Composition dependence of the glass transition of polymer–diluent mixtures: 2. Two concomitant glass transition processes as a general feature of plasticized polymers

M. Scandola, G. Ceccorulli and M. Pizzoli

Centro di Studio per la Fisica delle Macromolecole del CNR, Dipartimento di Chimica 'G. Ciamician', Via Selmi 2, 40126 Bologna, Italy

The available theoretical and empirical treatments concerning the glass transition temperature, T_g, of polymer–diluent mixtures do not account for the occurrence of the 'cusp' in the T_g/composition dependence or of the two concomitant glass transitions recently reported by these authors. The only treatment predicting a change of curvature in T_g vs. concentration, due to Braun and Kovacs, does not describe satisfactorily the behaviour of the seven polymer–diluent systems examined. In order to compare the results with the available literature data, a normalization procedure is developed, whose main effect is to evidence that the T_g/concentration dependence of all polymer–diluent systems is composed of two branches. It is concluded that in polymer–diluent mixtures still considered homogeneous at a macroscopic level two different mobilization phenomena occur, related to mobilization of 'hindered diluent' and 'plasticized polymer', respectively. The possibility of revealing the two phenomena individually depends strongly on the technique being used as well as on the peculiar physical properties of the binary system being examined.

INTRODUCTION

A number of polymer–diluent systems recently examined by these authors have shown a dual dependence of the glass transition temperature (T_g) on composition[1-4]. Such behaviour can be summarized as follows: the glass transition of the polymer is strongly depressed by diluent additions, while the glass transition of the diluent is hindered by the presence of dissolved polymer molecules and its temperature increases with polymer content. The phenomena are present in the same macroscopically homogeneous mixture and can be easily revealed, the former at low, the latter at high diluent content. As regards the intermediate range of concentrations, it is often difficult to assign the broad glass transition observed to either of the two relaxation processes. In some special cases (polystyrene–tritolylphosphate and poly(vinyl chloride)–butylacetate) two transitions have been revealed concomitantly[3,4], both moving to lower temperature with increasing diluent content.

Until recently, the occurrence of such a dual composition dependence of the glass transition has been regarded as an 'anomaly' with respect to the predicted behaviour of a single glass transition whose temperature regularly decreases from the T_g of the polymer to the T_g of the diluent. Apart from the results of the present authors[1-4], in recent years a number of papers reporting the occurrence of 'cusps' or 'changes of curvature' in the compositional dependence of the glass transition of both polymer blends and plasticized polymers have appeared in the literature[5-10].

The aim of this paper is to examine and compare literature data and our own results to demonstrate that,

what has been considered an 'anomaly', is probably normal behaviour that has to be expected for all polymer–diluent systems.

EXPERIMENTAL

The instrumentation, experimental procedures as well as the source of polymers and diluents are described in the previous paper[4]. In the present paper the following abbreviations will be used: poly(vinyl chloride) (PVC); polystyrene (PS); polycarbonate (PC); poly(methyl methacrylate) (PMMA); phthalates: di-methyl (DMP), di-ethyl (DEP), di-n-propyl (DPP), di-n-butyl (DBP), di-octyl (DOP); tritolylphosphate (TTP); n-butyl-acetate (BuAc); di-octyladipate (DOA); di-ethylbenzene (DEB).

RESULTS AND DISCUSSION

A number of theoretical treatments[11-14], as well as empirical equations[15-17], have been proposed to describe the composition dependence of the glass transition temperature of polymer–diluent mixtures. None of the available treatments allows for a dual dependence but one—based on 'free volume' considerations—from Braun and Kovacs[18]. According to the 'free volume theory', the fractional free volume f_2 contributed by the polymer to the mixture at a given temperature T is given by:

$$f_2 = f_{g2} + \alpha(T - T_{g2}) \tag{1}$$

where f_{g2} is the fractional free volume at the polymer glass

transition temperature T_{g2} and α is the thermal expansion coefficient of the free volume. Braun and Kovacs[18] (B–K) pointed out that f_2 must be always ≥ 0, therefore the above equation defines a critical low temperature limit $T_c = T_{g2} - f_{g2}/\alpha$ below which the polymer no longer contributes to the free volume of the mixture. A somewhat similar limit is implicitly contained in the thermodynamic theory from Gibbs and Di Marzio[12], who postulated the existence of a critical temperature T_2 ($T_2 \simeq T_g - 50\,\mathrm{K}$), corresponding to zero configurational entropy of the polymer. Braun and Kovacs proposed two different equations to describe the composition dependence of T_g above and below T_c:

$$T_g = \frac{\phi_2\Delta\alpha_2 T_{g2} + \phi_1\Delta\alpha_1 T_{g1}}{\phi_2\Delta\alpha_2 + \phi_1\Delta\alpha_1} \qquad T > T_c \qquad (2)$$

and

$$T_g = T_{g1} + (f_{g2}/\Delta\alpha_1)(\phi_2/\phi_1) \qquad T < T_c \qquad (3)$$

where ϕ_1 and ϕ_2 are the volume fractions, $\Delta\alpha$ the difference between the expansion coefficient above and below T_g and the subscripts 1 and 2 refer to diluent and polymer, respectively.

The B–K treatment predicts a T_g/composition dependence where a change of curvature occurs at T_c, the so-called 'cusp', but of course does not account for any coexistence of two glass transition phenomena in the same polymer–diluent mixture. As an example of the application of the B–K treatment to our T_g data, *Figures 1* and *2* show the results obtained for the PVC–DBP system using the value of 2.04 for $\Delta\alpha_1/\Delta\alpha_2$ and extrapolated experimental density data for the calculation of volume fractions at T_g. It can be clearly seen in *Figure 1* that, while equation (2) (which corresponds to the well known Kelley and Bueche equation[11]) gives a good fit to the experimental results up to T_c, equation (3) does not fit the data at intermediate concentrations. The reason for this result is clear in *Figure 2*, where a plot of T_g versus
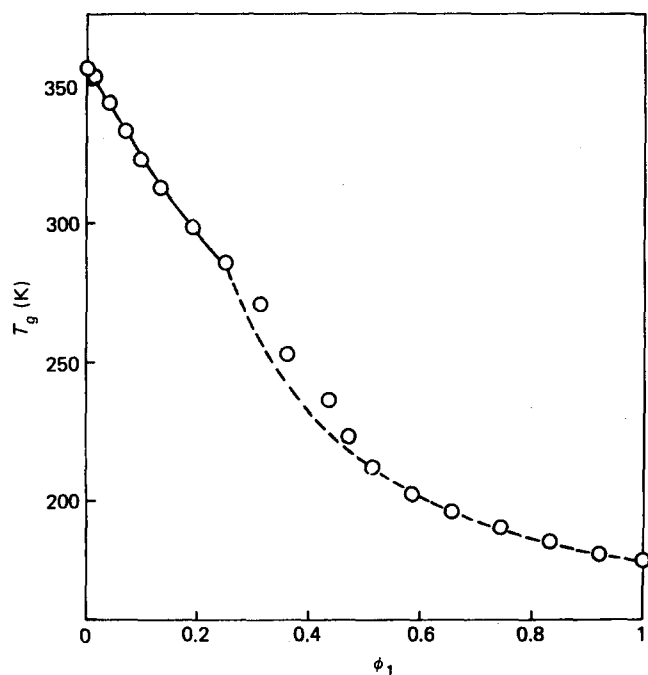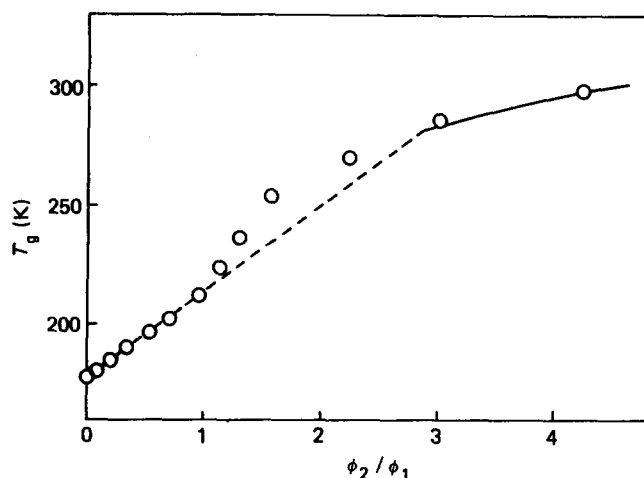

Figure 2 Glass transition temperature vs. the volume fraction ratio ϕ_2/ϕ_1 for PVC–DBP mixtures: (O) experimental results; (——) equation (2); (———) equation (3)
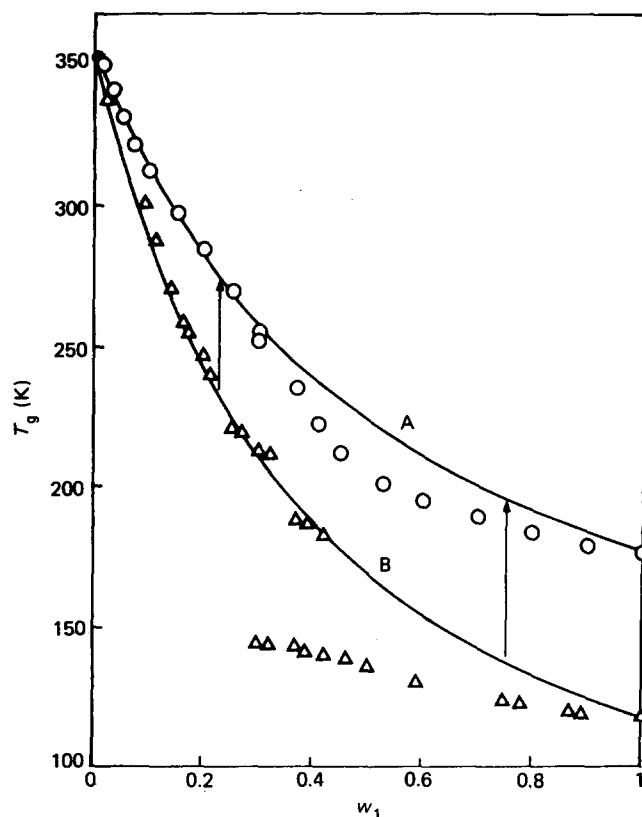

Figure 3 Graphical illustration of the normalization procedure according to equation (5). (O) PVC–DBP; ($\triangle$) PVC–BuAc. Curve A: equation (4) with $k = 0.54$; curve B: equation (4) with $k = 0.47$

ϕ_2/ϕ_1 according to equation (3) shows that there is no linear dependence up to T_c, the linearity ending at a much lower temperature. All other systems examined by these authors[4] exhibit similar behaviour to that shown in *Figures 1* and *2*.

Since T_c is determined only by polymer parameters, it has to be emphasized that the B–K treatment predicts a common value of the critical temperature for all PVC–diluent systems, irrespective of the low molecular weight component in the mixture. This is in contrast with our results, where—when present—the 'cusp' appears at different temperatures for the different PVC–diluent systems. It can be therefore concluded that the only available theoretical treatment predicting the occurrence

Figure 1 Glass transition temperature vs. volume fraction of diluent (ϕ_1) for PVC–DBP mixtures: (O) experimental results; (——) equation (2); (———) equation (3)

of a change of curvature in the concentration dependence of T_g does not apply satisfactorily to our experimental results.

The mixtures recently examined by these authors[3,4] refer to six diluents and two polymers. In order to compare experimental results for systems differing not only in T_{g2} and T_{g1} ($T_{g2} - T_{g1}$ ranging from 140 to 240 K) but also in the curvature of the T_g/w_1 dependence, as quantified by the adjustable parameter k in the equation:

$$\ln T_g = \ln T_{g2} + [\ln(T_{g1}/T_{g2})]/[1 + k(w_2/w_1)] \quad (4)$$

a 'normalization' of the experimental T_g values has been carried out. The procedure is illustrated graphically in *Figure 3*, where the experimental results for two of the systems, one of which is arbitrarily chosen as a 'reference', are shown together with the curves (solid lines in *Figure 3*) calculated by means of equation (4), where k has been adjusted to give the best fit to the experimental data in the composition range of polymer-rich mixtures. These calculated curves (c-curves) have been used in the normalization procedure: normalization consists in modifying all T_g data by the application of a 'normalizing factor' that brings to coincidence the c-curve of the system to be normalized with that of the system chosen as a reference. In practice this is achieved by applying to all T_g values a vertical shift equal to that needed to superpose the c-curves over the whole concentration range, as shown by the arrows in *Figure 3*. To this purpose the following equation is used:

$$\ln T_g^* = \ln T_{g2}^a + \ln(T_g^b/T_{g2}^b) \cdot \frac{\ln(T_{g1}^a/T_{g2}^a)}{\ln(T_{g1}^b/T_{g2}^b)}$$

$$\cdot \frac{1 + k^b w_2/w_1}{1 + k^a w_2/w_1} \quad (5)$$

where superscripts 'a' and 'b' correspond to the 'reference' and to the system to be normalized, respectively. Application of equation (5) to six PVC–diluent and one PS–diluent systems is shown in *Figure 4*, where the solid line represents the reference c-curve, common to all systems. The interesting result of the
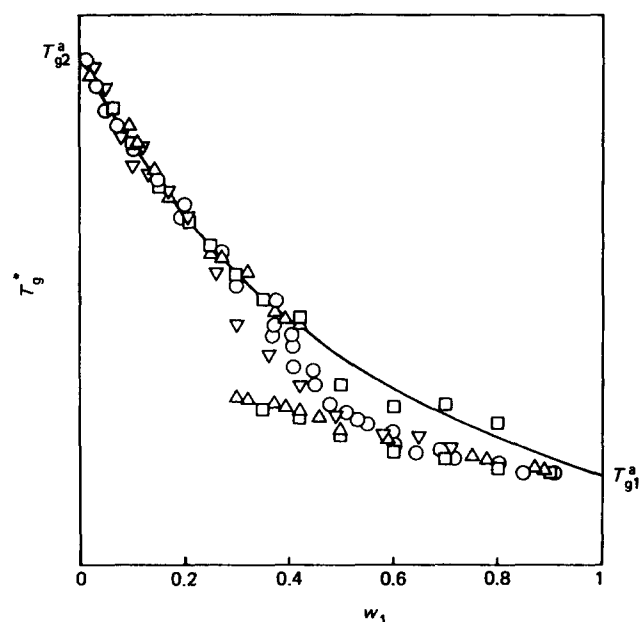
Figure 4 Normalized T_g^* values vs. w_1 for mixtures of PVC with: (O) phthalates, (△) BuAc, (▽) TTP and of PS with: (□) TTP, some points omitted for the sake of clarity
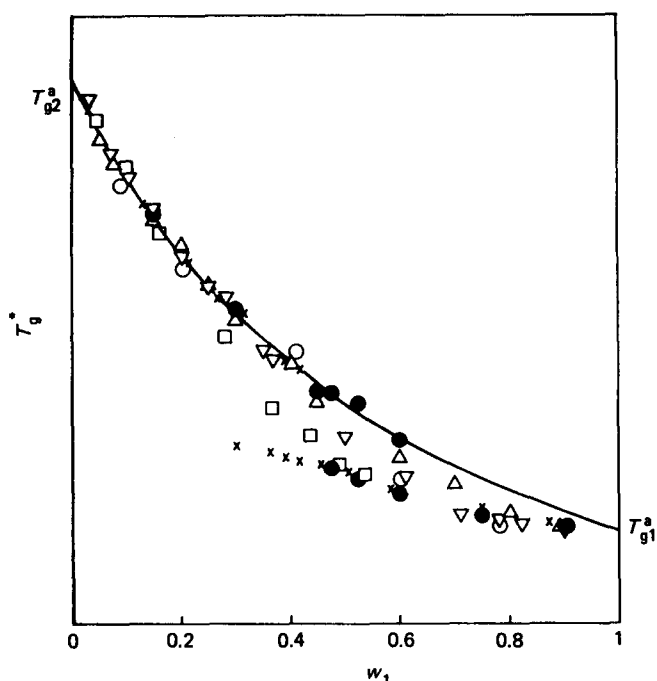
Figure 5 Normalized T_g^* values vs. w_1 for the following systems: (O) PS–toluene[5]; (□) PVC–DOA[7]; (●) PS–TTP[19]; (▽) gelatin–glycerol[20]; (△) PC–TTP[21]; (×) PVC–BuAc (this work)

normalization procedure is that bringing to coincidence the concentration dependence of T_g at low diluent concentrations carries as a consequence the appearance of a common trend of the normalized T_g^* values for all systems at $w_1 > 0.6$.

For the two systems that show two concomitant glass transitions at diluent contents higher than about 30%, PVC–BuAc and PS–TTP, it may be observed that both T_g's decrease with increasing w_1, the upper following the c-curve, the lower along the trend suggested by the behaviour of all systems at $w_1 > 0.6$. With regards to PS–TTP, we recall that the scatter of the T_g^* data in *Figure 4* reflects the difficulty in accurately detecting the upper glass transition temperature[3]. The remaining PVC–diluent systems show a transition of the T_g^* values from one dependence to the other in the central composition region, the change being more or less abrupt depending on the diluent.

Among the polymer–diluent systems for which 'anomalous' T_g/w_1 dependences have been reported in the literature, unforunately only a few can be selected to be 'normalized'. The reason for this is mainly the insufficient amount of experimental data over the entire concentration range, the lack of an experimental value for the glass transition temperature of the diluent as well as the use of composition variables other than weight fraction. Moreover, very little tabulated T_g data are available, so that readings from plots have to be carried out.

Figure 5 shows the 'normalized' data for the polymer–diluent systems taken from the literature, for which the above difficulties have been overcome. We recall that the first step of the normalization procedure is the selection, for each system, of the curvature parameter (k in equation (4), becoming k^b in equation (5)) that gives the best fit to the T_g data in the composition range of low w_1. Introducing k^b, T_{g1}^b and T_{g2}^b in equation (5) and using as system 'a' the same reference system previously chosen, the T_g^*/w_1 plot of *Figure 5* is obtained. For the sake of

comparison also one of our PVC–diluent systems is shown in *Figure 5* (PVC–BuAc, some values omitted for clarity). The data taken from the literature may be divided into two groups: the first[5,7,19] referring to polymer–diluent systems for which the original authors remarked an 'anomalous behaviour', the other[20,21] relative to binary systems whose T_g/composition dependence was considered satisfactorily fitted by an empirical equation[15] such as:

$$T_g = w_1 T_{g1} + w_2 T_{g2} + k w_1 w_2 \qquad (6)$$

In *Figure 5* it may be observed that the systems belonging to the former group (PS–toluene, PS–TTP, PVC–DOA) clearly follow the dual trend shown by all our systems. Unfortunately, due to the differing compositional variable (volume fraction), it is impossible to include a normalization of the T_g data by Czekaj *et al.*[6] on the PVC–TTP, PVC–DOP, PS–DEB and PMMA–DEP systems that exhibit a very clear 'cusp' in the composition dependence. The T_g^* values of the two remaining literature systems of *Figure 5*, gelatin–glycerol and PC–TTP, appear to fall on the lower branch of the T_g^*/w_1 dependence at high diluent contents ($w_1 > 0.7$ for gelatin–glycerol and $w_1 > 0.8$ for PC–TTP). This observation suggests that what has been interpreted as a single decreasing T_g curve[20,21] may be a very gradual transition from the upper to the lower section of the dual T_g/w_1 behaviour.

A very recent paper by Beirnes and Burns[22] reports the presence of two calorimetric T_g's, detectable over the whole range of concentrations from polymer to diluent, for the PVC–DOA and PVC–DOP systems. Both T_g's decrease with increasing diluent content. Rather surprisingly, only a single T_g value for each mixture as 'midpoint temperature for the region containing the two transitions' is reported in the original work[22]; therefore it is not possible to include the normalization of such data in *Figure 5*. Nevertheless, from the calorimetric curves reported by Beirnes and Burns it seems that the two transitions decrease with increasing diluent concentration much in the same way as found for our PVC–diluent systems (*Figure 4*).

Summing up the experimental evidence discussed above, it can be concluded that all observations support the view that in polymer–diluent mixtures two different mobilization phenomena coexist and may be evidenced in the form of two distinct glass transitions. The one at higher temperature is due to the transition from the glassy to the rubbery state of the macromolecules, facilitated by the presence of the mobile diluent. This phenomenon is the manifestation of the well-known 'plasticizing effect' of diluents on the polymer glass transition[23] and may be intuitively explained in terms of the free volume theory[24]. The transition occurring at lower temperature is related

to the mobilization of the diluent hindered by the dissolved polymer molecules. It has to be emphasized that the polymer–diluent system can still be considered a homogeneous solution, no heterogeneities at a macroscopic level in the form of a typical phase separation being revealed by any of the techniques used (see ref. 4). The ability to reveal both transitions for a single polymer–diluent mixture seems to be principally connected with important parameters such as a narrow distribution of relaxation times of the molecular units responsible for the glass transition of the polymer[4] and a sufficiently large distance between T_{g2} and T_{g1} in addition to the experimental technique employed[3].

ACKNOWLEDGEMENTS

REFERENCES

1   Scandola, M., Ceccorulli, G., Pizzoli, M. and Pezzin, G. *Polym. Bull.* 1982, **6**, 653
2   Pizzoli, M., Scandola, M., Ceccorulli, G. and Pezzin, G. *Polym. Bull.* 1983, **9**, 429
3   Pizzoli, M., Scandola, M. and Ceccorulli, G. *Eur. Polym. J.*, in press
4   Ceccorulli, G., Pizzoli, M. and Scandola, M. *Polymer* 1987, **28**, 2077
5   Adachi, K., Fujihara, I. and Ishida, Y. *J. Polym. Sci. Polym. Phys. Edn.* 1975, **13**, 2155
6   Czekaj, T. and Kapko, J. *Eur. Polym. J.* 1981, **17**, 1227
7   Fried, J. R. and Lai, S. Y. *J. Appl. Polym. Sci.* 1982, **27**, 2869
8   Bank, M., Leffingwell, J. and Thies, C. *Macromolecules* 1971, **4**, 43
9   Jonza, J. M. and Porter, R. S. *Macromolecules* 1986, **19**, 1946
10 Nandi, A. K., Mandal, B. M., Bhattacharyya, and Roy, S. K. *Polymer* 1986, **27** (*Commun.*), 151
11 Kelley, F. N. and Bueche, F. J. *J. Polym. Sci.* 1961, **50**, 549
12 Gordon, J. M., Rouse, G. B., Gibbs, J. H. and Risen, Jr. W. M. *J. Chem. Phys.* 1977, **66**, 4971
13 Couchman, P. R. and Karasz, F. E. *Macromolecules* 1978, **11**, 117
14 Chow, T. S. *Macromolecules* 1980, **13**, 362
15 Jenckel, E. and Heusch, R. *Kolloid-Z.* 1953, **130**, 89
16 Fox, T. G. *Bull. Am. Phys. Soc.* 1956, **1**, 123
17 Pochan, J. M., Beatty, C. L. and Pochan, D. F. *Polymer* 1979, **20**, 879
18 Braun, G. and Kovacs, A. J. in '*Physics of Non-Crystalline Solids*', North Holland, Amsterdam, 1965, p 303
19 Riande, E., Markovitz, H., Plazek, D. J. and Raghupathi, N. *J. J. Polym. Sci. Polym. Symp.* 1975, **50**, 405
20 Yannas, J. B. and Tobolsky, A. V. *J. Macromol. Chem.* 1966, **1**, 723
21 Onu, A., Legras, R. and Mercier, P. *J. J. Polym. Sci. Polym. Phys. Edn.* 1976, **14**, 1187
22 Beirnes, K. J. and Burns, C. M. *J. Appl. Polym. Sci.* 1986, **31**, 2561
23 Sears, J. K. and Darby, J. R. 'The Technology of Plasticizers', Wiley, New York, USA, 1982
24 Ferry, D. J. 'Viscoelastic Properties of Polymers', Wiley, New York, USA, 1980