

Optically Transparent Nanofiber Paper

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Glass has well-suited low thermal expansion for use in electronic devices, but it is fragile, and the search for a stronger, more flexible optically clear medium has gone on for many years. Plastics have been widely studied; however, most of them have large coefficients of thermal expansion (CTE, approx. 50 ppm K⁻¹), and foldable plastics in particular exhibit extremely large CTEs, in excess of 200 ppm K⁻¹. Further, the functional materials deposited on plastic substrates are prone to be damaged by the temperatures involved in the assembly and mounting processes due to the mismatch between CTEs from different materials. This article reports on what might be best described as optically transparent paper. It is a foldable nanofiber material with low thermal expansion (CTE <8.5 ppm K⁻¹) prepared using 15 nm cellulose nanofibers with the same chemical constituents as conventional paper and a production process also similar to that of conventional paper. The only difference is in the fiber width and the size of the interstitial cavities (Fig. 1). The foldable, low-CTE, and optically transparent nanofiber paper is the perfect candidate for substrates for continuous roll-to-roll processing in the future production of electronic devices, such as flexible displays, solar cells, e-papers, and a myriad of new flexible circuit technologies, and could replace the costly conventional batch processes based on glass substrates currently used.^[1–5] We project that it will also replace conventional paper as an advanced information medium, which can still be produced using traditional paper-making equipment that is used in production today.

Cellulose nanofibers are the main component of plant and wood pulp fibers. These tiny elements with diameters of 15–20 nm are composed of bundles of cellulose microfibrils smaller than 4 nm in width, which, in turn, are composed of long cellulose molecules laterally stabilized by hydrogen bonds forming highly crystalline domains. As such, cellulose nanofibers have a CTE of 0.1 ppm K⁻¹,^[6] which is as low as that of quartz glass, and an estimated strength of 2–3 GPa,^[7] rendering it five times stronger than mild steel. The nanofibers also exhibit good heat-transfer properties comparable to glass.^[8] Another significant property of the nanofibers is that light scattering can be suppressed.^[9,10] If the cellulose nanofibers are densely packed, and the interstices between the fibers are small enough to avoid

light scattering, the cellulosic material becomes transparent while maintaining the high performance of the material described before.

To obtain the nanofibers from plants and wood fibers, it is necessary to disassemble the fibers' original structure. The cell walls of the fibers are composed of several thin layers, in which the cellulose nanofibers are oriented in various directions and embedded in matrix substances. In order to extract uniform nanofibers from this complex structure, wood flour was used as a starting material. The wood flour was ground in a water-swollen condition after lignin and hemicelluloses were removed.^[11] Figure 2a shows the scanning electron microscopy (SEM) image of the resulting fiber that was recovered by freeze-drying a 0.1 wt.% water suspension. The sheet of nanofiber paper was obtained first by freeze-drying followed by mechanically compressing the sheet at 160 MPa under a vacuum to eliminate air and voids. This, however, did not result in transparency (Fig. 3a). The nanofibers were deformed under load but recovered after unloading, and the spaces created resulted in light scattering.

The thin cellulose nanofibers tend to collapse by capillary action during the evaporation of water, and the deformed condition is fixed by hydrogen bonds that form between hydroxyl groups of the cellulose, thus producing a high-strength material without the use of binders.^[12] Because of this, a 0.1 wt.% water suspension of well-dispersed cellulose nanofibers was slowly filtered so that nanofibers were piled uniformly in a wet sheet with a moisture content of 560 wt.%. The wet sheet was sandwiched between a combination of wire-mesh (#300 inner layer) and filter papers (outer layers), and dried at 55 °C for 72 h, while a pressure of approximately 15 kPa was applied. The SEM image of the resulting sheet is shown in Figure 2b. The

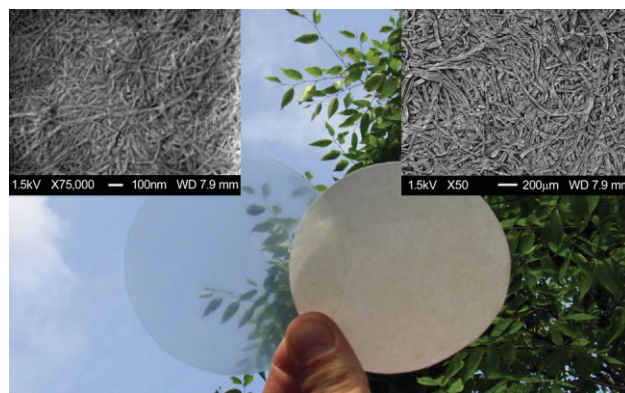


Figure 1. Optically transparent nanofiber paper (left) composed of 15 nm cellulose nanofibers (upper left, scale bar in inset: 100 nm) and conventional cellulose paper (right) composed of 30 μm pulp fibers (upper right, scale bar in inset: 200 μm).

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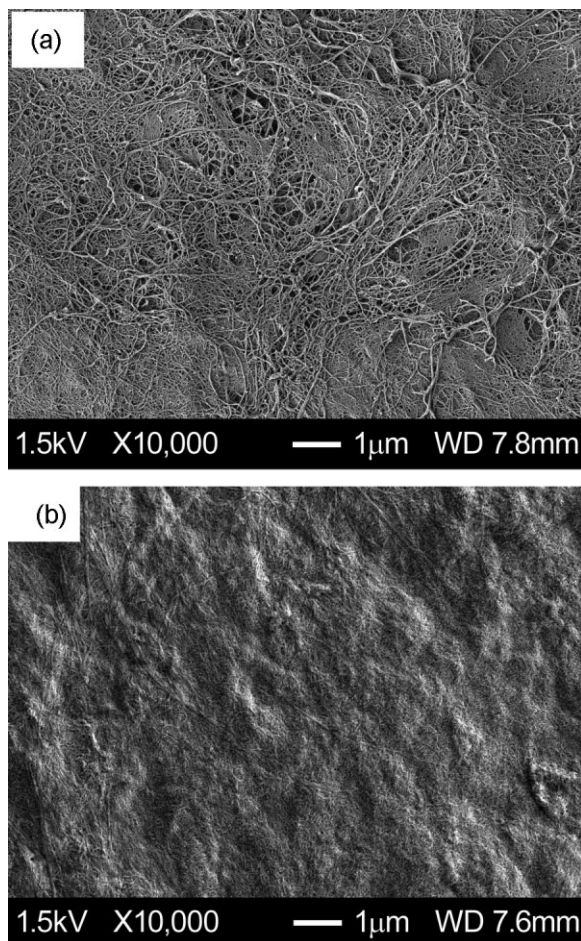


Figure 2. SEM images of a) freeze-dried and b) oven-dried nanofiber sheets.

nanofibers were so densely packed that individual fibers could not be observed. The density measured using a gas pycnometer (“Accupyc 1330”, Micromeritics Inc.) was 1.53 g cm^{-3} . Since the density of the cellulose crystallite is 1.59 g cm^{-3} ,^[13] this result implies that the cavities in the sheet were almost completely removed.

The dried sheet thus obtained was not optically transparent but translucent (Fig. 3a), and had a plastic film-like appearance indicating that light scattering in the bulk sheet was significantly suppressed. In other words, the lack of transparency seemed to be caused by surface light scattering. When the sheet was polished using emery paper (4000 grit followed by 15000 grit), it became transparent, as shown in Figure 3a. The regular light-transmittance levels of the sheet before and after polishing are compared in Figure 3a (sheet thicknesses were $60 \mu\text{m}$ before and $55 \mu\text{m}$ after polishing). The light transmittance of the cellulose nanofiber sheet upon polishing reached 71.6%, including surface reflection (Fresnel’s reflection) at a wavelength of 600 nm. Despite the plastic-like transparency, the sheet is as foldable as conventional paper (Fig. 3b). Therefore, we have designated this new material “cellulose nanofiber paper”. Since the optically transparent sheet consists of high-strength and low-thermal-expansion nanofibers, its Young’s modulus and tensile strength

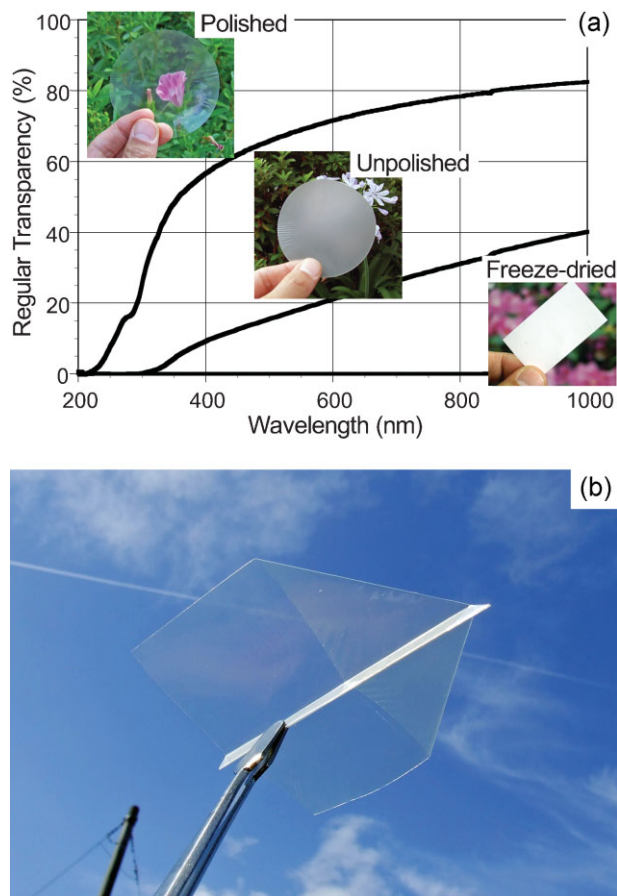


Figure 3. a) Light transmittance of the cellulose nanofiber sheets. The thicknesses of the oven-dried nanofiber sheet were $60 \mu\text{m}$ before and $55 \mu\text{m}$ after polishing. b) The sheet is as foldable as conventional paper.

are 13 GPa and 223 MPa, respectively. Its CTE is 8.5 ppm K^{-1} , which is comparable to that of glass. This is the first time a foldable, high-strength, low-CTE, and optically transparent cellulose nanofiber paper has been described.

The achievement of optical transparency in the nanofiber paper by smoothing the surface suggests various approaches for making functional transparent cellulose sheets. Smooth surfaces can be obtained by the lamination of optically transparent plastics, such as polycarbonate films, on the nanofiber paper by exploiting the thermal softening temperature of thermoplastics while avoiding thermal deterioration of cellulose (Fig. 4a). This would greatly contribute to the simplification of the roll-to-roll process as well. Another approach would be to deposit transparent resins on the surface (Fig. 4b), or even transparent conductive inorganic materials, like indium tin oxide (ITO), using a spin-coater. Ink-jet printers may allow the drawing of precise transparent and functional patterns on the sheet via the addition of functional nanoelements to the ink (Fig. 4c). As cellulose is highly hygroscopic, transparent-cellulose nanofiber sheets without chemical modification are liable to dimensional instability.^[14,15] These surface-smoothing approaches would impart not only high optical transparency but also act as moisture barriers to the cellulose nanofiber sheets.

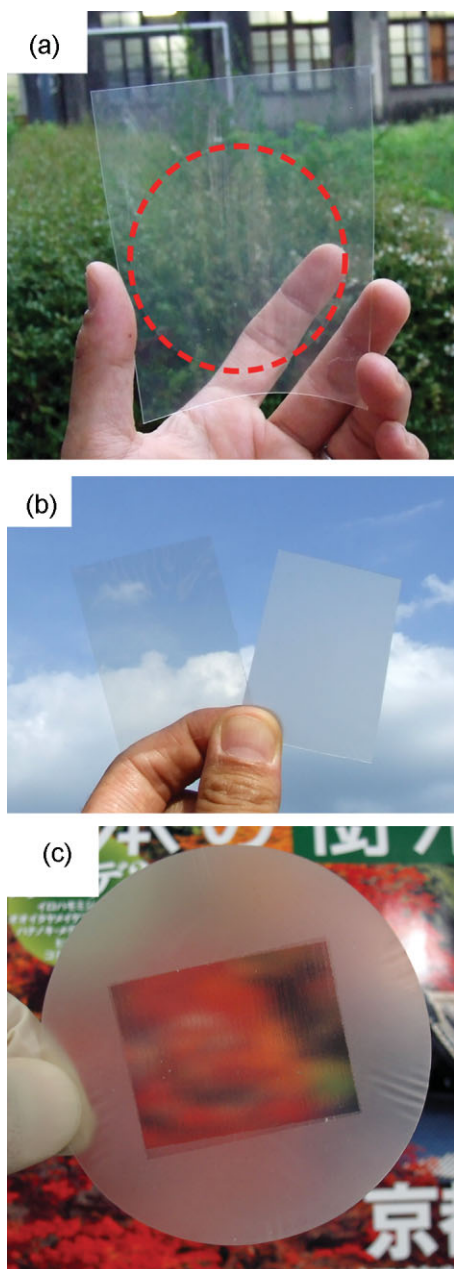


Figure 4. Various approaches to preparing functional transparent cellulose sheets. a) Lamination of optically transparent plastics (inside the red circle). b) Deposition of transparent resins on the surface of cellulose sheets (left: surface-coated sheet, right: uncoated sheet). c) Drawing of transparent patterns on the sheet using a domestic ink-jet printer.

In summary, this Communication reports the inception of a new kind of paper made of cellulose nanofibers, as opposed to micrometer-sized cellulose pulp fibers of ordinary paper. The raw material consists of the same cellulose obtained from trees and plants, but the down-sizing to the 15 nm nanofibers enables paper to have some fascinating properties, such as transparency (71.6% at a wavelength of 600 nm), high modulus (13 GPa), high strength (223 MPa), and minimal thermal expansion (8.5 ppm K⁻¹). Since paper was invented, it has played an important role as an information-transfer medium. This study shows the next

evolutionary step of paper in the form of cellulose nanofiber paper, with the potential to become an extremely important material supporting future generations of electronic devices. The nanofiber paper could play the same role as or an even greater role than conventional paper in information storage and transfer for perhaps another millennium to come.

Experimental

Cellulose Nanofibers: Wood flour from Douglas fir (*Pseudotsuga menziesii*) sieved under 60 mesh was used. It was first dewaxed in a Soxhlet apparatus with a 2:1 mixture of toluene/ethanol for 6 h. Afterwards, a sodium chlorite (NaClO₂) treatment, following the method of Wise et al. [16], removed mainly lignin, and an alkaline treatment with 5 wt% potassium hydroxide (KOH) at 20 °C for 24 h removed hemicelluloses. After the series of chemical treatments, the samples were filtered and rinsed with distilled water until the residues were neutralized. The α -cellulose content of the purified samples was 80–85%, as determined by extraction with 17.5 wt.% NaOH. The water slurry with 1 wt% undried purified sample was passed once through a grinder (MKCA6-3; Masuko Sangyo Co., Ltd.) at 1500 rpm.

Translucent cellulose nanofiber sheets: Fibrillated cellulose fibers were dispersed in water at a fiber content of 0.1 wt%, and the suspension was stirred overnight. 240 g of suspension was vacuum filtered for 3–4 h with a glass filter (KG-90, Toyo Roshi Kaisha, Ltd.) using a hydrophilic polytetrafluoroethylene membrane filter (H010A090C, Toyo Roshi Kaisha, Ltd.; pore size: 0.1 μ m).

Lamination of optically transparent plastics (Fig. 4a): Unpolished translucent-cellulose nanofiber sheets were put between polycarbonate films (50 μ m thick, MitsubishiPlastics, Inc.). They were hot-pressed at 160 °C for 3 min under 1 MPa and cooled down to 120 °C within 2–3 min keeping the pressure.

Deposition of transparent resins (Fig. 4b): Neat acrylic resin (tricyclodecane dimethanol dimethacrylate (TCDDMA), Mitsubishi Chemical Corp.) was dropped on the microscope slides. An unpolished translucent-cellulose nanofiber sheet was sandwiched between the slides and the resins were spread on the sheets by hand pressing. The resin was immediately cured using an UV curing equipment (20 J cm⁻², a F300S UV lamp system and a LC6 benchtop conveyor, Fusion UV Systems Japan).

Ink jet printing (Fig. 4c): Unpolished translucent-cellulose nanofiber sheets were printed on the both sides with transparent phenol-formaldehyde resin (RESITOP PL4414, Gun Ei Chemical Industry Co., Ltd.) diluted in methanol by a domestic ink-jet printer (PX-V630, SEIKO EPSON Corp.).

Light Transmittance: Regular light transmittances were measured using an UV spectrometer (U-4100, Hitachi High-Tech. Corp.) by placing the specimens 25 cm from the entrance port of the integrating sphere.

Tensile Tests: Tensile tests were performed using a universal materials testing machine (type 3365; Instron) for samples 20 mm long and 3 mm wide at a crosshead speed of 1 mm min⁻¹ and with a specimen gauge length of 10 mm.

Coefficient of Thermal Expansions: The CTEs were measured using a thermomechanical analyzer (TMA/SS6100, SII Nanotechnology Inc.). Specimens were 25 mm long and 3 mm wide with a 20 mm span. The measurements were carried out three times with a heating rate of 5 °C min⁻¹ in a nitrogen atmosphere in tensile mode under a load of 3 g. The CTE values were determined as the mean values at 20–150 °C in the second run.

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