Chemical Modification of Cellulose Nanofibers for the Production of Highly Thermal Resistant and Optically Transparent Nanopaper for Paper Devices

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ABSTRACT: Optically transparent cellulose nanopaper is one of the best candidate substrates for flexible electronics. Some types of cellulose nanopaper are made of mechanically or chemically modified cellulose nanofibers. Among these, nanopapers produced from chemically modified cellulose nanofibers are the most promising substrate because of their lower power consumption during fabrication and higher optical transparency (lower haze). However, because their thermal durability is as low as plastics, paper devices using chemically modified nanopaper often do not have sufficiently high performance. In this study, by decreasing the carboxylate content in the cellulose nanofibers, the thermal durability of chemically modified nanopaper was drastically improved while maintaining high optical transparency, low coefficient of thermal expansion, and low power consumption during fabrication. As a result, light-emitting diode lights illuminated on the chemically modified nanopaper via highly conductive lines, which were obtained by printing silver nanoparticle inks and high-temperature heating.

KEYWORDS: cellulose nanofiber, TEMPO oxidation, yellow index, transparency, printed electronics
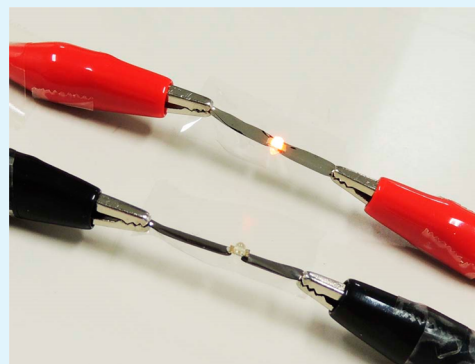
1. INTRODUCTION

In electronic devices, a continuous roll-to-roll process using flexible substrates has attracted much attention to realize flexible electronics with low cost. The processing temperatures for device processing have decreased from 300−500 °C to 150−200 °C by the development of device-processing technology. The decrease of the processing temperature has enabled the use of plastics substrates in electronic devices instead of rigid inorganic substrates. However, the temperature is not sufficiently low for the use of common plastics such as polyethylene terephthalate and polyethylene naphthalate. Therefore, developments in roll-to-roll processing have taken considerably longer than expected. Recently, paper substrates have also attracted attention because of their high flexibility and light weight.[1−5] Papers consisting of cellulose fibers have inherently high thermal resistance, but their rough surfaces make it difficult for them to accept device processes such as mounting or printing of device components.[6] Some papers have smooth surfaces, such as coated or photo paper, but they readily become yellow or brown under low-temperature heating because their surfaces are smoothed by coating with thermal sensitive polymers.[6] Therefore, the lack of flexible substrates with high thermal resistance is one of the barriers to develop the continuous roll-to-roll process.

In 2009, paper was produced with 3−15 nm wide cellulose nanofibers obtained by mechanical or chemical-assisted nanofibrillation, and it was called "nanopaper".[7,8] The nanopaper exhibited both high transparency and highly smooth surfaces, while retaining the light weight and high foldability of conventional paper. Moreover, nanopaper has a much higher thermal stability than traditional coated and photo paper because it consists of only cellulose without any polymers.[6,9] Therefore, nanopaper combined with heating processes resulted in various paper devices, such as conductive circuits,[6,10] flexible antennas,[11−13] transparent conductive electrodes,[14,15] transistors,[16−18] memory,[19] and solar cells.[20−22]

It is noteworthy that there were two temperature ranges in the device processes: >150 °C and <150 °C. In general, the higher process temperature increases the device performance, such as conductivity or mobility. Because nanopaper containing mechanically nanofibrillated nanofibers (hereafter referred to as mechanically modified nanopaper) has high thermal durability above 140 °C, it is annealed at 150, 180, or 200 °C after mounting of the device components.[6,10,16] As a result, the obtained paper devices show performance as high as electronic devices based on thermal resistant inorganic substrates. In contrast, when nanopaper composed of chemically modified nanofibrillated nanofibers (hereafter referred to as chemically modified nanopaper) is used, the process temperature is <140 °C and the obtained devices often show lower performance than electronic devices based on inorganic or plastic substrates.[13,15,17,18,21−24]

In chemically modified nanopaper, the starting cellulose pulp fibers are chemically modified by 2,2,6,6-tetramethylpyperidine-1-oxyl (TEMPO)-mediated oxidation[25,26] or carboxymethylation (CM)[27] as pretreatments for mechanical nanofibrillation (Figure 1). In these chemical modifications, carboxyl groups are
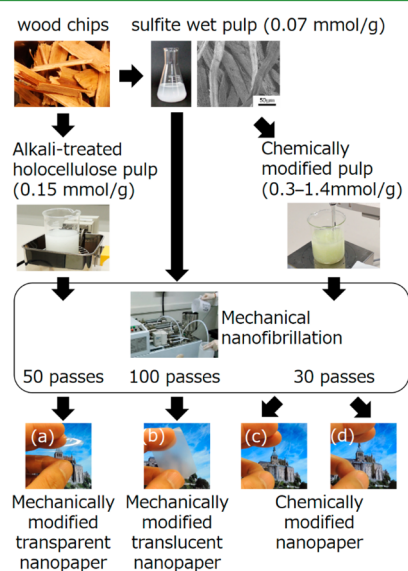
Figure 1. Procedures for the production of nanopaper from wood chips. (a) Mechanically modified transparent nanopaper. (b) Mechanically modified translucent nanopaper. (c, d) Chemically modified nanopaper: (c) TEMPO nanopaper and (d) CM nanopaper.

introduced into the microsized cellulose pulps. Under slight mechanical nanofibrillation, the modified pulps are homogeneously dispersed into 3−15 nm wide cellulose nanofibers by electrostatic repulsion and/or the osmotic effect.[25−29] After drying the chemically modified nanofiber dispersion, the obtained nanopaper has high transparency, highly smooth surfaces, low coefficient of thermal expansion (CTE), light weight, and high foldability like mechanically modified nanopaper.[8] Moreover, the production of chemically modified nanopaper consumes much less power in the nanofibrillation process compared with mechanically modified nanopaper. However, the thermal stability of chemically modified nanopaper is not as high as mechanically modified nanopaper.[26,30] Therefore, the low thermal resistance (<140 °C) is the only disadvantage of chemically modified nanopaper for application to electronic devices.

In this study, we evaluated the transparency and thermal stability of chemically modified nanopaper using TEMPO oxidation or CM and compared the properties with those of mechanically modified nanopaper. We then improved the thermal stability of chemically modified nanopaper, especially the protection of yellow or brown discoloration during heating in air, focusing on the carboxylate content of the cellulose nanofibers.

2. EXPERIMENTAL SECTION

2.1. Cellulose Pulps. For mechanically modified nanopaper, two types of cellulose pulps were used: a never-dried softwood dissolving sulfite pulp from Nippon Paper Group. Inc., Japan, and a holocellulose pulp with alkali treatment from wood chips of Japanese cedar (*Cryptomeria japonica*). The procedure for alkali treating the holocellulose pulp is summarized as follows. Wood chips (40 g) were first dewaxed by stirring in an acetone/water mixture (900

mL:100 mL) at room temperature overnight. The chips were then delignified by heating in an acetic anhydride/hydrogen peroxide mixture (500 mL:500 mL) at 90 °C for 2 h. Finally, the holocellulose pulp was treated with 5 wt % potassium hydroxide (KOH) at 20 °C for 2 h. The obtained alkali-treated holocellulose pulps had α-cellulose contents of 76−80% and Klason lignin of 0%

For chemically modified nanopaper, never-dried softwood dissolving sulfite pulps (Nippon Paper Group. Inc., Japan) were used as starting materials. In this study, two types of chemical modifications were applied: TEMPO oxidation[25,26] or CM.[27] The preparation of TEMPO-oxidized cellulose pulps with carboxylate contents of 0.27 and 1.35 mmol/g is summarized below. The wet sulfite pulp (dry weight 20 g) was suspended in distilled water (1500 mL) containing TEMPO (0.16 g) and NaBr (1.0 g). NaClO solution (4 wt %) of 0.5 or 10 mmol/g cellulose (15.4 or 308 mL) was added into the cellulose slurry at room temperature under continuous stirring. As a postreduction process, NaBH$_4$ (2 g, 0.1 g/g cellulose) was added into the cellulose slurry at room temperature under continuous stirring for 3 h.[26] Preparation of CM cellulose pulps with carboxylate contents of 0.33 or 1.38 mmol/g are summarized below. The wet sulfite pulp (dry weight 100 g) was solvent-exchanged by a graded ethanol series (50% → 70% → 90% → 100% → 100%) with centrifugation at 12 000 rpm for 3 min (model 7000, rotor A-5004, Kubota Corp.). The solvent-exchanged wet pulp was immersed in a solution of monochloroacetic acid (10 or 30 g) in isopropanol (500 mL) for 30 min. A solution of NaOH (15 or 50 g) in a mixture of methanol (250 mL) and isopropanol (1000 mL) was added into the cellulose slurry and then heated at 50 °C under continuous stirring for 60 min.

2.2. Nanofibrillation and Nanopaper. All of the cellulose pulps were disintegrated by the same water-jet nanofibrillation system. In this system, a 0.5 wt % pulp water dispersion of 2000 g was homogenized using a high-pressure water-jet system (Star Burst, HJP-25005 E, Sugino Machine Co., Ltd.) equipped with a ball-collision chamber. The slurry was ejected from a small nozzle with a diameter of 0.17 mm under a high pressure of 245 MPa.[9] The water dispersions of the chemically modified pulps, holocellulose pulp, and sulfite pulps were passed through this nozzle 30, 50, and 100 times, respectively. The cellulose nanofiber/water dispersions were dropped onto an acrylic plate using an applicator and then oven-dried at 50 °C overnight. The concentration of alkali-treated holocellulose and softwood dissolving sulfite nanofibers were 0.8 wt %, and that of TEMPO-oxidized and carboxymethylated nanofibers were 1.0 wt %. After drying, transparent 20-μm thick nanopapers were obtained.

2.3. Electrical Conductive Lines. A silver nanoparticle ink dispersed in an ethanol/ethylene glycol mixture was purchased from Cabot (CCI-300, Cabot Printing Electronics and Displays, U.S.A.). Inkjet printing was performed with a piezoelectric system (Dimatix DMP 2831, Dimatix-Fujifilm Inc., U.S.A.) equipped with a 10 pL cartridge (DMC-11610). The silver nanoparticle ink was impacted at a voltage of 22 V and a frequency of 5 kHz using a customized waveform. The substrate was maintained at room temperature during printing. The distance between the substrate and the nozzle was set to 1 mm, and dot spacing was set at 20 μm. The length of the printed lines was 40 mm. After printing, the lines on the TEMPO nanopaper with carboxylate content of 1.35 or 0.27 mmol/g were heated at 140 or 160 °C for 10 min in air.

2.4. Characterizations. The transparency of total transmittance was measured with a V-670 spectrophotometer (V-670, Jasco Corp.). Even transparent materials without any light absorption suffer reduced transparency because of light scattering. This light scattering is called haze. The haze was measured using a haze meter (HZ-V3, Suga Test Instruments Co., Ltd.). Thermogravimetric analysis was performed on a Q-50 (TA Instruments) under a nitrogen atmosphere (60 mL/min) at a heating rate of 10 °C/min. The thermal durability of the nanopaper was evaluated by the 5% weight loss point. The yellowness index (YI) was measured by a color meter (ZE 6000, Nippon Denshoku Industries Co., Ltd.). When the nanopaper was heated, the appearance changed from colorless transparent to yellowness transparent. We described the discoloration using the differential yellowness index (ΔYI) of the color before and after heating. The

Table 1. Characteristics of Nanopaper (Total Light Transmittance at 600 nm Wavelength, Haze, 5% Weight Loss Point under N$_2$ Gas, CTE, and Discoloration Time at 160, 180, and 200 °C in Air)

nanopaper (carboxylate contents)	total transmittance (%)	haze (%)	5 wt % loss point (°C)	ΔYI > 3 at 160 °C (min)	ΔYI > 6 at 180 °C (min)	ΔYI > 6 at 200 °C (min)	CTE (ppm/K)
mechanically modified translucent (0.07 mmol/g)	89.1	43.67	306.2	>120	90	20	7.2
mechanically modified transparent (0.15 mmol/g)	89.4	5.23	283.6	60	40	10	8.0
TEMPO (1.35 mmol/g)	90.5	1.21	229.5	30	10	2	7.3
CM (1.38 mmol/g)	89.5	0.67	236.2	15	6	2	13.3
TEMPO (0.27 mmol/g)	91.4	4.23	247.8	60	30	6	7.9
CM (0.33 mmol/g)	90.5	2.49	251.1	60	24	4	9.6

coefficient of thermal expansion (CTE) was measured using a thermomechanical analyzer (TMA/SS6100, SII Nanotechnology Inc.). The CTE values were determined as the mean values at 20–150 °C in the second run.

3. RESULTS AND DISCUSSION

Cellulose nanopaper was fabricated by drying cellulose nanofiber/water dispersions. The cellulose nanofibers were produced by mechanically and/or chemically assisted nanofibrillation from microsized cellulose pulp fibers (Figure 1). The mechanically modified nanopaper had different translucence and clear transparency depending on the starting pulp. For example, sulfite wet pulp could not be disintegrated into homogeneous cellulose nanofibers because the cellulose nanofibers in the pulp coalesced by irreversible hydrogen bonding of "hornification".[31] Thus, despite harsh 100 times mechanical nanofibrillation, the obtained nanopapers were translucent and their haze was 43.67% because of light scattering inside the nanopaper (Figure 1b, Table 1). In contrast, alkali-treated wet holocellulose pulp was easy to disintegrate into homogeneous nanofibers because residual hemicellulose inside the pulp acts as a surfactant in mechanical nanofibrillation.[31,32] When the homogeneous nanofiber dispersion is dried, the cellulose nanofibers are densely packed together by capillary action during the evaporation of the water and then light scattering does not occur inside the films.[7] As a result, the obtained mechanically modified nanopaper was optically transparent and the haze was only 5.23% after 50 times mechanical nanofibrillation (Figure 1a, Table 1). The total transmittances in the visible wavelength range of 400–800 nm were almost the same for the two types of nanopaper (~90%) (Figure 2a). In the ultraviolet (UV) wavelength range of 200–400 nm, the nanopaper from holocellulose pulp had lower total transmittance than the nanopaper from sulfite pulp. This is because holocellulose pulps have lower cellulose purity than sulfite pulp, and the holocellulose nanopaper absorbs incident light with UV wavelength well.

Hornificated sulfite pulp is easy to disintegrate into homogeneous nanofibers after chemical modification, such as TEMPO oxidation or CM.[25−27] In this study, TEMPO-oxidized or carboxymethylated pulps were made from sulfite wet pulps. The carboxylate contents of TEMPO-oxidized and carboxymethylated pulps were 1.35 and 1.38 mmol/g, respectively. These are similar carboxylate contents to other reported values.[28−30] As mentioned above, the nanopaper from sulfite pulp was translucent after 100 times mechanical nanofibrillation. In contrast, the nanopapers from TEMPO-oxidized and carboxymethylated sulfite pulp were clear transparent with only 30 times mechanical nanofibrillation
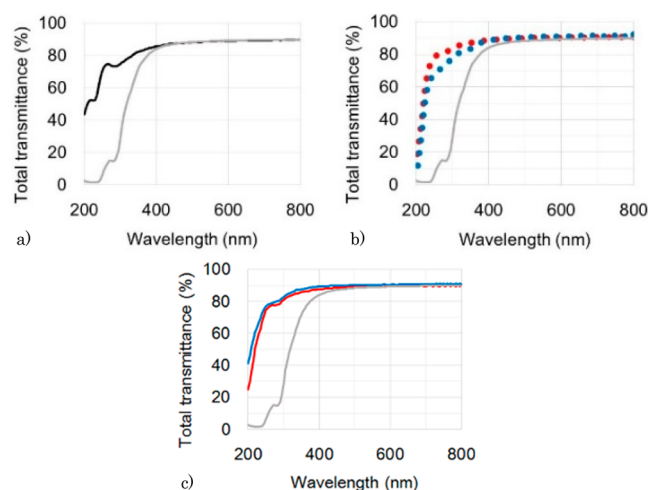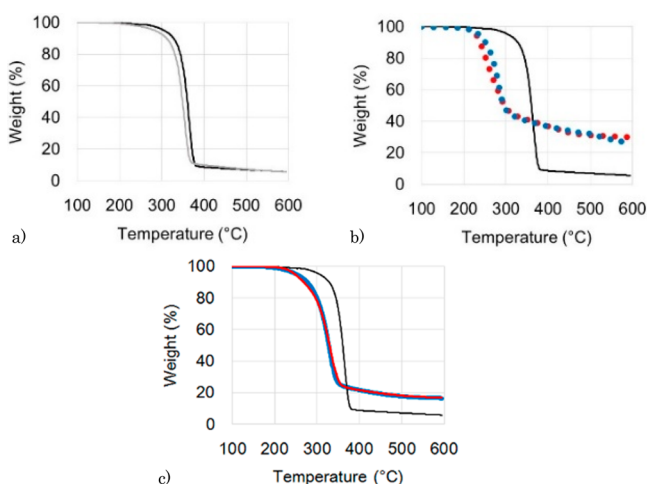

Figure 2. Total light transmittance of nanopaper. Black line in (a), mechanically modified translucent nanopaper (0.07 mmol/g); gray line in (a, b, c), mechanically modified transparent nanopaper (0.15 mmol/g); red dotted line in (b), TEMPO nanopaper (1.35 mmol/g); blue dotted line in (b), CM nanopaper (1.38 mmol/g); red solid line in (c), TEMPO nanopaper (0.27 mmol/g); blue solid line in (c), CM nanopaper (0.33 mmol/g).

(Figure 1c and d). The hazes of TEMPO and CM nanopaper were 1.21% and 0.67%, respectively (Table 1). Both of their total transmittances in the 400−800 nm wavelength range were as high as those of mechanically modified transparent or translucent nanopaper (Figure 2b). Moreover, their total transmittances in the 200−400 nm wavelength range were as high as those of mechanically modified translucent nanopaper, because of the high cellulose purity of their starting sulfite pulps.

In electronic devices, the processing temperatures have decreased to 150−200 °C by printed electronics. However, most plastics do not have sufficient high thermal durability against temperature. We have already reported that mechanically modified translucent and transparent nanopapers have sufficiently high thermal stability at 150−200 °C.[6,9] In this study, we evaluated the thermal stability of chemically modified nanopaper by thermal gravimetric analysis under nitrogen and investigated the color change in air.

First, as a measure of the thermal stability, the 5% weight loss points of the nanopaper were determined by heating under nitrogen. The mechanically modified translucent nanopaper had the highest 5% weight loss point (306.2 °C), the mechanically modified transparent nanopaper had the second highest (283.6 °C), and TEMPO and CM nanopaper had the lowest (229.5 and 236.2 °C, respectively) (Figure 3a, Table 1).

Figure 3. Thermogravimetric curves of nanopaper under nitrogen atmosphere. Black line in (a, b, c), mechanically modified translucent nanopaper (0.07 mmol/g); gray line in (a), mechanically modified transparent nanopaper (0.15 mmol/g); red dotted line in (b), TEMPO nanopaper (1.35 mmol/g); blue dotted line in (b), CM nanopaper (1.38 mmol/g); red solid line in (c), TEMPO nanopaper (0.27 mmol/g); blue solid line in (c), CM nanopaper (0.33 mmol/g).

These results indicate that the lower the haze of the nanopaper, the lower is the thermal stability. According to previous reports, lower-haze nanopaper is produced from TEMPO-oxidized pulp with higher carboxylate content.[25,33] Therefore, increasing the carboxylate content not only affects the optical transparency but also drastically reduces the thermal stability of the nanopaper. Thus, we developed a chemically modified nanopaper with not only low haze but also high thermal stability by adjusting the carboxylate content.

The starting sulfite wet pulp had a carboxylate content of 0.07 mmol/g. By adjusting the reaction conditions, sulfite pulps were produced with carboxylate contents of 0.27 mmol/g by TEMPO oxidation and 0.33 mmol/g by CM. When the modified sulfite pulps were mechanically nanofibrillated 30 times, the nanofibers were homogeneously distributed in the dispersion. Thus, transparent cellulose nanopaper was obtained by the same procedure as for the other nanopapers (Figure 1). Decreasing the carboxylate content to 0.27 or 0.33 mmol/g resulted in nanopapers with total transmittances of 91.4 and 90.5%, which are as high as those of nanopapers with higher carboxylate contents (Figure 2c, Table 1). In contrast, the haze of slightly chemically modified nanopaper increased from 1.21% to 4.23% in TEMPO nanopaper and from 0.67% to 2.49% in CM nanopaper (Table 1). Both the hazes are less than that of mechanically modified transparent nanopaper (5.23%). The 5% weight loss point increased from 229.5 to 247.8 °C for TEMPO nanopaper and from 236.2 to 251.1 °C for CM nanopaper (Figure 3, Table 1).

In electronics devices, transparent substrates should maintain their colorless transparency with exposure to temperature during device processing in air. The thermal stability was evaluated by the yellowness index (YI), which is a number calculated from spectrophotometric data that describes the change in color of a test sample from clear or white to yellow. In this study, the difference of YI (ΔYI) was calculated before and after heating at 140−200 °C in air. As references for the ΔYI values, transparent nanopapers on a white board are shown in Figure 4. Before heating, nanopaper is colorless
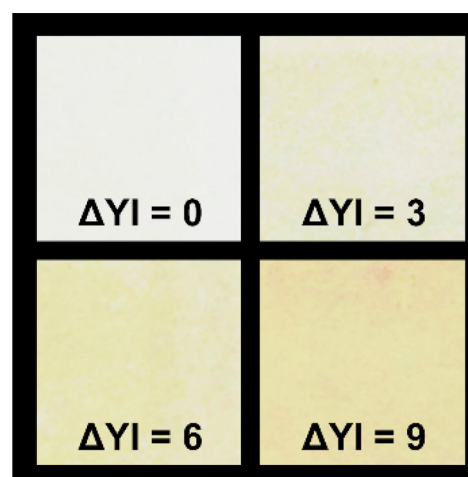
Figure 4. Transparent nanopaper samples with different ΔYI values on a white board (ΔYI = 0, before heating; ΔYI = 3, slight color change; ΔYI = 6, light yellow; and ΔYI = 9, obvious yellow).

transparent (YI = 0). After heating in air, the slight yellowness (ΔYI = 3) is difficult to visually detect, the yellowness (ΔYI = 6) is easy to detect, and the appearance clearly turns to transparent yellow or brown at ΔYI = 9.

Transparent plastics often turn yellow within 30 min at 140 °C. In contrast, after heating at 140 °C for 120 min, all of the transparent nanopapers retained colorless transparency with ΔYI < 3 (Figure 5a, Table 1). When the heating temperature
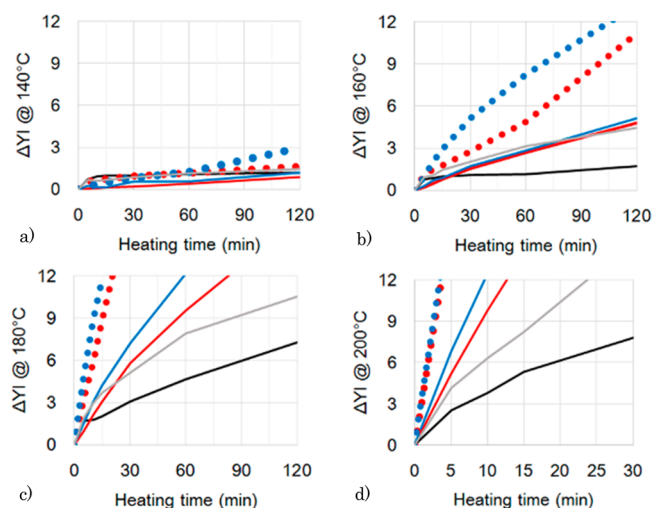

Figure 5. ΔYI curves of nanopaper in air at (a) 140, (b) 160, (c) 180, and (d) 200 °C. Black line, mechanically modified translucent nanopaper (0.07 mmol/g); gray line, mechanically modified transparent nanopaper (0.15 mmol/g); red dotted line, TEMPO nanopaper (1.35 mmol/g); blue dotted line, CM nanopaper (1.38 mmol/g); red solid line, TEMPO nanopaper (0.27 mmol/g); blue solid line, CM nanopaper (0.33 mmol/g).

was above 140 °C, the color change depended on the carboxylate content in the nanopaper. The mechanically modified translucent nanopaper had the lowest carboxylate content of 0.07 mmol/g, and they exhibited the highest color resistance. For example, their ΔYI was <3 after heating at 160 °C for 120 min and was <6 after heating at 180 °C for 90 min or at 200 °C for 20 min (Figure 5b−d). In printed electronics, the conductive patterns are often fabricated by high-temper-

ature heating at 150−200 °C. Therefore, high color resistant translucent nanopapers are used for such high-temperature heating to achieve high conductive patterns.[6,10] The second highest thermal resistive nanopaper was the mechanically modified transparent nanopaper, whose carboxylate content in the pulp was 0.15 mmol/g. The mechanically modified transparent nanopaper maintained ΔYI < 3 after heating at 160 °C for 60 min (Figure 5b−d). Thus, mechanically modified transparent nanopaper is used as thermal resistive transparent substrates in optoelectronic devices such as an organic thin-film transistors (TFTs).[16] In our previous study, mechanically modified transparent nanopaper endured high-temperature integration processes at 180 °C for 60 min, which are almost the same conditions as those used on a conventional glass substrate.[16] As a result, the obtained TFT array on the mechanically modified transparent nanopaper showed higher mobility than that on thermal-sensitive plastic substrate.

Traditional chemically modified nanopaper (>1.0 mmol/g) had the lowest color resistance. TEMPO nanopaper (1.35 mmol/g) exceeded ΔYI = 3 after heating at 160 °C heating for 30 min, and CM nanopaper (1.38 mmol/g) exceeded ΔYI = 3 after heating at 160 °C for 15 min (Figure 5b). Chemically modified nanopapers have been heated below 140 °C in device fabrications, and the obtained device performance was often inferior to plastic-based electronics.[13,15,17,18,21−24] However, decreasing the carboxylate content to 0.27 or 0.33 mmol/g increased their color resistance. This is because the lower carboxylate content decreased the aldehyde content in the pulp, which is one of the discoloration triggers during heating.[26,34] For example, at 160 °C heating, the discoloration time to exceed ΔYI = 3 in TEMPO nanopaper was prolonged from 30 to 60 min, and that in CM nanopaper was prolonged from 15 to 60 min (Figure 5b). At 180 °C heating, the discoloration time to exceed ΔYI = 6 in TEMPO nanopaper was also prolonged from 10 to 30 min, and that in CM nanopaper was prolonged from 6 to 24 min (Figure 5c).

We demonstrated the illumination of light-emitting diode (LED) light on nanopaper to confirm their improved thermal stability in device processing (Figure 6). When printed lines with silver nanoparticle inks were heated over 150 °C, the
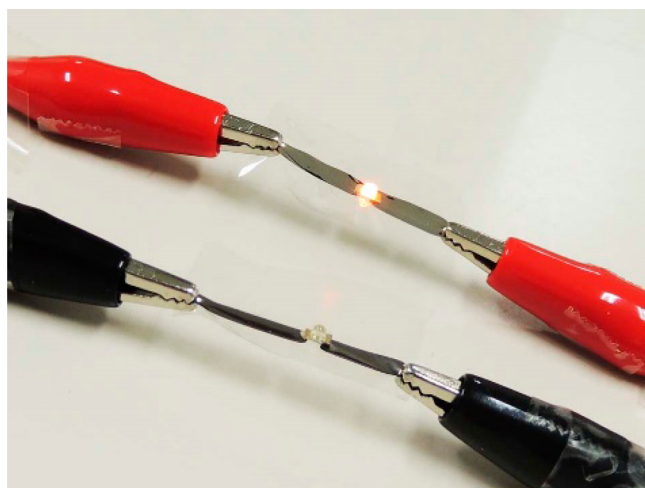
Figure 6. LED light and silver nanoparticle printed lines on nanopaper: TEMPO nanopaper (0.27 mmol/g) with 160 °C heating (top) and TEMPO nanopaper (1.35 mmol/g) with 140 °C heating (bottom).

electrical contacts between the silver nanoparticles were produced by heat sintering. As a result, the printed lines enhanced the high electric conductivity and illuminated LED lights mounted on them.[6,35] The maximum temperature for TEMPO nanopaper (1.35 mmol/g) was 140 °C to maintain their colorless transparency. When the printed lines were heated at 140 °C, the line could not enhance the high conductivity. As a result, an LED light on TEMPO nanopaper (1.35 mmol/g) did not illuminate. In contrast, TEMPO nanopaper (0.27 mmol/g) maintained its colorless transparency even after heating at 160 °C. Therefore, the printed line heated at 160 °C has sufficiently high conductivity, and the LED light was illuminated on TEMPO nanopaper (0.27 mmol/g).

The low CTE is well-known to be one of the advantages of nanopaper. As shown in Table 1, all of the nanopapers with or without chemical modification and with any carboxylate content exhibited incredibly low CTEs of 8−10 ppm/K. For CM nanopaper, the CTEs were relatively high: 9.6 ppm/K for low carboxylate content and 13.3 ppm/K for high carboxylate content. However, these CTEs are much lower than those of most plastics.

CONCLUSIONS

Chemical modification of pulp can produce cellulose nanofibers with high speed and low cost. Using the chemically modified nanofibers, transparent nanopapers with low haze and low CTE were obtained. However, the chemically modified nanopaper had lower thermal durability than mechanically modified nanopaper and some plastics. Although many low-temperature device processes have been developed, higher temperature generally increases the device performance. Our findings in this study reveal that decreasing the carboxylate content improves the thermal stability of the nanopaper. The slightly modified nanopaper enhanced the high thermal stability while maintaining high optical transparency and low CTE. Therefore, this new chemically modified nanopaper could play an important role in the development of future paper devices.

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Notes
The authors declare no competing financial interest.

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