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Pressure influence on the glass transition of polymers and polymer blends

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Dedicated to Prof. Dr. W. H. Stockmayer to his 80th birthday with the best wishes

SUMMARY

p-V-T measurements have been carried out on a broad series of polymers and polymer blends. The effect of pressure on the glass transition temperature, T_g, and on related properties - increments of the coefficients of expansion, $\Delta\alpha$, and compressibility, $\Delta\kappa$, at T_g - has been evaluated critically. The results are discussed in terms of the free volume, the order parameter, and the statistical mechanical theory. It is concluded that neither the simple 'free volume' theory, nor the order parameter theory in the one order assumption predict correctly the observed behaviour. A possible explanation of the phenomena observed is offered assuming an expansion of the free volume, which is independent of the nature of the polymer. For the blends binary contacts between the components are discussed, with respect to interaction energy and to conformational rearrangements.

INTRODUCTION

The effect of pressure on the glass transition temperature of polymers and related properties (increments of the coefficients of expansion, $\Delta\alpha$, and compressibility, $\Delta\kappa$, at T_g) has been in the focus of research activities for a long time. With respect to the theoretical interpretation of this phenomenon three major models have been discussed in literature.

- The **free-volume theory** (1) relates the glass transition temperature to a certain critical value, f_c, of the temperature and pressure dependent free-volume fraction, f,

$$f = f_c + \alpha_f (T-T_g) - \kappa_f p \qquad (1)$$

for $T>T_g$ and $f = f_c$, for $T \leq T_g$

The pressure dependence of T_g will be accordingly given by

$$dT_g/dp = \Delta\kappa/\Delta\alpha \qquad (2)$$

It is assumed, consequently, that T_g should increase linearly with pressure, p.

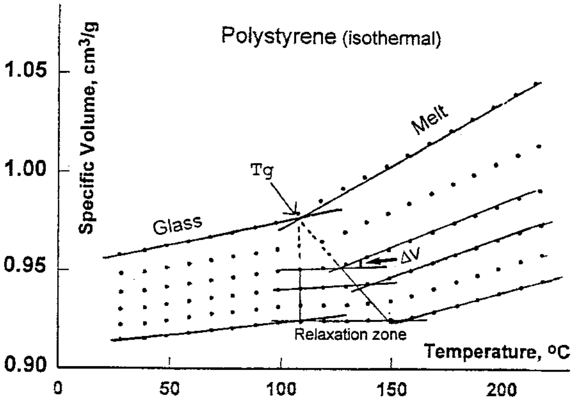

Figure 1 A: p-V-T meaurements • Specific volume vs. temperature of PS at various pressures

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Simha and Somcynsky (2) have extended the free volume theory in terms of statistical thermodynamics by introducing vacancies in a particular lattice model. The vacancies are considered via a statistical disorder function of the fraction of holes, h(V,T), which varies also far below T_g and which is responsible for persisting significant structural contributions to the thermodynamic functions even in the glassy state (3). The hole fraction is obtained by minimization of the configurational free energy. The result is a p-V-T equation of state, and the glass temperature is defined by the intersection of the p-V-T interfaces for the polymeric melt and the glass. The Simha-Somcynsky theory results, however, in very complicated analytical expressions for the pressure dependence of the increments of expansion coefficient and the compressibility at the glass transition.

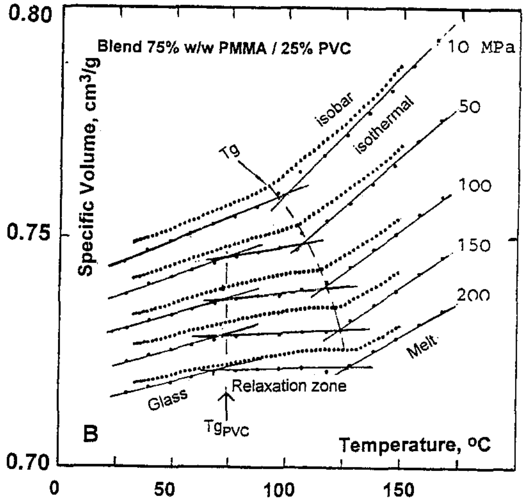


Figure 1 B: Specific volume vs. temp. of 75 % PMMA / 25 % PVC blend at various pressures

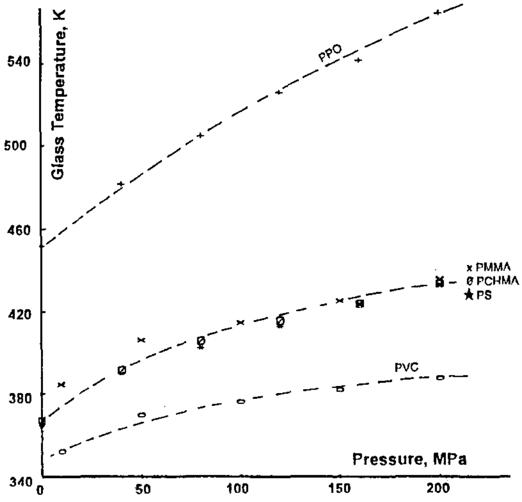


Figure 2 A: Glass temperature T_g vs. pressure for PPO, PMMA, PCHMA, PS and PVC

- The **order parameter theory** (4) describes the glass-forming system in terms of one or more order parameters. These order parameters have equilibrium values in the liquid state, and they are frozen-in within the glass. In the one order parameter treatment, the same linear correlation equ. (1) results between the glass temperature and pressure as in the free volume theory. The order parameter theory, however, predicts that the pressure dependence of T_g determined by isobar cooling may differ from that found in isothermal compression.

- Finally, according to the **statistical-mechanical theory** of Gibbs and DiMarzio (5), the glass temperature in polymers is associated with a thermodynamic second-order transition, defined by a vanishing configurational entropy of the system described by a S-V-T equation of state. In our context, the most important result of the Gibbs-DiMarzio theory is the prediction that with increasing pressure the changes of the glass transition and related properties are leveling off asymptotically. This is in accordance with experimental findings.

In the present paper we wish to analyze some data concerning the influence of pressure on the glass temperature and related properties of both polymers and compatible polymer blends.

Table I: Characteristics of the studied polymers

Polymer	M_n	M_w/M_n	T_g / K
PPO • Poly(2,5-dimethyl phenylene oxide)	13,100 [a]	2.73	451.7 [1]
PS • Polystyrene	42,000 [b]	1.03	364.7 [1]
PCHMA • Poly(cyclohexylmethacrylate)	62,000 [c]	1.44	366,9 [1]
PMMA • Poly(methyl methacrylate)	108,000 [d]	1.08	382,6 [2]
PVC • Polyvinylchlorid	37,400 [e]	2.23	354.6 [2]

1. T_g extrapolated from isobaric pVT measurement to 0 MPa
2. Isobaric T_g value for 10 MPa

a. BASF sample
b. BASF sample, anionic polymerization
c. Own anionic polymerization
d. Röhm sample, group transfer polymerization
e. Aldrich sample

EXPERIMENTAL

The polymers used for polymer blend preparation and their characteristics are given in Table I.

The p-V-T measurements were performed by the hydrostatic method using the GNOMIX p-V-T apparatus of Zoller in both the isothermal and isobaric mode. In the *isothermal mode* data are acquired along isotherms for well defined pressure steps. Starting measuring conditions being fixed for a pressure of 10 MPa, specific volumes at atmospheric pressure are extrapolated. In the *isobaric mode* the data are acquired in selectable time intervals during controlled heating or cooling of the apparatus. In the isobaric mode of measurement the cooling to room temperature is self-driven, however, by the temperature difference between environment and the hydrostatic pressure vessel, containing the piezometer cell with the polymer sample in mercury as the confining fluid.

The experimental data are usually presented in isobaric form - specific volume vs. temperature - as shown in Fig. 1A for PS measured in the isothermal mode. Beside the shift T_g to higher temperatures, the development of a volume relaxation zone is observed, which enlarges with increasing pressure.

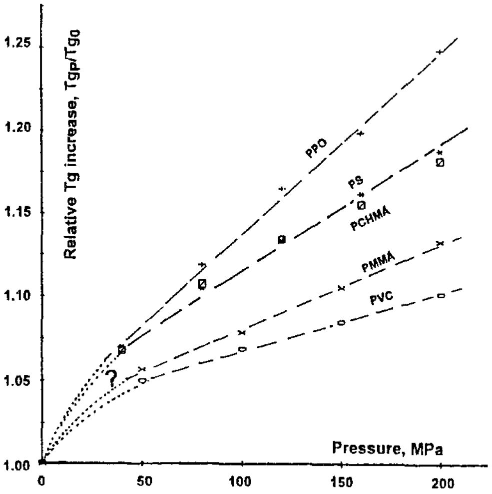


Figure 2 B: Relative T_g (T_{gp}/T_{go}) vs pressure for PPO, PS, PCHMA, PMMA, and PVC

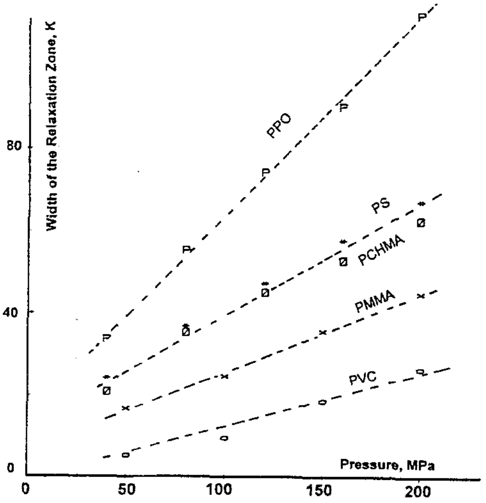


Figure 3: Pressure dependence of the width of the relaxation zone

In Fig. 1B the difference between p- V-T data measured in the isothermal and in the isobaric mode is illustrated for the blend of 75% w/w PMMA / 25% w/w PVC. As the reproducibility of data is assured in the isothermal measurement mode, further discussions will be restricted to isothermal p-V-T data.

RESULTS AND DISCUSSION

A - Homo- and copolymers

The pressure dependence of the glass temperature is illustrated in Fig. 2 A. It is defined, as sketched in Fig. 1, by the intersection of the extrapolated lines of the specific volume of the melt and of the glass or - for the higher pressures - of the relaxation zone. In accordance with literature data, as reviewed by Skorodumov and Godovskii (6), the increase of the glass temperature decreases asymptotically with increasing pressure. In a relative presentation, T_{gp}/T_{go}, the increase of the glass temperature is linear, however, as evidenced in Fig. 2B. It is remarkable that the pressure influence on the glass temperature is the higher, the higher the initial glass temperature of the polymer at atmospheric pressure. At the same time an increase of the width of the 'relaxation' zone is observed, which is defined by the temperature range of nearly no increase of specific volume with increasing temperature between glass and melt (see Fig. 1). It is interesting to note that, in the limit of experimental error, the lower temperature limit of the 'relaxation' zone coincides with the glass temperature of the polymer at atmospheric pressure. The same behaviour concerning the relaxation zone width has been observed by Zoller - Hoehn (7). However, in compatible polymer blends this lower temperature limit of the 'relaxation' zone seems to approach the glass temperature of the blend component with the lower T_g. This is at least valid for the PVC/PMMA blend (see Fig. 1B).

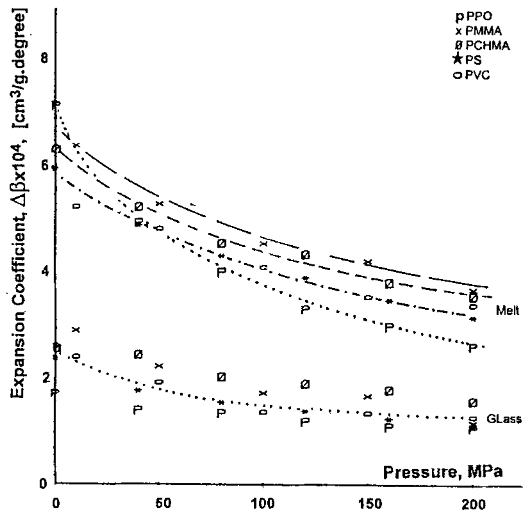


Figure 4 A: Expansion coefficients vs. pressure of polymer melts and glasses

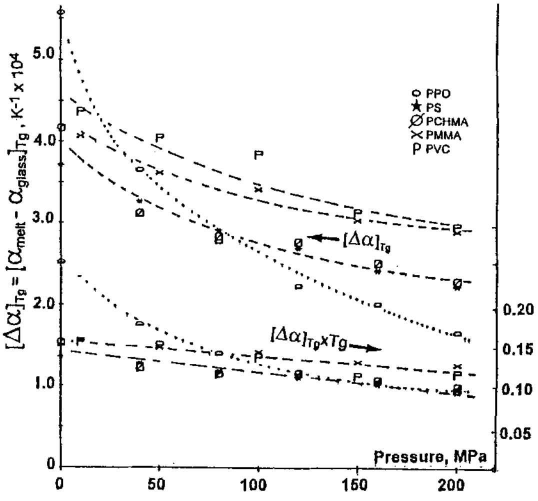


Figure 4 B: Increments of expansion coefficient at T_g, and Simha-Boyer rule vs. pressure

Accordingly to the two of the Simha-Boyer rules (8), which relate the expansion coefficients with T_g

$$\alpha_{melt}T_g = .164 \quad \text{and} \quad (\Delta\alpha)_{Tg}T_g = .113$$

$$\text{with } (\Delta\alpha)_{Tg} = (\alpha_{melt} - \alpha_{glass})_{Tg} \qquad (3)$$

an increase of the glass temperature with increasing pressure will be accompanied by a decrease of the expansion coefficients. This is illustrated in Fig. 4A for the influence of the pressure on the slopes, β = dV/dT (cm^3 g^{-1} deg^{-1}) (9), of the specific volumes of the polymeric glasses and melts, respectively. It is remarkable that the decrease of the expansion coefficient is the steeper, the steeper the increase of the glass temperature with pressure (compare data for PPO, i. e.) The effect is essentially evidenced by the polymer melts. The increments of the expansion coefficient at T_g, $(\Delta\alpha)_{Tg}$, were evaluated dividing the corresponding β-values by the respective specific volumes at T_g. The obtained data are shown in Fig. 4 B, together with the values of the product $(\Delta\alpha)_{Tg} \cdot T_g$. The latter product still shows a decreasing tendency with increasing pressure. Again, the effect is the larger for the polymer with the higher glass transition at atmospheric pressure, i. e. for PPO.

The temperature dependence of the compressibility coefficient, $\Delta\kappa = (1/V)\,(dV/dp)$, is evidenced in Fig. 5 A. The pressure dependences of the increments of the compressibility coefficient at T_g of the studied polymers, $(\Delta\kappa)_{Tg} = (\kappa_{melt} - \kappa_{glass})_{Tg}$, are shown in Fig. 5 B. They were evaluated starting with the differences of the specific volumes, ΔV, obtained by substracting the corresponding specific volume of the relaxation zone, extrapolated to the respective T_g, from the melt specific volume (see Fig. 1 A). Like the increments of the expansion coefficient at T_g (dashed lines), the compressibility coefficient increments at T_g (dotted lines) decrease with increasing pressure. However, the decrease is steeper for the latter (Fig. 6). The tendency of leveling off with increasing temperature is evidenced by both.

Taking into account the predictions of the simple free volume theory the pressure dependences of the two characteristic ratios of (1), $\Delta Tg/\Delta p$, and $\Delta\kappa/\Delta\alpha$, respectively, are compared in Fig. 7. It is remarkable that the two ratios have different values and are neither constant, nor pressure independent. In the same time both show a leveling off tendency with increasing pressure. Additionally the respective values are polymer specific, like

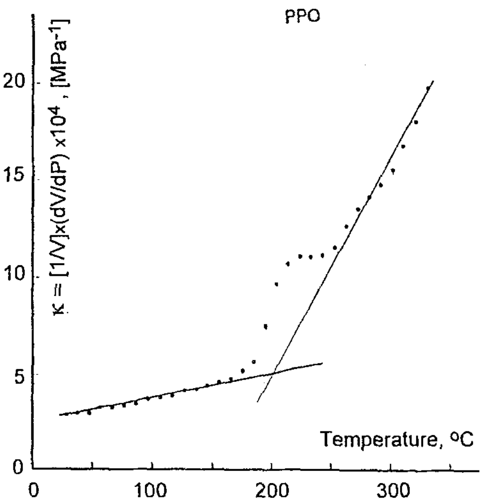


Figure 5 A: Temperature dependence of the compressibility of PPO

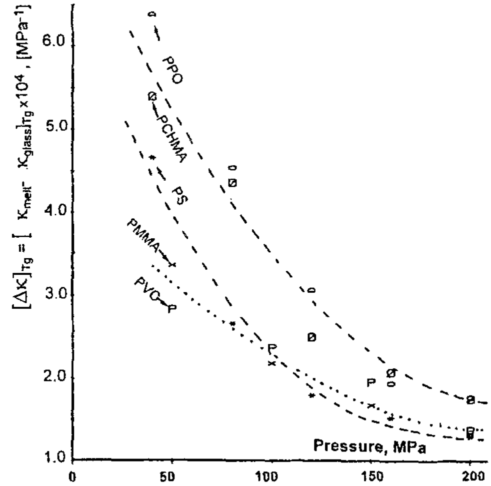


Figure 5 B: Increments of the compressibility coefficient at T_g vs. pressure

all other studied properties related with the polymer glass transition.

The obtained data concerning the pressure influence on T_g and related properties suggest that neither the simple 'free volume' theory, nor the order parameter theory in the one order assumption predict correctly the observed behaviour.

All studied characteristics show a strong tendency of asymptotical leveling off with increasing pressure. However, the observation is unexpected that, at T_g, the changes of glass temperature, expansion and compressibility coefficient as well of their increments are the more accentuated the higher the glass transition temperature of the polymer at atmospheric pressure. A stronger pressure effect concerning the shift of melting to higher temperatures (10) has also been observed for polymers with an initial larger bulk melting temperature at atmospheric pressure.

A possible explanation is offered assuming an expansion of the free volume, which is independent of the nature of polymer. Supposing that the need of 'free volume' generally increases with increasing T_g, at higher pressure more free volume has to be created by expansion in order to allow the characteristic mobilities for glass transition. As a consequence the pressure dependent shift of the glass temperature to higher temperatures will be more pronounced.

A correlation also may exist between the pressure dependent shift of T_g to higher temperatures and the enlargement of the relaxation zone observed at higher pressures (see Fig. 1). The observed relaxation zone at the higher pressures may be connected with the special working procedure applied: The isotherm measurement is always started at the lower fixed pressure of 10 MPa, the pressure being increased then stepwise to 200 MPa. During heating to the next higher temperature the pressure is relaxed in the same time to the initial value of 10 MPa, and the pressure cycle is repeated. The influence of the experimental procedure on the observed relaxation phenomenon will be analyzed in detail by further studies.

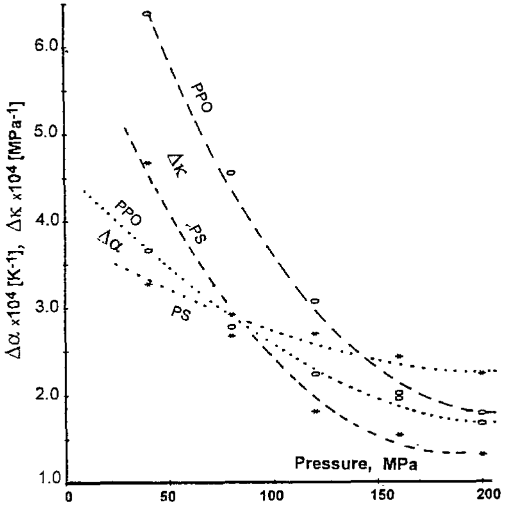


Figure 6: Pressure dependence of the increments of expansion and compressibility coefficients at T_g for PS and PPO

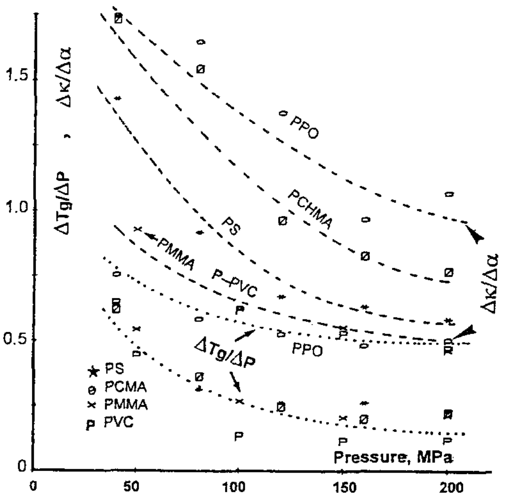


Figure 7: Pressure dependence of the ratios $\Delta\kappa/\Delta\alpha$ and $\Delta T_g/\Delta p$ of PS, PCHMA, PMMA, PVC

B - Polymer Blends

Finally, some preliminary results concerning the influence of pressure on the glass temperature of compatible polymer blends are presented.

The composition dependence of T_g for different pressures is illustrated in Fig. 8 for the blend PS/PPO, in Fig. 9 for PS/PCHMA, and in Fig. 10 for PVC/PMMA. All three blends exhibit positive deviation from the glass temperature at the lowest pressure, as predicted by the Fox equation (11) - dashed lines

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \qquad (4)$$

(5) The Fox equation results from the Gordon-Taylor equation (12)

$$T_g \approx (w_1T_{g1} + Kw_1T_{g2})/(w_1 + Kw_2)$$

which was derived in fact for random copolymers in the assumption of volume additivity of the components. w_i are the weight fractions of the blend components and the index 2 refers to the polymer with the higher glass transition.

The dotted lines evidence the adaption of experimental data by a 'virial' like concentration power equation, deduced in the assumption of specific binary interactions between the blend partners (13)

$$(T_g - T_{g1})/(T_{g2} - T_{g1}) = (1 + K_1)w_{2c} - (K_1 + K_2)w_{2c}^2 + K_2w_{2c}^3 \qquad (6)$$

$w_{2c} = Kw_2/(w_1 + Kw_2)$ is the weight fraction corrected for volume additivity by the Gordon-Taylor equation parameter, $K = \rho_1\Delta\alpha_2/\rho_2\Delta\alpha_1$.

Neglecting the differences between the densities of the polymers, ρ_i, the increments of the expansion coefficients may be replaced according to second of the Simha-Boyer rules - equ.3 - by the respective reciprocal glass temperatures. Then, the Gordon-Taylor parameter for volume additivity becomes $K = T_{g1}/T_{g2}$. With this assumption the Fox equation (4) results from the Gordon-Taylor equation (5) (14).

In (6) the parameter K_1 is characteristic mainly for the interaction energy of binary contacts between the blend components, and K_2 accounts for the conformational rearrangements due to the new created binary hetero-contacts.

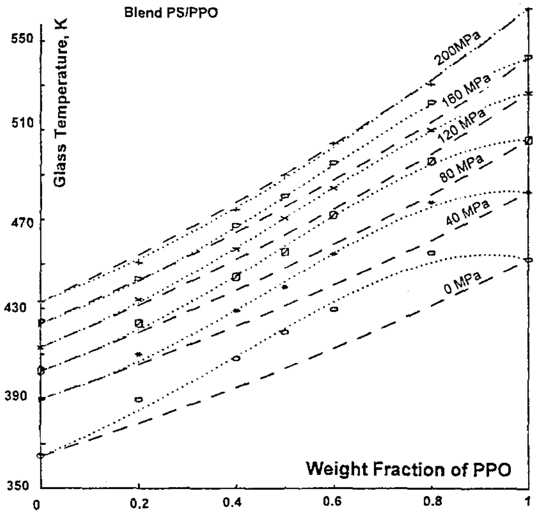


Figure 8: Pressure influence on the composition dependence of the T_g of PS/PPO blends

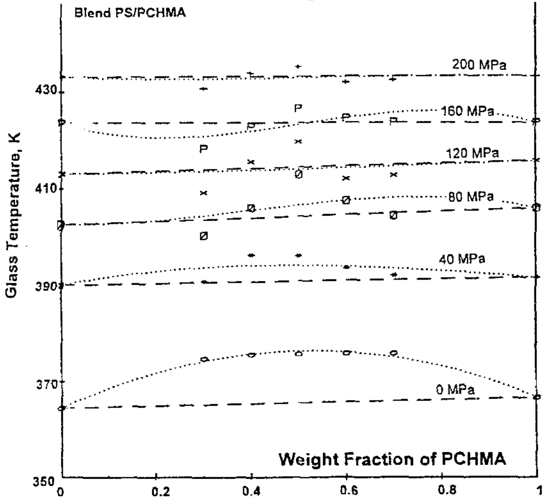


Figure 9: Pressure influence on the composition dependence of T_g of PS/PCHMA blends

It is remarkable that with increasing pressure the glass temperatures of the blends approach volume additivity behaviour. A more detailed analysis of the blend p-V-T data is in progress.

As expected, the difference between the glass temperatures of the blend partners increases because according to the data obtained for homopolymers the increase of T_g is higher for the component with the higher T_g. This is illustrated in Fig. 11.

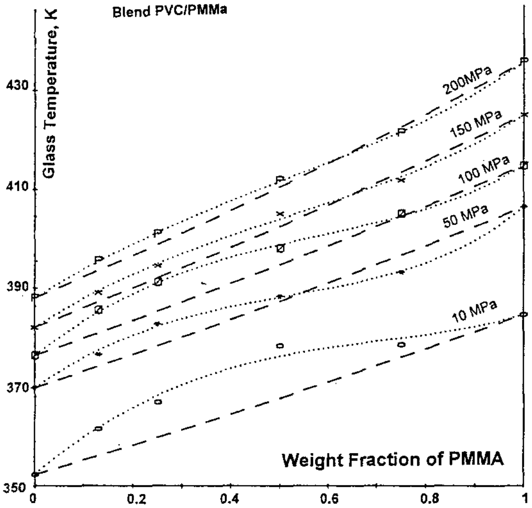
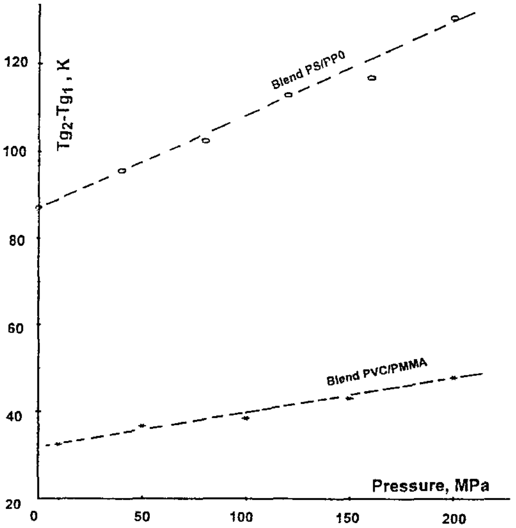


Figure 10: Pressure influence on the composition dependence of T_g of PVC/PMMA blends

Figure 11: Pressure dependence of the difference T_{g_p} - T_{g_o} of the blend components, PS/PPO and PVC/PMMA



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