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Effect of Agar on Physical Properties of Thermoplastic Starch Derived from Sugar Palm Tree

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ABSTRACT

Modification of thermoplastic starch with other natural polymer is a promising research since the combination of both material will produce a fully green polymer with modified properties. The aim of this paper is to investigate the effects of agar on physical properties of thermoplastic sugar palm starch (SPS). Various types of thermoplasctic SPS based polymer were prepared by blending SPS and agar with the presence of glycerol as a plasticiser. Agar with various contents (10, 20, 30, and 40 wt%) were mixed with thermoplastic SPS via melt mixing before compression moulded into 3 mm mould plate. The prepared laminates were characterised for the moisture content, density, water absorption, thickness swelling and water solubility. Results showed that incorporation of agar has slightly increased the moisture content and water absorption capacity of the blends. Slight increment in thickness swelling was observed for thermoplastic SPS after incorporation with agar (40 wt%). Water solubility of thermoplastic SPS was slightly increased with incorporation of agar (40 wt%). Similar density was recorded for all ratios of agar, which indicated that the incorporation of agar did not influence the density of thermoplastic SPS. In conclusion, the incorporation of agar has slightly increased the hydrophilic behaviour of thermoplastic SPS.

Keywords: Agar, starch, thermoplastic, thickness swelling, water absorption

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INTRODUCTION

Most plastic products currently used for various applications are made up of petroleum-based polymeric materials. Their use is widespread due to large scale availability, low production cost, lightweight, versatile and good mechanical properties (González & Igarzabal, 2013, pp. 289-296). However, these materials have certain disadvantages because they were synthesised from a non-renewable source, making them not readily biodegradable (Kasim et al., 2015, pp. 117-123). This characteristic leads to major source of generation and accumulation of non-degradable residues which make petroleum-based polymer as an environmental harmful waste (Bucci et al., 2005, pp. 564-571). Hence, the bio-polymer concept is getting serious attention since it is associated with the use of renewable raw materials such as polysaccharides extracted from agricultural, marine, animal or microbial sources (González & Alvarez Igarzabal, 2013, pp. 289-296). Among these sources, starch is one of the most promising materials due to certain advantages such as availability, economic, abundant, biodegradable, and renewable (Chang et al., 2014, pp. 285-393; Li et al., 2015, pp. 115-122). Starch is a heterogeneous material containing two microstructures called amylose and amylopectin. Amylose is a linear structure of α-1,4 linked glucose units, whereas amylopectin is a highly branched structure of short α-1,4 chains linked by α-1,6 bonds. The most common starch used to develop biopolymer includes cassava, corn, potato, sago and rice (Beilvert et al., 2014, pp. 242-248; Edhirej et al., 2015, pp. 1-16; Prachayawarakorn et al., 2011, pp. 88-95; Rahmat et al., 2009, pp. 2370-2377; Ramesh et al., 2012, pp. 701-706).

Sugar palm is of the Palmae family which also is known as *Arenga pinnata*. This natural forest species is known for the production of sugar known as *neera* sugar and it is recently used for producing bioethanol (Ishak et al., 2013, pp. 699-710). This palm tree is reported to be able to produce 50 to 100 kg of starch (Sahari et al., 2014. pp. 955-959). Sugar palm starch has comparable properties in terms of the amylose content (37%), which is higher than cassava (17%), potato (25%) and corn (28%) (Sahari et al., 2014. pp. 955-959). It is reported that amylose content in starch is essential for polymerisation efficiency (Zou et al., 2012, pp. 1583-1588). A recent study developed thermoplastic starch from sugar palm and characterised the physical, thermal and mechanical properties (Sahari et al., 2013, pp. 1711-1716).

Agar is a polysachharide obtained from marine alga such as *Gracilaria* and *Gelidium* sp. (Giménez et al., 2013, pp. 264-271). It consists of two main components; agarose and agaropectin. Agarose is a linear polymer based on the 3, 6-anhydro-α-L-galactopyranose unit, whereas agaropectin is a heterogeneous mixture of smaller molecules which have similar structures with agarose but with are slightly branched and sulfated (Atef et al., 2014, pp. 537-544). This polysaccharide is used for gelling and as a thickening agent in food and pharmaceutical industry. Recently, agar has received much attention in biopolymer development due to its promising properties such as good film forming ability, thermal stability and mechanical properties (Reddy & Rhim, 2014, pp. 480-488). It is reported that agar biopolymer has a relatively good water resistance than other seaweed polysachhride (Rhim, 2012, pp. 66-73).

Though there are numerous works done on the properties of agar film from solution casting, studies on agar behaviour as a blend component in thermoplastic starch are still rare.

Therefore, agar was selected to modify the properties of thermoplastic starch prepared from sugar palm tree. The objective of this work is to study the effects of agar on the properties of thermoplastic SPS prepared via melt mixing and hot pressing. Different ratios of agar were used to study the effects on thermoplastic SPS. Similarly, various techniques were used to characterise the physical properties of the blends including density, moisture content, water absorption, water solubility and thickness swelling behaviour.

MATERIALS AND METHODS

Materials

Sugar palm starch (SPS) was prepared from sugar palm tree at Jempol, Negeri Sembilan, Malaysia. The interior part of the trunk was crushed in order to obtain the woody fibres which contained the starch. This woody fibres were soaked in fresh water followed by squeezing them to dissolve the starch into the water. Water solution containing starch was filtered in order to separate the fibres from the solution. This solution was then left for sedimentation of the starch. The supernatant was discarded and the wet starch was kept in an open air for 48 hours followed by drying in an air circulating oven at 105°C for 24 h. Agar powder was procured from R&M Chemicals and glycerol was purchased from Sciencechem.

Sample Preparation

Thermoplastic SPS was prepared by adding glycerol (30wt% starch-based), followed by pre-mixing using a high speed mixer at 3000 rpm for 5 min. After this preliminary step, the resulting blend was melt-mixed using Brabender Plastograph at 140oC and rotor speed of 20 rpm for 10 min. These mixtures were granulated by means of a blade mill equipped with a nominal 2 mm mesh and thermo-pressed in order to obtain laminate plate with 3 mm thickness. For this purpose, a Carver hydraulic thermo-press was operated for 10 min at 140°C under the load of 40 tonnes. The same processes were also used for the preparation of different TPSPS blends. The property modification of different TPSPS blends was carried out by using different ratios of agar (10, 20, 30, and 40 wt%). All the samples were pre-conditioned at 53% RH for 2 days prior to testing.

Density

The density of SPS and agar powder was measured using gas intrusion under helium gas flow with AccuPyc 1340 pycnometer. Density determination balance (XS205 Mettler Toledo) was used to measure the density of TPSPS blends. Five measurements were conducted at 27°C and the average value was computed.

Moisture Content

Moisture content of samples was determined according to the previous study (Sahari, Sapuan, Zainudin, & Maleque, 2012). The samples (10 x 10 x 3 mm) were prepared for the moisture content investigation. All the samples were heated in an oven for 24 h at 105°C. Weight of samples, before (M_i) and after (M_f) the heating was measured in order to calculate moisture content. The moisture content was determined by using Eqn. 1.

$$\text{Moisture content (\%)} = \frac{M_i - M_f}{M_i} \times 100 \quad \text{[Eqn.1]}$$

The tests were conducted in five replications and the average value was computed.

Water Absorption

Specimens having dimensions of 10 × 10 × 3 mm were dried in an air circulating oven at 105°C ± 2 for 24 h to remove existing moisture, followed by immersing in water at room temperature (23 ± 1°C) for 0.5, 2 and 24 h, respectively, as mentioned in some previous studies (Lomelí Ramírez et al., 2011, pp. 1712-1722; Sahari et al., 2012, pp. 254-259). The samples were weighed before (Wi) and after the immersion (W_f) and water absorption of the laminates was calculated using the following equation:

$$\text{Water absorption (\%)} = \frac{W_f - W_i}{Wi} \times 100 \quad \text{[Eqn.2]}$$

The test was conducted in five replications and the average value was computed.

Thickness Swelling

In order to determine the percentage of thickness swelling, a similar testing parameter was used, as mentioned in water absorption. The samples were measured before (Ti) and after (Tf) the immersion using a digital vernier (Model: Mitutoyo) with 0.01 accuracy. The thickness swelling ratio of the laminates was calculated using the following equation:

$$\text{Thickness swelling (\%)} = \frac{T_f - T_i}{Ti} \times 100 \quad \text{[Eqn.3]}$$

The test was conducted in five replications and the average value was computed.

Water Solubility

Water solubility (WS) of the thermoplastic SPS blends was determined according to the method by Kanmani and Rhim (2014, pp. 708-716), with a slight modification. For this, a piece of sample (10 x 10 x 3 mm) was cut and dried at 105°C ± 2 for 24 h. The initial weight of samples (W_o) was measured before immersing into 30 mL of distilled water with a gentle stirring. After 8 h of immersion, the remaining piece of sample, taken from the beaker and filter paper, was used to remove the remaining water on the surface. Then, the film was dried again at 105°C ± 2 for 24 h to determine the final weight (W_f). The WS of the sample was calculated, as follows:

$$\text{Water solubility (\%)} = \frac{W_o - W_f}{Wo} \times 100 \quad \text{[Eqn.4]}$$

The test was conducted in five replications and the average value was computed.

RESULTS AND DISCUSSION

Thermoplastic SPS blends were been prepared by using different agar contents (0 to 40wt%) in order to investigate the effects of the agar content at proportionally increasing amount while maintaining SPS as the based material.

Figure 1 shows thermoplastic SPS blends prepared via melt mixing and hot pressing. Through the naked eyes, this polymer blends formed homogenous surface and there is no apparent phase seggregation observed, suggesting that SPS, agar, and glycerol had good miscibility via melt mixing process.

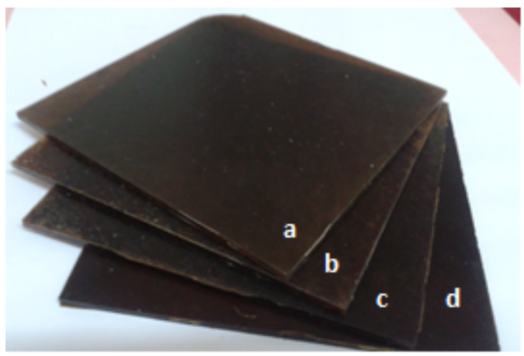

Figure 1. Thermoplastic SPS blends with agar (a) 10wt% (b) 20wt% (c) 30wt% (d) 40wt%

Density

Density of material is an important characteristic that should be taken into account during material selection process. This is because density might affect the performance of the end-product in various forms such as weight, manufacturing and handling processes, ease of use, transportation cost, as well as energy consumption (Al-Oqla & Sapuan, 2014, pp. 347-354). Hence, it is vital to investigate the effects of agar on the density of thermoplastic SPS to study the potential of this biopolymer as an alternative material to the existing non-biodegradable polymer.

The average densities of native SPS and agar powder obtained by helium pycnometer are 1.4854 ± 0.001 g/cm^3 and 1.4817 ± 0.004 g/cm^3, respectively. The density value obtained for SPS in this study is lower than that of potato (1.55 g/cm^3) and maize (1.5 g/cm^3) but slightly higher than tapioca starch (1.466 g/cm^3) (Alebiowu & Osinoiki, 2010, pp. 341-352). This finding shows that this alternative starch has comparable properties to the established starch in terms of the physical properties.

Figure 2 shows the density of thermoplastic SPS blends with agar. In general, there is no obvious trend observed on the variation of density with increasing amount of agar for the blends. This might be attributed to similar density of native SPS and agar, which led to a flat trend of density value for this biopolymer. This finding shows that agar incorporation does not affect the density value of this biopolymer. The density value recorded for thermoplastic SPS without the presence of agar (1.392 g/cm^3) is in consistent with the previous finding (1.400

g/cm^3) (Sahari et al., 2012). This value is comparable to conventional polymer such as epoxy (1.1 - 1.4 g/cm^3), polyester (1.2 - 1.5 g.cm^3) and vinyl ester (1.1 - 1.4 g/cm^3), which suggests that this biopolymer has a very promising property as a substitute material in plastic industry (Gao & Zhao, 2015, pp. 176-182).

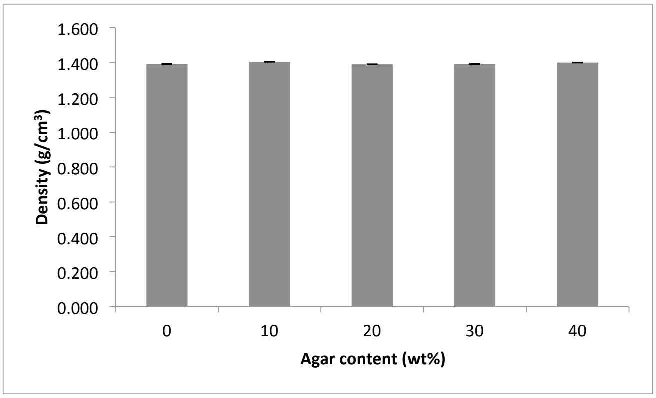

Figure 2. Density of Thermoplastic SPS blends

Moisture Content

Moisture content of material is an important criterion that can affect the dimensional stability of the end-product. A previous study has shown that moisture content has significant effects on water absorption and thickness swelling behaviour of material, whereby higher moisture content led to higher water absorption capacity and thickness swelling as well (Sahari et al., 2012, pp. 254-259). Figure 3 shows the moisture content of thermoplastic SPS blends. In general, incorporation of agar (0 to 40 wt%) onto thermoplastic SPS shows a slight increasing trend on its moisture content from 5.8 to 6.51 wt%. This finding might be attributed to a more hydrophilic behaviour of agar as compared to starch. The value reported for thermoplastic SPS in this finding is slightly lower than that of the previous study (11 to 13 wt%), which suggests that different preparation method and environment condition might affect the moisture content of thermoplastic starch (Sahari et al., 2012, pp. 254-259). Nevertheless, increment in the moisture content of thermoplastic SPS blend is not significant as compared to the amount of agar incorporated into it. This finding shows that this polysachharide indicates a relatively good compatibility since there was no sudden change in the trend as the amount of agar increased from 0 to 40 wt%. Moreover, a slight increment in moisture content shows that incorporation of agar gives a relatively minimum effect to the moisture content of thermoplastic SPS.

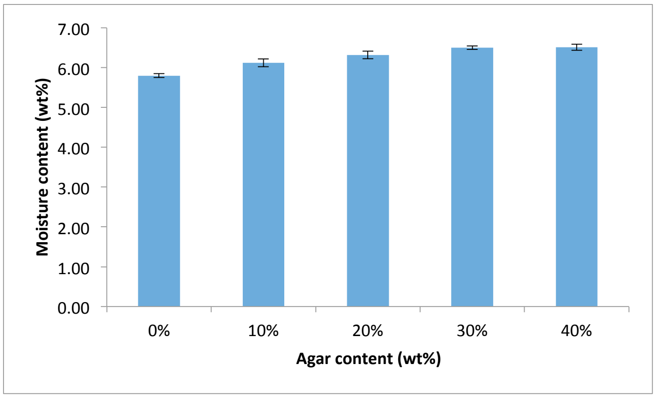

Figure 3. Moisture content of thermoplastic SPS blends

Water Absorption

Starch and agar are a form of polysachharide which is known to be very sensitive to moisture; thus, it is vital to investigate the water absorption capacity of the combination of these two materials. Starch consists of amylose and amylopectin whereas agar consists of agarose and agaropectin, which is hydrophilic in nature due to the formation of bond between hydroxyl group and oxygen bond with water (Lomelí et al., 2011, pp. 1712-1722; Shamsuri et al., 2014, pp. 440-453). This is one of the main reasons for the hydrophilic behaviour of thermoplastic starch and agar.

Figure 4 shows the water absorption capacity of thermoplastic SPS blends with agar. It can be seen that after 0.5h, thermoplastic SPS showed 15% water uptake, while the blends of SPS with 40% agar showed a slight increment to 26%. The effect of incorporating agar into thermoplastic SPS on water uptake was more evident after 2h and 24h, respectively. Water absorption capacity recorded for the thermoplastic SPS in this study is lower than that reported for thermoplastic waxy rice starch (Prachayawarakorn et al., 2011, pp. 88-95). Both thermoplastic SPS and blends presented slight differences in water uptake after 0.5h; however, after 24h, the blends absorbed much more water than the matrix, and as the agar content increased, the water uptake increased as well. This might be attributed to more hydophilic behaviour of agar compared to starch. Agar was sulfated polysaccharide and the presence of charged groups resulted in more extended chains with a higher hydrophilicity as compared to other polysachharide (Phan, Debeaufort, & Luu, 2005, pp. 973-981; Wu et al., 2009, pp. 299-304). Highest moisture content obtained by 40% agar also showed that moisture content affects the water absorption behaviour of thermoplastic SPS blends. This finding is in agreement with a previous study on characterisation thermoplastic starch from sugar palm (Sahari et al., 2012, pp. 254-259).

Nevertheless, high water absorption capacity shown by thermoplastic SPS blends might be attributed to the change in the structure of starch and agar following the gelatinisation process during melt mixing which broke down the intramolecular bonds of their molecules in the presence of heat and plasticiser allowing more hydrogen bonding sites to engage with water. Moreover, a previous study has shown that the presence of plasticiser also increased the affinity of thermoplastic starch to moisture (Mathew & Dufresne, 2002, pp. 609-617). Glycerol is a hydrophilic molecule which increases free volume and chain movements that reduce rigidity and heightens the molecular mobility of films (Maran et al., 2013, pp. 1335-1347; Wu et al., 2009, pp. 299-304). This facilitates the diffusion of water into the laminates leading to higher water absorption capacity.

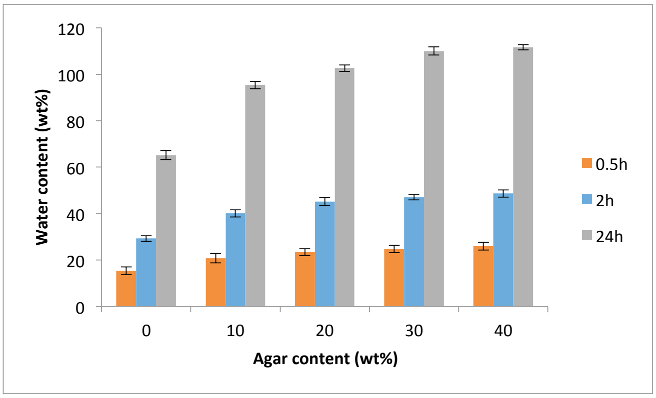

Figure 4. Water absorption capacity of thermoplastic SPS blends

Thickness Swelling

The dimensional stability of a material is an important property that affects the final performance of a product. The swelling behaviour of thermoplastic SPS blends was investigated using the swelling ratio described in Section 2.6 in order to investigate the effects of agar on the dimensional stability of this blend.

Figure 5 shows the swelling ratio percentage of thermoplastic SPS with various agar contents immersed in water at 23oC. In general, the thickness of the thermoplastic SPS and its blends increased gradually after immersing in water for 0.5, 2 and 24 h, respectively. This shows that the thickness of these new materials was affected by the immersion time, and the finding is in agreement with that of the previous studies (e.g., Ashori & Sheshmani, 2010, pp. 4717-4720; Deng & Catchmark, 2014, pp. 864-869; Talavera et al., 2007, pp. 1-7). This might be attributed to the fact that longer immersion time allows more water molecules to engage with hydrogen bonding sites of thermoplastic SPS blends which facilitated swelling. A similar increasing trend was observed for water absorption, suggesting that thickness swelling is dependent on water absorption behaviour of material (Lomelí et al., 2011, pp. 1712-1722). A similar finding has been reported for synthetic polymer as well as biopolymer from starch (Adhikary et al., 2008, pp. 190-198; Sahari et al., 2012, pp. 254-259).

It can also be seen that with the incorporation of agar, the swelling ratio increased as well. The matrix showed the lowest swelling while the blend with agar (40 wt%) showed the highest ratio. This might be attributed to the fact that agar has higher water absorption capacity than starch which leads to higher swelling ratio of this blend. Nevertheless, the increment in swelling ratio was insignificant with the addition of agar, whereby for 0.5 h immersion and the addition of 40% agar, the swelling ratio for thermoplastic SPS was increased by only 5%. As the immersion time increased to 24 h, the increment percentage dropped to only 4%, suggesting that incorporation of agar gives minor changes to the thickness swelling behaviour of thermoplastic SPS. Meanwhile, the thickness swelling ratio for the thermoplastic SPS measured in this study is slightly lower than the previously reported for cassava starch, indicating comparable properties of SPS among other starch (Lomelí et al., 2011, pp. 1712-1722).

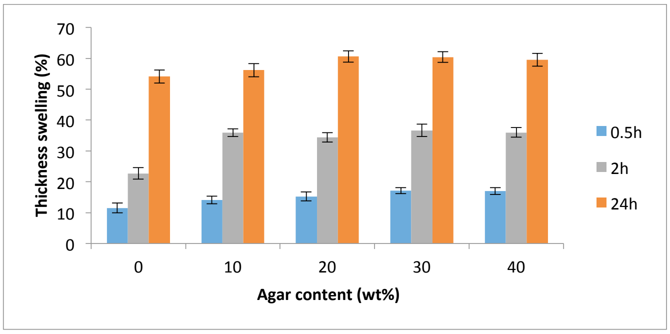

Figure 5. Thickness swelling capacity of thermoplastic SPS blends

Water Solubility

It is understood that water solubility is the measure of water resistance of a material. On the other hand, water solubility also shows degradation behaviour of material when disposed in water. Figure 6 shows the solubility of thermoplastic SPS blends with different amounts of agar. Thermoplastic SPS (0 wt% agar) prepared in this study showed lower solubility than rice starch (44.4%) but a similar solubility with cassava starch prepared in the previous studies (Arismendi et al., 2013, pp. 290-296; Belibi et al., 2014, pp. 220-226; Brindle & Krochta, 2008). This finding suggests that SPS has comparable properties to the commercial starch available in the market. It was observed that the solubility of thermoplastic SPS was slightly increased from 22.76 to 28.9% after the addition of agar (0 to 40 wt%). This result revealed that agar has the ability to increase the solubility of thermoplastic SPS. Nevertheless, the increment was very minor when compared to the amount of agar added into the blends. This finding also shows that SPS has slightly better water resistance compared to agar. This was also justified by the water absorption behaviour discussed in Section 3.3.

A previous study measured the solubility of agar film blended with carrageenan also reported increased solubility of materials as carrageenan component was added (Rhim, 2012, pp. 66-73). This phenomenon was attributed to more hydrophilic behaviour of carrageenan component as compared to agar, which is in good agreement with this study. In another point of view, this finding shows that agar has slightly improved degradability of thermoplastic SPS in water, which is favourable for sustainable waste disposal.

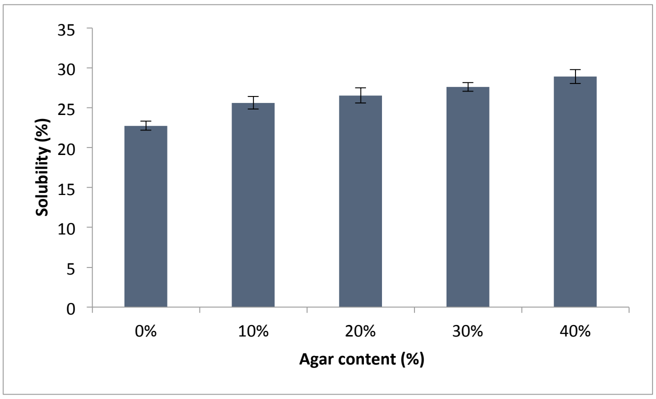

Figure 6. Solubility of thermoplastic SPS blends

CONCLUSION

Novel thermoplastic derived from SPS and agar was successfully prepared via melt mixing and hot press moulding. This biopolymer shows variation in its physical properties with incorporation of agar. These differences could be attributed to the different properties of these two polysachharides. It was found that moisture content, water absorption, solubility and thickness swelling increased with incorporation of agar. Thermoplastic SPS showed the lowest values for these properties whereas the blend with 40 wt% agar showed the highest value, indicating increasing trend of hydrophilic behaviour with the incorporation of agar. In addition, the density of thermoplastic SPS was observed to remain unchanged with the presence of agar.

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