Strong Cellulose-Based Materials by Coupling Sodium Hydroxide–Anthraquinone (NaOH–AQ) Pulping with Hot Pressing from Wood

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ABSTRACT: Natural cellulose-based materials (CBMs) have considerable potential as strong and lightweight materials for advanced structural applications. Herein, we demonstrate a mechanically strong yet lightweight CBM with highly aligned wood fibers by the coupling pulping of wood blocks with mechanical pressing, which exhibits a tensile strength of 719.0 ± 30.2 MPa, an elastic modulus of 19.0 ± 1.4 GPa, and a density of 1.32 g/cm³. The extraordinary mechanical properties of the CBM are mainly ascribed to the good orientation of wood fibers in the longitudinal direction as well as the dramatically increased hydrogen bonds among adjacent fiber cells due to the lignin removal and mechanical pressing. More significantly, the resulting sheet-like anisotropic CBMs can be used to fabricate anisotropic and isotropic bulk CBMs with maximum tensile strengths of 561 and 330 MPa, respectively, through a facile and scalable layer-by-layer stacking method. This work exploits the mechanical potential of cellulose and the large-scale production of anisotropic and isotropic bulk CBMs with extraordinary mechanical performance and may open up a range of novel applications to CBMs.

INTRODUCTION

Modern society has long been sought to achieve strong yet lightweight materials for advanced applications ranging from building, transportation, and medical instruments to electronics, power plant, and aerospace. Unfortunately, most of the current high-performance materials are nonrenewable and nonbiodegradable, which fails to fulfill the growing requirement of sustainable development.1–4 Cellulose-based materials (CBMs) from wood not only are earth-abundant, renewable, and environmentally beneficial but also have the potential to be mechanically strong, light weight, and stiff, which can be given high-priority consideration to alleviate our reliance on petroleum-based materials, steel, and concrete.5–7

From the structural point of view, crystalline cellulose of an elementary fibril has a tensile strength of 7.5–7.7 GPa and Young’s modulus of 110–220 GPa,8–10 exceeding those of glass, Kevlar, and steel fibers. Micro-sized cellulose fibers self-assembled by helically aligned elementary fibrils exhibit remarkably reduced mechanical properties, with a tensile strength of 0.3–1.4 GPa and Young’s modulus of 14–27 GPa.11 For bulk wood consisting of microscale cellulose fibers, 50–140 MPa tensile strength and 2–14 GPa modulus are obtained,12 indicating the sharp decrease of mechanical properties during the biosynthesis. Therefore, how to transfer the extraordinary mechanical performance of cellulose to bulk CBMs is an urgent issue to be overcome.

Recently, tremendous efforts have been devoted to produce strong CBMs by rational orientation of micro and nano-cellulose fibers, which enable the effective transformation of the superior mechanical properties of cellulose nanofibrils (CNFs) into bulk CBMs.13–20 For example, Nishino et al. developed an all-cellulose composite material by impregnating manually aligned ramie fibers into molecular cellulose solution. The resulting all-cellulose composite exhibited an ultimate tensile strength of 480 MPa and an elastic modulus of 45 GPa.21 Mechanical stretching is an efficient approach to orientate CNFs in the planar direction.13,17–20 Sehaqui et al. prepared strong nanopaper by cold drawing of the CNF hydrogel. After drawing, the tensile strength increased from 185 to 397 MPa while the modulus increased from 10.3 to 33.3 GPa.20

To further improve the mechanical properties of CBMs by mechanical stretching, Tang and co-workers demonstrated a macroscopic ribbon with strong tensile strength (576 ± 54 MPa) and modulus (32.3 ± 5.7 GPa) by grafting of CNFs with...
ethylene glycol which can prevent CNF agglomeration, thus facilitating the subsequent alignment of CNF during mechanical stretching. However, the inefficiency and complexity of these methods limited the scalable preparation of strong CBMs. Moreover, the mechanical performance of these CBMs is much lower than that of a single CNF. Lately, Hu's group proposed a facile top-down approach to process natural wood into a high-performance bulk CBM for structural applications. The resulting bulk CBM possesses a tensile strength of 548.8 ± 47.2 MPa, resulting from the utilization of well-aligned wood fibers in natural wood.

Herein, we demonstrated strong and lightweight CBMs with highly aligned micro-sized wood fibers. Wood blocks were treated with an aqueous sodium hydroxide–anthraquinone (NaOH–AQ) system to remove lignin while maintaining the well-aligned configuration of wood fibers in the longitudinal direction, and the delignified wood blocks were then mechanically pressed with a presser to increase the hydrogen bonds among cellulose fibers that facilitated the increase in strength.

Figure 1. (a) Schematic showing the transformation of a natural wood block into a strong CBM by lignin removal and mechanical pressing. (b) Color changes during the fabrication process. (c) Stress–strain curves of a strong CBM. (d) Comparison in tensile strength of strong CBM, other CBMs, and metals.

Figure 2. SEM images showing the good alignment of fiber cells in the longitudinal direction of (a) wood, (b) delignified wood, and (c) the as-prepared CBM. SEM images to show well-defined lumina of (d) wood and (e) delignified wood in the radial direction. (f) Cross-sectional SEM images showing the densely packed structure of the strong CBM obtained after mechanical pressing.
tensile strength of the as-prepared CBMs. More significantly, anisotropic and isotropic bulk CBMs with fascinating mechanical properties were presented by a layer-by-layer stacking approach. Our work exploits the mechanical potential of the cellulose and the large-scale production of bulk CBMs with superior mechanical performance, which may open up a range of novel applications to CBMs.

■ RESULTS AND DISCUSSION

Transferring the exceptional mechanical performance of the cellulose to bulk CBMs is still challenging. Herein, we fabricated CBMs with extraordinary mechanical properties by a combination of delignification and mechanical pressing. Figure 1a highlights a straightforward method to fabricate a strong CBM by delignification and mechanical pressing of natural wood. Wood blocks obtained by longitudinally cutting the wood trunk were cooked by NaOH−AQ liquor to remove the lignin and hemicellulose as much as possible, leading to softening of the well-aligned structure of wood fibers. Removing the lignin in the middle lamella can dramatically promote the subsequent formation of hydrogen bonding among aligned fiber cells during mechanical pressing. After this, the delignified wood block with aligned wood fibers was mechanically pressed to prepare a strong CBM (Figure 1b). The as-fabricated CBM notably exhibits a strong tensile strength of 773 MPa (Figure 1c), which is shown to be higher than those of typical metals (AlSi10Mg alloy 24 and high specific-strength steel 25), and even of lightweight titanium alloy (Ti6Al4V) 26 and those of other CBMs (polyethylene glycol-grafted CNF ribbon 19 and densified wood 23) as shown in Figure 1d.

A scanning electron microscopy (SEM) analysis was used to investigate the microscopic structure of natural wood, delignified wood, and CBM prepared from natural wood. SEM images in Figure 2a demonstrate the ordered orientation of wood lumina parallel to the growth direction of tree. The cell walls adhere to each other by a mixture of the lignin and hemicellulose. However, the tight adhesion between neighboring fiber cells becomes loose after pulping because the lignin in the middle lamella was removed (Figure 2b). Figure 2c shows the good preservation of the alignment feature of fiber cells during the fabrication process. The magnified SEM images in Figure 2d indicate that there are many rectangle-like pores (cell lumina) with a diameter of 30−50 μm, and the boundaries between adjacent cell walls are fuzzy due to the existence of the heavily lignified middle lamella. After delignification, visible gaps between adjacent cell walls appear due to the removal of the middle lamella (Figure 2e).

Mechanical pressing along the radial direction was applied to compress the loose configuration of delignified wood into a dense structure with approximately a six-time reduction in thickness. No conspicuous lumina is seen from the SEM images in Figure 2f, which suggests that more hydrogen bonding among aligned fiber are forming during mechanical pressing. Thus, the oriented arrangement of microstructures along with the rising numbers of hydrogen bonds leads to the super tensile strength of CBMs.

In summary, the preparation strategy proposed in this study not only preserves the ordered arrangement of fiber cells in wood but also promotes the formation of hydrogen bonds. The well-aligned arrangement of microscale structures along with the rising numbers of hydrogen bonds contributes to transferring the outstanding mechanical potential of wood fibers to CBMs.

Thanks to the good preservation of highly aligned microstructures and the increased number of hydrogen

| cooking time (h) | 0     | 1     | 2     | 3     | 4     |
|------------------|-------|-------|-------|-------|-------|
| lignin content (%) | 27.3 ± 0.09 | 12.8 ± 0.11 | 5.8 ± 0.08 | 3.76 ± 0.05 | 2.12 ± 0.06 |
| tensile strength (MPa) | 46.5 ± 5.10 | 470.3 ± 19.60 | 563.1 ± 26.40 | 719.0 ± 30.18 | 615.6 ± 25.50 |
| modulus (GPa) | 5.6 ± 0.30 | 10.5 ± 0.94 | 12.2 ± 0.85 | 19.0 ± 1.35 | 15.2 ± 1.97 |

Figure 3. (a) Comparison in tensile strength and modulus of natural wood and a strong CBM. (b) Tensile strength and modulus of the as-prepared strong CBMs with different cooking times. (c) Tensile strength of CBMs as a function of the lignin content. (d) Tensile stress in the direction perpendicular to the wood fiber alignment.
bonds among adjacent cell walls during the fabrication, the resulting CBMs exhibit excellent mechanical properties with an average tensile strength of 719.0 ± 30.2 MPa and Young’s modulus of 19.0 ± 1.4 GPa. The maximum stress of the CBM in the longitudinal direction is approximately 15 times stronger than that of original wood (46.5 ± 5.10 MPa), and its maximum Young’s modulus is nearly 4 times larger than that of original wood (Figure 4a, Table 1).

As we mentioned above, lignin removal in wood can facilitate the formation of hydrogen bonds at the interfaces of neighboring fiber cells in the subsequent mechanical pressing, which results in the strong strength of the CBMs. When the cooking time increasing from 1 to 3 h and the lignin content decreasing from 27.3 ± 0.09 to 3.8 ± 0.05%, both the tensile strength and modulus show a gradually growing trend (Figure 3b, Table 1). When the cooking time reaches 3 h, the as-prepared CBM exhibits average tensile strength and modulus of 719.0 ± 30.2 MPa and 19.0 ± 1.4 GPa, respectively. The result indicates that the increased numbers of hydrogen bonds among adjacent fiber cells after lignin removal primarily contributed to the full utilization of the exceptional mechanical properties of CBMs. However, as the cooking time increased to 4 h, the tensile stress and modulus of the as-prepared CBM begin to decline as shown in Figure 3b,c. The decrease in mechanical properties of the CBM may be due to the degradation of the cellulose.

Strong 2D submillimeter thick films and 1D microfibers are two types of CBMs that are widely reported in previous literature, which can limit their application in the fields where strong and lightweight bulk materials are needed. In this section, a facile and scalable layer-by-layer stacking approach was proposed to fabricate anisotropic and isotropic bulk CBMs with superb mechanical properties. Anisotropic bulk CBMs were fabricated by rationally stacking anisotropic CBMs along the axial direction of the fiber and gluing with 2% carboxymethylcellulose (CMC) solution, as shown in Figure 4a, followed by hot pressing at a temperature of 50 °C to accelerate drying. The upper images in Figure 4c show the anisotropic bulk CBMs with a dimension of 5 × 3.5 × 0.7 cm³ that presented an ultimate tensile stress of 561 MPa (Figure 4d).

Although anisotropic bulk CBMs exhibit excellent mechanical properties along the axial direction of the wood fiber, the tensile stress in the direction perpendicular to the fiber alignment is only 30 MPa (Figure 3d), which will restrict their uses in some areas that require excellent mechanical properties in all directions. Therefore, we fabricated isotropic bulk CBMs by stacking an anisotropic CBM with fiber alignment in the x direction, followed by the y direction and gluing with 2% CMC solution. Finally, the sample was dried by hot pressing at a temperature of 50 °C for 4 h. As a result, the fiber alignment between adjacent anisotropic CBMs is perpendicular, as shown in Figures 4b,c. The resulting isotropic bulk CBMs have a tensile stress and a modulus of approximately 330 MPa and 15 GPa, respectively (Figure 4d).

### CONCLUSIONS

In conclusion, we demonstrate a strong CBM with highly aligned wood fibers by a facile top-down method involving NaOH–AQ pulping of the wood block and subsequent mechanical pressing. The as-prepared CBM exhibits a record tensile strength as high as 773 MPa and a modulus of up to 21.7 GPa. The strong strength of the resulting CBM was primarily due to the good orientation of wood fibers in the longitudinal direction as well as the increased numbers of hydrogen bonds among adjacent fiber cells resulting from the lignin removal and mechanical pressing. Moreover, anisotropic and isotropic bulk CBMs with exceptional mechanical performance are successfully fabricated from aforementioned sheet-like CBMs by a facile and scalable layer-by-layer stacking approach, which show maximum strengths of 561 and 330 MPa, respectively. Such strong yet lightweight CBM sheds light on fully exploiting the extraordinary mechanical potential of the cellulose and has the potential to use as high-performance engineering materials in the areas that are traditionally dominated by artificial petroleum-based materials such as plastics, concrete, and metals.

### EXPERIMENTAL SECTION

**Materials.** Pine wood (*Pinus sylvestris* var. *mongolica* Litv.) blocks with a dimension of 100 × 35 × 3 mm³ were used in this work. Sodium hydroxide (>96%) and anthraquinone (>98%) were purchased from Guangzhou Jinhuada chemical reagent Co., Ltd.

**Fabrication of CBMs.** The delignification of wood blocks was performed in a 1 L stainless autoclave reactor (Parr 4523, USA). The delignification solution was prepared by dissolving sodium hydroxide (20 g) and anthraquinone (0.05 g) in 600 mL deionized (DI) water. The wood blocks and the delignification solution (wood/solution = 1:20) were added in the reactor and kept at 170 °C for 1, 2, 3, and 4 h, respectively. The delignified samples were then washed with DI water several times to remove the residual black liquor.

The delignified wood blocks were covered with filter paper and pressed with a hydraulic press at the pressure of 8 MPa for 3 h at room temperature. During this process, the filter paper should be replaced at intervals to ensure the removal of water in wood blocks. Finally, the delignified samples were pressed at 90 °C for 3 min with 8 MPa to obtain strong CBMs.
Characterizations. Microstructure of strong CBMs and wood blocks was characterized by a scanning electron microscope (Hitachi SU-70), and the cross-sections of the samples were cut with a Leica EM TIC 3X argon ion cutter microscope (Hitachi SU-70), and the cross-sections of the samples were cut with a Leica EM TIC 3X argon ion cutter first. The mechanical properties were carried out on an Instron 5565 universal tester using a 2 kN load cell. The lignin contents were measured based on Technical Association of Pulp and Paper Industry Standard Method T 222-om-83.

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Notes
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