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# Thermodynamic Aspects of the Glass-Transition in the Compatible Blend Poly(Styrene)-Poly(Vinylmethylether)

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**Dedicated to Prof. C. I. Simionescu's 65th Birthday**

## Summary

It is shown that composition dependence cf glass-transition in the compatible poly(styrene)-poly(vinylmethylether) blend exhibits deviations from additivity rules derived in the supposition of continuity of the thermodynamic excess functions of mixing. Only the acceptance of an additional adjusting parameter which accounts for interaction, enables the interpretation of experimental $T_g$-data. This adjusting parameter is quite different for the blends of PVME with oligomeric and high moleculare PS, respectively.

## Introduction

It is well known that the glassy state is not confined to high polymers only, but it is general to substances which easely can be cooled below their melting points without the occurance of crystallization. The transition to the glassy state involves an abrupt change in the thermodynamic state of the glassy-forming liquid, occuring in a rather narrow range of temperature.

For polymers a series of rules relate the observed changes at $T_g$ with the $T_g$ itself as pointed out by BOYER [1]. The most common relationships are respectively $\Delta\alpha T_g = K_1$ and $\Delta CpT_g = K_2$. $\Delta\alpha = \alpha_L - \alpha_G$ is the change of the cubical expansion coefficient at $T_g$ and similar $\Delta Cp = Cp_L - Cp_G$. Structural features, however, may be responsible for deviations from these rules.

The glass-transition is related to the mobility of the polymer chain and is caused by relaxational effects associated with the volume change. The dominant characteristic of $T_g$ is connected to the iso-free volume assumption. Discussion concerning the opinion the $T_g$ is also a thermodynamic phase transition of second-order is still actual [2].

Miscibility in polymer blends is restricted to amorphous phase only and compatible polymer mixtures exhibit a single $T_g$ which varies with the composition.

## Glass-transition of compatible polymer blends

Various empirical rules have been proposed to describe the composition dependence of $T_g$ and it has been suggested that all these rules can be derived accordingly to the thermodynamic mixing equations [3]. Some problems which arise, however, with the thermodynamic approach have been pointed out recently by GOLDSTEIN [4].

With the supposition that thermodynamic excess functions of mixing, $\Delta S_{mix}$, $\Delta H_{mix}$ and $\Delta V_{mix}$ are continous through the glass transition the following expressions are deduced for the $T_g$ of the binary mixture:

Entropy

$$\ln T_g = (X_A \Delta Cp_A \ln T_{gA} + X_B \Delta Cp_B \ln T_{gB})/(X_A \Delta Cp_A + X_B \Delta Cp_B) \quad (1)$$

Enthalpy

$$T_g = (X_A \Delta Cp_A T_{gA} + X_B \Delta Cp_B T_{gB})/(X_A \Delta Cp_A + X_B \Delta Cp_B) \qquad (2a)$$

Volume

$$T_g = (X_A V_A{}^0 \Delta\alpha_A T_{gA} + X_B V_B{}^0 \Delta\alpha_B T_{gB})/(X_A V_A{}^0 \Delta\alpha_A + X_B V_B{}^0 \Delta\alpha_B) \qquad (2b)$$

$X_i$ are the mole fractions and $V_i{}^0$ the molare volumes of the pure components.

Equations (1) and (2a) are compatible only if the ratio $T_{gA}/T_{gB}$ is not to different from unity so that the logarithmic terms can be developed and approximated in the usual manner. For most compatible polymer blends, however, this condition is hardly valid.

On the other hand, if both (2a) and (2b) are true, the ratio $\Delta Cp/\Delta\alpha V^0$ seem to be an universal constant for all polymers. But considering the wellknown relation $\Delta\beta\Delta Cp = \Delta\alpha^2 V^0 T_g$ ($\Delta\beta$ is here the difference of compressibility coefficient at $T_g$) – derived by PRIGOGINE and DEFAY $^{5)}$ according to the method of irreversible thermodynamics and independently by HIRAI and EYRING $^{6)}$ from the hole theory – in the rearranged form $\Delta Cp/\Delta\alpha V^0 = \Delta\alpha T_g/\Delta\beta$ and taking into account that $\Delta\alpha T_g$=constant, $\Delta\beta$ has to be an universal constant too for all polymers. This is contradicted by experimental data, however.

Neglecting for the moment the above evidenced difficulties arising from the assumption of simultaneous validitiy of the thermodynamic $T_g$-composition relations of compatible polymer blends, it is easy to show theyr connection with the reported empirical $T_g$-composition rules.

If the $\Delta Cp_i$ are expressed per unit mass, the mole fractions, $X_i$ in (1) and (2a) can be replaced by the mass fractions, $w_i$. On the other hand the products $X_i V_i{}^0$ in eqn. (2b) can be substituted by the volume fractions, $\Phi_i$, and taking into account the small differences in polymer densities, mass and volume fractions are interchangeable in first approximation. As a consequence weight fractions can be used in the $T_g$-composition relationships of compatible polymer blends.

For $\Delta Cp_A = \Delta Cp_B$ and $\Delta\alpha_A = \Delta\alpha_B$, respectively, equation (1) yields the logarithmic mean rule of POCHAN $^{6)}$, whereas equations (2a) and (2b) result in the arithmetic additivity rule of ideal behaviour. Both above equalities are, however, questionable for polymers.

Introducing $\Delta Cp_B/\Delta Cp_A = K$ or $\Delta\alpha_B/\Delta\alpha_A = K$, respectively, the nonlogarithmic equations (2) transform into a GORDON-TAYLOR $^{7)}$ type equation

$$T_g = (w_A T_{gA} + K w_B T_{gB})/(w_A + K w_B) \quad . \qquad (3)$$

Considering supplementary the above mentiond Boyer rules, the FOX $^{8)}$ relation is obtained

$$(T_g)^{-1} = w_A (T_g)_A{}^{-1} + w_B (T_g)_B{}^{-1} \quad . \qquad (4)$$

Negative deviations from ideal additivity behaviour are predicted by these two latter equations.

All these rules support rather symmetrical $T_g$-composition relationships for compatible polymer blends as evidenced in Figure 1.

The choosen $T_g$-values of the components A and B were in Fig.1 of 300 and 400 K, respectively. Taking into account real $\Delta Cp$ and $\Delta\alpha$ data of polymers, the K values of the Gordon-Taylor equation (3) range at most between additivity and 0.4 and the expected $T_g$ data of compatible polymer blends will be situated within the hatched surface in Figure 1. For comparison only, the Fox relation (F) which obeys the Boyer rules is presented too in both the Figure 1 and the following Figures.

Larger deviations from additivity and especially positive and asymmetric $T_g$-composition dependences observed experimental support supplementary the

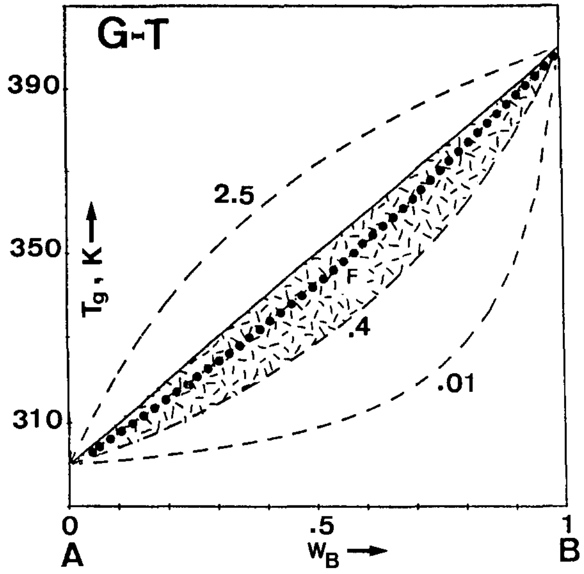

Figure 1. The Gordon-Taylor $T_g$-rule of compatible polymer blends. Values of the K-parameter are shown on the respective curves. The dotted curve represents the Fox (F) relation.

limitation of the simple thermodynamic mixing rules based on continuity of extensive thermodynamic functions only.

There have to be considerd two aspects. First, with respect to the $T_g$ of the blend the pure components are the one in the liquid and the second in the glassy state. Consequently it is necessary to reexamine the assumption of continuity of the thermodynamic excess mixing functions in such conditions. Second, are neglected possible differences in interactions between the components in the mixed phase which may occure in the glassy and in the liquid state.

These will result at least in a supplementary correction term of the Tg-composition relations of compatible polymer blends.

Assymetric $T_g$-composition curves can be reproduced by adding an quadratic term to the arithmetic additivity rule, as suggested by JENKEL and HEUSCH [9]

$$T_g = w_A T_{gA} + w_B T_{gB} + q w_A w_B \quad , \quad (5)$$

with $q=b(T_{gB}-T_{gA})$ in the original version of the relation, b being an empirical system dependent parameter.

KWEI [10] has recently shown that both assymetric deviations and S-shaped curves can be fited by adding the quadratic term to the Gordon-Taylor equation, to account for specific interactions,

$$T_g = (w_A T_{gA} + K w_B T_{gB})/(w_A + K w_B) + q w_A w_B \quad . \quad (6)$$

The shapes of both the corrected $T_g$-composition equations (5) and (6) are illustrated in Figure 2, assuming the experimentally justified limite value of K=0.4 and different b- and q-values, respectively.

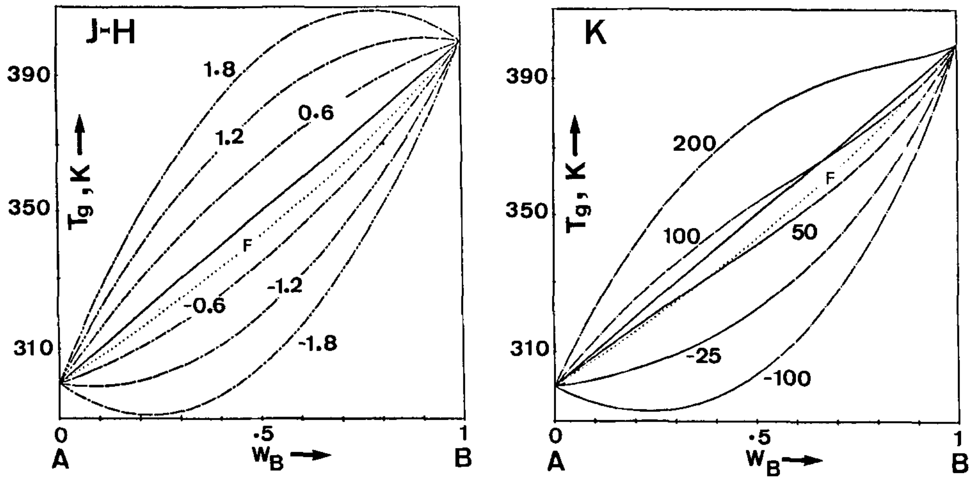

Figure 2. Asymmetric $T_g$ curves of compatible polymer blends according to Jenkel and Heusch (J-H) and Kwei (K) b- and q-parameters indicated on the curves.

Taking into account, however, the possible thermodynamic background of the relations, it seems more justified to use the Gordon-Taylor equation (2) as starting point for a corrected $T_g$-composition relation of compatible polymer blends as suggested by Kwei.

## Results and Discussion

BASF Poly(vinylmethylether) - PVME - of $M_w$=73,000 and special standard Poly(styrene) of Pressure Chemical of $M_w$=800, $M_w/M_n$=1.3 - $PS_{800}$ - and of $M_w$=75,000, $M_w/M_n$=1.06 - $PS_{75k}$ -, respectively, were used as blending components.

Experimental $T_g$-data of the studied PVME/PS blends are shown in Figure 3. $T_g$ temperatures were measured by DSC with a PERKIN-ELMER DSC-2, and are extrapolated for zero heating rate.

The blends with the high moleculare PS were obtained by freeze-drying from solutions in common solvent (toluene), whereas the blends with the oligomeric PS were prepared by mixing in the molten state.

For both the blends the best fit of the $T_g$-data is obtained by the Kwei relation, suggesting strong interactions in accordance with the reported data of FTIR measurements [13].

There arise, however, essential differences concerning the glass transition behaviour of the blends of PVME with the oligomeric and with the high molecular PS, respectively, as reflected in the values of both the K- and q-parameters.

The most striking aspect of these differences is related to the observation that in the latter blend the K-parameter is effectively equal to the $T_{g,PS}/T_{g,PVME}$ ratio, whereas in the blend with the oligomeric PS the fiting K-parameter is at all arbitrary. In both cases the additional q-parameter is negative.

The shape of the $T_g$-composition curves suggest that the free volume increase (i.e. the $T_g$ depression) is more accentuated in the blend with the high molecular PS. Taking into account the interaction between the components of the blend, it may be assumed that the oligomeric PS will adapt closer to the PVME chain introducing therefore less supplementary free volume than the high molecular PS.

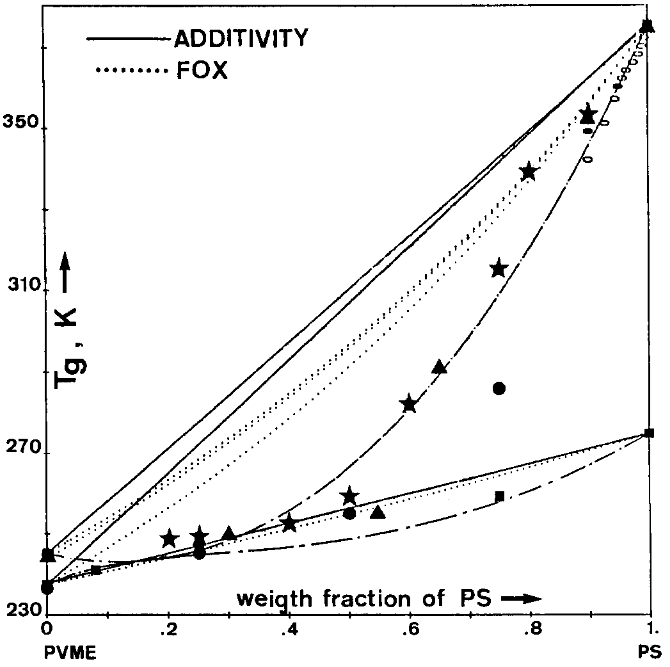

Figure 3. $T_g$-composition dependence of PVME/PS blends
Data of: ★BANK et al. [11], PVME $M_n$=524,000/PS, $M_n$=150,000
▲ Kwei et al. [12] PVME, [η]=0.51/PS, [η]=0.94 in benzen at 25°C
Monnerie et al. [13], PVME $M_w$=99,000 and PS, ○ $M_w$=106,000 and ● $M_w$=75,000
● PVME/PS$_{75k}$, fit K=$T_{gB}/T_{gA}$, q=-120, ■ PVME/PS$_{800}$, K=4.167, q=-73

At higher PS contents, only, the mobility of the chain ends in oligomeric PS will also contribute to an enlargement of the free volume of the blend as observed experimetal. In blends with high molecular PS although interaction is still efective, from the beginning the PS coil will be less adaptable with the PVME chain. This will create supplementary free volume in the blend causing the substantial depression of the $T_g$ temperature when compared with the additivity value.

Interaction of polymer chains, generally, will be accompanied by an orientation effect, contributing to an increased stiffnes as confirmed by viscoelasticity measurements [14, 15]. According to the above postulated model the simultaneous observed lowering of $T_g$ temperatures, although interaction is effective, is primary due to entropic configurational effects. This is not in contradiction with the observed flow behaviour as the mobility of the blend is guaranteed by the PVME chain. The stiffer PS is more or less only floated and as a consequence the hydrodynamic volume of the flowing unit will be enlarged suggesting an apparent increased stiffnes during flow.

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