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THERMAL TRANSITIONS AND POLYMER/POLYMER MISCIBILITY
II. PVC/EVA miscible systems

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Abstract

Poly(vinyl chloride) was blended with ethylene-vinyl acetate copolymer containing 70 wt% of vinyl acetate. The system shows a single glass transition temperature for all compositions, indicating their miscibility. The T_g *vs.* composition curves display an inflection, which changes with the chemical environment of the initial solution. The best fit to the shape of the curve was well reproduced by the Kovacs-Braun equation. The ΔT_g values reveal local heterogeneity, which means no total miscibility at a molecular level. Negative values of the Flory-Huggins interaction parameter were obtained from the calorimetric data.

Keywords: DSC, EVA, interaction parameter, polymer blends, PVC

Introduction

A formal treatment of the glass transition temperature, T_g, regards it as a quasi-second order transition [1]. With this, a relation between one thermodynamic function and the variation in the glass transition temperature, ΔT_g, can be derived [2]. A theory has been developed which involves a consideration of the importance of the enthalpy interactions as concerns the phase behaviour and its relation with the Flory-Huggins interaction parameter, χ. In this theory, the composition variation is related to the molar enthalpy of a mixture, H_m, and can be represented by

$$H_m = x_1H_1 + x_2H_2 + \Delta H_m \qquad (1)$$

where x_1 and x_2 are the respective molar fractions of polymers 1 and 2 in the mixture, H_1 and H_2 are the molar enthalpies of the two components and ΔH_m is the excess enthalpy of mixing.

The following equation represents the thermodynamics for the mixing process, where ΔH_1, ΔH_2 and ΔH_m are the changes in enthalpy when the temperature is raised from T_{g_1} to T_{g_2} at constant pressure:

$$\Delta H_m = x_1\Delta H_1 + x_2\Delta H_2 + \Delta H_m(T_{g_2}) - \Delta H_m(T_{g_1}) \qquad (2)$$

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From this relation, the theoretical considerations presented by Lu and Weiss [2] represent the enthalpy of mixing for a binary polymer blends as

$$\Delta H_m(T) = \chi RT\varphi_1\varphi_2 \tag{3}$$

where χ is the Flory-Huggins interaction parameter, R is the gas constant, T is temperature and φ_1 and φ_2 are the volume fractions of the two components 1 and 2.

Since the enthalpies change during the increase of temperature from T_{g_1} to T_{g_2} (glass transition temperatures of the pure components 1 and 2) since the respective enthalpy excesses ΔH_m (T_{g_1}) and ΔH_m (T_{g_2}) can be expressed as functions of the incremental changes in heat capacity, ΔC_p, which occur at the pure-component glass transition, and also since χ has a composition-dependent quadratic form

$$\chi = \chi_o + \chi_1 w_2 + \chi_2 w_2^2 \tag{5}$$

when T_{g_m} is known, a relationship can be used to calculate χ, as suggested by Lu and Weiss [2]:

$$T_{g_m} = \frac{w_1 T_{g_1} + K w_2 T_{g_2}}{w_1 + K w_2} + \frac{A w_1 w_2}{(w_1 + K w_2)(w_1 + b w_2)(w_1 + c w_2)^2} \tag{6}$$

where T_{g_m}, T_{g_1} and T_{g_2} are the glass transition temperatures, respectively, of the blend and its components, w_1 and w_2 are the weight fractions of the two components, respectively, and A can given by

$$A = \frac{-\chi R(T_{g_1} - T_{g_2})c}{M_1 \Delta C_{p_1}} \tag{7}$$

and K by

$$K = \frac{\Delta C_{p_2} - w_1 \delta C_{p_1}^{l}}{\Delta C_{p_1} - w_2 \delta C_{p_2}^{g}} \tag{8}$$

where $c=\rho_1/\rho_2$ is the component density ratio, ΔC_{p_1} and ΔC_{p_2} are the changes in specific heat of the components at T_{g_1} and T_{g_2}, δC_{p_1} and δC_{p_2} are the specific heat changes due to mixing in the liquid and solid phases, and $b=M_2/M_1$ is the molar mass ratio of the chain segments.

In this work, the thermodynamic miscibility of poly(vinyl chloride) (PVC) blended with ethylene vinyl acetate copolymer with 70 wt% of vinyl acetate (EVA 70) is analyzed by using the values of T_{g_m} in Eq. (6) to calculate χ from Eq. (7) with the experimental thermal parameters obtained from DSC data.

Experimental

Materials

The PVC used in this work was a commercial product of Companhia Petroquímica Camaçari, with a density of 1.390 g cm^{-3}. EVA 70 was obtained from Bayer. The polymers were characterized as described elsewhere [3].

Blends of PVC with EVA were prepared in solution by using tetrahydrofuran (THF) and methyl ethyl ketone (MEK) (Merck) as solvents, at appropriate concentrations of PVC and EVA to obtain PVC:EVA weight ratios of 9:1, 7:3, 5:5, 3:7 and 1:9. Films were prepared by casting PVC, EVA and the blends from 2% w/w filtered solutions onto glass plates, which were then kept in a desiccator at room temperature for one week. The films were removed from the support by immersion in distilled water, dried and stored at room temperature. The residual solvent was removed from the films by heating at 65±3°C for 72 h under vacuum. The samples were submitted to infrared spectrometry (Perkin Elmer, 1720X FT-IR spectrometer) to ensure the complete removal of the solvent; this was checked via the absence of the THF absorption band at 1065 cm^{-1} or the MEK carbonyl absorption band at 1720 cm^{-1}. The coprecipitated blends were obtained by precipitating the polymers from THF solutions with water, and the deposits were dried under vacuum at room temperature to constant weight.

Measurements

The calorimetric measurements were carried out in a Perkin-Elmer DSC-2 instrument calibrated with indium (T_m=429.86 K and ΔHf=6.8 cal g^{-1}) as standard. The samples weighing 15–20 mg were run at a heating rate of 20 K min^{-1} from 213 to 398 K under a nitrogen purge. To erase any thermal history effects, the samples were submitted to a heating/cooling cycle before T_g measurement. The glass transition temperature of each sample was determined as the temperature at the midpoint (1/2 ΔC_p) of the transition, as described by Wunderlich *et al.* [4]. The reproducibility of the measurements was checked and was found to be within at least ±5%. All procedures were run with at least duplicate samples.

Theoretical relationships

The T_g *vs.* composition relationship for the PVC/EVA 70 system can be described by the theoretical and empirical equations listed in Table 1. The theoretical equations arise from application of the thermodynamic theory to compatible polymer blends, as proposed by Couchman [5]; it supposes the connectivity constraint on the excess mixing entropy in the blends. Therefore, the theoretical relation for the composition dependence of T_g is given by Eq. (9) on the basis of temperature-independent heat-capacity increments. This equation can be reduced to other simplified relations when certain assumptions are applied:

a) If the ratio T_{g_1}/T_{g_2} approaches unity [5], the logarithmic terms of Eq. (9) may be approximated to give Eq. (10).

b) If it is assumed that $\Delta C_{p_i} \cdot T_{g_i}$ is constant [2, 5], Eq. (10) reduces to the Fox equation (Eq. (11)).

c) When $\Delta C_{p_1} = \Delta C_{p_2}$, Eq. (9) can be written as proposed by Pochan, Beatty and Pochan [5–8] (Eq. (12)).

d) If $T_{g_1}/T_{g_2} \approx 1$, the logarithmic functions from Eq. (12) can be suitably expanded and can be written as the rule of mixtures [7] (Eq. (13)).

e) Aubin and Prud'Homme [7] pointed out that, instead of setting $\Delta C_{p_1} = \Delta C_{p_2}$, a constant K given by the ratio $\Delta C_{p_1}/\Delta C_{p_2}$, can be introduced, and this gives Eq. (14), proposed by Utracki.

f) When the system interactions are very weak, Eq. (6) can be simplified to another form of Couchman's equation [2] (Eq. (15)).

As total entropy and total volume are continuous at glass transition temperatures, the derivation of a relation for T_g in terms of pure-component properties was outlined by Couchman and Karasz [9]; the resulting relation (Eq. (16)) includes the transition increment of isobaric volume thermal expansivity, α_i:

$$\alpha \equiv (1/V_i^0)(\partial V_i/\partial T)_p \tag{18}$$

The equation proposed by Couchman can be written for multicomponent systems by using the general expression presented by Utracki [10] (Eq. (17)).

By definition, $T_{g_1} < T_{g_2}$, and therefore $K = \Delta C_{p_2}/\Delta C_{p_1} < 1$. As pointed out by Lu and Weiss [2], Eq. (18) always predicts negative deviation for T_{g_m}.

Results and discussion

Figure 1 shows that the mixtures PVC/EVA 70 exhibited a single glass transition temperature for all compositions. It may be observed that the solvent can influence the transition *vs.* composition curves; these samples were cast films from THF solutions, cast films from MEK solutions, and mixtures obtained by coprecipitating

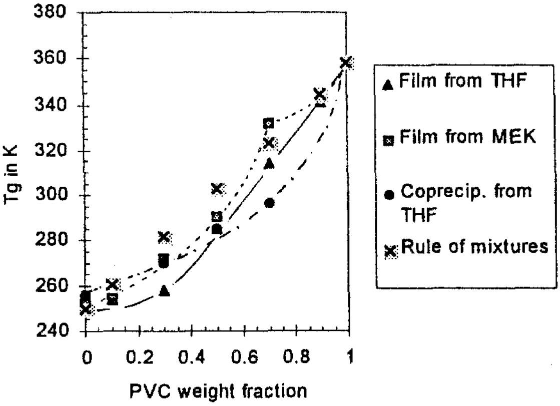

Fig. 1 T_g-composition relationship for PVC/EVA 70 blends

THF solutions of the two polymers in water. The T_g values increase with the PVC content in the blend, rising from 234 K (-39°C) (T_g of pure EVA 70) to 358 K (85°C) (T_g of pure PVC). The results obtained from the experimental data give curves which lie below the straight line predicted by the rule of mixtures.

The mixing method effect on the T_g *vs.* composition function can be explained by the distinct chemical environment during sample preparation. It indicates that the samples prepared from THF solution followed by slow evaporation gave a system that allows a higher interaction between the polymeric components with increasing EVA content. The curve can be outlined as a line which changes slope at a PVC composition of 0.3. The line from the blends made from THF solutions coprecipitated in water show the inflection at w_2=0.7, while the curve from those prepared by using MEK as solvent presents a cusp. The systems obtained from water coprecipitation and produced from MEK evaporation are more unstable. The former method is unfavourable for higher interaction between the components, and the latter uses a solvent that has less affinity with the polymers inducing the $\Delta\chi_{12}$ effect. However, since the Tg values were obtained by using the same instrumental conditions, any systematic error in the measurement will not affect the pattern of the curve.

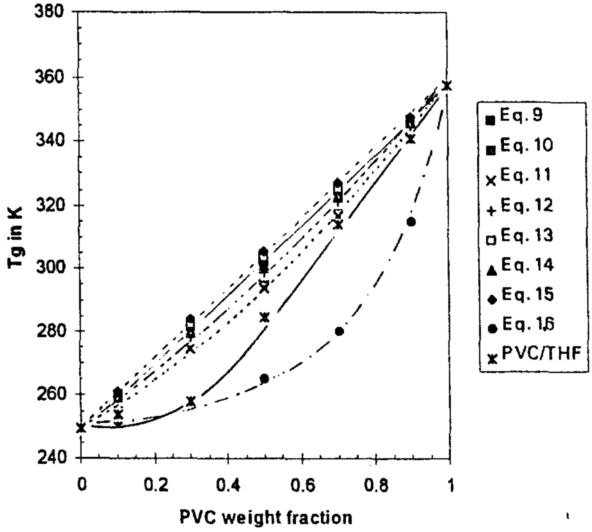

Fig. 2 Theoretical T_g-composition relationship for PVC/EVA 70 blends using Eqs (9) to (16)

The T_g *vs.* composition relationship for the PVC/EVA 70 system could be described by the equations presented in Table 1 (Eqs (9) to (17)) and depicted in Fig. 2. The profile of the experimental curve is similar to those presented before for polymer -diluent systems [11, 12] and polymer blends [13–16], but it represents a poor approximation to those predicted by the relations listed in Table 1. The literature [13, 17–19] describes that the discrepancy from linearity indicates the interaction between the components.

Table 1 Relationships used to predict composition dependence of T_g for compatible systems

Author	Equation	Remarks	Ref.	Eq.
Couchman	$\ln T_g = \dfrac{w_1\Delta C_{p_1}\ln T_{g_1} + w_2\Delta C_{p_2}\ln T_{g_2}}{w_1\Delta C_{p_1} + w_2\Delta C_{p_2}}$	based on connectivity constraint on excess mixing entropy	[5, 8]	(9)
Couchman	$T_g = \dfrac{w_1\Delta C_{p_1}T_{g_1} + w_2\Delta C_{p_2}T_{g_2}}{w_1\Delta C_{p_1} + w_2\Delta C_{p_2}}$	$T_{g_1}/T_{g_2} \cong 1$	[5]	(10)
Fox	$\dfrac{1}{T_g} = \dfrac{w_1}{T_{g_1}} + \dfrac{w_2}{T_{g_2}}$	$(\Delta C_{p_i}, T_{g_i})$ is constant, Eq. (10)$\Rightarrow$Eq. (11)	[2, 5, 8]	(11)
Pochan, Beatty and Pochan	$\ln T_g = w_1\ln T_{g_1} + w_2\ln T_{g_2}$	$\Delta C_{p_1} = \Delta C_{p_2}$, Eq. (9)$\Rightarrow$Eq. (12)	[5–8]	(12)
Rule of mixtures	$T_g = w_1T_{g_1} + w_2T_{g_2}$	empirical; expansion of logarithm term of Eq. (12)	[5, 7, 8]	(13)
Utracki	$\ln T_g = \dfrac{w_1\ln T_{g_1} + Kw_2\ln T_{g_2}}{w_1 + Kw_2}$	$K = \dfrac{\Delta C_{p_1}}{\Delta C_{p_2}}$	[7, 8]	(14)
Couchman	$T_g = \dfrac{w_1T_{g_1} + Kw_2T_{g_2}}{w_1 + Kw_2}$ and $K = \dfrac{\Delta C_{p_2}}{\Delta C_{p_1}}$	for very weak or no specific interactions; $T_{g_1}/T_{g_2} \cong 1$	[2, 7, 8]	(15)
Couchman and Karasz	$T_g = \dfrac{\varphi_1\Delta\alpha_1T_{g_1} + \varphi_2\Delta\alpha_2T_{g_2}}{\varphi_1\Delta\alpha_1 + \varphi_2\Delta\alpha_2}$	$\Delta V_m^{\text{glass}} \cong \Delta V_m^{\text{liquid}}$	[5, 9]	(16)
Utracki/Couchman	$\ln T_g = \dfrac{\Sigma w_n\Delta C_{p_n}\ln T_{g_n}}{\Sigma x_n\Delta C_{p_n}}$	for multicomponent systems	[10]	(17)

$\Delta\alpha_1$ and $\Delta\alpha_2$ are the differences in the expansivity of a component in the vitreous and the liquid states; n is the number of components.

Beirnes and Burns [20] reported that miscible polymer systems can display a monotonous glass transition temperature dependence on composition or an unusual pattern (cusp). These features have been discussed by many authors for polymer-plasticizers [8, 20–22] and polymer blends [7, 8, 12, 15, 17, 23–26], and correlated to the strength of the interaction [12, 13, 17].

The theoretical development of the Kovacs-Braun equation [19]:

$$T_g = T_{g_1} + \frac{\varphi_2 fg_2 + g\varphi_1\varphi_2}{\varphi_1\Delta\alpha_1} \tag{19}$$

where fg_2 is the free volume fraction of polymer 2 at T_{g_2}, considers the effect of the interaction between the components with a term, g, that is a function of the volume excess of the mixture:

$$g = (V_e/V)/\varphi_1\varphi_2 \tag{20}$$

V_e is the excess volume and V is the volume of the blend. In spite of some theoretical restrictions, this equation has been applied successfully [7, 8, 12] to data that present a cusp in the T_g *vs.* composition curve instead of a monotonous curve.

The Kovacs-Braun equation [7, 8, 19] foresees that, for blends whose T_g difference is higher than 52 K, the free volume of the polymers approaches zero at one critical temperature, T_c. This is the temperature where the polymer with higher T_g does not contribute to the free volume of the mixture. It matches a value where a real second-order transition is observed.

Thus, T_c and φ_c can be calculated by application of the equations

$$T_c = T_{g_2} - (fg_2/\Delta\alpha_2) \qquad \text{considering } T_{g_2} > T_{g_1} \tag{21}$$

$$\varphi_c = fg_2/[\Delta\alpha_1(T_{g_2} - T_{g_1}) + fg_2(1 - \Delta\alpha_1/\Delta\alpha_2)] \tag{22}$$

Prud'Homme *et al.* [7, 8, 17] have shown that, above T_c, T_g is given by

$$T_{g_2} - T_g = (\varphi_1\varphi_2)(\Delta\alpha_1/\Delta\alpha_2)(T_g - T_{g_1}) \tag{23}$$

and below T_c, T_g can be calculated as

$$T_g = T_{g_1} + (fg_2/\Delta\alpha_1)(\varphi_2/\varphi_1) \tag{24}$$

Equation (24) shows that T_g depends uniquely upon the parameters of polymer 1. As mentioned in the literature [7, 8, 12, 17], cusps in the T_g *vs.* composition curve can be theoretically predicted following the iso-free volume theory. According to this theory, $fg_2=0.025$ and, supposing that $\Delta\alpha_1=\Delta\alpha_2$ and the value of $\Delta\alpha_2=0.00048\ \mathrm{K}^{-1}$, the value of T_c is given by

$$T_c = T_{g_2} - 52 \tag{24}$$

where T_c depends only on T_{g_2}.

Accordingly, Eq. (19) can be used for the region below the 'critical point' (T_c, φ_c); $\varphi_c=0.55$ and $T_c=355$ K are obtained for the PVC/EVA 70 system. Above the 'critical point', a g value of 0.012 was used; the results are depicted in Fig. 3. The curve corresponds to the best fit for the experimental data on the PVC/EVA 70 system obtained from THF and shows that the Kovacs-Braun equation appropriately describes the behaviour of this system.

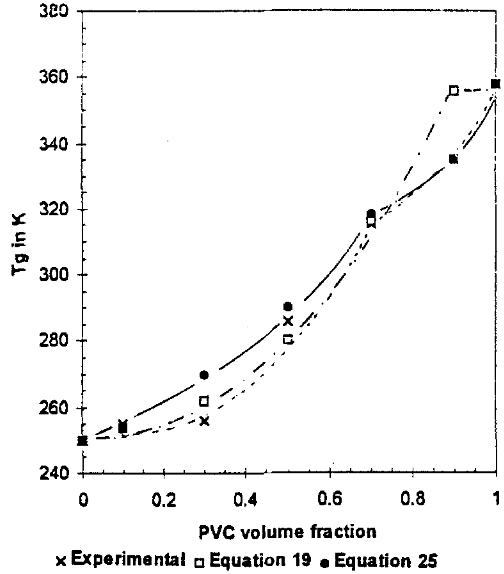

Fig. 3 Theoretical T_g-composition relationship for PVC/EVA 70 blends using Eqs (19) and (25)

Figure 3 also demonstrates that the interaction parameter g can be introduced into the Gordon-Taylor equation as reported by Aubin and Prud'Homme [7, 8]. Then, T_g is given by

$$T_g=\frac{\varphi_1 T_{g_1}+k\varphi_2 T_{g_2}+g\varphi_1\varphi_2}{\varphi_1+k\varphi_2} \tag{25}$$

where k and g have values of 0.8 and 0.1, respectively, for PVC/EVA 70 blends. Although this equation can not predict the cusp behaviour, a good approach is possible by variation of the fitting parameters.

The transition width in homogeneous mixtures, represented by ΔT_g, is usually 15°C. However, when $\Delta T_g>15$°C, less homogeneous mixtures appear, and for compositions rich in the more elastomeric component, the T_g of the blend is reduced and the transition range is expanded.

This expansion corresponds to a reduction in the miscibility due to the presence of heterogeneous domains and local microheterogeneity. Also, composition oscillations with different T_g are present and suggest that the system does not possess complete miscibility at the molecular level. The enlargement has been well documented for polyester/nitrocellulose [17] and PVC/polyester [26] blends.

The ΔT_g data as a function of the composition for PVC/EVA 70 are presented in Fig. 4. As assigned previously for a single glass transition, it indicates a better miscibility, independently of the sample preparation method. The increase in ΔT_g at the intermediate compositions reveals higher microheterogeneity than for the extreme compositions.

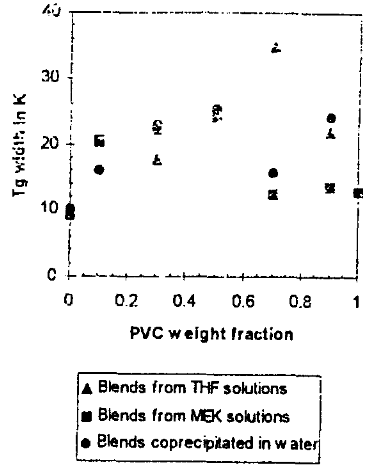

Fig. 4 ΔT_g-composition relationship for PVC/EVA 70 blends

The interaction parameter, χ_{12}, obtained from calorimetric measurements, was calculated from Eqs (6) to (8) and the T_g *vs.* composition experimental data, which were used with conditions and restrictions to the values of the unknown variables, and with the assumptions that A is a composition quadratic function and that K is a linear function expressed as

$$K = A' + Ew_2 \tag{26}$$

In this way, a minimization numeric method (Newton-Raphson) was applied in order to obtain the interaction parameter, χ_{12}. It must be borne in mind that, even without these restrictions, the obtained values are near the calculated values if it is assumed that both K and A are functions of the composition. The results are presented in Fig. 5.

As assigned previously from qualitative calorimetric observations, the blends obtained from THF solution exhibit more negative values, which means a better miscibility level. The samples coprecipitated from water and obtained from MEK solution display less negative χ_{12}, confirming the influence of the sample preparation procedure on the final miscibility. This parameter does not have any significant composition dependence. The dependence of χ_{12} on the composition, shown in Fig. 5, follows the same relation as for the preparation method.

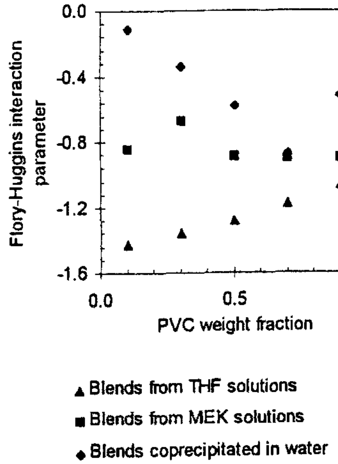

Fig. 5 Flory Huggins interaction parameter, χ, for PVC/EVA 70 blends as a function of PVC/EVA weight fraction

Conclusions

During the sample preparation, the T_g difference for PVC/EVA 70 blends in the distinct chemical environment indicates that the THF solutions result in systems involving a better interaction between the blend components as compared with those precipitated from water and the MEK systems.

The Gordon-Taylor equation gives the best fit to the experimental T_g *vs.* composition data, including the anomalous cusp. This was registered as an increase in the microheterogeneity at the intermediate compositions whereas high miscibility level was assigned for the extreme compositions. The values obtained for the interaction parameters are more negative for the blends obtained from THF solution, in agreement with the qualitative experimental calorimetric observations.

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