

CHARACTERISTICS OF COMPATIBLE BINARY POLYMER BLENDS DEDUCED FROM DSC THERMOGRAMS. 1. A STUDY ON POLYVINYL ALCOHOL – POLYVINYL PYRROLIDONE MIXTURES

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Effects of interchain interactions on the thermal processes of glass transition, melting and crystallization were evidenced for the mixture of polyvinyl alcohol and polyvinyl pyrrolidone. The experimental data were analyzed by using theoretical calculations to obtain information about the relative strength of the homo and hetero-interchain interactions. A deduction is that the known calculation expressions for the thermal parameters and effects are rather specific and, therefore, both the theory and the measurement accuracy should be still improved. The DSC method was exhaustively used.

INTRODUCTION

The miscibility and interactions between components are the most important aspects for defining polymer blends.¹ Interchain interactions have been much investigated as strength and influence on the thermal behavior.

The present article refers to the system of polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP). An initial study of this polymer mixture is due to Hefford,² who has analyzed miscibility aspects. Further articles show the compatibility of PVA with other natural polymers^{3,4} as well as the molecular weight influence on the crystallization of PVA in presence of PVP,⁵ study of miscibility in dilute solution and solid.⁶ Also, there are known several empirical equations intended to evaluate the effects, which the interchain interactions generally exercise on the processes of glass transitions,⁷ and melting⁸ in compatible polymer mixtures.

As known, atactic PVA is a semicrystalline polymer the glass transition temperature and melting point of which are about 70°C and 230°C, respectively. On the other side, PVP is a highly amorphous polymer with the glass transition at about 160°C. PVP thermally decomposes before reaching its molten state. The strongest homochain

interactions are due to the hydrogen bonds for PVA and the dipole-dipole attraction forces for PVP.

It is expected that the dominant heterochain interactions are the hydrogen bonds between the hydroxyl groups of PVA and the carbonyl groups of PVP. It will be shown in this paper that the order of interchain interaction strength in solid-state PVA-PVP blends is PVA-PVA < PVA-PVP < PVP-PVP. This conclusion is based on DSC observations carried out for the processes of glass transition, melting and crystallization.

RESULTS AND DISCUSSION

The samples analyzed in this study are given as chemical composition and codification in Table 1.

Glass transition process

One observes in Fig. 1 that each sample shows an only glass transition temperature (T_g), and the T_g values lie between 343 K (T_g of PVA) and 430 K (T_g of PVP). Besides, all experimental points are situated under the straight line that goes through the points corresponding to the two pure polymers (Fig. 2).

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Table 1

Sample notation and data of DSC measurement

Sample code	a	b	c	d	e	f	g	h	i	j	k
w = [PVP]	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
T _g (K)	343	347	353	358	350	368	378	396	404	417	430
T _m (K)	500	484	472	467	464	462	-	-	-	-	-
T _c (K)	470	468	463	459	443	440	-	-	-	-	-

w is the molar fraction of PVP in the sample.

Along the time, several equations have been established for the homogeneous binary blends. Two of them, the Gordon-Taylor¹³ (1) and Kwei⁷ (2) equations, have been much used. The significance of variables and parameters of these equations are as following: T_{g1} and T_{g2} are the glass transition temperatures of the polymers P1 and P2 which constitute the mixture, w is the weight

$$T_g = [T_{g1}(1-w) + kT_{g2}w] / (1-w + kw) \quad (1)$$

$$T_g = [T_{g1}(1-w) + kT_{g2}w] / (1-w + kw) + qw(1-w) \quad (2)$$

Three types of T_g = T_g(w) dependences can be derived from the equation 1: the case with k = 1, when the plot T_g vs w is the straight line that joins the points (0, T_{g1}) and (1, T_{g2}), the case with k > 1, when the plots are placed above the straight line for k=1, and the case with k < 1, when the plots are situated under the plot for k = 1. This means that, relative to the pure additive value T_g = (1-w)T_{g1} + wT_{g2} which corresponds to k = 1, the values corresponding to the same chemical composition are higher for k > 1 and lower for k < 1. By using the reliable supposition that the stronger interchain interaction the higher T_g values, one can state that the relative strength of the interaction between the two polymers of a binary blend, P₁ and P₂, is correlated with the values k as follows: P₁...P₁ ≤ P₁...P₂ ≅ P₂...P₂ for k = 1, P₁...P₁ < P₂...P₂ < P₁...P₂ for k > 1, and P₁...P₁ < P₁...P₂ < P₂...P₂ for k < 1. It results that the relative strength of interchain interactions could be evaluated by means of the deviation of T_g vs w plots from the straight line for k = 1.

Fig. 2 shows the experimental points (w, T_g) determined for the PVA-PVP blend. Also, there are drawn the plots of equation 1 for k = 1 and k = 0.479. The last value k corresponds to the best fitting with the experimental values, and indicates P₁...P₁ < P₁...P₂ < P₂...P₂, that can be explained by the following inequalities between the strengths of

fraction of the polymer P2, while k and q are empiric parameters the values of which must be established by seeking for an optimum fitting between the experimental and calculated T_g values. It is supposed that T_{g1} < T_{g2}, what is equivalent to the assumption that the interactions between the chains P₁ are weaker than those between the chains P₂, i.e. P₁...P₁ < P₂...P₂.

interchain interactions: P₁...P₁ hydrogen bonds < P₁...P₂ hydrogen bonds < P₂...P₂ dipole-dipole interactions (Figure 3). These inequalities are real ones because the oxygen atom is more acid in a carbonyl group than in a hydroxyl group, and the polarity of N-C=O groups is greater than that of O-H groups.

Nevertheless, the parameter k has not got a clear mechanistic meaning. What may be affirmed is that, apparently, the fraction of the more rigid phase P₂ decreases in the favor of the softer phase P₁ by a k/[1-(1-k)w] factor when k < 1, and conversely when k > 1. To improve this aspect, Kwei has introduced a second parameter q that, physically, is a temperature parameter. We think that the Kwei's equation 2 should be usually applied with k = 1 for two reasons: (i) the parameter k has not a clear physical meaning, and (ii) the solution of an optimization problem is more questionable for the case with two variables than for that with one variable. The term qw(1-w) is considered as a measure of the heterochain interactions. Two plots of equation 2 are given in Fig. 2: one corresponding to k = 1 and q = -335.15 K, where the fitting between the experimental and calculated values was obtained by considering q as only variable, and the other the values k = 1.71 and q = 383 K of which were determined by solving a problem of minimum with two variables.

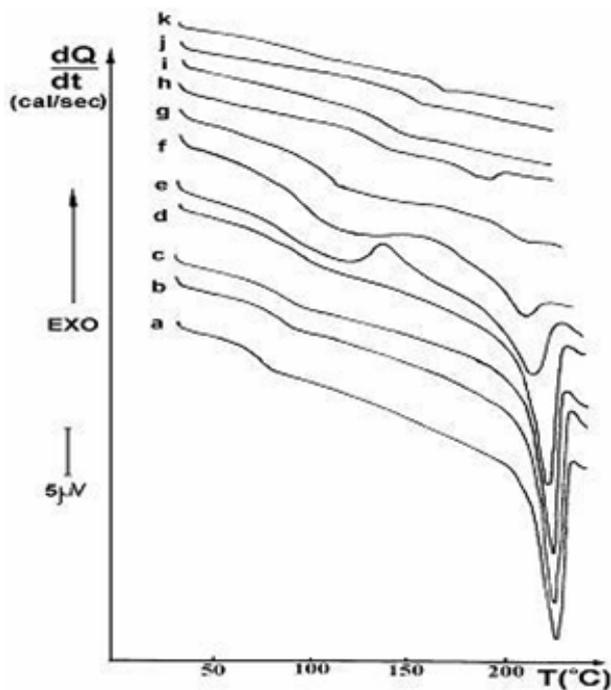


Fig. 1 – DSC thermograms recorded during the second heating, after a sample quench from 250 °C.

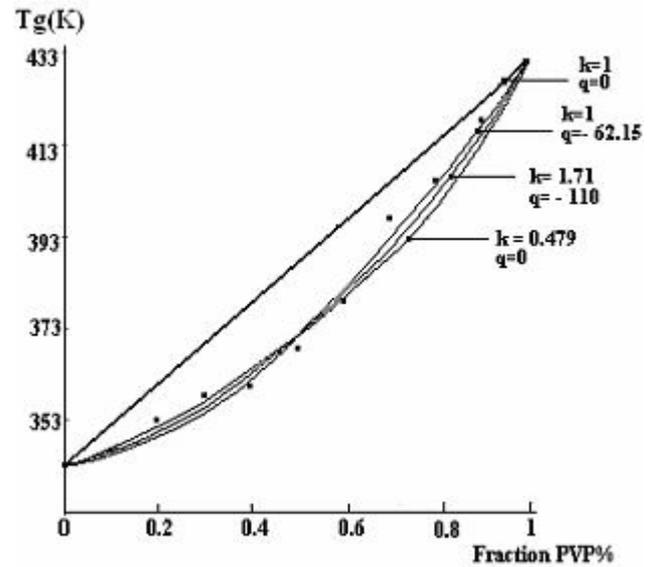


Fig. 2 – T_g vs w plots which result with the experimental data in Table 1 and equations 1 and 2.

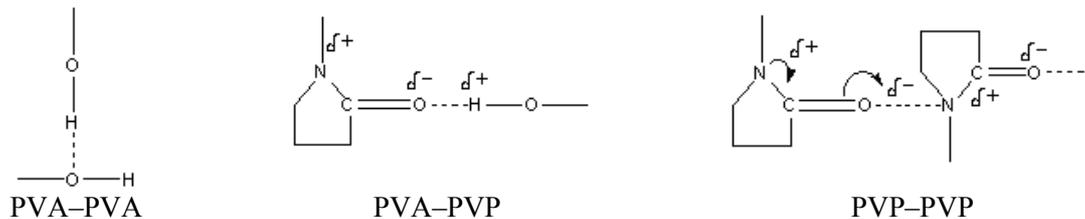


Fig. 3 – The most favorable interchain interactions in a PVA–PVP system.

A comment of the three curves in Fig. 2 is necessary. A first observation is that the differences between them are smaller than the experimental errors. Therefore, one results that the theoretical modeling must be performed on experimental data obtained with sufficiently high accuracy. And such a prerequisite is not easily accomplished for T_g measurements carried out by both the DSC technique and any other method. Nevertheless, the both equations, Gordon-Taylor¹³ and Kwei,⁷ correctly reproduce the relative strengths of the three of interchain interactions, P₁...P₁, P₁...P₂ and P₂...P₂.

Melting process

As PVP is a completely amorphous polymer and PVA is a semicrystalline one, the melting peak of DSC thermograms only arise from PVA. One observes on Fig. 1 that (i) the melting process is

visible when the content of PVA is higher than about 30 %, and (ii) the melting point decreases when the content of PVP increases. There are several equations which describe such a melting point depression, all of them being derived from the Flory-Huggins equation (3),^{9,10} which has been developed for systems composed of a polymer and a low molecular diluent. Subsequently, Scott¹¹ has modified this equation to be applicable to compatible semicrystalline polymer – amorphous polymer mixtures (equation 4).

$$1/T_m - 1/T_{m0} = (R/\Delta H_c)(V_c/V_d)(w - \chi w^2) \quad (3)$$

$$1/T_m - 1/T_{m0} = -(R/\Delta H_c)(V_c/V_d)\chi w^2 \quad (4)$$

The parameters and variables in the two equations are the followings: T_{m0} and T_m are the melting points of the crystalline polymer (PVA in this case) in pure state and in a binary mixture respectively, R is the universal gas constant, ΔH_c is

the heat of fusion per mole of crystalline polymer units, V_c is the molar volume of the repeating unit of the crystalline polymer, V_d is the molar volume of a low molecular diluent, V_a is the molar volume of the repeating unit of the amorphous polymer (PVP in the present paper), w is the volume fraction of the diluent in equation 3 and of the amorphous polymer in equation 4, and χ is the interaction parameter of the pair of components.

Unlike the case of polymer-diluent systems, the interaction parameter χ plays a decisive role on the

$$\Delta T_m / (T_m w) = (R/\Delta H_c)(V_c/V_a)T_{m0} - (R/\Delta H_c)(V_c/V_a)T_{m0}\chi w \quad (5)$$

The T_m values determined from the DSC thermograms are given in Table 1. When these data were plotted according to equation 5, a straight line was indeed obtained (Fig. 4). By using the initial ordinate and slope of this straight line and the parameter values known for the two polymers considered in this study, $V_a = 91.9 \text{ cm}^3/\text{mol}$ and $\rho = 1.25 \text{ g/cm}^3$ for PVP, and $V_c = 35 \text{ cm}^3/\text{mol}$ and $\rho_c = 1.35 \text{ g/cm}^3$ for PVA,¹⁴ the following parameter values were obtained:

$$\Delta H_c = 4.3 \text{ kJ/mol} \quad \text{and} \quad \chi = 1.14 \quad (6)$$

It is to be mentioned that the value 4.3 kJ/mol deduced for ΔH_c is acceptably different from the value 6.9 kJ/mol found for pure PVA.¹⁴

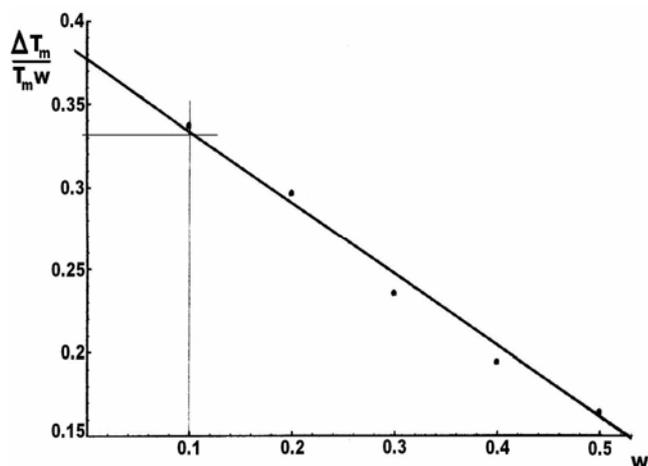


Fig. 4 – Plot results from equation (5); interaction parameter χ result from slope calculation.

melting behavior of the crystalline polymer-amorphous polymer systems.⁷ What is strange with equation 4 is the fact that the interaction parameter χ should be negative to explain the commonly observed depression of melting point ($T_m < T_{m0}$). For this reason, but not only, we consider that the equation 3 is more proper than equation 4 to be used for the case of polymer-polymer mixtures. If the equation 3 is rewritten under the form 5, where $\Delta T_m = T_{m0} - T_m$, the plot of $\Delta T_m / (T_m w)$ vs w should be a straight line.

Nevertheless, it is known that the temperature parameters in the equations 3-5 are in fact equilibrium melting points, *i.e.*, the melting points of infinitely thick crystals. Such parameters are extremely difficult to be determined and, consequently, their replacement with the temperatures where the DSC melting peaks are highest is a rather rough approximation. However the values of ΔH_c and χ determined as before for the system PVA-PVP must be well appreciated because they are rather plausible and the DSC technique is almost the only method that can be applied for polymer mixtures in solid state.

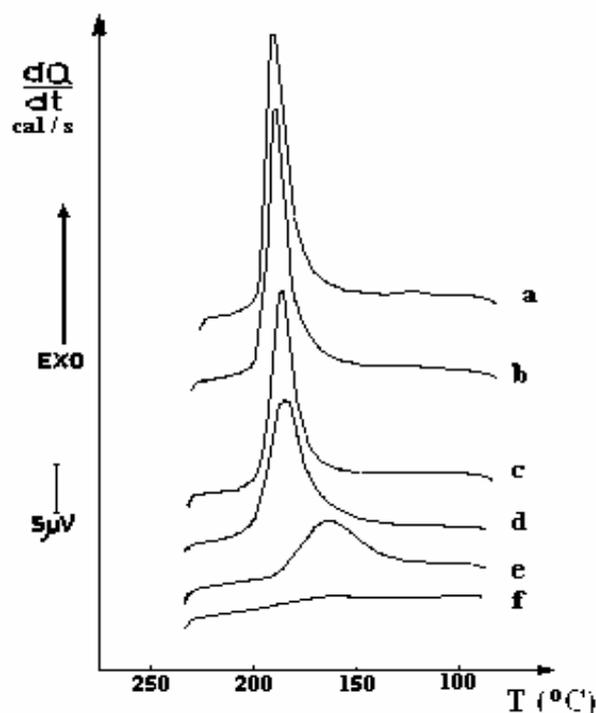


Fig. 5 – DSC cooling thermograms at a 10 °C/min rate.

On the other side, the sizes of crystallites and the crystalline fraction are dependent on the blend composition. So, an improved expression of T_m for binary polymer blends could be tried in two ways. One of them would start with the finding of an expression of dependence between the crystallite thickness L_c and the blend composition. Then the Thompson–Gibbs equation.¹²

$$T_m = T_{m0} [1 - 2\sigma / \Delta H_c \rho_c L_c (w)] \quad (7)$$

where σ is the crystallite specific fold surface free energy, and ρ_c is the crystal density, should be used. One other way would be developed by using the Flory-Huggins^{9,10} or Scott¹¹ equations, where the amorphous fraction w includes both the amorphous polymer and the amorphous fraction of the semi-crystalline polymer.

Crystallization process

The crystallization of PVA is observable in DSC cooling scans when the amount of PVP is lower than about 50% (Fig. 5). Two observations can be made when the fraction of amorphous polymer (PVP) increases: (i) the crystallization peak shifts to lower temperatures, and (ii) the peak width increases while the ratio of the peak area to sample mass seems to be constant. These characteristics can be explained by the assumption that the crystallizable polymer (PVA, here) forms crystals the sizes of which are the smaller so as the content of amorphous polymer increases. Such a situation seems to be contrary to that of crystallization from solution. However, it is interesting to study the crystallization in a mixture where the amorphous polymer has T_g lower than that of the crystallizable polymer.

EXPERIMENTAL

PVA from Moviol, with 98% hydrolyzation percentage and a viscosity index of 90 for a 4 % aqueous solution at 20°C, and PVP from Merck, with $M_w = 25000$, were used as received.

The samples were obtained under film form as follows. The polymers were separately dissolved in distilled water at reflux, for about 2 hours to obtain solutions of 2 %. The two solutions were mixed in desired PVP/PVA ratios, from 10/90

to 90/10, and stirred then for 2 hours at 60°C. By casting the mixed solutions on glass plates and drying at room temperature for 4 days, we obtained films of 0.10 - 0.15 mm.

The DSC thermograms were recorded in the temperature range from 20 to 230°C with a Mettler DSC 12E differential scanning calorimeter at a heating rate of 10°C/min. The samples were pieces of film of 7-8 mg weight, which were closed in aluminum pans. The calorimeter cell was purged with dry nitrogen at 2 l/h. The scales of temperature and enthalpy were calibrated with high purity indium. The T_g values were determined from the second heating cycle curves as the midpoint of discontinuity in heat flow, $\Delta C_p/2$.

CONCLUSIONS

Contrary to expectations, the thermal processes in binary blends of miscible polymer still offer interesting subjects of study. It is clear that the explanation and modeling of the glass transition are rather far from satisfactory solutions. On the other hand, the DSC observation is one of the few methods that give information about the polymer-polymer interactions in solid state. The melting and crystallization processes do not happen in the presence of an amorphous polymer like in a liquid solution. For this reason, new experimental and theoretical studies are much required.

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