



Open
Access

Physicochemical Characteristics of Bionanocomposites, Polycaprolactone/Starch/Cocoa Pod Husk Microfibrillated Cellulose

Dzun Noraini Jimat^{1,*}, Farahiyah Adi Putra¹, Sarina Sulaiman¹, Yusilawati Ahmad Nor¹, Nor
Fadhillah Mohamed Azmin¹, Sharifah Shahira Syed Putra¹

¹ Department of Biotechnology Engineering, Kulliyah of Engineering, International Islamic University Malaysia, 53100 Kuala Lumpur, Malaysia

ARTICLE INFO

ABSTRACT

Article history:

Received 27 October 2018

Received in revised form 23 November 2018

Accepted 13 December 2018

Available online 18 March 2019

The development of biocomposites has increased due to their biodegradability, renewability, and high specific strength which are comparable with other polymer composites. Even though, the conventional composites are still in high demand due to their durability, however, it cannot decompose and the accumulation of these wastes for a long period is harmful to the living things and to the environment. Therefore, in this study the biodegradable polymers, polycaprolactone (PCL) and starch were selected in this study to synthesize bionanocomposite incorporated with microfibrillated cellulose (MFC). The microfibrillated cellulose (MFC) was extracted from cocoa pod husk (CPH–MFC) and was mixed with PCL and starch, where its amount was varied between 3-10wt%. The prepared bionanocomposites were characterised in terms of its water uptake rate, and structural and thermal properties using Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). The morphology analysis using scanning electron microscope (SEM) shows that the CPH–MFC extracted was in nanoscale size. The percentage of water uptake of the prepared bionanocomposites increased with the amount of CPH–MFC. Meanwhile, the FTIR spectra of the prepared bionanocomposites showed almost similar characteristic peaks with the FTIR spectra of pure PCL. DSC analysis showed that the melting temperature increased as the amount of CPH–MFC increased. This study justifies that the incorporation of CPH–MFC with the PCL–starch matrix improved the water uptake rate and thermal properties but did not show significant changes to the structure of PCL.

Keywords:

Bionanocomposites, thermal properties,
water uptake rate

Copyright © 2019 PENERBIT AKADEMIA BARU - All rights reserved

1. Introduction

The amount of plastic being used is tremendously increasing with the increase of population. This leads to a high accumulation of plastic wastes all over the world. It is harmful to the environment and can cause water, land, and air pollutions. Due to its durability and non-biodegradability, it cannot

*Corresponding author.

E-mail address: jnoraini@iium.edu.my (Dzun Noraini Jimat)

decompose and the accumulation for this waste for a long period is harmful to the living things as well as to the environment.

Recycling plastic is one of the ways to tackle this problem, but recycling plastics means that people are still using plastics but for different purposes. Hence, this will not reduce the amount of plastics, so this is not the most effective way to cut off the plastic consumption. Therefore, the invention of biodegradable plastics which can be easily disposed could assist to reduce environmental pollution problems due to non-degradable plastics.

Polycaprolactone (PCL) has received much attention as one of the packaging materials due to its high flexibility and biodegradability as well as its hydrophobic nature. Unfortunately, commercial applications are limited since the production cost of PCL appears to be high. To overcome the limitations and create new materials with desired properties, PCL can be blended with low cost biodegradable natural biopolymers such as starch and chitin. Blending of PCL and starch could markedly reduce the cost and also enable flexibility. However, blending PCL with starch can cause problems due to poor compatibility between the two phases. Therefore, the compatibility of the two immiscible phases can be enhanced with the addition of a compatibiliser such as cellulose.

A new concept that incorporates waste materials from crops such as cocoa pod husk, coconut husks, sugarcane bagasse and rice straw into useful products such as biocomposite, adsorbent-based [1] and building materials [2] has prevented the increasing amount of waste disposal. Since it is low decomposable material, disposing too much of this waste material needs a high cost and is a time-consuming process. In addition, the usage of cellulose from crop waste as the compatibiliser saves the cost of biocomposite production. Thus, this study investigates the characterisation of the prepared PCL–starch incorporated with microfibrillated cellulose from cocoa pod husks. This type of biocomposite is potential to be used as bio-based packaging materials such as dairy products [3].

In Malaysia, cocoa fruits have its own economic value to produce commercialised products such as cocoa butter, chocolate, and cocoa powder. There is a huge amount of cocoa pod husk discarded as waste after going through fruits processing. In 2010, there was over 20,643 hectares of cocoa plantations around Malaysia [4]. It is estimated about 700–750 kg of cocoa waste will be produced from each tonne of cocoa fruit which leads to waste management problem. Currently, the waste is used as fertiliser for cocoa tree after decomposition process of cocoa pod husk whilst a few farmers utilise it to feed the animal. Perhaps, by converting this by-product of cocoa into valuable new products which could be commercialised, it can improve the sustainability of our environment and also diversify the economic aspects of cocoa. In fact, this huge quantity of cocoa pod husk contains a large quantity of cellulose which is good to be used in bionanocomposite production.

Cellulose is the most widespread natural polysaccharide and the most abundant organic compound derived from lignocellulosic biomass [2]. Cellulose fibre is naturally made by microfibrils linked together and it is composed of large polymer chains with an empirical formula $(C_6H_{10}O_5)_n$ and has varied molecular weights. The application of cellulose fibres in bionanocomposite has a great potential to improve the performance of polymeric matrix in mechanical resistance aspect. In comparison with others, it has some unique advantages and properties such as renewability, biodegradability, biocompatibility, recyclability, relatively high resistance, and stiffness [5]. Due to these improved properties, there are many potential applications for cellulose-based bionanocomposites such as packaging products, electronics, cosmetics, and medical applications. Microfibrillated cellulose (MFC) consists of particles that contain multiple elementary fibrils with a high aspect ratio, high surface area, and segregated amorphous and crystalline regions [6]. It is about 10–40 nm thick fibrous cellulose structures with the length of several tens of microns [7]. Cellulose microfibrils are flexible and the long nanoparticles and these fibrils can form a network or web-like structure which are suitable for mechanical reinforcement of nanocomposite.

PCL is a semicrystalline polymer and an increase in molecular weight tends to decrease its crystallinity [8]. It is commonly prepared by using stannous octoate catalyst through ring-opening polymerisation process of ϵ -caprolactone [9]. Compared with other polymers, PCL has many advantages such as biodegradable, biocompatible, good in mechanical strength, and can be shaped at ease. In many industrial applications, starch is seen as a good material to make biocomposites since it is cheap and abundant. Blending pure starch with synthetic biopolymer such as PCL can be applied to improve both PCL and starch properties by complementing each other's weaknesses. Biodegradable polymers such as PCL have been blended with starch to enhance strength of the foams and water resistance [10]. Due to its advantages such as biodegradable, renewable, and has high strength and stiffness, nanoscale cellulose fibre such as microfibrillated cellulose (MFC) is widely used to produce bionanocomposites. Research study on development of high performance and/or functional polymer materials using nanoparticles is greatly increased in designing attractive composite to expand its application industry [11]. It is an unique challenge to obtain the desired properties of polymer composites as different approach would produce different final product [12]. Only few studies were carried out in incorporating MFC into the polymer nanocomposites, specifically PCL [13,14] or PCL/starch blends [15,16]. Hence, this project investigated the characteristics of the prepared PCL–starch incorporating with microfibrillated cellulose from cocoa pod husk (CPH–MFC) in terms of its physicochemical structure, water uptake rate, and thermal property. The usage of extracted MFC from cocoa pod husks is not only provide a new alternative route of CPH wastes but also alternative sources of nanocellulose which would enhance the features of synthesized polymer biocomposite (PCL-starch) for this study.

2. Methodology

2.1 Materials

Cocoa pod husks were obtained from the Malaysian Cocoa Board in Jengka, Pahang. Caprolactone ($C_6H_{10}O_2$) and sodium hydroxide (NaOH, 99%) were purchased from Merck, Germany. Hydrogen peroxide (H_2O_2 , 35%), dichloromethane (CH_2Cl_2), methanol (CH_3OH), and sulfuric acid (H_2SO_4 , 98%) were supplied by Friendemann Schmidt Chemical, Australia. Stannous octoate [Tin(II) 2-ethylhexanoate, 100%] was purchased from Sigma, USA. Starch ($C_6H_{10}O_5$)_n and chloroform ($CHCl_3$) were purchased from System, Malaysia and R&M Chemical, U.K respectively. All the reagents were of analytical reagent grade (AR).

2.2 Extraction of Microfibrillated Cellulose from Cocoa Pod Husk (CPH–MFC)

The extraction of microfibrillated cellulose (MFC) was performed as described by Jimat *et al.*, [17]. The ground and sieved cocoa pod husk was mixed with 2% (w/v) of NaOH before it was placed in a water bath at 80 °C. Prior to placing it again in a water bath at 75 °C, the cellulose was bleached with 1:1 aqueous solution of H_2O_2 . Then, the material was treated with 12% (w/v) of NaOH before placing it again in a water bath at 80 °C followed by washing and filtration. Next, the cellulose was mixed with 1% (w/v) of H_2SO_4 and were placed in a water bath (Memmert, WB/OB 7-45 WBU 45) at 80 °C. Finally, the resulting cellulose was filtered and washed sufficiently with distilled water. Then, the extracted CPH–cellulose was sonicated using ultrasonicator at 70 amplitude (FB-705 Fischer-Scientific™ Ultrasonic Dismembrator). After that, the samples were centrifuged (Heraeus Multifuge X1R, Germany) for 20 min at 10000 rpm and at 5 °C. Then, the MFC suspension was kept at 4 °C until further analysis.

2.3 Preparation of Polycaprolactone (PCL)

The procedure for the preparation of PCL was adapted from a previous study with some modifications [18]. The ring-opening polymerisation reaction of ϵ -caprolactone monomer was done with the help of stannous octoate catalyst. A mixture of 30 mL of caprolactone and 0.25 g of stannous octoate was placed in a 250 mL conical flask. The mixture was stirred constantly at 140 °C for 2 h. As the reaction proceeded, the mixture became highly viscous and it was subsequently dissolved in dichloromethane and precipitated out in methanol. Later, the solution was poured into glass petri dishes and placed in an oven (Memmert, INE400-E406) at 45 °C for a day.

2.4 Preparation of Bionanocomposites PCL–Starch Incorporated with CPH–MFC

The bionanocomposites were prepared based on a study done by previous researchers [19]. The PCL pellets were dissolved in chloroform and stirred constantly using a magnetic stirrer (IKA C-MAG HS7, Germany) at 40 °C. After PCL were fully dissolved, starch and CPH–MFC were added and the mixture was continuously stirred for 2 h. The mixture was poured into glass petri dishes and allowed to dry at room temperature for 2 days. Each of the sample was prepared in triplicates. The composition of the prepared bionanocomposites is shown in Table 1.

Table 1
The composition of prepared bionanocomposites

PCL (wt/wt%)	Code	Starch (wt/wt%)	Microfibrillated Cellulose (wt/wt%)	Glycerol (wt/wt%)
100	Pure PCL	0	0	0
	PCL-1	25	3	2
70	PCL-2	23	5	2
	PCL-3	18	10	2
	PCL-4	20	3	2
75	PCL-5	18	5	2
	PCL-6	13	10	2
	PCL-7	15	3	2
801	PCL-8	13	5	2
	PCL-9	8	10	2

2.5 Characterisation Analyses

2.5.1 Water uptake rate

The water uptake rate was done by weighing about 0.5 g of each biocomposite. Each sample was placed in a beaker containing 10 mL of water. After 1 h, the biocomposite was taken out from the beaker, the excess water was wiped, and the final weight was measured. The percentage of water uptake of biocomposite was determined using Equation 1:

$$\text{Percentage water uptake, \%} = \frac{\text{Final weight} - \text{Initial weight}}{\text{Final weight}} \times 100\% \quad (1)$$

2.5.2 Field emission scanning electron microscopy (FESEM) analysis

Field emission scanning electron microscope (FESEM, Merlin, Zeiss, Germany) with an accelerating voltage of 10.0 kV was used to investigate the morphology of the extracted CPH–MFC.

The cellulose suspensions were dropped on the holder with a double sided cellophane tape and left to dry for 24 h before coating with iridium for 15 min.

2.5.3 Fourier transform infrared spectroscopy (FTIR) analysis

The FTIR spectra of CPH–MFC, PCL, and biocomposites were determined using Nicolet IS50 FTIR model (Thermo Scientific, US). The spectra were recorded in the range of 4000–400 cm^{-1} .

2.5.4 Differential scanning calorimetry (DSC) analysis

The thermal analysis on the biocomposite and pure PCL was performed on a Mettler Toledo Star System DSC-1 apparatus (Switzerland). About 7–15 mg of the sample was placed in the aluminium pan and put inside the machine slot. The heating rate of 10 $^{\circ}\text{C}/\text{min}$ was used while the temperature was varied from 25 to 150 $^{\circ}\text{C}$.

3. Results

3.1 Morphology of Chemical Treated and Sonicated of CPH–MFC

The FESEM images of raw cocoa pod husk (a) and extracted CPH–MFC (b) are shown in Figure 1. Figure 1(a) shows a native cellulose fibre structure before treatment process that comprised thick-walled fibre and intact structure. While, the extracted CPH–MFC after chemo-physical treatment appeared as long interconnected fibrils that tied to a three-dimensional (3D) network. This proves that the lignin and hemicellulose were successfully removed and the fibre was separated into individual cellulose microfibril. The fibres were in range of 10-20 nm in diameter and several micrometer in length.

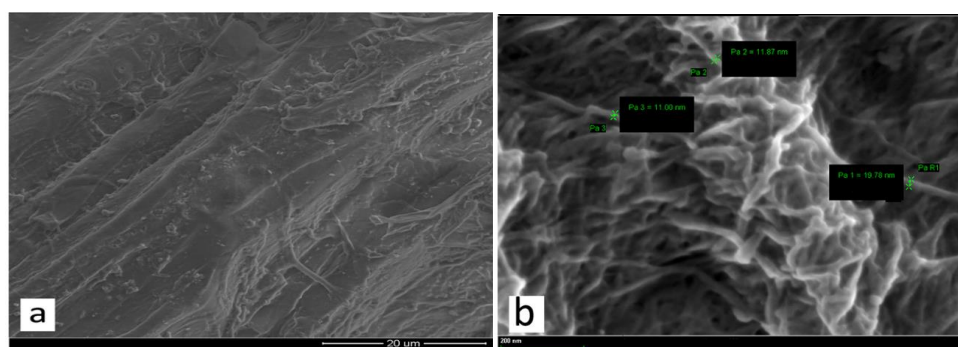


Fig. 1. FESEM images of (a) crude cocoa pod husk (2000 \times magnification) and (b) extracted CPH-MFC via chemical–physical treatment (100,000 \times magnification)

The FTIR spectrum of CPH–MFC is shown in Figure 2. The absorption peak at 3333.4 cm^{-1} was assigned to hydroxyl groups stretching. The peaks at 2891.83 and 1367.29 cm^{-1} were assigned to stretching and deformation vibrations of C–H group in glucose unit. Meanwhile, β -glycosidic linkage between glucose units was justified by the absorption peak at 894.29 cm^{-1} . The peak at 1023.72 cm^{-1} was assigned to C–O– group of secondary alcohols and ethers functions existing in the cellulose chain backbone. This CPH–MFC FTIR spectrum proves that the absorption peaks correspond to CPH–MFC.

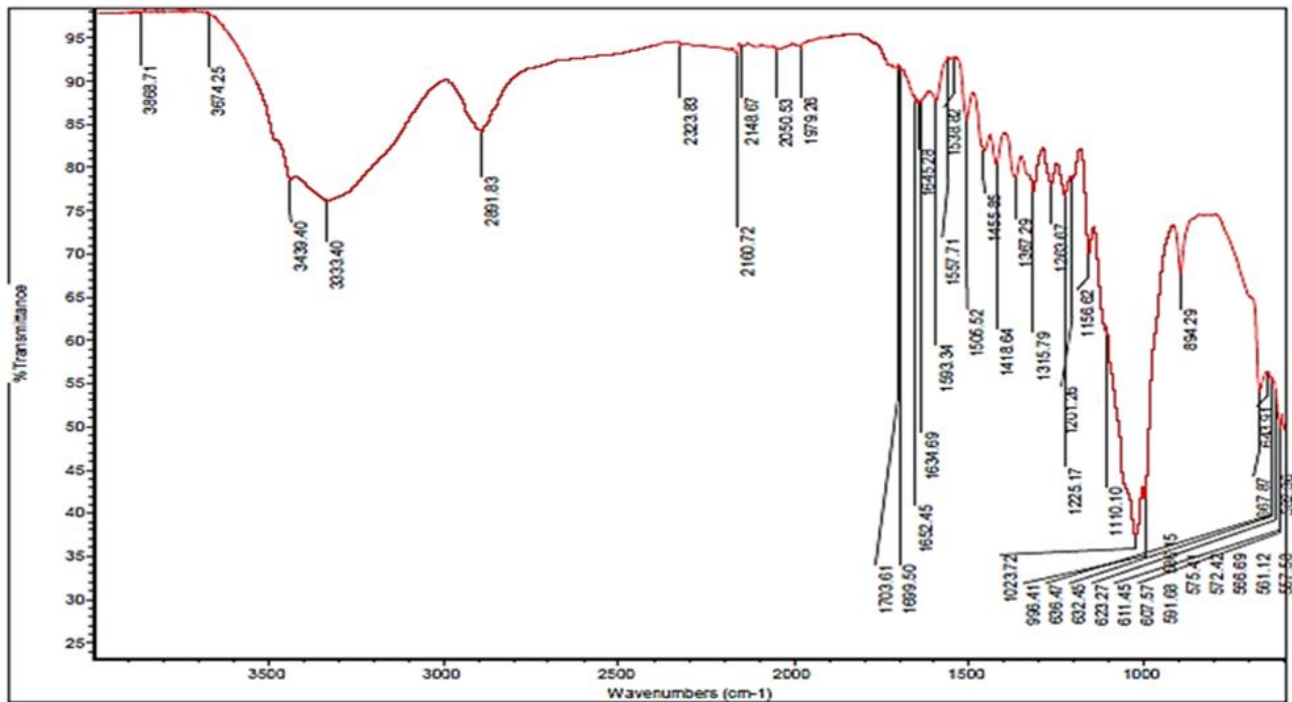


Fig. 2. FTIR spectrum of CPH-MFC

3.2 Characterisation of Polycaprolactone (PCL) and Bionanocomposites

Polycaprolactone/Starch/Cocoa Pod Husk Microfibrillated Cellulose (CPH-MFC) Water Uptake Rate

Figure 3 represents the percentage of water uptake of the prepared bionanocomposites. The pure PCL (100 wt% of PCL) had the least percentage of water uptake compared with those of the bionanocomposites containing 70, 75, and 80 wt% of PCL, because PCL has hydrophobic property and does not interact with water. A study reported that the percentage of water uptake increased as the amount of CPH-MFC increased [20]. The biocomposites with 3 and 10 wt% of CPH-MFC showed the lowest and highest percentage of water uptake, respectively, due to the hydrophilic property of the cellulose where its hydroxyl groups can form hydrogen bondings with water molecules. The best sample group which showed the least percentage of water uptake was the bionanocomposite containing 75 wt% of PCL (PCL-4, PCL-5, and PCL-6).

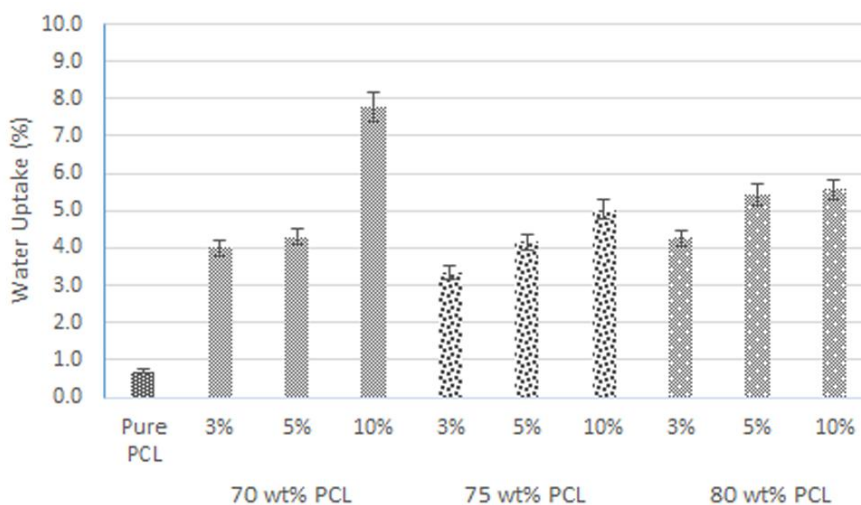


Fig. 3. Water uptakes of the prepared bionanocomposites

3.3 FTIR Analysis of Bionanocomposites

Figure 4 represents the FTIR spectra of the samples of pure PCL, PCL-4, PCL-5, and PCL-6. PCL was prepared through the ring opening polymerisation reaction of caprolactone monomer using stannous octoate catalyst and it was analysed using FTIR. The absorption peaks at 2944.32 and 2864.73 cm^{-1} were assigned to the C–H hydroxyl groups asymmetric stretching and C–H hydroxyl groups symmetric stretching, respectively. In addition, the C=O stretching vibrations of the ester carbonyl was justified by the absorption peak at 1720.65 cm^{-1} . The absorption peaks at 1238.34 and 1167.24 cm^{-1} were assigned to C–O–C asymmetric stretching and C–O–C– symmetric stretching, respectively. These FTIR spectra prove that the absorption peaks correspond to PCL.

The FTIR spectra of PCL-4, PCL-5, and PCL-6 showed almost similar characteristic peaks like pure PCL. All the characteristic peaks representing starch and CPH–MFC were not distinctive due to the overlapping of very intense bands of PCL. Overall, there were no significant differences between the characteristics peak of PCL–starch Incorporated with CPH–MFC with the pure PCL. This may be due to the low amount of starch and CPH–MFC added in the prepared biocomposites thus the characteristics peaks of PCL were more dominant.

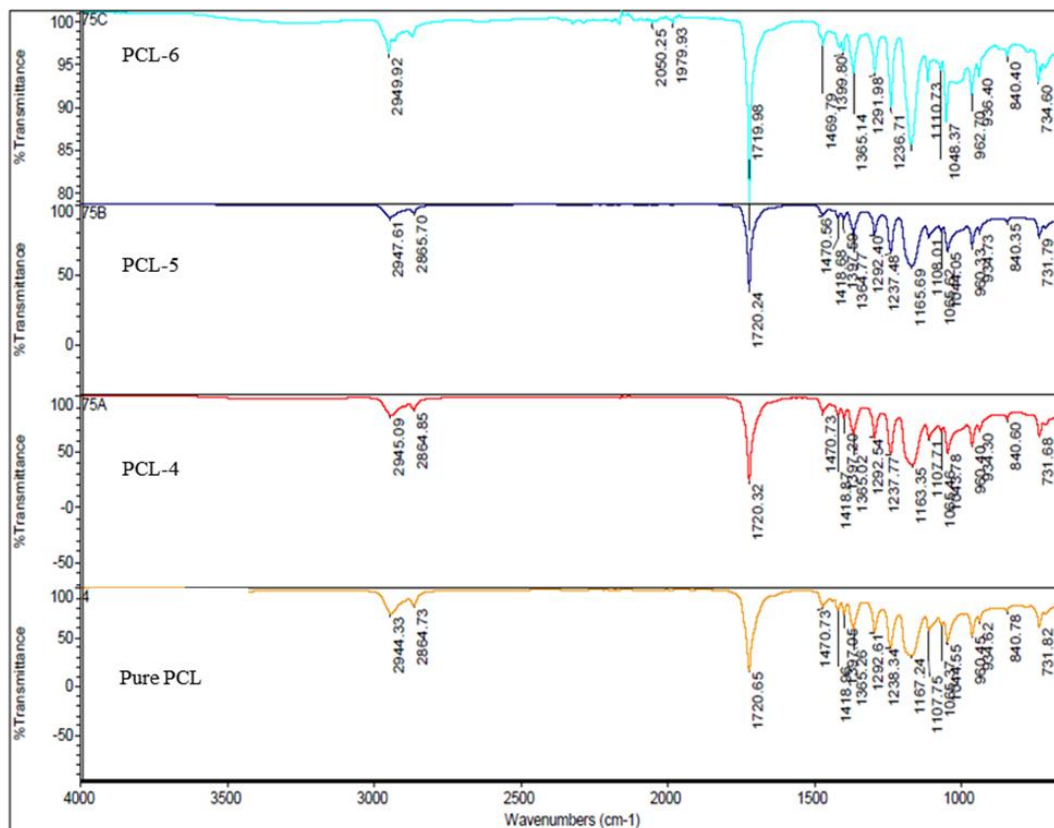


Fig. 4. FTIR spectra of pure PCL, PCL-4, PCL-5, and PCL-6

3.4 Thermal Analysis of Bionanocomposites

Table 2 shows the melting behaviour of the prepared bionanocomposites probed by DSC whereas Figure 5 represents the DSC thermograms of the pure PCL and bionanocomposites PCL-4, PCL-5 and PCL-6. The melting temperature of pure PCL obtained was 60.44 $^{\circ}\text{C}$ which satisfies the actual melting temperature of PCL polymer [21]. However, the melting temperature of the sample PCL-4 decreased to 59.15 $^{\circ}\text{C}$ when starch and 3 wt% CPH–MFC were added. The addition of starch to PCL reduced the

melting temperature of PCL possibly due to the PCL molecular weight reduction. For the samples PCL-5 and PCL-6, the melting temperature increased to 62.20 and 62.35 °C, respectively. A study stated that the melting temperature of bionanocomposites increased as the amount of CPH–MFC increased [22]. This is due to the cellulose that acts as a compatibiliser, improving the thermal property as it ties the molecules between PCL and starch phases. Besides that, the thermal property was improved since there was a higher amount of hydrogen bonds between the cellulose chains which led to a more ordered or packed cellulose regions. However, from Figure 5, the addition of CPH–MFC only gave some minimal changes to the melting temperature of bionanocomposites PCL-4, PCL-5, and PCL-6. Further studies are necessary in order to investigate mechanical and barrier properties of this developed bionanocomposite (PCL/starch/CPH–MFC) which are critical features for being used as bio-based packaging material such as dairy products [3].

Table 2
Melting temperatures of the prepared bionanocomposites

Sample	Melting Temperature T_m (°C)
Pure PCL	60.44
PCL-4	59.15
PCL-5	62.20
PCL-6	62.35

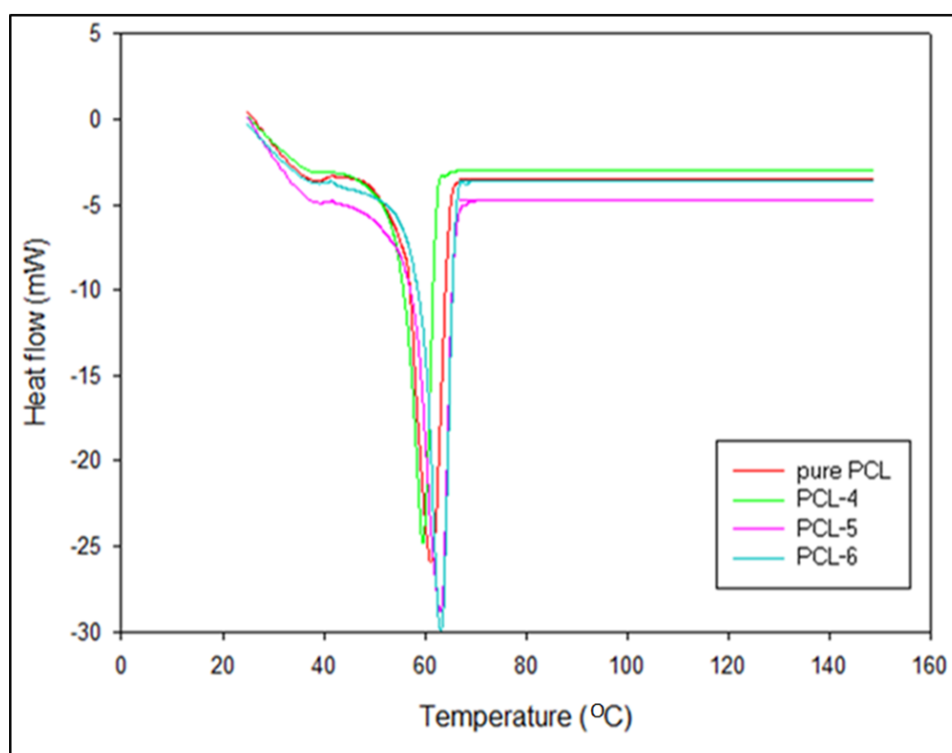


Fig. 5. DSC thermogram of the pure PCL and bionanocomposite PCL-4, PCL-5, and PCL-6

4. Conclusion

The microfibrillated cellulose was successfully extracted from cocoa pod husk through chemical pretreatment and sonication. In addition, bionanocomposites based on PCL–starch incorporated

with CPH–MFC were prepared and characterised in terms of water uptake rate, FTIR and DSC analysis. The water uptake of the prepared bionanocomposites increased as the amount of CPH–MFC added increased. For structural analysis using FTIR, it was observed that the characteristic peaks of PCL dominated because a less amount of starch and CPH–MFC were added. For thermal analysis using DSC, the melting temperature of the bionanocomposites increased as the amount of CPH–MFC increased. Thus, the incorporation of CPH–MFC within the PCL–starch matrix improved the water uptake rate and thermal property but did not show significant changes to the structure of PCL.

Acknowledgement

The authors thanked the International Islamic University Malaysia (IIUM) for providing the equipment, chemicals, and instruments for this research. We also thanked the Malaysian Cocoa Board for supplying cocoa pod husk (CPH).

References

- [1] Basri, W. N. F. W., Jun-Wei Lim, Mohamed Hasnain Isa, Lavania Baloo, Yoshimitsu Uemura, Mohammed JK Bashir, Yen-Cheong Lee, and Dennis Ling Chuan Ching. "Sugarcane bagasse-based adsorbent as an alternative to enhance the harvesting process of *Chlorella vulgaris* biomass." *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences* 46, no. 1 (2018): 106-113.
- [2] Din, Abdul Talib, Norzawahir Mohd Hafiz, and Anika Zafiah Mohd Rus. "Exploration to Find Green Building Materials from Recycled Solid Wastes." *Journal of Advanced Research in Materials Science* 12 (2015): 12-23.
- [3] Jakobsen, Marianne, V. Holm, and G. Mortensen. "Biobased packaging of dairy products." In *Environmentally compatible food packaging*, pp. 478-495. Woodhead Publishing, 2008.
- [4] Daud, Zawawi, Halizah Awang, Mohd Kassim, Angzzas Sari, Mohd Hatta, Mohd Zainuri, and Ashuvila Mohd Aripin. "Cocoa pod husk and corn stalk: Alternative paper fibres study on chemical characterization and morphological structures." In *Advanced Materials Research*, vol. 911, pp. 331-335. Trans Tech Publications, 2014.
- [5] Mondragon, G., S. Fernandes, A. Retegi, C. Peña, I. Algar, A. Eceiza, and A. Arbelaiz. "A common strategy to extracting cellulose nanoentities from different plants." *Industrial crops and products* 55 (2014): 140-148.
- [6] dos Santos, Fernanda Abbate, Gisele CV Iulianelli, and Maria Inês Bruno Tavares. "The use of cellulose nanofillers in obtaining polymer nanocomposites: properties, processing, and applications." *Materials Sciences and Applications* 7, no. 05 (2016): 257.
- [7] Siró, István, and David Plackett. "Microfibrillated cellulose and new nanocomposite materials: a review." *Cellulose* 17, no. 3 (2010): 459-494.
- [8] Woodruff, Maria Ann, and Dietmar Werner Hutmacher. "The return of a forgotten polymer—Polycaprolactone in the 21st century." *Progress in polymer science* 35, no. 10 (2010): 1217-1256.
- [9] ÇAKMAN, Gülce, and Nursel DILSİZ. "Preparation and Physical, Thermal Properties of Polycaprolactone/m-Halloysite Nanocomposite." *J. Multidiscip. Eng. Sci. Stud.* 2 (2016): 842-848.
- [10] Soykeabkaew, Nattakan, Chuleeporn Thanomsilp, and Orawan Suwantong. "A review: Starch-based composite foams." *Composites Part A: Applied Science and Manufacturing* 78 (2015): 246-263.
- [11] Chakrabarty, Arindam, and Yoshikuni Teramoto. "Recent advances in nanocellulose composites with polymers: a guide for choosing partners and how to incorporate them." *Polymers* 10, no. 5 (2018): 517.
- [12] Kargarzadeh, Hanieh, Marcos Mariano, Jin Huang, Ning Lin, Ishak Ahmad, Alain Dufresne, and Sabu Thomas. "Recent developments on nanocellulose reinforced polymer nanocomposites: A review." *Polymer* 132 (2017): 368-393.
- [13] Tian, C., S. Y. Fu, Q. J. Meng, and Lucian A. Lucia. "New insights into the material chemistry of polycaprolactone-grafted cellulose nanofibrils/polyurethane nanocomposites." *Cellulose* 23, no. 4 (2016): 2457-2473.
- [14] de Oliveira Aguiar, Vinícius, and Maria de Fatima Vieira Marques. "Composites of Polycaprolactone with Cellulose Fibers: Morphological and Mechanical Evaluation." In *Macromolecular Symposia*, vol. 367, no. 1, pp. 101-112. 2016.
- [15] Jimat, Dzun N., Faridah Ariffin, Maimunah Asem, and Sarina Sulaiman. "Characterization of biodegradable composite based on polycaprolactone/starch reinforced with sugarcane bagasse microfibrillated cellulose." *Journal of Advanced Research in Materials Science* 39 (2017): 32-39.
- [16] Arun, S., KA Ajith Kumar, and M. S. Sreekala. "Fully biodegradable potato starch composites: effect of macro and nano fiber reinforcement on mechanical, thermal and water-sorption characteristics." *International Journal of Plastics Technology* 16, no. 1 (2012): 50-66.
- [17] Asem, M., W. M. F. W. Nawawi, and D. N. Jimat. "Evaluation of water absorption of polyvinyl alcohol-starch

- biocomposite reinforced with sugarcane bagasse nanofibre: Optimization using Two-Level Factorial Design." In *IOP Conference Series: Materials Science and Engineering*, vol. 368, no. 1, p. 012005. IOP Publishing, 2018.
- [18] Sivabalan A, Harihara R, Meenarathi B, Palanikumar S, Anbarasan R. "Synthesis and Characterization of poly (ϵ -caprolactone: A comparative study." *Int J Sci Res Eng Technol*. (2014): 30–1.
- [19] Azmi, Nurulhusna, A. Aznizam, A. Sani, and A. Nur. "Preparation and Characterization of Tapioca Starch Filled Polycaprolactone Composite Films." *Malaysian Journal of Analytical Sciences* 18, no. 3 (2014): 612-617.
- [20] Su, Jianyu, Ling Chen, and Lin Li. "Characterization of polycaprolactone and starch blends for potential application within the biomaterials field." *African Journal of Biotechnology* 11, no. 3 (2012): 694-701.
- [21] Thompson, Richard C., Charles J. Moore, Frederick S. Vom Saal, and Shanna H. Swan. "Plastics, the environment and human health: current consensus and future trends." *Philosophical Transactions of the Royal Society B: Biological Sciences* 364, no. 1526 (2009): 2153-2166.
- [22] Zoppe, Justin O., Maria S. Peresin, Youssef Habibi, Richard A. Venditti, and Orlando J. Rojas. "Reinforcing poly (ϵ -caprolactone) nanofibers with cellulose nanocrystals." *ACS applied materials & interfaces* 1, no. 9 (2009): 1996-2004.