# PROPERTIES OF NANOFIBRILLATED CELLULOSE PREPARED BY MECHANICAL MEANS

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Nanofibrillated celluloses (NFCs) were prepared from four different sources of cellulose, namely, hardwood, softwood, cotton linter and cattail, by using a Super Masscolloider mechanical fibrillation device. The NFCs had the average diameters in the range of 30 to 70 nm and the average lengths of several micrometers. Their aspect ratio was found to be of 70-150. Cattail fiber turned out to be a valuable NFC source due to the least energy needed for NFC preparation. Nevertheless, cattail NFC showed high tensile and excellent thermal properties, similarly to wood cellulose NFCs. It was also found that the α-cellulose contents, the degrees of polymerization and the crystallinity indices of the NFCs all decreased greatly because of the grinding treatment. The NFCs were used as reinforcing materials in preparing unrefined hardwood (Hw) handsheets (with various Hw:NFC ratios) and a great improvement in bonding properties was observed. The NFC films exhibited Young's moduli of 8-10 GPa, while cotton linter NFC presented the least film strength among them because of lack of hemicelluloses.

***Keywords***: nanofibrillated cellulose (NFC), α-cellulose, crystallinity, cupriethylenediamine (CED) viscosity, cotton linter and cattail fibers

## INTRODUCTION

Recently, nanocellulose materials have gained much attention and research interest due to its potential applications. There are three main types of nanocellulose materials: nanofibrillated cellulose (NFC), which is also sometimes called microfibrillated cellulose; cellulose nanocrystals (CNC), which are also sometimes called nanocellulose whiskers; and bacterial cellulose (BC).[1] The nanocellulose materials are biodegradable, renewable, recyclable, environmentally friendly and abundantly available nearly everywhere in the world. Many researchers have mentioned that nanocellulose materials could be used in medicines, biocomposites, pharmaceuticals, batteries, biosensors, aircraft, paper coatings, tissue engineering and many other applications. Researchers seem to be more interested and more focused on NFC than on CNC. According to Lavoine *et al*., more than 80% of the scientific research published on nanocellulose materials is conducted on NFC, and only approximately 20% is dedicated to CNC and BC.[1]

To define nanocellulose materials, many different methods have been used to determine the morphologies of the fibers. Researchers have used field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM) and other methods to determine the morphologies of nano-sized materials.[2-7] Cellulose from various sources has been used to produce nanofibrillated cellulose (NFC).[3] In the research performed by Abraham *et al*.,[3] raw cellulose materials underwent steam explosion accompanied by chemical treatment to produce NFC. They discussed the cellulose contents and the crystallinities of the raw materials for the steam exploded fibers and the bleached fibers, respectively.

The authors showed that the increase in the cellulose content and crystallinity is due to the removal of lignin, hemicelluloses and amorphous areas during the treatment.[3] In the study by Yousefi *et al*.,[8] the properties of micro-paper, nano-paper and bacterial nano-paper were compared. They reported that the crystallinity index of the NFC was 7 units lower, compared to that of the micro-paper (69%). The authors also mentioned that the high shearing and pressure forces created between the grinding disks led to the reduction of the crystallinity and crystal size of the NFC. Later, a decrease in the crystallinity index and CED viscosity was also confirmed by Winuprasith and Suphantharika.[9]

Different equipment can be used for creating NFC, such as a microfluidizer, a mechanical grinder and an ultrasonication device.[10,11] According to Chen *et al*.,[11] nanocellulose materials could open new ways for creating bio-nanocomposites, tissue engineering scaffolds, filtration media, packaging and other materials. NFC plays an important role in bonding and reinforcement for composites with better strength. The strength properties of nanocellulose reinforced materials with different types of polymers have been widely researched and published.[2,10,12-17] According to Al-Turaif,[14] an addition of 0.1% of NFC increased stress, strain, toughness and Young's modulus by 121%, 73%, 300% and 64%, respectively. NFC reinforcement led to high strength properties due to a high surface area, which is beneficial for achieving fiber contacts and for the reinforcement of the polymer composite.[15] A nano-composite made by blending 16.5% of NFC with polyurethane indicated that the strength was improved by 500% and the elastic modulus by 3000%, compared to pure polyurethane.[12] The mechanical grinding process decreased the CED viscosity and the degree of polymerization (DP). Lower DP indicates lower strength of the material.[1,13,18,19] Furthermore, the strength and stiffness of the composite were negatively affected by size non-homogeneity of NFC. Therefore, it is necessary to have even size distribution of the NFC for use in composite materials.[13]

There has been little research describing the use of cotton linter and cattail fibers for the production of NFCs, even though much research has been conducted on cotton linter nanocrystalline cellulose. This study aimed to compare the nano-fibrillation behaviors and the morphologies of celluloses from four different sources: hardwood, softwood, cotton linter and cattail fiber, when Super Masscolloider grinding was applied. In addition, this research made observations on the changes of α-cellulose contents, CED viscosities and the crystallinity indices of the NFCs. The reinforcing effects of the NFC from different sources were evaluated by adding NFC to the unrefined hardwood handsheets. Also, NFC films were made to evaluate their mechanical properties.

## EXPERIMENTAL

### Materials and methods

Four different types of raw materials were used, namely hardwood (Hw), softwood (Sw), cattail fibers and cotton linter (Table 1). The materials were soaked in water for at least four hours before being disintegrated. All the fibers were diluted to the consistency of around 1.3% before being ground by the Super Masscolloider (Masuko Sangyo Co. Ltd., Japan), which is an ultra-fine grinding machine for the nanofibrillation process. It consists of two grinding stones; the stone at the top is fixed and the stone at the bottom is rotated at a high speed. Cellulose materials fed into the hopper are ground between these two grinding stones. In this research, the cellulose materials were ground at 2,000 rpm and at an input current of 2.0 A. There should be a criterion to finish the grinding. Each batch of grinding was counted as one pass, and the materials passed the grinder repetitively until all the ground materials passed a 200 mesh screen. From our experience, most of the materials become NFC at that time, and the number of passes was counted as a measure of easiness for making NFC.

To evaluate the NFC morphologies, three different types of equipment were used: an Itplus optical microscope, AFM and FE-SEM. For the AFM and FE-SEM tests, one drop of 0.05% NFC solution was deposited and air-dried on the circle of mica glass with a 10 mm diameter, and each sample was scanned at least at four different positions. The samples for the FE-SEM were coated with platinum for 45 seconds before measurement. The morphology of individual NFC was measured by digitizing the magnified FE-SEM micrograph, where individually separated NFCs were shown. Fifty length and width measurements were made for each NFC source. An X-ray diffractometer (XPERT-PRO) was used to measure the crystallinity of the raw materials and NFC samples.[21] The raw materials and NFCs for the crystallinity evaluations were air dried. The measurements were carried out over a range from 3° to 40° with a step size of 0.1050422°. The XRD was operated at 40 kV and 30 mA. The testing methods and the equipment for handling fibers were listed in Table 2.

### Thermogravimetry analysis (TGA)

The thermal degradation of the four different celluloses and NFC samples was studied using thermogravimetry analysis instruments (TGA, Mettler

Toledo). The samples were heated at a heating rate of 10 °C/minute in the range of 25 °C to 500 °C, under nitrogen atmosphere.

**Reinforced hardwood handsheets and NFC films**

Four different types of NFCs were used as reinforcing materials for hardwood handsheets to determine their reinforcing capability with the ratios of 10:0, 9:1 and 8:2 (Hw:NFC). Tensile strengths and densities were measured according to the methods described in Table 2.

NFC films were made in the following way. Initially, the aqueous solution of NFC was vacuumed for at least 30 minutes, while stirring, to release the air. Then, a fixed amount of it was spread on a flat glass in a predetermined area and dried in an oven drier at 95 °C for around 2-3 hours. The wet NFC film, which became a half-dried wet sheet, was detached from the glass and pressed between blotting papers in a wet press to remove water further. Finally, the wet NFC films were dried in a drum drier at 130 °C. The dried NFC films were stored in a conditioned room for two days before the analysis of mechanical properties.

Table 1
Fiber information

| Fibers | Viscosity as received (cP) | Origin |
|---|---|---|
| Hardwood | 14.6 | Mixture of aspen and poplar bleached kraft pulp from Canada |
| Softwood | 15.6 | Mixture of hemlock, Douglas fir and cedar bleached kraft pulp from Canada |
| Cattail (*Typha latifolia*) | 8.9 | Cattail fiber, soda and anthraquinone pulping, from Chungnam National University, South Korea (Kim *et al.*)[20] |
| Cotton linter | 50.1 | Cotton linter from KOMSCO (Korea Minting & Security Printing Corporation) |

Table 2
Testing methods

| Test name/equipment | Used method/standard |
|---|---|
| Alpha cellulose content (α) | Tappi T203 cm-99 (Korea Standard M 7044) |
| CED viscosity | Tappi T230 om-89 |
| Crystallinity | X-ray diffraction/Segal's method[21] |
| Valley beater | Tappi T 200 sp-96 |
| Tensile strength | Tappi T 404/T 494 |
| Thickness | Tappi T 411 om-97 |
| Handsheet formation | Tappi T 205 om-88 |
| PFI mill | Tappi T 248 cm-85 |

**Tensile strength of NFC films**

NFCs films were kept in a conditioned room (23 °C, 50% RH) for two days before mechanical testing. The size of the NFC film specimens was 15 x 120 mm and at least 5 replication tests were performed using a Micro 350 tensile tester (Testometric Co. Ltd., England).

## RESULTS AND DISCUSSION

### Morphology of NFCs

The NFCs were observed using AFM and FE-SEM to determine their morphologies. The widths of the fibers before grinding were observed using an optical microscope and the average fiber widths were of 16, 25, 10 and 14 μm for hardwood, softwood, cattail and cotton linter, respectively. Figure 1 reveals that the widths of the fibers were changed from the micro level (ITplus microscope) to nanosize (FE-SEM and AFM) due to the grinding process. On average, the NFC widths of hardwood, softwood, cattail and cotton were of 30, 40, 46 and 70 nm, respectively, as shown in Table 3. The width and length of nanofibrillated cellulose was determined by FE-SEM.[22]

**Alpha cellulose contents, CED viscosities and crystallinity indices of the samples**

Table 4 shows the number of passes needed to prepare NFCs, and the alpha cellulose contents, CED viscosities and crystallinity indices of the

NFC samples. For cotton linter, a refining pretreatment was needed before using the Super Masscolloider because of its long length. Cotton linter was refined by the Valley beater to 100 CSF before grinding. It was observed that all the fibrillated materials from Sw, Hw, cattail and cotton linter passed through a 200 mesh screen after 18, 14, 11 and 21 replicated passes in the Super Masscolloider, respectively. The different number of passes may be due to several factors, such as the degree of polymerization (DP), the crystallinity index, the cellulose source and the structure of the fibers. The results indicated that cattail fiber was the easiest one to produce NFC, among the others. In contrast, the cotton linter sample was the most difficult sample to convert to NFC: it needed 21 passes in the Super Masscolloider, plus the Valley beater refining before grinding.

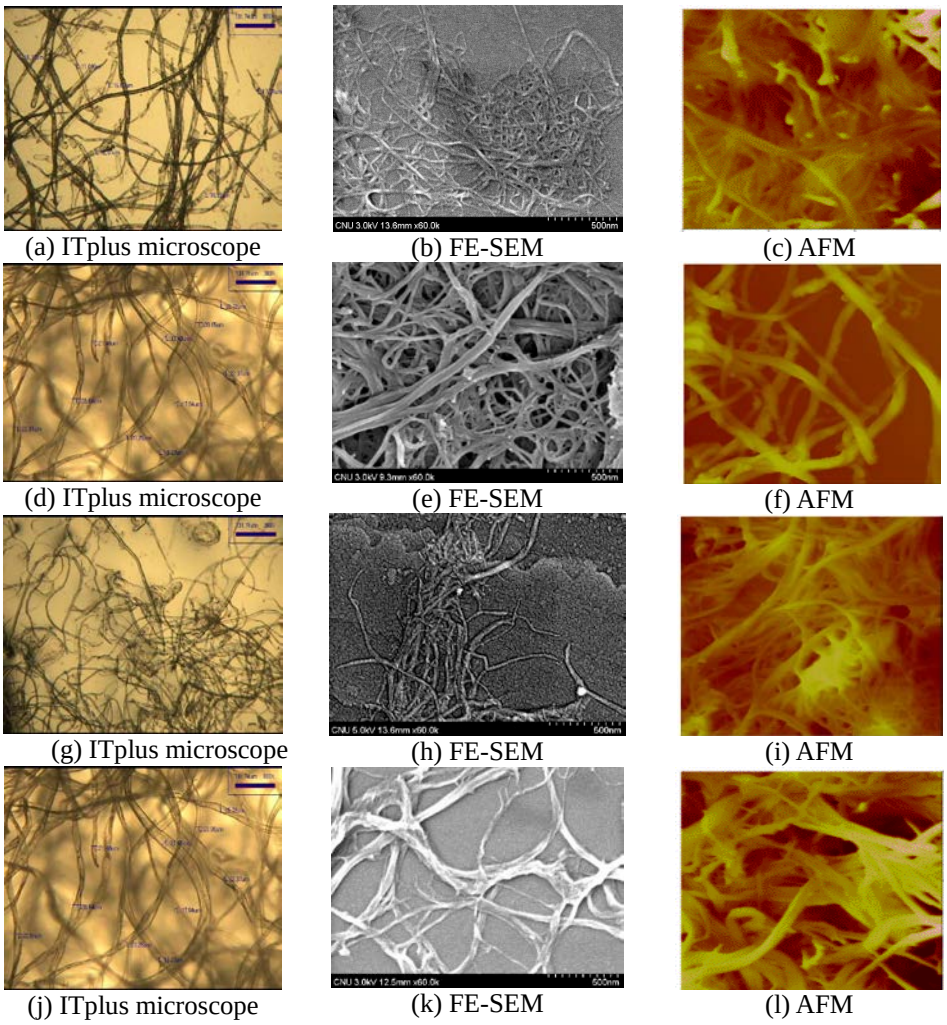



Figure 1: Fiber morphology observed by an ITplus optical microscope (fiber morphology before grinding) – scale bar 131 µ x 300; and NFC morphologies by FE-SEM and AFM (hardwood (Hw) and Hw-NFC (a to c); softwood (Sw) and Sw-NFC (d to f); cattail and cattail-NFC (g to i); and cotton linter and cotton linter-NFC (j to l))

Table 3
Lengths, widths, and aspect ratios of NFCs of four cellulose sources (average of 50 measurements)

| Parameters | Sw-NFC | Hw-NFC | Cattail-NFC | Cotton-NFC |
|---|---|---|---|---|
| Length (nm) | 6,740 | 6,458 | 3,185 | 5,454 |
| Width (nm) | 46 | 40 | 30 | 70 |
| L:W ratio | 147 | 161 | 106 | 78 |

*Hw: hardwood; Sw: softwood; NFC: nanofibrillated cellulose; L:W: length:width

The results in Table 4 indicate that the alpha cellulose contents of all of the samples decreased because of the grinding process. These decreases in alpha cellulose contents can be explained by the reduction in the degree of polymerization (DP) of the cellulose. It was shown that the cotton linter had the smallest drop in its alpha cellulose content. We believe that is because the DP of cotton linter before grinding was relatively too high to go down to the molecular weight level of beta cellulose.

The CED viscosities of all of the samples were decreased after being ground in the Super Masscolloider. The highest change of viscosity was for cotton linter, which had a viscosity of 50.1 cP before grinding that dropped to 20.1 cP for the cotton linter-NFC. The next largest viscosity drop was for the softwood fiber, which exhibited a viscosity drop from 15.6 to 8.4 cP. The CED viscosity losses could lead to lower strength properties.[1,12,17,19,24] Figure 2 indicates that a higher number of passes in the Super Masscolloider causes larger drops in CED viscosity.

As Table 4 indicates, the crystallinity indices of the NFCs decreased because of the grinding process. One more observation was that the number of passes in the Super Masscolloider increased proportionally to the initial crystallinity indices of the celluloses (regression coefficient $R^2$ = 0.986). The cattail fiber had the lowest initial CrI; hence, it had the lowest number of passes through the grinder to produce the NFC.

**Strength properties of reinforced HW-NFC**

Unrefined hardwood fibers were used to prepare handsheets, including NFCs as reinforcing materials. The handsheet made only of the unrefined hardwood fibers had a density of only 470 kg/m$^3$ and a tensile index of 17.6 Nm/g. By the addition of 10% and 20% of NFCs, the tensile strengths and the densities of the unrefined hardwood handsheets all increased proportionally to their addition levels (Fig. 3). For comparison, a hardwood PFI refining curve was also included. It turned out that the addition of NFC to unrefined hardwood caused the tensile strength to increase more than PFI refining did at the same density. The Sw-NFC reinforced handsheet had the highest tensile strength increase and the cotton linter-NFC – the lowest. It was believed that the cotton linter-NFC had the lowest hemicellulose content (mostly α-cellulose in Table 4), and thereby caused the least inter-fiber bonding.

Table 4
Alpha cellulose contents, CED viscosities and crystallinity indices (CrI%) of the samples

| Name | α-Cellulose content (%) | CED viscosity (cP) | Crystallinity index (%) | Number of passes in Super Masscolloider |
|---|---|---|---|---|
| Hardwood | 85.8 ± 0.3 | 14.6 ± 0.1 | 77.7 | - |
| Softwood | 89.7 ± 0.2 | 15.6 ± 0.1 | 79.9 | - |
| Cotton linter | 99.1 ± 0.4 | 50.1 ± 0.4 | 82.5 | - |
| Cattail | 85.6 ± 0.4 | 8.9 ± 0.1 | 74.6 | - |
| Hw-NFC | 64.7 ± 1.1 | 10.3 ± 0.3 | 69.2 | 14 passes |
| Sw-NFC | 76.1 ± 1.0 | 8.4 ± 0.4 | 63.0 | 18 passes |
| Cotton linter-NFC | 97.2 ± 1.3 | 20.1 ± 0.6 | 79.4 | 21 passes |
| Cattail-NFC | 71.2 ± 0.5 | 6.9 ± 0.1 | 69.2 | 11 passes |

*Hw: hardwood, Sw: softwood, NFC: nanofibrillated cellulose

**NFC films mechanical properties**

The mechanical properties of the NFC films from four different cellulose sources are shown in Table 5. The NFC films in the table had Young's moduli of 8-10 GPa, which is consistent with the results (6-15 GPa) reported by Moon *et al.*[8,14,23] The Sw-NFC film had the highest tensile index in comparison with the others, but its CED viscosity, NFC length, aspect ratio, α-cellulose content and crystalline index could not explain clearly which factor contributed most to its high strength. Cattail-NFC and HW-NFC showed similar values in Young's moduli and tensile indices, even though the NFC length (Table 4) and CED viscosity (Table 5) were very different.

So, the NFC length and CED viscosity might not be the major factors to decide the tensile strength of NFC films. Cotton-NFC showed low tensile index because of lack of hemicellulose content, as expected.

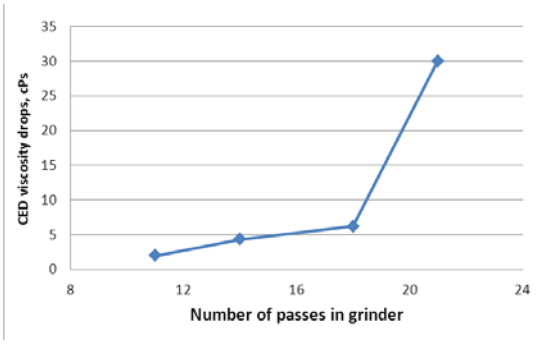



Figure 2: CED viscosity as a function of the number of passes in the grinder for cotton linter

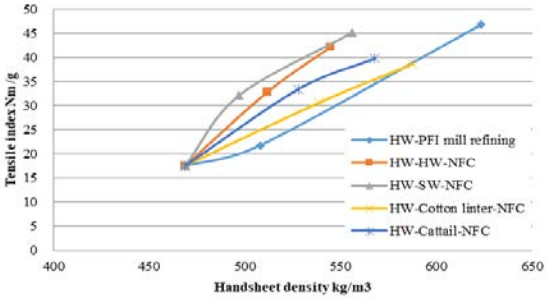
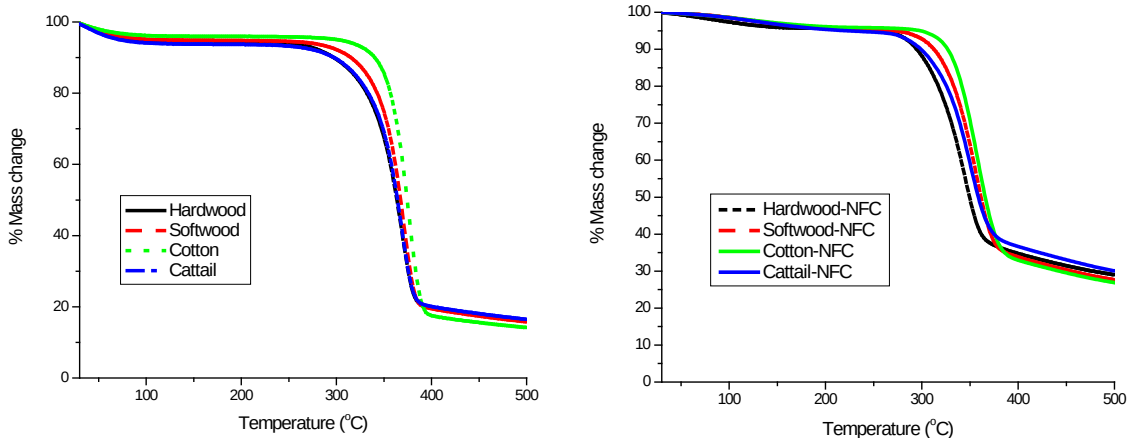



Figure 3: Tensile index of unrefined hardwood fibers reinforced with different NFCs and that of Hw-PFI mill refining (amount of NFC increased from the leftmost point to the right by 0, 10 and 20%)

Table 5
Mechanical properties of NFC films

| Samples | Peak stress (MPa) | Strain at break (%) | Young's modulus (GPa) | Tensile index (Nm/g) |
|---|---|---|---|---|
| Hw-NFC | 111.2 ± 16.9 | 3.68 | 10.4 ± 0.8 | 82.0 |
| Sw-NFC | 107.4 ± 11.9 | 3.50 | 9.3 ± 0.3 | 109.3 |
| Cotton linters-NFC | 56.7 ± 9.7 | 1.25 | 8.7 ± 0.7 | 55.0 |
| Cattail-NFC | 104.9 ± 6.7 | 4.21 | 10.3 ± 0.7 | 90.3 |




a) b)

Figure 4: Thermal stability of raw cellulose materials (a) and NFCs (b)

Table 6
Thermal decomposition temperature of cellulose raw materials and their NFCs

| Samples | Thermal decomposition temperature, °C | |
|---|---|---|
| | Raw cellulose | NFC |
| Hardwood | 361 | 337 |
| Softwood | 363 | 349 |
| Cotton linters | 369 | 350 |
| Cattail | 361 | 342 |

**Thermogravimetry analysis (TGA)**

The thermal decomposition temperature of raw cellulose materials was around 360-370 °C, and the cotton linter showed the highest temperature, in comparison with the others (Fig. 4 and Table 6). Cattail and hardwood were very close, with a similar thermal decomposition temperature at 361 °C. Due to the grinding treatment, the NFC

thermal decomposition temperature was decreased greatly (19-24 °C differences in Table 6). Still, Cotton-NFC had the highest thermal decomposition resistance.

## CONCLUSION

Cellulosic fibers from four different sources, including hardwood, softwood, cattail and cotton linter, were ground by mechanical means to be turned into nano-fibrillated celluloses (NFCs), and their morphologies were examined by means of an IT-plus microscope and by FE-SEM observation (width: 30-70 nm, length: 3-7 μm, aspect ratio: 70-150). Cattail fibers could be a new potential cellulose source for NFC due to the fact that it required the least energy for NFC preparation, as well as due to its high mechanical properties and high thermal stability, in comparison with wood celluloses. The CED viscosities, alpha cellulose contents and crystallinity indices all decreased because of the grinding treatment. The tensile indices of the unrefined hardwood handsheets reinforced by NFCs increased more significantly than those from the hardwood refined in the PFI mill at the same density. So, it meant that bulkier and stronger sheet could be made from the NFC reinforced fiber furnish. The tensile strengths of NFC films were dependent upon their hemicellulose content, but not strongly dependent upon the molecular weight or the morphologies of their NFCs. Cotton linter needed the highest energy to make NFC, but showed low bonding properties.

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