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A new approach to PVC–plasticizer interaction by using a T_g concentration power equation

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The concentration power equation recommended by Brekner, Schneider and Cantow for adapting the compositional dependence of the glass temperature, T_g, of compatible binary polymer blends has been used to correlate the experimental T_g data obtained for PVC-plasticizer systems. It is demonstrated that the T_g vs composition data for such systems can be adapted with the condition that two different concentration power equations are applied separately to the two branches of the curves separated by the cusp typical for these systems. Accordingly, different values are obtained for the parameters of the concentration power equation for the two branches of the T_g vs composition curves. A certain significance is attributed to the cusp, characterized by a critical composition of the system. Below the critical composition the plasticizer will be fixed by energetic driven hetero-interaction preferentially in the 'interdomains' within the amorphous PVC matrix, causing a stiffening of the blend. Above the critical concentration the plasticizer will still penetrate these domains, but this time due to plasticizer–plasticizer homocontacts which thus contribute to an increase of the mobility and consequently of the entropy of the blend. This different behaviour is characterized by means of the different parameters of the concentration power equations for the two branches of the T_g vs composition curves. Additionally it is shown that the parameters can be correlated with the usual compatibility criteria of the plasticizer ranking. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: T_g–composition dependence; concentration power T_g vs composition equation; cusp)

INTRODUCTION

Glass transition temperatures, T_g, of binary PVC–plasticizer systems show non-monotonic composition dependences; i.e., T_g vs composition curves appear discontinuous as if they were composed of two different bends, which intersect in a given point called the 'cusp'. This cusp defines a certain critical composition of the PVC–plasticizer blend[1]. Two-bended T_g vs composition curves were predicted theoretically by Braun and Kovacs[2] by assuming that at temperatures below the glass temperature of the critical blend the polymer does not further contribute to the 'free volume' changes of the mixture.

The presence of cusps within T_g vs composition curves has been experimentally observed for different PVC-plasticizer blends[3–9], suggesting the questionablility of any monotonics function based on additivity suppositions for the description of the composition dependence of the composition dependence of the blend T_g[10–18]. The failure of any equation based on additivity is explained by the neglect of the specific PVC–plasticizer interactions. Considering the effect of these experimentally proven interactions[19–21], new T_g vs composition relations were recommended which improved the fit of the experimental data[22–25]. Among these relations, the most exact are those of Righetti *et al.*[24,25], who extended the expressions of Couchman[16] by introducing a supplementary term comprising an additional parameter for the better fit of the experimental data. However, the major deficiency of these equations is that no correlation is offered for relating the additional fitting parameter to the structure of the plasticizer.

The present paper attempts to extend the concentration power equation developed by Brekner *et al.*[26,27] for the composition dependence of the T_g of compatible polymer blends in order to characterize the effect on the glass transition temperature of plasticizers commonly used for PVC.

The T_g vs composition equation for polymer blends has been derived by assuming both the energetic effects of binary heterocontact formation driven by interaction and the entropic contributions due to the simultaneously induced conformational redistributions in the neighbourhood of the contacts. The result is a third-power concentration equation which includes, beside the

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Gordon–Taylor parameter characteristic for supposed volume additivity, two additional parameters:

$$(T_g - T_{g_1})/(T_{g_2} - T_{g_1}) = (1 + K_1)w_{2_c} - (K_1 + K_2)w_{2c}^2 + K_2 w_{2c}^3 \qquad (1)$$

T_g is the glass temperature of the blend and T_{g_i} are the glass temperatures of the blend components. w_{2_c} is the weight fraction of the component with the higher T_{g_2}, corrected for the different volume expansivity of the blend components:

$$w_{2_c} = K_{GT} w_2 / (w_1 + K_{GT} w_{2_c}) \qquad (2)$$

w_i are the weight fractions of the blend components and K_{GT} the Gordon–Taylor parameter[10], defined as:

$$K_{GT} = (\rho_1/\rho_2) \cdot (\Delta\alpha_2/\Delta\alpha_1) \qquad (3)$$

ρ_i are the densities and $\Delta\alpha_i = (\alpha_m - \alpha_{Gl})_i$ the increments of the expansion coefficients at T_g of the blend components.

Assuming the validity of the Simha–Boyer rule, $\Delta\alpha T_g = \text{constant}$[28], the Gordon–Taylor parameter may be expressed as[29]:

$$K_{GT} = (\rho_1/\rho_2) \cdot (T_{g_1}/T_{g_2}) \qquad (3')$$

The Gordon–Taylor equation[10] for supposed volume additivity holds for both $K_1 = 0$ and $K_2 = 0$, i.e.

$$T_g = (w_1 T_{g_1} + K_{GT} w_2 T_{g_2})/(w_1 + K_{GT} w_2) \qquad (1')$$

Neglecting the contribution of the different densities of the blend components, i.e. considering $K_F = T_{g_1}/T_{g_2}$, the Gordon–Taylor expression can be reformulated, the result being the Fox relation[11]:

$$1/T_g = w_1/T_{g_1} + w_2/T_{g_2} \qquad (1'')$$

K_1 and K_2 are the additional parameters of the concentration power equation (1), defined as

$$K_1 = \{[(E_{12\text{-}1} + E_{12\text{-}2}) - (E_{11\text{-}1} + E_{22\text{-}2})] - [(e_{12\text{-}2} - e_{12\text{-}1}) + (e_{11\text{-}1} - e_{11\text{-}2})]\}/(T_{g_2} - T_{g_1}) \qquad (4)$$

and

$$K_2 = [(2e_{12\text{-}1} - e_{11\text{-}1} - e_{22\text{-}1}) - (2e_{12\text{-}2} - e_{11\text{-}1} - e_{22\text{-}2})]/(T_{g_2} - T_{g_1}) \qquad (5)$$

$E_{ij\text{-}k}$ represents the interaction energy stored in an ij binary contact located in a k neighbourhood which has to be overcome at the T_g of the blend, and $e_{ij\text{-}k}$ are the energetic contributions to the contact energies due to the induced conformational redistributions by binary heterocontact formation.

K_1 mainly depends on the difference between the interaction energies of the binary hetero- and homocontacts. We also consider, via $e_{ij\text{-}i}$, entropy changes due to induced conformational redistributions, expressed as energetic contributions to the contact energies. K_2 accounts only for the additional energetic contributions due to conformational entropy changes during binary heterocontact formation.

Taking into account that miscibility claims the predominant energetic effects of heterocontacts, the first term of K_1, i.e. $[(E_{12\text{-}1} + E_{12\text{-}2}) - (E_{11\text{-}1} + E_{22\text{-}2})]$, >0. Positive values of K_1 thus indicate prevailing energetic effects due to heterocontact formation, accompanied by locally induced chain orientation in the neighbourhood of the heterocontacts. Negative values of K_1 are due to predominant entropic effects caused by conformational rearrangements during heterocontact formation.

Prevailing energetic contributions of the heterocontacts accompanied by local chain orientations will result in a decrease of the free volume and consequently in an increase of the blend T_g compared to the predicted additive value. Increasing conformational entropy contributions are accompanied by an increase of the free volume and thus by a decrease of the blend T_g. It may thus be concluded that, as in polymer solutions, additivity is in fact the result of compensation of energetic and entropic effects during blend formation.

The attempt to apply the concentration power equation to PVC-plasticizer blends is based on the assumption that miscibility is caused by both energetic and entropic effects. The very tempting prospect of quantifying, by means of the K_1 and K_2 parameters, the influence of the plasticizer structure upon its interaction with PVC is additionally considered.

EXPERIMENTAL

The PVC was supplied by Fluka (K value of 69–71). The characteristics of the three plasticizers used in this study (of min. 99.5% purity) are presented in *Table 1*.

A total of nine PVC–plasticizer blends (consisting of 5 g PVC and increasing amounts of plasticizer, weighed with a precision of ±2 mg) were prepared for each plasticizer. The blends were dry-blended at 40°C and subsequently annealed for 24 h at 20°C. For d.m.a. measurements test pieces (50 × 5 × 2 mm) were prepared

Table 1 General characteristics of the plasticizers studied

	Plasticizer code		
Characteristic	S 141[a]	DEHP[b]	DIDA[c]
Supplier	Monsanto	Solventul	Solventul
Molecular weight ($g\,mol^{-1}$)	362.44	390.62	426.76
Density ($g\,cm^{-3}$)	1.091	0.983	0.918
Glass transition temperature T_g (K)	188.0	188.3	176.2
Critical solution temperature CST (°C)	95	117	156
Solubility parameter δ ($(cal\,cm^{-3})^{1/2}$)	9.32	8.85	8.08
Interaction parameter B ($cal\,cm^{-3}$)	0.3136	1.061	3.240
Interaction parameter χ	−0.23	−0.03	0.28

[a] S 141: 2-ethylhexyl-diphenyl-phosphate
[b] DEHP: di-2-ethylhexyl-phthalate
[c] DIDA: di-isodecyl-adipate

from the PVC–plasticizer blends, adding Cd and Zn as thermal stabilizers (in a proportion of 2 phr, i.e. w/w parts per hundred parts of polymer) by roll-milling at 160°C and press-moulding at 170°C.

T_g temperatures were determined by using the Perkin-Elmer DSC-7 apparatus. Indium and high-purity cyclohexane were used for temperature calibration. Each blend sample was first quenched to a temperature of about $T_g - 50\,\mathrm{K}$ and subsequently heated at a rate of $10\,\mathrm{K\,min^{-1}}$ up to a temperature of about $T_g + 50\,\mathrm{K}$. For each heating scan the glass temperature was determined as the transition midpoint ($1/2\,\Delta c_p$) temperature. The T_g data finally considered are the arithmetic mean values of two subsequent scans, differing by less than 1 K from each other.

Dynamic mechanical measurements were carried out on a Rheometrics RSA II visco-elastometer equipped with a dual-cantilever device. Strain and frequency (0.16 Hz) were kept constant during the measurement of the dynamic storage (E') and loss (E'') moduli as well as the loss tangent, tan δ (E'/E''), over a selected temperature range (between $T_g - 40\,\mathrm{K}$ and $T_g + 40\,\mathrm{K}$), using a heating rate of $2\,\mathrm{K\,min^{-1}}$.

The critical solution temperatures (CST) were determined according to DIN 53 408. The solubility parameters, δ, were calculated by using the Coleman rule[30], whereas the Flory–Huggins interaction parameters, χ, were taken from literature[31]. Compatibility between PVC and plasticizer increases with decreasing CST, χ, and the difference between the solubility parameters of the blend components related to the interaction parameter $B = (\delta_{\mathrm{PVC}} - \delta_{\mathrm{plasticizer}})^2$[32], where $\delta_{\mathrm{PVC}} = 9.88\ (\mathrm{cal\,cm^{-3}})^{1/2}$.

RESULTS AND DISCUSSION

The composition dependences of the glass temperature of the three PVC–plasticizer blends investigated are illustrated in *Figures 1–3*. The presence of cusps is obvious in all cases. The critical concentration of the plasticizer at the cusps, $w_{1c}^* = 1 - w_{2c}^*$, increases with the compatibility of the plasticizer, expressed by the three commonly recommended criteria CST, δ and χ shown in *Table 1*. At the beginning, w_{1c}^* values of the cusps were identified visually on the d.s.c. scans as those concentrations where hypothetical T_g–w_{2c} curves (not shown in the figures) appear broken. Subsequently, d.m.a. analysis supplied a more accurate criterion for establishing the exact position of the cusps.

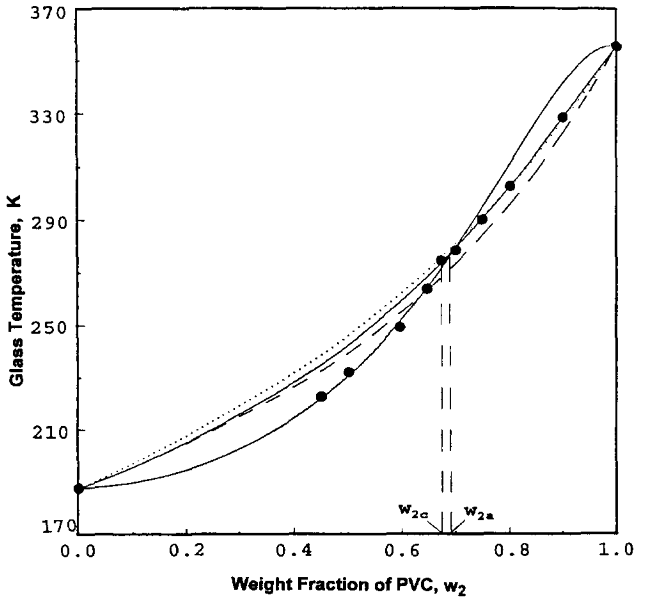

Figure 1 T_g vs composition of the PVC–S 141 blend: dashed line—Gordon–Taylor equation; dotted line—Fox equation; full lines—concentration power equation (for significance of w_{2c} and w_{2a} see text)

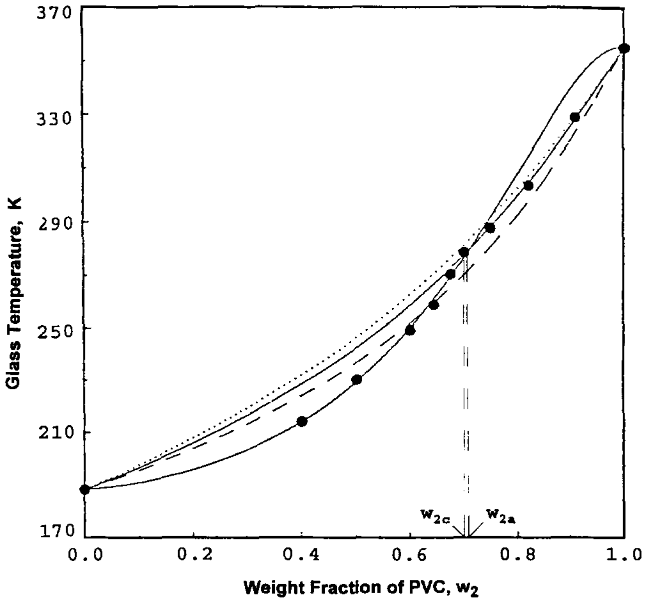

Figure 2 T_g vs composition of the PVC–DEHP blend

It is well known that the tan δ peaks (characterizing the α transition of the plasticizer) of the d.m.a. spectra start to flatten and broaden with increasing plasticizer content, but finally sharpen again at higher plasticizer concentrations[33]. On the basis of d.m.a. results we concluded that the lowest and broadest tan δ peak of the PVC–plasticizer blends is characteristic of the very critical composition of the cusps. This is illustrated in *Figure 4* by the tan δ curve 3, corresponding to the critical

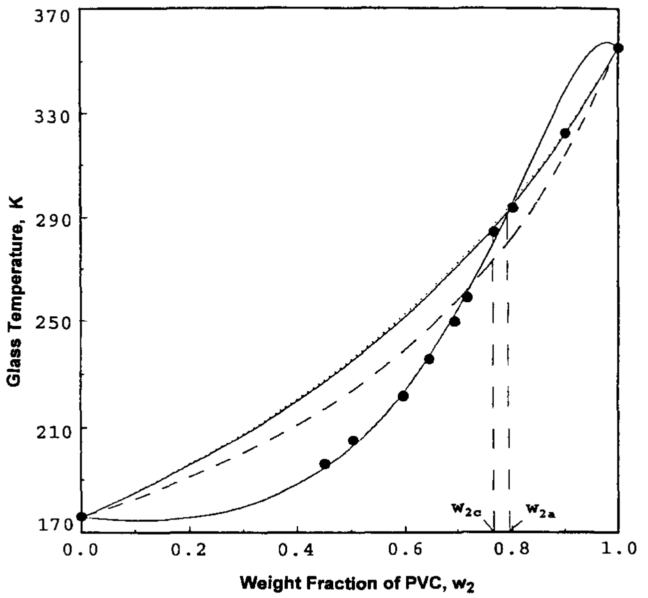

Figure 3 T_g vs composition of the PVC–DIDA blend

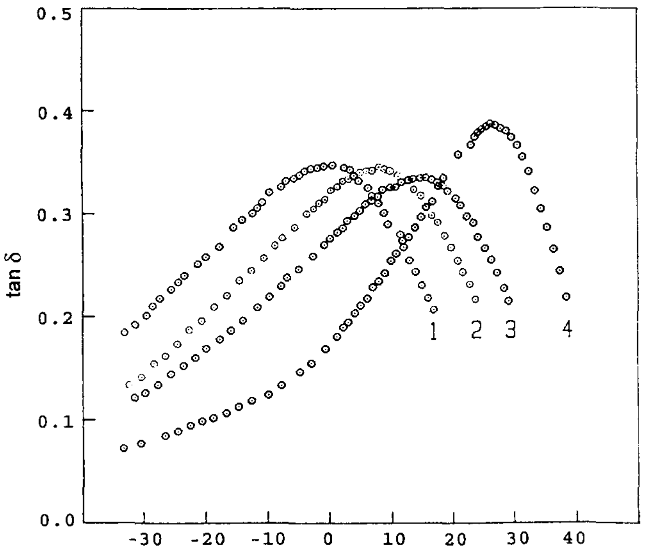

Figure 4 Composition dependence of the shape of the loss tangent of the PVC–DEHP blend. Weight fraction of DEHP: 1—0.35; 2—0.325; 3—0.30 = w_{1c}; 4—0.275

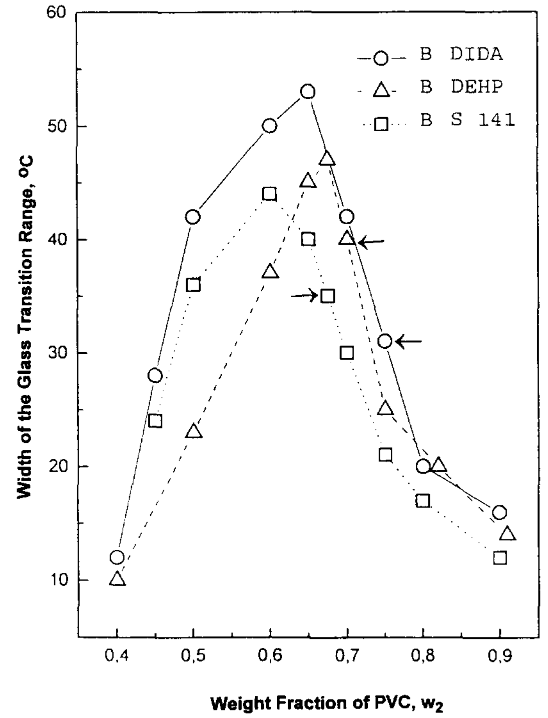

Figure 5 Composition dependence of the width of the glass transition range for PVC–plasticizer blends. The critical concentrations of PVC (w_{2c}) are indicated by arrows

composition of the PVC–DEHP blend. The explanations offered for the change of shape of the tan δ peak with blend composition are, however, still inconsistent. Some authors suggest that what is responsible for the observed cusps is the changing homogeneity of the system, which first decreases and then increases with increasing plasticizer content of the blend[34]. Accordingly the cusp characterizes the most heterogeneous PVC–plasticizer blend. Other authors, on the contrary, consider that the lowest tan δ peak corresponds to the blend of maximum homogeneity[35].

Our d.m.a. results in the sub-T_g range support better the first hypothesis. The observed flattening of the low temperature β peak, being finally covered by the α peak shifted to lower temperatures, was associated with the growing heterogeneous character of the blend[36]. Correspondingly, the width of the glass transition, ΔT_g (established by d.s.c.), increases with the plasticizer content (see *Figure 5*). At the critical composition, the glass transition has not yet reached its maximum width, but still broadens. Accordingly the heterogeneous character of the blend is still growing. This supposition is also supported by the PVC–plasticizer interaction criteria.

The results from the T_g vs composition data based on d.s.c. measurements of the three PVC–plasticizer blends studied cannot be fitted either by the Gordon–Taylor equation (1′)—dashed lines—or by the Fox relation (1″)—dotted lines (see *Figures 1–3*). Even the attempt to fit the data by using a single concentration power equation (1) for the whole concentration range fails (for clarity the respective curves are not shown in the figure). Applying, however, individual concentration power equations for the two concentration ranges separated by the cusps (i.e. for $0 - w^*_{2c}$ and $w^*_{2c} - 1$, respectively), the fit of the experimental data is remarkable. The two T_g vs composition bends intersect at an extrapolated analytical d.s.c. cusp (w^*_{2a}) which correlates surprisingly well with the 'experimental' one (w^*_{2c}) corresponding to the lowest tan δ curve in d.m.a. The respective values are shown in *Table 2*, together with the K_1 and K_2 parameters corresponding to the two concentration ranges mentioned above.

It is obvious that both the K_1 and K_2 parameters differ markedly, suggesting a change of the nature of the respective plasticizer–PVC interaction. In the low concentration range of plasticizer (between 1 and w^*_{2c}) the positive K_1 values suggest a prevailing energetic effect of the heterocontacts. This is also confirmed by the values

Table 2 Analytical data of the PVC–plasticizer blends studied

	Plasticizer code^a		
Characteristic	S 141	DEHP	DIDA
Experimental critical concentration of PVC w_{2c}	0.67	0.70	0.75
Analytical critical concentration of PVC w_{2a}	0.69	0.71	0.79
Gordon–Taylor constant K_{GT}	0.44	0.41	0.36
[1 − w^*_{2c}] concentration range: K_1	0.00	0.15	0.34
[1 − w^*_{2c}] concentration range: K_2	−0.28	−0.05	0.11
[w^*_{2c} − 0] concentration range: K_1	−0.85	−0.74	−1.34
[w^*_{2c} − 0] concentration range: K_2	−1.95	−1.83	−2.76

^{a} Plasticizers as in *Table 1*

of the difference between the parameters K_1 and K_2.

$$K_1 - K_2 = \{[(E_{12\text{-}1} + E_{12\text{-}2}) - (E_{11\text{-}1} + E_{22\text{-}2})] - [(e_{12\text{-}1} - e_{12\text{-}2}) + (e_{22\text{-}2} - e_{22\text{-}1})]\} / (T_{g_2} - T_{g_1})$$

which is positive too, suggesting that the substitution of the plasticizer molecule by polymer sequences in the neighbourhood of the heterocontacts, quantified by small values of K_2, is really negligible. The values of the parameters decrease, however, as the compatibility of the plasticizer increases.

At higher plasticizer content, the parameters tend to have large negative values, suggesting that an increasing contribution to the mobility of the blend of the increasing number of plasticizer–plasticizer homocontacts is responsible for increasing the entropic effects. Again, the least compatible plasticizer—DIDA—exhibits the lowest values of K_1 and K_2.

According to classical theory, compatibility is related to the PVC–plasticizer interaction forces[37]. The lower the respective values of CST, χ or the B compatibility criteria are, the more compatible with PVC is the plasticizer. A very recent viscosimetric method used for estimating the χ interaction parameter indicates the same decrease of compatibility in the order: S141 > DEHP > DIDA[38]. Other authors claim that the solvency criterion[39], which is related to the aromaticity of the plasticizer structure[40], describes the PVC–plasticizer interaction more accurately. Solvency can be evaluated by means of the final gelation temperature of plastisols. According to both criteria (solvency and aromaticity), the order of plasticizer compatibility is again: S141 > DEHP > DIDA.

Unfortunately the question is still open to discussion. Three very different methods (d.m.a., s.e.m. and SALS), used recently for classifying plasticizer activity, proved that an aliphatic plasticizer (di-butyl sebacate) is the better solvent for PVC than the aromatic di-isooctyl phthalate[41].

The K_1 values indicate, however, opposite trends. In the $(1 - w^*_{2c})$ plasticizer low concentration range the energy of the heterointeractions decreases with both the increasing compatibility (in classical terms) and the solvency (defined according to reference 41), whereas in the $(w^*_{2c} - 0)$ plasticizer high concentration range the aliphatic–aromatic plasticizers exhibit the stronger heterointeraction.

In a further study we will present a more detailed discussion concerning the correlation of the K_1 and K_2 parameters with the plasticizer structure, using both our own and literature data.

The use of different T_g concentration power equations for the two ranges of T_g vs composition data of PVC–plasticizer blends offers the advantage of outlining the cusp. According to the respective K_1 values up to the critical concentration w^*_{1c}, the plasticizer is fixed mainly through heterointeraction forces predominant in the 'interdomains' of the amorphous matrix. The solvency of the plasticizer in the amorphous regions of the 'domains' will, however, be greater the better its compatibility with PVC[36]. The amount of located plasticizer (solvating the polymer) will thus be proportional to the compatibility. After consuming its interaction possibilities within the amorphous PVC matrix (i.e. above w^*_{1c}), the plasticizer will still penetrate the domains, this time due to plasticizer–plasticizer homocontacts contributing by their larger mobility to an increase of entropy of the blend. Accordingly, the heterogeneous character of the system is further increasing. Depending on the compatibility of the plasticizer, there is, however, a reduced chance of solvating crystallites.

CONCLUSIONS

By applying different T_g concentration power equations for the two ranges of PVC–plasticizer compositions, separated by the cusp (characterized by a critical plasticizer content, w^*_{1c}), an excellent correlation of the experimental data can be obtained. The cusps indicate changes of the PVC–plasticizer interaction. In the low plasticizer concentration range plasticizer–PVC heterocontacts are established predominantly, while in the high concentration range plasticizer–plasticizer homocontacts prevail. The heterogeneous character of the blend is thus still increasing above the critical composition, as is illustrated by the increasing width of the glass transition range (evidenced by d.s.c.).

The changing nature of the PVC–plasticizer interaction is supported by the large difference between the values of the two parameters K_1 and K_2 of the T_g concentration power equations applied to the two concentration ranges mentioned above. Additionally, K_1 and K_2 can be correlated with the classical compatibility criteria for PVC–plasticizer systems.

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