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Physico-chemical properties of biodegradable films of polyvinyl alcohol/sago starch for food packaging

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Abstract

In this study, polyvinyl alcohol (PVA) was blended with sago starch (SS) films in presence of glycerol as plasticizer. The solution was prepared using solution casting method prior irradiation using electron beam for crosslinking process. The effect of incorporation of sago starch into the PVA matrix was studied using various techniques using tensile test, FTIR, SEM and AFM-3D. FTIR spectroscopy was used to check the sago presence in the PVA matrix. Obtained results from the AFM-3D shows that PVA/SS films have relatively rougher surface topography which contributed to the chemically attached sago starch onto the PVA materials as compared to the raw films. Tensile test results revealed that film without starch has higher tensile strength compare to films with starch

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1. Introduction

Global production of plastic has continued to rise due to higher demand from the consumer. In 2013, 299 million tons of plastics were produced and this represent 4 percent increase over 2012 [1]. Plastic production in worldwide has expand rapidly as the durable, petroleum replaced materials like glass and metal. Even though recycling and recovery has been practiced, but it is not sufficient and millions of tons of plastics ends in landfills and ocean each year. These situation has led to serious ecological problems and contributing to the environmental pollution

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Common conventional plastics that is used for food packaging include polyethylene terephthalate (PET), polyvinyl chloride (PVC), low density polyethylene (LDPE), polyvinyl chloride (PVC), polystyrene (PS), polypropylene (PP). The materials used to package the food is mostly one-time application where it will be discarded when its useful life is over. Advantages of these conventional polymers which is low-cost, good mechanical properties (tensile and elongation), good barrier properties to water, oxygen and others. However, all these plastics from petroleum based materials in non-biodegradable thus contributing to the environmental problems.

In the view of biodegradable packaging, starch is commonly used as the raw materials due to its advantages which is abundant, low cost and renewable [2, 3]. Azhari, N.A [4], prepared blend films of PVA/Corn Starch via casting method and found that PVA films contain starch has high biodegradation rate compare to control films of PVA that does not contain any starch. In Southeast Asia, sago is widely produced from the metroxylon sago palm tree at relatively low cost compare to common starch such as cereal and potato starch [3]. However, hydrophilic nature of the starch has causing poor mechanical properties which limit its usage widely. This could be overcome by modified the starch either chemically or physical by adding plasticizer and polymer additives [4]. Starch based-films have many advantages includes no colour, odour and taste compare to plastics films that have good barrier properties. Oxygen barrier property plays an important role to preserve foods like fruits, meats and salads and starch based film can offer that where it has selective permeability to some substances, examples like oxygen thus make it a good modified atmosphere packaging (MAP).

Previous studies have primarily concentrate on blending starch with polyvinyl alcohol (PVA) as a potential biodegradable polymer[4-7]. Blend of starch-PVA has shown great film-forming properties that leads to flexible materials with homogenous and smooth surface [8]. PVA is a water soluble synthetic polymer, non-toxic, flexible, and widely used in food packaging application due to its excellent barrier properties. PVA also acknowledge as one of the polymer that has higher biodegradation rate due to the presence of hydroxyl group which determine the hydrophilic condition of this polymer. PVA is a high cost polymer compare to thermoplastic materials and blending it with cheap natural polymer will decrease the cost and also enhance biodegradability of this material.

The aim of this study was to develop and characterize biodegradable packaging incorporated with starch as for food packaging to replace petroleum based materials.

2. Experimental

2.1. Materials

PVA was purchased from Sigma Aldrich (hydrolysis rate:99%, density:1.19 g/cm³). Sago starch with approximately 12% moisture and glycerol was purchased from SIM Company Sdn. Bhd. (Penang, Malaysia). Glycerol (glycerine, C₃H₈O₃) with density of 1.267 g/cm³ from SIM Company Sdn Bhd (Penang, Malaysia) was used as plasticizer to decrease glass-transition temperature (T_g) to increase flexibility and workability of starch and PVA since starch is only partially compatible with PVA

2.2. Preparation of PVA/SS films

The ratio of sago starch solution and PVA solution is 1:3 while the amount of glycerol is 1% from the total amount of the solution. The solution was according to a method described by Nouri et al [3] 5% (w/w) of PVA solution were added into sago starch 5% (w/w) at 650 °C for starch gelatinization and stirred continuously for 45 minutes to complete homogeneity and gelatinization in the solution. 1% plasticizer, glycerol was added into the solution and the temperature of the mixture is maintained at 60 °C since the solution tend to separate when the temperature dropped below 60 °C. 30 ml of the solution will be cast in the petri dish that can yield 10cm x 10cm film forming area before undergo irradiation using electron beam (EPS 3000, Malaysian Nuclear Agency) operated at 2MeV at 30kGy with a 10kGy per pass for cross-linking process [9]. Then the films will be kept on the fridge for 24 h to remove bubbles before dried in the oven for another 24 h. The film will be peeled off after drying and kept inside zipper bag until further use.

3. Characterizations

3.1. Mechanical properties

Mechanical properties of the films were characterized using a universal testing machine (SHIMADZU Autograph Tensile Test Machine Model AGS-G) according to a standard method (ASTM 882). The gauge length was set at 6 mm and the cross head speed of 20 mm/min was used and the test was performed at 25 ± 3 °C. The tensile strength (σ_b), elongation at break, (ϵ_b) were determined. Average value of four replicates were taken for each sample.

3.2. FTIR Analysis

Attenuated total reflection Fourier transform Infrared (ATR-FTIR) of the samples were recorded on Brucker, Tensor II. Samples were taken at the wavelength range $4000 - 400$ cm^{-1} . FTIR was used to obtain information about the interactions between sago starch and the poly vinyl alcohol films.

3.3. Scanning electron microscopy (SEM)

Morphology of PVA/SS films was observed by a scanning electron microscopy (SEM, Model JEOL JSM-6460 LA). The films were frozen in liquid nitrogen then snapped immediately. All the samples the specimens were fixed on stubs with double-sided tape and then sputtered with gold in sputter coater. Then, the specimens were examined with scanning electron microscope under high vacuum condition and at an accelerating voltage of 10.0 kV to surface (200 x) and 15.0 kV to cross-section (2000 x).

3.4. Atomic force microscopy (AFM)

Surface topography of the PVA film and PVA/SS film was investigated by atomic force microscopy using an AFM SHIMADZU SPM -9500J2

4. Results and discussion

Indication of the strength and elasticity of the films are provided by the tensile properties. Tensile strength and percent of elongation at break represent force per unit area required to tear the film and ability of the film to stretch. Fig. 1 (a) and (b) shows tensile strength (TS) and elongation at break (EB) of PVA film (control) and PVA/SS films.

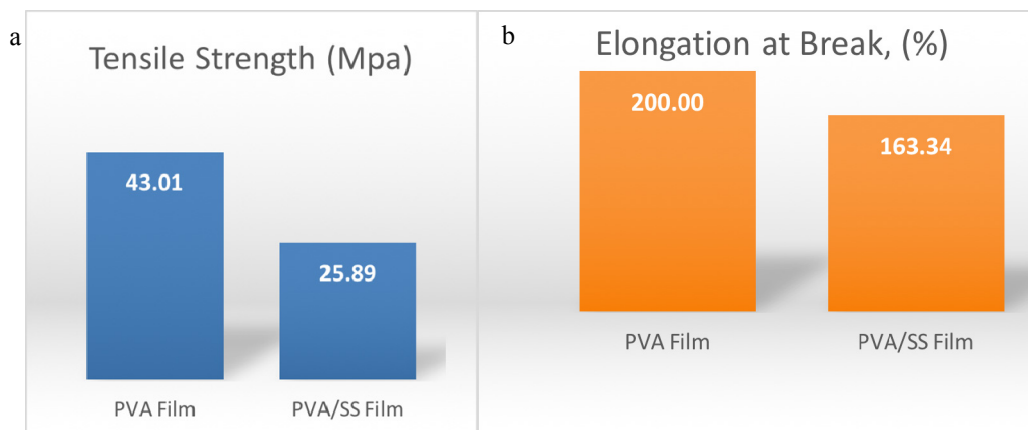


Fig. 1. (a) Tensile strength of pure PVA film and PVA/SS film; (b) Elongation at break of pure PVA film and PVA/SS film

The values for tensile strength (TS) and elongation at break (EB) for the PVA film (control) are 43.09 MPa and 200% respectively while for PVA/SS film, values of TS and EB is 25.90 Mpa and 163.34% respectively. TS and EB values of control film (PVA Film) was higher than the film with sago starch (PVA/SS Film) where the EB value of PVA film and PVA/SS film were 200.00% and 163.34% respectively while the TS were 43.01 MPa and 25.89 MPa. This might be due to the compatibility between the PVA and the sago starch. As reported by Yun et al. (2008), in the PVA/starch composite, starch just partially compatible with PVA [10]. It was reported that the tensile strength, elongation at break and the transparency of the PVA/starch composite decrease with an increase of the starch content. However, the TS and EB might be increased by certain treatment such as cross-linking process or grafting process. Shen et al. in her study obtained the value of TS and EB for control film were higher than the film with addition of potassium sorbate [11]. When the addition of potassium sorbate was increased, the TS of the films decreased progressively.

The decreasing values after incorporation of SS into the PVA matrix could be explained by low interfacial interaction between the PVA and SS in the films and this would lead to low mechanical strength at the blends interface. Similar behaviours was also observed by other researcher which found that increasing amount of starch in the blends lead to decreased value of tensile strength [4, 12].

FTIR microscopy was used to study the interaction between film matrix and sago starch. The spectra of PVA film (control) and films incorporated with sago starch and glycerol (plasticizer) is shown in Fig. 2 below.

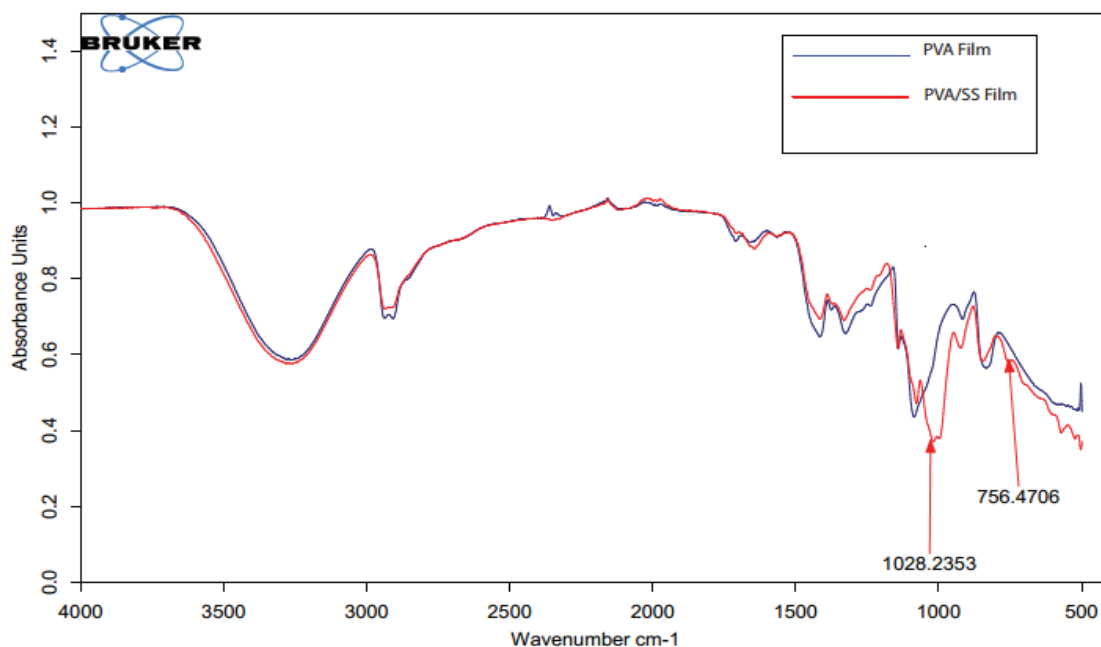


Fig. 2. FTIR spectra of PVA and PVA/SS film

In Fig. 2, both PVA (control) and PVA/SS (1% plasticizer) shared same characteristics where broad band were observed at $\sim 3290\text{cm}^{-1}$ which referring to the $-\text{OH}$ stretching that indicate there were plenty of water hydroxyl in the films. Meanwhile the band attributed to $-\text{CH}$ and $-\text{CH}_2$ deformation vibration in CH_2OH were presented in peak (c) in the range between $1640 - 1650\text{ cm}^{-1}$ which similar to the observation by Ismail H. et al [13]. By comparing spectra of PVA film and PVA/SS film, PVA/SS film have showed new peaks which if profound at 1028cm^{-1} that is attributing to the C-O stretch of glycerol which is used as plasticizer in this experiment. This indicates hydrogen bond interactions between starch and glycerol, indicating that the sago starch successfully participated in PVA film. These analyses is in agreement with Priya et al. [14]. Therefore, it clearly showed both sago and PVA peak appeared in spectrum of PVA/SS film indicating that the successful of sago starch crosslinked with PVA.

Effect of incorporation of the sago starch in the PVA film was studied using scanning electron microscopy and the results are presented in Fig. 3. This analysis provides information about the surface morphology and internal microstructure of the films. It can be clearly seen that the surface of PVA film was smooth and without pores or cracks and homogenous. Different situation observed for PVA/SS film where the surface was rougher in appearance due to certain agglomeration of the sago starch particle.

While for PVA/SS film, cross section images show obvious segregation between starch and PVA film which might be occurred during film formation. Same result obtained by Chen et al who explained that aggregations of starch and micro-phase separation between pea starch and PVA occurred during film formation, due to the lack of total miscibility[10].

The cross section of this PVA films shows some irregularities typical of semi-crystalline structures, associated with the ordered arrangement of some segments of the polymer chains. In fact, PVA has been reported to present a high degree of crystallinity around 54%. Cano et al. in his study also obtained the same result which the surface of PVA film was smooth was spherical shaped [15].

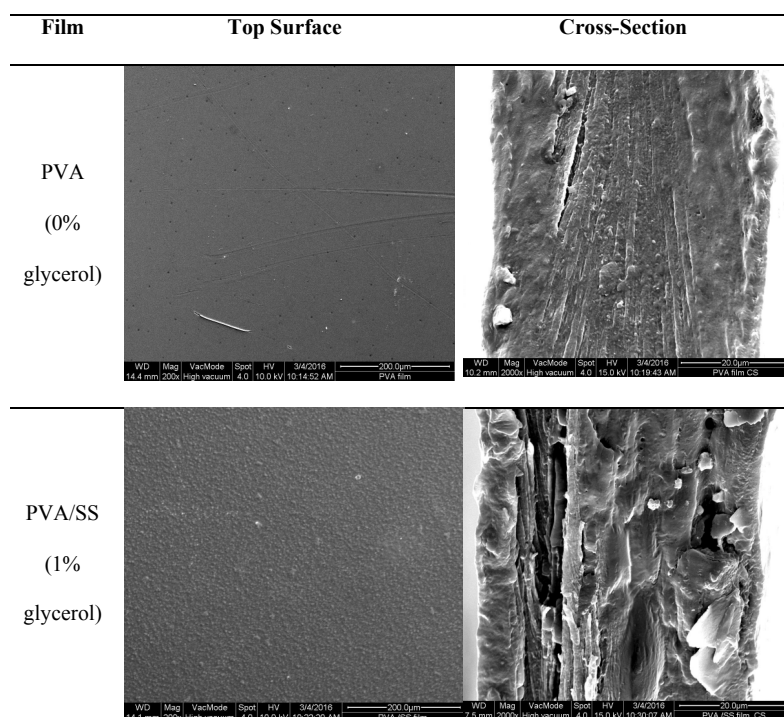


Fig. 3. Microscopy SEM images of PVA film (control) and PVA/SS film

In order to quantify the impact of the incorporation of the sago starch into PVA film (matrix), AFM analysis was performed. Fig. 4 (a) and (b) shows three-dimensional (3D) of AFM images of the PVA film (matrix) and biofilm containing the starch, PVA/SS. The micrograph image of the PVA/SS film presented high number of rounded and homogeneously peaks compared to the matrix, PVA film. It is also observed that there are some agglomerated particles which present in the PVA/SS film. The agglomeration caused an increases of roughness and created a deep valleys and high peaks. The agglomerated particles might be sago starch that formed during film preparation since sago starch is easy to agglomerate when the temperature drop down. The observations from the topographic images were confirmed with the values of the surface roughness of each system (RMS), resulting 76.17 nm and 53.41 nm for PVA and PVA/SS film respectively.

These results shows that sago starch is successfully incorporated into the PVA film matrix. Salarbashi et al. in her study obtained the same results, where the particles for control film were mono-dispersed while some particles of blended film were aggregated [16].

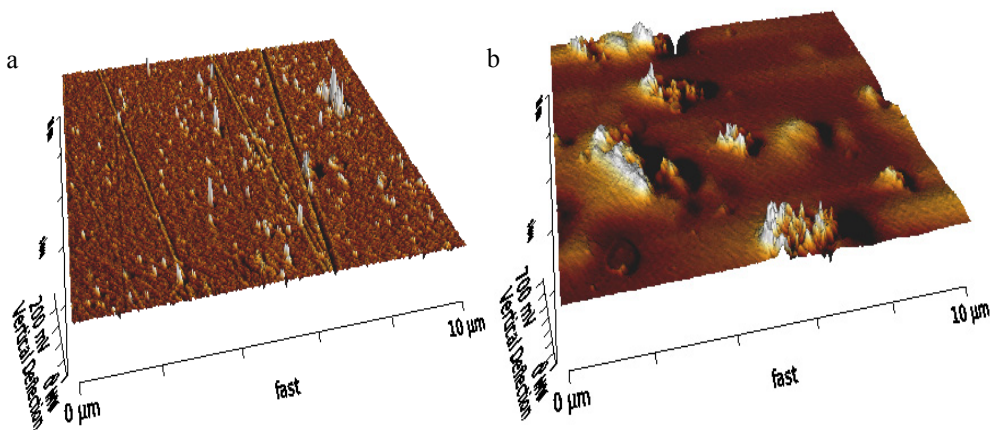


Fig. 4. AFM micrographs of (a) PVA film and (b) PVA/SS film

5. Conclusion

Cross-linked of polyvinyl alcohol (PVA) with sago starch (SS) and glycerol used electron beam radiation with 30 kGy were studied to develop a biodegradable film. The successful preparation of cross-linked film was confirmed using Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM). FTIR analyses has confirmed presence of sago starch and glycerol in the PVA/SS film since there is a peak that indicated C-O bond appear in the PVA/SS spectra. SEM was used to obtain sub-microscopic images of the film surfaces prior to modification. This technique confirms some of the expected properties of the surfaces related to addition of sago starch and 1% glycerol and also confirms that the addition makes the surface change. AFM is a well establish technique for probing surface topography and has been applied to polymer surfaces. The three-dimensional Atomic Force Microscopy (AFM) shows that PVA/SS (1% glycerol) have relatively rougher surface topography which contributed to the chemically attached SS onto PVA surface as compared to the raw film.

The effect in tensile properties of polymeric material after the incorporation with sago starch and glycerol was investigated. It was found that sago starch decreased the tensile strength (TS) and elongation at break (EB).

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