Journal of Thermal Analysis, Vol. 49 (1997) 227-234

THERMAL TRANSITIONS AND POLYMER/POLYMER MISCIBILITY
I. PVC/EVA immiscible systems

C. Thaumaturgo[1] *and E. C. Monteiro*[2]

[1]Instituto Militar de Engenharia (IME) Praça General Tibúrcio 80, CEP 22290-270, Rio de Janeiro
[2]Instituto de Macromoléculas, IMA/UFRJ Caixa Postal 68525, CEP 21945-970, Rio de Janeiro, RJ, Brazil

Abstract

In order to provide additional information on the miscibility of the PVC/EVA system, calorimetric parameters such as ΔC_{p_i}, T_{g_i} and ΔT_{g_i} were obtained with a different approach. A qualitative and quantitative measure of the blend composition at the interface was obtained. This indicated that the domains are rich in each component and the presence of the second component in the phase has little effect on the main chain relaxation. The PVC fraction in the EVA-rich phase is always larger than the EVA fraction in the PVC-rich phase. Positive and small values of the Flory-Huggins interaction parameter were obtained from calorimetric data.

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

Introduction

A qualitative measurement of the miscibility degree in polymer blends can be obtained by comparison of the measured and calculated ΔC_{p_M} of the mixture, that is the Fried ratio [1], F:

$$\Delta C_{p_{M_{\mathrm{calculated}}}} = x_1\Delta C_{p_1^\circ} + x_2\Delta C_{p_2^\circ} \quad \text{and} \quad \Delta C_{p_{M_{\mathrm{experimental}}}} = x_1\Delta C_{p_1^\circ} + x_2\Delta C_{p_2^\circ}$$

where x_1 and x_2 are the mass fractions and $\Delta C_{p_1^\circ}$ and $\Delta C_{p_2^\circ}$ are the heat capacity variations of the pure components 1 and 2.

One estimate of the interfacial fraction of partially miscible blends can be obtained from calorimetric measurements. The value F described above gives qualitative information on the extent of the diffusion interface. It should be borne in mind that this is obtained with the total mass fractions x_1 and x_2, which gives a higher F value. However, the composition remains constant only well away from the interface, where ΔC_{p_i} and T_{g_i} can be assumed constant.

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

The interface between the components involves a fraction of the material of the mixture [2], w_i, which is material not in phases I and II and which can be expressed as a function of the ΔC_p and T_g data as

$$w_i = 1 - \frac{\Delta C_{p_2}[\Delta C_{p_2^\circ} \ln(T_{g_2^\circ}/T_{g_2}) - \Delta C_{p_1^\circ} \ln(T_{g_1^\circ}/T_{g_2})]}{\Delta C_{p_1^\circ}\Delta C_{p_2^\circ} \ln(T_{g_2^\circ}/T_{g_1^\circ})} - \frac{\Delta C_{p_1}[\Delta C_{p_2^\circ} \ln(T_{g_2^\circ}/T_{g_1}) - \Delta C_{p_1^\circ} \ln(T_{g_1^\circ}/T_{g_1})]}{\Delta C_{p_1^\circ}\Delta C_{p_2^\circ} \ln(T_{g_2^\circ}/T_{g_1^\circ})}$$

where $T_{g_1^\circ}$, $T_{g_2^\circ}$, $\Delta C_{p_1^\circ}$ and $\Delta C_{p_2^\circ}$ are the glass transition temperatures and the heat capacity variations of pure components 1 and 2. T_{g_1}, T_{g_2}, ΔC_{p_1} and ΔC_{p_2} are, respectively, the glass transition temperatures and the heat capacity variations of the domains rich in components 1 and 2.

These basic principles have been used to investigate immiscible blends of poly(vinyl chloride) (PVC)/ethylene vinyl acetate copolymer (EVA) with low vinyl acetate (VA) content.

Experimental

The PVC used in this work was a commercial product of Companhia Petroquímica Camaçari, with a density of 1.390 g cm^{-3}. Six EVA copolymers with VA contents of 31(EVA31), 41(EVA41), 45(EVA45), 50(EVA50) and 70(EVA70) wt% were obtained from commercial sources. Pertinent parameters of the polymers studied were described elsewhere [3].

Pure polymers and blend films were obtained by casting 1% solutions in tetrahydrofuran (THF) or methyl ethyl ketone (MEK) onto a glass plate in a desiccator at 298 K with saturated solvent vapor for a minimum of 72 h. The obtained films were dried in vacuum at 338 K±3°C for 72 h. Residual solvent was verified by absence of infrared absorption at 1065 cm^{-1} (THF) and 1720 cm^{-1} (MEK). The absence of MEK was also verified by absence of the volatilization peak in the DSC curve.

For DSC investigations, 15 to 20 mg samples were heated in nitrogen atmosphere from 213 to 398 K. The heating rate applied was 10 K min^{-1}, the cooling rate was 320 K min^{-1} and the sensitivity was 5 mcal.

In order to eliminate the thermal history of the samples, a heating/cooling cycle was applied. The data obtained in this analysis were the glass transition, T_g, the T_g width, ΔT_g, the heat capacity variation, ΔC_p, and the melt fusion, T_m.

Results and discussion

The calorimetric curves registered the glass transitions of different PVC/EVA pairs. The transition width, the transition enthalpy and the heat capacity variation were also obtained. Figures 1A to 1D show T_g as a function of the composition of the mixture for PVC/EVA pairs.

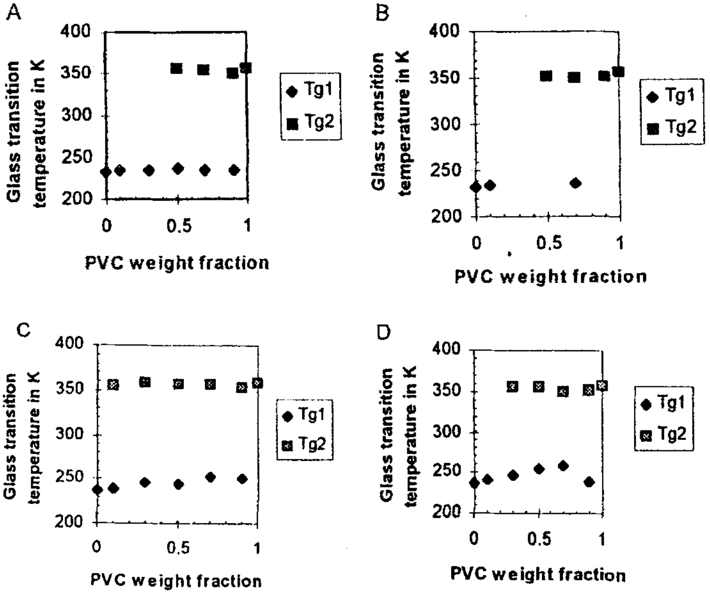

Fig. 1 T_g-composition relationship for PVC/EVA blends. A – PVC/EVA31; B – PVC/EVA41; C – PVC/EVA45; D – PVC/EVA50

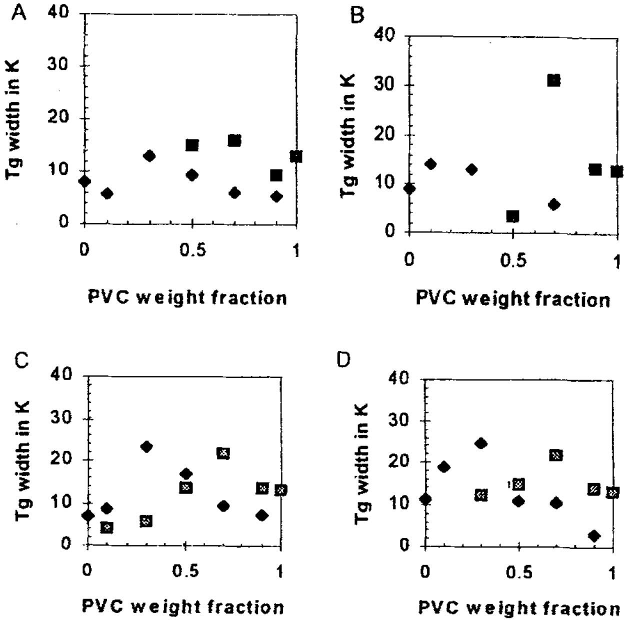

Fig. 2 ΔT_g-composition relationship for PVC/EVA blends. A – PVC/EVA31; B – PVC/EVA41; C – PVC/EVA45; D – PVC/EVA50. ◆ ΔT_{g_1}, ■ ΔT_{g_2}

Table 1 Composition of phases in PVC/EVA blends

Blend	PVC mass fraction	EVA (%), x_1^{I}	PVC (%), x_2^{II}
EVA50			
5019	0.1	0.929	–
5037	0.3	0.820	0.994
5055	0.5	0.703	0.995
5073	0.7	0.668	0.996
5091	0.9	0.958	0.975
EVA45			
4519	0.1	0.921	0.990
4537	0.3	0.924	0.994
4555	0.5	0.942	0.995
4573	0.7	0.867	0.995
4591	0.9	0.887	0.980
EVA41			
4119	0.1	0.994	–
4137	0.3	–	–
4155	0.5	–	0.975
4173	0.7	0.991	0.970
4191	0.9	–	0.974
EVA31			
3119	0.1	1.000	–
3137	0.3	0.998	–
3155	0.5	0.992	0.996
3173	0.7	0.997	0.989
3191	0.9	0.999	0.973

Phase I: EVA rich-composition; phase II: PVC-rich composition.

Except for the PVC/EVA70 blend, two clear T_g's can be observed for all mixtures. The mixtures with low acetate content in the copolymer (EVA31, EVA41, EVA45 and EVA50) exhibit T_g values very near to that for the pure component. This indicates that the domains are composed of each component and the presence of the second component in the domain has little effect on the main chain relaxation. Some transitions in the PVC-rich domain of the blends with lower VA content were masked by residual melt fusion of the long ethylene sequences that had yet to be crystallized.

The composition has little effect on the T_g shift of these systems. This increased as the acetate content was raised. It was actually null for the EVA31 and EVA41 blends, whereas in the EVA45 blends, the compositions with high acetate, the EVA-rich domains present some T_g shift.

The PVC/EVA50 blends showed some EVA50 influence on the lower glass transition, T_{g_1}. T_{g_1} and T_{g_2} (transitions in the blend) are far from $T_{g_1}^{o}$ and $T_{g_2}^{o}$ (transitions of the pure components) when the composition reaches 1:1, which means that rich domains are highly contaminated by the second component.

The T_g width, ΔT_g, for the EVA45 blends displayed some variation with composition, but the values were less than 15°C, which means that the heterogeneity here is smaller than for mixtures with low VA content (EVA31 and EVA41) (Figs 2A to 2D).

For PVC/EVA50, ΔT_g in the EVA domain, ΔT_{g_1}, reveals significant variations in the EVA-rich composition, whereas ΔT_g in the PVC-rich domain, ΔT_{g_2}, remains unaffected by the composition. In the intermediate composition, both ΔT_{g_1} and ΔT_{g_2} have values higher than 15°C, which indicates a higher heterogeneity than for the extreme compositions.

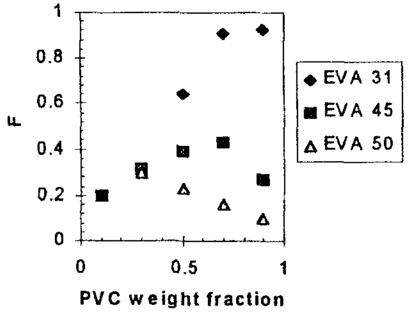

Fig. 3 Fried ratio F-composition relationship for PVC/EVA blends

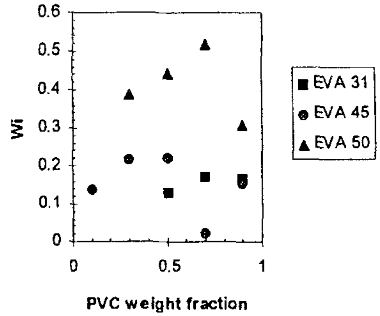

Fig. 4 Interface weight fraction-composition relationship for PVC/EVA blends

The two transitions point to the presence of two phases, two domains, two distinct microstructures, both rich in each component and contaminated to some degree with the other component. The composition of each component in both phases can be quantified by using the T_g *vs.* composition relationship for a mixture.

The phase composition of the semi-miscible and immiscible blends can be calculated by using the experimental T_g and ΔT_g values with the Couchman T_g-composition equation, yielding

$$x_1^{\mathrm{I}} = \frac{\Delta C_{p_2}^{\circ} (\ln T_{g_1} - \ln T_{g_2}^{\circ})}{\Delta C_{p_1}^{\circ} (\ln T_{g_1}^{\circ} - \ln T_{g_1}) - \Delta C_{p_2}^{\circ} (\ln T_{g_1} - \ln T_{g_2}^{\circ})}$$

for the component 1 – rich phase (I) and $x_2^{\mathrm{I}}=1-x_1^{\mathrm{I}}$;

$$x_1^{\mathrm{II}} = \frac{\Delta C_{p_2^\circ}(\ln T_{g_2} - \ln T_{g_2^\circ})}{\Delta C_{p_1^\circ}(\ln T_{g_1^\circ} - \ln T_{g_2}) - \Delta C_{p_2^\circ}(\ln T_{g_2} - \ln T_{g_2^\circ})} \quad \text{and } x_2^{\mathrm{II}} = 1 - x_1^{\mathrm{II}}$$

for the component 2 – rich phase (II), which express the compositions of components 1 and 2 in phases I and II. $\Delta C_{p_1^\circ}$, $\Delta C_{p_2^\circ}$, $T_{g_1^\circ}$, $T_{g_2^\circ}$, ΔC_{p_1}, ΔC_{p_2}, T_{g_1} and T_{g_2} remain the same as described above. Table 1 lists the calculated x_1^{I}, x_2^{I}, x_1^{II} and x_2^{II} for the studied blends.

Table 2 Flory-Huggins, interaction parameter, χ_{12}, and critical interaction parameter, χ_{crit}, for PVC/EVA blends

Blend	PVC mass fraction	φ_1^{I}	φ_2^{I}	φ_1^{II}	φ_2^{II}	$\chi_{12}\times10^4$	$\chi_{\mathrm{crit}}\times10^5$
EVA50/PVC							6.08
5019	0.1	0.948	0.052	–	–	–	
5031	0.3	0.865	0.135	0.008	0.992	1.8	
5055	0.5	0.768	0.232	0.008	0.992	18.6	
5073	0.7	0.738	0.262	0.046	0.954	11.7	
5091	0.9	0.969	0.031	0.034	0.976	12.5	
EVA45/PVC							7.01
4519	0.1	0.993	0.007	0.013	0.987	19.7	
4537	0.3	0.994	0.006	0.008	0.992	21.9	
4555	0.5	0.958	0.042	0.007	0.993	22.9	
4573	0.7	0.903	0.097	0.007	0.993	2.3	
4591	0.9	0.917	0.083	0.027	0.973	16.4	
EVA41/PVC							6.96
4119	0.1	0.996	0.004	–	–	–	
4137	0.3	–	–	–	–	–	
4155	0.5	–	–	0.035	0.965	–	
4173	0.7	0.994	0.006	0.041	0.959	14.6	
4191	0.9	–	–	0.036	0.954	–	
EVA31/PVC							7.60
3119	0.1	0.999	0.001	–	–	–	
3137	0.3	0.998	0.002	–	–	–	
3155	0.5	0.994	0.006	0.006	0.994	26.4	
3173	0.7	0.998	0.002	0.001	0.999	21.4	
3191	0.9	0.999	0.001	0.038	0.962	16.9	

Table 1 indicates that the fraction of PVC in the EVA-rich phase (phase 1) is much larger than the fraction of EVA in the PVC-rich phase (phase II).

These results suggest that only a proportion of the molecules in the blend actually participate in the observed transitions, in agreement with the former qualitative observations (ΔT_{g_1}, ΔT_{g_2}, T_{g_1} and T_{g_2}).

The values of the Fried ratio, F, as a function of composition are presented in Fig. 3. These values are higher for blends with low VA content. Further, the higher values for the intermediate compositions indicates that in these blends low quantities of this material are present in the interfacial region. However, EVA50 blends afford F values that diminish as the PVC content is increased, which means higher miscibility in these compositions.

All the biphase blends have domains rich in one component but contaminated by the other, in agreement with the increase in the T_g widths (ΔT_{g_1} and ΔT_{g_2}) due to oscillations in phase homogeneity as a result of the differences in the interaction of the chains with their environment.

The difference between the measured and the calculated ΔC_p indicates that part of the mixture does not contribute to the glass transitions, forming a distinct region that is not related with any domain. This region can be defined as an interfacial diffusion region, composed by an equilibrium layer. For less immiscible blends, this layer will be more extensive.

The fractions of the components of the mixture in the interface w_I calculated for these blends were always lower than the $1-F$ values. This is due the fact that in the calculation of F the initial mass fractions were used (x_1 and x_2). Thus, F has a qualitative character, while in the w_I calculation, the real mass fractions in each phase were used (x_1^I, x_2^I, x_1^{II} and x_2^{II}). The quantity of material in the interface diminishes as the VA content diminishes in accordance with the degree of interaction between the components (Fig. 4).

For immiscible blends, very few methods are known whereby the Flory-Huggins interaction parameter, χ_{12}, can be determined. Most of them involve ternary phase solutions with a solvent. However, χ_{12} and the critical interaction parameter, χ_{crit}, can also be obtained from calorimetric measurements [4] as described below by

$$\bar{\chi}_{crit} = \chi_2/V_o = 1/2\left[\frac{1}{(N_1V_1)^{1/2}} + \frac{1}{(N_2V_2)^{1/2}}\right]^2$$

and

$$\chi_{12} = \frac{\ln\frac{\varphi_1^{II}}{\varphi_1^{I}} + \left(1 - \frac{N_1}{N_2}\right)(\varphi_2^{II} - \varphi_2^{I})}{N_1(\varphi_2^{12} - \varphi_2^{112})}$$

where φ_1^I, φ_2^I, φ_1^{II} and φ_2^{II} are, respectively, the volume fractions of each component in phases I and II. V_o is the reference volume $V_o = 105\ \mathrm{cm^3\ mol^{-1}}$), V_1 and V_2 are the molar volume of the repetitive units, and N_1 and N_2 are the respective polymerization degrees. If it is assumed that these systems involve a phase equilibrium, if the molecular weight fractionation dissimilarities between the phases are neglected, and if the phase compositions are used, it is possible to calculate the interaction parameter for the PVC/EVA systems. Table 2 lists the results.

As expected, all χ_{12} values were positive and near zero, including values higher than χ_{crit}, which means that all blends are thermodynamically immiscible. Although the composition has no significative influence on the χ_{12} values, the intermediate mixtures yield χ_{12} values higher than those of the extreme composition blends, in agreement with the qualitative observations above.

Conclusions

The T_g widths, ΔT_g's, provide good qualitative information about the miscibility in each blend domain. For the PVC/EVA system, the PVC fraction in the EVA-rich phase (phase I) is always larger than the EVA fraction in the PVC-rich phase (phase II). The high F values confirm that a small proportion of the material is in the interfacial region; this quantity diminishes as the VA content in the EVA phase becomes lower.

The interaction parameters in this system are in agreement with the experimental observations and the intermediate compositions exhibit χ_{12} values larger than those of the extreme composition blends.

* * *

Support for this research by CNPq, FINEP and CAPES is appreciated.

References

1 J. R. Fried, F. E. Karasz and R. McKnight, Macromolecules, 11 (1978) 150.
2 H. Yang, S. Ricci and M. Collins, Macromolecules, 24 (1991) 5218.
3 E. E. C. Monteiro and C. Thaumaturgo, Polymer Bulletin, 30 (1993) 697.
4 X. Lu and R. A. Weiss, Macromolecules, 25 (1992) 3242.