Isolation and characterization of microcrystalline cellulose extracted from banana fiber in poly(lactic acid) biocomposite produced from solvent casting technique

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Abstract. The purpose of this project is to extract Microcrystalline Cellulose (MCC) from Banana fiber to produce Poly(Lactic Acid)/Microcrystalline Cellulose, (PLA/MCC) biocomposite film using a solvent casting technique. The initial phase is the production of MCC from Banana fiber by involving three steps; alkaline treatment, bleaching and acid hydrolysis. MCC produced from the different concentration of Nitric acid in the acid hydrolysis process, were used to analyze the morphological and crystalline properties using SEM and XRD respectively. MCC produced from the higher concentration of Nitric acid shows good morphological properties and higher % crystallinity. Then, MCC compounded into PLA with different filler loading to produce PLA/MCC biocomposite film using a different solvent which is Chloroform and Dichloromethane. Results show that lower MCC loading, induces good filler matrix interaction and this evidences by the improvement of the Tensile strength and Young’s Modulus, as well as shows improvement in loss factor and storage modulus which studied from DMA. Moreover, the addition of MCC slightly improved the thermal stability of PLA. From using a different solvent to produce PLA/MCC biocomposite film, Dichloromethane solvent improves the tensile strength and Young’s modulus of biocomposite film, while Chloroform reduces the tensile properties of biocomposite film.

1 Introduction

Poly (lactic acid), (PLA) thermoplastic is a biocompatible polymer derived from renewable resources such as corn, sugar beets, potato, cheese and whey by fermentation processes [2]. PLA can be processed similarly like polyolefins such as Polyethylene and Polypropylene, moreover, PLA have good stiffness and strength [1,2]. PLA is mainly used in commodity areas, for instance, in packaging, textile and composite with the aid of new technologies and for large scale of production [3]. PLA have better properties, but its low deformation at break, high modulus, hydrophilic properties and low heat resistance have limited its application

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primarily to rigid thermoformed packaging [4]. In this study, PLA based biodegradable composites are prepared with microcrystalline cellulose as the reinforcing phase.

Banana plantation in Malaysia covers 26,000 hectares and it is the second most widely cultivated fruit with the total production of 530,000 metric ton yearly. For every cycle of banana production, four times of waste are generated. Somehow, the leaves can use for wrapping, but the waste stems getting accumulated in banana growing areas. Thus, recycling consideration of banana stem will solve the country’s agriculture disposal problem in eco-friendly way. These agriculture wastes are least cost and also containing cellulose richly, which about 60-65% [5]. In this study, banana fibers chosen to be the raw material to obtain microcrystalline cellulose.

Microcrystalline cellulose, (MCC) is purified, partially depolymerized, non-fibrous form of cellulose that occurs as white. Generally, MCC is odourless, tasteless crystalline powder composed of porous particles and consist of linear homopolysaccharide of β-(1,4) linked anhydro D-Glucose units [6]. MCC which is extracted from natural fiber widely being used in various field such as pharmaceutical, cosmetics, food, plastic composites because of its, compatibility, hydrophilicity, acid-insolubility and biodegradability. There are few methods to extract MCC from lignocellulosic material. In this study, MCC from banana fiber extracted using two steps including cellulose extraction using alkaline pretreatment and MCC preparation through acid hydrolysis method.

MCC in PLA as reinforcing filler has a better dispersion and have ability to improve its properties when using suitable amount of MCC to compound. Moreover, the techniques used to produce PLA/MCC composite also affect the properties of composite produced. Technique used in this study is solvent casting technique; which is a simple technique that used to produce polymer composite with uniform thickness distribution, high optical purity with low haze [7]. Solvents used in this study are Dichloromethane and Chloroform; both solvents are good solvents in order to dissolve PLA [8].

2 Experimental

2.1 Materials

The Poly (lactic acid), PLA is supplied by TT Biotechnology Sdn. Bhd., Penang. Hydrogen Peroxide is supplied by Bendosen Company, while Nitric acid, and Sodium Hydroxide supplied by HmbG Chemicals. Banana fiber obtained from locally in Perlis. The fibers were cut into small pieces and dried under sunlight for 1 week, then crushed to have fine powders.

2.2 Microcrystalline preparation

40g of Banana fibers were soaked in 1000 ml of 1 M Sodium Hydroxide solution overnight. Then the mixture was stirred and heated at 70-80°C for 4 hours. The treated banana stems were bleached using 10% hydrogen Peroxide in 15% Sodium Hydroxide solution at 90°C for 45 min. Bleached banana fibers were washed using distilled water until becomes neutral. Acid hydrolysis process was conducted on bleached fibers using 0.5M, 1.0M and 1.5M of Nitric acid in the reflux system, respectively. The hydrolysis process was conducted for 2.5 hours at 70-80°C. Then, the suspension obtained was filtered and washed to obtained microcrystalline cellulose (MCC). The obtained MCC was dried in an oven at 70°C for 1 day and ground to obtain the fine powder.
2.3 Preparation PLA/MCC biocomposite

Poly (Lactic Acid), PLA pellets were dissolved completely in 45ml of Dichloromethane solvent and stirred at room temperature. Subsequent PLA pellets dissolve completely, 5 php of Microcrystalline cellulose powder which hydrolyzed using 0.5M Nitric acid was slowly added and stirred for 40min. Then, 45 ml of PLA/MCC mixture was cast on the glass mold of 15cm X 15cm and make sure no air bubble present. Following that, the PLA/MCC composite was let to be dried in room temperature for 24 hours. The steps were repeated to form a composite film of PLA/MCC by using different MCC loading which hydrolyzed using different concentration of Nitric acid followed by another solvent, which is Chloroform. The formulation of PLA/MCC biocomposite film with different concentration of Nitric acid hydrolyzed MCC, different loading of Microcrystalline cellulose powder and the different solvent are shown in Table 1.

Table 1. Formulation of PLA/MCC biocomposite produced from Dichloromethane and Chloroform solvents.

| Material                     | PLA/MCC - Dichloromethane solvent | PLA/MCC - Chloroform solvent |
|------------------------------|-----------------------------------|------------------------------|
| PLA, php                     | 100                               | 100                          |
| Concentration of Nitric acid, M | 0.5, 1.0, 1.5                     | 0.5, 1.0, 1.5                |
| MCC loading, php             | 5, 10                             | 5, 10                        |

*php= part per hundred polymer

2.4 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy was used to identify the changes in the functional group of raw fiber and MCC powder prepared using different acid concentration. It can prove that obtained powders from the isolation process were MCC. Raw fiber and MCC powder tested from Perkin Elmer Spectrometer 2000 using Attenuated total reflection (ATR) method. The scan range was set from 600-4000cm⁻¹ at room temperature.

2.5 Scanning Electron Microscope (SEM)

Scanning electron microscope (SEM) machine model JEOL JSM-6460 LA was used to study morphology of MCC powder and tensile fracture surface of biocomposite film. The sample was mounted onto aluminium stubs and coated with a thin layer of palladium to provide a conductive coating. The system was running at 15kV and studied the morphology of samples at a magnification of 500x, 1000x and 1500x.

2.6 X-ray Diffractometer (XRD)

X-ray diffraction (XRD) analysis is used to study the crystallinity behavior of raw banana fiber and MCC powder. An X-ray diffractometer model of Bruker D2 Phaser was used and the test carry out using Ni-filtered Cu Kα radiation with the scan of 10° to 50° (2θ angle range) and scan rate is 2°/min. The crystallinity of Raw Banana fiber powder and MCC powder were calculated using Crystallinity Index (CRI) shows Equation 1.

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\text{CRI (\%)} = \frac{I_{002} - I_{am}}{I_{am}} \times 100\% 
\]  

(1)
2.7 Tensile Properties

The tensile properties of PLA/MCC biocomposite were identified using Universal Tensile Machine (UTM) Instron 5590. Tensile properties such as Tensile strength, Young’s Modulus and Break elongation for each sample were obtained by following ASTM D 882 method. The test was conducted at crosshead speed of 10 mm/min and the sample dimension was 80mm×15mm.

2.8 Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis (DMA) is used to identify the thermomechanical properties of PLA/MCC biocomposite film formed using two different MCC loading. Perkin Elmer DMA 8000 model was used to test the sample with 50mm×5mm dimension in tension mode. The heating rate used is 2ºC/mm, the frequency used is 1 Hz and the temperature range set from 30ºC-120ºC.

3 RESULT AND DISCUSSION

3.1 Properties of MCC powder produced from different concentration of Nitric acid in acid hydrolysis process

3.1.1 Fourier Transform Infrared (FTIR) Spectroscopy

Fig. 1(a) shows the FTIR spectra of Raw fiber and peak at 3289cm⁻¹ is assign for O-H stretching vibration from cellulose. The peak at wavelength of 2917 cm⁻¹ indicates the C-H stretching while peak at 1011cm⁻¹ indicates C-O stretching of primary alcohol of cellulose. Peak at wavelength of 1604 cm⁻¹ corresponded to C=O vibration of aromatic skeletal of lignin. In Fig. 1(b-d), same peaks can be observed as in Raw fiber which are at 3317-3319 cm⁻¹, 2890-2893 cm⁻¹, and 1014-1016 cm⁻¹. Except peaks at 1325-1326 cm⁻¹ and 1644 cm⁻¹. Thus, peak at 1644 cm⁻¹ in MCC powder spectra belongs to the strong absorption of water by cellulose which proves that low amount of hemicellulose presence in MCC powder. While peak between 1325-1326 cm⁻¹ indicates the presence of crystalline cellulose. Moreover, in the MCC spectra, elimination of 1604cm⁻¹ peak evidences the removal of aromatic skeleton of lignin.

3.1.2 X-Ray Diffraction

Fig. 2 shows the X-ray diffraction patterns and the relative degrees of cellulose crystallinity. From Fig. 2, it can be observed, all samples the peaks were at 2θ = 16º, 22.5º, and 36º, where 2θ = 22.5º is belongs to (002) crystallographic peak. From Fig. itself, it is very obvious that, the crystallinity have increased when compared the peaks intensity of MCC powders with its Raw fiber. The crystallinity index, % for all samples were calculated and summarized in the Table 2. The Crystallinity index of 1.5M Nitric acid hydrolyzed MCC is higher compared to other samples which is 51.3% and the Raw fiber has the lower crystallinity % which is 37.5%. The higher the concentration of acid, the higher crytsallinity of MCC powder produced.
Fig. 1. FTIR analysis of Raw fiber and MCC produced from different concentration of acid.

Fig. 2. X-Ray Diffraction results of Raw fiber and 0.5 M, 1.0M, 1.5M Nitric acid hydrolyzed MCC powders.

Table 2. Crystallinity Index of MCC powder.

| Sample     | Crystallinity (%) |
|------------|-------------------|
| Raw fiber  | 37.5              |
| 0.5M MCC   | 47.0              |
| 1.0M MCC   | 48.6              |
| 1.5M MCC   | 51.3              |
Fig. 3(a) and Fig. 3(b) shows SEM micrograph of 0.5M and 1.5M Nitric acid hydrolyzed MCC at ×500 magnification respectively. 0.5M MCC have very rough surface with irregular shape and the particle seems long in length. 1.5M MCC have rough surface with almost regular shapes and the MCC particles seems short in length.

3.2 Effect of different loading of MCC on the properties of PLA/MCC biocomposite film

3.2.1 Tensile Strength

Fig. 4. depicts the effect of different MCC loading on the tensile strength of PLA/MCC biocomposite film. 5 php MCC filled films have the highest tensile strength compared to 10 php MCC filled films. For instance, the maximum tensile strength is holds by 1.5M/5php MCC/DC film. Lower MCC content in PLA can have better dispersion and better interfacial bonding with matrix. This will eventually increase the tensile strength of biocomposite film. Higher MCC content in PLA tend to flocculates and deteriorates the properties of biocomposite film, which proven by the lower tensile strength of 10php MCC filled PLA/MCC film.

Fig. 4. Effect of different MCC loading in the tensile strength of PLA/MCC biocomposite.
Fig. 5 shows the Young’s modulus of PLA/MCC biocomposite films with different MCC loading. The highest value for Young’s modulus is shown by 1.5M/5php MCC/DC. As explained earlier, lower MCC loading will have good dispersion and interfacial bonding with PLA matrices. Thus, higher force is needed to break the samples. The lower Young’s modulus is shown by 1.5M/10php MCC/C film. 10 php of MCC loading in PLA matrix tend agglomerate and unable to distribute the stress well under tension. Thus, higher MCC loaded film possess lower Young’s modulus.

Fig. 5. Effect of different MCC loading in Young’s Modulus of PLA/MCC biocomposite.

### 3.2.2 Thermomechanical Properties

Fig. 6 shows the loss factors of PLA/MCC biocomposite films with different MCC loading. Tan delta can be defined as dimensionless parameter which measures the ratio of loss modulus to storage modulus [9]. When compares the MCC filled PLA films with Neat PLA/DC, the tan delta peak slightly shifted to higher temperature. Thus, the addition of MCC restricts the movement of molecules and there are some interactions presence between PLA and MCC in filled PLA [1]. Tan delta peaks of Neat PLA/DC which accurately measured at 70.3ºC is lower than 1.5M/5MCC/DC (72.0ºC) and 1.5M/10MCC/DC (73.3ºC) composites. From Fig. 6, the tan delta of three composites exhibit in following order, Neat PLA>1.5M/10MCC/DC> 1.5M/5MCC/DC. Thus film containing 5 php MCC possess low tan delta which proves low loss of energy and good interfacial interaction between PLA matrix and MCC filler.
3.3 Effect of different solvent on the properties of PLA/MCC biocomposite film

Fig. 7 shows the tensile strength of 1.5M/5MCC/C, 1.5M/10MCC/C, 1.5M/5MCC/DC, and 1.5M/10MCC/DC. From the Fig. it is known that, the tensile strength of 1.5M/5MCC/DC is higher compared to other ratios. Dichloromethane solvent have lower boiling point, thus have the shorter evaporation time. So, when the PLA pellets are dissolved by the Dichloromethane solvent, it will evaporate in short period of time and will not provide the chances for the MCC to flocculate in the PLA matrix. This will result in PLA/MCC film with good dispersion of filler among the matrix which leads to higher tensile strength. PLA/MCC biocomposite film produced from Chloroform solvent have lower tensile strength compared to film produced from Dichloromethane solvent. Chloroform with longer evaporation time results in the flocculation of MCC in the PLA matrix, especially in the film of using 10php MCC. The flocculation deteriorates the dispersion of MCC in the PLA matrix and reduce the properties of PLA/MCC biocomposite film. This can be proven from the lower tensile strength of 1.5M/5MCC/C and 1.5M/10MCC/C compared other two films.

Fig. 8 shows the effect of using different solvent on the break elongation of PLA/MCC biocomposite. Fig. 8.0 reveals that the break elongation of Chloroform film is higher than
Dichloromethane films. This can be relate with the crystallinity of sample, where the break elongation will be reduced with increase in crystallinity. Good dispersion of MCC in PLA matrix increases the crystallinity of PLA biocomposite films as well as decreases the break elongation.

Fig. 8. Effect of different solvent on the Break Elongation of PLA/MCC biocomposite film.

3.3.1 Morphology of PLA/MCC biocomposite film

Fig. 9(a) and Fig. 9(b) shows the SEM micrograph of tensile fractured morphology of PLA/MCC/C and PLA/MCC/DC PLA biocomposite film at magnification of ×500 respectively. In Fig. 9(a), fractured surface of 1.5M/5MCC/C seen to be very rough. The rough surface of the fractured sample is the effect of using Chloroform, which induced a greater chain mobility of the polymer causes a rough surface of the film due to its slow evaporation rate [8]. Moreover, from Fig. 9.0(a) it can be clearly observed the MCC pullout and holes. This indicates that, there are least interfacial bonding between the PLA matrix and MCC filler.

Fig. 9(b), shows the morphology of 1.5M/5MCC/DC film’s tensile fractured surface at ×500 magnification. The fractured surface of 1.5M/5MCC/DC is smoother than 1.5M/5MCC/C in Fig. 9(a). Fig. 9(b) reveals that, there are interfacial interactions between the PLA matrix and MCC surfaces. It also can be concluded that, there are least level of pulled out of MCC from PLA matrix. In Fig. 9(b) also have the evidence for the adherence of PLA matrix on the MCC surface. Thus, it can be concluded that, Dichloromethane providing good interfacial bonding between PLA matrix and MCC filler.
Fig. 9. Morphology of fractured surface of (a) PLA/MCC/C and (b) PLA/MCC/DC biocomposite film.

4 CONCLUSIONS

MCC produced from higher concentration of Nitric acids shows higher Crystallinity Index and have smaller size as well as particles with almost regular shape. Incorporation of lower loading of MCC in PLA matrix, improves the tensile strength and Young’s modulus in biocomposite. Moreover, MCC in PLA slightly improves the thermal stability and reduces the loss factor. From using different solvents, Dichloromethane have improved the tensile strength and Young’s modulus but reduced the break elongation of biocomposite film. PLA/MCC biocomposite film formed by Chloroform solvent shows lower tensile properties. Dichloromethane solvent induces good interaction between PLA and MCC, which can be observe by SEM micrograph, while Chloroform solvent induces poor interaction between PLA and MCC.

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