COMPATIBILIZATION STUDY OF BLENDING POLYMERS PLA-PCL WITH FILLERS CATECHIN-CHITOSAN AS NEW MATERIALS FOR BIOPLASTIC MANUFACTURE

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ABSTRACT

The use of agents in the form of nanochitosan to develop active bioplastics offers a new way to modify the transport properties and release of active compounds while increasing the mechanical resistance and compatibility between polymers. This study aims to study the effect of mixing two polymers in the form of polylactic acid (PLA) and polycaprolactone (PCL) as a matrix and 10% (w/v) filler. The matrix for bioplastic film-forming was prepared by mixing 8 g PLA and 2 g PCL. The internal film and surface microstructures were characterized by scanning electron microscopy (SEM) and interactions between the particles using FT-IR. Mechanical physical properties were reviewed using ASTM D638. The results show that amount of filler composition promotes a significant change in the microstructure of the film and is associated with improving properties. The amount of nanochitosan (0.9 g) and catechin (0.1) was homogeneously distributed. As a consequence. However, when the filler composition is varied in other quantities, the tensile strength will fluctuate.

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1. INTRODUCTION

Concerns about non-biodegradable plastic waste and limited petroleum resources have increased global interest in using bio-based, biodegradable...
Compatibilization Study of Blending Polymers PLA-PCL with Fillers Catechin-Chitosan as New Materials for Bioplastic Manufacture

Biodegradable packaging materials are a viable alternative to synthetic packaging materials based on petrochemical products. Biodegradable polymers are becoming more affordable, they have the potential to be used as an environmentally friendly alternative to plastic packaging. Polymers such as polylactic acid (PLA) and polycaprolactone (PCL) can be used as biodegradable packaging materials to replace traditional plastics. PLA and PCL are biopolymers with a high potential to replace traditional plastics.

Previous research has shown that PLA, PCL, and other polymers are all biodegradable. However, it is still not widely used due to a number of drawbacks. Incorporating polymers rather than chemical modification or customized macromolecular synthesis is one method for improving the thermal resistance and mechanical strength of biodegradable polymers, resulting in balanced properties. PLA (polylactide) is a biodegradable polymer made from renewable sources. PLA is made from lactic acid polymers, whereas lactic acid can be made through enzymatic processes using starch as a raw material. PLA has a wide range of applications (biomedical, packaging, textile fiber and technical goods). Under the influence of heat, bacteria, and light, PLA degradation can occur naturally. Furthermore, PLA can be degraded in the body without causing harm. Plants like corn and potatoes can be used as feedstock for PLA production. PLA's properties are comparable to those of fossil-based polymers.

Ring-opening polymerization (ROP) of e-caprolactone and polycondensation of 6-hydroxyhexanoic acid are two methods for producing polycaprolactone. The ROP method is preferred because it produces polymers with lower polydispersity index (PDI) values and higher molecular weight, as well as better mechanical properties. PCL is typically synthesized without a catalyst using ring-opening polymerization, but its low melting point results in high production costs and commercial limitations. Because PCL is used primarily in biomedical and pharmaceutical fields, it should be produced with caution to avoid the presence of toxic compounds that may cause side effects in users or organisms. As a result, combining PLA - PCL with other biofillers can cause deformation and affect its end-of-life characteristics under a variety of environmental conditions. Chitosan is a polysaccharide derived from the deacetylation of chitin found in marine waste, specifically crustacean shells like shrimp, oyster, crab, and lobster. Chitosan has been widely used in the production of edible films. It has high film-forming ability, broad antimicrobial activity, selective permeability to gases (CO2 and O2), and is compatible with vitamins, minerals, and antimicrobial agents. With the addition of chitosan, PLA's ability to crystallize and antibacterial properties can be improved. Research in Catechins were used as natural plastic antioxidants to protect the polymer matrix from thermal treatment. Because catechins have a high hydroxyl group, they can interact with polymer groups, including PLA and PCL, via hydrogen bond interactions.

Based on the advantages of the PLA polymer and several studies, the addition of filler to the PLA matrix and PCL matrix has not produced strong characteristics,
so an innovation will be carried out in this study by adding a combination of both catechin and chitosan fillers into the PLA-PCL matrix, which is expected to produce a new biocomposite that has strong characteristics and overcomes the shortcomings of Biodegradable composite.

2. MATERIALS AND METHODS
2.1. MATERIALS
The materials used for the extraction of catechins are jamblang seeds and methanol. The materials used for the manufacture of plastic wrap are PLA, PCL, Nanochitosan, jamblang seed (Lokal agriculture plant), PEG and chloroform all those materials were purchased from sigma aldrich, Jakarta.

2.2. METHODS
2.2.1. EXTRACTION OF CATECHINS USING SOXHLET EXTRACTION
Extraction was carried out using a conventional Soxhlet apparatus referring to the research conducted by previous research. Rihayat (2010) The distillation flask is placed in a bath, thimble holder and condenser. Jamblang seeds are cleaned of flesh, washed and then dried in the sun for 3 hours. The dried seeds are blended until they become powder. Jamblang seed powder is packed in filter paper and placed in a thimble holder. The solvent in the form of methanol was put into a distillation flask. When the boiling point is reached, the liquid moves through the siphon and is lowered back into the distillation flask, bringing the extracted solute into the liquid. The extraction process was carried out for 6 hours. In a solvent flask, the solute is separated from the solvent by the distillation method.

2.2.2. SAMPLE PREPARATION
PLA, PCL, Nanochitosan, Catechins, Aluminum foil, Analytical Balance, Beaker glass, Hotpress, Petri dish and Rod mold. PLA 8 g and PCL 2 g were mixed using a DSM Xplore co-rotating extruder at a melting temperature of 180°C and a screw speed of 100 rpm. Furthermore, it is inserted into the ASTM 638 D Type I Standard specimen mold which is coated with aluminum foil, then compressed using a hot press at a temperature of 180°C for 20 minutes under atmospheric pressure. The formed biocomposite was allowed to stand at room temperature until it solidified completely for further FTIR, and SEM testing.

Table 1

<table>
<thead>
<tr>
<th>No</th>
<th>Sample</th>
<th>Fillers</th>
<th>Nanochitosan</th>
<th>Catechin</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Xa1</td>
<td>0.9</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Xa2</td>
<td>0.8</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Xa3</td>
<td>0.7</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Xa4</td>
<td>0.6</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Xa5</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Xa6</td>
<td>0.4</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Xa7</td>
<td>0.3</td>
<td>0.7</td>
<td></td>
</tr>
</tbody>
</table>
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2.3. CHARACTERIZATION TECHNIQUE

2.3.1. TENSILE STRENGTH

Engineering tensile tests are mostly carried out to complement the basic design information for the strength of a material and as supporting data for material specifications. In the tensile test, the test object is given an axial tensile force load which increases continuously, at the same time observing the elongation experienced by the test object.

2.3.2. FT-IR (FOURIER TRANSFORM INFRARED)

Fourier Transform Infrared (FT-IR) is used to identify the type of functional group bonding possessed by materials including plastics. The purpose of FT-IR analysis on plastic film samples is to see the wavelength and characteristic peaks in the sample. This wavelength indicates the presence of certain functional groups in the sample, because each functional group sample has a characteristic peak that is specific to that functional group.

2.3.3. SCANNING ELECTRON MICROSCOPY (SEM)

Scanning Electron Microscope (SEM) is an electron microscope that is used to view the image surface of a material, besides that it can also provide information regarding the chemical composition of a material, both conductive and non-conductive materials. This microscope uses electromagnetic and electrostatic to control the incoming light and the appearance of the resulting image. Salim et al. (2021)

3. RESULTS AND DISCUSSIONS

3.1. TENSILE STRENGTH

Researchers used PLA-PCL as a matrix to investigate the effect of chitosan content on the mechanical strength of bioplastic samples. The resulting tensile strength increases as the chitosan content increases. Because nanochitosan, as an immiscible component, has low ductility and is a brittle material, its addition stiffens the mixture. Furthermore, good interfacial adhesion between chitosan and PLA-PCL matrix was caused by good dispersion of chitosan particles as a result of chitosan's high solubility with acetic acid solvent. When the total amount of nanochitosan content in the mixture is considered, our results show higher tensile strength at 9% by weight of nanochitosan content. The even dispersion of chitosan particles is due to the constituent materials' good compatibility and immiscibility. Chuesiang et al. (2021)

The effect of catechins and nanochitosan as active agents on the mechanical properties of PLA-PCL films is dependent on the molecular structure of the Active Agents, processing techniques, and conditions.
The mechanical properties of PLA films changed more as the concentration of active agents increased. In general, the tensile strength of PLA-PCL films decreased with active agent incorporation. This is primarily due to the plasticizer effect, which occurs between the PLA-PCL chains. When a agent is added, the free volume increases, chain attachment decreases, and chain mobility and flexibility increase. Nanochitosan, on the other hand, acts as a reinforcing filler in PLA-PCL and limits the movement of the PLA-PCL segmental chains. Because of the stiffness of these polysaccharide chains and the resulting interaction between PLA-PCL and nanochitosan, the film stiffness increases. Suryani et al. (2018) This interaction can take the form of hydrogen bonds between PLA (carbonyl or hydroxyl end groups) and nanochitosan hydroxyl/amine/acetamide groups.

### 3.2. FTIR OF BIOPLASTIC

FT-IR is an instrument that uses the principle of spectroscopy. Infrared spectroscopy/FTIR is used for identification of organic compounds because of its very complex spectrum consisting of many peaks (qualitative analysis). FTIR is also to determine the types of functional groups that can indicate the general composition of a material. Initially, tests were carried out for conventional plastic samples and for bioplastic. For this reason, two measurements at different locations were obtained from each bioplastic sample. These measurements are presented in Figure 2, with an offset between them to show the true similarity. As shown, the measurements were very consistent based on the absorption functional groups of the components.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wavelength number (cm⁻¹)</th>
<th>Functional groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PLA/PCL (SNI)</td>
<td>3330-3500</td>
<td>O – H</td>
</tr>
<tr>
<td></td>
<td>2840-3000</td>
<td>C – H</td>
</tr>
<tr>
<td></td>
<td>1540-1820</td>
<td>C = O</td>
</tr>
<tr>
<td></td>
<td>1000-1300</td>
<td>C – O</td>
</tr>
</tbody>
</table>
This analysis was carried out to identify the functional groups present in the produced PLA-PCL/Chitosan-Catechin samples and conventional plastics as a comparison using a Fourier Transform Infrared (FT-IR) Spectrophotometer. FT-IR is a widely used method to investigate intermolecular interactions and phase behaviour between polymers. In Figure 1, the sample in the form of conventional plastic as a comparison shows the characteristics of the wave number area of
2870.06 cm\(^{-1}\), 1743.65 cm\(^{-1}\) and 1166.93 cm\(^{-1}\) which shows the C - H and C = O and C - O groups. In Figure 3 with samples of PLA-PCL 0.9 g chitosan and 0.1 g catechins which are the best results from the research that has been carried out, it shows the characteristics of the wave number area of 3348.42 cm\(^{-1}\), 2927.94 cm\(^{-1}\) and 1163.08 cm\(^{-1}\) which shows the O – H, C – H, and C – O groups, while for the C = O group there is an increase which should be in the range 1640-1820 but the results obtained are 1892.17 cm\(^{-1}\). In this study, it was shown that the addition of a new functional group in the form of O – H which was not found in the plastic sample was used as a comparison.

Based on the comparison between ordinary plastics and biodegradable plastics, it was found that the FTIR results of biodegradable plastics were very close to the plastics used as comparisons, so that the resulting products had very similar properties to ordinary plastics, although there was a new functional group, namely, O-H. This is because the constituent materials and compositions used are different so that they will not produce the same functional group and wave number.

### 3.3. SEM CHARACTERIZATION OF BIOPLASTIC

SEM testing as an additional test in this study aims to support the results of the best samples taken from the main tests of tensile tests and thermal degradation tests. The samples tested were samples with a variation of (a) Xa1, (b) Xa7, and (Xa10) based on Table 1. This test aims to see the morphological structure of PLA-PCL biocomposite using a microscope that relies on electron beams to describe the surface shape of the analyzed material. The following is a picture of the results of the analysis under an electron microscope (SEM).

![Figure 4](image)

**Figure 4** SEM Image of Each Bioplastic (a) Xa1, (b) Xa7, and (Xa10)

The image above shows the sample’s surface structure at x100 magnification, which shows a smooth surface and a good interfacial bond between the matrix and filler. This is due to the fact that when PLA polymer is combined with PCL polymer, it has superior mechanical and surface properties, resulting in good exfoliation or union with PLA polymer and high miscibility. The ability of one liquid to completely dissolve in another liquid solvent is referred to as miscibility. Suryani et al. (2018) When we have a miscible solution, no distinct layer between the two liquids forms. Thus, immiscibility occurs when a distinct layer forms in a mixed solution.

### 4. CONCLUSIONS AND RECOMMENDATIONS

The composition of 0.9 g Chitosan: 0.1 g Catechins with C - H, O - H, C = O, and C - O groups produced the best results. The SEM test revealed a smooth surface with good interfacial bonds formed between matrix and filler; however, there is still
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insoluble chitosan residue due to the inhomogeneous blending process and the use of incompatible solvents.

CONFLICT OF INTERESTS
None.

ACKNOWLEDGMENTS
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