Effect of glycerol and sorbitol plasticizers on physical and thermal properties of sugar palm starch based films

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Abstract: - The aim of this study was to characterize and compare the effect of glycerol and sorbitol plasticizers on physical and thermal properties of sugar palm starch (SPS) films. Film samples were prepared using conventional casting technique. Sorbitol plasticized SPS films (S-SPS) have higher thickness and density. Whereas, the moisture content and solubility of SPS films containing glycerol (G-SPS) were higher than those of S-SPS. The addition of sorbitol to SPS films elevated the thermal degradation temperature to higher values and thus, increased the thermal stability of S-SPS than G-SPS.

Key-Words: - Sugar palm; Starch; Glycerol; Sorbitol; Biodegradable films

1 Introduction

Up to date, the packaging industry heavyly depends on crude oil for the production of petroleum base plastics [1]. Plastics have been widely utilized as packaging materials due to their good barrier properties, outstanding mechanical performance and so on [2]. However, the non-biodegradable nature of petroleum based plastics has led to enormous environmental pollution. Hence, the growing environmental awareness throughout the world has attracted the development of environmentally friendly plastic materials which are biodegradable and from renewable sources [3]. There has been increasing importance in biodegradable films made from biopolymers.

Of late, several stduies were conducted on starch based films as potential substitute for conventional packaging plastics. Starch has been considered as one of the most promising natural renewable resources due to its large availability, relatively low cost, and biodegradability. Starch based films are reported to have good oxygen and carbon dioxide barrier properties which are relevant for effective packaging. On the other hand, they have drawbacks in mechanical and water vapor permeability properties. In addition, native starches are brittle and not processable. Therefore, plasticizers are generally added to native starch to overcome brittleness as well as improve flexibility and workability. The most commonly used plasticizers for starch based films are polyols including glycerol, sorbitol etc. Many researchers studied the effect of various polyols on the properties of starch films derived from different sources [4]–[11]. So far, little work is found on the effect of various polyols (glycerol and sorbitol) on sugar palm starch. Sahari et al. [12] was reported to study the effect of glycerol on sugar palm starch. Sugar palm is a multipurpose tree commonly found in Tropical countries. Besides

producing sugar, almost all parts of the sugar palm tree are used for making useful traditional products such as mats, brooms, fishing ropes etc [13]. Starch is also extracted from the inner part of the trunk [14] which is a potential biopolymer for film preparation.

The aim of this study was to develop, characterize and compare the effect of glycerol and sorbitol plasticizers on physical and thermal properties of sugar palm starch films.

2. Methodology

2.1. Film preparation

Pure sugar palm starch was weighed and dissolved in distilled water to obtain film forming suspension (8 w/w % starch concentration). The film forming suspension was heated at $95 \pm 2°C$ for 15 mins under continuous stirring before adding 30 % of plasticizer. The plasticized solution was later allowed to cool down to 40 °C. Film forming solution was casted on petri-dishes (10 cm diameter) and let it dry for 24 h.

2.2. Film thickness

Film thickness was determined using a digital micrometre (Mitutoyo Co., Japan) with 0.001mm sensitivity. The thickness measurements were obtained from five different film areas for each sample. The mean value of measurements for individual sample was utilized.

2.3. Film density

Density of the developed films was determined usingdensimeter (Mettler-Toledo (M)Sdn. Bhd). The immersing liquid used in this work was Xylene instead of distilled water to avoid water uptake by the hydrophilic film samples. Secondly, the density of the liquid should be less than the film to ensure that the film does not float. Hence, Xylene is more suitable compared to water due to its lower density.The film sample was weighted (m) before immersing it in the liquid. The amount of liquid displaced after immersing film into the liquid was recorded as *V*. Eq. (1) was utilized to calculate the density (ρ). The test was performed in quadruplicate.

$$\rho = \frac{m}{V} \qquad (1)$$

2.4. Film moisture content

Moisture content of film samples were determined by initially weighting (W_i) each sample using a digital weighting scale. The samples were then dried in an oven at 105°C for 24 hand reweighted (W_f). Eq. (2) was formulated to calculate moisture content of each film sample. The test was carried out in triplicate and the final moisture content for each film was recorded as the mean of results.

$$Moisture\ content = \left[\frac{W_i - W_f}{W_i}\right] \times 100 \qquad (2)$$

2.5. Film water solubility

Three samples (2cm diameter) were obtained from each film and dried in an oven at 105°C for 24 h. The samples were weighted to determine the initial dry matter of each film (W_i). Each sample was immersed in 30 mL of distilled water and kept at $23 \pm 2°C$ for 24 h. The sealed beaker was stirred periodically. The insoluble portion of film sample was removed from soluble matters in distilled water and dried in an oven at 105°C for 24 h. The oven dried samples were reweighted to know the weight of the solubilized dry matter (W_o). Water solubility of each film was determined by Eq. (3).

$$Solubility(\%) = \left[\frac{W_i - W_o}{W_i}\right] \times 100 \qquad (3)$$

2.6. Thermal-Gravimetric Analysis (TGA)

Thermogravimetric tests were performed using (brand) TGA analyzer under 20 ml/min flow rate of nitrogen atmosphere. The tests were carried out at temperature range from 25 °C to 800 °C with a heating rate of 10 °C/min. Film sample of 5 – 15 mg was placed in the sample pan and heated. The weight loss as function of temperature and the

differential of the thermogravimetric curves were analyzed.

3. Results and Discussion

3.1. Film thickness

Fig 1 reveals that the type of plasticizer immensely influences the thickness of films. S-SPS films exhibited thicker films than G-SPS films. The observed differences in the film thickness may be ascribed to the difference in molar mass of glycerol and sorbitol. Therefore, low film thickness of G-SPS films can be possibly ascribed to its smaller molar mass compared to S-plasticizer. Ghasemlou et al. [1] also reported that sorbitol plasticized films produce thicker films than glycerol plasticized films.
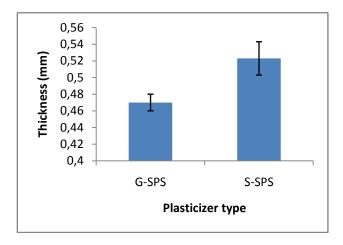

Fig. 1 Effect of glycerol and sorbitol on the thickness of plasticized SPS films

3.2. Film density

Fig 2 shows the effect of plasticizer type on the density of SPS films. The addition of plasticizers decrease the density of unplasticized SPS films from 1.54 g/cm^3 to 1.44 g/cm^3 and 1.51 g/cm^3 for G-SPS and S-SPS films, respectively. The type of plasticizer significantly affects the density of films such that G-SPS films were lower than S-SPS films. This could be attributed to the low molar mass of glycerol (92.09 g/mol) which is almost twice less than sorbitol (182.17 g/mol). This result concurs with those reported by Razavi et al. [8].
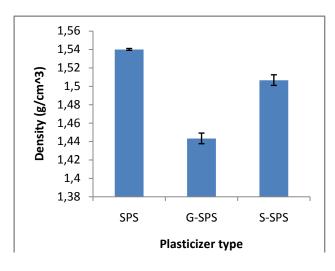

Fig. 2 Effect of glycerol and sorbitol on the density of plasticized SPS films

3.3. Film moisture content

S-SPS films demonstrated lower moisture content as compared to glycerol containing (G-SPS) films (see Fig 3). This may be attributed to the high molecular structure resemblance of glucose units to that of sorbitol, causing stronger molecular interactions between the sorbitol and the intermolecular polymer chains. Consequently, the chances of sorbitol interacting with water molecules become lesser. On the contrary, the hydroxyl groups in glycerol have strong affinity with water molecules; enabling glycerol containing films to easily retain water within their matrix and form hydrogen bond [15]. Hence, glycerol acts as water-holding agent whereas sorbitol entertains less interaction with water molecules.
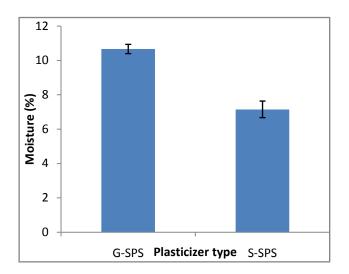
Fig. 3 Effect of glycerol and sorbitol on the moisture content of plasticized SPS films

3.4. Film solubility

It can be observed in Fig 4 that G-SPS has higher solubility (38.58%) compared to S-SPS (26.39 %). The high water-solubility of G-SPS films over their counterpart may be ascribed to the strong affinity of glycerol to water molecules, as well as, its lower molecular weight which easily facilitate its entrance between the polymer chains to increase the free space volume between the chains [1], [16].
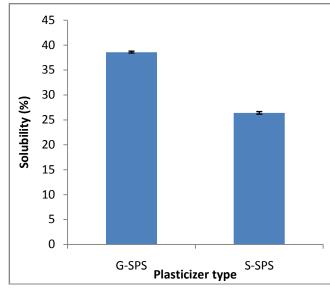

Fig. 4 Effect of glycerol and sorbitol on the solubility of plasticized SPS films

3.5. Thermal-Gravimetric Analysis

Thermal-gravimetric analysis technique was utilized to determine the thermal decomposition and stability of unplasticized and plasticized SPS films. The changes in film weight as a function of temperature increase has been shown in Fig 5. It can be observed that the TGA curve of unplasticized SPS film is similar to that of G-SPS and S-SPS. The thermal decomposition of films occurred in three-main steps. This result generally conforms with the three thermal degradation events of most starch based films reported in the literature [17]–[21].

The first thermal event commences shortly after the heating started and ends before 100 °C. At this stage, water molecules in the film samples are eliminated by evaporation. In addition, G-SPS demonstrated drastic weight loss as compared to S-SPS. This observation may be attributed to the high moisture content of G-SPS as shown in Fig 3. The second stage of thermal weight loss occurs between 100 – 290 °C which was associated with the disappearance of plasticizer compounds. The last level of film thermal degradation was attributed to the decomposition and depolymerization of starch carbon chains [22].
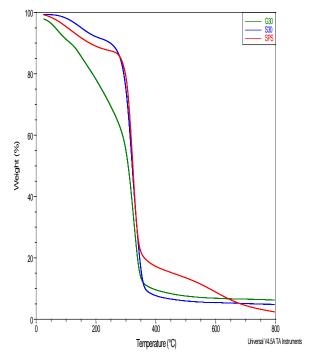

Fig. 5 TGA curves of glycerol and sorbitol plasticized SPS films

Comparing the TGA curves, the addition of sorbitol to SPS films adjusted the degradation temperature to higher values and thus, increasing the thermal stability of S-SPS.

4. Conclusion

The current study manifested that sugar palm starch is a potential film-forming biopolymer which could

be used for developing biodegradable films. Without plasticizers, SPS films are brittle with many visible cracks and not easily peelable from the casting surface. Hence, the introduction of plasticizers helps to overcome brittleness and, enhance flexibility and peelibility of SPS films. Different plasticizer types and concentrations were exploited to investigate their effect on physical and chemical properties of SPS films. The results demonstrated that plasticizer type and concentration influences film thickness, density, moisture content, solubility, swelling capacity and water absorption. However, further research regarding the mechanical, thermal, and barrier properties of SPS films should be conducted to select the most suitable film for food packaging application.

Acknowledgements

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