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Characterization of biodegradable composite based on polycaprolactone/starch reinforced with sugarcane bagasse microfibrillated cellulose



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ARTICLE INFO	ABSTRACT
Article history: Received 2 July 2016 Received in revised form 1 February 2017 Accepted 4 August 2017 Available online 30 November 2017	Biodegradable polymers have been extensively studied in order to substitute the synthetic polymers since they are non-biodegradable which is harmful to environment. Polycaprolactone (PCL) could be a good candidate to substitute synthetic polymer since it can be slowly degraded by microbes. PCL was synthesized by ring-opening polymerization of Σ -caprolactone with stannous octoate as catalyst. To improve the mechanical strength of PCL, it was reinforced with microfibrillated cellulose (MFC) and starch acts as filler. MFC was extracted from sugarcane bagasse (SCB) through chemo-mechanical treatments. Characterizations of the PCL-starch composite reinforced with MFC-SCB with respect to its morphology and structural changes as well as its thermal degradation were evaluated. In this study, amount of tapioca starch was fixed at 40%. Meanwhile, the composition of PCL and MFC-SCB were varied from 50% to 58% and 2% to 10% respectively. Initial observation from microscopy images showed that there were significant changes of morphology of PCL after adding starch and SCB-MFC. As shown in SEM images, the surface of biocomposite PCL-starch-MFC-SCB was quite uniform and smooth with less 5% of MFC-SCB due to the presence of sugarcane bagasse microfibril cellulose.
microfibrillated cellulose, composite	Copyright © 2017 PENERBIT AKADEMIA BARU - All rights reserved

1. Introduction

The interests in biodegradable based composites have increased rapidly. Most of the research focuses on the green polymeric materials which can be obtained from renewable sources [1]. Natural polymers like cellulose and their derivatives are available in huge quantities. They can be

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extracted from various renewable sources like from plant or from their residue such as sugarcane bagasse. Most importantly, they are biodegradable and have some unique properties, thus making them as a suitable candidate for reinforcing agent in composites production. In general, cellulose is light and eco-friendly polymers. Cellulose is also low cost, high specific strength and modulus.

Sugarcane bagasse is the solid waste generated from the process of sugarcane refining, or in other words, after sugarcane stalks were crushed in order to obtain their juice [2]. It can be used in pulp and paper production, products-based on fermentation and many others. When this bagasse undergone suitable modifications and manufacturing processes, the bagasse showed improved mechanical properties like tensile strength, hardness, and impact strength. Furthermore, this bagasse is also known for its easiness to be modified and treated with chemicals, as well as mixing with other materials to form new types of composite materials like blending the fibers with polymers [4]. The cellulose content of bagasse is quite high with 43.6% [3]. The high content of cellulose in bagasse makes it an ideal material to be used as reinforcement in nanocomposite. Microfibrillated cellulose (MFC) is consisting of particles that contain multiple elementary fibrils with a high aspect ratio, high surface area, and segregated amorphous and crystalline region [4]. Therefore, in this study, MFC was extracted from this recyclable, reusable, and biodegradable material, sugarcane bagasse.

One of the synthetic biodegradable polymer that can be used to produce the composites is polycaprolactone (PCL) which is use in food packaging and tissue engineering [5]&[6]. In general, PCL is a linear, hydrophobic, partially crystalline polyester, and the best part is, it can be slowly degraded by microorganisms. Basically, PCL can be prepared through ring-opening polymerization of ε -caprolactone. There are many advantages of PCL compared to other synthetic biopolymer such as (polyglycolid acid) (PGA) and poly (L-lactide) (PLA). PCL has very good thermal stability which shows its degradation temperature in the range of 280°C to 330°C [7]. PCL degrades in nature within only few years whereas conventional plastics takes hundreds and thousand years to fully dispose.

However, some limitation such as high costs, low melting temperature and low mechanical properties of PCL, impede its usage in industries [8]. Blending PCL with other biocompatible materials such as starch and reinforcing agent, cellulose is a possible way to overcome those limitations. Despite that, hydrophobic issues is the limitation to the tissue regeneration using PCL scaffolds, which may affect its rate of degradation and the cell adhesion [9]. Since, PCL is highly hydrophobic and shows high crystallinity, blending PCL with other polymer such as starch is expected to improve its hydrophilicity as well as its biodegradable characteristics.

Starch based materials including pure starch or cassava starch are said to be as the most ideal hydrophilic polymers to be blend with PCL since it is high in hydrophilicity. Many previous studies showed that the blending of PCL-starch based material was a good combination since they completed each other weakness. The weakness of starch based material such as high shrinkage has been overcome by the blending with PCL. Since the morphology and internal interaction of starch will be changed by water molecules, its mechanical properties, glass transition temperature (Tg) and the dimension depend on the water content [10]. Blending starch with degradable hydrophobic polymers can improve its degradation rate. The mechanical properties of these two mixtures are depends on their composition. Previous study reported that physical properties of PCL become significantly worse when blended with starch due to the poor compatibility between the two phases [11]. Therefore, the addition of reinforcing agent like cellulose into the PCL-starch blend can improve the physical properties of the blend. In this study, the microfibrillated cellulose of sugarcane bagasse (MFC-SCB) would be reinforced into polycaprolactone-starch composite and its properties were determined.



Application of biocomposites as alternative material for petroleum-derived products are essential as they are biodegradable materials and could reduce carbon emission and facilitate recycling process [12]. Thus, investigation of structural and thermal properties of bionanocomposite, PCL-starch reinforced with different loading of MFC-SCB was carried out in this study.

2. Experimental Study

2.1 Materials

Chemicals used in this research work were caprolactone (Merck), stannous octoate, dichloromethane (Bendosen), methanol (HmbG Chemicals), cassava starch (Systerm) and chloroform (Systerm ChemAR). Sugarcane bagasse was collected from local night market.

2.2 Preparation of Microfibril Cellulose (MFC)

A 0.25g of solid sugarcane bagasse that already bleached with hydrogen peroxide (H_2O_2) was put in microtube and the distilled water was added until it nearly full. Then, after mixing with vortex, the sample was sonicated using ultrasonication followed by centrifuging for 15 minute at 6000 rpm. The pellet was collected and freeze dried prior use. The freeze dried sample was stored in dessicator until further use.

2.3 Preparation of Polycaprolactone (PCL)

The procedure for synthesis of polycaprolactone (PCL) was adapted from Arun and co-workers [1]. The polymerization of caprolactone monomer was done using stannous octoate as the catalyst. The reaction was held on the hot plate with constant stirring by using magnetic stirrer at 140°C. The mixture became highly viscous as the reaction proceeds. Then, the viscous polymer was dissolved in dichloromethane and precipitated out in methanol. The precipitated polymer was filtered by washing it with water and collected after that.

2.4 Preparation of PCL-starch-MFC-SCB

PCL-starch-MFC-SCB composite was prepared based on the study performed by Hossain and coworkers [13] with some modifications. A homogenous suspension of microfibril cellulose in chloroform was prepared first by stirring and sonication. While, the PCL pellet was dissolved in chloroform (10% w/v) and stirred constantly at 40° C by using magnetic stirrer.

Table 1				
Formulation and Sample Codes For The Nanocomposites				
Codes PC	PCL	Cassava Starch	MFC-SCB (wt%)	
	(wt %)	(wt %)		
C-1	58%	40%	2%	
C-2	55%	40%	5%	
C-3	52%	40%	8%	
C-4	50%	40%	10%	

Then, cassava starch was added after PCL has fully dissolved along with microfibril cellulose suspension in chloroform that prepared before, and stirred for 2 hour. Then, the composite was poured into glass petri dish and allowed to evaporate at room temperature (25^oC). After 24 hour,



the resulting films were dried in a vacuum oven at 50° C for 48 hour and ready for analysis. The composition for the composites preparation is as in Table 1.

2.5 Characterization of the Nanocomposites

2.5.1 Field Emission Scanning Electron Microscope (FESEM) analysis

Morphology of all prepared samples was examined using Jeol JSM-6700F Field Emission Scanning Electron Microscope (FESEM). The dried sample was stamped on the holder with the 1cm x 1cm double-sided cellophane tape.

2.5.2 Differential Scanning Calorimetry (DSC)

The thermal behaviour of the samples was carried out using DSC-1 differential scanning calorimeter (Mettler Toledo Star System). Sample was placed inside the aluminium pan for about 7mg to 19mg and placed inside the machine slot. The heating rate of 100C/min was used while the temperature was varied from 250° C to 1000° C.

2.5.3 Fourier transform infrared (FTIR) spectroscopy Analysis

Fourier transform infrared (FTIR) spectroscopy analyses of the samples were performed by scanning in transmittance mode in the region of 4000 and 550cm⁻¹ (wave numbers) using Thermo Scientific Nicolet iS50 FT-IR Spectrometer machine. The samples were analyzed in triplicates.

3.0 Results and Discussions

Microscopy images of all samples were shown in Figure 1. Surface morphology of native PCL was smooth continuous phase compared to PCL blends with starch or MFC or both. It was observed that the surface of the sample PCL with starch was rough, while PCL-starch-MFC has some aggregates, and the fracture occurred through the interface at some locations probably due to the high concentration of starch.



Fig. 1. Compound microscope images of nanocomposites obtained after 48 hour drying. (A) neat PCL, (B) PCL with MFC, (C) PCL with starch, and (D) PCL with MFC and starch





Fig. 2. FESEM image of neat PCL

Figure 2 shows the smooth surface of neat structure of PCL and Figure 3 shows the FESEM images of prepared PCL-starch blends with different composition of SCB-MFC via solvent-casting. Surface morphology of PCL-starch with 2% MFC-SCB (Figure 3a) was smooth compared to other samples. However, when the composition of MFC-SCB was increased, the appearance of individual microfibril cellulose could be seen on the surface of other samples (Figure 3 b-d). It seems that the individual microfiber cellulose was not well-embedded in the PCL-starch blends.



Fig. 3. SEM images of biocomposites obtained after 48 hour drying. PCL-starch with (a) 2% of SCB-MFC, (b) 5% of SCB-MFC, (c) 8% of SCB-MFC and (d) 10% of SCB-MFC

DSC tests for neat PCL and composites were carried out in order to investigate the melting temperature of the samples. Figure 4 shows the DSC curve of the nanocomposites in which A, B, C and D represent PCL-starch reinforced with 2%, 5%, 8% and 10% MFC-SCB respectively, while E is for neat PCL.





Fig. 4. DSC thermogram of the neat PCL and nanocomposites in which A, B, C and D represent PCL-starch with 2%, 5%, 8% and 10% NC respectively, and E is for neat PCL

As shown in Figure 4, the addition of MFC-SCB into the PCL gave minimal changes to the melting temperature. As expected, the melting temperature of the PCL component increased slightly with an increase in the NC loading. When compared with previous study performed by Zoppe and coworkers [14], the melting temperature obtained is quite similar and had the same trend (when NC loading increased, melting temperature also increased). The melting temperature of neat PCL in this study ranges from 53.23°C to 53.71°C which is in the range of previous study 53.40°C. However, other study by Tsujimoto and co-workers [15] found that the melting temperature for neat PCL was quite high which is 58.6°C while for the composites the melting temperature ranging from 50.6°C to 52.8°C which is quite low. Their study observed that when the loading increased, the melting temperature decreased. This might be due to different source of reinforcing agent used which is epoxidized soybean oil.

Presence of peaks at 1720.96 cm⁻¹ and 1173.51 cm⁻¹ as showed in Figure 5(I) were corresponding to C=O and C-O acyclic stretching of ester group of the sample. Other peaks, 2944.09 cm⁻¹ and 2864.50 cm⁻¹ represent C-H stretching. These results showed that the prepared polymer was polycaprolactone. The same spectra pattern of PCL-starch-MFC-SCB samples was observed with one wide band in the range 3500 - 3000 cm⁻¹ that attributed to the vibrations of O-H (Figure 5II) of starch and carboxylic acid groups from PCL [9]. The peaks at 2915.61 cm⁻¹ and 1316.14 cm⁻¹ represent the C-H stretching and bending of $-CH_2$ groups respectively. While, the peak 1158.42 cm⁻¹, corresponds to the presence of C-O-C stretching bridge of glucose ring structure of cellulose could not be detected. The peak at 1031.08 cm⁻¹ which shows the presence of C-O stretching in the saccharide structure also disappeared. The dispearance of these peaks might be due to the over lapping of very intense bands in PCL and starch as reported in previous studies [9].

The results indicated that MFC-SCB can be a potential reinforcement agent to PCL-starch composite. Its presence slightly improved the thermal properties of PVA-starch composite. However, further studies are needed in evaluating its mechanical strength as well as its water barrier property which may offer good opportunities to various industry applications.





Fig. 5. FTIR spectra of (I) neat PCL and (II) PCL-starch with (A) 2% of SCB-MFC, (B) 5% of SCB-MFC, (C) 8% of SCB-MFC and (D) 10% of SCB-MFC

4.0 Conclusion

This work has demonstrated the potential of using sugarcane bagasse microfibrillated cellulose (MFC-SCB) in the development of biocomposite PCL-starch. It can be concluded that, the developed biocomposite has slightly improved its thermal degradation compared to the original polycaprolactone (PCL).

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