

IMPROVEMENT THE PROPERTIES OF POLY(L-LACTIDE) FILMS WITH CELLULOSE FIBER FROM RICE STRAW WASTE IN AGRICULTURAL PRODUCTS

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ABSTRACT: The poly(L-lactide) films properties were improved by using cellulose from rice straw. The cellulose was extracted by hydrolysis method and that was confirmed the property by using Fourier transforms infrared spectroscopy (FT-IR). The sample films were prepared by mixing poly(L-lactide) with cellulose at different weight ratios (100/0, 98/2, 96/4, 94/6, 92/8, 90/10). Physical, mechanical and thermal properties of the films were analyzed by X-Ray diffraction (XRD), Scanning Electron Microscope (SEM), Thermogravimetric Analysis (TGA) and Tensile testing. It was found that after increasing the concentration of the cellulose to 2 %wt, the tensile strength increases from 24.949 to 37.108 MPa and Young's Modulus slightly increase from 0.112 to 0.189 GPa. The thermal stability of the sample films increased slightly. These results showed that cellulose from rice straw was enhanced to develop the thermal and mechanical properties of poly(L-lactide) film. The water uptake increased with the addition of cellulose.

Keywords: *Poly(L-lactide), Cellulose fiber, Rice straw*

1. INTRODUCTION

Nowadays, polymers are used in the daily life of human which used mostly from petroleum. Because the polymers are lightweight, inexpensive and high strength but it is hard to be degradable. Therefore, the biodegradable polymer is one choice to substitute polymer from fossil fuel. The biodegradable polymers are classified according to their origin into two groups which are natural polymers for example chitosan[1], chitin[2], starch[3] and silk fibroin[4] and synthetic biodegradable polymers such as poly(glycolic acid)[5], poly(caprolactone)[6] and poly(l-lactide). In the decade the researchers are interested in poly(l-lactide) due to nearby properties with the petrochemical origin. The outstanding properties of poly(l-lactide) are renewable[7], biodegrading[8], transparent properties[8]. However, poly(l-lactide) is very brittle[9] and low toughness, which limits in applications that need plastic deformation under high stress[10]. Thus, the disadvantages of poly(l-lactide) were improved by composite with bamboo charcoal[11], cotton gin waste [12], oil palm [13] and cellulose fiber[14]. Thailand is one of rice country so there is a lot of leftover rice straw after the harvest of rice. Although the straw is useful for animal feeding or used as a material for cultivation of straw mushroom however the quantity of rice straw is still rested a lot. Therefore, farmers need to get rid of rice straw by burning, which resulted in

the environmental impact. As rice straw is a marginal feed compared to other cereal grain straw and a problematic fuel source due to high ash generation, exploring more viable options to utilize rice straw is pressing, particularly as an environmental concern. The composition of rice straw is cellulose (38.3%), hemicellulose (31.6%), lignin (11.8%) and silica (18.3%)[15]. In this work reducing the problems of the environment and adding value to the rice straw was studied. Improvement the mechanical properties and thermal properties of the poly(l-lactide) films with cellulose fiber from rice straw was studied in different ratios (0%, 2%, 4%, 6%, 8% and 10% of cellulose fiber).

2. MATERIALS AND METHODS

2.1 Materials

The poly(l-lactide) (PLLA, molecular weight = 100,000), used in this study was supplied by Assoc. Prof. Dr. Yodthong Baimark. Sodium hydroxide (NaOH, AR grade, Ajax Finechem), hydrogen peroxide (H₂O₂, 30-32%, ANAPURE), sulfuric acid (H₂SO₄, 98%, ANAPURE) and Chloroform (CHCl₃, AR grade, LLC) were used as received.

2.2 Preparation of Cellulose from Rice Straw

Rice straw from agriculture was cut in the length of

1-2 cm, washed 3-4 times with tap water for removing dust and dried at 100 °C for 24 hours. NaOH (2M) was added to rice straw (1 g/NaOH 20 ml) and boiled under constant stirring at 80 °C for 1 hour. After that, it was washed with distilled water. Fibers were bleached with 18.5% H₂O₂ (v/v) for 3 hours, then washed with distilled water. The cellulose fibers were hydrolyzed using 50% H₂SO₄ (v/v) at 45°C for 1 hour under constant stirring as a previously reported method [7]. After hydrolysis, it was diluted with cold water to stop the hydrolysis reaction. Then the samples were washed with water until neutral pH to remove the excess sulfuric acid. The suspension was sonicated [7] at 45 °C for 30 minutes and evaporated in an oven at 100 °C for 12 hours. Then, it was ground into a powder, the powdered cellulose fibers were selected in the size 150-250 µm before stored in a desiccator.

2.3 Fabrication of Poly(L-Lactide)/Cellulose Composite Film

Adding the chloroform 15 ml into poly(l-lactide) and stirred until 1 hour. Then it was mixed with cellulose for 30 minutes. It was poured into the petri dish and dried in an oven at 50°C for 1 hour. After that, it was also deeply dried in a vacuum oven at 50°C for 24 hours and then it was stored in a desiccator. The ratio of poly(l-lactide)/cellulose was 100/0, 98/2, 96/4, 94/6, 92/8 and 90/10 (w/w).

2.4 Characterization of Poly(L-Lactide)/Cellulose Composite Film

FT-IR spectra were obtained using Fourier Transform Infrared Spectroscopy; FTIR (Perkin Elmer model Spectrum GX). The measurements were scanned in the range 400 - 4000 cm⁻¹. X-ray diffraction; XRD was widely used for the identification of unknown crystalline materials and measured by the machine models D8 ADVANCE (Bruker). The crystallinity of cellulose was extracted from rice straw, films sample were scanned by scattering 2 angles from 5-40 degree with a rate of 0.2 sec/degrees. Scanning Electron Microscope; SEM (JEOL, JSM-64606V) was used to study surface and morphology (shape, pattern, size) of the samples. The cellulose powder samples were prepared into the carbon tape on the stub and coated with gold. The film samples were prepared by immersion in liquid nitrogen before it was broken to study the cross-section morphology. The film pieces were also mounted on the stub to study morphology. Thermogravimetric Analysis; TGA samples were heated from 40 to 800 °C at a rate of 10 °C/min under nitrogen atmosphere. Tensile

testing of the film samples was studied on a universal testing machine (LLOD INSTRUMENTS, AS500) at room temperature. The film samples were cut 1 × 8 cm. (repeat 5-10 times). The water uptake capacity [16] of each film was studied by cut the film to size 1 x 1 cm and was immersed into distilled water at room temperature for 90 minutes. Then it was taken off from water and weighed. The water uptake was determined using this equation

$$\% \text{ Water uptake} = \frac{M_2 - M_1}{M_1} \times 100$$

where M₁ is the weight of the dry film before immersion and M₂ is the weight of the film after immersion.

3. RESULTS AND DISCUSSION

The extracted cellulose was filtered with the sieves and the size of cellulose was 150-250 µm. The result was showed in Fig 1. The result of FT-IR was presented in Fig 2, the 3500-3000 cm⁻¹ range characterized by a broad spectrum and high intensity of OH stretching and 1650 cm⁻¹ was OH bending showed at a lower range than adsorbed water. At 1450-1420 cm⁻¹ was C-H stretching and the range of 1382-1375 cm⁻¹ was CH bending. At 902-893 cm⁻¹ was associated with cellulosic β-glycosidic linkages, at 1155 cm⁻¹ was C-C ring stretching, and C-O-C at 953 cm⁻¹ was glycosidic ether. The results were similar to Ping Lu's *et al* [17] results.



Fig. 1 Rice straw cellulose powder

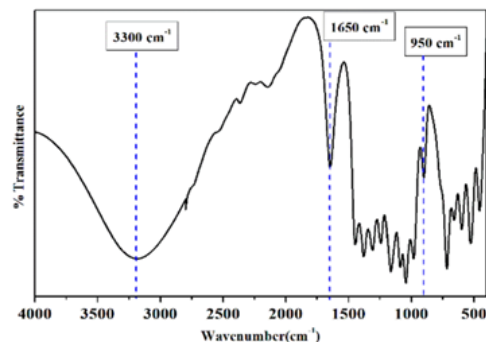


Fig. 2 FT-IR spectrum of rice straw cellulose

The XRD results (Fig. 3) showed that the crystalline peaks of cellulose were at 15.3° , 22.5° , and 34.5° . It could be asserted that the extraction of cellulose could be accomplished by hydrolysis. Lignin and hemicellulose were amorphous structure. The crystalline peaks are found in the same area as the research by Anuj Kumar *et al* [18]. It was also found that when the improved chemical was increased the crystallization was also increased due to the amorphous removal. Fig 4 shows that the appearance of cellulose powder was small and uncertain shape may be due to the hydrolysis process.

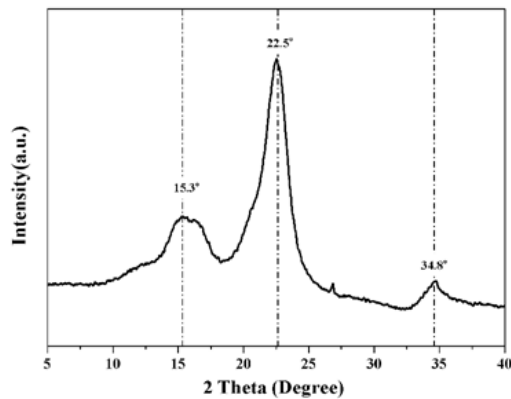


Fig. 3 XRD spectrum of rice straw cellulose

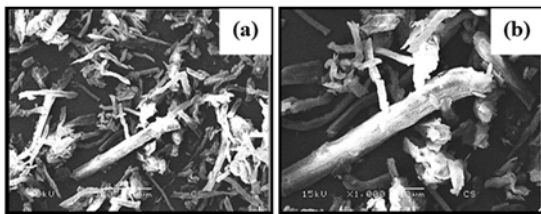


Fig. 4 Morphology of rice straw cellulose powder from SEM 500X (a) and 1000X (b)

3.1 Characterization of Poly(L-Lactide) Films Mixed with Rice Straw Cellulose Fiber

The physical appearance of the poly(l-lactide) films (Fig. 5) was smooth and clear. The best cellulose distribution compared to other ratios was PLLA98/CS2. When adding more cellulose, the film became darker and the cellulose was clumped due to the polarity of the cellulose. The results obtained by FT-IR analysis (Fig. 6) show that (a) was a 100% cellulose spectrum. The dominant function of the $3500\text{--}3000\text{ cm}^{-1}$ spectrum was broad spectrum and high intensity of OH stretching. The range of $1450\text{--}1420\text{ cm}^{-1}$ was C-H stretching and at 950 cm^{-1} was C-O-C glycosidic ether and (g) was the spectrum of poly(l-lactide) film. The 1750 cm^{-1} function group was a function of C=O and the range

of $1450\text{--}1420\text{ cm}^{-1}$ was C-H stretching. The (b-f) spectrum was poly(l-lactide) film mixed with cellulose. The range of $3500\text{--}3000\text{ cm}^{-1}$ was OH stretching. It has broad-spectrum and high intensity compared to poly(L-lactide) film (spectra g). As a result, there was a large number of hydroxyl groups (OH) in cellulose. The 1750 cm^{-1} was a function of carbonyl (C=O), which was prominent in poly(l-lactide). C-H stretching was a common group of poly(lactic acid) and cellulose (950 cm^{-1}). C-O-C was a glycosidic ether that was prominent in cellulose. The range of $1450\text{--}1420\text{ cm}^{-1}$ was C-H stretching, which was found in poly(l-lactide) and cellulose. As 950 cm^{-1} was a C-O-C glycosidic ether that is prominent in cellulose. The results of FT-IR can be confirmed that the sample film (b-f) were contained cellulose. [17]

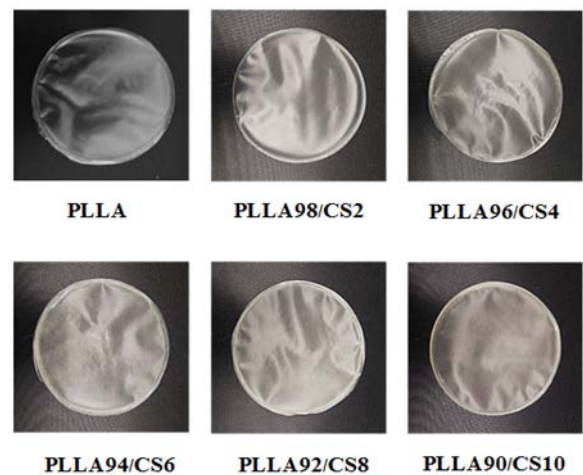


Fig. 5 Physical characteristics of films

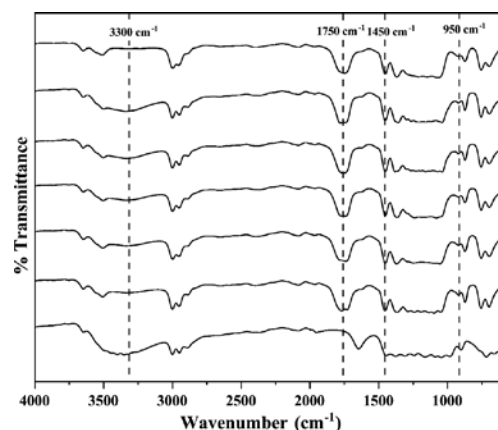


Fig. 6 FT-IR spectra of the film in various ratios (a) CS100, (b) PLLA98 / CS2, (c) PLLA96 / CS4, (d) PLLA94 / CS6, (e) PLLA92 / CS8 (f) PLLA90 / CS10 and (g) PLLA 100.

The crystallinity of polylactide film at 16.7° and

22.6° was shown in Fig. 7. According to Ping Lu *et al.* [18], 2 θ values of cellulose were found at 15.3° 22.5° and 34.5°. When the cellulose was mixed into the poly(l-lactide), it was observed that the crystallinity of the film was increased, and the highest increase was the PLLA98 / CS2 ratio film. Surface characteristics of films were shown in Fig.8. It was found that the surface appearance of poly (l-lactide) film was smooth and less rough which was different to the films that mixed with cellulose, which were more roughly textured, the ratio of cellulose increases. However, PLLA98/CS2 was a good dispersion of the cellulose, making the least rugged surface film when compared to the others. The poorly distributed cellulose, resulting in a rough surface. The cross-section of ratio each film was investigated. It was found that the poly(l-lactide) contains rough surface texture somewhat less than film mixed with cellulose. The results were in the same direction as the surface characteristics of the film, as shown in Fig. 9. The cellulose was inserted into the films. It was known that poly(l-lactide) and cellulose were not homogeneous because non-polar properties of poly(l-lactide) and that the cellulose was polar properties. So, it was less homogeneous. But it can be seen that the cellulose can be inserted into the poly(l-lactide) as a result of adhesion. It could be said that cellulose has a rough surface when poly(l-lactide) melts into a liquid and could be inserted into the gap in the roughness of the cellulose when the poly(l-lactide) solidifies it causes adhesion. It also described the adhesion of the chemical bonding. Many hydroxyl groups of cellulose could build up hydrogen bond between molecules of cellulose and poly(l-lactide) [19,20]

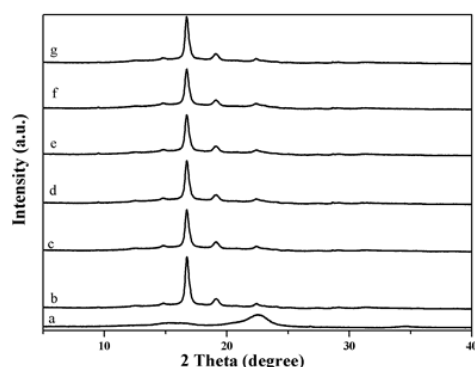


Fig. 7 XRD spectra of the film in various ratios (a) CS100, (b) PLLA98 / CS2, (c) PLLA96 / CS4, (d) PLLA94 / CS6, (e) PLLA92 / CS8 (f) PLLA90 / CS10 and (g) PLLA 100.

Thermogram analysis was shown in Fig.10. The decomposition of poly(l-lactide) at 320 °C and cellulose decomposition showed at 360 °C, so it

was showed only one component. Decomposition of hemicellulose (250 °C) and lignin (365 °C) were not found [21]. When the cellulose was mixed into the poly(l-lactide), the degradation was 1 stage at 300-400 °C. The decomposition of each ratio varies. It was noted that when the cellulose content increases, the temperature of the decomposition of the film increases slightly as shown in Table 1

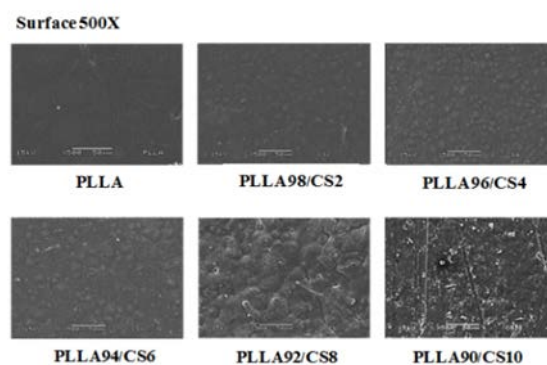


Fig. 8 The surface of PLLA, PLLA98 / CS2, PLLA96 / CS4, PLLA94 / CS6, PLLA92 / CS8 and PLLA90 / CS10 500X

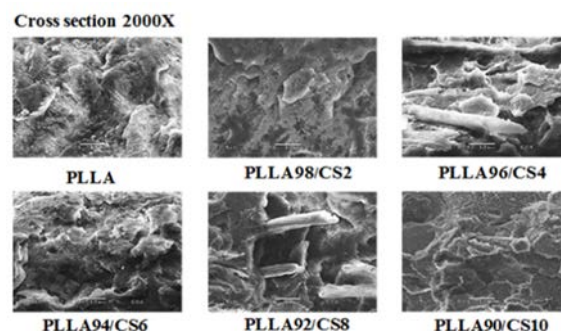


Fig.9 The cross section of PLLA, PLLA98 / CS2, PLLA96 / CS4, PLLA94 / CS6, PLLA92 / CS8 and PLLA90 / CS10 2000X

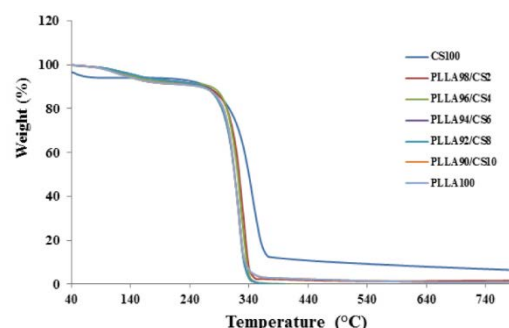


Fig. 10 TG thermograms of PLLA100, PLLA98 / CS2, PLLA96 / CS4, PLLA94 / CS6, PLLA92 / CS8, PLLA90 / CS10 and CS100.

Tensile testing of poly(l-lactide) film and cellulose mixed films in various ratios were found that cellulose affects the mechanical properties of poly(l-lactide) films. When mixing the cellulose in the poly(l-lactide) films, the tensile strength, elongation at break and Young's modulus of films were increased. These values indicated the strength of the film (The results are shown in Table 2). However, the highest test values were from PLLA98/CS2 film. This may be due to the amount and dispersion of cellulose in the film, which affected the strength. The results of this study were consistent with the findings of Sanyang ML *et al.* [16] and also consistent with SEM results. The good dispersion of cellulose resulted in a stronger film. Due to the uniform dispersion, the mixed film was very strong adhesion. Thus the mixed films were better tensile properties than the poly(l-lactide) film without cellulose blends. However, when the amount of cellulose mixture was increased at more than 2% the films were reduced strength. Because the more cellulose, the formation of cellulose was poor dispersion and less adhesion between poly(l-lactide) and cellulose.

Table 1 Temperature decomposition of cellulose and films

| Sample | T _{d(max)} (°C) |
|-------------|--------------------------|
| CS100 | 360 |
| PLLA | 320 |
| PLLA98/CS2 | 340 |
| PLLA96/CS4 | 340 |
| PLLA94/CS6 | 330 |
| PLLA92/CS8 | 330 |
| PLLA90/CS10 | 330 |

Table 2 Tensile testing of the films

| Sample | σ^a (MPa) | ϵ^b (MPa) | E ^c (GPa) |
|-------------|------------------|--------------------|----------------------|
| PLLA100 | 24.95±3.95 | 6.47±1.36 | 1.11±38.31 |
| PLLA98/CS2 | 37.92± 1.03 | 13.55±3.45 | 1.12 ±45.28 |
| PLLA96/CS4 | 35.46±1.12 | 10.70±2.04 | 1.18 ±77.58 |
| PLLA92/CS8 | 30.60±1.09 | 10.31±0.96 | 1.02 ±88.79 |
| PLLA90/CS10 | 29.98±1.39 | 7.12±2.06 | 1.15±94.63 |

^a Tensile strength ^b Elongation at break ^c Young's Modulus

The water absorption results were present in Fig. 11. The poly(l-lactide) film was the lowest water absorption while the water absorption of mixed films was increased because of the hydroxyl groups

of cellulose. The water absorption increased with an increasing amount of cellulose. When comparing PLLA with PLLA98/CS2, the values were slightly different[16].

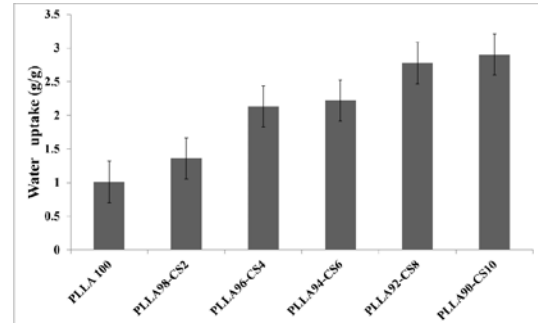


Fig. 11 The water absorption ratio of films

4. CONCLUSION

The rice straw cellulose was mixed in poly(l-lactide) by the solvent method. The ratio of poly(l-lactide)/cellulose was 100/0, 98/2, 96/4, 94/6, 92/8 and 90/10. Physical characteristics of the film were darker color when cellulose content was increased. The surface fracture of the films was more uneven surface as the ratio of cellulose increased. The thermal stability of the films was slightly increased with the addition of cellulose blends. The cellulose content increased also increasing the tensile strength, Elongation at break, and Young's Modulus. However, when the amount of cellulose is increased, the formation of cellulose results in poor distribution and less adhesion between the poly(l-lactide) and the cellulose. It could be concluded that the cellulose extracted from rice straw was used as a reinforcement to increase the thermal and mechanical properties of poly(l-lactide). The film with 2% cellulose blend was the best thermal and mechanical properties due to the addition of ingredients in the right proportion and well dispersed in the poly(l-lactide) of cellulose.

5. ACKNOWLEDGMENTS

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6. REFERENCES

- [1] J. Bonilla, E. Fortunati, M. Vargas, A. Chiralt, and J. M. Kenny, "Effects of chitosan on the physicochemical and antimicrobial properties of PLA films," *J. Food Eng.*, vol. 119, no. 2, pp. 236–243, 2013.
- [2] R. Nasrin, S. Biswasa, T. U. Rashid, S. Afrina,

- R. A. Jahan, P. Haque, and M.M.Rahman, "Bioactive Materials Preparation of Chitin-PLA laminated composite for implantable application," *Bioact. Mater.*, vol. 2, no. 4, pp. 199–207, 2017.
- [3] M. A. Shirai, M. V. E. Grossmann, F. Yamashita, P. S. Garcia, and C. M. O. Muller, "Development of biodegradable flexible films of starch and poly (lactic acid) plasticized with adipate or citrate esters," *Carbohydr. Polym.*, vol. 92, no. 1, pp. 19–22, 2013.
- [4] S. L. Jackman, C. H. Chen, S. N. Chettih, S. Q. Neufeld, I. R. Drew, C. K. Agba, I. Fiaquer, A. N. Stefano, T. J. Kennedy, J. E. Belinsky, K. Roberston, C. C. Beron, B. L. Sabatini, C. D. Harvey, and W.G. Regehr, "Silk Fibroin Films Facilitate Single-Step Targeted Expression of Optogenetic Proteins Resource Silk Fibroin Films Facilitate Single-Step Targeted Expression of Optogenetic Proteins," *CellReports*, vol. 22, no. 12, pp. 3351–3361, 2018.
- [5] K. Lee, K. U. K. R. O. Yoon, S. I. H. L. Woo, and I. S. Choi, "Surface Modification of Poly (glycolic acid) (PGA) for Biomedical Applications," *J. Pharm. Sci.*, vol. 92, no. 5, pp. 933–937, 2003.
- [6] T. Patricio, M. Domingos, A. Gloria, and P. Bartolo, "Characterisation of PCL and PCL / PLA scaffolds for tissue engineering," *Procedia - Soc. Behav. Sci.*, vol. 5, pp. 110–114, 2013.
- [7] M. Kaseem, K. Hamad, H. W. Yang, F. Deri, and Y. G. Ko, "Properties and medical applications of polylactic acid: A review," *EXPRESS Polym. Lett.*, vol.9, no.5, pp. 435–455, 2015.
- [8] M. Murariu and P. Dubois, "PLA composites: From production to properties," *Adv. Drug Deliv. Rev.*, vol. 107, pp. 17–46, 2016.
- [9] L. T. Lim, R. Auras, and M. Rubino, "Processing technologies for poly (lactic acid)," *Prog. Polym. Sci.*, vol. 33, no. 8, pp. 820–852, 2008.
- [10] R. M. Rasal, A. V. Janorkar, and D. E. Hirt, "Progress in Polymer Science Poly (lactic acid) modifications," *Prog. Polym. Sci.*, vol. 35, no. 3, pp. 338–356, 2010.
- [11] M. Ho, K. Lau, H. Wang, and D. Hui, "Improvement on the properties of polylactic acid (PLA) using bamboo charcoal particles," *Compos. Part B*, vol. 81, pp. 14–25, 2015.
- [12] R. M. Bajracharya, D. S. Bajwa, and S. G. Bajwa, "Mechanical properties of polylactic acid composites reinforced with cotton gin waste and flax fibers," *Procedia Eng.*, vol. 200, pp. 370–376, 2017.
- [13] M. K. M. Haafiz, A. Hassan, Z. Zakaria, I. M. Inuwa, M. S. Islam, and M. Jawaid, "Properties of polylactic acid composites reinforced with oil palm biomass microcrystalline cellulose," *Carbohydr. Polym.*, vol. 98, no. 1, pp. 139–145, 2013.
- [14] H. Kyutoku, N. Maeda, H. Sakamoto, H. Nishimura, and K. Yamada, "Effect of surface treatment of cellulose fiber (CF) on durability of PLA/CF bio-composites," *Carbohydr. Polym.*, vol. 203, no.1, pp. 95–102, 2019.
- [15] A. Ecology, M. Tayyab, F. Agriculture, S. Waheed, and F. Agriculture, "Bioethanol production from lignocellulosic biomass by environment-friendly pretreatment methods: A review," *Appl. ecol. environ. res.*, vol. 19, no. 1, pp. 225–249, 2015.
- [16] M. L. Sanyang, S. M. Sapuan, M. Jawaid, M. R. Ishak, and J. Sahari, "Development and characterization of sugar palm starch and poly (lactic acid) bilayer films," *Carbohydr. Polym.*, vol.146, no. 1, pp. 36–45, 2016.
- [17] P. Lu and Y. Lo Hsieh, "Preparation and characterization of cellulose nanocrystals from rice straw," *Carbohydr. Polym.*, vol. 87, no. 1, pp. 564–573, 2012.
- [18] A. Kumar, Y. S. Negi, V. Choudhary, and N. K. Bhardwaj, "Characterization of Cellulose Nanocrystals Produced by Acid-Hydrolysis from Sugarcane Bagasse as Agro-Waste," *Mater. Chem. Phys.*, vol. 2, no.1, pp. 1–8, 2014.
- [19] C. Miao and W. Y. Hamad, "Alkenylation of cellulose nanocrystals (CNC) and their applications," *Polym.*, vol. 101, pp. 338–346, 2016.
- [20] E. Luiz, D. Paula, V. Mano, E. Aparecida, R. Duek, and F. Vargas, "Hydrolytic degradation behavior of plla nanocomposites reinforced with modified cellulose nanocrystals," *Quim. Nova*, vol. 38, no. 8, pp. 1014–1020, 2015.
- [21] S. Hyun, Y. Chang, and J. Han, "Development of polylactic acid nanocomposite films reinforced with cellulose nanocrystals derived from coffee silverskin," *Carbohydr. Polym.*, vol. 169, pp. 495–503, 2017.