

Thermal and Mechanical Properties of Poly(vinyl alcohol) Plasticized with Glycerol

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Received 1 April 2010; accepted 25 January 2011

DOI 10.1002/app.34229

Published online 7 July 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Thermomechanical behavior of membranes based on blends of poly(vinyl alcohol) (PVA) with different weight percentage (wt %) of glycerol has been studied. Solid-state PVA/Glycerol polymer membranes were prepared by a solution casting method. The films were studied for thermal characteristics by differential scanning calorimetry (DSC) and thermogravimetric analysis and for the mechanical properties including hardness and modulus by nanoindentation method. The dispersion of glycerol within the polymer matrix was examined using scanning electron microscopy. Fourier transform infrared spectroscopy was used to confirm the formation of hydrogen bonding between the

plasticizer and PVA in their blends and also to provide information on compatibility and physical interactions between the glycerol and PVA. It was found that the thermal properties particularly the melting point (T_m) for PVA blends exhibit a reduced value proportional to the glycerol content. The hardness and elastic modulus were also found to decrease with an increase in plasticizer content. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3102–3109, 2011

Key words: differential scanning calorimetry; thermogravimetric analysis; mechanical properties; nanoindentation; poly(vinyl alcohol)

INTRODUCTION

In recent years, the extent of research interest involving the synthesis and characterization of biodegradable films has increased substantially, mainly due to interest in minimizing the ecological impact caused by using synthetic polymers in food packaging industry. A significant proportion of past research on films has been focused on using biopolymers from renewable sources, that is, products or byproducts derived from agriculture or from agro-industries.¹

Poly(vinyl alcohol) (PVA) is a synthetic polymer, which is soluble in water, and its solubility in water being influenced by a number of factors like; the degree of hydrolysis, molecular weight and molecular weight distribution, particle size distribution, and crystallinity. It is one of the hydrogels often used in biomedical applications due to its excellent film forming properties, adhesion, and emulsifying characteristics.² 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 hy-

drolysis.³ Since 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, this corresponding to different amounts of hydroxyl groups present in the polymer back-bone.⁴ PVA is well suited for making biodegradable blends with natural polymers due to its good film-forming capability⁵ and water solubility. It has been used in several studies on biopolymer based materials produced by casting or extrusion.⁶ In case of films produced by casting from aqueous solution, the studies have involved blends of PVA with polysaccharides, such as starch,^{7–9} gellan,¹⁰ and with proteins, such as wheat gluten,¹¹ collagen,^{12,13} and gelatin.^{14–16}

Room temperature ionic liquids; also known as plasticizers have been widely used as organic solvents and supporting electrolytes in many scientific fields due to their excellent properties such as high conductivity, nonvolatility, and nonflammability.^{17–22} Because of the substantial improvement of plasticizers to the conductivity, thermal, and electrochemical properties of polymers, the incorporation of plasticizers into different polymers have been reported.^{23–25} 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.^{26,27} Glycerol is a

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syrupey, colorless, water soluble high-boiling point liquid with a distinctly sweet taste. Its soothing qualities make it useful in many industrial applications namely, shaving cream and soaps and in medical application as cough drops and syrups. It also widely used as plasticizer. Plasticizers, are low-molecular-weight compounds, which, when blended with polymers, will increase the free volume of the material or the macromolecular mobility of the polymer, and consequently the polymeric network becomes less dense due to the decrease in intermolecular forces, thus improving the extensibility and flexibility of the films.²⁸ A number of plasticizers, for example, water and polyols^{29–31} have been essayed to decrease the melting temperature and increase the flexibility and workability of biopolymer-based films.^{32–41} 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.⁴²

In this work, we investigated the effect of glycerol (plasticizer) percentages on thermal and mechanical properties of PVA films. In addition, the melting and plasticizing behavior of PVA were also examined according to the amount of plasticizer, thermal history, and PVA blend.

MATERIALS AND METHODS

Materials

Glycerol was obtained from Quatek (NC) Polyvinyl alcohol PVA-124 was purchased from σ -Aldrich (St. Louis, Missouri, US) Chemical having molecular weight of 124,000–186,000 g/mol with 99% hydrolyzed. All other laboratory reagents were also purchased from σ -Aldrich and used as supplied. Distilled water was used in the preparation of the polymer films.

Material and membrane preparation

The solid-state PVA/glycerol polymer membranes (glycerol with 0.5, 1, and 2% of weight) were prepared by a solution casting method. PVA (degree of polymerization = 1700, degree of hydrolysis > 99%) was dissolved in distilled water (10 mL) with a concentration of 5 wt % (0.5 mg) in a conical flask and kept on a magnetically stirred hotplate at 90°C. The solution was heated and stirred until it was completely dissolved. Then 0.9 mL (for 0.5 wt %) of glycerol and 8.8 mL ethanol were added to PVA solution and mixed together under continuous stirring condition at the temperature of 90°C for 6 h or until the solution becomes completely homogeneous and clear. The resulting homogeneous polymer solution was then poured onto a PTFE plate to form a thin

film. The excess water and methanol were evaporated slowly at 80°C in a vacuum oven. The other two samples (1 and 2 wt %) PVA/glycerol blends were prepared using the same procedure.

Thermogravimetric analysis (TGA)

TGA analysis of PVA and PVA/Glycerol membranes were performed using a Thermogravimetric Analyzer TGA Q50 V20.10 Build 36 Model (TA Instruments, Water LLC) containing a TGA Heat Exchanger system. The samples (~ 10 mg) after weighted 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.

Differential scanning calorimetry (DSC)

DSC analysis of polymeric membranes were performed using a differential scanning calorimeter DSC Q200 V24.4 Build 116 Model (TA Instruments, Water LLC) containing a refrigerator cooling system. The sample (~ 10 mg) was placed in hermetically sealed aluminum pans and heated from –50 to 400°C with a heating rate of 10°C/min under nitrogen atmosphere.³⁴ An empty hermetically sealed aluminum pan was used as the reference cell. The results were analyzed using the TA Universal Analysis 2000 V4.5A Build 4.5.05 (TA Instruments) software. The glass transition temperature corresponded to the temperature where a baseline inflection occurred, and the melting temperature was determined as the peak temperature of the endothermic event of the DSC curves.

Nanoindentation

All nanoindentation experiments of PVA/glycerol membranes were performed by a Nano Test Materials Testing Platform Two (Micro Materials, Wrexham, UK) that was equipped with a three-sided pyramid diamond indenter tip (Berkovich type).⁴³ The nanoindentation tests were carried out as follows: A constant displacement rate of 0.0167 mN/s was maintained during the increment of load until the indenter reached a depth of 1827 nm into the surface. The load was then held at maximum value (1 mN) for 30 s to avoid creep that may significantly affect the unloading behavior. The indenter was then withdrawn from the surface at the same rate until 10% of the maximum load, followed by the indenter being completely removed from the material. Here, constant displacement rate was chosen to load the samples to avoid strain-hardening effects on the measurements.⁴⁴ At least five indents were performed on each sample and the distance between the

indentations was 50 μm to avoid interaction. The nanoindentation loading-unloading curves are shown in Figure 1(a–c) for various PVA/glycerol blends.

The hardness (H) and the elastic modulus (E) were calculated from the load-displacement data. As the indenter was allowed to penetrate into the specimen, both elastic and plastic deformation occurred and only the elastic portion of the displacement was recovered during unloading. Nanoindentation hardness is defined as follows⁴⁵:

$$H = \frac{P_{\max}}{A} = \frac{P_{\max}}{24.5h_c^2} \quad (1)$$

where P_{\max} is the load measured at a maximum depth of penetration (h) in an indentation cycle; A is the projected contact area; and h_c is the contact depth of the indentation, which is given by

$$h_c = h - 0.75 \frac{P_{\max}}{S} \quad (2)$$

where S is the slope, $\frac{dP}{dh}$, of the initial portion of the unloading curve at $h = h_{\max}$ and 0.75 is a constant that depends on the indenter geometry. The elastic modulus of the specimen was inferred from the initial unloading contact stiffness S . The relationship among contact stiffness, contact area, and elastic modulus was derived as follows.⁴⁶

$$S = 2\beta E_r \sqrt{\frac{A}{\pi}} \quad (3)$$

where β is a constant that depends on the geometry of the indenter ($\beta = 1.034$ for a Berkovich indenter) and E_r is the reduced elastic modulus, taking into account the elastic deformation of both the tested specimen and the indenter. For evaluating E_r , the contact stiffness (S), and the contact area A could be determined accurately from load against displacement graph measured during the indentation process. The specimen's elastic modulus (E_s) was then calculated as follows

$$E_s = \frac{1 + \nu_s^2}{\frac{1}{E} - \frac{1 - \nu_i^2}{E_i}} \quad (4)$$

where ν_s and ν_i (0.07) are the Poisson's ratios of the specimen and indenter, respectively, whereas E_i is the modulus of the diamond indenter (1141 GPa). In all calculations, the estimated value of ν_s of semi-crystalline polymeric materials is 0.35.⁴⁷

Fourier transform infrared spectroscopy (FTIR)

Transmission infrared spectra of all films were recorded at room temperature using FTIR (NEXUS-

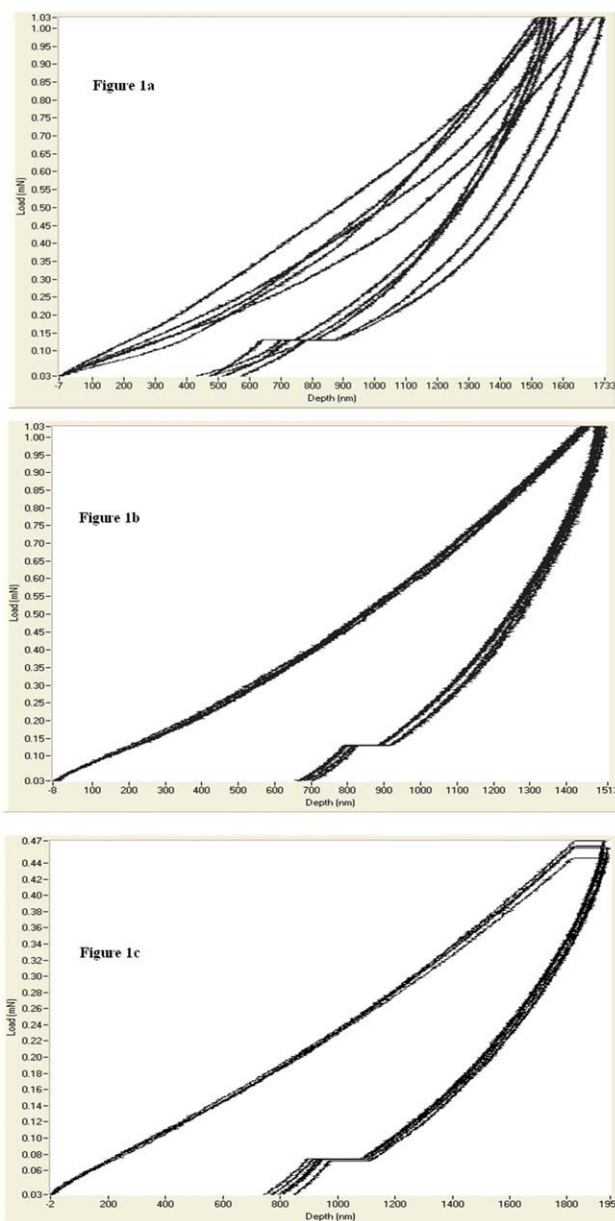


Figure 1 Nanoindentation (loading-unloading curves) of the PVA/glycerol polymer blends. (a) Nanoindentation curve for PVA containing 0.5% glycerol. (b) Nanoindentation curve for PVA containing 1.0% glycerol. (c) Nanoindentation curve for PVA containing 2.0% glycerol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

470, Thermo Nicolet, Golden Valley, Minnesota, US) spectrophotometer in the range of wavenumber from 4000 to 400 cm^{-1} during 32 scans, with 2 cm^{-1} resolution. The film was mounted directly in the sample holder and data was collected after scanning the background.

Scanning electron microscopy (SEM)

SEM was conducted on a Jeol model JSM-5600 instrument at an accelerating voltage of 10 KV and

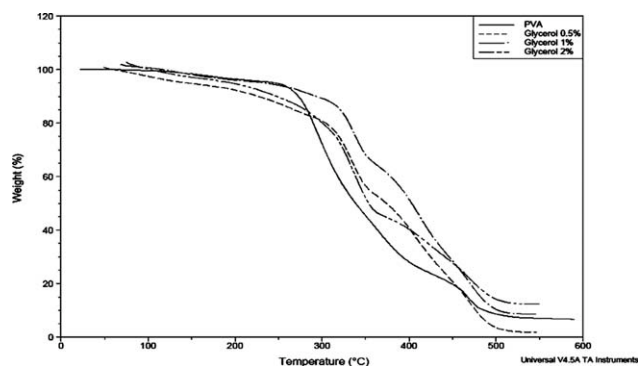


Figure 2 TGA thermograms of the PVA and PVA/glycerol blends.

18–300,000 magnifications with guaranteed resolution of 3.5 nm. Sample film was dehydrated at room temperature using ethanol for 1 h, dried in air and then sputter-coated with thin film of gold. The film was cut and SEM examined the cutting surface.

RESULTS AND DISCUSSION

Thermal properties

Thermal degradation of polymeric materials is a consequence of the fact that the organic macromolecules within the polymer matrix as well as low-molecular-weight organic molecules are stable only up to a certain temperature range. Their stability depends on the inherent characteristics of the sample as well as the specific interactions associated between the different macromolecules or molecules present in the polymer. These interactions are due to the dipole-dipole interaction, van der Waals, London, and hydrogen bonding forces. Since molecules/macromolecules consist of atoms or group linked together by covalent bonds, and the strength of these bonds are limited, a high thermal stability of the blend can be explained at the molecular level because of the less scission of chemical bonds under the influence of heat. Chain scission or bond dissociation takes place when the supplied thermal energy exceeds the bond dissociation energy of the respective bond or group. The plasticizers are low-molecular-weight molecules, that when added to polymeric materials modifies the tridimensional organization of the polymeric matrix, decreasing the intermolecular attraction forces and consequently, increasing the free volume and the mobility of the polymeric chain. This is done via hydrogen bonds between its hydroxyl groups and the polar functional groups of some amino acid residues.^{32–34}

Thermogravimetric (TGA) analysis

TGA were conducted on pure PVA and PVA/glycerol membranes to determine their thermal stability

and the corresponding degradation stages in response to temperature as well as their moisture content in the membrane. Decomposition temperature (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.^{48,49} Figure 2 shows all the combined TGA curves of PVA and PVA/glycerol membranes. Both the PVA and PVA/glycerol polymer membranes exhibit two-stage degradation. The first stage was between 300 and 380°C, and it was due to the degradation of the main chain of PVA composite membrane; the total weight loss corresponds to this stage is given in Table I for all the membranes.

It has been observed that for the pure PVA, the onset decomposition temperature started at 250°C, which was less than that of the PVA/glycerol membranes. This was directly related to the plasticizing effect of the glycerol causing the decomposition temperature increases to a higher value. The second stage around 380–480°C was due to the carbonation of polymer matrix followed by a final decomposition of the polymer chains that begins around 500°C. There was 90% weight loss or more for all samples at above 500°C. TGA data was given in Table I.

The onset decomposition temperature for PVA blends starts at 300°C. After this temperature, the PVA/glycerol polymer membrane becomes greatly degraded. It has been clearly evidenced that the PVA/glycerol membrane samples are relatively stable in the temperature range of 100–300°C.

DSC analysis

The DSC thermograms of the PVA/glycerol blends are presented in Figure 3 for various glycerol contents. There is no thermal history present in these blends or subjected to since they were all casted from solution. All thermograms were obtained from the initial heating run from 50 to 400°C. Three endothermic peaks were observed on the DSC curve of the pure PVA as well as PVA/glycerol blends. The first relaxation observed at 50–150°C, is due to the

TABLE I
The Weight Loss (%) of the PVA and PVA/Glycerol Polymer Blends at Different Temperatures Obtained from TGA Analysis

Glycerol Weight Percentage (wt %)	Temperature (°C) Region		
	50–200°C	300–380°C	400–500°C
0.0	4.28	52.02	41.36
0.5	8.77	43.22	36.42
1.0	5.78	45.18	36.08
2.0	8.22	50.51	23.45

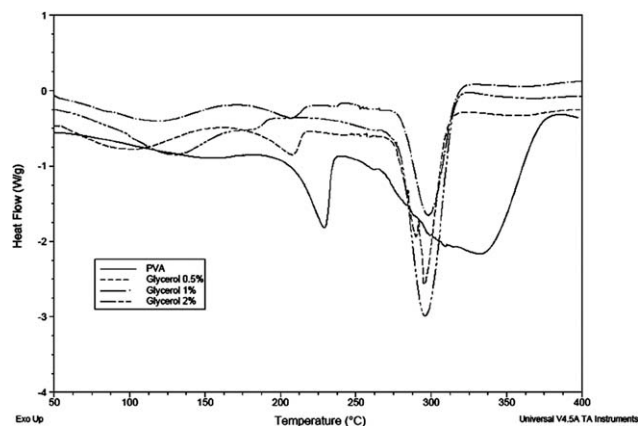


Figure 3 DSC thermograms of pure PVA and PVA/glycerol blends.

relaxation in the PVA crystalline domains. The second relaxation in the temperature range of 175–225°C is caused by the melting of the crystalline domains of PVA, and the third peak starting from 250°C is due to the decomposition of the PVA.⁵⁰

When glycerol is incorporated into the PVA film, it can be seen that the thermal degradation onset is shifted to a higher temperature (also from TGA data) while the melting peak is shifted to a lower temperature, and that these effects increase with increasing glycerol content. These behaviors are better visualized in the peak temperature data shown in Table II.

The depression of the melting temperature (T_m) and the peak broadening indicate that the ordered association of the PVA molecules was decreased by the presence of glycerol.⁵¹ It can be interpreted that glycerol increases the segmental mobility of PVA and decreases the crystallite region of a PVA. With the water evaporation by dehydration, the glycerol will become more concentrated. Thus, the formation of the biopolymeric matrix will take place via electrostatic, hydrophobic, and Van der Waals interactions, as well as hydrogen bonds among adjacent PVA chains and between the glycerol.⁵² FTIR spectroscopy experiment confirmed the formation of hydrogen bonding between glycerol and PVA in

TABLE II
Glass Transition Temperature (T_g), Melting Temperature (T_m) and Decomposition Temperature (T_d) of the PVA/Glycerol Polymer Blends with Increasing Glycerol Weight Percentage

Glycerol Weight Percentage (wt %)	T_g (°C)	T_m (°C)	T_d (°C)
0.0	152.9	230.1	331.2
0.5	99.2	206.4	293.5
1.0	115.6	203.6	292.7
2.0	124.5	177.8	290.4

their blends as explained in more details in Section FTIR characterization.

Mechanical properties

The mechanical properties of PVA/glycerol blends were performed by nanoindentation. Figure 3 shows the loading-unloading curves of three PVA/glycerol blend samples. It has been seen that the plasticizers plays an important role on the mechanical properties of polymers. Generally, the tensile strength decreased and the elongation at break increased as the percentage of plasticizers increased.⁵³ The hardness and elastic modulus of PVA blends as the function of glycerol concentration are shown in Table III.

As the glycerol percentage increased, the residual glycerol in the blends played a role as the plasticizer, which reduced the interactions among the macromolecules and resulted in the decrease of the hardness as well as elastic modulus. The presence of glycerol had a significant plasticizing effect on PVA by reducing both the glass transition and melting temperature of PVA membrane and storage modulus drop. This plasticizing effect could be attributed to their low-molecular-weight and hydroxyl groups leading to the formation of polymer-plasticizer interactions to the detriment of polymer-polymer interactions. Smaller molecules of glycerol embed themselves between the PVA chains, increasing the spacing and free volume, and allowing them to move past one another even at lower temperatures.

FTIR characterization

FTIR was used to characterize the presence of specific and important chemical groups in the materials. Pristine PVA film and PVA containing varying percentage of glycerol were obtained as 1–2 mm thick films and were analyzed using FTIR in a transmittance mode. Figure 4 shows the FTIR spectra for pure glycerol, neat PVA polymer, and three (PVA/glycerol) blends with different glycerol percentage namely 0.5, 1.0, and 2 wt %. All major peaks related to hydroxyl, and methyl groups were observed. In

TABLE III
Nanoindentation Results of a Neat PVA and PVA/Glycerol Blends

Glycerol Weight percentage (wt %)	Hardness (GPa)	Elastic Modulus (GPa)
0.0	0.133724	1.242050246
0.5	0.102452	0.796296442
1.0	0.032235	0.297138235
2.0	0.010538	0.067103394

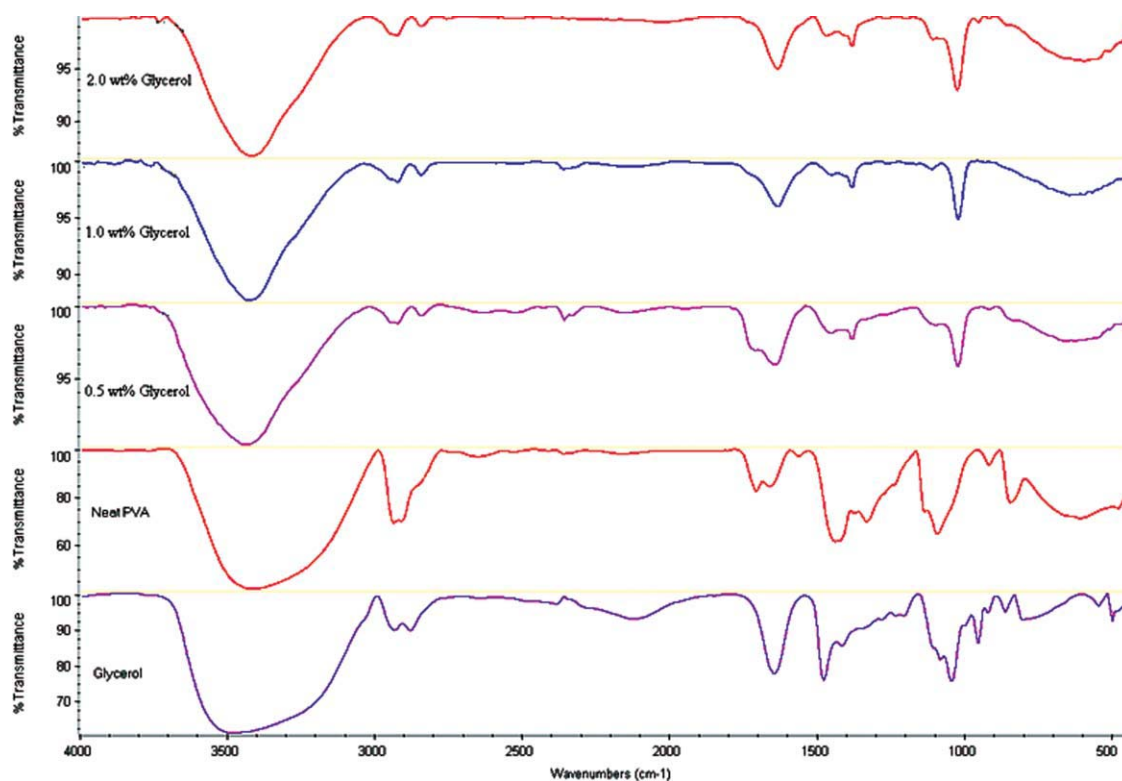


Figure 4 FTIR Spectra for all samples including neat glycerol, pure poly(vinyl alcohol) and their blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

pristine PVA, intramolecular and intermolecular hydrogen bonds are expected to occur between hydroxyl groups attached to the main chain due to high hydrophilic forces.⁵⁴ The broad band observed in all samples between 3400 and 3500 cm^{-1} was linked to the stretching O—H from the intermolecular and intramolecular hydrogen bonds. The vibrational band observed at 2900 cm^{-1} refers to the stretching C—H from alkyl groups, which is clearly visible in the glycerol spectra and neat PVA. It was observed that the intensity of this peak decrease as the glycerol percentage increase. The peaks between 1000 and 110 cm^{-1} are due to the stretching of C—O group, which once again present in all samples. These peaks become sharper are shifted to lower frequencies as the glycerol ratios in the sample are increased.

When PVA is dissolved in deionized water and then mixed with various ratios of glycerol, the chemical structure of PVA undergoes significant transformation in which the hydrogen bonding is dominating the structure. Clear evidence can be observed from the presence of a very broad and large band linked to the stretching of O—H group in the range from 3100 to 3600 cm^{-1} in all samples but more evident in pristine PVA sample. The broad peak was shifted progressively to higher wavelength region and become sharper and more defined as the glycerol

weight percentage was increased. This indicates the hydrogen bonding is switched from among PVA chains to PVA/glycerol. Furthermore, the reduction of intensity of the O—H peaks present in the glycerol containing PVA samples, indicating a possible formation of a random chains rearrangement of the physical crosslinking of PVA with glycerol destroying the crystalline domains. This may be explained by the formation of amorphous domain structure, which may present between glycerol and PVA in which the polymer chains are starting to unfold. This examination gives support to the reduction in mechanical properties, which was observed for PVA sample containing different percentages of glycerol plasticizer.

SEM observations

Photo 1 shows the SEM micrograph of the dehydrated surface of the highest percentage of glycerol blended with PVA (2 wt % glycerol/PVA). As seen from the micrograph the domain of the plasticizer is well blended within the polymer matrix and no segregation was observed. This evaluation suggests that the glycerol is entirely compatible with PVA Also revealed that the glycerol is a compatible plasticizer to PVA and interacts fully with the polymer by distributing itself consistently within the polymer

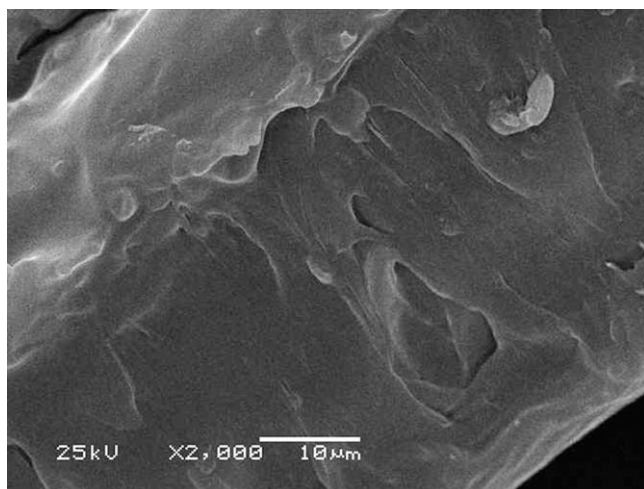


Photo 1 Scanning electron micrograph of 2 wt % glycerol blended with poly(vinyl alcohol).

matrix creating an additional free volume. Blending efficiency and compatibility depends on the chemical structure, molecular weight, and functional groups of the plasticizer; therefore, the polymer and the plasticizer are having similarity in solubility parameters and polarity (hydrogen bonding) to form a homogenous blend.⁵⁵ This was examined and confirmed by both SEM and FTIR.

CONCLUSIONS

All polyvinyl alcohol blends with various weight percent of glycerol, have an excellent film forming characteristics. The blended films produced were colorless and homogenous and transparent. This work demonstrates that glycerol form favorable interactions with PVA through the intermolecular hydrogen bonding interactions. As the glycerol percentage increased, the melting temperature of PVA decreases along with broadening of endothermic peak, which indicate that the ordered association of the PVA molecules decreased. The residual glycerol in the blends played a role of a plasticizer, which reduces the interactions among the macromolecules, which resulted in the decrease of the hardness as well as elastic modulus. FTIR spectroscopy was used to confirm the presence of major functional groups present in PVA/glycerol blends and used to confirm the formation of intermolecular attraction forces between PVA and the glycerol. The distribution and dispersion of glycerol within the polymer matrix was observed using SEM and confirmed by FTIR.

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