The Impact of Chitosan Incorporation on the Mechanical Characteristics of Biodegradable Packaging based on PLA/PCL Blend

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Abstract. The development of environmentally sustainable plastics has gained prominence due to their eco-friendliness and renewable nature. In this research, eco-friendly plastic was formulated by blending Polylactic Acid (PLA) and Polycaprolactone (PCL) with the incorporation of chitosan as a filler. The primary objective of this study is to scrutinize and delineate the influence of varying compositions of PLA/PCL/chitosan on the mechanical attributes of eco-friendly plastics. This was achieved through hot pressing methods at a temperature of 200°C for a duration of 1 hour. The composition ratios for PLA/PCL were set at 2/8 g, 3/7 g, 5/5 g, 7/3 g, and 8/2 g, while chitosan compositions ranged from 0.2 g to 0.6 g. Comprehensive assessment of the eco-friendly plastics involved biodegradability tests, tensile strength measurements, elongation evaluations, functional group analyses, and examination of plastic film morphology. Optimal performance, ascertained through characterization, was achieved with a composition of PLA/PCL/Chitosan at 8/2/0.6 g, yielding a 38.8% degradation rate, a tensile strength of 42.53 MPa with a composition of PLA/PCL/Chitosan at 8/2/0.4 g, and an elongation of 6.96% with a composition of PLA/PCL/Chitosan at 8/2/0.2 g. The functional groups identified included N-H, C-H, C=O, and C-O groups, indicating a blending process without the formation of new functional groups. Morphology testing revealed a smooth surface, although some undissolved chitosan particles were evident, likely due to non-uniform blending.

1 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

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because it has several advantages. However, this plastic polymer cannot be destroyed naturally (non-biodegradable) [1,2]. To address this issue, Polylactic Acid (PLA) has emerged as a promising biopolymer that can replace traditional plastics. PLA is derived from renewable natural materials, such as starch, through lactic acid fermentation, rendering it both renewable and biodegradable. Despite its robust, transparent, and waterproof properties, PLA does exhibit rigidity and low permeability. To ameliorate these limitations and enhance biocomposite characteristics, other polymers are often incorporated into the PLA matrix [3-5].

Polycaprolactone (PCL) is one such polymer with the potential to enhance the properties of PLA. PCL is an aliphatic polyester known for its biocompatibility and good permeability. Although it boasts high crystallinity, a slow degradation rate, and a low melting point, its mechanical properties are suboptimal. Nonetheless, its relatively low melting point facilitates processing through conventional methods [5,6]. PLA and PCL share hydrophobic and biodegradable traits, but differ significantly in their physical attributes. PLA is transparent, highly flexible, and robust, whereas PCL is non-transparent, brittle, and prone to fracture. By combining these two materials, it becomes possible to address the limitations of the individual polymers [7]. The pursuit of environmentally friendly plastic technology is moving quickly, with ongoing research examining the effects of fillers, particularly chitosan, which is widely used. Variations in the composition of raw materials and fillers, on the other hand, have produced inconsistencies in mechanical properties, morphology, and biodegradability, leading researchers to seek more consistent formulations [8]. Chitosan is a biodegradable and renewable material derived from chitin found in crustacean shells. It's well-known for its biocompatibility, antibacterial properties, and ability to form films with high barrier properties. These properties make chitosan an ideal candidate for food packaging, as it can increase product shelf life, reduce food waste, and reduce the need for synthetic packaging materials with negative environmental consequences [9].

Several studies have been carried out to produce the best characteristics of biodegradable plastic. Study [10] by Rustianto et al., (2019) using taro starch in making biodegradable plastic with the addition of chitosan and glycerol as plasticizers. From the research results, the optimum composition was obtained, by glycerol and chitosan to produce a tensile strength of 2.32 MPa and a water resistance percentage of 44.62%. Excess chitosan can cause agglomeration or clumping of chitosan particles within the polymer matrix. These agglomerations can create stress concentration points within the material, making it more susceptible to failure under tensile loads. Another study prove that using glycerol as a plasticizer diminishes the intramolecular cohesive forces between starch chains, thereby facilitating the formation of hydrogen bonds between glycerol and starch molecules [11]. This phenomenon leads to a reduction in tensile strength while concurrently enhancing flexibility. Therefore, to improve plastic mechanical properties, PLA need to blend with PCL as it has different hydrophobicity levels. PLA is more hydrophilic, while PCL is more hydrophobic. This blend can offer a balance between these properties, making it suitable for a broader range of applications. Additionally, the hydrophilic nature of PLA can facilitate chitosan dispersion and interaction within the blend. The combination of PLA, PCL, and chitosan can improve the compatibility and dispersion of chitosan within the polymer matrix. This is important for achieving uniform properties and behavior in the resulting material.

The objectives of this research are 1. To determine the effect of the PLA/PCL ratio on the mechanical properties of eco-friendly plastic; To determine the mass of chitosan on the mechanical properties of eco-friendly plastic; To find out the characteristics of the eco-friendly plastic produced.

2 Research and Method

This Research was conducted at the Analytical Chemistry Laboratory of the Chemical Engineering Department of Lhokseumawe State Polytechnic and the Fugha Mandiri Workshop on Jl. Elak, Jeuleukat, Kec. Blang Mangat, Lhokseumawe City.

Materials and Tools : The materials used are analytical scales, stirring rods, hot press, aluminum foil, analysis tools namely UTM; SEM; FTIR

Raw Material Preparation : Polylactic Acid (PLA), Polycaprolactone (PCL), Chitosan

Dependent Varaible :

1. Biodegradation test
2. Tensile strength test (best sample based on biodegradation test)
3. Functional group test (best sample based on biodegradation test)
4. Morphology test (best sample based on biodegradation test).

2.1 Eco Friendly Plastic Manufacturing Process

The polymers (PLA, PCL, and chitosan) weight as much as its variables. Subsequently, all materials were introduced into the extruder. The blending procedure for these polymers took place in a single-screw extruder, with the temperature maintained at 160°C for a duration of 45 minutes. The resulting polymer blend was then poured into a mold that adhered to the ASTM 638 D Type I Standard and had been lined with aluminum foil. Compression was applied by employing a hot press at a temperature of 180°C for 20 minutes under atmospheric pressure. Following this, the resulting film was allowed to cool to room temperature 28 ^{0} C.

2.2 Biodegradation Test Work Process

Prepare the sample planting site, prepare and cut the samples to a size of 2 x 2 cm each. Next, weigh the initial weight of the sample before planting. Plant each sample in the soil simultaneously for 1 week. After reaching 1 week, the sample was taken, then cleaned from the soil and dried in sunlight. Weigh the final weight of the sample after the biodegradation process

2.3 Tensile Strength Test Work Process

Samples that have been printed to size are placed on both ends of the clamp on the pulling tool. The pulling machine switch and the graph recorder switch are turned on together according to the pulling machine speed. From the test results of this machine, a relationship will be obtained between the tensile force and the increase in length. Tensile strength testing specimens refer to the ASTM D-638 standard.

2.4 SEM Test Work Process

The analysis of the surface morphologies of both the unmodified and the harmoniously blended film samples post-fracture was conducted through the utilization of a Scanning Electron Microscope (SEM), specifically the JEOL JSM-7800F model, at an accelerating voltage of 20 kV. To prepare for scanning, the fractured surfaces underwent a gold sputtering coating process and were affixed onto stubs using double-sided carbon adhesive tape.

2.5 FT-IR Test Work Process

Fourier Transform Infrared (FT-IR) spectroscopy serves as a valuable tool in the characterization of materials, including plastics, by aiding in the identification of the specific functional groups that contribute to their chemical composition. The primary objective of conducting FT-IR analysis on plastic film samples is to examine the wavelengths and distinctive peaks exhibited within the samples. These wavelengths provide insights into the existence of particular functional groups within the material, as each functional group demonstrates a unique and characteristic peak in the FT-IR spectrum, enabling the differentiation and identification of these functional groups (600 cm -1 to 4000 cm -1).

3 Result

This research aims to make Eco-Friendly Plastic or also called biodegradable plastic from biopolymers which have great potential to be developed as a substitute for conventional plastic, namely blending Polylactic Acid (PLA), Polycaprolactone (PCL) and also adding chitosan as a filler by varying each of them. that material. Research on the manufacture of Eco-Friendly Blang Mangat, Lhokseumawe City and analysis of mechanical properties was carried out, namely tensile strength test, functional group test, morphology test and biodegradation test.

Table 1. Experimental Methode

PLA/PCL (gram)	Chitosan (grams)	Initial Weight (grams)	Final Weight (grams)	Degradation Percent (%)
2/8	0,2	1,43	1,13	21,0
	0,3	1,41	1,13	19,9
	0,4	1,45	1,16	20,0
	0,5	1,47	1,15	21,8
	0,6	1,50	1,10	26,6
3/7	0,2	1,50	1,18	21,3
	0,3	1,45	1,15	20,7
	0,4	1,53	1,20	21,6
	0,5	1,47	1,19	19,1
	0,6	1,42	1,13	20,4
5/5	0,2	1,40	1,10	21,4
	0,3	1,43	1,11	22,4
	0,4	1,47	1,14	22,5
	0,5	1,48	1,12	24,3
	0,6	1,48	1,10	27,1
7/3	0,2	1,53	1,09	27,3
	0,3	1,46	1,05	28,1
	0,4	1,55	1,09	29,7
	0,5	1,50	1,04	30,6
	0,6	1,54	1,06	31,2
8/2	0,2	1,49	1,03	31,8
	0,3	1,53	1,00	34,6
	0,4	1,56	1,01	35,3
	0,5	1,51	0,95	37,1
	0,6	1,47	0,90	38,8

3.1 Biodegradation Analysis

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. The biodegradation process can occur by hydrolysis (chemical degradation), bacteria or fungi, enzymatic degradation, wind and abrasion (mechanical degradation) and light (photodegradation). This process can also be carried out anaerobically and aerobically.

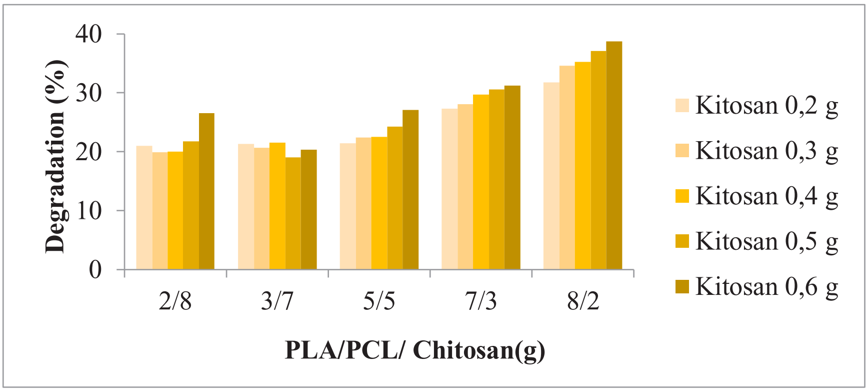

Fig 1. The Relation between PLA/PCL/Chitosan Composition and Percent Degradation

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 g, 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 [12]. PLA and PCL are biopolymers that have the ability to degrade biologically in the soil because they are obtained from renewable sources. The process of blending PLA and PCL with the best composition can increase the percentage of plastic film degradation.

3.2 Tensile Strength Analysis

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 g of PLA/PCL and 0.2 g of chitosan; 0.4 and 0.6 g.

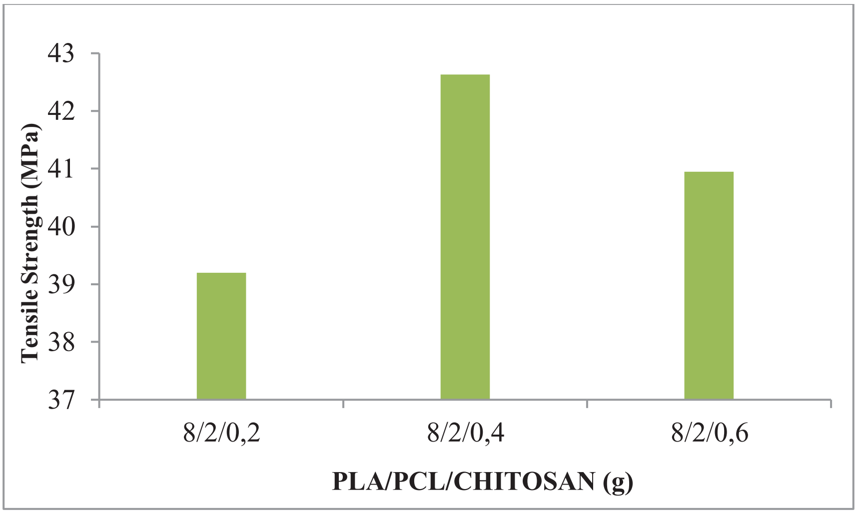

Fig 2. Graph of the Relationship between PLA/PCL/Chitosan Composition and Tensile Strength

The graph above 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 g, 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 g, it turned out that the tensile strength of the plastic film decreased to 40.65 MPa. It can be seen that the highest tensile strength value is found in the 0.4 g 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 [13]. The crystalline phase provides strength, stiffness and hardness so that it can cause the plastic film to break more easily [14]. 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) g. According to research conducted by [15], 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.

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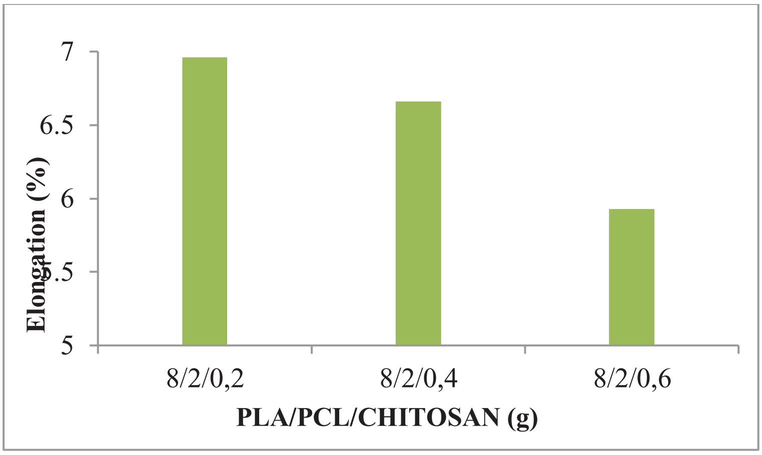

Fig 3. Graph of the Relationship between PLA/PCL/Chitosan Composition and Elongation

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. 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 g (2% w/w) producing an elongation of 6.96%

3.3 SEM Analysis

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 biocomposite process 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.

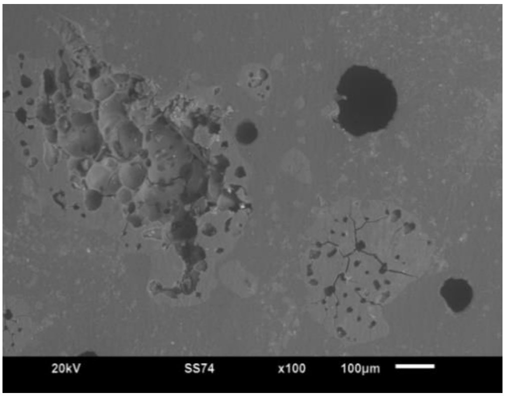

Fig. 4 Morphology Test Results for PLA/PCL/Chitosan Samples (8/2/0.4) g

Figure 4 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 blending process is not homogeneous. This is because the heating and blending 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.

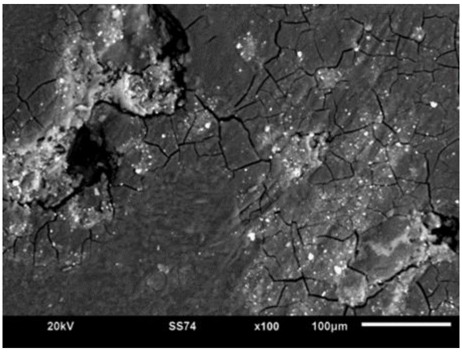

Fig 5. Morphology Test Results for PLA/PCL/Chitosan Samples (8/2/0.6) g

Figure 5 shows the morphological structure of 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 groups, causing the distribution of chitosan in the plastic film layer to be unevenly distributed 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 blending process at the gelatinization temperature, it will easily combine the chitosan particles, thereby strengthening the plastic film. SEM images also provide bubbles scattered on the surface of the plastic film. This shows that too much chitosan molecules have a tendency to form hydrogen bonds with each other due to their chemical structure resulting in agglomeration. Futhermore, high viscosity of chitosan, making it difficult to mix thoroughly with the base polymer [16]. The high viscosity can impede the even distribution of chitosan, promoting agglomeration.

3.4 Compound Functional Group Analysis With FT-IR

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.

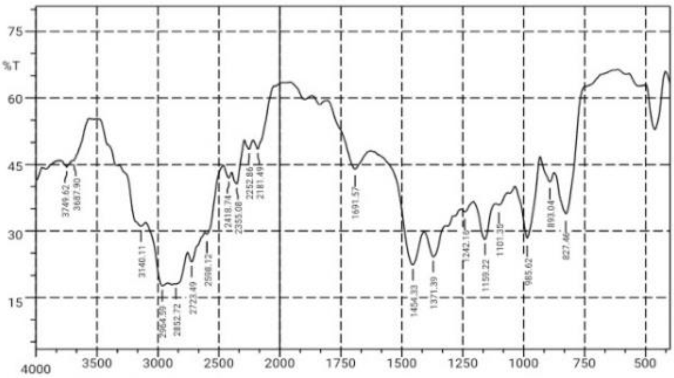

Fig 6 . FT-IR Spectrum of PLA/PCL/Chitosan Sample (8/2/0.4) g

Figure 6 shows the results of a blending sample of Polylactic Acid (PLA)/Polycaprolactone (PCL)/chitosan 8/2/0.4 g 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 absorption 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 cm^{-1} where there is a C – O group. These results indicate the functional groups that make up by chitosan interaction.

From the results of identifying functional groups in table, it shows that all 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. The results of identifying functional groups also 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. it is only a blending process without any reaction to the constituent ingredients. This causes the resulting plastic biocomposite to still have the properties of its constituent components.

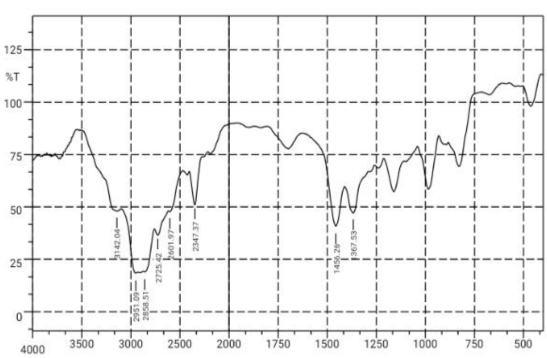

Fig 7. FT-IR Analysis Polylactic Acid (PLA)/Polycaprolactone (PCL)/chitosan 8/2/0.6 g

Figure 7 shows the results of the blending sample of Polylactic Acid (PLA)/Polycaprolactone (PCL)/chitosan 8/2/0.6 g which has been carried out that there is an absorption at 3142.04 cm^{-1}, which is 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 there is an absorption of 2951.09 cm^{-1} where there is a C - H group, in the 2500 – 2000 cm^{-1} area there is an absorption of 2347.37

cm^{-1} where there is a C = O group and in the 1500 – 1250 cm^{-1} area there is absorption at 1456.26 cm^{-1} where there is a C - O group. The results of identifying functional groups in table also 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. However, it is only a blending process without any reaction to the constituent ingredients. This causes the resulting plastic biocomposite to still have the properties of its constituent components.

4 Conclusion

Based on the results obtained in this research, it can be concluded as follows: A greater ratio of Polylactic Acid (PLA) to 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 g. 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%.

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