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Glass-Transition Temperatures of PVME - PS Blends
Influence of the Molecular Weight of PS

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SUMMARY

Glass-transition temperatures of compatible PVME/PS blends show, beside the well-known composition dependence, a predominant influence of the molecular weight of the blend components, mainly that of PS. This influence can be reproduced by an extended Gordon-Taylor equation only. The values, however, of the parameters of the extended Gordon-Taylor equation show molecular specific correlations.

INTRODUCTION

It has recently been shown that the composition dependence of the glass-transition in compatible poly(vinylmethylether) - PVME -/ poly(styrene) - PS - blends can be explained by accepting an additional adjusting parameter, which accounts for the interaction between the components of the blend. The impossibility of representing Tg-composition data for the compatible PVME/PS blends by the usual FOX and GORDON-TAYLOR relation has been remarked upon by BANK et al. (ref.1).

This adjusting parameter is quite different for blends with oligomeric and high molecular PS, respectively (ref.2). Molecular weight specific differences are also observed in rheological measurements (ref.3).

The aim of this paper is to extend the Tg study to an increased number of compatible PVME/PS blends by varying the molecular weight of both the components, in expectance of a better insight into the molecular weight influence on the Tg-composition dependence of compatible polymer blends.

Tg - COMPOSITION RELATION FOR POLYMER BLENDS

It is known that miscibility in polymer blends, restricted to the amorphous phase only, is related to the existence of a single composition-dependent glass-transition temperature, Tg.

Different rules have been proposed to describe the composition dependence of Tg and, in a series of papers, COUCHMAN (ref.4) has suggested that these rules can all be supported by thermodynamic mixing equations for the extensive functions, assuming continuity at Tg of the excess functions of mixing. The problems that arise with this thermodynamic approach are shown by GOLDSTEIN (ref.5) and are illustrated by the different Tg equations, derived for entropy, S,

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$$\ln Tg = (X_A \Delta Cp_A \ln Tg_A + X_B \Delta Cp_B \ln Tg_B)/(X_A \Delta Cp_A + X_B \Delta Cp_B) \qquad (1)$$

and enthalpy, H, respectively

$$Tg = (X_A \Delta Cp_A Tg_A + X_B \Delta Cp_B Tg_B)/(X_A \Delta Cp_A + X_B \Delta Cp_B) \qquad (2)$$

Here, X_i are the mole fractions and ΔCp_i the discontinuities at Tg of the heat capacities.

The corresponding equation for the continuity of the volume of mixing at Tg is also of nonlogarithmic form:

$$Tg = (X_A \Delta\alpha_A V_A^o Tg_A + X_B \Delta\alpha_B V_B^o Tg_B)/(X_A \Delta\alpha_A V_A^o + X_B \Delta\alpha_B V_B^o) \qquad (3)$$

$\Delta\alpha_i$ are the discontinuities of the expansion coefficient and V_i^o the molar volumes of the pure components

PREST and PORTER (ref.6) have published an almost identical expression, which was derived assuming the validity of the "iso-free volume" state supposition for Tg of WILLIAMS, LANDEL and FERRY (ref.7).

Taking into account the WLF temperature-dependence of the free volume

$$f = f_g + \Delta\alpha (T - Tg) \qquad (4)$$

with $\Delta\alpha = \alpha_L - \alpha_{Gl}$, the expansion coefficient of the free volume (identical in the iso-free volume state assumption with the discontinuity of the expansion coefficient at Tg) and accepting additivity for both the free volume and the expansion coefficient of the free volume, equation (5) results:

$$Tg = (\Phi_A \Delta\alpha_A Tg_A + \Phi_B \Delta\alpha_B Tg_B)/(\Phi_A \Delta\alpha_A + \Phi_B \Delta\alpha_B) \qquad (5)$$

Φ_i are the volume fractions of the components. The identity of equs. (3) and (5) is evident considering the correlation between volume and mole fraction, $\Phi_i = X_i V_i^o/(V/n)$, with V the global volume and n the global number of moles of the mixture. Volume fraction can also obviously be replaced by the respective weight fraction.

Rearranging equ.(3), the GORDON-TAYLOR expression (ref.8) is obtained:

$$Tg = (X_A Tg_A + K X_B Tg_B)/(X_A + K X_B) \qquad (6)$$

with $K = \Delta\alpha_B V_B^o / \Delta\alpha_A V_A^o$.

Accepting the SIMHA - BOYER rule (ref.9), $\Delta\alpha\, Tg = \text{const}$, the expression for K becomes: $K = (V_B^o/V_A^o)(Tg_A/Tg_B) = K'(Tg_A/Tg_B)$. For $K'=1$, the FOX expression (ref.10) results:

$$(Tg)^{-1} = (X_A/Tg_A) + (X_B/Tg_B) \qquad (7)$$

The Gordon-Taylor expression (6) explains only monotonous deviations, either negative ($K<1$) or positive ($K>1$) from additivity (ref.2). To account for specific interaction, which may perturb the free volume additivity in the polymer mixture, KWEI (ref.11) added to the Gordon-Taylor equation the quadratic term, $qX_A X_B$. S-shaped curves can then be explained, but only with positive deviations from additivity in the low Tg range and negative deviations in the high Tg range, as shown in Fig.1a. To reproduce negative deviations in the low Tg range and positive deviations in the high Tg range, an additional correction term has to be used (see Fig.1b.)

The extendet Gordon-Taylor equation is therefore further used for reproduction of the experimental Tg dependence on polymer composition.

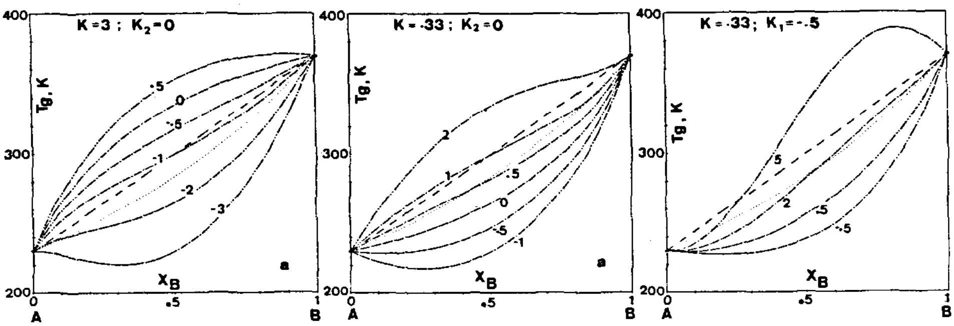

Fig.1 Theoretical Tg vs. composition curves of compatible polymer blends predicted by the extended Gordon-Taylor equation
a. $K_2 = 0$ (in fact the Kwei relation (ref.11)), influence of the K_1 parameter (shown on the curves) for constant K-values
b. Influence of the K_2 parameter for constant K and K_1 values

$$Tg = (X_A Tg_A + K X_B Tg_B)/(X_A + K X_B) + (Tg_B - Tg_A) X_A X_B (K_1 + K_2 X_B) \qquad (8)$$

The multiplicator $(Tg_B - Tg_A)$ in the correction term is preferred, taking into account a suggestion of JENKEL and HEUSCH (ref.12). The justification for the use of this multiplicator is supported by experimental data, as will be seen below.

Defining a free volume related mole fraction, $X_A' = \Phi_A \Delta\alpha_A / (\Phi_A \Delta\alpha_A + \Phi_B \Delta\alpha_B)$, the Gordon-Taylor equation reduces to a mathematically simple additivity rule, which, in terms of X_B' only, may be written in the form:

$$Tg = X_A' Tg_A + X_B' Tg_B = Tg_A + (Tg_B - Tg_A) X_B' \qquad (9)$$

taking into account that $X_A' = (1 - X_B')$.

The extended Gordon-Taylor equation can be reformulated in a similar way to a virial equation for Tg of polymer mixtures showing deviations from the supposed free volume additivity.

$$Tg = Tg_A + (Tg_B - Tg_A) X_B' (1 + K_1' X_B' + K_2' X_B'^2 + \dots) \qquad (10)$$

presenting thermodynamic support for the use of the $(Tg_B - Tg_A)$ multiplicator in the correction term for deviations from additivity due to molecular interaction.

EXPERIMENTAL

The characteristics of the polymers used for PVME/PS blend preparation are shown in TABLE 1. All blends were obtained by freeze-drying from toluene solution.

TABLE 1. **Characteristics of the Polymers used for Blend Preparation**

Polymer	Provenance	M_w	M_w/M_n	Tg, K
PS_{800}	Pressure Chem.Corp.	800	1.30	260.8
PS_{9500}	Dr.Möller	9500	1.75	346.3
PS_{73500}	Pressure Chem.Corp.	73500	1.08	371.3
$PVME_{1000}$		1000	1.41	210.7
$PVME_{10500}$	BASF	10500	2.01	235.8
$PVME_{97500}$	BASF	97500	2.06	241.9

PS_{800} and PS_{73000} were Special Polystyrene Standards of Pressure Chemical Company. The anionic PS_{9500} was kindly supplied by Dr. Möller from our Institute.

$PVME_{10500}$ and $PVME_{97500}$ were supplied by BASF. $PVME_{1000}$ was prepared via quasicationic polymerization in toluene at -40°C, using the initiator systheme J_2/HJ. After termination with $NaOH/NH_3$ the product was washed with $Na_2S_2O_3$-solution and then purified by repeated precipitation from water solution. All PVME samples were dissolved in water (25 % w/w solution) and extracted with toluene at 0°C. Subsequently partial reduction of polydispersity was assured through precipitation from the aqueous solution by heating at about 40°C.

Molecular weights of the samples were determined by GPC and by osmometry and vapour osmometry, respectively. Glass-transition was observed by DSC at different heating rates, using a PERKIN-ELMER DSC 7. The temperatures referring to the onset of the abrupt increase in heat capacity were designated as Tg and the values given in Table 1 are those extrapolated for zero heating rate.

RESULTS AND DISCUSSION

The experimental Tg data of the PVME/PS blends confirm the molecular weight specific dependence and, as illustrated in Fig.2, this molecular weight specificity is related essentially to the molecular weight of the PS component.

Independent of the molecular weight of PVME, all blends with PS_{800} show mainly additivity in the low PS content range and negative deviations in the high PS content range (Fig.2a). On the contrary, blends with the higher molecular weight PS show negative deviations in the low PS content range. The high PS range exhibits positive deviations for PS_{9500} (Fig.2b) and small negative deviations, approaching additivity, for the higher molecular weight PS_{73000} (Fig.2c), respectively.

Fig. 2d compares the Tg data of the $PVME_{97500}/PS_{73500}$ blend with available literature data.

The data of BANK et al. (ref.1) refer to the blend PVME, M_n=524000/PS, M_n=150000 and were measured by DSC at a heating rate of 20 K/min. The higher Tg values of the pure components are therefore explicable. The same conditions for Tg determination were used by HALARY et al. (ref.14) for blends of PVME, M_n=46500, M_w/M_n=2.12 and PS, M_n=100000, M_w/M_n=1.06. The Tg data of KWEI et al. (ref.13) were evaluated from volume-temperature curves and refer to PVME, $[\eta]$=0.51 (under benzene at 25°C) and PS, $[\eta]$ =0.94 (under the same conditions). Our former data, also obtained by DSC, refer to PVME, M_w=73000 (as supplied by BASF) and PS, M_n=73500, M_w/M_n=1.06.

The similarity of the extended Gordon-Taylor plots is evident. Taking into account that the literature data give K_1=-0.7, the same value was also used for the $PVME_{97500}/PS_{73500}$ blend, although in Fig. 2c the value -0.5 was used for all blends of PS_{73500}, including that with $PVME_{97500}$.

All Figures show additivity by dashed lines and the Tg behaviour predicted by the Fox relation by dotted lines. The composition of the blends is always expressed in mole fraction of monomeric styrene unit.

The constants of the extended Gordon-Taylor equation (8), obtained using the trial and error method, used for the reproduction of the experimental Tg data of the studied blends are shown in TABLE 2.

Although apparently the K value varies, the correlation with the Tg_{PVME}/Tg_{PS} ratio is confirmed by the invariance of the respective K' multiplicator for all PVME/PS blends.

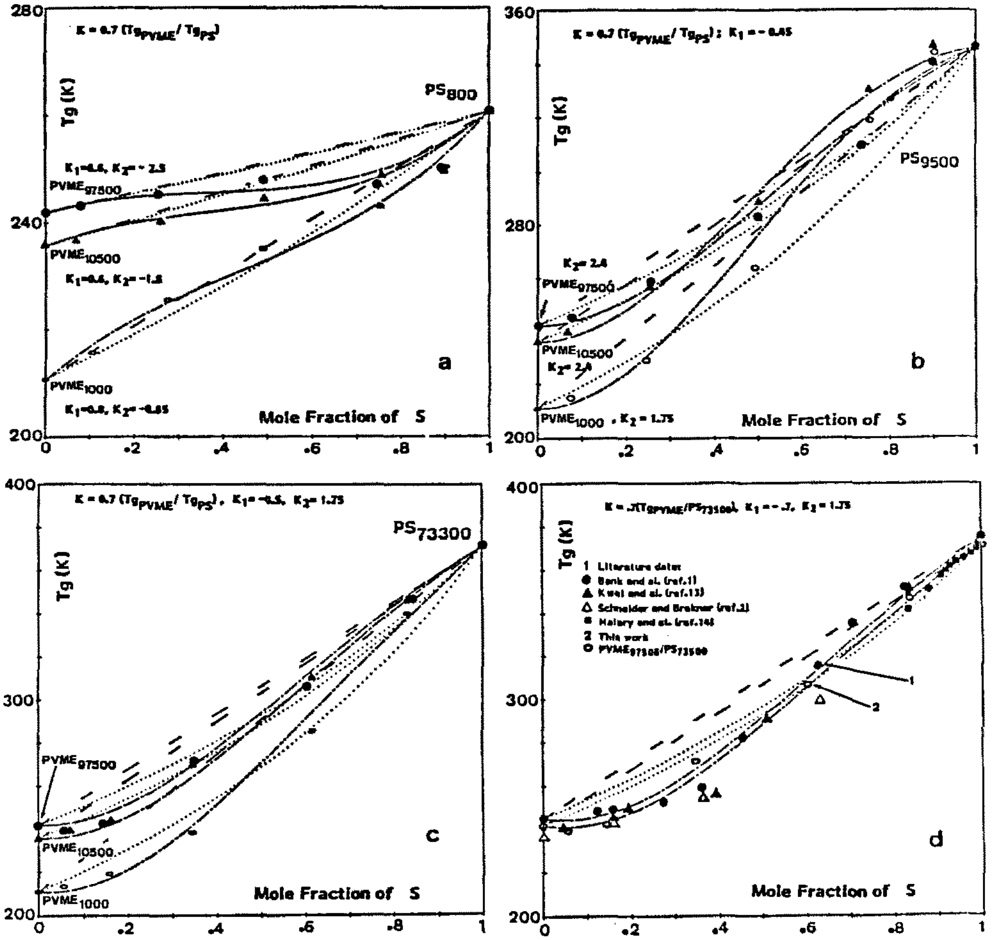

Fig. 2 Tg vs. composition curves of PVME/PS blends
PVME blends with a - PS_{800}, b - PS_{9500} , c - PS_{73500} and
d - comparison between literature data and $PVME_{97500}/PS_{73500}$;
the values of the parameters of the extended Gordon-Taylor equation
are specified

It may therefore be assumed that the K' constant is characteristic for the given polymer blend. The constants K_1 and K_2 are determined by both specific interactions and by the molecular weight of the components. The suggested correlation of these latter constants with the difference between the Tg values of the components, (Tg_{PS}-Tg_{PVME}), is supported by the fact that the respective values are at least constant for groups of blends. They vary with the molecular weight of the polymer components and all data suggest the

TABLE 2. Constants of the extended GORDON-TAYLOR Relation

Polymer Blend	$K = K'(Tg_A/Tg_B)$		$(Tg_B-Tg_A)(K_1+K_2X_B)$	
PVME/PS	K	K'	K_1	K_2
1000/800 x)	0.557	0.7	0.8	-0.85
10500/800	0.623	0.7	0.6	-1.8
97500/800	0.640	0.7	0.6	-2.5
1000/9500	0.419	0.7	-0.45	2.4
10500/9500	0.470	0.7	-0.45	2.4
97500/9500	0.482	0.7	-0.45	1.75
1000/73500	0.391	0.7	-0.5	1.75
10500/73500	0.438	0.7	-0.5	1.75
97500/73500	0.449	0.7	-0.7	1.75

x) The figures indicate the molecular weight of the components

predominant influence of the molecular weight of the less flexible PS component. Further studies are needed, including measurements on other compatible polymer blends, for clarification of the molecular correlation, mainly of the K_1 and K_2 constants.

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