International Journal of Biological Macromolecules 89 (2016) 575–581

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac

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

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ARTICLE INFO

Article history:
Received 6 January 2016
Received in revised form 20 April 2016
Accepted 9 May 2016
Available online 10 May 2016

Keywords:
Thermoplastic starch
Starch
Agar

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.

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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http://dx.doi.org/10.1016/j.ijbiomac.2016.05.028
0141-8130/

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 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 widley 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 ($10 \times 10 \times 3$ 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, Wi 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:

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

To determine the percentage of thickness swelling, the samples were measured before, *Ti* 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:

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

2.8. Statistical analysis

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