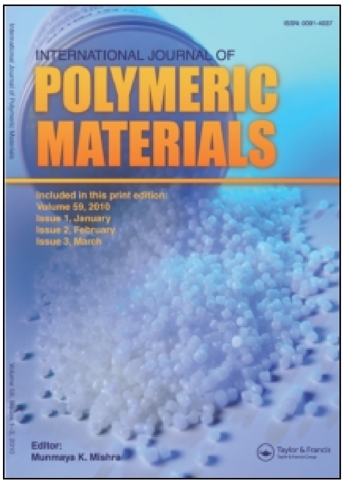

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Roy, Saroj K. , Brown, G. Ronald and St-pierre, Leon E.(1983) 'The Influence of Thermodynamic Interactions on the Glass Transition of Poly (Vinyl Chloride)-Benzylbutylphthalate Mixtures', International Journal of Polymeric Materials, 10: 1, 13 — 20

To link to this Article: DOI: 10.1080/00914038308077987

URL: http://dx.doi.org/10.1080/00914038308077987

Intern. J. Polymeric Mater., 1983, Vol. 10, pp. 13–20
0091–4037/83/1001–0013 $18.50/0

Printed in Great Britain

The Influence of Thermodynamic Interactions on the Glass Transition of Poly(Vinyl Chloride)-Benzylbutylphthalate Mixtures

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(*Received April 23, 1982*)

The glass transition temperature and the interaction parameters, χ, for poly(vinyl chloride) plasticized with benzylbutylphthalate have been determined over a wide range of concentrations. The classical iso-free volume theory of the glass transition fails to explain the experimental results. However, 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

In general polymers used industrially contain some additive that alters the physical properties to suit the application. The addition of plasticizers is common in the case of poly(vinyl chloride), PVC. The plasticizers, which are generally compounds with a low vapour pressure in the temperature range of application, e.g., dioctylphthalate, cause a decrease in the viscosity and in the glass transition temperature, T_g. Although large quantities of plasticized PVC are used commercially in such varied forms as flexible wire insulation, floor covering, automobile interiors, etc., there are still many important unsolved problems associated with the use of such mixtures. For example, "bleeding" of plasticizer is a real concern in the use of PVC tubing for transfusions.[1–3]

Plasticization technology has advanced only slowly during the past four decades, largely because of an incomplete understanding of the nature of the interaction between the polymer and the plasticizer as well as of the effect of specific interactions on the properties of the final product.

As early as 1947, Boyer and Spencer[4] suggested that a relationship exists between the T_g of plasticized PVC samples and the Flory-Huggins interaction parameter, χ, of the components. An adequate explanation of the effect of χ on T_g, shown in Figure 1, has not been given. It seems possible that the behaviour at high values of χ may result from the formation of a suspension of polymer in plasticizer, rather than a true solution. It should be kept in mind that the well-known variation in χ with volume fraction was apparently ignored in developing this relationship.[4]

The present paper gives results for the effect of concentration of benzylbutylphthalate on the χ parameter and on T_g over a wide range of volume fractions. An effort is made to rationalize the shift in T_g in terms of χ.

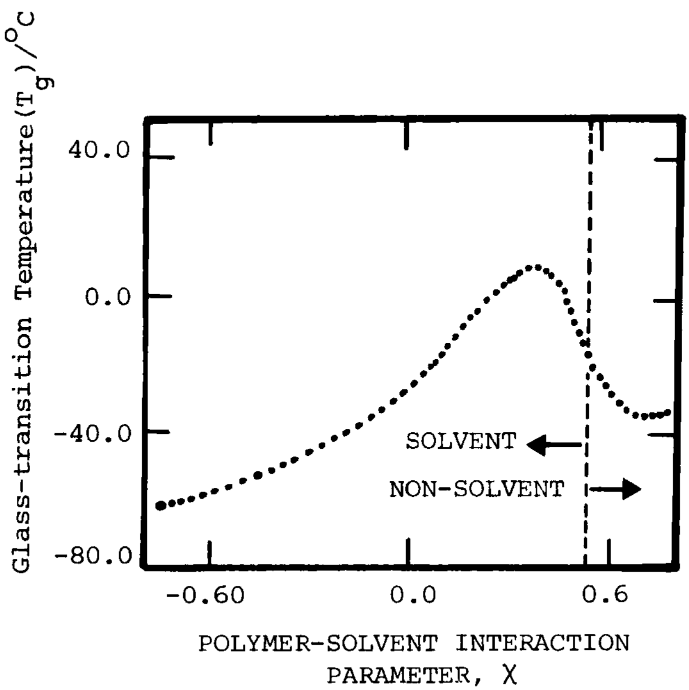

FIGURE 1 Glass transition temperature (T_g) as a function of polymer-solvent interaction parameter (χ) at 30 volume % plasticizer.[4]

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 1 wt. % free-flowing, non-plasticizing sulfur containing *T*-35 organotin stabilizer (M&T Chemicals). X-ray studies did not detect any crystallinity in the samples.

The plasticizer benzylbutylphthalate was used as received from Monsanto Chemicals.

Procedure

Measurements of T_g were made by differential scanning calorimetry with a Perkin Elmer DSC-2C. The PVC samples were solution-cast from THF and solvent was removed at 62–65°C under vacuum.

The interaction parameters, χ, were determined† by the gas-liquid chromatography (GLC) technique[6] using an instrument that has been described previously.[7] Usual procedures were followed in the preparation of column materials and in their packing.

RESULTS AND DISCUSSION

The plasticizer BBP causes a depression in the T_g of plasticized PVC (Figure 2). For these solution-cast samples T_g decreases in a nonlinear fashion as the volume fraction of BBP, ϕ_d, is increased. Indeed at $\phi_d \sim 0.25$ a cusp, labelled T_c in Figure 2, is evident. Similar, "cusp behaviour" has been reported for PVC with other plasticizers.[8-10]

The dotted line in Figure 2 indicates the decrease in T_g expected on the basis of iso-free volume theory.[11,12] According to this theory free volume fractions of polymer and of plasticizer, f_p and f_d respectively,‡ are

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

$$f_d = f_{g,d} + \alpha_{l,d} (T - T_{g,d}) \tag{2}$$

where f_g is the free volume fraction of the pure component at T_g, $\Delta\alpha_p$ represents the difference in thermal 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. The free volume fraction of the mixture is assumed to be equal to the sum of the free

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† A detailed description of the experimental procedures and the data from which the χ values were derived is contained in the thesis of S. K. Roy.[5]

‡ The subscripts *p* and *d* denote polymer and plasticizer, respectively.

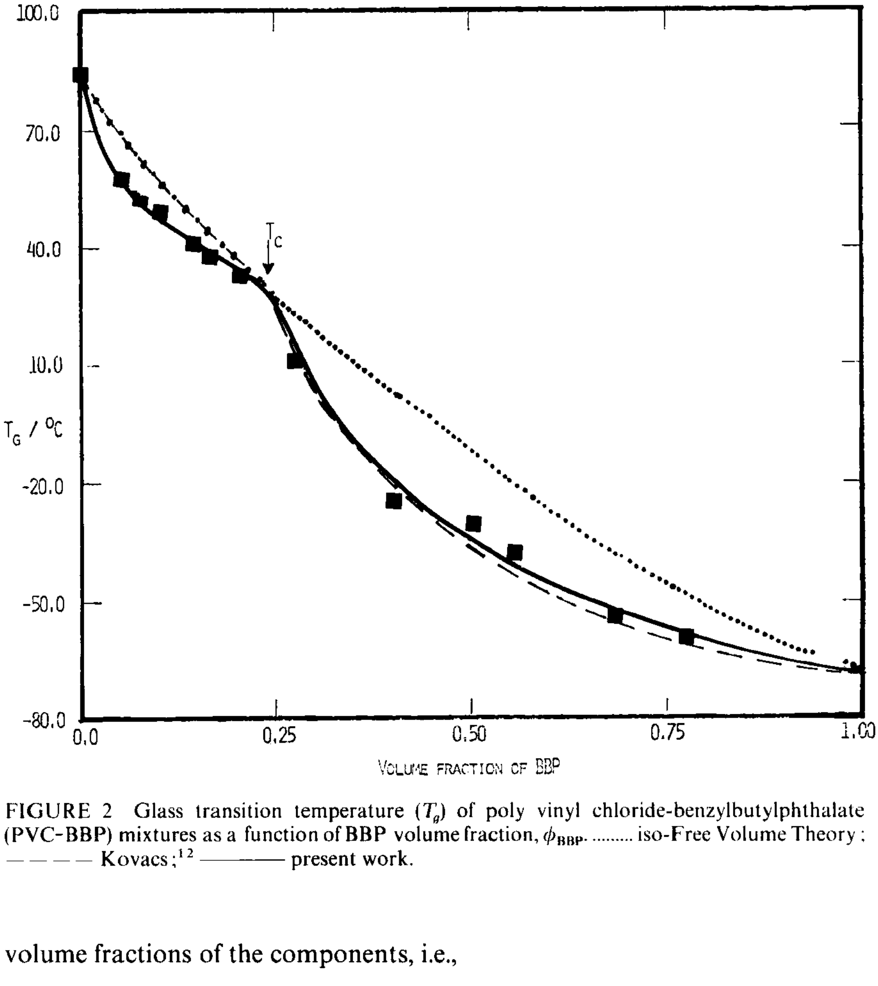

FIGURE 2 Glass transition temperature (T_g) of poly vinyl chloride-benzylbutylphthalate (PVC-BBP) mixtures as a function of BBP volume fraction, ϕ_{BBP}. .... iso-Free Volume Theory; — — — — Kovacs;[12] ———— present work.

volume fractions of the components, i.e.,

$$f = \phi_p f_p + \phi_d f_d \tag{3}$$

$$= \phi_p f_{g,p} + \phi_d f_{g,d} + [\phi_p \Delta\alpha_p (T - T_{g,p}) + \phi_d \alpha_{l,d} (T - T_{g,d})] \tag{4}$$

According to the iso-free volume theory, at $T = T_g$, $f = (\phi_p f_{g,p} + \phi_d f_{g,d}) = 0.025$ and the term in the square bracket of Eq. (4) equals zero. The iso-free volume theory description of the compositional variation of T_g of the mixture is obtained by replacing T of Eq. (4) by T_g so that

$$T_g = \frac{\phi_p \Delta\alpha_p T_{g,d} + \phi_d \alpha_{l,d} T_{g,d}}{\phi_p \Delta\alpha_p + \phi_d \alpha_{l,d}} \tag{5}$$

It is evident that the dotted line in Figure 2 derived with this expression is a poor approximation to the experimental results, except in the region of T_c. However, as pointed out by Kovacs,[12] for temperatures below $T_{g,p}$, the second term on the right-hand side of Eq. (1) signifies a decreasing contribution to the free volume fraction of the mixture by the polymer. The f_p resulting from the polymer becomes zero at some critical temperature, T_c, given by

$$T_c = T_{g,p} - \frac{f_{g,p}}{\Delta\alpha_p}$$

The critical concentration of plasticizer, $\phi_{d,c}$, corresponding to T_c is

$$\phi_{d,c} = \frac{f_{g,p}}{\alpha_{l,d}(T_{g,p} - T_{g,d}) + f_{g,p}\left(1 - \frac{\alpha_{l,d}}{\Delta\alpha_p}\right)} \qquad (7)$$

For the plasticizer concentration $\phi_d > \phi_{d,c}$, Eq. (5) no longer applies because at these temperatures the polymer would add "negative" free volume which is a physically absurd concept. The variation of T_g with concentration beyond the critical point, T_c, is then given by

$$T_g = T_{g,d} + \frac{f_{g,p}}{\alpha_{l,d}} \frac{\phi_p}{\phi_d} \qquad (8)$$

A plot of this expression yields the dashed line in Figure 2.

It is evident that the agreement of the experimental data with the Kovacs treatment is excellent beyond the cusp (T_c). However, to the left of that point the data fall considerably below the predicted values. This is thought to be due to the fact that Kovacs simplified his original approach by neglecting any contribution to f which might result from the excess volume of mixing, V^E. When excess volume fraction of mixing is also considered to contribute to f, Eq. (3) becomes

$$f = \phi_p f_p + \phi_d f_d + \frac{V^E}{V}$$

where V is the molar volume of the mixture. This excess volume is a function of the enthalpy of mixing, ΔH^M or H^E.[13] The magnitude of the excess volume of mixing for the system natural rubber-benzene has been found by Eichinger and Flory,[14] using the Hildebrand-Scott approach, to be about one-tenth of one percent. Although this appears to be negligible 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.

It seems probable that the formation of a PVC-BBP solution would not be an athermal process. However, heats of mixing for such system are very difficult to measure. Hence, the interaction parameter, χ, was determined instead over the complete concentration range. The results are shown in Figure 3.

It is evident from these data that below 0.36 volume percent plasticizer the χ values exceed the theta value of 0.61, indicating an endothermic heat of mixing. In such a case the V^E would be positive,[12] and it would be expected that the free volume in the mixture would be increased by the amount of V^E. This would result in a T_g below that predicted for an athermal mixture, in agreement with the data in Figure 2. The excess volume fraction of mixing required to cause the experimentally observed shift in T_g, ΔT_g, at plasticizer concentrations less than $\phi_{d,c}$ is

$$\frac{V^E}{V} = \Delta T_g(\phi_p \Delta\alpha_p + \phi_d \alpha_{l,d}) \tag{9}$$

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

A plot of calculated V^E of mixing *vs.* χ is given in Figure 4. The linearity of the plot suggests a 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 term,[15] a direct calculation of the enthalpy of mixing cannot be made at the present time from the χ values. Further work is now underway in an effort to elucidate the enthalpic and entropic contributions to χ. From these results direct calculations of V^E and in turn T_g will be attempted.

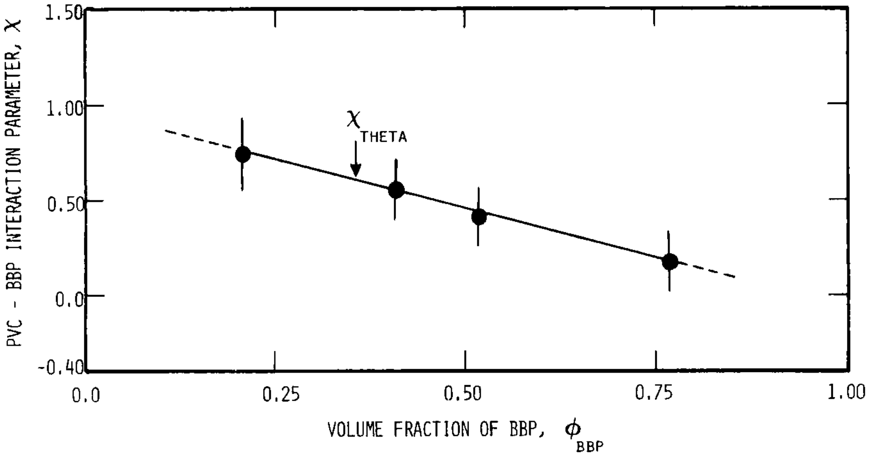

FIGURE 3 Polyvinyl chloride-butylbenzylphthalate (PVC-BBP) interaction parameter (χ) as a function of BBP volume fraction, ϕ_{BBP}.

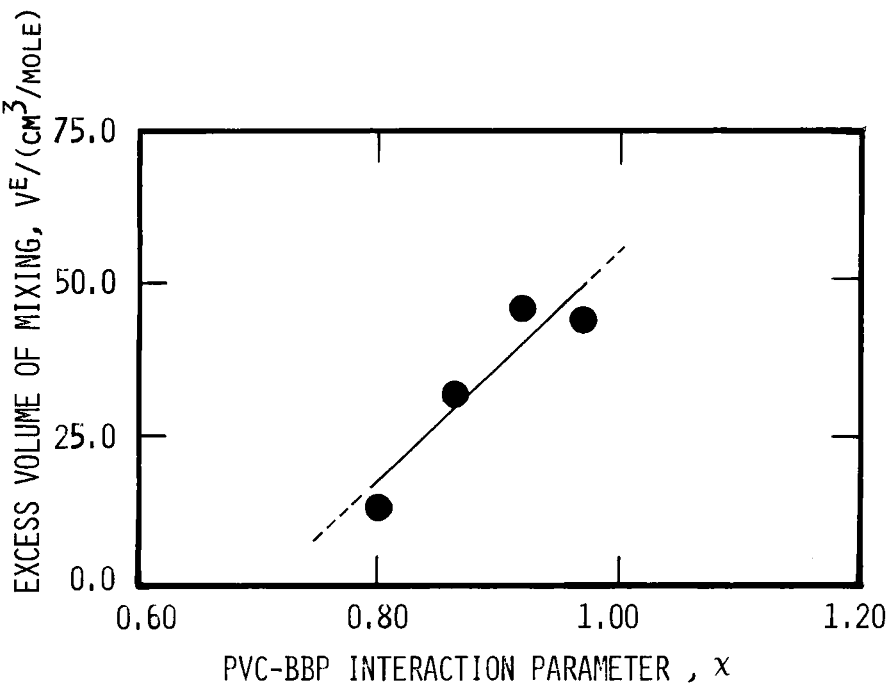

FIGURE 4 Molar excess volume of mixing (V^E) as a function of polyvinyl chloride-butylbenzylphthalate (PVC-BBP) interaction parameter (χ).

SUMMARY

The shifts in the T_g of PVC with volume fraction plasticizer, benzylbutylphthalate, which do not follow the classical iso-free volume theory have been rationalized on the basis of the contribution of the excess volume of mixing to the free volume. The latter value has been related to the enthalpy of mixing through the Flory-Huggins interaction parameter χ.

Acknowledgements

Support for this work through grants from Imperial Oil and the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. We are also grateful for the many helpful discussions with Dr. V. P. Gupta and Professor D. D. Patterson.

References

1. W. Geertz, K. Dyer, D. Johnson, B. Miller, B. Taylor and W. Sharp, *Trans. Am. Soc. Artif. Intern. Organs* **20**, 42 (1974).

2. R. J. Rubin and C. A. Schiffer, *Transfusion* **16,** 330 (1976).
3. P. Blais, *Can. Res.* **14,** 13 (1981).
4. R. F. Boyer and R. S. Spencer, *J. Polym. Sci.* **2,** 157 (1947).
5. S. K. Roy, M.Sc. thesis, McGill University, 1982.
6. J. R. Conder and C. L. Young, *Physicochemical Measurements by Gas Chromatography*, John Wiley and Sons, New York (1979).
7. D. Deshpande, D. Patterson, H. P. Schreiber and C. S. Su, *Macromolecules* **7,** 530 (1974).
8. S. K. Roy, G. R. Brown and L. E. St-Pierre, *Korean J. Polym Sci.* (in press).
9. J. R. Fried, S.-Y. Lai, L. W. Kleiner and M. E. Wheeler (Proceedings of the Third International Symposium on PVC), *J. Macromol. Sci.* (in press).
10. G. Pezzin, A. Omacini and F. Zilio-Grandi, *La Chimica e L'Industria* **50,** 309 (1968).
11. M. C. Shen and A. Eisenberg, *Rubber Chem. Technol.* **43,** 95 (1970).
12. A. J. Kovacs, *Adv. Polym. Sci.* **3,** 394 (1963).
13. J. H. Hildebrand and R. L. Scott, *The Solubility of Non-Electrolytes*, 3rd ed., Dover Publications Inc., New York (1964).
14. B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.* **64,** 2035 (1968).
15. D. Patterson, *Macromolecules* **2,** 672 (1969).