basis of an athermal mixture.

Assuming that the excess free volume represented by the T_g shift derives from the V^E , a calculation of the latter value can be accomplished from eqs. 6 and 10-12.

$$T_{g(V^E=0)} = \frac{\phi_p \Delta \alpha_p T_{g,p} + \phi_d \alpha_{l,d} T_{g,d}}{\phi_p \Delta \alpha_p + \phi_d \alpha_{l,d}} - \left[\frac{V^E}{V} / (\phi_p \Delta \alpha_p + \phi_d \alpha_{l,d}) \right] \quad (10)$$

$$\text{Therefore } T_{g(V^E=0)} - T_{g(V^E \neq 0)} = \left[\frac{V^E}{V} / (\phi_p \Delta \alpha_p + \phi_d \alpha_{l,d}) \right] = \Delta T_g \quad (11)$$

$$\text{and } \frac{V^E}{V} = \Delta T_g (\phi_p \Delta \alpha_p + \phi_d \alpha_{l,d}) \quad (12)$$

where V^E/V is the excess volume fraction of mixing which has been assumed to be totally contributory to 'extra' free volume of the system.

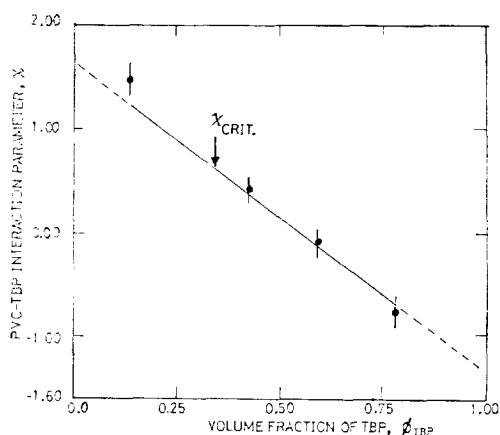


Fig. 3. Polyvinyl chloride-tributyl phosphate (PVC-TBP) interaction parameter (χ) as a function of TBP volume fraction, ϕ_{TBP}

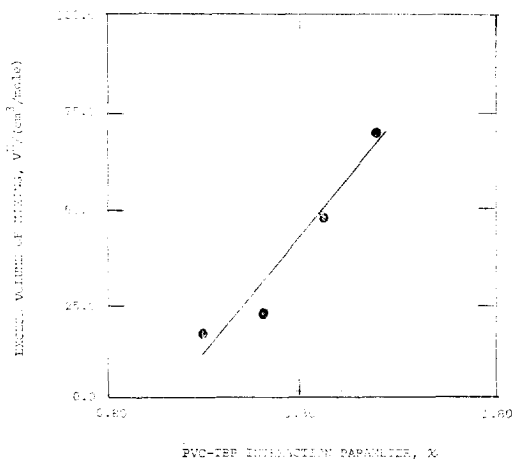


Fig. 4. Molar excess volume of mixing (V^E) as a function of polyvinyl chloride-tributyl phosphate (PVC-TBP) interaction parameter (χ)

A plot of calculated V^E of mixing versus χ is given in fig.4. The linearity of the plot indicates a direct relationship between χ and the V^E and hence between χ and T_g . Since the χ value has been demonstrated to be something more than a simple enthalpic term⁷, a direct calculation of the enthalpy of mixing cannot be made at the present time from the χ values. Further work is now underway which will hopefully elucidate the relationship between the χ value and the enthalpy of mixing.

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