Super-stretchable paper-based materials for 3D forming

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ABSTRACT

Paper is renewable, recyclable, sustainable and biodegradable material and, as a result, paper-based materials are widely used in the world packaging market. However, paper-based materials cannot compete with plastics in terms of processability into various 3D shapes. This is due to poor formability of paper, which is closely associated with its toughness. To improve paper formability, we report on a facile and green method that combines fiber and paper mechanical modifications at different structural levels as well as biopolymer treatment via spraying. As a result, a remarkable elongation of ~30% was achieved after proposed combined approach on the laboratory scale. At the same time, a significant increase in tensile strength and stiffness (by ~306% and ~690%, respectively) was observed. Overall, an inexpensive, green, and scalable approach is introduced to improve formability of fiber networks that in turn allows preparation of 3D shapes in the processes with fixed paper blanks such as vacuum forming, hydroforming, hot pressing, etc.

INTRODUCTION

There is a tremendous potential for wood-fiber based materials such as paper and paperboard to contribute to lightweight structures in several different applications such as vehicle components, building materials and packaging, among others. Fiber-based packaging materials have important benefits in comparison to fossil-based plastics regarding biodegradability, recyclability and renewability. However, paper exhibits several drawbacks that today seriously limit its potential, that includes moisture sensitivity, barrier properties and limited formability[1]. While barrier properties and moisture resistance can be improved by

surface modification and by introducing functional coating and films[2], there are no simple methods to enhance the convertibility of paper into 3D objects.

The term “formability” describes the ability of a material to undergo plastic deformation without damage, and therefore it is strongly associated with the toughness[3]. The main properties of fiber-based products to meet the requirements of 3D shaping have been recently investigated[1,4] and methods to improve the respective material extensibility (formability) have been highlighted[5].

Generally, the extensibility of paper relies on three principal factors: properties of single fibers, character of inter-fiber bonds, and the structure of the fiber network formed during the papermaking process. In earlier publications it has been shown that certain mechanical treatments of the fibers improve the extensibility of paper[6], the inter-fiber bonding can be affected by chemical modifications[7] or by application of different additives[8–10] as well as the structure of the fiber network can be altered by in-plane compaction[11] and/or drying shrinkage[12]. In this work, mechanical modification of fibers, addition of biopolymers and in-plane compaction of the fiber web were combined to improve 3D formability of paper, which was also assessed with press-forming experiments.

EXPERIMENTAL

Materials.

Bleached, once-dried softwood kraft fibers were obtained from a Finnish pulp mill. The mechanical treatment of fibers included high consistency (HC) treatment in wing defibrator, and low-consistency (LC) refining in PFI mill. The physical properties of the mechanically-treated fibers were investigated with a Kajaani FiberLab analyzer (Metso Automation, Kajaani, Finland) and a Leica DM750 optical microscope. Handsheets were prepared according to ISO 5269-1:2005 standard except that a grammage of 70 g/m^2 was used. Guar gum galactomannan (GG) was purchased from Sigma-Aldrich (no. 232-536-8) and was used as received. Prior to use, GG was dissolved in water at 85 °C for 6 h and then cooled to room temperature under constant stirring. Gelatin from porcine skin (Type A, ~300 g Bloom gel strength, no. 232-554-6) was purchased from Sigma-Aldrich. A commercial polylactic acid (PLA) latex (Landy PL-3000) was obtained from Miyoshi Oil & Fat Co., Ltd., Japan. The latex was provided with a dry solids content of 40.2 wt%, and a mean particle size of 1.2 μm was determined by dynamic light scattering. The minimum film forming temperature (MFFT) of 20 °C was provided by the manufacturer. Biopolymer-modified paper was prepared by spraying of aqueous 4 wt.% biopolymer solution (with respect to dry cellulose fibers) on freshly prepared cellulosic fiber handsheets before wet pressing. All the characterizations were conducted for

the freely dried samples. To estimate the contribution of sprayed polymers on drying shrinkage as well as to assess the dimensional changes of paper subjected to in-plane compaction, shrinkage of paper was calculated according to eq 1 that compares the perimeter of a square formed by four small holes punctured at each corner of the handsheet, before and after drying:

$$Shrinkage = \frac{P_w - P_d}{P_w} \times 100\% \qquad (1)$$

where P_w and P_d are the perimeter of the square in wet and dry handsheet, respectively. Measurements were performed at least from eight sheets using a high-resolution scanner (UMAX PowerLook 2100XL-USB) and a software code developed for this purpose.

Methods.

In-Plane Compaction of Paper. In-plane compressive treatment of paper was performed by using a tailor-made compaction unit developed by VTT in Jyväskylä (VTT, Jyväskylä) (see Figure 3). In this device, paper is placed between two strained rubber bands (Poisson's ratio is 0.49), and the bands are pressed together by a piston-driven plate. Once paper was pressed between the bands, tension was released, and the bands started to spring back to restore their original length. Consequently, paper was contracted along the deformed rubber bands. The strain and the strain recovery of the rubber bands was 13%. Paper was compacted at ~40% water content and dried without restraint after treatment. Reference sample was moisturized to 60% dry solids content and freely dried.

Tensile Strength. Mechanical properties of prepared papers were measured with a MTS 400/M (MTS Systems, USA) vertical tensile tester with a load cell of 200 N equipped with TestWorks 4.02 measuring program (according to ISO 1924-3:2005 standard). At least 10 replicates of each sample type were measured, and the average values are reported.

Formability. Formability strain of modified fiber networks was measured using a 2-D formability tester developed by VTT, Jyväskylä (see Figure 4). This unit was equipped with a double-curved heated press, a bottom support (temperatures up to 250 °C), and blank holders. In typical experiments, a paper sample with a grammage range from 80 to 300 g/m^2, was rapidly preheated to the die temperature within 0.5−0.7 s. This allowed the paper forming to occur under temperatures that were close to that of the die. The testing proceeded as follows: a paper sample (20 mm wide and ~110 mm long) was fixed by the two blank holders. The press was then moved into contact with the sample (at ~3% strain) and retained still for 0.5 s in order to preheat the sample. Then, the press continued a downward movement until sample failure. The velocity of the forming press was 1 mm/s. The formability strain of the samples was measured as an average value collected from 10 samples at die temperatures of 23 (room

temperature), 60, 75, 90, 105, and 120 °C. Prior to testing, the samples were conditioned at 75% RH and 23 °C. Formability strain was measured in the direction of compaction.

3D Press Forming with Fixed Blank. Press forming process with MiniMould developed at Lappeenranta University of Technology Pilot testing line was used to prepare rectangular trays (90 × 80 × 35 mm, depth can be varied) from modified networks[13]. The maximum depth of the trays was investigated with respect to proposed paper modification strategy since the material formability is justified by this criterion in the fixed blank process. Samples were prepared following the same procedure as described above, with the exception that a high grammage paper (~220 g/m2) was used. The following forming parameters were used: pressing speed 60 mm/s, pressing force 30 kN, dwell time 600 ms, male mould temperature 22 °C, female mould temperature 120 and 160 °C, blank holding force 4800 kN. Prior to forming, the samples were conditioned overnight at 75% RH and 23°C.

RESULTS AND DISCUSSION

Mechanical treatment of fibers and it's effect on paper toughness

Mechanical treatments of fibers at high solids content (HSC) induce fiber deformations (microcompressions, curls, dislocations, etc.), (Figure 1) that are known to positively contribute to the paper extensibility[14]. On the other hand, moderate beating at low solids content (LSC) tends to straighten the fibers (Figure 1), which leads to improved bonding within the fibers thus providing additional strength, while micro-compressions and dislocations in the fibers are mainly preserved while keeping the dewatering properties of the furnish on acceptable level, Table 1. Industrially, combination of these methods is used to improve the tensile energy absorption (TEA) of paper for the production of sack and bag paper grades[15].

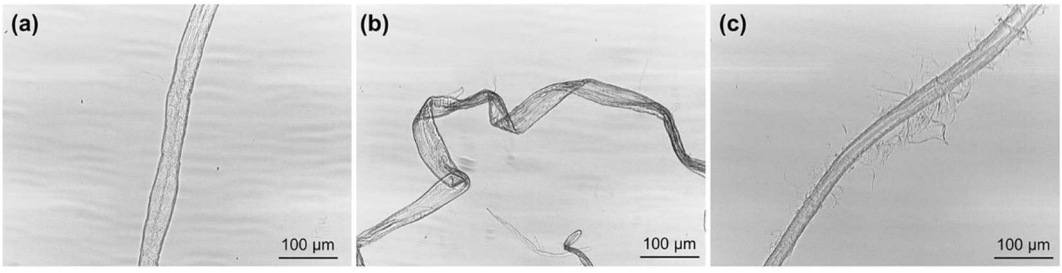


Figure 1. Optical microscope images of an unmodified fiber (a), WD treated fiber (110 °C and 40% DS) (b) and a fiber after a combined WD+PFI treatment at 2000 revolutions (c).

The data in Table 1 show the effect of suggested individual (HC wing defibrator treatment and LC PFI refining) treatments as well as their combination on the mechanical properties of paper dried without restraint. HC wing defibrator treatment increased the elongation of paper but had

only a minor effect on the tensile strength despite improved bonding between the fibers based on the Scott bond values. The results indicate that PFI refining can also be quite effective in improving the strength and extensibility of freely-dried paper. However, when these treatments applied subsequently, the extent of fiber-fiber bonding was significantly enhanced, which is indicated by the increased paper density and considerably improved toughness. Extensibility of the paper was improved from 4.9 to 8.2 %, as a result of the HC treatment, and to 11.9 % for combined HC and LC treatment. Increase in the extensibility was accompanied with increases in drying shrinkage and tensile strength.

Table 1. The effect of HC wing defibrator (WD) treatment at 40% solids content and 110°C, LC PFI refining at 2000 revolutions and their combination on fiber properties and drainage resistance and on mechanical properties of paper (free drying). TSI – Tensile strength index, TEAI – Tensile energy adsorption index, SB – Scott bond, DS – drying shrinkage

Treatment	Fiber length (mm)	Kink (1/mm)	Curl (%)	SR	WRV (g/g)	Density, kg/m^3	TSI, Nm/g	Breaking strain, %	TEAI kJ/kg	SB, J/m^2	DS %
Reference	2.3	1.5	18.9	12	1.1	512	22.7	4.9	0.8	99.4	3.0
WD	2.0	2.9	27.1	12	1.4	534	28.7	8.2	1.6	298.3	5.1
PFI	2.3	1.5	20.0	19	1.7	589	63.1	8.9	3.3	680.4	5.8
WD+PFI	2.1	1.5	20.2	25	1.7	573	53.7	11.9	3.9	1757	7.4

Standard deviation is less than 5%

Mechanical performance of biopolymer-modified paper

Biopolymer-treated papers were obtained by spraying aqueous biopolymer solutions (only 4 wt % biopolymer mass with respect to dry cellulose fibers). Due to addition of the biopolymers, the grammage of the handsheets was slightly higher than the initial value, in the range of 75−78 g/m^2, which indicates that the biopolymers were adsorbed on the fiber surfaces and were likely to fill the free volume of the web; thus, it was expected that they increased the interfiber contact area and bonding. For example, on Figure 2 cross-section SEM micrographs of the gelatin-treated paper is illustrated, from where it is apparent that despite its surface application, gelatin does not accumulate on the surface of the paper but rather partially penetrates throughout the fiber network.

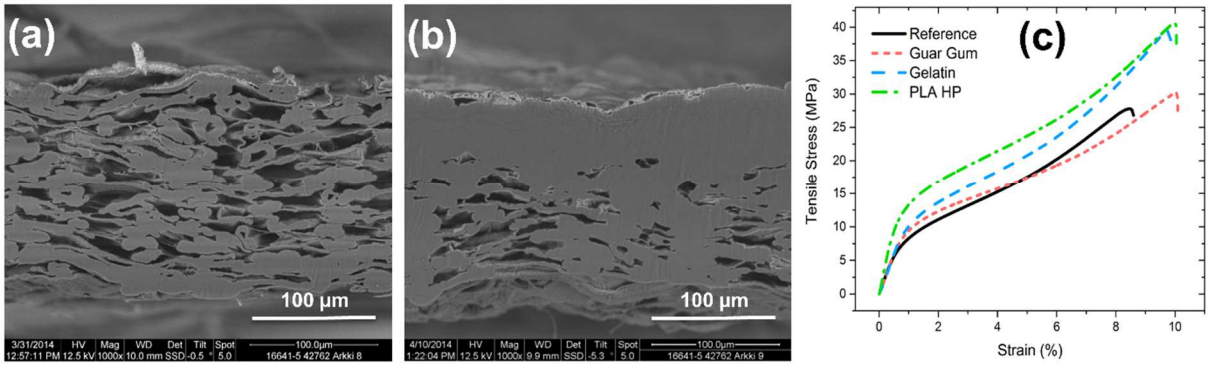


Figure 2. Cross-section SEM micrographs of reference sample (a), gelatin-treated paper (4 wt.% gelatin) (b) and stress-strain curves of biopolymer-treated paper (biopolymer addition amount was 4 wt% with respect to dry fibers) (c).

PLA-treated samples were hot-pressed in order to activate the latex. In order to subject all samples to the same conditions used for PLA-treated systems, therefore, allowing better comparison, all the samples were hot-pressed. (Note: hot-pressing was found to have a negligible effect on the mechanical properties; data not shown.) Activation of latex by hot pressing facilitated spreading of the latex on the fiber surface and, consequently, was assumed to improve the relative bonded area in the network. In fact, the results indicated improved mechanical properties of the sample, while the structural density was not affected (Figure 2c).

Mechanical properties of biopolymer-treated, in-plane compacted paper.

Typical stress−strain curves of the networks modified by in-plane compaction are presented in Figure 3, including measurement in both the machine (compaction) (MD) and cross-machine (CD) directions. *Note:* only randomly oriented papers from a laboratory sheet former were used, and therefore MD and CD refer here to the direction of compaction; i.e., they are not to be confused with the dominant direction of the fibers in the paper network. The most relevant mechanical properties are reported in Table 2, where untreated (non-compacted) reference paper is included for evaluation. To facilitate comparisons, some data were normalized by using the apparent density, i.e., presented as indexed values (tensile, TEA, and stiffness indices). The extent of compaction was followed by shrinkage measurements. The narrow standard deviations associated with the shrinkage values indicate a good reproducibility of this method and also demonstrate the repeatability of the in-plane compaction process.

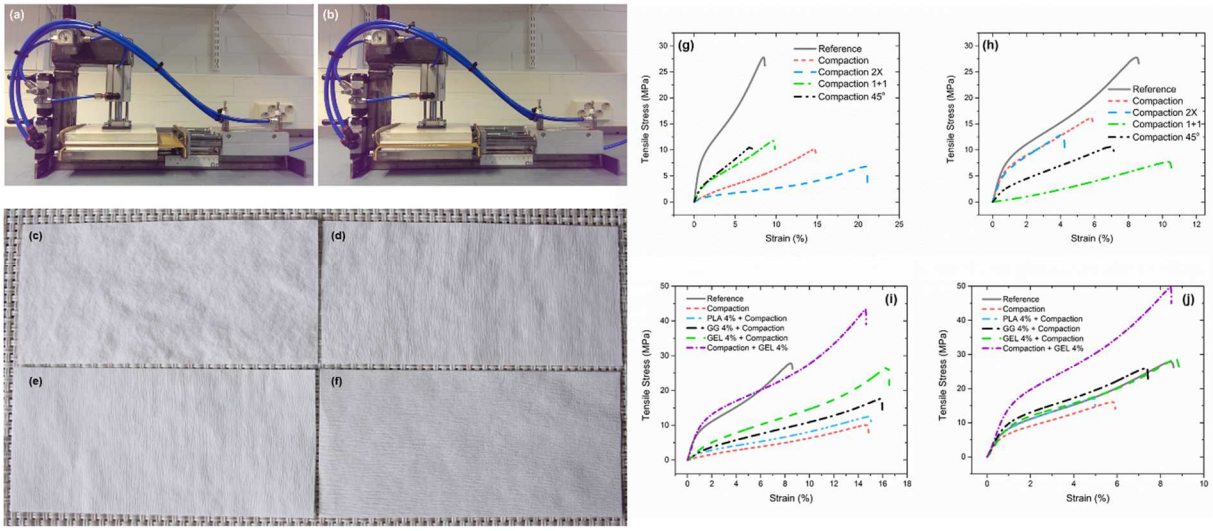


Figure 3. Left: Compaction device shown in operation in the strained (a) and non-strained (b) positions. Structure of unmodified paper (c), compacted once (d) and twice (e) as well as paper compacted in both directions (f) during MD compaction at a rubber recoiling of 13%. Right: Stress−strain curves of in-plane compacted paper in MD without (g) and with biopolymer modification (i) and in CD without (h) and with biopolymer modification (j). “2×” means compaction was performed twice; “1+1” means biaxial compaction was performed, first in MD and then in CD; “45°” means mechanical properties measured at 45° relative to the direction of compaction. Reference: unmodified paper. Biopolymer addition amount was 4 wt% with respect to dry fibers. Note the different scales on the horizontal X-axes for the strain.

As it is apparent from Figure 3, application of in-plane compaction increased the MD strain while the strength and stiffness indices were reduced. The increase in strain and the decrease in tensile strength index became even more pronounced when the compaction was performed twice (“Compaction 2×”). Such treatment resulted in more profound micro-creeped structure, which had a lower load-carrying ability and higher stretch potential due to the increased deformations (Figure 3e). In order to favor a lower anisotropy upon compaction, the operation was performed in both directions (biaxial compaction, also referred to as “Compaction 1+1”). This approach improved the extensibility in both directions while maintaining the strength properties at satisfactory levels. In addition to two-directional compaction, mechanical properties were also measured at 45° relative to the direction of compaction. This was carried out in order to geometrically equalize the contributions of both MD and CD deformations. However, the extensibility from such measurement was higher only for CD.

The effect of PLA latex on the mechanical properties of compacted paper was negligible in MD and somewhat even negative in CD (Figure 3). As can be seen from Table 2, the mechanical properties in MD were almost the same as those for the compacted sample without any polymer treatment. Guar gum (GG), on the other hand, afforded a clear improvement of the mechanical properties of the compacted paper, even in both directions. Compared to

biopolymer-free systems, compaction of GG-containing paper resulted in 13% and 63% increases in MD extensibility and strength, respectively. If measured in the CD direction, the aforementioned properties improved by 23% and 31%, respectively. In-plane compaction of gelatin-treated paper resulted in a significant improvement of the strain to failure and tensile strength, i.e., 20% and 125% increase in MD, respectively. In CD, these properties improved by 60% and 70%. Also, an attempt was made to further reinforce the compacted paper structure, i.e., by introducing gelatin after compaction (sample "Compaction + Gel"). Table 2 indicates that application of gelatin onto in-plane compacted structures further improved the mechanical properties, both in MD and CD (Figure 3i-j). Improvements in paper tensile stiffness of 690% in MD and 50% in CD were noted, respectively. Overall, the results presented point to the fact that in-plane compaction is a powerful technique to improve the extensibility of paper and associated with such treatment deterioration of strength properties could be compensated via application of an aqueous dispersions of biopolymers, applied either before or after compaction.

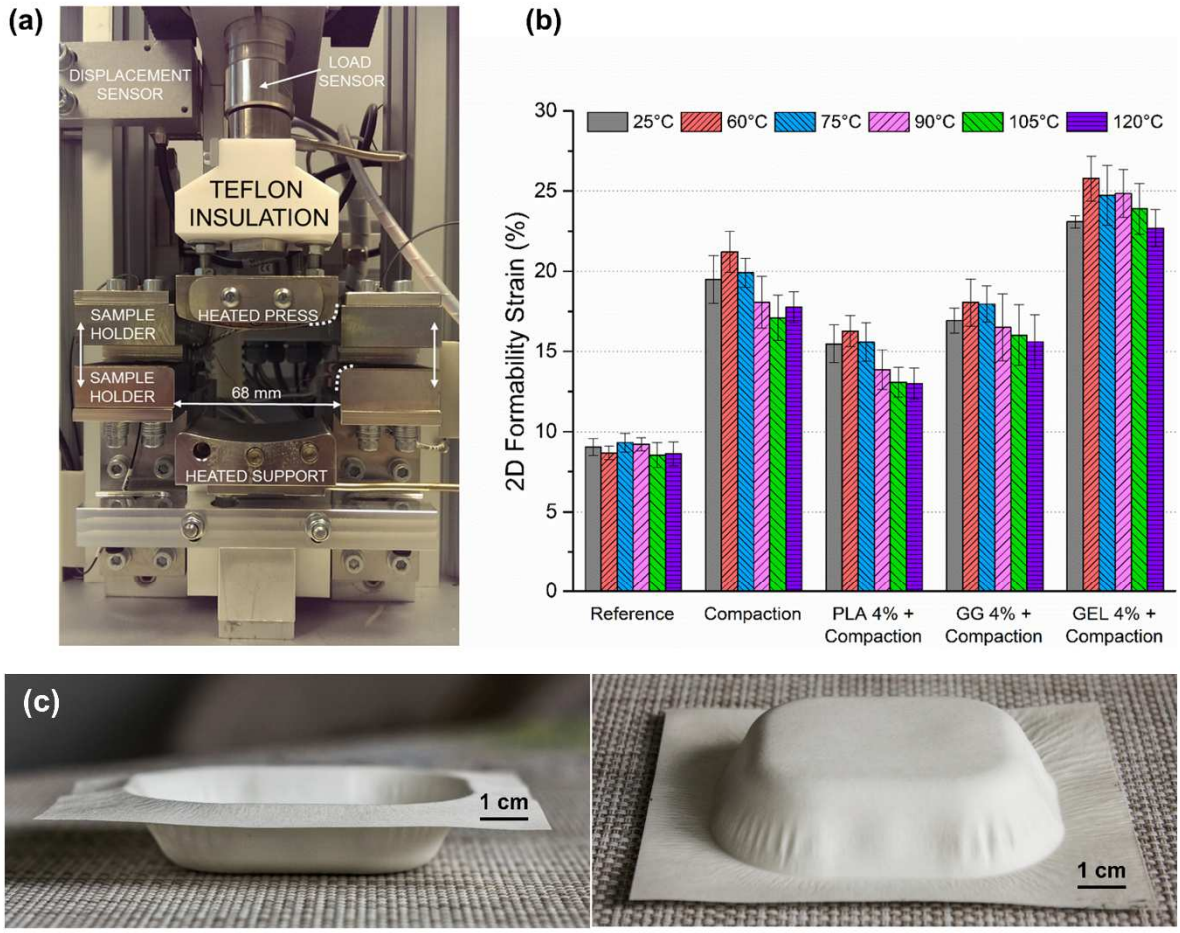
Table 2. Mechanical properties of in-plane compacted paper treated with 4 wt.% of bio-based aqueous dispersions (the abbreviation "Com" is used to indicate "Compacted"). Poly(lactic acid) (PLA) latex and guar gum galactomannan (GG) were added by spraying before compaction. Gelatin (Gel) was introduced either before ("Gel + Com") or after ("Com + Gel") compaction. Biopolymer addition amounted to 4 wt.% with respect to dry fibers. Reference is unmodified paper.

Sample	Apparent density (kg/m^3)	Strain to failure (%)	Shrinkage (%)	Tensile Strength (MPa)	Tensile strength index (Nm/g)	TEA index (J/g)	Tensile stiffness index (kNm/g)	Young's modulus (GPa)
Reference	554	8.5 ± 0.3	4.5 ± 0.2	28.0 ± 0.9	50.4 ± 1.5	2.4 ± 0.1	2.02 ± 0.22	1.11 ± 0.12
Mechanical properties in longitudinal direction (MD)								
Compaction	444	14.0 ± 1.4	11.3 ± 1.1	10.6 ± 1.4	23.8 ± 3.1	1.7 ± 0.2	0.22 ± 0.04	0.10 ± 0.01
PLA + Com	541	14.6 ± 0.5	10.9 ± 0.6	12.4 ± 0.8	22.8 ± 1.6	1.7 ± 0.1	0.43 ± 0.06	0.23 ± 0.03
GG + Com	479	15.9 ± 1.5	10.0 ± 1.2	18.7 ± 1.8	38.9 ± 3.8	3.4 ± 0.5	0.53 ± 0.17	0.25 ± 0.08
Gel + Com	498	16.7 ± 0.9	9.7 ± 0.9	26.7 ± 2.2	53.6 ± 4.3	4.3 ± 0.4	0.63 ± 0.15	0.32 ± 0.07
Com + Gel	640	14.6 ± 0.8	8.3 ± 0.8	43.1 ± 2.4	67.3 ± 3.7	5.4 ± 0.4	1.74 ± 0.33	1.11 ± 0.21
Mechanical properties in lateral direction (CD)								
Compaction	444	5.6 ± 1.2	1.6 ± 0.7	15.9 ± 2.2	35.6 ± 4.9	1.3 ± 0.3	2.22 ± 0.49	0.99 ± 0.22
PLA + Com	541	4.9 ± 0.4	-0.5 ± 0.3	17.9 ± 1.1	33.8 ± 2.1	1.1 ± 0.1	3.00 ± 0.10	1.63 ± 0.06
GG + Com	479	6.9 ± 0.9	1.3 ± 0.5	24.6 ± 2.8	46.6 ± 4.4	2.0 ± 0.3	2.2 ± 0.23	1.16 ± 0.12
Gel + Com	498	8.9 ± 1.1	1.5 ± 0.6	29.6 ± 2.8	59.7 ± 4.7	3.1 ± 0.5	2.24 ± 0.54	1.11 ± 0.27
Com + Gel	640	8.3 ± 0.5	2.1 ± 0.3	52.2 ± 3.2	81.1 ± 4.9	3.8 ± 0.2	3.40 ± 0.46	2.19 ± 0.29

± values correspond to standard deviations from 10 replicates. Shrinkage denotes to the dimensional changes induced by the drying shrinkage and compaction. Reference sample was moisturized to 60% dry solids content and freely dried.

2D formability and 3D structures by press forming of biopolymer-modified, in-plane compacted samples.

A 2D formability unit was employed to simulate the process conditions of thermoforming. The formability strains of modified paper samples were examined as a function of the forming temperatures. As evident from Figure 4, compaction was an effective strategy to improve the paper formability. A 2-fold increase in formability strain was observed (from ~9% to ~20%). PLA modification, however, was found to limit the formability strain of compacted paper. Modification of compacted paper with guar gum did not improve the formability strain, which was surprising considering the previously observed impact of GG on the mechanical properties of the treated paper. Interestingly, the application of gelatin significantly improved the formability strain of compacted paper; values up to 3-fold higher than those of the non-compacted reference sample were recorded (from ~9% to ~27%). It is also worth to mention that for most of the samples, 60 °C appears to be the temperature at which the maximum strain is achieved. Gelatin treatment was combined with paper in-plane compaction to produce advanced 3D shapes by direct press forming, which eliminated the pre-creasing step. It was found that the paper formability in fixed blank forming processes was mainly governed by the extensibility and tensile strength of paper. Therefore, the performance of the material was assessed by measuring the peak depth of rectangular trays that were fabricated with the systems (Figure 4). It is evident from Figure 4 that the highest peak depths and corresponding strains were achieved by using the biaxial compaction, 1+1 method. Moreover, the samples containing gelatin displayed the highest potential for 3D structures and impressive peak depth, and strain values were recorded. The optimal processing temperature and humidity were found to be 120 °C and 75% RH (moisture content of ~9%), respectively. In addition, the developed 3D shapes (trays) presented smooth edges, Figure 4, which indicated that the material is able to sustain vacuum sealing or deposition of an additional barrier layer as a post processing steps toward preparation of packaging materials. Furthermore, the processability of gelatin-treated, compacted paper is expected to allow other types of advanced forming processes [16,17].



Test point	120°C	160°C	120°C	160°C
	Average peak depth, (mm)		Corresponding strain (%)	
Compaction 2x	14	13	16.4	14.8
Compaction 1x	16	14	19.9	16.4
Compaction 1+1	17.5	16	22.6	19.9
Gel 4% + Compaction 2x	18	19	23.5	25.3
Gel 4% + Compaction 1x	20	18.5	27.1	24.4
Gel 4% + Compaction 1+1	21	20	28.9	27.1

Figure 4. Top: 2D formability tests (a) and 2D formability strain of modified papers at different temperatures (b). Reference: unmodified paper. Poly(lactic acid) (PLA) latex, guar gum galactomannan (GG) and gelatin (GEL) were added by spraying before compaction. Biopolymer addition amount was 4 wt.% with respect to dry fibers. Samples were conditioned overnight at 75% RH. Bottom: Photo of samples manufactured by the press forming method with a fixed blank by using the sample “Gel 4% + Compaction 1+1” (c). The table shows average peak depths and corresponding material strain of produced rectangular trays as a function of different in-plane compaction methods. 2X: compaction was performed twice; 1+1: compaction was performed in both directions, first in MD followed by compaction in CD. Paper samples had a basis weight ~220 g/m2 and were conditioned overnight at 75% RH. The female mould temperature during forming was 120°C and 160°C.

Combined approach for improved 3D formability of paper.

A combined approach to improve paper extensibility is proposed, as illustrated in Figure 5. First, wood fibers can be processed with a judicious combination of low and high consistency treatments under moderate temperatures. After forming the network, a subsequent in-plane compaction can be conducted. It is expected that the tensile strength and stiffness are significantly reduced after this process. Following, the compacted paper can be treated with water-soluble biopolymers (e.g., gelatin) and dried without restraint. Finally, a proper softening of polymers during the forming step can be promoted by controlling the moisture and temperature, depending on the type of forming unit. The proposed approach contains a certain degree of flexibility; i.e., some of the treatment steps can be modified, interchanged, or even replaced. For example, water-soluble polymers may be replaced by thermoplastics. Moreover, the proposed approach to improve fiber network extensibility/formability can be implemented within the existing papermaking environments without addition of major capital costs.

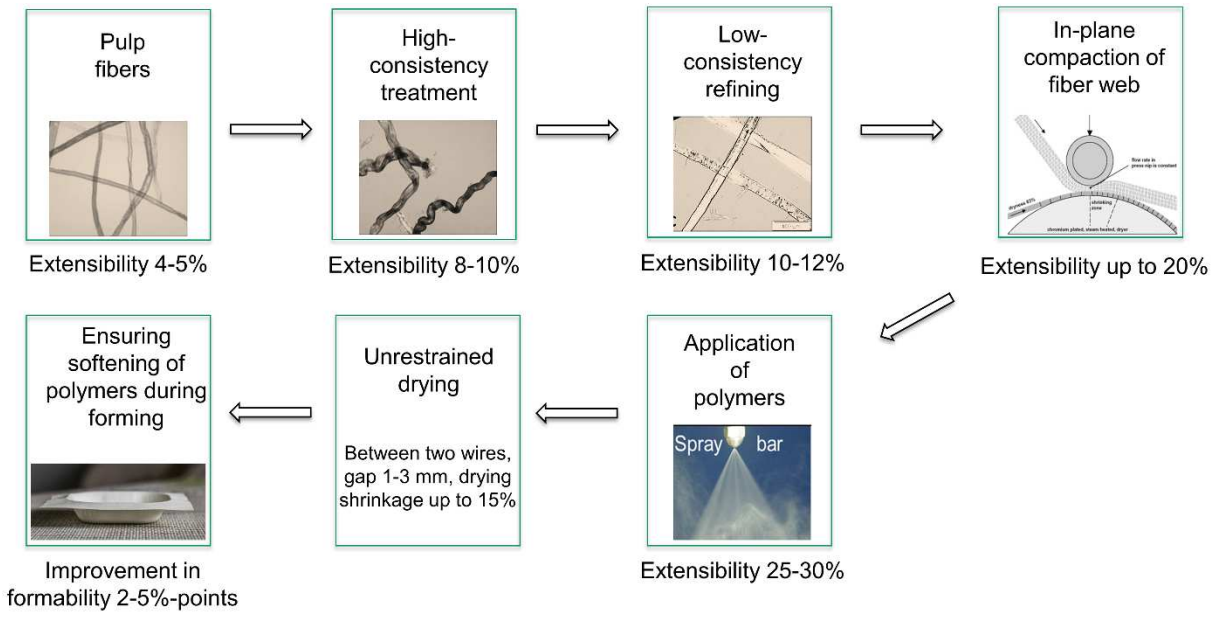


Figure 5. Proposed approach to improve paper extensibility/formability via combined mechanical and polymer treatments.

CONCLUSIONS

We propose a combination of fiber mechanical treatment with in-plane compression of paper and biopolymer treatment for the preparation of extensible/tough fiber networks. First, extensibility of paper was improved by modifying the fiber properties, fiber bonding and fiber network via performing combined high- and low-consistency mechanical treatment without deterioration of drainage of paper. In-plane compaction effectively contributed to network

extensibility in the direction of compression. However, it led to a significant reduction of tensile strength and stiffness. Application of water-soluble polymers, guar gum and gelatin, resulted in further improvement of paper extensibility and tensile strength. For instance, the extensibility of paper increased from 8.5% for untreated sample to 14.0% for the compacted paper and 16.7% for the compacted paper with the addition of gelatin; likewise, the tensile strength index changed from ~50 to 24 N·m/g and became ~54 N·m/g for the compacted paper with the addition of gelatin. The 2D formability strain of compacted paper upon gelatin addition reached values as high as 27%. Finally, press forming experiments of gelatin-loaded, compacted paper evidenced 21 mm deep rectangular trays prepared with the fixed blank process, which corresponds to unprecedented material extensibility of ~29%. The proposed approach provides an attractive platform for the preparation of advanced 3D shapes using fiber-based, biodegradable materials.

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