Mechanical Properties and Morphology Biocomposites of Polycaprolactone (PCL)/Modified using Trisodium Trimetaphosphate

Marpongahtun[1*], Cut Fatimah Zuhra[1], Sovia Lenny[1], Darwin Yunus Nasution[1], Aulya M.[1], Suci A. Amaturrahim[1], Mahmud[2], Fitria Puspa Dewi[1] and Irmayani[1]

[1]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Jl. Bioteknologi No. 1 Kampus USU Padang Bulan, Medan 20155, Indonesia*

[2]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Medan, Sumatera Utara, Indonesia*

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Abstract: The determination of the mechanical properties and morphology of polycaprolactone (PCL) / breadfruit polytocyte biocomposites tied up with trisodium trimetaposphate was performed. The breadfruit starch is tied with trisodium trimetaposphate to produce pospat starch. The highest degree of substitution was obtained in variation of trisodium weight of trimetafosfat 3%, that is 0,0633. PCL / Starch Biocomposite was prepared by mixing method between PCL in chloroform solvent with modified 3% sodium starch then printed at 75˚C since 10 minutes. Mechanical properties, functional group, and morphological of PCL/Modified breadfruit starch biocomposite was analyzed. The result of evaluation showed an optimal tensile test value of 90%: 10% with tensile strenght of 7,4287 MPa and Modulus Young's of 27,852 MPa. The functional group analysis of phosphate starch showed asymmetric P-O-C group at wave number 1018,41 cm^{-1}. Analysis with FT-IR from PCL/Modified Breadfruit Starch Biocomposite showed of physical interaction occurred between PCL and modified breadfruit starch. Morphological analysis using SEM showed smooth and homogeneous surface of biocomposite.

1 INTRODUCTION

Biocomposite is a type of composite that one of the constituents, namely the padding or matrix derived from natural materials (Xanthos, 2005). The matrix used in this study is the polymer matrix.

Polymer matrixs that derived from nature were start being selected by the community in the manufacture of biocomposites because they were considered more environmentally friendly. This study uses matrix padding in the form of breadfruit starch derived from breadfruit. Breadfruit is high in carbohydrates and a valuable source of starch. Breadfruit produced 18.5 grams/ 100 grams of starch with 98.86% purity, 27.68% of amylose and 72.32% of amylopectin (Rincon and Padilla, 2004).

Biocomposite in this study was made by mixing breadfruit starch with polycaprolactone (PCL) with the aim for improving the mechanical properties of biocomposite. PCL is generally used as one of the basic ingredients for making biomaterials. PCL has good mechanical properties, that biocompatible with many types of polymers. The use of PCL for tissue regeneration is very limited due to its hydrophobic nature which affect cell regeneration and degradation rate. A simple way to increase its hydrophilicity, by mixing PCL with natural polymers (Wang *et al.*, 2009).

Starch modification and processing techniques have developed rapidly, natural starch can be modified so it has better properties. Because the starch industry wants a stable thickness of starch at both high and low temperatures, good endurance to mechanical treatment, and thickening power that resistant to acidic and high temperature. (Koswara, 2009).

(Wang *et al.*, 2005) conducted a study of thermal and thermomechanical behavior of polycaprolactone

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and starch/ polycaprolactone compound for biomedical applications, corn starch was used where a compound of corn starch with 30/70% weight of PCL (SPCL), and used a commercial PCL. After conducting thermal analysis, the melting peak temperature and melting enthalpy for PCL is higher than SPCL which is equal to 58.40 ^{0}C and 59.80 ^{0}C at SPCL crystallization rate is much higher than PCL which is equal to 47.60 ^{0}C, this indicates that starch acts as an agent for PCL .

(Sujito, Munawaroh and Purwandari, 2013) conducted a study of the mechanical properties and ability of biodegradation of poly lactic acid biocomposite with amplifier of thin bamboo sheets and sengon wood, biodegradation test of biocomposite was carried out using the land fill method where the materials was buried in the soil for 4 weeks and watered with ± 150 cc / day. Observation of the test material was carried out every week by calculating the percentage changes in relative mass and physical changes from the material using a microscope. The results showed a decrease in the quality of biocomposite synthesized materials due to burial.

(Zuhra and Marpongahtun, 2016) conducted a study of breadfruit starch modification by crosslinking method using trisodium trimetaphosphate with various weight of sodium trimethaphosphate 1%, 2%, 3% and 30, 60, and 90 minutes of reaction times. Results from the research using IR spectroscopy phosphate starch was formed asymmetric P-O-C vibrations at wave numbers 1050-995 cm^{-1} and 1643 cm^{-1}. The effect of increasing Trisodium trimetaphosphate concentration increases the value of substitution degree and decreases the swelling power value. The highest degree of substitution was 0.003 gram at 3% concentration and 60 minutes of reaction time.

Starch can be divided into 2 types, native starch which has not been modified and modified starch. Modifications made to improve the properties of native starch, including producing higher brightness starch, lower viscosity and gel formed, starch granules break more easily and higher gelatinization time and temperature (Koswara, 2009).

Cross-linking is a method that can be used to modify starch by replacing -OH groups with groups of added crosslinking agents such as esters, ethers or phosphates (Siswanto, Manurung and Budiyati, 2012). The advantage of using the crosslinking method is to produce starch with little swelling power. This will strengthen starch granules so that it is not easily broken during heating and make the starch more resistant to acidic and heat media. In addition, it strengthens hydrogen bonds in granules with chemical bonds that act as bridges between starch molecules. As a result, when starch is heated in water, the granules will expand that make the hydrogen bonds weaken (Koswara, 2009).

In this study, a combination of polycaprolactone and modified starch was mixed homogeneously through perfect stirring. That is produce a thin membrane formed by pouring and evaporating the solvent at room temperature. Characterization carried out is the mechanical strength test, functional group analysis and surface morphology analysis.

2 MATERIALS AND METHODS

2.1 Equipment

Tools used in this research are analytical scale, measuring cup, hotplate, stirrer, glass funnel, beaker glass, oven thermometer, desiccator, aquadest bottle, measuring flask, aluminum foil, hot press, magnetic stirrer, pH meter, spectrophotometer FT-IR, tensile testing equipment, Scanning Electron Microscopy (SEM), and whatman filter paper No.1.

2.2 Materials

Materials used in this study include: breadfruit, trisodium trimetafosfat (TMP), vanadate-molybdate reagent, Na_2CO_3, KH_2PO_4, 0.5 N NaOH, 0.5 N HCl, polycaprolactone (PCL), chloroform, aquadest and water.used in this study include: breadfruit, trisodium trimetafosfat (TMP), vanadate-molybdate reagent, Na_2CO_3, KH_2PO_4, 0.5 N NaOH, 0.5 N HCl, polycaprolactone (PCL), chloroform, aquadest and water.

2.3 Methods

2.3.1 Isolation Starch from Breadfruit

Breadfruit that has yellowed peeled and removed the stalks of fruit, then washed from dirt and sap. Then cut into small pieces and mashed with blender. Furthermore, filtered the mashed breadfruit using gauze and left until precipitate. Washed the precipitate repeatedly with water until the top layer is clean. The obtained starch is dried in the oven at 45 °C for 24 hours. Ground and sifted the crude starch. Then, analyzed breadfruit starch using FT-IR.

2.3.2 Phosphate Starch Manufacture

Dissolved 30 grams of breadfruit starch with 45 mL aquadest until a suspension was formed and then added 1% trisodium trimetaphosphate while stirring to pH 10 by dripping 1 M NaOH. Then heated the compound at 45 °C while stirring for 60 minutes. Furthermore, neutralized the obtained starch porridge to pH 6.5 with 1 M HCl then washed thoroughly using distilled water. Phosphate starch then dried at 40° for 24 hours. Ground and sifted the coarse phosphate starch. Used the same procedure for trisodium trimetaphosphate 2 and 3% weight. Furthermore, the obtained phosphate starch was characterized by FT-IR and calculated the degree of substitution (DS).

2.3.3 Determination of Degree of Substitution for Crosslink Starch (Phosphate Starch)

Determination of phosphate substitution degrees was carried out according to (Deetae *et al.*, 2008) as 1.5 grams of sodium carbonate were dissolved in 5 mL aquadest. Then added 2.5 grams of starch phosphate to the sodium carbonate solution and put into the kiln at 550 °C for 6 hours to be ignited. Dissolved the sample that has been ignited with 2 mL of 25% HCl and stirred until it dissolves. Then added aquadest until it reach 50 mL volume of solution. Piped 10 mL from the solution and added vanadate-molybdate reagent, then left at room temperature for ± 45 minutes. After that, observed the samples using a UV-Visible spectrophotometer at a 435nm wavelength should be aligned to the center with linespace exactly at 13-point. The text must be set to 11-point.

2.3.4 Manufacture of Modified Starch Biocomposite with PCL

Dissolved 9 grams of PCL with chloroform at 60 °C. Then added with 1 gram of starch phosphate while being distirer until homogeneous for 30 minutes, then cooled and dried. Next, put it into the mold and pressed with a Hot Press tool at 75 °C for 10 minutes. Use the same procedure on the manufacture of biocomposite according to predetermined variations. Then carried out biocomposite characterization of tensile test analysis, FT-IR and SEM.should appear aligned to the center including organisation, address and e-mail.

3 RESULT AND DISCUSSION

3.1 Phosphate Starch Manufacture

Phosphate starch is starch obtained from cross-linking reaction between starch and trisodium trimetaphosphate in the presence of sodium hydroxide which acts as a catalyst.

The reaction between starch and sodium hydroxide starts with the attack of Na atom from sodium hydroxide on C2 starch atom. Sodium hydroxide will break the C2-C3 bond which has a secondary alcohol group to form the phosphate starch. And the secondary -OH group on C2 starch atom attacks H atoms of C3 starch atoms to produce water. Then the C2-C3 bond is cut off and the electron is displaced to produce phosphate starch.

3.2 FT-IR Spectrum Analysis of Breadfruit Starch and Modified Starch

Function group analysis using FT-IR for starch and modified starch from the breadfruit isolation can be seen from FT-IR spectroscopic data. The FT-IR spectrum of breadfruit starch (Figure 1) shows the group contained in starch, where the wave number 3379.29 cm^{-1} shows the –OH group; 2924.09 cm^{-1} shows the –CH group; 1643.35 cm^{-1} shows the C = O group. The results of FT-IR spectrum analysis showed that starch isolation was successfully carried out can be seen in Figure 1.

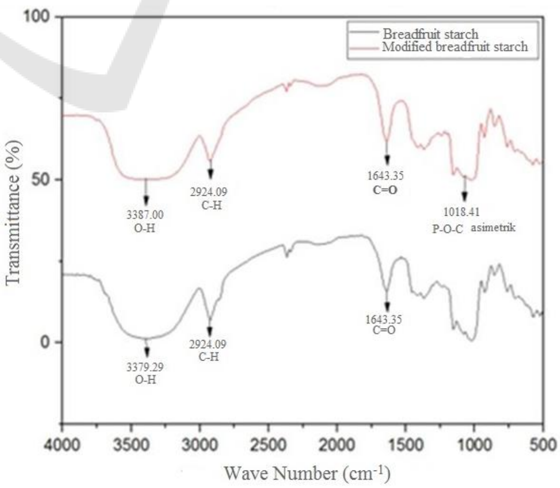

Figure 1: FT-IR Spectrum Breadfruit Starch and Modified Breadfruit Starch.

The FT-IR spectrum phosphate starch supports the emergence of a vibration peak in the wave number 1149 cm^{-1} – 1018,41 cm^{-1} indicating the presence of a P=O aliphatic group that supported by band absorption which indicate the presence of asymmetric P-O-C groups in the wave number 1080,14 cm^{-1}. The vibration peak at the wave number 1643 cm^{-1} shows the hydrogen intramolecular bond and the break-off of the hydrogen bond so that the -OH group is converted into phosphate ester (Li and Yeh, 2001). This absorption comes from an added crosslinking agent, namely trisodium trimetaphosphate which replaces the -OH group in starch molecules. This shows the addition of new groups to the modified starch.

3.3 Determination of Phosphate Percentage and Degree of Substitution (DS)

Determination degree of substitution was carried out using UV-visible spectrophotometry. The results of determining the degree of substitution can be seen in Table 1.

Table 1: Results of determination degree of substitution of variations in the trisodium trimetaphosphate weight.

Treatment	Phosphate Percentage	Degree of Substitution (DS)
0,3 g TMP	0,9592	0,0520
0,6 g TMP	1,1585	0,0633
0,9 g TMP	1,2426	0,0681

Results of the substitution degrees obtained ranged from 0,0520 – 0,0681. The highest value of 0,0681 was obtained from phosphate starch with a variation weight of 0,9 gram trisodium trimetaphosphate with 60 minutes reaction time. The more crosslinking agents were added and the longer the reaction time, the more phosphate groups can substitute the -OH group. This is because the longer the contact time between trisodium trimetaphosphate and starch, the weakens the hydrogen bonds found in starch molecules.

3.4 FT-IR Spectrum Analysis of PCL Biocomposite/Modified Breadfruit Starch

FT-IR spectroscopy was used to determine the characteristics of composite membranes functional groups. The FT-IR spectrum of polycaprolactone (PCL) and PCL biocomposite/modified breadfruit starch can be seen in Figure 2.

The FT-IR spectrum of polycapolactone shows the -OH, -CH, C=O group at wave numbers respectively 3448,72 cm^{-1}, 2931,80 cm^{-1}, 1620,21 cm^{-1}.

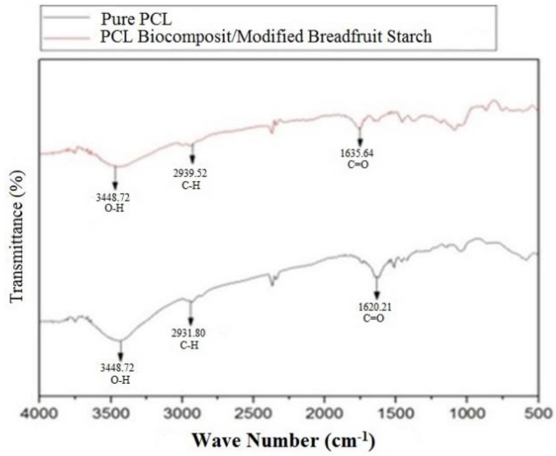

Figure 2: FT-IR Spectrum of Pure PCL and Biocomposite PCL/ Modified Breadfruit Starch.

The FT-IR spectrum of biocomposite PCL/ breadfruit starch showed –OH, C–H, and C=O groups at wave numbers of 3448,72 cm^{-1}, 2939,52 cm^{-1}, and 1635,64 cm^{-1}, respectively.

Based on FT-IR analysis, it can be seen that the functional groups formed are a combination of specific functional groups found in their constituent components. The functional group reappeared on the spectrum compound between polycaprolactone and breadfruit starch where the intensity was almost same and new functional group was not found. This proves that the compound of PCL/ breadfruit starch produced is a physical mixing process.

3.5 Mechanical Properties Analysis of Biocomposite PCL/Modified Breadfruit Starch

Tensile strength is the ability of a material to hold a load without breaking the material. Mechanical properties are carried out to determine the tensile strength and biocomposite elasticity produced.

Composites with good mechanical properties can be obtained if the padding material is well dispersed in the matrix. Fillers and matrixs must be compatible, that is, they are suitable when mixing. In this study, the fillers used were starch and the matrix was polycaprolactone. The results of the mixture between PCL / breadfruit starch and the results of tensile strength analysis can be seen in Figures 3 and Figure 4 and in Table 2.

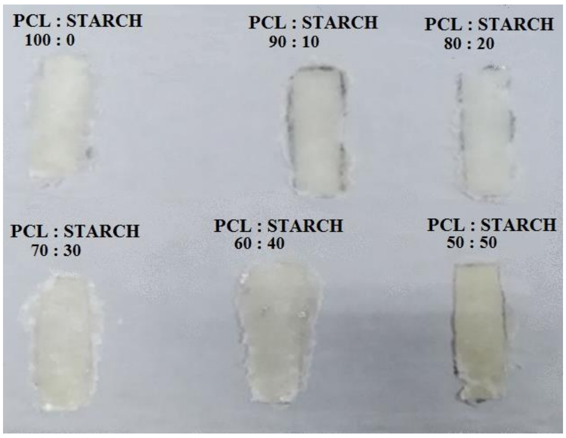

Figure 3: PCL Biocomposite/ Modified Breadfruit Starch.

Table 2: Result of Tensile Strength and Modulus Young's from Pure PCL Pure and Biocomposite PCL / Modified Breadfruit Starch.

NO	Material Type	Tensile Strenght (MPa)	Modulus Young (MPa)
1	Pure PCL (100% : 0%)	5.5473	4.9771
2	Biocomposite PCL/Modified Breadfruit Starch (90% : 10%)	7.4287	27.852
3	Biocomposite PCL/Modified Breadfruit Starch (80% : 20%)	3.2615	58.126
4	Biocomposite PCL/Modified Breadfruit Starch (70% : 30%)	2.6466	13.309
5	Biocomposite PCL/Modified Breadfruit Starch (60% : 40%)	2.2155	4.732
6	Biocomposite PCL/Modified Breadfruit Starch (50% : 50%)	1.7954	42.968

The comparison of the tensile strength result and Modulus Young's can be concluded that biocomposite with a ratio of 90%: 10% has the most optimum value, with 7.4287 Mpa of tensile strength and 27.852 Mpa of Modulus Young's.

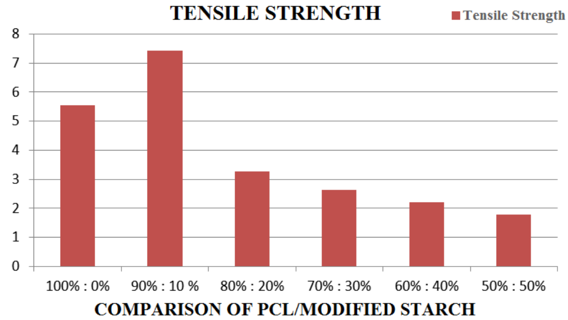

Figure 4: Tensile Strength Graph of Pure PCL and Biocomposite PCL / Modified Breadfruit Starch.

The mixing process is more stable and the mixture of starch added is less so that it increases the value of the tensile strength produced. The value of the tensile strength mixture is decreases with increasing starch. This is consistent with (Sabo *et al.*, 2013) which states that the more starch mixtures werw added, the lower the tensile strength value, because starch molecules will interact with the polymer chain structure which causes the polymer chain to be difficult to move because of the intermolecular forces between starch molecules.

3.6 Morphological Analysis with SEM

Surface morphology analysis with SEM was carried out to provide information about the shape and change of surface from pure PCL and modified biocomposite PCL /breadfruit starch. Figures 5 and 6 are SEM results of pure PCL and modified PCL / modified breadfruit starch with a ratio of 90%: 10% that obtained from the most optimum tensile test analysis result. Morphological analysis was carried out using a ZEISS device with a magnification of 2500 times with a power of 15,0 kV.

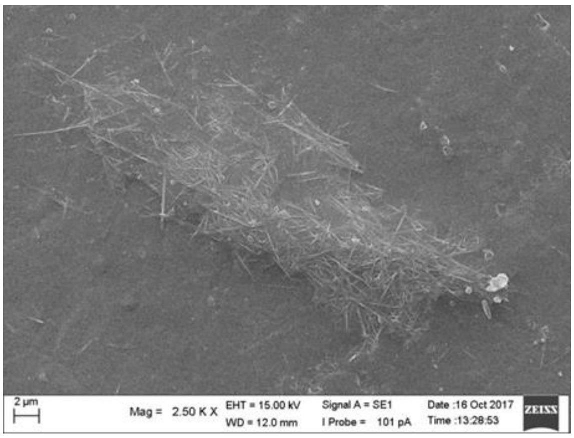

Figure 5: SEM Analysis of Pure PCL.

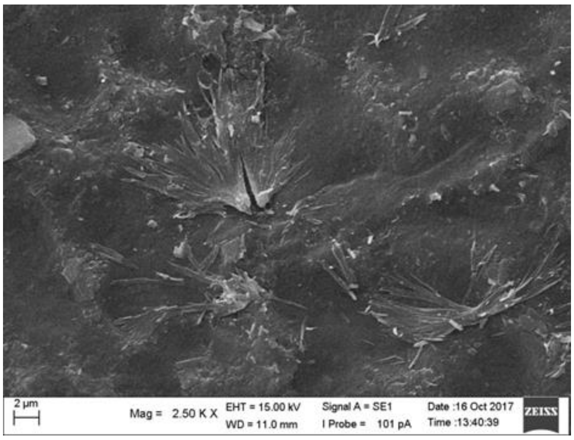

Figure 6: Biocomposite PCL/Modified Breadfruit Starch (90%: 10%).

From the SEM results, it can be seen that PCL has more evenly surface, because PCL is not filled with padding so that it produces a more evenly and smooth surface (Panindia, 2015) .Meanwhile, biocomposite PCL/breadfruit starch shows that starch can be distributed evenly on the PCL surface with the presence of physical interactions that produce a more evenly and smoothly surface. PCL and starch have the ability to mix with each other because both have good properties and characteristics so that they have compatibility when mixing to produce a smooth and more evenly surface morphology.

4 CONCLUSIONS

The results from the research conducted can be concluded that phosphate starch in the variation of the weight of trisodium trimetaphosphate 3% is the most optimum condition with the highest value of Substitution Degrees which is 0,0681. Mechanical biocomposite analysis of PCL/Starch Breadfruit with 90%: 10% showed an optimum conditions with tensile strength values of 7,4287 MPa and 27.852 Mpa of Modulus Young's. FT-IR analysis on optimum biocomposite showed the occurrence of physical interactions between starch molecules and PCL. Morphological analysis shows the formation of a homogeneous surface and evenly distributed on the surface of the biocomposite.

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