Development of Poly Lactic Acid/Kitosan Elastomer with Essential Oil Addition to Improved Performance Antibacterial Materials

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Abstract. Consumer demand for high quality food without chemical preservatives is a challenge for the food industry. Therefore, food packaging is needed which can extend the shelf life of food products by protecting from external factors such as microorganisms, moisture, and ultraviolet light. In this study, we synthesize Poly Lactic Acid (PLA) derived from environmentally friendly materials and the addition of chitosan to produce a material that are resistant to the development of microorganisms in food packaging applications which is a new concept innovation of biodegradable active packaging, where packaging is developed this has an ability to reduce or inhibit the growth of microorganisms on the food surface. The results obtained in this study are as follows: the addition of turmeric as essential oil and chitosan have been shown to increase antibacterial activity. Elastomer biofilms produced are able to fight S.aureus and E. coli bacteria on exposure for 72 hours in an open room. They are more effective against gram-positive bacteria when compared to gram-negative. Maximum biofilm tensile strength in 4-gram chitosan variation, 0.3 mL TEO and 0.5 mL glycerol with tensile strength of 40.01 MPa. The maximum decomposition temperature of the biofilm is obtained at 315.74°C with 4 grams chitosan variation, TEO 0.3 mL and 0.5 mL glycerol. The addition of TEO into the chitosan biofilm is also able to bind molecules of chitosan and evenly distributed molecules on the surface.

1. Introduction
PLA or Poly Lactic Acid is an aliphatic linear polyester produced from lactic acid polycondensation. PLA comes from renewable materials, namely starch which is usually obtained from agricultural products, such as cassava, bananas, corn, potatoes, rice, sago and others which are easily digested by microbes (Rola Mansa, et al., 2015). Investors will support PLA mass production with known profitability and the availability of cheap raw materials from agricultural sources in the long term. PLA technology uses renewable raw materials with minimal carbon values. Poly Lactic acid also has properties that support it for packaging both food and non-food because it has good barrier properties especially for moisture and moisture. In addition, if it is used specifically as a package of lactic acid
food (PLA) is included in the GRAS (Generally Recognize as Save) group, so it is safe from the migration of hazardous materials from packaging.

The breakthrough of biodegradable plastic continues to be developed and researched considering the reasons for its use which provide benefits to humans and the environment. Conventional plastic that is often used in the wider community contains carcinogenic substances that can reduce health problems. Therefore, especially for food packaging made from biodegradable plastic material. For example, meat packaging, dairy products, or bread using film and foam forms, can also be used in bottles and disposable cups for packing water, juice and other drinks. In food packaging, antimicrobials affect the nature of blocking bacteria-exposed material, so that it can increase product expiration and quality.

Chitosan is a polysaccharide obtained by deacetylation of chitin and has many applications because of its excellent oxygen blocking, antimicrobial, biodegradation, biocompatibility and non-toxicity properties. One of the important characteristics of chitosan is the ability to interact with cellular cells and lysoenzymes that are able to degrade microbes in vivo. The functional group contained in chitosan also allows for modification of diverse chemical bonds including reactions with cross-bonding intermediates, thus allowing their use as a mixture of bioplastics, namely plastics which can be degraded and do not pollute the environment (Skurtys et al., 2009).

To further enhance the antimicrobial activity of many herbs and extracts which are used as additional ingredients in chitosan film. The composition, structure and functional groups of the extract play an important role in determining antimicrobial activity. Usually compounds with the most effective phenolic groups include turmeric. Turmeric is one of the active substances against S. aureus and E. coli because phenolic compounds contained in turmeric such as curcuminoids. Essential oils, alkaloids, curcumin, turmerol and veleric acid are the compounds most associated with antimicrobial activity in turmeric (Nisar, 2015). In addition to the antibacterial properties of essential oils or their components has been shown to show antimitotic, antitoxigenic and antiphrastic properties, these characteristics may be related to the function of these compounds in plants (Mitelut, et al, 2015).

With the existence of these problems, in this study aims to form PLA / Chitosan elastomer biofilm with the addition of essential oil from turmeric to create a food plastic packaging material that is effective and has resistance to microbial contamination.

2. Material and Method

2.1. Material

The main PLA material used was obtained from powdered Natre Work Co. The material used for making chitosan comes from waste, namely shrimp skin. While the additional ingredients used are turmeric oil from turmeric which is the result of local plantations. The plasticizer used to form elastomers is food grade glycerol and bacteria used for antibacterial tests are Staphylococcus aureus and E. coli. A set of extraction tools. Magnetic stirrer, Oven, Hot plate, Sieve, Filter paper, Glass Beaker, Stirrer and Measuring cup.

2.2. Method

2.2.1. Preparation of Chitosan

100 grams of shrimp skin is cleaned with clean water and boiled for 1 hour, then washed and dried in an oven for 2 hours at 160oC, then pureed into powder. The demineralization stage of shrimp skin powder uses HCl with concentrations ranging from 0.25-2 M (ratio 1:10 (b / v)) to the heating and stirring process for 1-2 hours. Then it is filtered and dried for 24 hours. Deproteinization steps use 0.5-2M NaOH solution with a soaking time for 10-400 minutes at a temperature of 200C-100oC. Then filtered, washed with distilled water and dried until thoroughly dried, producing chitin powder. The
decolorization stage uses acetone ratio of 1:10 (b / v) soaking for 10 minutes. Dry for 2 hours at 28°C. Bleaching chitin powder with 0.315% NaOCl for 5 minutes. Deacetylation stage of chitin powder uses 50% NaOH with a ratio of 1:20 (b / v) heated for 3-5 hours at a temperature of 80-100°C, washed with aquadest: alcohol (80%), strain and then dried for 24 hours produced chitosan powder.

2.2.2. Turmeric Extraction

20 grams of turmeric are mashed with a pounder, then put the soft turmeric into the socket. The isolation process of turmeric oil by adding 200 mL of ethanol for several hours until no condensate falls again and the temperature is maintained at 78°C. The isolation of turmeric is concentrated again by distillation. Turmeric essential oil is produced.

2.2.3. Preparation POLY LACTIC ACID / KITOSAN ELASTOMER

2 grams of chitosan powder was dissolved in 30 mL of 1% acetic acid then added 70 mL of aquadest. Then the PLA powder is added with a little glycerol. The solution is homogenized with stirrer at 70°C for 60 minutes until the film solution is suspended completely. In the final treatment, the film solution is added with turmeric essential oil. Then the film solution is homogenized for 30 minutes with a magnetic stirrer. The film solution is poured on a mold that has been cleaned with 96% ethanol. The film is dried for 3 days or until it is completely dry. The dried film is then removed from the mold. Dry films are ready for analysis.

3. Characterization Technique

3.1. Characterization of Mechanical Properties (Tensile Strength)

2 grams of chitosan powder were dissolved in 30 mL of 1% acetic acid then 70 mL of aquadest were added. Then PLA powder is added with a little glycerol. The solution is homogenized with stirrer at 70°C for 60 minutes until the film solution is completely suspended. In the last treatment, the film solution was added with turmeric essential oil. Then the film solution was homogenized for 30 minutes with a magnetic stirrer. The film solution is poured on the mold that has been cleaned with 96% ethanol. The film is dried for 3 days or until it is completely dry. The dried film is then removed from the mold. The dried film is ready for analysis.

3.2. FT-IR Characterization

FT-IR (Fourier Transform InfraRed) is one of the characterization methods of chemical properties using infrared spectroscopy. The sample before modification was tested at an infrared wavelength range of 600 cm⁻¹ to 4000 cm⁻¹. KBr is used as back ground in powder sample analysis (solid). Whereas 5% by weight of the sample was homogenized with 95% KBr using mortar and then pressed in pell.

3.3. SEM Characteristics (Scanning Electron Microscopy)

SEM analysis aims to determine the morphology of solids. Scanning Electron Microscope is a type of electron microscope that describes the surface of the sample through a scan process using high energy emission from electrons in a raster scan pattern. Electrons interact with atoms that will make the sample generate signals and provide information about the surface of the sample topography, composition and other properties such as electrical conductivity.
4. Result and Discussion

4.1. Tensile Strength of PLA/Chitosan Elastomer

Tensile test is the simplest and most basic mechanical test, and uses international standards for testing. Tensile test is carried out using a sample based on the size of ASTM D-638 type 4 standard for plastic. The sample of the tensile test (specimen) with a length of 6,000 mm, thickness of 0.500 mm and with a given load of 1.0 mm / s obtained the test results as shown in Figure 4.2 below.

![Graphs showing tensile strength analysis](image)

**Figure 1.** The results of tensile test analysis on variations of chitosan 2 grams, TEO 0 mL and glycerol 0 mL / biofilm 1 (a), 3 grams chitosan, TEO 0.3 mL and glycerol 0.5 mL / biofilm 2 (b) and 4 grams chitosan, TEO 0.3 mL and glycerol 0.5 mL / biofilm 3 (c).

Based on Figure 4.7 can be seen clearly the comparison of the three samples that have been tested. Samples that have the greatest strength are samples with 4 grams chitosan variation, TEO 0.3 mL and glycerol 0.5 mL / biofilm 3 with tensile strength of 40.01 MPa. This occurs because the mass of chitosan is greater than that of biofilm 1 with a tensile strength of 23.34 MPa and biofilm 2 with a tensile strength of 19.28 MPa. In addition to being antibacterial, chitosan is also an amplifier from film materials, so biofilm 3 has the greatest tensile strength.

Adding large amounts of glycerol will reduce the tensile strength of the biofilm. This is because of the nature of glycerol as a plasticizer for biofilms by reducing the strength of the biofilm itself. So that the biofilm produced breaks faster when tensile tested.
Plasticizer reduces the strength of inter and intra molecular and increases mobility and flexibility of film. The more use of plasticizers will increase solubility. The type and concentration of plasticizers will affect the solubility of starch-based films. The more use of plasticizers, the solubility will also increase.

4.2. **FT-IR Analysis Results PLA / Chitosan Elastomer Biofilm**

Biofilm functional group analysis using Fourier Transform Infrared (FTIR). Based on the results of the analysis there is a biofilm sample of 1 O-H group whose wavelength is 3649.32 cm⁻¹ and N-H wavelength 3498.87 cm⁻¹. It can be seen clearly that in biofilm 2 and biofilm 3 it experienced a significant decrease. This occurs due to the addition of TEO and glycerol. In biofilms 2 O-H groups are wavelength 3647.39 cm⁻¹ and N-H wavelengths are 3493.08 cm⁻¹. As well as in biofilm 3 O-H groups with a wavelength of 3643.33 cm⁻¹ and N-H at a wavelength of 3494.08 cm⁻¹ as seen in the figure below.

![Image of FT-IR analysis results](image_url)

**Figure 2.** The results of tensile test analysis on variations of chitosan 2 grams, TEO 0 mL and glycerol 0 mL / biofilm 1 (), chitosan 3 grams, TEO 0.3 mL and glycerol 0.5 mL / biofilm 2 () and chitosan 4 grams, TEO 0.3 mL and glycerol 0.5 mL / biofilm 3 ()

4.3. **Scanning Electron Microscopy (SEM) analysis on biofilms**

Scanning Electron Microscopy (SEM) works based on the principle of gun electrons producing electron beams and accelerating with the anode. Then the magnetic lens focuses the electrons towards the sample. The focused electron beam scans the entire sample by being directed by the scanner coil. When electrons hit the sample, the sample will emit new electrons that will be received by the detector and sent to the monitor.
Figure 3. SEM analysis results on variations of chitosan 2 grams, TEO 0 mL and glycerol 0 mL / biofilm 1 (a), chitosan 3 grams, TEO 0.3 mL and glycerol 0.5 mL / biofilm 2 (b) and chitosan 4 grams, TEO 0.3 mL and glycerol 0.5 mL / biofilm 3 (c).

Based on Figure 4.11, the results of SEM analysis on biofilm 1 showed that chitosan particles were still spaced and the surface morphology of biofilm still had empty space because there was no addition of glycerol (binder). In the biofilm 2 particles chitosan starts to spread evenly and has a tight structure due to the addition of TEO and glycerol. And in 3 biofilms, chitosan was spread evenly on the surface, but had a thinner structure due to the addition of less glycerol compared to biofilm 2.

The addition of TEO to biofilms is proven to be able to bind the biopolymer element in chitosan to become a good bond and produce a complex biofilm surface. The interaction of the two biopolymer elements is an attraction that can replace the inorganic material of the filmmaker.

5. Conclusion
The addition of turmeric as essential oil and chitosan have been shown to increase antibacterial activity. Elastomer biofilms produced are able to fight S. aureus and E. coli bacteria on exposure for 72 hours in an open room. Maximum biofilm tensile strength in 4-gram chitosan variation, 0.3 mL TEO and 0.5 mL / biofilm glycerol with tensile strength of 40.01 MPa. The maximum decomposition temperature of the biofilm is obtained at 315.74°C with 4 grams chitosan variation, TEO 0.3 mL and 0.5 mL glycerol. The addition of TEO into the chitosan biofilm is also able to bind molecules of chitosan and evenly distributed molecules on the surface.
References

[1] Rola Mansa, et al., 2015. Preparation and characterization of novel bentonit/PLA nanocomposites. "Applied Bentonit Science, 115, 87-96

[2] Fernanda, et al., 2013, “Thermoplastic starch/poly(lactic acid) sheets coated with cross-linked kitosan”, Polymer Testing, 32, 94–98)

[3] Lee Tin Sin, et al., 2013. Polylactic Acid, PLA Biopolymer Technology and Application. USA: Elsevier

[4] J.P. Mofokeng, et al., 2015. "Morphology and thermal degradation studies of melt-mixed poly(lactic acid) (PLA)/poly(e-caprolactone) (PCL) biodegradable polymer blend nanocomposites with TiO2 as filler. Polymer Testing, 45, 93-100

[5] Boukeur, et al., 2015. "Synergy between fillers in organomontmorillonite/graphene–PLA nanocomposites." Applied Bentonit Science, 116-117, 69-77).

[6] A.M. Motawie, et al., 2014. "Electrophysical characteristics of polyurethane / organo-bentonite nanocomposites." Egyptian Journal of Petroleum, 23, 379–387

[7] Skurtys et al., 2009. Food Hydrocolloid Edible Films and Coatings. Department of Food Science and Technology, Universidad de Santiago de Chile. Chile. pp 34