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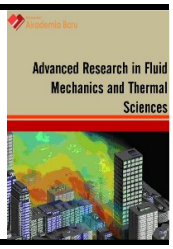

Effect of Agar on Dynamic Mechanical Properties of Thermoplastic Sugar Palm Starch: Thermal Behavior

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ABSTRACT

The aim of this work is to study the behavior of thermoplastic sugar palm starch (SPS)/agar blends when subjected to increasing temperature. Thermoplastic SPS/agar blends were prepared by incorporation of agar into thermoplastic SPS in the range of 10 to 40 wt%. The mixture was melt-mixed and then hot pressed at 140°C for 10 min. Dynamic mechanical testing was conducted on all samples at a temperature range of 25 to 140°C. The results show that the storage modulus of all samples decreased gradually with increase in temperature. This phenomenon indicates higher molecular movement of the materials when subjected to increasing temperature. Increasing agar weight fraction from 10 to 40wt% has decreased the storage modulus of the thermoplastic SPS/agar blends. These findings were accompanied by a decrease in the loss modulus of thermoplastic SPS which indicates less viscosity of the material when agar was introduced. The damping factor that indicates the molecular mobility of the material display increasing trend with an increase in agar concentration. In conclusion, the addition of agar has increased the molecular mobility of thermoplastic SPS which enhanced the polymer chain movement of the material at high temperature.

Keywords:
Thermoplastic starch, Dynamic mechanical analysis, Sugar palm, Thermal behavior

1. Introduction

Depleting petroleum resources for the production of petroleum-based polymer and the threat of the non-biodegradable plastics to the environment has attracted the attention of researchers to develop more environmental-friendly material as the alternative [1-3]. In recent, the research on the

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development and improvement of composites by using natural resources has gained increasing attention from all over the world. This includes both natural fibre and a natural filler such as kenaf and eggshell [4-6]. Apart from that, biopolymer derived from renewable resources are highly potential alternative to the conventional synthetic polymer due to the biodegradable characteristics. The examples of renewable resources are starch, alginate, chitosan, cellulose etc which commonly extracted from green plant or macroalgae. Among these biopolymers, starch is one of the most favorable material due to the abundance, low cost, biodegradable, and highly renewable [7-9].

Starch is a polysaccharide produced by the green plant as the energy storage. It consists of two microstructures namely amylose and amylopectin. Starch posses an interesting characteristic where it can be transformed into plastic in the presence of plasticizer and heat [9]. In this process, the starch granules will break down and the starch molecules will form a homogeneous melt known as thermoplastic starch (TPS) [10]. Previous studies have reported the characteristics of TPS derived from various resources such as cassava, corn, potato, rice, sago etc [11-14]. Even though this biopolymer display excellent environmental-friendly characteristics, however, TPS have some limitations such as poor mechanical properties and highly sensitive to moisture [8,15].

Agar is a sulfated polysaccharide which is extracted from marine algae of the class Rhodophyceae such as such as Gelidium sp. and Gracilaria sp [16,17]. This polysaccharide consists of two main components i.e agarose and agaropectin. This biopolymer is widely used as a gelling and thickening agent for food and pharmaceutical industry. Due to the good film-forming ability, this polysaccharide has received much attention from the researcher for the development biopolymer such as packaging film [18-20]. Similar to starch, agar also requires the presence of heat and plasticizer in order for this material to transformed into bioplastic. A study conducted on tropical climate has reported good biodegradable characteristics of the biopolymer [21]. A study conducted by Wu *et al.,* [22] shows that incorporation of agar into potato starch film has increased the mechanical properties of the material. The author attributed this improvement to the formation of intermolecular hydrogen bonding between starch and agar and the compact structure of the film. In addition, the increased in mechanical properties were associated to the more entangled structure of agar than the starch. However, most of the studies conducted on the development of agar biopolymer were focusing on solution casting technique to produce a thin film, hence, the research on the behavior of agar when transformed into rigid material such as thermoplastic starch are very rare to find.

Sugar palm is a natural forests species which belongs to Palmae family. This tree is known for producing *neera* sugar, a traditional sweetener in Asean country. Apart from that, this tree is able to produce up to 100 kg of starch from a single trunk [23,24]. The development of TPS from sugar palm has been reported earlier by Sahari *et al.,* [24] where the thermal, mechanical, and physical properties of the biopolymer were presented. In general, the neat TPS from sugar palm shows poor mechanical properties where tensile strength reported is only 2.42 MPa. Therefore this material requires further modification to improve the properties. In our earlier study [25], the modification of thermoplastic SPS with agar has shown positive findings on the mechanical properties of the material. The reported tensile strength of the thermoplastic SPS/agar is 13 Mpa. However, the increase in the mechanical properties was accompanied by a decrease in the thermal stability of the polymer blend. Therefore, it is important to study the dynamic mechanical properties of thermoplastic SPS/agar blends in order to investigate the behavior of this material when subjected to increasing temperature. Although several studies on the modification of thermoplastic starch have been reported, however, it clear from the literature that no study carried out the dynamic mechanical analysis of thermoplastic sugar palm starch modified with agar.

2. 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 fibers which contain the starch. These woody fibers were 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 left for the 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 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 (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 140 ^{o}C and rotor speed of 20 rpm for 10 min. This mixture was granulated by means of a blade mill equipped with a nominal 20 mm mesh and thermo-pressed in order to obtain a 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. Prior to the pressing, the samples were pre-heated at 140^{o}C for 10 min. Hot press film was placed in between the mold in order to facilitate the removal of the sample. Prior to removal, the samples were transferred to cold pressing for 4 minutes. The cooled sample was slowly removed from the mold in order to avoid cracking of the samples. Similar processes were used for the preparation of thermoplastic SPS/agar blends. The thermoplastic SPS was modified by incorporating a different amount 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 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) for thermoplastic SPS/agar blends were conducted according to ASTM D5023 standard. The measurements were carried out using a DMA instrument (TA Instruments (New Castle, DE) model Q800 V20.24 Build 43) operated in flexure mode at a frequency of 1Hz in a nitrogen atmosphere. The dimensions of the samples were 50 mm x 10 mm x 3 mm. The samples were mounted on a specimen holder in three-point bending condition. The dynamic storage modulus, loss modulus, and tan delta were recorded as a function of temperature from ambient temperature (25°C) to 150°C, at a constant heating rate of 2°C/min.

3. Results and Discussions

In this study, the DMA characterization was conducted in order to evaluate the viscoelastic properties of the thermoplastic SPS/agar blends. The storage modulus, loss modulus, and tan delta were measured as a function of increasing temperature and constant frequency. The elastic portion of the samples was examined based on the storage modulus. The energy dissipated (heat) was identified through the loss modulus, which shows the viscous region of the samples [26].

3.1 Storage Modulus

In general, storage modulus represents the elastic modulus of a material that defines the recoverable strain energy of the materials. These properties signify the elastic behavior of the materials when subjected to increasing temperature. The storage modulus also characterizes the stiffness of the materials.

The variation of storage modulus as a function of temperature for thermoplastic SPS/agar blends are shown in Figure 1. In general, the DMA curves of thermoplastic SPS and thermoplastic SPS/agar blends show similar trends regarding the variation of storage modulus with temperature. The storage modulus of the sample decreased continuously when the temperature increased from 25 to 140°C. This finding is typical for glassy amorphous solids [27]. Similar results were reported in the previous studies for modified thermoplastic cassava starch and thermoplastic corn starch [27-29].

It can be seen that the storage modulus of thermoplastic SPS decreased as the loading of agar increase from 0 to 40wt%. This finding might be attributed to the lower thermal stability of agar than thermoplastic SPS which led to decrease in the storage modulus of the material when subjected to increasing temperature. Lower onset degradation temperature of native agar than SPS has been reported in the previous study [25]. A similar finding was reported for the modification of thermoplastic corn starch with oxidized starch [28]. A study conducted on the effect of plasticizer on the dynamic mechanical properties of sugar palm starch film also reported a decrease in the storage modulus of the material following the incorporation of plasticizer which was attributed to the lower rigidity of the material with the addition of plasticizer [26].

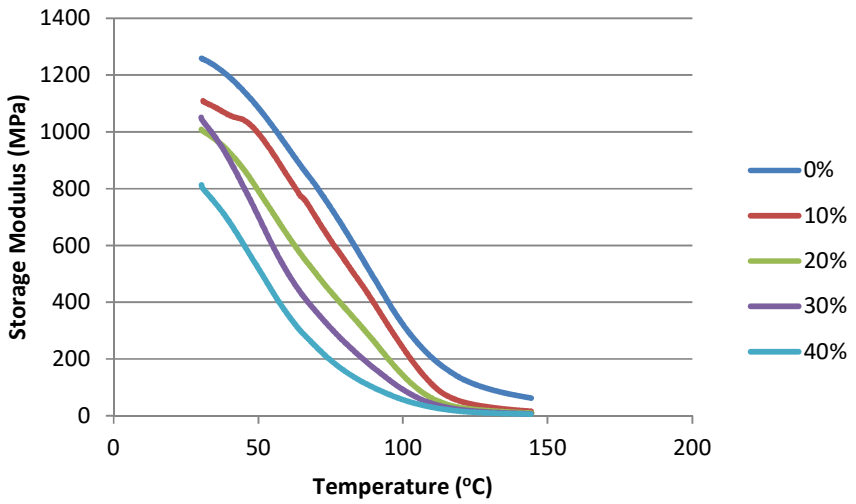

Fig.1. Storage modulus of thermoplastic SPS with different agar concentration

3.2 Loss Modulus

In general, loss modulus can be defined as the viscous response of a material. This parameter indicates the dissipation of energy in the form of heat when subjected to deformation [30,31]. It can be seen that the loss modulus of thermoplastic SPS/agar blends shows a slightly different trend with the storage modulus (Figure 2). The loss modulus curves for thermoplastic SPS with 0wt%, 10wt% and 20wt% agar content increased first, then gradually decreased as the temperature raised from 25 to 140°C. Meanwhile, the loss modulus of thermoplastic SPS with 30wt% and 40wt% agar decreased

as the temperature increased. In general, it can be seen that the loss modulus curves reached the maximum values for the dissipation of the energy and then decreased at higher temperatures. This phenomenon might be associated with the increased of free movement of the polymer chain as the temperature increases [30].

It is known that as the temperature increase, the energy from heat will be absorbed by the molecules which will trigger the molecules to vibrate faster. Hence, the space between the molecules increased and lower the rigidity of the materials. Increasing agar concentration from 0 to 40wt% was observed to decrease the loss modulus of thermoplastic SPS. Again, this phenomenon might be attributed to the lower thermal stability of native agar than the native SPS. Another study conducted on the modification of low density-polyethylene with agar also reported a decrease in the loss modulus of the matrix following the incorporation of agar at high concentration[32]. Meanwhile, a decrease in the loss modulus of material was also reported for the plasticized starch film which was attributed to the low molar mass character of the plasticizer, which decreases the viscosity of the starch films [26].

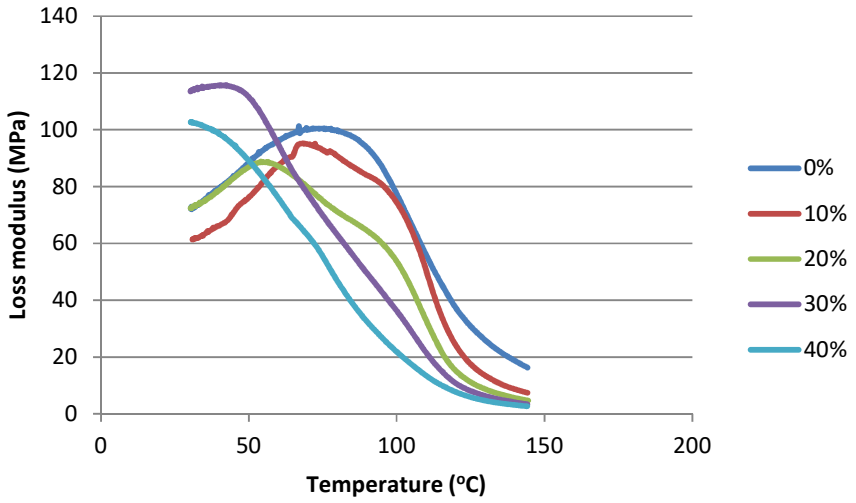

Fig. 2. Loss modulus of thermoplastic SPS with different agar concentration

3.3 Damping Factor (Tan Delta)

In general, the damping factor (tan delta) can be defined as the ratio of loss modulus to that of storage modulus. In composites, these properties enable the identification of interlocking bonding between the fiber and matrix. In this study, the damping factor can be used to identify molecular mobility of the thermoplastic SPS/agar with respect to temperature. Fig. 3 displays the effect of agar on the damping factor of thermoplastic SPS.

It can be seen that the damping factor for all samples increased gradually with increased in temperature and decreased after reaching a peak, regardless of agar concentration. This finding shows that the molecular mobility of all samples increased with increasing temperature which is in good agreement with the previous studies conducted on other materials such as thermoplastic cassava starch, low density-polyethylene and chitosan-starch film [32-34]. Increase in the damping factor with increasing temperature might be attributed to the higher mobility of the chain segment due to higher molecular energy. Hence, lower damping factor represents the lower degree of molecular mobility [30].

Incorporation of agar from 10 to 40wt% was observed to increase the damping factor of thermoplastic SPS matrix. This phenomenon might be associated with the low thermal stability of native agar, hence, the tendency of the molecules to move freely when subjected to increasing temperature is higher than the SPS. The higher damping factor of LDPE when incorporated with 10% agar was also reported in the previous study [32].

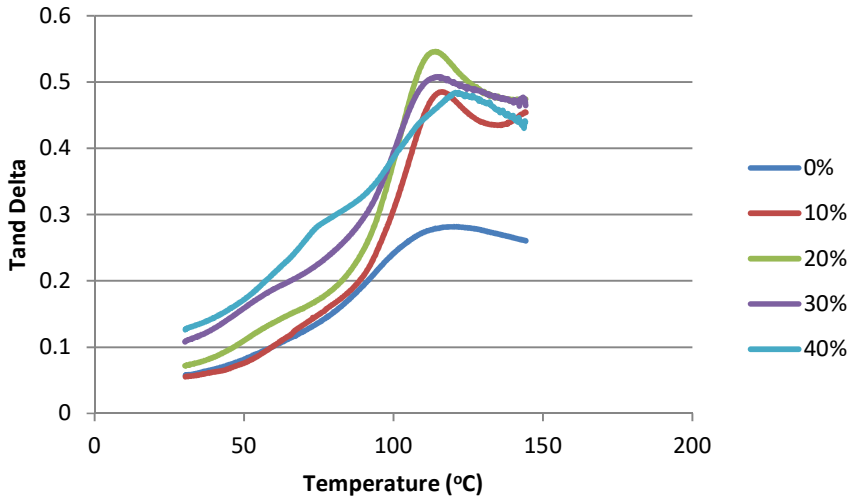

Fig. 3. Damping factor of thermoplastic SPS with different agar concentration

4. Conclusions

The influence of agar concentration on the dynamic mechanical properties of thermoplastic SPS was investigated. It was found that the storage modulus of all thermoplastic SPS/agar blends decreased with increasing temperature from 25 to 150°C. This trend was attributed to the higher mobility of polymer chain in the material when subjected to increasing temperature. Incorporation of agar was observed to decreased the storage modulus of the thermoplastic SPS matrix. Thermoplastic SPS with 40wt% agar concentration shows the highest degree of polymer chain mobility, hence leading to low storage modulus. The viscosity of thermoplastic SPS matrix was found to decrease with increasing agar concentration which was indicated through the lower loss modulus of the materials. The damping factor of the thermoplastic SPS was increased following the incorporation of agar which shows higher molecular mobility of the materials. Overall, incorporation of agar into thermoplastic SPS increased the molecular mobility of the materials.

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