Lyocell Fibers from Pulps with High Mannan and Xylan Content – Part 2: Mechanical Properties

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Abstract

For sustainability reason, it is beneficial to utilize additional wood components like hemicelluloses for the production of cellulosic man-made fibers. In this study, we showed that mannan and xylan in softwood kraft pulps could be used successfully in the lyocell process at mill scale to spin holocellulosic fibers. Mannan was preserved throughout the process up to 96.6% while xylan was degraded more readily. Overall, fiber strength properties were in the range of market fibers. Dry elongation – reaching 11.7 to 14.3% - was even raised while dry tenacity – reaching 29 to 37cN/tex – was only slightly deteriorated by low molecular weight polymers. Wet elongation, in contrast, was clearly favored by a high share of long polymer chains. Overall, an indication was found that softwood-xylan showed to be a beneficial hemicellulose in lyocell fibers within the limits of our study.

Keywords: *kraft pulp, mannan, xylan, lyocell fiber, strength properties*

Introduction

About 20 years ago the US and European apparel industry was moving towards Asia due to significant cost advantages. But times are changing. 80% of the international chief procurement officers (CPOs) of the fashion industry now name speed-to-market and in-season-reactivity as the top priorities of their business *(Andersson et al. 2018)*. They have to meet customer desires of circular value chains with high sustainability and fast fashion at the same time. The pressure on profitability is enormous. The market is based on the pull-model, where products are produced in smaller charges and delivered on demand, and no longer on the push-model. Nearshoring and new delivery models are the key issues. Even if labor costs in China and Bangladesh are still lower compared to Western Europe and the US, the gap has decreased during the past decade and will continue to equalize. Due to savings in freight and duties, production sites are already now moving to Mexico, Turkey or Morocco. E.g., the production costs of denim for the European market can even be 3% lower when shifted from China to Turkey *(Andersson et al. 2018)*.

At the same time, a groundbreaking technology development for the sewing industry takes place: automated sewing technology using robotics is one example. Automating sewing is a problem by the nature of the fabric itself. These material problems like flexibility and stretchability have been overcome by a research group from Georgia Tech's Advanced Technology Development Center guided by Stephen Lang Dickerson *(US9085081B2, WO2008112842A2, US8573145B2, US2015122164A1)*. The new SewBot® technology can reduce production costs and the output will increase. As an example, only three to five workers can run 21 automated sewing lines. The production costs for a T-shirt made in the US are said to become comparable to those produced in Bangladesh. Additionally, the textile industry can realize on-demand replenishment easily.

Nearshoring and automation are two important factors for a circular economy. Sustainable raw material is the third and at least as important as the other two. According to the market volume, cellulose is the choice of renewable raw material. Certified wood or even textile waste produced in a biorefinery can provide dissolving pulp that is subsequently processed in the lyocell process to yield biodegradable and sustainable products. Lyocell fibers have always been an almost luxury fiber product with special properties. Why shouldn't we produce a new generation of fibers more suitable for the mass-market that will meet the requirements of circular value chain? This mill-study suggests an approach by using a bigger part of the raw material wood, not only cellulose but also hemicelluloses, creating holo-cellulosic man-made fibers.

Experimental

Material

Four different softwood market pulps were chosen for the production of lyocell fibers. Market pulps 1, 2 and 3 with their increased mannan and xylan content were produced by modified kraft pulping with subsequent ECF-bleaching. Pulp 1 and 3 originated from the same mill. The raw materials used were *Pinus ssp*.. Market pulp 4 was a standard dissolving pulp for lyocell fiber production with a low hemicellulose content made from *Picea abies*. The pulping process applied was the acid sulfite process combined with TCF bleaching.

All pulps were processed in the lyocell process at mill scale using NMMO as a solvent without major changes in production parameters. For this study, non-wovens fibers with a titer of about 1.8dtex have been chosen.

Methods

All analyses of pulp and fibers were performed according to Tappi-, ISO- and SCAN-standards.

The determination of neutral sugar monomers was performed by anion exchange chromatography (AEC) with pulsed amperometric detection (PAD) after a total hydrolysis with H_2SO_4 according to *Sixta et al. (2001)*.

Table 1: *Pulp properties of the hemicellulose rich softwood kraft pulps in comparison to a sulfite dissolving pulp.*

Analysis	Unit	Market pulp 1	Market pulp 2	Market pulp 3	Market pulp 4 - Reference
Wood		*Pinus ssp.*	*Pinus ssp.*	*Pinus ssp.*	*Picea abies*
Pulping process		Modified Kraft	Modified Kraft	Kraft	Sulfite
Glucan	%	84.1	85.7	82.2	96.0
Xylan	%	7.3	6.9	6.9	1.4
Mannan	%	5.5	5.1	5.7	1.3
Xylan/Mannan ratio	-	1.33	1.35	1.21	1.08
Arabinan	%	0.3	0.2	0.3	<0.1
Rhamnan	%	<0.1	<0.1	<0.1	<0.1
Galactan	%	0.2	0.2	0.2	<0.1
Sum of hemicelluloses	%	13.3	12.4	13.1	2.7
Brightness	%	90.4	89.1	91.6	94.2
Viscosity	mL/g	345	380	370	410
Kappa No.	-	0.3	0.7	0.3	0.1
R10	%	84.6	86.3	83.7	87.6
R18	%	88.2	89.8	87.4	94.5
COOH	µmol/g	40.0	33.5	44.1	25.2
Copper No	%	1.1	0.5	1.4	1.3
Acetone extractives	%	0.02	0.04	0.03	0.06
Ash 850°C	%	0.05	0.05	0.04	0.05
Fe	mg/kg	7.8	1.4	1.60	1.3

Results and Discussion

The three commercial softwood kraft pulps 1, 2 and 3 were not considered as dissolving pulps and so far have not been used for the lyocell process in plant scale. In general, they are used for other applications like e.g. fluff. For comparison, a sulfite dissolving pulp from softwood was added (market pulp 4). Pulp properties are described in detail in table 1. All softwood pulps showed the same level of viscosity required for application in the lyocell process. They differed in hemicellulose content and subsequently R18 and in the ratio of xylan to mannan. All other specifications like inorganics or extractive content satisfied the expectations of the demanding process.

The use of softwood pulps gave the advantage of observing effects from both hemicelluloses mannan and xylan, while hardwood as the raw material only gives the chance of monitoring mainly xylan. In this study, even a differentiation between both hemicelluloses was possible. A relative hemicellulose yield could be calculated by setting the cellulose yield to 100%. The results showed that xylan was more readily degraded than mannan during processing. This could be observed by lower relative xylan yields compared to relative mannan yields (see table 2). Even the reference pulp with its very low hemicellulose concentration, market pulp 4, showed the same tendency. The high relative mannan yield was observed for all pulps tested.

It is well known that mannan more readily associates with cellulose, which may lead to a stabilization of the polymer. *Corbett and Kidd (1958*) investigated the degradation behavior of mannan and xylan in akaline medium with 25 *N* NaOH at 100°C, which may give an indication for the lyocell process. Xylan was more readily removed from the pulp than mannan as observed in our study. *Ono et al. (2018)* suggested a more detailed hypothesis for mannan reaction mechanisms: The formation of non-phenolic lignin/polysaccharide α-ether bond structures is more likely for glucomannan than for xylan because of the steric hindrance of the C6-OH-group. The reaction occurs preferentially at high lignin concentration under acidic conditions at high temperature. This is the case during prehydrolysis before kraft pulping or during sulfite pulping. These bonds are subsequently cleaved under alkaline conditions via quinone methide formation in subsequent alkaline process steps like kraft pulping or oxygen delignification. In contrast, if the preceding acidic treatment is missing, the cellulose-mannan-structure can be assumed to result a more stable and more branched structure. This was the case for market pulps 1 to 3, and this may lead to a better incorporation of mannan into lyocell fibers compared to xylan. The mannan was obviously not much degraded due to

Table 2: *Lyocell fiber properties produced from hemicellulose rich softwood kraft pulps in comparison to a sulfite dissolving pulp.*

Analysis	Unit	Fiber 1	Fiber 2	Fiber 3	Fiber 4
Pulp used		Market pulp 1	Market pulp 2	Market pulp 3	Market pulp 4 - Reference
Titer	dtex	1.9	1.9	1.8	1.3
Tenacity dry	cN/tex	29.2	31.1	37.4	34.5
Elongation dry	%	11.9	11.7	14.3	12.6
Tenacity wet	cN/tex	24.9	28.7	32.0	29.3
Elongation wet	%	17.0	18.6	17.0	14.8
Tenacity wet/Tenacity dry	-	0.85	0.93	0.85	0.85
Elongation wet/Elongation dry	-	1.43	1.59	1.19	1.18
Xylan in fiber	%	6.8	5.9	7.1	1.4
Mannan in fiber	%	5.3	4.7	5.4	1.1
Sum of hemicelluloses	%	12.1	10.6	12.5	2.5
Xylan/Mannan in fiber	-	1.28	1.26	1.31	1.27
Xylan yield (rel.)	%	93.5	85.7	n. d.	85.7
Mannan yield (rel.)	%	96.6	92.8	95.4	87.0

Table 3: *Molecular weight distribution of hemicellulose rich lyocell fibers.*

Analysis	Unit	Fiber 1	Fiber 2	Fiber 3	Fiber 4
Mn	kg/mol	51	67	67	41
Mw	kg/mol	382	469	160	156
PDI	-	7.5	7.1	2.4	3.8
<DP80	%	5.2	3.3	2.5	6.2
<DP100	%	7.1	4.7	3.6	7.9
>DP2000	%	28.6	33.1	11.0	12.3

the mechanism described above while the xylan was degraded and partly dissolved in the spinning bath.

The mechanical properties of the resulting lyocell fibers were analyzed (see table 2). The tenacity decreased when pulp with high hemicellulose content was used (see figure 1). The difference of 8.2cN/dtex for a titer of 1.9dtex was significant. Despite high contents of hemicellulose of 10.6 to 12.5%. All the same, the strength data were still at the high level known for lyocell fibers. Although fiber 4 showed a much lower titer of 1.3dtex, it provides an indication of properties of conventional lyocell market fibers. These findings match exactly with the literature *(Nypelö et al. (2018), Ma et al. (2017), Sixta et al. 2006, Chen et al. (2015), Zhang and Tong (2007), Zhang et al. (2008)). Nypelö et al. (2018)* correlated the strength reduction with the lower cellulose content. Lower cellulose content leads to a decrease in polymer orientation, and therefore a loss in strength.

In our case, the cellulose content was decreased by increased hemicellulose content (see figure 1). Even the lyocell fiber produced from low hemicellulose sulfite pulp fitted into the scheme regarding the correlation of sum of hemicellulose and tenacity, but not regarding the share of low MW polymers. Obviously, this was due to the lower chain length of hemicelluloses and to their chemical structure, which may have hindered the formation of more oriented areas in the final fiber (see table 3). Our findings emphasize the explanation of *Nypelö et al. (2018)*.

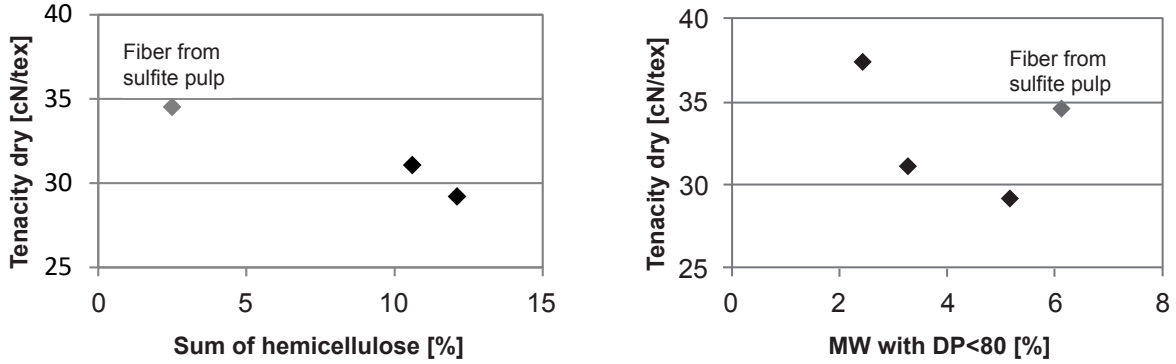

Figure 1: *Correlation of dry fiber strength with hemicellulose contents and low MW polymers of the lyocell fibers.*

For the lyocell process with NMMO, *Fink et al. (2004)* stated that there is no memory with respect to crystalline order of the starting pulp and that different pulp types and morphologies do not significantly alter the supramolecular fiber structure. They attributed variations in fiber strength to the influence of different DPs of the polymers although they used unbleached hardwood organosolv pulps with increased lignin and xylan content. No significant changes in fiber mechanical properties were observed assuming nearly equal supramolecular order and orientation.

In our study, there was a clear correlation between fiber tenacity and pulp viscosity determined by the SCAN-method, but not with Mw of the fibers determined from molecular weight distribution (see table 2 and 3). Overall, the dry tenacity was a function of cellulose chain length and cellulose content, and it was still at a high level despite a hemicellulose content of up to 12.5%.

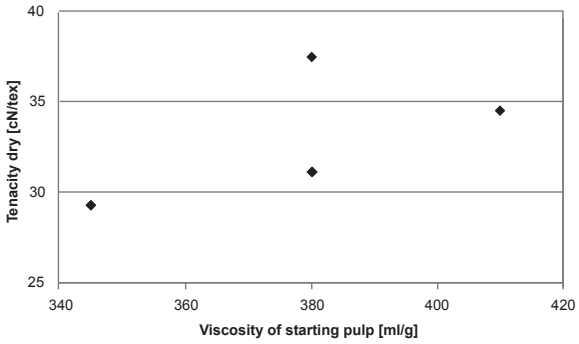

Figure 2: *Influence of pulp viscosity on fiber tenacity.*

The wet tenacity decreased with increasing hemicellulose content. Obviously, the water uptake was higher for lyocell fibers with higher hemicellulose content due to a higher content of accessible OH-groups originating from hemicelluloses. This fact resulted in lower wet tenacity.

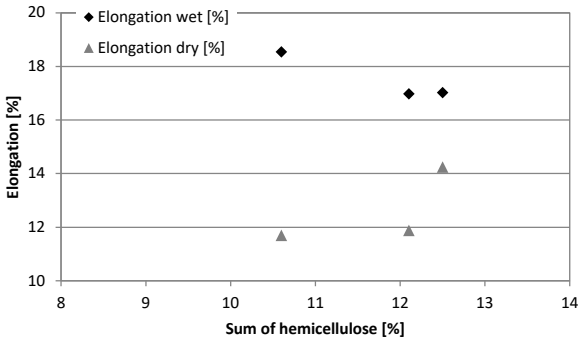

Figure 3: *Effects of hemicellulose contents of lyocell fibers on wet and dry elongation.*

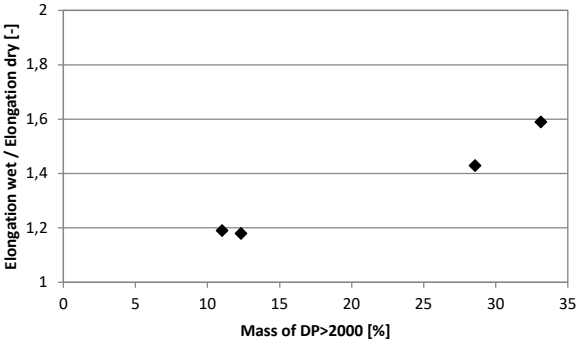

Figure 4: *Effects of high molecular weight polymers of lyocell fibers on wet to dry elongation.*

Within the range of this study, dry elongation was favored by higher hemicellulose content (see figure 3). Although *Nypelö et al. (2018)* described the elongation of lyocell fibers as almost constant using a lyocell process with an ionic liquid as solvent. Contradictory, wet elongation decreased with higher hemicellulose contents. This effect showed a more complex role of hemicelluloses in lyocell fiber strength buildup.

In general, wet fiber properties are strongly depending on the fiber structure. The more porous core swells stronger than the denser skin. Therefore, the skin hinders swelling of the core and thus helps for better wet properties. *Nypelö et al. (2018)* observed no skin for xylan and lignin enriched Ioncel F fibers. The core-shell-organization was revoked for lignin and xylan rich lyocell fibers. We described the same for our hemicellulose rich lyocell fibers *(Schild et al. (2019))*. This should have a negative effect on wet elongation. There may also be a second more prominent effect on wet elongation. Lyocell fibers have a high orientation and therefore a high dimensional stability, which results in a high wet modulus, which is observed from figure 3. Both properties were altered when we raised the concentration of hemicelluloses in the fibers. The skin was diminished and the orientation of the polymers was interfered. This may also explain lowered wet properties for fibers with higher hemicellulose content (see figure 3).

While dry strength properties increased with a lower part of low MW polymers wet elongation was favored by a high share of long chain polymers, here measured as DP>2000 (see figure 4). Fibers 1 and 2 showed a lower dry elongation due to the high amount of low MW polymers. But for wet elongation their values increased over proportionally due to their high share of high MW polymers (see table 2 and 3). The long polymer chains were presumably bridging between structure elements resulting in better elasticity in the wet state.

Nevertheless, a differentiation between xylan and mannan as natural wood polymers is of main interest. In this study, a higher share of xylan compared to mannan favored fiber strength properties, both dry fiber elongation and dry fiber tenacity as can be seen from figures 5 and 6. The fiber tenacity could be raised from about 30cN/tex to 37.4cN/tex. Elongation was increased significantly from 11.9% to 14.3% by only raising the ratio of xylan to mannan in the fiber. The effects on fiber properties were clearly recognizable taking into account that this study was not a single lab experiment, but it comprises mill trails over several days.

It is well known from polymer science, that short chain polymers have a positive effect on elasticity and give rise to higher elongation at break. At the same time, they affect tenacity negatively. Short chains do not participate in stiffness and buildup of strength. Mannan has the longer chain length of both hemicelluloses and associates more readily with cellulose. Therefore, it should be favorable for fiber formation

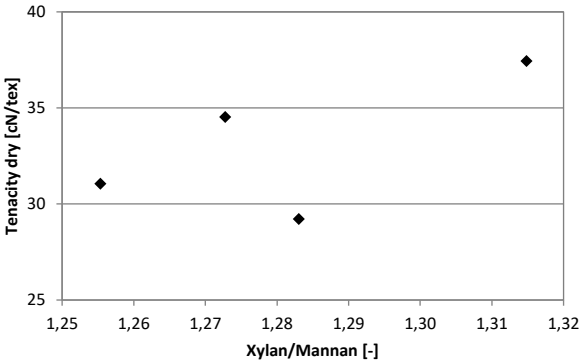

Figure 5: *Influence of xylan to mannan ratio on tenacity of dry lyocell fibers.*

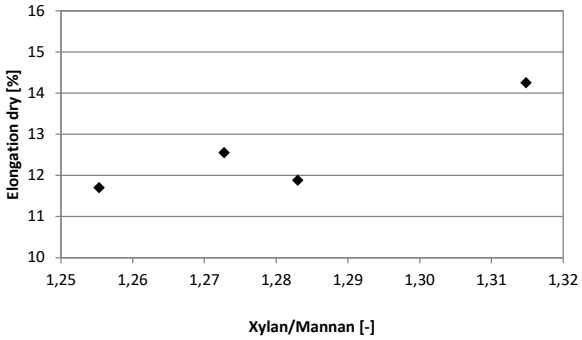

Figure 6: *Influence of xylan to mannan ratio on elongation of dry lyocell fibers.*

and strength properties. But the opposite was the case for our study. A higher share of xylan in the lyocell fibers showed a beneficial effect on fiber strength properties. It even seamed to compensate for negative impacts of mannan on elasticity.

The results of *Park et al. (2020)* indicated the same unexpected correlation for hardwood xylan and tensile strength. They used the hardwood *Liriodendron tulipifera* as raw material. Therefore, the predominant hemicellulose was xylan. Results showed that in the case of wet-spun cellulose nanofibers hardwood-xylan could increase the tensile strength.

Berglund et al. (2020) conducted more fundamental research on the role of softwood hemicelluloses in combination with cellulose hydrogels. They treated bacterial cellulose with galactoglucomannan (GGM) and arabino-4-*O*-methylglucuronoxylan (AGX) isolated from spruce wood. GGM interacted closely with cellulose, especially after alkaline treatment. This phenomenon facilitated cellulose crystallization and therefore, the overall crystallinity increased slightly. AGX, in contrast, hindered the packing of cellulose chains and by that reduced the crystallinity. This gave rise to a dramatic increase of elongation at break under tension. The purpose of this basic research by *Berglund et al.* was to elucidate the cell wall 2 (S2) and therefore, did not cover the process of fiber spinning. Nevertheless, this study explained two effects found in our mill trails: first, the loss of crystallinity for the lyocell fibers with high xylan content as published in *Schild et al. (2019)*; second, the increase of elasticity due to a higher xylan content. Still there is no explanation for the increase in fiber tensile strength by xylan in regenerated cellulosic fibers as described in our study and by *Park et al. (2020)*.

Although fundamental know how of hemicellulose structures and functions in native wood cell walls and regenerated fibers is available, an explanation of the role of different hemicelluloses during fiber forming seems not that simple. More investigations on this topic are important to generate a valid hypothesis.

Conclusions

Softwood kraft pulps with increased xylan and mannan contents could be demonstrated to be a promising new raw material for the production of holocellulosic lyocell fibers. Using additional wood polymers like hemicelluloses would increase resource efficiency and sustainability. Beneficial aspects of these holocellulosic fibers dominate since the overall yield will be higher at fiber strength levels comparable to conventional market fibers, and the chemical consumption during pulping will be lower. Therefore, the proposed new fiber type will be of significant economic interest. Production trials at industrial scale showed a realistic way of completion. Prolonged production trials are inevitable to study the impacts of hemicelluloses on closed process loops and recovery.

Nevertheless, lab investigations may be of interest for a better understanding of the roles of the different hemicelluloses xylan and mannan in fiber forming and their impacts on fiber properties.

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