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Study of the miscibility and thermodynamics of cellulose diacetate–poly(vinyl pyrrolidone) blends

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The miscibility of blends of cellulose diacetate (CDA) and poly(vinyl pyrrolidone) (PVP) was extensively studied by means of differential thermal analysis and dynamic mechanical thermal analysis, tensile test, measuring viscosity of diluted and concentrated solutions of blends in acetone–ethanol mixture and morphological observations. A single glass transition temperature is observed, which is intermediate between the glass transition temperatures associated with each component and depends on composition. A synergism in mechanical properties of blends was found. The absolute viscosity and the intrinsic viscosity of solutions of blends are much higher than the weight average values of solutions of CDA and PVP. Optically clear and thermodynamically stable films were formed in the composition range of CDA/PVP = 100/0 to 50/50 w/w. Fourier transform infrared was used to investigate the nature of CDA–PVP interaction. Hydrogen bonds were formed between hydroxyl groups of CDA and carbonyl groups of PVP. Heats of solutions of CDA/PVP blends and their mechanical mixtures were measured by using a calorimeter. Mixing enthalpy obtained with Hess's law approach was used to quantify interaction parameters of this blending system. It was found that mixing enthalpies and interaction parameters were negative and composition dependent. © 1997 Elsevier Science Ltd.

(Keywords: miscibility; interaction parameter; cellulose diacetate)

INTRODUCTION

Owing to the combinatorial entropy being very small for a polymer couple their miscibility in most cases is the result of specific interactions present between different molecular chains. Furthermore, a negative enthalpy which brings a negative Gibbs free energy can be expected[1]. Specific interactions can be classified as dipole–dipole, hydrogen-bonding, ion–ion, acid–base and donor–acceptor interactions. Among them the hydrogen-bonding is the most popular. Cellulose diacetate (CDA) and poly(vinyl pyrrolidone) (PVP) are a possible miscible couple. The reason is that hydroxyl groups on CDA molecular chains can form hydrogen-bonding with carbonyl groups on PVP molecular chains when their adjacent distance is near enough.

However, to our knowledge no papers have been published on the miscibility of this couple in spite of several research groups having worked on blends of cellulose derivatives with PVP mainly with the aim of preparing membranes. Kozakiewicz *et al.*[2] dissolved CDA in N-vinyl-pyrrolidone monomer and conducted a free radical polymerization to prepare molecular composites. Phase separated films were obtained. Kurokawa[3] dissolved cellulose acetate phthalate and

PVP (1/1 mole ratio) in DMF and cast the solution on glass plates. The films obtained were used for reverse osmosis rejection of organic solutions. Shuey[4] fabricated haemodialysis membranes by blending CDA and PVP to give a membrane having insulin and albumin permeabilities of 83 and 0.6%, respectively. Schultz and his group[5] adopted CDA–PVP blends as reverse osmosis membranes for desalination.

In this paper the detailed characterizations of the miscibility of CDA–PVP binary blends were carried out by means of differential scanning calorimetry (d.s.c.), dynamic mechanical thermal analysis (d.m.t.a.), tensile tests, viscometry, optic microscopy, etc. Fourier transform infrared (*FT*i.r.) was used to investigate the nature of any specific interaction. As is well known, evaluation of the heat of mixing (or enthalpy of mixing), ΔH_{mix}, is of prime relevance to understanding polymer miscibilities. Therefore, ΔH_{mix} parameters were measured by determination of heats of solutions of blended and non-blended CDA and PVP and estimated with a Hess's law approach[6,7]. The dependence of the miscibility on blending compositions was quantified with the absolute values of negative enthalpy of mixing or the thermodynamic interaction parameters χ_{12}. Here, due to the glass transition temperatures of CDA and PVP being 182°C and 126°C respectively, it is quite difficult to use the equation-of-state theory developed by Flory *et al.*[8–11]

to evaluate the χ_{12} parameters. A simpler expression for the free energy of mixing based on Flory–Huggins treatment[1,12] was adopted to evaluate the χ_{12} parameters:

$$\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}} \tag{1}$$

$$\Delta H_{\mathrm{mix}} = (v_1 + v_2)[B - T(\partial B/\partial T)]\phi_1\phi_2 \tag{2}$$

$$\Delta S_{\mathrm{mix}} = -(v_1 + v_2)(\partial B/\partial T)\phi_1\phi_2 \tag{3}$$

$$BV/RT = \chi_{12} \tag{4}$$

where ΔG_{mix}, ΔH_{mix} and ΔS_{mix} are the free energy of mixing, enthalpy of mixing and entropy of mixing, respectively. v_i and ϕ_i are the volume and the volume fraction of component i. V is the molar volume of the repeating unit of polymers. R is the gas constant and T is the Kelvin temperature.

EXPERIMENTAL

Materials and preparation of blends

Cellulose diacetate was obtained from Novaceta Co. of Italy. Its acetyl content is 40.5% and the substitution degree, DS, is 2.5. The raw material was fractionated by using a fractional precipitation method with acetone as the solvent and ethanol as the precipitant. The fraction which has a weight average molecular weight ($\bar{M}_w$) of 10.5×10^4 and molecular weight distribution ($\bar{M}_w/\bar{M}_n$) of 1.52 was adopted in this work.

Poly(vinyl pyrrolidone) was purchased from SERVA. The molecular parameters characterized by g.p.c. are: $\bar{M}_w = 7.4 \times 10^3$, $\bar{M}_n = 4.9 \times 10^3$ and $\bar{M}_w/\bar{M}_n = 1.51$.

CDA/PVP blends were prepared by using solution casting method with acetone–ethanol mixture (8/1, volume ratio) as the common solvent. Concentrations of CDA/PVP were about 5–6% w/v. Solutions were cast on glass plates and then quickly transferred to an oven with forced circulation air at 50–55°C until dry. Films were finally dried *in vacuo* for 48 h and stored in a vacuum desiccator.

Techniques

The optical clarity of CDA/PVP films were checked by visual examination and by using optical microscopy, Reichert Zetopan. Thermal stability and possible phase separation were investigated with the optical microscope equipped with a Mettler FP52 hot stage.

Glass transition temperatures (T_g) of CDA/PVP blends were evaluated by using d.s.c. and d.m.t.a. D.s.c. tests were carried out in a Perkin Elmer DSC-7 differential scanning calorimeter calibrated with indium and lead standards. The heating and cooling rates were 10 and -20 K min^{-1}, respectively. The weight of samples was about 20 mg. In order to avoid the influence of water absorbed and possible solvents entrapped into films, two heating runs were performed for each sample in the range of temperature 300–500 K. Thermograms of the second runs were used to take T_g values. Reproducible T_g for each sample was obtained by using the midpoint criterion[13]. D.m.t.a. tests were performed by means of a dynamic mechanical thermal analysis apparatus, Polymer Laboratories (UK). The vibration frequency, in tension, was 3 Hz and the heating rate of 3 K min^{-1} was maintained through the temperature range of 373–523 K. The position of maximum of the tan δ peak was taken as the T_g of a specimen.
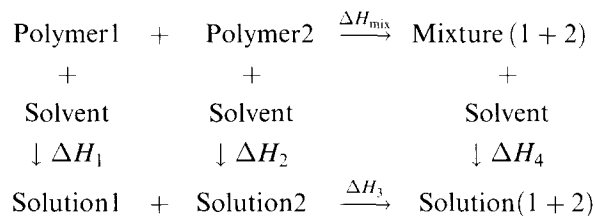
Dumb-bell specimens (gauge length 28 mm) were cut from the as-cast films. Tensile tests were performed at room temperature under dry nitrogen medium by using an Instron test machine, Model 1121. The cross-head speed was 10 mm min^{-1}. Before testing, specimens were kept in a vacuum oven at least for 24 h in 60°C. Young modulus E, tensile strength δ_b and elongation at break ϵ were calculated from stress–strain curves.

Absolute viscosities of solutions of CDA/PVP blends were measured at 303 K with a Brookfield Digital Viscometer. The CDA concentration was fixed at 5.6 g/100 ml solvent. The concentration of PVP was varied and dependent upon the CDA/PVP ratio. A mixture of acetone and ethanol with the volume ratio of 8/1 was taken as the common solvent. Intrinsic viscosities of CDA in solutions of PVP were determined with a Schott–Gerate Automatic Viscometer. A mixture of acetone and ethanol with volume ratio of 8/1 was used as the solvent of PVP. Concentrations of PVP are 0, 0.3, 0.8, 1.6 and 3.4 g/100 ml, respectively.

Infrared spectra of thin films of CDA/PVP binary blends were taken by means of a Nicolet MX-1 *FT* i.r. spectrometer. Seventy-two scans of 2 cm^{-1} resolution were signal-averaged and stored on a magnetic disc system. The accuracy of the frequency of the apparatus was 0.2 cm^{-1}. To remove the solvent completely and avoid water contamination CDA/PVP films were kept in a vacuum oven at 80°C for 48 h and then stored in a vacuum desiccator until used.

Heat of mixing measurements

Owing to the very slow interdiffusion of two polymers and to the small heat effect, it is very difficult to measure the heat of mixing for a polymer blending system. A more convenient approach is to follow an indirect route according to the following thermodynamic cycle based on Hess's law[6,7]:

Polymer1 $+$ Polymer2 $\xrightarrow{\Delta H_{\mathrm{mix}}}$ Mixture $(1+2)$

$+$ $+$ $+$

Solvent   Solvent   Solvent

$\downarrow \Delta H_1$ $\downarrow \Delta H_2$ $\downarrow \Delta H_4$

Solution1 $+$ Solution2 $\xrightarrow{\Delta H_3}$ Solution$(1+2)$

From the above cycle, ΔH_{mix} is calculated from

$$\Delta H_{\mathrm{mix}} = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 \tag{5}$$

Measurements of ΔH_1, ΔH_2, ΔH_3 and ΔH_4 were carried out by means of a Setaram C80D calorimeter using the mixture of acetone and ethanol with the volume ratio of 8/1 as the common solvent. Prior to tests all samples were heated to 140°C, kept at this temperature for 10 min and then cooled to room temperature by means of d.s.c. Mettler TA-3000 System. Therefore all samples had the same thermal history. A reversal mixing equipment was adopted to improve the dissolution speed in this test. According to the recommended procedure, a sample was placed in the lower container and the solvent in the upper one of the measuring cell. A mercury seal and a lip were used to separate the two containers. And the same quantities of the solvent and mercury were filled in the reference vessel. The mass of samples and the volume of solvent were established to obtain final concentrations of less than 0.2% w/v. A temperature of 24.5°C was used through all the experiments.

Repeated tests under the same conditions indicated that heats of solution measured were affected by an error of less than 5%. The reported heats of solution were calculated from the average of at least four measurements for the same sample.

Due to the measuring temperature for heats of solution being much lower than the glass transition temperatures of two components and their blends (126–182°C), values of heats of mixing of CDA/PVP blends obtained at 24.5°C should be corrected to the related values of liquid states assumed. And then equations (2) and (4) could be used to calculate interaction parameters of CDA/PVP blends. In this work Petrie–Marshall theory[14] was adopted for correction and the following procedures were adopted: curves of specific heats of CDA, PVP and their blends both in their glass states and liquid states were obtained by using d.s.c., Mettler TA-3000 System with heat scanning rate of 10°C min^{-1}. Curves of specific heats at assumed liquid states were obtained by extrapolating the curves of specific heats in the real liquid states to the related glass states. Excess glass enthalpies ($\Delta H'_{mix}$) of samples were calculated by using

$$\Delta H'_{mix} = \int_{T_g}^{24.5} w_1 [C_p^l(CDA) - C_p^g(CDA)] \, dT$$
$$+ \int_{T_g}^{24.5} w_2 [C_p^l(PVP) - C_p^g(PVP)] \, dT$$
$$- \int_{T_g}^{24.5} [C_p^l(blend) - C_p^g(blend)] \, dT \quad (6)$$

where C_p^l is the specific heat in the hypothetical liquid state, C_p^g is the specific heat in the glass state, w_i is the weight fraction of component i and T is temperature. Heats of mixing of CDA/PVP blends corresponding to their hypothetical liquid state at 24.5°C were defined as the differences between values of heats of mixing measured by means of the calorimeter and the excess glass enthalpies, $\Delta H'_{mix}$, obtained from equation (6).

RESULTS AND DISCUSSION

Optical clear films

Transparency is usually used as the first proof for the judgement of polymer miscibility. Visual examination and OM observation showed that CDA/PVP films prepared by using solution casting method are completely transparent in the composition range of 95/5 to 50/50 w/w. It is well known that if the difference of refractive indices of two polymers is lower than 0.005–0.01, transparent films with negligible light scattering can be obtained for their blends, independent of their miscibility[15]. Or, if two blending components are layered one upon the other one, or they are highly dispersed in microphases having dimensions lower than the wavelength of visible light (0.4–0.7 μm), optical clear films may also be obtained. The refractive index of CDA is 1.473–1.478 and 1.53 for PVP[16]. Their difference is 0.04–0.05 and much larger than the above limit. Also a structure layered with one component upon the other cannot be formed for CDA/PVP blends since solutions of blends used to cast films are completely miscible. Therefore a preliminary conclusion that CDA and PVP are miscible can be drawn.

It was found that films with different compositions were still transparent when they were heated to 230°C which is far higher than T_g values of the blends. This feature implies that blends are thermodynamically stable.

Glass transition temperature

The most widely used criterion for the judgement of the miscibility of polymer blends is the existence of a single glass transition temperature occurring between those of the pure polymers which varies in a regular way with compositions[1]. D.s.c. thermograms of CDA/PVP blends with varied composition ratios were shown in *Figure 1*. A single T_g between the T_g values of CDA and PVP was detected for each blend. This feature suggests that CDA/PVP blends are miscible in all the range of compositions. The T_g dependence on compositions is shown in *Figure 2*. The curve A corresponds to T_g values measured by using d.s.c. Curves B and C correspond to those calculated on the base of weight of average of T_g values of pure components and the Fox equation[16], respectively.

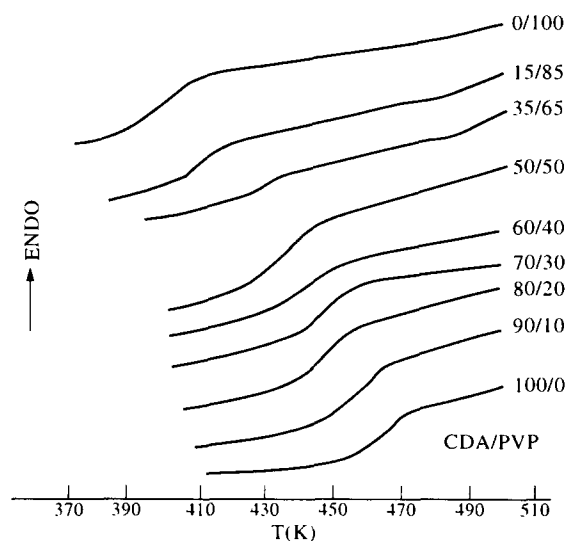$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (7)$$

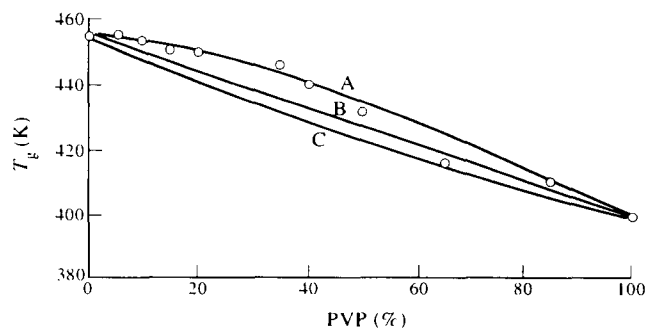**Figure 1** D.s.c. curves of CDA/PVP blends, numbers denote the wt% of CDA/PVP

Figure 2 Dependence of glass transition temperatures on composition ratio of CDA/PVP. (A) Experiment, (B) weight average, (C) Fox equation

where w_i and T_{g_i} are the weight fraction and the glass transition temperature of component i, respectively. A marked positive deviation from the prediction of the Fox equation is observed from *Figure 2*. As is well known the Fox equation assumes that random mixing at the segmental level is present in a polymer blending system. This deviation can be tentatively explained by specific interactions establishing between CDA and PVP molecular chains[17], which introduces hindering of the movement of segments of the blending system.

Usually, d.m.t.a. is more sensitive than d.s.c. for the detection of T_g values of polymers. In order to verify the conclusion obtained from calorimetric data, dynamic mechanical relaxation behaviour was investigated for CDA and CDA/PVP blends, 90/10, 80/20, 70/30, 60/40 and 50/50 w/w. As shown in *Figure 3* all blends are characterized by a single tan δ peak, which suggests that a single T_g is present and shifts toward lower temperature with increasing the content of PVP blends. The observed feature is consistent with that obtained by d.s.c. It is also found that sharpness of tan δ peaks of blends is similar to that of pure CDA, providing further evidence of high extent of miscibility for this blending system[1].

Mechanical properties

Figure 4 shows Young's modulus and tensile strength of CDA/PVP blends as a function of their compositions. Both modulus and tensile strength have a maximum for the blend containing 5% PVP (by wt). Nearly constant values were obtained in the composition range of CDA/PVP = 80/20 to 60/40. Due to the difficulty for preparation of the pure PVP film by using the solution casting method it was impossible to get Young's modulus and tensile strength for PVP used in this work. However, its modulus and tensile strength prepared by using moulding methods can be obtained and are less than 2×10^3 MPa and 40 MPa, respectively. According to calculations based on the weight average of modulus and tensile strength of the pure CDA and PVP, these two mechanical parameters of CDA/PVP blends are much higher than calculated values, which suggests that there is a synergism of mechanical properties present in CDA/PVP blends. This feature has been observed in several miscible blends[18] and attributed to the contraction of free volume or densification. Here, we prefer to explain tentatively that the possible specific interaction present between CDA and PVP lead to better molecular packing, as suggested by Jacques[19] and Feldman[20].

Viscosity of solutions of CDA/PVP blends

As shown in *Figure 5*, absolute viscosities of PVP solutions are quite low and increase very slightly with concentrations. In order to evaluate the effect of the content of PVP on absolute viscosities of CDA/PVP solutions, the concentration of CDA was fixed at 5.6 g/100 ml for each CDA/PVP solution and the concentrations of PVP was varied on the base of composition ratio of CDA/PVP (95/5, 90/10, 75/25, 60/40, 45/55, 30/70, 15/85). The absolute viscosity of the pure CDA solution having the concentration of 5.6 g/100 ml is 46 CP. It can be observed from *Figure 5* that absolute viscosities of all CDA/PVP solutions are much higher than weight average values of viscosities of the pure CDA and PVP. This feature suggests that molecular chains of CDA and PVP are strongly
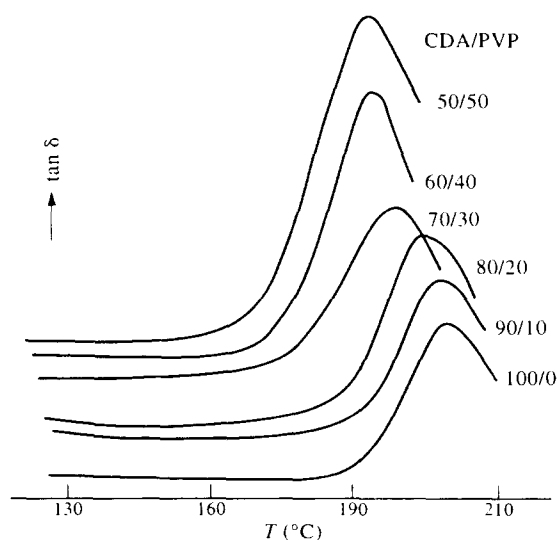
Figure 3 Temperature dependence of mechanical loss tan δ of CDA and CDA/PVP blends, numbers denote the wt% of CDA/PVP
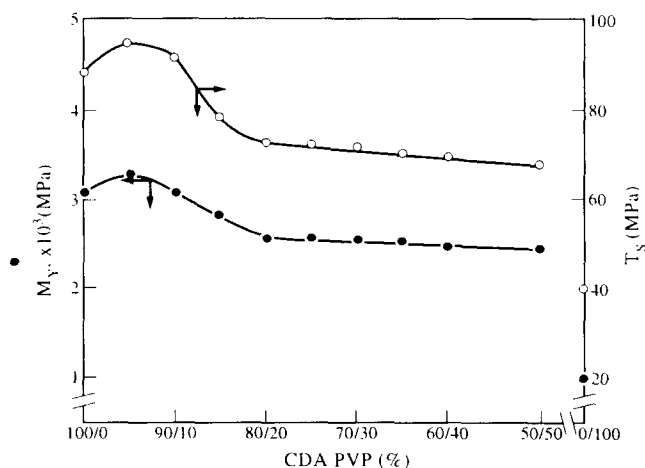
Figure 4 Young's modulus and tensile strength of CDA/PVP blends as a function of compositions
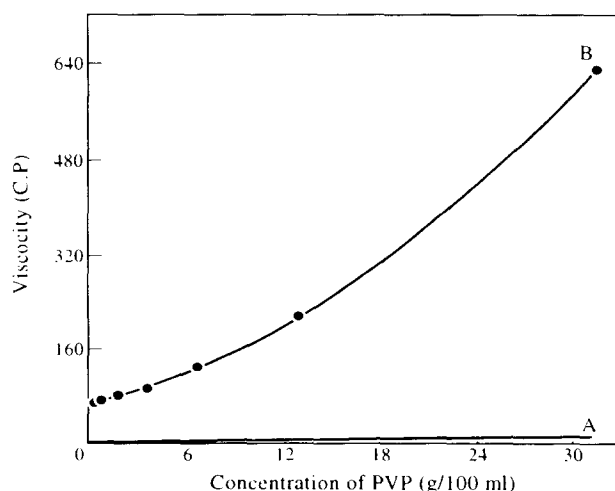
Figure 5 Absolute viscosities of solutions of CDA/PVP blends as a function of PVP concentrations (CDA concentration was fixed at 5.6 g/100 ml)
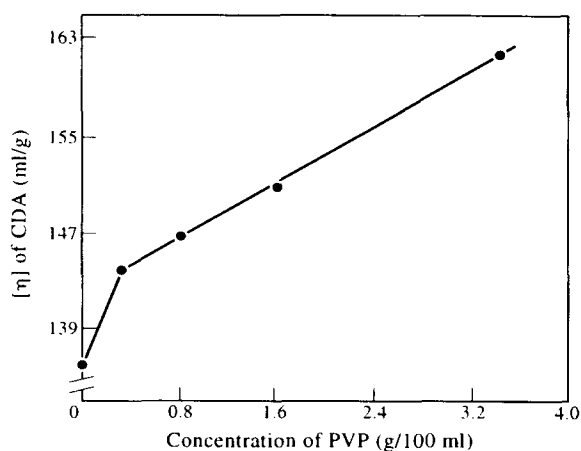
Figure 6 Dependence of intrinsic viscosities of CDA on PVP concentrations

associated together in the common solvent. PVP molecules in solutions may bridge different CDA chains by the hydrogen-bonding specific interaction, which causes aggregation of CDA molecules.

Intrinsic viscosities of CDA in solutions containing different contents of PVP in acetone–ethanol (8/1 by volume) were shown in *Figure 6*. With enhancing PVP concentrations intrinsic viscosities of CDA increased remarkably. It meant that the size of coils of CDA molecular chains expanded. Undoubtedly this feature should arise from the interaction between CDA and PVP. The extent of this kind of interaction can be estimated in terms of a parameter K_{12}. The viscosity $\eta(c_1, c_2)$ of a dilute solution containing two polymers (1 and 2) at concentrations (c_1, c_2) can be expressed as

$$\frac{\eta(c_1, c_2)}{\eta_0} = 1 + c_1[\eta_1] + c_2[\eta_2] + c_1^2 b_1 + c_2^2 b_2$$
$$+ 2c_1 c_2 b_{12} + \cdots \qquad (8)$$

where $[\eta_i]$ is the intrinsic viscosity of polymer i in pure solvent, η_0 is the viscosity of the solvent, b_i is a characteristic of interaction between similar molecules, b_{12} is a complex interaction parameter in which hydrodynamic and thermodynamic interactions are included.

$$b_{12} = K_{12}[\eta_1][\eta_2] \qquad (9)$$

where K_{12} is similar to Huggins' coefficient K_i. Using equation (8) $[\eta_1]$ of polymer 1 in a solution of polymer 2 at the concentration c_2 can be expressed as

$$[\eta_1]_{C_2} = \lim_{C \to 0} \frac{\eta(c_1, c_2) - \eta(c_2)}{\eta(c_2) c_1} \qquad (10)$$

where $\eta(c_2)$ is the viscosity of polymer 2 solution. Hence to a first approximation

$$\frac{[\eta_1]_{C_2}}{[\eta_1]} = \frac{1 + 2K_{12}[\eta_2]c_2 + \cdots}{1 + [\eta_2]c_2 + K_2[\eta_2]c_2^2} = \frac{1 + 2K_{12}[\eta_2]c_2}{(\eta_{r,2})_{C_2}} \qquad (11)$$

where $(\eta_{r,2})_{C_2}$ is the relative viscosity of a solution of polymer 2 at the concentration c_2. By plotting $([\eta_1]_{C_2}/[\eta_1])(\eta_{r,2})_{C_2}$ against $[\eta_2]c_2$ the K_{12} parameter characterized the extent of interaction between a couple of polymers can be obtained from the slope of the plot. The plot was shown in *Figure 7* for CDA/PVP solutions. The
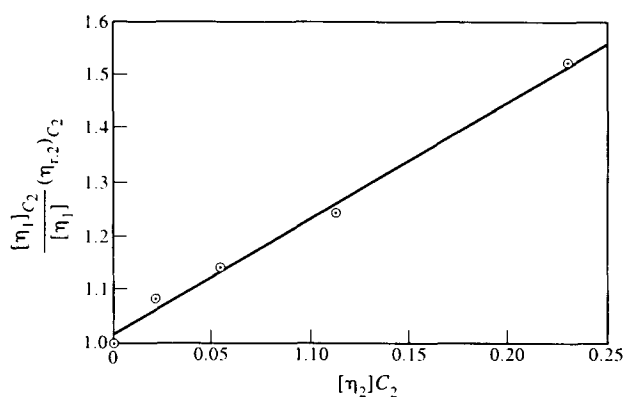

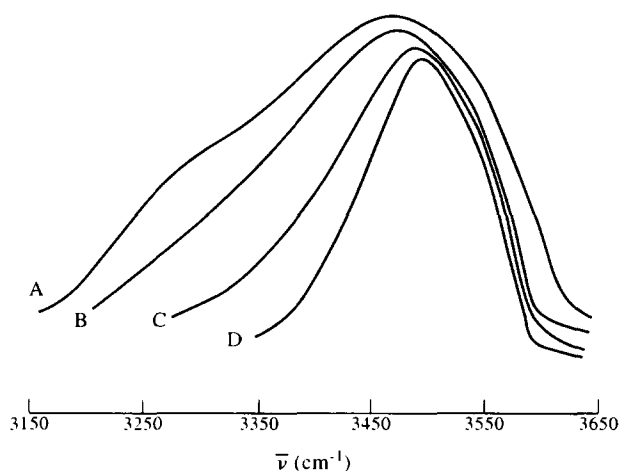**Figure 7** Plot of $([\eta_1]_{C_2}/[\eta_1])(\eta_{r,2})_{C_2}$ vs $[\eta_2]_{C_2}$

Figure 8 *FT*i.r. spectra of CDA/PVP blends in the range of 3250–3650 cm^{-1}

	CDA/PVP (wt.%)	Peak position of –OH of CDA (cm^{-1})
A	20/80	3460
B	40/60	3467
C	70/30	3481
D	100/0	3490

parameter K_{12} calculated from the slope of the plot is 1.1. This value is much higher than those generally obtained (0.37–0.60) from miscible blends[22], suggesting a strong interaction present in CDA/PVP blends.

Interacting groups—FTi.r. studies

In previous discussions good evidence verified that there was a strong interaction present between CDA and PVP. This interaction possibly arises from hydrogen-bonding between carbonyl groups of PVP and hydroxyl groups of CDA. *FT*i.r. experiments supported this assumption. *Figure 8* showed *FT*i.r. spectra of CDA/PVP blends and CDA in the range of 3250–3650 cm^{-1}, characteristic of the hydroxyl (–OH) vibrating frequency. With increasing the content of PVP, significant shifts and broadening of peaks could be observed. For instance, comparing with the pure CDA the hydroxyl peak of the blend with CDA/PVP = 20/80 shifted about 30 cm^{-1} toward lower frequency and a remarkable broadening was observed. *FT*i.r. spectra of carbonyl groups of PVP and CDA in blends of CDA/PVP = 100/0, 70/30, 40/60, 20/80 (w/w) were shown in *Figure 9*. With decreasing content of PVP the vibrating frequency of carbonyl groups obviously decreased. Since
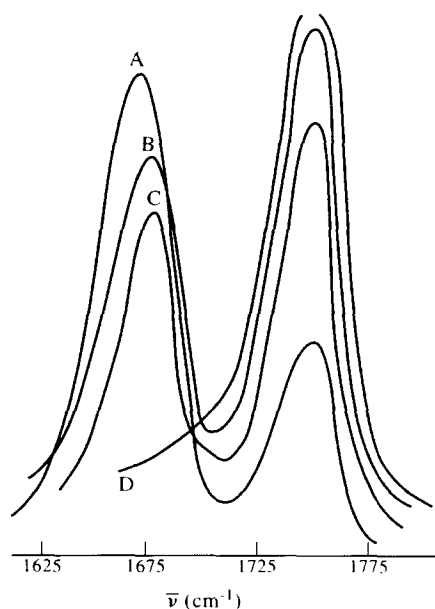
Figure 9 *FT* i.r. spectra of CFA/PVP blends in the range of 1625–1775 cm^{-1}

	CDA/PVP (wt%)	Peak position of –CO of PVP (cm^{-1})	CDA (cm^{-1})
A	70/30	1672	1752
B	40/60	1677	1752
C	20/80	1678	1752
D	100/0	—	1752

it was impossible to get a pure PVP film by a solution casting method, we did not obtain the *FT* i.r. spectrum of the pure PVP. Comparing the sample, CDA/PVP = 70/30 with the other one having CDA/PVP = 20/80, the difference of vibrating frequencies of their carbonyl groups is 6 cm^{-1}. These features can be attributed to the shift of the electron density that lowers the vibration transition energies associated with hydroxyl groups of CDA and carbonyl groups of PVP due to the formation of hydrogen-binding. The lower the content of CDA, the more the possibility of forming hydrogen-bonding, and the smaller the frequency of hydroxyl groups of CDA. Similar trends can be observed for the shift of peaks of carbonyl groups of PVP. As shown in *Figure 9* there was no shift for peaks of carbonyl groups of CDA which means that no hydrogen-bonding interaction is present in these groups.

Heating of mixing and evaluation of interaction parameters

Calorimetric data of mechanical mixtures and solution casting blends of CDA and PVP were shown in *Table 1*. Negative values of heat of mixing were obtained in all the composition range. A direct proof of miscibility of CDA and PVP is given here. The negative values of heat of mixing can be attributed to the specific interaction of hydrogen-bonding of two components. As shown in *Table 1* the absolute values of heat of mixing increase with enhancement of the CDA content of CDA/PVP blends. This feature suggests that the extent of their miscibility is strongly dependent upon their compositions.

As it is well known, the extent of polymer–polymer interactions can be qualified by means of a thermo-dynamic interaction parameter, χ_{12}. This parameter can

Table 1 Calorimetric data of CDA/PVP blends measured at 24.5 °C

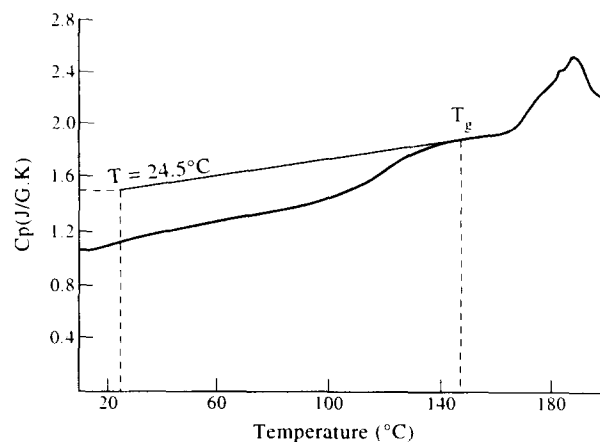| CDA/PVP (wt/ ratio)	$\Delta H_1 + \Delta H_2 + \Delta H_3$ (J g^{-1})	ΔH_4 (J g^{-1})	ΔH_{mix} (J g^{-1})
90/10	−38.4	−35.7	−2.6
65/35	−35.5	−33.2	−2.3
40/60	−26.0	−24.6	−1.4
15/85	−22.2	−21.7	−0.5

Figure 10 Typical C_p (specific heat) curve of a CDA/PVP blend (40/60) obtained by d.s.c.

Table 2 Specific heats of the glass state C_p^g and the hypothetical liquid state C_p^l, excess glass enthalpy of mixing $\Delta H'_{mix}$ and corrected enthalpy of mixing $\Delta H''_{mix}$

CDA/PVP (wt.ratio)	C_p^g (J g.K^{-1})	C_p^l (J g.K^{-1})	$\Delta H'_{mix}$ (J g^{-1})	$\Delta H''_{mix}$ (J g^{-1})
100/0	1.14	1.63	·	·
90/10	1.12	1.57	2.6	−5.2
64/35	1.12	1.56	3.0	−5.3
40/60	1.15	1.53	0.7	−2.7
15/85	1.16	1.51	0.2	−0.7
0/100	1.19	1.43	–	–

be simply estimated by using the free energy of mixing based on the Flory–Huggins treatment as mentioned in the Introduction. Due to the fact that heats of mixing measured here correspond to the glass state of this blending system, they should be corrected to the related hypothetical liquid state which is obtained by extra-polating the specific heat curve of the liquid state to the corresponding glass state. A typical extrapolating procedure was shown in *Figure 10*. Specific heats in the glass state and the hypothetical liquid state, the excess glass enthalpy of mixing as well as the corrected heat of mixing for this blending system, were shown in *Table 2*. Interaction parameters calculated on the basis of equations (1)–(4) as a function of compositions were shown in *Figure 11*. Here we assume $\Delta S_m = 0$. Values of v_1(CDA) and v_2(PVP) are 0.769 cm^3 g^{-1} [23] and 0.826 cm^3 g^{-1} [24], respectively. The average molar volume of the repeating unit of CDA and PVP, 148.3 cm^3 g mol^{-1}, is used as the parameter, V, of equation (4). As shown in *Figure 11*, negative interaction parameters were obtained in all the composition ranges of this blending system. The absolute values of interaction parameters increase monotonically with the content of CDA. These
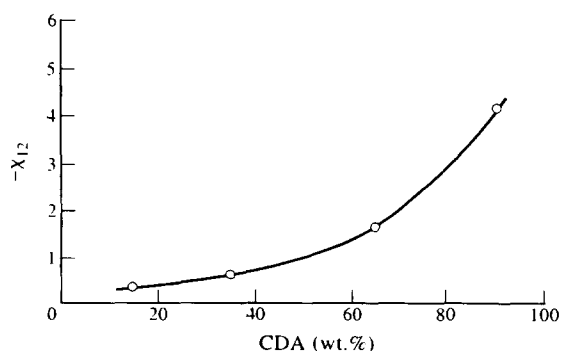
Figure 11 Interaction parameters, χ_{12} of CDA/PVP blends as a function of compositions

features indicate again that the CDA and PVP couple is miscible and the miscible extent is dependent upon the content of CDA. We should point out here that for well-known reasons interaction parameters obtained in this work are very approximate and only used qualitatively to characterize the extent of miscibility.

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