Analysis on the barrier properties of thin film PLA/PBAT reinforced with microcrystalline cellulose

Sitti Fatimah Mhd Ramle¹, Aqilah Abdul Rahim¹, Nur Hafizzah Jusoh¹, Nurul Fazita Mohammad Rawi² and Che Ku Abdullah Che Ku Alam²

¹Forest Resources Technology Programme, Faculty of Bioengineering and Technology, Universiti Malaysia Kelantan, 17600 Jeli, Kelantan, Malaysia.
²Division of Bio-Resources Technology, School of Industrial Technology, Universiti Sains Malaysia, 11800 Pulau Pinang, Malaysia.

Email: fatimah.m@umk.edu.my

Abstract. In recent times, awareness on plastic pollution had increase which brings innovation on new productions to be environmental friendly. Various polymers has been used to analyse the suitability to produce thin films. In this study, Poly lactic acid (PLA) and Polybutylene adipate terephthalate (PBAT) reinforced with microcrystalline cellulose (MCC) were investigated. MCC were produced from selected bamboo for obtaining cellulose, then followed by an acidic hydrolysis process for the processing of microcrystalline cellulose (MCC). In this study, the thin film are focusing on the barrier properties such as water absorption, solvent resistance and absorption test. From the results shows that, the lowest rate of water absorption rate is 1.9% by 1% B-MCC/PLA/PBAT, meanwhile, the highest rate of water absorption is 60.1% by 5% C-MCC/PLA/PBAT. The water absorption rate decrease gradually with the decreasing of amount of MCC in the samples. Lastly, the thin film samples can resist with oleic acid solvent as the condition of thin film samples is still remain but they were not resistance with xylene as the thin film samples were shrinked and degraded. This thin film have a potential to replace the non-biodegradable petrochemical polymer based on their properties such as food contact, availability and cost.

1. Introduction
During the modern period nowadays, people start taking care of the environment due to many pollutions as many industries start developing in many countries. One of the corruptions is the plastic pollution is due to the some of the community that do not have an awareness to recycle the plastics to reduce pollution that contribute to ocean pollution and become threats to the aquatic living things [1]. One of the way to prevent the plastic pollution is by substitute the non-biodegradable polymer to biodegradable polymer [2] such as polylactic acid polymer that can be process using the standard method for processing polymer.

In this study polylactic acid (PLA) and polybutylene adipate terephthalate (PBAT) were used to produce thin film incorporate with microcrystalline cellulose (MCC) derived from bamboo. PLA or polylactic acid is derived from renewable sources and is a thermoplastic aliphatic polyester that commonly used in the food industry. Polylactic acid have the potential to replace the non-biodegradable petrochemical polymer based on their properties such as food contact, availability and cost [3]. Polylactic acid has many advantages as a biodegradable polymer that has better water vapour barrier properties [4].
For polybutylene adipate terephthalate or PBAT, PBAT is a random copolymer that is biodegradable and can easily thermoform and moulded. Polybutylene adipate terephthalate or PBAT is a biodegradable polymer that has excellent ductility [5]. PBAT has many benefit properties such as has low stiffness, puncture toughness [6]. For this research study, the objectives is to analyse the barrier properties of PLA/PBAT incorporate with MCC such as the moisture content determination and solvent resistance of the thin film to know their potential as an alternative bio plastic in the food industry.

2 Materials and Methods

2.1 Cellulose preparation
Kraft pulping method was used to prepare the cellulose from the bamboo sample [7]. 100g of bamboo chip was used in Kraft pulping method. The bamboo chip was cooked with NaOH solution and Na2S solution and the black liquor was removed. Then the sample was undergo the bleaching process using [8] method, to get the white cellulose.

2.2 Microcrystalline cellulose preparation
Microcrystalline cellulose (MCC) ware obtained by using acid hydrolysis method [9] 2.5N HCl at 105°C ± 2 was used to hydrolyse pulp fibres for 30 minutes with the 1:20 ratio of pulp to liquor. The reaction mixture was washed with 5% diluted ammonium hydroxide (NH4OH). Then, to make sure the mixture is acid-free, the mixture was washed with distilled water repetitively. From this process, the microcrystalline cellulose (MCC) that derived bamboo pulp fibres was filtered in the room temperature (23-26°C) and until the constant weight is achieved [10]. The MCC was dried in the vacuum oven at 105°C. After this process, the MCC produced was ground until form to a fine powder by using a ceramic mortar. The final product form of MCC was a fine, white to yellowish colour and snowy powder. The MCC derived from bamboo named B-MCC while commercial MCC named C-MCC which compared in this study.

2.3 Preparation of thin film
PLA and PBAT pellets, MCC were dried for one day in the oven [11]. The B-MCC/PLA/PBAT and C-MCC/PLA/PBAT composites were prepared by melt-mixing with 50 ml chloroform in the beaker at temperature 60°C.

2.4 Characterization of thin film
The bamboo powder, cellulose, B-MCC, C-MCC, B-MCC/PLA/PBAT thin film, C-MCC/PLA/PBAT thin film were characterized on the barrier properties such moisture content (MC), solvent resistance and absorption test.

2.4.1 Determine the moisture content of thin film
Xylene and oleic acid were the solvent that used for the absorption and resistance of solvent test for all samples. For two day (48h), the properties of solvent resistance for all different solvents that the samples were immersed and observed with camera at temperature of 30°C [12]. The weight for initial samples and the weight of samples after immersion were recorded to know the absorption of solvent. The SAR (ratio of solvent absorption) formula was in equation 1:

\[
SAR = \left( \frac{w_f - w_0}{w_0} \right) \times 100\%
\]  

(1)

The weight of samples before immersion in the solvent is \( w_0 \), and the weight of samples after taken out from immersion of solvent is \( w_f \) [11].
2.4.2 Determine the solvent resistance of thin film

The thin film of B-MCC/PLA/PBAT and C-MCC/PLA/PBAT were cut into 5cm x 5cm regarding to ASTM D570. The mass of each samples were measured according to different temperature. Three temperatures used for water absorption test which were 23°C, 100°C and equilibrium state (23°C, 50% RH). Each of the samples were immersed in the beaker containing distilled water that were set at different temperatures for 24 hours. Then, the weight of each samples were measured again after 24 hours [13]. The formula of increase in weight percentage is equation 2:

\[
\text{Percentage of weight (\%) = } \frac{\text{wet weight} - \text{conditioned weight}}{\text{conditioned weight}} \times 100\%
\]

3 Results and Discussion

3.1 Moisture content of thin film

From the figure 1, the moisture content of thin film samples were shown. The highest moisture is 4.3% by PLA/PBAT thin film sample followed by 1% B-MCC/PLA/PBAT (3.9%), 5% B-MCC/PLA/PBAT (3.4%), 3% B-MCC/PLA/PBAT (3.1%), 1% C-MCC/PLA/PBAT (1.5%), 3% C-MCC/PLA/PBAT (1.2%), 5% C-MCC/PLA/PBAT (0.5%) respectively.

The moisture content of thin film samples decrease gradually with the increase in the microcrystalline cellulose. This is because the gradually growing concentrations of MCC encouraged the creation of further hydrogen bonds between PLA/PBAT and MCC molecules and increased the compactness of the thin films [14]. In the other hand, the hygroscopicity of thin films with significant volumes of MCC was weak due to the lower hydrophilicity. Overall, in this moisture content analysis, the more the amount of MCC content in the thin film, the lower the moisture content in the thin film such as 5% C-MCC/PLA/PBAT which only absorbed 0.5% of moisture content.

![Figure 1. Moisture content of thin film samples.](image_url)

3.2 Solvent resistance of thin film

From table 1, the solvent resistance of thin film samples were shown. The condition of the thin film samples are different according to the solvents used such oleic acid and xylene. Xylene solvent made the thin films samples become hard and degrade after the immersion. As the amount of MCC increase in the thin film, the thin film samples were less degrade and less ruptured than PLA/PBAT thin film.
samples as it was not reinforced with MCC [15]. Meanwhile, oleic acid solvent only made the thin film samples absorbed the solvents but there were no changes in the condition of thin film samples.

Xylene is a solvent that were used in many industries as a raw material to produce films, dyes and fibres [16]. In this study, the properties of thin film samples is not resistance with the xylene as it made them degrade and non-functional. Yet, oleic acid solvent is resistance with the thin film samples and still functional.

**Table 1. Solvent resistance of thin film samples**

| Thin film samples | Oleic Acid | Xylene |
|-------------------|------------|--------|
| PLA/PBAT          | ![Image]   | ![Image] |
| 1% C-MCC/PLA/PBAT | ![Image]   | ![Image] |
| 1% B-MCC/PLA/PBAT | ![Image]   | ![Image] |
| 3% C-MCC/PLA/PBAT | ![Image]   | ![Image] |
| 3% B-MCC/PLA/PBAT | ![Image]   | ![Image] |
| 5% C-MCC/PLA/PBAT | ![Image]   | ![Image] |
(Continued…)

### Thin film samples

|          | Oleic Acid | Xylene |
|----------|------------|--------|
| 5% B-MCC/PLA/PBAT | ![Oleic Acid](image1.png) | ![Xylene](image2.png) |

3.3 Absorption rate of thin film

From the figure 2, the solvent absorption rate percentage for two solvents is shown. Generally, for Xylene solvent, the bio plastic thin film samples absorbed lesser amount of solvent then oleic acid solvent in the bio plastic thin film samples [17]. The highest rate of solvent absorption is 1% C-MCC/PLA/PBAT thin film (Oleic acid: 62.07%, Xylene: 35.06%) followed by 1% B-MCC/PLA/PBAT thin film (Oleic Acid: 60.31%, Xylene: 25.95%). Meanwhile, the lowest rate of solvent absorption is 5% B-MCC/PLA/PBAT (Oleic acid: 11.99%, Xylene: 8.32%) thin film followed by 5% C-MCC/PLA/PBAT thin film (Oleic acid: 15.50%, Xylene: 11.60%).

Xylene is an organic hydrocarbon chemical and oleic acid is categorised as one of fatty acid. Oleic acid resulted the increase of solvent absorption rate percentage while xylene resulted the decrease of solvent absorption rate percentage [18]. The decreasing of amount of MCC in the thin film samples made the increasing of solvent absorption rate. This is because there are many porous space in the thin film samples as there are less amount of MCC that reinforced with PLA/PBAT. Then, the solvents can penetrate into the thin films and increase the absorption rate.

![Figure 2. Percentage of solvent absorption percentage of thin film samples](image3.png)

4. Conclusion

In this study the thin film of PLA/PBAT reinforced with microcrystalline cellulose has been studied. The results shows that the moisture content of the thin film decrease as the MCC is higher due to high amount of hydrogen bonds that made the thin films more compacted. Other than that, the rate of water absorption can decrease as the decreasing of permeability. This is because the pore structure of thin
film play the main part in the absorption of water. For solvent absorption, the thin film absorb more amount of oleic acid than the xylene as the percentage of solvent absorption for oleic acid is more higher than the percentage of solvent absorption for xylene. In addition, the thin film samples have no resistance with xylene solvent is because they shrink and degraded after the immersion for 48 hours. Meanwhile, the thin film samples have resistance with oleic acid solvent because the thin film samples structure is remained and stable after the immersion. So this thin film are appropriate with certain function of thin film in the future.

References
[1] Cózar A, Echevarría F, González-Gordillo J I, Irigoien X, Úbeda B, Hernández-León S and Duarte C M 2014 Proc Natl Acad Sci (USA)
[2] Johnson R D J, Prabu V A, Amuthakkannan P and Prasath K A 2017 Rev. Adv. Mater. Sci. 49 112
[3] Muller J, González-Martínez C and Chiralt A 2017 Materials 10 952
[4] Rhim J W, Hlong S I and Ha C S 2009 LWT-Food Sci. Technol. 42 612
[5] Wu N and Zhang H 2017 Mater. Lett. 192 17
[6] Muthuraj R, Misra M, Defersha F and Mohanty A K 2016 Compos. Part A Appl. Sci. Manuf. 83 120
[7] Mosier N, Wyman C, Dale B, Elander R, Lee Y, Holtzapple M and Ladisch M 2005 Bioresour Technol. 96 673
[8] Boon J G, Hashim R, Sulaiman O, Sugimoto T, Sato M, Salim N, Amini M H M, Nor Izaida I and Sitti Fatimah M R 2017 ARPN J. Eng. Appl. Sci. 12 33
[9] Mohamad Haafiz M K, Hassan A, Arjmandi R, Zakaria Z, Marliana M M, Syakir M I and Nurul Fazita M R 2016 Polym. Polym. Compos. 24 675
[10] Siti Fatimah M R, Othman S, Rokiah H, Zubaïdah Aimé A H, Arai T, Kosugi A and Murata Y 2019 AIP Conf Proc. 2068 020039
[11] Siti Fatimah M R, Nur Ayuni A, Nurul Fazita M R, Nur Salsabilah Z and Boon J G 2020 IOP Conf. Ser. Earth Environ. Sci. 596
[12] Yoshinori M, Satoshi K, Eiji T, Sitti Fatimah M R, Othman S, Rokiah H, Wan A I, Kosugi A, Akiko H and Abe H 2015 Ind crops and products 190
[13] Chen J, Long Z, Wang J, Wu, M, Wang F, Wang B and Lv W 2017 Cellulose 24 4449
[14] Nor Amira Izzati A, John W C, Nurul Fazita M R, Najieha N, Azniwati A A and Abdul Khalil H P S 2020 Mater. Res. Express 7 015336.
[15] Cao X, Chen Y, Chang P R and Huneault M A 2007 J Appl Polym Sci. 106 1431
[16] Chuayjuljit S, Su-Uthai S and Charuchinda S 2010 Waste Manag Res 28 109
[17] Nedovic V, Kalusevic A, Manojlovic V, Levic S and Bugarski B 2011 Procedia Food Sci 1 1806
[18] Wang J, Gardner D J, Stark N M, Bousfield D W, Tajvidi M and Cai Z 2018 ACS Sustain Chem Eng. 6 49

Acknowledgement
This research was funded by Matching Grant University Scheme between Universiti Malaysia Kelantan and Universiti Sains Malaysia (R/SGPP/A1300/00801A/003/2019/00696).