Starch Based Biocomposite from Sago (*Metroxylon sagu*) with Nano-Chitosan Reinforcement: Mechanical and Thermal Characteristics

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ABSTRACT

A biocomposite system incorporating sago starch and nano-chitosan (SS/NCS) were developed by casting and solvent evaporation method. The purpose of this experiment for characterization of the film based on sago starch (SS) with a variation of the addition of nano-chitosan (0, 2, 4, 6 and 8% by weight starch) and analyze its effect on mechanical properties, thermal properties, and morphological characteristics of mixed film (SS / NCS). Possible intermolecular interactions between SS and NCS were confirmed by Fourier-transform infrared spectroscopy (FTIR) and the reduction of crystallinity in XRD. The experimental data showed that the incorporation of nano-chitosan resulted in an increase in film solubility, tensile strength and elongation at break and a decrease in Young’s modulus. Elongation at break of the (SS/NCS) films increased with increasing of nano-chitosan concentration. The water vapor permeability (WVP) of (SS/NCS) films increased with an increase of chitosan concentration and the same tendency observed for the moisture content. Based on thermogravimetric analysis (TGA), the percentage of nano-chitosan content in starch-based films can increase thermal stability. Scanning electron microscope (SEM) shows the surface morphology and interface of NCS/SS composite films and suggests sufficient homogenization of starch and chitosan in biodegradable composite films.

Keywords: sago starch, nano-chitosan, starch-based film, biocomposite

INTRODUCTION

Sago starch as an abundant natural resource in the tropics has high potential to be used as industrial raw material. One of the potentials of the sago starch is its utilization as a raw material for bioplastics and biocomposites. A variety of starch-based film applications are used in the packaging industry, industries made from plastic, to the technology and medical industries. Starch has the potential to be processed into plastic films with good oxygen barriers. However, starch-based plastic films have hydrophilic properties thus making the mechanical properties of the films produced brittle and low tensile strength [1, 2], their application is limited due to poor moisture barrier properties, fragility and low tensile strength. To improve functional properties and overcome these weaknesses, starch is combined with other natural biopolymers or modified and with the addition of plasticizers [3].

Starch with a ratio of amylose and amyllopectin will affect functional properties, the higher the amylose content, the better the ability to form films. The ratio also determines the
ability of the film process, mechanical properties as well as the ability of the film to barrier properties [1, 4, 5]

The process and application of starch-based films are constrained because they are fragile and hydrophilic. To improve the ability of starch films to hydrophilic and brittle properties, starch modification can be done or by adding other polymers both synthetic and natural polymers such as aliphatic polyester [6], mixed with natural rubber [7] or zein [8] and composite with fiber [9]. One of the natural polymers that most widely used to overcoming this problem is the addition of chitosan, specifically to improve the mechanical characteristics and process capability of starch films.

Chitosan is a long-chain polymer of glucosamine, 2-amino-deoxyglucose which is obtained from the deacetylation of chitin from the skin and head of hard-skinned invertebrate animals using the base of sodium hydroxide. The second organic polymer after cellulose which is the most abundant and easily found in nature is chitin where found in various animal species both land and water. Chitosan is a form of cationic polysaccharide derived from deacetylation of chitin, which comes from the crustacean shell and exoskeleton of an insect) which has biocompatibility, biodegradability, film formation, non-toxicity and antimicrobial properties. Application of chitosan today has been widely used in the food industry and bioengineering as an encapsulation material, enzyme immobilization, control in drug delivery, and in agriculture as a support for plant growth and microbial agents [10-12]. The characteristics of chitosan are insoluble in water and strong base solution, slightly soluble in HCl, HNO₃, and 0.5% H₃PO₄ while in H₂SO₄ it is not soluble. Chitosan is also insoluble in some organic solvents such as alcohol, acetone, dimethyl formamide and dimethylsulfoxide, but chitosan is slightly soluble in hydrochloric acid and nitric acid and dissolves both in weak acids such as formic acid and concentrated acetic acid (0.2 -100)% in water [13].

Researches related to starch and chitosan based films have been carried out with various methods and variations but in principle the use of starch and chitosan has fragile properties with low mechanical properties [14] [15] [16] [17]. However, to overcome these problems, the process of adding plasticizers such as glycerol and other polyols will reduce friction in the polymer chain which will also increase the flexibility of the resulting film [18] [19] [20] [21] [22]. In general, the starch-based film making process is carried out by the method of pre-gelatinization of starch by a heat stirring process, then chitosan is added to the starch solution for later pouring into the mold [22-24]. The addition of other components such as gelatin, cellulose, starch, polyamide, vinyl alcohol, and ethylene glycol are also able to improve the properties of chitosan films so that the mechanical characteristics of the film become better [25-28]. In this study, chitosan was dissolved into an emulsifier solution and then mixed with a starch solution that had reached pre-gelatinization. The final mixture is then poured into the mold by casting method to evaluate the effect of adding chitosan on the mechanical properties of the film, thermal properties, and film morphology

EXPERIMENT
Materials
Chitosan powder from CV Chimultiguna, Indramayu, Indonesia is a blue crab shell extract with a molecular weight specification of 102 kDa and the degree of deacetylation reaches 96.24%. Sago starch containing 23% amylose and 73% amylopectin (Sapapua), was supplied by CV Rajawali New Glory, Sorong, West Papua. Glycerol (99.0% purity) from Merck, and acetid acid were purchased from PT Kimpo Indotama (Indonesia).
Characterization
Mechanical properties
Measurement of tensile strength, elastic modulus, and maximum elongation at break from sago-chitosan films were carried out by the ASTM D882-09 method and using the AI-7000-S universal testing machine model (Gotech, Taiwan). Preparation of the test sample is done by cutting the film that has been printed with dimensions of width 15 mm and 100 mm length which is done with several replications.

Fourier transform infrared spectroscopy (FTIR)
Fourier Transform Infrared Spectroscopy measurements were obtained using a FTIR model IRPrestige 21 Spectrophotometer Shimadzu 8400S Vertex 70 Bruker, Germany. Spectra were recorded at a spectral range between 3500 and 6000 cm\(^{-1}\) at a scan rate of 180 scans and spectral resolution of 2 cm\(^{-1}\). The FTIR spectrum was employed in the transmittance mode. FTIR analyses were performed to study the effect of the addition of thermoplastic chitosan in thermoplastic starch, to verify possible interactions among starch, chitosan and glycerol.

The purpose of using the FTIR method is to determine the level of influence of the addition of nano-chitosan to sago starch films and to determine the interaction between components of both starch, chitosan and glycerol. FTIR analysis using the FTIR IRPrestige 21 Spectrophotometer Shimadzu 8400S Vertex 70 Bruker, Germany. The spectrum used is in the spectral range between 3500 and 6000 cm\(^{-1}\) with a spectral resolution of 2 cm\(^{-1}\) and a scan speed of 180 scans.

X-ray diffraction (XRD)
The crystal structures of film were analyzed from diffraction patterns obtained on a model Philips PW 1710 X-ray diffractometer. Samples were scanned from 5 to 40 using a scan rate of 1° min\(^{-1}\). The diffraction patterns were fitted using Gaussian curves, after peak deconvolution using a dedicated software (Origin 8.0\textsuperscript{TM}). Crystallinity index (CI) of NCS and blends were estimated based on areas under the crystalline and amorphous peaks after baseline correction. The IC of SS was estimated as a function of the B and Vh crystal form according to \cite{25}.

Water vapor permeability (WVP)
Water vapor barrier properties on the film function to avoid or reduce the flow of moisture between the plastic film and the surrounding atmosphere. Preparation of film samples was carried out by cutting a 45 mm diameter film to be stored in a desiccator with an RH setting of 50 ± 5% and 25 °C for seven days. The cut film is then stored tightly in a plastic bottle that has been filled with 30 mL distilled water (100% RH). The bottle is closed and sealed using Vaseline to prevent moisture leakage. Before the bottle is inserted, the bottle is weighed to determine the initial mass and then stored in a closed desiccator (1000 g silica gel) at 25 °C. For every three hours weighing for 24 hours using Kenko with a precision level of up to 0.1 mg. Average WVP results are calculated through the equation below

\[
WVP = \frac{(dW \times L)}{(dt \times dp \times A)}
\]
where \( dW \) = weight loss of the plastic bottle (g), \( L \) = film thickness (m), \( A \) = the exposed area of film sealing top of a plastic bottle (m\(^2\)), \( dt \) = the time under the partial water vapor pressure gradient (dP=2533 Pa). Three samples per treatment were tested.

**Scanning electron microscopy (SEM) analyses**

Morphological analysis of the cross section of starch-chitosan films was carried out using SEM (Scanning Electron Microscopy) JEOL JSM-6510. Edible film sample are attached to the set holder with double adhesive, then coated with gold metal under vacuum. The sample is put into place in the SEM, then the topographic image is observed and magnified 3000 times.

**Thermogravimetric measurements**

Characterization of thermal properties can be measured using a Thermogravimetric Analyzer (TGA). TGA analysis (SETARAM TGA-24S) is carried out with the aim of finding out thermal stability on the starch-chitosan film. Analysis of thermal properties can provide information about the physical changes of the film.

The output of the TGA is a thermogravimetric curve obtained under conditions of synthetic air atmosphere. Samples were prepared in platinum containers provided that each sample of 6 mg was then heated at a heating rate of 10 °C min\(^{-1}\) from 25 to 600 °C.

**Procedure of reaction**

Starch solution (SS) (3 g/50 mL) prepared by the method of putting sago starch into a glass then adding deionized water then stirring at 450 rpm for 10 min, then stirring again 65° C and stirring with 450 rpm for 5 min to pre-gelatinization. Nano chitosan (NCS) with variations (0.2, 0.4, 0.6, and 0.8 wt%) was put into a glass containing 100 mL of 0.1 M acetic acid aqueous solution at 100° C with stirring of 450 rpm for 15 min. Glycerol was added to the mixing SS and NCS at weight ratio of 1:1 to fabricate the SS/NCS films at 70 °C with stirring of 450 rpm for 20 min. SS/NCS film solution was prepared to be poured into a petri dish and dried at 40 °C for 20 hours. The dried chitosan starch film was then removed at room temperature for about 10 minutes and before it is used for testing it must be stored at room temperature and 75% RH for 48 hours.

**RESULT AND DISCUSSION**

**Mechanical properties**

The tensile strength and elongation at break of thermoplastic starch with chitosan variations are shown in Table 1. The stress and strain curves are shown in Figure 1 of the SS / NNCS blend polymer of a ratio of 1: 0.2 wt% to 1: 0.8 wt%. The pattern of starch-based plastic material seen in the stress strain curve shows that the plastic zone increases until it reaches the deformation phase and ends at the final zone where the sample is broken.

The tensile strength of starch-based plastic films can be seen in Table 1 showing that it addition of chitosan to starch film has a significant effect, but with the addition of glycerol as a plasticizer will reduce the tensile strength and improve the brittle nature of the film due to its hydrophilic nature. The results given the starch–nanochitosan ratio ranging from 1 : 0.2 wt% to 1: 0.8 wt%, the tensile strength gradually increased. In addition, the breaking elongation first increased and then decreased as starch content increased. The comparison between the stress and strain curves showed that the elongation reached 55.4% when the chitosan–starch ratio was 1 : 0.6 wt% and that the tensile strength reached 2.6 MPa.
Figure 1. Stress–strain curves of SS/NCS films with 0.2 to 0.8 wt.% chitosan ratio. SS/NCS films with 0.6 wt% chitosan have a good tensile strength and elongation.

Table 1. Mechanical properties of SS/NCS films

| Film     | Thickness (mm) | Tensile strength (MPa) | Elongation at break (%) |
|----------|----------------|------------------------|-------------------------|
| SS/NCS0.2wt% | 0.085 ± 0.006<sup>a</sup> | 1.2 ± 0.66<sup>a</sup> | 20.0 ± 5.2<sup>a</sup> |
| SS/NCS0.4wt% | 0.094 ± 0.004<sup>b</sup> | 1.7 ± 1.53<sup>b</sup> | 43.4 ± 2.3<sup>b</sup> |
| SS/NCS0.6wt% | 0.088 ± 0.002<sup>a</sup> | 2.6 ± 1.54<sup>a</sup> | 53.8 ± 3.8<sup>b</sup> |
| SS/NCS0.8wt% | 0.099 ± 0.008<sup>b</sup> | 2.8 ± 1.39<sup>a</sup> | 22.3 ± 3.9<sup>a</sup> |

The difference in the letter code indicates a significant difference between the formulations (p < 0.05). Values are mean ± standard deviation (n = 4).

**X-ray diffraction (XRD)**

Figure 2 shows the diffraction patterns formed in the XRD pattern of SS / NCS films displayed vertically to avoid overlapping patterns. The SS / NCS spectrum displayed a broad diffraction peak shape against a large amorphous background background, this shows the characteristics of a semi-crystalline polymer with a low degree of crystallinity. Based on Figure 2, two major reflection peaks that affect the crystallinity of the film were detected at 12.6 and 19.4. The same thing was done by Shi et al. [26] which saw two sharp peaks with values of 13.5 and 20.9 and were referred to as V-type structures. Crystal structure is formed due to the amylose crystallization in a single helix involving glycerol or lipids [27]. The crystallinity of the force is induced by thermal processing in which the strong interactions between the hydroxyl groups of starch molecules are replaced by hydrogen bonds formed between plasticizer and starch during thermoplastic processing [28].

The process of dispersion of native starch granules that has been well integrated during processing is in the absence of reflected peaks which correspond to the type-A crystal structure, characteristic of cereal starch [29]. The greater the chitosan in the film has an increase in the degree of crystallinity of the SS / NCS film matrix, although the difference is not significant as shown in Figure 2.
Figure 2. XRD spectra of films based on sago starch film combined with nano chitosan (SS/NCS). Starch–nano-chitosan ratio ranging from 1 : 0.2 wt% ; 1: 0.4 wt% ; 1:0.6 wt% ; and 1: 0.8 wt%.

Figure 3. FTIR spectra of sago starch film (SSF) and sago starch-chitosan blend (SS/NCS).

FTIR

The FTIR analysis method makes it possible to see the phenomenon of intermolecular interactions between the various constituent components of starch-chitosan films in a composite system. The phenomenon of changes in the chemical structure of Sago Starch (SS) / Nano-Chitosan (NCS) films because SS and NCS are incorporated into the formulation can be seen from FTIR spectra. A broad peak of a hydroxyl (O-H) group stretching was observed at 3255 cm⁻¹ for the SS/NCS film and 3268 cm⁻¹ for SS. The different peaks between those films demonstrated the increased amount of O–H groups inside the film as the new formulations were developed.
The carbonyl group (C=O) is conjugated and the amide group (N-H) is bent as the functional groups of amides I and II appear at 1645 cm\(^{-1}\) and 1560 cm\(^{-1}\). The films differed in terms of the peak spectra shown by SS at 1643 cm\(^{-1}\) for the C=O stretch. The distinct peaks of the films portrayed the incorporation of SS and NCS inside the film. In addition, the SS spectrum showed a peak for the aromatic ring of C=C at 1426 cm\(^{-1}\). The band was observed to be sharper and shifted to 1416 cm\(^{-1}\) after the combination of SS and NCS. The appearance of NCS in the spectra acts as a peak transition, this is because the chemical structure is in a closed hydrocarbon circle.

Another characteristic of absorption frequency was shown at 1075 cm\(^{-1}\), which is attributed to C–O stretching in SSF. It became sharper and shifted to 1080 cm\(^{-1}\) when other materials were added into the solution. The broad peak at 835 cm\(^{-1}\) demonstrated the symmetric P=O of the SS/NCS film. These peaks revealed the crosslinking of NCS with acetic acid in the transformation of chitosan nanoparticles.

Table 2. WVP properties of different SS/NCS films

| Film      | WVP (10\(^{-10}\) g/Pa·m·s) |
|-----------|-------------------------------|
| SS/NCS0.2wt% | 1.31 ± 0.226\(^a\)             |
| SS/NCS0.4wt% | 1.88 ± 0.145\(^b\)             |
| SS/NCS0.6wt% | 2.54 ± 0.211\(^a\)             |
| SS/NCS0.8wt% | 2.97 ± 0.138\(^b\)             |

The difference in the letter code indicates a significant difference between the formulations (p< 0.05). Values are mean ± standard deviation (n = 4).

**Water Vapor Permeability**

The function of water vapor barrier properties is to avoid or reduce the exchange of moisture between the plastic film and the surrounding atmosphere. Addition of chitosan will improve the film's water vapor barrier properties. WVP values of SS/NCS films show values in the range 1.31-2.97 \(\times 10^{-10}\) g.m\(^{-1}\)s\(^{-1}\)Pa\(^{-1}\). The highest WVP of SS/NCS films can be attributed to the greater number of free hydroxyl groups and hydrophilic glycerol addition. The free hydroxyl group increases interaction with water molecules, supports the transmission of water vapor through film, while the addition of glycerol as a plasticizer can increase the distance between molecules and reduce intra-molecular hydrogen bonds, this affects the characteristics of starch tissue to be less dense and increases the adsorption and desorption of water molecules. The hydrophobic nature of chitosan is influenced by the presence of a long hydroxyl and amino group in its chemical structure so that it is possible to increase the WVP value of SS / NCS films with the increasing addition of chitosan. An increase in bond interactions between hydrogen molecules in starch and chitosan materials will increase the permeability value of the film.

**Thermogravimetric analyzes**

The thermal stability and decomposition temperature of plastic films were evaluated by TGA. SS/NCS films which had optimum mechanical properties were analyzed at a heating rate of 10 °C/min under nitrogen flow. In this study, the temperature used for the analysis was between 50 °C and 500 °C. There were three consecutive stages of film decomposition. The
first stage was due to the loss of water, whereas the second stage corresponded to the decomposition of the partially decomposed film. The final stage signified the maximum decomposition phase of the sample. The thermograms for SS/NCS samples showed similar patterns for those three stages. The initial stage for the decomposition process occurs at temperatures 50 °C and 150 °C. At this stage, the weight loss for SS/NCS film was 5%. The first stage occurred by the phenomenon of the loosely bound water.

The second stage of the decomposition occurred at 200 °C. The weight loss during this stage was 33 % for the SS/NCS film. Finally, the third stage was examined above 250 °C. The thermograms exhibited the final value of weight loss of 60% at 385 °C for SS/NCS film. The weight loss for the final stage was 60 % due to the split of the aliphatic ring side chain from the aromatic ring with the breaking of C–C linkages between the NCS structural units.

**Figure 4.** SEM micrographs of (1) SS/NCS 0.2 wt% film surface; (2) SS/NCS 0.4 wt% film surface; (3) SS/NCS 0.6 wt% film surface; (4) SS/NCS 0.8 wt% film surface.

**SEM Characterization**

Morphological characteristics of SS/NCS films can be seen in the SEM surface micrograph results of the film surface and also the fracture surface of the starch-chitosan film. Morphological test results can be seen in Figures 4 (1-4) which show the surface morphological structure of biodegradable plastic film samples with different levels of chitosan. In the Figures 4 (1-2), the morphological structure with chitosan amplifiers 0.2 and 0.4 wt% respectively showed white dots that describe the chitosan particle size distribution. The percentage of chitosan 0.6 wt% as shown in Figure 4 (3) shows smoother film surface which shows that the agglomerated chitosan particle distribution is more evenly distributed to the entire surface of the starch matrix. In Figure 4 (4) there are rather large white lumps.
which indicate that chitosan particles are not evenly distributed so that they experience agglomeration clustering at a point.

Based on morphological test results, it can be seen that the surface of biodegradable plastic appears flock. This is due to the temperature and the drying time of the biodegradable film affecting the surface structure of the biodegradable plastic produced. High temperature and drying time will accelerate the evaporation of water vapor contained in the material, so that the particles of material will move up and cause the layers between cells to fuse and result in the appearance of pores on the surface of the film. The drying time and temperature which gives the optimum mechanical properties of starch film are at 50 °C for 6 hours [30]. Morphological analysis with SEM aims to determine the homogeneity of the film, surface structure, cracking and surface smoothness. Analysis results SEM with 3000x magnification can be seen for films with SS/NCS ratio was 1: 6 %wt, show that the resulting is homogeneous. This is indicated with the distribution of chitosan in the form of granules that are uniform and scattered evenly distributed in all parts of the surface.

CONCLUSION

The tensile strength of sago-chitosan starch thermoplastic films with glycerol plasticizers increased with the addition of chitosan, with tensile strength and elongation at break obtained at the composition of sago-chitosan 1: 0.6 wt% reached 2.6 MPa and 53.8 %, respectively. Increased chitosan content will increase tensile strength, but also reduce bioplastic elongation. FTIR spectrum analysis shows that mixing occurs physically. The results of the TGA show that SS/NCS films in the composition of chitosan 0.6 wt% against starch showed a value of 60% weight loss achieved at 385 °C. SEM photo shows the morphology of the formation of air pores due to temperature and film drying time. There is a relationship between the distribution of chitosan on the starch matrix to the mechanical properties and surface quality of the film. The better distribution of chitosan particles on the starch matrix and the optimal temperature and drying time will increasing the mechanical properties of the film. The results of thermal analysis showed an increase in melting point with the addition chitosan content in the film. This study shows that the combination of chitosan on starch films can improve mechanical properties of bioplastics produced and the potential for further research into medical use.

CONFLICT OF INTERESTS

Authors declare that there is no competing interest.

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