Use of mechanically ground lignocellulosic native fines (LF) in the all-cellulosic composite filaments: fines properties and plasticizers

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Abstract The influence of the physical and colloidal properties of W-stone ground lignocellulose native fines (LF) on the properties of lignocellulosic composite filaments was investigated. W-stone ground LF is a low-cost material exhibiting a microfibrillar structure with the chemical structure of native wood. The physical properties of manufactured LFs were investigated by utilising SEM imaging, turbidity measurements and image-based particle analysis using a Kajaani fibre analyser. The properties of LFs were varied by adjusting the process energy input that altered the produced material's particle size and shape and subsequent fractionation with a wire. The reduction in particle size was observed to increase the colloidal stability of produced LFs, but no significant changes in the chemical profile of the LFs were observed. The effect of the properties of LF on the manufacture of composite filaments with

carboxymethyl cellulose (CMC) was studied by using a dry-jet wet spinning approach. The smaller particle size had a positive effect on the mechanical properties of composite filaments (tenacity increased from 5.5 to up to 7.6 cN/tex). The compatibility of different plasticisers with LF–CMC composite filaments was also studied. It was observed that the number of free hydroxyls per a monomer unit of the plasticiser had a positive correlation with the plasticisation effect in the LF–CMC composite filaments. Regenerated cellulose filaments are often rather expensive to be used in many applications such as composites. The investigated filaments could thus be used in low-cost applications requiring a fully biodegradable material profile. Here, the presence of lignin may increase the structural compatibility of the produced matrix.

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Graphical abstract

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Introduction

Global awareness of global warming has increased the motivation and need to develop carbon neutral materials in order to decrease the use of fossil-based materials (Schlamadinger and Marland 1996). Ligno-cellulose materials are likely to play an increasing role in solving this issue since these materials are produced by nature via photosynthesis. Photosynthesis is nature's tool for recycling carbon dioxide (Halmann and Steinberg 1999; Ragauskas et al. 2006). Moreover, lignocellulose is an extremely flexible raw material because of its easy physical and chemical processability, permitting the manufacture of a wide

range of applications such as regenerated polymeric structures, cellulose nanofibril (CNF) based films, papers and boards, and timber materials.

Wood itself is a composite material comprising mainly cellulose (40–45%), hemicellulose (25–35%) and lignin (20–30%) in an oriented manner (Sjöström 1993; Alen 2000). The disintegration of wood cell walls, via mechanical or chemical pulping, is required when wood fibres are utilised in paper and board applications. The main difference between the two disintegration strategies is in the utilisation of the intercellular lignin. In chemical pulping, lignin is removed and usually incinerated for energy production whereas, in mechanical disintegration, lignin remains on the surface of the fibres (Sixta 2006). It should be noted that mechanical pulping methods are not capable of disintegrating intact fibres from the cell wall; fibres are generally broken down at some level and the resulting furnish includes a fraction of small particles known as “fines” (McDonald et al. 2004).

Recently, the reduction in particle size of wood-based materials well below cell level has attracted increasing interest. Such micro and nanomaterials (also called “cellulose nanofibrils”, CNF) have a very high specific surface area and can be applied to many high-tech applications including solid films, aerogels and filaments (Klemm et al. 2011). This further disintegration of the wood cell wall can be carried out using extensive mechanical treatment with or without chemical pre-treatments (Moon et al. 2011). However, CNF is usually made from chemically-pulped fibres, in which the lignin has been removed from the middle lamellae, since most CNF manufacturing processes do not tolerate a high lignin content (Spence et al. 2010; Rojo et al. 2015). Lignin has many interesting properties and is currently being researched intensively for new areas of application (Azadi et al. 2013). Lignin (like wood) is a hydrophilic material (Mantanis and Young 1997; Notley and Norgren 2010) that binds proteins (Leskinen et al. 2017), and has a compatibilising effect on composites (Chirayil et al. 2014; Leskinen et al. 2017).

Recently, a W-stone grinding method, which is a low-cost approach to producing fine lignin containing fibrillated cellulose material directly from wood and which retains all the chemical components of wood, was introduced (Saharinen et al. 2016b). W-stone grinding is based on the perpendicular grinding of native wood with a W-shaped rotating stone in water (Saharinen et al. 2016a). In this method, cellulose micromaterial is released via a strong shear force resulting from the frictional forces under elevated temperature. The properties of the manufactured lignocellulosic native fines (LF) are dependent on the processing conditions and differ significantly from pulp fibres, and may reach the LF yield up to 90% (Brodin and Theliander 2013; Heinemann et al. 2016). Typically, the produced material resembles pulp fines with an overall structure on a micrometre scale and a fine structure on a nanometre scale. (Pulp fines refers to particles that can pass through a 200 mesh screen with an aperture of 76 μm —Tappi Testing Method T 261 pm-80). In the grinding process, mechanical forces disintegrate the lignin from the middle lamellae; it is then spread over the surface of the fine material. This is one reason why mechanically ground fines have been reported to have a limited bonding ability (Retulainen et al. 1998; Kangas and Kleen 2004; Vainio and Paulapuro 2007). The use of lignin

and lignocellulosic materials in composite applications has been subject to extensive study due to the compatibilizing effect of lignin between the cellulose and polymeric matrices (Thakur et al. 2014).

Cellulose materials have typically low elongation and high strength properties because of the strong hydrogen bonding patterning between cellulose chains (Gardner and Tajvidi 2016). This may be a problem in many applications. Thus, additives (softeners, plasticisers) have typically been used to improve the flexibility and workability of the material by preventing the internal bonding of the material (Wypych 2004; Vieira et al. 2011). Plasticisers replace cellulose–cellulose hydrogen bonding with cellulose–plasticiser–cellulose hydrogen bonding that permits the interfaces to slide under tension. (Thus, “bond” has a broad meaning below—not only does it refer to hydrogen bonds between lignocellulosic surfaces, but to any mechanical link between lignocellulosic particles.)

We introduced the utilisation of W-stone ground LF in lignocellulosic composite filaments with carboxymethyl cellulose (CMC) and aluminium crosslinking in Orelma et al. (2017). In this study, we continued this investigation by varying the energy input in grinding and subsequent LF fractionation and studied its effect on the physical and colloidal properties of LFs. Our aim was to investigate how the properties of LF influence the performance of LF–CMC filaments. The secondary goal was to investigate the plasticising of the formed filament by varying the free hydroxyl numbers of monomers of the plasticisers and studying their effect on the plasticisation of the produced LF–CMC composite filaments. The observed behaviours give an indication of the performance and utilisation of the mechanically ground lignocellulosic fines in all-lignocellulosic composite materials. The low cost LF based composite filaments may find applications e.g. in biodegradable composites.

Experimental

Materials

The raw material of lignocellulosic native fines (LF) comprised debarked spruce softwood obtained from Espoo, Finland. Carboxymethyl cellulose (CMC,

degree of substitution (DS) of 0.7 and molecular weight of 700 kDa) and aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$) were obtained from Sigma Aldrich (Finland). As plasticisers, we used methyl groups containing triacetin and hydroxyl groups containing ethylene glycol (melting point $-12.9\text{ }^\circ\text{C}$), glycerol (mp. $17.8\text{ }^\circ\text{C}$), and sorbitol (mp. $95\text{ }^\circ\text{C}$) (Fig. 1). The molecular weights and the number of available hydroxyls of these molecules vary. All other chemicals used were laboratory grade and were used as received.

W-stone grinding of LF

The lignocellulosic native fines (LF) were produced by utilising a custom-made W-stone grinder at VTT in accordance with the procedure presented earlier (Saharinen et al. 2016b). The custom grinder comprises a special grinding stone with a serrated grinding surface. The grinding setup was identical to the one used in our previous study (Orelma et al. 2017). The grinding conditions and sample codings are presented in Table 1. Prior to the milling, the logs were manually debarked. The dry matter content of wood was approximately constant, 45%, in all grinding trials. The diameter and width of the stone were 30 cm and 5 cm, respectively. Grinding was carried out by initially cutting a log into smaller sections (dimensions $34 \times 34\text{ mm}^2$). The wood blocks were then pressed one by one to make contact with the grinding stone. Two specific energy input levels were used: 2.6 and 4.8 kWh/kg. The stone was sprinkled with shower water at a temperature of $65\text{ }^\circ\text{C}$; this prevented the overheating of both the stone and the sample.

The fibre orientation of the wood blocks was parallel to the shaft of the grinding stone. The angle used ensured that the fibres in the wood blocks

disintegrated into fine particles instead of disintegrating from the cell wall (Saharinen et al. 2016b). With the given operational conditions, the wood was ground to a micrometre scale LF with a yield of 90%. The non-fibrillated material was removed by initially filtering the ground material with successive mesh sizes of 14 and 48, respectively. Then a 200 mesh filter (with a sieve size of 0.090 mm) was utilised to fractionate a portion of 4.8-LF (see Table 1). The small pass-through fraction (code 4.8 m-LF) obtained was utilised in the experiments. Finally, the filtrates were concentrated by rotary evaporation. The concentrated LF samples were stored in a refrigerator until they were used in composite filament spinning trials.

Methods

Preparation of composite filaments from LF

The composite filaments were produced from LF using carboxymethyl cellulose (CMC) as a matrix polymer. The CMC stock solution was prepared dissolving 5 wt% CMC in Milli-Q water. The LFs and CMC solutions were mixed into a final dry consistency of 5 wt% by using an equal 50/50 mixing ratio that we had observed to be a good compromise for producing composite filaments in our previous study (Orelma et al. 2017). The mixture was concentrated to 10 wt% by a rotary evaporator. The filaments were then dry-jet wet spun into 2 wt% aluminium sulphate dissolved in Milli-Q water that precipitated the CMC of the filament by chelation of neighbouring carboxyl groups (counter ions were changed from Na^+ to Al^{3+}) (Braihi et al. 2014). Spinning was carried out with a constant flow rate of 5 ml/min by utilising converging nozzles with diameters of 0.28 mm and 0.41 mm (plastic

Fig. 1 The molecular models of ethylene glycol, glycerol, sorbitol and triacetin

Table 1 Sample coding of prepared LF grades

Sample code	Specific energy input (kWh/kg)	Grinding stone	Peripheral speed of the grinding stone (m/s)	Fractionation through a 200 mesh filter
2.6-LF	2.6	Norton 701L12VGP	20	No
4.8-LF	4.8	Norton A601-N5VG	10	No
4.8 m-LF	4.8	Norton A601-N5VG	10	Yes

tapered flexible tip, Drifcon, Denmark). The filaments were kept in an aluminium solution for a short period and then flushed with water, and dried in laboratory conditions under tension to prevent drying shrinkage.

The ability of common plasticisers to increase the ductility of LF–CMC filaments was tested with triacetin, ethylene glycol, triacetin, glycerol and sorbitol. In all cases, the dosage was 50 wt% of the dry content of LF–CMC. The spinning of the LF–CMC filaments was similar both with and without an added plasticiser. Table 2 shows the densities of the used compounds.

Topography of the LF grades using SEM and optical microscopy

Scanning Electron Microscopy (SEM) imaging was performed using a Merlin Field Emission (FE)-SEM (Carl Zeiss NTS GmbH, Germany) without a sputter coating. The samples were prepared by drop casting the diluted LFs on PEI-coated silicone oxide surfaces, which were dried in laboratory conditions prior to SEM imaging. The SEM imaging was performed using a secondary electron detector (SE2) at 1.5 keV electron energy. The pixel resolution was 2048×1536 . The image analysis was carried out using the image analysis software ImageJ.

Optical microscopy imaging was performed using a Nikon H550S optical microscope with a $40\times$ TU Plan Fluor objective. The filament samples were taped from

each end onto a microscope glass. The thicknesses of the filaments were calculated from the microscopy images by utilising Nikon imaging software.

Particle size of produced LF grades using a Kajaani fibre tester

The physical characteristics of the produced LF grades were investigated by using a Kajaani FS300 fibre analyser (Metso Automation Inc., Helsinki, Finland). The device measures fibre length, width, curl, and kink index optically. The measurement principle is based on the tendency of individual fibres to change their light polarisation as they pass through a narrow capillary.

Surface charge of LF grades by zeta potential

The surface charge of the produced LF grades was investigated using a Mütéc SZP-06 System Zeta Potential analyser. The samples were prepared by diluting the concentrated LFs with ion exchanged water to a mass consistency of 0.4%. All measurements were duplicated.

Sedimentation speed of LF grades by turbidity

The colloidal stability of cellulose materials is known to correlate to a long sedimentation time (Hubbe and Rojas 2008). The stability of the LF particles was

Table 2 Densities (general literature data), carbon/hydroxyl (C/OH ratios), and molar masses of the used compounds

Material	Density (g/m ³)	C/OH ratio	Molar mass g/mol
Cellulose	1.50	8/3 (glucose unit)	192 (glucose unit)
CMC	1.59	10/2 (monomer)	249 (monomer, DS 1)
Ethylene glycol	1.11	2/2	62
Glycerol	1.26	3/3	92
Sorbitol	1.49	6/6	182
Triacetin	1.16	9/0	218

investigated by sedimentation measurements using a Turbiscan Lab Expert (Formulation, Toulouse, France). The method is based on an optical measurement of vertical back-scattering light profiles versus time. The LF concentrates were diluted in a 1.0 w/v% concentration with Milli-Q water. Then the turbidity measurements were carried out at 1-h intervals. In the measurements, the clarification zone formed above the turbid colloid was observed by measuring the height of the opaque bottom column as a function of storage time.

Hydrophilicity of produced LF grades using a contact angle goniometer (CAM)

The hydrophilicity of produced LF materials were characterised using a contact angle goniometer (Attension Theta Optical Tensiometer, Biolin, Sweden) (Kwok and Neumann 1999). The samples were prepared by vacuum filtration of a 20 ml LF sample with Millipore membrane filters. After filtration, the samples were dried between blotting boards under a 1 kg weight in an oven overnight at 50 °C. Prior to the measurement, the samples were stabilised at standardised laboratory conditions (50% relative humidity and 23 °C). The CAM measurement was carried out using Milli-Q water with a droplet size of 4 µl. At least three parallel measurements were carried out per measurement point.

Mechanical characteristics of LF–CMC filaments

The mechanical characteristics of LF–CMC filaments were measured using a Lloyd LS5 tensile tester equipped with a 100 N sensor (AMETEK Measurement & Calibration Technologies, Florida, USA). The measurements were carried out in standardised conditions (50% relative humidity and 23 °C). Prior to the measurements, the filaments were kept overnight, as a minimum, in standardised conditions. The filament tenacity, breaking force of a filament normalised with its linear density (weight/length), was then measured and calculated. It should be noted that a unit often used to measure linear density, or fineness, is tex/dtex, which is the mass in grams of a 1000/10,000 m long filament. The span length between the filament holders was 20 mm. The measurements were carried out using a constant 2 mm/min strain rate. All test points were repeated at least five times.

Efficiency of the load bearing

The stress–strain curves of filaments were normalized with the efficiency factor, which is the ratio of Young's moduli of a studied curve to the highest Young's modulus of the group of interest. The efficiency factor describes the efficiency of stress transfer. During straining, the fibre segments between bonded regions tend to straighten (i.e. are activated, see Lobben 1975) until the elongation potential has been utilised. In an ideal case, when the level of bonding is the only changing factor, the normalized stress–strain curves are identical; only the failure point is different.

The efficiency factor concept has previously been used to describe changes in inter- and intra-fibre bonding that are reflected in the shape of the stress–strain curve of paper (Seth and Page 1981; Coffin 2012). The fibres in the filaments are likely to form an aligned fibre network, but the efficiency factor concept should be useful also here; it provides, for example, an estimate of whether the plasticiser chemicals cause changes in the fibre filament activation.

Results

Manufacture and properties of lignocellulosic native LF

The topography of the produced materials was investigated using FE-SEM from drop-cast LF films. The LF ground with 2.6 kWh/kg specific energy (2.6-LF) comprised mainly well fibrillated (Fig. 2a) wood material, although the number of larger pieces of wood fibres was considerable. These pieces were typically more than 50 µm long and their width was between 5 and 15 µm (aspect ratio up to 10). They included strips with a thickness of 0.5–2 µm and a length of tens of microns. The 2.6-LF material obtained also contained a micro-fraction (diameter below 1 µm). Overall, this material was similar to what is present in thermomechanical pulps in smaller fractions (Kangas and Kleen 2004). When the specific energy was increased to 4.8 kWh/kg, the material obtained (4.8-LF) clearly had a finer structure. Contrary to 2.6-LF, it did not contain pieces of wood fibres (Fig. 2b). 4.8-LF included a small fraction of tens of micron long strips (aspect ratio above 80), whose

Fig. 2 SEM images of the produced LF samples with different energy input and fractionation. **a** 2.6-LF, **b** 4.8-LF, **c** 4.8 m-LF. For sample codes, see Table 1

dimensions were typically $1\text{--}4\text{ }\mu\text{m} \times 0.25\text{--}1\text{ }\mu\text{m}$. When 4.8-LF was further fractionated with a 200 mesh wire, the filtrate material (4.8 m-LF) was made up of clearly finer particles than 4.8-LF (Fig. 2c). The particle length was below $50\text{ }\mu\text{m}$ and particle thickness was on a micrometre scale. Moreover, a very fine fraction (particle length $1\text{--}2\text{ }\mu\text{m}$) was also present. The produced LF materials were similar to what was reported for W-stone ground wood LF in (Heinemann et al. 2016). It should be noted that the aspect ratio of the three differently produced LFs varies. It could be expected that particles with a higher aspect ratio are likely to give a higher resilience when used in the composite filaments.

Characterisation of produced LF grades

The properties of produced LF grades were investigated using an optical particle size analyser (Kajaani) that has been developed for wood fibre materials (Hirn

and Bauer 2006). The 2.6-LF contained over 50% of small-sized material (particle length below $200\text{ }\mu\text{m}$) (Table 3). Thus, the measured optical particle sizes should only be used for a rough estimate of the dimensions of the particles present in the produced LF grades. Nevertheless, the measured particle sizes of the LF grades correlated well with the length scales seen in SEM images. The length weighted particle length was $250\text{ }\mu\text{m}$; this is significantly lower than the length of softwood kraft pulp fibres, which is approx. 2.7 mm , similar to softwood kraft fibres (Brodin and Theliander 2013). This suggests that the measured particles were branched upon fibrillation. The increased grinding energy from 2.6 to 4.8 kWh/kg did not significantly alter the optically measured length weighted average fibre length. However, the curl of the material increased slightly, and the kink index increased significantly with increased energy consumption. Both these changes indicate increased fibrillation. When fractionation with a 200-mesh wire

Table 3 Physical properties of the produced LF samples

	Unit	2.6-LF	4.8-LF	4.8 m-LF
Arithmetic av. fibre length	mm	0.12	0.11	0.06
Length weighted av. fibre length	mm	0.24	0.26	0.12
Weight weighted av. fibre length	mm	0.39	0.48	0.29
Length < 0.2 mm	%	51.27	51.3	85.9
Fibre curl	%	12.8	15.2	23.1
Kink index	1/m	89	553	75
Fibre width	µm	23.5	28.7	42.9
Zeta potential	mV	− 28.5	− 25.4	− 38.1
Contact angle (10 s)	°	49 ± 3	46 ± 2	52 ± 2

was applied to the 4.8-LF, the fine fraction increased significantly (the mass fraction of particles shorter than 200 µm increased from 51 to 86%). A similar conclusion was also reached by inspecting the SEM images.

The stability of the produced LF colloids was analysed using the turbidity measurement. The sedimentation of the 2.6-LF sample was rather slow (Fig. 3). After 12 h, the 2.6-LF sample had sedimented to 15% of the original value. The plateau was reached after 10 days, when the height of the colloid pillar was approximately 50% of the original value. We also observed similar results for this LF grade in our previous article (Orelma et al. 2017). When the energy input in the W-stone grinding was increased from 2.6 to 4.8 kWh/kg to achieve the 4.8-LF grade, the kinetics and intensity of the sedimentation were significantly reduced. After 12 h, the 4.8-LF sample had sedimented only 1% from its original value, and the height of the water pillar of the colloid was 68% of the original value after 10 days. As discussed above, the 4.8-LF grade was post-fractionated to further decrease the particle size using a 200 mesh wire. During the turbidity measurement, we did not see any sedimentation within 30 days for this (4.8 m-LF) grade. The observed significant improvement of the colloidal stability of the LF with decreasing particle size can be explained by the relative increase of Brownian forces relative to the gravitational forces (Larson 1999).

The stability of colloids can also be analysed in the context of the DVLO theory, which combines the effects of the van der Waals attraction and electrostatic repulsion resulting from the double layer of counterions (Tadros 1987). The surface charge of the 2.6-LF and 4.8-LF grades was anionic, their zeta potentials

being below − 25 mV (Table 3). This indicates the presence of an ionic double layer, which generally increases the colloidal stability of cellulosic materials (Hubbe and Rojas 2008). The reason for the anionic surface charge is the emerge of hemicelluloses from the cell wall layer during grinding (Willför et al. 2005). The fractionated grade 4.8 m-LF had an even higher negative zeta potential (− 38.1 mV), further explaining the observed negligible sedimentation in the turbidity measurement.

The dispersion of the lignin on the particle surfaces was studied using a contact angle measurement (with water). The investigation was carried out using solvent cast films from the LF grades. The contact angles of the 2.6-LF, 4.8-LF, and 4.8 m-LF grades were similar (approximately 49°, 46° and 52°, respectively, see Table 3). The observed contact angle was slightly lower than that of native spruce wood, which has the same contact angle of 60° as pure lignin surfaces (Notley and Norgren 2010). In comparison, the contact angle varies between 26 and 31° for pure cellulose surfaces. The observed contact angles indicate that grinding draws out hydrophilic carbohydrates from the wood cell wall (Mantanis and Young 1997). Furthermore, LF materials clearly contain some lignin on the material surfaces, since all the measured contact angles were between those reported for pure cellulose and pure lignin surfaces (Notley and Norgren 2010). However, our characterisation shed no light on the dispersal of lignin on the material surfaces; the coverage is probably uneven.

Fig. 3 The stability of the produced LF samples at 1.0 w/v%. The curves show the location of the interface between the transparent and turbid phases as a function of time in a sedimentation experiment. **a** The dashed lines show the

sedimentation level of each sample after 3 weeks. The sample 4.8 m-LF did not display any sedimentation within the 3 weeks' trial. The inserts on the right show the respective situations: after 42 h for **b** 2.6-LF, and after 46 h for **c** 4.8-LF and **d** 4.8 m-LF

Effect of the LF grade on the mechanical properties of LF–CMC composite filaments

The produced LF grades were spun into composite filaments using CMC. Figure 4a shows, as an example, the optical microscopy of the surface morphology of the prepared 2.6-LF–CMC composite filament. It

can be seen that the filament surface appears to be relatively soft looking. In the SEM image (Fig. 4b), longitudinal stripes caused by the spinning nozzle are visible. Otherwise, the surface structure of the prepared filament is rather uneven. Table 4 summarises the properties of the produced LF–CMC filaments: thickness, fineness, Young's modulus, maximum

Fig. 4 Optical microscopy image of the 2.6-LF–CMC composite filament (**a**). Morphology of the surface of the 2.6-LF–CMC composite filament using SEM imaging (**b**)

strain, tenacity and toughness. The correlation coefficient between tenacity and tensile strength was 0.93, and thus we have excluded the discussion of the tensile strengths from the discussion.

The type of LF grade had a significant effect on the strength properties of composite filaments. Figure 5a shows examples of the tenacity-strain curves used for calculating the mechanical properties of the filaments. The tenacities of 2.6-LF, 4.8-LF and 4.8 m-LF were approximately 5.6 ± 0.4 , 7.6 ± 0.6 , and 5.7 ± 0.6 cN/tex, respectively (Table 4). The Young's modulus followed a similar trend and was clearly higher for filaments made from 4.8-LF (4450 MPa) compared to those made from 2.6-LF (3110 MPa) or 4.8 m-LF (3030 MPa). It is likely that the highly irregular particle shape of 4.8-LF (due to strong fibrillation) strengthens particle-particle contacts thereby improving the compatibility of LF with CMC. It could also be speculated that the smaller particle size may cause a more uniform distribution of LF in the CMC matrix. Figure 5b shows the scaled stress-strain curves and the efficiency factors of the

LF filaments. The load bearing and filament activation of the 4.8- and 4.8 m-LF filaments was similar until reaching 4% strain. On the other hand, the lowest efficiency factor of the 4.8 m-LF in this group indicates that lower inter-particle bonding of LF may have enabled higher elongation. Mechanism behind the better elongation may be tangential sliding or twist of LF particles or the plasticiser taking larger role in bonding the LF by preventing particle-particle contacts. However, it is obvious that these values are the result of the combined effect of multiple material properties. There is not many references in the literature to make comparison, The Young's modulus of pure cellulose (microcrystalline cellulose) is of the order 25,000 MPa. (Eichhorn and Young 2001) Thus, Young's modulus of the produced LF-CMC filaments was always clearly one order of magnitude lower than reported for microcrystalline cellulose.

The strength of the LF-CMC composite filaments achieves the levels required in many filament applications. As an example, cotton filament and pulp-based fibre filament crosslinked with polyacrylic acid

Table 4 Mechanical properties of the produced LF filaments

CMC (%)	LF (%)	Plasticiser (%)	Thickness (μm)	Fineness (tex)	Young's modulus (MPa)	Maximum strain (%)	Tenacity (cN/tex)	Toughness (J/kg)
2.6-LF, 0.41 mm nozzle								
50	50	–	139 ± 13	20.3	3110 ± 430	4.1 ± 0.7	5.6 ± 0.4	1540 ± 170
25	25	50 (Glycerol)	151 ± 17	29.0	520 ± 160	11.6 ± 2.4	1.3 ± 0.1	930 ± 120
4.8-LF, 0.41 mm nozzle								
50	50	–	136 ± 11	16.8	4450 ± 380	4.6 ± 1.2	7.6 ± 0.6	2210 ± 400
25	25	50 (Glycerol)	127 ± 15	19.2	2770 ± 620	12.1 ± 2.0	5.1 ± 0.5	4110 ± 420
25	25	50 (Sorbitol)	167 ± 22	31.7	750 ± 70	15.7 ± 3.1	2.2 ± 0.2	2330 ± 320
25	25	50 (Ethylene glycol)	129 ± 16	16.1	5430 ± 420	7.2 ± 0.7	7.4 ± 0.3	4320 ± 280
25	25	50 (Triacetin)	127 ± 12	18.3	3970 ± 300	5.8 ± 2.1	4.8 ± 0.4	2050 ± 440
4.8 m-LF, 0.41 mm nozzle								
50	50	–	138 ± 15	17.6	3030 ± 150	6.7 ± 9	5.7 ± 0.6	4010 ± 510
25	25	50 (Glycerol)	176 ± 19	29.6	240 ± 40	20 ± 5	1.6 ± 0.2	2360 ± 240
4.8-LF, 0.28 mm nozzle								
50	50	–	91 ± 9	8.1	5190 ± 270	3.8 ± 1.4	7.0 ± 0.9	1830 ± 470
25	25	50 (Glycerol)	109 ± 10	15.2	2510 ± 375	6.8 ± 2.2	3.1 ± 0.2	1510 ± 270
25	25	50 (Sorbitol)	106 ± 11	12.3	1670 ± 250	8.2 ± 2.0	2.7 ± 0.5	1890 ± 310
25	25	50 (Ethylene glycol)	90 ± 9	9.8	6000 ± 480	3.7 ± 0.4	6.4 ± 0.6	1460 ± 130
25	25	50 (Triacetin)	109 ± 11	11.2	3700 ± 530	3.6 ± 0.7	4.9 ± 0.6	1240 ± 180

Fig. 5 **a** Examples of tenacity–strain curves. **b** Normalised stress–strain curves. Efficiency factors in the **b**: 4.8-LF: 0.98; 2.6-LF: 1.0; 4.8 m-LF: 0.93. The filaments were made in both cases with the 0.41 mm nozzle without a plasticiser

(PAA) have been reported to reach a tenacity level of 15 and 5 cN/tex, respectively (Tenhunen et al. 2016). However, the prepared filaments did not achieve the strength level of regenerated cellulose filaments made by NaOH/urea carbamate or by novel ionic liquid processes (tenacities up to 37 cN/tex) (Qi et al. 2008; Hauru et al. 2014).

Compatibility of plasticisers with LF–CMC composite filaments

Cellulose materials are typically rather rigid with low elongation due to the strong inter-hydrogen bonding. Thus, plasticisers are often used to improve the ductility of cellulose materials. We tested four plasticisers with 4.8-LF filaments: methyl group substituted triacetin, and hydroxyl substituted ethylene glycol, glycerol and sorbitol. The trials were carried out with a constant 50% plasticiser loading. Figure 6a shows typical tenacity–strain curves for the filaments with tested plasticisers and Fig. 7 shows a detailed comparison of the Young’s modulus, tenacity, maximum strain and toughness. Excluding the toughness, the 0.41 mm and 0.28 mm nozzles expressed similar qualitative behaviour.

All the plasticisers improved the filament elongation, at least to some extent. The maximum strain of the produced composite filaments increased as a function of the number of available hydroxyl groups of the plasticiser. The effects of triacetin on maximum strain was marginal compared to the reference with no plasticiser, but it decreased the strength considerably.

Triacetin obviously failed to adhere properly to the fibre surfaces and only weakened the fibre–fibre bonds. Ethylene glycol increased the maximum strain of the filament by 60% with no reduction in filament strength. Here, the possible weakening of fibre–fibre bonds was fully compensated by the additional bonds between fibres and ethylene glycol polymers. The glycerol and sorbitol increased the maximum filament strain by approximately 180% and 290%, respectively. However, the strength properties dropped correspondingly, particularly with sorbitol. Here, the fibre–fibre bonds were probably totally replaced by plasticiser bridges between the fibres.

Figure 5b shows the scaled stress–strain curves of the various 4.8-LF filaments. We see that up to 2.5% of the strain behaviour of the filaments was similar. The bonds of the reference, ethylene glycol, and triacetin, were already fully activated here, as they only tended to break with slightly higher strains (this manifested as a strong bending of the curve, which preceded the filament breakage). The curves of the reference, ethylene glycol, and triacetin, were very similar (Fig. 6b). This suggests that their composite structures are also qualitatively similar to the plasticisers, increasing their bonding efficiency only moderately. On the other hand, the bonding efficiency of glycerol and sorbitol is very high, which is reflected in the much higher maximum strain. It is likely that glycerol and sorbitol play a significant role in load bearing, either by increasing flexible bonding with an improved elongation ability between the LF particles or by creating a continuous stretchable material matrix

Fig. 6 **a** Typical tenacity–strain curves of the 4.8-LF-CMC filaments with and without a plasticiser. **b** Scaled stress–strain curves of the 4.8-LF-CMC filaments with and without a plasticiser. Efficiency factors in the **b**: No plasticiser: 0.90;

Ethylene glycol: 1.0; Triacetin: 0.94; Glycerol: 0.52; Sorbitol: 0.19. The plasticiser content of 50 wt% to the combined dry mass of LF and CMC was used. The 0.41 mm nozzle was used during spinning

Fig. 7 The effects of the plasticiser on the 4.8-LF filament properties **a** Young's modulus, **b** tenacity, **c** maximum strain and **d** toughness. All plasticisers were tested with two spinning needle sizes (0.41 and 0.28 mm)

around the LF particles and by assuming the primary role in load bearing.

The results indicate that ethylene glycol with its two available hydroxyls per a molecule is already capable of preventing the formation of cellulose–cellulose hydrogen bonding patterns. The glycerol and

sorbitol demonstrated a strong plasticisation effect that reduces the material strength significantly. Triacetin is a widely utilised plasticiser with polylactic acid (PLA) and other plastics. However, its plasticisation effect on this occasion was rather small. It has been reported with poly(N-vinyl pyrrolidone) that the

plasticisation effect of hydroxyl containing plasticisers increases as a function of available hydroxyls in the plasticiser molecule (Feldstein et al. 2001). It appears that with cellulosic materials, the used plasticiser should contain at least one hydroxyl per a molecule (monomer) to achieve a reasonable plasticisation effect. However, it is important to note that we did not analyse the effect of the loading levels of the plasticisers on the filament properties. This may have a significant effect on the observed plasticisation effects.

Conclusions

The effect of energy input on the properties of mechanically ground LF particles and the subsequent properties of LF–CMC composite filaments were studied. The increase in the energy input decreased the particle size of the LF material and increased the specific surface area. The lowered particle size had an enhancing effect on the colloidal stability of the LF. The increased specific surface area of the LF and lowered particle size permit the formation of a more homogenous filament structure, which increases the filament's mechanical resistance. Thus, when compared to 2.6-LF filaments, the increased specific surface area and smaller particle size increased the tensile strength (4.8-LF) and the maximum strain (4.8 m-LF) of the composed filaments, respectively. The compatibility of plasticisers in the LF–CMC matrix was also investigated. The plasticisation effect increased as a function of the number of available hydroxyl groups per monomer of the plasticiser. The studied filaments could find applications from disposable and low-cost applications in which biodegradability is a required character.

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