

Biodegradable Blends Based on Polyvinyl Pyrrolidone for Insulation Purposes

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ABSTRACT: Polyvinyl pyrrolidone/polyvinyl alcohol (PVP/PVA) and polyvinyl pyrrolidone/starch (PVP/St) blends were prepared with different compositions. The compatibility studies indicate that PVP/PVA is compatible while PVP/St is incompatible. The addition of glycerol and glutaraldehyde can improve to some extent the phase separation behavior between PVP and St. The permittivity ϵ' and the dielectric loss ϵ'' were measured in the frequency range 0.01 Hz up to 10 MHz and temperatures from 30 up to 90°C. It is found that the blend ratio (50/50) of both investigated systems is preferable for insulation purposes in comparable with the other blends under investigation. The data of the loss electric modu-

lus M'' was calculated from the dielectric parameters ϵ' and ϵ'' and analyzed into three relaxation mechanisms ascribing the cooperative motion of the main and side chains τ_1 ($\alpha\beta$), the side chain motion τ_2 (β) and the segmental motion of the groups attached to the side chains τ_3 ($\beta\gamma$). The activation energy corresponds to the second relaxation process ΔH_2 was calculated using Arrhenius equation and found to be in the range which justifies the presumption of β -relaxation process. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3879–3891, 2012

Key words: biodegradable polymers; blends; dielectric; compatibility

INTRODUCTION

Biodegradable polymeric materials have potentials in electric and electronic applications such as fabrication of cellular phones or computer laptop casings.¹

Polyvinyl pyrrolidone (PVP) and polyvinyl alcohol (PVA) are water soluble, synthetic biodegradable polymers and form high degree of complexes with large variety of additives/dopants.^{2–5} Ragab et al. studied the structural and electrical properties of PVA/PVP (50/50) blend filled with different concentrations of NiCl₂ to use the final product in some technical application. The X-ray diffraction analysis demonstrated the complexation between the filler and the polymers blend, which takes place in the polymeric network. This is because the interaction between the blend and the filler leads to decrease in intermolecular interaction between the polymers blend chains.⁶

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.⁷

Starch is a natural polymer that is totally biodegradable in a wide variety of environments.^{8,9} Owing to its complete biodegradability,¹⁰ low cost, and renewability,¹¹ starch is considered as a promising candidate for developing sustainable materials for conserving the petrochemical resources, reducing environmental impact and searching more applications.^{12–14}

Films prepared from starch are often too fragile to stand handling, e.g., bending or stretching. Those films have to be plasticized using low molecular weight substances, such as glycerol. Plasticizer is added to the film to give better handling properties like flexibility and elasticity.¹⁵ However plasticized starch alone swells and deforms on exposure to moisture.^{16–18} The crosslinking of starch macromolecules with glutaraldehyde is one of the most common way to reduce the solubility of polysaccharides by formation of intermolecular bridges between the polysaccharide macromolecular chains.¹⁹

Recently, much attention has been paid to the development of polymeric blends. 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.⁷ An important factor in the development of new materials based on polymeric blends is the miscibility between the polymers in the mixture, because the

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degree of miscibility is directly related to the final properties of polymeric blends.²⁰ Therefore, to obtain a one-phase system in polymer blends, it is usually necessary to ensure that favorable specific intermolecular interaction exists between two base components of the blend, for example, hydrogen bonding.^{21–23}

The miscibility of PVA/PVP blends was studied using viscosity measurements of dilute solutions of blend,²⁴ SEM,²⁵ DSC,^{7,25,26} and FTIR.^{27–29} The authors found that the (SEM) micrographs of PVA/PVP blend showed a smooth area²⁵ and exhibit single glass transition temperature as was evidenced from the (DSC) results.^{7,25,26} It was also found that there is hydrogen bonding between the hydroxyl group of PVA and the carbonyl group of PVP as it was evidenced from the FTIR^{27–29} which indicates the homogeneity between the polymer blends.

Blending of PVP with starch also form hydrogen bonds between OH in starch and C=O of pyrrolidone group in PVP.³⁰

The polymeric materials need further evaluation of dielectric properties which included space charge distribution, permittivity, conductivity, and dielectric strength³¹ to fulfill electrical safety standards as well as resistance to fire.³² 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.⁷

Several authors have studied the blend miscibility by comparing the dipolar losses at glass transition and have shown how both the glass transition temperature and the width of the loss peaks are affected by the miscibility of the components.^{33–35}

Therefore, the aim of this study is to develop eco-friendly biodegradable polymer blends based on PVP with low environmental loads (i.e., PVP is a biodegradable polymer so it doesn't add pollution to the environment) which can be easily decomposed and recommended to be used as electrical insulating materials. The compatibility of such blends will be investigated through the scanning electron microscopy and viscosity studies. In this work, a review on their various dielectric properties is studied.

EXPERIMENTAL

Materials

Poly (*N*-vinyl-2-pyrrolidone) PVP with an average molecular weight of (40,000) supplied by Merck from Germany. Polyvinyl alcohol PVA with an average molecular weight (85,000) supplied by Qualikems from India. Potato starch with an average

molecular weight of the monomer (162.14) n supplied by Fluka from United States. Glutaraldehyde (25%) supplied by Qualikems from India. Glycerol supplied by Fluka from United States.

Preparation of the polymer blend by the solution casting technique

A series of PVA/PVP and PVP/starch blends were prepared with different compositions (100/0.0, 75/25, 50/50, 25/75, and 0.0/100) by the solution casting method. Aqueous solutions of individual polymers of PVA and PVP were prepared separately. First, PVA solution was prepared by dissolving 3.5 g PVA in 75 ml distilled water (95°C) for 30 min then PVP solution was prepared by dissolving 3.5 g PVP in 75 mL distilled water at room temperature for 10 min. For PVP/St blend, first starch and glycerol in the ratio (70/30 wt/wt) were mixed together with water using magnetic stirrer for 10 min, then glutaraldehyde with concentration 10% (based on starch weight) was added as crosslinking agent for starch. The mixture were mixed with stirring for 30 min at 60°C and kept at 90°C for 15 min. After mixing, the mixture was poured into glass Petri dishes packaged with Teflon paper to avoid the adherence of the casted films. The cast solution was allowed to dry at 60°C in an oven for 24 h. after evaporation, the films were removed from the Petri dishes and kept in vacuum desiccators to ensure the total elimination of the water and then used for further studies.

Viscosity measurements

All measurements were performed at (30 ± 0.1°C) with an Avs 350 automatic Ubbelohde-type capillary viscometer from Schott-Geraete (Hofheim, Germany). The instrument was also equipped with a model K100 thermo stated bath. Stock solutions of each system were prepared and diluted to yield five concentrations (1, 0.8, 0.7, 0.6, and 0.4 g/100 mL) made by the addition of appropriate amounts of water to the stock solutions. The elution time of each solution is then determined as the average of three readings. In this case, the liquid meniscus was sensed optoelectronically at the measuring levels. These precision devices always ensured the high accuracy of the capillary viscometer.

Scanning electron microscopy

SEM model JSM-T20 JEOL, Japan was used to characterize the blend morphology. SEM was performed by mounting the polymer blend samples on standard specimens tub, and then created with very thin layer of gold by deposit.

Broad-band dielectric relaxations measurements

Circular discs with a diameter of 12 mm were used for dielectric studies. These studies were carried out using an impedance analyzer (Schlumberger Solartron 1260), an electrometer, amplifier, and measuring cell as described before.³⁶ The permittivity ϵ' , loss factor $\tan \delta$, and ac resistance $R_{a.c}$ were measured at different temperatures and different frequencies 1–5 MHz. The measurements were automated by interfacing the impedance analyzer with a personal computer through a GPIB cable IEE488. A commercial interfacing and automation software Lab VIEW was used for acquisition of data. The error in ϵ' and $\tan \delta$ amounts to 1 and 3%, respectively. The temperature of the samples was controlled by a temperature regulator with Pt 100 sensor. The error in temperature measurements amounts 0.5°C. To avoid moisture, the samples were stored in desiccators in the presence of silica gel. Thereafter the sample was transferred to the measuring cell and left with P₂O₅ until the measurements were carried out.

RESULTS AND DISCUSSION

Compatibility study

Viscosity measurements

Viscosity measurement has been applied to investigate the compatibility of both PVP/PVA and PVP/St blends in dilute solution with different blend composition (100/0, 75/25, 50/50, 25/75, 0/100). The nature of viscosity of dilute polymer solutions is based on analyzing hydrodynamic properties related to the movement of macromolecules in solutions. The two phase structures of polymer mixtures and deformation of drops in flow mixture depend not only on the component ratio but also on the value of the viscosity, which is estimated from the degree of deviation of viscosity from the initial viscosity. The compatibility of the polymer blends can be deduced from³⁷:

$$(\eta_{sp}/C) = [\eta_i] + K[\eta_i]^2 C$$

where η_{sp} is the specific viscosity, C is the concentration in g/100 mL, $[\eta_i]$ is the intrinsic viscosity, and K is constant. A linear relationship is obtained by plotting η_{sp}/C against the concentration C as shown in Figures 1(a) and 2(a) for PVP/PVA and PVP/St respectively. From the intercept of these lines with the y -axis, the intrinsic viscosity $[\eta_i]$ is obtained. The plots of $[\eta_i]$ versus the PVP content are illustrated graphically in Figure 1(b) for PVP/PVA and Figure 2(b) for PVP/St. It is clear that the values of $[\eta_i]$ are coincide with the line connecting the two individuals for PVP/PVA blends within the

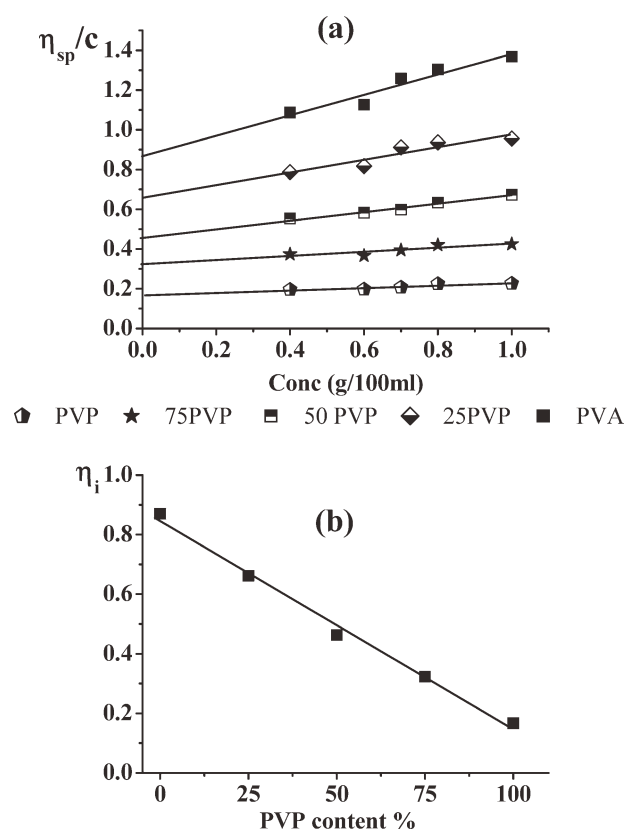


Figure 1 (a) Variation of the specific viscosity η_{sp}/c versus concentration (b) Variation of the intrinsic viscosity $[\eta_i]$ versus PVP content in PVP/PVA blend at 30°C.

experimental error (do not exceed 2%). This means that these blends are compatible. This compatibility could be attributed to the hydrogen bond interactions between the C=O groups of PVP and OH groups in PVA, in the amorphous zone of the blend.

On the other hand, the values of $[\eta_i]$ are found to be negatively deviates from the line connecting the two individuals for PVP/St blends (i.e., these values are lower than the theoretical values calculated from the line connecting the two individuals). This deviation could lead to some sort of incompatibility in such blends. Glycerol was chosen as a low molecular weight material that is added to PVP/St blends as a plasticizer to starch and at the same time as a compatibilizer agent for such system. Also glutaraldehyde is added as a crosslinking agent. In solution, glutaraldehyde is added as a crosslinking agent to starch and it acts as a compatibilizer agent to PVP/St blends. So it is easy to measure the viscosity of the solution contains PVP/St blends with both glycerol and glutaraldehyde.

Figure 3(b) represents the variation of $[\eta_i]$ versus the PVP content in PVP/St blends after the addition of glycerol and glutaraldehyde. It is seen from this figure that the values of $[\eta_i]$ are coincide with the

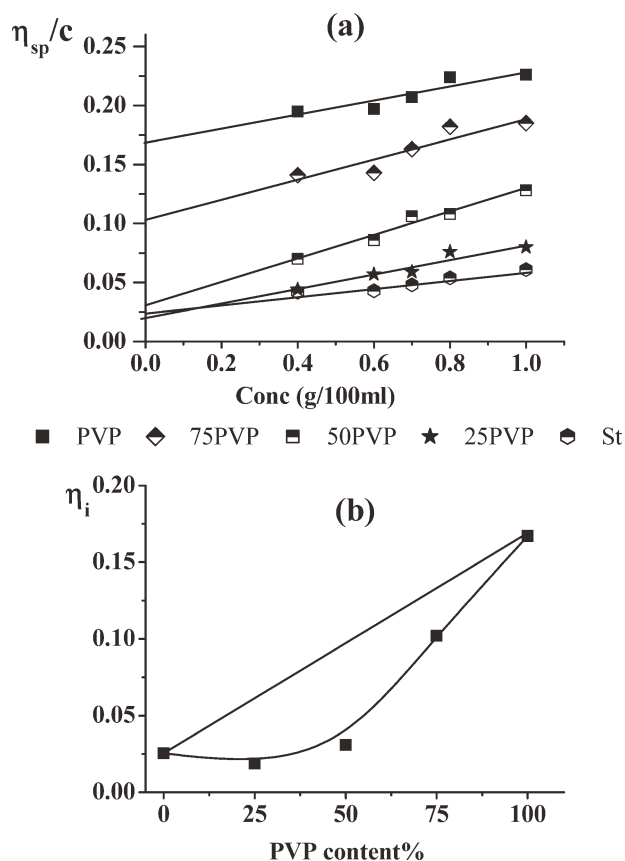


Figure 2 (a) Variation of the specific viscosity η_{sp}/c versus concentration (b) Variation of the intrinsic viscosity $[\eta_i]$ versus PVP content in PVP/St blend without glycerol and glutaraldehyde at 30°C.

line connecting the two individuals which indicates that the addition of glycerol and glutaraldehyde solve to some extent the problem of phase separation of such blends.

Scanning electron microscopy

The SEM micrographs of PVP, PVA, and the blend of PVP/PVA with ratio (50/50) are shown in Figure 4. From this figure it is clear that a fine morphology is observed for the sample PVP/PVA (50/50) blend where the surface appeared to be smooth and uniform indicating the compatibility between PVP and PVA.

The SEM micrographs of PVP, starch and the blend of PVP/St (50/50) with glycerol and glutaraldehyde are compared with that of the sample without glycerol and glutaraldehyde as shown in Figure 5. From this figure it is seen that the sample PVP/St (50/50) before the addition of glycerol and glutaraldehyde shows two phases as the starch granules appear very easy to aggregate due to the strong interaction of intermolecular and intramolecular hydrogen bonds of starch molecules³⁸ and show a tendency to form clusters as implied by the presence

of elongated cavities, and droplet coalescence probably started taking place, indicating the less compatibility between PVP and starch.³⁰ These results are also due to the large difference between the relative viscosity of PVP and starch.³⁰ After the addition of glycerol and glutaraldehyde the surface appeared to be smooth and uniform with no exposed starch granules where there is better dispersion of starch in the PVP matrix. The addition of small molecules of plasticizer can weaken the hydrogen-bond interactions of starch molecules preventing their close packing through the formation of hydrogen bonds between the plasticizer and starch thus the starch granule aggregates can be destroyed providing the starch thermoplastic ability and processibility as normal plastics.³⁸ The solubility of PVP in glycerol is due to the formation of hydrogen bonds between the carbonyl groups of PVP monomer units and the hydroxyl groups of the glycerol molecules (heterogeneous H-bond in the PVP- glycerol blends).³⁹ The addition of glutaraldehyde formed a covalent bond at the PVP/starch interface, so that the interfacial adhesion was enhanced indicating improvement in compatibility between PVP and starch.

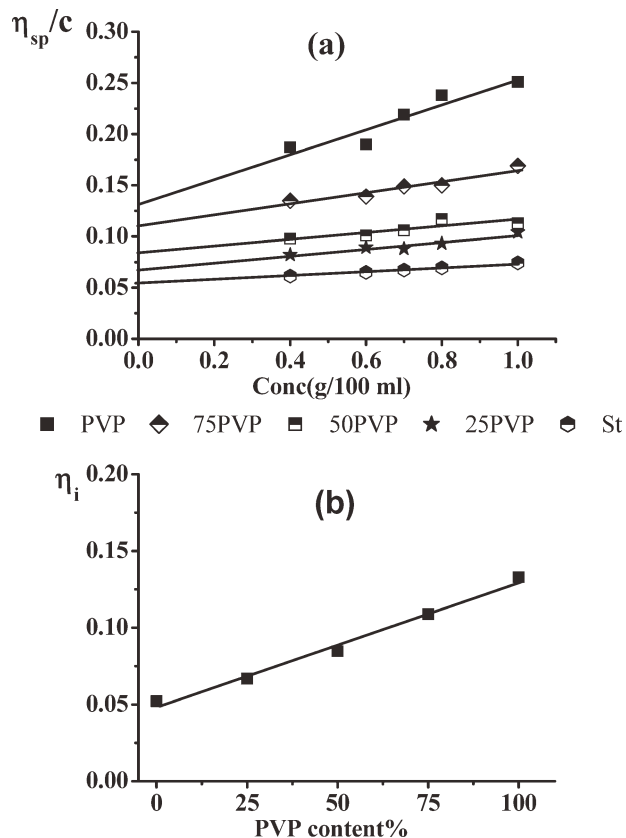


Figure 3 (a) Variation of the specific viscosity η_{sp}/C versus concentration (b) Variation of the intrinsic viscosity $[\eta_i]$ versus PVP content in PVP/St blend with glycerol and glutaraldehyde at 30°C.

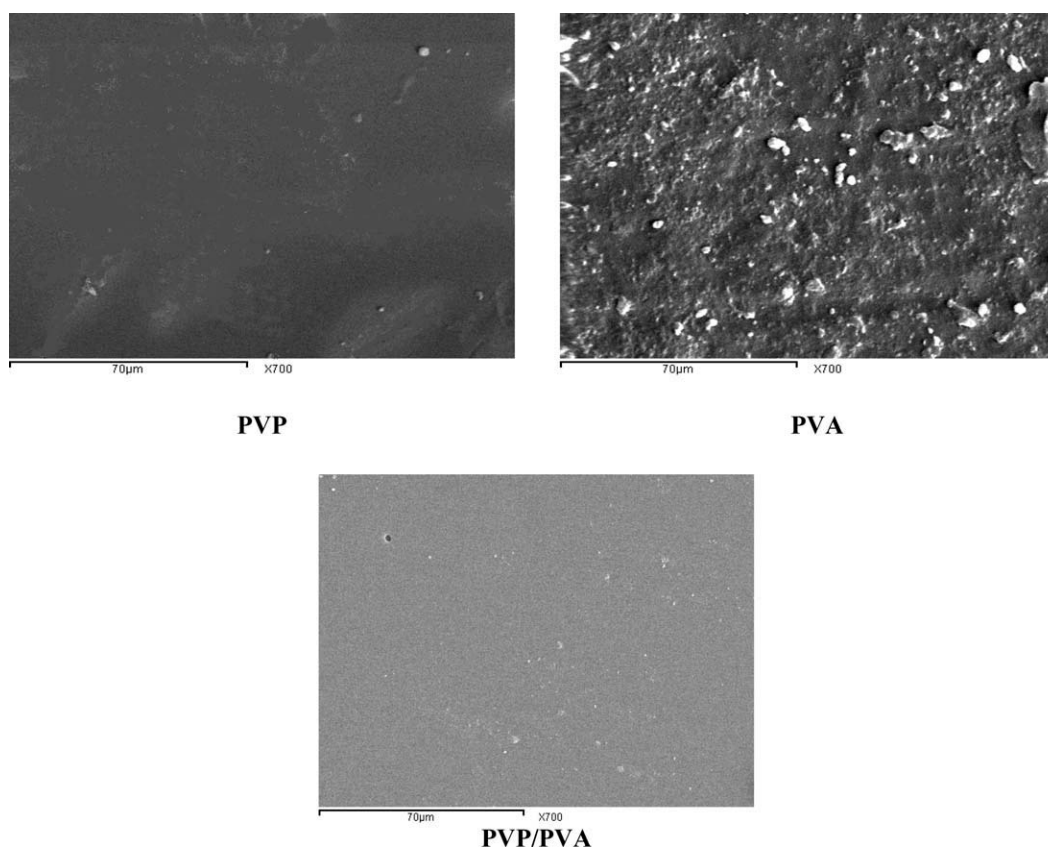


Figure 4 The scanning electron micrograph of PVP/PVA blend.

DIELECTRIC STUDY

PVP/PVA blends

The permittivity ϵ' and the dielectric loss ϵ'' were measured in the frequency range 0.01 Hz up to 10 MHz and temperatures from 30 up to 90°C for PVP/PVA blend with different blend ratios (0/100, 75/25, 50/50, 25/75, and 100/0). Example of the obtained data is illustrated graphically in Figure 6(A) for 30°C (a) and 90°C (b). From this figure it is seen that the values of ϵ' and ϵ'' are very high at low frequency and high temperature, but at higher frequencies these are relatively constant. Similar behavior was observed in a number of polymers.^{7,40,41} Such high values of ϵ' may be due to the interfacial effects within the bulk of the sample and the electrode effects.^{42,43} The values of both ϵ' and ϵ'' are found to be comparable with those found before in literature.⁴⁴

When an electric field is applied to the materials, the long-range drift of ions and barrier layer formation on the electrode surface result large values of permittivity and dielectric loss.^{45,46} 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 a decrease in the values of ϵ' and ϵ'' .^{47,48}

The permittivity ϵ' is plotted graphically versus PVP content at fixed frequency ($f = 100$ Hz) and at 30°C as shown in Figure 7. The linear relationship obtained indicates that PVA/PVP blends are compatible.

It was observed that the PVA rich blend has higher ϵ' values, because of the higher strength of hydrophilic effect of PVA system, i.e., the presence of many hydroxyl groups whereas the PVP rich blend show the lower ϵ' values because of the less hydrophilic effect of PVP, and in between these the ϵ' value of PVA / PVP blend systems. From these observations it can be concluded that around equal volume concentration of the blend, the net enhancement in polarization is zero. This may be due to neutralization of the PVA hydrophilic effect contribution in polarization by the PVP hydrophobic effect.⁴³

To understand the variation of both ϵ' and ϵ'' with temperatures, both values were plotted graphically in Figure 8 versus temperature at fixed frequency $f = 100$ Hz. From this figure it is clear that both ϵ' and ϵ'' increase with increasing temperature. This increase may be due to the presence of polar groups and the amorphous nature of both types of polymers.

From this figure it is also notable that the increase of ϵ' is accompanied by an acceptable increase in ϵ''

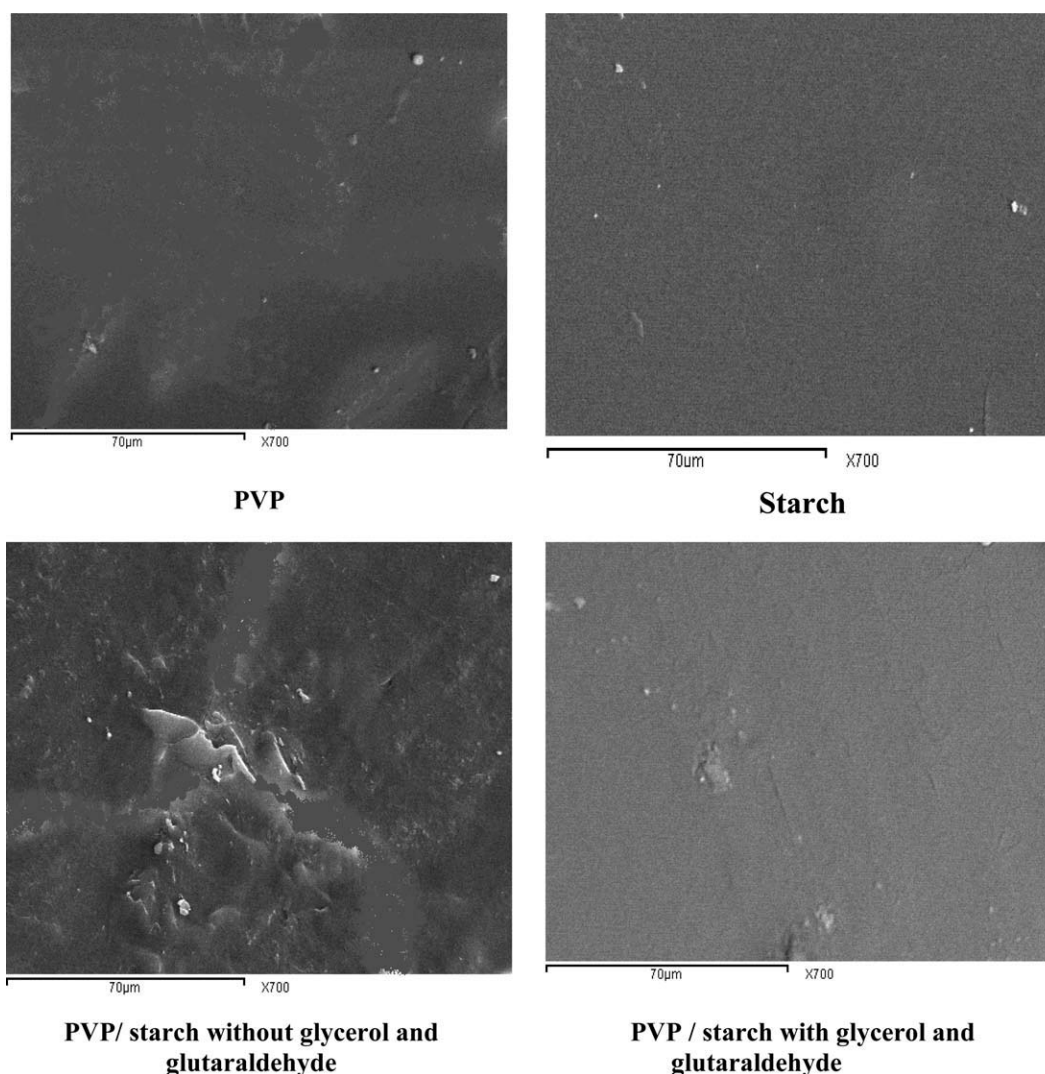


Figure 5 The scanning electron micrograph of PVP/St blend.

uptill concentration of 50% of PVA. After this concentration the increase in ϵ' is accompanied by a higher increase in ϵ'' values which loose to some extent these concentrations their insulation properties. For such reason and in order to get high performance insulating properties it is preferable that the concentration of PVA does not exceed 50% and also for the same reason the temperature does not exceed 50°C as the loss values are less than 1 for frequencies higher than 100 Hz.

The dielectric spectra ϵ'' versus the applied frequency f , as shown from Figure 6(A), seem to be complicated to be analyzed due to the superposition of more than one microdynamic process in addition to the electrical conductivity term. For such reason, the loss electric modulus M'' was calculated according to the relation⁷ and the obtained data are illustrated graphically in Figure 6(B).

$$M'' = \frac{\epsilon'^2}{\epsilon'^2 + \epsilon''^2}$$

The main advantage of this formalism is that the space charge effects often do not mask the features of the spectra, owing to the suppression of high capacitance phenomena in $M''(f)$ spectra thus the electrode effect can suppressed.⁷

The obtained data were analyzed for all blend ratios and at various temperatures in terms of three superimposed processes using the proper functions by using a computer program design especially for such purpose.⁴⁴

Example of the analyses was given in Figure 9 for PVP, PVP/PVA (50/50), and PVA respectively at 30°C.

The first relaxation process τ_1 in the low frequency range was fitted by Havriliak–Negami function and

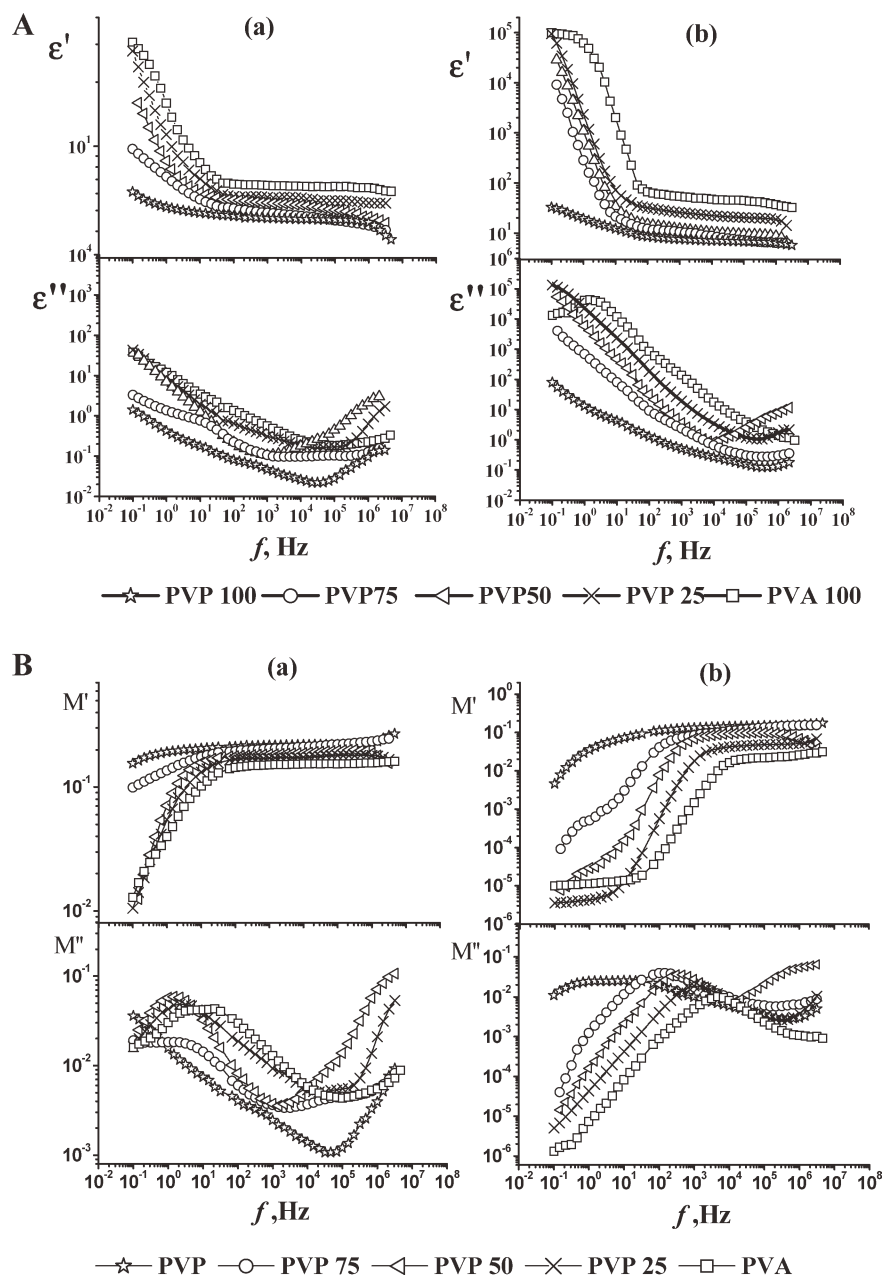


Figure 6 (A) Permittivity ϵ' and dielectric loss ϵ'' versus frequency f of PVP/PVA blend at: (a) 30°C (b) 90°C. (B) Real part of modulus M' and loss part of modulus M'' versus frequency f of PVP/PVA blend at: (a) 30°C (b) 90°C.

found to be highly affected by increasing temperature. According to Arrhenius equation⁴⁴ the activation energy ΔH corresponds to this relaxation process was calculated and found to be in the range 16.72–25.08 kcal mol⁻¹. This mechanism has been attributed to a crankshaft type of motion of the main polymeric chain in which a few segments are involved ($\alpha\beta$).⁴⁹

The third relaxation process τ_3 which lies at the higher frequency range with a maximum out of the available frequency range and fitted by Fröhlich function with distribution parameter $P = 3$ could be attributed to the segmental motion of the groups attached to the side chains ($\beta\gamma$). This may be due to

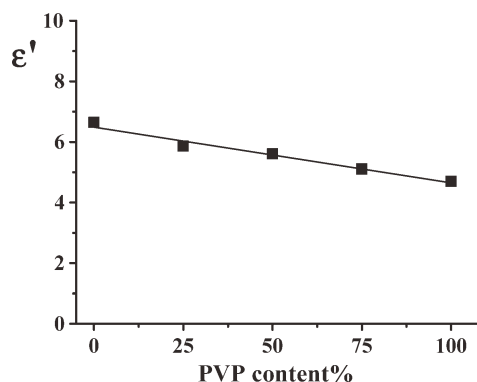


Figure 7 Variation of the permittivity ϵ' at $f = 100$ Hz 30°C versus PVP content in PVP/PVA blend.

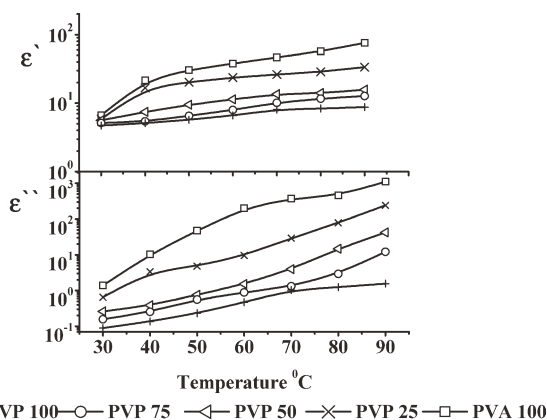


Figure 8 The permittivity ϵ' and dielectric loss ϵ'' at $f = 100$ Hz versus temperature in PVP/PVA blend.

TABLE I
The Relaxation Time For PVP/ PVA Blends at Different Temperatures

Sample	τ_1 s	τ_2 s	τ_3 s
At 30°C			
PVP	3.642	8.745E-6	2.336E-8
(PVP 75/PVA 25)	1.223	6.213E-6	1.997E-8
(PVP 50/PVA 50)	0.1842	4.757E-6	1.715E-8
(PVP 25/PVA 75)	0.15	3.748E-6	1.252E-8
PVA	0.05359	2.5E-6	1.137E-8
At 40°C			
PVP	3.285	5.862E-6	1.901E-8
(PVP 75/PVA 25)	0.5082	4.006E-6	1.75E-8
(PVP 50/PVA 50)	0.1552	3.152E-6	1.675E-8
(PVP 25/PVA 75)	0.02353	2.53E-6	1.061E-8
PVA	0.00965	1.8E-6	9.252E-9
At 50°C			
PVP	1.301	3.95E-6	1.775E-8
(PVP 75/PVA 25)	0.2418	2.858E-6	1.7E-8
(PVP 50/PVA 50)	0.0594	2.237E-6	1.658E-8
(PVP 25/PVA 75)	0.02051	1.775E-6	9.576E-9
PVA	9.362E-4	1.32E-6	8.639E-9
At 60°C			
PVP	0.4196	1.8E-6	1.715E-8
(PVP 75/PVA 25)	0.119	1.665E-6	1.686E-8
(PVP 50/PVA 50)	0.02699	1.292E-6	1.602E-8
(PVP 25/PVA 75)	0.00708	1.177E-6	6.499E-9
PVA	2.543E-4	9.12E-7	5.724E-9
At 70°C			
PVP	0.1606	1.143E-6	1.654E-8
(PVP 75/PVA 25)	0.07415	1.073E-6	1.62E-8
(PVP 50/PVA 50)	0.01106	8.272E-7	1.548E-8
(PVP 25/PVA 75)	0.00236	7.519E-7	6.131E-9
PVA	1.52E-4	6E-7	5.53E-9
At 80°C			
PVP	0.09936	6.999E-7	1.548E-8
(PVP 75/PVA 25)	0.03774	6.253E-7	1.504E-8
(PVP 50/PVA 50)	0.00262	5.672E-7	1.456E-8
(PVP 25/PVA 75)	7.115E-4	5E-7	5.53E-9
PVA	1.196E-4	3.8E-7	4.991E-9
At 90°C			
PVP	0.0594	4E-7	1.5E-8
(PVP 75/PVA 25)	0.0042	3.898E-7	out of range
(PVP 50/PVA 50)	7.62E-4	3.477E-7	out of range
(PVP 25/PVA 75)	2.294E-4	3.24E-7	out of range
PVA	4.576E-5	2.5E-7	out of range

TABLE II
The Relaxation Time For PVP/Starch Blends at Different Temperatures

Sample	τ_1 s	τ_2 s	τ_3 s
At 30°C			
PVP	3.737	7E-6	8.987E-9
(PVP 75/St 25)	3.735	1.711E-5	9.825E-9
(PVP 50/St 50)	0.3677	7.546E-5	1.571E-8
(PVP 25/St 75)	0.01515	2.078E-4	2.6E-8
St	Out of range	7.76E-4	3.672E-8
At 40°C			
PVP	3.216	4E-6	8.032E-9
(PVP 75/St 25)	3.2	1.066E-5	9.183E-9
(PVP 50/St 50)	0.306	2.7E-5	1.223E-8
(PVP 25/St 75)	0.00392	1.4E-4	2.357E-8
St	Out of range	5E-4	2.528E-8
At 50°C			
PVP	1.637	2.071E-6	7.177E-9
(PVP 75/St 25)	1.653	4.905E-6	9.763E-9
(PVP 50/St 50)	0.2111	1.178E-5	out of range
(PVP 25/St 75)	7.01E-4	4.7E-5	1.667E-8
St	Out of range	1.4E-4	2.327E-8
At 60°C			
PVP	0.4572	1.136E-6	out of range
(PVP 75/St 25)	0.1668	2.497E-6	out of range
(PVP 50/St 50)	0.05286	5.999E-6	out of range
(PVP 25/St 75)	6.124E-4	2E-5	out of range
St	Out of range	6.001E-5	1.863E-8
At 70°C			
PVP	0.2242	6.472E-7	out of range
(PVP 75/St 25)	0.15	1.2E-6	out of range
(PVP 50/St 50)	0.01677	3.611E-6	out of range
(PVP 25/St 75)	1.878E-4	9.997E-6	out of range
St	Out of range	3.042E-5	1.741E-8
At 80°C			
PVP	0.08141	4.126E-7	out of range
(PVP 75/St 25)	0.0858	6.601E-7	out of range
(PVP 50/St 50)	0.00651	1.9E-6	out of range
(PVP 25/St 75)	9.241E-5	5.3E-6	out of range
St	Out of range	1.4E-5	1.373E-8
At 90°C			
PVP	0.0519	2.35E-7	out of range
(PVP 75/St 25)	0.0389	4E-7	out of range
(PVP 50/St 50)	0.0031	8.502E-7	out of range
(PVP 25/St 75)	3.972E-5	2.6E-6	out of range
St	Out of range	8.002E-6	1.1E-8

the orientation of the polar groups N—O, O—H, and C=O present in the side chain of the polymers. This type of relaxation is called a dipolar group relaxation.⁷ In amorphous regions, the chains are irregular and entangled whereas in crystalline regions the chains are regularly arranged. Thus, the chains in the amorphous phase are more flexible and are capable of orienting themselves relatively more easily and rapidly than the crystalline state. Since (PVP/PVA) polymer blend is amorphous in nature, the dipolar molecules OH, N—O, and C=O in the side chain of the polymer blend should be able to orient themselves from one position to another more easily with certain frequencies governed by the elastic restoring force which binds the dipoles to their

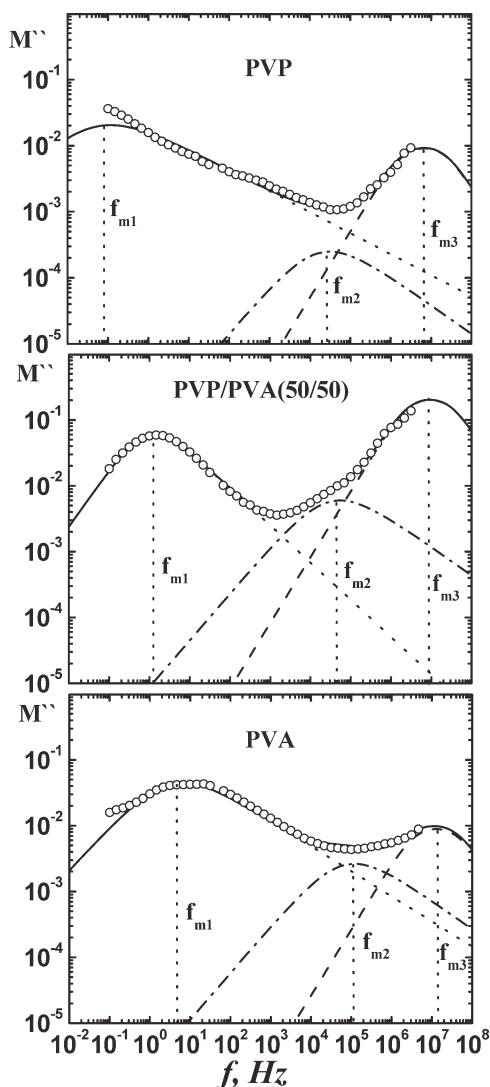


Figure 9 Example of the analysis for PVP/PVA blend at 30°C. The data are fitted by using two Havriliak–Negami functions and a Fröhlich one.

equilibrium positions and the rotational frictional forces exerted by neighboring dipoles and will contribute to absorption over a wide frequency and temperature range.⁷

The second relaxation process τ_2 which is considered to be our interest in this study as its maximum lies in the available range of frequency could be attributed to the β -relaxation. This may be due to the orientation of the side chains in the polymer blends.⁴⁴

According to Arrhenius equation⁴⁴ the activation energy ΔH_2 corresponds to this relaxation process was calculated and found to be in the range 8.36–11.43 kcal mol⁻¹ which justifies the presumption that this process is a β -relaxation. The obtained data are illustrated graphically in Figure 10.

The variation of τ_2 with PVP content at various temperatures was plotted graphically in Figure 11. From this figure it is notable that τ_2 increases line-

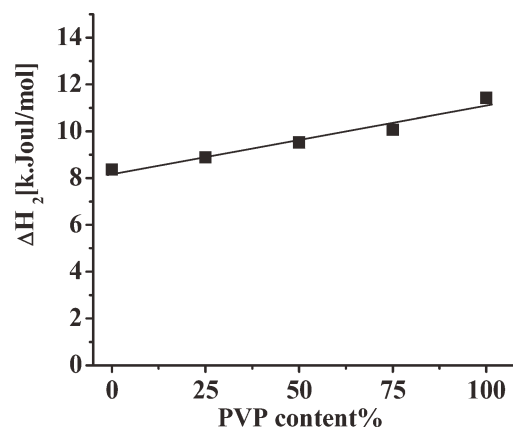


Figure 10 Variation of the activation energy of the second process (ΔH_2) versus PVP content in PVP/PVA blend.

arly by increasing PVP content. It was shown 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.⁵⁰

It is also notable that τ_2 decreases by increasing temperature. The linear relationship obtained indicate that PVA/PVP blends are compatible which is consider to be another justification to the results obtained by viscosity measurements and scanning electron microscopy micrographs.

PVP/starch blends

The permittivity ϵ' and the dielectric loss ϵ'' were measured in the frequency range 0.01 Hz up to 10 MHz and temperatures from 30 up to 90°C for PVP/St blend with different blend ratios (0/100, 75/25, 50/50, 25/75, and 100/0) after the addition of glycerol and glutaraldehyde. Example of the obtained data is given in Figure 12(a) for 30°C (a) and 90°C (b). From this figure it is clear that the values of ϵ' and ϵ''

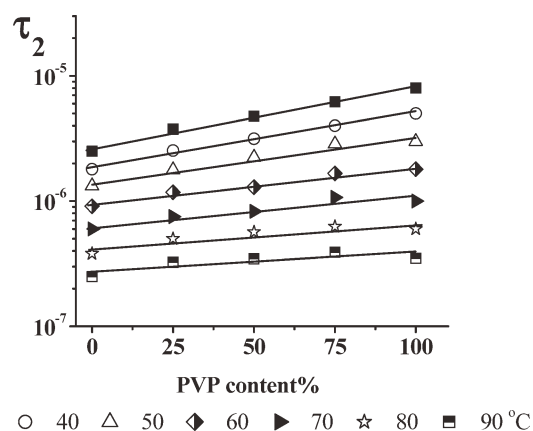


Figure 11 Variation of the relaxation time of the second process τ_2 versus PVP content in PVP/PVA blend.

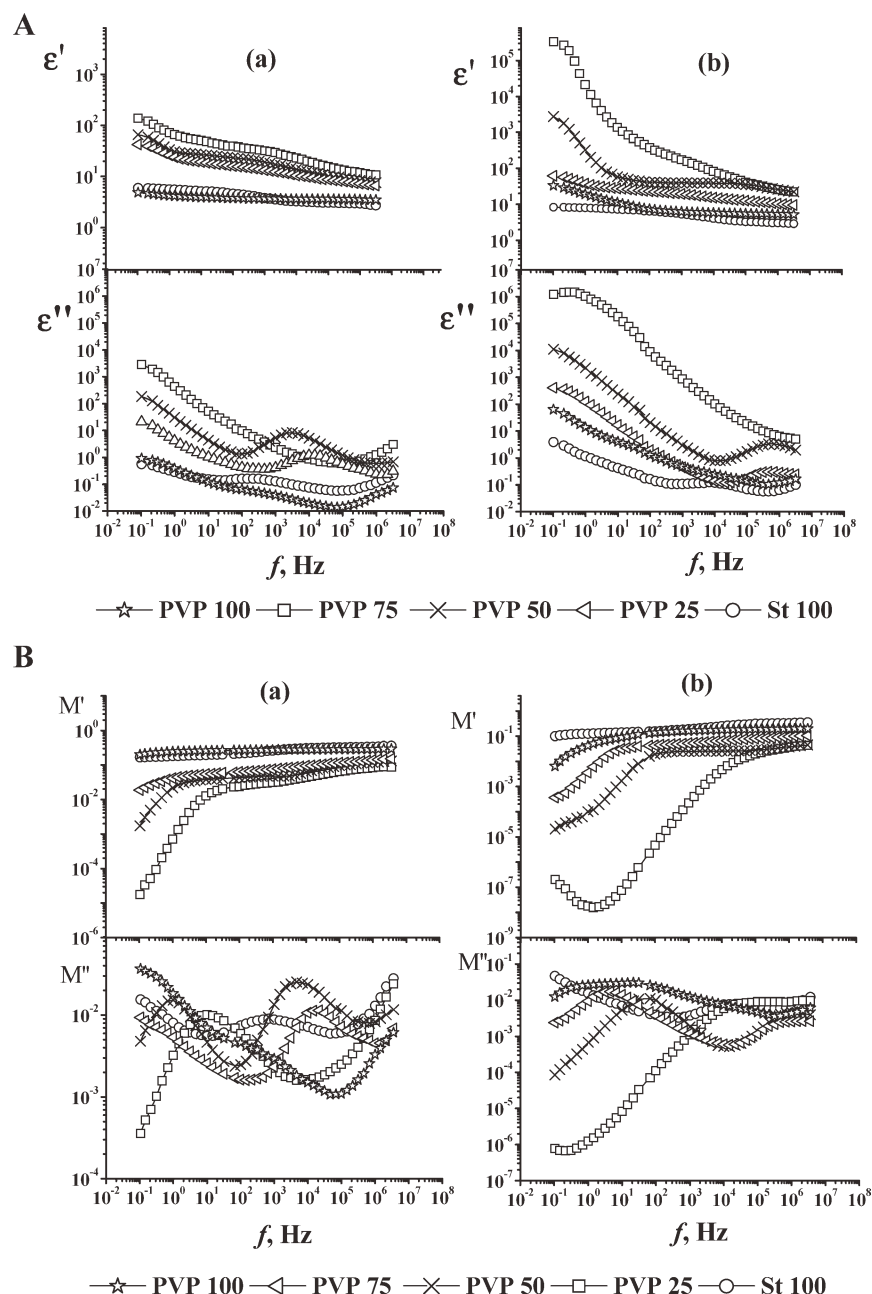


Figure 12 (A) Permittivity ϵ' and dielectric loss ϵ'' versus frequency f of PVP/St blend at: (a) 30°C (b) 90°C. (B) Real part of modulus M' and loss part of modulus M'' versus frequency f of PVP/St blend at: (a) 30°C (b) 90°C.

are highly affected by increasing temperature due to the presence of polar groups in both polymers.

Also it is of great interest to find that ϵ' of the blends are higher than those of both PVP and starch themselves. To understand this behavior ϵ' is plotted graphically versus PVP content at fixed frequency ($f = 100$ Hz) and at 30°C as shown in Figure 13. From this figure it is clear that this relation does not represent by a straight line as that for PVP/PVA blends Figure 7 but the deviation from linearity is positive. This positive deviation increases by increasing starch content in the blend. This finding may be due to the fact that the pyrrolidone ring in PVP contains a

proton accepting carbonyl moiety (C=O), with the starch presents hydrogen donor hydroxyl moiety (OH) as side groups. Therefore hydrogen bonding interaction may take place between these two chemical moieties in a blend of PVP and starch. Also, they are hydrogen bonds between starch/glycerol and starch/glutaraldehyde. These hydrogen bonds are responsible for the orientation of the starch and PVP chain segments for increasing the net polarization. Therefore, the higher values of ϵ' of the PVP/starch blends than those of the individuals starch and PVP.

This finding suggests that this blend may exhibit insulating properties better than either PVP or

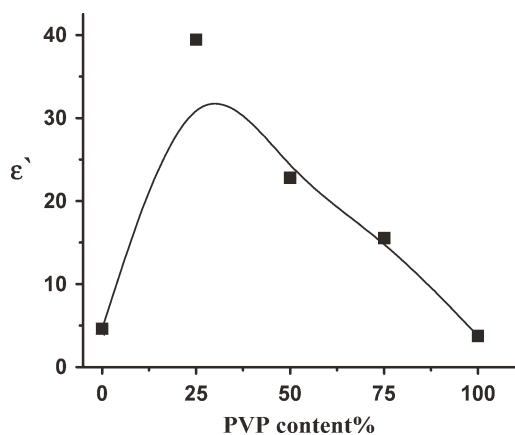


Figure 13 Variation of the permittivity ϵ' at $f = 100$ Hz and 30°C versus PVP content in PVP/St blend.

starch, which suggests a major synergistic improvement in practical utility for insulating purposes.⁵¹

To follow up the temperature dependence of such blends, the permittivity ϵ' and the dielectric loss ϵ'' were plotted graphically in Figure 14 versus temperature at fixed frequency ($f = 100$ Hz). From this figure it is seen that the values of ϵ' and ϵ'' of the individuals are lower than those for the PVP/starch blend ratios at different temperatures. Also it is seen that a positive temperature coefficient is observed for both ϵ' and ϵ'' due to the polar dipoles N—O and C=O in the side chain of the PVP in addition to the OH polar groups in starch, glycerol and glutaraldehyde molecules which are responsible for such increase.

For insulation purposes, it is preferable that the starch content does not exceed 50% as the increase in the permittivity ϵ' is accompanied with a pronounced increase in the dielectric loss ϵ'' . Also for the same reason it is better to use temperature does not exceed 50°C as the loss values are less than 1 for frequencies higher than 100 Hz.

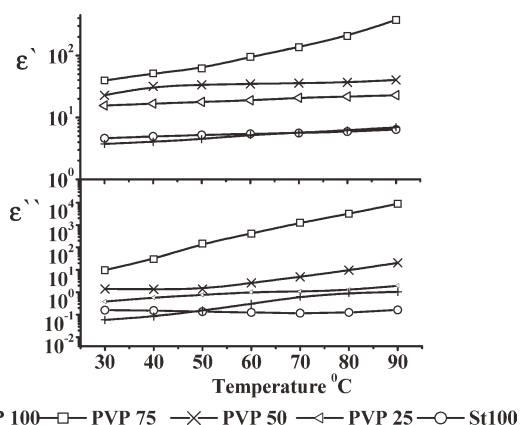


Figure 14 The permittivity ϵ' and dielectric loss ϵ'' at $f = 100$ Hz versus temperature in PVP/St blends.

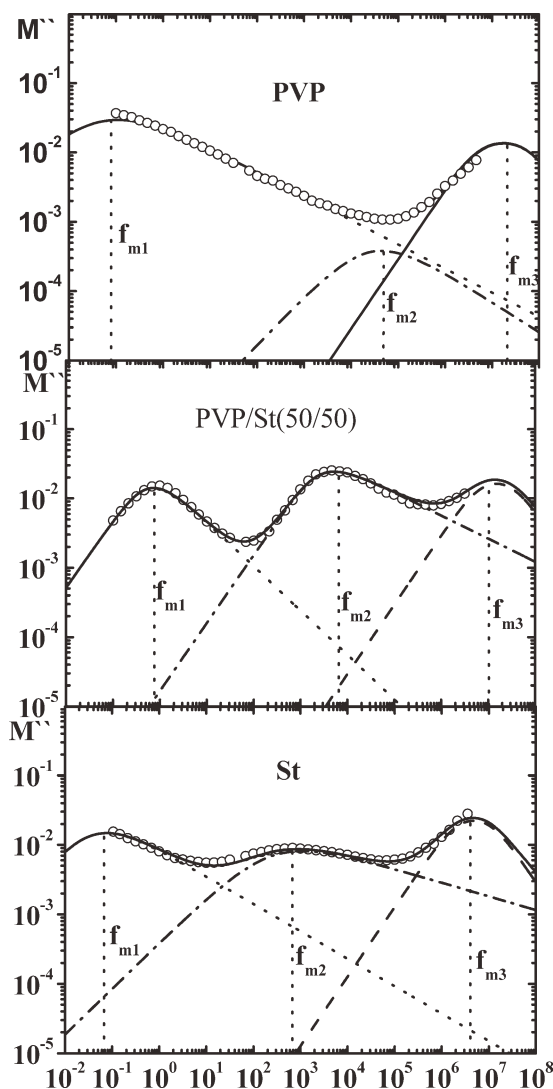


Figure 15 Example of the analysis for PVP/St blend at 30°C . The data are fitted by using two Havriliak–Negami functions and a Fröhlich one.

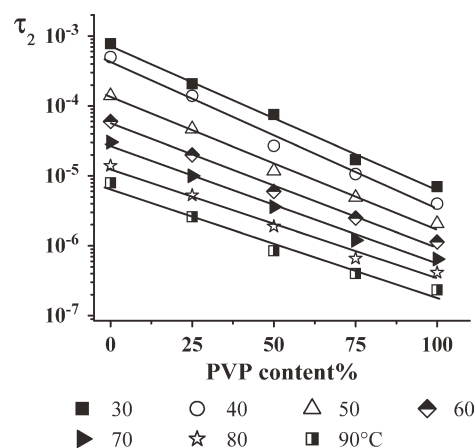


Figure 16 Variation of the relaxation time of the second process τ_2 versus PVP content in PVP/St blend.

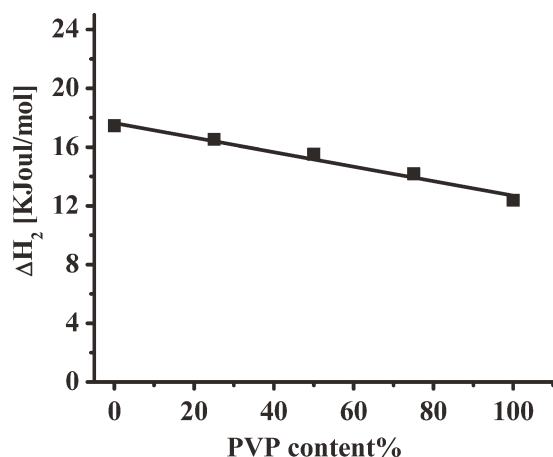


Figure 17 Variation of the activation energy of the second process (ΔH_2) versus PVP content in PVP/St blend.

The curves relating ε'' and the applied frequency shown in Figure 12(A) indicate that more than one relaxation process in addition to the electrical conductivity are present. The loss electric modulus M'' was calculated as mentioned above and illustrated graphically in Figure 12(B). The analyses were done in the same way as before for all blend ratios and at various temperatures. The analyses reveal three relaxation processes as in case of PVP/PVA system. Example of the analyses was given in Figure 15 for PVP, PVP/St (50/50), and St, respectively at 30°C.

In addition to the relaxation process in the lower frequency range τ_1 and that at the higher frequency τ_3 another relaxation process τ_2 was obtained which it is of our interest in this study and could be attributed to the β -relaxation.

The obtained values of τ_2 were illustrated graphically versus PVP content at various temperatures in Figure 16. From this figure it is seen that τ_2 increases by increasing starch content in the blend. This may be due to the increase in the molar volume of the rotating unites and consequently the relaxation time. This increase may be due to the crosslinking between starch chains by the addition of glycerol and glutaraldehyde which lead to the formation of more hydrogen bridges.

It is also notable that τ_2 decreases by increasing temperature. The linear relationship obtained indicates that PVP/St blends are compatible which is consider to be another justification to the results obtained by viscosity measurements and scanning electron microscopy micrographs.

The activation energy ΔH_2 associated with this process was calculated using Arrhenius equation.⁴⁴ The obtained values of ΔH_2 were found to be in the range 12.37–17.46 kcal mol⁻¹ which also justifies the presumption that this process is a β -relaxation. The obtained data are illustrated graphically in Figure 17.

CONCLUSION

- Two series of biodegradable blends based on polyvinyl pyrrolidone (PVP) with polyvinyl alcohol (PVA) and starch were prepared to be investigated through the compatibility and dielectric studies.
- The compatibility which was studied through viscosity, scanning electron microscope, and dielectric measurements indicates that PVP/PVA is compatible while PVP/St is in compatible.
- The incompatibility of later blend is improved by the addition of glycerol and glutaraldehyde.
- The dielectric measurements indicate that, at lower frequencies, the electrode polarization phenomena contributed significantly in the values of ε' and ε'' of the PVP/PVA and PVP/St blends.
- The permittivity ε' increases by increasing PVA content in PVP/PVA blend while in PVP/St the value of ε' of the blends are higher than those of both PVP and starch individuals. This positive deviation increases by increasing starch content in the blend. The maximum value is found at PVP/St (25/75) blend ratio. At this concentration the hydrogen bonds between starch/PVP, starch/glycerol and starch/glutaraldehyde are responsible for the increase in the net polarization and correspondingly in ε' .
- For both blends, the permittivity ε' and the dielectric loss ε'' are found to increase by increasing temperature.
- It is found that the concentration 50% of PVP in both blends is preferable for insulation purposes with temperature do not exceed 70°C.
- From the analysis data of the loss electric modulus M'' three different relaxation mechanisms are obtained which ascribe the motion of the main chain and its related motions; the crank shaft type of motion ($\alpha\beta$), the side chain motion (β) and the segmental motion of the groups attached to the side chains ($\beta\gamma$).
- The relaxation time of the second process τ_2 is found to decrease by increasing PVA content as the strength of the hydrogen bonding in PVP/PVA blend is PVA/PVA < PVP/PVA < PVP/PVP.
- On the other hand τ_2 increases by increasing starch content in PVP/St blend as a result of increasing the crosslinking density between OH groups in starch, glycerol and glutaraldehyde.

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