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Effect of Plasticizer Type and Concentration on Tensile, Thermal and Barrier Properties of Biodegradable Films Based on Sugar Palm (*Arenga pinnata*) Starch

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Abstract: The use of starch based films as a potential alternative choice to petroleum derived plastics is imperative for environmental waste management. This study presents a new biopolymer (sugar palm starch) for the preparation of biodegradable packaging films using a solution casting technique. The effect of different plasticizer types (glycerol (G), sorbitol (S) and glycerol-sorbitol (GS) combination) with varying concentrations (0, 15, 30 and 45, *w*/*w*%) on the tensile, thermal and barrier properties of sugar palm starch (SPS) films was evaluated. Regardless of plasticizer types, the tensile strength of plasticized SPS films decreased, whereas their elongation at break (E%) increased as the plasticizer concentrations were raised. However, the E% for G and GS-plasticized films significantly decreased at a higher plasticizer concentration (45% *w*/*w*) due to the anti-plasticization effect

of plasticizers. Change in plasticizer concentration showed an insignificant effect on the thermal properties of S-plasticized films. The glass transition temperature of SPS films slightly decreased as the plasticizer concentration increased from 15% to 45%. The plasticized films exhibited increased water vapor permeability values from 4.855×10^{-10} to 8.70×10^{-10} g·m^{-1}·s^{-1}·Pa^{-1}, irrespective of plasticizer types. Overall, the current study manifested that plasticized sugar palm starch can be regarded as a promising biopolymer for biodegradable films.

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1. Introduction

On the basis of biodegradability, availability, renewability, non-toxicity and affordability, starch is one of the most promising of all the potential biopolymer materials [1–4]. The use of starch in packaging promotes sustainability and addresses the negative impact non-biodegradable plastics pose on the environment [5,6]. Thus, starch has attracted a great deal of interest as a potential alternative to conventional plastics for packaging applications. Several studies have investigated the development and characterization of starch based films from corn [4,6–8], potato [9–13], cassava [14–20], banana [21], yam [22,23], pea [1], sago [24–26], rice [27–30], maize [31–34], Kudzu [35] and agar [36–39]. According to Sahari *et al.* [40] sugar palm starch is also a potential biopolymer material for making biodegradable films.

Sugar palm is a multipurpose tree which is found in most tropical countries. Almost all the components of the tree are utilized for making local products such as ropes, brushes, brooms, mats, cushions, palm wine, neera syrup, vinegar and many others [41]. Sugar palm starch (SPS) is normally extracted from sugar palm trees that are unable to produce fruits or yield *neera* sap. They are mainly obtained from the inner part of the sugar palm trunk [42]. Sahari *et al.* [43] reported that one tree can produce approximately 50–100 kg of starch. Wina *et al.* [44] also reported that the starch content of a tree ranged from 10.5% to 36.7%.The amylose content of SPS ranged from 37.0% (*w/w*) to 37.6% (*w/w*) as reported by Adawiyah *et al.* [45] and Sahari *et al.* [46]. This means that SPS has higher amylose content compared to most commercial film forming starches such as tapioca (17%), potato (20%–25%), wheat (26%–27%), maize (26%–28%) [46] and yam (30%) [23]. According to the report of Adawiyah *et al.* [45], the amylose content of SPS and sago starch are not significantly different, yet the former has higher amylose content. The proportion of amylose content in starch is among the most relevant criteria that influences the properties of starch based films [46]. On this basis, SPS can be considered a suitable raw material for developing biodegradable films. However, limited information about the functional properties of SPS has been reported compared to commercial starches like cassava, corn, wheat, *etc.*

Despite the numerous advantages of starch, it does not possess thermoplastic properties and cannot be used directly as packaging material [47]. In addition, its end products have poor dimensional stability and mechanical properties [3,6,48]. Native starch based materials are reported in many

investigations to be very brittle with many surface cracks and are difficult to handle. However, these drawbacks can be resolved by the addition of plasticizers to pure starch to improve its workability and suppress film brittleness [10,49]. The ultimate role of plasticizers is to enhance the flexibility and processibility of starch by reducing the strong intermolecular interactions between starch molecules [22,50]. As a result, the mobility of polymeric chains increases, which improves the flexibility, extensibility and ductility of plasticized films. On the contrary, the addition of plasticizers decreases film mechanical resistance. The type and concentration of plasticizer employed has significant effect on the physical, thermal, mechanical and barrier properties of films [35,50–52]. The most common plasticizer utilized for starch based films are polyols such as glycerol and sorbitol, amongst many others. Several researches have been conducted regarding the effect of polyols (especially glycerol and sorbitol) on the properties of films based on various starch origins [10,52–57].Of recent, Sahari *et al.* [40,43] investigated the effect of glycerol content (15, 20, 30 and 40 *w/w*%) on the physical and thermo-mechanical properties of SPS. They concluded that 30 *w/w*% glycerol plasticized SPS exhibited better mechanical properties.

Many studies have reported the plasticization effect of glycerol and sorbitol on various starches from different sources to prepare biodegradable or edible films. Nevertheless, Mikkonen *et al.* [58] reported that glycerol does migrate from film matrix atimes; when used alone as a plasticizer. Kuutti *et al.* [59] and Suyatma *et al.* [60] also observed similar trends with oat-starch films and chitosan films plasticized with only glycerol, respectively. On the other hand, when sorbitol alone is used as plasticizer, they easily crystallize from starch films as reported by Krogars *et al.* [32] and Talja *et al.* [10], in the case of corn and potato starch films. Hence, Krogars *et al.* [32] described that a 1:1 combination of glycerol-sorbitol as plasticizer for maize starch films was found to be more stable than using glycerol and sorbitol separately. According to Adhikari *et al.* [61], when multiple plasticizers are utilized in film matrix, strong interactions may occur between the plasticizers (plasticizer–plasticizer interactions); which can improve certain functional properties of the film. Elsewhere, Muscat *et al.* [62] also emphasized the significance of blending two plasticizers, especially polyols, at different concentrations to evaluate their effectiveness in developing starch based films.

To the best of our knowledge, little work has been published about the effect of different plasticizer types and concentrations on the tensile, thermal and barrier properties of a novel film forming starch, SPS. Therefore, in the present study, SPS was employed for the formulation of biodegradable films using casting solution method. The effect of glycerol, sorbitol and glycerol–sorbitol combination as plasticizer at different concentrations (0%, 15%, 30% and 45% dry starch based) on the tensile, thermal and barrier properties of SPS films was investigated.

2. Experimental Section

2.1. Materials

The native sugar palm starch utilized in the study was extracted from the core of a sugar palm tree at Jempol, Negeri Sembilan, Malaysia. The starch extraction method was adapted from Sahari *et al.* [40] with slight modifications. Glycerol and sorbitol were used as film plasticizers and were supplied by LGC Scientific, Selangor, Malaysia. Distilled water served as the solvent for preparing filmogenic solutions.

2.2. Film Preparation

The sugar palm-based films were prepared by conventional solution-casting technique. Glycerol (G), sorbitol (S) or glycerol-sorbitol (1:1) combination (GS) ratio were used as plasticizers to investigate the effect of each individual plasticizer on the developed 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 min 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 min at 95 ± 2 °C. The film forming solutions were left to cool down, prior to their casting in glass petri-dishes. The glass petri-dishes served as casting surfaces, enabling the film to have a smooth and flat surface. The fresh casted 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.

2.3. Tensile Properties

The mechanical properties of the films were tested using a standard method D882-02 (ASTM, 2002). Tensile strength and elongation at break were determined by using Instron 3365 universal testing machine with a load cell of 30 kg. Films were cut in the form of strips with dimension of 10 × 70 mm. The strips were clamped between two tensile grips and the initial gauge length was set at 30 mm. Films were pulled using a crosshead speed of 2 mm/min. During the stretching, force (N) and deformation (mm) were recorded. Measurements were carried out on 10 different specimens. The mechanical properties were calculated as average value from the obtained results.

2.4. Thermal-Gravimetric Analysis (TGA)

Thermo-gravimetric tests were performed using Mettler Toledo thermal analyzer (TA Instructments, New Castle, PA, USA).The tests were carried out at temperature range from 25 to 800 °C with a heating rate of 10 °C/min under nitrogen gas. Film sample of 5–15 mg was placed in the sample pan and heated. The weight loss as function of temperature was depicted as thermal-gravimetric analysis (TGA) curve.

2.5. Differential Scanning Calorimetry (DSC)

The film samples were conditioned (52% ± 1% for 48 h) prior to their analyses using differential scanning calorimetry (Universal V3-9A TA Instrument, New Castle, PA, USA). The calibration of the equipment was conducted using indium as standard. For differential scanning calorimetry (DSC) analyses, 5 mg of film samples were weighted and placed in an aluminum sample pan which was immediately sealed. An empty sample pan was used as reference. Film samples were heated from 35 to 265 °C at a rate of 10 °C/min. Nitrogen gas was used to flush the DSC cell at a flow rate of 20 mL/min to maintain an inert environment. The transition temperatures were determined from the thermogram results.

2.6. Water Vapour Permeability (WVP)

Prior to the water vapour permeability (WVP) test, the film samples were conditioned in a desiccator with relative humidity of 50% at 25 °C. The WVP test was conducted according to ASTM E96–95 with slight modifications. Circular film samples were mounted and sealed on the open mouth of cylindrical cups containing 20 g of silica gel. The test cups were measured before being kept in a relative humidity chamber (25 °C, relative humidity 75%). The weight of the test cups was determined by periodic measurement till the equilibrium state was reached. Weight increments of the test cups were recorded and WVP was calculated as follows:

$$\text{WVP} = \frac{(m \times d)}{(A \times t \times P)} \tag{1}$$

where *m* (g) is the weight increment of the test cup, *d* (mm) is the film thickness, *A* (m^2) is the area of film exposed, *t* (s) is the duration for permeation, and *P* (Pa) is the water vapor partial pressure across the films. The results were expressed in $g \cdot mm \cdot s^{-1} \cdot m^{-2} \cdot Pa^{-1}$.

3. Results and Discussion

3.1. Mechanical Properties

3.1.1. Tensile Strength of Sugar Palm Starch (SPS) Plasticized Films

The effect of different plasticizer types and concentrations on the tensile strength of SPS films is shown in Figure 1. The presence of plasticizer at lower concentration of 15% demonstrated high tensile strength value of 28.35 MPa for S-plasticized films, 15.82 MPa for GS-plasticized films and 9.59 MPa for G-plasticized films. The possible reason for the high tensile strength at low plasticizer concentration is the domination of strong hydrogen bonds produced by starch–starch intermolecular interaction over starch–plasticizer attraction. However, the addition of plasticizers from 15% to 45% caused significant reduction in the tensile strength of films, regardless of plasticizer type. The tensile strength of G-plasticized films notably decreased from 9.59 to 1.67 MPa and that of S-plasticized films dropped from 28.35 to 5.84 MPa as plasticizer concentration increased from 15% to 45%. In the case of GS-plasticized films, tensile strength reduction was observed from 15.82 to 3.99 MPa at the same range of plasticizer concentration. The decrease in tensile strength of starch based films as plasticizer concentration increased were reported by numerous authors [6,7,30,52,58–67]. This phenomenon can be explained through the role of plasticizers in diminishing the strong intra-molecular attraction between the starch chains and promoting the formation of hydrogen bonds between plasticizers and starch molecules. Thus, it reduces the tensile strength of SPS plasticized films by subsequently weakening the hydrogen bonds between starch chains [6,61].

As the glycerol concentration increased from 15% to 45%, G-plasticized films showed the highest reduction in tensile strength as compared to S- and GS-plasticized films. These results revealed that glycerol has higher efficiency in plasticizing SPS films than sorbitol. Razavi *et al.* [53] and Muscat *et al.* [6] reported a similar observation that glycerol induces greater tensile strength reduction compared to other polyols. This tendency can be ascribed to the smaller molar mass of glycerol (92.0928 g/mol; sorbitol 182 g/mol) which facilitate easy interaction between glycerol–starch molecular

chains. Tapia-Blácido *et al.* [68] also testified that glycerol is a more effective plasticizer for most edible films.
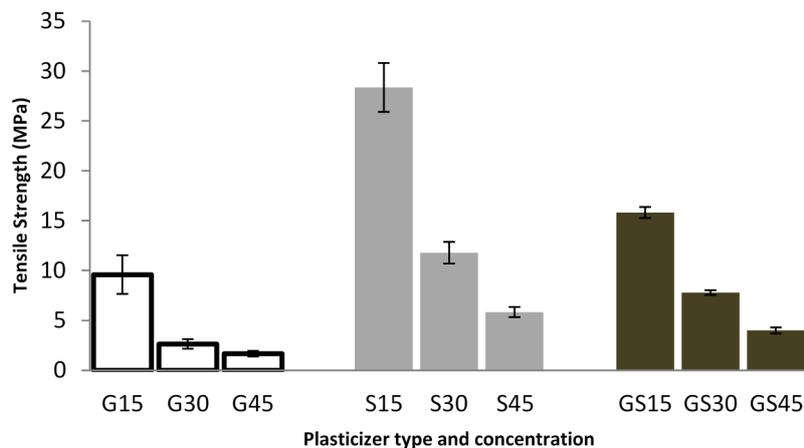

Figure 1. Effect of plasticizer type and concentration on the tensile strength of sugar palm starch (SPS) films.

Figure 1 clearly shows that S-plasticized films demonstrated superior tensile strength over their counterparts at a constant plasticizer concentration. For example, the tensile strength values of S-plasticized films are 28.35, 11.79 and 5.84 MPa compared to 9.59, 2.64 and 1.67 MPa for G-plasticized films at 15%, 30% and 45% plasticizer concentrations, respectively. These results are consistent with the findings of Tapia-Blácido *et al.* [68] and Tapia-Blácido *et al.* [50], who reported that sorbitol plasticized flour films are more resistant to breakage than films plasticized with glycerol at constant proportions. Interestingly, GS-plasticized films exhibited a tensile strength between individual G- and S-plasticized films. For example, the tensile strength value of GS30 is 7.79 MPa, which is between the tensile strength of 2.64 MPa for G30 and 11.79 MPa for S30 films. This is because GS-plasticized films are a combination of glycerol and sorbitol plasticizers. Therefore, the resulting films (GS-plasticized films) improve the low tensile strength of G-plasticized films and compromise the high tensile strength of S-plasticized films.

The tensile strength values of plasticized SPS films were higher than the reported values for films of corn starch with glycerol and stearic acid [69], corn starch with glycerol and xylitol [62], corn starch with glycerol alone [70], glycerol plasticized rice starch [71], amaranth flour plasticized with sorbitol or glycerol [68], cassava starch with glycerol [72], cush–cush yam starch [73], and pea starch with glycerol [74]. On the other hand, their tensile strength values were lower than LDPE and polystyrene [63].

3.1.2. Elongation at Break of SPS Plasticized Films

Elongation at break is the extendibility of film length from initial length to the point of break. Moraes *et al.* [75] defined elongation at break (E%) as the ability of films to deform before finally breaking. This parameter (E%) helps to determine the flexibility and stretchability of films. The desired flexibility of biopackaging films depends on their intended application and subsequent transportation, handling and storage of packaged foods.

The effect of plasticizer concentration (15%–30%) on the elongation of SPS plasticized films has an inverse behaviour (see Figure 2) compared with their correspondent tensile strength. As anticipated, the increase of plasticizer concentration from 15% to 30% registered considerable increase in film elongation: 26.52%–61.63% for G-plasticized films, 5.38%–34.5% for S-plasticized films and 15.1%–46.65% for GS-plasticized films. Similar film elongation behaviour has been reported by Kurt and Kahyaoglu [76], Suppakul *et al.* [77], Muscat *et al.* [6], Talja *et al.* [10] and Mali *et al.* [78]. The observed increase in film elongation is because plasticizers decrease the intermolecular bonds between amylose, amylopectin and amylose–amylopectin of the starch matrix and thus, substitute them with hydrogen bonds formed between plasticizer and starch molecules. Such disruption and reconstruction of starch molecular chains reduce the rigidity and promotes flexibility of films by allowing more chain mobility. Zavareze *et al.* [9] reported that the elongation of polymeric materials depends on the mobility of their molecular chains.

The results presented in Figure 2 verified that film elongation increased as the concentration of plasticizers was adjusted. However, the elongation of G- and GS-plasticized films significantly decreased from 61.63% to 28.39% and 46% to 34.27%, respectively, when plasticizer content increased from 30% to 45%. Sahari *et al.* [43] also reported a dramatic drop in the elongation of plasticized sugar palm starch when 40% glycerol was used. This occurrence can be explained by the anti-plasticization behavior or phase separation of highly plasticized starch films.
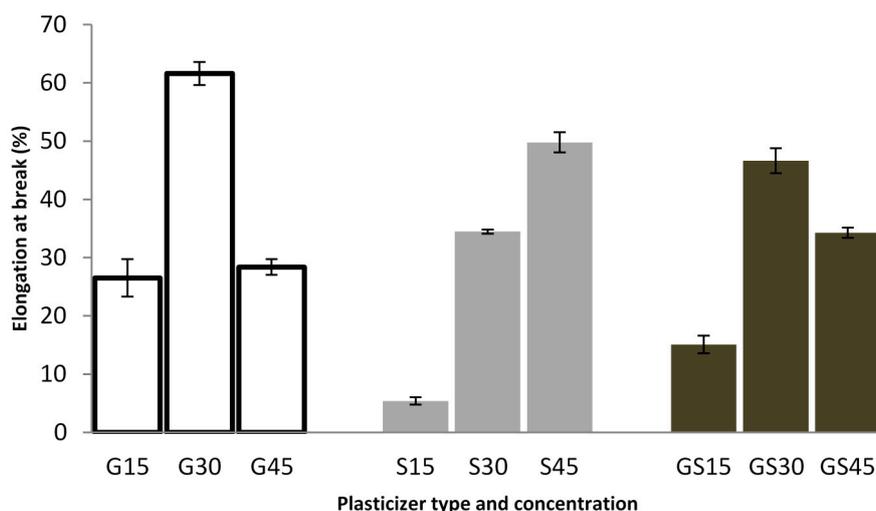

Figure 2. Effect of plasticizer type and concentration on the tensile strength of SPS films.

The anti-plasticization effect of plasticizers on starch based films depends on their concentration level [14,79,80]. The stress–strain curves in Figure 3 clearly shows the decrease of film tensile strength and increase of flexibility as plasticizer concentration increased. S15 films (Figure 3) demonstrated high stress coupled with low strain and, thus, were regarded as very brittle. Increasing the concentration of sorbitol enhanced the ductility of S30 and S45 films which is manifested by their large deformation before fracture. Suppakul *et al.* [77] observed an anti-plasticization effect on the elongation at break of cassava flour films at 50% sorbitol concentration. However, such anti-plasticization behaviour was not observed even in S45 films.
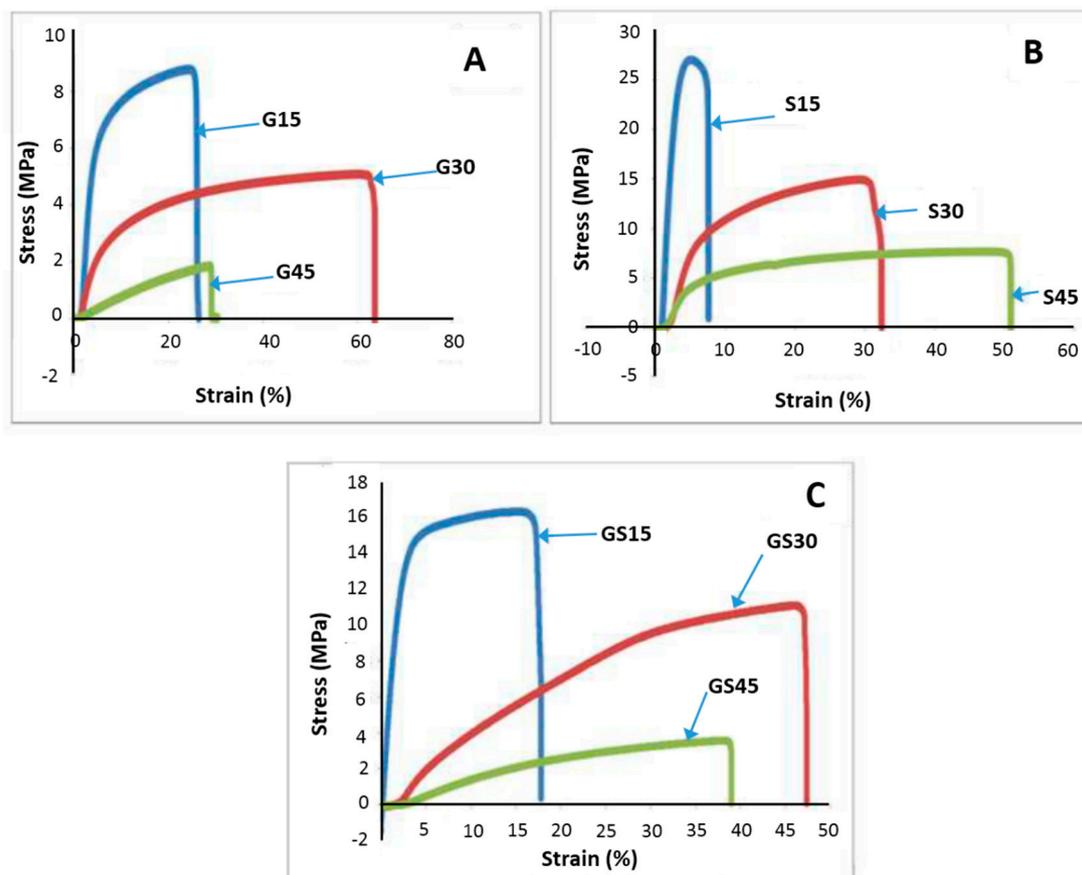
Figure 3. Stress-strain curve graph of (**A**) glycerol (G)-plasticized films; (**B**) sorbitol (S)-plasticized films; and (**C**) glycerol-sorbitol (GS)-plasticized films.

SPS films with higher strain (*i.e.*, G30, S45 and GS30) exhibited superior flexibility and approach fracture in a slower and smoother rate. Chang *et al.* [81] stated that the increasing concentration of plasticizers alter the fracture mechanism from swift brittle fracture at low strains to elastoplastic fracture at higher strains. Conversely, it appears from the stress–strain curve (Figure 3) that G45 and GS45 films displayed anti-plasticization effect at higher plasticizer concentration (*i.e.*, 45%). Such anti-plasticization phenomena at higher plasticizer concentration are associated with stronger interaction between plasticizer and starch molecules (amylose/amylopectin) that hinders macromolecular mobility [18,75]. According to Zhang *et al.* [82] anti-plasticization of plasticized starch based films occurs when the amount of plasticizer molecules increased above the critical value. Consequently, the interactions between starch polymers become weaker and the cohesive force of the polymer chains is decreased, resulting in a decrease in E% values. Laohakunjit and Noomhorm [27] reported that plasticized starch films outside the range of 20%–45% plasticizer content are either too brittle (<20 wt.%) or too tacky (>45 wt.%).

Alternatively, the observed decrease in E% of G45 and GS45 can also be attributed to the formation of glycerol-rich and starch-rich areas, due to glycerol migration from film matrix. The migration of glycerol from the film matrix enables the starch intermolecules to strongly interact once more and thus, reduce the E% of the films. This phenomenon happens when the plasticizer concentration is more than its compatibility limits, subsequently, causing phase separation. The phase separation in G45 and GS45 can possible justify the high stickiness of these films reported in the authors' previous work [83].

3.2. Thermal-Gravimetric Analysis (TGA)

Thermal-gravimetric analysis technique was utilized to determine the thermal decomposition and stability of unplasticized and plasticized SPS films. The results of the TGA curves were presented in Figure 4 in which the mass (mg) losses of film samples were plotted as a function of temperature (°C). As seen in the TGA curves,the thermal decomposition of all SPS 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 [3,71,84–86].

The initial stage of thermal degradation of films occurred at temperature less than 100 °C. The mass loss at this stage can be associated with the evaporation or dehydration of loosely bound water and low molecular weight compounds in the films [3,13,77]. G-plasticized films showed higher mass loss compared with the unplasticized SPS films at temeprature lower than 100 °C. On the contrary, the unplasticized films demonstrated higher mass loss compared to S-plasticized films. This indicates that G-plasticized films has higher moisture content than S-plasticized films.

The second stage of the thermal degradation range from ~125–290 °C corresponded to the evaporation of plasticizer compounds (*i.e.*, glycerol) together with chemisorbed water molecules. The degradation tememeperature of G-plasticized films (Figure 4) concurred with the findings of Sahari *et al.* [43] who also worked on plasticized sugar palm starch. Zhong and Li *et al.* [35] reported the degradation temperature of glycerol-rich phase of kudzu starch-based edible films between150 and 280 °C.

Further heating beyond 290 °C induced the highest thermal degradation rate which is reflected by the drastic weight reduction of both unplasticized and plasticized SPS films. The onset of thermal decomposition of starches occurred around 300 °C for plasticized films. According to Nascimento *et al.* [87], this stage corresponds with the elimination of hydrogen groups, decomposition and depolymerization of the starch carbon chains.

It can be observed in Figure 4 that the increase of glycerol concentration significantly increase the thermal degradation rate of G-plasticized film compared to the unplasticized films at constant temperature. For example, the percentage weight loss at 300 °C was 37% for G15, 45% for G30 and 52% for G45; while that of the unplasticized SPS films was 20%. In other words, the increase of glycerol concentration from 15% to 45% reduces the thermal resistance of SPS films. This observation can be attributed to the glycerol–starch molecular interaction which weakens the strong intermolecule bonds between starch molecules and thus, lowers the thermal resistance of G-plasticized films. For S-plasticized films, the increase of thermal degradation temperature up to 350 °C has an insignificant effect on their thermal stability, regardless of plasticizer concentration. Comparing the weight loss of SPS plasticized films, it can be seen that S-plasticized films are more thermally resistant than G- and GS-plasticized films at temperatures below 300 °C.
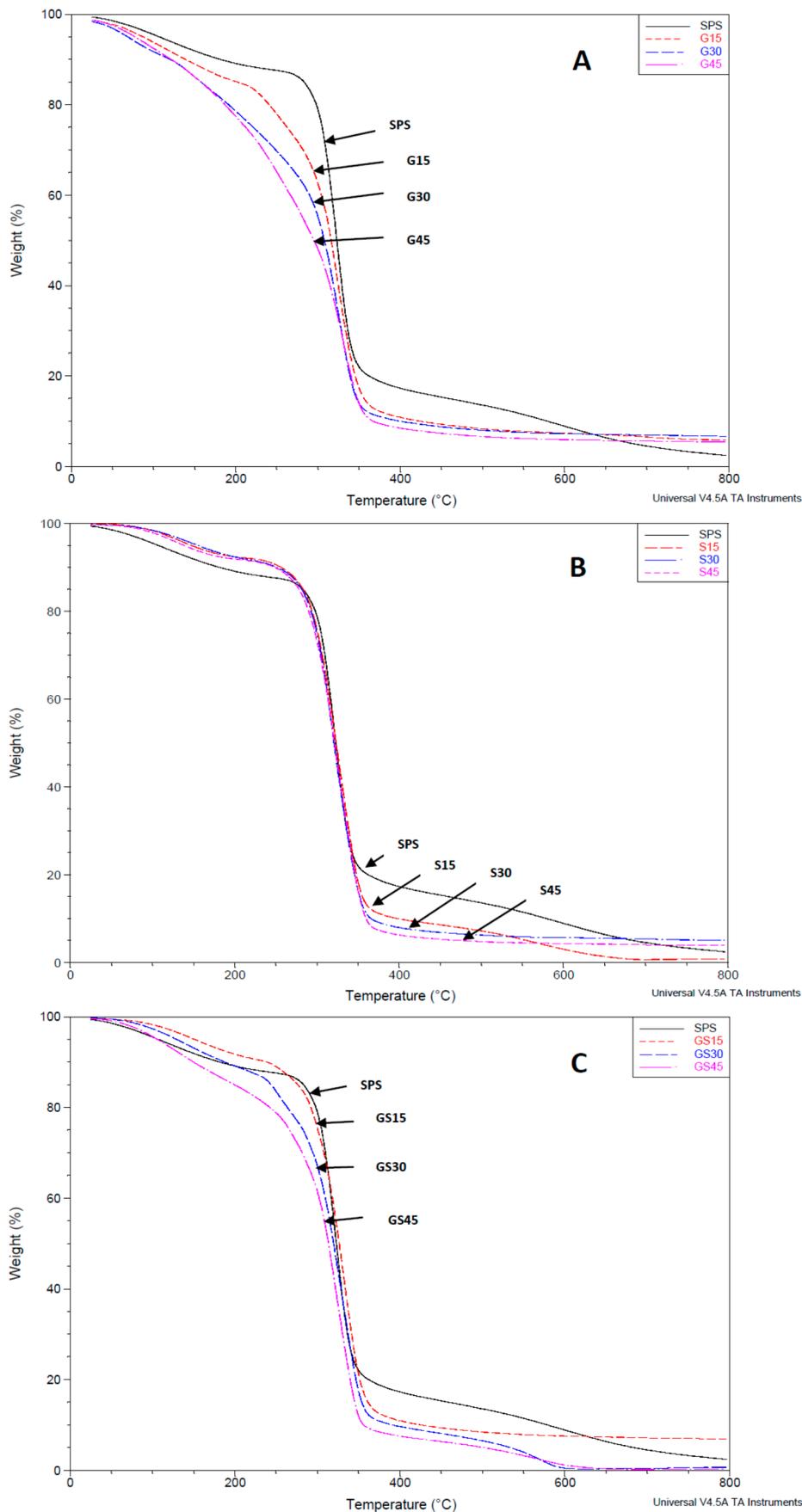
Figure 4. TGA curves of G-plasticized (**A**); S-plasticized (**B**); and GS-plasticized films (**C**) at different concentrations (15%, 30%, and 45%) compared to unplasticized SPS films.

3.3. Glass Transition Temperature (T_g)

Glass transition temperature (T_g) is considered as one of the most essential thermophysical transitions for starch based films. By definition, T_g is the temperature at which the forces binding the amylose and amylopectin of the starch are relaxed to allow large-scale molecular movements [82]. Hence, T_g of unplasticized and different plasticized SPS films were obtained from the differential scanning calorimetry (DSC) results as shown in Table 1. The results of this investigation show that the unplasticized SPS film has a T_g of 145.19 °C. The addition of plasticizers into unplasticized SPS films reduced the T_g, irrespective of plasticizer type. The obtained results agree with numerous findings that reported the decrease of T_g as plasticizers are incorporated into starch based films. Subsequently, the polymer matrix becomes less dense and the mobility of polymer chains increases [83,84]. However, in the present study, the decrease of T_g values of SPS films are insignificant as plasticizer concentrations increased from 15% to 45%.

G-plasticized films demonstrated greater T_g reduction when compared to S-plasticized films. This observation is attributed to the high hygroscopic character of glycerol. It tends to easily retain water into the matrix of the films. The addition of glycerol in SPS films generates more hydrophilic hydroxyl groups as active sites which could be occupied by water molecules. Thus, films with higher glycerol concentration reflected higher moisture content as previously reported by the authors [83] and consequently, lower the T_g values. It is well established that moisture content of starch based films affects their T_g because water has a plasticizing effect and could be considered as a polymer inter-chain mobility enhancer [78]. These authors also reported that higher glycerol concentration offer more chances of plasticizer–starch, plasticizer–water and plasticizer–plasticizer interactions. Thus, increasing free volume of films, which in turn lowers their T_g values.

As seen in Table 1, S-plasticized films exhibits the highest T_g values at equal concentration with its counterparts (G and GS-plasticized SPS films). This observation corresponded with its low moisture content as previously reported by the authors [85]. Sorbitol forms strong interaction with the intermolecular chains of SPS due to its high molecular structure resemblance with glucose units, thus, reducing the possibility of plasticizer–water molecule interactions occurring. Chiumarelli and Hubinger [88] reported that T_g may be related to tensile properties of films. On the basis of that, the high T_g values of S-plasticized films can be correlated with its high tensile strength compared to G and GS plasticized SPS films.

Interestingly, the T_g of GS-plasticized SPS films are the lowest at the same plasticizer concentration with its counterparts. Though, GS-plasticized films were anticipated to provide intermediate T_g values as in the case of Figures 1 and 2, where their tensile strength and elongation at break values are between G and S-plasticized films. However, the observed phenomenon for the Tg of GS-plasticized films can be elucidated based on their moisture content. It was reported in the previous work of the authors [83] that GS-plasticized films possessed the highest moisture content followed by G-plasticized films. Chang *et al.* [81], who studied the effect of water and glycerol on the T_g of tapioca starch films, reported that the higher the moisture content and plasticizer concentration of a film, the lower its T_g.

Table 1. Effect of plasticizer type and concentration on T_g and water vapour permeability (WVP) of SPS films.

Samples	Type of Plasticizer	Plasticizer Content (%)	T_g (°C)	WVP $\times 10^{-10}$ (g·s^{-1}·m^{-1}·Pa^{-1})
SPS	–	0	145.19	–
G15		15	139.77	5.820 ± 0.01
G30	Glycerol	30	138.71	6.642 ± 0.07
G45		45	138.51	8.700 ± 0.01
S15		15	141.65	4.855 ± 0.03
S30	Sorbitol	30	139.59	5.824 ± 0.01
S45		45	138.54	6.180 ± 0.02
GS15		15	137.42	5.561 ± 0.04
GS30	Glycerol-Sorbitol	30	137	6.360 ± 0.01
GS45		45	123.46	8.514 ± 0.02

3.4. Water Vapor Permeability (WVP)

The ability of packaging materials to refrain or minimize moisture transfer between the food and the surrounding environment is a crucial property for effective food packaging [4,23]. Hence, the WVP of the packaging material should be as low as feasible. The effect of plasticizer type and concentration on the WVP of SPS films is presented in Table 1. The WVP values of unplasticized SPS films are not provided as the films cracked and crumbled into small pieces due to their brittleness.

As shown in Table 1, WVP values of plasticized SPS films increased with plasticizer content (15%–45% *w/w*). The results show that increasing the plasticizer concentration from 15% to 45% increased WVP values from 5.820×10^{-10} to 8.70×10^{-10} g·s^{-1}·m^{-1}·Pa^{-1} for G-plasticized films, 4.855×10^{-10} to 6.180×10^{-10} g·s^{-1}·m^{-1}·Pa^{-1} for S-plasticized films, and 5.561×10^{-10} to 8.514×10^{-10} g·s^{-1}·m^{-1}·Pa^{-1} for GS-plasticized films. The plasticized films exhibited increased WVP values regardless of plasticizer type. Similar findings have been recently reported by Muscat *et al.* [6]. The SPS films with 15% plasticizer showed much lower WVP. This could be related to the strong starch–starch molecule interactions which are dominant at lower plasticizer concentrations, resulting in a dense and more compact starch network and structure. Thus, the lower the WVP values. Further increments of plasticizer concentration to 45% promote the mobility and flexibility of starch network chains due to the structural modification of the starch–starch molecular interaction to a looser network. Consequently, the film matrices became less dense and their WVP values eventually increase.

It can be seen that G-plasticized films have the highest WVP values compared to S- and GS-plasticized films. This observation can be attributed to the hydrophilic nature of glycerol which induces favourable sorption of water molecules. Cuq *et al.* [89] reported that glycerol is acknowledged to demonstrate superior plasticizing effect compared to sorbitol. However, the former presents higher WVP at a constant plasticizer concentration. Likewise, Muscat *et al.* [6] also reported that low-amylose and high-amylose corn starch films plasticized with glycerol (at 30% and higher) manifested higher WVP compared to films containing xylitol and the glycerol-xylitol combination.

In contrast, S-plasticized films showed the lowest WVP values. The likely explanation for this result may be the low moisture content of less than 8% of S-plasticized films as previously reported by the authors [83]. Low water content in the film matrix leads to more compact hydrogen bonds of

starch–water interaction than starch–starch intermolecular chains. Gaudin *et al.* [80] also reported that lower water content results in decreased permeability in hydrophilic biopolymer films. With low water content, a high number of free hydroxyl groups of the starch are available to interact with the active sites of sorbitol. Consequently, the chances of sorbitol interacting with water molecules become lower.

From Table 1, it can be observed that the WVP of GS-plasticized films are quite similar to that of G-plasticized films at a constant plasticizer concentration. Nonetheless, the GS-plasticized films exhibit slightly lower WVP values than G-plasticized films. This indicates that the glycerol concentration has more influence than sorbitol on the WVP of GS-plasticized films. However, the presence of sorbitol in GS-plasticized films helps to minimize their WVP values as compared to films plasticized with glycerol alone.

Overall, plasticized SPS films have WVP values higher than 0.0036×10^{-10} g·s^{-1}·m^{-1}·Pa^{-1} of low-density polyethylene (LPDE). The inherent hydrophilic character of starch is responsible for the high WVP of starch based films compared to synthetic plastic films [90]. However, the WVP values of plasticized SPS films with different concentrations have similar permeability with glycerol plasticized yam starch, corn starch and cassava starch films [18,23,81]. Regardless of plasticizer type, the WVP of 15% and 30% plasticized SPS films were lower than those of other starch based films such as glycerol or sorbitol plasticized pea starch films [74], rice starch films with glycerol or sorbitol [30], corn starch films containing glycerol [69], and cassava starch films with glycerol plasticizer [72].

4. Conclusions

The different plasticizers utilized in the film-forming solution have remarkable effects on the tensile, thermal and barrier properties of the resulting films. In all the plasticized SPS films, the tensile strength decreased with plasticizer content from 15%–45%. The reduction of hydrogen bonds between starch intermolecular chains due to the formation of starch (amylose)–plasticizer complexes was responsible for the plasticizing effect of different plasticizer concentrations. An antiplasticization effect was observed for the E% of G- and GS-plasticized films at 45% plasticizer concentration, while plasticization behavior was found at lower concentrations. This phenomenon was not observed for the E% of S-plasticized films. Interestingly, GS-plasticized films enhance the tensile strength of G-plasticized films and reduce the brittleness of S-plasticized films. Thus, better tensile properties with acceptable thermal stability were achieved by SPS films plasticized with a combination of glycerol and sorbitol (GS). The thermal degradation of the plasticized SPS films occurred in three different stages: (1) evaporation of loosely bound water (less than 100 °C); (2) evaporation of plasticized compounds (125–290 °C); and (3) decomposition of starch (more than 300 °C). The plasticized SPS films demonstrated good barrier properties compared to many biodegradable starch based films. This implies that plasticized SPS films may be suitable for food packaging applications. Generally, the current study verified that plasticizer type and concentration affects the mechanical, thermal and barrier properties of plasticized SPS films. In summary, this paper presents a potential biopolymer for the development of biodegradable films.

Acknowledgments

Author Contributions

The paper was designed and conceived by all the authors. The first author (Muhammed L. Sanyang) who is a PhD student conducted the entire experimental work under the supervision of Salit M. Sapuan (project leader), Mohammad Jawaid, Mohamad R. Ishak and Japar Sahari. All the authors helped in analysing the experimental results obtained. The manuscript was finally written by Muhammed L. Sanyang.

Conflicts of Interest

The authors declare no conflict of interest.

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