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Glass transition temperatures of plasticized polyarylate

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Summary

Glass transition temperatures of different Polyarylate/plasticizer systems with plasticizer concentrations limited to 30 wt.% have been determined by Differential Scanning Calorimetry. Experimental results have been compared to the predictions of three different expressions: the logarithmic rule of mixtures, the Fox equation and the Couchman-Karasz equation. The degree of homogeneity of the different systems has been related to the width of the simple Tg. The data for the different PAr/plasticizer mixtures seem to fit the Fox equation more closely than the other equations tested.

Introduction

When a polymer is mixed with a plasticizer, one of the main effects produced is that of a depression in the glass transition temperature (Tg) of the polymer, which allows a decrease in the processing temperature. Consequently, it is very important in these systems to know the variation of the Tg of the mixture with composition. Over the years, numerous equations have been used in an attempt to relate the glass transition temperature of polymer-polymer and polymer-plasticizer mixtures to component properties and mixture composition (1-6). Some of these equations are totally empirical, whereas others are based on theoretical treatments. Couchman and Karasz (5) have obtained an equation based on the continuity of mixture entropy at Tg. This equation, which appears to be applicable in several systems (4), reduces, under certain restrictions, to other well known equations, such as the simple rule of mixtures, the logarithmic rule of the mixtures or the Fox equation. In this work, we have studied the glass transition temperatures in mixtures of different compositions containing a copolyester of Bisphenol A and an equimolar mixture of isophthalic and terephthalic acids (Polyarylate, PAr) with several commercial plasticizers. The plasticizer concentration has been limited to 30 wt.% for practical reasons.

Experimental

Polyarylate (PAr, Arilef U-100) was obtained from Solvay & Cie.. Their average molecular weights, determined by GPC in THF at 30°C, were $\bar{M}n$=21500 and $\bar{M}w$=51400. The plasticizers were: dimethylphthalate (DMP, Palatinol M, BASF), diethylphthalate (DEP, Palatinol A, BASF), diisobuthylphthalate (DIBP, CEPSA) and dioctylphthalate (DOP, CEPSA). PAr/plasticizer mixtures were prepared by casting in chloroform. Adequate amounts of both components were dissolved in chloroform to give an approximate concentration of 10 wt.% in the solution. The solvent was removed by evaporation at room temperature under a stream of air. The films obtained were dried in a vacuum

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oven at 40 °C to eliminate any traces of solvent. Thermal analysis of the mixtures was carried out by Differential Scanning Calorimetry (DSC), using a PERKIN-ELMER DSC-2 calorimeter. The samples were conditioned before taking the DSC measurements by heating them from 300 K to 423 K at 20 K/min. After this, the samples were maintained at 423 K for 5 min and cooled quickly to 160 K. A second scan from 160 K to 500 K was carried out at 20 K/min. During this scan , the Tg and the width of the glass transition (w) were determined in the way indicated in Figure 1.

Results and Discussion

Figures 2-5 show the Tg values obtained for pure PAr and plasticizer and those found for the the different PAr/plasticizer mixtures. As can be observed, the Tg's for the different plasticizers are very similar. Dioctylphthalate shows a glass transition temperature of 170 K, which is somewhat lower than that obtained by Fried et al. (7) for the same plasticizer. The difference observed may be caused by the different heating rate used. We have obtained our thermograms at 20 K/min, whereas a heating rate of 40 K/min was used by Fried. We have not found in the literature Tg values for the other plasticizers.

On the other hand, it is clear from Figures 2-5 that all the plasticizers have approximately the same influence on the Tg of PAr, which may be a consequence of the similarity of the plasticizers' Tg's.

As we have already mentioned, Couchman and Karasz have obtained an equation which attempts to relate the Tg of a polymeric mixture with the composition and the properties of pure components. The equation, which is based on the continuity of mixture entropy at Tg may be written as follows:

$$\ln (Tg/Tg_1) = [w_2 \,\Delta Cp_2 \ln(Tg_2/Tg_1)] / [w_1 \,\Delta Cp_1 + w_2 \,\Delta Cp_2] \qquad /1/$$

where Tg is the glass transition temperature of the mixture, and Tg_1, Tg_2 those of the pure components, ΔCp the difference in specific heat between the liquid and glassy states at Tg, and w the weight fraction. In this equation, component 1 is the low temperature component.

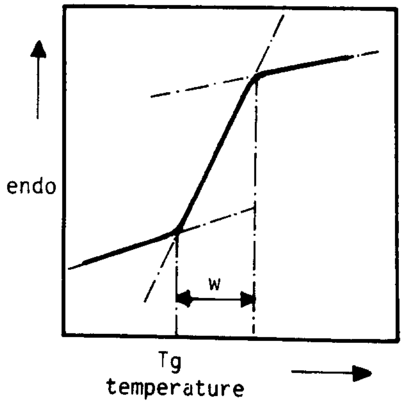

Figure 1.- Evaluation of the glass transition temperatures and width of the transition.

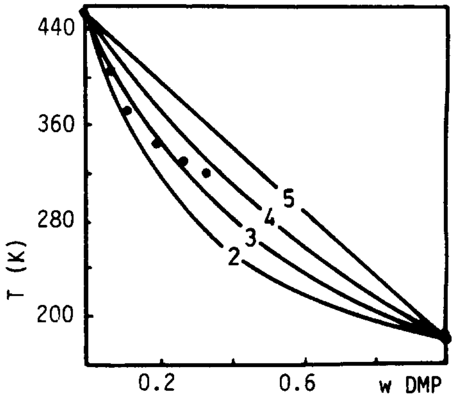

Figure 2.- Tg's of different PAr/DMP compositions. Numbers 2,3,4 and 5 refer to equations in the text.

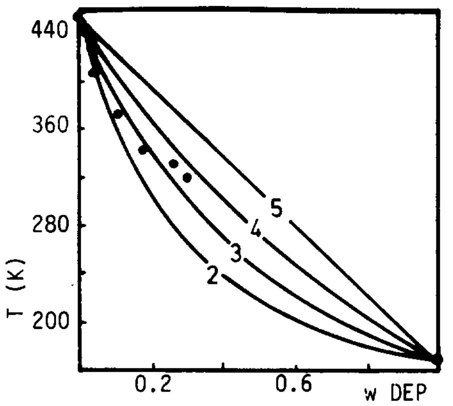

Figure 3.- Tg's of different PAr/DEP compositions. Numbers 2,3,4 and 5 refer to equations in the text.

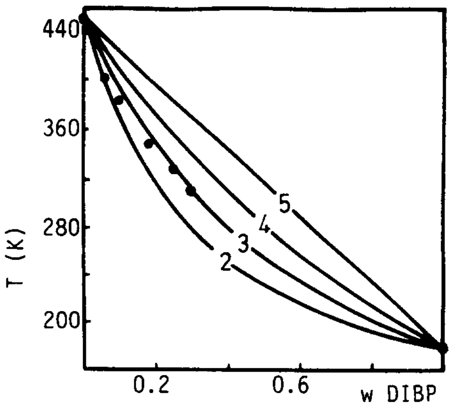

Figure 4.- Tg's of different PAr/DIBP compositions. Numbers 2,3,4 and 5 refer to equations in the text.

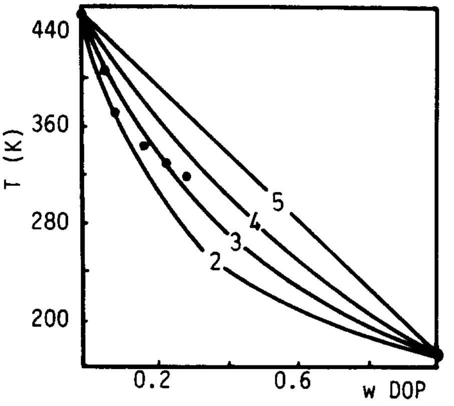

Figure 5.- Tg's of different PAr/DOP compositions. Numbers 2,3,4 and 5 refer to equations in the text.

The Couchman-Karasz equation has been applied to predict the Tg-composition relationships in several polymer-polymer and polymer-plasticizer mixtures (4, 7, 8). The application of this equation requires the knowledge of ΔCp and these values are rarely included in the literature. However, equation 1 may be simplified by taking into account the Simha-Boyer (9) empiric rule which states that for a number of polymers, $Tg.\Delta Cp$ is approximately constant. So, equation /1/ is transformed into:

$$\ln(Tg/Tg_1) = [\, w_2 \ln(Tg_2/Tg_1) \,] \;/\; [\, w_1 \, (Tg_2/Tg_1) + w_2 \,] \qquad /2/$$

In the limiting case where $Tg_1 \approx Tg_2$, equation /2/ may be transformed into the Fox equation:

$$1 \,/\, Tg = w_1/Tg_1 + w_2/Tg_2 \qquad /3/$$

On the other hand, if $\Delta Cp_1 = \Delta Cp_2$, equation /1/ reduces to the logarithmic rule of mixtures:

$$\ln Tg = w_1 \ln Tg_1 + w_2 \ln Tg_2 \qquad /4/$$

If the ratio of the two components' Tg's is not very far from unity, equation /4/ may be modified to give the additive rule of mixtures:

$$Tg = w_1\, Tg_1 + w_2\, Tg_2 \qquad /5/$$

Figures 2-5 also show the curves corresponding to equations /2-4/ for the different PAr/plasticizer mixtures. Equation /1/ has not been applied because of the difficulties in determining ΔCp values for the plasticizers. On the other hand, only the ΔCp value for DOP has been found in the relevant literature. Consequently, we have applied equation /2/, taking into account that we have verified that the Tg. ΔCp product for PAr is equal to 26.7 cal/gr, which is in good agreement with the constant value Tg. ΔCp = 27.5 proposed by Boyer . Also Fried et al. (7) have obtained a value Tg. ΔCp= 27.0 for DOP and similar values for other plasticizers; consequently we may expect the Tg. ΔCp product to be constant for the rest of plasticizers we have used in our work.

As can be observed in Figures 2-5, equations /4/ and /5/ do not adequately reproduce the Tg-composition relationships obtained experimentally. This could be expected if we take into account the conditions for which these equations are valid. If we look at equation /2/ and /3/, it appears that equation /3/ (Fox equation) is the equation which best agrees with the experimental data. This is an unexpected result. We have already mentioned that equation /2/ reduces to the Fox equation when $Tg_1 \approx Tg_2$ and this condition is not accomplished by the PAr/plasticizer mixtures. We have not been able to find any explanation for this result at the present moment. As can be observed in Figures 2-5, the Tg values obtained experimentally are greater than those predicted by the Couchman equation. The higher the plasticizer content in the mixture, the greater deviations observed. Other authors have found similar positive deviations in polymer/plasticizer mixtures. For example, Beirues and Burus (8) have observed in PVC/DOP and PVC/dioctyladipate Tg values somewhat higher than those predicted by the Couchman equation when the weight fraction of the plasticizer is lower than 40%. For plasticizer weight fractions higher than 40% there is a more clear agreement between theoretical and experimental Tg values.

The reason for the observed positive deviations of the experimental Tg values with respect to the values predicted by the Couchman equation may be that such an equation is based on the assumption that both components are homogeneously mixed on a microscale. However, if there are specific interactions between the components of the mixture, these may give rise to an inhomogeneity in the mixtures, rendering the equation invalid.

In the PAr/phthalate mixtures, the positive deviations may be attributed to the existence of specific interactions between the components, similar to those which have been proposed as responsible for the miscibility in PAr/poly(butylene terephthalate) blends (10).

Although all the PAr/plasticizer mixtures show a single glass transition, indicating their miscibility, it appears that the different mixtures have a different degree of homogeneity. First, PAr/DMP, PAr/DEP and PAr/DIBP mixtures are totally transparent at all compositions. On the contrary PAr/DOP mixtures are opaque. This seems to indicate the existence of a certain microheterogeneity in PAr/DOP mixtures. These visual observations seem to be confirmed by the variation of the width of the glass transition with the mixture composition in the different PAr/plasticizer mixtures. As can be seen in Table 1, the Tg width is greater in the mixtures than in the pure components. On the other hand, the Tg width increases as the plasticizer content in the mixtures increases. Similar results have been explained by several authors on the consideration that the width of the Tg in a mixture, can be relate to the phase homogeneity. Thus, Fried et al. (11) have observed a widening in the Tg of Poly(2,6-dimethyl-1,4-phenylene oxide)/Poly (styrene-co-4-chlorostyrene) mixtures as the copolymer compositions approach the region in which the mixtures are immiscible, that is, as the inhomogeneity of the phases present in the mixtures increases.

TABLE 1

Glass transition width for PAr/plasticizer mixtures

Composition PAr/DMP	width (K)	Composition PAr/DEP	width (K)
100/0	14	100/0	14
93/7	12	96/4	14
88/12	13	89/11	15
80/20	17	82/18	16
73/27	13	74/26	16
67/33	13	70/30	20
0/100	5	0/100	4

Composition PAr/DIBP	width (K)	Composition PAr/DOP	width (K)
100/0	14	100/0	14
94/6	14	94/6	20
90/10	16	91/9	20
82/18	21	83/17	26
75/25	27	77/23	24
70/30	25	71/29	30
0/100	5	0/100	6

According to these ideas, it appears that the different PAr/plasticizer mixtures have a different degree of homogeneity. The greater the aliphatic character of the alcoholic rest in the plasticizer, the lower the homogeneity. These results seem to indicate that the compatibility of the different plasticizers with PAr depends on the aliphatic character of the alcoholic rest, and diminishes the greater is the aliphatic character. This tendency is in good agreement with that expected from the solubility parameters of PAr and of plasticizers. Although the solubility parameter rule as a method of predicting miscibility is not very accurate, partly because of the difficulties in determining solubility parameters with precision, the lower the difference between the solubility parameters of the blends constituents, the greater the miscibility degree expected. In this sense, if we compare the solubility parameter of PAr, $\delta = 9.9$ (12), with the solubility parameters indicated in Table 2, it seems clear that the greater compatibility degree should correspond to the PAr/DOP system, in good agreement with the result obtained from the glass transition widths, as previously exposed. We have not found in the literature the solubility parameter for DIBP, and thus, it has been calculated by the Fedors' contribution group method.

From the results obtained in this work by means of calorimetric analysis in PAr/plasticizer mixtures it can be concluded that: i) the homogeneity of the mixtures depends on the chemical composition of the plasticizer,

TABLE 2

Solubility parameters for several plasticizers

Plasticizer	δ $(cal/cm^3)^{1/2}$
DMP	10.7
DEP	10.0
DIBP	9.7
DOP	7.9

and ii) it is the Fox equation which gives rise to the best reproduction of the Tg-composition data for the different PAr/plasticizer mixtures.

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