

Mechanical Properties of Poly(lactic acid) Sheet Reinforced with Microfibrillated Cellulose from Corn Cobs

Prapatsorn Deejam¹, Sireerat Charuchinda^{2,a}

¹*Interdisciplinary Program in Petochemistry & Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok 10330 Thailand*

²*Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok 10330 Thailand*

Abstract. In this study, cellulose was extracted from corn cobs by successive hot NaOH solution and followed by H₂O₂ bleaching. XRD pattern show characteristic peak of Cellulose I. Microfibrillated cellulose (MFC) was successfully prepared by dissolving the extracted cellulose in NaOH/urea solution, shearing in a homogenizer and finally by freezing and thawing. To improve strength of MFC, MFC was physically crosslinked using PVA by freezing and thawing. The crosslinked MFC/PVA was added to poly(lactic acid) (PLA) to improve its mechanical properties. The non-crosslinked MFC/PVA was also prepared by only stirring the solution without freezing and thawing. MFC/PVA reinforced PLA films with various ratios of PLA and MFC/PVA at 100:0, 99:1, 97:3 and 95:5 were prepared through a solution casting method. Tensile strength and elongation at break of PLA films increased with the addition of physically crosslinked MFC/PVA at 1%wt, whereas, the addition of non-crosslinked MFC/PVA decreased elongation at break. Crosslinking of MFC/PVA can improve tensile strength of PLA. It can render better tensile strength than that of non-crosslinked MFC/PVA. However, when MFC/PVA contents increase, tensile strength of PLA films reinforced with non-crosslinked and crosslinked MFC/PVA decreased. Morphology of fracture surfaces reveals good dispersion and adhesion between 1% crosslinked MFC/PVA and PLA matrix.

1 Introduction

Bio-based material has been attracted in both academic and industrial fields due to the growing concern about environmental protection and the rising cost of fossil fuel [1]. Nowadays, poly(lactic acid) (PLA) which is an aliphatic polyester made up of lactic acid (2-hydroxy propionic acid) [2] are widely used for bioplastic. The main limitations for application of PLA are their poor thermal and mechanical properties which can be improved by reinforcing with natural fibers such as microfibrillated cellulose (MFC) [3]. MFC is a cellulosic material, composed of expanded high-volume cellulose, greatly expanded in surface area and its diameter is in the range 20–60 nm with a length of several micrometers. It exhibits both amorphous and crystalline parts and presents a web-like structure that has a very good ability to form a rigid network [4]. Additionally, its properties can be improved with different methods such as grafting, chemical crosslinking and physical crosslinking [5].

Thus, the purpose of this study is to improve mechanical property of PLA reinforced with MFC. Since corn cobs are actually agricultural and feed industrial wastes in Thailand, in this study, cellulose was extracted from corn cobs by successive hot NaOH solution and followed by H₂O₂ bleaching. The MFC solution was prepared using NaOH/urea aqueous solution. To improve strength of MFC, MFC was then taken to physical

crosslink with PVA. PLA films reinforced with MFC/PVA were prepared using a solution casting method. The structure and mechanical properties of films were characterized by X-ray diffractometer (XRD) scanning electron microscope (SEM) and tensile testing machine.

2 Experimental

2.1 Materials

Poly(lactic acid) (PLA) (NatureWork™ PLA 4043D) in pellet form was purchased from NatureWork® LLC, Minnetonka, MN USA. Corn cobs were obtained from Nakornsawan Province in Thailand. Poly(vinyl alcohol) (PVA) was purchased from Ajax Finechem, Australia.

2.2 Preparation of MFC

Ground corn cobs and 1 M NaOH were heated at 70 °C with slow stirring for 2 h. The NaOH extraction was repeated two times and followed by bleaching with 2% H₂O₂ at 80 °C for 4 h. After cooling, the suspension was filtered and washed with water until pH 7. The obtained cellulose powder was placed in the oven at 60 °C for 24 h and kept in desiccator. A cellulose solution was then

^aCorresponding author: sireerat.c@chula.ac.th

prepared according to Chang et al method [6]. Three grams of cellulose powder was dispersed into NaOH/urea aqueous solution and was homogenized with high speed homogenizer (10000 rpm) for 20 minutes and then was frozen under refrigeration (-20 °C) for 24 h. The frozen solid was thawed and stirred at room temperature to obtain a transparent MFC solution.

2.3 MFC/PVA crosslinking

The MFC/PVA crosslinking was followed by Chang et al method [5]. PVA (3wt%) was dissolved in NaOH/urea aqueous solution at 90°C for 2 h. The physical crosslinked MFC/PVA was prepared by mixing MFC/PVA solutions in the ratios 70/30 (w/w) and subsequently freezing the mixtures under refrigeration for 24 h, then thawing to room temperature over 2 h. This freezing/thawing cycle was repeated 5 times as shown in Table 1. The crosslinked MFC/PVA was kept in refrigerator. The non-crosslinked MFC/PVA preparation was similar to the crosslinked MFC/PVA by stirring at room temperature over 2 h but without freezing/thawing.

2.4 Preparation of PLA and PLA films reinforced with MFC/PVA

A 5 wt% solution of PLA was prepared by stirring PLA pellets in chloroform at 60 °C for 2 h until fully dissolved. The PLA solution was immediately subjected to cast film on glass plates and left at room temperature for 24 h. The PLA film was then dried at 60 °C 24 h to evaporate solvent and noted as neat PLA. To prepare the PLA/MFC/PVA films, 5 wt% solution of PLA was mixed with non-crosslinked MFC/PVA (20N) and with crosslinked MFC/PVA (20P) in various ratios as shown in Table 1. The mixtures were homogenized at 4000 rpm for 5 min. The suspension was then sonicated for 10 min and was immediately casted on a clean glass plate. After removal of the solvent, PLA/MFC/PVA films were obtained.

Table 1. Formulations of PLA films reinforced with non-crosslinked and physically crosslinked MFC/PVA (homogenize for 20 min) through solution casting process.

Formula	PLA [wt%]	MFC/PVA [wt%]	Times of freezing/thawing cycle
99:1 PLA/MFC-20N	99	1	-
97:3 PLA/MFC-20N	97	3	
95:5 PLA/MFC-20N	95	5	
99:1 PLA/MFC-20P	99	1	5
97:3 PLA/MFC-20P	97	3	
95:5 PLA/MFC-20P	95	5	

3 Characterization

X-ray diffraction (XRD) was carried out using the X-ray Power Diffractometer (BRUKER axs, D8). Powder samples were scanned from 3 to 40 degrees 2 theta.

3.1 Mechanical testing

Tensile test was done using material testing machine (LLOYD, LF plus). Sample was cut into rectangular pieces about 0.3 mm thick, 0.5 mm wide and 5 mm long. The sample gauge length was 25 mm and the testing speed at 1 mm/min. The results were taken as an average of five tests.

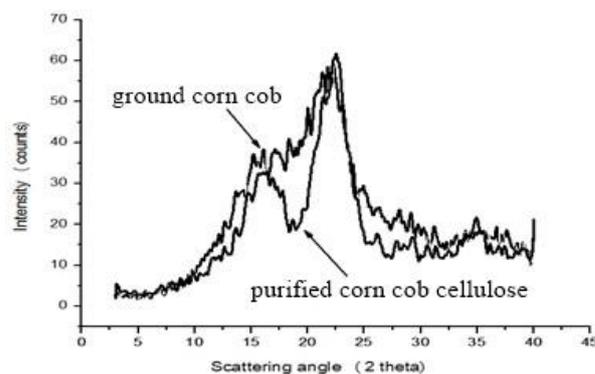
3.2 Morphology

Morphology of film samples was examined using a scanning electron microscopy (SEM, Jeol JSM 6400) at 15 kV with resolution of 1000X. The neat PLA and PLA/MFA/PVA film samples were analyzed.

4 Results and Discussion

4.1 Structure of corn cob cellulose

XRD patterns of purified corn cob cellulose and ground corn cobs are shown in Figure 1. The both XRD patterns show characteristic peak of cellulose I at 16 and 22 degrees two theta. The pattern of ground corn cobs is similar to the purified corn cob cellulose but broader due



to the presence of non-crystalline hemicelluloses and lignin [7].

Figure 1. X-ray diffraction patterns of ground corn cobs and purified corn cob cellulose.

4.2 Mechanical properties of PLA and PLA films reinforced with MFC/PVA

Tensile strength, Young's modulus and elongation at break of neat PLA and PLA films reinforced with MFC/PVA films are shown in Figure 2.

Tensile strength, Young's modulus and elongation at break of neat PLA were 20.50 MPa, 740.40 MPa and 21.23%, respectively. After addition of 1wt% crosslinked MFC/PVA, tensile strength and elongation at break increased to 26.21 MPa and 23.21% respectively but Young's modulus did not improve. This indicated that the

addition of 1wt% crosslinked MFC/PVA rendered good interaction between the PLA and MFC which resulted in better tensile strength than that of neat PLA. However, the addition of 3 and 5wt% crosslinked MFC/PVA led to a decrease in both tensile strength and elongation at break. This may be attributed to aggregation of the MFC due to the filler-filler interaction becomes greater than filler matrix interaction [1].

The effect of crosslinking MFC using PVA on mechanical properties indicated that crosslinking can improve tensile strength of PLA films because inter- and intra-molecular hydrogen bonds between MFC and PVA molecular chains were strong. These results demonstrated that MFC and PVA molecular chains had been compactly accumulated when freezing/thawing cycles were completed. This led to a decrease in the free volumes and a high strength [5].

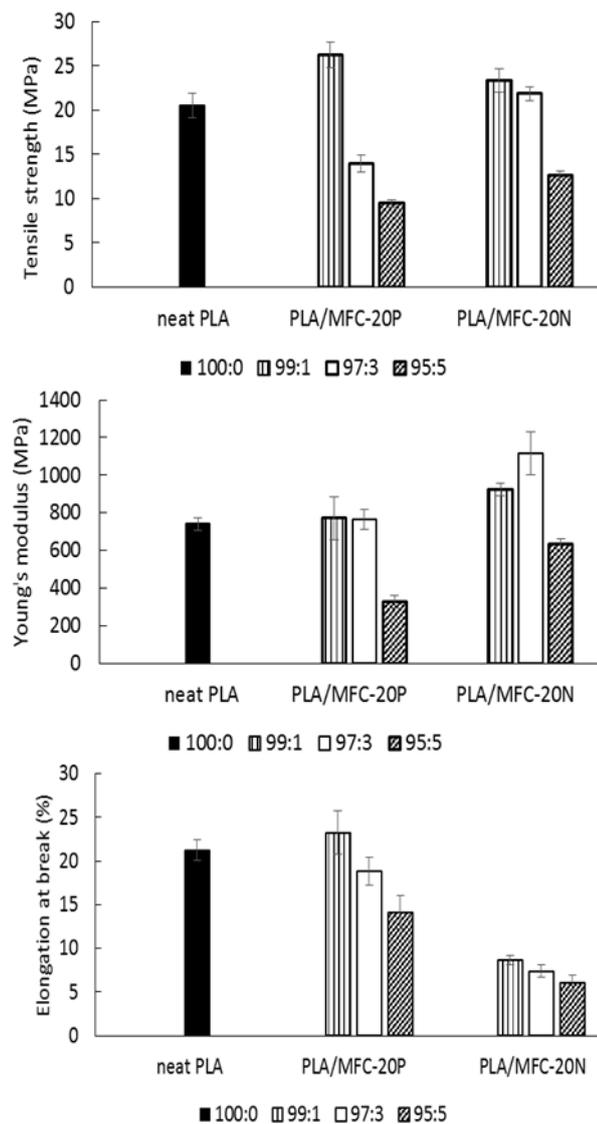


Figure 2. Mechanical properties of neat PLA and PLA reinforced with non-crosslinked and crosslinked MFC/PVA films.

4.3 Morphology

The morphology of fractured cross-sectional surfaces of PLA and PLA films reinforced with crosslinked MFC/PVA was studied by SEM as shown in Figure 3. The neat PLA (Figure 3a.) is categorized as ductile fracture because the fibrils remained on the fracture surface [1]. After crosslinked MFC/PVA added into PLA, the fracture surface showed irregular protrusion and holes as indicated by white arrow in Figure 3b-3d. This indicated a brittle fracture. The fracture surface of PLA films reinforced with crosslinked MFC/PVA at the ratios of 99:1 (Figure 3b) seems similar to neat PLA. This reveals good dispersion and adhesion between crosslinked MFC/PVA and PLA matrix. The SEM results agreed with the mechanical properties of composite films [1,8].

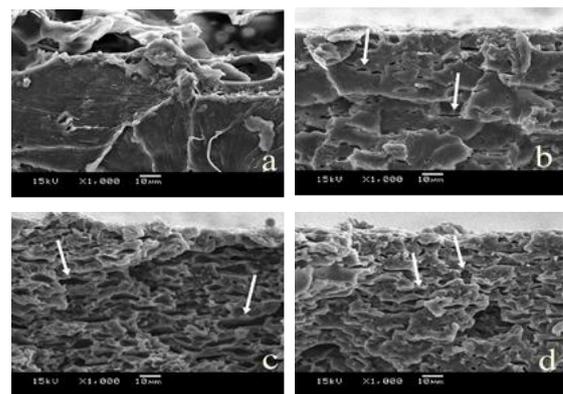


Figure 3. SEM micrographs of the fracture surface of PLA/MFC/PVA films (a) neat PLA (b) 99:1 PLA/MFC-20P (c) 97:3 PLA/MFC-20P and (d) 95:5 PLA/MFC-20P

5 Summary

Cellulose was extracted from corn cobs by successive hot NaOH solution and followed by H₂O₂ bleaching. The transparent microfibrillated cellulose (MFC) solution was prepared by dispersing extracted cellulose powder using NaOH/urea aqueous solution. To improve strength of MFC added to PLA, MFC was then taken to physical crosslink with PVA under freezing/thawing cycles. PLA films reinforced with non-crosslinked MFC/PVA and with crosslinked MFC/PVA were prepared using a solution casting method. It was found that PLA films reinforced with crosslinked MFC/PVA at 1 wt% has greater tensile strength than that of reinforced with non-crosslinked MFC/PVA at the same contents. However, when MFC contents increase, tensile strength decreased due to the filler-filler interaction which was found both in PLA films reinforced with non-crosslinked and crosslinked MFC/PVA. Morphology of fracture surfaces reveals good dispersion and adhesion between 1% crosslinked MFC/PVA and PLA matrix.

Acknowledgements

This research has been supported by the Ratchaphiseksomphot Endowment Fund 2013 of Chulalongkorn University (CU-56-416-AM).

References

1. M.K. Mohamad Haafiz, A. Hassan, Z. Zakaria, I.M. Inuwa, M.S. Islam M. Jawaid, *Carbohydr. Polym.* **98**, 139 (2013)
2. M. Jonoobi, J. Harun, A.P. Mathew, K. Oksman, *Compos. Sci. Technol.* **70**, 1742 (2010)
3. A.K. Bledzki, A. Jaszkievicz D. Scherzer, *Compos. Part A-Appl. S.* **40**, 404 (2009)
4. L. Brinchi, F. Cotana, E. Fortunati J.M. Kenny, *Carbohydr. Polym.* **94**, 154 (2013)
5. C. Chang, A. Lue L. Zhang, *Macromol. Chem. Physic.* **209**, 1266 (2008)
6. C. Chang, L. Zhang, J. Zhou, L. Zhang J.F. Kennedy, *Carbohydr. Polym.* **82**, 122 (2010)
7. R.L. Shogren, S.C. Peterson, K.O. Evans J.A. Kenar, *Carbohydr. Polym.* **86**, 1351 (2011)
8. P. Qu, Y. Gao, G. F Wu L. P. Zhang, *BioRes.* **5**, 1811 (2010)