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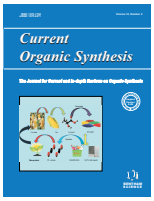
REVIEW ARTICLE



Effect of Agar on Flexural, Impact, and Thermogravimetric Properties of Thermoplastic Sugar Palm Starch

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Abstract: Development of a new polymer from renewable resources is getting serious attention from researchers due to the environmental issue caused by petroleum based polymer. The aim of this paper is to study the behavior of sugar palm starch (SPS) based thermoplastic containing agar in the range from 10 to 40 wt%. The thermoplastics were melt-mixed and then hot pressed at 140 °C for 10 minutes followed by flexural, impact and thermogravimetric analysis. Thermogravimetric analysis (TGA) showed that incorporation of agar increased the char residue content from 9.17 to 10.87 wt%. For mechanical properties, the addition of agar improved the flexural strength and modulus of SPS/agar blends. The impact strength of thermoplastic SPS was increased respectively with the addition of agar. However, at higher agar content (30 wt% to 40 wt%), the impact strength was decreased which attributed to high rigidity of the material at this ratio. In conclusion, incorporation of agar has improved the flexural, impact and thermal properties of thermoplastic SPS which widened the potential application of this biopolymer in future.

Keywords: Biopolymer, thermoplastic, agar, starch, sugar palm, flexural, impact, thermal.

1. INTRODUCTION

Environmental friendly polymer has gained increasing amount of attention due to waste management concerns of non-degradable petroleum based polymer. This material, often referred to as a biopolymer, is made from renewable resources such as starch, chitosan, carrageenan, agar, and cellulose or synthetic polymer from natural monomer and microbial fermentation such as polylactide acid (PLA) and polyhydroxybutyrate (PHB). Various studies were conducted on these biopolymers in order to analyze their potential as alternative material for short life application such as packaging material [1, 2]. Starch is one of the most promising materials for biopolymer development since it is renewable, widely available, has low cost and is totally biodegradable without toxic residue [3]. Starch is stored in carbohydrate in plants such as cassava, corn, wheat, rice, potatoes and sugar palm [4, 5]. Starch is composed of two polymers namely 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. Amylose molecules consist of 200-20,000 glucose units which form a helix as a result of the bond angles between the glucose units. Amylopectin contains short side chains of 30 glucose units attached to every 20–30 glucose units along the chain. Amylopectin molecules may contain up to two million glucose units [6, 7]. The linear structure of amylose makes it closely resemble the behavior of conventional synthetic polymers. Meanwhile, branched structure of amylopectin reduces the mobility of the polymer chains and interferes with any tendency for them to become oriented closely enough to permit significant levels of hydrogen bonding [8]. Even though biopolymer derived from starch has a lot of advantages in terms of environmental concern, however, it possesses certain limitations such as poor mechanical properties compared to synthetic polymers. Hence, various works were performed to improve the mechanical properties of starch based polymers. Previous study reported modification of thermoplastic cassava starch by blending with low-density polyethylene (LDPE), carrageenan and cotton fiber, which resulted in improved mechanical strength and modulus of the composites [9].

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 the production of bioethanol [5]. It is reported that sugar palm tree is able to produce 50 to 100 kg of starch [10]. Sugar palm starch (SPS) has comparable properties in terms of the amylose content (37%) which is higher than cassava (17%), potato (25%) and corn (28%) [10]. Previous study reported that the degree of polymerization efficiency was dependent on amylose content of the starch [8]. Fig. **1** shows SPS after extraction extraction process.

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Fig. (1). Sugar palm starch.

Fig. (2). Agar powder.

Agar is a polysachharide that consists of two main components namely agarose and agaropectin. This polysaccharide is obtained from marine algae of the class Rhodophyceae such as such as Gelidium sp. and Gracilaria sp. [11, 12]. Agarose is a linear polymer based on the 3, 6-anhydro-α-L-galactopyranose unit whereas agaropectin has similar structure with agarose but is slightly branched and sulfated. Agar is known for its gelling and thickening properties in the food and pharmaceutical industry. Apart from that, agar has received much attention among researchers due to its ability to form biopolymer. Fig. **2** shows agar powder in its native form. Previous study showed that agar film has promising properties as alternative packaging material [13-15]. Agar also shows environmental friendly characteristics due to its biodegradable properties as mentioned in the previous study [16]. In terms of mechanical properties, previous study showed that agar film possessed higher strength than starch film [17].

Most of the studies on agar biopolymer were focused only on thin film development *via* solution casting. To the best of our knowledge, there are very few studies that investigated the behavior of agar when processed under high temperature in order to produce single laminates or polymer blends. In our earlier work, the characteristics of thermoplastic SPS incorporated with agar *via* melt-mixing and hot pressing showed improvement in the properties of the prepared materials [18]. However, it is clear from the literature that there are no studies on the thermogravimetric, flexural and impact behavior of thermoplastic SPS/agar blend. Therefore, the objective of this work is to investigate the flexural, impact and thermogravimetric properties of thermoplastic SPS when incoporated with agar. 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 flexural, impact and thermogravimetric analysis (TGA).

2. MATERIALS AND METHODS

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 fibres which contain starch. These woody fibres were soaked in fresh water followed by squeezing, in order to dissolve the starch into water. Water solution that contained starch was filtered in order to separate the fibers 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 ^{o}C for 24h. Agar powder was procured from R&M Chemicals and glycerol was purchased from Sciencechem.

2.2. Sample Preparation

Preparation of thermoplastic SPS was conducted according to the previous work [18]. Thermoplastic SPS was prepared by addition of glycerol (30wt% 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 ^{o}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 ^{o}C under the load of 10 tonnes. 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%).

2.3. Flexural Tests

Flexural tests were conducted according to ASTM D-790 at the temperature of 23 ± 1 ^{o}C and relative humidity of 50 ± 5%. The samples were prepared with dimensions of 130 mm (L) x 13 mm (W) x 3mm (T). 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 2 mm/min. All samples were pre-conditioned at 53% RH for 2 days prior to testing.

2.4. Impact Tests

Izod impact tests were conducted according to ASTM D256 at the temperature of 23 ± 1 ^{o}C and relative humidity of 50 ± 5%. The samples were prepared with dimensions of 60 mm (L) x 13 mm (W) x 3mm (T). The tests were performed on 5 replications using a digital INSTRON CEAST 9050 pendulum impact tester. The impact strength was calculated based on the impact energy and cross section area of the specimen (Eq. 1). All samples were pre-conditioned at 53% RH for 2 days prior to testing.

$$\text{Impact strength} = \text{Impact energy (J)} / \text{area (mm}^2\text{)} \qquad \text{Eq. 1}$$

2.5. Thermogravimetric Analysis (TGA)

TGA was used to analyze thermal degradation behavior of material with respect to weight loss due to increase in temperature.

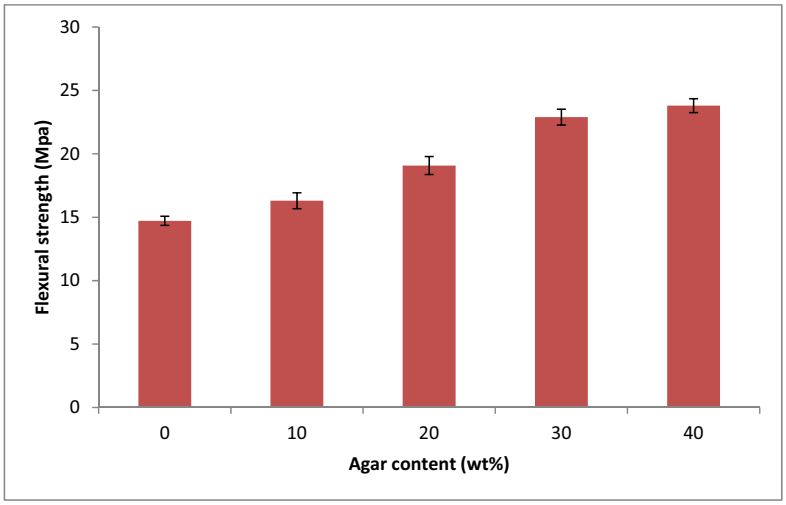

Fig. (3). Flexural strength of thermoplastic SPS blended with agar.

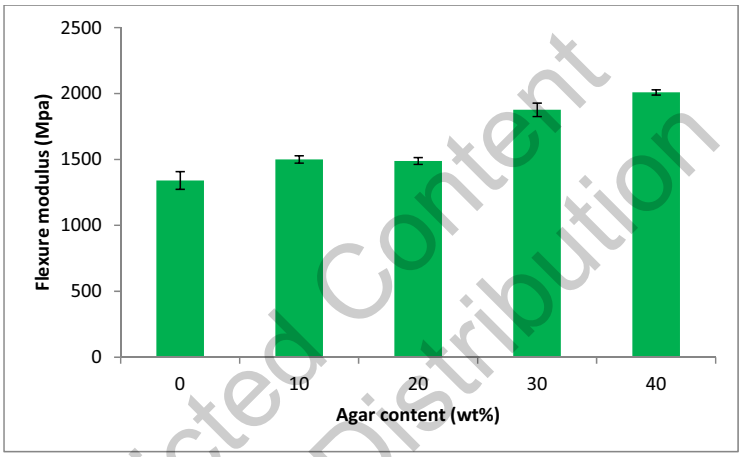

Fig. (4). Flexural modulus of thermoplastic SPS blended with agar.

TGA was performed with a Q series thermal analysis machine from TA Instrument. The analysis was carried out in aluminum pans under a dynamic nitrogen atmosphere in temperature range 25 to 600 °C at a heating rate of 10 °C/min. Samples were pre-conditioned at 53% RH for at least 2 days prior to testing.

2.6. Statistical Analysis

Statistical analysis of the mechanical properties was carried out by one-way analysis of variance (ANOVA) and the significance of each mean property value was determined ($p<0.05$) with the Duncan's multiple range test.

4. RESULTS AND DISCUSSION

4.1. Flexural Tests

Flexural strength is a mechanical parameter for rigid material that represents the ability to resist deformation under bending load. Figs. **3** and **4** show the flexural strength and modulus of thermoplastic SPS blended with different amounts of agar (10 to 40 wt%). Incorporation of agar into thermoplastic SPS was observed to increase the flexural strength by 61.9% ($p<0.05$). The flexural modulus of thermoplastic SPS also showed increasing trend with incorporation of agar where the modulus was improved by 49.8% ($p<0.05$). Increase in flexural strength and modulus of thermoplastic SPS might be attributed to several factors. Firstly, SPS and agar have good miscibility that can be attributed to their identical hydrophilic behavior and quite similar chemical structure of polysachharide. Miscibility of agar and starch was confirmed by a previous researcher who investigated the shifting in glass transition temperature value to intermediate value of individual polymer of starch and agar [19]. Secondly, agar has more entangled network structure which exhibits more resistance to deformation when subjected to stress [17]. Hence, increasing amount of agar in thermoplastic SPS increased the number of entangled network structure in the blends leading to higher strength and modulus of elasticity of their blends. The flexural strength and modulus of thermoplastic SPS prepared in this study show higher values compared to the previous study where the preparation methodology did not include melt mixing process [20]. This might be attributed to better dispersion of glycerol in SPS matrix during melt mixing process than mixing by mechanical stirring alone. In addition, it is well known that mixing of two or more components in melt condition produces better mixing results compared to mixing in their solid state. This finding is in agreement with our previous work which reported improvement in tensile strength and Young's modulus of thermoplastic SPS with incorporation of agar [18].

Statistical analysis of flexural test results was carried out by one way ANOVA and the results are shown in Table **1**. Since the P-value of the test was less than 0.05, hence, there was a statistically significant difference in mean flexural strength and modulus of the thermoplastic blends between the mixtures.

4.2. Impact Tests

Impact strength is the measure of impact resistance of material that indicates the ability to withstand a suddenly applied load. Fig. **5** shows the impact strength of thermoplastic SPS with different contents of agar. It can be seen that incorporation of agar (0 to

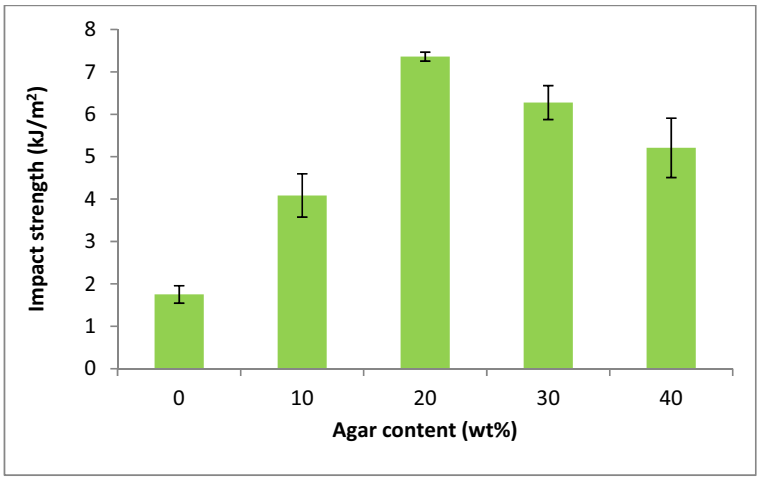

Fig. (5). Impact strength of thermoplastic SPS blended with agar.

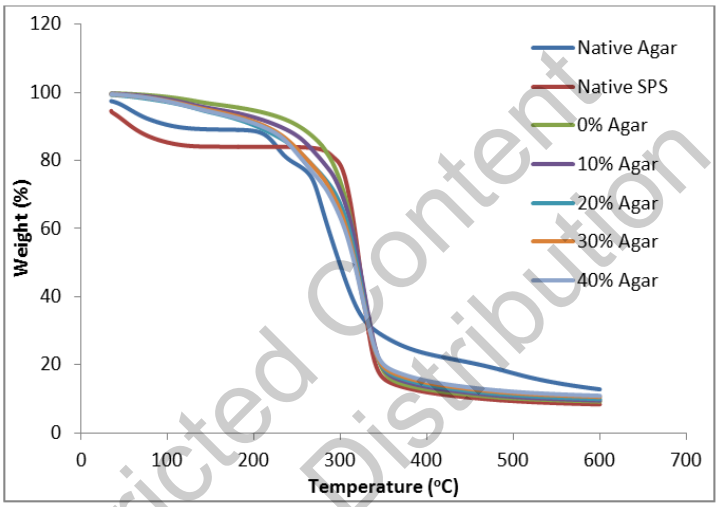

Fig. (6). TGA curve of native agar, native SPS, and thermoplastic SPS blends.

Table 1. Summary of the analysis of variance (ANOVA) of thermoplastic SPS/agar.

Variables	df	Flexural Strength	Flexural Modulus	Impact Strength
Mixture	4	0.00*	0.00*	0.00*

Note: *Significantly different at p≤0.05.

20wt%) increased the impact strength of thermoplastic SPS by 321% ($p<0.05$). This finding shows that good miscibility of SPS and agar does improve the ability of thermoplastic SPS to absorb the impact energy. However, further incorporation of agar led to decrease in the impact strength. This finding might be associated to the behavior of flexural modulus of this biopolymer. It is known that flexural modulus represents the rigidity of material (resistance to deformation upon bending) and this property is essential for the impact strength [21]. However, the decrement in impact strength at higher agar content (30 to 40 wt%) might be attributed to the fact that at very high rigidity, the polymer becomes more brittle and might lose its capacity of absorbing energy under impact conditions [22]. In addition, high impact strength is often associated with good flexibility of a material which enables it to absorb impact energy. For thermoplastic starch, this property can be altered easily by increasing the amount of plasticizer in the thermoplastic. This is due to the fact that plasticizer interferes the polymer chain and hydrogen bonding of starch resulting in more ductile and flexible material [20].

Statistical analysis of impact test data was conducted by one way ANOVA and the results are shown in Table **1**. Since the P-value of the test was less than 0.05, hence, there was a statistically significant difference in mean impact strength of the thermoplastic blends between the mixtures.

4.3. TGA Analysis

Thermal degradation behavior of thermoplastic starch based material is an important criterion in order to identify the limitation of material in the processing, treatment and operation [23]. Figs. **6** and **7** show the TGA and DTG curves of native agar, SPS, and their blends where the percentage loss of the sample weight and the derivative of the weight loss due to the volatilization of the degradation products are monitored as a function of temperature. The degradation step occured below 100 ^{o}C might be attributed to evaporation or dehydration of loosely bound water and low molecular weight compound [24]. Meanwhile, degradation which occured at around 130-250 ^{o}C can be associated to evaporation of glycerol [23]. Previous study reported thermal degradation of plasticizer for agar film occurring at temperature range of 190-250 ^{o}C [25]. This is due to the fact that the boiling point of glycerol is 198 ^{o}C [26]. The degradation that occured above 270 ^{o}C can be associated with degradation of agar [27]. Meanwhile, large degradation above 310 ^{o}C can be associated with elimination

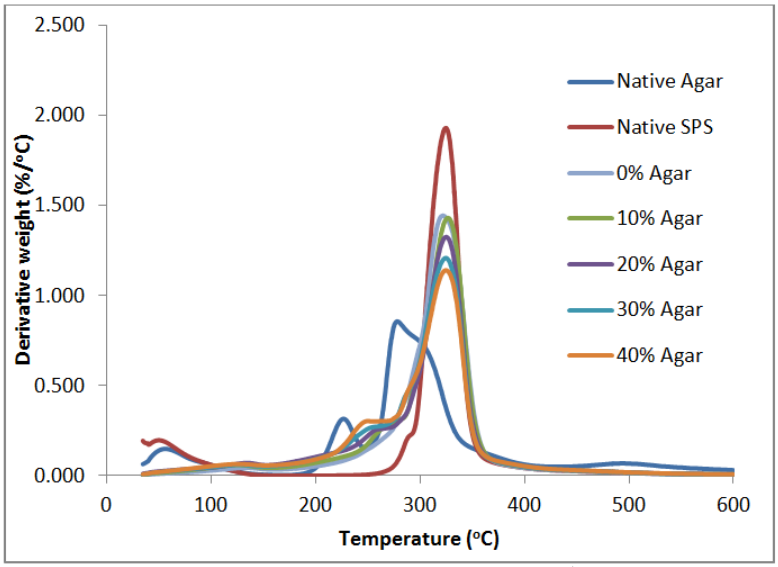

Fig. (7). DTG curve of native agar, native SPS, and thermoplastic SPS blend.

of hydrogen groups, decomposition and depolymerization of the starch carbon chains [28].

Incorporation of agar (0 to 40wt%) was observed to decrease the initial decomposition temperature of thermoplastic SPS from 283 to 274 °C. This might be attributed to the properties of native agar that has lower initial decomposition temperature compared to SPS. Char residue content of thermoplastic SPS was observed to increase with incorporation of agar. The minimum percentage of residue was recorded by thermoplastic SPS with 0% agar (9.2 wt%) whereas 40% agar (10.9 wt%) showed the highest residue content. This might be attributed to higher ash content of agar compared to starch [25]. Meanwhile, the DTG curve of thermoplastic SPS slowly changed according to native agar curve as the content of agar increased. The degradation at maximum decomposition temperature was reduced from 1.4 to 1.1 %/°C with incorporation of agar from 0 to 40wt%. Since maximum decomposition temperature was attributed to decomposition of starch compound, hence this phenomenon might be attributed to lower amount of starch in the blends as agar content increases. The maximum decomposition temperature was observed to be in the range of 314-315 °C. Maximum decomposition temperature of starch polymer was reported in the range of 310-330 [29]. This temperature was determined according to the maximum decomposition rate represented by the peak of the curve. Table **2** summarizes the TGA results.

Table 2. TGA results of thermoplastic SPS/agar.

Samples	T_{on} (°C)	T_{max} (°C)	Char at 600°C (wt%)
Native Agar	211	278	12.77
Native SPS	304	325	8.35
0% Agar	283	314	9.17
10% Agar	285	315	9.48
20% Agar	283	315	9.92
30% Agar	276	315	10.54
40% Agar	274	315	10.87

T_{on}- initial decomposition temperature; T_{max}-maximum decomposition temperature.

CONCLUSION

Novel biopolymer derived from sugar palm starch and agar was successfully prepared in this study. Effect of agar on thermoplastic SPS was experimentally studied with different agar contents. It can be clearly observed from results that incorporation of agar in thermoplastic SPS enhanced the flexural, impact and thermal properties (char residue content) of the blends. The thermoplastic SPS blends with 40 wt% agar exhibited the highest flexural strength of 11.53 MPa and flexural modulus of 288.27 MPa. Highest impact strength was exhibited by thermoplastic SPS blends with 20wt% agar. Addition of agar into thermoplastic SPS has improved the properties of thermoplastic SPS, widening the potential application of this biopolymer in green material development.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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DISCLOSURE

Part of this article has been reproduced from the previous publication in "International Journal of Biological Macromolecules Volume 89, August 2016, Pages 575-581; http://dx.doi.org/10.1016/j.ijbiomac.2016.05.028".

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