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Physical Properties of PVA Doped with Algal Glycerol

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ABSTRACT: Physical behavior of membrane blends of poly(vinyl alcohol) (PVA) doped with different weight percentage (wt %) of algal glycerol is reported. Solid-state PVA/glycerol membranes were prepared by the solution casting method. Electrical impedance measurements were conducted to test the effect of varying the percentage of glycerol on the conductivity of the membranes. The measurements were made in the frequency and temperature ranges 1 Hz–1 MHz and 303–423 K, respectively. It was observed that the ionic conductivity increased with the increase of glycerol concentration as well as temperature. The thermal properties of the films were characterized. It was found that the thermal properties, particularly the melting point (T_m), for PVA blends exhibit a reduced value proportional to the algal glycerol content. Fourier transform infrared spectroscopy was utilized to evaluate the interactions between the glycerol and PVA. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 4482–4489, 2013

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INTRODUCTION

Solid polymer electrolyte materials are attracting growing interest in recent years because of their potential applications in ionic devices such as rechargeable batteries, super capacitors, fuel cells, gas sensors, and electrochromic display devices/smart windows.¹⁻⁴ Among solid polymer electrolytes, protonconducting polymer electrolytes have received considerable attention and have been extensively investigated for advanced electrochemical applications.⁵ Obtaining high ionic conductivity at ambient temperature becomes crucial for the realization of these technological applications.⁶ Ploy(vinyl alcohol) (PVA) is a water-soluble organic polymer that has many excellent characteristics, such as film forming property, high bonding strength, anti-static properties, and pollution free. It is harmless, soluble, and biodegradable under certain conditions. It can be used as a raw material for applications in the field of coating, adhesive agent, surfactant, emulsifier, dispersants, and films.^{7,8}

With respect to dry polymer, as in the case of thin films, the properties of the PVA are especially affected by the molecular weight and the degree of hydrolysis.⁹ As PVA is usually obtained by the hydrolysis of poly(vinyl acetate), different types of PVA can be produced, depending on the degree of hydrolysis involved, corresponding to different amounts of hydroxyl groups present in the polymer back-bone.¹⁰ However, it remains

insoluble in solution because of the presence of crosslinks. The degree of hydrolysis, or the content of acetate groups in the polymer and polymerization has an overall effect on its chemical properties, solubility, and the crystallizability of PVA.^{11,12} PVA must be crosslinked in order to be useful for a wide variety of applications, specifically in the areas of medicine and pharmaceutical applications. A hydrogel can be used as a hydrophilic cross-linked polymer (network), which swells when placed in water or biological fluids.¹³

Room temperature ionic liquids; also known as plasticizers have been widely used as organic solvents and supporting electrolytes in many scientific fields because of their excellent properties such as high conductivity, low volatility, and inflammability.¹⁴⁻¹⁹ Polymer properties such as modulus, flexural strength, hardness, impact resistant, and electrical conductivity can be improved or tailored to a specific application by several methods including blending with selected plasticizer. It is the role of these additive materials that make the polymers what they are and what they are for. PVA would have different properties without plasticizer and difficult to process in injection molding machine. In many cases it is only possible to process polymer products on a commercial basis by incorporating a plasticizer this case is extensively applied for Polyvinyl Chloride. Because of the substantial improvement of plasticizers to the conductivity, thermal, and electrochemical properties of polymers, the incorporation of

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plasticizers into different polymers have been reported.^{20–22} Addition of a plasticizer is necessary to overcome the brittleness of films, to improve flow and flexibility, and to increase toughness, to impact resistance of film coating, and to prevent them from cracking during packing and transportation.^{23,24} The selection of a plasticizer for a specified system is normally based on the compatibility and permanence of the plasticizer, the amount necessary for plasticization, and the desired physical properties of the films.²⁵

There is a large number of commercially available plasticizers (the current database of commercially manufactured plasticizers contains more than 1200 items), which are added to polymers and biopolymers to provide the necessary and desirable processing, mechanical, and thermal properties also to prevent film brittleness in film forming plastics. The most commonly used plasticizers are ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, and oligosaccharides.⁴¹

Recently, many studies have focused on the use of natural and/ or biodegradable plasticizers because of their specific advantages such as lower cost, low toxicity, and good compatibility with variety of plastics, resins, and rubber.¹⁴ We have reported the effect of plasticizers such as sorbitol and glycerol on the electrical and mechanical properties of PVA and PVA-PAA blends.⁴²⁻⁴⁴ In this study, a new plasticizer (algal glycerol) is introduced. Oil from algae is considered a primary alternative to green fuel. Algal glycerol was obtained as a byproduct from the conversion of algae oil to biodiesel in a transesterification process. The algal glycerin was mixed 1 : 1 wt : wt with choline chloride to form glycerol ionic liquid. Blends of PVA and algal glycerol ionic liquid were prepared by a solution casting method. The thermal properties of the blends were studied using differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA). To study molecular interactions of the blends, Fourier transform infrared spectroscopy (FTIR) was used. In addition, the effect of adding this plasticizer to PVA on electrical conductivity was investigated.

MATERIALS AND METHODS

Materials

Algae Oil Preparation. Two types of microalgae were used for oil extraction namely *Ankistrodesmus braunii* and Nannochloropsis. Microalgae were cultured to obtain sufficient cell counts.²⁶ Algae cells were collected from the culture media. The separation of algae from water was done by centrifugation, drying, and filtration. Fifty-milliliter tubes with the algae–water mixture were loaded in the centrifuge machine to obtain the sediment of algae. The algal sediment obtained were further dried to remove moisture and used for the oil extraction process.²⁶

Oil extraction was performed by ultrasonication and soxhlet extraction. Ultrasonication was done using a Branson Sonifier 450 sonicator to rupture the cell wall of microalgae resulting in the release of algal oil. In the soxhlet extraction, hexane was evaporated and circulated through the powdered and dry algae sample that was placed in the soxhlet apparatus. The vapor of hexane condensed, mixed with the algae dissolves the oil and finally returned to the bottom where there was a boiling hexane. The cycle was repeated several times. Finally the hexane–oil mixture was removed from the apparatus, and hexane was evaporated off to give algae oil. Oil of 12–15% amount by volume was extracted from *A. braunii* and 10% from Nannochloropis sp. Algal glycerol was extracted from algae oil by mixing 1 L of algae oil with 200 mL of methanol. The mixture was kept magnetically stirring on a hotplate at 55°C for nearly 2 hours. The solution was then kept static for 1/2 hour. Two major products were found in the solution: glycerin and biodiesel. A 150–200 mL of dense glycerine is deposited at the bottom of the vessel and can be drawn off. The glycerol was then mixed 1 : 1 (wt : wt) with choline chloride to form glycerol ionic liquid.

Commercial PVA-124 was also purchased from Sigma-Aldrich Chemical with a molecular weight of 124–186 kg/mol and 99% hydrolyzed.

Membrane Preparation

The solid-state PVA/glycerol polymer membranes with glycerol to PVA weight percentage up to 6 wt % were prepared by the solution casting method. Five milligram of PVA was dissolved in distilled water (100 mL) inside a flask under continuous stirring on a hotplate at 90°C until it was completely dissolved. Then different wt % of glycerol were added to the PVA solution and mixed under continuous stirring condition at 90°C until the solution becomes completely homogenous and clear. The resulting homogenous solution was then poured on a PTFE plate to form a thin film. The excess water was evaporated slowly at a 70°C inside a vacuum oven for 24 hours.

Electrical Impedance Tests

A capacitor scheme was created by sandwiching each PVA/glycerol membrane between two spring-loaded electrodes. AC impedance tests were performed using a Solartron impedance-gain/ phase analyzer model SI 1260 controlled by computer. Z-view software was used to control the measurements and model the measured results with combinations of resistors and capacitors.

Fourier Transform Infrared Spectroscopy

A small amount of potassium bromide (KBr) powder was placed into a mould along with a small chip of polymeric film, and the mould was pressed at 5 tons for 2 minutes in a cold press machine to produce a KBr pellet. Transmission infrared spectra of the polymer pellets were recorded at room temperature using a NEXUS-470 - Thermo Nicolet Corporation FTIR spectrophotometer in the range of 4000–400 cm⁻¹, with 2 cm⁻¹ resolution. Each pellet was mounted directly on the sample holder, and the data were collected after scanning the background.

Differential Scanning Calorimeter Test

A DSC (TA Instruments, Water LLC model Q200) containing a cooling system was used to examine the evaluation in transition temperature (T_g) and melting temperature (T_m) for the different samples. Each sample of weight around 5 mg was placed inside a hermetically sealed aluminum pan and heated with a constant heating rate of 10°C/min from -20°C to 400°C under nitrogen atmosphere. An empty hermetically sealed aluminum pan was used as a reference cell. The results were analyzed using the TA Universal Analysis 2000 V4.5A software. The glass transition



Figure 1. Impedance spectra for different PVA/algal glycerol blends at 298 K. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperature was determined where a base line inflexion occurred, and the melting temperature was determined as the peak temperature of endothermic event of the DSC curves.

Thermogravimetry Analysis Test

TGA analysis of PVA/glycerol membranes were performed using Thermogravimetric Analyzer TGA Q50 V20.10 Build 36 Model (TA Instruments, Water LLC) containing a TGA heat exchanger system. The samples (\sim 10 mg each) after weighing in a pan were placed inside a tube furnace, which was heated to 600°C at a rate of 10°C/min under nitrogen atmosphere. The results were analyzed using the TA Universal Analysis 2000 V4.5A Build 4.5.05 (TA Instruments, Wilmington, Delaware, US) software.

RESULTS AND DISCUSSION

We have reported the effect of different plasticizers on PVA and PVA-PAA polymeric membranes.^{42–44} The electrical conductivity, mechanical properties, and thermal properties are altered as a function of the plasticizer content. Here, we present the electrical and thermal properties of PVA as a result of increasing algal glycerol in the film.

Electrical Properties

The ac impedance of the PVA/glycerol films was measured in the frequency range of $1-10^6$ Hz. Nyquist plots were constructed for the measured ac impedance, and the results are shown in Figure 1. The values of conductivity σ at different

temperatures are listed in Table I. The complex impedance plot of PVA/ glycerol (4 wt %) polymer electrolyte at different temperatures is shown in Figure 2. This figure shows two welldefined regions; a high frequency semicircle related to the parallel combination of a resistor and a capacitor and a low frequency semicircle representing formation of double layer capacitance at the electrode–electrolyte interface because of migration of ions at low frequency.²⁷ It can be seen from Figure 2 that the magnitude of bulk resistance decreases with the increase in temperature. It can also be seen that the low frequency semicircle vanishes at higher values of temperatures.

Ionic conductivity of the solid polymer electrolyte was calculated from the measured bulk resistance, area and thickness of the polymer film using $\sigma = l/RA$, where *l* is the thickness of the PVA/glycerol film (cm), *A* is the area of the blocking electrode (cm²), and *R* is the resistance of the PVA/glycerol film.

At room temperature, the highest ionic conductivity value was found to be 2.85×10^{-07} S cm⁻¹ for PVA/ (4 wt %) glycerol.

Effect of Temperature on Ionic Conductivity. Figure 3 shows the variation of $\log(\sigma)$ with inverse of the absolute temperature of pure PVA and PVA/algal glycerol polymer electrolytes doped with different glycerol concentrations. From the plot, it is evident that as the temperature increases the ionic conductivity increases for all the complexes, which is in agreement with the theory of Armand et al.²⁸ The increase in conductivity with temperature may be because of the decrease in viscosity that increase chain flexibility.²⁹ This can be explained on the basis of the free volume model³⁰ and hopping of charge carriers between localized states.³¹

The activation energies were calculated from log σ versus 1000/ *T* plots (Figure 3) using the Arrhenius relation:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{KT}\right)$$

where σ_0 is a constant, E_a is the activation energy, *K* is Boltzmann's constant, and *T* is the absolute temperature in kelvin. The conductivity and activation energy values of the polymer electrolytes are shown in Table II. The variations of the activation energy (E_a) values obtained from the Arrhenius plots shown in Figure 4. A minimum activation energy of $E_a = 0.099$ eV was noticed at 4 wt % algal glycerol, which enhances the values obtained from ac impedance test.

Table I. Conductivity for Neat PVA and PVA/Algal Glycerol Polymer Electrolyte Systems

	σ (S.cm ⁻¹) at different temperatures				
Sample description	298 K	323 K	348 K	373 K	398 K
Neat PVA	5.04E-09	4.59E-08	2.03E-07	3.47E-07	3.88E-07
PVA+1 wt % Algal Glycerol	1.20E-08	1.38E-07	5.67E-07	6.53E-07	1.21E-06
PVA+2 wt % Algal Glycerol	3.24E-08	1.37E-07	1.49E-07	1.01E-07	4.33E-07
PVA+3 wt % Algal Glycerol	4.46E-08	1.48E-07	2.39E-07	7.11E-07	1.11E-06
PVA+4 wt % Algal Glycerol	2.62E-07	8.50E-07	2.02E-06	3.60E-06	1.84E-06
PVA+5 wt % Algal Glycerol	1.16E-07	4.55E-07	7.05E-07	1.11E-06	1.55E-06
PVA+6 wt % Algal Glycerol	8.26E-08	3.83E-07	1.11E-06	1.61E-06	

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Figure 2. Impedance spectra for PVA/algal glycerol (4 wt %) blend at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 3. Arrhenius plot for pure PVA and PVA/algal glycerol complexes polymer electrolytes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Dielectric Analysis. The complex dielectric constant of a system is defined by:

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

where ε' is the real part of dielectric constant (dielectric permittivity) and ε'' is the imaginary part of dielectric constant (dielectric loss). Both real and imaginary parts of the complex

 Table II. Conductivity and Activation Energy of PVA: Algal Glycerol

 Polymer Electrolytes

Sample	Conductivity (S cm ⁻¹) at 298 K	Activation energy (eV)
Pure PVA	5.04E-09	0.15
PVA+1 wt % Algal Glycerol	1.20E-08	0.12
PVA+2 wt % Algal Glycerol	3.24E-08	0.12
PVA+3 wt % Algal Glycerol	4.46E-08	0.14
PVA+4 wt % Algal Glycerol	2.62E-07	0.10
PVA+5 wt % Algal Glycerol	1.17E-07	0.11
PVA+6 wt % Algal Glycerol	8.26E-08	0.17



Figure 4. Activation energy of algal glycerol based electrolytes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dielectric constant ε^* are of particular significance in ion conducting polymers.

Figure 5(a,b) shows the variation of the dielectric permittivity (ε') and the dielectric loss (ε'') of the films with frequency for





Figure 5. (a) Frequency dependence of the real part $\varepsilon'(\omega)$ of dielectric permittivity for the optimized system (PVA/4wt % algal glycerol) blend with different glycerol at 298 K.(b) Frequency dependence of the imaginary part $\varepsilon''(\omega)$ of dielectric loss for the optimized system (PVA/4wt % algal glycerol) blend with different glycerol at 298 K. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]





Figure 6. Dependence of ionic conductivity on algal glycerol concentration for PVA/algal glycerol polymer complex at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the PVA: algal glycerol (4 wt %) polymer electrolyte at different temperatures. Dielectric constant describes the stored energy, whereas the dielectric loss describes the dissipated energy. From the plots, it is clear that the dielectric permittivity and the dielectric loss decrease monotonically with increasing frequency and attains a constant value at higher frequencies. Similar behavior was observed in a number of other polymers.^{32–36} For low frequencies, the dielectric permittivity and the dielectric loss are high, but as the frequency is raised, the permittivity begins to drop, which could be because of the dipoles are not being able to follow the field variations at high frequencies³⁷ as well as because of electrode polarization effects.²⁹ For higher frequencies, the periodic reversal of the electric field occurs so

 Table III. Thermal Characteristics by DSC of the Films of Neat PVA and Blends of PVA/Algal Glycerol

Sample description	Т _д (°С)	<i>T_m</i> (°C)	<i>T</i> _d (°C)
Neat PVA	139.48	220.13	331.21
PVA+1 wt % Algal Glycerol	89.17	213.44	299.92
PVA+2 wt % Algal Glycerol	91.25	207.56	287.52
PVA+3 wt % Algal Glycerol	127.52	193.33	293.35
PVA+4 wt % Algal Glycerol	106.56	188.95	273.26
PVA+5 wt % Algal Glycerol	132.19	179.86	279.84
PVA+6 wt % Algal Glycerol	94.4	180.70	273.05

fast that there is no excess ion diffusion in the direction of the field. The low frequency dispersion region is attributed to charge accumulation at the electrode–electrolyte interface.

From Figure 5, it is also clear that the dielectric permittivity increases with increasing temperature for the PVA: algal glycerol (4 wt %) polymer electrolyte system. The variation of dielectric permittivity with temperature is different for nonpolar and polar polymers. In general, for nonpolar polymers, the ε' is independent of temperature but in the case of strong polar polymers the ε' increases with temperature. The behavior of ε' in the present investigations is typical of polar dielectric, where dipole orientation is facilitated by the increase in temperature resulting in an increase in dielectric permittivity.

Figure 6 represents the ionic conductivity of PVA/algal glycerol polymer film as a function of glycerol concentration. Two characteristic regions can be easily distinguished doped PVA polymer electrolytes. It has been found that the conductivity is



Figure 7. DSC thermograms for neat PVA and PVA/glycerol blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 8. TGA thermograms of the neat PVA and PVA/algal glycerol blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

maximum at 4 wt % glycerol (to 2.62×10^{-07} S cm⁻¹) then decreases as the percentage of glycerol increases. This may be attributed to the increase in number of mobile charge carriers and also to the increase in amorphous nature of the polymer electrolyte, which reduces the energy barrier thereby facilitating the fast ion transport.³⁸ However, a decrease in conductivity is observed beyond 4 wt % of glycerol. This may be because of the aggregation of ions, leading to the formation of ion clusters, thus decreasing the number of mobile charge carriers.

DSC Analysis. The DSC measurements for PVA/algal glycerol blends are represented in Figure 7 for various glycerol percentages. All DSC results were obtained from the initial heating run between -25° C and 400°C. Three endothermic peaks were observed on the DSC curves for neat PVA and PVA/ glycerol blends. The first relaxation was observed between 50°C and 125°C this is because of the relaxation in the PVA crystalline domains. The second relaxation between 170°C and 220C is caused by melting of crystalline domains of PVA and the third peak starting from 250°C is because of the degradation of the PVA.

The thermal characteristics of the pure PVA and PVA/glycerol blends are listed in Table III. Neat PVA has a glass transition temperature of 139.48°C, whereas the blends show a shift of glass transition temperature to lower temperature as shown in Figure 7. The thermal analysis of PVA/glycerol blends by DSC shows that the melting temperature T_m shift is because of the interaction of the blend. The melting peak temperature and the degradation temperature are shifted to lower temperature when the percentage of glycerol is increased.

Thermogravimetric Analysis. TGA tests were conducted on pure PVA and PVA/algal glycerol membranes to determine their thermal stability and the corresponding degradation stages as a function of temperature as well as their moisture content in the membrane. Decomposition temperate (T_d) for each sample was computed by the instrument's software. Thermal degradation of PVA has been extensively reported. Below 300°C, the main degradation product reported is water, produced by elimination of the hydroxyl side group.^{39,40} Figure 8 shows all the combined TGA curves of PVA and PVA/algal glycerol membranes. Both

Table IV. The Weight Loss (%) of the PVA and PVA/Algal Glycerol Polymer Blends at Different Temperatures Obtained from TGA Analysis

	Temperature (°C) region			
Sample description	50-220	220-350	400-500	
Neat PVA	6.43	75.44	10.14	
PVA+1 wt % Algal Glycerol	11.07	55.18	13.53	
PVA+2 wt % Algal Glycerol	14.90	64.59	13.31	
PVA+3 wt % Algal Glycerol	23.74	48.87	15.07	
PVA+4 wt % Algal Glycerol	36.99	40.52	15.53	
PVA+5 wt % Algal Glycerol	35.59	35.63	16.77	
PVA+6 wt % Algal Glycerol	34.51	37.28	15.52	







Figure 9. FTIR spectra for neat PVA polymer, algal glycerol, and different PVA/glycerol percentages. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the PVA and PVA/algal glycerol polymer membranes exhibit two-stage degradation. The first stage is between 250°C and 350°C, and it is because of the degradation of the main chain of PVA composite membrane. The total weight loss corresponds to this stage is given in Table IV for all the membranes. It has been observed that for the pure PVA, the onset decomposition temperature started at 250°C, which is less than that of the PVA/algal glycerol membranes. This is directly related to the plasticizing effect of the glycerol causing the decomposition temperature to increase to a higher value. The second stage is around 380-500°C, and it is because of the carbonation of polymer matrix followed by a final decomposition of the polymer chains that begin around 500°C. There is a 90% weight loss for all samples at above 500°C. TGA data are presented in Table IV. The onset decomposition temperature for PVA blends starts at 300°C. After this temperature, the PVA/algal glycerol polymer membrane becomes greatly degraded. It is clearly evidenced that the PVA/algal glycerol membrane samples are relatively stable in the temperature range of 50–150°C.

Fourier Transform Infrared Spectroscopy. FTIR was used to characterize the presence of specific and important chemical groups in the materials. Pure PVA film and PVA containing varying percentage of glycerol were obtained as 0.1–0.3 mm thick films and were analyzed using FTIR in a transmittance mode. Figure 9 shows the FTIR spectra for neat PVA polymer, algal glycerol and four (PVA/glycerol) blends with different glycerol percentage. All major peaks related to hydroxyl, and methyl groups were observed. In neat PVA, intra-molecular and intermolecular bonds are expected to occur between hydroxyl groups attached to the main chain because of high hydrophilic forces.⁸

The broad band observed between 3000 and 3600 cm⁻¹ was linked to the O-H stretching from intermolecular and intramolecular hydrogen bonds. It was observed that as the percentage of glycerol was increased, the broad band decreases and peak intensity increases. The vibrational band observed at 2950 cm⁻¹ refers to the stretching of C-H bond from alkyl groups. It was observed that the intensity of this peak decreases and split into two peaks as the percentage of glycerol increases. The two peaks between 1650 and 1750 cm⁻¹ diminish to one sharp peak as the glycerol

percentage increases. A C-O stretch bond exists in all samples at the range of 1100 cm^{-1} . The presence of broad band linked to the stretching of O-H group in the range of 3000 to 3600 cm⁻¹ is a clear evidence that the hydrogen bonding is the dominating structure this broad peak is more evident in neat PVA and becomes sharper and more defined as the percentage of glycerol increases. The broad peak is shifted progressively to higher wavelength region and becomes sharper and more defined as the glycerol weight percentage is increased. This indicates that the hydrogen bonding is switched from among PVA chains to PVA/ glycerol. This examination gives support to the increase in the conductivity, which was observed for PVA samples containing different weight percentage of glycerol plasticizer.

CONCLUSION

Algal glycerol based polymer electrolytes were prepared by solid solution casting and characterized. The analysis showed that the plasticizer affects the ionic conductivity of the polymeric films. The ionic conductivity results of all analyzed samples as a function of temperature obey predominantly an Arrhenius relationship and the samples were stable up to 150°C. Ionic conductivity results of 2.62×10^{-07} S cm⁻¹ at room temperature and 3.60×10^{-06} S cm⁻¹ for 4 wt % of algal glycerol at 373K were obtained. As the glycerol percentage increased, the melting temperature of PVA decreased along with the broadening of endothermic peak, which indicated that the ordered association of the PVA molecules decreased. From the FTIR analysis, it was evident that algal glycerol formed favorable interactions with PVA through the intermolecular hydrogen bonding interactions. It was confirmed the presence of the major functional groups in PVA/glycerol.

REFERENCES

- 1. Mac Callum, J. R.; Vincent, C. A. Eds., Polymer Electrolytes Reviews; Elsevier: Amsterdam, **1987**.
- Gopalan, A. L.; Santhosh, P.; Manesh, K. M.; Nho, J. H.; Chul-Gyun Hwang, S.; Lee, K. P. J. Membr. Sci. 2008, 325, 683.
- 3. B.P. Tripathi, V.K. Shahi, Polym. Sci. 2011, 36, 945.
- 4. Bhide, A.; Hariharan, K. Eur. Polym. J. 2007, 43, 4253.
- Lasseques, J. C. In: Colomban, P. Ed., Proton Conductors: Solid Membranes and Gel—Materials and Devices; Cambridge University Press: Cambridge, (Chapter 20), 1992.
- Natesan, B.; Karan, N. K.; Rivera, M. B.; Aliev, F. M.; Katiyar, R. S. J. Non Cryst. Solids 2006, 352, 5205.
- Springer, T. E.; Zawodzinski, A.; Wilson, M. S.; Golfesfeld, S. J. Electrochem. Soc. 1996, 143, 2.
- Mansur, H. S.; Orefice, R. L.; Mansur, A. A. P. Polymer 2004, 45, 7193.
- 9. Pal, K.; Banthia, A. K.; Majumdar, D. H. J. Biomater. Appl. 2006, 21, 75.
- Mansur, H. S.; Sadahira, C. M.; Souza, A. N.; Mansur, A. P. Mater. Sci. Eng. C 2008, 28, 539.
- 11. R.K. Tubbs, J. Polym. Sci. 1996, A1 4, 623.
- 12. Finch, C. A. Poly(vinyl alcohol): Properties and Applications; Weily: New York, **1973**.

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- 13. Peppas, N. A. Hydrogels in Medicine and Pharmacy, Polymers; CRC press: Boca Raton, FL, Vol. 1, **1987**.
- 14. Singh, B.; Sekhon, S. S. Chem. Phys. Lett. 2005, 414, 34.
- Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A.E.; Rogers, R. D. Chem. Commun. 1998, 1765.
- Matsumi, N.; Sugai, K.; Miyake, M.; Ohno, H. *Macromole*cules 2006, 39, 6924.
- Sekhon, S. S.; Lalia, B. S.; Kim, C. S.; Lee, W. Y. Macromol. Symp. 2007, 249, 216.
- 18. Jiang, H.; Fang, S. B. Polym. Adv. Technol. 2006, 17, 494.
- Ogihara, W.; Sun, J. Z.; Forsyth, M.; MacFarlane, D. R.; Yoshizawa, M.; Ohno, H. *Electrochim. Acta* 2004, 49, 1797.
- 20. Kim, K. S.; Park, S. Y.; Choi, S.; Lee, H. J. Power Sources 2006, 155, 385.
- Shin, J. H.; Henderson, W. A.; Tizzani, C.; Passerini, S.; Jeong, S. S.; Kim, K. W. J. Electrochem. Soc. 2006, 153, A1649.
- 22. Cheng, H.; Zhu, C. B.; Huang, B.; Lu, M.; Yang, Y. *Electrochim. Acta* **2007**, *52*, 5789.
- 23. Aydinli, M.; Tutas, M. Food Sci. Technol. 2000, 33, 63.
- 24. Barreto, P. L. M.; Pires, A. T. N.; Soldi, V. Polym. Degrad. Stab. 2003, 79, 147.
- Cheng, L. H.; Karim, A. A.; Seow, C. C. J. Food Sci. E Food Eng. Phys. Properties 2006, 71, 62.
- 26. Haik Y., Selim M. Y., Abderahman. Energy 2011, 36, 1827.
- Ravi, M.; Pavani, Y.; Kiran Kumar, K.; Bhavani, S.; Sharma, A.K.; Narasimha Rao, V. V. R. *Mater. Chem, Phys.* 2011, 130, 442–448.
- Armand, M. B.; Chabagno, J. M.; Duclot, M. J. In Vashishta, P.; Mundy, L. N.; Shenoy, G. (Eds.), Fast Ion Transport in Solids; North Holland: Amsterdam, 1979, p 131.

- 29. Ramesh, S.; Yahana, A. H.; Aroof, A. K. Solid State Ionics 2002, 152, 291.
- 30. Pillai, P. K. C.; Khurana, P.; Trilateral, A.; J. Mater. Sci. Lett. 1986, 5, 629.
- Chetia, J. R.; Maullick, M.; Dutla, A.; Dass, N. N. Mater. Sci. Eng. B 2004, 107, 134.
- 32. Vijayalakshmi Rao, R.; Sridhar, M. H. Mater. Lett. 2002, 55, 34.
- Hilker, B.; Fields, K. B.; Stern, A.; Space, B.; Peter Zhang, X.; Harmon, J. P.; *Polymer* 2010, *51*, 4790.
- 34. Yang, S.; Benitez, R.; Fuentes, A.; Lozano, K. Compos. Sci. Technol. 2007, 67, 1159.
- 35. Raja, V.; Sharma, A. K.; Narasimha Rao, V. V. R. Mater. Lett. 2004, 58, 3242.
- Mohamed, N. S.; Hashim Ali, S. A.; Arof, A. K. Indon. J. Phys. 2004, 15, 3.
- Tareev, B. Physics of Dielectric Materials; MIR Publications: Moscow, 1979.
- Hema, M.; Selvasekarapandian, S.; Arunkumar, D.; Sakunthala, A.; Nithya, H. J. Non Cryst. Solids, 2009, 355, 84.
- Ballistreri, A.; Foti, A.; Montaudo, G.; Scamporrino, E. J. Polym. Sci. Polym. Chem. Ed. 1980, 18, 1147.
- 40. Krumova, M.; Flores, A.; Balta Calleja, F. J.; Fakirov, S. *Colloid Polym. Sci.* **2002**, *280*, 591.
- Vieira, M. G. A.; da Silva, M. O.; Santos, L. O.; Beppu, M. M. Eur Polym. J. 2001, 254, 47.
- 42. Josh, V.; Haik, M. Y.; Ayesh, A.; Mohsin, M. A.; Haik, Y. J. Appl. Polym. Sci. 2012, 128, 3861.
- 43. Ayesh, A.; Mohsin, A., Haik, M., Haik Y. *Current Appl. Phys.* **2012**, *12*, 1223.
- 44. Mohsin, M. A., Hossin, A.; Haik, Y. Mater. Sci. Eng. A 2011, 528, 925.