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Structure and properties of a pulp fibre-reinforced composite with regenerated cellulose matrix

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ABSTRACT Fully bio-based cellulose–cellulose composites were produced by partly dissolving beech pulp fibres in lithium chloride/dimethylacetamide (LiCl/DMAc) and subsequent regeneration of matrix cellulose in the presence of undissolved fibres. Compared to cellulose–epoxy composites produced from the same fibres, a two-fold increase in tensile strength and elastic modulus was observed for cellulose–cellulose composites. From scanning electron microscopy and nanoindentation it is concluded that changes in the fibre cell wall during LiCl/DMAc treatment, improved matrix properties of regenerated cellulose compared to epoxy, and improved fibre–matrix adhesion are responsible for the superior properties of cellulose–cellulose composites.

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1 Introduction

With a tensile strength of up to 1500 MPa and an elastic modulus of 40 GPa to 120 GPa, natural fibres are a potential alternative to glass fibre for the reinforcement of polymer matrix composites [1]. However, the mechanical performance of natural fibre-reinforced composites is limited by a number of factors, among which high natural variability of mechanical fibre properties, hygroscopicity of natural fibres, and insufficient fibre–matrix adhesion are most important [2]. In order to improve fibre–matrix adhesion, surface modification is often needed [3], which increases the cost of natural fibre-reinforced composites, making them less competitive. Recently, Nishino et al. [4] presented a new approach to natural fibre-reinforced composites by combining unidirectionally aligned ramie reinforcement fibres with a matrix of regenerated cellulose. Since fibre and matrix are chemically identical in such a cellulose–cellulose composite, fibre–matrix adhesion should be maximum. This is expressed by a comparably high tensile strength of up to 480 MPa measured for unidirectional ramie fibre-reinforced all-cellulose composites [4]. Being composed of a single, bio-based material, such composites possess the advantage of being biodegradable; however, consisting of cellulose, they still bear the disadvantage of hygroscopicity and perform best only in dry conditions [2].

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In the present paper, we produce a cellulose–cellulose composite by partial dissolution of random-oriented beech pulp fibres and use wide-angle X-ray scattering (WAXS), nanoindentation, tensile testing, and scanning electron microscopy (SEM) to characterise its structure and properties.

2 Materials and methods

Dissolving-grade beech pulp discs with a diameter of 12 cm and a thickness of 1.5 mm were activated in distilled water at 20 °C for 6 h, and subsequently dehydrated twice in methanol and acetone, and in dimethylacetamide (DMAc, Aldrich 27,101-2) for 1 h each. In order to dissolve a certain amount of cellulose, a pulp disc was then placed in a solution of 8-g lithium chloride (LiCl, Fluka 00621) in 100-mL DMAc for 10 h. Dissolved cellulose was precipitated from solution by immersing the pulp sheets into a bath of distilled water. For complete removal of LiCl/DMAc, the distilled water in the bath was exchanged repeatedly during 5 days. Thereafter, the sheet was gently compressed between tissue paper to remove excess water and subsequently dried between sheets of paper in a hot press at a temperature of 80 °C and a pressure of 200 MPa. During drying in the press, the pressure was increased slowly in order to prevent fibre displacement. High pressure was applied to compact the composite and to avoid the formation of pores due to the shrinkage of regenerated cellulose during drying. Dry composite sheets consisted of ∼ 80 vol. % fibres and 20 vol. % regenerated cellulose matrix. For comparison, pulp sheets were vacuum impregnated with epoxy resin (Epoxy resin L, no. 236 349, Conrad, Germany) and cured at ambient temperature and a pressure of 200 MPa. After pressing the composite sheets were ∼ 1-mm thick and the fibre volume fraction was 72%. Sheets of pure regenerated cellulose were produced by dehydrating 1-g pulp and dissolving overnight in 100-mL LiCl/DMAc at ambient temperature. Regenerated cellulose sheets were precipitated in water, washed in distilled water, dehydrated, and pressed as described above.

The structural properties of the composite were characterised using X-ray diffraction. The preferred orientation in the composite was evaluated 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).

Additionally, $\theta/2\theta$ scans were performed by integrating 2D detector images acquired with Nanostar.

Ten strips each with a length of 80 mm and a width of 5 mm were cut from composite sheets and fixed in the grips of a Zwick/Roell universal testing machine. Samples were loaded to failure at a cross-head displacement rate of 1 mm/min and elongation was recorded by means of Zwick macrosense clip-on displacement sensors.

Small pieces containing the fracture surface were cut from specimens tested in tension, sputter coated with gold, and observed in high-vacuum mode at an acceleration voltage of 10 kV in a Philips Environmental Scanning Electron Microscope.

In order to study mechanical properties of matrix and fibres in cellulose–epoxy composites and dried LiCl/DMAc-treated pulp fibre sheets, nanoindentation experiments were performed. Small samples were embedded in epoxy resin and smooth surfaces were cut by means of an ultramicrotome equipped with a diamond knife. Samples were glued to metal discs with epoxy resin and mounted onto the stage of an atomic force microscope (Digital Instruments DI Dimension 3100) equipped with an add-on indentation device (Hysitron Triboscope). In a force-controlled mode, indents were performed by means of a Berkovich-type triangular diamond pyramid, applying a peak force of 250 μN. Material hardness and elastic modulus were evaluated according to Oliver and Pharr [5].

3   Results and discussion

Wide-angle X-ray scattering revealed a near-random distribution of fibre orientation in pulp sheets (Fig. 1). Integrated data from the 2D detector images is shown in Fig. 2. The $\theta/2\theta$ scan of untreated beech pulp corresponds to cellulose I, which shows highest scattering intensity at 22.7° [6], whereas regenerated cellulose contains primarily cellulose II crystallites, which show highest scattering intensity at 20.4° [7]. The pulp sheet treated with LiCl/DMAc primarily shows characteristics of cellulose I, but small changes in the intensity distribution indicate the presence of cellulose II. On the one hand, the scattering intensity peak in the treated pulp sheet has shifted to a smaller angle of 21.6°. On the other hand, the normalised scattering intensity at the angle characteristic of cellulose II (20.4°) in the treated pulp sheet increases by 20% compared to untreated beech pulp. From this, it is concluded that the treatment of pulp with LiCl/DMAc leads to the dissolution of a certain
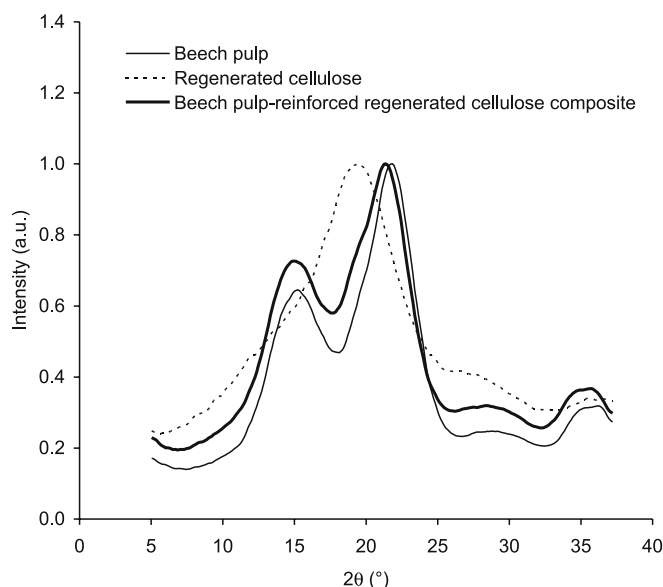

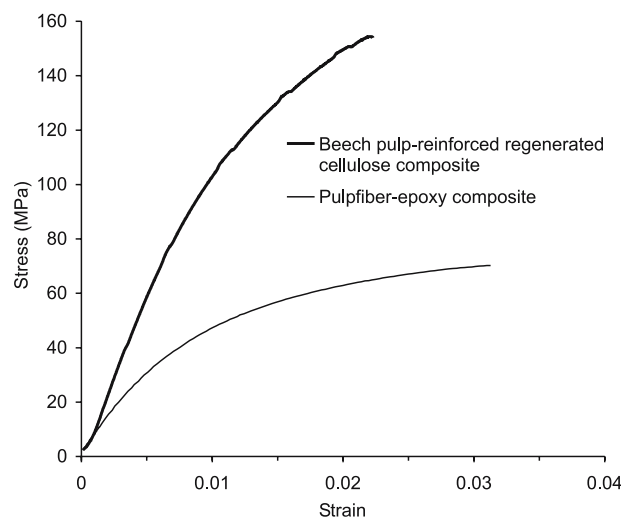**FIGURE 2** $\theta/2\theta$ scans derived from WAXS 2D detector images

FIGURE 3   Stress–strain graphs from tensile tests

amount of cellulose, which serves as matrix between undissolved fibres after precipitation from solution and drying. The treated pulp sheet may thus be regarded as a composite of regenerated cellulose reinforced with random-oriented pulp fibres.
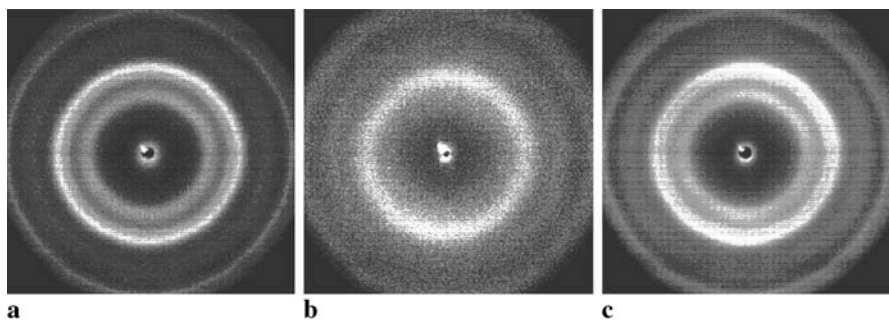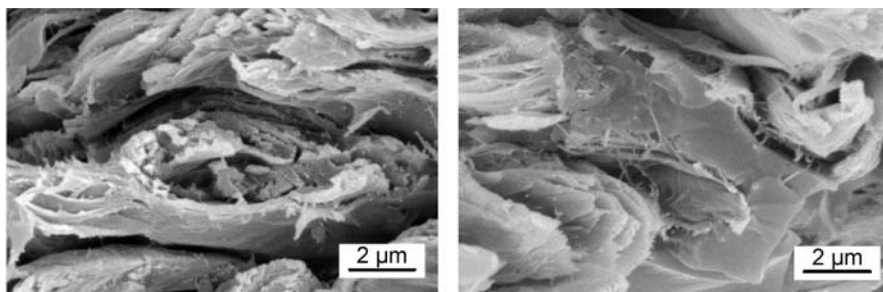

FIGURE 1   WAXS 2D detector images of a beech pulp sheet (**a**), pure regenerated cellulose (**b**), and a beech pulp sheet after treatment with LiCl/DMAc (**c**)

FIGURE 4 SEM images of fracture surfaces from a beech pulp-reinforced regenerated cellulose composite (*left*) and a pulp fiber–epoxy composite (*right*). Note the smooth fracture surface of epoxy in the centre of the *right-hand image*

Tensile tests with this composite showed a tensile strength of 154 ± 17 MPa and an elastic modulus of 12.2 ± 0.9 GPa (Fig. 3). This compares very favourably with the mechanical properties of other random-oriented natural fibre reinforced composites, which typically show a tensile strength of 15 to 140 MPa and an elastic modulus of 1 to 13 GPa [8–13]. Considering that cellulose–cellulose composites produced by Nishino et al. [4] were reinforced by unidirectionally aligned ramie fibres, the strongest natural cellulosic fibre [2], the quality of the random-oriented pulp fibre-reinforced cellulose–cellulose composite produced in the present study ($\sigma = 154$ MPa) is comparable to the ramie-reinforced composite ($\sigma = 480$ MPa). With 70 ± 8 MPa and 5.8 ± 0.7 GPa the tensile strength and elastic modulus, respectively, of the pulp fibre-reinforced epoxy composite produced for direct reference was only 50% of the cellulose–cellulose composite. Since reinforcement fibres and fibre volume fraction were similar in the cellulose–cellulose and the cellulose–epoxy composites, the observed changes in mechanical performance by a factor of two may be explained by differences in matrix properties and fibre–matrix interaction.

SEM of fracture surfaces revealed important microstructural differences between the cellulose–epoxy and the cellulose–cellulose composites (Fig. 4). In the cellulose–epoxy composite, fibre and matrix can be easily identified by their different fracture patterns, particularly the smooth surface of fractured epoxy. By contrast, the matrix in the cellulose–cellulose composite fractures in a lamellar way, which makes it difficult to distinguish it from the reinforcement pulp fibres. Since no clear boundaries between fibre and matrix were identified by SEM of cellulose–cellulose composites, it is concluded that there is a much better compatibility and better interfacial adhesion of fibre and matrix in these composites compared to cellulose–epoxy composites, which was also observed by Nishino et al. [4].

Results of nanoindentation experiments performed in the matrix and fibres of cellulose–epoxy and cellulose–cellulose composites are shown in Figs. 5 and 6. Both hardness and elastic modulus were about twice as high in the regenerated cellulose matrix compared to epoxy. Also, the hardness and elastic modulus of reinforcement fibres were higher in fibres embedded in cellulose than fibres from the epoxy composite. This indicates that not only are matrix properties superior in the cellulose–cellulose composite, but also fibre properties are significantly improved by LiCl/DMAc treatment. Presumably, cellulose not only from the fibre surface was dissolved and transformed to regenerated cellulose serving as matrix. Also, a certain amount of cellulose inside the fibre
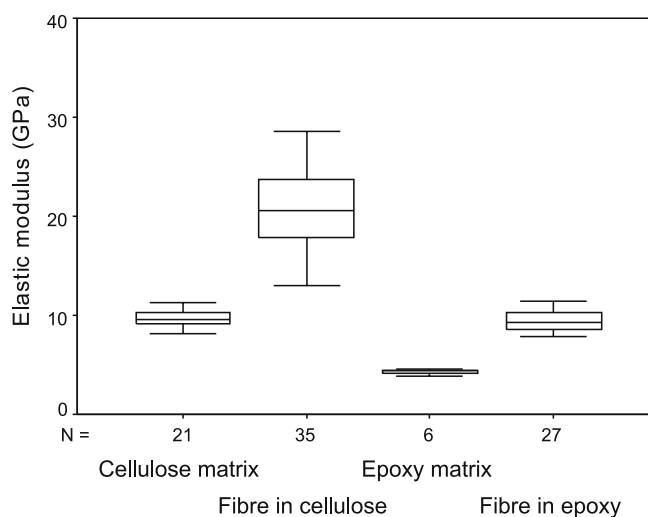
FIGURE 5 Elastic modulus derived from nanoindentation experiments
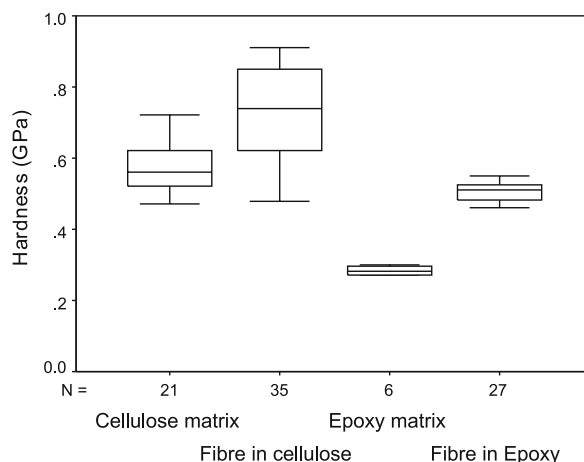
FIGURE 6 Hardness derived from nanoindentation experiments

cell walls was apparently dissolved and regenerated within the cell wall during solvent removal. Thus, the regenerated cellulose within the fibre cell walls acts as cell wall matrix holding cellulose I microfibrils together, which improves cell wall hardness and elastic modulus.

4 Conclusion

Structural changes in the fibre cell walls together with improved matrix properties and fibre–matrix adhesion are the cause for the two-fold increase in tensile strength and

elastic modulus observed for cellulose–cellulose composites compared to cellulose–epoxy composites.

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