



# Hierarchical wood cellulose fiber/epoxy biocomposites – Materials design of fiber porosity and nanostructure



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## ABSTRACT

Delignified chemical wood pulp fibers can be designed to have a controlled structure of cellulose fibril aggregates to serve as porous templates in biocomposites with unique properties. The potential of these fibers as reinforcement for an epoxy matrix (EP) was investigated in this work. Networks of porous wood fibers were impregnated with monomeric epoxy and cured. Microscopy images from ultramicrotomed cross sections and tensile fractured surfaces were used to study the distribution of matrix inside and around the fibers – at two different length scales. Mechanical characterization at different relative humidity showed much improved mechanical properties of biocomposites based on epoxy-impregnated fibers and they were rather insensitive to surrounding humidity. Furthermore, the mechanical properties of cellulose-fiber biocomposites were compared with those of cellulose-nanofibril (CNF) composites; strong similarities were found between the two materials. The reasons for this, some limitations and the role of specific surface area of the fiber are discussed.

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## 1. Introduction

New sustainable products from renewable resources are desirable as environmental concerns are growing in the society. One of the most important biological resources available for new environment friendly materials is wood. Wood is a “green” resource; available in large quantity with the added advantage that the infrastructure and logistics for wood handling are available in almost every region. The wood cell wall is a complex hierarchical structure, where cellulose fibrils (3–5 nm wide) are the primary load bearing units. These fibrils are arranged as aggregates (20–50 nm wide) [1,2] in different layers of the cell wall and are embedded in a matrix of hemicellulose and lignin. During recent years, substantial research has focused on extracting these fibrils from fibers and using them to prepare nanocomposites and other advanced products [3–6]. A promising future of polymer matrix nanocomposites based on cellulose nanofibrils (CNF) is foreseen [7–10] but some fundamental problems remain. One practical disadvantage with CNF is that nanoscale entities are difficult to

process on a large industrial scale. For instance, the viscosity of hydrocolloidal suspensions of CNF is very high at a low concentration, and it is therefore extremely time-consuming to filter a nanocellulose suspension. To filter a network of nanofibers can take 3–24 h in contrast to just a few seconds with fibers. There are also drawbacks related to storage and transport – nanofibrils are often isolated as gels, typically at 2% solid content, and drying them to a higher solid content (above a critical level) causes agglomeration [11,12]. The use of nanostructured cellulosic wood fibers therefore offers many interesting advantages in a processing context, provided that the fibrils inside the fiber can be fully utilized. Moreover, in order to disintegrate the fibrils from a pulp fiber, an energy-intensive process (usually a high pressure homogenizer) may be required, and the dispersion of these nanofibrils in polymer/monomers without agglomeration is also a challenge. Surface modification of the fibrils is a common strategy to overcome this problem [13,14].

The use of the inherent nano-structure of cellulose fibers is an alternative approach. After delignification, the fibril aggregates in the fiber wall are arranged in an open structure with a surface area of approximately 150 m<sup>2</sup>/g [15,16]. Svensson et al. [17] used mild TEMPO-mediated oxidation followed by careful solvent exchange to preserve the open structure in the dry state. Yano et al. [18] used acetylation to avoid the irreversible collapse of the fiber wall by

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limiting the formation of irreversible bonds. They further impregnated the acetylated fiber sheets with acrylic resin and obtained transparent composites. Fang et al. [19] developed a nanostructured paper with high transparency and haze, suitable for solar cell applications. These studies show the growing interest in the utilization of the native structure of cellulose fibers for the preparation of new advanced materials.

In the present study, the open structure of cellulose pulp fibers is considered to be a porous template consisting of nanostructured fibril aggregates. The potential for using such fibers to prepare composites with unique properties is explored and the main objective is to utilize the nanostructure of the cell wall to prepare biocomposites based on plant fibers and compare their properties with biocomposites from collapsed fibers as well as with CNF nanocomposites.

The study also aimed to evaluate the effect of changes in supramolecular structure of the fibers on the properties and performance of the final composite. It is known that oxidation of cellulose fibers (in this case, TEMPO-mediated oxidation) increases the fiber wall volume (i.e. the fibers swell in water) and modifies the fibril aggregate structure inside the fiber wall. Attempts were made to impregnate these fibers with epoxy resin. Structural changes in the fiber wall and epoxy impregnation may affect the composite performance. Therefore, composites prepared with fibers oxidized to different charge densities (having open pore structure) were evaluated. This served to relate the structural changes inside the fiber wall with the performance of the composites.

Furthermore, the properties of pulp fiber composites were compared with cellulose nanofibril (CNF) composites [20]. This comparison further emphasized the importance of interface/surface area, size/dispersion of the reinforcing unit and fiber network characteristic in determining the composite properties.

## 2. Experimental

### 2.1. Material and method

The epoxy resin used was monomeric Bisphenol A Diglycidyl Ether (abbreviated DGEBA) purchased from TCI chemicals and Jeffamine D-400 polyetheramine (abbreviated D400), kindly provided by Huntsman, USA, was used as the cross-linker. The ratio between the two components was determined experimentally and was different for different materials (see results and discussions). Dissolving pulp (60% Norwegian spruce and 40% Scots Pine) was obtained from Domsjö, Örnsköldsvik, Sweden. The glucose content was above 96% as determined by sugar analysis.

### 2.2. Processing

The pulp was oxidized using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) catalyst to charge densities of  $600 \pm 50 \mu\text{eq/g}$  and  $1300 \pm 50 \mu\text{eq/g}$  [21,22]. The charge density was measured by conductometric titration [23] and the pulp was thereafter converted into its sodium form according to an earlier described procedure [24]. The reference, with a collapsed fiber wall, was an unoxidized pulp ( $20 \mu\text{eq/g}$ ), converted into its sodium form using the same procedure.

Fiber sheets with a grammage of approximately  $110 \text{ g/m}^2$  were prepared using a Rapid Köthen (RK) sheet forming device (PTI, Vorchdorf, Austria). To remove the excess water, sheets were dried for 2 min 30 s at  $93^\circ\text{C}$  under vacuum. These drying conditions made it possible to remove the excess water but at the same time avoid collapse of the fiber wall, and sheets with a solid content of 20% were obtained after this initial dewatering as shown in earlier investigation [17]. Rectangular strips (50 mm by 10 mm) were cut from these wet fiber sheets and placed in methanol for at least 24 h, the methanol was changed at least three times during this period. The methanol-soaked fiber network was then placed in a bulk impregnation

mixture (DGEBA and D400) and kept under vacuum. After impregnation for ca. 4 h, the fiber samples were removed, gently wiped with filter paper to remove excess liquid resin from the surface and then placed between Teflon sheets and cured in Rapid Köthen for 1 h at  $93^\circ\text{C}$ . The slight underpressure (95 kPa) drained any excess epoxy from the networks. The composites were then cured in an oven at  $90^\circ\text{C}$  for 2 h and postcured at  $120^\circ\text{C}$  for 2 h. Composites with unoxidized fibers were prepared in a slightly different way – the fiber sheets were prepared in RK as before and rectangular strips were cut and dried completely in air (to collapse the cell wall). The dried fiber strips were soaked in methanol and then impregnated and cured as described earlier. The fiber content, based on the initial dry weight of the fibers and final composite weight was  $18 \pm 1 \text{ wt}\%$  and the thickness was in the range of 0.48–0.50 mm. The density of the composites, as calculated based on the dimensions and total weight, was  $1.05\text{--}1.1 \text{ g/cm}^3$  for all the composites. The composites are referred to as Pulp/EP Ox-0, Pulp/EP Ox-600 and Pulp/EP Ox-1300 depending on the charge density of the fibers.

### 2.3. Characterization

A simplified water retention value measurement (WRV, SCAN 68:00) was performed using 5-mL disposable centrifuge filters (Millipore Ultrafree-CL Centrifugal Device, Millipore, Billerica, MA, USA) equipped with  $5\text{-}\mu\text{m}$  PVDF membranes. Approximately 1–2 g of wet fibers were placed in the filter and centrifuged at 3000g for 30 min at room temperature. The dry content of the fibers was determined gravimetrically by drying in an oven at  $105^\circ\text{C}$  overnight. The dimensionless mini-WRV value was then determined as the mass of water divided by the mass of dry sample (g/g).

Differential Scanning Calorimetry (DSC) was performed with a Mettler Toledo instrument. Samples weighing ca. 20 mg and sealed in 100  $\mu\text{L}$  aluminum pans were heated to  $120^\circ\text{C}$  to remove any thermal history. The glass transition temperature ( $T_g$ ) was calculated from the second scan, which was between  $-20$  and  $150^\circ\text{C}$  at a rate of  $5^\circ\text{C}/\text{min}$ .

Tensile tests were performed with an Instron 5944 with a 500 N load cell. Samples (50 mm by 7 mm) and thickness between 0.480 and 0.500 mm were tested at a strain rate of 10%/min. Prior to testing, the samples were conditioned at a relative humidity of 50% (or 98%) and  $23^\circ\text{C}$  for at least 2 days. Moisture uptake was calculated as the weight increase based on the dry weight. To measure the strain accurately, a differential speckle photography (vic 2D, LIMESS) device was used. The modulus was calculated from the initial elastic region, typically between 0.1% and 0.3% strain.

The distance,  $h$ , between fibers in the composite was estimated using a model for unidirectional and cylindrical fibers and assuming square packing [25], see Eq. (1):

$$h = 2 \left[ \left( \frac{\pi}{4f} \right)^{1/2} - 1 \right] \quad (1)$$

where  $r$  = radius of fibers (15  $\mu\text{m}$ ) or fibrils (2 nm),  $f$  = volume fraction of fibers in the composite.

Dynamic Mechanical Thermal Analysis (DMTA) was performed with a TA Q800 in tensile mode for rectangular strips (15 mm by 4 mm). Measurements were taken at an amplitude of 10  $\mu\text{m}$  and a frequency of 1 Hz between  $-20^\circ\text{C}$  and  $200^\circ\text{C}$ . The  $T_g$  was calculated from the peak in the loss modulus curve.

SEM microscopy images were obtained using FE-SEM (Hitachi S-4800) after coating the surface with platinum–palladium. Smooth cross sections were prepared by cutting the samples with an ultramicrotome (Leica Ultracut UCT) using a diamond knife (Diatome). Cross sections of samples fractured during tensile test were also studied.

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