

Effect of plasticizer type and concentration on physical properties of biodegradable films based on sugar palm (*arenga pinnata*) starch for food packaging

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Abstract In this study, sugar palm starch (SPS) films were developed using glycerol (G), sorbitol (S) or their combination (GS) as plasticizers at the ratio of 15, 30 and 45 (wt)% using casting technique. The addition of plasticizers to SPS film-forming solutions helped to overcome the brittle and fragile nature of unplasticized SPS films. Increased plasticizer concentration resulted to an increase in film thickness, moisture content and solubility. On the contrary, density and water absorption of plasticized films decreased with increasing plasticizer concentration. Raising the plasticizer content from 15 to 45 % showed less effect on the moisture content and water absorption of S-plasticized films. Films containing glycerol and glycerol-sorbitol plasticizer (G, and GS) demonstrated higher moisture content, solubility and water absorption capacity compared to S-plasticized films. The results obtained in this study showed that plasticizer type and concentration significantly improves film properties and enhances their suitability for food packaging applications.

Keywords Sugar palm · Starch · Biodegradable films · Plasticizer · Glycerol · Sorbitol

Introduction

Petroleum based plastics are dominantly used in packaging industries owing to their outstanding versatility, mechanical and barrier properties (Farris et al. 2009; González and Alvarez Igarzabal 2013; Siracusa et al. 2008; Tharanathan 2003). In spite of their numerous advantages, petroleum based plastics are a great source of environmental pollution, as they are non-biodegradable. Packaging products made from these non-biodegradable polymers are highly resistant to microbial attacks and thus persist in the environment for several decades after disposal. Therefore, petroleum based plastics are considered as one of the primary cause of solid waste generation and accumulation in the environment. In addition to being non-biodegradability, they are also from non-renewable sources. The rapid depletion of petroleum reserves coupled with the non-biodegradable nature of petroleum based polymers have triggered increasing concerns regarding their wide usage for packaging. Such concerns fuelled the growing interest in replacing petroleum based plastics with renewable and biodegradable polymer materials. In that regard, biopolymers such as polysaccharides derived from agricultural sources are potential alternatives to mitigate the above mentioned succinct disadvantages of petroleum based plastics. Numerous studies testified to the mounting attention for the use of starch from different sources to prepare biobased packaging films. Recent studies by Sahari et al. (Sahari et al. 2012a) had brought sugar palm tree on the spotlight as a promising source for starch extraction as biopolymer.

Sugar palm (*arenga pinnata*) is known to be a versatile tree and indigenous to tropical countries, most especially in South-

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East Asia (Sahari et al. 2012b; Ticoalu et al. 2012). The tree is popular for its numerous economic uses. It provides significant products such as palm sap, fresh palm juices, palm neera, brown sugar, vinegar, palm wine, bio-ethanol and black fibers as raw materials for furniture making, brooms, handicraft, house construction, water resistant shipping ropes and other uses (Elberson and Oyen 2010; Ishak et al. 2013). Starch can also be obtained from sugar palm trunk, preferably when the tree no longer produces sugar and fruits (Adawiyah et al. 2013). Sugar palm starch has been traditionally used as raw material for glue substances (Sahari et al. 2011; Sahari et al. 2012a). However, it has not yet received the much needed attention required for developing it as an industrial starch biopolymer.

Starches are considered as one of the most promising biopolymers due to their biodegradability, renewability, abundant availability and low cost (Imre and Pukánszky 2015; Jiménez et al. 2012; Peelman et al. 2013; Zhang et al. 2014). They are counted as the main carbohydrate resources found in cereal and tuber plants, such as corn and cassava, respectively. Starches are polysaccharides composed of two different macromolecules, amylose and amylopectin. The ratio of linear homopolymer amylose and highly branched amylopectin depends on the botanical origin of the starch and can affect their behaviour during processing and the properties of the final product (Talja et al. 2007, 2008). From the packaging industry perspective, starch based materials are gaining more attention in the bio-based polymer market for various packaging applications. However, native starches are brittle and does not possess any thermoplastic properties. Hence, products made from native starches easily crumble into bits when dried in ambient conditions. Strong intermolecular hydrogen bonding between the amylose and amylopectin macromolecular network chains (Ma and Yu 2004; Zhang and Rempel 2012) are responsible for the brittle nature of starches. The introduction of plasticizers together with elevated temperatures and shear, increases the flexibility of native starches similar to conventional thermoplastic polymers. The process of curing the brittleness of native starches is known as the plasticization of starch. Glycerol had been used in previous studies for sugar palm starch plasticization (Sahari et al. 2012a; 2013, 2014).

To date, there is little work done pertaining to the influence of various plasticizer types and concentration on sugar palm starch films. Hence, the aim of this current investigation is to determine the effect of different plasticizer type (glycerol, sorbitol, and glycerol: sorbitol) and concentrations (15, 30 and 45 %) on the physical properties of sugar palm starch based films.

Materials and methods

Materials

Sugar palm starch was obtained from sugar palm trunks at Jempol, Negeri Sembilan (Malaysia). The glycerol (99 %

purity, food grade) and D-sorbitol plasticizers (99 % purity) were purchased from a supplier, LGC Scientific (Selangor, Malaysia).

Extraction of sugar palm (*Arenga pinnata*) starch

The SPS extraction procedures adopted were similar to Sahari et al. (Sahari et al. 2012a, 2013, 2014) with slight modifications. The sugar palm tree was cut and the trunk was then split lengthwise to remove the woody fiber together with the starch powder from the inner soft core of the sugar palm trunk. Gradually, water was introduced into the fiber and starch mixture obtained from the tree trunk and was thoroughly kneaded by hand. The mixture was then filtered to allow the water to flow through the sieve with starch granules in suspension. The starch was granted enough time to settle at the bottom of the container and the water decanted. Thereafter, the starch was kept in an open air for a moment and later dried in an air circulating oven at 120 °C for 24 h.

Film preparation

The sugar palm-based films were prepared by conventional solution-casting technique. Glycerol (G), sorbitol (S) or their 1:1 combination (GS) ratio were used as plasticizers to investigate the effect of each individual plasticizers on SPS films. The film preparation procedures are described as follows: Initially, 8 % (w/w) aqueous dispersion of gelatinized sugar palm starch was prepared by heating the film forming solution at 95±2 °C for 15 mins under constant stirring in a hot water bath. This step helps to provide homogeneous dispersion by disintegrating the starch granules. Thereafter, the different plasticizers were added into the dispersions at 0, 15, 30 or 45 % (w/w, starch basis). The heating process continued for an additional 15 mins at 95±2 °C. The film forming solutions were left to cool, prior to their casting in glass petri-dishes. The glass petri-dishes serving as casting surface, enables the film to have a smooth and flat surface. The freshly cast films were placed in an oven (40 °C) to allow evaporation. All films were prepared in triplicate including films without plasticizers which were used as controls. After 24 h of drying, films were peeled from the casting surfaces and stored in desiccators with 53±1 % relative humidity (RH). The film preparation process has been presented in Fig. 1.

Film thickness

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

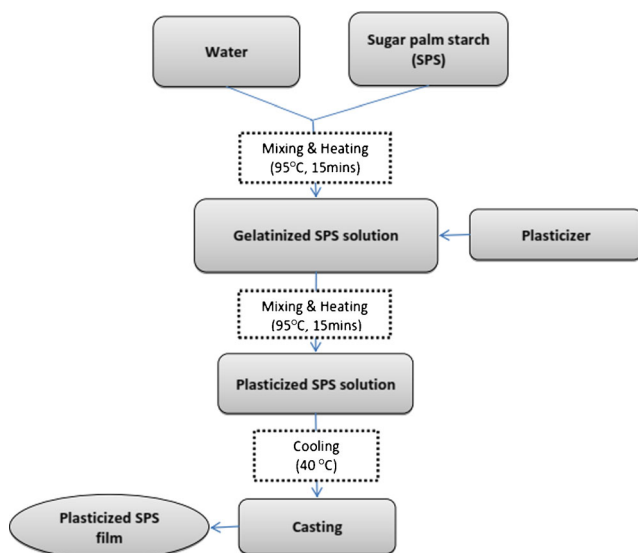


Fig. 1 Film preparation flow chart

Film density

Density of the developed films was determined using densimeter (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. In addition, the density of the liquid had to be less than the film to ensure that the film does not float. Hence, Xylene is much 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.

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

Film moisture content

Moisture content of film samples were determined by initially weighing (W_i) each sample using a digital weighing scale. The samples were dried in an oven at 105 °C for 24 h and reweighed (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 the result.

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

Film solubility in water

Three samples (2 cm diameter) were obtained from each film and dried in an oven at 105 °C for 24 h. The samples were

weighed 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 ± 2 °C for 24 h. The sealed beaker was stirred periodically. The insoluble portion of film sample were removed from soluble matters in distilled water and dried in an oven at 105 °C for 24 h. The oven dried samples were reweighed to know the weight of the solubilized dry matter (W_o). Water solubility of each film was determined by Eq. (3).

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

Film swelling index

The water sorption capacity of each film was studied by immersing a known mass of film sample into distilled water at room temperature (23 ± 2 °C). The Film was periodically removed from the distilled water and reweighed until constant film mass was attained. The test was performed in triplicate. The water uptake was determined using Eq. (4):

$$\text{Swelling index}(\%) = \left[\frac{M_{\text{Swollen}} - M_{\text{Dry}}}{M_{\text{Dry}}} \right] \times 100 \quad (4)$$

Where M_{Dry} and M_{Swollen} represents initial and swollen mass of film sample, respectively. This method was adapted from (González and Alvarez Igarzabal 2013).

ATR-FTIR

Infrared spectra of the film samples were analysed using Fourier Transform Infrared Spectroscopy in Attenuated Total Reflectance mode (FTIR-ATR). Firstly, a film sample was mounted on a sample holder in contact with ZnSe crystal and then placed on an attenuated total reflectance accessory. FTIR spectra were collected by recording 42 scans with a resolution of 4 cm^{-1} in a $4000\text{--}400 \text{ cm}^{-1}$ wave range. The ZnSe crystal which possesses high reflective index was thoroughly cleaned after each measurement.

X-ray diffraction (XRD)

X-ray diffractometer (APD2000, Italy) equipped with copper anode X-ray tube was utilized to obtain X-ray diffraction patterns for each film sample. X-ray diffractograms of films were recorded for 2θ and the scanning region was between 5° to 40° at scan rate of 2° min^{-1} . The XRD analysis of film samples were conducted with $\text{Cu K}\alpha$ radiation of 1.542 \AA , under a voltage of 40 kV and a current of 40 mA.

Scanning electron microscope (SEM) images

The morphology of the films was investigated using scanning electron microscope (brand) at an acceleration voltage of 5 kV. The film samples were mounted on aluminium stubs with double-sided adhesive tapes. Thereafter, the samples were coated with gold to avoid charging.

Statistical analysis

The statistical analyses of the obtained experimental results were performed by analysis of variance (ANOVA) using Minitab 16 software. Mean comparisons were conducted using Turkey's test at a 0.05 level of significance.

Results and discussion

General appearance sugar palm starch (SPS) plasticized films

Figure 2 shows the photographic images of the obtained plasticized and unplasticized SPS films, whereas, Table 1 describes their visual appearance. SPS films prepared without plasticizers were wavy, brittle, rigid and fragile. Many cracks were observed on the surface of the films. They crumble into bits, making it difficult to peel and handle. This observation could be attributed to the strong inter/intra molecular hydrogen bonds of SPS which provide less mobility to the macromolecular chains, resulting in brittle and rigid films with surface cracks. This observation is in agreement with the findings of Suppakul et al. (2013) and Talja et al. (2007), who prepared cassava flour and potato starch films, respectively.

The introduction of plasticizers to SPS films renders them flexible with smooth and homogeneous surface. SPS films

with 45 % plasticizers were observed as more flexible and the flexibility reduces as the plasticizer concentration decreases, irrespective of the plasticizer type. In other words, the increase of plasticizer concentration of the various plasticizer types (G, S, and GS) enhances flexibility of SPS plasticized films. The low molecular size of the plasticizers enables them to creep within the intermolecular spaces of polymer chains, reducing the intermolecular hydrogen bond strength, hence, increasing the molecular mobility. The intermolecular hydrogen bond of SPS films weakened as the plasticizer concentration increased from 15 to 45 %. Nonetheless, at the same plasticizer concentration, the change in plasticizer type significantly affected the flexibility of their resulting films. Hence, it was noticed that GS-plasticized films demonstrated higher flexibility, followed by G-plasticized films.

SPS films prepared with low plasticizer concentration (15 %) were difficult to peel. Increasing plasticizer concentration to 30 % and finally to 45 %, reduced the force required for peeling the films from the casting surface. Among the plasticized SPS films, S15 films required stronger force to peel due to their brittle and fragile nature. Further addition of plasticizers helped in conquering the brittleness of the starch by softening their three-dimensional molecular network structure which in turn generated an increase in the molecular free volume. G-plasticized films were easier to peel as compared to S and GS-plasticized films of same plasticizer concentration. It can be assumed that glycerol is relatively easier to interpose itself within the intra/intermolecular spaces of the starch because of its smaller molecular weight. The strong bond between glycerol and SPS reduced the cohesive tension of the starch molecules; thus, G-plasticized films became easy to peel. Furthermore, the appearance of all the plasticized films was clear and transparent. However, S-plasticized films illustrated clearer and more transparent view than G- and GS-plasticized films as shown in Fig. 2.

Fig. 2 SPS films prepared using different plasticizer type and concentration



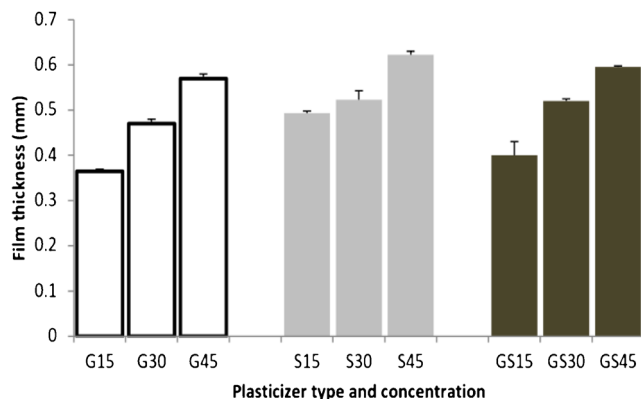
Table 1 Appearance of unplasticized and plasticized SPS films

Sample	Plasticizer type	Plasticizer concentration (%)	Appearance of films
SPS	–	0	Transparent, brittle and fragile, surface cracks, rigid, difficult to peel
G15	Glycerol	15	Transparent, not brittle, not fragile, no surface cracks, flexible, not sticky, peelable
G30	Glycerol	30	Transparent, more flexible than G15, slightly sticky
G45	Glycerol	45	Transparent, more flexible than G30, slightly elastic, sticky, easy to peel
S15	Sorbitol	15	More transparent than G15 and GS15, brittle and fragile, less flexible than G15, not sticky, slightly difficult to peel and handle, not sticky
S30	Sorbitol	30	More transparent than G30 and GS30, not brittle and fragile, more flexible than S15 but less than G30, peelable, not sticky
S45	Sorbitol	45	More transparent than G45 and GS45, flexible, easy to peel and handle, not sticky
GS15	Glycerol:Sorbitol	15	Transparent, not brittle and fragile, not rigid, flexible, easy to peel, not sticky
GS30	Glycerol:Sorbitol	30	Transparent, more flexible than G30, stickier than G30
GS45	Glycerol:Sorbitol	45	Transparent, more flexible than G45, stickier than GS30 and G45

Film thickness

Figure 3 shows film thickness increase from 0.365 to 0.570 mm, 0.493 to 0.622 mm and 0.40 to 0.596 mm in response to increase in G, S and GS concentration from 15 to 45 %, respectively. The results illustrated significant increase in film thickness by raising plasticizer concentration, irrespective of plasticizer type. This may be attributed to the role of plasticizers in disrupting and restructuring of intermolecular polymer chain networks, creating more free volumes which translate into thicker film thickness. Similar effect of plasticizer concentration on film thickness was reported by Razavi et al. (2015), Jouki et al. (2013), Ahmadi et al. (2012), Ghasemlou et al. (2011) and Imran et al. (2010).

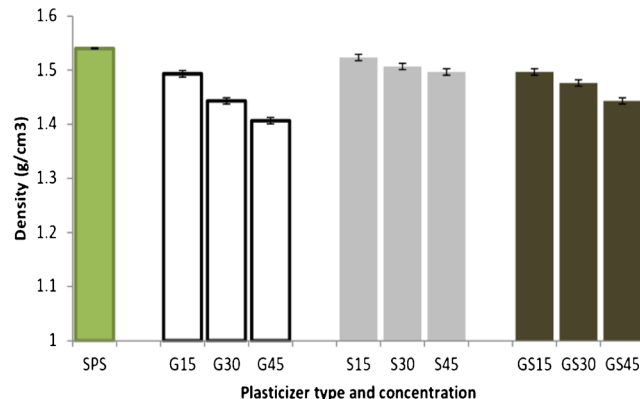
In addition, varying the plasticizer type reveal significant influence on film thickness as displayed in Fig. 3. S-plasticized films exhibited thicker films than GS- and, then, G-plasticized films. The differences in film thickness of various plasticizers may be ascribed to their molar mass because the film forming solution formulation was constant. Low film thickness expressed by G-plasticized films at constant

**Fig. 3** Thickness of SPS films with different plasticizer type and concentration

concentration can be possibly ascribed to its smaller molar mass compared to S-plasticizer. Ghasemlou et al. (2011) also reported that S-plasticized films produce thicker films than G-plasticized films.

Film density

The addition of plasticizer lowers the density of SPS (1.54 g/cm³). Hence, all the plasticized films exhibit lower density than the unplasticized SPS film. Figure 4 shows the effect of plasticizer type and concentration on the density of SPS films. Raising the concentration of plasticizers from 15 to 45 % causes slight decrease in the density of G- (1.493–1.407 g/cm³), S- (1.523–1.496 g/cm³) and GS-plasticized films (1.497–1.443 g/cm³). It can be evidently seen that the density of the films slightly decreased by increasing the proportion of plasticizers from 15 to 45 %, regardless of plasticizer type. The results of G-plasticized films are in agreement with those reported by Sahari et al. (2012a), who plasticized sugar palm starch with glycerol (15, 20, 30 and 40 %) using dry processing technique (hot pressing).

**Fig. 4** Density of SPS films with different plasticizer type and concentration

The density values did not demonstrate much significant difference between the various plasticizer types. However, the order of density reduction at the same plasticizer concentration is registered as follows: S- GS- G-plasticized films. This phenomenon may be ascribed to the differences in molecular weight and density of the plasticizers. The molar weight of the plasticizers also follows similar trend as the aforementioned density reduction. Razavi et al. (2015) also observed no significant difference between sage seed gum (SSG) films containing glycerol and sorbitol, even so, glycerol plasticized films revealed lower density than sorbitol below 60 % concentration.

Film moisture content

For all plasticized SPS films, the moisture content increased significantly as plasticizer concentration increases from 15 to 45 %; with the exception of S-plasticized films. Generally, starch based films turn out to be more hydrophilic with an increase in plasticizer concentration. Thus, several investigations reported that the moisture content of hydrocolloid films increases by adding more plasticizer (Ghasemlou et al. 2011; Hernández-Munoz et al. 2003; Kristo and Biliaderis 2006; Zhang and Han 2006). However, the effect of sorbitol on the moisture content of SPS films was not obvious as that of G- and GS-plasticized films. Figure 5 shows constant moisture content for S-plasticized films with increasing plasticizer concentration. Similar findings were reported by Aguirre et al. (2013), Ghasemlou et al. (2011), Osés et al. (2009), and Arvanitoyannis and Biliaderis (1999). Possible explanation for the low moisture content of S-plasticized films as compared to glycerol containing films (i.e., G- and GS-plasticized films) may be due 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

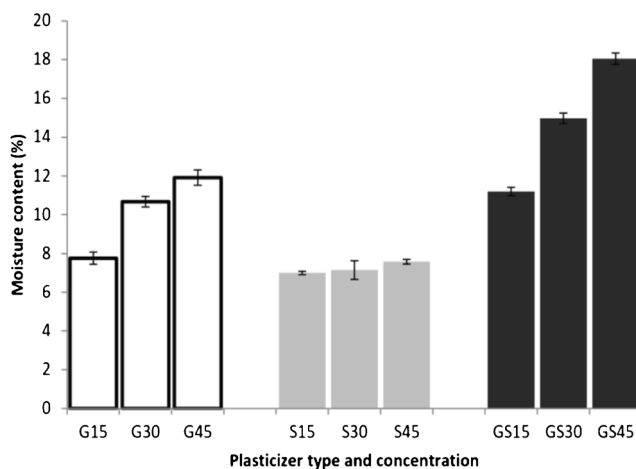


Fig. 5 Moisture content of SPS films with different plasticizer type and concentration

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 (Cerqueira et al. 2012). Hence, glycerol acts as water-holding agent whereas sorbitol entertains less interaction with water molecules.

Although, Sahari et al. (2012a) reported a decrease in moisture content of SPS films (13.2, 12.5, 11.9 and 10.3 %) with increase in glycerol concentration (15, 20, 30, and 40 %, respectively), the moisture content of G-plasticized films (7.76, 10.66 and 11.91 for 15, 30 and 45 % glycerol concentration, respectively) obtained in this study is generally lower.

Film solubility

Film solubility in water is an essential property in selecting suitable food packaging plastics. For most food applications, films with good water insolubility are required to provide water resistance and boost shelf-life of food products (Perez-gago and Krochta 2001; Yin et al. 2007). Conversely, for some food products, packaging films are designed to be water-soluble before consumption of the product (Aguirre et al. 2013; Perez-gago and Krochta 2001).

Plasticization of SPS films significantly increase film solubility in water as presented in Fig. 6. Regardless of the plasticizer type, the solubility of plasticized SPS films in water increased with increased plasticizer concentration. Similar trend was reported in previous studies, regarding the effect of plasticizer concentration on biodegradable film solubility in water (Aguirre et al. 2013; Chiumarelli and Hubinger 2014; Maran et al. 2013). Due to the hydrophilic nature of plasticizers (particularly polyols), they perform essential role in weakening the interaction between polymer molecular chains, increasing the free space volumes between the chains. This in turn promotes water diffusion into the film matrix and, consequently, increasing the solubility of plasticized films.

Chiumarelli and Hubinger (Chiumarelli and Hubinger 2014) and Müller et al. (Müller et al. 2008) reported that

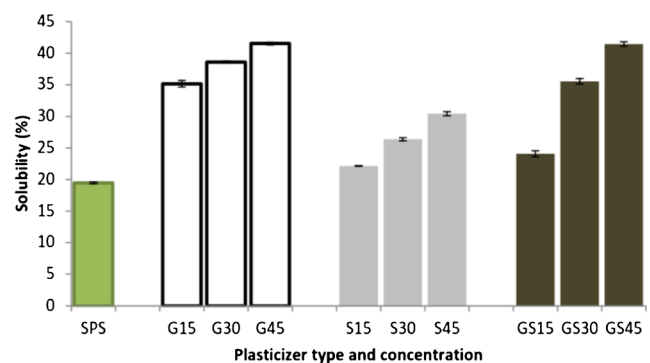


Fig. 6 Solubility of SPS films with different plasticizer type and concentration

plasticizer type and concentration has strong impact on film solubility. Figure 6 uncovers the influence of plasticizers on SPS film solubility in water; the results obtained were 35.14–41.52 % for G-plasticized films; 22.14–30.44 % for S-plasticized films and 24.09–41.43 % for GS-plasticized films at concentration range of 15–45 %. G-plasticized films display higher solubility in water as compared to its counterparts at similar concentration. The high water-solubility of G- and GS-plasticized films over S-plasticized films may be attributed to the strong affinity of glycerol to water molecules, as well as, its lower molecular weight which uncomplicated its entrance between the polymer chains (Cuq et al. 1997; Ghasemlou et al. 2011).

Water absorption and swelling index

Films were emerged in water to verify the effect of plasticizer type and concentration on the hydrophilic nature of starch based films. Water diffuses into the network chains of the films, thus, causing the film to swell. The swelling of all the films were rapid during the initial 6 h and later followed by slower swelling rate until they reach equilibrium. This phenomenon may be due to the abundant active hydroxyl groups of films which were vacant at the initial stage of absorption process. However, the active sites were gradually saturated until they could no longer accommodate any water molecule. This point is referred to as equilibrium state.

It can be observed in Fig. 7 that the addition of plasticizers effectively decreased the swelling and water retaining capacity of SPS films. For all concentration, S-plasticized films are more water resistant and less hygroscopic than G- and GS-plasticized films, due to their strong hydrogen bond formation with the starch intermolecules. As a result, they significantly reduce the interaction between water molecules and the intermolecular hydrophilic functional groups of starch molecules. Increase of plasticizer content from 15 to 45 % effectively influence the swelling capacity and water uptake of plasticized SPS films; but this was not the case with S-plasticized films because they were less affected by plasticizer concentration. Müller et al. (2008) also reported similar results, when they

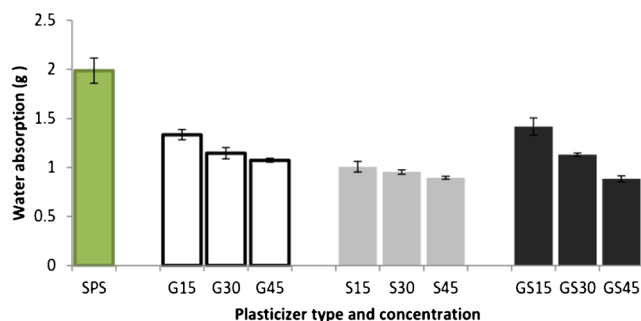


Fig. 7 Water absorption of SPS films with different plasticizer type and concentration

evaluated the effect of glycerol and sorbitol on cassava starch films.

FTIR analysis

The IR spectra of unplasticized and plasticized SPS films are presented in Fig. 8. The broad absorption bands visible at $3600\text{--}3020\text{ cm}^{-1}$ are attributed to the hydrogen bonds formed by the interaction of O-H groups at the end of polymer chains of starch and in the plasticizers. Similar peaks were reported by Kurt and Kahyaoglu (2014), Sahari et al. (2014), and Tongdeesontorn et al. (2012). The hydrogen bond between SPS and plasticizers are identified by the frequency shift of the broad bands of hydroxyl functional groups in SPS. The peaks around 2950 cm^{-1} are ascribed to C-H aliphatic absorption peaks, whereas, the low intensity peaks 1680 cm^{-1} are indicative of bond water molecules within the starch (Park et al. 2000; Sahari et al. 2014). The characteristic peaks at 1004 cm^{-1} are assigned to C-O bond stretching of C-O-C groups in the anhydro-glucose ring of SPS. Similar peaks were observed on native and plasticized starch by Shirai et al. (2013) at $1020\text{--}995\text{ cm}^{-1}$; Sahari et al. (2014) at $1030\text{--}990\text{ cm}^{-1}$; Dai et al. (2009) at $1082\text{--}1029\text{ cm}^{-1}$ and; Kurt and Kahyaoglu (2014) at $1150\text{--}1033\text{ cm}^{-1}$.

These results manifested that all films showed absorption peaks in the same regions, irrespective of plasticizer type and concentration. This reveals that they possess similar functional groups. Though, the plasticizer types utilized during film preparation were different, they are all classified as polyols.

Film crystallinity

The X-ray diffraction patterns of SPS based films plasticized with G, S and GS at different concentrations (0, 15, 30 and 45 %) are presented in Fig. 9. As observed, the unplasticized SPS film shows a large amorphous area with crystalline peaks

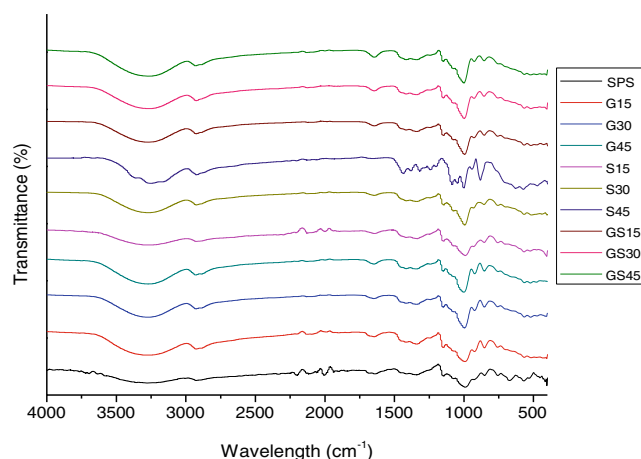


Fig. 8 FTIR spectra of SPS films with different plasticizer type and concentration

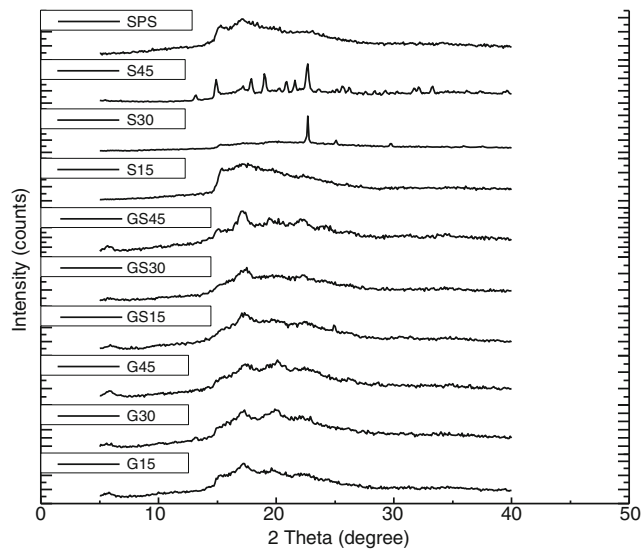


Fig. 9 XRD patterns of unplastized and plasticized SPS films

imbedded. The prime reflection peaks which contributed to the crystallinity of SPS films are located at 15.2, 17.1 and 23.1° which correspond to B-type diffraction pattern (BeMiller and Whistler 2009). Similar observation was made by Zhong and Li (2014) who suggested that peak 2 θ at 17° exhibited the formation of double-helical B- type crystalline.

The X-ray diffraction patterns of unplastized SPS films are similar to that of films containing glycerol (G- and GS-plasticized films). However, a newly defined peak immersed at $\sim 19^\circ$, which was attributed to the addition of glycerol to G- and GS-plasticized films. The peak observed at 19° corresponds to V-type crystalline structure which indicates the existence of amylose-glycerol interactions. García et al. (2009) suggested that amylose favors strong interaction with glycerol. Gutiérrez et al. (2015) and Perez et al. (2012) reported that the amylose within the starch is mainly responsible for the crystallinity of starch based films. Thus, the V-type structure illustrated in G- and GS-plasticized films might be due to the single helical structure formed by amylose and glycerol interaction during processing. In other words, the addition of glycerol to starch dispersion solution disrupted their double helix conformations by the establishment of stable single chain V-conformations helices. This phenomenon led to the formation of glycerol-amylose complexes (Bodirlau et al. 2013; Gutiérrez et al. 2015; Lopez et al. 2014). Furthermore, it can be seen that the intensity of diffraction peaks increased as glycerol concentration increased from 0 to 45 % for G- and GS-plasticized films. Zhong and Li (2014) who studied the effect of glycerol on the properties of Kudzu starch films found that crystallinity of the films was enhanced as glycerol concentration increased from 0 to 40 %. Bergo et al. (2008) also reported similar results regarding the crystallinity of cassava starch films with glycerol content from 0 to 45 %.

The X-ray diffraction patterns of S-plasticized films revealed high increase in the intensity of a peak at 22.7°. The distinction of the peak became more explicit as sorbitol concentration increased from 0 to 45 %. The increase of sorbitol concentration (0–45 %) has a strong effect on the crystallinity of SPS films which is manifested by their sharp and well defined peaks coupled with insignificant amorphous region. On this basis, S30 plasticized films can be classified as highly crystalline as compared to S15 plasticized films; which shows lesser crystallinity from the broad hump diffraction pattern. Further addition of sorbitol concentrations until 45 %, increased the crystallinity of S45-plasticized films as reflected in the appearance of several sharp peaks. The high crystallinity of S30 and S45 films may be induced by the disruption and replacement of hydroxyl groups within starch intermolecules with hydrogen bonds formed between sorbitol and starch molecules during plasticization process.

Famá et al. (2005), Hu et al. (2009) and Gutiérrez et al. (2015) reported that an increase in crystallinity of starch films is strongly related to decrease in film moisture content. Therefore, the increase in crystallinity of S-plasticized films as observed (Fig. 9) concurs with their low moisture content obtained in this study.

Film morphology

Scanning electron microscopy (SEM) images of film samples at magnifications of 500 \times are presented in Fig. 10. The microstructure of the film surfaces was examined to determine the difference in surface morphology cause by plasticizer type and concentration. Micrograph of film surfaces showed significant difference between unplastized and plasticized SPS films. The surface of unplastized SPS films appears very irregular with discontinuity in polymer network structures. The observed rough surface can be linked with the remnants of SPS granules within the polymer matrix of SPS film. According to Sahari et al. (2012a) the SEM of native SPS were rounded and oval shaped granules with smooth surfaces. Hence, (in Fig. 8) the shape of the native SPS were partially disrupted and disordered by dissolving them in large amount of water under constant stirring and high temperature. Nonetheless, traces of rounded and oval like shapes of SPS granules were still visible in the SEM, indicated by arrows in the SPS micrograph. Amylose and amylopectin in native starch of films without plasticizers form biphasic structures (Dai et al. 2009).

The addition of plasticizers to starch based films helps in solubilizing starch granules completely; enhances the smoothness and cohesiveness of film surface microstructure (Dai et al. 2009). The surface microstructure of films prepared with 15 % plasticizer concentration shows relatively less rough and compact appearance compared to unplastized films, regardless of plasticizer type. However, with the exception of GS-

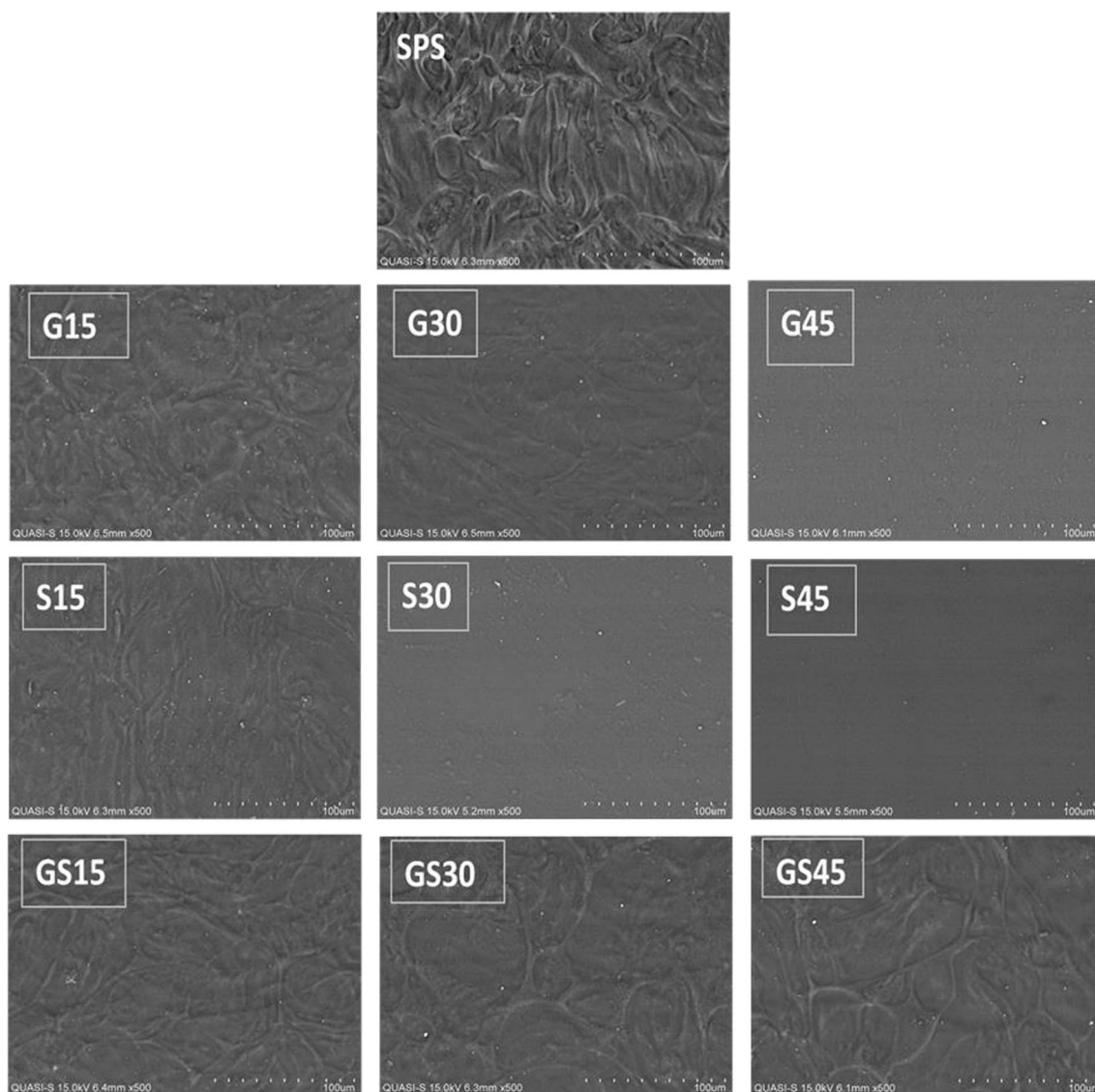


Fig. 10 SEM images of SPS films with different plasticizer type and concentration

plasticized films, further addition of plasticizer concentration (30 and 45 %) promotes more homogeneous, compact, and dense film surface. At 45 % plasticization, films with G and S-plasticizer showed no distinguishable surface difference. Their surface micrographs are smooth, uniform and continuous in appearance. This conforms with the findings of Chiumarelli and Hubinger (2014), Dai et al. (2009), Ghasemlou et al. (2011).

For all the different plasticizer concentrations, S-plasticized films proved to be relatively more smooth, homogeneous and compact. These SEM images manifest the effective interaction of sorbitol with SPS molecules to weaken intermolecular and intermolecular hydrogen bonds of the starch. The observed surface features of S-plasticized films explicitly explain their low moisture content, solubility, swelling and water absorption.

Conclusions

Without plasticizers, SPS films are brittle with many visible cracks and not easily peeled from the casting surface. Hence, the introduction of plasticizers helped to overcome brittleness and, enhance flexibility and peelability 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. Gradually increasing the plasticizer concentration from 15 to 45 % decreases the density and water absorption capacity of films; but increases film thickness, moisture content and solubility, regardless of the plasticizer type involved. However, moisture content and water absorption of S-plasticized films were the

least affected by plasticizer concentration. S-plasticized films exhibited lower moisture content, solubility and water absorption than G- and GS-plasticized films. In contrast, films containing G-plasticizers displayed lower film thickness and density compared to S-plasticized films. Overall, S-plasticized films showed the best performance with respect to physical properties. However, the effect of different plasticizers and concentrations on the mechanical, thermal and barrier properties of sugar palm starch based films should be evaluated be able to determine the best combination for developing biodegradable food packaging films.

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