

# Biodegradation of PCL/PCLacac Biocomposite with the Addition of Nanocellulose from Rice Stalk Waste as Filler in Soil Media

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**Abstract.** Biocomposites based on poly( $\epsilon$ -caprolactone) (PCL) and cellulose have been widely used in packaging, agriculture, materials, and biomedicine. PCL is a biocompatible and flexible polymer that can interact with cellulose. Meanwhile, cellulose is a natural filler that is renewable, environmentally friendly, and abundant in Indonesia. The combination of both is expected to produce a biocomposite with improved mechanical, thermal, and biodegradable properties. In this study, short-chain synthetic PCL (PCLacac) was used as a compatibilizer in the PCL matrix to enhance its interaction with the hydroxyl groups of cellulose filler. In the early stage, PCLacac was mixed with a commercial long-chain PCL matrix and nanocellulose derived from rice stalk using a reflux method to form a biocomposite. After that, the biodegradation rate was tested in soil media for 60 days which showed that the addition of 2.5% PCLacac to PCL resulted in the fastest degradation rate.

**Keywords:** Biocomposite, biodegradable, PCL, nanocellulose, and soil media

## 1 Introduction

Environmental problems caused by plastic waste and conventional materials are caused by their nature which is difficult to decompose naturally so that the accumulation of plastic waste in the soil and water is increasing. Although plastic has advantages such as light weight, resistance to moisture, strength, and low production costs, its durability actually causes the accumulation of waste that pollutes the environment [1]. The use of environmentally friendly materials is increasingly becoming a major concern in various industrial fields, especially to reduce the impact of synthetic waste on the environment [2], [3]. To overcome this problem, the use of biodegradable polymers such as poly( $\epsilon$ -caprolactone) (PCL) is a promising alternative solution.

PCL is a semicrystalline aliphatic polyester with high permeability, low toxicity, controlled degradation, and biocompatibility. Therefore, PCL is widely used in various applications such as food and beverage packaging, surgical sutures, tissue engineering, wound dressings,

implants, and drug delivery systems [4]–[8]. While PCL can degrade well, it has several weaknesses, such as being very brittle and stiff, making it very easy to break.

One method widely developed to overcome the weaknesses of PCL is to mix it with natural fillers such as cellulose to form biocomposites [9]. Currently, biocomposites based on poly( $\epsilon$ -caprolactone) (PCL) and cellulose have been widely used in the fields of packaging, agriculture, materials, and biomedicine [10], [11]. On the other hand, PCL is known as a biocompatible and flexible polymer. Therefore, it has great potential to be combined with natural fillers such as cellulose, which is derived from renewable and abundant resources in Indonesia [12].

Cellulose as a filler offers advantages such as sustainability, environmental friendliness, and the ability to improve the mechanical and thermal properties of biocomposites [13]. The combination of PCL and cellulose produces a material that not only has good physical performance but is also easily degraded in the environment [14]. This is an important solution to overcome the problem of materials that are difficult to decompose naturally and also provides added economic and ecological value.

In an effort to enhance the interaction between PCL and cellulose, this study developed the synthesis of short-chain PCL obtained using bis(acac)<sub>2</sub>Zr complex as a catalyst. The synthesized PCL (PCLacac) is expected to be able to interact better with the hydroxyl groups on the cellulose surface, thereby strengthening the structure of the resulting biocomposite. The mixing process between PCLacac and commercial PCL was carried out to obtain a polymer matrix with better compatibility properties. Meanwhile, the nanocellulose used in this study was obtained from rice stalk waste and is one type of agricultural waste in Indonesia. The use of rice stalk waste as a source of nanocellulose not only provides added value to organic waste, but also supports the principles of a circular economy and sustainable waste management.

This study will test the biodegradation of biocomposites by burying them in soil media for 60 days. The aim is to evaluate the biocomposite's ability to degrade naturally in the environment. The biocomposite tested is composed of a mixture of commercial poly( $\epsilon$ -caprolactone) (PCL) and PCL(acac), and uses nanocellulose obtained from rice stalk waste as a natural filler. This combination is expected to produce a biocomposite that not only has good mechanical strength but is also environmentally friendly.

## **2. Method**

### **2.1. Place and Time of Research**

This research was conducted at the Chemistry Research Laboratory, Universitas Negeri Medan. The research activities included the fabrication of a PCL/PCLacac biocomposite using rice stalk nanocellulose as filler, biodegradation testing, and water swelling testing.

### **2.2. Research Tools and Materials**

The equipment used in this study were a vacuum pump, hot plate (Thermo Scientific Cimarec SP88857105), oil bath, analytical balance (Fujitsu), condenser, two-neck flask, magnetic stirrer, thermometer, and ASTM D638 type IV mold. Meanwhile, the materials used included commercial PCL (CAPA 6800), PCL synthesis was obtained using bis(acetylacetonato)zirconium(IV) catalyst (PCLacac), chloroform, alcohol, and landfill.

### 2.3. Production of PCL/Nanocellulose Biocomposite from Rice Stalk

The process of preparing PCL/Nanocellulose biocomposite is carried out according to two predetermined ratios as shown in Table 1.

**Table 1.** Comparison of the composition of PCL, PCLacac, and nanocellulose in biocomposite manufacturing process.

Commercial PCL (g)	PCLacac (g)	Nanocellulose (g)
0,99	0	0,01
0,965	0,025	0,01

The biocomposite preparation begins by dissolving commercial PCL in chloroform. PCLacac is then added until homogeneous. Rice stalk nanocellulose is then added until dissolved. The mixture is then refluxed for one hour at 60 °C while stirring at a constant speed. The mixture is then poured into an ASTM D638 type IV mold to form a biocomposite film specimen.

### 2.4 Soil Biodegradation Test

To conduct the biodegradation test, the specimens were first cut into 2×2 cm pieces and weighed, after which the samples were buried in a landfill. Specimen measurements were taken periodically every ten days until the 60<sup>th</sup> day. The collected specimens were then cleaned using a mixture of 70% alcohol and distilled water. Afterward, the specimens were dried and reweighed. The rate of biodegradation was determined based on the decrease in mass of the specimens during the biodegradation process [15]–[17].

### 2.5 Water Swelling Test

The water swelling test was conducted according to ASTM D 570 and ISO-62 procedures. The samples were first cut into 2×2 cm pieces and then weighed, after which the specimens were immersed in water for twenty-four hours. After the soaking period was complete, the samples were cleaned and reweighed to determine their final weight [15]–[17].

## 3. Results and Discussion

### 3.1 Research Result

#### 3.1.1. PCL/PCLacac-Based Biocomposites with Nanocellulose Fillers

The manufacture of PCL/PCLacac-based biocomposites with nanocellulose fillers was carried out using a mixing technique followed by a solvent casting method. PCL functions as a matrix, PCLacac functions as a compatibilizer, and nanocellulose from rice stalk acts as a filler. PCL has a long chain with semi-crystalline, elastic, and biodegradable properties, but its biocompatibility still needs to be improved. Meanwhile, PCLacac with a shorter chain plays a role in improving biocompatibility and polarity between matrices, thereby strengthening the interaction between the matrix and nanocellulose phases.

The addition of PCLacac helps improve the compatibility between the hydrophobic phase (PCL) and the hydrophilic phase (nanocellulose). The carbonyl group in PCLacac can form hydrogen

bonds with the hydroxyl group in nanocellulose, resulting in a more homogeneous distribution of nanocellulose in the matrix.

### 3.1.2. Soil Biodegradation Test

Biodegradation testing of the biocomposite in soil was conducted for 60 days to simulate natural environmental conditions. The biocomposite was indicated to have undergone degradation due to the activity of microorganisms in the soil, as shown in Figure 1.



**Fig 1.** Biodegradation Test of Biocomposite in Soil Media with PCLacac Composition  
(a) 0% (b) 2.5%

The rate of biocomposite degradation due to burial in soil was measured by observing the change in specimen weight. Measurements were made based on the difference in mass before and after the biodegradation process using soil as the medium. The resulting percentage calculation represents the remaining specimen weight, as shown in Table 2 below.

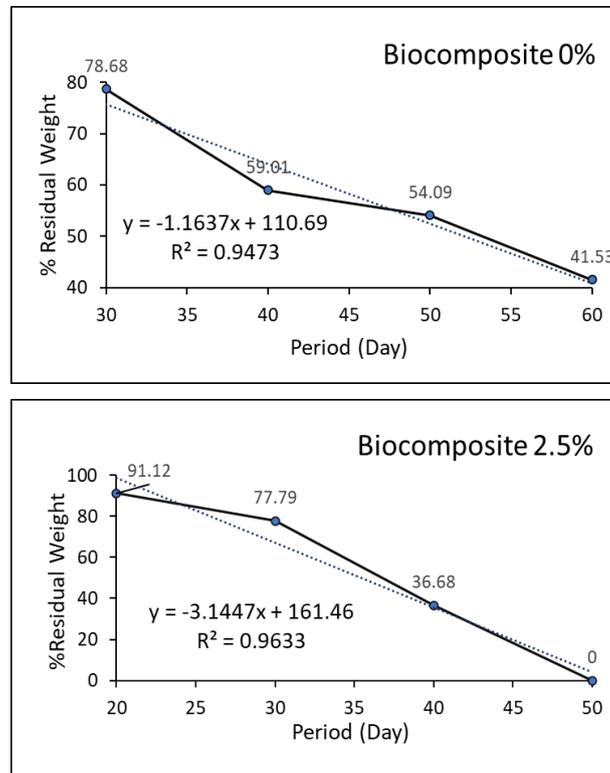
**Table 2.** Percentage of biodegradation results in biocomposites

PCLacac Biocomposite	Day No - (%)						
	0	10	20	30	40	50	60
0%	100	98.36	89.44	78.68	59.01	54.09	41.53
2.5%	100	96.79	91.12	77.79	36.68	0	0

Based on the data in Table 2, the degradation rate can be divided into two stages. The initial stage lasts from day 0 to day 30, during which no significant weight loss occurs. The second stage occurs between day 30 and day 60, marked by significant weight loss. Based on the biodegradation data in Table 2, the addition of 2.5% PCLacac showed the highest degradation rate, marked by complete degradation without leaving any biocomposite specimens at the end of the test. Conversely, the biocomposite without the addition of PCLacac (0%), produced the lowest degradation rate with a remaining specimen of 41.53%. These results indicate that the addition of PCLacac and nanocellulose can increase the biodegradability of the biocomposite [15]–[17].

### 3.1.3. Biodegradation Profile of Biocomposites

Based on the regression line equation as shown in Figure 2, the decomposition time of the biocomposite can be predicted up to 95% of its remaining weight.



**Fig 2.** Degradation Rate in Biocomposites (a) 0% (b) 2.5%

**Table 3.** Modeling of Biocomposite Decomposition Rate Up to 95% Remaining Weight

Biocomposite PCLacac	R <sup>2</sup>	Regression equation	t50% (day)	t95% (day)
0%	0.9473	-1.1637x+110.69	52	91
2.5%	0.9633	-3.1447x+161.46	35	50

Based on the data in Table 3 and Figure 2, the decomposition time of the biocomposite with 2.5% PCLacac was faster than the other biocomposites. This is likely due to the biocomposite becoming more hydrophilic, and more accessible to water and microorganisms. Consequently, the ester bond hydrolysis and enzymatic activity are faster.

On the other hand, the biocomposite without PCLacac addition (0%) had a slower biodegradation rate than the other biocomposites. Furthermore, the decomposition time of the biocomposite with 0% PCLacac addition until half the residue remained (t50%) was 52 days. Meanwhile, the decomposition time of the biocomposite with 0% PCLacac addition until 5% residue remained (t95%) was 91 days. [15]–[17].

### 3.1.4. Water Swelling Test

Figure 3 shows the results of the water swelling test on biocomposites with PCLacac compositions of 0% and 2.5%. This test was conducted to determine the percentage of water absorption in the biocomposite film within a 24-hour period. The water absorption rate reflects the material's resistance to water.



**Fig 3.** Water swelling test on biocomposite (a) 0% (b) 2.5%

Table 4 presents the results of the water swelling test on the biocomposites. The 2.5% PCLacac biocomposite showed the highest water absorption at 0.8%. In contrast, the biocomposite without PCLacac was 0.65%.

**Table 4.** Water Test Results on Biocomposites

Biocomposite PCLacac	Initial Weight (g)	Final Weight (g)	Absorption (%)
0%	0,0609	0,0613	0,65
2.5%	0,0618	0,0623	0,8

The high water absorption of the 2.5% PCLacac biocomposite is likely due to the lack of dominant hydrophobic molecules. As a result, water diffuses more easily into the material. Meanwhile, the low water absorption of the 0% PCLacac biocomposite after 24 hours of immersion is likely due to the formation of dominant hydrophobic molecules and the small number of PCL end groups. As a result, the molecules can associate with each others and form a waterproof area [15]–[17].

### 3.2. Discussion

Tables 2 and 3 show that the addition of 2.5% PCLacac to the biocomposite resulted in the highest degradation rate compared to the biocomposite without PCLacac addition (0%). This increased biodegradation rate is most likely due to the presence of short-chain PCLacac in the biocomposite matrix. These short chains increase the number of end groups per unit mass of polymer, thus expanding the area accessible to water, enzymes, or microorganisms. Thus, the hydrolysis process of the ester bonds in the PCL main chain becomes easier.

In addition to chemical factors, the morphological structure of biocomposites also plays a crucial role in accelerating degradation. The addition of hydrophilic nanocellulose can create microchannels within the polymer matrix. These microchannels serve as pathways for water and oxygen diffusion, facilitating water penetration and the movement and colonization of microorganisms into the interior of the biocomposite. This condition accelerates the formation

of hydrolytic enzymes by microorganisms, which in turn accelerates the polymer chain breakdown process.

The results in Table 4 also show that the biocomposite with the addition of 2.5% PCLacac also has the highest water absorption compared to the biocomposite without PCLacac. This increase in water absorption is in line with the observed increase in the biodegradation rate. This indicates that the addition of PCLacac not only changes the chemical structure of the polymer but also increases the hydrophilicity and water absorption capacity of the biocomposite. The absorbed water plays an important role in the degradation process because it triggers the initial hydrolysis reaction and accelerates the disintegration of the polymer structure.

Overall, these results indicate that the combination of short-chain PCLacac and hydrophilic nanocellulose provides a synergistic effect in increasing the water absorption and biodegradation rate of biocomposites. This modification can be an effective approach in designing biodegradable materials with adjustable degradation rates for biomedical applications and environmentally friendly packaging.

#### 4. Conclusion

Based on the research results, it can be concluded that the addition of 2.5% PCLacac to the PCL matrix with nanocellulose filler from rice stalk can significantly improve the biodegradation properties and water absorption capacity of the biocomposite. This formulation shows the best performance compared to the composition without PCLacac. Thus, the use of PCLacac as a compatibilizer is effective in modifying the PCL matrix, as well as opening opportunities for the development of environmentally friendly biocomposites that have the potential to be applied in various fields, especially biodegradable and sustainable materials. In addition, the results of this study can be an important basis for the development of green materials that support the reduction of material waste in the future.

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