

In Situ Lignin Adhesion for High-Performance Bamboo Composites

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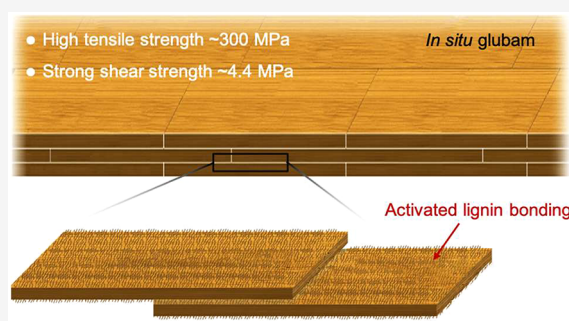
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Supporting Information

ABSTRACT: Bamboo composite is an attractive candidate for structural materials in applications such as construction, the automotive industry, and logistics. However, its development has been hindered due to the use of harmful petroleum-derived synthetic adhesives or low-bonding biobased adhesives. Herein, we report a novel bioadhesion strategy based on *in situ* lignin bonding that can process natural bamboo into a scalable and high-performance composite. In this process, lignin bonds the cellulose fibrils into a strong network via a superstrong adhesive interface formed by hydrogen bonding and nanoscale entanglement. The resulting *in situ* glued-bamboo (glubam) composite exhibits a record-high shear strength of ~4.4 MPa and a tensile strength of ~300 MPa. This *in situ* lignin adhesion strategy is facile, highly scalable, and cost-effective, suggesting a promising route for fabricating strong and sustainable structural bamboo composites that sequester carbon and reduce our dependence on petrochemical-based adhesives.

KEYWORDS: bamboo engineering, bamboo composite, biomass adhesive, structural materials, environmental sustainability



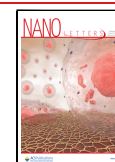
Bamboo, one of the world's fastest-growing plants, is an attractive candidate as a structural material for various structural engineering applications (e.g., construction, the automotive industry, logistics, etc.) because of its availability worldwide, high renewability (yield within 3–5 years), and superior mechanical properties, being simultaneously hard, tough, lightweight, and malleable.^{1,2} Additionally, bamboo displays outstanding carbon sequestration capacity, making bamboo products a sustainable, cost-effective, and environmentally friendly alternative to traditional structural building materials, such as steel or concrete.^{3,4} However, natural bamboo has inherent structural defects, namely a hollow, jointed structure.^{5,6} Additionally, the narrow width of raw bamboo restricts the size and scale of products manufactured from it, limiting its use in large-scale applications where there could be enormous potential for decarbonization.^{7,8} As a result, adhesives are typically used to fabricate engineered bamboo materials and composites with larger desired dimensions. Synthetic adhesives, such as phenolic and urea-formaldehyde resins, enable high performance by providing good bonding strength. However, such adhesives are derived from nonrenewable fossil resources and require energy-intensive and complex manufacturing processes, which additionally contribute to global warming. Furthermore, such synthetic adhesives can be harmful to human health due to the emission of carcinogenic formaldehyde gas.^{9,10} Consequently, to make bamboo and other biomass-based composites a viable alternative to conventional structural materials, we need to develop greener strategies for adhesion.

To address these challenges, researchers have explored novel biobased adhesives^{11,12} derived from abundant natural materials (e.g., lignin,^{13,14} tannin,¹⁵ protein,¹⁶ and starch¹⁷), which are cost-effective and more eco-friendly, compared to conventional adhesives. For example, lignin is a natural polymer widely found in plants like wood, bamboo, and straw, where it acts as a natural glue in cell walls and bonds with cellulose and hemicelluloses to provide structural stability to the plants.^{18,19} Lignin is also particularly attractive for commercial applications as it is abundantly available from the waste stream of paper mills and biomass refineries, making it an inexpensive feedstock material.²⁰ Researchers usually modify the lignin structure to improve its reactivity by introducing more functional groups (active sites) for adhesive bonding between interfaces through methods such as oxidation,²¹ phenolization,²² and hydroxylation.²³ However, these lignin-based adhesives continue to feature poor adhesive performance when applied directly in composites due to weak chemical cross-linking with regard to rigidity and construction.^{24,25} Additional cross-linking agents or manufacturing procedures are generally required to achieve the desired bonding strength, but lignin-based adhesives still fail to meet the

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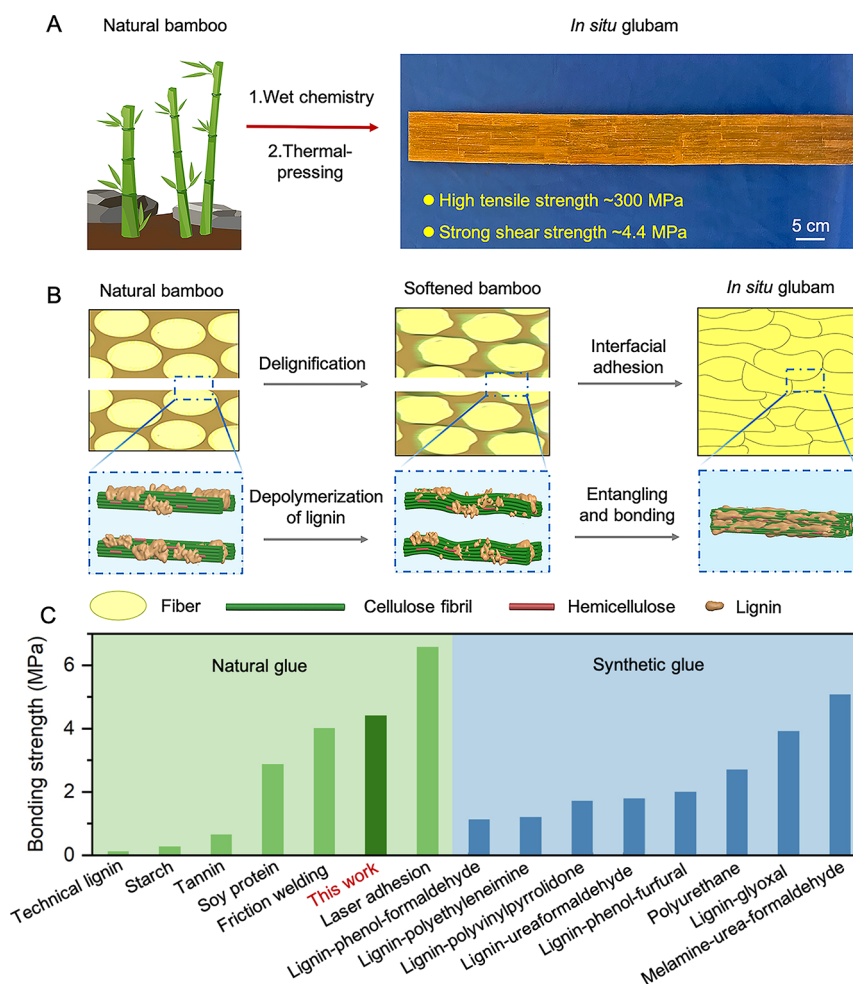


Figure 1. (A) Natural bamboo is processed into scalable *in situ* glubam via alkaline and thermal-pressing treatment. (B) Schematic illustration of the transformation of natural bamboo into *in situ* glubam. Natural bamboo fiber consists of a solid matrix of cellulose, hemicelluloses, and lignin. During step 1 of the delignification treatment, the lignin and hemicelluloses are partially dissolved and removed (through washing) from the bamboo, exposing and softening the cellulose fibrils. The remaining lignin in the cell wall is depolymerized into low-molecular weight segments. In step 2, the softened bamboo is hot-pressed at 140 °C, causing the remaining lignin to penetrate and embed in the voids of the cellulose fibers and spread on the fiber surface. The process results in a strong adhesive interface via mechanical entanglement and hydrogen bonding between the lignin and cellulose fibrils. (C) Bonding strength of the *in situ* lignin glue compared to those of other natural and synthetic adhesives.^{14,17,21,28–37}

performance of established synthetic glues even with supplemental processing.^{26,27} Therefore, alternative approaches to biobased adhesion must be considered to develop sustainable and high-performance bamboo and other natural-material composites with a robust adhesive interface.

In this work, we report a novel bioadhesion strategy based on *in situ* lignin bonding that can convert natural bamboo into a multiscale, high-performance composite with a performance that exceeds the mechanical performance of conventional structural materials (Figure 1A). As shown in Figure 1B, in this process, natural bamboo is first chemically treated in a solution of NaOH to partially remove lignin and hemicelluloses from the bamboo matrix. This treatment generates wrinkles and pores in the bamboo structure and softens the bamboo, which exposes more surface functional groups of the lignin and cellulose nanofibrils. Subsequent hot-pressing treatment (140 °C and 20 MPa) compresses the bamboo fibers into a close-packed structure, while ensuring the lignin continues to partially penetrate the pores of bamboo fibers and cover some fiber surface. As a result, this process allows the residual lignin to interact tightly with the aligned cellulose nanofibrils via

enhanced hydrogen bonding and physical adhesion. The hydrogen bonding and physical entanglement in the lignin/cellulose complex create a super strong adhesive interface leading to a 4.4 ± 0.3 MPa bonding strength of the *in situ* glued-bamboo composite (glubam), which is the highest among biobased adhesives and comparable to synthetic glues and physical adhesion (Figure 1C). The *in situ* glubam composite can also be fabricated at different lengths and scales as needed for various applications by simply staggering the chemically treated bamboo layers before hot-pressing. This study highlights the importance of physical interaction for interfacial glues and demonstrates a practical approach for making bamboo-based sustainable large-scale structural engineering composites that could provide a significant decarbonization impact and promote sustainable forestry practices.

To fabricate the *in situ* glubam (Figure S1A), we first used a wet-chemistry method^{38,39} to autoclave natural bamboo strips at 160 °C in a 20 wt % NaOH solution for 1 h (5:1 liquid:bamboo ratio). After this process, the mass loss of natural bamboo was 41.4 wt % due to partial removal of the lignin and hemicelluloses from the bamboo matrix. Then, we took two sheets of these

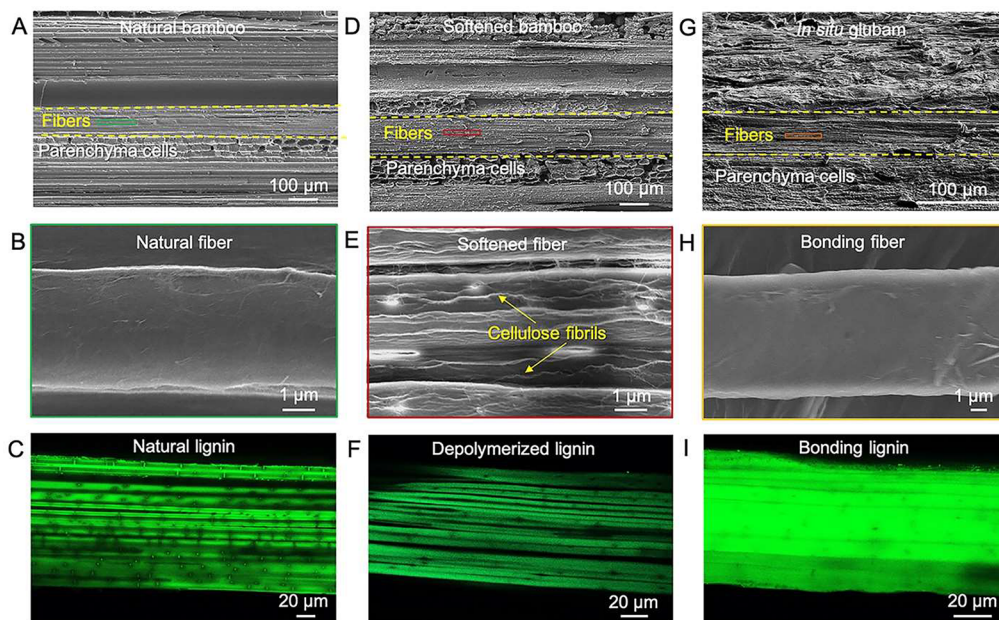


Figure 2. Morphological and microstructural evolution from natural bamboo to *in situ* glubam. (A) Side-view SEM image of natural bamboo, which is composed of long highly aligned fibers and short parenchyma cells. (B) Magnified SEM image of a single fiber of natural bamboo, demonstrating a solid structure. (C) Confocal fluorescent image of lignin in natural bamboo. (D) Side-view SEM image of the softened bamboo, demonstrating the separation of the fibers and parenchyma cells after the wet-chemistry process. (E) Magnified SEM image of a single fiber of the softened bamboo, showing the exposed and curly cellulose fibrils. (F) Confocal fluorescent image of lignin in softened bamboo. (G) Side-view SEM image of the *in situ* glubam, showing completely collapsed fibers and parenchyma cells forming a densified structure. (H) Magnified SEM image of a bonding fiber from the *in situ* glubam, demonstrating its nonporous structure. (I) Confocal fluorescent images of lignin in the *in situ* glubam.

softened bamboo strips, stacked them along the axial (parallel to the fiber growth) direction, and bonded them together by hot-pressing (140 °C and 20 MPa) to form the final *in situ* glubam, which featured an approximately 94.2% increase in density compared with that of natural bamboo (Figure S1B). The wet-chemistry treatment significantly changes the composition of softened bamboo and *in situ* glubam compared with that of natural bamboo. Specifically, the characteristic functional groups of lignin, which are represented by peaks at 1593, 1505, and 1462 cm^{-1} , as well as the functional groups of hemicellulose peaks at 1736 and 1235 cm^{-1} ,⁴⁰ are attenuated in the softened bamboo and *in situ* glubam. This suggests that the hemicellulose and lignin contents of the softened bamboo and *in situ* glubam are lower than those of the natural bamboo (Figure S2A). For a more quantitative analysis of the different components, we performed acid hydrolysis, as reported in the literature.³² Compared with the natural bamboo starting material, the lignin and hemicellulose contents of the softened bamboo decreased from $29.8 \pm 1.5\%$ to $17.5 \pm 2.7\%$ and from $22.5 \pm 1.1\%$ to $11.5 \pm 1.5\%$, respectively (Figure S2B), demonstrating the effectiveness of the wet-chemistry treatment. After hot-pressing, the resulting *in situ* glubam was mainly composed of cellulose ($72.5 \pm 2.5\%$) with remaining lignin ($18.3 \pm 2.2\%$) and hemicelluloses ($8.6 \pm 1.4\%$).

Scanning electron microscopy (SEM) revealed the structural evolution from natural bamboo to *in situ* glubam. In the natural bamboo material, the long fibers are remarkably well-aligned and parallel to the growth direction. Additionally, the short parenchyma cells are neatly stacked around the fiber bundles (Figure 2A). From the cross section of the natural bamboo, we can see that the fiber bundles consist of many solid elementary fibers, surrounded by hollow parenchyma cells (Figure S3A,D). When a magnified view of a single fiber in natural bamboo is

observed, its structure is fairly smooth without visible pores (Figure 2B). Each fiber consists of cellulose fibrils within an amorphous matrix of lignin and hemicelluloses. We used polarization microscopy to observe the morphology of the cellulose fibrils, which demonstrated bright birefringence under polarized light. The polarized images show that the natural cellulose fibrils are well aligned along the growth direction of bamboo (Figure S4A). Additionally, confocal fluorescence microscopy was used to observe the distribution of lignin, which combined intensity from excitation of 405, 488, 561, and 640 nm. Figure 2C shows that lignin is continuous and uniformly distributed around the bamboo fiber bundles. After the partially removal of lignin and hemicelluloses by the wet-chemistry treatment, the fibers and the cell walls of the parenchyma cells become more porous, separating from each other and creating voids in the adhesive matrix between the cells of the softened bamboo sample (Figure 2D and Figure S3B,E). Nanocellulose fibrils and nanopores appear between the fibers at the nanometer level, in which cellulose fibrils become curly and soft, with more cellulose fibril surfaces exposed (Figure 2E and Figure S4B). The wet-chemistry treatment also partially removes lignin, breaking up the formerly continuous lignin distribution (Figure 2F). After the hot-pressing process, the porous cell walls and fiber bundles collapse completely, forming a highly dense structure along the bamboo growth direction in the *in situ* glubam (Figure 2G and Figure S3C,F). At a higher magnification, we can see that the voids of the softened fibers have disappeared, forming densified bonding fibers (Figure 2H). Additionally, as shown in Figure 2I, the lignin is aggregated and becomes more uniform again, with almost no visible gaps, suggesting a compact, highly entangled structure. Above all, under the action of hot-pressing, the lignin penetrates into the voids of the cellulose fibers that had been opened by the wet-

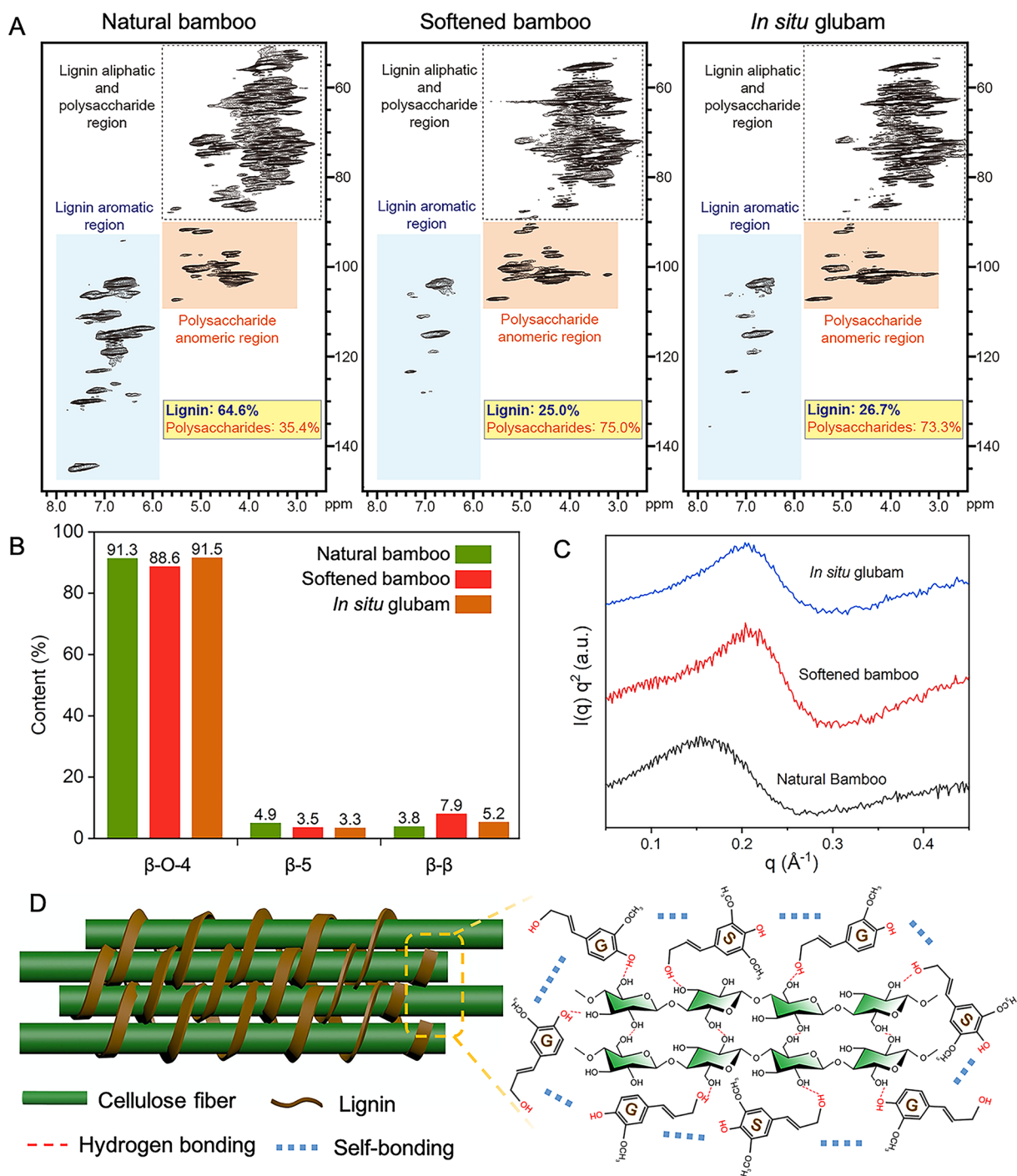


Figure 3. Chemical structure of the *in situ* glued lignin and the interaction between lignin and cellulose. (A) 2D HSQC NMR spectra of whole cell walls from natural bamboo, softened bamboo, and *in situ* glubam. (B) NMR quantification of lignin aliphatic structures in natural bamboo, softened bamboo, and *in situ* glubam. (C) SAXS spectral patterns of natural bamboo, softened bamboo, and *in situ* glubam. (D) Mechanism of structural linkages between *in situ* glued lignin and cellulose.

chemistry process and homogeneously spreads over the fiber surface, which we hypothesized could act as a glue within the *in situ* glubam by physically entangling with the highly oriented fibers to form a strong and tough matrix.

To gain further insight into the transformation of the molecular structure of lignin during the two-step treatment, we recorded the two-dimensional (2D) nuclear magnetic resonance (NMR) spectra of natural bamboo, delignified bamboo, and *in situ* glubam. Lignin consists of phenylpropane monomeric units that are connected primarily by ether bonds

(e.g., β -O-4) and carbon-carbon bonds (e.g., β - β or β -5).^{40–42} As shown in panels A and B of Figure 3, despite a decrease in the overall amount of lignin following the treatments, no significant changes were observed in the linkages. In the *in situ* glubam, the β -O-4 ether bond accounts for ~91.3% of the total ether linkages of the lignin. In the side-chain region, syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H) in substructures are linked via β -O-4, β - β , and β -5 bonds, respectively (Figure S5). Probable condensation peaks appeared near the S2/6 units after the delignification process. Lignin

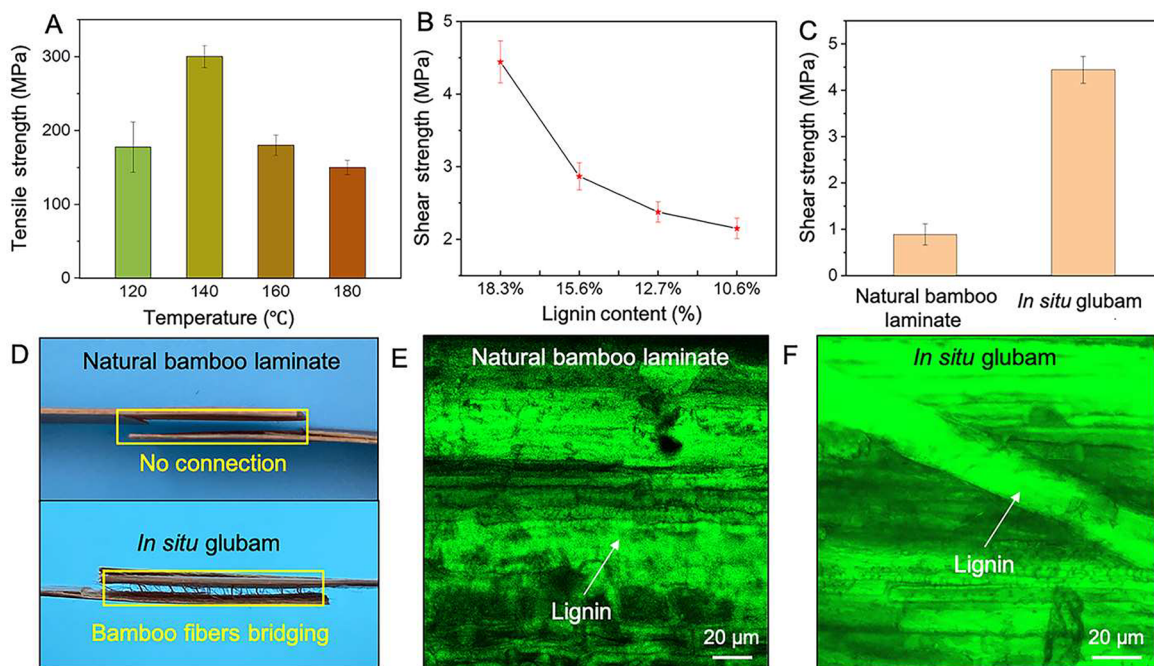


Figure 4. Mechanical properties of an *in situ* glubam. (A) Tensile strength of the *in situ* glubam fabricated at different hot-pressing temperatures. (B) Shear strength of *in situ* glubam featuring different lignin contents. (C) Shear strength of the natural bamboo laminate and *in situ* glubam. (D) Optical images of the natural bamboo laminate and *in situ* glubam after tensile. Confocal fluorescent images of (E) the natural bamboo laminate and (F) the *in situ* glubam.

depolymerization generated and exposed more active sites (functional groups such as phenolic hydroxyl) on the lignin surface. This increase in the number of active sites not only strengthens the hydrogen bonding between lignin and cellulose but also improves the self-bonding reactivity of the lignin fragments under hot-pressing.

Furthermore, we used X-ray diffraction to analyze the nanostructures of cellulose macrofibers in natural bamboo, softened bamboo, and *in situ* glubam. Small-angle X-ray scattering (SAXS) was used to determine the molecular alignment of the cellulose chains that comprise the nanofibrils.⁴³ Figure 3C shows the SAXS curves, plotted using the scattered intensity perpendicular to the fibril direction as a function of scattering vector q , defined as $q = (4\pi/\lambda) \sin \theta$, with λ and θ being the X-ray wavelength and half of the scattering angle, respectively. Interfibril distances d can be quantified using Bragg's law $d = 2\pi/q_m$, where q_m is the q value at the peak position in the SAXS curves. The calculated interfibril distances are 40.9, 31.6, and 30.3 nm for natural bamboo, softened bamboo, and *in situ* glubam, respectively. The interfiber distance of the *in situ* glubam is 25.9% shorter than that of natural bamboo and is close to that of dry softened bamboo. In the dry state of the softened bamboo, cellulose microfibrils tend to be in close contact, due to the decrease in the lignin content between the microfibrils. The major effect of hot-pressing was that it strengthened the cellulose microfibril "bondage" mediated by the remaining lignin molecules, resulting in the enhancement of the cross-linking hydrogen bonding force between the cellulose and cellulose and between the cellulose and lignin in the *in situ* glubam.

We used 2D wide-angle X-ray scattering (WAXS) to examine the organization of cellulose chains in the crystal. It turned out that cellulose I remained as the predominant crystal polymorph in the softened bamboo and *in situ* glubam, as revealed by indexing Bragg's peaks in the WAXS data (Figure S6). In

addition, the degree of cellulose crystalline orientation was calculated, on the basis of the azimuthal scan of the scattered intensity in the vicinity of the (200) reflection, using Hermans's orientation function, denoted P_2 (Figure S7 and eq Sp1). P_2 values of the natural bamboo and *in situ* glubam were 0.90, and 0.81, respectively, suggesting that crystals in the *in situ* glubam are more misoriented, an effect due to the high-pressure processing. Such misorientation might be able to cause microfibril entanglement, which is another factor that accounts for enhanced mechanical performance. Cellulose microfibril entanglement structure is beneficial for obtaining a better-bonded structure with depolymerized lignin in the *in situ* glubam. The schematics shown in Figure 4D explain the gluing mechanism of the *in situ* glubam. In the absence of chemical adhesives, the reinforced filling and bonding effect of lignin with cellulose microfibrils creates a powerful bridge network via intermolecular hydrogen bonding interaction, explaining the bonding strength of the *in situ* glubam.

We investigated the tensile mechanical properties of the *in situ* glubam at different hot-pressing temperatures (120, 140, 160, and 180 °C). The *in situ* glubam displayed a tensile strength of 300 ± 15 MPa at a hot-pressing temperature of 140 °C, likely because this temperature is close to the glass transition temperature of lignin (Figure 4A and Figure S8). We also evaluated the macroscopic tensile shear adhesion strength of the *in situ* glubam at different degrees of delignification by controlling the alkaline treatment time using a lap shear test. When the lignin content was $18.3 \pm 2.2\%$ (treated for 1 h), the interfacial bonding strength reached a maximum value of 4.4 ± 0.3 MPa (Figure 4B). With a decrease in the lignin content, the interfacial bonding strength of the *in situ* glubam gradually decreased. There were still gaps between the nanofibers that could not be completely closed at the molecular level in the *in situ* glubam without lignin (Figure S9). The absence of a dense structure in the composite indicates that lignin plays a key role as

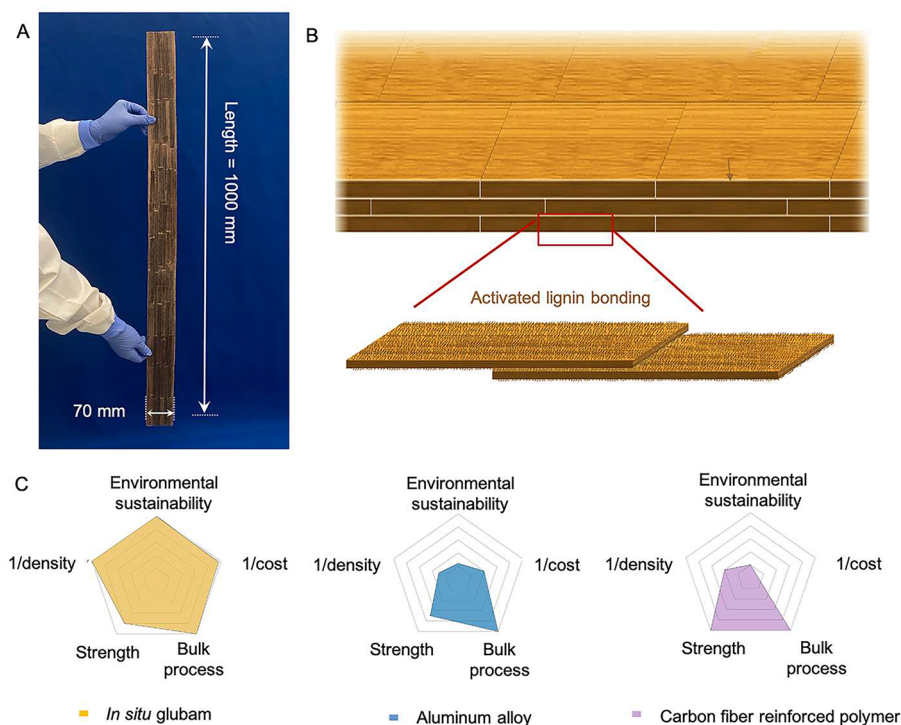


Figure 5. (A) Large-scale *in situ* glubam (1000 mm × 70 mm × 1.2 mm). (B) Schematic of stacking softened bamboo into a multilayer *in situ* glubam board using lignin as the only *in situ* glue. (C) Radar chart comparing various properties of *in situ* glubam, aluminum alloy, and carbon fiber-reinforced polymer, which normalizes the results by the maximum value of each characteristic.

an adhesive agent. However, when we prepared a natural bamboo laminate, in which no alkaline treatment was applied, just hot-pressing at 140 °C, the material displayed a shear strength of just 0.88 MPa (Figure 4C). Figure 4D shows that there was no penetration or embedment observed in the natural bamboo laminate after conducting the shear strength test. In contrast, we observed from the interfacial joints of the *in situ* glubam after the shear strength test that a large number of oriented fiber bundles of bamboo were peeled off, which played a major role in connecting and bridging the two bamboo strips after hot-pressing. We observed the morphology of the natural bamboo laminate and *in situ* glubam. As shown in Figure S10, it is challenging to hot-press the natural bamboo laminate into a completely compact structure. Despite the application of 20 MPa of pressure, there were still many gaps between the lumens and fiber bundles. In contrast, the *in situ* glubam has a densified microstructure in which the fully collapsed fiber bundles are tightly packed along their cross section. Additionally, fluorescence imaging of lignin on the adhesion interface of the natural bamboo laminate shows that the lignin is in a dispersed state, despite the fact that the fluorescence intensity of lignin is very high (Figure 4E). In contrast, fluorescence imaging of lignin on the adhesion interface of *in situ* glubam shows that the surface lignin clumps together, particularly in the bamboo fiber part (Figure 4F). These results show that lignin cannot achieve bonding by hot-pressing directly without alkaline treatment.

As shown in Figure 5A, we can prepare a large *in situ* glubam board with dimensions of 1000 mm × 70 mm × 1.2 mm using the delignification and hot-pressing treatment without the addition of any additional adhesives. By stacking the softened bamboo strips (Figure 5B), we can fabricate the *in situ* glubam to different lengths sufficient for practical use (e.g., ≤1 m long). Even at these larger sizes, the mechanical properties of the *in situ*

glubam remain stable. Figure S12A shows the stress–strain curves of randomly selected small samples containing nodes from a large *in situ* glubam board, which features a similar tensile strength of 195 ± 30 MPa. In addition, applying additional lignin (e.g., kraft lignin) and resin (e.g., epoxy) at the interface can further improve the interfacial binding between sheets of bamboo laminate (Figure S11). The mechanical test results show that the tensile strength of *in situ* glubam was greatly improved, reaching 245 ± 21 or 357 ± 17 MPa, even though only 5 wt % kraft lignin or epoxy, respectively, was added (Figure S12B). These results demonstrate this method has great potential for producing scalable and strong structural materials. Compared to the costly and complex processes involved in traditional bamboo-laminated timber that uses additional adhesive, our approach for *in situ* glubam is facile and eco-friendly with fewer processing steps. In comparison to metals and polymer composites, the *in situ* glubam composite is cost-effective and ecologically friendly and generates minimal processing pollution. These factors increase its potential to serve as a sustainable alternative for a wide range of applications (Figure 5C). For example, wind power is a sustainable industry, but the biggest concern of composite blades is that the main materials (e.g., glass fiber-reinforced plastics and carbon fiber-reinforced plastics) of the composite blades currently used are nonbiodegradable and nonrecyclable. Recycling means that bamboo composites could be reprocessed into a variety of other bamboo products after they have reached the end of their life cycle. *In situ* glubam, as an exclusive biomass material, contains only cellulose, hemicelluloses, and lignin, giving it potential to be recycled and biodegraded. By virtue of helping to reduce environmental pollution and minimize waste generation, our *in situ* glubam holds great potential in reinforced materials for applications such as wind turbine blades.

In conclusion, we have successfully demonstrated a facile and cost-efficient *in situ* lignin bonding strategy for manufacturing *in situ* glubam, a material that is strong, scalable, and sustainable. Our approach involves a wet-chemistry method and thermal pressing of bamboo, both of which are common industrial operations that can be readily adopted. The remaining lignin after the chemical treatment acts as a natural glue that tightly wraps, adheres, and cross-links the cellulose nanofibrils together via hydrogen bonding networks and physical entanglement of lignin. The resulting *in situ* glubam exhibits an impressive shear strength of 4.4 ± 0.3 MPa and a high tensile strength of 300 ± 15 MPa. With this approach, we successfully demonstrated the production of strong and scalable bamboo-laminated lumber without the need for additives. The final product demonstrates an affordable and eco-friendly sustainable alternative to synthetic fiber-reinforced composites, particularly in lightweight structural applications. Moreover, the process reduces energy demands and increases carbon storage, making it an environmentally conscious choice.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.3c01497>.

Materials, chemicals, characterization, fabrication of *in situ* glubam, density, FTIR spectra, corresponding composition content, SEM images, polarized light microscopy images, 2D NMR spectra, 2D WAXS patterns for all compounds, optical pictures, and tensile stress–strain curves of multilayer *in situ* glubam board (PDF)

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Author Contributions

T.M. and Y.D. contributed equally to this work. L.H. conceived the concept. T.M., Y.D., X.P., and L.H. designed and carried out the experiments. T.M., Y.L., Z.L., and Y.D. contributed to the *in situ* glubam process and characterization. Y.M. contributed to the analysis of the crystalline structure. J.G. contributed to the collection of the SEM and digital images. H.K. collected and analyzed NMR data. T.M., Y.D., and L.X. collaboratively analyzed the data and wrote the manuscript. All authors commented on the final manuscript.

Notes

The authors declare no competing financial interest.

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