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Mechanical properties of Poly(lactic acid) Composites Reinforced with Microfibrillated Cellulose Prepared Using High Speed Blending

Supachok TANPICHAI* **and Jatuphorn WOOTTHIKANOKKHAN**

King Mongkut's University of Technology Thonburi, Bangkok, Thailand 10140

Abstract

Bamboo fibers, as a raw cellulose source, were used to prepare microfibrillated cellulose (MFC) using a high speed blender at 20,000 rpm for 60 minutes. Nanofibers with the width of less than 100 nm were disintegrated from the fibers. MFC networks were then prepared, and embedded in poly(lactic acid) resin using a compression molding at temperature of 180ºC and a pressure of 10 MPa. Mechanical properties of poly(lactic acid) composites reinforced with MFC were investigated. The interaction between MFC fibrils and PLA resin was observed. As a result, Young's modulus and tensile strength of the composites increased to 3.1 GPa and 39 MPa respectively, compared to values of 2.4 GPa and 33 MPa for Young's modulus and tensile strength of pure poly(lactic acid) resin. This indicates the stress can be transferred from the matrix to the reinforcement phase. The improvement of mechanical properties of the composites confirms that MFC prepared using a high speed blender can be used as reinforcement.

Keywords : Microfibrillated cellulose, Stress transfer, Composite, Mechanical properties, Bamboo fibers
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Introduction

Microfibrillated cellulose (MFC), a web-like structure of interconnected cellulose fibrils with diameters in the range of 10-100 nm, was firstly introduced by Turbak et al.(1) and Herrick et al.(2) in 1983. A wood pulp suspension was passed through a high pressure homogenizer to produce MFC. Until now, many techniques have been developed to produce a large quantity of MFC fibrils such as grinding(3,4), high speed blending(5) and high intensity ultrasonication.(6,7) The mechanical properties of MFC fibrils are found to be dependent on the cellulose source and mechanical treatment.(8)

MFC have attracted more attention as an alternative material to glass fibers to strengthen polymers such as poly(lactic acid) (PLA)(9-11), polypropylene(12,13), poly(vinyl alcohol)(6,14,15), to name a few polymers due to the advantages such as superior mechanical properties, high aspect ratio, optical transparency, low thermal expansion, low density and biodegradability.(8,13,16-19) Siqueira et al.(20) studied the reinforcing effect of cellulose nanowhiskers (CNWs) and MFC on the enhancement of the mechanical properties of nanocomposites. It was found that the higher mechanical properties of composites with the addition of MFC can be observed, compared to with the same content of CNWs. This may be due to the higher aspect ratio of MFC in the nanocomposites. Moreover, with the addition of only 2 wt% of MFC in poly(vinyl alcohol), tensile strength and Young's modulus of the composites increased to 103 MPa and 5.2 GPa, compared to 93 MPa and 4.3 GPa of neat poly(vinyl alcohol).(6) Lu J. et al.(15) also studied properties of poly(vinyl alcohol) composites reinforced with MFC and found that mechanical properties of the composites increased with the addition of MFC.

The aim of this study is to prepare networks of MFC from bamboo fibers using a high speed blender. PLA composites reinforced with these networks were then fabricated using a compression molding. Mechanical properties of the composites and networks were investigated, compared to those of neat PLA resin. A few studies of the preparation of MFC using a high speed blender have been introduced. This study, therefore, should broaden the possibility of the use of the high speed blender to prepare MFC fibrils from bamboo fibers, and confirm the MFC prepared in this work can enhance mechanical properties of neat PLA resin.

Materials and Experimantal Procedures

Bamboo fibers with length of ~1 cm and diameters of 11.3 ± 1.7 µm were purchased from a local market in Bangkok, Thailand. Poly(lactic acid) (PLA), 4043D, used as a raw material were supplied by NatureWorks company. The density is 1.24 g cm^{-3}

*Corresponding author E-mail : supachok.tan@kmutt.ac.th

MFC network preparation

Prior to mechanical treatment, bamboo fibers were repeatedly washed to remove impurities. 1 g of bamboo fibers were subsequently soaked in 100 ml distilled water for 24 hours to swell the fibers. A high speed blender with 20,000 rpm (PANASONIC MXAC400) was used to disintegrate MFC fibrils for 60 minutes. The cellulose solution was then poured into a Petri dish, and dried in an oven at temperature of 60°C for 7 days. The MFC networks with the thickness of ~270 µm were finally formed.

Composite preparation

The MFC network was placed between two PLA films. The films were then compressed for 3 minutes at temperature of 180°C and a pressure of 10 MPa. The prepared composite with a thickness of ~300 µm was produced. The composite had a composition of ~47 wt% fiber and ~53 wt% PLA.

Scanning electron microscopy

The morphology of bamboo fibers with 60 minutes treatment time and without mechanical treatment was studied using a scanning electron microscope (SEM JSM6610LV) equipped with a secondary electron detector under an accelerating voltage of 10 kV. Before the analysis, the samples were sputter coated with a thin layer of gold to avoid charging. The fractured surface the composite reinforced with MFC was investigated.

Tensile testing

Tensile properties of MFC networks, neat PLA films and composites were performed using a LLOYD LR 50 K universal testing machine equipped with a load cell of 1 kN. Samples with the width of 5 mm were tested with a gauge length of 40 mm and a crosshead speed of 1 mm minute^{-1}. The samples were mounted in the grips with a padding of filter paper. The width and thickness of the specimens were measured using a vernier caliper and micrometer, respectively. The Young's modulus was calculated from the initial part of the slope of the stress-strain curve. At least five samples were tested for each material to obtain means and standard deviations.

Results and Discussion

1 wt% cellulose suspensions of untreated bamboo fiber and 60 minutes-treated bamboo fibers are shown in Figure 1. The raw bamboo fibers were precipitated at the bottom of the bottle after mixing with distilled water. However, no sedimentation of fibrils mechanically treated for 60 minutes can be observed after 24 hours. This indicates the higher degree of fibrillation and more surface area of MFC fibrils can be obtained.[(9,21)] The similar behavior has been found from aqueous suspensions of cellulose nanofibers pre-treated using high pressure homogenization and sonication.[(9,21]

(A) (B) Figure 1. Suspensions of (A) bamboo fibers and (B) MFC fibrils after 60 minutes treatment time.

SEM micrographs of the raw bamboo fibers and MFC fibrils after mechanical treatment for 60 minutes are shown in Figure 2. The web-like structure and highly entangled MFC fibrils can be observed.[22] This confirms that MFC fibrils with diameters in the range of 100-500 nm can be prepared from raw bamboo fibers using a high speed blender. The wide range of diameters and widths for MFC fibrils has been also found using ultrasonication to fibrillate lyocell fibers.[6,7] It is worth noting that the shear stress produced from the high speed blender used in this project may be not enough to fully fibrillate nanofibrils from the bamboo fibers.

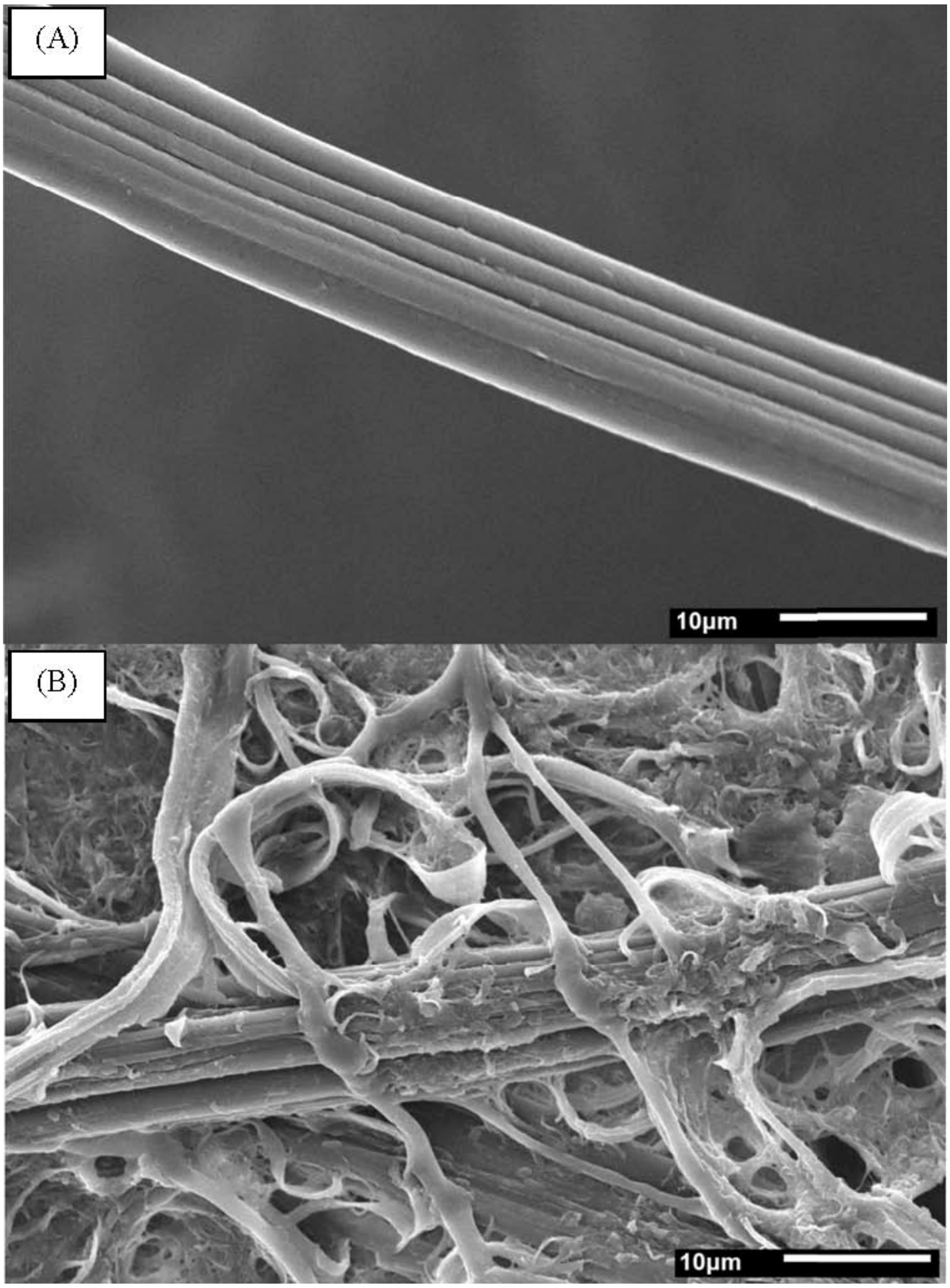

Figure 2. SEM pphotographs of (a) the uuntreated bbamboo singgle fiber annd (b) MFC fibrils after mmechanical treatment fofor 60 minutes.

The fractured surface of the MFC reinforced PLA composite after tensile testing is shown in Figure 3. PLA can be observed to penetrate the MFC network to interact with MFC fibrils as the network had high porosity. The effect of fibril network porosity on stress transfer in composites has been discussed.[9] It is difficult for PLA resin to penetrate into a dense network of bacterial cellulose with 10% porosity. The interaction of the less porosity network and polymer matrix can be found only on the top layer of the network and the matrix.[10] The better interaction between the fibrils and polymer matrix, on the other hand, can be found for composites reinforced with high porosity networks because the polymer resin can easily penetrate through the bigger pores between fibrils into the network.[9]

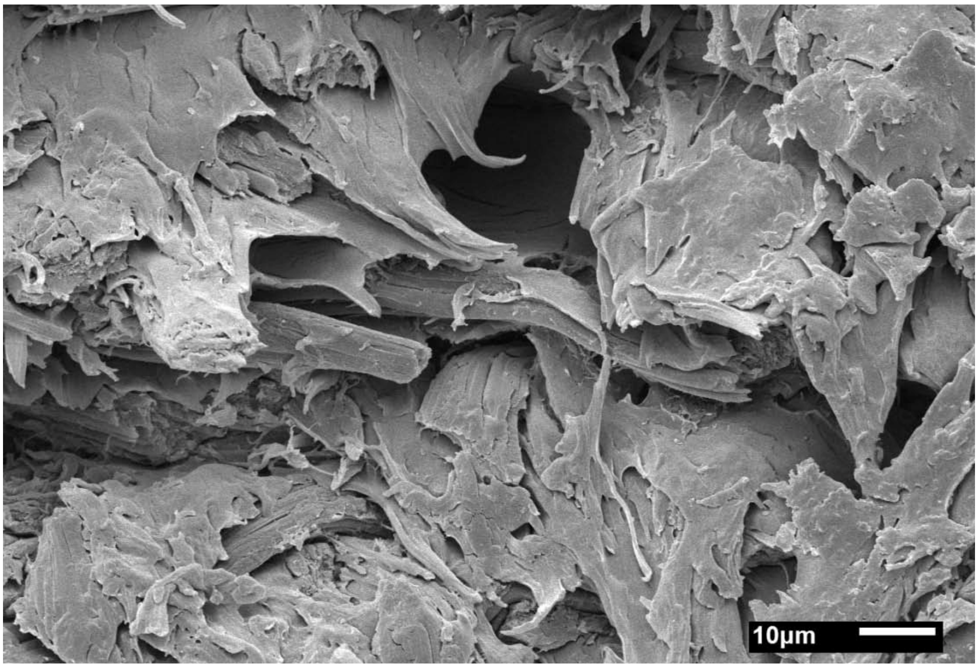

Figure 3. SEM image of the fractured structure of the MFC reinforced PLA composite after tensile testing.

Mechanical properties

The tensile properties of the neat PLA films, MFC networks and MFC reinforced PLA composites are summarized in Table 1. Young's modulus and tensile strength of MFC networks are 0.2 GPa and 2.6 MPa, respectively. Although these values of the MFC networks are very low, compared to values of 2.4 GPa and 32.8 MPa for Young's modulus and tensile strength of neat PLA films, after embedding the MFC network in PLA resin Young's modulus and tensile strength of MFC reinforced PLA composites were found to increase by ~30% and ~18% to 3.1 GPa and 38.7 MPa, respectively. This results from the penetration of PLA into the network and better interaction between MFC fibrils and PLA resin, as shown in the SEM image. This improvement also confirms that MFC fibrils prepared from bamboo fibers using a high speed blender can be used as reinforcement with PLA.

Similar increase of mechanical properties has been previously reported for composites reinforced with cellulose nanofiber networks.[9,10,12,14,18] MFC networks were prepared using the combination techniques of homogenization and high intensity sonication, and PLA composites reinforced with these networks were fabricated using a compression molding. Tensile modulus and strength of the composites were found to be improved by 60% and 14%, compared to those of the neat PLA films.[9] Moreover, Cheng et al.[12] studied the effect of two different types of lyocell fibers (untreated lyocell fiber and mechanically treated lyocell fiber) on mechanical properties of composites. Young's modulus and tensile strength of composites reinforced with treated lyocell fibers were found to be superior to those of untreated lyocell fiber reinforced composites. This is due to the higher aspect ratio of fibrils isolated from fibers after mechanical treatment.

Table 1. Tensile properties of PLA films, MFC networks and MFC reinforced PLA composites. Errors are reported in parentheses.

Materials	Tensile modulus (GPa)	Tensile strength (MPa)	Strain (%)
Pure PLA film	2.4 (0.2)	32.8 (5.3)	3.2 (2.0)
MFC network	0.2 (0.1)	2.6 (0.3)	7.1 (1.3)
MFC /PLA composite	3.1 (1.4)	38.7 (2.8)	1.9 (0.2)

Conclusions

MFC fibrils with the wide range of diameters and sizes were successfully prepared form 11 µm-diameter bamboo fibers using a high speed blender, and laminated bionanocomposites of poly(lactic acid) and porous MFC networks were subsequently prepared using a compression molding. Mechanical properties of neat polymer resin, composites and MFC networks were investigated. It can be found that the addition of the MFC network in the PLA resin can increase Young's modulus and tensile strength from 2.4 to 3.1 GPa and 32.8 to 38.7 MPa, respectively. Strain of the composites, however, was found to be lower, compared to neat polymer. The higher mechanical properties of the composites may be due to the good interaction between MFC fibrils and matrix.

References

1. Turbak, A.F., Snyder, F.W. and Sandberg, K.R. (1983). Microfibrillated cellulose, a new cellulose product: Properties, uses, and commercial potential. *J. Appl. Polym. Sci. Appl. Polym. Symp.* **37** : 815-827.

2. Herrick, F.W., Casebier, R.L., Hamilton, J.K. and Sandberg, K.R. (1983). Microfibrillated Cellulose : Morphologyand accessibility. *J. Appl. Polym. Sci. Appl. Polym. Symp.* **37** : 797-813.

3. Abe, K., Iwamoto, S. and Yano H. (2007). Obtaining cellulose nanofibers with a uniform width of 15 nm from wood. *Biomacromolecules*. **8** : 3276-3278.

4. Iwatake, A., Nogi, M. and Yano, H. (2008). Cellulose nanofiber-reinforced polylactic acid. Compos. Sci. Technol. **68(9)** : 2103-2106.

5. Uetani, K. and Yano, H. (2011). Nanofibrillation of wood pulp using a high-speed blender. *Biomacromolecules.* **12(2)** : 348-353.

6. Cheng, Q., Wang, S. and Rials, T.G. (2009). Poly (vinyl alcohol) nanocomposites reinforced with cellulose fibrils isolated by high intensity ultrasonication. *Compos. Part A* Appl. Sci. Manuf. **40(2)** : 218-224.

7. Wang, S. and Cheng, Q. (2009). A novel process to isolate fibrils from cellulose fibers by high□intensity ultrasonication, Part 1: Process optimization. *J. Appl. Polym. Sci.* **113(2)** : 1270-1275.

8. Siro, I. and Plackett, D. (2010). Microfibrillated cellulose and new nanocomposite materials : A review. *Cellulose.* **17(3)** : 459-494.

9. Tanpichai, S., Sampson, W.W. and Eichhorn, S.J. (2012). Stress-transfer in microfibrillated cellulose reinforced poly(lactic acid) composites using Raman spectroscopy. *Compos. Part A Appl. Sci. Manuf.* **43(7)** : 1145-1152.

10. Quero, F., Nogi, M., Yano, H., Abdulsalami, K., Holmes, S.M., Sakakini, B.H. and Eichhorn, S.J. (2010). Optimization of the mechanical performance of bacterial cellulose/poly(L-lactic) acid composites. *ACS Appl. Mater. Interfaces.* **2(1)** : 321-330.

11. Kowalczyk, M., Piorkowska, E., Kulpinski, P. and Pracella, M. (2011). Mechanical and thermal properties of PLA composites with cellulose nanofibers and standard size fibers. *Compos. Part A Appl. Sci. Manuf.* **42(10)** : 1509-1514.

12. Cheng, Q., Wang, S., Rials, T.G. and Lee., S.H. (2007). Physical and Mechanical Properties of Polyvinyl Alcohol and Polypropylene Composite Materials Reinforced With Fibrils Isolated From Regenerated Cellulose Fibers. *Cellulose*. **14(6)** : 593-602.

13. Iwamoto, S., Yamamoto, S., Lee, S.H. and Endo, T. Mechanical properties of polypropylene composites reinforced by surface-coated microfibrillated cellulose. *Compos. Part A Appl. Sci. Manuf.* **59** : 26-29.

14. Tang, C. and Liu, H. (2008). Cellulose nanofiber reinforced poly(vinyl alcohol) composite film with high visible light transmittance. *Compos. Part A Appl. Sci. Manuf.* **39(10)** : 1638-1643.

15. Lu, J., Wang, T. and Drzal, L.T. (2008). Preparation and properties of microfibrillated cellulose polyvinyl alcohol composite materials. *Compos. Part A Appl. Sci. Manuf.* **39(5)** : 738-746.

16. Tanpichai, S., Quero, F., Nogi, M., Yano, H., Young, R.J., Lindstrom, T., Sampson, W.W., Eichhorn, S.J. (2012). Effective young's modulus of bacterial and microfibrillated cellulose fibrils in fibrous networks. *Biomacromolecules*. **13(5)** : 1340-1349.

17. Sanchez - Garcia, M.D. and Lagaron, J.M. (2010). On the use of plant cellulose nanowhiskers to enhance the barrier properties of polylactic acid. *Cellulose*. **17(5)** : 987-1004.

18. Jonoobi, M., Aitomäki, Y., Mathew, A.P. and Oksman, K. (2014). Thermoplastic polymer impregnation of cellulose nanofibre networks: Morphology, *mechanical and optical properties*. **58** : 30-35.

19. Eichhorn, S.J., Dufresne, A., Aranguren, M., Marcovich, N.E., Capadona, J.R., Rowan, S.J., Weder, C., Thielemans, W., Roman, M., Renneckar, S., Gindl, W., Veigel, S., Keckes, J., Yano, H., Abe, K., Nogi, M., Nakagaito, A.N., Mangalam, A., Simonsen, J., Benight, A.S., Bismarck, A., Berglund, L.A. and Peijs, T. (2010). Review: current international research into cellulose nanofibres and nanocomposites. *J. Mater. Sci.* **45(1)** : 1-33.

20. Siqueira, G., Bras, J. and Dufresne, A. (2009). Cellulose whiskers versus microfibrils: Influence of the nature of the nanoparticle and its surface functionalization on the thermal and mechanical properties of nanocomposites. *Biomacromolecules*. **10(2)** : 425-432.

21. Chen, W.S., Yu, H.P., Liu, Y.X., Chen, P., Zhang, M.X. and Hai, Y.F. (2011). Individualization of cellulose nanofibers from wood using high - intensity ultrasonication combined with chemical pretreatments. *Carbohydr. Polym.* **83(4)** : 1804-1811.

22. Chen, W.S., Yu, H.P., Liu, Y.X., Hai, Y.F., Zhang, M.X. and Chen, P. (2011). Isolation and characterization of cellulose nanofibers from four plant cellulose fibers using a chemical - ultrasonic process. *Cellulose*. **18(2)** : 433-442.