Difference between bamboo- and wood-derived cellulose nanofibers prepared by the aqueous counter collision method

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KEYWORDS: Bamboo pulp, Cellulose nanofiber, Aqueous counter collision, Emulsion droplet, Amphiphilic property

SUMMARY: Bamboo pulps whose crystalline and hierarchical structures differ from those of wood pulps were subjected to the aqueous counter collision (ACC) method, which makes it possible to overcome interfacial interactions between cellulose molecules in order to produce cellulose nanofibers (CNFs) and hence highlights differences between surface properties. At first, the CNFs derived from both bamboo and wood were compared in studies of the sedimentation behavior of 0.05% (w/w) aqueous CNF dispersions. Then, changes in mechanical properties of CNF sheets under various humidity conditions, as well as the CNF emulsion droplets formed by mixing with *n*-hexane, both of which were prepared from aqueous CNF dispersions, were examined. These investigations focusing on the interaction of CNFs with water indicated totally different inherent nature in the surface properties between bamboo and wood CNFs, which were prepared by the ACC method. Moreover, the different character in the two CNF emulsion droplets also indicates that the surface on bamboo-derived CNFs prepared by this method was likely to exhibit more hydrophobic properties than wood CNFs without any chemical modification.

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"Bamboo", a tribe of the grass family, contains cellulose fibers as a main frame component similarly to wood, although their adult forms are far different from one another. The response to beating of bamboo pulps of micro-sized width differs from that of wood, because the orientation directions of the microfibrils in the individual cell wall layers are different (Wai et al. 1985). However, once the pulps assemble to form a paper sheet, differences in physical properties become much smaller, except for the ones related to fiber length, and the deterioration due to degree of polymerization (Win, Okayama 2011).

Amada et al. (1997) and He et al. (2007) reported that the crystalline structure of bamboo cellulose differs from that in wood, but this does not necessarily induce a characteristic difference in the fibers of micro-sized width. If any, the structural difference is likely to result in the smaller scaled characteristics appearing in cellulose nanofibers (CNFs).

Although various methods of preparing CNF have been proposed (Nakagaito, Yano 2005; Saito et al. 2006), the aqueous counter collision (ACC) method developed by Kondo et al. (2008), which allows to cleave interfacial interactions among cellulose molecules using dual high speed water jets, is one of the best tools to clarify the above differences. This method disintegrates native fibers into CNFs without chemical modification, which in fact will expose inherent structural difference of raw materials. According to Kose et al. (2011a), the ACC nano-pulverizing process depends on differences in crystalline forms and hierarchical structures of the cellulose fibers. Thus, the size-reducing behavior for bamboo-derived pulps would be different from that for wood pulps.

In this study, we focused on the differences in surface properties between the bamboo- and wood-derived CNFs prepared by the ACC method. In particular, the aqueous dispersion states of CNFs produced by the ACC treatments were examined in terms of interaction with water. In the CNF sheet forms, changes in the tensile strength were compared between bamboo and wood origins under various humidity conditions. The surface nature of CNFs was investigated by observing the formation of emulsion droplets when aqueous CNF dispersions were mixed with *n*-hexane. Finally, the authors want to propose that the ACC method would be able to reveal inherent properties on the nano-scales by employing raw materials having hierarchical structures.

Materials and Methods

Preparation of CNFs by aqueous counter collision (ACC)

Two kinds of bleached kraft pulps from bamboo and hardwood (Chuetsu Pulp & Paper Co., Ltd., Toyama, Japan) were employed as starting materials. Prior to CNF preparation, bamboo bleached kraft pulps were refined by repeating filtration with a nylon mesh (62 μm in diameter) in order to substantially remove tissue parenchyma cells.

An aqueous counter collision system (Sugino Machine Co., Ltd., Toyama, Japan) was used to prepare CNFs (*Fig 1*). In this equipment, jets of aqueous suspensions containing micro-sized fibers are expelled through two nozzles, so that the two streams collide against one another under high pressure, resulting in rapid, wet pulverization and the formation of an aqueous dispersion of nano-sized objects (Kondo et al. 2008). The diameter of each nozzle was 160 μm in this study. The number of ejection steps and the ejection pressure may be adjusted to subject the sample to the desired quantity of pulverizing cycles (or "passes").

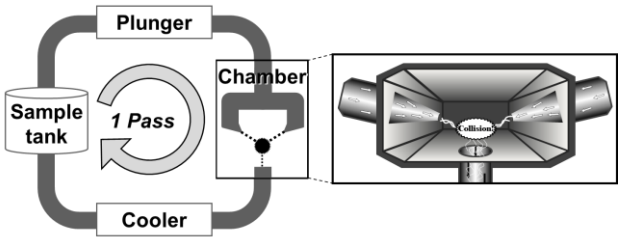

Fig 1 - Schematic view of the aqueous counter collision (ACC) method

The micro-sized pulp samples were subjected to ACC treatments; typically dispersing of wet pulps corresponding to either 0.39 g or 0.78 g as dried weight in 780 g of water to produce either 0.05% (w/w) or 0.10% (w/w) pulp suspensions, respectively. These aqueous suspensions were then transferred into the sample tank of the ACC apparatus and ejected through the pair of water jets, leading to collision of the resulting streams at the chosen pressure of 180 MPa. The pulverization process could potentially be repeated 10, 30, 50, 70 and 90 passes. After the desired number of collisions had occurred, an aliquot of the treated suspension was taken from the sample tank and various analyses were conducted, as described in the following section.

Apparent comparison of CNFs dispersion states

The sedimentation behavior of aqueous CNF dispersion from bamboo and wood were compared by visual inspection. Dispersions were prepared by the ACC treatments at 0.05% (w/w) and 0.10% (w/w) and the sedimentation was observed after 1, 3, 5, 7 and 10 days of settling after shaking.

Preparation of CNF sheets

Bamboo- and wood-derived CNF sheets were prepared by vacuum filtration of aqueous CNF dispersions prepared from 0.10% (w/w) of the individual pulp suspensions. Filtrations were performed through a filter membrane with a pore size of 0.22 μm in diameter (GVWP, Merck Millipore, Billerica, MA, USA) in a glass filter funnel with a diameter of 35 mm. Two kinds of drying process for the wet CNF sheets after filtration were carried out at room temperature (23-30°C) in the range of 40-60% of relative humidity (RH) for over 3 days, and 130°C for 1 day, respectively.

Densities and water contents for CNF sheets

Densities and water contents of CNF sheets were measured under the three kinds of humidity-conditions; (A): 50% RH at 23°C for over 3 days, (B): at 130°C for 1 day following (A), and (C): 50% RH at 23°C for over 3 days following (B). Densities of CNF sheets were determined by dividing weight by volume at each condition. The volume was calculated based on thickness and areas of sample specimens before tensile tests, measured by Digital Micrometer (Series406-Non-Rotating Spindle Type 406-250, Mitutoyo Corp., Kawasaki, Japan) and Digital Caliper (ABSOLUTE Digimatic Caliper 500 Series 500-181-20, Mitutoyo Corp., Kawasaki, Japan). Water contents were calculated by the following equation;

$$water\ contents\ (\%) = \frac{W_{sample} - W_{(B)}}{W_{sample}}$$

where W_{sample} is the weight of CNF sheets at respective humidity-conditions, and $W_{(B)}$ is the weight of CNF sheets at condition (B), where water contents were assumed 0%.

Tensile tests

Tensile tests of CNF sheets were performed using a Material Testing Instruments (STA-1225, ORIENTEC Co., Ltd., Tokyo, Japan) equipped with a 100 N load cell. Sample specimens were prepared by cutting the CNF sheets into 30-35 × 7 mm strips. The sample specimens were measured at 20 mm of active length at 10% min^{-1} strain rate under the three kinds of humidity-conditions.

Emulsification of aqueous CNF dispersion with *n*-hexane

In order to obtain indication of how surface properties of individual CNFs may or may not differ, the emulsifying behaviors of the aqueous CNF dispersions with *n*-hexane were examined. Aqueous CNF dispersions (10 ml) were mixed with 10 ml of *n*-hexane (Wako Pure Chemical Industries, Ltd., Osaka, Japan), immediately after the ACC treatment with 90 passes at 0.10% (w/w), and then the mixture was subjected to ultrasonic treatments for 2 min to result in emulsified states.

Transmission electron microscopy (TEM)

TEM images of dispersed CNFs were used to determine fiber width. A drop of aqueous CNF dispersions was mounted on a copper grid before air-drying and subsequent negative-staining by 4% aqueous uranyl acetate, and finally air-dried. CNFs on a grid were observed with a JEM-1010 (JEOL Co., Ltd., Tokyo, Japan) at an 80 kV accelerating voltage. The negative films of the acquired images were scanned to be digitized for the measurement of the fiber width. The fiber width of dispersed CNFs was measured from the TEM images acquired at a magnification of 25k using the open access software Image J; the mean values were calculated from the measured values of more than 50 fibers.

Optical microscopy

Optical microscopy was carried out to compare the cloudy phases formed in the emulsified samples described above. Droplets in the cloudy phases were picked up and then put on a slide glass, before observation using an optical microscope (BHA, OLMPUS Co., Tokyo, Japan).

Scanning electron microscopy (SEM)

The emulsified states in the cloudy phases were observed by using SEM. Prior to the observation, a drop of the sample on a stub was rapidly frozen in liquid nitrogen and then fractured before freeze-drying. Samples thus prepared were observed by JSM5600LV (JEOL Co., Ltd., Tokyo, Japan) after coated with Au.

Results and Discussion

Comparison of CNFs dispersion states

Kose and Kondo (2011b) reported that aqueous CNF dispersions prepared from bacterial cellulose pellicle by ACC treatments exhibited well dispersed states. In the present study, aqueous CNF dispersions prepared from bleached kraft pulps from bamboo and hardwood also exhibited well dispersed states in the concentration of 0.10% (w/w) after treated with 10 passes. Aqueous CNF dispersions prepared from bleached kraft pulps from both bamboo and hardwood also exhibited well dispersed states in the concentration of 0.10% (w/w) after treatment with 10 passes. However, a different sedimentation behavior of CNFs was observed in the aqueous dispersions of the bamboo and wood-derived CNFs at the lower concentration of 0.05% (w/w) (*Fig 2*). For bamboo-derived CNFs, the sedimentation was observed at 50 or more passes of the ACC treatment, whereas it was not observed for wood treated with the corresponding passes. The sedimentation rate for suspensions treated with less than 50 passes also differed from those treated with 50 or more passes (see Supporting Information: *Fig S1*). These results indicate that the sedimentation behaviors are different at either less or more 50 passes.

In order to investigate the width size distribution of nanofibers produced, TEM observation was carried out for CNFs contained in the supernatant and sedimentation areas after ACC-treated at 30 and 90 passes (*Fig 3*). For the samples at 30 passes, a number of CNFs having thicker fiber width were observed in the sedimentation areas, whereas there was no significant difference in fiber width observed for the samples in the both areas at 90 passes (*Table 1*). Therefore, differences in sedimentation behavior may be dependent on the width of nanofibers produced. In general, the sedimentation can be due to the entanglement among nanofibers. Thus, appearance of the different behavior as seen in the thinner bamboo nanofibers might be influenced by the other contribution of some interfacial interactions with water, as well as the entanglement of fibers.

Characterization of CNF sheets

Interactions between H_2O and both bamboo- and wood-derived CNFs were compared at agglomerated state like a sheet form, in order to reveal some appearance of differences in the surface properties between the both CNFs. For that, shrinkage behaviors of CNF wet sheets in drying processes were compared by changing the water evaporating rates through two kinds of drying temperatures, room-temperature and 130°C. Moreover, interactions between "moisture" and CNFs were examined by measuring physical properties of dried

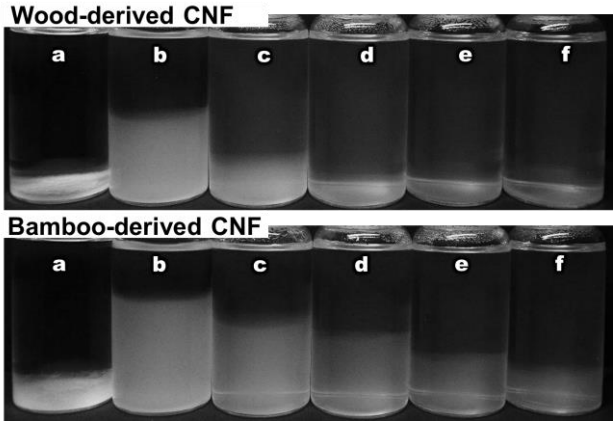

Fig 2 - Photographs of aqueous dispersions of wood-derived (above) and bamboo-derived (bottom) CNF after 10 days of sedimentation. The samples were ACC treated at 0.05% consistency for (a) 0, (b) 10, (c) 30, (d) 50, (e) 70 and (f) 90 passes, respectively.

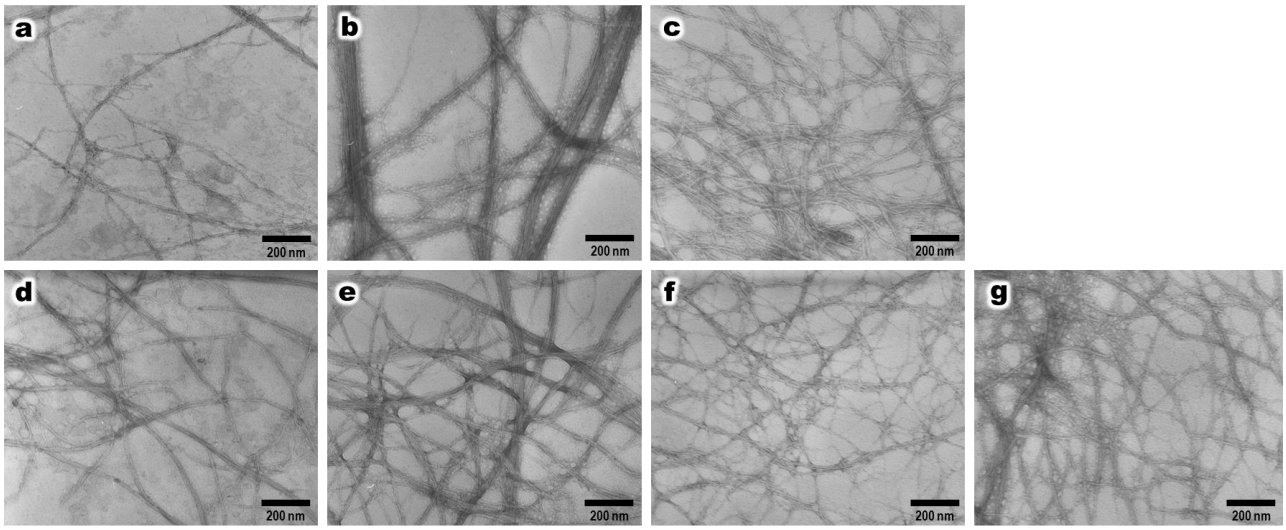

Fig 3 - TEM images of CNFs in respective aqueous CNF dispersions prepared by the ACC treatments with 30 and 90 passes. (a) supernatant and (b) sedimentation area of wood-derived with 30 passes, (c) dispersed area of wood-derived with 90 passes, (d) supernatant and (e) sedimentation area of bamboo-derived with 30 passes, (f) supernatant and (g) sedimentation area of bamboo-derived with 90 passes, respectively.

Table 1 - Fiber width of CNFs

		Fiber width (nm)	
		Supernatant	**Sedimentation**
30 passes	Wood-derived CNFs	20.8 ± 6.1	32.8 ± 21.6
	Bamboo-derived CNFs	20.4 ± 7.7	33.4 ± 19.4
90 passes	Wood-derived CNFs	22.3 ± 12.4	-
	Bamboo-derived CNFs	20.7 ± 8.3	23.8 ± 10.3

Table 2 - Physical properties of CNF sheets at the respective humidity-conditions; (1)-(6) correspond to procedures in *Fig 4*.

				Tensile test			
		Density	**Water content**	**Young's modulus**	**Tensile strength**	**Strain-to-failure**	**Slope in the plastic region**
		(kg/cm^3)	**(%)**	**(GPa)**	**(MPa)**	**(%)**	**(GPa)**
Wood-derived CNF sheets	(1)	1442 ± 61	7.6 ± 0.9	6.5 ± 0.6	170 ± 1	7.3 ± 0.9	1.51 ± 0.08
	(2)	1349 ± 16	-	7.1 ± 0.4	233 ± 11	6.4 ± 0.7	-
	(3)	1454 ± 8	6.7 ± 0.1	6.9 ± 0.3	164 ± 10	6.9 ± 0.8	1.22 ± 0.10
	(4)	1490 ± 71	6.5 ± 0.7	7.2 ± 0.5	167 ± 9	4.9 ± 0.4	2.04 ± 0.01
	(5)	1420 ± 16	-	7.7 ± 0.3	216 ± 14	4.5 ± 0.4	-
	(6)	1530 ± 24	6.8 ± 0.2	7.1 ± 0.1	139 ± 3	3.8 ± 0.1	1.75 ± 0.11
Bamboo-derived CNF sheets	(1)	1412 ± 89	8.2 ± 0.1	6.3 ± 0.2	195 ± 12	8.0 ± 0.3	1.70 ± 0.01
	(2)	1332 ± 21	-	7.0 ± 0.2	239 ± 10	5.6 ± 0.5	-
	(3)	1447 ± 12	7.2 ± 0.2	6.7 ± 0.5	151 ± 12	5.6 ± 0.7	1.23 ± 0.04
	(4)	1394 ± 37	6.0 ± 0.9	6.7 ± 0.5	174 ± 20	5.5 ± 1.0	1.91 ± 0.06
	(5)	1321 ± 9	-	6.8 ± 0.2	189 ± 9	3.7 ± 0.3	-
	(6)	1422 ± 15	7.0 ± 0.2	7.0 ± 0.1	226 ± 3	9.7 ± 0.4	1.55 ± 0.05

sheets under various humidity-conditions with sequences as shown in *Fig 4*. The included free and bound water in dry sheets would be absorbed or desorbed by changing humidity-conditions. In general, it would appear that the free water are easily absorbed or desorbed by an environment change, whereas the bound water is not desorbed unless it is under a high temperature. Desorption of free and bound water is assumed to occur under the humidity-condition as 0%RH at 130°C in *Fig 4B*, and then the moisture is supposed to absorb to the CNF sheets under the humidity-condition as 50%RH at 23°C in *Fig 4C*. In this regard, absorption behavior of bound water would result in difference depending on the CNF surface properties as either hydrophilic or hydrophobic. In the experiments, such changes in physical properties due to the difference were observed as listed in *Table 2*.

The densities of CNF sheets dried at the two temperatures were different between bamboo- and wood-derived CNF sheets (*Fig 5*). In the case of wood-derived CNF sheets, the density of 130°C-dried sheets was higher than that of room temperature-dried sheets at all conditions. In contrast, bamboo-derived CNF sheets exhibited an opposite behavior. The fiber network structures in the CNF sheets would be affected by the entanglement of fibers. The influence would be strongest for the wet sheets and less pronounced at the drying process. Namely, the results indicate that individual CNFs were affected by the difference of interfacial interactions with water, as well as the entanglement of fibers.

Fig 6 shows stress-strain curves of samples obtained by the same preparation procedure. Stress-strain curves of the CNF sheets exhibited a similar trend regardless of raw materials and drying temperature. More specifically, the change in stress due to the load initially increased linearly (this region is called the elastic region), then curved gently (this point is called the yield point) and finally increased slowly and linearly again (this region is called the plastic region). The yield point disappeared after complete drying process, (A) to (B) shown in *Fig 4*. The initial behavior with a yield point and a plastic region was recovered by moistening, i.e., process (B) to (C). These results indicate that the yield point and the plastic region were clearly affected by the moisture in the CNF sheets. On the other hand, there was no significant difference in the Young's modulus corresponding to the slope in the elastic region by changing the humidity-conditions. Thus, it seems that the fiber network structures, once formed in the CNF sheets, were not significantly affected by the adsorption or desorption of moisture, because it is mainly the elastic region that is affected by the general sheet structure.

Fig 7 shows the linear relationship between density and Young's modulus for the individual CNF sheets under completely dried conditions, water content 0% in *Fig 4B*, indicating that the physical entanglement of fibers in the network structures of bamboo-derived CNFs were similar to that composed of wood-derived CNFs.

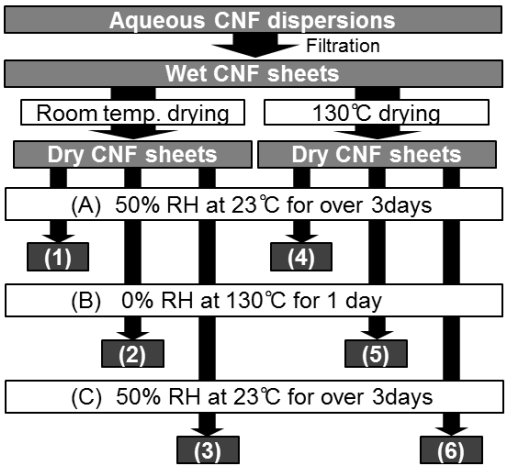

Fig 4 - Sequences of test scheme

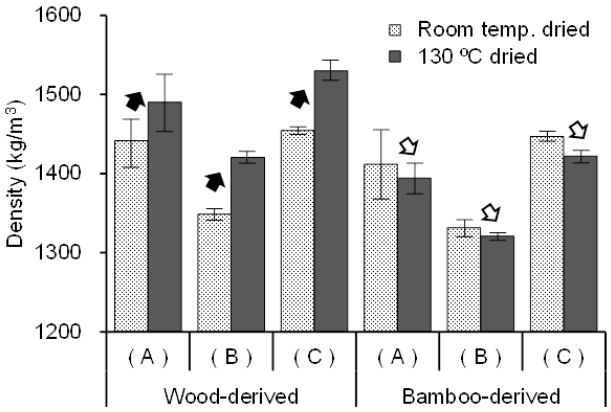

Fig 5 - Densities of wood- and bamboo-derived CNF sheets after dried at room temperature and 130°C, respectively. Humidity-conditions (A), (B) and (C) in measurements were indicated in *Fig 4*.

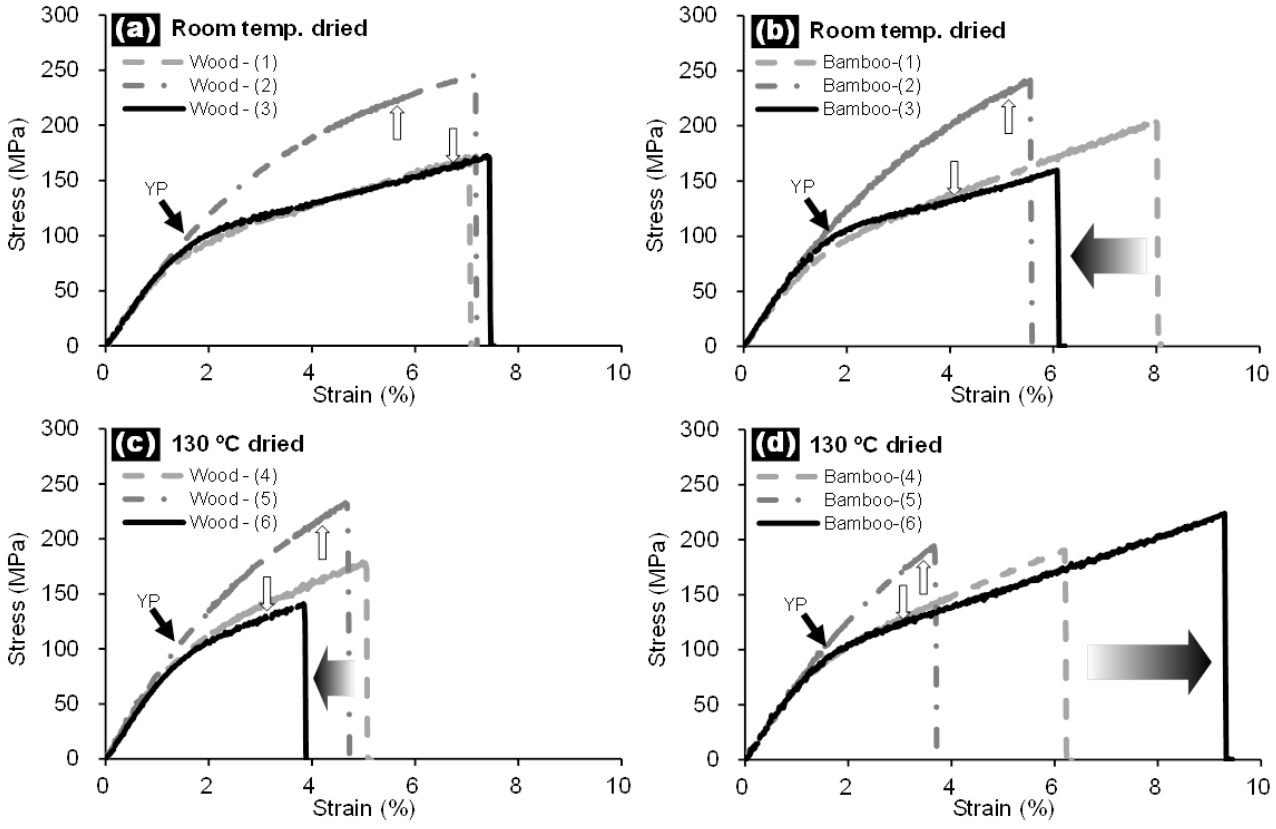

Fig 6 - Tensile stress-strain curve of room temperature-dried CNF sheets derived from wood (a) and bamboo (b), and of 130°C dried CNF sheets derived from wood (c) and bamboo (d). Measurement conditions of the sheets (1)-(6) were indicated in *Fig 4*. The close arrows (YP) indicate the yield points. The larger arrows indicate changing of strain-to-failure followed by desorption and subsequent absorption of water. The open arrows indicate change of stress-strain curve by changing humidity-condition. The slash areas indicate elastic regions.

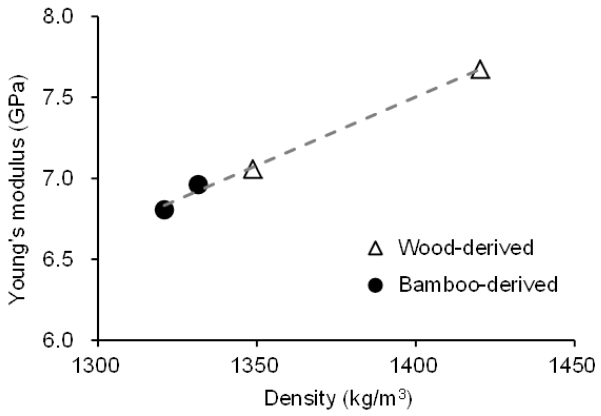

Fig 7 - Relationship between densities and Young's moduli of the individual CNF sheets at condition-(B)

The behavior of strain-to-failure in 130°C-dried bamboo-derived CNF sheets was different from the others sheets (*Fig 6*). By desorption of the moisture with dehydration from (A) to (B), strain-to-failure ratio was decreased or not changed. Then, when CNF sheets were re-moistened by changing from (B) to (C) in *Fig 4*, strain-to-failure did not return any more to the position of the humidity-condition (A) state. However, only when bamboo-derived CNF sheets were dried at 130°C, strain-to-failure increased drastically from 5.5% to 9.7% (see the larger arrows in (a)-(d) of *Fig 6*). These results indicate that the behavior in the plastic region, which would be affected by moisture in the CNF sheet, were different among bamboo- and wood-derived CNFs. There were some reports concerning the slippage among the CNFs that would occur in the plastic region (Eichhorn et al. 2001; Sehaqui et al. 2011). As reported by Henriksson et al. (2008), the slope *n* in the plastic region would depend on both the porosity of the CNF sheets and frictional resistance to slippage of individual CNFs. In this study, the slope *n* in the plastic region in any sheets at humidity-condition in *Fig 4C* was lower than those in the cases of *Fig 4A*. The frictional resistances to slippage of individual CNFs decreased in the drying process of the humidity-condition in *Fig 4B*. The difference in the slope of the humidity-condition in *Fig 4 A and 4C*, Δn, was expressed as follows:

$$\Delta n = n_C - n_A$$

where n_A is the slope in the humidity-condition in *Fig 4A*, and n_C is the slope in the humidity-condition in *Fig 4C*. The Δn of wood-derived CNFs were -0.29 at both room temperature and 130°C dried sheets. On the other hand, the bamboo-derived CNF sheets were -0.47 and -0.36, respectively (*Table 2*). As Δn corresponding to the frictional resistances decreased, bamboo-derived CNFs exhibited a larger loss of Δn than wood. The detailed mechanism is still unknown.

CNFs are a uniaxially oriented aggregate of amphiphilic cellulose molecular chains, but these generally exhibit a hydrophilic property by exposing the OH groups on the surfaces (Goussé et al. 2002; Khalil et al. 2012), although there are reports that CNF surface property depends on the media (Johansson et al. 2011). The ACC method reduces micro-sized pulps into CNFs by cleaving the interfacial interactions among cellulose molecules. Therefore, this method may expose not only hydrophilic but also hydrophobic surfaces due to the glucopyranose ring, when cleaving ways of pulp fibers are varied by the individual collision of dual water jets. It seems that the difference in the proportion of the exposed hydrophobic surface can affect the above measurements which are susceptible to water, such as sedimentation behavior, sheets densities and strain-to-failure in tensile tests. Namely, the results so far obtained indicate that the CNF network interactions may be dependent on how much hydrophobic sites were exposed on the CNF surfaces of either bamboo- or wood-derived CNFs.

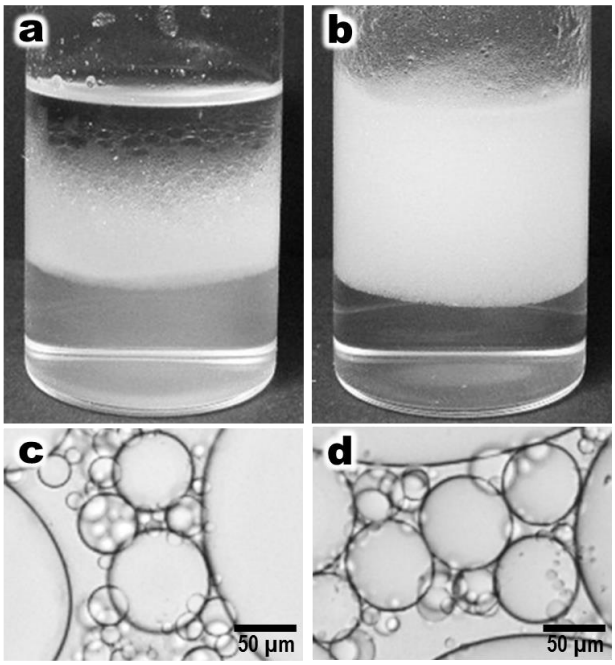

Fig 8 - Appearance of water / *n*-hexane emulsions containing (a) wood-derived and (b) bamboo-derived CNF observed five days after mixing. Optical microscopy images of cloudy phase for samples containing (c) wood-derived and (d) bamboo-derived CNF, respectively.

Comparison of emulsification with *n*-hexane

In order to more directly compare the surface properties of CNFs from bamboo and wood, the respective aqueous CNF dispersions were emulsified with *n*-hexane as a hydrophobic solvent. Mixture of water and *n*-hexane was phase-separated and soon it resulted in two layers without mixing. Emulsions were formed by ultrasonic treatment of the mixtures. These were separated into a clear and a cloudy layer on the next day, and kept stable state for more than 5 days. The emulsified states exhibited different manners among bamboo and wood CNFs, but the similar emulsion droplets were observed by optical microscopy in the cloudy layer after 5 days (*Fig 8*).

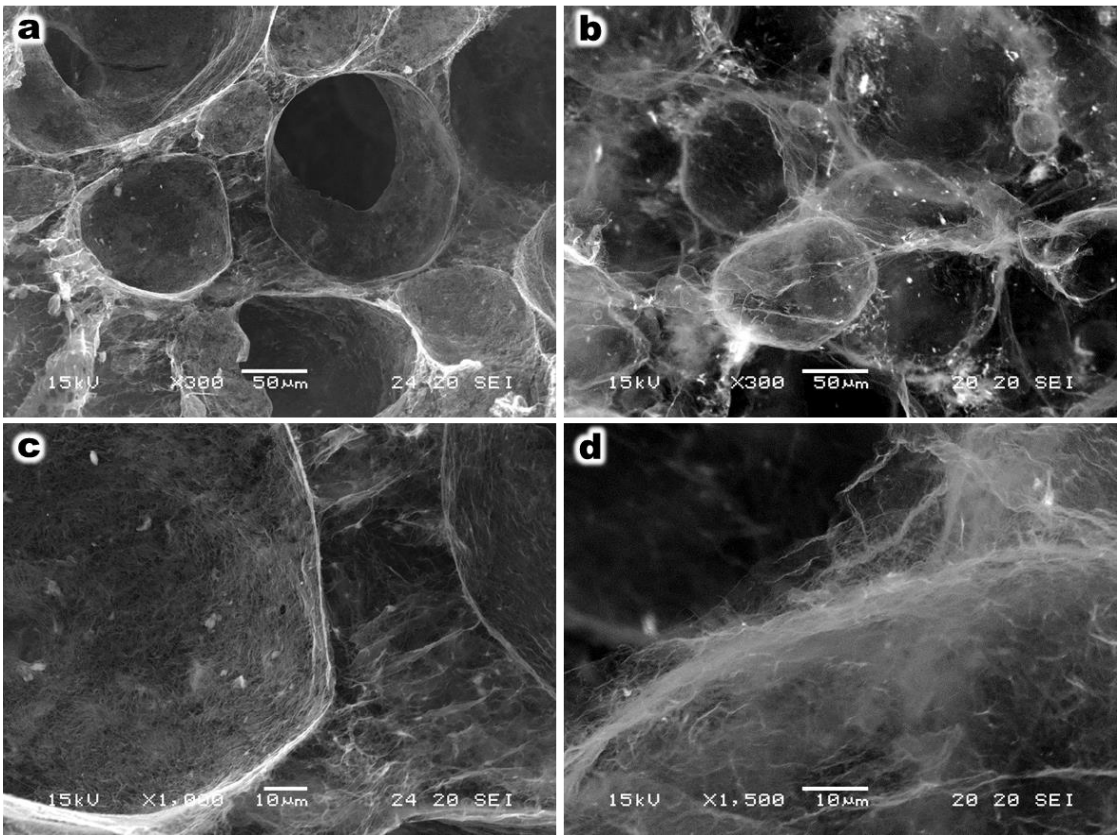

Fig 9 - SEM images of cloudy phases in emulsions between (a) wood-derived and (b) bamboo-derived aqueous CNF dispersions were emulsified with *n*-hexane. (b) is the magnified image of (a), (d) is the magnified image of (b).

In wood-derived aqueous CNF dispersion, cavities were observed inside the emulsion droplets by SEM observations, and there were CNFs outside the droplets (*Fig 9a* and *c*). In the bamboo-derived CNF dispersions, spherically-agglomerated CNFs were observed in the void spaces (*Fig 9b* and *d*). These results might be due to the difference of surface properties among bamboo- and wood-derived CNFs, although the details in the emulsion droplets formation are unknown. We need further detailed studies in the future to elucidate what type of emulsions and the details how they are formed.

Conclusions

This study attempted to clarify the difference between bamboo- and wood-derived cellulose nanofibers prepared by the aqueous counter collision method. The ACC method was capable of nano-pulverizing from the pulps to the CNFs by overcoming interfacial interaction among cellulose molecules. The two CNFs prepared by the ACC method exhibited the differences in sedimentation behavior of the aqueous CNF dispersions, as well as in the physical properties of formed sheets. Moreover, when the emulsion droplets were formed by mixing the aqueous CNF dispersions with *n*-hexane, bamboo-derived CNFs formed spherically-agglomerated CNFs, whereas wood-derived CNFs formed the emulsion having cavities like a sponge. The results suggested that the CNFs from bamboo and wood might have different surface properties on hydrophilic-hydrophobic relationship.

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Supporting Information

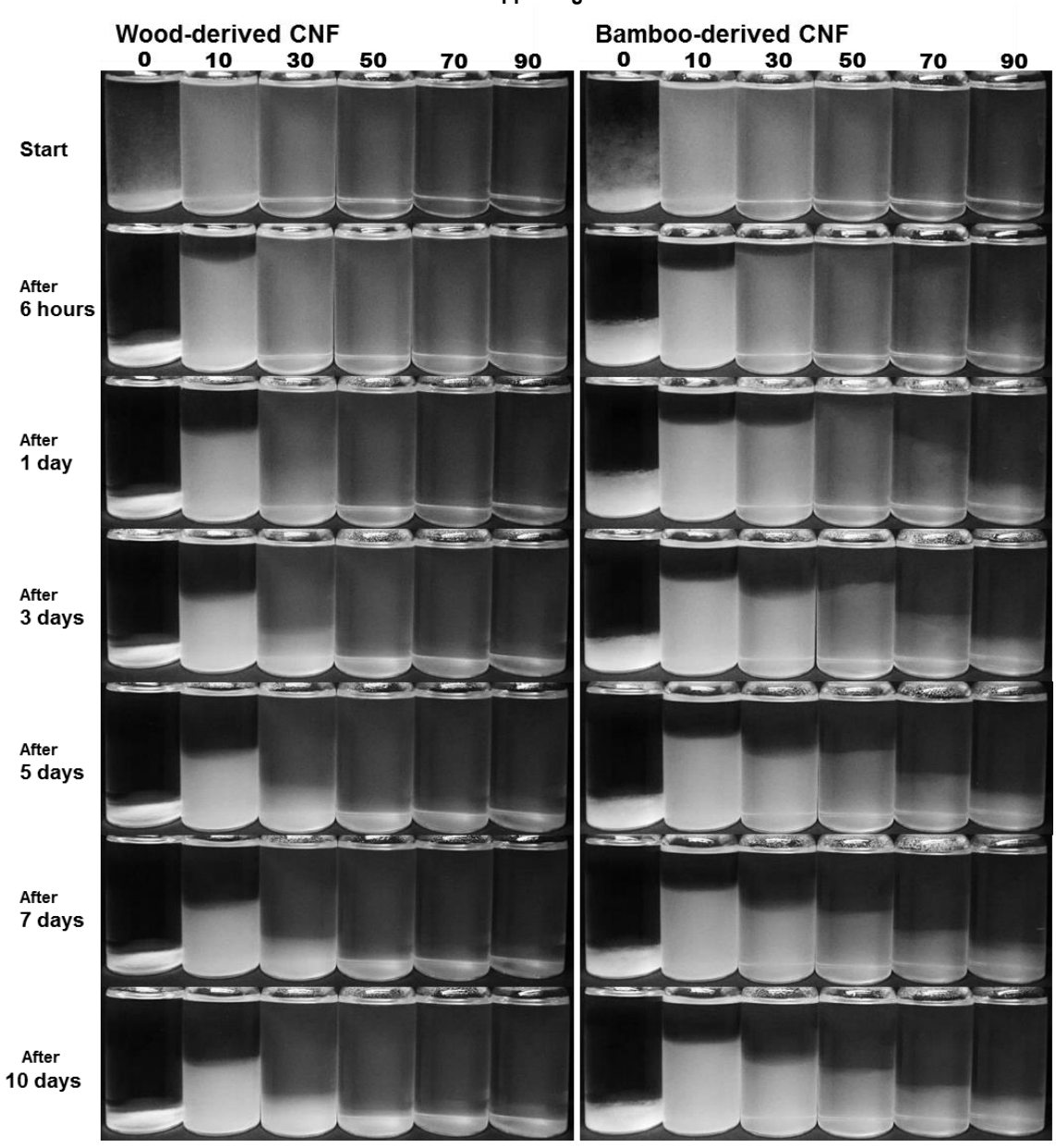

Fig S1 - Photographs of aqueous dispersions of wood-derived (left) and bamboo-derived (right) CNF. These images are the photographs observed the sample states changes with passage of time. The samples were ACC treated at 0.05% consistency for 0, 10, 30, 50, 70 and 90 passes, respectively.