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# 3 nm Thick Lignocellulose Nanofibers Obtained from Esterified Wood with Maleic Anhydride

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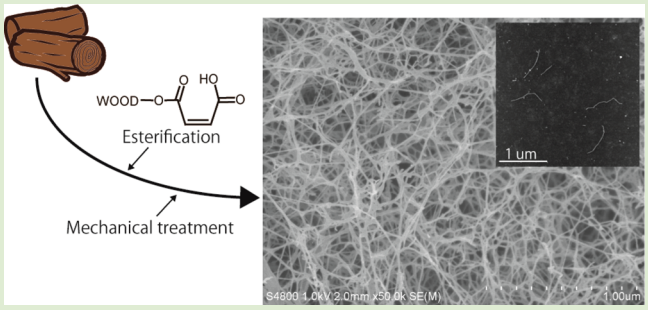
**ABSTRACT:** Esterification with maleic anhydride before mechanical treatments enabled wood to fibrillate into thin and uniform thick lignocellulose nanofibers. The esterification did not affect the crystal structure of the cellulose, and carboxyl groups introduced by the esterification facilitated the fibrillation of the wood. Moisture in the reaction system caused hydrolysis of some of the lignin and hemicellulose, thereby assisting the fibrillation. The esterification significantly reduced the number of passes through the disk mill required for the production of lignocellulose nanofibers with large specific surface areas. By using a high-pressure homogenizer, 97 wt % of the esterified wood was fibrillated into 3 nm thick lignocellulose nanofibers.




Biomass has attracted attention as a resource with the potential to replace present petrochemical-based materials for the realization of a carbon-neutral and consequently sustainable society. Wood is the most abundant biomass resource. Its main constituent, cellulose, is organized in microfibrils with thickness of 3 nm in the wood cell wall, indicating that disintegration of the wood can provide large quantities of bionanofibers. The wood cell wall consists of cellulose microfibril bundles adhered by lignin and hemicellulose, and in general, the wood-based bionanofibers are made from purified cellulose. The exception, which were lignin-containing cellulose nanofibers made from chemi-thermo mechanical pulp, was reported by Abe et al.[1] Previously, we reported that whole wood can be fibrillated into lignin-containing bionanofibers called lignocellulose nanofibers (LCNFs) without cellulose purification.[2] However, when thin LCNFs with specific surface areas of more than 100 $m^2$ $g^{-1}$ were obtained by fibrillation using a disk mill, 15 passes through the disk mill were required. Therefore, the high energy consumption required for LCNF preparation should be reduced in order to utilize this material in the industrial field. Here, we show that esterification of wood with maleic anhydride enables the reduction of the pass number required for LCNF preparation. Furthermore, it is also shown that extremely thin LCNFs are obtained from the esterified wood.

Wood pulp, which is purified cellulose from wood, is used as a cellulose nanofiber (CNF) source. The fibrillation of wood pulp is achieved using a disk mill,[3−5] high-pressure homogenizer,[6,7] or ultrasonic homogenizer.[8] The resultant CNFs have been investigated for their potential utilization as high strength,[9−11] transparent,[12−14] and high gas barrier films,[15] wet and aero gels,[16−20] composite fillers,[2,21−23] and electronic devices.[24,25] Although wood pulp can be fibrillated into CNFs only through mechanical treatments, chemical modification and pretreatments have been effective in producing thin and uniform thick CNFs and in reducing the energy needed for fibrillation.[16,26,27] In addition, it has been reported that wood pulp oxidation using a TEMPO catalyst changes hydroxyl groups into carboxyl groups on the cellulose microfibril surface.[28,29] Since the carboxyl groups help the dispersion of cellulose microfibrils in water by swelling of the pulp fibers and osmotic pressure effects, in these studies, the TEMPO oxidation facilitated the fibrillation of wood pulp into CNFs of 3 nm thickness and consisting of single cellulose microfibrils.

We previously reported on LCNFs with specific surface areas of 107 $m^2$ $g^{-1}$ (Figure 1a). Improved dispersion of the LCNFs in the polypropylene matrix enhanced the mechanical properties of the composites.[2] Although the wood was passed 15 times through the disk mill, the obtained LCNFs had a wide thickness distribution, from 20 nm to 1 $\mu$m. When there is an only difference of aspect ratio in the LCNFs, the reinforcement effect of the thinner and more uniform thick LCNFs was significant, due to their large aspect ratios. However, the chemical modification of wood for effective fibrillation has not been examined, and this study demonstrates that the introduction of carboxyl groups by esterification facilitates fibrillation.

The esterification of wood to introduce carboxyl groups was achieved by causing the wood to react with maleic anhydride.[30] Ring-opened maleic anhydride forms ester bonds with hydroxyl groups of lignin, hemicellulose, and cellulose in the reaction, resulting in carboxyl groups being borne on the wood constituents. The reaction used here proceeded without solvents, which is an advantage with regard to industrial

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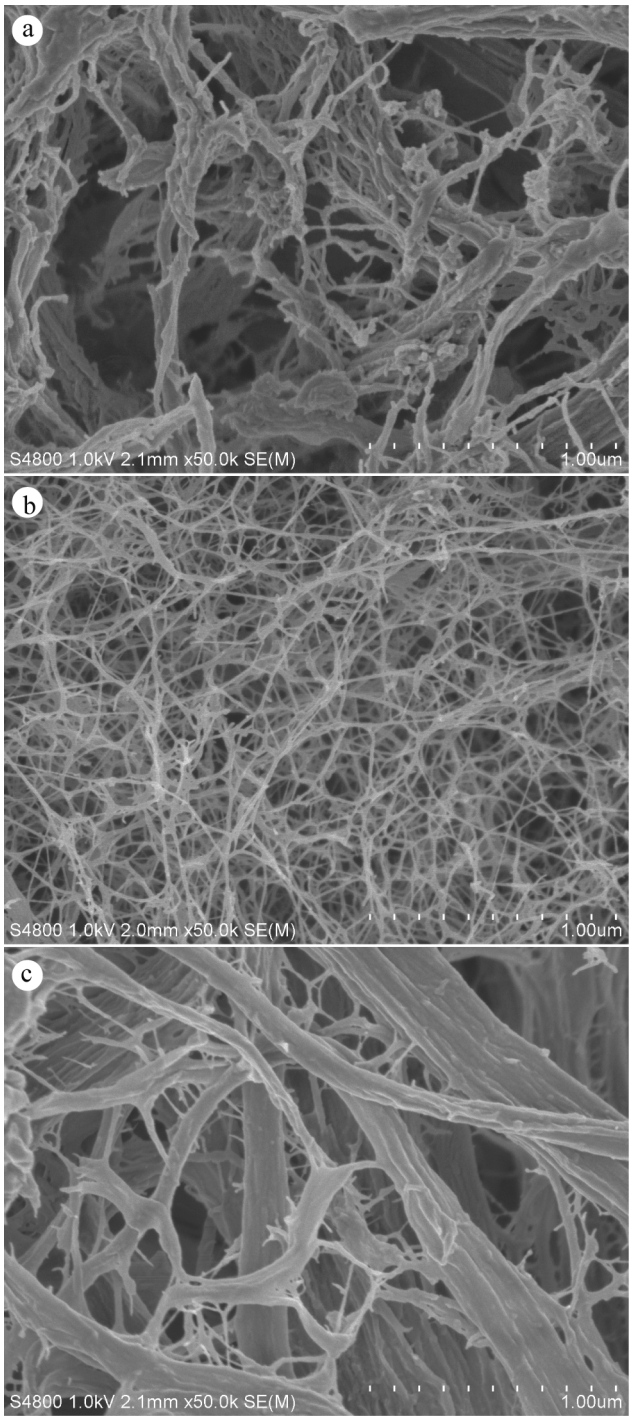


**Figure 1.** SEM images of LCNFs prepared by (a) 15 passes through the disk mill of unmodified wood and 3 passes through the disk mill of esterified wood under (b) 18% moisture content and (c) dry conditions.

application. In this study, wood flour with a moisture content of 0 and 18% reacted with maleic anhydride at 120 °C for 3 h. After the introduced carboxylic acid was changed into $Na^+$-carboxylate groups by neutralization using sodium hydroxide, the esterified wood suspension (0.3 wt %) was passed 3 times through the disk mill to prepare the LCNFs.

Figure 1b is a scanning electron microscopic (SEM) image of the LCNFs prepared from esterified wood with 18% moisture content. Their thickness distributions were uniform compared to the LCNFs prepared from unmodified wood and requiring 15 passes through the disk mill (Figure 1a). The thicknesses of the majority of the esterified wood-based LCNFs were less than 10 nm (measured using SEM), and their specific surface area was 289 $m^2\ g^{-1}$. It was determined that the esterified wood with maleic anhydride was fibrillated into uniform and thin LCNFs with one-fifth of energy for the mechanical treatments. On the other hand, the fibrillation efficiency in the esterified wood under dry conditions (Figure 1c) was lower than that in the esterified wood with 18% moisture content. Furthermore, there was no significant difference between the LCNFs prepared from the unmodified and esterified wood under dry conditions.

Table 1 shows the constituents of the unmodified and esterified wood, measured using high performance liquid chromatography. Although the esterification of the dry wood caused a little change in the wood constituents, the esterification of the moisture-containing wood reduced the lignin and the hemicellulose-derived sugars by 56% and 41%, respectively. The maleic anhydride in the reaction system was hydrolyzed into maleic acid by the moisture in the wood, and the maleic acid then hydrolyzed the lignin and hemicellulose, dissolving them in water.

The amount of grafted maleic acid in the esterified products of the dry wood was larger than that of the moisture-containing wood. It was indicated that the larger amount of esterified lignin and hemicellulose remained in the esterified products of the dry wood, in comparison with the moisture-containing wood. Note that it has been reported that hemicellulose does not hinder the fibrillation of wood pulp.[5] Considering the amount of grafted maleic acid, not only the introduction of carboxyl groups but also the removal of part of the lignin by the esterification of the moisture-containing wood facilitated the fibrillation.

The glucose content of the esterified products of the moisture-containing wood was larger than that of the other samples, indicating that cellulose was difficult to be hydrolyzed by the maleic acid. Furthermore, X-ray diffraction analysis (Figure 2) revealed that the esterification did not change the cellulose I crystal structure, either with moisture or without. This result revealed that the esterification did not occur inside of the cellulose crystals.

The 0.3 wt % suspension esterified wood with 18% moisture content was passed 3 times through a high-pressure homogenizer to produce LCNFs in a high yield. In our experience, this fibrillation efficiency is higher than that of the disk mill. After centrifugation of the obtained suspension, 97 wt % of solid was included in the supernatant. The suspension supernatant had a brown-colored transparent appearance, and an atomic force microscopic (AFM) image of this substance is shown in Figure 3a. The thicknesses and lengths of the observed LCNFs were 3.1 ± 0.5 nm and 642 ± 359 nm, respectively. Their cross-section profiles are shown in Figure 3b, evidencing the narrow thickness distribution of the LCNFs. Considering the thicknesses of the cellulose microfibrils in the wood cell wall, it can be determined that the obtained LCNFs consisted of completely individualized microfibrils. Also, lignin and hemicellulose seemed to coat the microfibrils in the LCNFs, which was difficult to determine by morphological observation.

This study revealed that esterification with maleic anhydride before mechanical treatments enabled wood to fibrillate into thin and uniform thick LCNFs. The esterification significantly reduced the number of passes through the disk mill required for



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**Table 1. Amount of Grafted Maleic Acid and Change of Wood Constituents in Unmodified and Esterified Wood under 18% Moisture Content and Dry Conditions[a]**

| | | wood constituents | | | | |
|---|---|---|---|---|---|---|
| | maleic acid (wt %) | lignin (wt %) | glucose (wt %) | mannose (wt %) | xylose (wt %) | galactose (wt %) |
| unmodified wood | 0 | 32.2 | 45.0 | 15.7 | 4.5 | 2.6 |
| esterified wood (18% moisture content) | 18.8 | 14.2 | 72.4 | 11.0 | 1.8 | 0.6 |
| esterified wood (dry) | 26.7 | 29.1 | 46.2 | 19.5 | 3.3 | 1.9 |

[a]Sum of wood constituents was corrected to 100%.

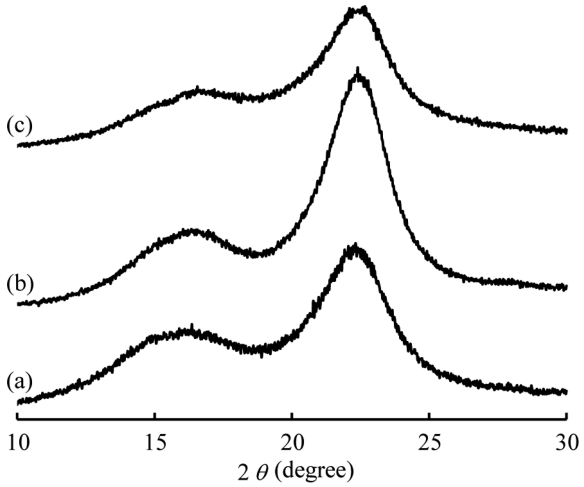


**Figure 2.** X-ray diffraction spectrum of (a) unmodified wood and esterified wood with maleic anhydride under (b) 18% moisture content and (c) dry conditions.

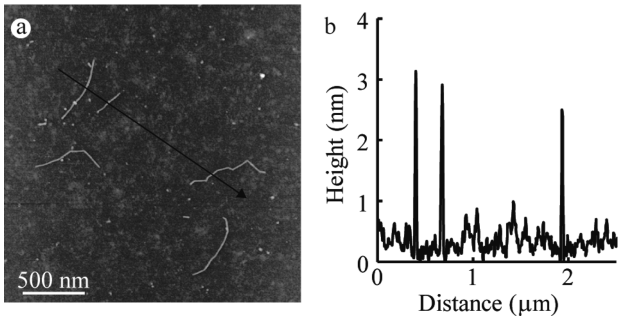


**Figure 3.** (a) AFM image of LCNFs prepared by 3 passes through the high-pressure homogenizer of esterified wood with 18% moisture content and (b) roughness along the indicating black arrow in the AFM image.

the production of LCNFs with large specific surface areas. By using a high-pressure homogenizer, 97 wt % of the esterified wood was fibrillated into 3 nm thick LCNFs.

## EXPERIMENTAL SECTION

Oven-dried and 18-%-moisture-content wood flour (particle size <0.2 mm; Japanese cypress; soft wood) were used. The wood flour (5 g, dried weight) reacted with maleic anhydride (25 g) at 120 °C for 3 h without stirring. The reactants were washed with acetone and then with distilled water until pH of filtrate water was 7.

NaOH solution (1 mol $L^{-1}$) was added into the esterified wood–water suspension until the suspension pH reached 11, in order to neutralize the introduced carboxylic acid. Subsequently, the excess NaOH was washed with distilled water, and the unmodified wood was also treated with NaOH.

The fibrillation was demonstrated using a disk mill (Supermasscolloider, MKCA6-3, Masuko Sangyo Co., Japan) and a high-pressure homogenizer (Masscomizer X, Masuko Sangyo Co., Japan) under wet conditions. The disk mill grinds samples between rotating stones. In order to obtain the LCNFs, the 0.3% water suspensions of unmodified and esterified wood were passed 15 and 3 times, respectively, through the disk mill. The rotational speed was 18 000 rpm. During the first pass, the gap between the grinding stones was narrowed to 50 μm from the initial contact distance, while the additional passes were conducted using a 100 μm narrow gap measured from the initial contact distance.

The high-pressure homogenizer injects a sample suspension into a tight flow path at a high speed, generating shear and colliding forces. In our experience, its fibrillation efficiency is higher than that of the disk mill. However, the unmodified wood suspension could not be treated using the high-pressure homogenizer since the unmodified wood was too rigid to inject into the tight flow path. On the other hand, the esterified wood under the moisture-containing conditions was significantly swollen by water after the neutralization. The esterified wood–water suspension was passed 3 times through the high-pressure homogenizer at 200 MPa to obtain the LCNFs. Then, the unfibrillated fraction was removed from the LCNF suspension using a centrifuge at 18 500*g* for 5 min to assess the LCNF yield.

The dilute LCNF suspension (0.001 wt %) prepared from the esterified wood under moisture-containing conditions by the high-pressure homogenizer treatment was deposited on mica precoated with polyethylenimine. The LCNFs were examined using AFM in the tapping mode. The lengths and thicknesses of 50 LCNFs were measured from the AFM images using software included in the AFM system. Their thicknesses were defined as being the height difference between the mica surface and the tops of the LCNFs.

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### Author Contributions

The manuscript was written through contributions of all authors.

### Notes

The authors declare no competing financial interest.

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## REFERENCES

(1) Abe, K.; Nakatsubo, F.; Yano, H. *Compos. Sci. Technol.* **2009**, *69*, 2434–2437.
(2) Iwamoto, S.; Yamamoto, S.; Lee, S. H.; Endo, T. *Cellulose* **2014**, *21*, 1573–1580.
(3) Taniguchi, T.; Okamura, K. *Polym. Int.* **1998**, *47*, 291–294.
(4) Iwamoto, S.; Nakagaito, A. N.; Yano, H. *Appl. Phys. A: Mater. Sci. Process.* **2007**, *89*, 461–466.
(5) Iwamoto, S.; Abe, K.; Yano, H. *Biomacromolecules* **2008**, *9*, 1022–1026.
(6) Turbak, A. F.; Snyder, F. W.; Sandberg, K. R. *J. Appl. Polym. Sci. Appl. Polym. Symp.* **1983**, *37*, 815–827.



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*ACS Macro Lett.* 2015, 4, 80–83

(7) Herrick, F. W.; Casebier, R. L.; Hamilton, J. K.; Sandberg, K. R. *J. Appl. Polym. Sci. Appl. Polym. Symp.* **1983**, *37*, 797−813.
(8) Zhao, H. P.; Feng, X. Q.; Gao, H. *Appl. Phys. Lett.* **2007**, *90*, 073112.
(9) Nakagaito, A. N.; Yano, H. *Appl. Phys. A: Mater. Sci. Process.* **2004**, *78*, 547−552.
(10) Nakagaito, A. N.; Yano, H. *Appl. Phys. A: Mater. Sci. Process.* **2003**, *80*, 155−159.
(11) Sehaqui, H.; Zhou, Q.; Ikkala, O.; Berglund, L. A. *Biomacromolecules* **2011**, *12*, 3638−3644.
(12) Nogi, M.; Iwamoto, S.; Nakagaito, A. N.; Yano, H. *Adv. Mater.* **2009**, *21*, 1595−1598.
(13) Yano, H.; Sugiyama, J.; Nakagaito, A. N.; Nogi, M.; Matsuura, T.; Hikita, M.; Handa, K. *Adv. Mater.* **2005**, *17*, 153−155.
(14) Iwamoto, S.; Nakagaito, A. N.; Yano, H.; Nogi, M. *Appl. Phys. A: Mater. Sci. Process.* **2005**, *81*, 1109−1112.
(15) Fukuzumi, H.; Saito, T.; Iwata, T.; Kumamoto, Y.; Isogai, A. *Biomacromolecules* **2009**, *10*, 162−165.
(16) Pääkkö, M.; Ankerfors, M.; Kosonen, H.; Nykänen, A.; Ahola, S.; Osterberg, M.; Ruokolainen, J.; Laine, J.; Larsson, P. T.; Ikkala, O.; Lindström, T. *Biomacromolecules* **2007**, *8*, 1934−1941.
(17) Olsson, R. T.; Azizi Samir, M. A. S.; Salazar-Alvarez, G.; Belova, L.; Ström, V.; Berglund, L. a; Ikkala, O.; Nogués, J.; Gedde, U. W. *Nat. Nanotechnol.* **2010**, *5*, 584−588.
(18) Sehaqui, H.; Salajkova, M.; Zhou, Q.; Berglund, L. A. *Soft Matter* **2010**, *6*, 1824−1832.
(19) Svagan, A. J.; Samir, M. A. S.; Berglund, L. A. *Adv. Mater.* **2008**, *20*, 1263−1269.
(20) Abe, K.; Yano, H. *Carbohydr. Polym.* **2011**, *85*, 733−737.
(21) Suzuki, K.; Okumura, H.; Kitagawa, K.; Sato, S.; Nakagaito, A. N.; Yano, H. *Cellulose* **2013**, *20*, 201−210.
(22) Wang, B.; Sain, M. *Polym. Int.* **2007**, *546*, 538−546.
(23) Zimmermann, T.; Pöhler, E.; Geiger, T. *Adv. Eng. Mater.* **2004**, *6*, 754−761.
(24) Nagashima, K.; Koga, H.; Celano, U.; Zhuge, F.; Kanai, M.; Rahong, S.; Meng, G.; He, Y.; De Boeck, J.; Jurczak, M.; Vandervorst, W.; Kitaoka, T.; Nogi, M.; Yanagida, T. *Sci. Rep.* **2014**, *4*, 5532.
(25) Koga, H.; Nogi, M.; Komoda, N.; Nge, T. T.; Sugahara, T.; Suganuma, K. *NPG ASIA Mater.* **2014**, DOI: 10.1038/am.2014.9.
(26) Wagberg, L.; Decher, G.; Norgren, M.; Lindstroem, T.; Ankerfors, M.; Axnaes, K. *Langmuir* **2008**, *24*, 784−795.
(27) Henriksson, M.; Henriksson, G.; Berglund, L. a.; Lindström, T. *Eur. Polym. J.* **2007**, *43*, 3434−3441.
(28) Saito, T.; Nishiyama, Y.; Putaux, J.-L.; Vignon, M.; Isogai, A. *Biomacromolecules* **2006**, *7*, 1687−1691.
(29) Isogai, A.; Saito, T.; Fukuzumi, H. *Nanoscale* **2011**, *3*, 71−85.
(30) Matsuda, H. *Wood Sci. Technol.* **1987**, *21*, 75−88.



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