

Development and Compatibility Assessment of New Composite Film Based on Sugar Beet Pulp and Polyvinyl Alcohol Intended for Packaging Applications

Zhu Shen, Mehran Ghasemlou, Donatien Pascal Kamdem

School of Packaging, College of Agriculture and Natural Resources, Michigan State University, East Lansing, Michigan 48824
Correspondence to: M. Ghasemlou (E-mail: ghasemlo@msu.edu) and D. P. Kamdem (E-mail: kamdem@msu.edu)

ABSTRACT: In this study, interaction and compatibility between sugar-beet pulp (SBP) and polyvinyl alcohol (PVA) in blend films was assessed. Film-forming dispersions of different ratios of SBP to PVA (100/0, 75/25, 50/50, and 25/75) were cast at room temperature. The effects of adding PVA to SBP on the resulting film's physical, mechanical and barrier properties and thermal stability were investigated. X-ray diffraction and environmental scanning electron microscopy (ESEM) were used to characterize the structure and morphology of the composites. When PVA was also added to the composite films, the films became softer, less rigid and more stretchable than pure SBP films. The addition of PVA gave significantly greater elongation at break (12.45%) and lower water vapor permeability ($1.55 \times 10^{-10} \text{ g s}^{-1} \text{ m}^{-1} \text{ Pa}^{-1}$), but tensile strength did not markedly change, remaining around 59.68 MPa. Thermogravimetric analysis also showed that SBP/PVA film had better thermal stability than SBP film. The ESEM results showed that the compatibility of SBP50/PVA50 was better than those of other composite films. These results suggest that when taking all the studied variables into account, composite films formulated with 50% PVA are most suitable for various packaging applications. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41354.

KEYWORDS: casting method; composite film; physical properties; sugar-beet pulp; thermal stability

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INTRODUCTION

Over the past two decades, the use of plastic from synthetic polymers has increased significantly. These polymers—polyethylene, polypropylene, polyethylene terephthalate, polystyrene (PS) and polycarbonate—are usually petroleum-based and are regarded as non-degradable.¹ One of the current research trends is the replacement of synthetic polymers with biodegradable plastics made of renewable raw materials. This is closely connected with growing consumer demand for high-quality and long-shelf-life products and increased awareness of environmental problems with non-degradable packaging.² The interest in the study of natural-polymer films has attracted much attention due to their excellent biodegradability and biocompatibility, and the range of their potential applications. However, films based on these biopolymers are usually sensitive to environmental conditions, and their physical and mechanical properties are not adequate for many applications.³ As a result, several studies have been carried out to develop films based on mixtures of biopolymers and synthetic polymers.^{4,5}

Sugar-beet pulp (SBP) is a lignocellulosic byproduct from the sugar refining industry and is mainly used for animal feeding.

The United States sugar industry discarded about 26.7 million tons of SBP in dry-matter equivalent in 2011.⁶ On a dry-weight basis, SBP contains 75–80% polysaccharides, consisting of roughly 22–24% cellulose; 30% hemicelluloses, mainly arabinans and (arabino) galactans; 25% pectin. There are also small amounts of fat (1.4%), protein (10.3%), ash (3.7%) and lignin (5.9%).⁷ Of these compounds, SBP cellulose has been shown to have a strong potential for a number of packaging applications. Unlike most cellulose originating from secondary-wall fibers, the cellulose obtained from SBP is a typical primary-wall cellulose.⁷ SBP has been traditionally employed as an excellent emulsifier, thickener or stabilizer, along with a number of potential non-food industrial applications.⁸ Dufresne et al.⁹ showed that SBP can produce films with good appearance and satisfactory mechanical properties; it appears to have good potential as a film forming agent. However, to the best of our knowledge, limited studies have been carried out to evaluate the effectiveness of biodegradable films made from SBP for possible applications as packaging material.

Polyvinyl alcohol (PVA), as a non-toxic and water-soluble synthetic polymer with excellent film-forming properties and chemical resistance, as well as good biodegradability, has been

widely used in the preparation of blends and composites with several natural, renewable polymers.¹⁰ Many researchers have studied various biodegradable composite packaging films made from PVA and other renewable biopolymers such as corn starch,¹¹ chitosan,¹² sodium alginate¹³ and carboxymethyl cellulose.¹⁴ Nevertheless, to our knowledge this is the first study that explores various characterizations of PVA–SBP blend films.

Based on these considerations and the need for fundamental research into and potential industrial applications of biodegradable films, the aim of this study was to develop new biocomposite, biodegradable films by blending PVA with SBP using a simple casting method, with sorbitol as a plasticizer, and to evaluate some characteristics of these films, such as their mechanical, barrier, thermal stability, crystallinity and microstructural properties, to examine their potential applications as packaging material.

EXPERIMENTAL

Materials

Sugar-beet pellets were donated by the Michigan Sugar Company (Bay City). The pellets were dried and ground into powder fine enough to go through an 80-mesh sieve using a high-speed Laboratory Wiley Mill. The moisture content of the powders was around 7% (d.b.), according to the provider. They were stored at room temperature (23°C) until used. All chemical reagents used in this research were purchased from Sigma–Aldrich Chemical Co. (St. Louis, MO) and were of analytical grade. Millipore water (deionized and filtered) was used in the preparation of the film-forming dispersion (FFD).

Preparation of SBP. The dried and ground SBP was defatted by extraction with 200 mL in a Soxhlet apparatus for at least 24 h in accordance with ASTM E1690.¹⁵ The dewaxed samples were allowed to stand in a mild acid aqueous solution (1 M H₂SO₄) adjusted to a convenient pH (1.5 or 2) inside an Erlenmeyer flask with the temperature set at 75°C. Mild acid hydrolysis was chosen as the most appropriate system for the selective hydrolysis of hemicellulose in SBP.¹⁶ The residual was then filtered and washed with distilled water several times until its pH was neutral. After acid treatment, the bleaching process was used to remove the lignin. Forty grams of the acid treated sample was heated in a water bath for 24 h at 70–80°C together with 160 mL of water containing 40 g of hydrogen peroxide (30% solution) and 200 g of acetic acid. The residue was hand-squeezed in a nylon cloth and washed with distilled water and boric acid (2%). Distilled water was added to the residue up to 800 mL; the sample was placed in a 1-L aluminum vessel (Chicago Boiler Company, Chicago) and homogenized using 250 g glass beads and 50 g ceramic bead abrasives for 15 h at room temperature and 610 rpm. All purified SBP was refrigerated at 4°C in bottles covered with aluminum foil to prevent direct exposure to light until further analysis.

Chemical Composition of SBP. The chemical composition of the SBP at the initial and final stages of treatment was determined according to the standards provided by the Technical Association of Pulp and Paper Industry, taking into account the modification described by Silvério et al.¹⁷ This method is

based on the sequential extraction and separation of three fractions of lignocellulose. Briefly, lignin content was determined as specified in the ASTM standard E1721.¹⁸ This method is based on the isolation of lignin after hydrolysis of the polysaccharides (cellulose and hemicellulose) and its dissolution with concentrated sulfuric acid (72%). The holocellulose (hemicellulose + cellulose) content was estimated according to ASTM standard D1104¹⁹ through selective degradation of the lignin by sodium chlorite at 70°C. The cellulose content was determined by the removal of the hemicellulose from the holocellulose using sodium hydroxide (NaOH) at room temperature. The hemicellulose content was found by subtracting the cellulose content from the holocellulose content. The ash content was also determined by considering the percentage difference before and after calcination for 6 h at 500°C.

Preparation of Films. SBP/PVA composite films were manufactured by casting and evaporation as follows. A PVA solution was prepared by dissolving 5 g of PVA in 50 mL distilled water under magnetic stirring at 40°C for 1 h. SBP/PVA composite films were prepared by mixing different levels of 1% (w/w) purified SBP solutions (created as described in the previous section) with various levels of PVA solutions (denoted as SBP100, SBP75/PVA25, SBP50/PVA50, and SBP25/PVA75). To achieve complete dispersion, each mixture was stirred constantly for 40 min using a magnetic stirrer at 500 rpm on a hot plate. The films prepared without plasticizer were brittle and cracked on the casting plates during drying. Thus, plasticizer was incorporated into the FFD to achieve more-flexible films. Preliminary experiments were performed to compare the effectiveness of using sorbitol or glycerol as a plasticizer. It was revealed that sorbitol gave significantly better results than glycerol, with the latter producing wet films that were difficult to peel. Accordingly, the dispersions were mixed with sorbitol as a plasticizer at a loading of 10% (w/w) of the total solid weight. Following the addition of plasticizer, stirring was continued for a further of 15 min. The resulting dispersions were rested for several minutes to allow natural removal of most of the air bubbles incorporated during stirring. The FFDs were spread over PS petri dishes (15-cm diameter, 30 g of FFD per plate), which were placed on a leveled surface and allowed to dry for approximately 48 h at 30% RH and 22°C. Dried films were peeled off the casting surface and maintained at 22°C and 53% relative humidity (produced with saturated Ca(NO₃)₂ solution) in a conditioning desiccator until further evaluation. For each test, three different samples were prepared by taking three portions from each film at different positions (two at the edges and one at the center) with the exception of the water vapor permeability (WVP) analysis, where the whole sample was used, and replicates of each type of film were evaluated.

Film Characterization. Film thickness. Film thickness was determined using a hand-held digital micrometer (Mitutoyo No. 293-766, Tokyo, Japan) with a precision of 0.0001 mm. Measurements were carried out on at least five random locations, and the mean thickness value was used to calculate the permeability and mechanical properties of the films.

Film density. To determine film density, samples of $1 \times 1 \text{ cm}^2$ were maintained in a desiccator with calcium sulfate desiccant (0% RH) for 20 days and weighed. Dry-matter densities were calculated using eq. (1):

$$\rho_s = \frac{m}{A \times \delta}$$

where A is the film area (1 cm^2), δ is the film thickness (cm), m is the film dry mass (g) and ρ_s is the dry-matter density of the film (g/cm^3).²⁰ The film density was expressed as the average of three determinations.

WVP. The WVP of films was determined gravimetrically in accordance with ASTM E96/E96M²¹ with some modifications. Films without pinholes or defects were cut into discs with a diameter slightly larger than the diameter of special glass cups with a circular opening of 0.000324 m^2 . Each cup was completely filled with calcium sulfate desiccant (0% RH) and covered with a disc, leaving an air gap of 1 cm between the film underside and the desiccant. The whole system was then placed in a desiccator containing a saturated sodium chloride solution (75% RH). The RH inside the cell was always lower than outside, and water-vapor transport was determined from the weight gain of the permeation cell at a steady state of transfer. The cups were weighed to the nearest 0.0001 g every 1 h during the first 9 h and finally at 24 h intervals over the rest of a 4-day period. Changes in the weight of the cup were recorded and plotted as a function of time. The slope of each line was calculated by linear regression using Microsoft® Office Excel 2010 (the lines' regression coefficients were > 0.998). The water vapor transmission rate was obtained by dividing the slope (g/h) by the effective film area (m^2). This was multiplied by the thickness of the film and divided by the pressure difference between the inner and outer surfaces to obtain the WVP value, which was expressed as $[\text{g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}]$ and calculated according to eq. (2):

$$\text{WVP} = \frac{\Delta m X}{A \Delta t \Delta p}$$

where $\Delta m/\Delta t$ is the weight of moisture gain per unit of time (g/s), X is the average film thickness (m), A is the area of the exposed film surface (m^2) and Δp is the water vapor pressure difference between the two sides of the film (Pa). WVP was measured for three replicated samples for each type of film.

Mechanical Properties. The mechanical properties of the composite films were determined at 22°C and 30% RH with an Instron 5565 Universal Testing machine (Instron, Canton, MA) according to ASTM standard method D882.²² Films were cut in rectangular strips of 50-mm long and 6.35-mm wide. The films were fixed with an initial grip separation of 25 mm and stretched at an extension speed of 0.8 mm/min. A microcomputer was used to record the stress-strain curves. Tensile strength (TS), elongation at break (EB) and elastic's modulus (EM) were calculated. At least four replicates of each test sample were run to achieve dependable data.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was performed to evaluate the thermal stabilities of SBP100, SBP75/PVA25, SBP50/PVA50, and SBP25/PVA75 using a TGA 2950 running with the Universal Analysis Software pack-

age V3.9a (TA Instruments, New Castle, DE). Samples of approximately 5 mg were heated from 50 to 500°C at $15^\circ\text{C}/\text{min}$ heating rate under a nitrogen flow of $70 \text{ mL}/\text{min}$. Weight losses of samples were measured as a function of temperature. TGA (weight loss as a function of temperature) and derivative thermogravimetry (DTG) curves were recorded. All the measurements were conducted at least in duplicate.

X-ray Diffraction. X-ray diffraction (XRD) patterns of the composite films were taken using a Bruker D8 advanced X-ray diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) operated at 40 kV and 40 mA, equipped with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). Samples were scanned over a diffraction angle (2θ) range of 10 – 40° , with a scanning rate of $2^\circ/\text{min}$ at room temperature. The d -spacing was calculated using Bragg's diffraction equation, $\lambda = 2d \sin \theta$, where λ is the wavelength of the X-ray radiation used ($\lambda = 1.5406 \text{ \AA}$), d is the spacing between diffractive lattice planes and θ is the measured diffraction angle. Data was collected in duplicate.

Film Microstructure. An environmental scanning electron microscope (Phillips Electroscan 2020 equipped with a Lab6 filament) at 20 kV acceleration voltage was used to observe the surface characteristics of the composite films. All composite samples were fractured in liquid nitrogen, and the fractured surfaces were sputter-coated with gold film using a Denton sputter coater to improve image quality.

Statistical Analysis. The results were presented as the mean \pm standard deviation of each treatment. Statistics on a completely randomized design was performed using analysis of variance, analyzed using SAS software (version 9.3; Statistical Analysis System Institute, Cary, NC). Duncan's multiple range tests were used to compare the differences among the mean values for the films' properties at the level of 0.05.

RESULTS AND DISCUSSION

Chemical Composition of SBP

Table I shows the chemical composition of the SBP samples before and after purification. The cellulose content before purification was $22.2 \pm 0.76\%$; the hemicellulose content was $19.3 \pm 0.43\%$; the lignin content was $5.9 \pm 1.23\%$; and the ash content was $6.3 \pm 0.10\%$. After bleaching, the cellulose content was almost three times more than the original value, while the hemicellulose content was approximately half, and the lignin content was significantly removed. These results indicated that the chemical treatments (acid treatment followed by bleaching) can effectively break down the lignocellulosic structure of SBP, leading to cleavage of hemicellulose-lignin bonds and resulting in the almost total removal of lignin. The ash and lignin contents were much lower than those reported by Concha Olmos and Zúñiga Hansen.²³ In terms of cellulose content, Toğrul and Arslan²⁴ reported lower values (17–32%), than those obtained in this work. It was found that the increase in cellulose content brings about improved crystallinity of the SBP samples together with improved thermal properties; this result agrees with Li et al.²⁵

Appearance and Physical Properties of the Films

The SBP films were flexible and resistant when handled. The composite films formed from SBP and PVA were visually

Table I. Chemical Composition of SBP Samples Before and After Treatment

Materials	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)
Raw samples	22.18 ± 0.72b	19.25 ± 0.40a	5.89 ± 1.21a	6.31 ± 0.11a
Bleached samples	78.43 ± 0.55a	12.46 ± 0.53b	1.01 ± 0.11b	1.65 ± 0.23b

Values of the chemical composition represent the mean ± standard deviation of three replicates. Values in a column having different letters were significantly different ($P < 0.05$).

homogeneous, with no bubbles or cracks, and had good handling characteristics. This meant that these films could be easily peeled from the casting plates without tearing. Those without PVA were relatively whitish; however, with the inclusion of PVA in the formulation, they became more transparent (data not shown here). Moreover, it was observed that the color intensified and the transparency increased as the content of PVA increased. The films' thicknesses were found to be similar, with an average thickness between $48 \pm 2 \mu\text{m}$ and $53 \pm 2 \mu\text{m}$; addition of PVA did not change the average thickness of the films significantly ($P > 0.05$). The thicknesses were controlled well because all FFDs were weighed to the same mass prior to casting. The film density which increased upon PVA addition varied from $1.06 \pm 0.01 \text{ g/cm}^3$ to $1.18 \pm 0.01 \text{ g/cm}^3$; demonstrating that the composite films were significantly ($P < 0.05$) more dense than the SBP films.

WVP

One of the main functions of food packaging is to avoid or minimize moisture transfer between the food and the surrounding atmosphere. WVP should therefore be as low as possible to optimize the food package environment and potentially increase the shelf-life of the food product.²⁶

Figure 1 shows the WVP for different composite films made with SBP and PVA. The WVP was $1.78 \text{ g s}^{-1} \text{ m}^{-1} \text{ Pa}^{-1} \times 10^{-10}$ for the plasticized SBP film sample. In this study, the WVP of the SBP/PVA composite films was not significantly ($P > 0.05$) affected by the inclusion of 25% of PVA compared to SBP films. The further addition of PVA up to 50% to SBP resulted in a decreased WVP for the resulting composite films ($1.61 \text{ g s}^{-1} \text{ m}^{-1} \text{ Pa}^{-1} \times 10^{-10}$); this was most likely associated with interactions between SBP and PVA molecules that have the effect of preventing water molecules from diffusing through the films, thus decreasing WVP values. However, when a PVA content of 75% was incorporated, the results did not significantly ($P > 0.05$) affect the WVP of the blend films. The same behavior was shown in research by Limpan et al.,²⁷ who found that increases in PVA concentration decreased the WVP of myofibrillar protein/PVA composite films. The results presented in this study are more promising than those reported by Bonilla et al.,³ who prepared biodegradable films based on PVA and chitosan and reported relatively high WVP values between 6.14 and $19 \text{ g s}^{-1} \text{ m}^{-1} \text{ Pa}^{-1} \times 10^{-10}$. However, the WVP values obtained in this work were high compared to those of high-barrier synthetic polymers: $0.0127 \text{ g s}^{-1} \text{ m}^{-1} \text{ Pa}^{-1} \times 10^{-10}$ for PVC, $0.0092 \text{ g s}^{-1} \text{ m}^{-1} \text{ Pa}^{-1} \times 10^{-10}$ for LDPE and $0.0023 \text{ g s}^{-1} \text{ m}^{-1} \text{ Pa}^{-1} \times 10^{-10}$ for HDPE.²⁸ Nevertheless, the WVP values for the SBP/PVA films were slightly higher than those of cellophane

($0.84 \text{ g s}^{-1} \text{ m}^{-1} \text{ Pa}^{-1} \times 10^{-10}$),²⁹ and there is indeed some scope for their use in some food packaging applications.

Mechanical Properties

The mechanical properties of the films were characterized by measuring the TS, EB and EM, which are key elements of a film's strength and flexibility. Thus, determination of these properties is of great importance not only in scientific but also technological and practical application of these films. Results of the mechanical tests are shown in Figure 2.

Neat SBP films exhibited average TS and EB values of $50.24 \pm 1.22 \text{ MPa}$ and $4.10 \pm 0.41\%$, respectively; these are in the same range as those reported by other authors.^{30,31} SBP/PVA composites with a PVA content of 25% by weight were less elastic and less resistant, and had significantly ($P < 0.05$) lower TS and EB values than neat samples; trends in the values were not clear, and these properties are still under study. Ghasemlou et al.³² have discussed the plasticization effectiveness of glycerol and sorbitol in detail. They suggested that the larger size of sorbitol molecules compared to glycerol molecules would make them less effective in trapping hydrophilic sites; this could probably explain this behavior. Nevertheless, the composite films in which the PVA concentration was more than 50% (SBP50/PVA50) had significantly ($P < 0.05$) higher TS values ($59.68 \pm 4.22 \text{ MPa}$). However, further increases in PVA content did not show a further increase ($P > 0.05$) in TS value

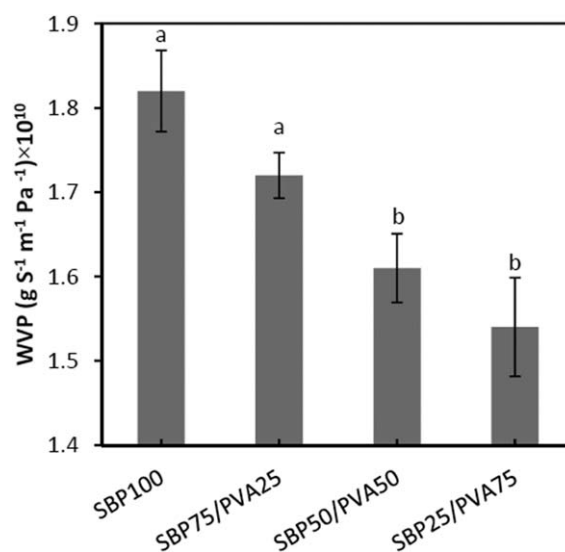


Figure 1. WVP of the different composite films made of sugar beet pulp (SBP) and PVA. Note: a, b, and c are different letters represent significant differences ($P < 0.05$) between the means obtained in Duncan's test.

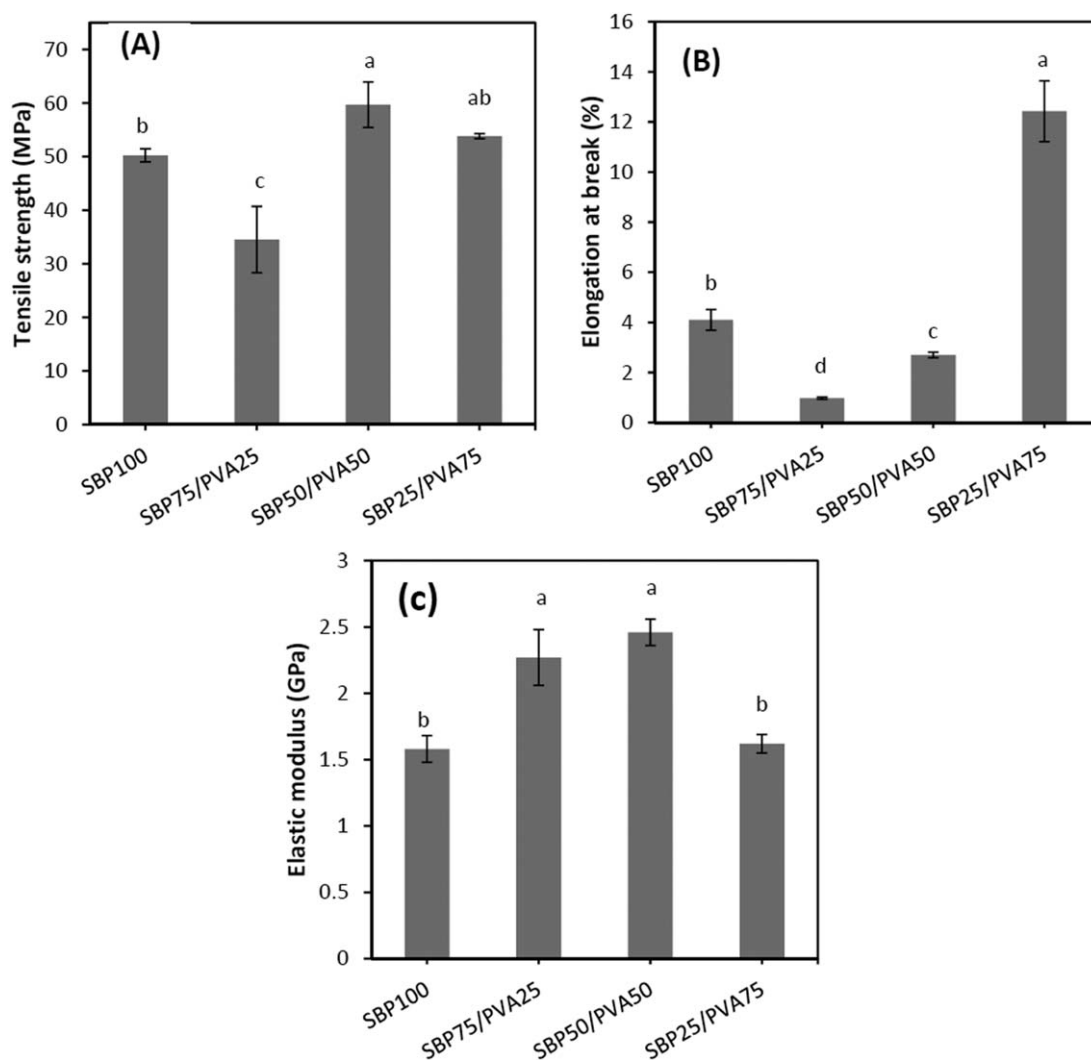


Figure 2. TS (A), EB (B) and Elastic modulus (C) of the different composite films made of sugar beet pulp (SBP) and PVA. Note: a, b and c are different letters represent significant differences ($P < 0.05$) between the means obtained in Duncan's test.

(53.84 ± 0.45 MPa) for composite films in this study. The PVA fraction thus contributed to increase in TS such that a higher force was required to rupture those films, but our study on the SBP/PVA composite films—that is, replacing some fractions of SBP by PVA—did not similarly strengthen the composite film. This result might be attributed to such factors as the poor hydrogen bonding interaction between the two main components and the plasticizer, or the weak plasticizing effect of water absorbed in the films. This observation did not agree with the findings of Zhang et al.,³³ who investigated the mechanical properties of wheat protein/PVA blend films and found that the TS values for the composite films were significantly better than those of neat films. These results were not also in accordance with the work of Bahrami et al.,⁵ who reported that chitosan/PVA films showed higher TS and substantially reduced EB values. They suggested that the formation of intermolecular hydrogen bonds between $-\text{OH}$ groups of PVA and $-\text{NH}_2$ groups of chitosan can improve the mechanical properties of the blend films. However, these are only assumptions, and these authors did not display or measure interactions actually involved in

their systems. Although comparison of the TS of the composite films containing PVA with those of SBP films did not show any striking change, the EB of the resulting composite films was greatly affected by the addition of PVA: there was a significant ($P < 0.05$) increase in EB, especially in films with a PVA content of 75% ($12.45 \pm 1.21\%$). The EM increased with higher PVA contents up to 50%, and then decreased at PVA contents higher than 50%.

Thermal Stability Assessment by TGA

The thermal stability of SBP/PVA films was evaluated by TGA.

Figure 3 shows the TGA weight loss and the DTG curves for the pure films and SBP/PLA composites in the temperature range of 50–500°C. Previous studies showed that the thermal degradation of SBP follows a two-step weight loss.³⁴ The first weight loss, which was observed at 50–150°C, is generally due to the loss of free water adsorbed in the film. The weight loss in second stage, which corresponds to the elimination of hydroxyl groups and the decomposition and depolymerization of the carbon chains, occurred at 170–270°C. PVA had the similar trend

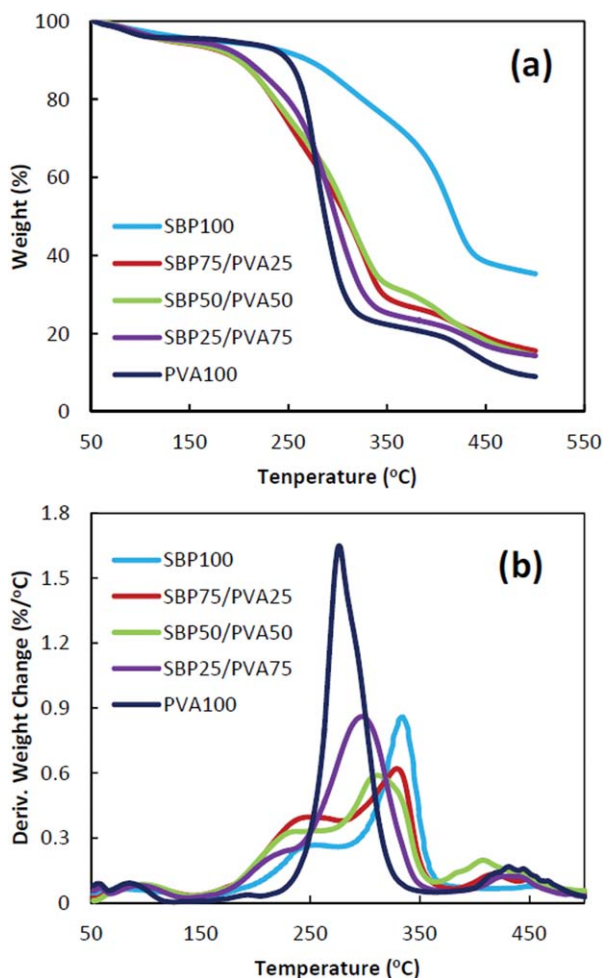


Figure 3. TGA (a) and DTG (b) curves for the sugar beet pulp (SBP) and PVA and different composite films made of SBP and PVA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of degradation because PVA also consists of hydroxyl groups. Our results indicated that a PVA level of 25% did not influence the matrix's thermal degradation. However, it was found that with the addition of PVA up to 50%, SBP/PVA films began thermal degradation at lower temperatures. This could be associated with the interaction between the SBP and PVA matrix, which might delay the thermal degradation of the composite films. It can be seen from Figure 3 that the onset degradation temperatures of the composites are found to be slightly higher ($\sim 15^\circ\text{C}$) with the addition of PVA. However, there was no definitive trend with increases in the loading content of PVA. Correspondingly, there are two major peaks in DTG curves: one is due to dehydration and second is due to decomposition and carbon burning. A complete weight loss with a maximum at 333 and 278°C for pure SBP and PVA, respectively, was detected. A similar behavior with SBP was observed in SBP75/PVA25, with a maximum at 331°C , corresponding to the thermal decomposition of the polymer. However, in the SBP25/PVA75 composite films, a shift to lower temperatures of about 40°C was detected, indicating that the thermal degradation of

SBP25/PVA75 happened at lower temperatures. It appears that blending SBP with a synthetic polymer like PVA could improve the thermal stability of the composite polymer.

Assessment of Compatibility of Blend Films by XRD

The films based on blends of SBP and PVA produced in the present work were subjected to XRD analyses. Some typical examples of the results obtained from these analyses are shown in Figure 4.

A very broad peak appeared at around $2\theta = 22.27^\circ$ ($d = 0.395\text{ nm}$), which is characteristic of typical cellulose structure and agrees well with the results obtained by Li et al.³⁵ in their work with pure SBP fibers. PVA showed an obvious diffraction peak at $2\theta = 19.58^\circ$ ($d = 0.453\text{ nm}$). Similar XRD patterns can be observed in the studies of Xiao et al.³⁶ for pure PVA films. While the pattern of the composite films should be the superposition of those of the two components, we expected that the composite films made from SBP and PVA would be partially crystalline materials, because the films made with both pure SBP and pure PVA showed partially crystalline structures. The diffraction peaks at $2\theta = 22.27^\circ$ of SBP crystal and $2\theta = 19.58^\circ$ of PVA crystal were also obvious in the XRD of composite SBP/PVA film, as shown in Figure 4. This shows that blending SBP and PVA cannot effectively break the SBP and PVA crystals; this suggests that the addition of PVA had no influence on the internal structure of the film, although the intensity of the diffraction peak decreased. With an increase in

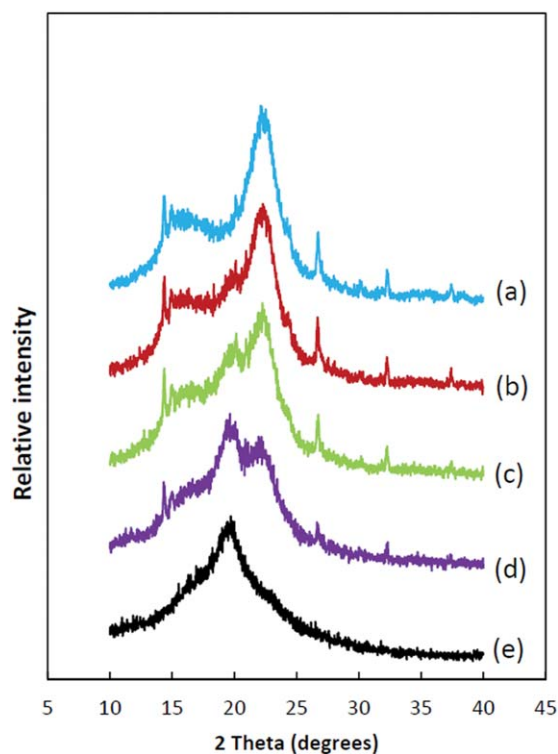


Figure 4. X-ray diffractograms of SBP/PVA composite films (a) SBP/PVA ratio of 100/0 (v/v), (b) SBP/PVA ratio of 75/25 (v/v), (c) SBP/PVA ratio of 50/50 (v/v), (d) SBP/PVA ratio of 25/75 (v/v) and (e) SBP/PVA ratio of 0/100. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

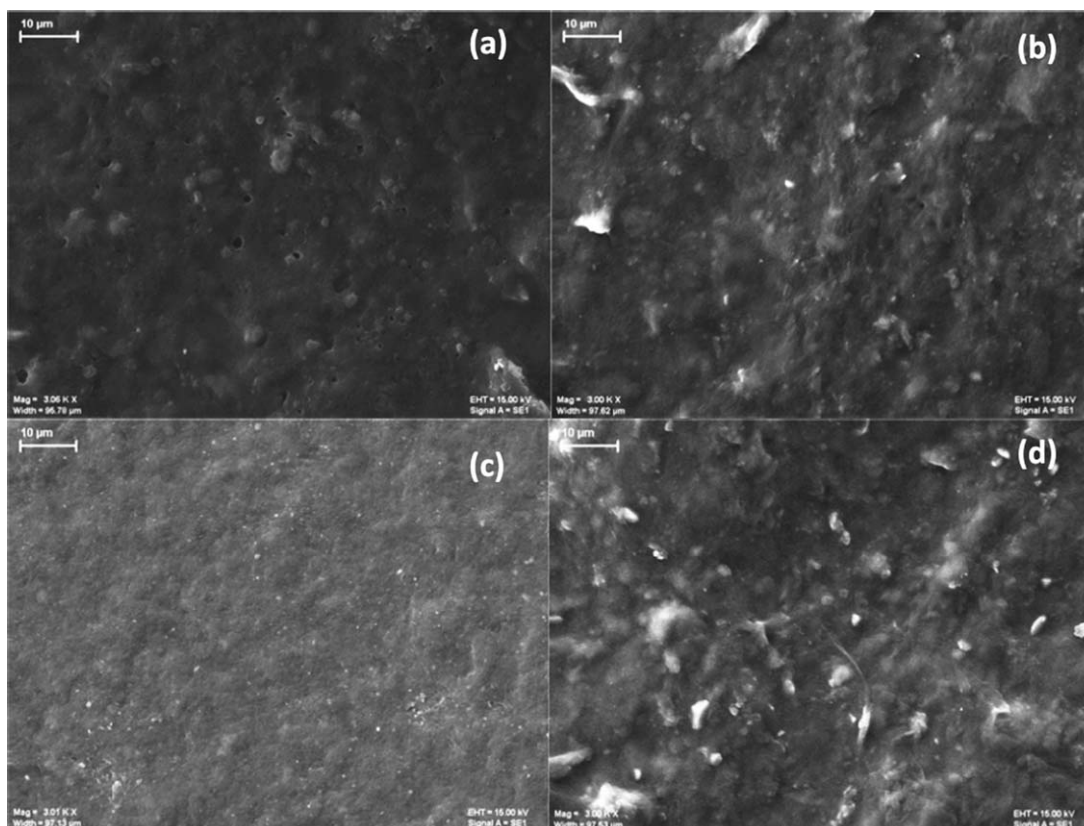


Figure 5. Typical scanning electron micrographs of SBP/PVA composite films (a) SBP/PVA ratio of 100/0 (v/v), (b) SBP/PVA ratio of 75/25 (v/v), (c) SBP/PVA ratio of 50/50 (v/v), and (d) SBP/PVA ratio of 25/75 (v/v).

the PVA content up to 75%, the intensity of the diffraction peak of the blend film became flatter and broader than those of either SBP or PVA. It could be assumed that intermolecular interactions between SBP and PVA existed, which means that these two polymers have relatively good compatibility. This conclusion was in agreement with previous work of Xiao et al.,³⁶ who reported that films made with blends of PVA and konjac glucomannan showed partially crystalline structures.

Surface Morphology of Blend Films

Figure 5 shows representative electron scanning micrographs of the surfaces of SBP/PVA composite films plasticized with sorbitol. The surface of the SBP films was relatively smooth and homogeneous, without any pores or cracks and with good structural integrity, similar to those reported by Li et al.³⁵ Even though macroscopically both pure SBP and composite films showed similar surface characteristics, the addition of higher percentages of PVA brought out notable differences in the films' surface microstructure. Exposures of insoluble SBP blended with PVA were visible in SBP75/PVA25 [Figure 5(b)] films under scanning electron microscopy, indicating that SBP and PVA cannot dissolve each other sufficiently. SBP50/PVA50 [Figure 5(c)] was comparatively smooth and the distribution was more uniform (although with some particles remaining), indicating good compatibility of PVA and SBP. An apparent phase separation was observed in the SBP25/PVA75 composite films, as shown in Figure 5(d). This is most likely due to the fact that

when the PVA content in the blend is beyond a certain threshold, the samples' miscibility deteriorates. Despite this observation, all composite films generally had a compact matrix with good demonstrated structural integrity, leading to acceptable mechanical properties; this was confirmed by the mechanical results. These results were similar to those of Chen et al.,³⁷ who attributed phase deterioration in their work to the relatively poor compatibility between starch and PVA.

CONCLUSION

This is the first report that demonstrates the feasibility of forming biodegradable films made from SBP and PVA via casting and solvent-evaporation. SBP could be a promising raw material for the preparation of biodegradable films and coatings. The mechanical properties, water resistance and thermal stability of the SBP/PVA films were better than those of the neat SBP film. XRD results revealed that SBP and PVA are compatible, and that the addition of PVA reduces the crystallinity of SBP/PVA blends. The results generated in this study clearly indicate that there is a major requirement to understand how preparation processing would affect biodegradable-film manufacture. While successful films were produced during this study, it is clear that further studies are required to improve film formulations, composition and properties. Moreover, further studies need to be conducted using FT-IR spectroscopy to provide evidence for the presence of interaction between SBP and the PVA matrix.

Additionally, thermal analysis using DSC needs to be performed to study the thermal properties of the resulting composite films.

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REFERENCES

1. Yoon, S.-D.; Park, M.-H.; Byun, H.-S. *Carbohydr. Polym.* **2012**, *87*, 676.
2. Ghasemlou, M.; Khodaiyan, F.; Oromiehie, A.; Yarmand, M. S. *Food Chem.* **2011**, *127*, 1496.
3. Bonilla, J.; Fortunati, E.; Atarés, L.; Chiralt, A.; Kenny, J. *Food Hydrocoll.* **2014**, *35*, 463.
4. Kanatt, S. R.; Rao, M.; Chawla, S.; Sharma, A. *Food Hydrocoll.* **2012**, *29*, 290.
5. Bahrami, S. B.; Kordestani, S. S.; Mirzadeh, H.; Mansoori, P. *Iranian Polym. J.* **2003**, *12*, 139.
6. WPO Market Statistics and Future Trends in Global Packaging. *Brazil: Formato Design-Brazil*. Available at: <http://www.worldpackaging.org>. **2008**. p. 1–44.
7. Sun, R.; Hughes, S. *Carbohydr. Polym.* **1999**, *38*, 273.
8. Mishra, R.; Banthia, A.; Majeed, A. *Asian J. Pharm. Clin. Res.* **2012**, *5*, 1.
9. Dufresne, A.; Cavaillé, J. Y.; Vignon, M. R. *J. Appl. Polym. Sci.* **1997**, *64*, 1185.
10. Chiellini, E.; Corti, A.; D'Antone, S.; Solaro, R. *Prog. Polym. Sci.* **2003**, *28*, 963.
11. Luo, X.; Li, J.; Lin, X. *Carbohydr. Polym.* **2012**, *90*, 1595.
12. Yang, X.; Yang, K.; Wu, S.; Chen, X.; Yu, F.; Li, J.; Ma, M.; Zhu, Z. *Radiat. Phys. Chem.* **2010**, *79*, 606.
13. Jegal, J.; Oh, N. W.; Park, D. S.; Lee, K. H. *J. Appl. Polym. Sci.* **2001**, *79*, 2471.
14. El-Sayed, S.; Mahmoud, K.; Fatah, A.; Hassen, A. *Physica B Condens. Matter* **2011**, *406*, 4068.
15. ASTM E1690. Annual Book of ASTM; American Society for Testing and Materials: Philadelphia, PA, **2008**.
16. Harmsen, P.; Huijgen, W.; Bermudez, L.; Bakker, R. Literature Review of Physical and Chemical Pretreatment Processes for Lignocellulosic Biomass; Food & Biobased Research: Wageningen UR, **2010**.
17. Silvério, H. A.; Flauzino Neto, W. P.; Dantas, N. O.; Pasquini, D. *Ind. Crops Prod.* **2013**, *44*, 427.
18. ASTM E1721. Annual Book of ASTM; American Society for Testing and Materials: Philadelphia, PA, **2001**.
19. ASTM D1104. Annual Book of ASTM; American Society for Testing and Materials: Philadelphia, PA, **1956**.
20. Jouki, M.; Khazaei, N.; Ghasemlou, M.; HadiNezhad, M. *Carbohydr. Polym.* **2013**, *96*, 39.
21. ASTM E96/E96M. Annual Book of ASTM; American Society for Testing and Materials: Philadelphia, PA, **2012**.
22. ASTM D882 Annual Book of ASTM; American Society for Testing and Materials: Philadelphia, PA, **2012**.
23. Concha Olmos, J.; Zúñiga Hansen, M. *Chem. Eng. J.* **2012**, *192*, 29.
24. Toğrul, H.; Arslan, N. *Carbohydr. Polym.* **2003**, *54*, 63.
25. Li, M.; Wang, L.-J.; Li, D.; Cheng, Y.-L.; Adhikari, B. *Carbohydr. Polym.* **2014**, *102*, 136.
26. Salarbashi, D.; Tajik, S.; Ghasemlou, M.; Shojaee-Aliabadi, S.; Shahidi Noghabi, M.; Khaksar, R. *Carbohydr. Polym.* **2013**, *98*, 1127.
27. Limpan, N.; Prodpran, T.; Benjakul, S.; Prasarpran, S. *J. Food Eng.* **2010**, *100*, 85.
28. Smith, S. A. In *Polyethylene, Lowdensity*; Bakker, M., Ed.; The Wiley Encyclopedia of Packaging Technology; John Wiley and Sons, New York, **1986**.
29. Tajik, S.; Maghsoudlou, Y.; Khodaiyan, F.; Jafari, S. M.; Ghasemlou, M.; Aalami, M. *Carbohydr. Polym.* **2013**, *97*, 817.
30. Liu, L.; Liu, L.; Fishman, M. L.; Hicks, K. B.; Liu, C.-K. *J. Agric. Food Chem.* **2005**, *53*, 9017.
31. Liu, B.; Zhang, J.; Liu, L.; Hotchkiss, A. T. *J. Polym. Environ.* **2011**, *19*, 559.
32. Ghasemlou, M.; Khodaiyan, F.; Oromiehie, A. *Carbohydr. Polym.* **2011**, *84*, 477.
33. Zhang, X.; Burgar, I.; Loubakos, E.; Beh, H. *Polymer* **2004**, *45*, 3305.
34. Yilgin, M.; Deveci Duranay, N.; Pehlivan, D. *Energy Convers. Manage.* **2010**, *51*, 1060.
35. Li, W.; Coffin, D. R.; Jin, T. Z.; Latona, N.; Liu, C. K.; Liu, B.; Zhang, J.; Liu, L. *J. Appl. Polym. Sci.* **2012**, *126*, E362.
36. Xiao, C.; Liu, H.; Gao, S.; Zhang, L. *J. Macromol. Sci., Pure Appl. Chem.*, **2000**, *37*, 1009.
37. Chen, Y.; Cao, X.; Chang, P. R.; Huneault, M. A. *Carbohydr. Polym.* **2008**, *73*, 8.