The Structural Origins of Wood Cell Wall Toughness

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The remarkable mechanical stability of wood is primarily attributed to the hierarchical fibrous arrangement of the polymeric components. While the mechanisms by which fibrous cell structure and cellulose microfibril arrangements lend stiffness and strength to wood have been intensively studied, the structural origins of the relatively high splitting fracture toughness remain unclear. This study relates cellulose microfibril arrangements to splitting fracture toughness in pine wood cell walls using in situ electron microscopy and reveals a previously unknown toughening mechanism: the specific arrangement of cellulose microfibrils in the cell wall deflects cracks from the S2 layer to the S1/S2 interface, and, once there, causes the crack to be repetitively arrested and shunted along the interface in a zig-zag path. It is suggested that this natural adaptation of wood to achieve tough interfaces and then deflect and trap cracks at them can be generalized to provide design guidelines to improve toughness of high-performance and renewable engineering materials.

From the point of view of mechanical function, wood structure can be summarized as a fibrous composite at both the cell- and cell wall-level. At the cell level, softwoods such as pine beside parenchyma cells primarily consist of cylindrically shaped tracheid cells, with the cylinder axis aligned longitudinally in the tree and containing cell walls surrounding the cell lumens. The walls of the tracheid cells are composed of layered arrangements of cellulose microfibrils which have a high tensile strength and stiffness embedded in a matrix of lignin which has a low strength and stiffness in tension, but high in compression. Both are connected by hemicellulose, which has a tensile/compression strength and stiffness between those of cellulose and lignin. The compound middle lamella (CML) consisting of the middle lamella and the primary wall connects the cells, while the secondary cell wall is composed of three layers: S1, S2, and S3. The layers differ in their molecular composition, but more importantly for mechanical properties, they differ in the microfibril arrangement. A widely accepted model describes a helical arrangement within the cell wall with the S1, S2, and S3 layers of the cell wall distinguishing themselves by the angle of the microfibrils (MFA) relative to the cell axis (Figure 1c). However, further details of the ultrastructure are frequently controversially discussed, including MFA variations within a given cell wall layer, the existence of a radial component to the microfibril direction, and the structure at the interfaces between the secondary cell wall layers.

The fracture behavior of wood has been the subject of many studies and is influenced by whether the cracks propagate across the grain, thereby deforming and rupturing the wood cells, or along the grain. The energy of fracture or toughness for cracks that propagate across the grain is quite high, ≈10 kJ m⁻², which is comparable to engineering Al alloys or medium C steels. The main toughening mechanism is believed to be plastic buckling of the cell walls under tension due to the helical arrangement of the cellulose microfibrils. In contrast, the energy of splitting fracture along the grain is roughly 10 times smaller. Although mode I splitting cracks typically grow unstably, showing brittle behavior, investigations of their morphology reveal toughening from microcracking and crack bridging involving several to many wood cells, which contribute to the modest toughness. A closer look shows that splitting cracks either connect up the lumen by propagating through the cell walls between the lumen (transwall fracture), or propagate entirely within the cell walls (intrawall fracture or intercell fracture). Although transwall fracture would clearly be energetically favorable if the cell walls were isotropic material, wood frequently exhibits intrawall fracture. For example, pine wood regularly splits by intrawall fracture at the S1/S2 interface, as well as in the CML or the S1 layer. Although the anisotropic arrangement of microfibrils in the cell wall is clearly important in determining the crack path and the toughness, its detailed role in splitting fracture has received little attention to date.

In this work, we perform in situ electron microscopy studies of the propagation of axial splitting cracks in the cell walls of pine latewood. The goal is to understand how cell-wall level toughening mechanisms and crack path selection depend on local microfibril arrangements and account for the splitting fracture toughness of wood. Pine wood is chosen because of its relatively simple cell structure and because of its tendency for intrawall fracture.

Specimens for ultrastructure characterization by transmission electron microscopy (TEM) were prepared by microtome and focused ion beam (FIB) machining (Figure 1d, for details...
see Experimental Section and Supporting Information). The FIB is used here rather than the more routinely employed ultramicrotome, because it allows unembedded wood specimens to be prepared in the complex double cantilever beam geometry, and embedding must be avoided when performing mechanical tests since it completely changes the mechanical response. TEM images of both radial-tangential (r–t) and radial-longitudinal (r–l) sections are used to reconstruct the 3D microfibril arrangements in the outer portion of the cell wall (Figure 2). The CML is identifiable on the right-lower side or right-side of both sections (Figure 2a,b) from the darker staining contrast due to its higher lignin content. The quality of the images from the FIB-prepared specimens is similar or somewhat worse than from ultramicrotome prepared specimens,[17–22] but allows the projected microfibril directions to be clearly detected. The radial component of the MFA in the r–l section \( \theta_r \) (Figure 2b) depends on the distance from the CML, increasing from 0 to 5° at \( \approx 1 \) µm distance, to almost 90° at 200 nm distance, and then decreasing to around 60° ± 20° in the S1 layer at the interface to the CML. We associate the region of maximum \( \theta_r \) with the

Figure 1. Pine latewood cell structure with approximate dimensions and specimen geometry showing both the tree (\( \hat{L}\hat{T}\hat{R} \)) and cell (\( \hat{I}\hat{T}\hat{R} \)) cylindrical coordinate systems. a) Tangential–longitudinal (\( \hat{T}\hat{L}\hat{R} \)) tree sections are prepared by microtome from latewood rings of a pine tree trunk. b) SEM image of part of a \( \hat{T}\hat{L}\hat{R} \) tree section. c) Tracheid cell showing the widely accepted cellulose microfibril arrangements in the secondary cell wall, as well as typical cell dimensions for pine latewood arrangements in the coordinate system of the cell. d) Specimen geometries for TEM characterization and in situ double cantilever beam fracture tests. A tip is used to pry apart the cantilevers causing crack propagation from the notch.

Figure 2. Microfibril structure in pine latewood cell wall. a,b) 120 keV TEM images of KMnO4 stained \( \hat{r}\hat{l}\hat{l} \) (a) and \( \hat{r}\hat{l}\hat{l} \) (b) sections overlaid with arrows showing the projected microfibril directions. Approximate positions of the wood cell wall layer interfaces are indicated with dashed lines. c) Reconstructed 3D arrangement of the cellulose microfibrils in the outer part of the cell wall.
S1/S2 interface, since pine S1 layers are typically 100 to 200 nm thick and the S1/S2 interface is often defined by a change in the handedness of the helical arrangements. The radial component of the MFA in the $\mathbf{r} - \mathbf{t}$ section (Figure 2a) also depends on position, starting at almost 90° at approximately 1 µm away from the CML and rapidly decreasing to zero in the S1. Both section images are representative of the structure observed in a number of $\mathbf{r} - \mathbf{l}$ and $\mathbf{r} - \mathbf{-l}$ sections of the pine latewood and are in good agreement with extensive ultrastructure studies in the literature using ultramicrotome and TEM as well as different wood species, tree ages, and sample positions in the tree (tree height, number of annual ring). In particular, there are consistent observations of the non-zero radial component of the MFA. A possible reconstructed 3D microfibril arrangement is presented in Figure 2c, showing a complex helical arrangement in pine latewood that deviates from a purely circular helical or lamellar structure.

In situ studies of axial splitting crack propagation are performed in a scanning electron microscopy (SEM) on ≈200 nm thick $\mathbf{r} - \mathbf{-l}$ sections of pine latewood cell walls under a constant crack opening rate using a modified double cantilever beam geometry (Figure 3c) (see Experimental Details for descriptions of the specimen preparation and fracture tests). A summary of the in situ tests is provided in Table S1 (Supporting Information). For cases where the notch is located within the S2 layer, the cracks propagate unstably (moving a distance of almost 10 µm in less than 1 s) in a straight path along the microfibril direction (determined before testing using TEM). The smooth and straight crack surfaces and the lack of any crack bridging or microfibril pull-out prove the absence of obvious toughening mechanisms (see Figure S1 in Supporting Information).

In contrast, clearly nonbrittle behavior is observed when the notch is located near the S1/S2 interface (Figure 3). While prying the cantilevers apart, the crack is deflected along the microfibril direction from the notch to the S1/S2 interface region where it arrests (Figure 3a, image number 1). Then, after slow propagation of the crack a short distance through the S1 layer, the crack abruptly changes direction and moves rapidly back across the S1/S2 interface region within a single SEM image frame (in less than 0.5 s) where it is again arrested (Figure 3a, image number 2). There, it slowly moves a few hundreds of nanometers into the S2 layer before changing direction and propagating back across the S1/S2 interface where it is again arrested (Figure 3a, image number 3). The crack tip performs stop-start motion along a zig-zag path around the S1/S2 interface (Figure 3b).

The force needed to pry apart the cantilevers at a constant rate (Figure 3c) correlates with the stop-start motion: it increases when the crack is arrested, and rapidly decreases as soon as the crack propagates, leading to a saw tooth profile. The measured force includes friction effects and plasticity in the
cantilevers, but is nonetheless a measure of the driving force needed in the crack tip region to overcome the material resistance to fracture. It confirms that toughening mechanisms are active during crack tip arrest.

The SEM images reveal that crack tip arrest and crack deflection are associated with crack bridging and crack tip blunting in the S1/S2 interface region, suggesting that these are the active toughening mechanisms (Figure 4a). Bridging typically involves microfibril aggregates that diagonally span the crack (Figure 4c,d) and result from a secondary crack forming ahead of the arrested primary crack. Bridging may also involve fine ligaments that perpendicularly span the crack, and which is reminiscent of crazing, where the polymer molecules align along the tensile axis during deformation (Figure 4e). Bridging is expected to reduce the stresses at the crack tip thereby increasing the toughness. Crack tip blunting occurs slowly during crack arrest (Figure 4e), indicating extensive viscoelastic processes in the surrounding material and increasing the work of fracture.

According to fracture mechanics concepts, cracks propagate when the crack driving force (characterized by fracture mechanics parameters such as $K$, $G$, or $J$) exceeds the material resistance to crack extension, which reflects the deformation processes that occur in the material ahead of and behind the crack tip and is generally a function of crack extension (the so-called $R$ curve). For the approximate Mode I double cantilever beam geometry used here with compliant displacement-controlled loading, the crack driving force is expected to remain roughly constant during crack extension. This means that splitting cracks in the S2 layer far away from the S1/S2 interface must have a falling or constant $R$ curve, consistent with the absence of obvious toughening mechanisms such as microfibril pull-out and bridging. In contrast, the change in direction of the microfibrils at the S1/S2 interface leads to a variety of toughening mechanisms (Figure 4) and a rising $R$ curve. During crack arrest in the S1/S2 interface, viscoelastic deformation of the matrix material occurs which leads to crack tip blunting and an increase in the size of the highly stressed region ahead of the crack tip. For example, hydrogen bonds in the amorphous matrix around the cellulose microfibrils can break and recover, resulting in a velcro-like stick-slip movement of the polymer molecules along each other. Propagation of the arrested crack can proceed once secondary cracks are nucleated in the region ahead of the primary crack tip, where the stress normal to the microfibrils exceeds a critical value. The secondary crack will propagate along the microfibril direction toward the S1/S2 interface where it will be arrested, leading to the observed stop-start, zig-zag behavior. The bridge left behind...
at the site of crack arrest contributes to toughening and will eventually rupture.

These observations reveal a previously unknown toughening mechanism for splitting fracture in the cell walls of wood. Axial cracks that are within the S2 layer—the majority volume fraction of wood cell walls—are deflected along the microfibril direction towards the S1/S2 interface, where the local microfibril arrangements lead to crack arrest, crack tip blunting and eventually to crack renucleation and bridging along the S1/S2 interface. The changes in sign of $\theta$, with distance along the S1/S2 interface, which manifest as a whorl-like microfibrillar structure (Figure 4b), have been observed in several TEM sections in this study, so that cracks propagating in either axial direction in the S2 layer should eventually be deflected to the S1/S2 interface.

Note that an essential requirement for deflecting an axial crack and constraining it to “zig-zag” along the S1/S2 interface is the radial component of the microfibril direction ($\theta$). Although microfibril radial components have previously been clearly observed in TEM using ultramicrotome prepared specimens,22–27 the radial component remains a point of some contention, possibly because it is not easily compatible with accepted physiological models for cell wall formation.3 However, the complexity of the microfibril arrangements in the wood cell walls24 and the possibility that they may wrinkle due to growth stresses, offer promising directions for investigation and discussion that may provide a resolution to the conflict.

It is well known that the fracture behavior is moisture dependent and the vacuum-tested samples have a lower moisture content (~0%) than of wood in use (moisture content of 10%–20%). However, preliminary in situ experiments in a 0.8 mbar water vapor atmosphere show the same effect of the MFA and the S1/S2 interface on fracture, despite more pronounced viscoelastic behavior of the wood (see Table S1 and Figure S2, Supporting Information). Other test conditions which differ from the conditions found in living wood or wood products, including the effects of electron and ion beam damage and chemical changes from staining, have been minimized and judged to not significantly affect the observed structure or fracture behavior (see Section III in Supporting Information). Thus, it is highly probable that the observed effect of the ultrastructure of pine late wood on controlling splitting fracture in the cell walls has direct implications on the fracture behavior of cellulose microfibril-based biological composites with similar ultrastructure. A radial component to the cellulose MFA has been observed in different wood species, and other biological composites, to improve their splitting fracture toughness.

Nature has evolved a variety of structural tactics for increasing toughness. A common tactic in hard biocomposites is the presence of weak interfaces between highly compliant and low toughness materials that basically increase the toughness of the composite material by crack deflection and path length increase.10 Here, we have identified an entirely new but intuitive tactic: a highly anisotropic structure that not only generates tough interfaces but also deflects and localizes cracks at these interfaces. This cell wall-level toughening mechanism should be active to some extent in all woods and under different ambient conditions, suggesting that the specific arrangement of the microfibrils in the cell wall may be a natural adaptation to enhance the toughness of living wood. The concept of using fibril arrangements to design interfaces that are tough and then guide and capture the cracks there is a design principle that is adaptable to engineering composites and fulfills two important engineering goals at one time: to control toughness and also select the failure site.

**Experimental Section**

**Sample Preparation:** A Sartorius 31A30 sledge microtome was used to cut 60–100 $\mu$m thick latewood T–L sections (Figure 1a) from pine sap wood pieces that had been stored under ambient conditions. The sections were stained with a KMnO$_4$ (wt1%) solution, washed with distilled water, and cut into 2 mm high and 1 mm wide slices with a razor blade. The slices were dried on a heating plate at 100 °C for a few min, glued on TEM semicircular copper grids with the wood cells aligned perpendicular to the straight edge of the semicircle, and coated with several nanometers of amorphous carbon using a Balzers Union CED 010 carbon coater (Figure 1b). Next, a FEI Nova 600 NanoLab FIB was used to machine double cantilever beam fracture specimens at the top of the sections using 30 keV Ga ions. As a first step, a 9 $\mu$m wide, 6 $\mu$m thick, and 20–25 $\mu$m high block was prepared using a high current of 20 nA. It was composed of two adjacent tracheid cell walls with an S1/S2 interface located near the middle. Next, a 3 $\mu$m wide and 20–25 $\mu$m high radial–longitudinal (r–l) lamella with a thickness of 80–200 nm was prepared in the middle of the block using beam currents from 1 nA down to 10 pA, leaving two 3 $\mu$m wide and 6 $\mu$m thick beams or cantilevers to the left and to the right of the lamella. After TEM investigations of the upper part of the lamella to determine the ultrastructure, the TEM-damaged part of the lamella was removed with FIB, leading to a height difference of 1.5 $\mu$m between the top of the lamella and the cantilevers. Finally, a notch was prepared at the top of the lamella using a beam current of 10 pA. The FIB preparation process is described in more detail in the publication of Kelling et al.20

**Sample Precharacterization in TEM:** The exact position of the S1/S2 interface and the microfibril arrangement within the lamella was determined in a Philips CM 12 TEM at 120 keV before performing the in situ SEM fracture tests.

**In Situ SEM Fracture Tests:** In situ mode I fracture experiments using a modified double cantilever beam geometry29 were performed in a FEI Nova Nano SEM 650 operated at 5 keV (Figure 1d). Piezo stages were used to displace the fracture specimens (Figure 1d) at a constant displacement rate against a wedge-shaped tip with an opening angle of 120° in order to pry apart the double cantilevers and drive TL crack propagation from the FIB-prepared notch through the ~200 nm thick lamella. The crack face normal is in the tangential direction (T) in the coordinates of the macroscopic wood and in the radial direction (F) in the coordinate system of a single cell, and propagates in the longitudinal direction (L, l). A FemtoTool FT-S Microforce Sensing Probe was used to measure the force on the tip and thereby the resistance to crack tip displacement. The crack driving force in this geometry is constant or slightly decreasing with crack length30 which allows even semibrittle cracks to be stably propagated. Note that due to friction between the cantilever beams and the wedge-shaped tip and plastic deformation of the cantilevers, the measured force on the tip was higher than the actual crack driving force needed to overcome the material resistance to fracture. The thinness of the lamella provided an approximate 2D section and allowed local structure to be directly related to crack propagation and toughening mechanisms without complications from the complex 3D microfibril structure.
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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