Miscible Blends of Cellulose Acetate Hydrogen Phthalate and Poly(vinyl pyrollidone) Characterization by Viscometry, Ultrasound, and DSC

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ABSTRACT: Miscibility characteristics of cellulose acetate hydrogen phthalate (CAP) and poly(vinyl pyrollidone) (PVP) have been investigated by solution viscometric, ultrasonic, and differential scanning calorimetric (DSC) methods. From viscosity measurements, Krigbaum and Wall polymer–polymer interaction parameter Δb was evaluated. Ultrasonic velocity and adiabatic compressibility have been plotted versus blend composition and are found to be linear. Variation of T_g with composition follows Gordon–Taylor equation. T_g values have also been calculated from the Fox equation. The results obtained reveal that CAP forms a miscible blend with PVP in the entire composition range. Compatibility may be due to the formation of hydrogen bonding between the carbonyl group of PVP and the free-hydroxyl group of CAP. Compatibility has also been confirmed from dielectric measurements. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 859–867, 2000

Key words: polymer blend; miscibility; interaction parameter; dielectric properties

INTRODUCTION

In this article, we report on the miscibility of a new blend system of cellulose acetate hydrogen phthalate (CAP) and poly(vinyl pyrollidone) (PVP). CAP and PVP have been selected for the present study due to their pharmaceutical applications.[1,2] Polymer–polymer miscibility is generally considered as a result of specific interaction between polymer segments. The specific interactions include donor–acceptor, dipole–dipole, hydrogen-bonding, ion–ion, acid–base, and ion–dipole interactions.[3–6] It is well known that proton acceptor polymerlike PVP forms miscible blends with hydroxyl-containing polymers such as poly(vinyl phenol), poly(vinyl alcohol), poly(hydroxy ethyl methacrylate), etc.[7–9] The specific interaction is hydrogen bonding. Polymer–polymer miscibility can be detected by a number of techniques such as DSC, neutron scattering, morphology studies by optical and electron microscopy, dynamic mechanical measurements, infrared spectroscopy, ultrasound, and viscometry.[10–13] Hence, blends of PVP and CAP have been prepared by solution-casting method and characterized by DSC, solution viscometry, and ultrasonic measurements, and miscibility has been predicted.

EXPERIMENTAL

Polymers used in the present study, CAP and PVP, were obtained from CDH Chemical Ltd. (New Delhi, India) and purified. The structures of CAP and PVP are as follows:
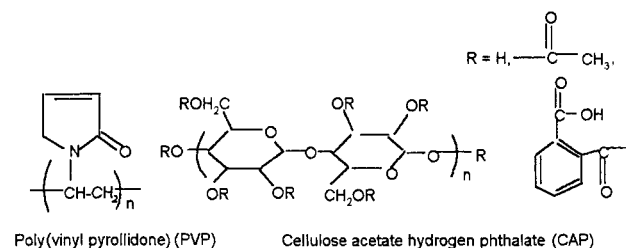
Poly(vinyl pyrollidone) (PVP)   Cellulose acetate hydrogen phthalate (CAP)

Table I   Values of Relative Viscosity and Reduced Viscosity of CAP/PVP Blends

Blend Composition (CAP/PVP)	Relative Viscosity (Concentration used 2%)	Concentration (g/mL)	Reduced Viscosity of Blend Compositions				
			0/100	30/70	50/50	70/30	100/0
0/100	1.5	0	0.145	0.236	0.289	0.347	0.430
10/90	1.61	0.2	0.150	0.240	0.295	0.365	0.460
20/80	1.73	0.4	0.155	0.255	0.315	0.395	0.490
30/70	1.86	0.6	0.160	0.265	0.335	0.420	0.525
40/60	1.98	0.8	0.160	0.280	0.350	0.445	0.555
50/50	2.11	1.0	0.165	0.295	0.370	0.475	0.585
60/40	2.23	1.2	0.170	0.305	0.390	0.500	0.615
70/30	2.35	1.4	0.175	0.320	0.410	0.525	0.645
80/20	2.47	1.6	0.180	0.330	0.425	0.560	0.675
90/10	2.59	1.8	0.185	0.345	0.445	0.580	0.715
100/0	2.71	2.0	0.190	0.365	0.460	0.610	0.745

Films with thickness on the order of microns were used for DSC studies. Polymer solution was used for viscometric and ultrasonic studies. Stock solutions (2% w/v) of each polymer was prepared in the common solvent dimethyl formamide (DMF). Blend solutions of CAP and PVP (2% w/v) at different compositions of 30/70, 50/50, and 70/30 were then prepared. Relative viscosities of the component polymer solutions and their blend compositions were measured at 31°C by using an Ubbelohde viscometer. Reduced viscosities of polymer solutions and their blends for various concentrations were also measured. Ultrasonic velocity of the 3% blend solutions was measured at 30°C by using ultrasonic pulse echo interferometer (SD UI-003). For DSC studies, thin films of CAP, PVP, and their blends were prepared by solution casting by using DMF as a common sol-
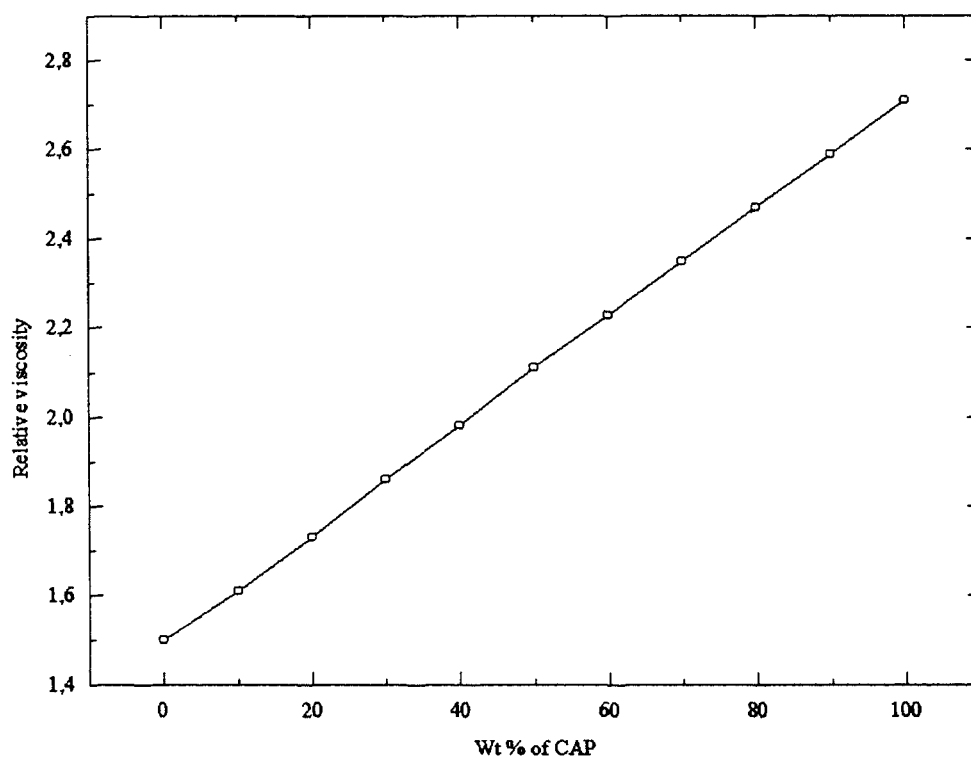
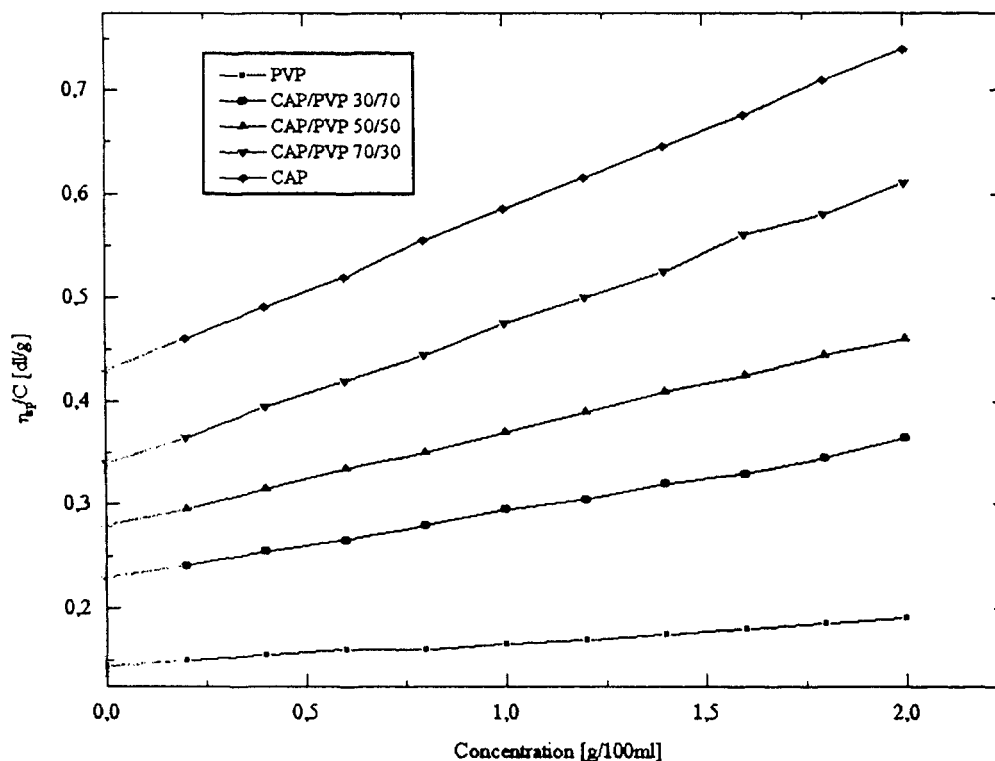**Figure 1**   Relative viscosity versus blend composition of CAP/PVP blends.

Figure 2   Reduced viscosity versus concentration for CAP, PVP, and CAP/PVP blends.

vent. Films were dried in vacuum for 2 days. DSC measurements were performed in Shimadzu DSC-50; the scan rate was 10 K/min.

RESULTS AND DISCUSSION

Relative and reduced viscosities of individual polymers and blends are given in Table I. The relative viscosity is plotted against the blend composition (Fig 1). The curve is linear for the entire composition range, characteristic of miscible blend system.[14] Reduced viscosities of the compo-

nent polymers and their 30/70, 50/50, and 70/30 blend compositions are plotted against concentrations (Fig. 2). The plots are linear and no crossover is seen, showing that the blends are compatible. A sharp crossover in the plots of reduced viscosity versus concentration is characteristic of incompatible blends.[15] The intrinsic viscosity values of the individual polymers and their blend compositions are obtained from the reduced viscosity versus concentration plots by extrapolating to zero concentration (Fig. 2). The experimental intrinsic viscosities of the blends are compared with their intrinsic viscosity values predicted

Table II   Intrinsic Viscosity and Interaction Parameter of CAP/PVP Blends

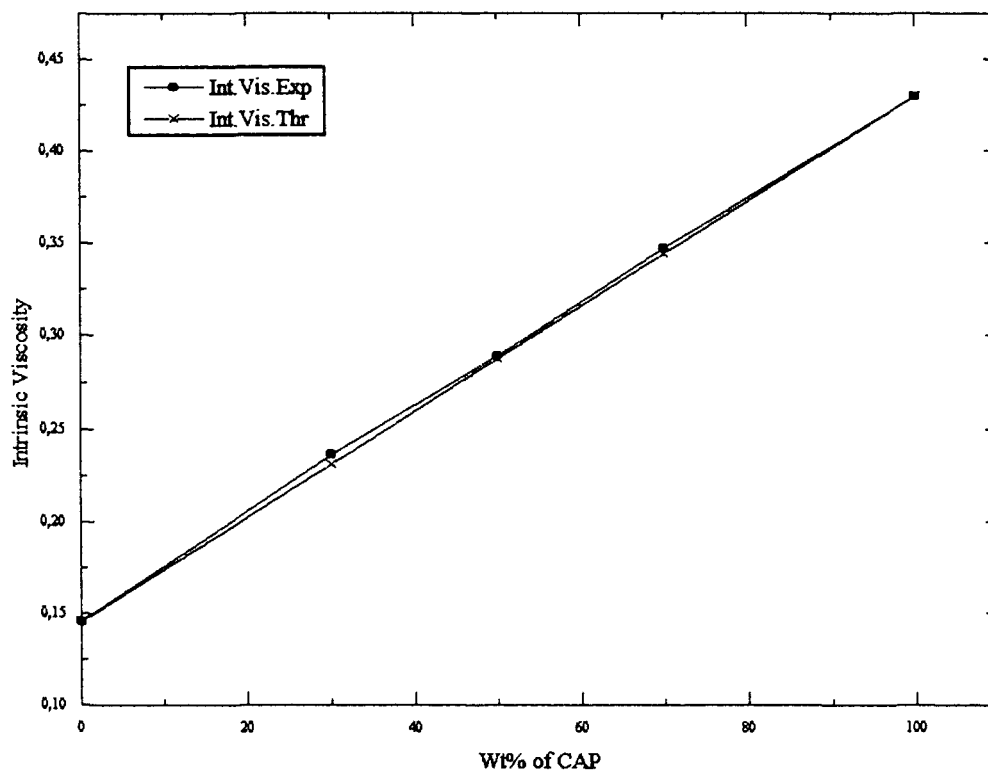| Blend Composition CAP/PVP	Intrinsic Viscosity		Slope of Red Viscosity vs Concentration	Experimental b_{12} Value	Theoretical b_{12}^* Value	Δb	μ
	Experimental (dL/g)	Theoretical (dL/g)					
0/100	0.145	0.145	0.01875	—	—	—	—
30/70	0.236	0.2305	0.100	0.1827	0.0541	0.1286	1.5834
50/50	0.289	0.2875	0.125	0.1625	0.0541	0.1084	0.3342
70/30	0.347	0.3445	0.1375	0.1407	0.0541	0.0866	1.0660
100/0	0.430	0.430	0.15625	—	—	—	—

Figure 3 Intrinsic viscosity versus composition of CAP/PVP blends.

from the weighed averages and are presented in Table II. The experimental intrinsic viscosity values are slightly higher than the theoretical values (Fig. 3). For immiscible systems, it was observed that intrinsic viscosity always shows a negative deviation due to repulsive interaction between polymers.[16]

The interaction parameter b of the component polymers and their blend compositions are found from the plots of the reduced viscosity versus concentration and given in Table II. The slope of the curve gives corresponding b values. Evalua-

tion of b is done on the basis of the classic Huggins equation.[17] Krigbaum and Wall interaction parameter Δb[18] of the blends is found from the difference between the experimental and theoretical values of the interaction parameters b_{12} and b_{12}^*. Polymer 1–Polymer 2 interaction parameter Δb can be calculated as follows:

$$\frac{(\eta_{sp})_m}{C_m} = [\eta]_m + b_m C_m \qquad (1)$$

Table III Ultrasonic Velocity and Adiabatic Compressibility of CAP/PVP Blends

Blend Composition (CAP/PVP)	Ultrasonic Velocity (m/s)	Density (ρ kg m^{-3})	Adiabatic Compressibility β (kg^{-1} m s^2)
0/100	1535	955.9	4.428×10^{-10}
10/90	1529	956.9	4.470×10^{-10}
30/70	1513	957.9	4.560×10^{-10}
50/50	1499	958.9	4.641×10^{-10}
70/30	1483	959.4	4.739×10^{-10}
90/10	1468	958.9	4.839×10^{-10}
100/0	1459	957.4	4.907×10^{-10}
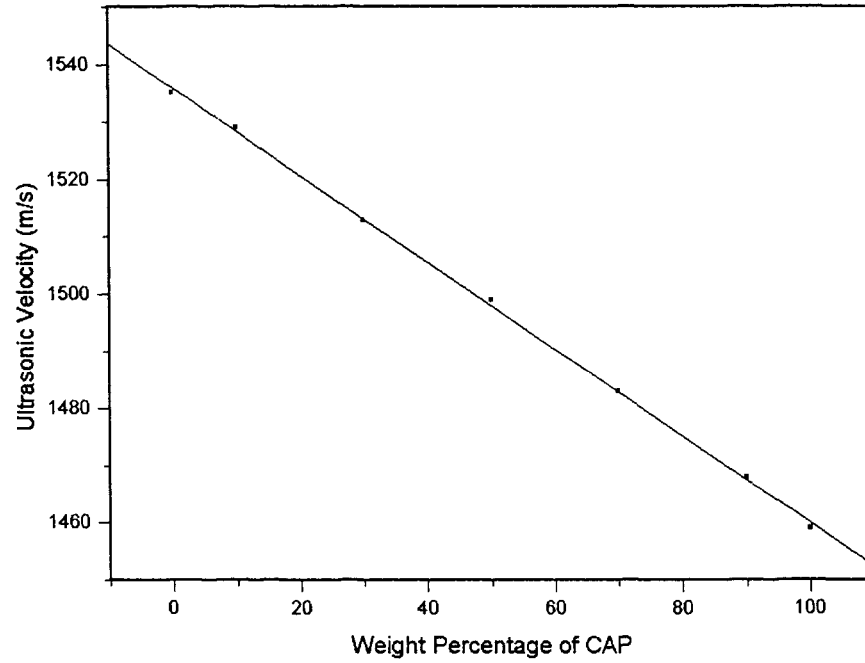
(a)
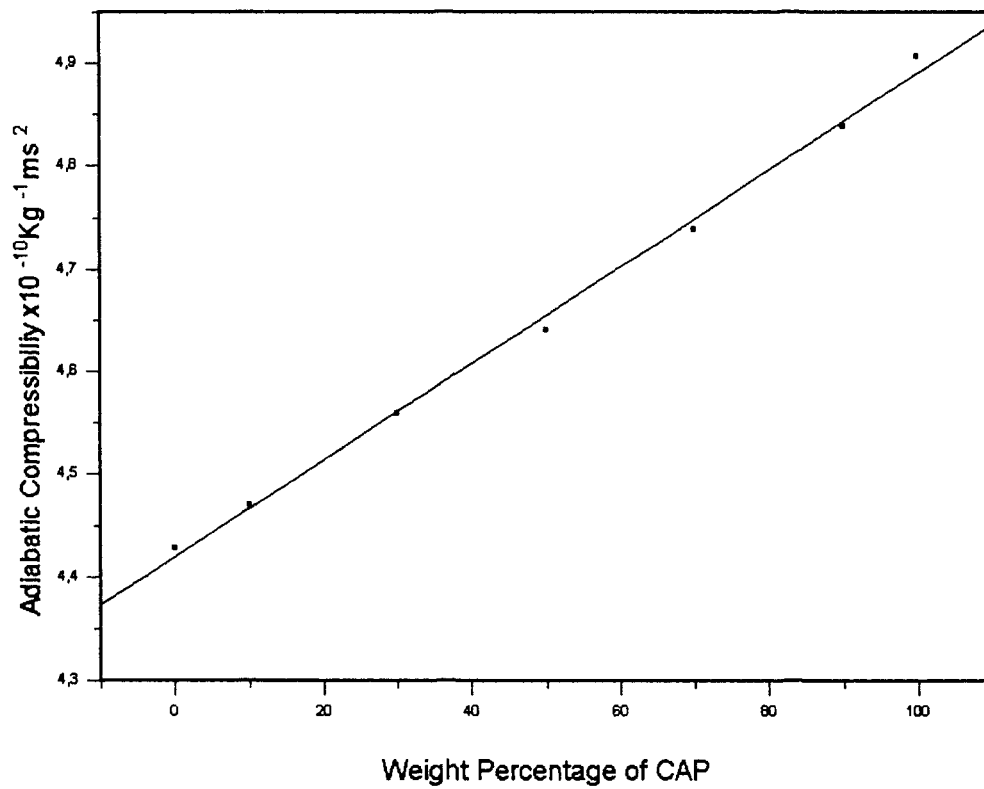
(b)

Figure 4   (a) Ultrasonic velocity versus weight percentage of CAP/PVP blend at room temperature. (b) Adiabatic compressibility versus composition of CAP/PVP blends at 30°C.
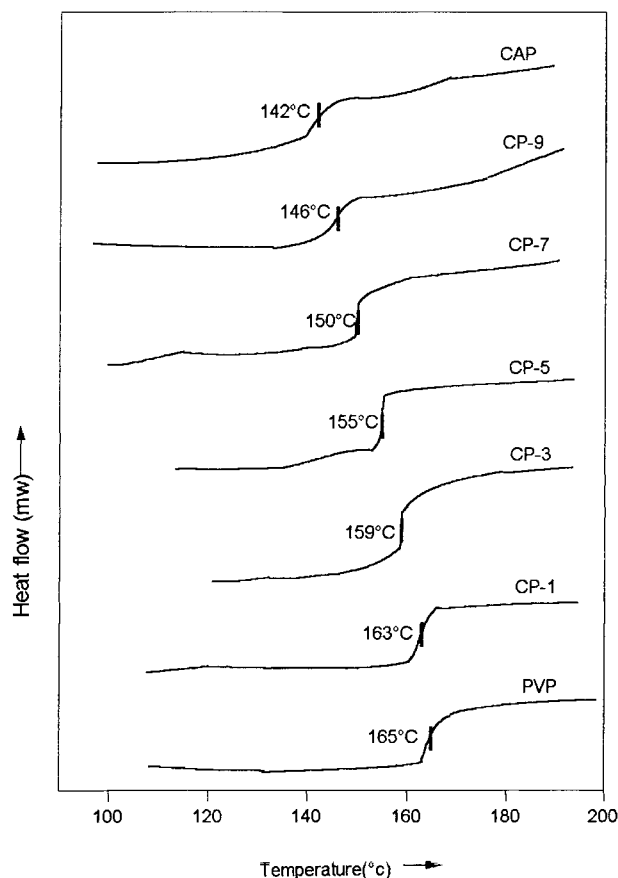
Figure 5 DCS thermogram of CAP/PVP blends.

where C_m is the total concentration of polymers ($C_1 + C_2$) and $[\eta]_m$ is the intrinsic viscosity of blend. $[\eta]_m$ can be theoretically defined as:

$$[\eta]_m = [\eta]_1 X_1 + [\eta]_2 X_2 \qquad (2)$$

(for a noninteracting system), where X_1 and X_2 are weight fractions and $[\eta]_1$ and $[\eta]_2$ are intrinsic viscosities of Polymer 1 and Polymer 2, respectively. Δb_{12} is the interaction parameter which is defined by the equation:

$$b_m = X_1^2 b_{11} + 2X_1 X_2 b_{12} + X_2^2 b_{22} \qquad (3)$$

where b_m defines the global interaction between all polymeric species. b_{12} may be obtained experimentally by eqs. (3) and (1):

$$b_{12}^* = (b_{11} b_{22})^{1/2} \qquad (4)$$

where * is the theoretical value.

$$\Delta b = (b_{12} - b_{12}^*) \qquad (5)$$

$\Delta b > 0$ signifies miscibility and $\Delta b < 0$ indicates phase separation. It is found that Δb values are positive for the blend compositions predicting compatibility (Table II). If η_1 and η_2 are sufficiently far apart, a more effective parameter μ can be used to predict miscibility:

$$\mu = \frac{\Delta b}{(\eta_2 - \eta_1)^2} \qquad (6)$$

The values of μ are also found to be $+ve$ (Table II) and a high value of μ may be attributed to a strong interaction between the polymers.[19–21] In the present system, it may be due to a specific interaction of hydrogen bonding between the polymers. Ultrasonic velocities, densities, and adiabatic compressibilities of blends are given in Table III. Adiabatic compressibility is calculated using the formula:

$$\beta_{ad} = \frac{1}{v^2 \rho} \qquad (7)$$

where v is the ultrasonic velocity and ρ is the density. Ultrasonic velocity of blends is plotted against the blend composition (Fig. 4) and is found to be linear. For incompatible blend solutions, ultrasonic velocity versus composition curve is nonlinear showing a distinct phase inversion at intermediate composition.[22] Adiabatic compressibility also varies with blend composition and a linear relationship is observed (Fig. 4).

Table IV   Experimental and Theoretical Glass Transition Temperature (T_g) of CAP/PVP Blends

Blend Composition (CAP/PVP)	Experimental T_g Values (°C)		Theoretical T_g Values	
	DSC	Dielectric	Neilson Equation	Fox Equation
100/0	142	142	—	—
90/10	146	—	144.3	144
70/30	150	151	148.9	148.2
50/50	155	156	153.5	152.6
30/70	159	160	158.4	157.35
10/90	163	—	162.7	162.37
0/100	165	163	—	—
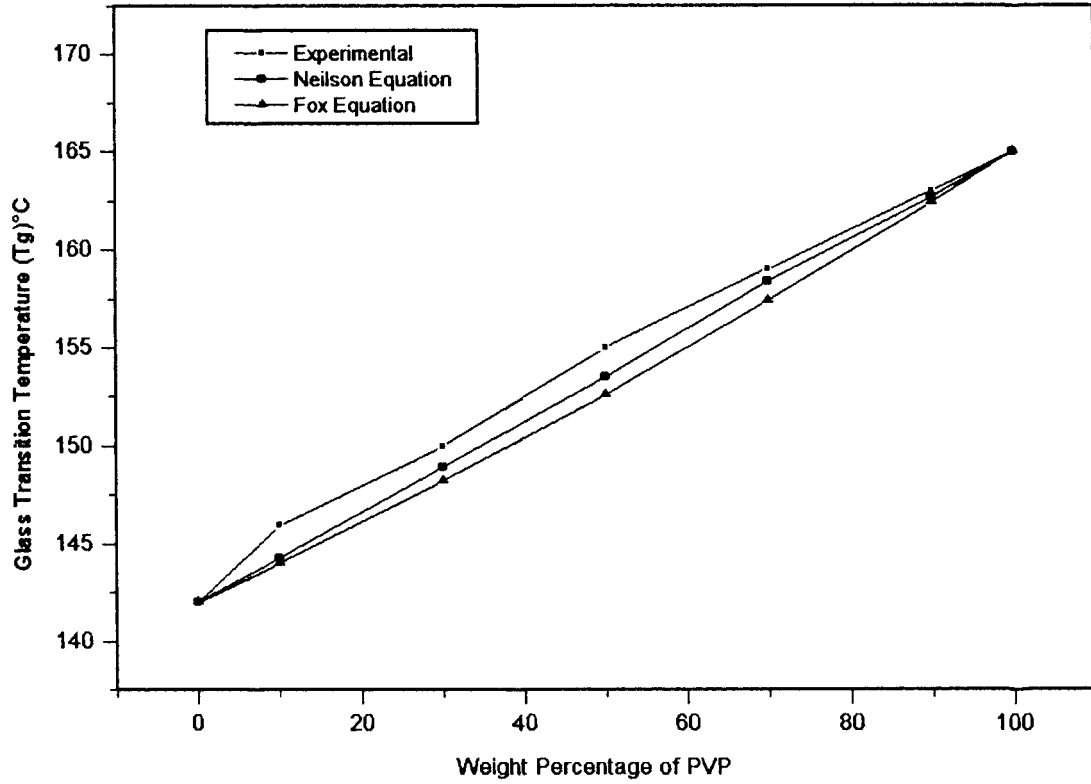
(a)
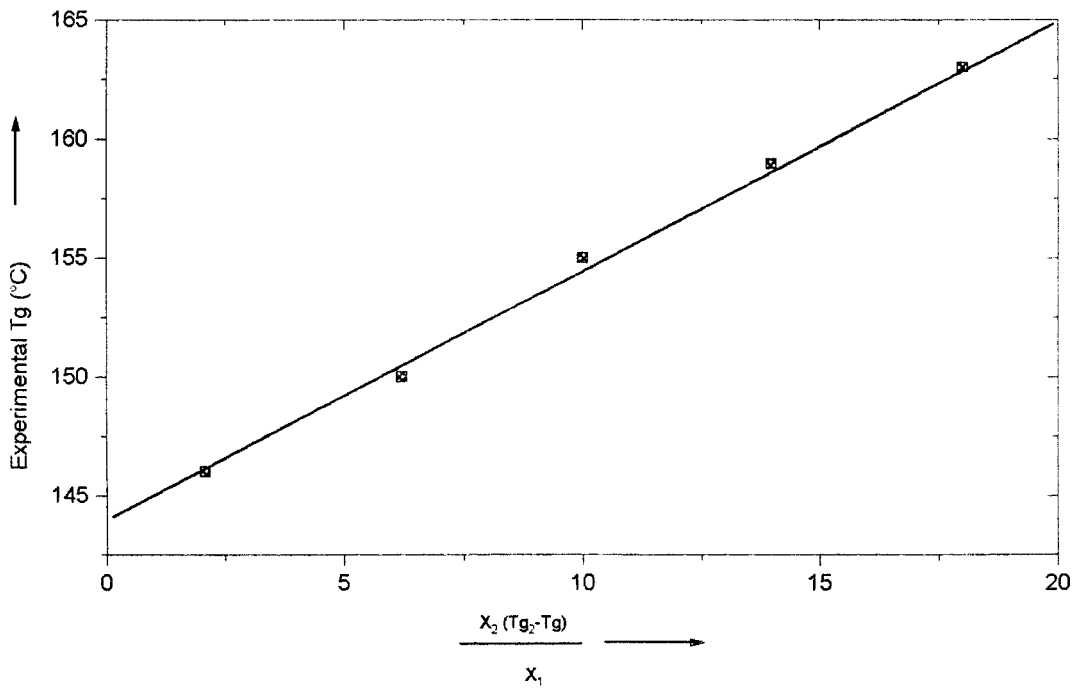
(b)

Figure 6   (a) T_g values versus composition (experimental and theoretical) of CAP/PVP blends. (b) Verification of Gordon–Taylor equation for CAP/PVP blend.
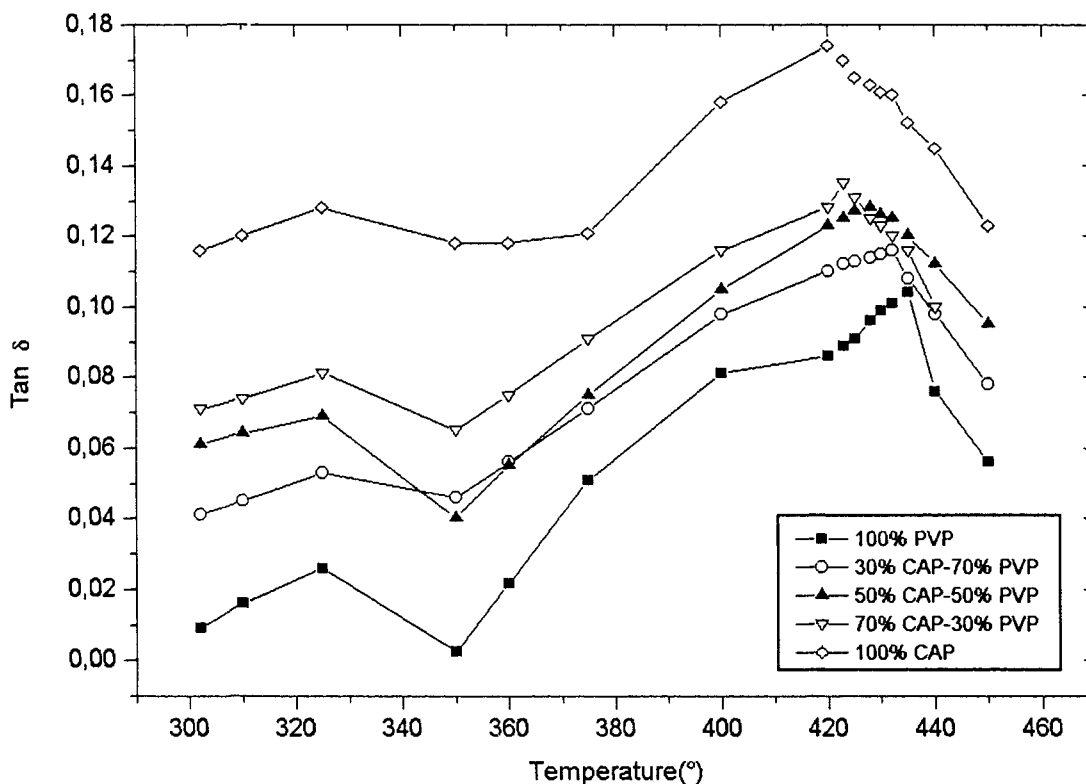
Figure 7 Tan δ as a function of temperature for different CAP/PVP blend composition at 50 Hz.

The glass transition temperature (T_g) of individual polymers and their blends are recorded from the DSC endotherm (Fig. 5 and Table IV). Blends exhibited a single T_g, intermediate to those of CAP and PVP. The T_g of miscible blends can be predicted by using the Fox equation[23] and Gordon–Taylor equation:[24]

$$\frac{1}{T_g} = \frac{X_1}{T_{g_1}} + \frac{X_2}{T_{g_2}} \quad \text{(Fox equation)} \qquad (8)$$

$$T_g = \frac{X_1 T_{g_1} + k X_2 T_{g_2}}{X_1 + k X_2} \quad \text{(Gordon–Taylor equation)} \qquad (9)$$

where X_1, X_2, T_{g1}, and T_{g2} are the weight fractions and glass transition temperatures corresponding to Polymer 1 and Polymer 2, respectively. k is a constant which gives a semiquantitative measure of the degree of interaction between the polymers. T_g values calculated from the Fox equation and the Gordon–Taylor equation and their theoretical values calculated from Neilson's equation[25] (Table IV)

are plotted against the blend composition [Fig. 6(a,b)]. Blends show positive deviation from Fox equation implying intermolecular interaction between the polymers. Plots are linear and slope (k) of the curve for Gordon–Taylor equation is found to be 1.1. [Fig. 6(b)] The value of k has been calculated theoretically using the Fox equation and the Gordon–Taylor equation and are found to be 0.86. Experimental k value (1.1) is found to be higher than the theoretical value showing higher interaction between the components and hence compatibility. The intercept of Gordon–Taylor equation curve is found to be 142°C, which is the T_g of pure CAP.

Compatibility has been further confirmed from dielectric measurements.[26] In blends, dielectric loss as a function of temperature displayed a single peak corresponding to T_g and the temperature of loss peak shifted regularly between the two composition extremes corresponding to CAP and PVP (Fig. 7). T_g values agree well with those obtained from DSC (Table IV).

All these observations show that there is specific interaction between CAP and PVP and CAP

forms miscible blends with PVP for all compositions. The miscibility may be due to the formation of hydrogen bond between the CO group of PVP and the free-hydroxyl group of CAP.

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