Comparative study of paper and nanopaper properties prepared from bacterial cellulose nanofibers and fibers/ground cellulose nanofibers of canola straw

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Nanopaper was prepared using ground cellulose nanofibers (GC) from canola straw and bacterial cellulose nanofibers (BC). The characteristics of GC and BC nanopapers were investigated and compared. Micropaper was also prepared from as-bleached cellulose microfibers of canola straw, used as a control sample to evaluate the effect of grinding on the properties of cellulose nanofibers and nanopaper. The average diameters for the microfiber, GC and BC were 26 μm, 32 nm and 45 nm, respectively. Micropaper had crystallinity and crystallite size of 69% and 5.5 nm, respectively. As the result of grinding, the crystallinity and crystallite size of GC nanopaper dropped to 62% and 5.1 nm, respectively. BC nanopaper showed the highest values, with 80% and 6.2 nm, respectively. GC nanopaper had a lower onset temperature (270 °C) and thermal stability than that of both micropaper (275 °C) and BC nanopaper (320 °C). Micropaper was permeable to air while GC and BC nanopapers showed very high barrier property. Grinding had a drastic positive effect on mechanical properties: the tensile strength and Young’s modulus of GC nanopaper increased 11 times on average over those of micropaper, reaching 114 MPa and 13.6 GPa, respectively. BC nanopaper had the highest tensile strength and Young’s modulus, with 185 MPa and 17.3 GPa, respectively. GC and BC nanopapers are regarded as highly tough, fully bio-based, fully biodegradable and multi-performance materials.

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1. Introduction

Today, nanometer-sized materials such as nanotubes, nanoplates and nanofibers have attracted much attention from researchers as well as industries. The ability to see materials down to nanoscale dimensions (top-down downsizing) and to control how materials are constructed at the nanoscale (bottom-up synthesis) is providing the opportunity to develop new materials and products in previously unimagined ways (Berglund and Peijs, 2010; Gatenholm and Klemm, 2010).

Bio-based nanomaterials such as nanocellulose, nanochitin and nanostarch potentially have crucial importance. Nanocellulose has been studied intensively for potential use in a range of applications such as biomedicine, biomaterials engineering, membranes, magnetic and electronics and polymer nanocomposites (Gatenholm and Klemm, 2010; Siro and Plackett, 2010; Lavoine et al., 2012; Eichhorn et al., 2010; Ummartotin et al., 2012). The importance of nanocellulose can be attributed to properties like its biodegradability and renewability, high specific strength and stiffness, high reinforcing potential and high specific surface area (Siro and Plackett, 2010; Klemm et al., 2011). In addition, due to increased concerns about possible cancer hazards from carbon nanotubes, currently one of the most popular nanomaterials (Poland et al., 2008), the more environmentally friendly characteristics of bio-based nanomaterials such as nanocellulose are driving increased interest in their uses and synthesis.

Several approaches have been introduced to produce nanocellulose; these can be classified into top-down and bottom-up approaches. In top-down approaches such as acid hydrolysis (Randay, 1949), homogenizing (Turbak et al., 1983), grinding (Taniguchi and Okamura, 1998), electrospinning (Frey et al., 2003), enzymatic hydrolysis (Janardhan and San, 2006), TEMPO-mediated oxidation (Saito et al., 2007; Isogai et al., 2011) and solvent-based isolation (Yousefi et al., 2011b), nanocellulose is isolated from cellulose fibers using chemical, mechanical or chemomechanical forces. In this study, ultra-fine friction grinding was used: this process, in which microscale cellulose fibers are forced through a gap between rotary and stator stone disks, is fast, simple,
one-step and high-yield. Fig. 1 shows the silicon carbide (SiC) grinding stone used in this study at macro- and microscales. There are several grooves on the stones' surface through which a microfiber suspension moves outward as the result of centrifugal forces; repeated cyclic pressure and shearing stresses result in the nanodefinition of the cellulose fibers (Abe et al., 2007; Yousefi et al., 2011a).

There are wide varieties of wood and non-wood resources for nanocellulose production. Using non-wood resources such as agricultural residues is interestingly increasing due to shortage of wood resources and environmental concerns (Hedjazi et al., 2009; Bras et al., 2010). For example, canola straw—used as one of the raw materials of current study—is a low value agricultural residue reported to be suitable for manufacture of cellulose-based products (Yousefi, 2009). Canola seeds are basically used for the production of edible oil, but, high volume of its straw (3 tons/ha) is annually ploughed into the ground or burnt (Yousefi, 2009).

Bacterial synthesis was used as a bottom-up approach to produce BC nanofibers (Brown, 1886). Instead of obtaining nanocellulose by fibrillating fibers, bacterial cellulose is produced by bacteria in “reverse” by synthesizing cellulose and building up bundles of nanofibers by some bacteria species especially Acetobacter xylinus in aqueous culture media during a time period of days up to two weeks (Brown, 1886; Soykeabkaew et al., 2009; Gatenholm and Klemm, 2010).

Nanopaper is defined as a sheet made completely of cellulose nanofibers. Most of its characteristics including its physical and mechanical properties have been reported to be much superior to those of ordinary papers (Henriksson et al., 2008; Sehaqui et al., 2011; Yousefi et al., 2011a). Owing to its high physical and mechanical properties and biodegradability, nanopaper is considered to be a multi-performance material.

Nanocellulose produced using the different approaches of top-down and bottom-up are assumed to have different properties. The present study aimed to examine and compare the properties of nanopaper produced by ground and bacterial cellulose nanofibers. Another objective was to compare the properties of fibers and ground nanofibers of canola straw and their corresponding paper and nanopaper.

2. Experimental

2.1. Raw materials

Canola straw, obtained from fields in Karaj, Iran, was used as raw material for this study. The purification of cellulose from canola straw, resulted in alpha cellulose amount of 92 ± 1%, has been described elsewhere (Yousefi et al., 2011a). The resulting water slurry with 1 wt.% as purified fibers of canola straw was passed once through a grinder (MKCA6-3; Masuko Sangyo Co., Ltd., Japan) at 1500 rpm to produce the ground cellulose nanofibers (GC). Bacterial cellulose nanofiber (BC) pellets were prepared from Fuji Co., Japan. The BC pellets were mechanically fragmented using stirring.

Well-dispersed suspensions (0.2 wt.%) of purified fibers, GC and BC were filtered by vacuuming, followed by drying at ambient temperature. They were then hot-pressed at 100 °C, 2 MPa for 1 h. This produced as-prepared micropaper (from fibers) and nanopapers (from GC and BC) with thickness of 80–90 μm and 40–60 μm, respectively. The micropaper, GC nanopaper and BC nanopaper were then conditioned at a relative humidity of 60% and a temperature of 25 °C.

2.2. Measurements

The micro- and nanopapers were dried in a vacuum and coated with platinum/palladium (Pt/Pd). The specimens were observed with a field emission scanning electron microscope (FE-SEM, JSM-6700F; JEOL, Tokyo, Japan) at an accelerating voltage of 5 kV. The diameters of 300 micro- and nanofibers were measured on FE-SEM micrographs using AutoCAD software (Autodesk, San Rafael, CA, USA).

X-ray diffraction was performed using an X-ray diffractometer (RINT-2100, Rigaku Co., Japan) operating by CuKα radiation at 40 kV and 20 mA. The X-ray profile was prepared in the range of 2θ = 10–40° at a scanning speed and interval of 1.2 °/min and 0.02°, respectively. After subtracting the air scattering, the diffraction profile was curve-resolved into non-crystalline scattering and crystalline reflections using Fityk software. The apparent crystallinity was measured based on the ratio of crystalline and non-crystalline areas (Garvey et al., 2005; Nishino and Arimoto, 2006). The integral width of the [2 0 0] reflection was corrected for the CuKα doublet and instrumental broadening. The crystallite size of the cellulose was estimated by Scherrer’s Eq. (1) (Alexander, 1969):

\[
D = \frac{\lambda}{\beta \cos \theta}
\]

where \(D\) is the crystallite size, \(\lambda\) is the X-ray wavelength (0.15418 nm), \(\theta\) is the diffraction angle for the [2 0 0] plane and \(\beta\) is the corrected integral width.

The thermal decomposition was performed using a thermogravimetric analyzer (SII TG/DTAS2000, Seiko Instruments Inc., Japan). The specimens of micropaper, GC nanopaper and BC
nanopaper (two specimens each) were heated from 50 to 600 °C at a heating rate of 10 °C/min in a nitrogen atmosphere.

Burst test was carried out according to TAPPI T403 om-02 standard using burst tester (Frank-pti Co., Germany). The burst strength was normalized based on the paper grammage (weight in grams per square meter) of each specimen to obtain burst index.

The stress–strain curves of micropaper, GC nanopaper and BC nanopaper (eight specimens each) were measured using a tensile tester (Autograph AGS-1kND, Shimadzu Co., Japan) at room temperature. The specimens, which measured 20 mm long by 4 mm wide, were tested using 1000 N load cell at extension rate of 1 mm/min. The average value of the tensile strength (σ, max), Young’s modulus (E) and strain at break (ε, max) were evaluated. The tensile strength was also normalized based on density and grammage of each specimen to obtain specific tensile strength and tensile index, respectively. On each graph bar, 95% confidence intervals are shown to indicate the differences in means.

3. Results and discussion

Fig. 2 shows (a) photographs of as-bleached microfiber, as-produced GC and as-received BC pellicle at macroscale, and (b) FE-SEM micrographs of micropaper, GC and BC nanopapers. The as-bleached microfibers were on average, 26 ± 9 μm thick; they were reduced almost three orders of magnitude to GC with an average diameter of 32 ± 10 nm through the highly effective, fast, one-step, top-down method of grinding. The average dimension of the BC nanopaper was 45 ± 8 nm, which was 11 nm thicker than that of the GC. Giving average diameter of 32 ± 10 nm, the lateral disconnection between adjacent nanofibrils within cellulose fiber is found to be the main fragment point in the top-down approach of grinding. As a comparison, the fragment point of cellulose nanostructures in the TEMPO-mediated oxidation is the lateral gap between adjacent elementary fibrils giving nanofiber 3–4 nm in width and a few microns in length (Saito et al., 2007). On the other hand, bacteria assemble cellulose chains, crystallites and elementary fibrils hierarchically to make nanofibrils, or nanofibril bundles giving an average diameter of 45 ± 8 nm (Nakagaito et al., 2005).

Fig. 3 shows the X-ray diffraction profiles and photographs of micropaper, GC nanopaper and BC nanopaper. The strongest peak in all patterns appeared in the 2θ = 22.5–22.7° assigned to the atomic plane of [2 0 0] of cellulose crystallite. The X-ray diffraction photographs perpendicular to the sheet surface showed a constant equatorial distribution scattering intensity in Debye–Scherrer rings corresponding to the different crystallite reflections. This indicates that a perfectly random orientation of crystallites contributed to the formation of a random network structure during vacuum filtration of microfiber and nanofiber suspension. The X-ray diffraction photograph of BC nanopaper showed clearer and more distinctive Debye–Scherrer rings compared to those of micropaper and GC nanopaper. This result is consistent with the X-ray diffraction profiles, in which the profile of BC nanopaper presents narrower and sharper peaks compared to those of micropaper and GC nanopaper.

The Debye–Scherrer rings are directly affected by crystallinity and crystallite size (Nishino and Arimoto, 2006; Yousefi et al., 2011a,b). Table 1 presents the integral width for the peak of [2 0 0] plane, crystallinity and crystallite size for micropaper, GC nanopaper

![Fig. 2](image-url)

<table>
<thead>
<tr>
<th>Microfiber</th>
<th>GC</th>
<th>BC</th>
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</thead>
<tbody>
<tr>
<td>a. Macroscale photograph</td>
<td></td>
<td></td>
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<tr>
<td>Microfiber</td>
<td>GC nanopaper</td>
<td>BC nanopaper</td>
</tr>
<tr>
<td>b. FE-SEM micrographs</td>
<td>Ave. 26 ± 9 μm</td>
<td>Ave. 32 ± 10 nm</td>
</tr>
<tr>
<td></td>
<td>100 μm</td>
<td>2 μm</td>
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<tr>
<td></td>
<td>Ave. 45 ± 8 nm</td>
<td>2 μm</td>
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</table>

![Fig. 3](image-url)

**Fig. 3.** X-ray diffraction profiles perpendicular to the sheet surface of micropaper, GC nanopaper and BC nanopaper, with their corresponding X-ray diffraction photographs.
and BC nanopaper. The integral-width values of micropaper, GC nanopaper and BC nanopaper were 1.63 ± 1.78 and 1.44, respectively. The peak for GC was broader than those for micropaper and BC nanopaper. The crystallinities of micropaper, GC nanopaper and BC nanopaper were 69%, 62% and 80%, respectively. The crystallinity of micropaper was higher than that of GC nanopaper, but lower than that of BC. Similarly, the crystallite sizes of micropaper, GC nanopaper and BC nanopaper were 5.5, 5.1 and 6.3 nm, respectively. As these results show, the thicker the crystallite, the smaller the integral width. The higher crystallinity and crystallite size of BC is attributed to the origin of the cellulose and the mechanism of bottom-up synthesis used by bacteria. The crystallinity and crystallite size of cellulose derived from lignocellulosic sources are less than those of BC (Gao et al., 2010). Grinding had a significant effect on the loss of crystallinity and crystallite size; this is due to the high shearing and pressure forces created between the grinding stones (Abe et al., 2007; Yousefi et al., 2011a). Iwamoto et al. (2007) also reported the degradation of fibrillated pulps during the grinding treatment.

Fig. 4 shows the thermogravimetric traces for micropaper, GC nanopaper and BC nanopaper. First, a slight weight loss occurred at low temperature due to the release of absorbed water. Rapid decomposition occurred in the temperature range of 260–360 °C for micropaper and GC nanopaper, and 320–380 °C for BC nanopaper. The decomposition-onset temperature of GC nanopaper (270 °C) was slightly lower than that of micropaper (275 °C). BC nanopaper showed the highest decomposition-onset temperature of 320 °C. The lower onset temperature indicates a lower thermal stability for GC compared to that for microfiber and BC; this is attributed to GC’s lower crystallinity. In contrast, BC’s higher crystallinity made a dense structure at nanoscale; consequently, it shows higher thermal stability (Gao et al., 2010). As the temperature increased above 400 °C, the ultra-fine network structures of GC and BC fibers made them more likely to form pyrolysis products (Gao et al., 2010). Therefore, the final weights of GC and BC nanopaper were about 13% of their original weights, whereas the corresponding reduction for the micropaper was only 3.5%. The char formation was initiated by the cross-linking and re-polymerization of pyrolysis products of non-crystalline cellulose. In the degradation process, non-crystalline cellulose was initially attacked; therefore, GC nanopaper, which has a lower crystallinity compared to that of BC nanopaper, exhibited a rapid degradation rate and an increase in initial char formation (Switalski et al., 2002).

Table 2 presents the air-permeability values for micropaper, GC nanopaper and BC nanopaper. The micropaper had a structure highly permeable to air (42 ± 7 μm Pa⁻¹ s⁻¹), while GC and BC nanopapers formed complete barrier structures. The superior barrier quality of GC and BC nanopapers is attributed to their multi-layered highly packed nanostructures containing impermeable cellulose crystals (Fendler et al., 2007; Syverud and Stenius, 2009; Yousefi et al., 2011a).

Table 3 shows grammage values of micropaper, GC nanopaper and BC nanopaper together with their corresponding burst strength and burst index. There was a significant difference between the corresponding grammage, burst strength and burst index of the specimens. For example, the burst index of micropaper, GC nanopaper and BC nanopaper obtained 0.4 × 10³, 2.78 × 10³ and 3.84 × 10³ Nm/g, respectively. The higher burst index of nanopapers is contributed to their fully consolidated structures, higher specific surface area and hydrogen bonding position in nanofibers network. Fig. 5 shows the mechanical properties, including $\sigma_{\text{max}}$, $E$ and $\varepsilon_{\text{max}}$, of micropaper, GC nanopaper and BC nanopaper. The values for $\sigma_{\text{max}}$ of micropaper, GC nanopaper and BC nanopaper were 9.5, 114 and 185 MPa, respectively. The values for $E$ were 2, 13.6 and 17.3 GPa, respectively. The values for $\varepsilon_{\text{max}}$ were 1.5%, 5.7% and 6.5%, respectively. These results show significant differences among means. Table 4 presents the density of micropaper, GC nanopaper and BC nanopaper together with their corresponding specific tensile strength and tensile index. The density of micropaper (0.85 g/cm³) was significantly lower than those of GC nanopaper (1.3 g/cm³) and BC nanopaper (1.3 g/cm³) as the compressibility of microfibers was less than that of cellulose nanostructures. The specific tensile strength and tensile index of micropaper were much lower than those of GC and BC nanopapers. For example, the specific tensile strength of micropaper obtained 11.2 Nm/g while those of GC and BC nanopapers were 87.7 and 142.3 Nm/g, respectively. This is because the specific surface area of nanofibers is larger than that of microfibers. The larger surface area directly affects the

![Table 1: Integral width, crystallinity and crystallite size.](image)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Integral width (°)</th>
<th>Crystallinity (%)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micropaper</td>
<td>1.63</td>
<td>69</td>
<td>5.5</td>
</tr>
<tr>
<td>GC nanopaper</td>
<td>1.75</td>
<td>62</td>
<td>5.1</td>
</tr>
<tr>
<td>BC nanopaper</td>
<td>1.44</td>
<td>80</td>
<td>6.3</td>
</tr>
</tbody>
</table>

![Table 2: Air permeability of micropaper, GC nanopaper and BC nanopaper.](image)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Micropaper</th>
<th>GC nanopaper</th>
<th>BC nanopaper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability</td>
<td>42 ± 7</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

![Table 3: The values of grammage, burst strength and burst index.](image)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Grammage (g/m²)</th>
<th>Burst Strength (kPa)</th>
<th>Burst Index ($\times 10^3$ Nm/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micropaper</td>
<td>78</td>
<td>31</td>
<td>0.4</td>
</tr>
<tr>
<td>GC nanopaper</td>
<td>73</td>
<td>203</td>
<td>2.78</td>
</tr>
<tr>
<td>BC nanopaper</td>
<td>69</td>
<td>205</td>
<td>3.84</td>
</tr>
</tbody>
</table>

![Table 4: The values of density, specific tensile strength and tensile index.](image)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Density (g/cm³)</th>
<th>Specific tensile strength (Nm/g)</th>
<th>Tensile Index ($\times 10^3$ Nm/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micropaper</td>
<td>0.85</td>
<td>11.2</td>
<td>0.122</td>
</tr>
<tr>
<td>GC nanopaper</td>
<td>1.3</td>
<td>87.7</td>
<td>1.562</td>
</tr>
<tr>
<td>BC nanopaper</td>
<td>1.3</td>
<td>142.3</td>
<td>2.681</td>
</tr>
</tbody>
</table>

![Fig. 4: Thermogravimetric traces of micropaper, GC nanopaper and BC nanopaper.](image)
numbers of hydrogen bonding positions and mechanical properties (Sehaqui et al., 2011). Although cellulose microfibers are naturally composed of nanoscale units called nanofibrils, the lack of connectivity of nanofibrils within microfibers network negatively affects the mechanical properties. This means tensile stress is not properly transferred through the whole micropaper network (Yousefi et al., 2011a,b).

Although BC nanopaper possesses the highest mechanical properties in this study, they are inferior to the initial mechanical properties of BC sheets reported in the literature (Soykeabkaew et al., 2009). The main reason for the high initial strength of the BC sheets is due to the continuity of the fibrils, which are not necessarily linear, but possess “three-way branching points,” as observed by Yamanaka et al. (1989). When BC pellicles were mechanically fragmented and sheets prepared, the mechanical properties decreased compared to the values of sheets from nondisintegrated BC pellicles (Gee et al., 2007). This is attributed to the loss of continuity in the original network structure (Soykeabkaew et al., 2009; Gee et al., 2007). BC nanopaper possesses higher mechanical properties than GC nanopaper. The degree of polymerization of BC has been reported to be up to 8000 (Siro and Plackett, 2010), while that of cellulose from lignocellulosic sources is commonly reported to be around 1200–1400 (Henriksson et al., 2007). On the other hand, the degree of polymerization is reported to correlate strongly with the aspect ratio of the nanofibers (Siro and Plackett, 2010). Therefore, with an increased degree of polymerization, the aspect ratio increases, the bonding position of each nanofiber expands and the entanglement of nanofibers in the whole network increases, resulting in higher mechanical properties.

BC is produced as a highly hydrated and relatively pure cellulose nanofiber, and therefore no chemical treatments are needed to remove lignin and hemicelluloses, as is the case for plant cellulose (Barud et al., 2008); hence, BC fibers keep their intrinsic properties. But in the case of the top-down approach of grading, multiple chemical-purification steps are applied to the cellulose of lignocellulosic materials (Iwamoto et al., 2007; Abe and Yano, 2009; Yousefi et al., 2011a). In addition, grading itself is a mechanical-based method by which cellulose microfibers are downsized through high shearing and compression forces; therefore, the nanofibers are expected to be damaged during both purification and grading (Iwamoto et al., 2007; Abe and Yano, 2009; Yousefi et al., 2011a).

The properties of BC nanopaper were consistently superior to those of nanopaper prepared from GC. Both nanopapers prepared in this study are regarded as high-performance, multi-functional materials expected to have wide variety of applications in areas such as packaging, electronics, magnets, medical engineering and textiles.

4. Conclusions

High-performance nanopapers were prepared from GC and BC nanofibers. The study showed that canola straw, a low-value agricultural residue, can be turned into nanopaper, a valuable product. The top-down method of grading had a negative effect on the crystallinity, crystallite size and thermal stability of GC nanopaper compared to those of micropaper. However, it significantly increased the mechanical properties and air impermeability of GC nanopaper. The crystallinity, crystallite size, thermal stability and mechanical properties of BC nanopaper were higher than those of GC nanopaper and micropaper. Nanopapers as high-performance materials have a wide variety of potential applications.

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