Dielectric spectroscopy studies on (PVP + PVA) polyblend film

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Abstract

The thermal behavior of (PVP + PVA) polyblend film have been examined using differential scanning calorimetry and scanning electron microscopy. Capacitance and loss tangent values of polyvinyl pyrrolidone (PVP) + polyvinyl alcohol (PVA) polyblend film were measured in the frequency range 1–100 kHz and temperature range 298–423 K. Dielectric permittivity of real part (ε') was obtained from capacitance data and dielectric permittivity of imaginary part (ε'') was obtained from real part of dielectric permittivity and loss tangent values. The decrease in dielectric permittivity was observed with increasing frequency and also observed increase in dielectric permittivity with increasing temperature. The complex dielectric constant (ε^*) has been described by the electric modulus $M^* = (1/\varepsilon^*) = M' + iM''$. The data of M^* has been analysed by the stretched exponential decay of the electric field, $\Phi(t) = \exp-(t/\tau_0)^\beta$.
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1. Introduction

The dielectric properties of heterogeneous polymer materials play an important role in device applications such as high performance capacitors, electrical cable insulation, electronic packing and components. From the fundamental point of view, dielectric relaxation spectroscopy has been widely used to realize the microscopic dynamical relaxation process in complicated systems. The detailed investigation of the dielectric loss, an electrode and interfacial polarization effect of polymers is of great importance.

Polymer blending is a useful technique for designing materials with a wide variety of properties. An important commercial advantage is that polymer blends offer a way to produce new materials by using already existing polymers, which thus reduces development costs. Polyvinyl pyrrolidone (PVP) deserve a special attention among the conjugated polymers because of good environmental stability, easy processability, moderate electrical conductivity

and rich physics in charge transport mechanism. The local modification of the chemical structure induces drastic changes in electronic properties. The composite materials consisting of conducting medium in the insulating polymer matrix provide satisfactory mechanical as well as electrical properties. Polyvinyl alcohol is a potential material having a very high dielectric strength (>1000 kV/mm), good charge storage capacity and dopant-dependent electrical and optical properties. Both of the PVP and PVA are water-soluble and miscible in all proportions, PVA was selected as the component in the blend.

The study of dielectric loss as a function of temperature and frequency was used to characterize the molecular motion and dielectric relaxation behavior of the polymer [1,2]. In the present work, we have investigated systematically the dielectric properties of (PVP + PVA) polyblend film in range of frequency 1–100 kHz and temperature 298–423 K.

2. Experimental

Film (thickness 100 μm) of (PVP + PVA) polyblend was prepared in the weight percent ratio (50:50) with triple distilled water as a solvent using a solution-cast technique. The solution was stirred for 10–12 h and then poured into

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polypropylene dish and allowed to evaporate slowly at room temperature. The final product was vacuum dried thoroughly at 10^{-3} Torr.

For the DSC measurements a Netzsch DSC 200, operating in dynamic mode (heating rate = 10 K/min), was employed. Samples of ≈ 5 mg weight were placed in sealed aluminium pans. Prior to use the calorimeter was calibrated with metal standards; an empty aluminium pan being used as a reference. The morphology of the samples was characterized by an JSM-5610LV scanning electron microscope (SEM).

Dielectric measurements were made using Aglient 4294A precision impedance analyzer in the range 1–100 kHz and temperature range 298–423 K. The temperature was measured by copper–constantan thermo couple. The specimen is placed in a vacuum jig with uniform pressure contact to avoid stay capacitance.

3. Results and discussion

The interaction parameter (α) for this blend is positive and the variation of ultrasonic velocity with blend composition is found to be linear. These two observations indicate that the blend is miscible in all proportions. So there will not be any phase separation.

DSC results show that there is a single glass transition temperature (T_g) in the region 95–100 °C (Fig. 1), evidencing the blend miscibility.

By using the SEM technique, the morphology of PVP/PVA blend was studied. It is a uniform type, but with differing degrees of roughness (Fig. 2). Which suggest that the PVP molecules may disperse in the soft-segment phase with little influence on the microphase separation and mixing of the hard and soft segments. Thermal stability was evaluated on the basis of TG data. It has been found that in this blend under investigation degrade thermally through a similar step route (Fig. 3).

The initial decomposition temperature (IDT) was it reached 175 °C. The maximum rate of decomposition was
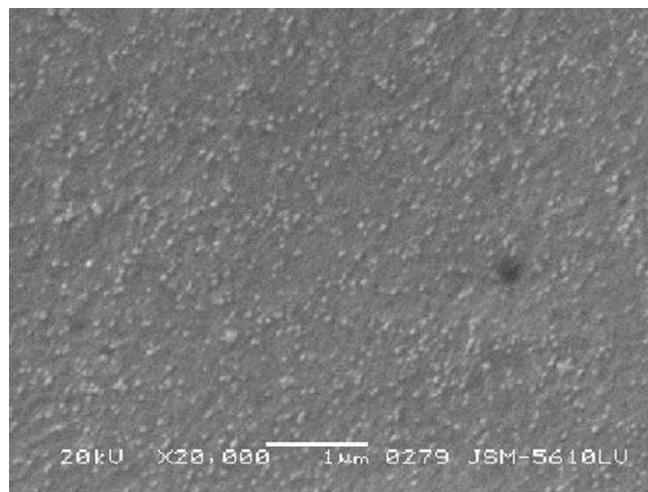

Fig. 2. SEM microphotograph of (PVP + PVA) polyblend film.

ascertained on the basis of first derivative of TG curve and lay in the range 400–475 °C it seems that conditions of diffusion of gaseous products through polymer matrix are decisive for better stability of this polymer blend. It is note worthy that for the blend under investigation the 1:1 w/w composition of PVP/PVA was still retained, as described in the material part of the experimental.

It is however, essential to note that this sample thermally stable up to 150 °C which is usually high enough temperature for processing and storage. However, in special thermoplastic processing under high temperature and shear stresses, and in reaction injection moulding during which the temperature in the center of the mould may exceed 150 °C owing to the high reaction exotherm, thermal degradation may occur. This thermal dissociation may not be totally disadvantageous from the processing point of since it allows molecular rearrangements by breaking the already made vinyl alcohol bonds.

The dielectric response is generally described by the complex permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, where real ε' and imag-
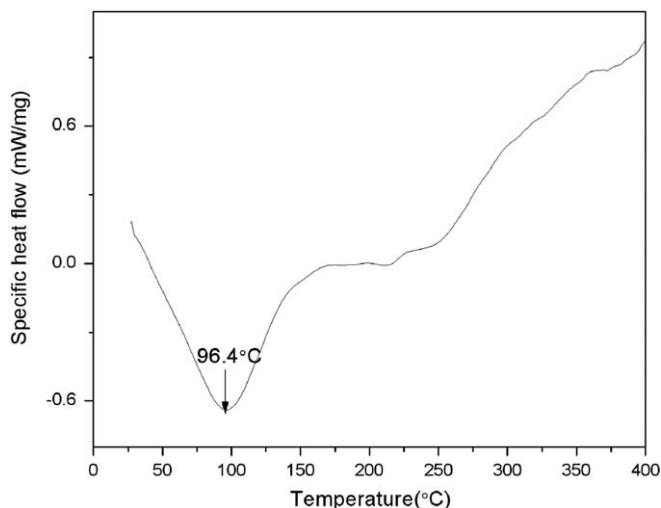

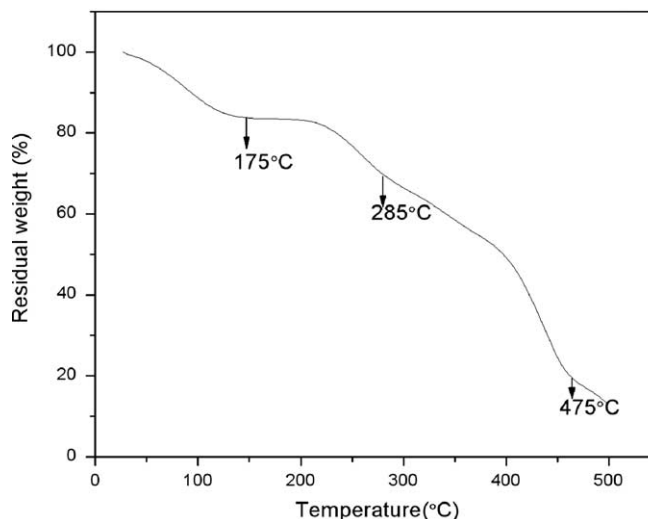Fig. 1. DSC curve of (PVP + PVA) polyblend film.

Fig. 3. TG curve of (PVP + PVA) polyblend film.

inary ε'' components are the storage and loss of energy in each cycle of applied electric field. The frequency dependence of ε' and ε'' for the film of (PVP + PVA) at various temperatures is shown in Fig. 4(a) and (b). The values of ε' and ε'' are very high at low frequency and high temperature, but at high frequency these are relatively constant with frequency. Similar behavior was observed in a number of polymers [3–7]. Such high values of ε' may be due to the interfacial effects with in the bulk of the sample and the
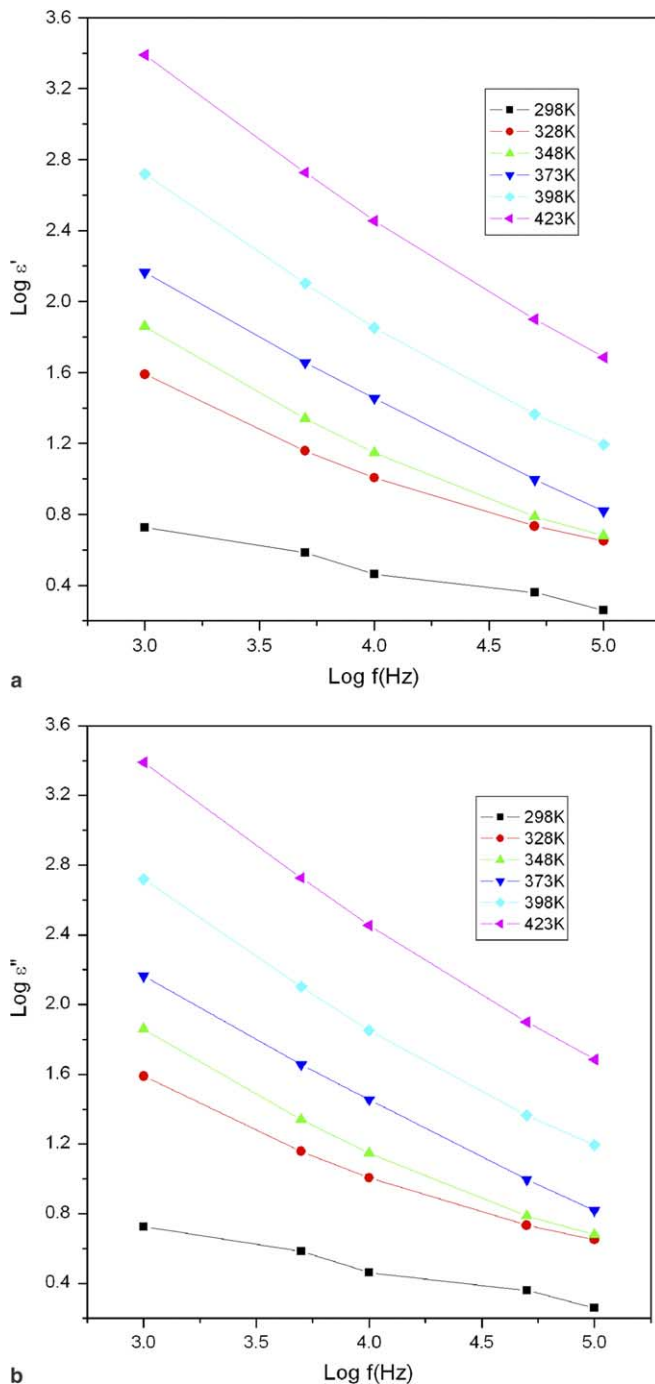

a

b

Fig. 4. (a) Plots of log of real part of dielectric permittivity vs. log of frequency at different temperatures. (b) Plots of log of imaginary part of dielectric permittivity vs. log of frequency at different temperatures.

electrode effects [8]. At high frequencies, the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. The polarization due to the charge accumulation decreases, leading to the decrease in the values of ε' and ε'' [9,10]. The large value of ε'' is also due to the motion of free charge carrier with in the material. As a result of it, a power law dispersion in ε'' is observed and it does not reveal any peak in the measure frequency range.

From Fig. 4(a) and (b), it is also clear that the dielectric permittivity real and imaginary values are found to increase with increasing temperature and attains a constant value at higher frequencies. The variation of ε' and ε'' with temperature is different for non-polar and polar polymers. In general, for non-polar polymers the ε' and ε'' are independent of temperature, but in the case of strong polar polymers the dielectric permittivity increases as the temperature increases. However, since the specific volume of the polymer is temperature dependent, i.e., it increases, as the temperature increases, the dielectric permittivity decreases with increase of temperature in the case of weak polymers [11].

Different formalisms [12] such as complex permittivity ε'', complex electric modulus M^*, complex impedance Z^* have been explored to interpret the dielectric spectra. The main advantage of M^* formalism is that the electrode effect can suppressed [13]. As the electrode effect is important in the system, we have analyzed the dielectric spectra by M^* which can be evaluated from the following relations:

$$M' = \varepsilon'/(\varepsilon'^2 + \varepsilon''^2), \tag{1}$$

$$\text{and } M'' = \varepsilon''/(\varepsilon'^2 + \varepsilon''^2). \tag{2}$$

The calculated values of M' and M'' are shown in Fig. 5(a) and (b) at various temperatures for the film (PVP + PVA). The asymptotic values M_∞ (high frequency limit of M') increase with increasing of temperature. The almost zero values of M' at low frequency indicate the removal of electrode polarization. The spectrum of M'' shows an asymmetric peak approximately centered in the dispersion region of M'. The peak shifts to higher frequencies with the increasing temperature.

The broad and asymmetrical shape of electric modulus are generally described by the stretched exponential decay function of the electric field [14] as

$$\Phi(t) = \exp -(t/\tau_0)^\beta. \tag{3}$$

The stretching parameter $\beta = 1.14/w$, where w being the full-width at half-maximum (FWHM) and it is 1.14 for Debye relaxation. The complex electric modulus [15] has been estimated as

$$M^* = M_\infty[1 - \int_0^\infty -\mathrm{d}\Phi(t)/\mathrm{d}t \cdot \exp(-\mathrm{i}wt)\,\mathrm{d}t]. \tag{4}$$

The spectra of M' and M'' are well fitted by Eq. (4) as indicated in Fig. 6(a) and (b). The best fitted value of $\beta = 0.912$ for (PVP + PVA) film, which gives w is 1.25. The peak frequency f_p as a function of temperature can be described by Arrhenius equation as,
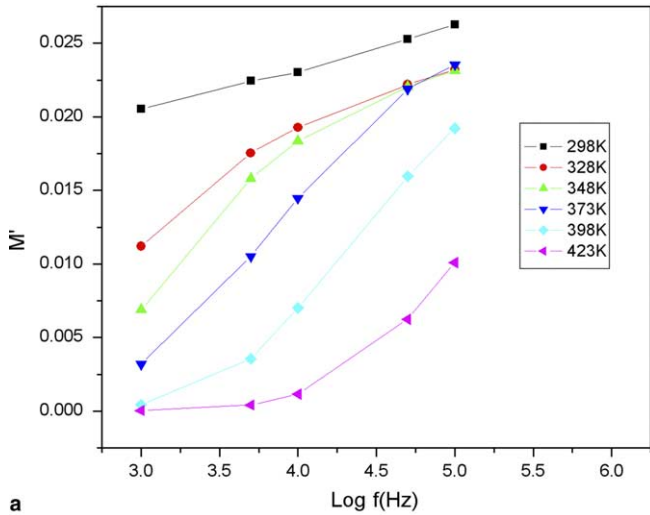
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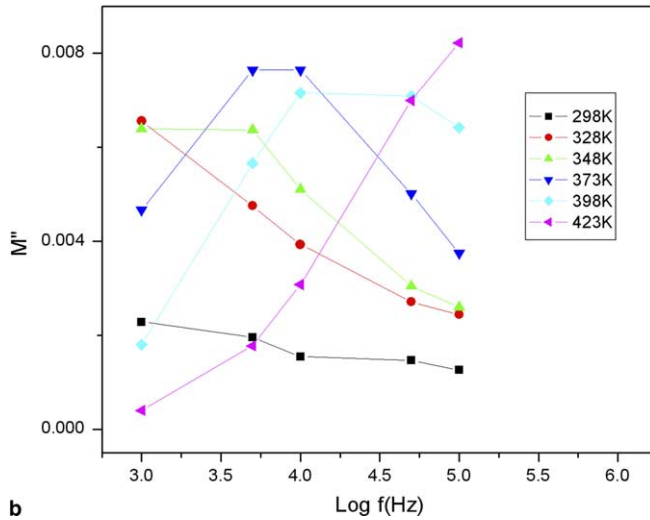
b

Fig. 5. (a) Plots of the electric modulus of real part (M') vs. log of frequency (log$f$) at different temperatures. (b) Plots of the electric modulus of imaginary part (M'') vs. log of frequency (log$f$) at different temperatures.

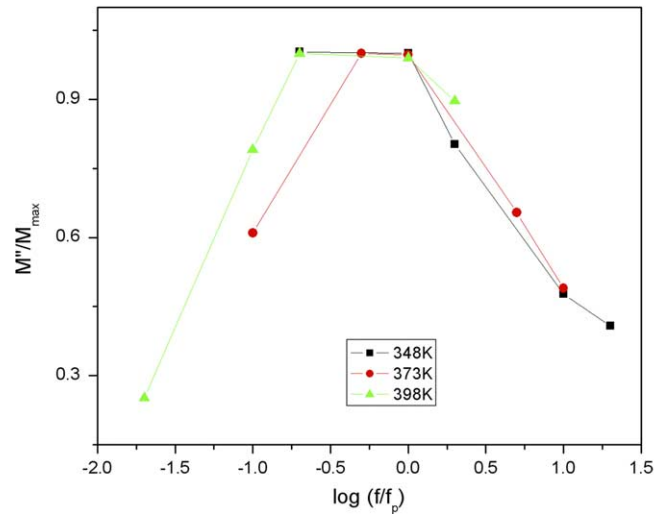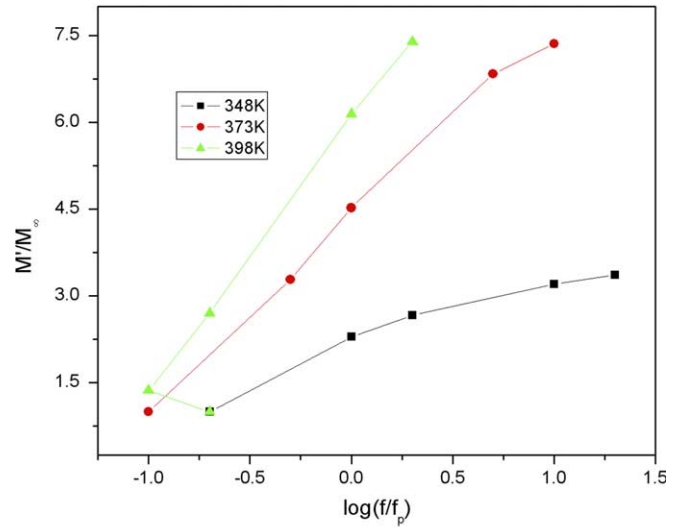Fig. 6. (a) Plots of the M'/M_∞ vs. log(f/f_p) at different temperature. (b) Plots of the M''/M_{max} vs. log(f/f_p) at different temperatures.

$$f_p = f_{p0} \exp(-E_a/kT), \qquad (5)$$

where f_{p0} is a constant and k is the Boltzman constant. The calculated value of the activation energy $E_a = 0.065$ eV.

The shape of M'' is constant with temperature but it may be changes with the variation of composition. Thus M'' spectra at different temperature can be scaled so that it collapse on to a master curve as shown in Fig. 6(b).

Fig. 7 shows the variation of loss tangent (tanδ) with temperature at frequencies 1, 5, 10 and 100 kHz. From the plots, it is clear that a loss peak was observed at a temperature (368 K), i.e., below the melting temperature (383 K) for a field frequency of 1 kHz. In general, polymers posses three dielectric relaxations, α, β and γ in decreasing order of temperature. For amorphous polymers α-peak is absent, β and γ peaks occur at temperature less than the melting temperature in that order. XRD studies revealed the amorphous nature of the (PVP + PVA) polyblend film. The relaxation peak in the present investigations may be
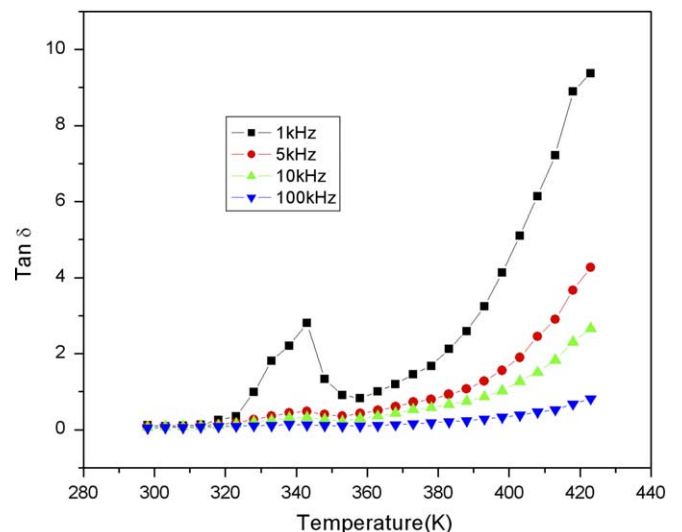

Fig. 7. Plots of the loss tangent (tanδ) vs. temperature at different frequencies.

attributed to β-relaxation, which may be due to the orientation of the polar groups N–O, O–H and C=O present in the groups of polymer blend. This type of relaxation is called a dipolar group relaxation [16]. In amorphous regions, the chains are irregular and entangled where as in crystalline regions the chains are regularly arranged. Hence, it is very easy to move the molecular chains in the amorphous state rather than the crystalline state. The molecular packing in the amorphous state is weak and so the density is smaller than that of crystalline regions. Thus, the chains in the amorphous phase are more flexible and are capable of orienting themselves relatively more easily and rapidly. The dipoles N–O and C=O in the side chain of the polymer blend will orient themselves with certain frequencies governed by the elastic restoring force which binds the dipoles to their equilibrium positions and the rotational frictional forces exerted by neighboring dipoles. In the amorphous phase, dipolar molecules should be able to orient from one equilibrium position to another relatively more easily and contribute to absorption over a wide frequency or temperature range. Since (PVP + PVA) polymer blend is amorphous in nature, the dipolar molecules should be able to orient from one position to another more easily and will contribute to absorption over a wide frequency and temperature range [3,17]. Further work is in progress to understand the role of different compositions of the PVP/PVA on the dielectric behavior of the polymer blend.

4. Conclusions

Thermal characteristics of (PVP + PVA) blend have been assessed by thermal analysis method. Decomposition route was found to be of a two-step process. The large value of ε' at low frequency arises from the electrode polarization rather than the interfacial polarization within the material. The components of electric modulus at various temperatures follow the scaling law with stretching parameter $\beta = 0.912$. The relaxation time satisfies the Arrhenious relation having the activation energy 0.065 eV. The dielectric behavior exhibits a β-relaxation peak; this may be due to orientation of the polar groups present in the polymer blend matrix.

Acknowledgement

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