



Polyvinyl Alcohol Impact on the Physio-Chemical, Morphological, Barrier, Mechanical and Biodegradable Properties of Water Chestnut Starch Biocomposite Film

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ABSTRACT

A biodegradable film based on Water Chestnut Starch (WCS) with Polyvinyl Alcohol (PVA) at different proportions (100:0, 70:30 and 50:50 wt%) were prepared by casting technique. To study the impact of incorporation of PVA into the film matrix, physical, barrier and mechanical properties were examined. Scanning electron morphology was performed to explain the film morphology and structural properties. Results showed that PVA addition increased the swelling index and solubility but decreased the thickness. PVA enhances the Tensile Strength (TS) but found to be gradually decreased at high PVA concentration. Highest TS values were 31.33 MPa and 27.14 MPa for sorbitol and glycerol respectively at 30% PVA concentration. However, the elongation at break (%E) was minimum at lower concentration of PVA and then increased with PVA concentration. The Water Vapour Permeability (WVP) was decreased with higher PVA concentration from 2.585×10^{-10} to 1.714×10^{-10} $\text{gs}^{-1}\text{m}^{-1}\text{Pa}^{-1}$ and 1.476×10^{-10} to 1.232×10^{-10} $\text{gs}^{-1}\text{m}^{-1}\text{Pa}^{-1}$ for sorbitol and glycerol plasticized films respectively. Furthermore, the result showed that PVA incorporation delayed the film biodegradability, but their dissolution property allowed for food packaging with no ecological harmful effects.

Keywords: Biodegradable film; Polyvinyl alcohol; Plasticizer; Water chestnut starch; Polymer blend

INTRODUCTION

Synthetic plastic were a material of choice for various packaging applications due to their superior mechanical and barrier properties, low price, availability on a large scale and ease of application. In contrast, the extensive use of these petroleum based synthetic plastic during past few decades has caused severe environmental pollution, as they are hydrophobic and persisted in the environment due to their non-biodegradable nature [1]. This has lead the researchers to explore the potential of naturally occurring bio-polymers like starch, lignin and cellulose etc, for the development of biodegradable and eco-friendly plastic materials [2,3]. This bioplastic can be utilized in food packaging applications without producing environmental hazardous non-biodegradable waste [4,5]. Starch being biodegradable and of low cost, stands out among biopolymers as a material of promise for developing eco-friendly packaging films [6].

Starch is a polymeric carbohydrate, comprised of two major bi-macromolecules: amylose (mainly linear) and amylopectin (hyper-

branched) [3,6]. The presence of a huge number of hydroxyl groups on starch chains and the resulting hydrogen bonding provides its high hydrophilic properties [6]. Starch is derived from cereal like wheat, rice and corn and also from tubers like potato and cassava. The thickening capacity of starches makes them functionally suitable for various food industry applications [7]. The wheat, rice, corn, potato and tapioca were the most abundantly used starches in the food processing industry and hence were the subject of extensive research. Non-conventional starch sources have now taking into consideration for making biodegradable film. One such novel, low cost and modernistic candidate is Water Chestnut Starch (WCS). Water chestnut is an alternative source of carbohydrate, locally known as 'Singhara'.

Water chestnut (*Trapa natans*), is an aquatic plant from Trapaecea family and its genus is *Trapa bispinosa* roxb. It floats freely in water ponds and shallow water bodies, found in tropical and sub-tropical regions [8]. Water chestnut fruit color varies from dark green to brown and it has spikes on its outer cover in which the kernel is

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enclosed. The edible white tuber meat has about 5 g a normal weight. Approximately 70% carbohydrate on dry weight basis presents in white meat. About 4.7% protein, with the higher biological value presents in seeds than wheat protein. The presence of calcium, iron, phosphorus, thiamine and ascorbic acid in high amount make it a valuable food source [9,10]. The edible part is generally consumed as snacks or also as a component of other foods. In subcontinent, people eat it raw or after boiling or roasting. The fruit is dried and ground to form flour for various commercial and industrial applications [11]. Due to its high starch content of about 90%, it is a suitable component of various household and commercial food preparations [12]. On heating, it acquires a stiff and crispy form which facilitates in film fabrication [13]. As the potential of water chestnut as a new source of starch has remained unexploited by the food industry, this research will provide useful data that facilitate its utilization in various industrial applications in future. Although, it is in low cost and easy availability, pure starch is very brittle, lacks the mechanical strength, water resistibility, processibility, thermal stability, and high moisture sensitivity, resulting their limited use in extensive applications [14-17].

To improve these drawbacks, the starch was modified by certain physical and chemical processes like blending, preparation of its derivatives and copolymerization [6]. Biodegradable composite materials based on starch blended with some synthetic polymers of appropriate mechanical strength could help in reducing environment degradation [18].

Generally, aliphatic polyesters, Poly Vinyl Alcohol (PVA) and biopolymers are being blended with starch. The degradation polyesters like Poly (β -hydroxyalkanoates) (PHA), and Polylactide (PLA) or Poly (ϵ -caprolactone) (PCL), derived from chemical polymerization, are commonly blended with low cost starch to reduce the cost and maintain the desired properties of the resulting composites [19]. The common biodegradable properties of starch and polyesters help in mutual compatibility for blending, while PVA being water soluble is easily and evenly mix with starch. PVA-starch blends have been extensively studied due to the superior compatibility of PVA with starch and its excellent film forming capacity [20]. Many of these blends were investigated for their potential use in biodegradable packaging materials [21].

PVA, a semi-crystalline, non-toxic synthetic polymer, is water soluble, slightly soluble in alcohol and insoluble in organic solvents, having low permeability and high water absorption capacity [5,22-24]. The structural backbone of PVA molecule primarily consists of C-C bonds and among synthetic polymers. PVA is a rare example which is completely biodegradable [3,5]. PVA finds its use in various sectors like food, pharmaceuticals, coatings, adhesives, packaging materials etc. [3,25]. It has an ability to produce thin film which exhibits excellent performance and thermal stability [22]. PVA can also act as a cross-linking agent to form transparent films of improved mechanical and barrier properties with other suitable materials [5]. The hydroxyl groups of PVA make it highly biocompatible through their hydrogen bonding capacity. Starches of various origins have been used in making starch-PVA blend films by solution casting technique [3]. Starch is a natural polymer manufactured inside the plants through a complex photosynthesis process. It occurs in the form of very minute granules having a diameter between 15-100 μ m. Starch and PVA, both being biodegradable and water soluble, are easily and evenly miscible with each other; consequently create a magnificent couple for blending [23]. The starch-PVA composites fabrication and their characteristics were well studied but research

on their biodegradation property was minimal [1]. This study aims to develop a biodegradable film to minimize the adverse impact on environment due to landfill disposal of non-biodegradable polymers. In this manner, WCS was used to prepare composites with PVA by solution casting method. Sorbitol and glycerol were used as plasticizers. The impact of varying compositions of starch and PVA on the physical, barrier and mechanical properties of WCS-PVA blend film was examined.

MATERIALS AND METHODS

Materials

Water chestnuts were obtained from local market of Karachi, Pakistan. Polyvinyl Alcohol (PVA), glycerol, sorbitol and all other chemicals were of analytical grade and obtained from Sigma chemical company (Sigma-Aldrich GmbH, Germany). Distilled water is used in all experiments.

Isolation of starch

The isolation of WCS was performed by following the method of Zehra et al. [26]. Firstly, water chestnuts were washed, sun-dried and ground to powder. Mixing of 1 kg WCS in 2 L distilled water was carried out, following the addition of 0.2% solution to maintain pH 9.0. The resultant slurry was filtered through 200 mesh sieves and kept the filtrate in fridge for 24 h. After removing upper brown protein layer, washing was carried out with water and ethanol to remove other residues. The starch was then air dried in an oven at $45 \pm 1^\circ\text{C}$ overnight. The starch was ground gently with a mortar and pestle to pass it through a 100 mesh sieve (149 μ m), packed in plastic bags and stored at room temperature in a cool and dry place for film characterization.

Film preparation

Solution casting method was used for preparing WCS-PVA bio composite film. An aqueous solution containing 2% (w/v) of WCS-PVA in three different compositions (100:0, 70:30, and 50:50) was prepared according to the mass ratios given in Table 1. The film forming solution was prepared by mixing WCS and PVA in 100 mL distilled water, then placed on a hot magnetic stirrer with continuous agitation for 30 min at 90°C to encourage starch gelatinization completely. Afterwards, sorbitol and glycerol (20%, w/w on dry basis of solid content) were added and further mixing the resulting dispersions for 15 minutes. Finally, 25 mL of each warm mixture was casted on petri dishes (100 \times 20 mm) and then air dried at 45°C for 24 h [27]. Finally, the films were peeled off carefully and stored in plastic bags. The films were labelled as WxPy, where x and y represent the weight ratio of water chestnut starch (W) and PVA (P) respectively.

Table 1: Composition of the films based on blends of Water Chestnut Starch and PVA plasticized with both glycerol and sorbitol.

Sample	WCS: PVA (wt %)	WCS (g)	PVA (g)	Plasticizer (g)
W1P0	100:00:00	2	0	0.2
W7P3	70:30:00	1.4	0.6	0.2
W5P5	50:50:00	1	1	0.2

Moisture content

Moisture content of film samples was determined by following the method of Zehra et al. [26].

Film thickness

Film thickness was measured from five different positions by using a digital micrometer 0.001 mm accuracy and the average value was calculated [28].

Swelling index and water solubility

Swelling index and water solubility of the films was determined by using the method of Hadi et al. [29] with some modifications. The swelling index was performed by immersing the initially weighed (W_d) film sample in distilled water for 2 minutes. By removing the excess water with filter paper, the film samples were reweighed (W_s) and calculated the swelling index by the Equation. (1):

$$S = [(W_s - W_d) / W_d] \times 100 \quad (1)$$

In water solubility test, weighed (W_i) the initial film samples (2 × 2 cm), then immersed in 20 mL distilled water for 24 h under continuous magnetic agitation. Afterwards, dried the film samples at 105°C in an oven and reweighed (W_f). The water solubility of the films was calculated by following Equation. (2):

$$\text{Solubility (\%)} = [(W_i - W_f) / W_i] \times 100 \quad (2)$$

Scanning Electron Microscopy (SEM)

The film morphology of the surface and cross-section were examined by scanning electron microscopy (JSM, 6380A, Jeol, Japan) under high vacuum mode at an acceleration voltage of 10 kV. Sample were cut into small pieces and then placed on aluminium stub with double sided adhesive tape followed by gold coating for 180 seconds to enhance film conductivity and then photomicrographed at a magnification of 1300x.

Water vapor permeability

Water vapour permeability values were calculated by using the method of Nawab et al. [30].

Mechanical properties

Universal Testing Machine (Zwick Roell AG, Ulm, Germany) was used to investigated the mechanical properties of WCS-PVA composite film and analysed the data by Zwick software (Test Expert V11.02) according to the standard technique of ASTM D-882 [31].

Biodegradability in soil

Soil burial test was conducted to observed biodegradation of film samples according to the method reported by Jaramillo et al. [32] with some modifications. Film samples (2 × 2 cm) were firstly dried at 105°C for 24 h and initial weights (W_i) of the films was measured, then buried in agricultural soil in plastic cups and exposed to atmospheric condition where moisture were maintained by spraying water. Samples were taken out carefully from soil after every fifth day and gently cleaned with a tissue paper, washed with distilled water and then finally they were dried in a vacuum oven at 50°C for 12 h and weighed (W_f). The percentage of Weight Loss (WL) was calculated by using the Equation. (3):

$$WL\% = (W_i - W_f) / W_i \times 100 \quad (3)$$

Statistical analysis

All of the experiments were performed at least in 3 replicates. Samples were analyzed in triplicate and one-way Analysis of

Variance (ANOVA) was applied on the data followed by Duncan's multiple range tests to distinguish the treatments at p<0.05. The statistical analyses were performed using SPSS version 17.01 for window program (SPSS Inc., Chicago, IL, USA).

RESULTS AND DISCUSSION

Appearance and moisture content of film

The visual appearance of WCS-PVA composite films plasticized with both glycerol and sorbitol was smooth, clear and flexible comparatively to pure WCS film which was slightly brittle, rigid and fragile. Furthermore, WCS-PVA composite films were homogenous and translucent, without bubbles or any phase separation visible, showing their affinity between WCS and PVA during processing and in the ultimate product. The increase of PVA content improved flexibility of WCS-PVA films and were easier to peel off film without conditioning as compared to pure WCS films. The promising reason might be the efficient interfacial bonding force between WCS and PVA, which improved the surface smoothness by reducing the cohesive tension of starch molecules; thus, composite films became easy to peel [33]. Tang and Alavi found that the PVA addition to corn starch-glycerol blends prohibited cracks on the film surface, representing a good compatibility of starch and PVA [17].

The moisture content of WCS-PVA composite films with varying concentration of PVA were shown in Table 2. For all WCS-PVA composite films, moisture content indicated direct relationship with the PVA concentration as it is evident from the fact that composite films with higher PVA concentration turned out to be more hydrophilic. The incorporation of PVA increased free hydroxyl groups which allowed producing hydrogen bonds with water molecules and hence, moisture content is increased. The moisture content increased from 1.73% to 5.63% for G-plasticized films and from 4.77% to 6.17% for S-plasticized films. The obtained value of moisture content for WCS-PVA biocomposite films were lower to those obtained for pea starch/PVA with glycerol (6.3%) and similar to boiled rice starch/PVA films (5.18%) [34,35].

Table 2: Effect of compositions on thickness, moisture content, swelling index, and water vapour permeability of WCS-PVA composite films.

Sample	Plasticizer type	Thickness (mm)	Moisture content (%)	Swelling index (%)	WVP 10-10 (g/Pams)
W1P0	Glycerol	0.094 ± 0.0021 ^b	1.73 ± 0.032 ^b	40.45 ± 2.01 ^c	1.4762 ± 0.03 ^a
W7P3	Glycerol	0.092 ± 0.0034 ^c	5.15 ± 0.024 ^a	124.25 ± 1.42 ^c	1.3095 ± 0.05 ^b
W5P5	Glycerol	0.074 ± 0.0045 ^d	5.63 ± 0.046 ^c	197.91 ± 1.09 ^a	1.2328 ± 0.02 ^a
W1P0	Sorbitol	0.093 ± 0.0028 ^c	4.77 ± 0.039 ^b	118.94 ± 1.88 ^d	2.5849 ± 0.10 ^c
W7P3	Sorbitol	0.089 ± 0.0019 ^a	5.50 ± 0.062 ^d	154.08 ± 1.25 ^b	2.0369 ± 0.09 ^c
W5P5	Sorbitol	0.083 ± 0.0043 ^d	6.17 ± 0.081 ^c	159.93 ± 1.19 ^b	1.7143 ± 0.04 ^b

Note: Values are means ± SD of triplicates. Values in the same column with different superscript are significantly different (P<0.05).

Film thickness

The thickness values for WCS-PVA based biodegradable films reduced with increasing PVA concentration from 0.094 to 0.074 mm and 0.093 to 0.083 mm for glycerol and sorbitol respectively as shown in Table 2. Film thickness is influenced by the chemical compositions, molecular structure, as well as the interaction of starch and PVA in film formation steps [36]. Pure WCS film (W1P0) exhibited the maximum thickness. WCS contains 30% amylose (linear chains) and 70% amylopectin (branched chains). PVA is a linear chain polymer, it arranged in a more orderly manner when forming a film. Films containing higher linear chains possess lower thickness, conversely, higher thickness with branched polymer chains. The incorporation of PVA into starch molecules increased the amount of linear chains in the matrix which decreased the film thickness of the resulting material. This is in conformity of Carlos et al. who observed that the PVA addition to potato starch films decreased the film thickness [37]. On comparison with other biopolymer films, WCS/PVA films exhibited low thickness as compared to those obtained for corn starch/PVA (0.12 mm) [34].

Swelling index and water solubility

Swelling index is a significant factor that should be determined for selecting a food packaging material, because the food can be spoiled in films that exhibited high water holding capacity [38]. The swelling behaviour of the WCS-PVA composite film was illustrated in Table 2. The addition of PVA increased the swelling index from 40.45% to 197.91% and 118.94% to 159.93% when plasticized with glycerol and sorbitol respectively. Amylopectin content is responsible for the swelling actions while amylose content retards the swelling property in existence of lipids [39]. PVA addition increased the amount of free hydroxyl groups in the polymer matrix, thus improving the moisture uptake ability and the film become sensitive to water and moisture. This is in conformity of Basiak et al. who reported an enormous increase in swelling index by addition of whey protein isolate in wheat starch films [2].

Water solubility is an important criterion should be evaluated for biocomposite films which composed of water-sensitive biopolymer like starch, and a water-soluble synthetic polymer like PVA [3]. The solubility values of different concentrations of WCS and PVA are depicted in Table 2. Results indicated that the solubility of pure WCS film (W1P0) was the lowest, while the incorporation of PVA significantly increases the solubility values from 11.43% to 59.70% and 9.28% to 71.32% for glycerol and sorbitol respectively, primarily because of the increment in hydroxyl groups [37]. This trend could be demonstrated by the fact that solubility increased because of bonding strength between starch, PVA, and additives [40]. However, the solubility of WCS/PVA biocomposite film was found to be higher at all plasticizer concentrations than those reported for boiled rice starch/PVA film (6.71%) [34]. Higher solubility of WCS-PVA composite film was related with the weak bond, principally hydrogen bonds, between starch and PVA. This film could be hydrated in the existence of water, consequential ease of solubilisation [41]. Similar trend was reported by numerous authors [4,23,37]. In contrast, Elizondo et al. reported the significant reduction in solubility of *Amaranthus cruentus* flour and PVA blend film with more than 10% PVA [42].

Scanning Electron Microscope (SEM)

Micrograph assessment is an extremely important to examine

the physical structure and properties of the polymer blends film (Figure 1). The surface appearance and cross-section micrographs of the composite films prepared from different concentrations of WCS and PVA at 1300X magnification are shown in Figures 2a and 2b. Pure WCS (W1P0) film exhibited irregularities that could be associated to impurities or residues from the raw material used from water chestnut starch extraction that persist in the film. Conversely, composite films with different WCS concentrations were not exhibited these kind of unevenness, representing a uniform, homogenous structure. The composite WCS-PVA films are seemed to be comparatively smooth, homogeneous, and a continuous matrix devoid of any pores or cracks with superior structural integrity. This phenomena is due to the fact that starch/PVA have excellent intermolecular bonding force, so the compatibility of the film components enhanced by improving the dissolution and reaction between WCS and PVA, which decreased the undissolved materials, thus the smoothness of surface of the composite film enhanced [37]. The micrographs also indicated that the phase structures in the WCS-PVA blend films with different concentrations of WCS and PVA are very different. W7P3 film showed slight rougher and brittle surface as compared to the W5P5 film. In W7P3, PVA fibers are uniformly distributed in WCS molecules, however meanwhile the starch molecules merged extensively. This might be due to the higher viscosity of starch than that of PVA. However, in W5P5, WCS molecules implanted in the PVA network and the PVA fibers gathered the starch molecules on the surface [18]. Therefore, it is concluded that the starch granules scatter efficiently in PVA polymeric network when the WCS/PVA is equal to 50/50. The excellent dispersion of starch granules is beneficial to enhance the mechanical properties of WCS-PVA composites. Elizondo et al. (2009) [42] observed an opaque and irregular upper surface of *A. Cruentus* flour/PVA blend film, but without any cracks. Sreedhar et al. [43] reported that the addition of PVA into starch causing alteration in the biopolymer structure at both molecular and morphological levels, decreasing its inflexibility. Jayasekara et al. [44] found smooth surface of wheat starch/PVA with no cracking.

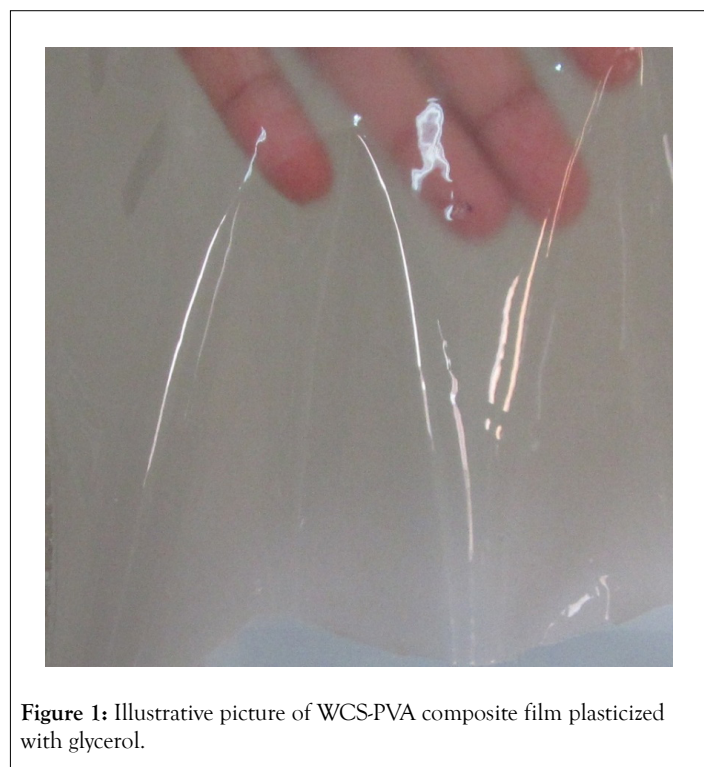


Figure 1: Illustrative picture of WCS-PVA composite film plasticized with glycerol.

Moreover, Figures 2a and 2b showed the cross-section of the composite WCS-films represented a significant amount of well-distributed micro-pores, for example in an mixture, possibly due to the homogenization technique used to advance the miscibility between water chestnut starch and PVA [42]. The cross-section

images showed that the increment in PVA concentration produced a more apparent lamellar structure and decreased the space among the lamellae. This could be explained by the fact that the hydroxyl groups of PVA make strong hydrogen bonds with WCS [45].

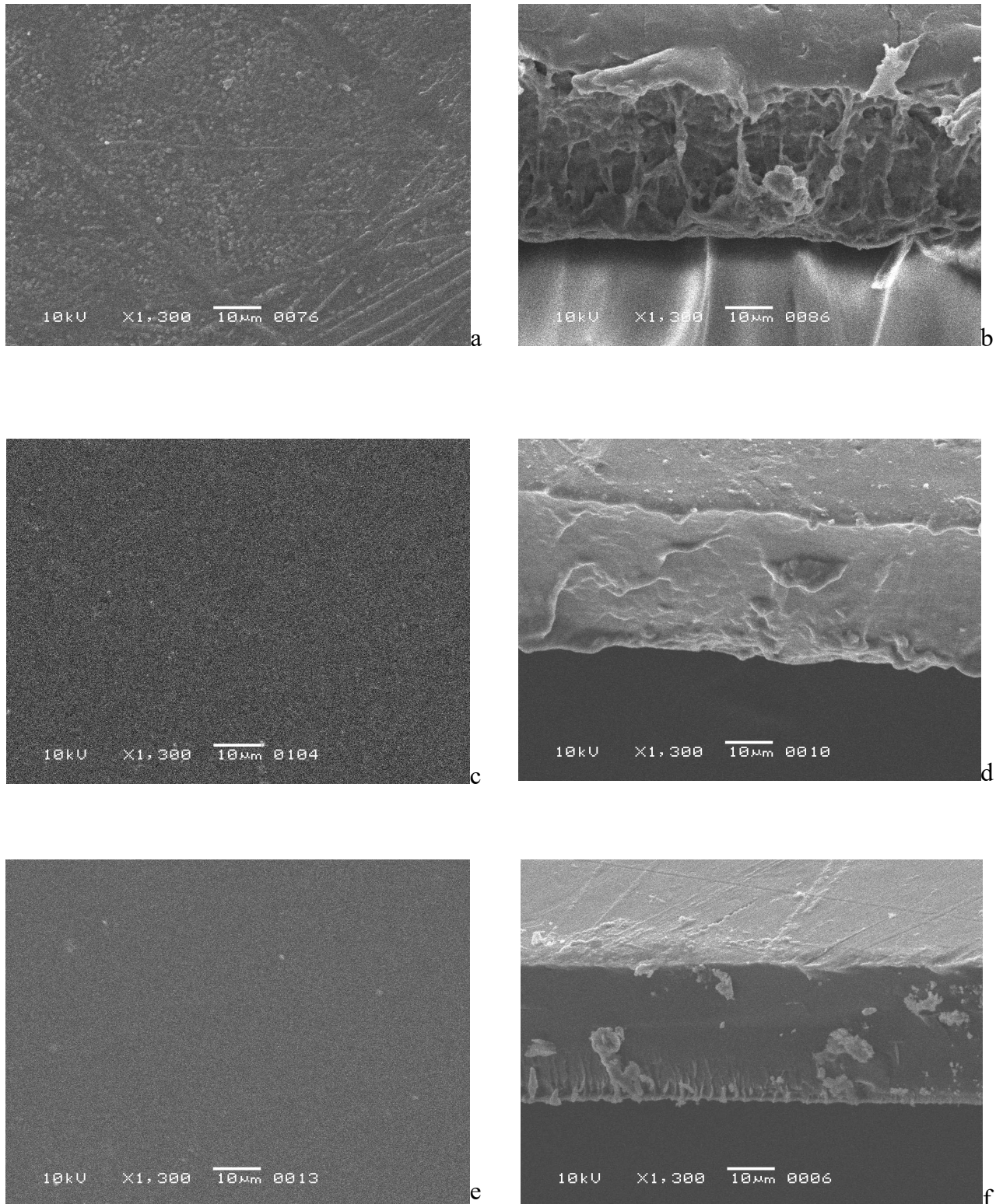


Figure 2a: Scanning electron micrographs of the surface (left) and cross section (right) of WCS-PVA composite films viewed at a magnification of 1300 × (a) and (b) W1P0, (c) and (d) W7P3, (e) and (f) W5P5 plasticized with glycerol.

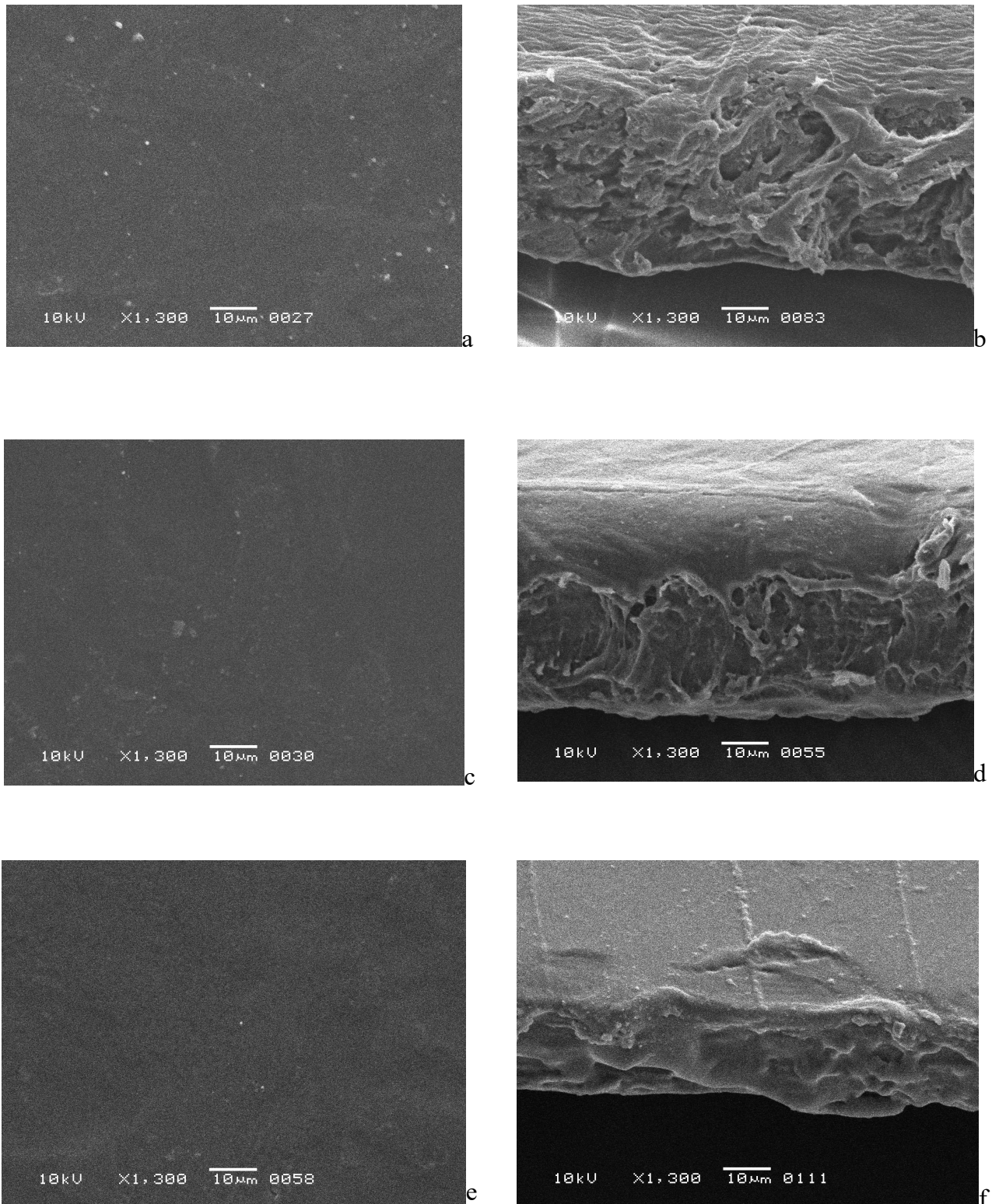


Figure 2b: Scanning electron micrographs of the surface (left) and cross section (right) of WCS-PVA composite films viewed at a magnification of 1300 × (a) and (b) W1P0, (c) and (d) W7P3, (e) and (f) W5P5 plasticized with sorbitol.

Water vapour permeability

Water vapor permeability is a significant characteristic of films for their appliance because water plays an important role in disintegrative reactions [46]. Table 2 represent the water vapor permeability (WVP) values of the studied films. WVP of WCS-PVA composite films were altered with an increase of PVA proportion. W1P0 films were more permeable, possessed a porous structure and irregular surface because of the presence of different molecules in the starch film like protein and lipids. Therefore, pure WCS films had higher WVP values compared to WCS-PVA biocomposite film. The incorporation of PVA reduced the WVP values from 1.476×10^{-10} to $1.232 \times 10^{-10} \text{ gPa}^{-1}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$ in films plasticized with glycerol and from 2.584×10^{-10} to $1.714 \times 10^{-10} \text{ gPa}^{-1}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$ in the films containing sorbitol (Table 2). The promising reason could be the semi-crystalline structure of PVA, producing an additional well-organized molecular structure than the starch. Furthermore, the greater number of hydroxyl groups escalating the polarity and the crystallinity of WCS-PVA biocomposite films. Gas or vapour molecules permeation is lowered because of the strong interactions between the polymeric structural matrixes, which caused a decrease in WVP values as the proportion of PVA increased [37] observed in Table 2. In similar researches, Dominguez et al. found that the PVA addition to chitosan film lowered the WVP values of the composed films [37].

Mechanical properties

Mechanical properties specify the potency of the films and their capacity to improve the mechanical reliability of foods. The sample thickness, processing method, test speed, specimen shape, etc can affect the mechanical properties. Tensile Strength (TS) and Percent Elongation at Break (%E) represent the force per unit area required to tear the film and the ability of the film to stretch [15]. In general, TS and %E of the films were significantly modified by the insertion of PVA into the polymeric network.

TS of WCS-PVA composite film increased significantly from 18.50 MPa to 27.14 MPa and 17.82 MPa to 31.33 MPa for glycerol and sorbitol respectively, by the addition of PVA (Table 3). The promising reason may be the development of inter-and intra-molecular hydrogen bonds particularly when the PVA amount is $\geq 30\%$. Because of its linear chains structure, PVA occupy the small intermolecular spaces available between polymeric chains of starch reducing secondary forces in these chains. The incorporation of PVA at a particular level increases the strength and flexibility of the composite film. However, the addition of higher amount of PVA resulted in poor mechanical properties due to an extreme amount of PVA-starch interactions, which could have competed with the interactions between PVA and starch [37]. Thus, it reduces the TS of WCS-PVA composite films by subsequently weakening the hydrogen bonds among starch chains. Similar results were found by Gouhua et al. (2006) regarding methylated cornstarch and PVA [47]. Ke and sun (2003) reported the similar result for cornstarch and poly (lactic acid) with different concentrations of PVA [48].

Table 3: Effect of compositions on solubility, tensile strength, and elongation at break of WCS-PVA biocomposite films.

Sample	Plasticizer type	Water solubility (%)	Tensile strength (MPa)	Elongation at break (%)
W1P0	Glycerol	11.43 ± 3.02^f	18.50 ± 0.85^d	28.89 ± 1.34^d

W7P3	Glycerol	49.54 ± 0.12^a	27.14 ± 1.32^e	7.14 ± 0.31^e
W5P5	Glycerol	59.70 ± 1.28^c	16.35 ± 0.45^b	19.41 ± 1.25^b
W1P0	Sorbitol	9.20 ± 0.34^b	17.82 ± 0.63^c	6.10 ± 0.28^b
W7P3	Sorbitol	40.86 ± 2.54^d	31.33 ± 1.51^f	1.54 ± 0.04^a
W5P5	Sorbitol	71.32 ± 2.98^c	6.43 ± 0.21^a	42.68 ± 1.72^c

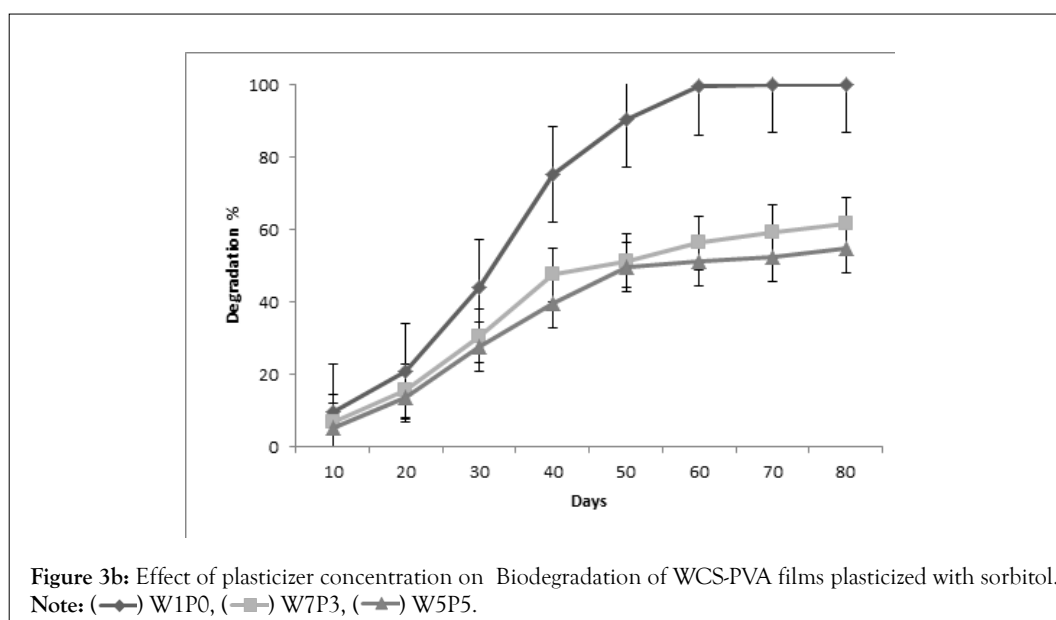
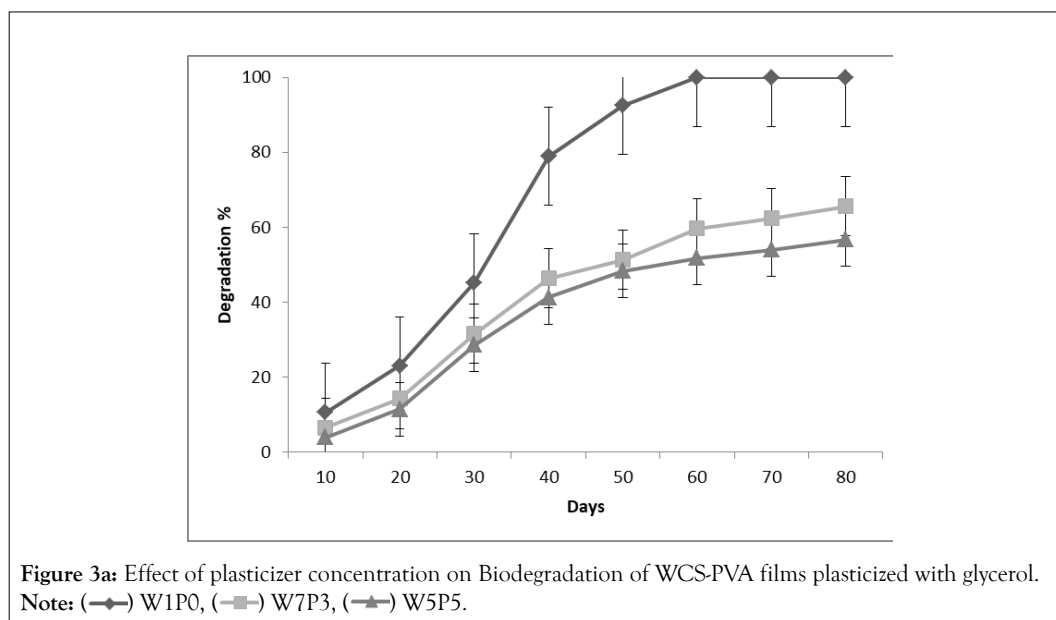
Note: Values are means \pm SD of triplicates. Values in the same column with different superscript are significantly different ($P < 0.05$).

The increase in %E of WCS-PVA composite film could be explained by the disruption of crystalline structure of starch. Starch, containing 70% amylopectin which are branched molecules, having empty spaces between polymeric chains. PVA could promote a tri-dimensional reordering of the polymeric matrix, resulting intermolecular disturbance of hydrogen bonds among starch molecules and the making of hydrogen bonds among PVA and starch, thus lowering the energy necessary for the movement of molecules supporting an enhancement of free volume [5]. Consequently, the %E increased whereas the TS decreased.

Biodegradation

Polymer degradation is a decisive functionality to use for packaging material. At present, no authorized standard technique was found to calculate the biodegradability of polymers. Many researchers have been used the enzyme method, the microbiological method and the soil burial method. In this research work, the soil burial test was conducted. The soil burial test is an open-air testing which gives a naturalistic atmosphere in which soil humidity, temperature, and type and amount of microorganisms are less controlled and vary with period of time [15].

The size and shape of the tested specimen should be same in order to minimized their influence on biodegradability [49]. The biodegradability of the films was calculated by assessment of their weight loss before and after periodic intervals of burial in soil is shown in Figures 3a and 3b. The nature of the microorganism type in the soil and the composition of the polymeric mixture affected the weight losses of the film sample [50]. The maximum values of weight loss were obtained for pure starch W1P0 film and the percentage of weight loss decreased with increasing PVA concentration in the WCS/PVA blends. PVA manifested a greater resistance against soil burial biodegradation, by forming an opaque structure between the polymeric chains that lowered the infiltration velocity of the microorganisms, consequential providing a stable support medium for starch [51]. Guohua et al. (2006) [15] proposed two-stage degradation took place in soil burial test: (a) the swelling of the film occurred by dispersion of water molecules into the film samples that facilitates the microorganisms growth: (b) enzymatic and other selected degradation caused a weight loss and disruption of the film sample. Pure WCS film despoiled rapidly in the initial 15 days and entire degradation was achieved within 60 days. In WCS-PVA composite film, a quick degradation obtained in the preliminary 40 days and 55 days for W7P3 and W5P5 respectively, followed by a slow degradation and reached 56.66% after 80 days at the end of the test. The result indicated that the WCS/PVA blend was not capable to be totally biodegrade in a small time duration in the natural atmosphere [23]. Chai et al. reported that the addition of PVA increased the biodegradation time of the starch/PVA blend films [23].



Similar results reported by other authors [15,19,52-57] therefore, the biodegradation examination concluded that starch is the main components to encourage the disintegration rate of the WCS/PVA blend, the biodegradability of the PVA/starch blends considerably was strengthened by higher starch and low PVA contents of the WCS/PVA composite film[23]. Furthermore, as the film components (WCS, PVA, and plasticizer) possess hydrophilic nature, dissolution of WCS and PVA making them completely biodegradable which support the decomposition of material without causing hazardous environmental damage [2].

CONCLUSION

WCS/PVA composite films prepared with different compositions showed momentous changes on the physio-chemical, barrier, mechanical and biodegradation properties. It was found that the addition of PVA manifestly increased the moisture content, swelling power and solubility. The WVP values and biodegradation were found to be higher for pure WCS film while the incorporation of PVA inhibits the moisture or vapour transmission. The TS increased with the addition of PVA but decreased at higher PVA concentration. Overall, the research work revealed that composite

films were colourless, transparent and showed superior properties than pure WCS film. The several functionalities of WCS and PVA assured the required results and meet the demand to be used as packaging films that will be useful for both food and non-food industrial applications.

CONFLICT OF INTEREST

The authors certify that they have NO affiliations with or involvement in any organization or entity with any financial interest, or non-financial interest in the subject matter or materials discussed in this manuscript.

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