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Valorization of Active Agent Nanochitosan-Catechin in Development Mechanical Properties Based on Polylactid Acid (PLA)- Polycaprolactone (PCL) Mixture

Suryani[1,*], Teuku Rihayat[1], Fitria[2], Aida Safitri[3], Isra Adelya Izzati[1]

1 Department of Chemical Engineering, Lhokseumawe State Polytechnic, Jl. Banda Aceh-Medan Km. 280,3, Buketrata, Mesjid Punteut, Blang Mangat, Kota Lhokseumawe, Aceh 24301, Indonesia
2 Department of Dermato Venereology, Medical Faculty, Syiah Kuala University, Aceh 23111, Indonesia
3 Department of Chemical Engineering, Faculty of Engineering, Universitas Sumatera Utara, Kota Medan 20222, Indonesia

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ABSTRACT

The circular economy was created to convert waste resources into economic products by implementing various strategies, two of which are: using materials from renewable sources and producing biodegradable products. The aim of this research is to manufacture polylactid acid (PLA) which is usually made from fermented plant starch, and a mixture of polycaprolactone (PCL), a biodegradable polyester, to investigate its potential use as a substitute for oil-based commodity plastics. The PLA/PCL mixes were mixed in batches using a lab-scale internal mixer and then printed. The mechanical strength of the resulting bioplastic was tested using the UTM d638 tool. It has been found that incorporating PCL into the PLA matrix can produce materials with tensile strengths ranging from 8.67 to 44.48 mPa. The incorporation of PCL significantly increases the toughness of PLA, increasing the energy required to fracture the specimen. Based on the results of GC-MS compounds like Beta elemene, Caryophyllene, Methanodrostonole, Alpha humulene, and Gamma gurjenene from jamblang seeds have good antioxidant activity. The addition of active compounds in the matrix must be considered in the study of the durability and stability of the PLA-PCL packaging film. When the active ingredient was added more than 7%, the tensile strength decreased drastically due to the only interaction between the active agent in the form of catechin and chitosan. Overall, the obtained PLA/PCL blends were found to be a strong and environmentally friendly alternative to oil-based commodity materials.

1. Introduction

Food waste is a global environmental issue that necessitates far more sustainable practices all over the world. The awareness of this issue is growing, and environmental scientists are developing solutions. It is critical to continue to address the issue of food waste. Food packaging waste is a significant environmental degrading aspect of the food industry that many consumers overlook [1-

* *Corresponding author.*
E-mail address: suryani.salimpnl@gmail.com

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3]. Every year, approximately one-third of the food produced is wasted due to a variety of factors such as environmental conditions, mechanics, spoilage, transportation, microbial spoilage, oxidation, and so on. Furthermore, packaging technology requirements vary from one food to the next. As a result, the food industry must adapt packaging systems to provide valuable features for food preservation [4].

To maintain food quality and freshness, the packaging system must optimize the integrated interaction of chemical, physical, and biological processes between the food and the packaging system [5]. Active packaging system research is now receiving widespread attention in order to develop efficient packaging films to protect food products from both innate and external factors. High-density polyethylene, low-density polyethylene, polypropylene, and polyethylene terephthalate are the most commonly used thermoplastics, with a lifetime of less than a year before being discarded [6-8]. Because of their short lifespan, plastic waste accumulates quickly in the environment. Each year, approximately 10-20 Mt of plastic ends up in the ocean as a result of currents and wind spreading throughout the marine environment, harming its ecosystem and wildlife [9]. It also leads to the transfer of microplastic, containing toxic additives, into the food chain fresh cut vegetables and fruits are highly favored by consumers because of the need for new and natural products and changes in consumer lifestyles, especially during the pandemic [10]. However, the food industry faces the challenge of maintaining the fresh features of meat, vegetable and cut fruit products for long storage periods. Vegetables and fruits are important components of a balanced diet [11,12]. When separated from the tree, plants, especially vegetables and fruit, do not undergo metabolism so over a period of time, the qualities related to color, taste, weight, and nutritional value continue to deteriorate. Loss of water is an important element that plays an important role in decreasing the quality of vegetables and fruits and can result in loss of nutritional value, soft texture, shriveling, and wilting [13].

Considering the limited use of packaging derived from petroleum-derived products, scientists have agreed to use biological materials as a substitute for petrochemical packaging. Among these many biological materials, PLA was chosen as the main polymer for the packaging production process because it has good water vapor barrier properties so that it is suitable for use as raw material for packaging and is included in the GRAS (Generally Recognize as Save) class [14-18]. Along with these advantages, there are disadvantages of PLA which is very sensitive to ultraviolet (UV) light, making it difficult to use in the outdoor environment for a long time and has high fragility so another compatible polymer is needed in the form of a thermoplastic polymer called PCL (Polycaprolactone) [19]. PCL is a linear aliphatic biodegradable polyester which can improve the physical and mechanical properties of the material through the bonding between polymers.

Chitosan, a polysaccharide polymer, can be added to materials to improve the mechanical properties of polymers, as is well known. Additionally, another component, such as an antioxidant, can be added to smart packaging. However, in this study, we investigated the effect of chitosan addition based on the blending of polymeric materials based on their mechanical characteristics and morphological structure.

2. Methodology

The materials used for the extraction of catechins are jamblang seeds and methanol. The materials used for the manufacture of plastic are PLA, PCL, chitosan, catechins, acetic acid and chloroform. All material was purchased in Sigma Aldrich, Jakarta, Indonesia.

2.1 Extraction of Catechins using Soxhlet Extraction

Extraction was carried out using a conventional Soxhlet apparatus referring to the research conducted by Fuente *et al.,* [20]. 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 Smart Packaging Production

To obtain the PLA-PCL biofilm, 50 g of PCL and 950 grams of PLA were dissolved in 1420.5 mL and PCL in 750 mL of chloroform solvent, each 0.067 g/mL, in a beaker separately. The mixing process is carried out by the solvent casting method using a 5 L glass beaker and heat is obtained from the hot plate. The polymer was mixed with the solvent using a magnetic stirrer at a speed of 700 rpm. After mixing for 20 minutes, the sample was evaporated using a rotary evaporator and then prepared for filler mixing. Each filler was catechin and chitosan will be added based on 10 w/w. Before addition, chitosan will be diluted in an acetic solution. Table 1 shows the mixture of chitosan on PLA-PCL packaging.

Table 1
The mixture of chitosan on PLA-PCL packaging

Matriks (PLA/PCL)		Chitosan (g)	Sample code	
9/1	8/2	0.2	X1	X6
		0.4	X2	X7
		0.6	X3	X8
		0.8	X4	X9
		1	X5	X10

3. Results
3.1 Tensile Strength of Bioplastic

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 (refer to Figure 1). Because chitosan, 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 chitosan content in the mixture is considered, our results show higher tensile strength at 6% by weight of nanochitosan content. The addition of plasticizer in the form of PEG influences the result of increasing tensile strength. The even dispersion of chitosan particles is due to the constituent materials' good compatibility and immiscibility. Too much acetic acid solvent in the sample causes a significant decrease in tensile strength because it is corrosive and breaks the cross-linking.

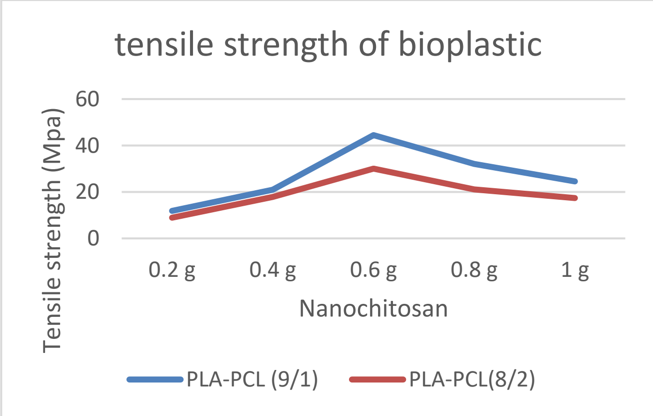


Fig. 1. Graph of the tensile strength

3.2 Characterization of Antioxidant Capacity

Fruit's antioxidant activity is thought to be the most important in the fight against a variety of degenerative diseases. Jamlang fruit seeds contain many phenolic compounds, including catechins, epicatechins, p-coumaric acid, caffeic acid, ferulic acid, and their esters, in addition to saccharides, organic acids, mineral elements, and vitamins A, B, and C. This compound demonstrated strong antioxidant activity. The majority of the apricot peel extract solutions demonstrated antioxidant activity. Table 2 shows the GC-MS analysis for jamblang seed.

Table 2
GC-MS analysis for jamblang seed

Compound name	Retention time
Beta elemene	12.827
Caryophyllene	13.136
Methanodrostonole	13.228
Alpha humulene	13.460
Gamma gurjenene	13.654

An enolic is a compound having an aromatic ring with one or more hydroxyl groups attached to the carbon atom of the aromatic ring. The hydroxyl group in phenolic compounds contributes directly to antioxidant activity and plays an important role in scavenging free radicals because the hydroxyl group of phenolic compounds can donate hydrogen atoms to stabilize free radicals. Phenolic compounds in the syzigium family consist of simple and complex phenolic compounds. A study by Li *et al.,* [21] states that catechins are the most important flavonoid group as an antioxidant compound. The high content of flavonoids is also related to the high content of phenolic in the extract of jamblang seeds, where flavonoids are a subset of phenolic compounds. Therefore, the high content of phenolic in a material indicates the high content of flavonoids in the material.

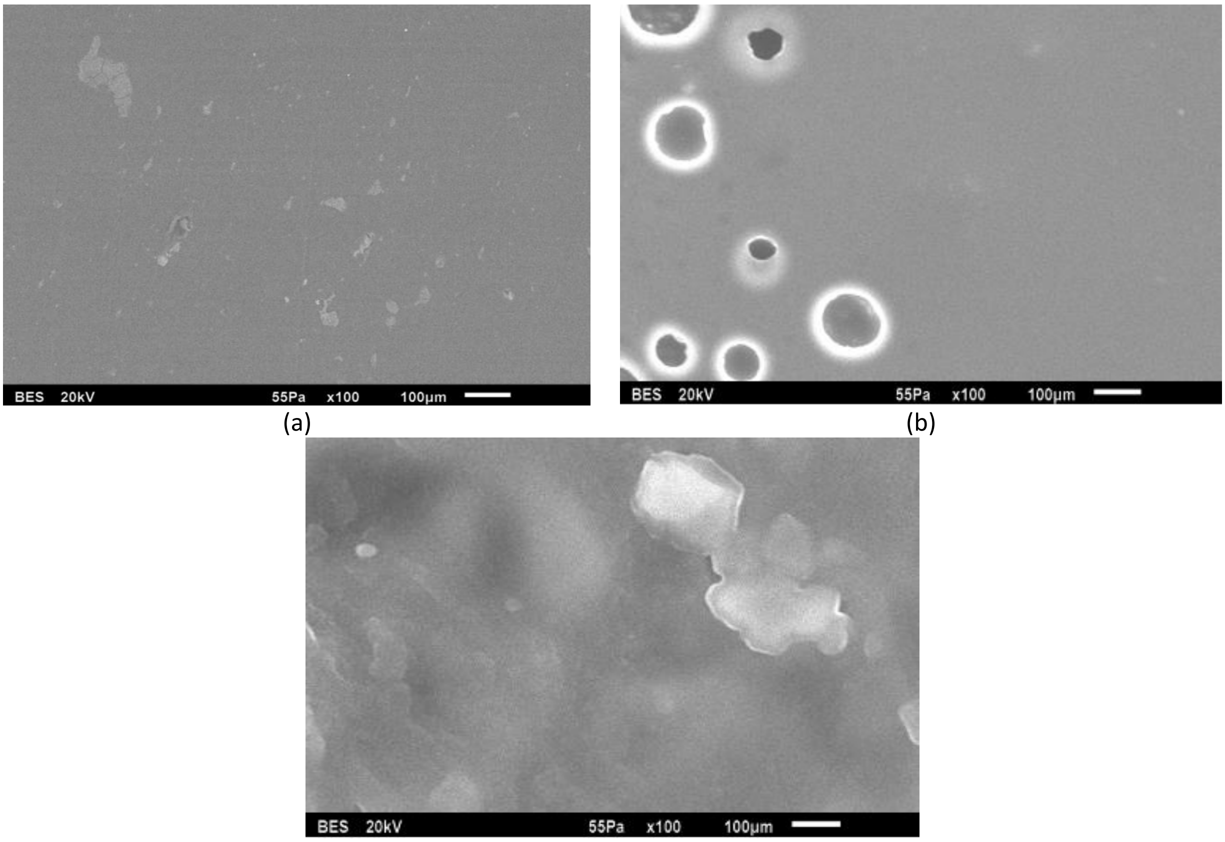
Another study used the DPPH method to assess the antioxidant properties of solvent casting PLA-PCL films loaded with different amounts of catechin and found that radical inhibition was greater than 70% and proportional to catechin content. Similarly, in a recent study by Olewnik *et al.,* [22], different concentrations of propolis extract were incorporated in PLA via solvent casting to protect the sausage from oxidation. The Folin-Ciocalteu method was used to determine the PC in the sausage, and the PC values increased due to the phenolic constituents released from the active films.

3.3 Morphological Structure Test Results with Scanning Electron Microscopy (SEM)

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. The following is a picture of the results of the analysis under an electron microscope (SEM).

Nanochitosan and catechins don't mix well with the PLA-PCL matrix, as seen in Figure 2. Since bioplastics are melted, they are more soluble. Since the interaction between the particles of the active agent and the matrix determines how soluble bioplastics are, it appears that nanochitosan has a different affinity for the matrix. As a result, lumps form, as observed on the surface and cross-section of the bioplastic. The bioplastics have low transparency due to their rough surfaces. Bioplastics' surface morphology and cross-section reveal details on the compactness of their film-forming constituents.

However, when the nanochitosan concentration was increased further, the nanochitosan did not completely blend with the matrix solution. The study by previous author Ma *et al.,* [23] relates to many nanochitosan microparticles formed on the bioplastic surface. The surface structure was smoother at higher nanochitosan concentrations. A high nanochitosan concentration in the polymer bioplastic may prevent anions and cations from attracting each other. Due to the lack of anion in the matrix molecular structure, the cation from nanochitosan may form intramolecular bonding in their molecules rather than intermolecular bonding with starch Ma *et al.,* [24]. Intramolecular bonding caused phase separation between nanochitosan and starch, reducing their rigidity and tensile strength.



(c)

Fig. 2. SEM image of each bioplastic (a) Xa1, (b) Xa7, and (Xa10)

4. Conclusions

The combined use of PLA-PCL to design smart packaging for food packaging by incorporating Active Agents via various processing techniques has been extensively researched in recent decades. According to the GC-MS results, the combination of the matrix and the agent in the form of jamblang seeds resulted in good antioxidant activity abilities. The addition of the active compound in the matrix must be considered in the study of the PLA-PCL packaging film's durability and stability. The mechanical properties show that film containing 0.6 g chitosan provides better properties than any other sample. SEM image also shows that the sample with a rough surface resulted from adding too much nanochitosan because it weakens the intermolecular bound between the matrix and filler. Another factor that will impact the physical/mechanical properties of PLA-PCL is primarily related to thermal decomposition, photo-oxidation, hydrolysis, thermo-oxidation at high temperatures, and natural weathering. Monitoring the functionality of active PLA-PCL films over time, on the other hand, is one of the topics that researchers should consider for future industrial applications.

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