

Studies on Dielectric Relaxation and ac Conductivity of Cellulose Acetate Hydrogen Phthalate–Poly (vinyl pyrrolidone) Blend

Vijayalakshmi Rao, P. V. Ashokan, J. V. Amar

Department of Materials Science, Mangalagangothri-574199, D. K. India

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ABSTRACT: The dielectric constant, dielectric loss, and ac conductivity of polyblends of cellulose acetate hydrogen phthalate (CAP) and poly (vinyl pyrrolidone) (PVP) of different compositions were measured in the temperature range of 300–430 K and in the frequency range of 50 Hz–100 kHz. In the blends, the dielectric constant as well as the dielectric loss as a function of the temperature display a single peak corresponding to the glass transition temperature (T_g) in the region between the T_g values of the pure

polymers. The T_g values observed agree well with those values obtained from DSC. Dielectric studies show that CAP forms a miscible blend with PVP. Ac conductivity values were calculated from the dielectric data and the conduction mechanism is discussed. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1702–1708, 2002

Key word: miscibility; dielectric properties; blends; glass transition

INTRODUCTION

Dielectric measurements such as the dielectric constant and the dielectric loss reveal significant information about the chemical and physical state of polymers. These properties are drastically affected by the presence of another polymer or a dopant in the polymer.^{1–5} Study of the dielectric relaxation provides valuable information about the intermolecular interaction and, hence, the miscibility. Paul and Newman⁶ and Olabisi et al.⁷ reviewed the methods of determination of polymer–polymer miscibility in blends. The methods included T_g determination (by DSC, dielectric relaxation, mechanical relaxation, and dilatometry), optical clarity, IR spectroscopy, SEM, ultrasonic, and viscometry. However, dielectric relaxation studies in polymer blends are found to be very limited. Hence, in this article, we report on dielectric relaxation studies of a new blend system of cellulose acetate hydrogen phthalate (CAP) and poly(vinyl pyrrolidone) (PVP) and attempt to understand the interaction involved in blending PVP with a proton donor polymer CAP. CAP and PVP were selected for the study because of their pharmaceutical applications.^{8,9} PVP is a proton-acceptor polymer and it forms miscible blends with hydroxyl-containing polymers such as poly (vinyl phenol), poly (hydroxyethyl methacrylate), and poly (vinyl alcohol).^{10–12} The specific interaction is hydrogen bonding.

EXPERIMENTAL

The Polymers used in the study, CAP and PVP, were obtained from commercial sources. The structure of CAP and PVP are as follows [Fig. 1(g)]: phthalate content: 30–40%; acetyl content: 19–24%; hydroxyl content: 36–51%; viscosity-average molecular weight of PVP, $M_v = 43,200$; and viscosity-average molecular weight of CAP, $M_v = 70,000$.

Thin films of 5- μ m thickness of CAP, PVP, and their blends of compositions of CAP/PVP_e of 70/30 (CP-7), 50/50 (CP-5), and 30/70 (CP-3) were grown by an isothermal immersion technique, using dimethylformamide (DMF) as a solvent.¹³ Films were grown on predeposited aluminum electrodes on a clean glass substrate. The top electrode of aluminum was vacuum-deposited on the dried polymer film to form a sandwich configuration of Al–polymer–Al. The dielectric properties (capacitance and $\tan \delta$) of the blends and individual polymers were measured as a function of temperature using a Gen. Rad. 1689 Precision RLC Digibridge in the frequency range of 50 Hz–100 kHz. The accuracy of the measurements was $\pm 0.1\%$. The sample temperature was monitored with a copper-constantan thermocouple in the range of 300–450 K using a digital multimeter with an accuracy of $\pm 0.5\%$. Sample films were annealed before actual measurements, to remove the solvent and obtain constant loss peak temperatures.

Correspondence to: V. Rao (vijrao@yahoo.com).

RESULTS AND DISCUSSION

The dielectric constant and $\tan \delta$ of CAP, PVP, and CAP–PVP blend films as a function of the field fre-

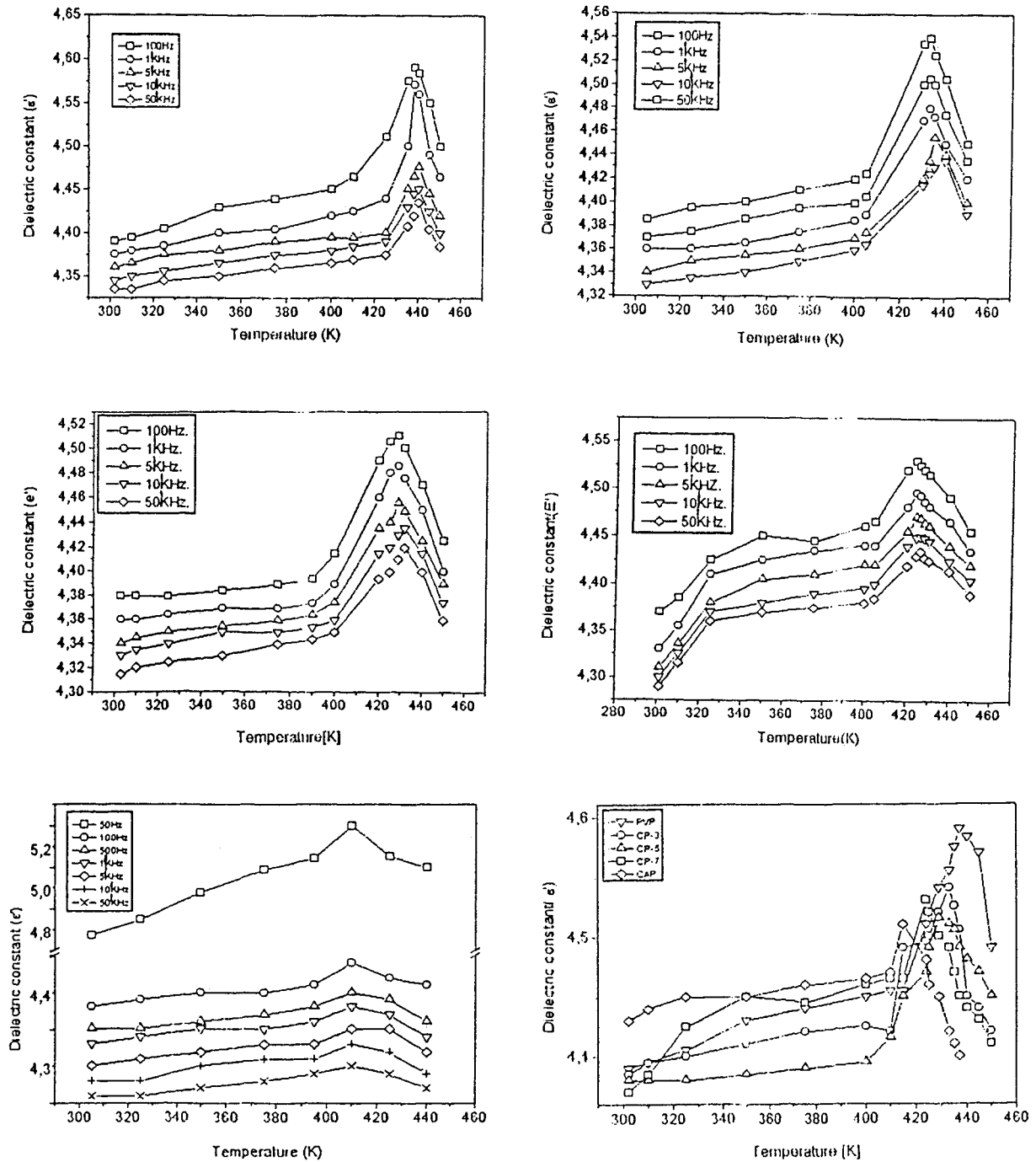


Figure 1 (a–e) Variation of dielectric constant with temperature at different frequencies for PVP, CP-3, CP-5, CP-7, and CAP, respectively. (f) Variation of dielectric constant with temperature for different blend compositions at 100 Hz. (g) Structures of CAP and PVP.

quency and temperature and ac conductivity values are shown in Figures 1–5.

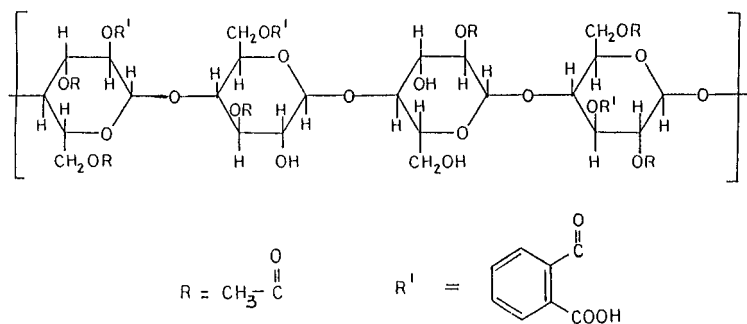
Variation of dielectric constant with temperature and frequency

The dielectric constant increases with increasing temperature, reaches a maximum, and then begins to decrease for all the blends studied and for pure CAP

and PVP. The temperature corresponding to the maximum is found to be the glass transition temperature of the corresponding blend/polymers [Fig. 1(a–e)].

The variation of the dielectric constant with the temperature is different for polar and nonpolar polymers. The dielectric constant is independent of the temperature for a nonpolar polymer, whereas, for strong polar polymer, it increases with the tempera-

Structure of cellulose acetate hydrogen phthalate (CAP)



Structure of poly vinyl pyrrolidone (PVP)

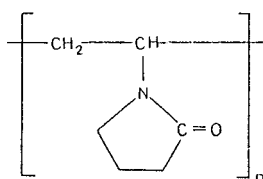


Figure 1 (Continued from the previous page)

ture. However, since the specific volume of the polymer is temperature-dependent, that is, it increases as the temperature increases, the dielectric constant decreases with an increase of temperature.¹⁴

The slow increase of the dielectric constant below the T_g in the present system may be due to the facilitation of the orientation of dipoles present in the polymers, while above the T_g , the decrease in the dielectric constant may be due to the increase in the thermal oscillations of the molecules and the diminishing degree of orientation of the dipoles. In addition to this, the decrease in the dielectric constant is also caused by

an increase in the specific volume of the polymer. Figure 1(f) shows the effect of blending CAP with PVP. The dielectric constant decreases with increasing frequency in the case of PVP, CAP, and all the blends. A typical plot is shown in Figure 2. This may be due to the tendency of the induced dipoles in the polymer to orient themselves in the direction of the applied field.¹⁵

Variation of $\tan \delta$ with temperature and frequency

Figure 3(a-e) shows the variation of $\tan \delta$ with the temperature for field frequencies between 50 Hz and

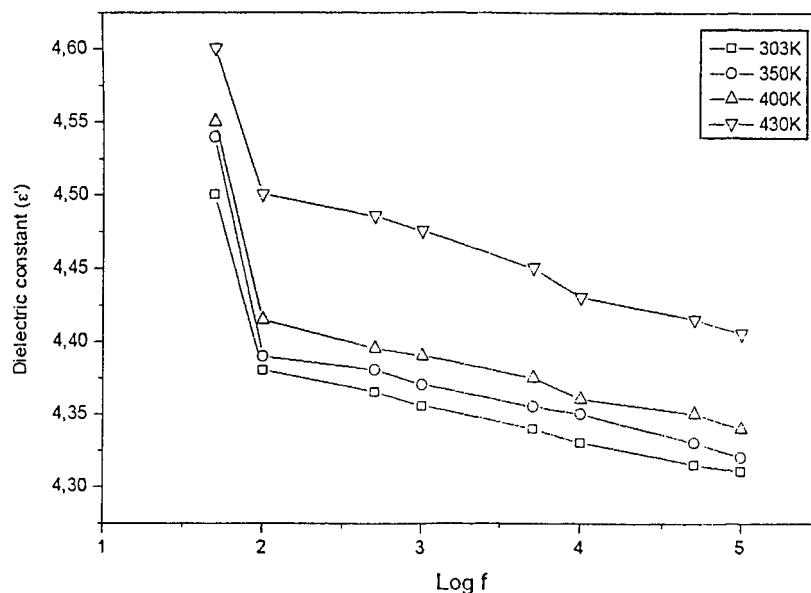


Figure 2 Variation of dielectric constant with frequency at different temperatures of the CP-5 blend.

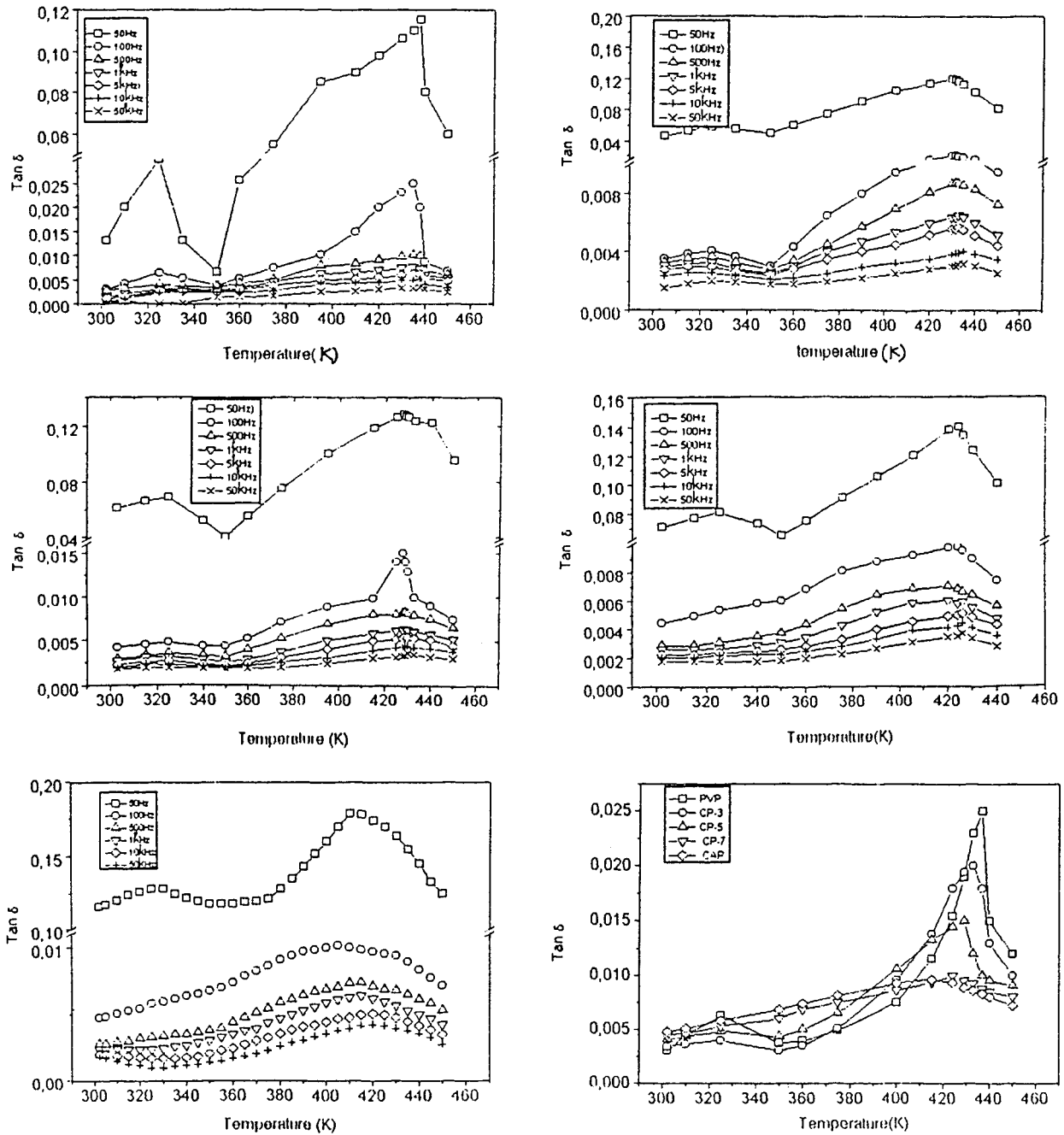


Figure 3 (a–e) Tan δ as a function of temperature at different frequencies for PVP, CP-3, CP-5, CP-7, and CAP, respectively. (f) Tan δ as a function of temperature for different blend compositions at a frequency of 100 Hz.

100 kHz for the blends and components. A loss peak is observed at the T_g of the blend and the peak shifted to the high-temperature side with increases in the frequency. The study of the miscibility in blends by dielectric relaxation involves the assessment of one or more loss peaks and the accurate location of these temperature maxima. In a binary blend, there is either one or multiple loss peaks. A single loss peak corresponds to the miscibility of the blend. From Figure 3(f), it is seen that a single loss peak is observed corresponding to the T_g for all the compositions stud-

ied and the temperature of the loss peak shifts regularly between the two composition extremes corresponding to PVP and CAP. The T_g values obtained from the loss peak agree well with the T_g values observed in the DSC measurements. The single T_g observed in the blends indicates that CAP forms a miscible blend with PVP. Also, the miscibility may be due to the interaction between the free OH group of CAP and the CO group of PVP. A low-temperature β -relaxation peak is also observed, which may be due to OH or CO groups that are not involved in the

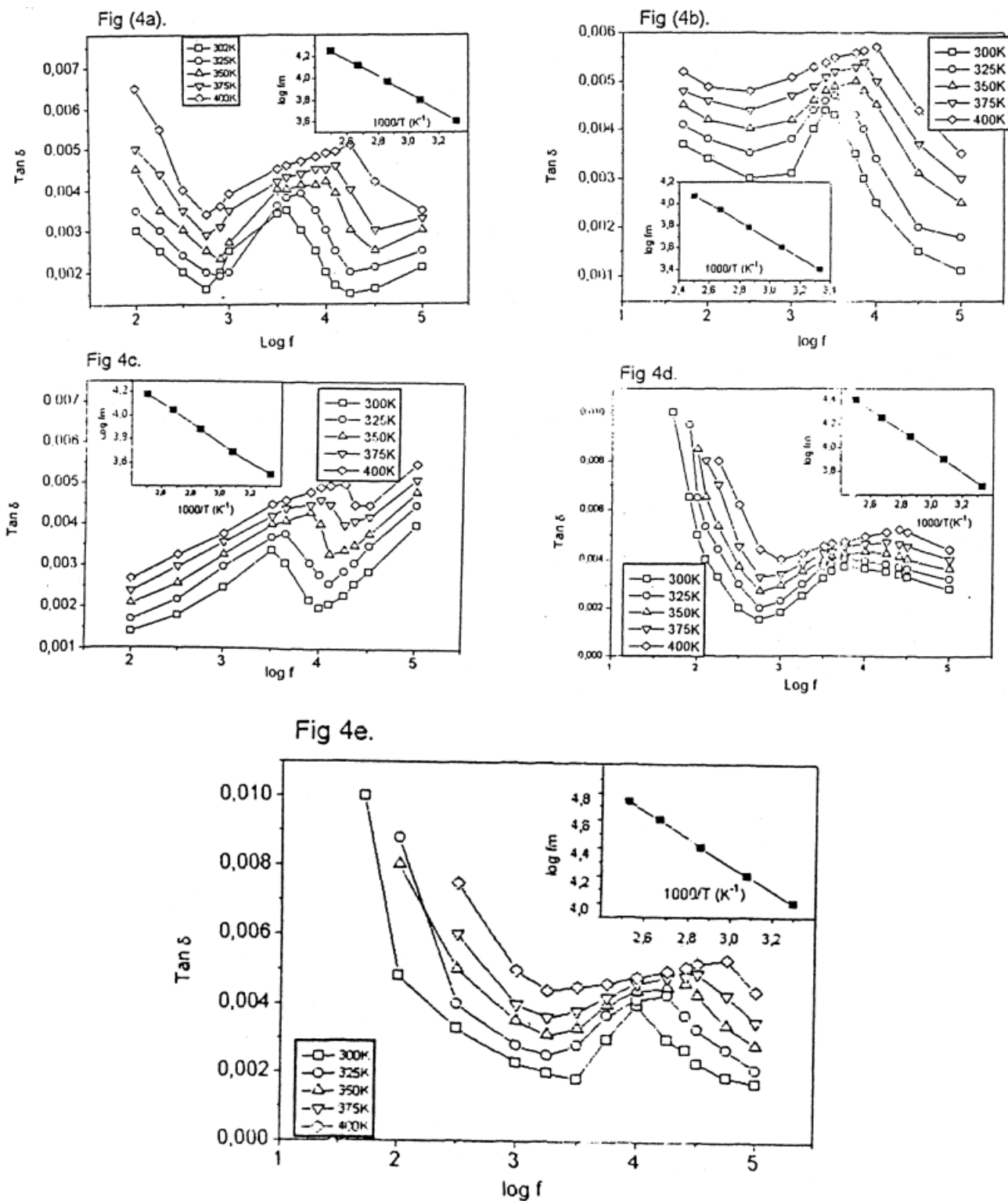


Figure 4 (a–e) Variation of $\tan \delta$ as a function of $\log f$ at different temperatures for PVP, CP-3, CP-5, CP-7, and CAP, respectively.

interaction. We have already studied in detail the miscibility and interaction in these blends by methods such as DSC, thermogravimetry, viscometry, and FTIR.¹⁶ From all these methods, we found that CAP/PVP blends are miscible. In the FTIR spectrum of a

blend, a shift of the hydroxyl and carbonyl stretching vibration to lower frequency and subsequent slight broadening of these bands are observed, showing that there is some specific interaction between hydroxyl and carbonyl groups, leading to hydrogen bonding.

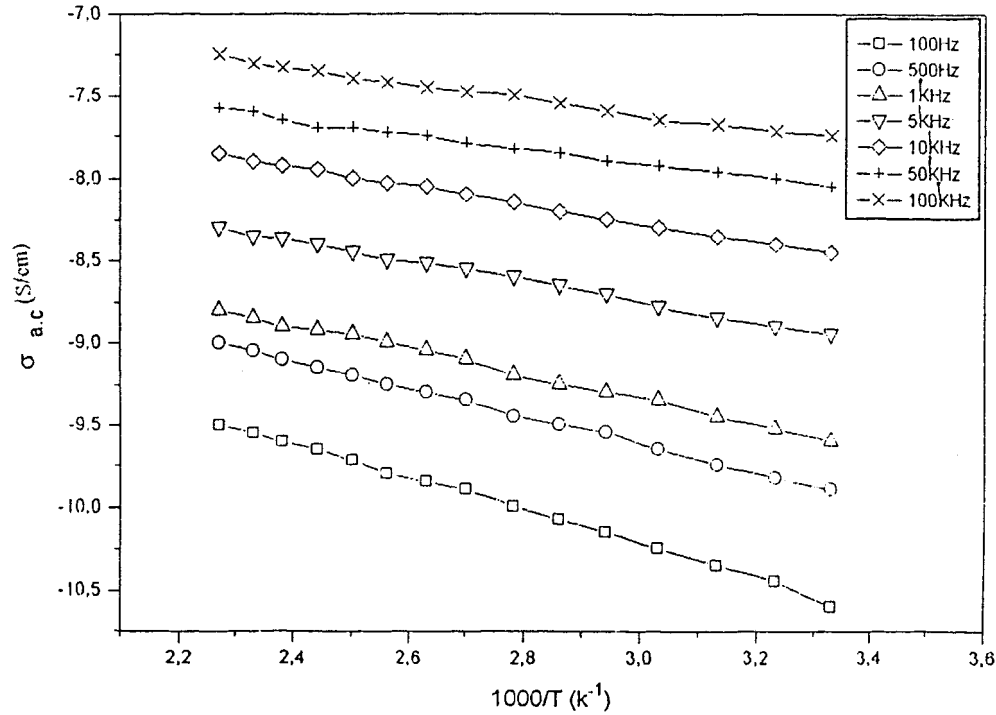


Figure 5 Variation of ac conductivity with temperature at different frequencies for CP-5 blend.

The variation of $\tan \delta$ with the field frequency at a fixed temperature is shown in Figure 4(a–e). $\tan \delta$ exhibits a relaxation peak around 10 kHz at a temperature corresponding to the T_g of the blends. The peak frequency is found to shift to higher frequency with an increase in the temperature. The activation energies of relaxation are calculated based on the following equation¹⁴:

$$f_m = f_0 e^{(-E/k_B T)} \quad (1)$$

where f_m is the frequency at the relaxation peak; f_0 , a constant; E , the activation energy; k_B , Boltzmann's constant; and T , the absolute temperature. The logarithm of the frequency corresponding to the $\tan \delta$ maximum is plotted against $1/T$ [Fig. 4(a–e)] and the activation energy is calculated from the slope. The activation energy of the blends and individual polymers are given in Table I. The activation energy lin-

early varies with increase in the content of CAP. As the temperature is increased, the β -relaxation shifts to a higher frequency, with the activation energies ranging between 0.06 and 0.08 eV.

Ac conductivity as a function of temperature and frequency

Ac conductivity (σ_{ac}) values are calculated from dielectric measurements using the following expression¹⁴:

$$\sigma_{ac} = f \epsilon' \tan \delta / 1.8 \times 10^{10} \quad (2)$$

The conductivity of an amorphous substance is governed by

$$\sigma_{ac} \propto f^n \quad (3)$$

TABLE I
 T_g Activation Energy, and n Value of CAP-PVP Blends

Blend composition CAP/PVP	T_g values (°C)		Activation energy (eV)		n Value
	DSC.	Dielectric relaxation (Accuracy, $\pm 2^\circ\text{C}$)	Dielectric relaxation	Ac conductivity	
0/100 (PVP)	165	164	0.0678	0.0738	0.883
30/70 (CP-3)	159	160	0.0678	0.0699	0.850
50/50 (CP-5)	155	156	0.0732	0.0914	0.920
70/30 (CP-7)	150	151	0.0753	0.0861	0.980
100/0 (CAP)	142	142	0.0820	0.0799	0.855

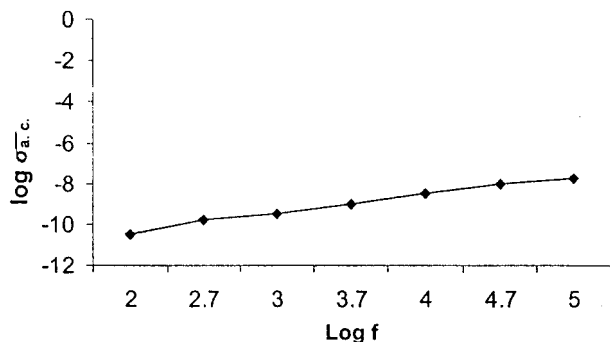


Figure 6 Variation of ac conductivity as a function of frequency at 300 K for CP-5 blend.

The index n is temperature-dependent and is within the limits $0.5 < n < 1$; n decreases with an increase in temperature. In the present study, σ_{ac} varies as a function of n , which lies between 0.85 and 0.98 for all blends in the frequency range of 100 Hz–50 kHz. A very weak temperature dependence is observed for PVP, CAP, and their blends (a typical plot is shown in Fig. 5). An increase in ac conductivity with the frequency and weak temperature dependence indicates that there may be charge carriers, which are transported by hopping through the defect sites along the chains.¹⁶ A representative plot of $\log \sigma_{ac}$ versus the frequency, $\log f$ (at 300 K for a CAP / PVP blend composition of 50/50), is given in Figure 6.

CONCLUSIONS

1. The dielectric constant and dielectric loss exhibit a single relaxation peak, corresponding to the T_g ,

for blends, and the temperature of the loss peak shifts between the two composition extremes extremes corresponding to PVP and CAP, showing that PVP forms a miscible blend with CAP.

2. From the relaxation behavior, the activation energy is found to lie between 0.06 and 0.08 eV.
3. Ac conductivity was deduced from the dielectric loss measurements, and a similar magnitude order of the activation energy for the dielectric relaxation and ac conductivity were observed.

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