

## Thermodynamics of mixing of poly(vinyl chloride) and poly(ethylene-*co*-vinyl acetate)

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### Abstract

The miscibility of poly(vinyl chloride) (PVC) and an ethylene–vinyl acetate copolymer with 85 wt% of vinyl acetate units (EVA85) has been studied by measuring the glass transition temperature and the enthalpy of mixing of several mixtures covering the whole composition range. An accurate thermal characterization as regards the specific heat of the two polymers and their blends has also been obtained. The enthalpy of mixing has been found negative for all the mixtures, indicating that specific interactions are involved between the polar groups of the two components. Particular attention has been paid also to the excess specific heat, which comes out positive for the PVC-rich blends and with a small negative value in a narrow region at high contents of EVA85. This finding is in agreement with negative and positive deviations that are observed for the glass transition temperature. Modelistic considerations about the type of interactions and the organization between PVC and EVA85 in the blends are proposed. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Polymer blends; Enthalpy of mixing; Excess specific heat

### 1. Introduction

Blends of poly(vinyl chloride) (PVC) and ethylene–vinyl acetate (EVA) copolymers have been extensively studied by many authors by means of different techniques [1–15]. The great interest for PVC/EVA mixtures is due to the fact that EVA, being a highly flexible polymer, can act as plasticizer of PVC, with the advantage to avoid the addition of low molecular plasticizers. In fact the migration of these latter in PVC matrices is a considerable problem, especially as regards the stiffening of the final products as well as the potential health risks for medical and food packaging applications. PVC/EVA is an interesting system also because it is an example of homopolymer–copolymer miscible blend although the homopolymers from the three repeating units are immiscible among themselves: PVC is immiscible with polyethylene and also with poly(vinyl acetate), but forms miscible mixtures with EVA within a specified range of copolymer composition. It has been suggested that the dependence of miscibility on the

copolymer composition is due to repulsion forces between the two different copolymeric units [16,17].

The phase behaviour of PVC/EVA blends is quite complex [10]. EVA copolymers with vinyl acetate content ranging from 45 to 85 wt% have been found miscible with PVC. Discrepancies between the results are found in the literature as regards the temperature at which phase separation occurs. Such disagreements have been explained as due to different molecular weight of the components and to different methods of blend preparation [10].

It is well known that thermodynamic miscibility is possible only if the free energy of mixing  $\Delta_{\text{mix}}G$  is negative, being  $\Delta_{\text{mix}}G$  given by [18]

$$\Delta_{\text{mix}}G = \Delta_{\text{mix}}H - T\Delta_{\text{mix}}S \quad (1)$$

where the enthalpy and entropy of mixing,  $\Delta_{\text{mix}}H$  and  $\Delta_{\text{mix}}S$ , respectively, are both function of composition, temperature and molecular weight. A negative  $\Delta_{\text{mix}}G$  is necessary but insufficient condition for miscibility. In order to obtain phase stability, additional requirements have to be satisfied [18]

$$\left( \frac{\partial^2 \Delta_{\text{mix}}G}{\partial w_i^2} \right)_{T,P} > 0 \quad (2)$$

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where  $w_i$  is the weight fraction of component  $i$ . Since the entropy of mixing of high molecular weight polymers is quite small, miscibility is assured by a negative value of  $\Delta_{\text{mix}}H$ , which corresponds to the existence of attractive interactions between the components. It is worth reminding that such specific interactions, as for example, hydrogen bonding and dipole–dipole interactions, operate in a system in addition to dispersive interactions, or London forces [19]. These latter act between groups not interacting specifically and are expected to contribute endothermically to the total enthalpy of mixing.

A direct measurement of  $\Delta_{\text{mix}}H$  cannot be performed due to the high viscosity and slow interdiffusion of the polymers. Two methods have been generally used in order to obtain experimental enthalpy of mixing. One takes into account the heat of mixing of low molecular weight compounds characterized by chemical structures similar to those of the repeating units [20]. This approach, named analogue calorimetry, not considering the effect of the chains' length, gives results approximate but qualitatively equivalent to the heat of mixing of a blend, being the enthalpic interactions primarily due to the nearest neighbour functional groups. The second one is an indirect method that consists of a thermodynamic cycle based on the Hess's law [21,22]

$$\Delta_{\text{mix}}H = w_1\Delta_{\text{sol}}H_1 + w_2\Delta_{\text{sol}}H_2 - \Delta_{\text{sol}}H_{\text{blend}} \quad (3)$$

where  $\Delta_{\text{sol}}H_1$ ,  $\Delta_{\text{sol}}H_2$  and  $\Delta_{\text{sol}}H_{\text{blend}}$  are the heats of solution in the same solvent of polymer 1, polymer 2 and their blend, respectively, and  $w_1$  and  $w_2$  are the weight fractions of the two polymers in the blend.

In this paper for the first time, an accurate thermal characterization of the blend PVC/EVA85 (EVA copolymer with 85 wt% of vinyl acetate units) is performed and illustrated. In addition the heat of mixing, measured by using the Hess's law approach, is reported in the whole composition range. Particular attention has also been paid to the temperature dependence of  $\Delta_{\text{mix}}H$ , which can be calculated from the excess specific heat,  $\Delta_{\text{mix}}c_p$ , according

to the following relationship [23]

$$\left(\frac{\partial \Delta_{\text{mix}}H}{\partial T}\right)_{P,w_i} = \Delta_{\text{mix}}c_p \quad (4)$$

with

$$\Delta_{\text{mix}}c_p = c_p - w_1c_{p1} - w_2c_{p2} \quad (5)$$

where  $c_p$ ,  $c_{p1}$  and  $c_{p2}$  are the specific heats of the blend and the two components, respectively. Finally, considerations about the nature and the type of interactions between PVC and EVA85 are deduced by comparing the composition dependence of the excess specific heat, the enthalpy of mixing and the glass transition temperature.

## 2. Experimental part

### 2.1. Materials

PVC was a Fluka commercial product ( $M_n = 48\,000$ ) and was used without further purification. EVA copolymer with 85 wt% of vinyl acetate units, EVA85, was supplied by Bayer AG. The material was purified via precipitation from chloroform solution with *n*-hexane. The filtered product was dried under high vacuum in oven at 333 K for 20 days and characterized in vinyl acetate content by thermogravimetric analysis [15]. Films of PVC/EVA85 blends, covering the whole range of composition, were prepared by solvent casting. The two components of the blends, in the desired proportions, were dissolved in THF to produce a 5 wt% homogeneous solution and kept under stirring for a few days. Successively the solutions were allowed to evaporate very slowly under an atmosphere nearly saturated of solvent. The films thus obtained were then dried under high vacuum in oven at 353 K for 4 days. The composition of the blends is reported in Table 1.

### 2.2. Specific heats measurements

Specific heat data were obtained via DSC analysis by using a Perkin Elmer DSC7. The external block temperature

Table 1  
Coefficients  $a$  and  $b$  of the relationship  $c_p = a + bT$  and heat of solutions  $\Delta_{\text{sol}}H$  in cyclopentanone at 298.15 K for PVC, EVA85 and their blends

Sample	EVA85 content (wt%)	Glassy state		Liquid state		$\Delta_{\text{sol}}H$ (J g <sup>-1</sup> )
		$a$ (J g <sup>-1</sup> K <sup>-1</sup> )	$b$ (J g <sup>-1</sup> K <sup>-2</sup> )	$a$ (J g <sup>-1</sup> K <sup>-1</sup> )	$b$ (J g <sup>-1</sup> K <sup>-2</sup> )	
PVC	0	0.088	0.00280	-0.032	0.00410	-28.0
BL05	5.0	0.087	0.00293	0.129	0.00378	-19.8
BL10	10.0	0.091	0.00303	0.135	0.00385	-15.9
BL20	20.0	0.091	0.00315	0.276	0.00357	-12.2
BL50	50.0	0.011	0.00379	0.687	0.00288	-4.8
BL80	80.0	0.055	0.00414	1.013	0.00241	-2.2
BL90	90.0	0.073	0.00420	1.022	0.00248	-0.7
BL95	95.0	0.100	0.00420	1.006	0.00262	-0.2
EVA85	100	0.089	0.00434	1.128	0.00234	-0.5

control was set at 203 K; dry nitrogen was used as purge gas. The instrument was calibrated with high purity standards. The temperature was known at  $\pm 0.1$  °C; the samples (5–8 mg) weighted to  $\pm 0.01$  mg. After a preliminary thermal characterization of the samples, performed in the temperature range between 240 and 480 K at  $20 \text{ K min}^{-1}$ , the following procedure was adopted: the samples were first heated up to 470 K (480 K for PVC) at  $20 \text{ K min}^{-1}$ , then quickly cooled below their glass transition. Successively, the specific heats were obtained at  $5 \text{ K min}^{-1}$  with the method based on three runs: the sample run, the blank run and the standard (sapphire) run. Care was taken to ensure that, for all the three runs, the initial and final isotherm levels were identical. The specific heat of the samples was calculated with a commercial software by Perkin Elmer. The error, estimated from repeated runs, was approximately  $\pm 0.015 \text{ J g}^{-1} \text{ K}^{-1}$ . The glass transition temperature  $T_g$  was taken as the intersection of the extrapolated pre- and post-transition enthalpy data. The error, from repeated scans, was approximately  $\pm 1$  K.

Temperature modulated differential scanning calorimetry (TMDSC) was also performed on some samples by means of the same Perkin Elmer instrument operating in modulated mode (DDSC). This kind of analysis resulted necessary for PVC and some PVC-rich mixtures in order to separate the cold crystallization process that occurs at temperatures slightly higher than the  $T_g$ . The underlying heating rate was set at  $2 \text{ K min}^{-1}$ , the temperature modulation was 1 K and the period 60 s.

### 2.3. Solution heats measurements

The calorimetric apparatus was a Calvet-type Setaram calorimeter (mod. BT 200), modified and improved as previously described [20]. A special cell was constructed for the dissolution of polymers, equipped with a stirrer driven by a stepping motor capable of reproducible rates in the range 10–60 rpm. In a single run from 10 to 100 mg of powder or thin flakes of the sample were introduced into a stainless steel (type 310) cylinder that is an integral part of the stirrer. The cell, whose volume is about  $10 \text{ cm}^3$ , was wholly filled with solvent to minimize the vapour space and sealed by a PTFE cap that allows the external connection with the stirring device and with the cell-opening device. After recording a steady baseline of the calorimetric signal under stirring, the cell is opened by applying a small pressure via a thin rigid steel wire. The working stirring rate was 20 rpm. The fast dissolution in cyclopentanone of the polymers allowed to run experiments lasting at most 45 min. In any case, the complete dissolution of the sample was checked at the end of each run. Experimental heats at 298.15 K were determined from the areas of thermograms, using a proportionality constant determined separately through a standard electric calibration. Calibration of the instrument was periodically performed using the  $1003.1 \text{ } \Omega$  calibration cell supplied by the manufacturer, applying an

electrical current in the range 1–3.2 mA generated by a constant current feeder. Calibration times, never shorter than 300 s, were measured manually with a 0.1 s resolution chronometer. The performance of the apparatus was checked by determining the heats of solution of KCl in water [24], resulting in an overall reproducibility of  $\pm 0.05 \text{ J mol}^{-1}$  and accuracy better than 2%. Each heat of solution value obtained is the average of four separate measurements.

### 3. Results and discussion

Fig. 1 shows the calorimetric curves at  $20 \text{ K min}^{-1}$  of (A) EVA85, (B) PVC and (C) the blend BL05 (5 wt% of EVA85). The first and the second scan, which was obtained after rapid cooling to a temperature below the glass transition, are both reported.

As regards EVA85, the curves have been plotted only up to 340 K because no thermal events were observed at higher temperature. An endothermic signal shift, corresponding to a glass-to-rubber transition, is observed for EVA85 at approximately 273 K, followed by a second endothermic phenomenon of lower intensity. In the second scan, the main event is observed at a slightly higher temperature, whereas the shape of the second process is found changed, corresponding to a typical glass transition event. Bearing in mind that the glass transition temperature of poly(vinyl acetate) is approximately in the range 300–310 K [25], this behaviour can be explained assuming the existence of long sequences of vinyl acetate units, firstly organized in

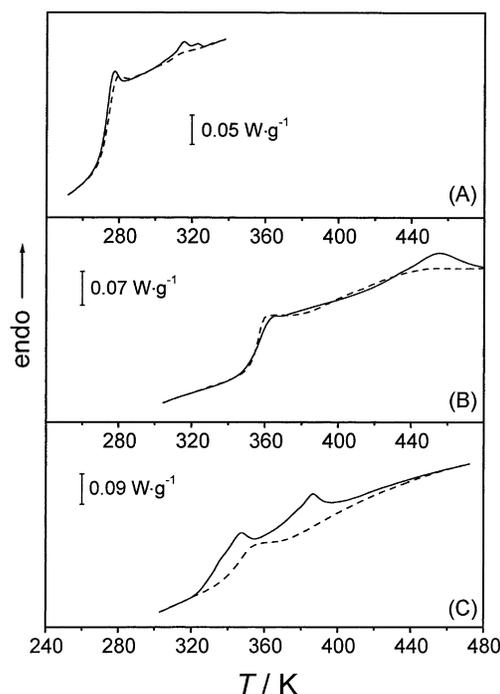


Fig. 1. DSC heating curves ( $20 \text{ K min}^{-1}$ ) of EVA85 (A), PVC (B) and blend BL05 (C): first scan (continuous line), second scan (broken line).

microdomains, which a thermal treatment at high temperature partly destroys (this can account for the main  $T_g$  raising in the second heating scan). The content of poly(vinyl acetate) blocks, remained after the thermal treatment, is approximately equal to 5% of the total EVA85 amount. However, the complex shape of the small thermal event observed in the first scan between 305 and 325 K could be explained assuming also the presence of a little amount of low-melting polyethylene crystalline phase, developed during the storage at room temperature. The fusion of this crystalline phase could merge with the glass transition of poly(vinyl acetate) blocks, may be overlapped by an enthalpy relaxation peak. The presence of a poor and imperfect polyethylene crystalline phase, melting at approximately 320 K, has been reported in EVA copolymer with 70 wt% of vinyl acetate [26]. A very similar behaviour is also shown by the EVA85-rich blends: BL95, BL90 and BL80.

Fig. 1(B) shows the calorimetric curves of the as-received PVC and after rapid cooling to a temperature below the glass transition. The broad melting peak, which is observed in the first scan extending from 400 to 480 K corresponds approximately to 6% of crystallinity, if one assumes as enthalpy of fusion of the fully crystalline PVC the value reported by the ATHAS data bank ( $\Delta H_f^0 = 177 \text{ J g}^{-1}$ ) [27]. Such determination is anyway quite approximate due to uncertainty in a so large baseline drawing. A similar behaviour characterizes also the quenched sample, with the difference that the melting endotherm is broader and smaller. A rough estimate of the enthalpy associated with the transition in this case leads to a crystallinity degree value of about 3%. In addition an exothermic peak, which has been attributed to a cold crystallization process, occurs in the second run at a temperature slightly higher than the glass transition (approximately 380 K). The phenomenon is more evident if the quenched sample is heated at a lower rate (10 or 5  $\text{K min}^{-1}$ ). A similar behaviour is also shown by PVC-rich blends. In order to obtain specific heat data independent of the crystallization event, i.e. without heat crystallization effects, TMDSC measurements were performed on PVC and BL05, BL10 and BL20 blends. The theoretical bases of TMDSC technique have been widely reported elsewhere [28–31]. As regards the cold crystallization process, it can be reminded that this process, occurring at high undercooling, below the melting region, has a strong irreversible character, in the sense that it cannot be reversed within the temperature range of the modulation. Cold crystallization takes place continuously during a TMDSC scan [31] and is observed as a non-reversing phenomenon. In Fig. 2 the specific heat data for quenched PVC by TMDSC and conventional DSC are shown and compared. Whereas  $c_p$  from conventional DSC accounts for the crystallization heat, the specific heat obtained by TMDSC shows a different trend, being the sum of  $c_p$  contributions from amorphous and crystalline phases, without the exothermic effect. A

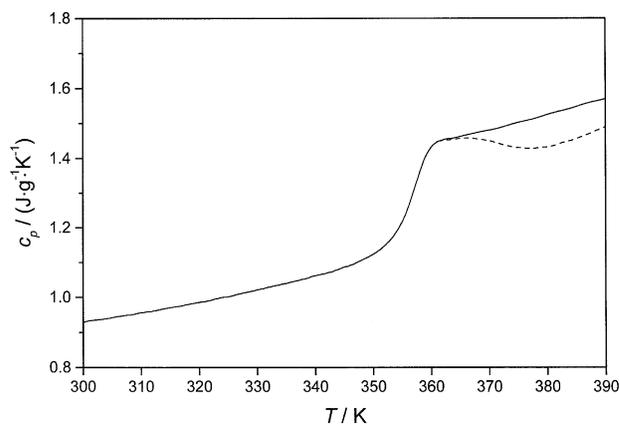


Fig. 2. Specific heat  $c_p$  of quenched PVC as determined by TMDSC (continuous line) and conventional DSC (broken line).

detailed paper on the determination of PVC specific heat by TMDSC is in preparation.

A well-defined melting peak at approximately 390 K, attributed to a separate PVC crystalline phase, is observed in the first scan of the PVC-rich blends BL05, BL10, BL20. An example is shown in Fig. 1(C) as regards the mixture BL05. The prolonged storage at the drying temperature (353 K), which is below the melting point of PVC but around its glass transition, produces a pure PVC crystalline phase, being the free energy of crystallization always considerably larger than that of mixing [32]. After heating up to 470 K, the sharp melting endotherm is no more present, being replaced by the broad fusion typical of pure PVC. A single glass transition is observed and the crystallinity degree, normalized for the PVC content, is approximately 2%. Since a single glass transition was observed for the PVC-rich blends BL05, BL10 and BL20 after heating up to 470 K, this treatment was considered appropriate to destroy the separate PVC crystalline phase, with the exception of a very little amount, and to produce one-phase amorphous systems, as also previously reported for other mixtures between PVC and EVA copolymers with different vinyl-acetate content [4–12].

The specific heat curves for the blends and the two pure components, all obtained after quenching from 470 K, are reported in Fig. 3: the data referring to PVC and the PVC-rich blends (BL05, BL10 and BL20) were obtained by TMDSC, all the others by standard DSC. The  $c_p$  data have been described by the linear relation  $c_p = a + bT$  both below and above the glass transition and the coefficients  $a$  and  $b$  are collected in Table 1. The heats of solution,  $\Delta_{\text{sol}}H$ , of PVC, EVA85 and their blends in cyclopentanone at 298.15 K are listed in Table 1, too.

Being the glass transition temperature of PVC and some blends higher than 298.15 K, it is not possible to obtain heats of solution referring to the thermodynamic equilibrium liquid state. Therefore, in order to get the enthalpy of mixing relative to the hypothetical liquid state ( $\Delta_{\text{mix}}H^l$ ), a correction has to be applied to the values of  $\Delta_{\text{mix}}H$  obtained

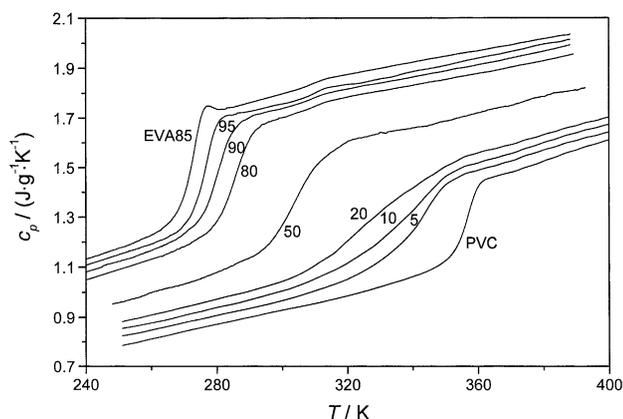


Fig. 3. Specific heats  $c_p$  of quenched EVA85, PVC and their mixtures. EVA85 weight percent is indicated on the curves. PVC and BL05, BL10, BL20 are analyzed by TMDSC, all the others by standard DSC.

by means of the Hess's cycle. Fig. 4 shows schematically the steps through which the correction was performed. The value in the point A is the enthalpy of mixing ( $\Delta_{\text{mix}}H$ ) calculated via Eq. (3) from the  $\Delta_{\text{sol}}H$  experimental data. The enthalpy of mixing at a temperature  $T_B$  higher than the  $T_g$  of PVC (point B) is obtained by integration of Eq. (4), i.e.

$$\Delta_{\text{mix}}H(T_B) = \Delta_{\text{mix}}H(298.15 \text{ K}) + \int_{298.15 \text{ K}}^{T_B > T_{g,\text{PVC}}} \Delta_{\text{mix}}c_p \, dT \quad (6)$$

where  $\Delta_{\text{mix}}c_p$  is the experimental excess specific heat defined in Eq. (5). Finally, the enthalpy of mixing at 298.15 K referring to the hypothetical undercooled liquid state (point C) is given by the following equation

$$\Delta_{\text{mix}}H^1(298.15 \text{ K}) = \Delta_{\text{mix}}H(T_B) + \int_{T_B > T_{g,\text{PVC}}}^{298.15 \text{ K}} \Delta_{\text{mix}}c_p^1 \, dT \quad (7)$$

where  $\Delta_{\text{mix}}c_p^1$  is the experimental excess specific heat in the liquid state:

$$\Delta_{\text{mix}}c_p^1 = c_p^1 - w_1c_{p1}^1 - w_2c_{p2}^1 \quad (8)$$

The values of the experimental enthalpy of mixing ( $\Delta_{\text{mix}}H$ )

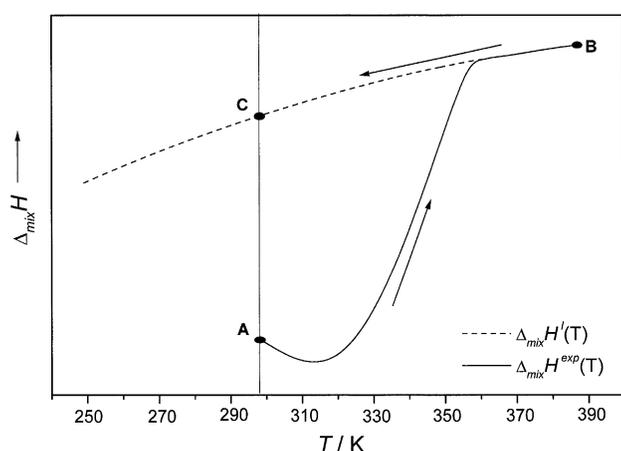


Fig. 4. Schematic plot of the method to obtain the enthalpy of mixing in the hypothetical liquid state (see text).

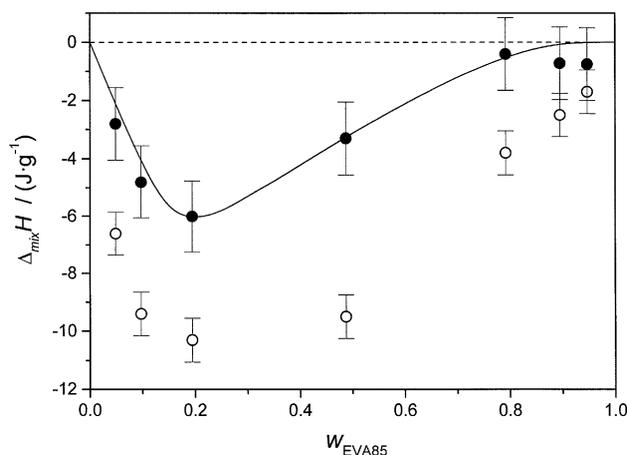


Fig. 5. Experimental enthalpy of mixing  $\Delta_{\text{mix}}H$  (O) and enthalpy of mixing in the hypothetical liquid state  $\Delta_{\text{mix}}H^1$  (●) at 298.15 K as a function of composition. The error bars are also indicated. The continuous line is the enthalpy of mixing  $\Delta_{\text{mix}}H^1$  calculated by means of Eqs. (3) and (13) (see text).

and the enthalpy of mixing relative to the hypothetical liquid state ( $\Delta_{\text{mix}}H^1$ ) at 298.15 K are shown in Fig. 5 as a function of blend composition. Both  $\Delta_{\text{mix}}H$  and  $\Delta_{\text{mix}}H^1$  are found negative for all the mixtures, indicating that specific interactions are involved between the two components. It is worth noting that the correction that can be introduced by normalizing the values of  $\Delta_{\text{mix}}H$  and  $\Delta_{\text{mix}}H^1$  for the effective amorphous phase content, i.e. neglecting the PVC crystalline phase percentage, is much lower than the experimental error.

As regards the nature of the intermolecular interactions active between PVC and the EVA copolymer, both a hydrogen bonding between the tertiary hydrogens of PVC and the carbonyl groups of EVA [4] and a dipole–dipole interaction between C=O and Cl–C [33] groups have been proposed. On the basis of additional studies [34], it is now generally assumed that the association occurs via hydrogen bonding. Further studies about this subject are in progress in our laboratory by using model liquids.

From the inspection of Fig. 5, one can observe that the minimum of both  $\Delta_{\text{mix}}H$  and  $\Delta_{\text{mix}}H^1$  vs concentration curves is found approximately in correspondence of the blend BL20, whose composition is close to the molar ratio of four PVC repeating units per one EVA85 repeating unit. This result is in excellent agreement with other data obtained on PVC/plasticizers systems: it has been found that about four/six PVC repeating units can bind to one polar plasticizer molecule containing carbonyl groups [35].

Fig. 6 shows the composition dependence of the glass transition temperature for the system PVC/EVA85. Also drawn is the glass transition curve predicted by the enthalpic Couchman equation [36]

$$T_g = \frac{w_1 \Delta c_{p1} T_{g1} + w_2 \Delta c_{p2} T_{g2}}{w_1 \Delta c_{p1} + w_2 \Delta c_{p2}} \quad (9)$$

where  $\Delta c_{pi}$ s are the specific heat increments of pure

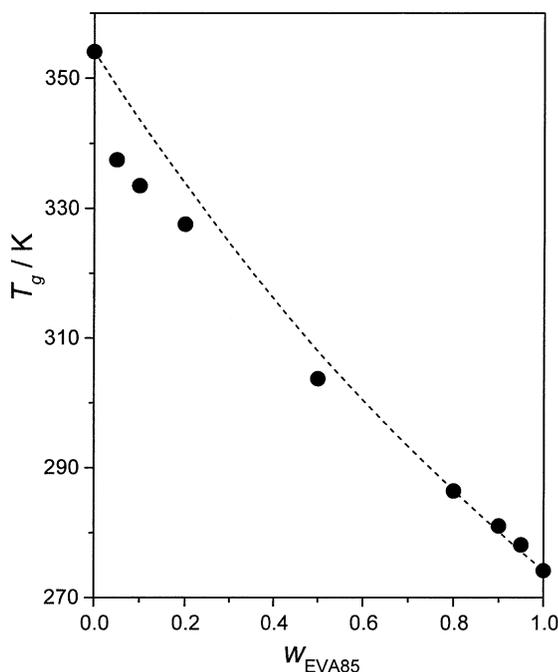


Fig. 6. Experimental  $T_g$  data (•) for PVC/EVA85 mixtures. The broken line is the theoretical curve calculated according to Eq. (9).

components at the respective  $T_{gi}$ s ( $\Delta c_{pi} = c_{pi}^l - c_{pi}^g$ ). This latter equation, which is obtained starting from the enthalpic treatment proposed by Couchman and assuming no temperature dependence of  $\Delta c_{pi}$ , i.e.  $\Delta c_{pi}(T) = \text{constant}$ , is used to predict approximately the glass transition temperature of blends in which specific interactions are absent. In this connection, any difference between the experimental and the calculated glass transition temperature has to be interpreted as due to specific interactions [37]. It has to be added that the parallel entropic equation and the enthalpic and entropic equations that can be derived by introducing the approximation  $\Delta c_{pi}(T) = \text{constant}/T$  produce curves that are not substantially different from that drawn in Fig. 6.

One can observe an asymmetry in the glass transition behaviour as a function of composition: the addition of EVA85 to PVC produces a remarkable lowering of the glass transition temperature. This lowering can be ascribed with confidence to specific interactions between the two components. As a matter of fact, the crystallinity degree of PVC in the PVC-rich blends is very small (see above) and the correction for the amorphous phase composition comes out negligible. Also the presence of separate nanophases of constrained amorphous PVC has to be excluded in PVC-rich blends. A 'rigid amorphous phase' [38] was not found in pure PVC, being the specific heat increment at the glass transition temperature very close to the value reported for the totally amorphous sample [27]. Since the thermal treatment for PVC and the blends was the same, the presence of a hypothetical PVC rigid amorphous phase in the more mobile mixed systems has to be rejected as a

possibility. At the other composition extreme of Fig. 6, a very little raising of  $T_g$  with respect to the Couchman prediction is observed. Evidently, the interaction that develops between PVC and EVA85, since modifies and partly destroys two different intermolecular structures, produces different effects on the physical properties in relation to the matrix that is considered.

In order to better understand how the strength of the interactions varies with the composition, the excess specific heat for the liquid state at 298.15 K has been calculated for all the blends by using the  $a$  and  $b$  parameters of Table 1. The  $\Delta_{\text{mix}}c_p^l$  data are shown in Fig. 7 as a function of composition. Also in this case two opposite behaviours are evidenced. The excess specific heat comes out positive for the PVC-rich blends, the range of positive values extending up to 80 wt% of EVA85, and with a small negative value for the two blends richest in EVA85. For the sake of comparison, the differences between the calculated and the experimental  $T_g$  data are reported, too.

The specific heat is a thermodynamic quantity related to the activation of molecular motions, being function of the degrees of freedom of a system. More mobile systems have higher  $c_p$  values. As a consequence, the excess specific heat can be considered as a measure of the molecular motions for a mixed system in comparison with the weighted average of pure components. A positive  $\Delta_{\text{mix}}c_p^l$  in the PVC-rich blends indicates that the number of degrees of freedom in the mixtures is higher than the weighted average of pure components. It is evident that the strong dipolar interchain interactions in pure PVC are partly destroyed by the presence of the copolymer EVA85 that creates a more mobile polymeric system in comparison with pure PVC. This finding is in agreement with the lowering of  $T_g$  in the mixtures with respect to pure PVC that, as general rule, occurs when the segment mobility and the free volume are enhanced. This is the evidence that EVA copolymer acts as plasticizer for PVC.

The opposite behaviour, which is observed in a very

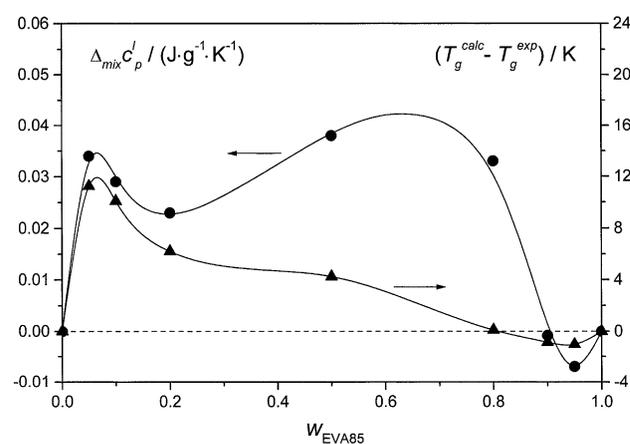


Fig. 7. Excess specific heat for the hypothetical liquid state  $\Delta_{\text{mix}}c_p^l$  at 298.15 K (•) and difference between the calculated and the experimental  $T_g$  (▲) as a function of composition.

narrow region at low contents of PVC, can be explained assuming a more rigid structure in the EVA-rich blends with respect to pure copolymer; this can be attributed to strong dipolar interactions between EVA85 and PVC, whose effect is to reduce the molecular mobility in the mixture. In fact in pure EVA85, the strong dipolar interactions between the ester groups are significantly hindered by the ethylene segments that, acting as diluents, lower and reduce the stabilization of the copolymer in comparison with pure poly(vinyl acetate).

It has been suggested that positive values of  $\Delta_{\text{mix}}c_p$  are an indication of directional specific interactions [39]. In our system, miscibility is assured by strong dipolar interactions, which are active in the whole composition range, as well as in pure PVC and EVA85. For this reason, the negative excess specific heat that is observed in the EVA85-rich composition extreme can be attributed not to non-directional dispersion forces, but to a balance between the specific heat of the mixture and the  $c_p$ s of the components, principally EVA85, whose  $c_p$  clearly dominates in this composition range [40].

Remarkable is the relative minimum observed in the  $\Delta_{\text{mix}}c_p^1$  curve in correspondence to the blend BL20, whose composition, as already pointed out, corresponds to the molar ratio of four PVC repeating units per one EVA85 repeating unit. An enthalpic favoured situation, due to the hypothetical formation of a sort of complex in which one EVA85 repeating unit coordinates four PVC units, can produce a higher stabilization of the blend and, as a consequence, a relative reduction of the degrees of freedom.

The stability of the complex can be defined by the equilibrium constant ( $K_{\text{eq}}$ ) of the following process



with

$$K_{\text{eq}} = \frac{X_{\text{PVC}_n\text{EVA85}}}{X_{\text{EVA85}}^n X_{\text{PVC}}^n} \quad (11)$$

where  $X_i$ s are the molar fractions of the components of each blend, all considered in the liquid state.  $K_{\text{eq}}$  can be written in terms of  $\alpha$ , the fraction of the initial moles of EVA85 involved in the complex, and  $R$ , the initial molar ratio between EVA85 and PVC ( $R = m_{\text{EVA85}}^0/m_{\text{PVC}}^0$ ):

$$K_{\text{eq}} = \frac{\alpha}{1-\alpha} \left[ \frac{1+R(1-n\alpha)}{1-n\alpha R} \right]^n \quad (12)$$

The heat of solution of the blend ( $\Delta_{\text{sol}}H_{\text{blend}}^1$ ) can be calculated according to the following relationship:

$$\begin{aligned} \Delta_{\text{sol}}H_{\text{blend}}^1 &= m_{\text{PVC}}^0(1-n\alpha R)\Delta_{\text{sol}}H_{\text{PVC}}^1 + \\ & m_{\text{EVA85}}^0(1-\alpha)\Delta_{\text{sol}}H_{\text{EVA85}}^1 + \alpha m_{\text{EVA85}}^0\Delta_{\text{sol}}H_{\text{PVC}_n\text{EVA85}}^1 \end{aligned} \quad (13)$$

Assuming  $n = 4$ , as suggested from the  $\Delta_{\text{mix}}H^1$  data, and  $\Delta_{\text{sol}}H_{\text{PVC}_n\text{EVA85}}^1 \approx 0$ , the best fit between the experimental

and the calculated solution heats was obtained for all the blends taking  $K_{\text{eq}} = 10$ . This value is in very good agreement with the equilibrium constant ( $K_{\text{eq}} = 16$ ) reported in Ref. [41], which was calculated from molecular modelling. The enthalpy of mixing  $\Delta_{\text{mix}}H^1$ , calculated by means of Eqs. (3) and (13), is drawn in Fig. 5 as continuous line. The supposition that the heat of solution of the hypothetical complex is zero can be reasonably justified by imaging the dissolution of the complex as a two-step process: the first step is the breaking of the complex in the two components and the second one is the dissolution of the polymers. Being  $\Delta_{\text{sol}}H_{\text{EVA}}^1 \approx 0$  (Table 1) and assuming similar enthalpy change for the dissolution of PVC in cyclopentanone and in EVA85, the result is that  $\Delta_{\text{sol}}H_{\text{PVC}_n\text{EVA85}}^1 \approx 0$ . The excellent agreement between the calculated and the experimental data showed in Fig. 5 confirms the reasonableness of the aforesaid assumptions.

By using the excess specific heat  $\Delta_{\text{mix}}c_p^1(T)$ , the enthalpy of mixing  $\Delta_{\text{mix}}H^1$  was calculated for all the blends at temperatures different from 298.15 K according to Eq. (4), as shown in Fig. 8, where the data are connected by a Redlich–Kister empirical polynomial [42], frequently used in describing excess thermodynamic properties

$$\Delta_{\text{mix}}H^1 = w_1w_2 \frac{\sum_{k=0}^{k=2} A_k(w_1 - w_2)^k}{1 + A_3(w_1 - w_2)} \quad (14)$$

with  $A_k$  and  $A_3$  as fitting parameters. The absolute value of  $\Delta_{\text{mix}}H^1$  decreases as the temperature increases and the enthalpy of mixing becomes positive at temperatures higher than 320 K in a narrow interval of composition.

As regards the free energy of mixing of PVC/EVA85 blends, we can presume that  $\Delta_{\text{mix}}G^1$  increases as temperature increases, since a lower critical solution temperature has been reported for other mixtures of PVC with EVA copolymers having different vinyl acetate content [1,8,10].

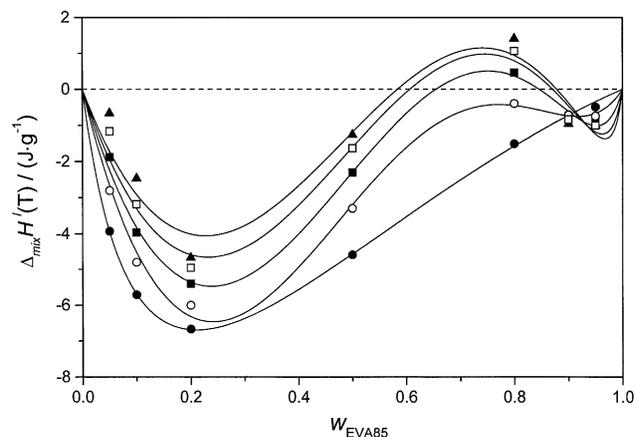


Fig. 8. Enthalpy of mixing in the hypothetical liquid state  $\Delta_{\text{mix}}H^1$  as a function of composition at 268.15 K (●), 298.15 K (○), 328.15 K (■), 358.15 K (□) and 388.15 K (▲). The data are connected by a Redlich–Kister type equation.

Moreover, taking into account that the temperature dependence of  $\Delta_{\text{mix}}G^l$  is given by

$$\left(\frac{\partial \Delta_{\text{mix}}G^l}{\partial T}\right)_{P,w_i} = -\Delta_{\text{mix}}S^l \quad (15)$$

negative values of the entropy of mixing  $\Delta_{\text{mix}}S^l$  are expected for this blend. A negative entropy of mixing is in agreement with the existence of strong directional interactions between the polar groups of the two polymers and compatible also with the hypothesis of a sort of complex between PVC and EVA85 and therefore with a more organized structure in the mixed system in comparison with pure components.

#### 4. Conclusions

The thermodynamics of mixing for the system PVC/EVA85 has been studied in order to obtain quantitative informations about the enthalpy of mixing. Particular attention has also been paid to the specific heat, a useful tool in order to gain informations about the interactions in a polymer mixture.

The thermal analysis on quenched samples showed a single glass transition for all the compositions, indicating one miscible phase that is stable up to 470 K. The  $T_g$ -composition curve exhibits a strong negative deviation from the behaviour predicted by the Couchman equation at high PVC contents and a very little positive deviation at high EVA85 contents.

The enthalpy of mixing is negative in the whole composition range. Very interesting is the  $\Delta_{\text{mix}}H$  vs composition curve, which presents a relative minimum in correspondence to the ratio 4:1 in the molar composition of the PVC/EVA85 system. A very simple model that assumes the formation of a stoichiometric complex between EVA85 and PVC units gives a surprising agreement with experimental  $\Delta_{\text{mix}}H^l$  data.

The behaviours of the excess specific heat as a function of composition parallels the  $T_g$  deviation of the Couchman prediction from the experimental data. The values are positive for the PVC-rich blends up to 80 wt% of EVA85, indicating that the mixtures are characterized by a higher molecular mobility with respect to pure components. On the contrary, negative values of  $\Delta_{\text{mix}}c_p^l$  and  $(T_g^{\text{calc}} - T_g^{\text{exp}})$  at very low content of PVC denote a more rigid structure in the blends in comparison with pure EVA85.

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