

Sugar beet cellulose nanofibril-reinforced composites

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Abstract Cellulose was isolated from sugar beet chips, a by-product of sugar production, by wet chemistry. Further processing of the cellulose with a high-pressure homogeniser led to the disruption of cell walls into nanofibrils. Cellulose sheets obtained by casting and slow evaporation of water showed higher strength and stiffness when homogenised cellulose was used compared to unhomogenised cellulose. These cellulose sheets showed significantly better mechanical performance than Kraft paper tested for reference. The addition of cellulose nanofibrils to a polyvinyl alcohol and a phenol-formaldehyde matrix, respectively, demonstrated excellent reinforcement properties. The best mechanical performance was achieved for a composite with a phenol-formaldehyde resin content of 10%, which showed a tensile strength of 127 MPa, a modulus of elasticity of 9.5 GPa, and an elongation at break of 2.9%.

Keywords Cellulose composites · Mechanical properties · Nanofibrils · Sugar beet cellulose

Introduction

Cellulosic fibres offer an alternative to glass fibres for composite reinforcement due to their good mechanical properties, to low weight, combined with low abrasiveness, renewability and abundance (Bledzki and Gassan 1999). Wood is certainly the most important source of cellulosic fibres, but competition among different markets, e.g., the use of solid wood and wood composites for building and furniture, the pulp and paper industry, and the combustion of wood for energy, together with the decline of tropical forests, will make it difficult to supply all users with the quantities they need at reasonable price in future. Apart from fibres from plants like flax, hemp, sisal, and others, the cellulosic part of by-products of the agricultural industry will become of more interest. Globally, by-products arising from the cultivation of corn, wheat, rice, sorghum, barley, sugarcane, pineapple, banana and coconut are the major sources of agro-based cellulosic fibre (Reddy and Yang 2005). In 1997 Dufresne and co-workers were the first to address the mechanical properties of paper sheets made from cellulose obtained by the purification of dried sugar beet pulp chips, a by-product of the sugar industry usually sold at very low price as cattle

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feed. Sugar beet pulp primary cell walls consist of roughly one-third cellulose, one third hemicelluloses, and one third pectin (Dinand et al. 1996, 1999). Dufresne et al. (1997) reported a significant improvement in strength and stiffness of paper sheets made from sugar beet cellulose when the purified cellulose was subjected to treatment by a high-pressure homogeniser. The high shear forces in a homogeniser lead to the disruption of cell walls and their separation into nano-scale cellulose fibrils with high length/diameter ratio (Dinand et al. 1996). Neither flocculation nor sedimentation of the nanofibrils in aqueous suspension occurs as long as some hemicelluloses and pectin is maintained on the fibril surface (Dinand et al. 1999). Electron diffraction of individual fibrils revealed almost unidirectional orientation of cellulose parallel to the fibril axis (Dinand et al. 1999). Therefore it may be assumed that the mechanical properties of such nanofibrils are close to the properties of the cellulose crystallite. The modulus of elasticity of cellulose I, which is the crystalline conformation typical of natural cellulose, is calculated as high as 138 GPa (Nishino et al. 1995). The tensile strength of cellulose I is also high, most probably in the order of- or higher than the tensile strength of 3.7 GPa estimated for perfectly parallel aligned regenerated cellulose (cellulose II) chains (Northolt et al. 2005). Due to these properties, sugar beet cellulose fibrils should be an excellent reinforcement for polymer composites. In spite of the obvious potential of this material, literature on sugar beet-derived cellulose nanofibril-reinforced composites is scarce. Azizi Samir et al. (2004) demonstrated the importance of network formation for the stiffness of a polymer latex reinforced with small amounts of sugar beet cellulose nanofibrils. In a similar procedure Dalmás et al. (2006) cast sheets from an aqueous mixture of polymer latex and sugar beet pulp-derived nanofibrils. At 6% fibril content, an increase of the modulus of elasticity of the polymer latex of about 150 times compared to the unreinforced polymer was observed.

In the present study, composites of polyvinylalcohol and phenol-formaldehyde, respectively, reinforced with cellulose nanofibrils at high fibre content were produced and their mechanical properties were evaluated by tensile tests.

Materials and methods

Preparation of cellulose nanofibrils

Dried sugar beet pulp chips as obtained after the removal of sugar in industrial sugar production were provided by Zuckerforschung Tulln, Austria. The chips were milled to a particle size of 1–5 mm before further treatment. 20 g dry chips were disencrusted in 200 ml 0.5 M NaOH at 80°C under frequent stirring for 2 h. After removal of excessive NaOH the pulp was washed in ~300 ml distilled water. Thereafter 100 ml NaOH were added, and washing was repeated after 15 min. Subsequently, the washed pulp was bleached by adding 10 g NaClO₂ at pH = 4.9 (acetate buffer made from 5 g acetic acid, 5 g sodium acetate, and 25 ml distilled water) at 70°C under frequent stirring for 2 h. The bleached pulp was repeatedly washed with distilled water before further processing. Aggregates of cells remaining after bleaching were disintegrated by means of an Ultra-Turrax mixer operated at 24,000 rotations min⁻¹. In order to disrupt the cell walls into individual cellulose nanofibrils, the cellulose suspension was run through a high-pressure APV-Gaulin laboratory homogeniser operated at 300 bar for 10–15 passes.

Cellulose nanocomposites

Diluted aqueous suspensions of cellulose fibrils (cellulose content approx. 0.5% wt) were mixed with water-soluble polyvinyl alcohol (PVA, Fluka 81381) and phenol-formaldehyde resin (PF, provided by Dynea, Austria), respectively. The amount of polymer added to the cellulose suspension was controlled in order to achieve fibre contents as desired. Subsequently, the aqueous cellulose-polymer mixture was cast into a petri dish with a diameter of 25 cm and placed in an oven maintained at a temperature of 40°C for 12 h. Thereafter, the Petri dishes were stored at ambient conditions (approx. 24°C and 45% rel. humidity) until complete evaporation of all water (1.5 to several weeks). The sheets obtained by this procedure had a thickness of 0.2 mm to 0.5 mm. PF composite sheets were cured in a hot press at 120°C and 10 MPa for 15 min. Pressure was applied to prevent the formation of air bubbles arising from water set free during the polycondensation of PF. All

composite sheets were stored in a climate chamber kept at 20°C and 65% rel. humidity for one month.

Morphological and mechanical characterisation

The structure of sugar beet cellulose before and after homogenisation was characterised by means of transmitted light microscopy and high-vacuum scanning electron microscopy.

In order to verify the orientation distribution of cellulose fibrils in the composite sheets produced in the present study, wide-angle x-ray scattering was performed using a *Nanostar* (Bruker AXS) system connected to a rotating anode generator with Cu target. The system is equipped with crossed Göbel mirrors, a pinhole system for a primary collimation with a beam diameter of 100 µm and a two dimensional (2D) wire detector (Hi-Star).

Mechanical testing was done on a Zwick 100 kN universal testing machine equipped with a 2.5 kN load cell and Zwick macrosense clip-on displacement sensors for accurate strain measurement. Strips with a width of 5 mm and a length of 50 mm were cut from the cellulose-reinforced polymer sheets and tested in tension at a displacement rate of 1 mm min⁻¹. Packaging-grade Kraft paper (60 g m⁻²) was chosen as a reference material. Since the fibres in this type of paper are not randomly distributed as opposed to the sugar-beet pulp specimens prepared in the present study, mechanical anisotropy was expected and tensile testing was performed parallel and transverse to the direction of production of the paper.

Results and discussion

Morphology of cellulose fibrils and composites

Transmitted light microscopy performed on a diluted suspension of purified and disintegrated sugar beet cellulose shows individual sugar beet cells with sizes ranging from 50 to 200 µm (Fig. 1). After treatment of the diluted cellulose suspension with a high-pressure homogeniser, cellulose nanofibrils were obtained. A scanning electron micrograph (SEM) of the surface of a dried homogenised cellulose sheet is shown in Fig. 2. The SEM image demonstrates that the obtained cellulose fibrils are nano-scale, with

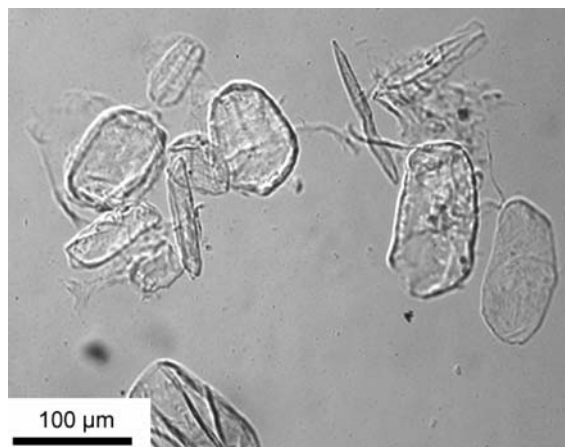


Fig. 1 Transmitted light microscopy image of individualised sugar beet pulp cells after removal of non-cellulosic substances and treatment with an Ultra-Turrax mixer

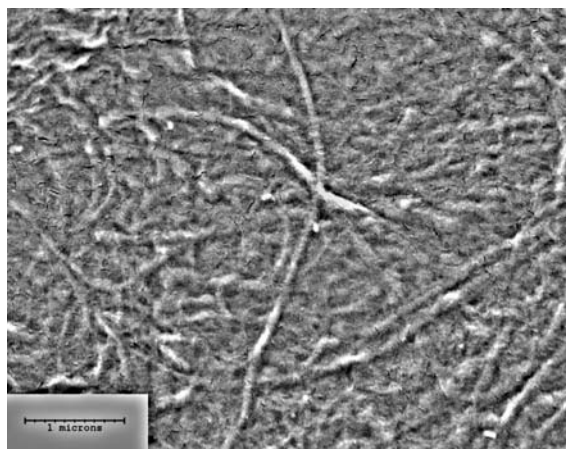


Fig. 2 Scanning electron microscopy image of sugar beet cellulose fibrils after treatment of purified pulp with a high-pressure homogeniser

diameters ranging from 30 nm to 100 nm and a length of several µm. Wide-angle x-ray scattering performed on a dried cellulose nanofibril sheet showed a homogeneous distribution of the scattering intensity originating from the cellulose (200) reflection, which is at an angle of 90° with respect to the crystallographic *c*-axis of the cellulose crystallite (Fig. 3). The homogeneous azimuthal distribution of scattering intensity confirms random orientation of the cellulose fibrils in the composite, which is an important prerequisite for the correct interpretation of mechanical test results.

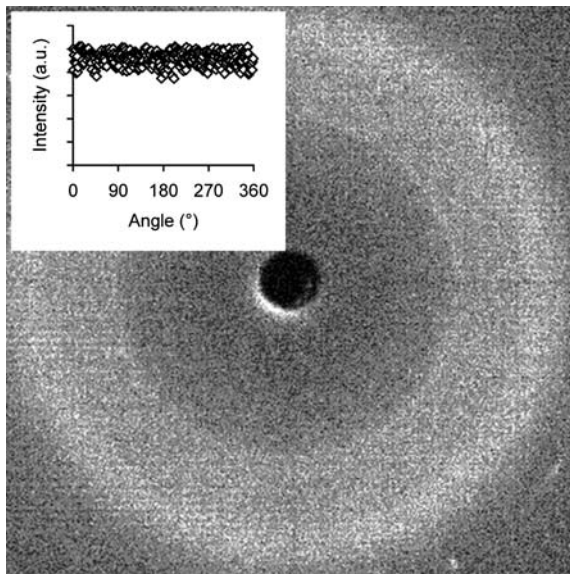


Fig. 3 Results of wide-angle X-ray scattering performed on a dried cellulose nanofibril sheet. The most intense reflection in the 2D detector image is the cellulose (200) reflection, which is at an angle of 90° with respect to the crystallographic c -axis of the cellulose crystallite. The inset shows the integrated azimuthal intensity distribution along the cellulose (200) reflection, demonstrating random orientation of the cellulose nanofibrils

Mechanical properties

The results of the mechanical characterisation of pure sugar-beet cellulose sheets, cellulose nanofibril-reinforced composites, and Kraft paper are summarised in Table 1. Representative stress strain curves from

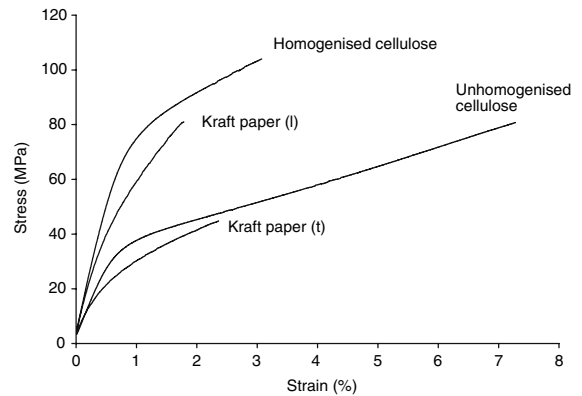


Fig. 4 Representative stress–strain curves from tensile tests of sheets of pure cellulose made from purified sugar beet pulp before and after the treatment with a high-pressure homogeniser compared to Kraft paper tested parallel (l) and transverse (t) to the direction of production

tensile tests of pure cellulose sheets are shown in Fig. 4. A clear increase in both the average modulus of elasticity and the tensile strength is observed after treatment with a high-pressure homogeniser. The observed increase of the modulus of elasticity by a factor two due to nanofibrillation in the high-pressure homogeniser (Table 1) agrees roughly with the increase in modulus reported by Dufresne et al. (1997). However the absolute values for the modulus of elasticity, with 1.3 GPa for unhomogenised cellulose and 2.3 GPa for homogenised cellulose sheets, respectively, observed by Dufresne et al. (1997), are much lower than the 4.6 GPa and 9.3 GPa, respectively, found in the present study. Values closer

Table 1 Summary of mechanical properties (E = modulus of elasticity, σ_f = tensile strength, ε_f = elongation at break; the cellulose content was estimated from the cellulose content of an aqueous suspension and the amount of polymer added)

Material	Cellulose content (% wt)	E (Gpa)	σ_f (Mpa)	ε_f (%)
Unhomogenised cellulose	100	4.6 ± 0.8	73 ± 10	7.2 ± 0.8
Homogenised cellulose	100	9.3 ± 0.9	104 ± 8	3.2 ± 0.8
Homogenised cellulose—PVA	50	5.3 ± 0.6	61 ± 12	1.6 ± 0.3
Homogenised cellulose—PVA	70	6.5 ± 1.0	72 ± 8	2.0 ± 0.4
Homogenised cellulose—PVA	90	7.7 ± 1.0	84 ± 15	1.7 ± 1.1
Homogenised cellulose—PF	50	5.2 ± 0.8	65 ± 10	3.2 ± 0.9
Homogenised cellulose—PF	70	7.1 ± 0.9	84 ± 10	3.1 ± 0.4
Homogenised cellulose—PF	90	9.5 ± 1.2	127 ± 5	2.9 ± 0.6
PVA	0	0.25 ± 0.06	17 ± 2	22.7 ± 0.9
Kraft paper (l)		9.2 ± 0.7	83 ± 6	1.9 ± 0.3
Kraft paper (t)		4.2 ± 0.3	45 ± 7	1.9 ± 0.7

to the results for the modulus of elasticity (9.3 GPa) and for the tensile strength (104 MPa) of cellulose nanofibril sheets obtained in the present study were measured by Zimmermann et al. (2004) for nanofibrillated softwood cellulose sheets (modulus of elasticity = 6 GPa, tensile strength = 100 MPa) and by Bruce et al. (2005) for cellulose sheets made from high-pressure homogenised swede root pulp (modulus of elasticity = 7 GPa, tensile strength = 100 MPa). Dinand et al. (1999) observed that disencrusted cell walls as shown in Fig. 1 consist of a loose network of cellulose fibrils and fibril bundles, and a similar range of fibril diameters was found both in the loose fibril network of disencrusted cell walls, and in suspensions of high-pressure homogenised cellulose. Since no additional chemical purification step was performed on the homogenised cellulose, the fact that individual fibrils or fibril bundles were separated from the cell-wall network is a possible cause for the observed improvement of mechanical properties. Cellulose fibrils will find contact to each other and become attached to each other by hydrogen bonds more easily in the course of solvent evaporation when they are individualised in suspension than when they are arrested in the network of the primary cell wall, as is the case before homogenisation. The contacting of cellulose fibrils is essential since it is the formation of an entangled network which provides high strength and modulus to cast cellulose sheets (Azizi Samir et al. 2004; Dufresne 2006) as demonstrated by the excellent mechanical properties achieved for homogenised cellulose without the presence of a matrix polymer. The excellent properties of cellulose nanofibril sheets are evident in comparison with packaging-grade Kraft paper tested for reference (Table 1, Fig. 4). Since the fibres in the paper show a certain degree of preferred orientation, the mechanical properties measured parallel to the direction of production differ significantly from the transverse direction (Table 1). In spite of the absence of preferred orientation, the mechanical properties of sheets of nanofibrillated cellulose are clearly superior to Kraft paper regarding both the modulus of elasticity and tensile strength. It is assumed that this difference is observed due to the higher strength and stiffness of individual nanofibrils and also due to the more intimately entangled network formed by nanofibrils, compared to Kraft pulp fibres. Therefore, specialty paper with high strength and stiffness seems

to be a potential application for nanofibrillated sugar-beet pulp.

The excellent reinforcement efficiency of sugar beet cellulose nanofibrils is demonstrated by the results of tensile tests with PVA and PF composites, respectively (Table 1). For PVA it was possible to cast a sheet of pure polymer which was also characterised in tension. At a cellulose content of 50%, the modulus of elasticity of PVA increased by a factor 20 and tensile strength increased by a factor 3.5, and both parameters increased further with a cellulose content of 70% and 90%, respectively (Fig. 5). However, the material turned rather brittle, as seen by the comparably low elongation at break in the order of 1.5% to 2% (Table 1, Fig. 6). In a random-oriented fibre reinforced composite, the in-plane modulus of elasticity is a function of the fibre and matrix moduli and their respective volume fractions (Chawla 2001). This corresponds very well with the systematic increase of the modulus of elasticity observed as a function of cellulose content (Fig. 5). Similarly the tensile strength of a fibre-reinforced composite is a function of fibre content, but other factors, particularly fibre-matrix adhesion, are also of great significance. The linear trend of increasing tensile strength with end points roughly at 0% and 100% cellulose content observed for PVA composites (Fig. 5) indicates that cellulose content is the major determinant of strength in these composites and that PVA does not contribute significantly to

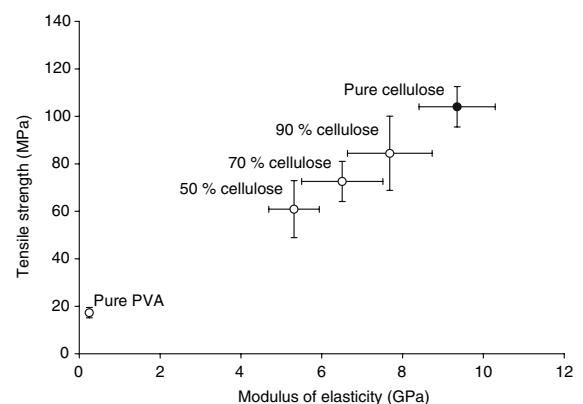


Fig. 5 Comparison of the average tensile strength and modulus of elasticity of sheets of pure poly(vinylalcohol) (PVA), pure cellulose, and composites with different fibril content (% wt) made thereof (error bars represent standard deviation)

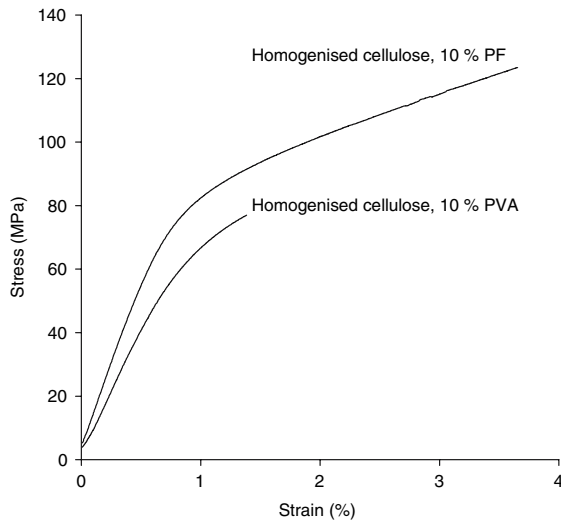


Fig. 6 Representative stress–strain curves from tensile tests with composites of poly(vinyl alcohol) (PVA) and phenol-formaldehyde (PF), respectively, reinforced with 90% wt cellulose nanofibrils

strength by creating additional, sufficiently strong bonds.

A different trend was observed for PF composites (Table 1, Fig. 7). Here, the modulus of elasticity is the same as in the PVA composite at 50% fibre content, but at higher fibre contents the modulus of PF composites is higher than for PVA composites (Table 1). Regarding the tensile strength, PF composites are stronger than PVA composites at a given fibre content. At 90% fibre content, the tensile

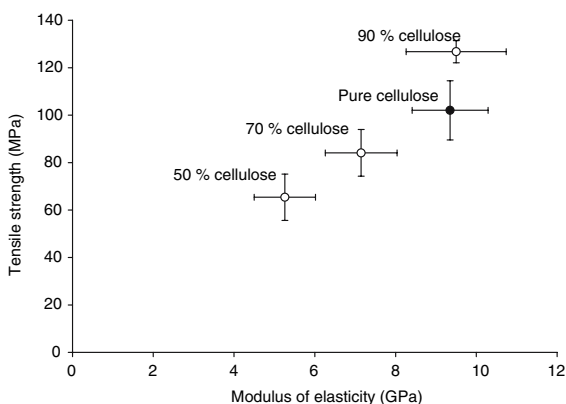


Fig. 7 Comparison of the average tensile strength and modulus of elasticity of sheets of pure cellulose, and composites with different fibril content (% wt) made of phenol-formaldehyde resin and cellulose fibrils (error bars represent standard deviation)

strength reaches a value of 127 MPa, which is significantly higher than the tensile strength of the corresponding pure cellulose sheet. This observation demonstrates that PF is capable of providing additional interfibrillar bonding to the cellulose nanofibril network, which improves tensile strength. It should be noted that the application of pressure during the curing of PF-bonded composites, which was not done for PVA-bonded composites, may also contribute to the better mechanical performance of the first. Finally, also regarding their failure strain PF composites show a clear advantage compared to PVA composites. With a typical elongation at break of 3%, PF composites proved to be much less brittle than PVA composites.

Conclusion

From the literature (Dufresne et al. 1997) it is already known that treatment of sugar beet cellulose with a high-pressure homogeniser leads to the disruption of cell walls into nanofibrils, which form strong cellulose sheets upon drying. The results presented above show that the mechanical properties of such cellulose sheets are superior to Kraft paper. In combination with a polymer matrix, the cellulose nanofibrils show excellent reinforcement properties. While a polyvinyl alcohol matrix does not contribute to a further improvement of the mechanical properties of the cellulose nanofibril sheets, the addition of a small amount of phenol-formaldehyde matrix polymer leads to a significant improvement of the tensile strength compared to the pure nanofibril sheets.

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