

Thermomechanical properties of poly(vinyl alcohol) plasticized with varying ratios of sorbitol

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ABSTRACT

The objective of this work is to study the thermal and mechanical properties of films based on blends of poly(vinyl alcohol) (PVA) with different weight percent of sorbitol. Solid-state PVA/sorbitol polymer membranes were prepared by a solution casting method. The characteristic properties of these polymer membranes were examined by thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC), nanoindentation methods and by Fourier Transform Infrared (FTIR) spectroscopy. It was found that the thermal properties (glass transition, T_g , melting point, T_m and decomposition temperature, T_d) for PVA blends showed a decrease proportional to the sorbitol concentrations. The hardness and elastic modulus obtained from nanoindentation test were also found to decrease with increase in plasticizer concentration. FTIR confirmed the reduction in hydrogen bonding between PVA chains in favour of formation new bonding between the plasticizer and the PVA chains.

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1. Introduction

Polymer blending constitutes a most useful method for the improvement or modification of the physicochemical properties of polymeric materials. Some of the polymer blends exhibit unusual properties, unexpected from homopolymers. An important property of a polymer blend is the miscibility of its components, because it affects the mechanical properties, the morphology, its permeability and degradation [1,2]. Numerous investigations regarding the miscibility in multi-component polymer systems have been carried out. Among them, the blends between biopolymers and synthetic polymers are of particular significance because they can be used as biomedical and biodegradable materials [3–13].

The Poly(vinyl alcohol) PVA is a hydrophilic semi-crystalline polymer produced by polymerization of vinyl acetate monomer to form poly(vinyl acetate) (PVAc), and subsequent hydrolysis of PVAc to PVA [14]. PVA is a water soluble synthetic polymer, non-toxic, with excellent film forming properties, which has been studied for medical and biomedical applications [14–16], recognized as biodegradable since the latest nineties [17]. For this reason, PVA has also been used in studies on biodegradable film production [18], including blended with proteins of various sources, such as

PVA/wheat [19], PVA/collagen hydrolysate [20,21], and PVA/gelatin [18,22–25].

PVA also offers flexibility, transparency, toughness as well as lower cost than other barrier polymer. Therefore, PVA has been developed as a barrier film for food packaging applications [26–29]. However, it is difficult to produce the film because the crystalline melting temperature (T_m) and decomposition temperature (T_{decom}) of PVA are close to each other. It is a limit for expanding into the market of food packaging application due to high manufacturing cost. Therefore, it is necessary to improve the thermal characteristic of PVA in order to suitability used in food packaging and film applications.

Room temperature ionic liquids 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, non-volatility, non-flammability and so on [30–35]. 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 [36–38]. 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 [39,40]. Water, oligosaccharides, polyols, and lipids are different types of plasticizers that are widely used in hydrocolloid-based films [41]. Independent of the moisture content, the production of films based on biopolymers normally demands the use of plasticizer agents to improve film workability. Plasticizers, which are low molecular

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components, 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 [42]. A number of plasticizers, e.g. water and polyols [43–45] have been utilized in order to lower the glass-transition temperature (T_g) and increase the flexibility and workability of biopolymer-based films [43,46–55]. 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 [56].

In this work, we investigated the effect of sorbitol (plasticizer) percentages on the physical and mechanical properties of the PVA films. In addition, the melting and crystallization behaviour of PVA were also examined according to the amount of plasticizer blended with the PVA. FTIR spectroscopy for all samples was also examined.

2. Materials and experimental methods

2.1. Materials

Sorbitol was obtained from Quartek Corp., NC, polyvinyl alcohol PVA-124 was purchased from Sigma–Aldrich Chemical Co. having molecular weight of 124,000–186,000 g/mol with acetyl hydrolysis rate of 99%. All other laboratory reagents were also purchased from Sigma–Aldrich and used as supplied. Distilled water was used in the preparation of the polymer films.

2.2. Material and membrane preparation

The solid-state PVA/sorbitol polymer membranes (sorbitol with 0.5%, 1% and 2% of weight) were prepared by solution casting method. PVA 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 is heated and stirred until it is completely dissolved. Then 0.9 ml (for 0.5 wt%) of sorbitol and 8.8 ml ethanol were added to PVA solution and mixed together under continuous stirring condition at the temperature of 90 °C for about 6 h. or until the solution becomes completely homogeneous. The resulting homogeneous polymer solution was then poured onto a PTFE plate to form a film. The excess water solvent mixture was further evaporated slowly at 80 °C in a vacuum oven. The other two (1 wt% and 2 wt%) PVA/sorbitol blends were prepared in the same procedure. All films obtained were transparent with a uniform thickness. Each film sample was stored in a sealable plastic bag and kept at room temperature.

2.3. Thermo gravimetric analysis (TGA)

TGA analysis of PVA/sorbitol 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) software.

2.4. 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 samples (~10 mg) were placed in hermetically sealed aluminium Tzero pans and heated from –50 °C to 400 °C with a heating rate of 10 °C/min under nitrogen atmosphere [48]. An empty hermetically sealed aluminium 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 inflexion occurred, and the melting temperature was determined as the peak temperature of the endothermic event of the DSC curves.

2.5. Nanoindentation

All nano-indentation experiments of PVA/sorbitol membranes were performed by a Nano Test Materials Testing Platform Two (Micro Materials Ltd., Wrexham, UK) that was equipped with a three-sided pyramid diamond indenter tip (Berkovich type) [57]. 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 in order to avoid the creep significantly affecting the unloading behaviour. 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 in order to avoid strain-hardening effects on the measurements [58]. At least five indents were performed on each sample and the distance between the indentations was 50 µm to avoid interaction.

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. Nano-indentation hardness is defined as follows [59]: (1) $H = \frac{P_{\max}}{A} = \frac{P_{\max}}{24.5h_c^2}$, 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 (2) $h_c = \frac{h - 0.75P_{\max}}{S}$ where S is the slope (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. As the indenter was allowed to penetrate into the sample, both elastic and plastic deformation occurred, and only the elastic portion of the displacement was recovered during unloading. 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 [60]: (3) $S = 2\beta E_r \left(\frac{A}{\pi}\right)^{1/2}$ 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 [57]: (4) $E_s = (1 - \nu_s^2) \left\{ \frac{1}{E_r} - \frac{(1 - \nu_i^2)}{E_i} \right\}^{-1}$ where ν_s and ν_i (0.07) [64] 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 semicrystalline polymeric materials is 0.35 [61].

2.6. Fourier transform infrared spectroscopy (FTIR)

Transmission infrared spectra of all films were recorded at room temperature using FTIR (NEXUS-470, Thermo Nicolet Corporation) 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 after scanning the background.

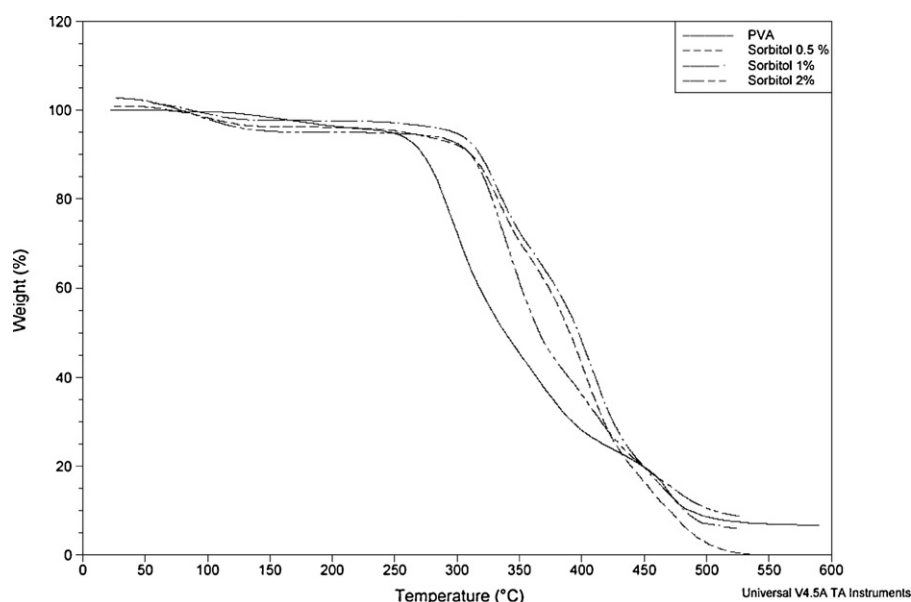


Fig. 1. TGA thermograph of the PVA/sorbitol polymers.

3. Results and discussion

3.1. 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 samples as well as the specific interactions associated between the different macromolecules or molecules present in the polymer. 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 [46–48].

3.1.1. TGA analysis

Thermo gravimetric analysis were conducted on pristine PVA thin film and PVA/sorbitol membranes to determine their thermal stability and the corresponding degradation stages in response to temperature as well as their moisture content in the membrane. Polymer membranes of three different PVA/ Sorbitol blends with sorbitol weight 0.5%, 1% and 2% were used in this study. Figure 1 shows all the combined the TGA curves of PVA and PVA/sorbitol membranes. There is a weight loss at the temperature of 100 °C for the PVA/sorbitol polymer membrane. It indicates that this polymer membrane contains some physical weakly and chemically strongly bound water in the matrix [62]. The higher the sorbitol content ratio, the higher percent of weight loss is for water at 100 °C. In addition, the PVA and PVA/sorbitol polymer membranes exhibit two-step degradation. The first step region is at around 300–380 °C is due to the degradation of PVA composite membrane; the total weight loss corresponds to this stage is given in Table 1 for all the membranes. It has been seen that for pristine PVA the decomposition start at 250 °C less than that of the PVA/sorbitol membranes which indicates that due to plasticizing effect of sorbitol the decomposition temperature increases. The second step around 380–480 °C was due to the carbonation of polymer matrix followed by a final decomposition of the polymer that

begins around 500 °C; there is a total weight loss for each sample at 500 °C is given in Table 1.

The onset decomposition temperature for PVA blends starts at 400 °C. After this temperature, the PVA/sorbitol polymer membranes becomes greatly degraded. It has been clearly evidenced that the PVA/sorbitol membrane samples are relatively stable in the temperature range of 100–300 °C.

3.1.2. DSC analysis

The DSC thermograms of the PVA/sorbitol blends are presented in Fig. 2 for various sorbitol contents. The first type of changes detected was related to the changes in heat capacity, which cause a shift in the base line of the DSC thermogram. Such shift is associated with the glass transition temperature (T_g). These changes were appeared at temperature range between 80 and 152 °C for all samples two endothermic peaks at higher temperature were also detected on the DSC curve for both pure PVA as well as PVA/sorbitol blends. The first relaxation in the temperature range of 200–230 °C is caused by the melting of the crystalline domains of PVA [63] and the second peak starting from 290 °C is due to the decomposition of the PVA. As the content of sorbitol increased, the first endothermic peak (T_m) of PVA blends became less intense and its value shifted to lower temperatures. Similar trend was observed for the T_g values of all samples see Table 2.

The depression of the melting temperature and the peak broadening indicate that the ordered association of the PVA molecules was decreased by the presence of sorbitol. It can be interpreted that sorbitol increases the segmental mobility of PVA and decreases the crystallite region of a PVA. With the water evaporation by dehydration, the sorbitol will become more concentrated. Thus, the formation of the biopolymeric matrix will take place via elec-

Table 1

The weight loss (percentage) of the PVA and PVA/sorbitol polymer membrane at different temperatures obtained from TGA analysis.

Sorbitol weight %	Temperature (°C) region		
	100	300–380	500
0	4.28	56.26	93.36
0.5	3.55	45.15	97.85
1	4.46	46.54	94.88
2	6.82	63.58	92.84

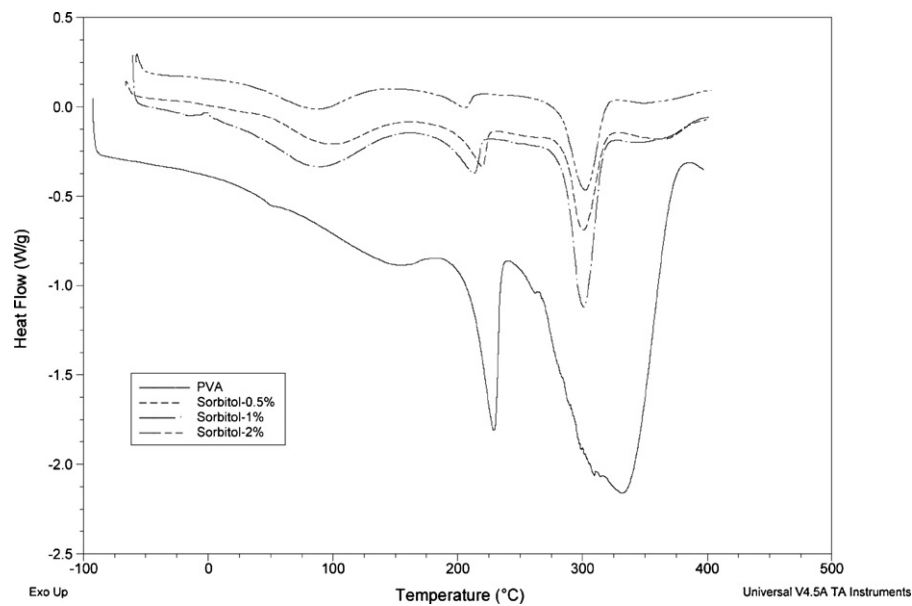


Fig. 2. DSC thermograph of the PVA/sorbitol polymers.

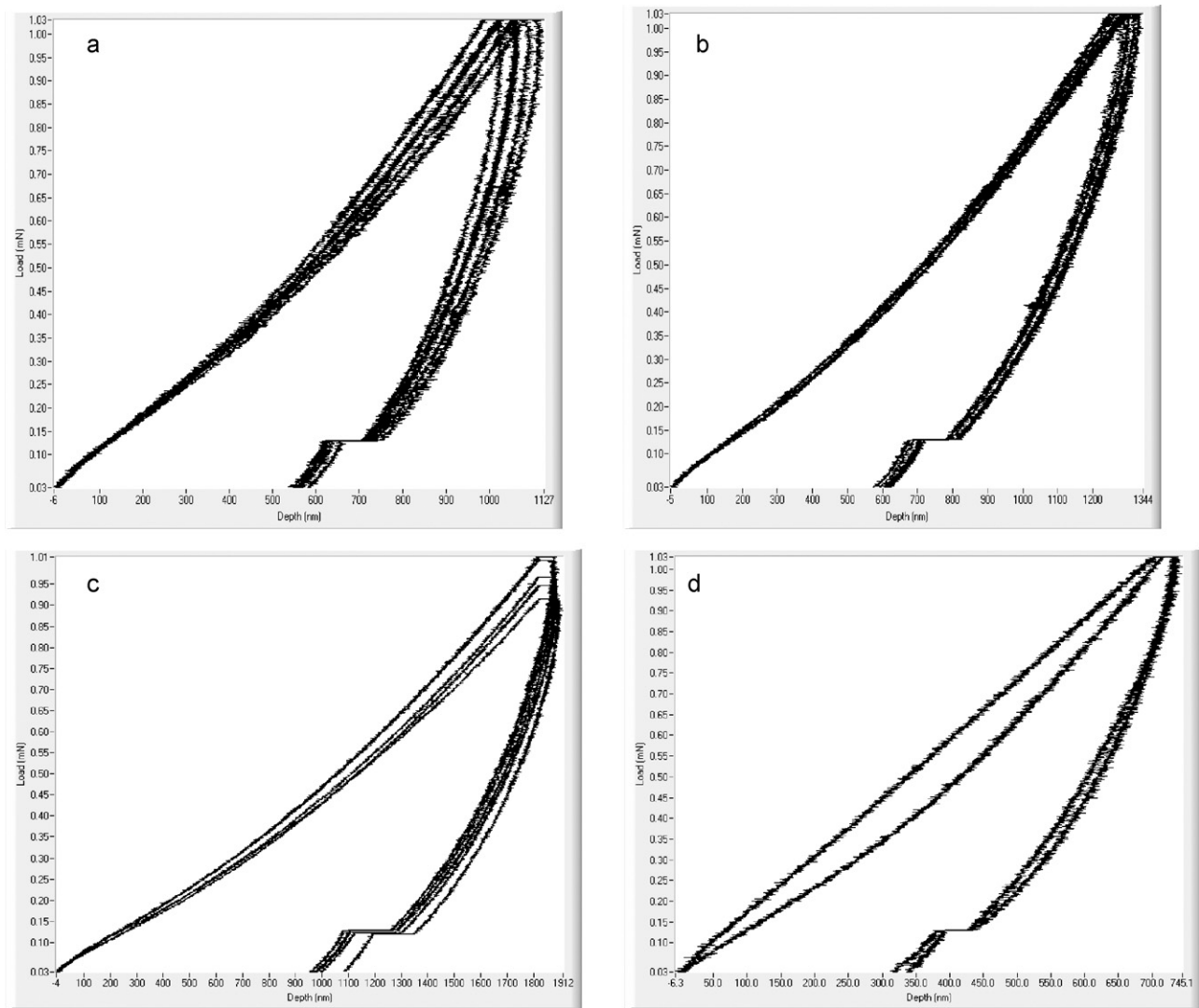


Fig. 3. Nanoindentation (loading–unloading curves) of the PVA/sorbitol blends. (a) Nanoindentation curve of PVA with 0.5% sorbitol. (b) Nanoindentation curve of PVA with 1% sorbitol. (c) Nanoindentation curve of PVA with 2.0% sorbitol. (d) Nanoindentation curve of PVA with 0.0% sorbitol.

Table 2

The transition temperature (T_g), melting temperature (T_m) and decomposition temperature (T_d) of the PVA/sorbitol polymer membranes with increasing sorbitol weight percent.

Sorbitol weight %	T_g , °C	T_m , °C	T_d , °C
0	152.9	230.1	331.2
0.5	96.6	218.4	299.3
1	85.5	209.2	297.3
2	80.2	200.4	296.8

trostatic, hydrophobic, and Van der Waals interactions, as well as hydrogen bonding between adjacent PVA chains and sorbitol molecules [64].

3.2. Mechanical properties

The mechanical properties of PVA/sorbitol blends were performed by nanoindentation. Figure 3(a–d) shows the loading–unloading curves of three PVA/sorbitol blend with 0.5, 1.0 and 2.0 weight percentage of sorbitol and for pure PVA, respectively.

It has been known that the plasticizer 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 [65]. The hardness and elastic modulus of PVA blends as the function of sorbitol concentration are shown in Table 3(a–c).

As the sorbitol percentage was increased, the residual sorbitol in the blends played a role of the plasticizer, which reduced the interactions among the macromolecules, which resulted in the decrease of the hardness as well as elastic modulus. The presence of sorbitol 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

Table 3

Nanoindentation of PVA/sorbitol blends with various sorbitol weight percent including pure PVA.

Data from Fig. 3	Sorbitol, weight%	Hardness (GPa)	Elastic modulus (GPa)
a	0.5	0.055	0.674
b	1	0.042	0.376
c	2	0.017	0.203
d	0.0	0.134	1.195

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 sorbitol embed themselves between the PVA chains, increasing the spacing and free volume, and allowing them to move past one another even at lower temperatures.

3.3. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) was used to characterize the presence of specific chemical groups in the materials. Pristine PVA film and PVA containing different percentage of sorbitol were obtained as 1–2 mm thick films and analyzed by FTIR using Transmittance mode. Figure 4 shows the FTIR spectra of pure sorbitol, pristine PVA polymer, and three PVA/sorbitol blends with different sorbitol content. All major peaks related to hydroxyl, and methyl groups were observed. In pristine PVA, intra-molecular and inter-molecular hydrogen bonds are expected to occur between hydroxyl groups attached to the main chain due to high hydrophilic forces [66]. The broad band observed between 3100 and 3500 cm^{-1} was ascribed to the stretching of hydroxyl groups (O–H) which contributed to from the intermolecular and intra-molecular hydrogen bonds [67]. The vibrational band observed at 3000 cm^{-1} refers to the stretching C–H from alkyl groups, which is clearly visible in the sorbitol spectra. It was observed that the intensity of this peak

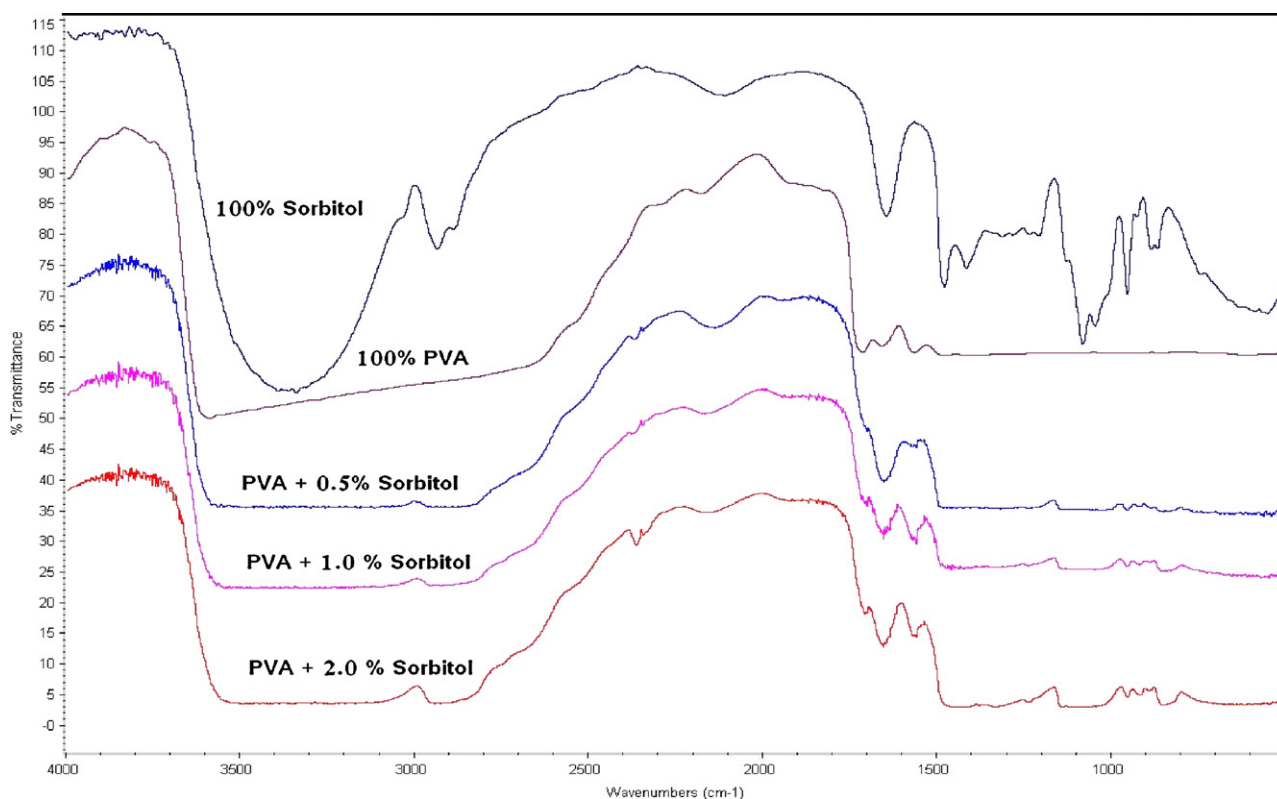


Fig. 4. FTIR spectroscopy for all samples including pure sorbitol.

increases as the sorbitol percentage increase. The peaks between 1550 and 1720 cm^{-1} are due to the stretching of C–O group. When PVA is dissolved in deionized water and then mixed with various ratios of sorbitol, 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. However, in pristine PVA sample, the peak was even broader due to the large number of hydroxyl groups present in contrast to the sorbitol, which has limited number of hydroxyl groups, which made the peak more resolved. The lower limit of the broad peak, containing various ratios of sorbitol, was shifted to higher wavelength region compared to the pure PVA due to hydrogen interaction of the sorbitol with hydroxyl groups of the PVA. This indicates the hydrogen bonding is switched from among PVA chains to PVA/sorbitol [68]. Furthermore, the reduction of intensity of the O–H peaks present in the sorbitol containing PVA samples, indicating a possible formation of a random chains rearrangement of the physical cross linking of PVA with sorbitol destroying the crystalline domains. This may be explained by the formation of amorphous domain structure, which may present between sorbitol and PVA in which the polymer chains are starting to unfold. This give support to the reduction in mechanical properties, which was observed for PVA sample containing different percentage of sorbitol.

4. Conclusion

This work demonstrates that sorbitol form favourable interactions (probably hydrogen bonds) with PVA. As the sorbitol percentage increased, the melting temperature of PVA decreases along with broadens of endothermic peak, which indicate that, the ordered association of the PVA molecules decreased. The residual sorbitol in the blends played a role as the plasticizer, which reduced the interactions among the macromolecules, which resulted in the decrease of the hardness as well as elastic modulus. FTIR spectroscopy confirmed the presence of PVA/sorbitol interactions.

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