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DSC and TMS study of polystyrene/(poly(α-methylstyrene) blends*

H. A. Schneider and Peter Dilger

Institut für Makromolekulare Chemie, Universität, Stefan-Meier-Strasse 31,
D-7800 Freiburg, Federal Republic of Germany

SUMMARY

It is shown that Tg data of PS/PaMS blends are influenced by the pressure applied during the preparation of compression-moulded samples. It is supposed the pressure favours the chain alignment of stiffer polymers in the neighborhood of binary contacts, contributing thus to the reduction of the freee volume. As a consequence compression-moulded samples will show increased Tg temperatures compared with those of the solution blended samples.

INTRODUCTION

The effect of molecular weight on the compatibility is emphasized in a series of papers concerning miscibility and phase separation of polystyrene/poly(α-methylstyrene) -PS/PaMS-blends[1-3]. Miscibility over the complet composition range confirmed by a single glass transition temperature, Tg, has been observed for blends of PS, Mn=51,000/PaMS, Mn=147,000[1]; PS, Mw=37,000/PaMS, Mw=90,000[2] and PS, Mw=20,400/PaMS, Mw=90,900[3]. The increase of the molecular weight of PS above Mw=100,000 was accompanied allways by phase separation, evidenced by two Tg.

Concerning the composition dependence of the Tg of the compatible blends, Saeki et al.[3] observed a pronounced depression in comparison with the Tg of the components and reported the failure of the Gordon-Taylor equation[4] for films obtained by solution blending and evaporation of the solvent at room temperature. The films were vacuum dried at 350 K for 24 h prior measurement. The shape of the Tg versus composition dependence suggests at the same time the primary influence of the molecular weight of the PaMS component with the higher Tg. Lin and Roe[5] on the contrary reported Gordon-Taylor like behaviour for blend samples obtained from the vacuum dried powder after solvent evaporation by compression-moulding at 1.25 kbar. The different composition dependences of these two series of PS/PaMS blends are shown in Fig. 1.

Taking into account the different methods used for blend preparation, pressure influence during sample preparation may be supposed and the goal of the present study is the verification of this assumption.

EXPERIMENTAL SECTION

Narrow mass polymers were purchased from the Polymer Standard Service, Mainz, FRG. Their characteristics are shown in Table I.

Films of the three series of blends PS1600/PaMS2500, PS12000/PaMS25000 and PS120000/PaMS76000 were made by solution blending from toluene, evaporation of the solvent at room temperature, followed by vacuum-drying for at least 72 h at 350 K.

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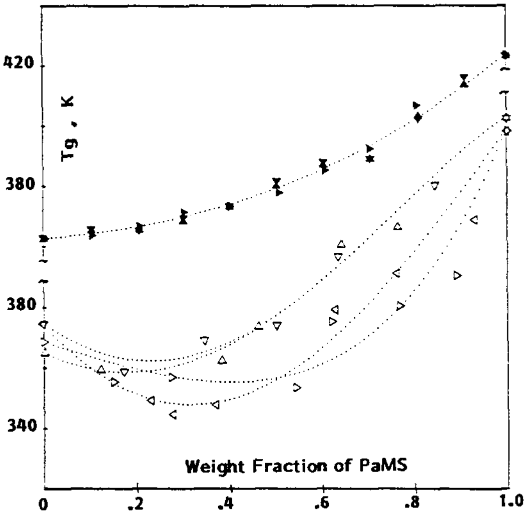


Fig. 1 Tg of PS/PaMS blends
Compression-moulded samples[5]:
▲ - 35,000/41,500 ;
▼ - 64,200/52,400 and
▶ - 55,100/55,000
Solution blended films[3]:
△ - 10,000/84,000 ;
▽ - 63,000/84,000 ;
◁ - 17,000/17,000 and
▷ - 37,000/17,000
(Numbers denote the molecular weights of the components)

Table I. Characteristics of the Polymers used for Blend Preparation

Polymer	M_w	M_w/M_n	Tg [a], K
PS 1,600	1,640	1.01	325.8
PS 12,000	11,900	1.06	359.0
PS 120,000 [b]	120,000	1.22	377.8
PaMS 2,500	2,510	1.15	366.3
PaMS 25,000	25,000	1.11	439.5
PaMS 76,500	76,500	1.10	447.8

[a] by DSC, extrapolated for zero heating rate
[b] obtained by anionic polymerization in our Institute

The Tg determination was performed by both power-compensation DSC and linear thermodilatometry.

For DSC measurements were used two series of polymer samples: the polymer films obtained by vacuum-drying and samples compression moulded after the vacuum-drying procedure at a pressure of 50 bar (5.10^3 KPa). Compression-moulded samples were also used for linear thermodilatrometric measurements.

The DSC measurements were performed on a PERKIN-ELMER DSC 7 using at least 8 different heating rates in the range 20-80 K/min. The Tg represent the extrapolated temperatures for zero heating rate (hr) of half-unfreezing, measured during the second heating scan after the previous controlled cooling down of the molten sample with a cooling rate (cr) of 80 K/min.

Linear expansion measurements were performed using the PERKIN-ELMER Thermomechanical Analyser System TMS-2 equipped with the Microprocessor Controller System 4.

For expansion coefficient determination were used also at least 8 different hr in the range 5-30 K/min or cr in the range 1-20 K/min, respectively. The Tg represent the temperatures extrapolated for zero hr or cr of the intersection points of the tangents to the linear parts of the expansion curves in the glassy and molten states, respectively.

The linear expansion coefficient is defined by the expression

$$\alpha_L = \Delta L / L_o \Delta T \qquad (1)$$

with L_0 the initial lenght of the sample, ΔL the change of this lenghts due to the temperature variation ΔT. The instrument calibration was cheked by measuring the expansion coefficient of the supplied Al standard.

Supposing isotrope expansion the volume expansion coefficient is given by

$$\alpha_V = 3\,\alpha_L + 3\,\alpha_L^{\;2} dT + \ldots \qquad (2)$$

i.e. $\alpha_V = 3\ \alpha_L$.

RESULTS AND DISCUSSION

The composition dependences of the Tg of the studied PS/PaMS blends are illustrated in Figs. 2 and 3.

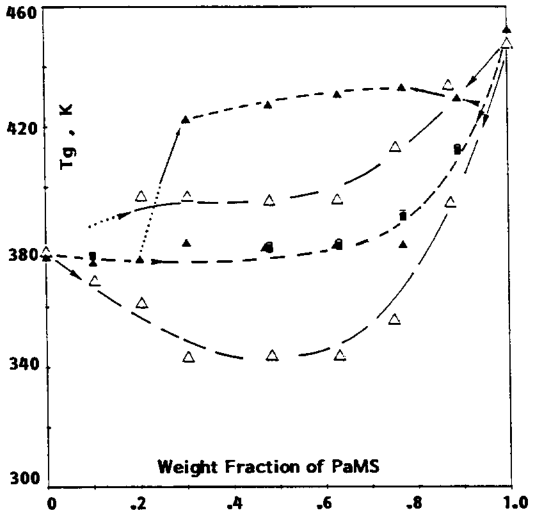


Fig. 2 Tg of the incompatible blend PS120000/PaMS76500

Compression-moulded samples by: ▲ - DSC and by TMS
■ - heating cycle
□ - cooling cycle

Solution blended films by:
△- DSC

As expected the blend PS120000/PaMS76000, with the PS component of Mw>100,000 is phase separated (Fig.2). The Tg data of the compatible blends are shown in Fig. 3. It is evident that except of the blend of the oligomeric components PS1600/PaMS2500, the compression-moulded samples show allways higher Tg, indifferent if the systeme is phase-separated or not. Obviously, increased pressure during blend preparation by compression-moulding improves chain alignment of the stiff polymers in the neighborhood of binary contacts and contributes thus to the reduction of free volume. Increased mobility of oligomeric components acts in the same manner, reducing consequently the influence of pressure. For all blends, however, are observed lower Tg than of the components in the range of small PaMS content.

The concordance of the Tg data for compression-moulded samples obtained by DSC and TMS, respectively, is satisfactory good. At the same time there is no essential difference between the extrapolated Tg data measured by TMS in the heating and cooling cycle, respectively.

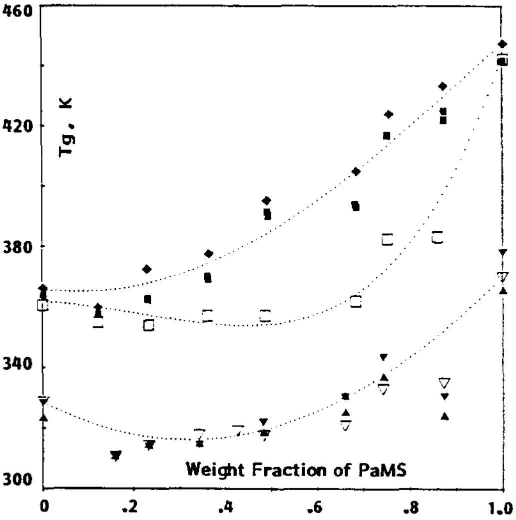


Fig. 3 Tg of compatible blends
PS12000/PaMS25000 (squares)
PS1600/PaMS2500 (triangles)

Compression-moulded samples:
◆ , ▲ - DSC data
■ , ▼ - TMS data

Solution blended films:
□, △ - DSC data

In Fig. 4 are compared the measured Tg data with the available literature values for PS/PaMS blends (are omitted the data of the blends of the oligomeric components PS1600/PaMS2500). To eliminate the inherend scatter of the reported Tg data of the pure components due to the different molecular weights, modalities of Tg evaluation and heating rates used by the different authors, a relative presentation was prefered of the ratio of Tg data $(Tg-Tg_1)/(Tg_2-Tg_1)$ versus w_2 the weight fraction of the PaMS component with the higher Tg_2.

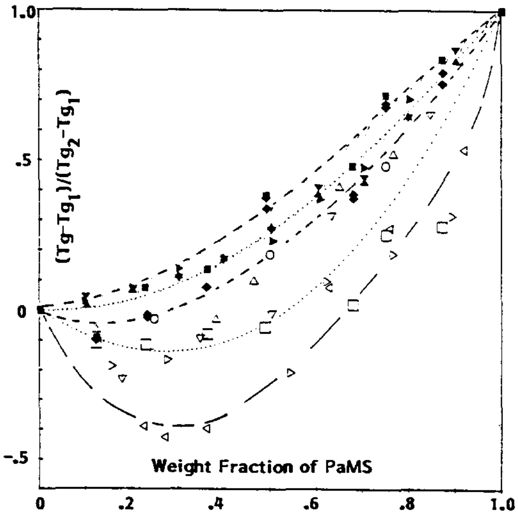


Fig. 4 Tg data of PS/PaMS blends according to equ. (3)

Compression-moulded samples:
Data of Lin and Roe5): ▲ ▼ ▶
(Significance of signs see Fig.1)
Data of this work:◆- DSC, ■- TMS

Solution blended films:
O - blend 37,000/90,000 2)
Data of Saeki et al.3) △ ▽ ◁ ▷
(Significance of signs see Fig.1)
Data of this work by DSC: □

Although the scatter of the data is large, mainly of that of the non compression-moulded samples (open signs), the quite different composition behaviour is evident compared to that of the compression-moulded samples (full signs). The depression of the Tg values of the blends (i.e. negative values of the ratio of the Tg differences, indicating smaller Tg values of the blend than of the components) is remarcable mainly for the non compression-moulded samples.

The dashed lines in Fig. 4 delimit the respective ranges of the Tg data of compression-moulded and non compression-moulded samples, whereas the dotted lines represent the best fit of the third-power equation

$$(Tg-Tg_1)/(Tg_2-Tg_1) = (1+K_1)\,w_{2c} - (K_1+K_2)\,w_{2c}^{\,2} + K_2\,w_{2c}^{\,3} \qquad (3)$$

which is obtained considering the influence of binary contact interaction between the blend components[6].

w_{2c} represents the corrected weight fraction of the component with the higher Tg_2 supposing volume additivity for the blend components:

$$w_{2c} = Kw_2/(1+(K-1)w_2) \qquad (4)$$

The significance of the constant K is given by the expression:

$$K = (\rho_1/\rho_2).(\Delta\alpha_2/\Delta\alpha_1) = K'(Tg_1/Tg_2) \qquad (5)$$

with ρ_i the densities of the components and $\Delta\alpha_i = \alpha_L - \alpha_{Gi}$, the difference between the expansion coefficients of the molten and glassy states at Tg.

Assuming the validity of the Simha-Boyer rule[7], $\Delta\alpha$ Tg=const, the second equality of equ. (5) may be uesd, with $K' = \rho_1/\rho_2$, the ratio of the densities of the components. Taking into acount the very similar densities of PS and PaMS, K' was admitted equal to unity.

The coefficients K_1 and K_2 characterize the interaction between the blend components and configurational redistribution due to orientation effects in the neighborhood of the binary contacts, respectively. Higher values of K_1 suggest stronger binary hetero-interaction, whereas higher values of K_2 better orientation effects of the hetero-contact interaction. For the assumed value of $K=Tg_1/Tg_2$, the respective coefficients for the compression-moulded samples are $K_1=-1.06$ and $K_2=-0.61$ and for the non compression-moulded samples $K_1=-2.15$ and $K_2=-0.38$, suggesting both stronger hetero-interactions and higher orientation effects in the neighborhood of the binary contacts in the compression-moulded samples. Both, stronger hetero-interactions and higher orientation effects will be accompanied by the reduction of the free volume, explaining the observed increase of the Tg.

Deviations of the Tg behaviour predicted by the Gordon-Taylor equation can by evidenced by representation of the data according to the reformulated third-power equation (3)

$$(Tg-Tg_1)/w_{2c}(Tg_2-Tg_1) = (1+K_1) - (K_1+K_2)w_{2c} + K_2 w_{2c}^{\,2} \qquad (6)$$

It has been shown[9] that volume additivity ($K_1=K_2=0$), is characterized by the expression $(Tg-Tg_1)/w_{2c}(Tg_2-Tg_1) = 1$, i.e. by the Gordon-Taylor equation

$$Tg = (w_1 Tg_1 + Kw_2 Tg_2)/(w_1 + Kw_2) \qquad (7)$$

with K defined by the equ. (5). Horizontal straight lines along unity are then the result of the representation of the ratio $(Tg-Tg_1)/w_{2c}(Tg_2-Tg_1)$ versus w_{2c}.

Straight lines of the slope K_1 suggest prevailing influences of the binary contact interaction and generally the Tg versus composition behaviour of such blends obey the Gordon-Taylor equation if a fitting parameter K_f is used, which differs of the value predicted by the coefficient K for volume additivity (equ.5).

Finally, important conformational rearrangements due to the binary hetero-interaction result in curved lines.

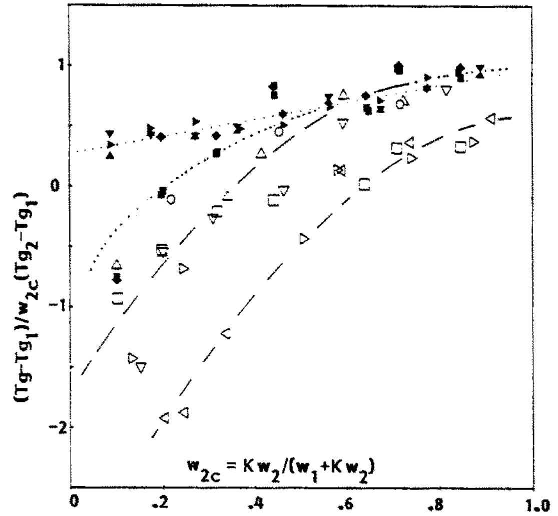
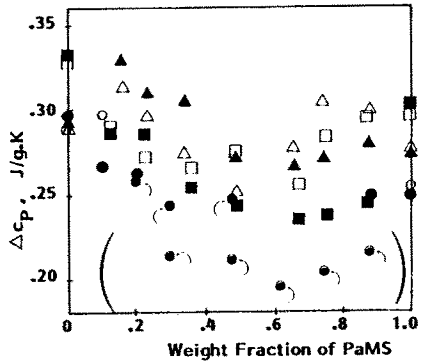


Fig. 5 Tg data of PS/PaMS blends according to equ. (6)

(Significance of symbols see Fig. 4)

From Fig. 5 it is evident that except of the data published by Lin and Roe[5] for samples compression-moulded at higher pressures, all the other analysed Tg data of the PS/PaMS blends suggest not only serious differences in binary contact interaction, but also conformational rearrangements in the neighborhood of the contacts, indifferent if the samples were compression-moulded or not. This explains why only Lin and Roe[5] confirmed the applicability of the Gordon-Taylor equation to their Tg data.

Subsequently are presented some observations concerning the increments at Tg of the heat capacities and of the coefficients of expansion. The composition dependences of these increments are shown in Fig. 6 and 7, respectively.



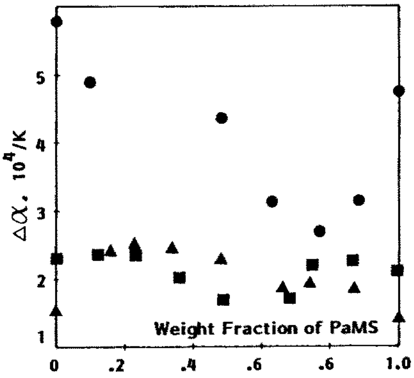


Fig. 6 Composition dependence of Δc_p at Tg of PS/PaMS blends

Fig. 7 Composition dependence of $\Delta\alpha$ at Tg of PS/PaMS blends

● and ○ – PS120000/PaMS76500 (arrows indicat the sum of Δc_p-data of phase separated blends showing two Tg)

■,□-PS12000/PaMS25000 and ▲,△ PS1600/PaMS2500 (full signs – compression-moulded samples)

Although the scatter of the data is large, a small depression is evident of the Δc_p-data of the blends compared to those of the pure components (Fig. 6). No essential differences are observed, however, between the data of compression-moulded and non compression-moulded samples.

The data marked by arrows represent the sum of the heat capacity increase observed for the two Tg in the phase separated PS120000/PaMS76000 blends.

Although the respective data of the PaMS components are somewhat too high, the concordance with heat capacity increase data at Tg published by Wunderlich[2] is satisfactory good. (The values raported by Wunderlich are of 0.295 J/gK for PS and of 0.213 J/gK for PaMS.)

Except of the data for the phase separated PS120000/PaMS760000 blends ($\Delta\alpha$ -values ranging between 4 and 6.10^{-4}/K) the data of the increments at Tg of the coefficients of expansion are relative composition independent and in the range of $2\text{-}3.10^{-4}$/K (Fig. 7). All the $\Delta\alpha$-values are, however, of the order of magnitude of increments at Tg of the coefficients of expansion shown in literature[10].

Taking into account the Simha-Boyer rules[7] for correlations between Tg and the increases of heat capacity and coefficient of expansion, respectively, in Table II are compared the values of the ratio Tg_1/Tg_2 with the respective ratios of the increments at Tg of the coefficients of expansion, $\Delta\alpha_2/\Delta\alpha_1$, and of the heat capacities, $\Delta c_{p2}/\Delta c_{p1}$.

Table II. Values of the Ratio of the Glass Transition Temperatures of the Components and of the Increments of the Coefficients of Expansion and Heat Capacities at Tg

Blend	Tg_1/Tg_2			$\Delta\alpha_2/\Delta\alpha_1$	$\Delta c_{p2}/\Delta c_{p2}$	
	TMS	DSC				
	a	a	b	a	a	b
PS120000/PaMS76500	–	0.832	0.845	0.838	0.854	0.886
PS12000/PaMS25000	0.824	0.818	0.816	0.928	0.913	0.903
PS1600/PaMS2500	0.891	0.851	0.887	0.929	0.929	0.955

[a] compression-moulded samples , [b] solution blended films

It is evident that the ratio of the increments at Tg can be substituted, in a first approximation, by the respective reversed ratio of the glass-transition temperatures to calculate the constant K (equ.3), which is used for the correction of the weight fractions of the components for supposed volume additivity in the blend.

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