Cellulose-Nanocomposites: Towards High Performance Composite Materials

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Summary: Strong cellulose fibres, e.g. flax and hemp, are increasingly used for composites. Despite substantial advantages, the tensile strength of these fibres is limited due to their complex structure and the unavoidable imperfections of the cell wall, inherent from growth or induced by processing. Essential improvements are possible by using highly crystalline cellulose fibrils ("whiskers") which can be isolated from the cell wall, thus eliminating the influence of adhesion and defects. Instead of complete fibrillation, which demands special time consuming processing, a partly fibrillation has been achieved by adapted textile finishing procedures which have the potential for mass production. By combining chemical and mechanical/hydro-mechanical treatments it is possible to produce finest fibrils with diameters from below 1 μm down to the nanometer range. The problem of fibril agglomeration during drying has been avoided by forming homogenous fibrous sheets in a wet-laid non-woven process. These sheets can be impregnated with thermosetting resins. Alternatively thermoplastic polymers can be directly integrated to form hybrid materials ready for moulding. The resulting composites show greatly enhanced mechanical properties.

Keywords: cellulose; fibres; fibrillation; nanocomposites; non-woven

Introduction

Natural fibre reinforced composites have found wide application, especially in the automotive industry, e.g. for door panels etc., and with time even for exterior parts such as under-shields. But their use is still limited to lower value parts, mainly because of the big variation of properties inherent to the natural products.[1,2] Whereas the average specific tensile strength of the strong bastfibres is comparable to glass fibres and the best single fibres are much stronger and almost comparable to aramide, the lower values are ten times weaker. These big variations result from the complex structure of the cell wall, containing highly crystalline cellulose fibrils embedded in a non-fibrous matrix of hemicellulose, pectin and lignin.[3,4] The mechanical strength of the fibres depends on the microfibrillar angle, the adhesion between cellulose microfibrils and the matrix and particularly on the unavoidable imperfections of the cell wall. These "kinks" (see Figure 1) are defects in the fibre structure originating from specific events during growth and more often induced by mechanical stress in the course of decortication and mechanical processing.[5–10]

The tensile strength of fibres increases with fibre fineness and decreases with increasing distance between the test grips, depending on the probability of the presence of defects along the fibre axis.[5–10] The relations can be described by Weibull statistics.[11–14]

The mechanical properties of fibre-reinforced composites are determined by: multiple factors:

1. Mechanical properties of components
   - Fibres/fibrils
   - Polymer matrix

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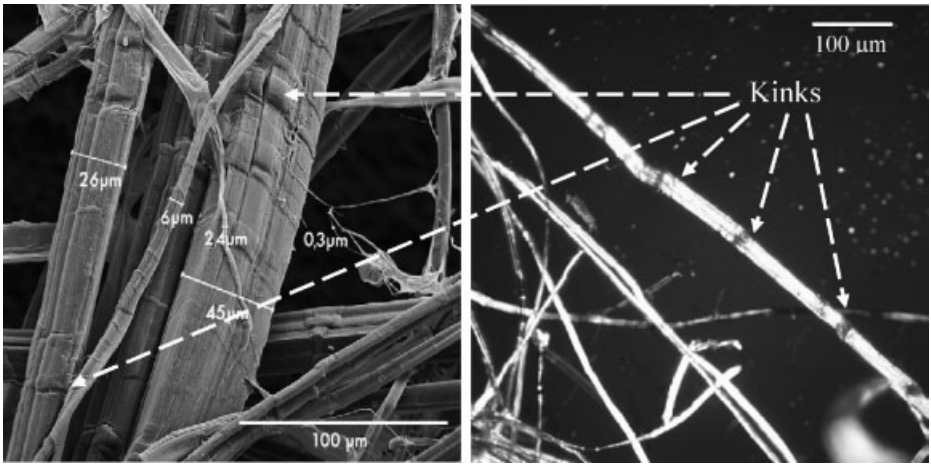

Figure 1.
Left: SEM micrograph of hemp fibres showing typical size variation and growth defects. Right: Single hemp fibres. Defects (kinks) are readily seen in the microscope, best in polarized light.

2. Composite structure
   - Fibre load (% - Vol.)
   - Fibre orientation
   - Fibre geometry (aspect ratio, critical length)
3. Fibre-Matrix-Adhesion

• Mechanical Factors
– specific interface
– mechanics of boundary layer (interphase)
• Chemical bonds
– secondary (van der Waals, Acid-Base)
– primary (covalent/ionic in special cases)

Besides the fibre load, the aspect ratio and the fibre-matrix adhesion are especially important. The aspect ratio of the fibres should be greater than 30 as a minimum, but should better exceed 100.

The fibre-matrix adhesion is determined by the number of binding sites and thus closely related to the specific surface of the fibres. Assuming a circular cross section of the fibres, the specific surface increases with the inverse of the fibre radius.

The increase in composite strength when using finer fibres with high specific surface has often been demonstrated.[5–7,15] An example is shown in Figure 1.

The basic idea to achieve further improved fibre and composite properties is to eliminate the macroscopic flaws by disintegrating the naturally grown fibres, and separating the almost defect free highly crystalline fibrils. In addition to the high strength of the single cellulose crystals, their extreme specific surface assures a greatly increased interfacial adhesion to the matrix.

The preparation of crystalline cellulose fibrils or ''whiskers'' with strength near to the theoretical value for cellulose, and their use for enhanced composites has long been reported in literature.[16–24] But, as can be seen from the references, which are by no means comprehensive, the work has been enormously intensified since 1999. More and more research groups have entered the field and the research on the topic is now rapidly expanding.[25–46] Unfortunately, the described procedures are still in a laboratory stage and require several quite complicated and time consuming steps. A specific problem is the fact that the fibrils are only stable in diluted suspensions, mainly in water. With increasing concentration and upon drying, they tend to entangle and clog together irreversibly. It is therefore difficult to produce polymer composites, and standard compound-

ing procedures are not applicable. The reported whisker composites have been prepared either by mixing the fibrils with water dispersions of polymers or by transferring the whisker suspension into an organic polymer solution. Because of these difficulties, cellulose nanocomposites have not yet attained practical relevance.

As a consequence and in order to proceed towards the practical applications of improved composites, we decided to dispense with the idea of a perfect fibrillation but instead to search for methods applicable to large scale production.

The objective was to develop fibrillated fibres with a highly increased specific surface by using standard fibre finishing processes common in the textile and/or paper industry.

Experiments and Results

Mechanically decorticated fibres of flax and hemp (''technical fibres'') were chosen as the raw materials. The fibres used for fibrillation experiments were used as such or after treatment by steam explosion (STEX).[47] After alkaline digestion of the fibres STEX splits the technical fibre bundles into single fibres. Furthermore, a major part of the hemicellulose and pectin (up to 20% of the raw fibre mass) is removed.[47] The result is shown on Figure 2.

Raw fibres as well as steam exploded fibres have been used for the screening experiments which included chemical treatment with acids and bases.

A typical processing sequence is:

1. Pre-wetting
2. Hydrochloric sequestering/scouring
3. Alkaline scouring
4. Neutralisation
5. Pulping or hollander beating
   (Total time 200 min)

It turned out that the chosen chemical processes alone, even after steam explosion, were not sufficient to fibrillate the fibres. Therefore, after the chemical treatment, the fibres were subjected to mechanical beating. A hollander beater, a laboratory blender and a pulper were used. The main factors are beating time, fibre concentration and filling volume.

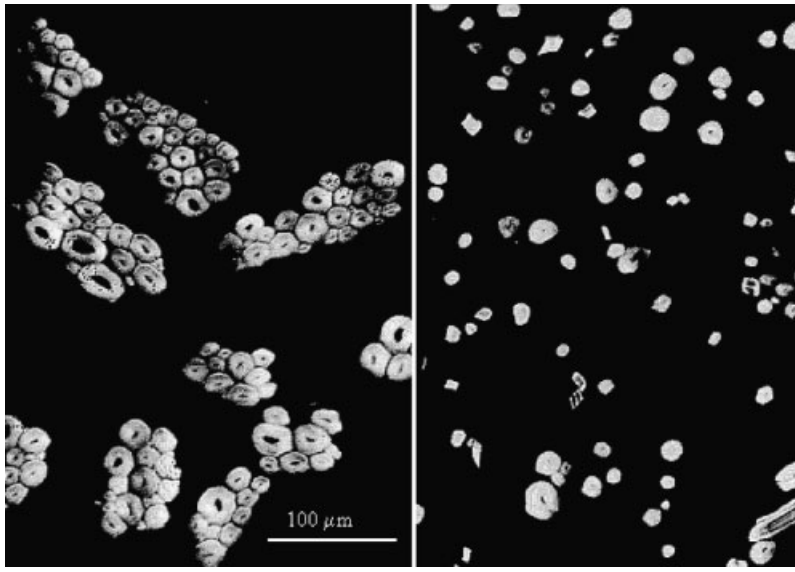

Figure 2.
Left: Bundles of raw flax fibres obtained from mechanical decortication. Right: Single fibres after steam explosion treatment of the raw fibre bundles.

Experimental design strategies have been used for the trials. But because of the many possible combinations of chemical and mechanical factors, a great number of experiments were still necessary.

Microscopy is most meaningful for evaluating the results, but because of the small sample size, numerous samples must be examined in order to obtain representative results. For routinely determining the fibrillation effect of a large number of samples, a simple and rapid method was required.

Two techniques for assessing the fibre fineness and the specific surface proved very useful:

1. The freshly prepared fibrillated fibre suspension was immersed into a Schopper-Riegler freeness tester. The drainage of water through the sheet formed by the settling fibres is correlated to the fibre fineness, a common method in the pulp and paper industry.

2. The fibre sheets formed during the freeness test are carefully removed and dried, and then used for porometry measurements in a PMI Porometer. The information obtained is the ''envelope surface'' of the fibres, a relative measure of the specific surface.The principle of the method is shown in Figure 3.

From the permeability curve the envelope surface is obtained using a modified Carman-Kozeny equation.[48]

$$\frac{Ql}{\Delta Pa} = \frac{\varepsilon^3}{k(1-\varepsilon)^2 S_v^2 \eta} + \frac{z\varepsilon^2 \pi}{(1-\varepsilon)S_v\sqrt{2\pi\rho\overline{P}}}$$

where Q = volume flow l = thickness of the powder bed ΔP = differential pressure across the sample bed a = cross sectional surface area of the sample bed ε = porosity of sample bed = void volume/total volume k = aspect factor, taken to be 5 S_v = total surface area of sample/volume of sample η = viscosity of the gas z = constant, taken to be $48\pi/13$ ρ = density of the gas P = mean pressure of gas in sample

Figure 4 illustrates the rather good correlation between the envelope surface from porometry and the specific surface determined with the BET-method using nitrogen adsorption, provided the fibres have similar surface structure. Different fibre types (e.g. cotton fibres) must be regarded separately.

The intensity of mechanical beating is lowest in the pulper, higher in the blender and very high in the hollander beater which also causes some fibre shortening by its cutting effect. Examples of results of the factorial experiments are shown in Figures 5 and 6.

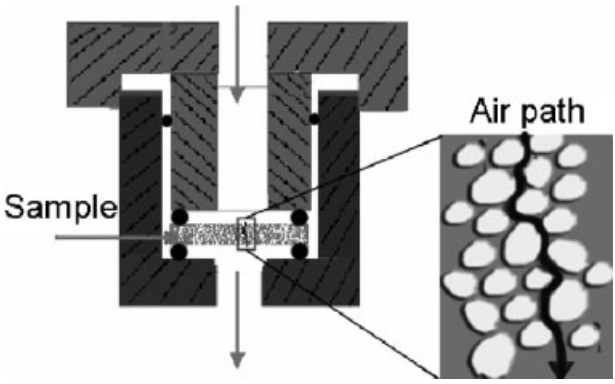

Figure 3.
The fibrous sheets are tightly fixed in the porometer cell. The air flow through the sample is measured as a function of the applied pressure.

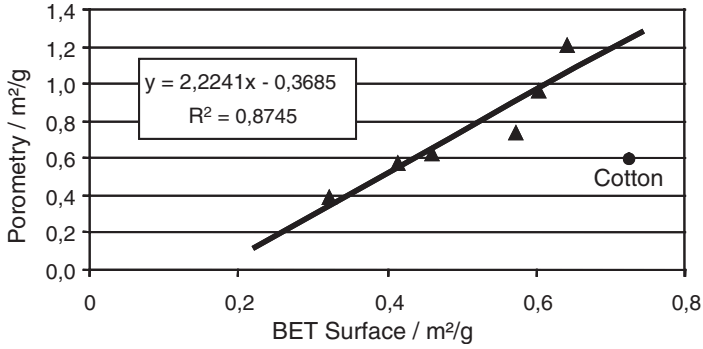

Figure 4.
Correlation between porometry envelope surface and the BET specific surface for the bast fibres flax or hemp (triangles). Cotton fibres have a different surface structure and would need a separate calibration.

Reduction of the filling volume in the respective beater increases the fibrillation effect. Extended beating time intensifies the fibrillation of hemp, but not of flax, as can be seen from the interaction graph Figure 6.

By choosing the proper chemical and mechanical treatment, a relevant proportion of the fibres is fibrillated. The resolution of the light microscope is insufficient to display details of the fibrils. Scanning electron microscopy (SEM) reveals more details and shows that the fibrils maintain a remarkable length and therefore have a very high aspect ratio.

Along the axis it seems that mainly the primary wall and eventually parts of the outer S1 layer of the fibres are readily fibrillated (Figure 7). Other observations are that fibrillation often begins at the fibre ends and that the fibre "kinks" are preferably attacked by hard chemical treatment.

Because the chosen processes are not sufficiently effective to achieve total fibrillation, still unaffected single fibres are always present. The significant length of

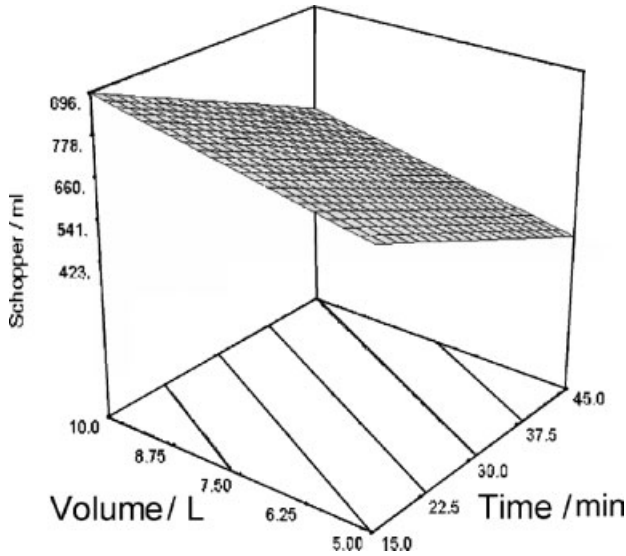

Figure 5.
Response surface illustrating the influence of filling volume in the beater and the beating time.

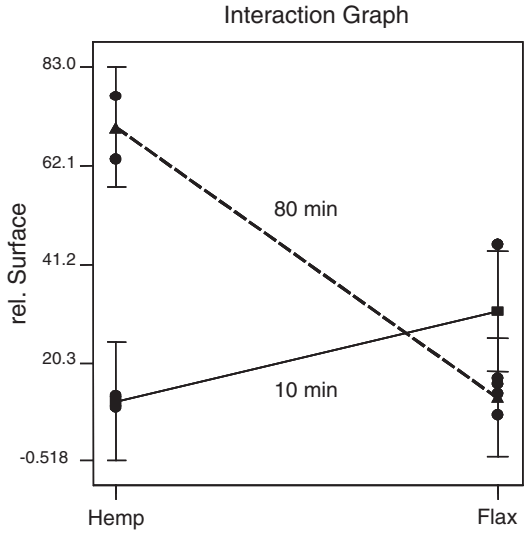

Figure 6.
The interaction graph shows the influence of the beating time on the different fibre types hemp and flax.

the fibrils, their residual connection to the fibre core and the presence of many normal fibres cause a strong tendency to entangle and clog together, forming knots (Figure 8).

Irreversible entanglement occurs upon uncontrolled drying of the fibrillated fibres. A homogenous re-dispersion in a polymer composite by common compounding processes becomes impossible.

In order to avoid clotting, it is very important to hold the fibres well separated in a diluted suspension, and to avoid strong stirring and mechanical agitation. By a gentle movement of the suspension, the entanglement can be sufficiently reduced.

The best method for preparing composites is therefore the forming of wet-laid non-wovens directly from the diluted fibre suspension. An inclined wire machine has been used to make non-woven sheets in which the fibres are quite homogenously and isotropically distributed. The wet-laid

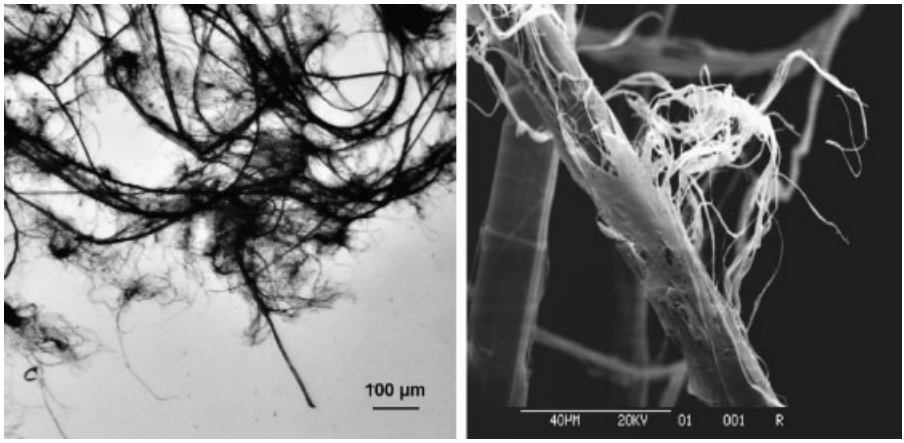

Figure 7.
Left: Light micrograph, fibrils are too fine to be clearly resolved. Right: SEM micrograph shows fibrillation of the outer layer.

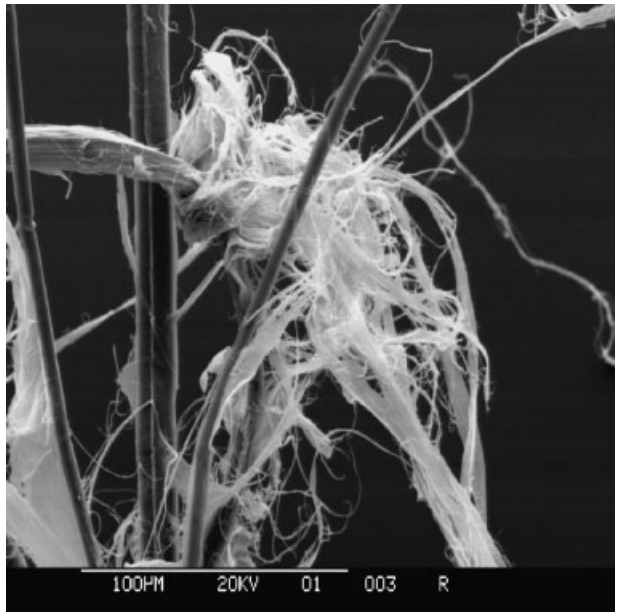

Figure 8.
Example of fibril entanglement.

process offers many advantages for preparing semi-finished materials. After drying, the fibrous sheets can be impregnated with thermosetting resins and moulded in the hot press.

Furthermore, it is easy to prepare hybrid sheets by adding thermoplastic polymers (e.g. polypropylene) in the form of fibres, or, if necessary, even powder together with other additives to the suspension. The resulting composite sheets are ready to be moulded in a hot press.

The obtained composites with the fibrillated fibres show superior mechanical properties as demonstrated in Figure 9–10.

As an example the treatment sequence III B which gave very good results is described. The chemical treatment was done in a programmable laboratory finishing apparatus (Ahiba). The fibre to liquor ratio was 1:10 by weight.

1. Pre-wetting

   2 g/l Felosan JET
   10 min., 40 °C, liquor drained off

2. Sequestering

   20 ccm/l Trilon TB (EDTA)
   heating 3 °C/min. to 80 °C
   adding of 20 ccm/l HCl conc.
   heating 3 °C/min to 95 °C
   10 min. 95 °C liquor drained off
   1× hot rinse, 60 °C, 10 min.
   1× warm rinse, 50 °C, 10 min.
   1× hot rinse, 80 °C, 10 min.
   1× cold rinse, 30 °C, 6 min.

3. Alkaline Scouring

   50 g/l NaOH (100%), cold
   heating 3 °C/min. to 95 °C
   90 min. at 95 °C liquor drained off
   1× hot rinse, 80 °C, 10 min.
   1× warm rinse, 50 °C, 10 min.
   1× cold rinse, 30 °C, 10 min.

4. Neutralization

   2 g/l Acetic acid (60%)
   15 min at 35 °C,

After the chemical treatment 2 g of the wet fibres were put into 500 ml of cold water

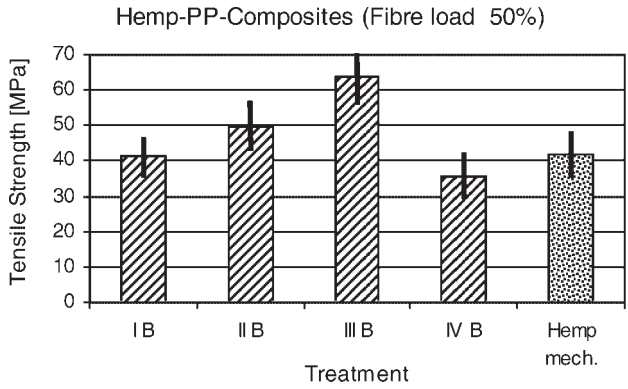

Figure 9.
Comparison of the tensile strength of composites, prepared by compression moulding of non-woven sheets containing hemp and PP fibres. I B – IV B denote different chemical and mechanical process sequences resulting in different grades of fibrillation. (see example III B below).

and this suspension was fibrillated by beating for 30 sec in a Waring-type laboratory blender. The suspensions were collected, transferred to the non-woven machine and formed to wet-laid sheets ready for the preparation of composites.

In additional experiments, the effect of hydro-mechanical treatment of wet-laid non-wovens by the ''Fleissner spunlace process'' has been investigated. In this process, the non-wovens are subject to very fine high-pressure water beams which impinge onto the fabric with extreme speed, thus entangling and bonding the fibres. The result is a homogenous non-woven with greatly increased tensile strength and high elongation. Furthermore, the high impact of the water jets effects an additional splitting of the fibres.

Epoxy composites prepared from such spunlaced non-wovens show slightly reduced tensile strength but substantially increased tensile modulus. Therefore the spunlace process offers an additional method for adapting the composite properties to different requirements.

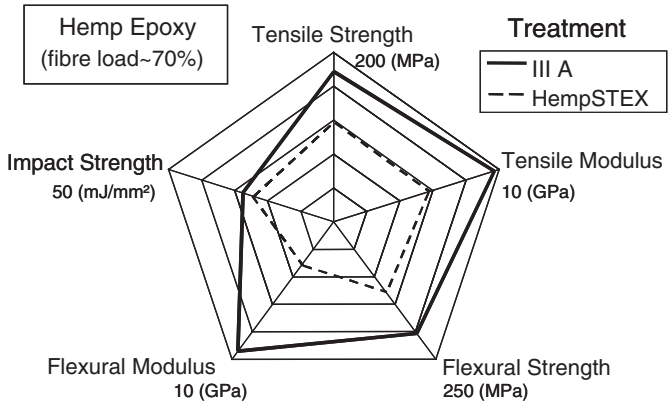

Figure 10.
The star plot demonstrates the significant improvement of the mechanical property profile of a composite prepared from fibrillated hemp (treatment sequence III A) compared to a composite with just steam exploded (STEX) hemp.

Conclusion

The mechanical properties of composites are greatly enhanced with increasing specific surface of the reinforcing fibres obtained by different degrees of fibrillation. In the case of natural fibres, an essential first improvement is achieved by splitting the bastfibre bundles into high quality single fibres by chemical processing, especially by alkaline scouring followed by steam-explosion.[47] The chemical treatment removes most of the non-fibrous substances hemicellulose, pectin and lignin. Depending on the retting degree of the raw fibres, the weight loss can amount to about 20%. Although the fine single fibres lead to considerably enhanced composite properties, their specific surface hardly exceeds 1 m^2/g. Furthermore, the maximum possible strength is limited by the existence of structural defects along the fibre axis.

The liberation of highly crystalline cellulose fibrils from the single fibres greatly increases the specific surface and also eliminates many of the macroscopic flaws. The complete disintegration of the complex fibre structure and preparation of true nanosized cellulose single crystals is still not available on an industrial scale due to the need of complicated and time consuming processing steps, but it has been demonstrated that a partial fibrillation is possible by modified finishing processes, which can easily be carried out in any textile finishing line and by additional mechanical beating.

Although the fibrillation is mostly restricted to the outer layers of the fibres, the specific surface available for bonding to the matrix is substantially increased and composites made of fibrillated fibres show considerably improved mechanical strength.

An easy method to circumvent entanglement and clotting of the fibrillated fibres and at the same time, to produce all types of composites has been found in the very flexible and effective wet-laid non-woven process, which also allows for mass production.

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