THERMOMECHANICAL AND MORPHOLOGY OF BIODEGRADABLE FILM MADE OF TARO STARCH AND CHITOSAN PLASTICIZED BY CASTOR OIL

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ABSTRACT

A biodegradable film made of taro starch and chitosan plasticized by castor oil was created through a casting solvent method. This study examined the influence of taro starch and chitosan composition on the thermo-mechanical and morphological properties of the film. We have successfully obtained a film with a smooth surface and compact structure of taro starch. The results showed that the higher proportion of chitosan in the polymer matrix succeeded in increasing the tensile strength and thermal stability of the film. The addition of chitosan into taro starch samples resulted in reducing the water uptake of the film. The film with a balanced ratio of taro and chitosan starch had excellent water resistance, its absorption of water is the lowest of all compositions.

Keywords: Biodegradable Film, Taro Starch, Chitosan, Castor Oil

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INTRODUCTION

The increasing problem of plastic waste to the environment increases the awareness of researchers to develop biodegradable plastics to replace conventional non-biodegradable petrochemicals plastic materials for various applications. Starch is one of the most widely used biodegradable plastic raw materials due to its multiple advantages, including its biodegradability property, renewable, non-toxic, inexpensive, and abundantly available¹⁻². Starch can be found in various sources of cereals and tubers, such as rice, potatoes, corn, yam, wheat, cassava, and taro³.

Starch is a macromolecule consists of amylose and amylopectin where the relative ratio of each component highly depends on the starch source itself. Corn starch, for example, contains 28 percent of amylose while it is only 17 percent in cassava⁴. Taro starch contains amylose ranging from 22.8 to 35.7 percent depending on its variety⁵. The thermomechanical, film formation and physical properties bioplastics made of starch depend on the ratio of amylose to amylopectin in starch. The higher the proportion of amylose to amylopectin in the starch, the more prominent the properties mentioned above⁶. Some of the flaws of starch-based films are that it is fragile and hydrophilic. People believed that starch is hard to process and has very limited use⁷. Many studies have been conducted to overcome the problem i.e blending the starch with various compounds, such as adding ZnO nanoparticles and montmorillonite⁸, blending cassava starch with Low Linear Density Polyethylene (LLDPE)⁹, adding green tea extract and basil into the cassava starch matrix¹⁰, and forming composites using microcrystalline cellulose¹¹. The other way to improve the thermomechanical properties of starch-based films is by adding chitosan.

Chitosan is the most widely available biopolymer in nature after cellulose. It is extracted by deacetylating the chitin found in the skin of shrimp, crabs and mushrooms. Many recent publications concerning the starch film formation report the addition of chitosan, especially blending chitosan with starch is aimed at

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improvement of various characteristics of starch-based films. Some examples of blending are chitosan-pumpkin starch¹² and bio-composite of corn starch and chitosan¹³. In general, studies reported that the chitosan addition could improve the thermomechanical properties of starch films. However, the films are still rigid and fragile. Therefore, plasticizers are often added to the starch-chitosan matrix to improve the properties. They not only maintain the thermomechanical properties but also reduce the rigidity by increasing the film elasticity which, in turn, expanding the application of starch-based plastic films. Some common plasticizers that employed to increase the elasticity of starch-based films include glycerol, sorbitol, polyol, and essential oils¹⁴⁻¹⁹. However, to date, there is no publication concerning the use of taro starch and chitosan plasticized by castor oil. Thus, the paper reports the characteristics of the plastic films made of taro starch and chitosan using castor oil as the plasticizer. The major objective in this work was to study the influence of taro starch and chitosan composition on the thermo-mechanical and morphological properties of the film.

EXPERIMENTAL

Material and Methods

The taro starch was originated from Aceh, Indonesia. The pretreatment involved blending it to create a fine powder, which was then immersed in distilled water for 36 hours. The precipitate was then dried at 70 °C for 6 hours in an oven. The chitosan was purchased from Tokyo chemical industry co., Ltd. Japan; and the acetic acid was purchased from Sigma-Aldrich.

Film Preparation

The film preparation method refers to Hasan et al²⁰ with a slight modification. The film was prepared by solvent evaporation where taro starch (TS) and chitosan (CH) were initially weighed following the experimental design (Table-1) and later dissolved in 50 mL of 2 percent acetic acid while continuously stirred for 5 h at 70°C. Next, castor oil was added, and the stirring continued for 45 minutes at 70°C¹². The mixture was poured in a petri dish and left at room temperature for one hour prior to solvent evaporation at 75°C for 6-7 h. The film was then removed from the oven and cooled at room temperature.

Table-1: Experimental Design

Sample	Weight of Chitosan (g)	Weight of Taro Starch (g)
CH100	2,0	0,0
CH70TS30	1,4	0,6
CH50TS50	1,0	1,0
CH30TS70	0,6	1,4
TS100	0,0	2,0

Structure Analysis

The structure of the bioplastic films product was analyzed using FTIR and XRD. FTIR spectra were obtained by Perkin Elmer 1800 series spectrometer and scanned in the wavenumbers ranging from 650 to 3900 cm⁻¹. The crystallographic analysis was carried out using a Shimadzu X-ray diffractometer. A thin film was placed at the sample holder and measured by using Cu-K α radiation at the wavelength (λ) of 0.1541 nm, 30 mA of electrical current, and accelerating voltage of 40 kV. The measurement was recorded with the scattering angle ranging from 10° to 80°.

The Analysis of Mechanical Properties

The tensile strength analysis was carried out using IK Tester MCT-2150 and the analysis procedure referred to ASTM 0638. A sample of 4 x 1 cm² was prepared and conditioned beforehand to the standard room temperature and humidity (23 $\pm$ 2°C, RH = 52%) for 24 h and was pulled at the speed of 2 mm/min.

The Analysis of Thermal Properties

Thermal properties examination aimed at determining the film resistance to the thermal contact influence. Thermal properties analysis was measured by the DSC-TGA of Linseis STA PT1600. The film was heated with a rate of 10 °C/min at the temperature between 25°C and 600°C.

Microstructure Analysis Using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM)

SEM was utilized to examine the surface area of the films and AFM was used for topographic analysis. The film samples of 5 x 5 mm² were mounted on gold-coated aluminum stubs. It was then observed using an SEM tool of KYKY-EM3200 (Philip: XL30 model) and an acceleration voltage of 25 kV. The topographic analysis of the film surface was conducted using Multimode AFM.

Water Uptake Test

This test referred to a modified method developed by Martucci et al.²¹ and Chen et al.²². A film of 2 x 2 cm² was weighed before being dipped in deionized water at room temperature. Subsequently, the film was periodically removed from the solution and was weighed to determine the water uptake using equation 1:

$$\text{Water Uptake} = \frac{W - W_o}{W_o} \times 100\% \quad (1)$$

W_o and W respectively represent the initial and final sample weight.

RESULTS AND DISCUSSION

Structural Analysis

Figure-1 shows the FTIR spectra of the functional groups of plastic films made of taro starch, chitosan, and castor oil while Table-2 presents the absorption peak analysis. The FTIR spectra of taro and chitosan starch films showed a typical absorption by functional groups of OH, NH, CH aliphatic, C=O and C-O, in the starch and chitosan molecules with castor oil plasticizer.

Fig.-1: FTIR Spectra of Film Taro Starch/Chitosan

The broad absorption peak of the O-H group in the chitosan molecule was indicated in the area of 3265.33 cm⁻¹, overlapping with the N-H group. The difference between the chitosan and starch was that chitosan had amine group that replaced the -OH group in amylose and amylopectin in starch. Another typical absorption distinguishing the chitosan and starch was the vibration of amine group at 1541.89 cm⁻¹ and the C-N group at 1406.29 cm⁻¹. The FTIR spectra of chitosan/taro starch indicate that no new

functional group in the plastic films of taro starch and chitosan using castor oil as a plasticizer. The only change was the shift of absorption wavenumber by the same functional group. This means that only physical interaction through the hydrogen formation and van der Waals force²³⁻²⁴. The absorption appearance in the area of 1743 cm^{-1} was typical of C=O carbonyl group, and the C-O ester at 1166 cm^{-1} was resulted by free fatty acids of the addition of castor oil as a plasticizer.

Fig. 2 displays the XRD pattern of the taro starch and chitosan film. The diffraction pattern indicates that the taro starch has a semi-crystalline structure, and a broad diffraction peak which is a characteristic of an amorphous structure. There are also some sharp peaks at $2\theta = 13.7^\circ$, 17.5° and 24.5° which are crystalline parts. The scattering peak at 13.7° and 17.5° indicates that taro starch has a Vh type crystal of the amylose complex⁴. The crystals were produced due to the presence of hydrogen bonds between the hydroxyl groups in the starch molecule chain and plasticizers. The peak at 13.7° was the characteristics of B type crystals. This type of crystals can be formed during processing, especially those involving heating²⁵. Similarly, the film made of chitosan formed a B type crystal, which is indicated by the scattering peak at 29.9° . The X-ray diffraction pattern of the sample mixture of starch and chitosan created a wide scattering peak in crystalline scattering region as respect to the interaction between the chains of starch and chitosan molecules that had modified the crystal structure of polymer molecules.

Table-2: Functional Group Analysis of Films by FTIR

Type of Vibration	Wave Number (cm^{-1})		
	TS100	CH100	TS50CH50
O-H stretching	3267.54	3265.33	3599.83
C-H stretching	2926,58	2921.29	2923.56
C=O stretching	1693,93	1743.63	1744,13
-CH ₂ - bending	1335.49	1406.29	1456,14
C-O stretching from the ester group	1145,25	1151,36	1151,15
-NH ₂	-	1636,99	1646,11

Fig.-2: XRD Pattern of the Film

Mechanical Properties Analysis

The test results of the mechanical properties of taro starch and chitosan films are presented in Table-3. The data indicated that tensile strength increased as the chitosan content rising, while the film elongation was more significant in those with a higher proportion of starch. This result is in line with several previous studies²⁶⁻²⁸. The increasing ratio of chitosan in the polymer matrix influences the interaction between polymers through the mechanism of hydrogen bond formation between the amine group of the

chitosan molecule chain and the hydroxyl group of starch molecules²⁹⁻³⁰. On the other hand, the increased chitosan will affect the formation of compact matrix structures resulting in the elongation value of plastic films to decrease³¹. The value is largely determined by how the polymer molecular chain easily moves, the easier the polymer molecule moves, the higher the elongation value.

Table-3: Mechanical Properties Result Test

Sample	Tensile Strength (MPa)	Elongation (%)	Modulus Young (MPa)
TS70CH30	7.470± 1.460	18.905± 2.696	9.802± 1.371
TS50CH50	9.849± 0.153	14.028± 0.685	14.751± 0.562
TS30CH70	11.740± 0.676	17.716± 0.033	8.519± 0.435

Thermal Properties Analysis

Thermal analysis data of the bioplastic films were shown in Fig.-3. The thermal degradation pattern of the bioplastic films seems to occur with a three stages mechanism. The first stage took place in temperature between 32.6 and 62.9 °C, used by the release of bound water molecules in the film matrix and other volatile components, resulting in 4.82 to 10.86 percent weight loss. The second stage occurred at the temperatures between 228.5 and 280 °C with 38.16 to 68.12 percent weight loss, concerning the decomposition of functional groups, i.e. amines and ethanol groups³². The final stage indicated weight loss ranging from 28.55 to 42.41%, concerning the final decomposition due to the polymer molecular chain termination³³.

Fig.-3: TGA Curve of Bioplastic Film from Taro Starch and Chitosan

Microstructure Analysis Using AFM

Figure-4 presents the AFM images of taro and chitosan starch sample films on various compositions, and Table-4 displays the surface roughness values. Figure-4 and the value of surface roughness parameter, Ra and Rq, show that chitosan films have higher surface roughness parameter values than other sample films. The particle size of chitosan contributed to this finding, while the Ra and Rq values of the taro starch and chitosan blend showed almost similar surface roughness that relatively low that can be considered as a smooth surface. Besides, the AFM image also proved that there was no phase separation between starch and chitosan. This finding is in line with the results of the SEM image (Fig.-5). Bonilla³⁴ reported similar

results concerning the surface of a film blending of wheat starch and chitosan. This means that the film produced is solid and as a result of the interaction between the starch and chitosan molecule chain. This data is supported by the data of FTIR measurements as well as thermal and mechanical properties.

Fig.-4: AFM Image of Film TS/CH Topography

Table-4: Roughness Parameter and Water Uptake of the Film

Sample	Roughness Parameter		Water Uptake (percent)
	Ra (nm)	Rq (nm)	
TS100	-	-	-
TS70CH30	210	260	121.13
TS50CH50	220	280	87.80
TS30CH70	150	180	108.40
CH100	730	850	-

Water Uptake Test

The tests were carried out to examine the maximum ability of bioplastic films to absorb water. The data concerning water uptake measurements on bioplastic TS/CH films are shown in Table-4. The data indicates that the sample containing a higher proportion of taro starch had a very high water uptake due to the hydrophilic character of the starch. The film with an equal ratio of taro and chitosan starch had good resistance to water with the lowest water uptake was at 87.8 percent. This is attributed by the interaction between the hydroxyl groups of starch and chitosan to form a hydrophobic matrix structure³⁴. The water uptake value reported in this study is relatively small compared to tapioca films who is ranging from 200 to 500 percent³⁵.

CONCLUSION

The study examined the influence of the composition of taro starch and chitosan additives using castor oil as a plasticizer. Films with a smooth surface have been successfully produced as evidenced by the AFM images (Fig.-3) with the relatively low Ra and Rq values for all films made of taro starch and chitosan. The polymer films produced have a compact structure, indicated by the FTIR spectra and the results of mechanical properties test. The higher proportion of chitosan in the polymer matrix corresponds to the higher tensile strength. However, the film elongation is getting smaller. Thermal stability of the films also improves as chitosan proportion increasing, indicated by a decrease in the weight loss of the samples

compared to taro starch to the temperature above 200 degrees Celsius. Adding chitosan into taro starch samples has successfully reduced film water uptake, the films made of an equal ratio of taro starch and chitosan have good water resistance, showing the lowest water uptake among all compositions.

Fig.-5: SEM Image, A-C: Surface Image of Sample CH100, CH50TS50, TS100, D-F: Fracture Image of Sample CH100, CH50TS50, TS100

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