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Further Evidence of an Unusual T_g-Concentration Dependence for Plasticized Polyvinylchloride

M. Scandola, G. Ceccorulli, M. Pizzoli, and G. Pezzin

Centro di Studio per la Fisica delle Macromolecole del C.N.R., Istituto Chimico „G. Ciamician", Bologna University, Via Selmi 2, I-40126 Bologna, Italy

Summary

The glass transition temperature-composition dependence for the systems PVC-dimethylphthalate and PVC-di-n-propylphthalate has been determined in the whole range of concentration. The glass transition temperature of the mixtures decreases with increasing diluent content and in both cases shows a discontinuity at a critical composition ($w_1 \simeq 0.4$). At diluent weight fractions lower than 0.4, the theoretical equations by Kelley-Bueche and Couchman-Karasz satisfactorily fit the experimental results. The marked changes in the glass transition parameters (T_g, Δc_p, width of the transition) which occur in the intermediate range of concentration ($0.4<w_1<0.6$), although difficult to visualize in physical terms, indicate an enhanced mobility of the relaxing units. Moreover, the properties of the mixtures in the high diluent concentration range seem to be dictated by the properties of the pure diluent.

Introduction

The glass transition temperature-composition dependence of polymer-diluent systems in the whole range of concentration, i.e. from the polymer to the pure diluent, has been reported in the literature for relatively few polymers (JENKEL and HEUSCH, 1953; BRAUN and KOVACS, 1965; PEZZIN et al., 1968; ONU et al. 1976; RIANDE et al., 1975). A regular decrease of the T_g of the mixture with increasing diluent weight fraction w_1 from the polymer glass transition temperature T_{g2} to the diluent T_{g1} is predicted by various equations; among them, the empirical equation by FOX (1956), the KELLEY and BUECHE (1961) "free volume" equation and the recent equations by COUCHMAN and KARASZ (1978) and CHOW (1980) based on thermodynamic treatments. There are, however, experimental data that suggest a different "shape" of the T_g-w_1 curve: rather than a single regularly decreasing curve, the T_g-w_1 dependence seems to be composed of two monotonically decreasing sections, having different curvatures and forming a cusp at a critical composition (BRAUN and KOVACS, 1965; PEZZIN et al., 1968; RIANDE et al., 1975).

This paper, based on a careful set of data on mixtures of Polyvinylchloride with di-methylphthalate and di-n-propylphthalate, gives additional evidence of the above mentioned complex behavior.

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Experimental

Di-methylphthalate and di-n-propylphthalate were obtained by esterification of equimolecular mixtures of phthalic acid and the corresponding alcohols, in the presence of p-toluensulphonic acid. The esters, whose purity was higher than 99%, were characterized by density and viscosity measurements from 23 to 80°C.

Commercial Polyvinylchloride (suspension polymerized at 60°C) was mixed with different amounts of plasticizer at 90°C for 30 min.

The glass transition temperature of the pure components and mixtures was determined by means of a Differential Scanning Calorimeter DSC-2 equipped with a Liquid Nitrogen Subambient Accessory and a Scanning Autozero for baseline linearization. DSC curves were recorded from 100 to 390°K at a scanning rate of 20°K/min. Owing to the width of the temperature range explored, the temperature was calibrated using three different high purity standards: lauric acid, benzene and n-octane. The glass transition temperature was determined by the method of the baseline deviation.

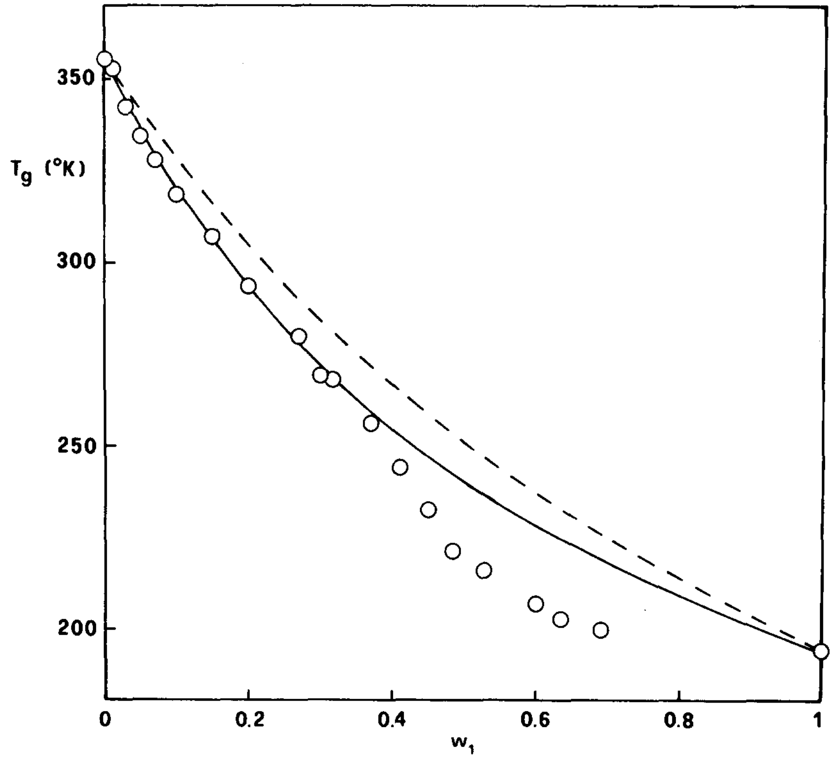

Fig. 1- Glass transition temperature of PVC-dimethylphthalate mixtures as a function of diluent weight fraction w_1.
○ : experimental data; —— : Couchman-Karasz equation;
- - - : Fox equation

As regards the pure diluents, whereas di-methylphthalate is easily vitrified on cooling but is able to crystallize and melt during scanning when heated above its T_g, di-n-propylphthalate does not crystallize and melt in similar conditions. The values of the glass transition temperature T_g and the specific heat increment at T_g, Δc_p are as follows:

di-methylphthalate: $T_{g1}= 194^{o}K$; $\Delta c_{p1}= 0.50\ J/g^{o}K$
di-n-propylphthalate: $T_{g1}= 180^{o}K$; $\Delta c_{p1}= 0.52\ J/g^{o}K$
Polyvinylchloride: $T_{g2}= 355.5^{o}K$; $\Delta c_{p2}= 0.27\ J/g^{o}K$.

Throughout the paper, subscripts 1 and 2 refer to diluent and polymer respectively.

Results and discussion

The mixtures studied in this work present a single T_g, which decreases with increasing diluent weight fraction w_1, as shown in Figs. 1 and 2. In Fig. 1 no T_g values for the PVC-dimethylphthalate

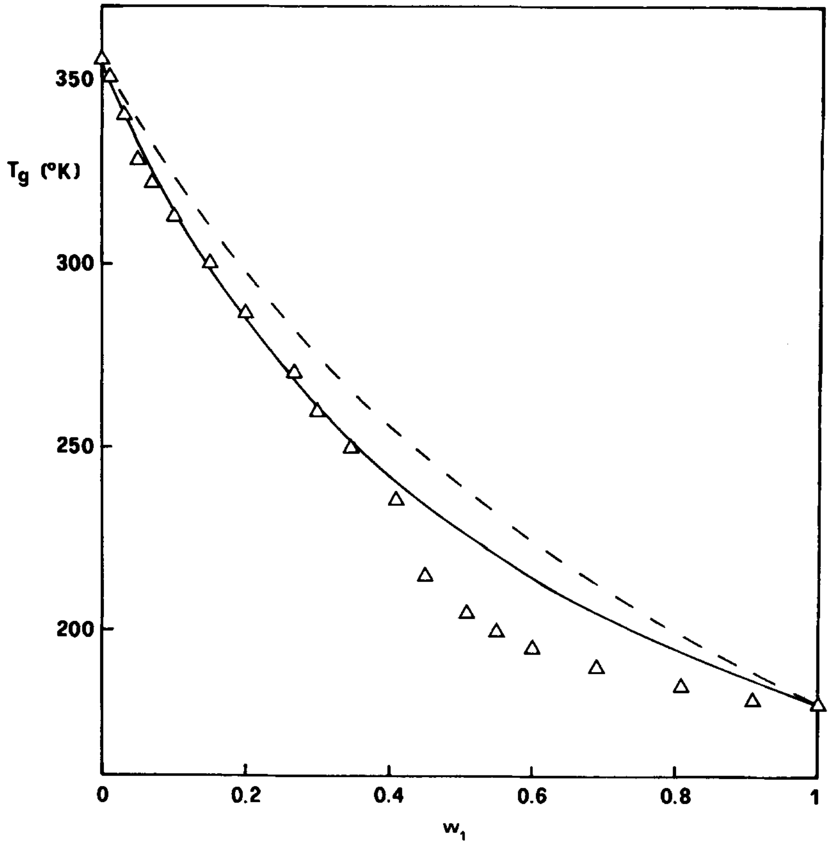

Fig. 2- Glass transition temperature of PVC-di-n-propylphthalate mixtures as a function of diluent weight fraction w_1.
△ : experimental data;——: Couchman-Karasz equation;
– – –: Fox equation

mixtures at $w_1 > 0.7$ are reported, owing to the occurrence of phase separation in the range of concentration $0.7 < w_1 < 1$. In fact, exo- and endothermic processes in the DSC curves - in the temperature range where pure di-methylphthalate crystallizes and melts - indicate that the pure diluent is present as a separate phase. At concentrations higher than $w_1 = 0.7$, the glass transition of the solvated polymer is difficult to determine due to the proximity of the pure diluent T_g.

The most striking feature of the two Figures is the abrupt change of slope of the curves at $w_1 \simeq 0.4$. This is clearly revealed when the experimental data are compared with the theoretically predicted curves. The FOX (1956) equation (dotted curves)

$$1/T_g = (w_2/T_{g2}) + (w_1/T_{g1}) \qquad [1]$$

clearly predicts values of T_g much higher than the experimental ones in the whole range of concentration.

The COUCHMAN and KARASZ (1978) equation (solid lines)

$$\ln(T_g/T_{g2}) = \left[w_1 \Delta c_{p1} \cdot \ln(T_{g1}/T_{g2})\right] / (w_1 \Delta c_{p1} + w_2 \Delta c_{p2}) \qquad [2]$$

appears to give a satisfactory description of the experimental data for both systems, when $w_1 < 0.4$. It has to be pointed out that no unknown parameters are required for the application of Eq. [2], the T_g and Δc_p values being available from the calorimetric measurements on the pure components.

A curve very close to that predicted by the Couchman's treatment is obtained by the use of the well known KELLEY and BUECHE (1961) equation:

$$T_g = (T_{g2}\alpha_2\phi_2 + T_{g1}\alpha_1\phi_1) / (\alpha_2\phi_2 + \alpha_1\phi_1) \qquad [3]$$

where α is the thermal expansion coefficient of the free volume and ϕ is the volume fraction. In practice, α_2 and α_1 are usually taken as $\Delta\alpha_2$ and $\Delta\alpha_1$, i.e. the difference between the expansion coefficient of polymer and diluent above and below their respective glass transition temperatures. From the literature (PEZZIN et al., 1968) $\Delta\alpha_2$ is known to be $3.4 \cdot 10^{-4}\ {}^{\circ}K^{-1}$ for PVC, while no $\Delta\alpha_1$ values are available - to our knowledge - for the two diluents. The best fit of the Kelley-Bueche equation to the experimental data in Figs. 1 and 2 requires the reasonable value $\Delta\alpha_1 = 7.4 \cdot 10^{-4}\ {}^{\circ}K^{-1}$ for both diluents and results in curves practically undistinguishable from the solid lines in the Figures.

In spite of the excellent agreement between the experimental data and the theoretical predictions in the low w_1 range, a description based on equations other than Eqs. [2] and [3] is clearly required in the range of concentrations from $w_1 = 0.4$ to the pure diluent. Two different approaches to the interpretation of this phenomenon may be advanced.

According to BRAUN and KOVACS (1965), in any treatment based on the "free volume" concept, the fractional free volume f_2 contributed by the polymer to the mixture is given by

$$f_2 = f_{g2} + \alpha_2 \cdot (T - T_{g2}) \qquad [4]$$

only at temperatures higher than a critical temperature T_c ($T_c = T_{g2} - f_{g2}/\alpha_2$) which only depends on polymer parameters. At temperatures lower than T_c, the meaningless result of a negative value for f_2 would be obtained from Eq. [4]. Therefore, in order to describe the concentration dependence of the glass transition temperature of mixtures over the entire composition range, two T_g vs. w_1 equations would be required rather than one. Braun and Kovacs, looking for experimental evidence for the "change of equation at T_c", found that the system Polystyrene-toluene does indeed exhibit the predicted features and described the $T_g - w_1$ dependence at $T_g < T_c$ with a new "free volume" equation.

Being the polymer the same for the systems studied in the present work, the Braun and Kovacs treatment would predict a common value of the critical temperature T_c, irrespective of the low molecular weight component in the mixture. On the contrary, Figs. 1 and 2 show that, as already pointed out, the experimental T_g data deviate from the theoretical predictions of Eqs. [2] and [3] at a common w_1 rather than a common T_g value. Therefore the basic theoretical requirement of a single T_c is not satisfied and the application of the Braun and Kovacs treatment, previously used by one of the Authors (PEZZIN et al., 1968), doesn't seem reasonable in the present case.

Any approach to the interpretation of the results has to consider that commercial plasticized PVC compounds, especially when poorly processed, are often heterogeneous and consequently exhibit multiple transitions (FOLDES and HEDVIG, 1981). On the

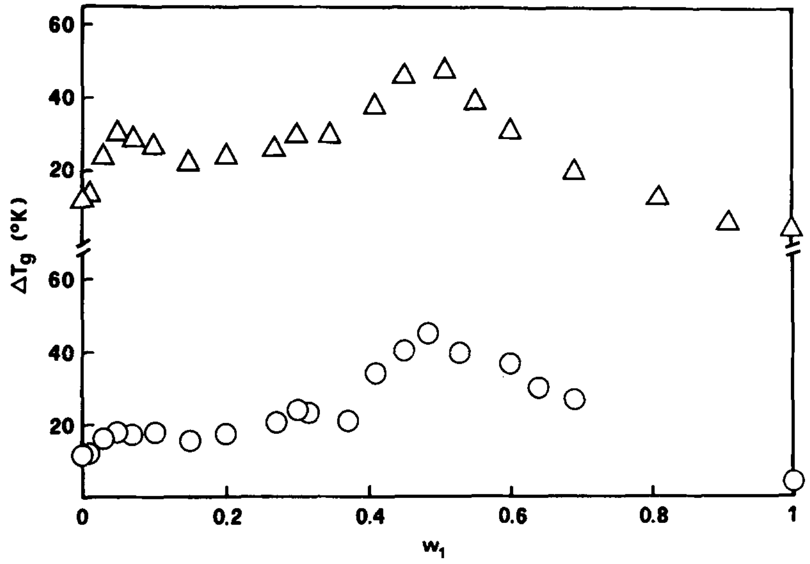

Fig. 3- Width of the glass transition region (ΔT_g) as a function of diluent content.
○: di-methylphthalate; △: di-n-propylphthalate

other hand, even in the absence of such multiple transitions, a broadening of the transition zone is usually found (HEDVIG, 1977). While the presence of a single T_g is taken as evidence of an extensive degree of compatibility, the broadening of the transition zone has been interpreted as indicative of incomplete miscibility at molecular level (AUBIN and PRUD'HOMME, 1980). As already mentioned, a single T_g was found in this work for all mixtures except for the system PVC-dimethylphthalate at $w_1>0.7$, i.e. at diluent contents well above the concentration where the cusp singularity appears.

At diluent weight fractions where the experimental T_g data are lower than the calculated values, the hypothesis that w_1 is underestimated can be made. An "actual" concentration of diluent in the mixtures higher than the "nominal" content can result only if the systems are heterogeneous, i.e. if part of the polymer is unavailable to diluent penetration. In other words, one of the two phases has to be either pure polymer or a very concentrated solution, whereas the second phase is the one whose vitrification gives rise to the "anomalous" T_g. In the absence of multiple T_g's and since PVC is a semicrystalline polymer, a tentative - although unlikely - suggestion is that the crystalline fraction segregates

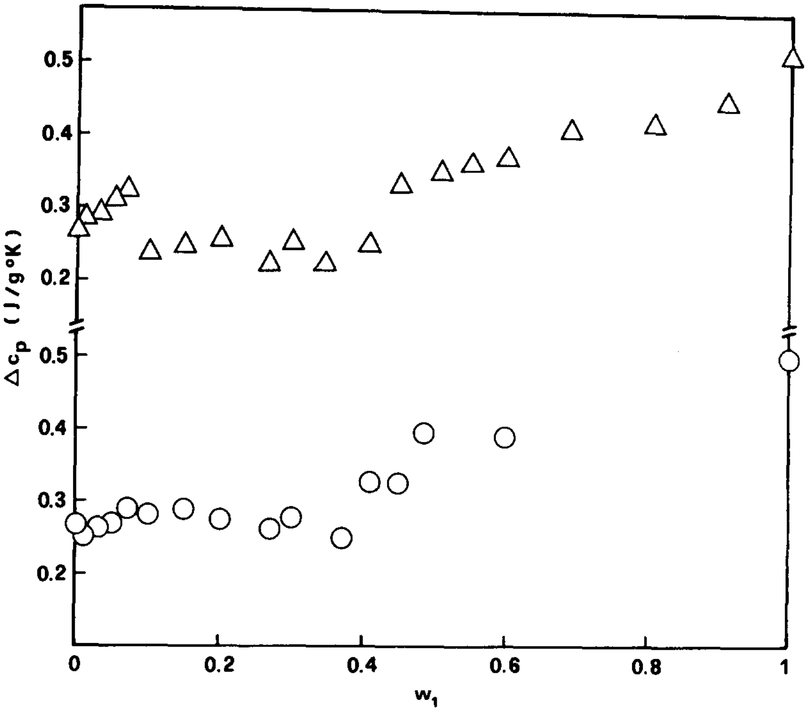

Fig. 4- Specific heat increment at T_g (Δc_p) as a function of diluent content.
○: di-methylphthalate; △: di-n-propylphthalate

at w_1>0.4. The results of Fig. 2 show that the nominal concentration w_1= 0.6 corresponds to w_1≃ 0.8 on the theoretical Couchman curve. If one assumes that the actual composition of the solution is w_1= 0.8, the undissolved (crystalline) polymer fraction should be as high as 62%, a value at least 3 times larger than the maximum amount of crystalline fraction accepted for conventional PVC. This interpretation has therefore to be ruled out.

Additional information on the transition can be obtained from the DSC curves, considering both the width (ΔT_g) of the glass transition region on the temperature scale and the corresponding specific heat increment Δc_p. These parameters are inevitably affected by uncertainties due to the graphical extrapolation employed; nevertheless, in spite of a certain scatter, a clear trend is found, as shown in Figs. 3 and 4, where the average values of ΔT_g and Δc_p are plotted as a function of diluent concentration. Both ΔT_g and Δc_p show a rapid increase in value at the diluent content (w_1≃ 0.4) where the T_g data start to deviate markedly from the theoretical predictions (see Figs. 1 and 2). The width of the glass transition zone of the mixtures is always larger than that of the pure components and goes through a maximum in the range of concentration from w_1= 0.4 to w_1= 0.6. It then decreases towards the diluent ΔT_g value which, as expected for a low molecular weight substance, is rather low (about 5 °K). Correspondingly, in the high diluent content range, Δc_p gradually increases tending to the value of the pure diluent.

From all the results so far considered, it can be observed that, in the range of concentration from w_1= 0.6 to w_1= 1, the properties of the mixtures seem to be controlled by the properties of the diluent. On the other hand, the changes occurring between w_1= 0.4 and w_1= 0.6 are difficult to visualize in physical terms. The relatively rapid decrease of T_g and increase of Δc_p in this range of concentration indicate an enhanced mobility of the relaxing units, i.e. of the solvated polymeric segments. Taking into account that the crystalline and morphological structure of PVC is very complex, and more than a single crystalline phase has been postulated (GUERRERO et al., 1980; BIAIS et al., 1980), the above described behavior could be tentatively attributed to some morphological transition of the polymeric chain taking place at the critical diluent concentration w_1≃ 0.4.

In order to get a better insight into the molecular mechanism responsible for the discontinuity observed in the glass transition temperature-composition curve, further investigations are needed and experimental work is currently in progress in our laboratories on different PVC-diluent mixtures.

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References

AUBIN, M. and PRUD'HOMME, R.E., Macromolecules, 13, 365 (1980).
BIAIS, R., GENY, C., MORDINI, C. and CARREGA, M., Br. Polym. J., 12, 179 (1980)
BRAUN, G. and KOVACS, A. J., "Physics of Non-Crystalline Solids", p. 303, North-Holland, Amsterdam 1965
CHOW, T.S., Macromolecules, 13, 362 (1980)
COUCHMAN, P. R. and KARASZ, F. E., Macromolecules, 11, 117 (1978)
FOLDES, E. and HEDVIG, P., J. Vinyl Technol., 3, 111 (1981)
FOX, T. G., Bull. Am. Phys. Soc., 1, 123 (1956)
GUERRERO, S. J., KELLER, A., SONI, P. L. and GEIL, P. H., J. Polym. Sci. (Phys.), 18, 1533 (1980)
HEDVIG, P., "Dielectric Spectroscopy of Polymers", Adam Hilger Ltd., Bristol 1977
JENCKEL, E. and HEUSCH, R., Kolloid-Z., 130, 89 (1953)
KELLEY, F. N. and BUECHE, F., J. Polym. Sci., 50, 549 (1961)
ONU, A., LEGRAS, R. and MERCIER, J. P., J. Polym. Sci. (Phys.), 14, 1187 (1976)
PEZZIN, G., OMACINI, A. and ZILIO-GRANDI, F., Chim. Ind. (Milan), 50, 309, (1968)
RIANDE, E., MARKOVITZ, H., PLAZEK, D. J. and RAGHUPATHI, N., J. Polym. Sci., Polym. Symp., 50, 405 (1975)

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