

EFFECT OF AGAR AND KAPPA-CARRAGEENAN ON THERMAL AND MECHANICAL PROPERTIES OF THERMO PLASTIC STARCH (TPS)

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ABSTRACT

EFFECT OF AGAR AND KAPPA-CARRAGEENAN ON THERMAL AND MECHANICAL PROPERTIES OF THERMO PLASTIC STARCH (TPS). Thermoplastic starch needs to be blend with other materials because of its limited properties. To gain the desired properties, the interaction between the added component (filler, plasticizer, second polymer, etc) must be concerned as it can affect the performances of the final product. Thermoplastic starch has been successfully made by mixing and compression molding with the addition of agar and kappa-carrageenan. The effect of the added material has been studied with FTIR, Tensile, DSC, and TGA to investigate their mechanical and thermal properties. The FTIR spectrum has shown the shifting around the methyl group (C-H), a carboxyl group (C-O), and a hydroxyl group (O-H). Thermal analysis results presented different patterns in melting and degradation behavior. Melting point of TPS/ agar/ kappa-carrageenan given a sharp peak in lower temperature which triggered by molecular transformation. They also experience a minimum mass loss compare to the neat one, which due to the change in structure or functional groups in bioplastics. Meanwhile, the tensile strength value did not show significant improvement with the presence of agar and kappa-carrageenan. It is shown that the addition of agar and kappa-carrageenan affects thermal behavior but does not significantly impact the mechanical properties.

Keywords: Starch, Agar, Kappa-carrageenan, Bioplastics

ABSTRAK

EFFECT OF AGAR AND KAPPA-CARRAGEENAN ON THERMAL AND MECHANICAL PROPERTIES OF THERMO PLASTIC STARCH (TPS). Bioplastik pati perlu dicampur dengan bahan lain karena sifatnya yang terbatas. Untuk mendapatkan sifat yang diinginkan, interaksi antara komponen yang ditambahkan (pengisi, pemlastis, polimer, dll) harus diperhatikan karena dapat mempengaruhi sifat produk. Campuran pati dengan penambahan agar dan karagenan telah berhasil dibuat dengan mixing dan compression molding. Pengaruh bahan yang ditambahkan telah dipelajari dengan FTIR, Pengujian Tensile, DSC, dan TGA untuk menyelidiki sifat termal dan mekaniknya. Spektrum FTIR menunjukkan pergeseran disekitar gugus metil (C-H), gugus karboksil (C-O), dan gugus hidroksil (O-H). Hasil analisis termal menunjukkan pola perilaku leleh dan degradasi yang berbeda. Titik leleh bioplastik, menunjukan puncak yang tajam pada suhu yang lebih rendah

yang disebabkan oleh adanya transformasi fasa. Adapun, pada hasil uji TGA, dengan penambahan agar dan kappa-carrageenan dapat memberikan perubahan struktur dan gugus fungsi sehingga pola degradasi campuran menunjukkan kehilangan massa yang lebih sedikit dibanding TPS saja. Sedangkan nilai kekuatan tarik tidak menunjukkan peningkatan yang signifikan dengan adanya agar dan kappa-carrageenan. Hal ini menunjukkan bahwa penambahan agar dan kappa-carrageenan berpengaruh terhadap perilaku termal tetapi tidak memberikan peningkatan yang signifikan terhadap sifat mekanik.

Kata kunci: Pati, Agar, Kappa-carrageenan, Bioplastik.

INTRODUCTION

Starch typically has thermoplastic behavior if were mixed with plasticizer as for example is glycerol or sorbitol. The plasticizer aims to reduce the hydrogen bonds in starch granules and conduct the multiple monomers into the polymer, the processed is so-called gelatinization. At high temperatures, mixed starch-plasticizer can be processed into thermoplastic starch (TPS) [1]. Starch generally found as semicrystalline and insoluble in water. Starch consist of two glucose polymer: amylose and amylopectin. During the thermal processing of starch into thermoplastic starch, the physicochemical transformation occurred. Thus, initiated the alteration of morphological characteristics, crystalline formation, and chemical structure of native starch [2]. Therefore, thermoplastic starch itself does not enough for most applications because of its limited properties. Consequently, starch usually blended with other materials to enhance their performances and strengthened their properties. But to gain the desired properties, the interaction between the added component (filler, plasticizer, second polymer, etc) must be good enough as it can affect the final performances [3].

Polymer blends that contain physical mixtures of structurally different polymers can interact with secondary bonding. The compatibility depends on molecular mixing [4]. Polymer-blends property greatly depends on the miscibility (compatibility) of the blend. Miscibility appears when specific interaction forces occur between the polymers. This can be formed as hydrogen bonding, charge transfer complexes, acid-base type interactions, dipole moments, and electron donor-acceptor complexes [5].

Agar is gelatinous substance derived from red algae. Agar is a mixture of polysaccharide agarose and a heterogeneous mixture of smaller molecules which is agaropectin [4]. Agar has ability to form reversible gels at even low concentration by simply cooling the hot aqueous solutions then the hydrogen bonding formed. This has provided a wide range of applications for agar,

such as thickening and gelling agent in food industries [6]. Kappa-carrageenan is generic name for a class of sulfated galactan polysaccharides and generally extracted from *Kappaphycus alvarezii* [7]. The chemical reactivity of carrageenans is due to their half-ester sulfate groups which strongly anionic and unstable free acid. The confirmation of the sugar chain associated with the cations can determine the physical properties of kappa-carrageenan. [8]. This study aims to investigate the effect between agar, kappa-carrageenan, and starch interaction in their thermal and mechanical properties.

EXPERIMENTAL METHOD

Materials and Instruments

Cassava Starch was obtained from Cv. Surya Pati Kencana, (Pati, Indonesia), Agar was purchased from Cv. Sari Mutiara Abadi (Malang, Indonesia), and Kappa-carrageenan was gained from Research Center for Marine and Fisheries Product Processing and Biotechnology, Ministry of Marine Affairs and fisheries Republic of Indonesia (Jakarta, Indonesia), Glycerol was purchased from PT. Wilmar Nabati Indonesia (Jakarta, Indonesia).

Morphology of bioplastics was observed using Scanning Electron Microscope (SEM) (JEOL, JSM IT-300, Japan), with thin layer gold coating before measurement. The interaction of functional groups was analyzed by Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) (Nicolet iS 5 ATR iD5, Thermo Scientific, USA) in the wavenumber of 4000 to 500 cm^{-1} . Thermal behavior was measured by Differential Scanning Calorimeter (DSC) 214 Polyma and Thermogravimetry Analyzer (TGA) 209 F1 Libra (Netzsch, Germany) under nitrogen atmosphere (30mL/min). The measurements were run from 40°C to 200°C for DSC and 25°C to 500°C for TGA, and the heating rate was 10°C/min for both. A universal testing machine (UCT-5T, Orientec Co.Ltd, Japan) was used to evaluate the tensile strength of bioplastics. The measurement was managed according to ASTM¹² D882-12 with an initial gauge

separation of 100mm and the crosshead speed of 50mm/min.

Method and Procedure

Thermoplastic starch/agar/kappa-carrageenan was prepared by mixing agar : kappa-carrageenan with the following formulation; 1:9 (% w/w), 5:5 (% w/w), and 9:1 (% w/w) respectively, then 10% (w/w) of the mixture were blended with 90% (w/w) of starch-glycerol (3:1) using Labo Plastomill (Toyoseki, Japan). Mixing process was run at 135 °C for 8 minutes with 50 rpm speed. The mixtures then poured into molds of 20x20 cm and pressed by compression molding at 135 °C under a load of 40 kg cm⁻² to form sheet.

RESULT AND DISCUSSION

The bioplastics of TPS, agar, and kappa-carrageenan with different composition as seen in Table 1, was analyzed using SEM at magnificent of 100x to observe the morphology on the fracture surface.

The SEM image of bioplastic has presented in Figure.1. It was shown the fracture surface morphology of sample (A) A9K1, (B) A5K5, and (C) A1K9. Some cavity seems to exist in the fracture surface of TPS using more agar (A9K1 and A5K5) which may be due to the imperfect process of plasticization. It is likely due to disparity of gelatinization temperature for starch and agar, which leads to poor miscibility. The viscosity of the mixture can also interfere this process [9]. On the other hand, for the TPS containing more carrageenan as seen in Figure 1 (c) shows no cavity but some granule seems to exist. This poor miscibility can also affect the mechanical properties of the samples which will be discussed in Figure 3.

Figure 2 shown the spectrum of neat TPS and the blends. No new peak appeared in the spectrum, but it is observed that some shifting occurred. The absorption peak at the wavenumber band of 1011 cm⁻¹ assigned to C-O stretch of starch. In addition, the broad peak at the band of 3500-3000 cm⁻¹ ascribed to O-H interaction [10]. S=O stretching of kappa-carrageenans showed in the

Table 1. Composition of TPS/Agar/Carrageenan bioplastics

Name of Sample	Agar (%)	Carrageenan (%)	Starch-Glycerol (3 : 1) (%)
TPS	-	-	100
A9K1	9	1	90
A5K5	5	5	90
A1K9	1	9	90

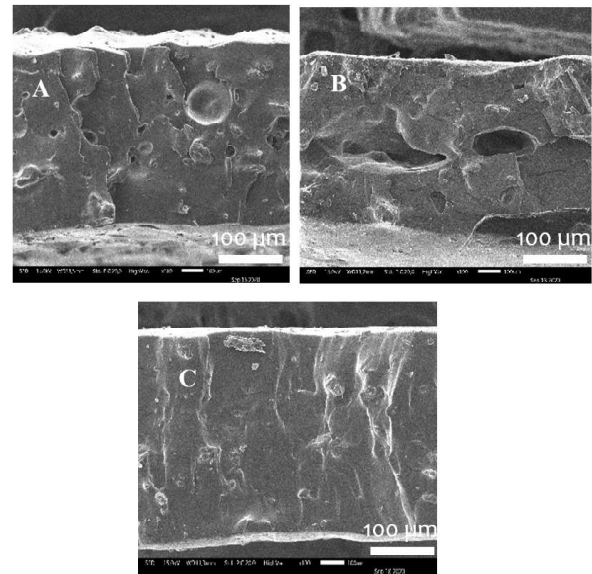


Figure 1. SEM Image of (a) A9K1, (b) A5K5, and (c) A1K9

band of 1262 cm⁻¹, and glycosidic linkage in the region of 1042 cm⁻¹ [11]. The shifting was revealed in the alkane group (CH₃ or CH₂) at the band of 2885 cm⁻¹ for starch to around 2900 cm⁻¹ region at the presence of agar and kappa-carrageenan. The absorption band in around 1750 cm⁻¹ and 1370 cm⁻¹ assigned to carbonyl group (C=O), absorption band in around 930 cm⁻¹ was ascribed as 3,6-anhydro-L-galactose, and absorption at about 890 cm⁻¹ was due to 1,3 beta-D-galactose. On the other hand, the absorption at wavenumber around 830 cm⁻¹ showed D-galactose-2-sulphate from agar, and around wavenumber region of 740 cm⁻¹ was ascribed as galactose bond [12], [13].

Figure 3, presented the tensile strength value of bioplastics. As can be seen, the strength value of the neat TPS and the mixtures did not have substantial differences due to insignificant amount of agar and

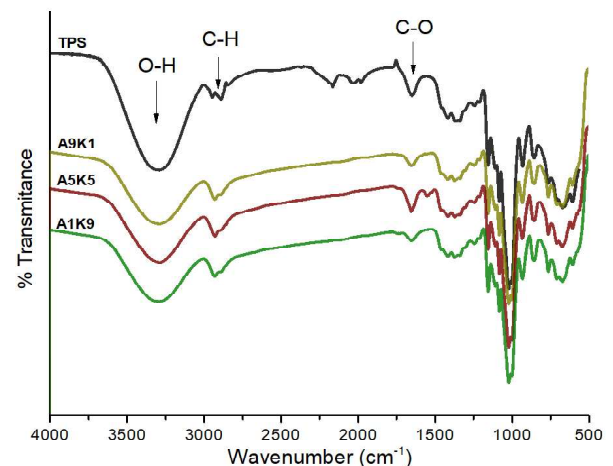


Figure 2. FTIR spectrum of TPS/Agar/Carrageenan bioplastic

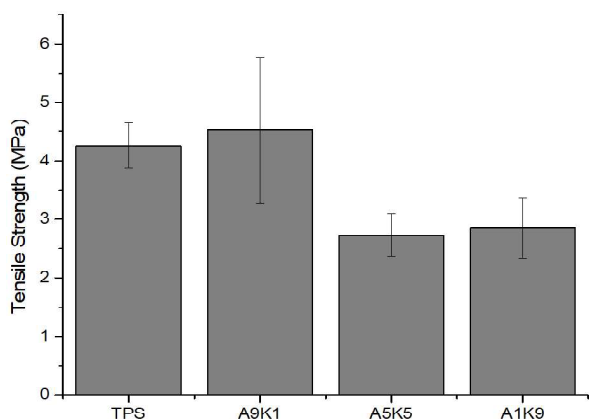


Figure 3. Tensile Strength of TPS/Agar/Kappa-carrageenan bioplastics

kappa-carrageenan in the bioplastics. The strength value of TPS and A9K1 was around 4,3 MPa and around 4,5 MPa respectively. The mechanical properties of A9K1 are similar to TPS, possibly because the composition and structure of starch (amylose and amylopectin) are almost the same as agar (agarose and agarpectin, rather than carrageenan. So that the interactions that occur are more miscible. Mechanical properties of A5K5 and A1K9 have almost the same values, however, they are both lower than TPS and A9K1 due to the higher carrageenan composition. The strength value of A5K5 and A1K9 was 3,7 MPa, and 3,8 MPa respectively. Kappa-carrageenans has low hydrophylic character because of an additional sulphate group in the anhydrous galactose residue, also the presence of amylose structure in starch and agar will restricts the miscibility of starch granules with kappa-carrageenan [9][14]. As a consequence, the mechanical properties of this composition has lower value than the others.

Differential Scanning Calorimeter of TPS/agar/kappa-carrageenan blends has presented in Figure 4.

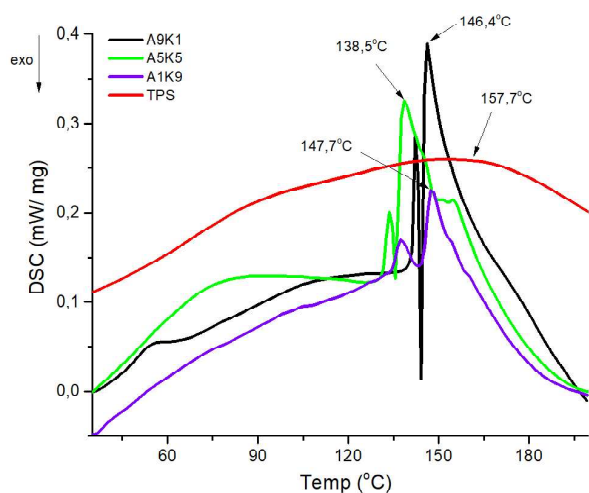


Figure 4. DSC curve of TPS with different blending composition

Remarkable differences were shown between TPS and the blends, it spotted that no significant endothermic peak appeared in the TPS curve, while the others exhibit two endothermic peaks. The dull and broad peak of TPS was considered as evaporation of water and glycerol. It is also proven with TGA measurement in Figure 5, which shows more mass loss in the first stage (until around 150 °C). Since starch was partially crystalline it gives some broad melting peak as a result of size distribution of crystallites [15][16]. Moreover, the existence of sharp endothermic peak for the mixture of A9K1, A5K5, and A1K9 reveals that the presence of agar and kappa-carrageenan were lead to molecular state transformation from the amorphous phase to crystalline phase. It can be seen in the change of board peak of TPS to sharp peak of A9K1, A5K5, and A1K9. It is assumed that this phase transformation was triggered by the change of intermolecular interaction which affects the chain mobility of polymer [4].

Thermal degradation behavior of bioplastics exhibits in Figure 5. The initial point of degradation varies between TPS and blends. The TPS experience more mass loss for about 11% loss in the first stage (30-150 °C) than the other samples. In contrast, the first stage loss of A9K1, A5K5, and A1K9 was about 4%, 5%, and 4% respectively. This loss experience was count as evaporation process of hydrate from OH groups of polymer and plasticizer. It is followed by second stage loss at the range of 150-250°C. The main degradation then took place at different temperatures for TPS and the mixtures. The maximum loss for TPS begins at about 300 °C, where maximum point loss for A9K1, A5K5, and A1K9 starts at around 250 °C. The differences of degradation patterns were due to difference in structure

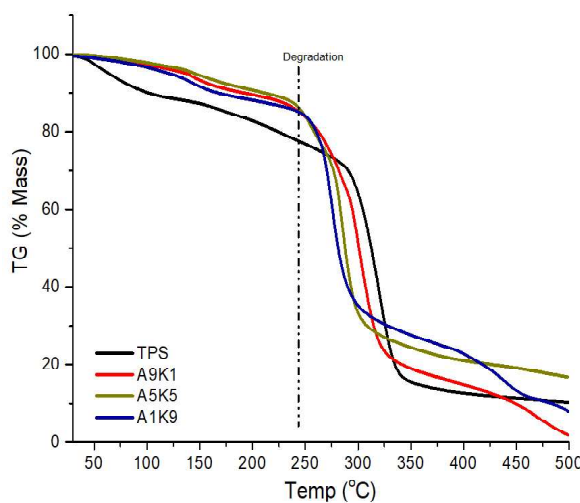


Figure 5. TG curve of TPS with different blending composition

or functional groups in bioplastics [17]. The greater the main chain bonding, the greater the energy needed to break the chain, as a result, the temperature for breaking the main chain became higher as seen in thermogram of TPS. Additionally, the presence of secondary bonding in A9K1, A5K5, and A1K9, as related to the above discussion on DSC results will lead to the weaker formation as a result the maximum loss became faster. It was also shown that the blends have more stability during the first and second stage, it is confirmed that the samples do not release as much water and volatile compound as the TPS during this stage.

CONCLUSION

The interaction of agar-kappa-carrageenan and thermoplastic starch was investigated with the IR spectrum and it spotted that the region of C-H band (2800 cm^{-1}), O-H band (3000 cm^{-1}), and C-O band (1700 cm^{-1}) experienced a shifting in wavenumber and intensity which indicated that secondary bond formed between materials. Hence, this phenomenon affected the chain mobility in polymer and caused a change in melting behavior. The molecular interaction between materials also influences the stability in degradation process. The TPS itself experience more mass loss before its degradation point, which was also caused by the hydrophilic nature of the plasticizer. Moreover, the mechanical properties did not improve meaningfully with the presence of agar and kappa-carrageenan, as the result of their unoptimum composition and miscibility properties.

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