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THE EFFECT OF ADDING CHITOSAN ON THE MECHANICAL PROPERTIES OF ECO-FRIENDLY PLASTICS BASED ON PLA/PCL

Dinda Alfatasya[1]*, Suryani[1]
[1]Chemical Engineering, Lhokseumawe State Polytechnic, Jl. Banda Aceh-Medan Km. 280.3, Buketrata, Mosque
*E-mail:dindaalfatasya@gmail.com

ABSTRACT

Research into making eco-friendly plastic has been developed because it is environmentally friendly and renewable. In this research, eco-friendly plastic was made from Polylactic Acid (PLA) and Polycaprolactone (PCL) with the addition of chitosan as a filler. The aim of this research is to study and determine the effect of mixing variations in PLA/PCL/chitosan composition on the mechanical properties of eco-friendly plastic using a hot press at a temperature of 200 0C for 1 hour. The PLA/PCL variations are 2/8 g, 3/7 g, 5/5 g, 7/3 g and 8/2 g while the chitosan composition is 0.2 g, 0.3 g, 0.4 g, 0, 5 g and 0.6 g. The characteristics of eco-friendly plastic can be seen through biodegradation tests, tensile strength tests, elongation tests, functional group tests and plastic film morphology tests. The results of the characterization of eco-friendly plastic with optimal performance are a composition of PLA/PCL/Chitosan 8/2/0.6 grams which produces 38.8% degradation percentage, a tensile strength value of 42.53 MPa with a composition of PLA/PCL/Chitosan 8 /2/0.4 grams, elongation percentage of 6.96% with a PLA/PCL/Chitosan composition of 8/2/0.2 grams. Meanwhile, the functional groups contained are the N – H, C – H, C = O and C – O groups. The results of the identification of functional groups show that no new functional groups are formed, but only a mixing process without any reaction in the constituent materials. Based on the results of the morphology test, it shows that the sample has a smooth surface. However, there is still chitosan that does not dissolve because the mixing process is not homogeneous.

***Keywords**:* Chitosan, Polycaprolactone (PCL), Polylactic Acid (PLA)

INTRODUCTION

The reduced availability of fossil resources and the increasing concentration of carbon dioxide in the atmosphere have become a concern for the development of bio-based plastics. This type of plastic derived from petrochemical polymers is a very popular plastic to use because it has several advantages. However, this plastic polymer cannot be destroyed naturally (non-biodegradable). Thus causing environmental pollution. One of the biopolymers that has great potential to be developed as a replacement for conventional plastic is Polylactic Acid (PLA). PLA is a type of plastic produced from renewable natural materials such as starch through lactic acid fermentation. PLA is a biopolymer that is renewable and biodegradable. PLA polymer has strong, transparent and waterproof properties. Apart from that, the weakness of PLA is that it is stiff and has low permeability properties. To improve the biocomposite properties of PLA, several other polymers are added with the aim of reducing deficiencies and improving the character of the biocomposite. Modification of PLA by blending with other polymers can increase the mechanical properties in the form of tensile strength, elongation at break and degradation of PLA (Rahmayetty, 2018).

One other polymer that has the potential to improve the characteristics of PLA is Polycaprolactone (PCL). PCL is an aliphatic polyester that is biocompatible and has good permeability. Apart from that, PCL also has high crystallinity, low degradation rate and low melting point so it has poor mechanical properties. However, with its relatively low melting point, it can be processed easily using conventional methods. PLA and PCL have the same properties, namely they are hydrophobic and can be degraded well. However, these two polymers also have different physical properties, namely PLA is transparent, very flexible and strong. Meanwhile, PCL is not transparent, very brittle and stiff so it breaks easily. If these two compounds are combined, the resulting polymer can improve the shortcomings of the properties of the original polymer (Eti Indarti, 2020).

Poly Lactic Acid was first produced in 1932 by Wallace Carothers who produced low molecular weight PLA and heated lactic acid under vacuum conditions. Poly Lactic Acid with the chemical formula (CH3CHOHCOOH)n is a plastic polymer that is biodegradable, thermoplastic and is an aliphatic polyester produced from natural raw materials. PLA can be formed through the esterification process of lactic acid which is obtained by fermentation by bacteria using starch or simple sugar substrates. Lactic acid is the simplest hydroxy acid compound consisting of an asymmetric carbon atom. This acid can be produced from carbohydrate fermentation by bacteria in the form of L-lactic acid or D-lactic acid (T Rihayat, 2019).

In 1973, a semicrystalline aliphatic polyester, namely Polycaprolactone (PCL), was discovered. Polycaprolactone with the chemical formula C6H10O2 is an aliphatic polyester which is biodegradable, biocompatible and has good permeability. PCL is an ideal type of polymer because it is non-toxic, can be absorbed after implantation and has good mechanical properties. This polyester is resistant to water, oil, solvents and chlorine, has low viscosity and is easy to shape. Apart from that, PCL also has several disadvantages, namely that it is hydrophobic, the biodegradation process is a little slow and it is sensitive to microbial activity. PCL has a melting point of around 60 ºC and a glass transition temperature (Tg) of -60 ºC. With this viscosity and melting point, PCL can be combined with other polymers and can also be processed easily. The nature of PCL, which is permeable to low molecular weight drugs (<400 Da) and non-toxic, makes PCL widely used in the biomedical field, such as surgical sutures and as a control matrix for drug delivery systems (Ridwan, 2018).

Polycaprolactone can be produced via two methods, namely ring opening polymerization (ROP) of e-caprolactone and polycondensation of 6 hydroxyhexanoic acid. The ROP method is more often used because it produces polymers with lower polydispersity index (PDI) values and higher molecular weights and better mechanical properties. PCL is usually synthesized without a catalyst using ring-opening polymerization. However, its low melting point results in high production costs and commercial limitations. The use of PCL is mainly in the biomedical and pharmaceutical fields, therefore it must be produced carefully to avoid the presence of toxic compounds that can cause side effects on the user or organism (Suryani, 2022).

PCL's ability to combine with other polymers through a blending process can overcome the shortcomings of these polymers. Blending is a physical mixing process between two or more types of polymers that have different structures and do not form covalent bonds between their components. The aim of this blending is the development of new biomaterials with a combination of properties that cannot be achieved by individual polymers. So as to obtain the desired material properties and adapt them to needs. Polyblend between PLA and PCL is expected to produce compatible polymers (Yessy Warastuti, 2017).

Chitosan concentration that is too high will reduce the tensile strength value because chitosan has a linear polymer chain structure. Where the linear chain structure tends to form a crystalline phase because it is able to arrange ordered polymer molecules. The crystalline phase provides strength, stiffness and hardness so that it can cause the plastic film to break more easily (Nur Indah Sari, 2022). PLA and

PCL in this study were produced from corn starch. Bioplastics made from starch have disadvantages, namely the low tensile strength of the bioplastics produced and the high level of water absorption. Therefore, starch-based bioplastics need to be mixed with chitosan (biopolymer) which can reduce the level of water absorption because it is hydrophobic. Because corn starch has stiff and brittle properties, chitosan is used as a reinforcement for biodegradable plastic (Angga Dwina Putra, 2019).

Table 1.1 Mechanical Properties of Biodegradable Plastics According to SNI 7818:2014

No.	Uraian	Persyaratan
1	Kuat tarik (N/mm^2)	Minimal 13,7 (13,7 – 139,74)
2	Kemuluran (%)	400 - 1120

Source: Ardimas Fauzan Huwaidi, 2022

Research Urgency

The development of environmentally friendly plastic technology is currently experiencing very rapid progress as well as research regarding the effect of adding fillers, especially the type of chitosan filler which has been widely used. Based on previous research, in general, we are developing the mechanical properties, morphology and biodegrability of bioplastics to replace conventional plastics by varying the composition of the raw materials and fillers used. However, the mechanical properties, morphology and biodegradability produced are inconsistent along with differences in the type and composition of the raw materials and fillers used, so these three variables are the main concern of researchers to make more representative bioplastics (Ummy Aisyah Rochaeni, 2017).

Biodegradable plastic packaging technology is one of the efforts made to get out of the problem of using non-degradable plastic packaging (conventional plastic), due to decreasing petroleum reserves, awareness and concern for the environment and health risks. Indonesia, as a country rich in natural resources (agricultural products), has the potential to produce various biopolymer materials, so biodegradable plastic packaging technology has good prospects. The price of biodegradable plastic is more expensive than conventional plastic, partly because production capacity is not yet optimal. Apart from that, there are no regulations regarding restrictions on the use of conventional plastic (Elmi Kamsiati, 2017).

Chitosan is a chitin compound that has had its acetyl group removed so that a free amine group remains. This causes chitosan to be polycationic. The natural polycationic (positively charged) nature of chitosan can inhibit the metabolism of damaging microorganisms and can coat the preserved product. The chitin compound can be isolated from the shells of crustacean animals such as shrimp shells. Shrimp shells contain 25-40% protein, 45-50% calcium carbonate, and 15-20% chitin (Ani Riani Kusmiati, 2020).

Based on the advantages of the PLA/PCL polymer and several studies, the addition of filler to the PLA and PCL matrix does not produce strong plastic characteristics. So in this research, PLA/PCL will be mixed with a variety of chitosan to improve the mechanical properties and biodegradability by mixing the polymer without reducing its quality.

Research Objectives, Benefits and Limitations

The types of biopolymers that can be used as substitutes for conventional plastic are Poly Lactic Acid (PLA) and Polycaprolactone due to their biodegradability so they are classified as biodegradable polymers. The prospect of developing PLA/PCL in Indonesia is estimated to be very potential, because Indonesia is rich in natural resources, especially starch as a basic ingredient for making PLA/PCL. High sources of starch can come from various types of plants such as corn, potatoes, cassava, cassava, sweet potatoes, sago and so on which can be obtained in abundance throughout the year. (T Rihayat, 2019).

The aim of this research is to determine the effect of the PLA/PCL/chitosan ratio on the mechanical properties of eco-friendly plastic. It is hoped that this material variation can produce biodegradable plastic which is produced from natural biopolymers and can be used to replace non-biodegradable plastic so that it will reduce environmental damage, namely polymer blending Polylactic Acid (PLA) and Polycaprolactone (PCL) with the addition of chitosan.

The limitation of this research is that the heating and mixing process of the plastic constituent materials, namely PLA/PCL/chitosan, is not perfect. Mixing the materials evenly can produce good plastic film characteristics. Another technology that can be used to ensure good heating and mixing is an extruder machine. This results in a perfect heating and mixing process. The resulting product will undergo several tests to determine the characteristics of the plastic film produced.

RESEARCH METHODS

Research methodology

The first stage of making this plastic film is by mixing PLA, PCL and chitosan polymers in ASTM D-638 Standard specimen molds coated with aluminum foil using a hot press at a melting temperature of 200 ºC for 1 hour. The PLA/PCL polymer ratio is mixed with various variations of chitosan where each mixture weighs 10 grams for each sample. The biocomposite that has been formed is left at room temperature until completely solidified and then subjected to tensile strength, SEM, FTIR and biodegradation tests.

Figure 1.1 Hot Press Machine

RESULTS AND DISCUSSION

This discussion includes the results of analysis carried out in research on making eco-friendly plastic. The analysis carried out includes mechanical properties analysis consisting of tensile strength and elongation analysis, biodegradation analysis, functional group analysis and morphological analysis.

Analisa Biodegradasi *Eco-Friendly Plastic*

Biodegradability is the main goal of making eco-friendly plastic based on biopolymers. The aim of the biodegradation test is to determine whether a material can be properly degraded in the environment so that it can be classified as an environmentally friendly polymer. In this research, the biodegradation process was carried out under aerobic conditions with the help of bacteria and fungi found in the soil for 7 days, because we wanted to see changes in a short time, whether there was a reduction in the mass of the planted samples.

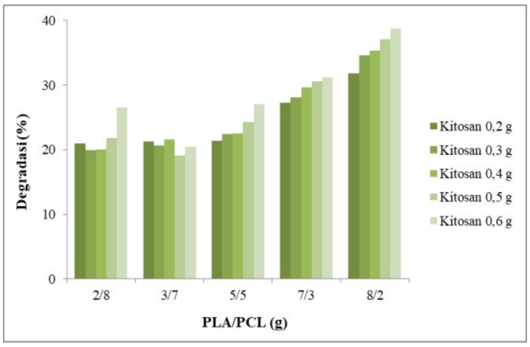

Figure 1.2 Graph of the Relationship between PLA/PCL/Chitosan Composition and Percent Degradation

From the graph above, it can be seen that the highest value obtained for the degradation percentage was with the composition PLA/PCL/chitosan 8/2/0.6 grams, namely 38.8%. The results obtained showed that the mass was lost after the plastic film was embedded in the soil for 1 week. Increasing the composition of chitosan can increase the amount of mass lost due to the degradation process, thereby increasing the percentage of plastic film degradation. Apart from that, the more PLA the composition, the better the biodegradation process will occur, this shows that PLA has good degradability. Meanwhile, using more PCL composition than PLA will give an irregular degradation percentage along with the addition of chitosan. PLA and PCL are biopolymers that have the ability to degrade biologically in the soil because they are obtained from renewable sources, namely produced from starch. So the process of blending PLA and PCL with the best composition can increase the percentage of plastic film degradation.

Effect of PLA/PCL/Chitosan Ratio on Tensile Strength of Eco-Friendly Plastic

The tensile strength analysis aims to determine the effect of variations in Polylactic Acid (PLA), Polycaprolactone (PCL) and chitosan on the tensile strength value and percent elongation of the plastic film produced. Tensile strength analysis was taken from the 3 (three) best samples from the biodegradation test, namely with a composition of 8/2 grams of PLA/PCL and 0.2 grams of chitosan; 0.4 and 0.6 grams.

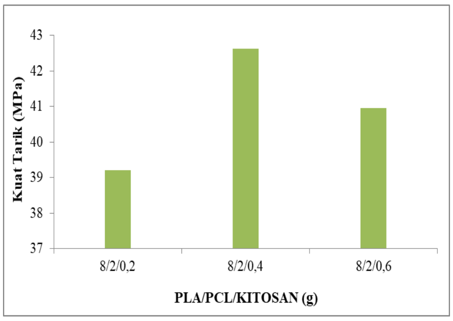

Figure 1.3 Graph of the Relationship between PLA/PCL/Chitosan Composition and Tensile Strength

This graph shows that the tensile strength of the plastic film produced has increased with the addition of chitosan from a composition of 0.2 to 0.4 grams, namely 39.20 to 42.63 MPa. The results obtained have reached the SNI value for the tensile strength of Eco-Friendly plastic. In general, chitosan functions as a reinforcing material which is mixed into plastic film samples. However, along with the addition of chitosan at a concentration of 0.6 grams, it turned out that the tensile strength of the plastic film decreased to 40.65. It can be seen that the highest tensile strength value is found in the 0.4 gram chitosan formulation. This shows that the addition of chitosan cannot continuously increase the tensile strength value of plastic film. This decrease in tensile strength is because chitosan has a linear polymer chain structure, where the linear chain structure tends to form a crystalline phase because it is able to arrange ordered polymer molecules. The crystalline phase provides strength, stiffness and hardness so that it can cause the plastic film to break more easily (Nur Indah Sari, 2022). Apart from that, this is also due to the saturated conditions in the bioplastic matrix, so that the filler added in large concentrations cannot be distributed and mixed with the matrix.

Apart from that, the composition of PLA and PCL also affects the tensile strength value. In this research, the tensile strength test was carried out, namely the composition of PLA/PCL (8/2) grams. According to research conducted by Fontelny, 2019, the optimal composition for the PLA/PCL mixture is 8/2 (w/w) resulting in a tensile strength value of 38 MPa. A PLA/PCL mixture with this composition can maintain the high stiffness of the PLA matrix and the PCL concentration is sufficient to achieve high toughness.

Effect of PLA/PCL/Chitosan Ratio on Percent Elongation of Eco-Friendly Plastic

The percent elongation test is a test carried out simultaneously with the tensile strength test, where the results of this test will obtain the percentage of plasticity properties and the maximum change in length when stretching occurs until the plastic film sample breaks. With this elongation test, the level of increase in length of the material can be determined.

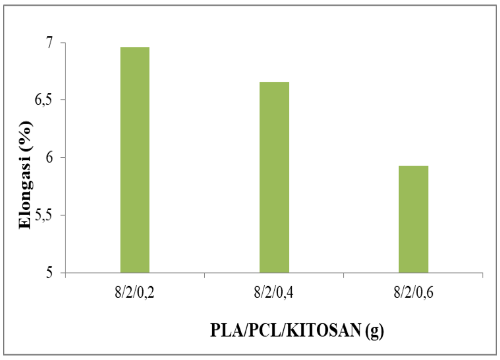

Figure 1.4 Graph of the Relationship between PLA/PCL/Chitosan Composition and Elongation

Based on the graph above, it can be seen that as the concentration of chitosan increases, the percentage of elongation decreases, this is directly proportional to the tensile strength value, meaning that the resulting plastic film breaks more easily. This decrease in elasticity is caused by the decreasing bond distance between molecules as they pass the saturation point, thereby reducing the intermolecular forces between chains. In this test, the highest elongation percentage was obtained with a chitosan composition of 0.2 grams (2% w/w) producing an elongation of 6.96%.

Morphological Analysis of Eco-Friendly Plastic

Morphological testing is an additional test in this research which aims to support the best sample results from the biodegradation test. This test aims to see the morphological structure of the PLA/PCL/chitosan blending process biocomposite using a microscope that relies on electron beams to describe the surface shape of the material being analyzed. The following is an image of the results of analysis using a Scanning Electron Microscopy (SEM) tool.

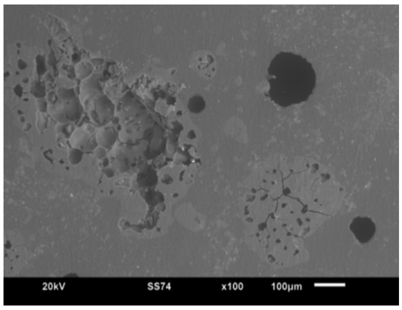

Figure 1.5 Morphology Test Results for PLA/PCL/Chitosan Samples (8/2/0.4) grams

The image above shows the morphological structure of the eco-friendly plastic film at 100x magnification. These results show that the surface structure of the sample still has a few white dots because the chitosan has not dissolved evenly. In this image you can also see bubbles scattered on the surface of the plastic film. This shows that the blending process between Polylactic Acid (PLA) and Polycaprolactone (PCL) was not perfect because the heating process was not good. The results obtained show that the sample has a smooth surface. However, there is still chitosan that does not dissolve because the mixing process is not homogeneous. This is because the heating and mixing process between chitosan and matrix is still not optimal. If the heating and stirring process is perfect, it will be easy to combine the chitosan particles with the matrix, thereby strengthening the resulting plastic film.

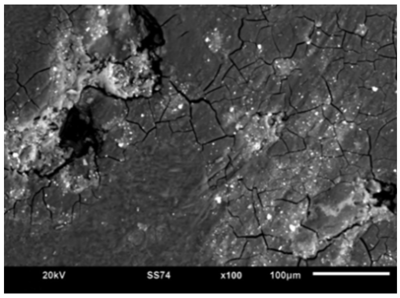

Figure 1.6 Morphology Test Results for PLA/PCL/Chitosan Samples (8/2/0.6) grams

The image shows the morphological structure of the eco-friendly plastic film at 100x magnification. These results show that the surface structure of the sample has white dots. This identifies that the chitosan particles experience agglomeration in clusters, causing the distribution of chitosan in the plastic film layer to not spread evenly due to the absence of proper treatment such as heating and stirring processes between chitosan and the matrix which causes uneven distribution of chitosan. If there is proper treatment such as good stirring during the mixing process at the gelatinization temperature, it will easily combine the chitosan particles, thereby strengthening the plastic film. In this image you can also see bubbles scattered on the surface of the plastic film. This shows that the blending process between Polylactic Acid (PLA) and Polycaprolactone (PCL) was not perfect because the heating process was not good. These results show that the sample has a less smooth surface, forming lumpy aggregates and a cracked plastic film surface due to poor bond formation between the matrix and filler. Pamilia Coniwanti's research, 2014, showed that the surface of the plastic film was not smooth because there was poor treatment during the stirring and heating process.

Functional Group Analysis of Eco-Friendly Plastic Compounds

This functional group analysis was carried out to identify the functional groups contained in plastic film samples using the Fourier Transform Infrared (FT-IR) tool. This analysis is based on the wavelength of the characteristic peaks of a sample. The wavelength of these peaks indicates the presence of certain functional groups in the sample because each functional group has characteristic peaks that are specific to certain functional groups. The spectrum of FT-IR analysis results can be seen in the image below.

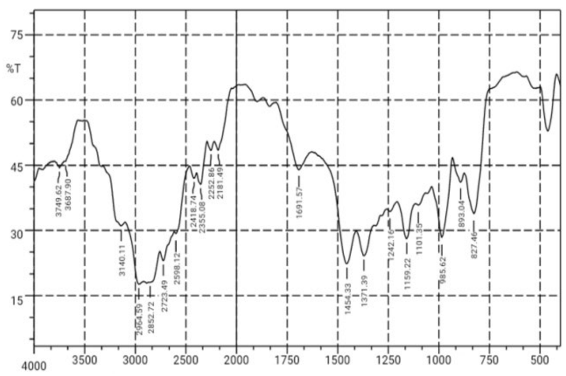

Figure 1.7 FT-IR Spectrum of PLA/PCL/Chitosan Sample (8/2/0.4) grams

The picture above shows the results of a blending sample of Polylactic Acid (PLA)/Polycaprolactone (PCL)/chitosan 8/2/0.4 grams which is the best result from research that has been carried out, that there is absorption at 3140.11 cm-1, which is proven to exist. N – H group, in accordance with the literature that the absorption width that appears in the 3300 – 3500 area is the absorption of the N – H group. Meanwhile in the 3000 – 2850 area there is an absorption of 2964.59 cm-1 where there is a C – H group, in the 2500 – 2000 area there is The absorption is at 2355.08 cm-1 where there is a C = O group and in the 1500 - 1250 area there is an absorption at 1454.33 cm-1 where there is a C - O group. These results indicate the functional groups that make up cellulose.

The results of the identification of functional groups show that all of the functional groups that appear are the same as the basic materials used, namely Polylactic Acid (PLA), Polycaprolactone (PCL) and chitosan, which do not show the formation of new functional groups. So it can be concluded that the process of making eco-friendly plastic is just a mixing process without any reaction to the constituent materials. This causes the resulting plastic biocomposite to still have the properties of its constituent components.

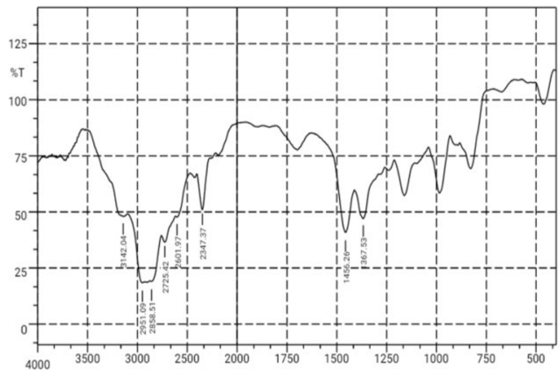

Figure 1.8 FT-IR Spectrum of PLA/PCL/Chitosan Sample (8/2/0.6) grams

From the picture above, it shows the results of the Polylactic Acid (PLA)/Polycaprolactone (PCL)/chitosan 8/2/0.6 gram blending sample which was carried out that there was an absorption at 3142.04cm-1, which was proven by the presence of an N – H group, in accordance with literature shows that the absorption width that appears in the 3300 - 3500 area is N - H group absorption. Meanwhile, in the 3000 - 2850 area there is an absorption of 2951.09cm-1 where there is a C - H group, in the 2500 - 2000 area there is an absorption of 2347.37cm-1 where there is a C = O group and in the 1500 - 1250 area there is absorption at 1456.26cm-1 where there is a C - O group. These results indicate the functional groups that make up cellulose. In research by Suryani, et al. 2022, in making environmentally friendly bioplastics from PLA/PCL with the addition of catechin and chitosan, similar results were obtained, namely that there were N – H, C – H, C = O and C – O groups formed in the bioplastic.

The results of the functional group identification show that all of the functional groups that appear are the same as the basic materials used, namely Polylactic Acid (PLA), Polycaprolactone (PCL) and chitosan do not show the formation of new functional groups. However, it is only a mixing process without any reaction to the constituent ingredients. This causes the resulting plastic biocomposite to still have the properties of its constituent components.

CONCLUSION

A greater ratio of Polylactic Acid (PLA) to Polycaprolactone (PCL) can increase the degradation percentage and tensile strength value of plastic film, because it can maintain matrix stiffness so as to achieve high toughness. The best composition was obtained at a PLA/PCL ratio of 8/2 grams. The addition of chitosan will increase the tensile strength value of plastic film. However, if the addition is greater it will also reduce the tensile strength and elongation percentage of the plastic film. The characteristics of the Eco-Friendly plastic produced have good mechanical properties in the form of a tensile strength value of 42.63 MPa and an elongation percentage of 6.96%.

REFERENCE

Coniwanti, Pamilia., Laila, Linda., Alfira, Mardiyah Rizka. 2014. Making Biodegradable Plastic Film from Corn Starch with the Addition of Chitosan and Glycerol Plasticizer. Journal of Chemical Engineering. Sriwijaya University. 4 (20) : 22-30

Darni, Y., Lismeri, L., Hanif, M., Sarkowi, S., & Evaniya, D. S. (2020). Increasing the Tensile Strength of Bioplastics with Microfibrillated Cellulose Filler from Sorghum Stems. Indonesian Journal of Chemical Engineering, 18(2), 37-41.

Fontelny, I., Ujcic, A., Fambri, L., & Slouf, M. (2019). Phase structure, compatibility, and toughness of PLA/PCL blends: A review. Frounties in Materials, 6, 206.

Huwaidi, A. F., & Supriyo, E. (2022). Making Biodegradable Plastic Sorbitol Plasticized Corn Starch with Cellulose Filler from Sugarcane Bagasse. Equilibrium Journal of Chemical Engineering, 6(1), 45-49.

Indarti, E., Marlita, A. S., & Zaidiyah, Z. (2020). Transparency and Permeability Properties of Bionanocomposite Film of

Polylactic Acid and Polycaprolactone, and Nanocrystalline Cellulose as a Filler. Journal of Agricultural Products Technology & Industry, 25(2), 81-89.

Kusmiati, A. R., & Hayati, N. (2020). Utilization of Chitosan from Shrimp Shells as an Adsorbent for the Heavy Metal Pb in Pharmaceutical Chemistry Practical Waste. Indonesian Journal of Laboratory, 3(1), 6-14.

Putra, A. D., Amri, I., & Irdoni, I. Synthesis of Bioplastics Based on Corn Starch with the Addition of Pineapple Leaf Fiber Cellulose Filler (Ananas cosmosus). Student Online Journal (JOM) Engineering and Science, 6, 1-8.

Rahmayetty, R., Kanani, N., & Wardhono, E. Y. (2018). Effect of PLA Addition to Glycerol Plasticized Starch on the Mechanical Properties of Blend Film. Semnastek Proceedings.

Ridwan, R., Wirjosentono, B., Tamrin, T., Siburian, R., Rihayat, T., & Nurhanifa, N. (2018, December). Modification of PLA/PCL/Aceh's bentonite nanocomposites as biomedical materials. In AIP Conference Proceedings (Vol. 2049, No. 1). AIP Publishing.

Rochaeni, U. A., Irdoni, H. S., & Bahruddin, B. Effect of Chitosan Filler and Glycerol Plasticizer Levels on the Properties and Morphology of Sago Starch-Based Bioplastics (Doctoral dissertation, Riau University).

Sari, N. I., Syahrir, M., & Pratiwi, D. E. (2022). The Effect of Adding Chitosan and CaCO 3 Fillers on the Bioplastic Characteristics of Gadung Tubers (Dioscorea Hispida Densst). Chemica, 23(1), 78-89.

Suryani, S., Rihayat, T., Fitria, F., & Safitri, A. (2022). Making Environmentally Friendly Bioplastics Based on PLA-PCL with Composite Catechin and Chitosan as a Substitute for Petroleum Based Plastics. Journal of Reaction Science and Technology, 20(01)

Warastuti, Y., Abbas, B., & Suryani, N. (2017). Preparation of irradiated polycaprolactone-chitosan-hydroxyapatite composite for biomaterial applications (Preparation of Irradiated Polycaprolactone-Chitosan-Hydroxyapatite for Biomaterial Application). Metallurgy, 28(2), 149-160.

Wirjosentono, B., & Rihayat, T. (2019). Preparation Of Chitosan PCL/PLA Nanocomposite Blended With Bentonite From Aceh, Indonesia. Rasayan Journal of Chemistry,12(4).