

Characteristics of thermoplastic sugar palm Starch/Agar blend: Thermal, tensile, and physical properties



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ABSTRACT

The aim of this work is to study the behavior of biodegradable sugar palm starch (SPS) based thermoplastic containing agar in the range of 10–40 wt%. The thermoplastics were melt-mixed and then hot pressed at 140 °C for 10 min. SEM investigation showed good miscibility between SPS and agar. FT-IR analysis confirmed that SPS and agar were compatible and inter-molecular hydrogen bonds existed between them. Incorporation of agar increased the thermoplastic starch tensile properties (Young's modulus and tensile strength). The thermal stability and moisture uptake increased with increasing agar content. The present work shows that starch-based thermoplastics with 30 wt% agar content have the highest tensile strength. Higher content of agar (40 wt%) resulted to more rough cleavage fracture and slight decrease in the tensile strength. In conclusion, the addition of agar improved the thermal and tensile properties of thermoplastic SPS which widened the potential application of this eco-friendly material. The most promising applications for this eco-friendly material are short-life products such as packaging, container, tray, etc.

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1. Introduction

Agriculture-based materials have gained increasing amount of attention over the last two decades due to environmental concerns and realization that petroleum resources are finite [1,2]. These biopolymers are very promising for short life applications such as disposable packaging, tray, container, etc. Renewable resources are normally referring to plant based resources such as starch, agar, and cellulose. In addition, synthetic polymer from natural monomers and microbial fermentation are also considered as renewable materials such as polylactide acid (PLA) and polyhydroxybutyrate (PHB). Among these biopolymers, starch is one of the most promising materials due to availability, economic, abundant, biodegradable, and renewable [3,4]. In general, starch is a heterogeneous material containing two microstructures which is amylose and amylopectin. Amylose is a linear structure of α -1,4 linked glucose units; and

amylopectin is a highly branched structure of short α -1,4 chains linked by α -1,6 bonds. The linear structure of amylose makes it closely resemble the behavior of conventional synthetic polymers [5]. In the presence of plasticizer and heat, starch undergoes spontaneous destructurization which results to formation of homogenous melt known as thermoplastic starch (TPS) [6]. Despite the promising environmental-friendly characteristic of TPS, it possess some limitations which limits the application i.e. mechanical properties. Blending TPS with other material is one of the most effective approaches since it is simple, rapid and cost effective [7]. Previous study shows that blending TPS with synthetic polymer i.e. poly (butylene succinate) (PBS) has improved the physical and mechanical properties of TPS [7,8]. The most common type of starch used for developing biopolymer includes cassava, corn, potato, sago, and rice [9–13].

Sugar palm (also known as *Arenga pinnata*) is a natural forest species that originates from the Palmae family. It is known for the production of *neera* sugar and recently for production of bioethanol [14]. It is reported that sugar palm tree is able to produce 50–100 kg of starch [15]. Sugar palm starch has comparable

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properties in terms of the amylose content (37%) which is higher than cassava (17%), potato (25%) and corn (28%) [15]. Previous study reported that degree of polymerization efficiency was dependent on amylose content of the starch [5]. Recent study developed thermoplastic starch from sugar palm and characterized the physical, thermal, and mechanical properties [16].

Agar is a polysaccharide with sulfate functional groups which is obtained from marine algae of the class Rhodophyceae such as *Gelidium* sp. and *Gracilaria* sp. [17,18]. It consists of two main components namely agarose and agaropectin. Agarose is a linear polymer based on the 3,6-anhydro- α -L-galactopyranose unit. Agaropectin is a heterogeneous mixture of smaller molecules which have similar structures with agarose but slightly branched and sulfated. Agar is widely used for gelling and thickening agent in food and pharmaceutical industry. This polysaccharide has received much attention in biopolymer development due to its ability to form film that possess good characteristics as alternative packaging material [19–21]. Previous study shows that agar biopolymer has relatively good water resistance as compared to other seaweed polysaccharide such as carrageenan [22]. Biodegradable characteristics of agar film was investigated in tropical climate and the results show that agar has good biodegradability and suits the criteria for environmental friendly material [23]. In addition, biopolymer derived from agar was reported to possess relatively higher tensile strength than starch based biopolymer [24]. However, all of these studies were focused only on development of thin films that prepared via solution casting which have some limitations for its potential application. To the best of our knowledge, there are very few studies that investigated the behavior of agar as blend component in thermoplastic starch [9]. It clear from literature review that no study carried out to modify the properties of thermoplastic SPS with agar. Therefore, the objective of this work is to study the effect of agar on tensile, morphological, thermal, and physical properties of thermoplastic SPS. Different ratios of agar were varied in order to study the properties of different thermoplastic SPS blends. Various techniques were used to characterize the properties of the blends including FT-IR, SEM, DSC, tensile testing, moisture absorption, and thickness swelling.

2. Materials and methodology

2.1. 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 fibre which contains the starch. This woody fibre was soaked in fresh water followed by squeezing in order to dissolve the starch into the water. Water solution that contained starch was filtered in order to separate the fibers from the solution. This solution was then leave for sedimentation of the starch. The supernatant was discarded and the wet starch was kept in an open air for 48 h 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.

2.2. Sample preparation

Thermoplastic SPS was prepared by addition of glycerol (30 wt% starch-based) followed by pre-mixing using high speed mixer at 3000 rpm for 5 min. After this preliminary step, the resulting blend was melt-mixed using Brabender Plastograph at 140 °C 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 10 t. The same processes were also used for the preparation of different thermoplastic SPS blends. The property modification of different thermoplastic SPS blends was carried out by using different ratios of agar (10, 20, 30, 40 wt%). All samples were pre-conditioned at 53% RH for at least 2 days prior to testing.

2.3. FT-IR analysis

Fourier transform infrared (FT-IR) spectroscopy was used to detect the presence of functional groups existing in thermoplastic SPS blends. Spectra of the material were obtained using an IR spectrometer (Nicolet 6700 AEM). FT-IR spectra of the sample (10 × 10 × 3 mm) was collected in the range of 4000 to 400 cm⁻¹.

2.4. Scanning electron microscope (SEM)

The morphology of tensile fractured surfaces was observed under scanning electron microscope (SEM), model Hitachi S-3400N with acceleration voltage of 10 kV.

2.5. Differential scanning calorimetry (DSC)

For differential scanning calorimetry (DSC) analysis, 5 mg of samples was weighed and placed in an aluminum sample pan which was immediately sealed. An empty sample pan was used as reference. The samples were heated from 35 to 265 °C at a rate of 10 °C/min using DSC equipment (Universal V3-9A TA Instrument, New Castle, PA, USA). 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. Tensile testing

Tensile tests were conducted according to ASTM D-638 at the temperature of 23 ± 1 °C and relative humidity of 50 ± 5%. The tests were carried out on 5 replications using a Universal Testing Machine (INSTRON 5556) with a 5 kN load cell; the crosshead speed was maintained at 5 mm/min.

2.7. Moisture absorption and thickness swelling

Thermoplastic SPS blends was stored in closed humidity chamber at 80 ± 2% relative humidity (RH) and 25 ± 2 °C in order to analyze moisture absorption behavior of the samples. Prior to the moisture absorption measurements, the samples with the dimension of 10 mm × 10 mm × 3 mm was dried at 105 °C ± 2 for 24 h.

The samples were weighed before, W_i and after absorption, W_f for certain period until constant weight is obtained. The moisture absorption of the samples was calculated using the following equation:

$$\text{Moisture absorption (\%)} = \frac{W_f - W_i}{W_i} \times 100 \quad (1)$$

To determine the percentage of thickness swelling, the samples were measured before, T_i and after, T_f storage using a digital vernier (Model: Mitutoyo) having 0.01 accuracy. The thickness swelling ratio of the laminates was calculated using the following equation:

$$\text{Thickness swelling (\%)} = \frac{T_f - T_i}{T_i} \times 100 \quad (2)$$

2.8. Statistical analysis

Statistical analysis of mechanical properties has been carried out by one-way analysis of variance (ANOVA) and the significance

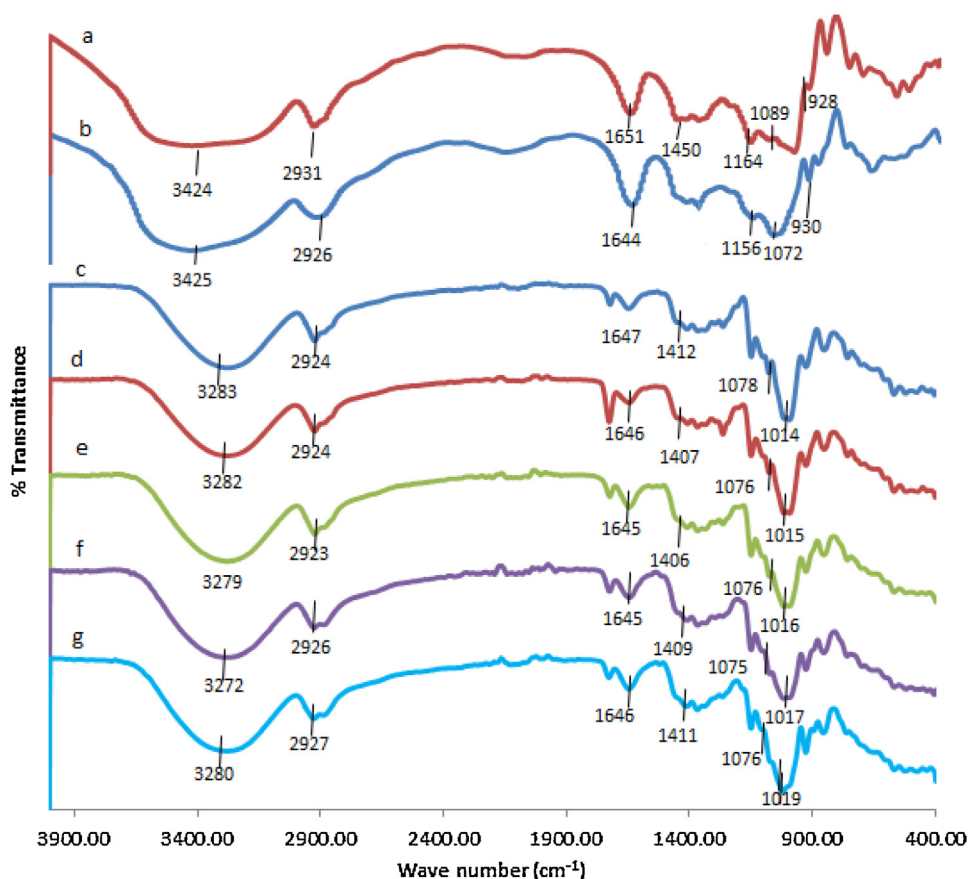


Fig. 1. FT-IR spectra of (a) native SPS and (b) native agar (c) neat SPS matrix (d) 10% agar (e) 20% agar (f) 30% agar (g) 40% agar.

of each mean property value was determined ($p < 0.05$) with the Duncan's multiple range test.

3. Results and discussion

3.1. FT-IR analysis

Fig. 1 shows the FT-IR data for native SPS, agar, and thermoplastic SPS blends respectively. The native SPS spectrum was similar to agar spectrum at the range of 4000 to 2000 cm^{-1} . These two materials had same broad bands from 3100 to 3700 cm^{-1} and this were attributed to hydrogen bonded hydroxyl group (O–H) from the complex vibrational stretching, associated with free, inter and intra molecular bound hydroxyl groups [24]. The bands at approximately 2900 cm^{-1} were characteristic of C–H stretching from CH_2 and/or CH_3 [9]. The peak at approximately 1640 cm^{-1} was attributed to tightly bound water present in the SPS. Meanwhile, the peak at 1644 cm^{-1} for native agar was caused by stretching of the conjugated peptide bond formed by amine (NH) and acetone (CO) groups [24]. The peaks in the range of 1400–1450 cm^{-1} were assigned for O–H bending. In SPS spectrum, three peaks appeared between 928 and 1164 cm^{-1} which were attributed to C–O bond stretching. The peaks at approximately 1089 and 1020 cm^{-1} were characteristic of the anhydro-glucose ring C–O stretch [24,25]. In agar spectrum, the peak at approximately 1070, 1030 and 930 cm^{-1} were assigned to the C–O of 3,6-anhydro-galactose [23].

FT-IR spectra of polymer blends enabled the interaction between the components to be identified were lower wavenumber indicates stronger interaction between the components [24]. The spectrum of thermoplastic SPS shows lower wavenumber of broad band at 3100–3700 cm^{-1} (O–H stretching) and single band

Table 1

Summary of the analysis of variance (ANOVA) of thermoplastic SPS/agar.

Variables	df	Strength	Modulus	Elongation
Mixture	4	0.00*	0.00*	0.00*

Note: *Significantly different at $p \leq 0.05$.

at approximately 1400 cm^{-1} (O–H bending) than native SPS. These peak position shifts indicates distinct interaction of hydrogen bonding between native SPS and glycerol in the thermoplastic. Since agar consists of polysaccharide (agarose and agarpectin) which have quite similar chemical structure with SPS, therefore, addition of agar into thermoplastic SPS does not show any distinct changes in the IR peak positions. However, similar peak position shifts of O–H group (3100–3700; 1400 cm^{-1}) to lower wave number were observed when agar was incorporated which assigned to increase of intermolecular hydrogen bonding. This phenomenon shows that agar and SPS were compatible and interaction exists between their chain upon blending.

3.2. Tensile properties

The change in composition of thermoplastic SPS initiated the change in mechanical properties of thermoplastic SPS as well. Table 1 shows the analysis of variance (ANOVA) of the mechanical properties. Since the P-value is less than 0.05, there is a statistically significant difference between the mean tensile strength, modulus, and elongation from one level of polymer blend to another. Effect of agar addition on tensile strength, modulus, and elongation were demonstrated in Figs. 2–4 respectively. The tensile strength of thermoplastic SPS blends showed significant

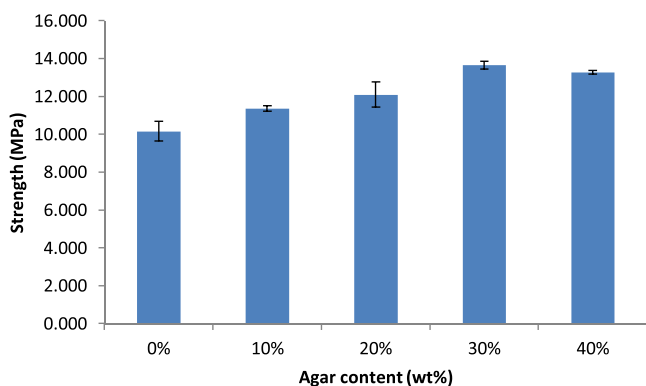


Fig. 2. Tensile strength of thermoplastic SPS/agar.

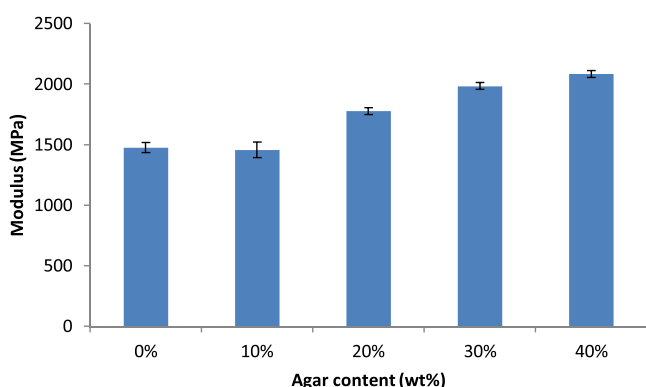


Fig. 3. Tensile modulus of thermoplastic SPS/agar.

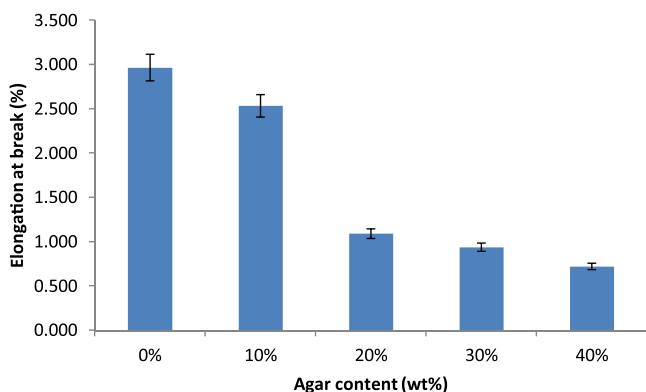


Fig. 4. Elongation at break for thermoplastic SPS/agar.

improvement ($p < 0.05$) with increasing agar content, while the elongation fall from 3.54% to 1.11% ($p < 0.05$). Addition of agar was seen to significantly ($p < 0.05$) enhanced the Young's modulus of thermoplastic SPS as well. When different ratios of agar were considered, it was noticed that the increasing content of agar tended to cause higher strength and Young's modulus of thermoplastic SPS. Highest strength was obtained from the thermoplastic SPS blends added by 30 wt% agar. At higher content of agar (40 wt%), the tensile strength was slightly decreased, and Young's modulus was slightly increase. SEM image showed that more rough cleavage fracture was observed at higher agar content compared to samples with low agar content. Nevertheless, the mechanical properties shown by thermoplastic SPS prepared via melt mixing in this study shows improved strength and modulus as compared to previous study that does not involved melt mixing during the preparation [16]. This might be attributed to better mixing and dispersion of plasti-

cizer and starch in melt form as compared to mechanical stirring alone. In addition, higher tensile strength and modulus of thermoplastic SPS in this study as compared to other published work on TPS might be associated to several reasons. Firstly, the amylose content of SPS is 37% which is higher than cassava (17%), potato (20–25%), corn (28%), rice (20%), and waxy rice (5%) [9,15]. It is known that higher amylose content led to higher degree of polymerization and previous study (comparing rice starch and waxy rice starch) reported that higher amylose content in rice starch led to higher tensile strength, lower elongation at break and better toughness of TPS [26,27]. Secondly, the amount of plasticizer also affects the properties of TPS, our TPS was develop by using 30 wt% of glycerol on starch basis (30:100 glycerol-starch) which produced higher rigidity and strength together with low ductility as compared to other study that using higher amount of plasticizer: starch ratio i.e. 50:50 [9], 65:35 [28], and 70:30 [29]. Higher amount of plasticizer is known to lower the strength and rigidity together with higher elongation attributed to the plasticizing effect that diminishes the strong intra-molecular attraction between the starch chains [30]. Different processing technique and parameters is another important factor that might affect the variation of mechanical properties obtained from TPS. High tensile strength of 8.8 ± 0.7 MPa [31] and 12.5 MPa [32] was also reported for characterization of TPS in previous studies.

A considerable increase of tensile strength with the increase of agar indicated that this polysaccharide has a great impact and able to form bonding with SPS. This might be attributed to the good miscibility caused by the similarity in chemical structure and phase compatibility of agar and starch [9]. This was justified by smooth and homogenous surface of fractured samples from SEM images with no phase segregation observed in SEM. In addition, FT-IR analysis also showed that addition of agar has considerably increase the hydrogen bonding of the blends indicating formation of bonding occurred between agar and starch. Moreover, agar has better mechanical properties due to more entangled network structure of agar compared to starch which explained the improved strength in their blends [24]. Previous study of thermoplastic waxy rice starch also reported slight increment in tensile strength with incorporation of agar [9]. However, this study only focused on the effect of agar at very low concentration (10 wt%) whereas behavior of agar at higher concentration were not reported.

3.3. SEM

Surface morphology of tensile fractured surface was investigated under scanning electron microscopy. The scanning electron microscopy allowed an overview of the structure of the thermoplastics and the fracture behavior as well. It should be noted that in thermoplastic starch, the starch granules should broke down and formed a continuous phase with glycerol. Fig. 5 shows that thermoplastic SPS formed a homogenous surface with no visible air pockets. This result indicated that prior melt mixing of starch and glycerol has improved the plasticization of starch. The circular phase observed in the micrograph was associated to the residue of starch granules after gelatinization [33]. Similar structure was observed in TPS from cassava [28,33]. After incorporation of agar into thermoplastic SPS, it can be seen that the blends showed a smooth surface without the presence of cluster which shows good miscibility and interaction between SPS and agar. In addition, there is no apparent phase of sugar palm starch and agar were observed from the micrograph indicating good miscibility of these two components. This finding is in good agreement with SEM micrograph of biopolymer derived from potato starch and agar [24]. As the content of agar increases from 10 to 40 wt%, it was observed that the fracture surface started to show cleavage structure which might be attributed to polymer-polymer bonding that resists deformation

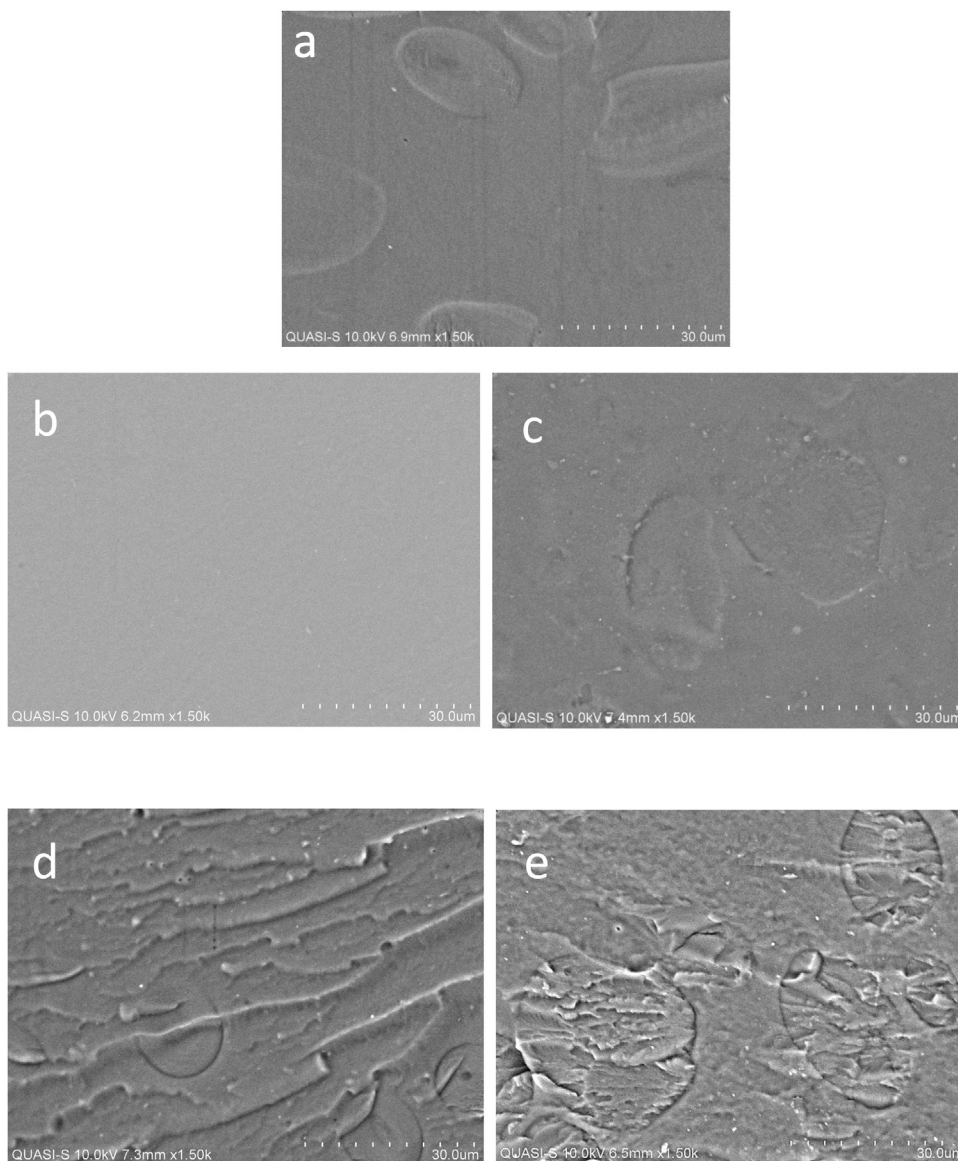


Fig. 5. SEM micrograph of fracture surface of thermoplastic SPS blended with different ratio of agar (a) 0 wt% (b) 10 wt% (c) 20 wt% (d) 30 wt% (e) 40 wt%.

under loading before fractured. In addition, more rough structure was evidence at higher agar content which can be attributed to higher filler content in TPS matrix.

3.4. DSC analysis

The glass transition temperature, T_g is where a material changes from glassy to rubbery state at a given heating rate. This is a very important parameter that determines the thermal, mechanical and dimensional stability of a material when subjected to high temperature. On the other hand, melting point, T_m of a polymer is essential for the processability of the material as well. **Table 2** shows the T_g and T_m value for native agar, SPS, and their blends respectively. For native SPS the T_g reaches 140.7 °C which is lower than reported for rice starch (235 °C) [34]. For thermoplastic SPS, the T_g value decreased to 137.9 °C with addition of glycerol as plasticizer. This finding is in good agreement with analysis of starch film prepared with different plasticizer amount [30]. Decreased in T_g value might be attributed to the role of plasticizer that interrupt the intermolecular forces between polymer chain which consequently reduced overall cohesion and reduction of T_g [16]. For thermoplastic SPS

Table 2

Glass transition, T_g and melting temperature, T_m of thermoplastic SPS/agar.

Samples	T_g (°C)	T_m (°C)
0% Agar	137.9	172.2
10% Agar	151.1	178.9
20% Agar	152.3	192.1
30% Agar	156.5	219.8
40% Agar	154.5	218.7
Native SPS	140.7	171.3
Native Agar	152.0	186.6

blends, it can be seen that incorporation of agar leading to increase in T_g value which can be associated with higher T_g value of native agar compared to SPS in this study. This was further justified by increased in intermolecular hydrogen bonding between SPS and agar as discussed in Section 3.2 that leading to decreased mobility of matrix chain, thus, increased the T_g value. In addition, increased in T_g value of the blends also indicates good miscibility between agar and SPS. Melting temperature of thermoplastic SPS blends show similar increasing trend with incorporation of agar, this might be attributed to similar discussions of T_g behavior. Again, higher

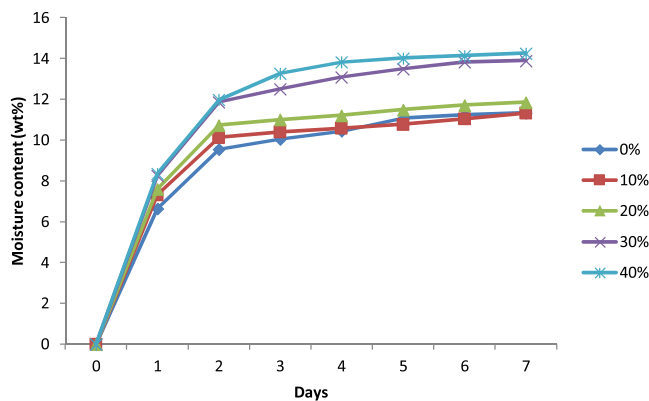


Fig. 6. Moisture absorption behavior of thermoplastic SPS with different amount of agar.

melting temperature of thermoplastic SPS blends as compared to native agar and SPS might be attributed to stronger interaction of molecular hydrogen bonding between agar, SPS, and glycerol as compared to the bonding forces in their native form as shown in FT-IR analysis.

3.5. Moisture absorption and thickness swelling

According to Sousa et al. [35], water absorption activity is based on thermodynamic principles that related to differences in the chemical potential of water molecules retained at the monolayer and upper layers of material. Thermoplastic starch consists of amylose and amylopectin whereas agar consists of agarose and agarpectin which is hydrophilic in nature due to formation of bond between the hydroxyl groups and oxygen bonds with water [36]. Though previous study has shown that agar biopolymer has better mechanical strength than starch, however, incorporation of agar into potato starch film prepared via solution casting is reported to caused increased in the moisture sensitivity [24]. Hence, moisture absorption behavior of thermoplastic SPS blends prepared via melt mixing and hot pressing were analyzed in order to study the effect of agar on moisture sensitivity of thermoplastic SPS.

Moisture sensitivity of thermoplastic SPS blends was evaluated at 25 °C by quantifying the equilibrium amount of water retained by the samples. Moisture absorption behavior of thermoplastic SPS blends was shown in Fig. 6. It was observed that moisture absorption was more rapid at the initial stages of storage and lower amounts of water were absorbed as time increased. This results is in agreement with previous study on water absorption behavior of starch based material [16,37,38]. In general, moisture absorption started to slow down after 3 days of storage and reached stability after 5–6 days. This finding is in good agreement with moisture absorption behavior of thermoplastic cassava starch which reported moisture stability after 5 days of absorption [39].

In general, incorporation of agar was observed to increased moisture absorption of thermoplastic SPS. This might be attributed to the fact that agar was sulfated polysaccharide and the presence of charged groups resulted in more extended chains with a higher hydrophilicity as compared to other polysaccharide such as starch [20,24]. However, it was noticed that the effect of agar (30 wt%) on moisture absorption of thermoplastic SPS after stability was less significant (3% increment) as compared on agar/potato starch film prepared in previous study (8% increment) [24]. This might be attributed to different processing condition under hot pressing method in this study compared to solution casting which resulted to lower moisture content and moisture absorption behavior as well.

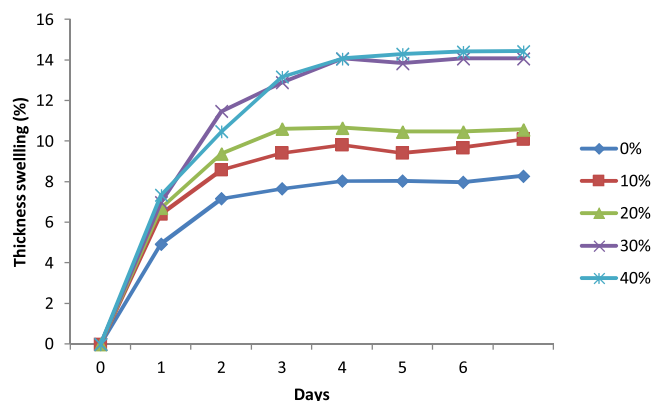


Fig. 7. Thickness swelling behavior of thermoplastic SPS blends with different amount of agar.

It is known that thickness swelling of material stored in humidity chamber is accompanied by the moisture absorption behavior of the respective material. The swelling behavior of thermoplastic SPS blends was investigated using the swelling ratio order to investigate the effect of agar on the dimensional stability of thermoplastic SPS. Fig. 7 shows that swelling behavior of thermoplastic SPS blends indicated similar trend with the moisture absorption behavior. This finding is in agreement with previous studies [36,40]. This might be attributed to accompany volume expansion from water absorption of the samples. Again, incorporation of agar into thermoplastic SPS leads to increase in swelling capacity which can be attributed to higher moisture absorption capacity of agar as discussed in this section earlier. Nevertheless, the increment in swelling capacity was insignificant (8%) compared to the amount of agar incorporated (40 wt%). This finding shows that incorporation of agar caused relatively insignificant effect on moisture sensitivity and dimensional stability of thermoplastic SPS.

4. Conclusions

Novel biopolymer derived from sugar palm starch and agar were successfully prepared via melt mixing and hot pressing in this study. The results shows that sugar palm starch and agar were compatible and the addition of agar improved the tensile properties (tensile strength and Young's modulus) and thermal properties of thermoplastic sugar palm starch in terms of glass transition temperature and melting temperature. Thermoplastic SPS blends with 30 wt% agar shows the highest tensile strength. Moisture sensitivities of thermoplastic SPS were slightly increased with addition of agar indicated by moisture absorption and thickness swelling behavior.

Conflicts of interest

The authors have declared no conflicts of interest.

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