



Printable highly transparent natural fiber composites

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ABSTRACT

In this study, we report the development of printable highly transparent natural fiber-reinforced composites based on raw flax fibers. The prepared composites exhibit superior transparency (>90% light transmittance), and the tensile performance is competitive to synthetic fiber-based counterparts. They also reveal excellent printability (<300 μm resolution) in additive manufacturing (AM) processes, allowing the fabrication of functional devices in multiplex geometries using plant-based materials. The findings indicate a novel and sustainable method to engineer transparent composites with excellent mechanical and processing characteristics.

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1. Introduction

Recently, the use of natural fibers to replace synthetic fibers in composite materials attracted significant attention. Natural fibers exhibit high specific mechanical strength, excellent thermal insulation, good flexibility, and superior biodegradability and compostability [1]. Numerous studies on natural fibers have demonstrated their potential for the field of high-performance composites [2–4]. While natural fibers are sustainable and inexpensive alternatives to synthetic fibers, their extensive variations in fiber dimensions and orientation can lead to inhomogeneous structures. To address the inhomogeneity issue, many surface-modification processes have been developed to convert raw fibers into a more appropriate form [5,6]. Nevertheless, the composites based on surface-modified fibers still suffer from inferior light transmittance, limiting their capability in potential optical applications. To increase the transparency of plant-based composites, methods based on high-pressure homogenizer treatment and grinder treatment have been explored [7]. These methods usually started from pre-fibrillated pulp instead of raw fibers, possibly due to the homogeneity considerations. Although the obtained light transmittance was outstanding, these processes still require >10 times of the physical treatment repetitions. Also, the fabricated composites are limited to simple macroscale geometries, and the compatibility of these natural fiber-reinforced composites with next-generation manufacturing technologies is relatively poor [6,7]. Against this background, we report the preparation of highly transparent

composites from raw flax fibers using a simple sonication/chemical treatment approach. The developed composites exhibit excellent printability in extrusion-based AM processes, which allows the fabrication of composite objects using plant-based materials. The findings in this study indicate a novel and sustainable method to engineer composites for future functional devices in multiplex geometries with transparent characteristics.

2. Materials and methods

Raw flax fibers (*Linum usitatissimum*) have irregular polygonal cross-sections and a hollow structure, consisting of approximately 53% cellulose, 23% hemicellulose, 23% lignin, and 1% pectin in a two-wall construction, as illustrated in Fig. 1a [8]. The primary wall (P) along the plant growth direction contains both cellulose and hemicellulose, with microfibrils disorderly arranged. The secondary wall, which consists of another three layers (S1–S3), is located inside the primary wall. Different from the primary wall, the microfibrils in the secondary wall are helically chain-structured, which provides overall mechanical strength and protection. Fig. 1b–d summarize the preparation processes of transparent flax fibers (TFFs) from such raw fibers. Long flax fibers with 20 to 200 μm diameter were first chopped into 1 to 3 mm pieces. As shown in Fig. 1b, plenty of large dark-colored bundles were observed under the microscope, which can degrade the homogeneity of the prepared composites. To eliminate the inhomogeneity and improve the dispersion of flax fibers, the chopped raw flax fibers were soaked in nitric acid (70%, Sigma-Aldrich) for 15 min to dissolve the pectin content for separating large bundles. Afterward, the acid-treated flax fibers were washed by deionized

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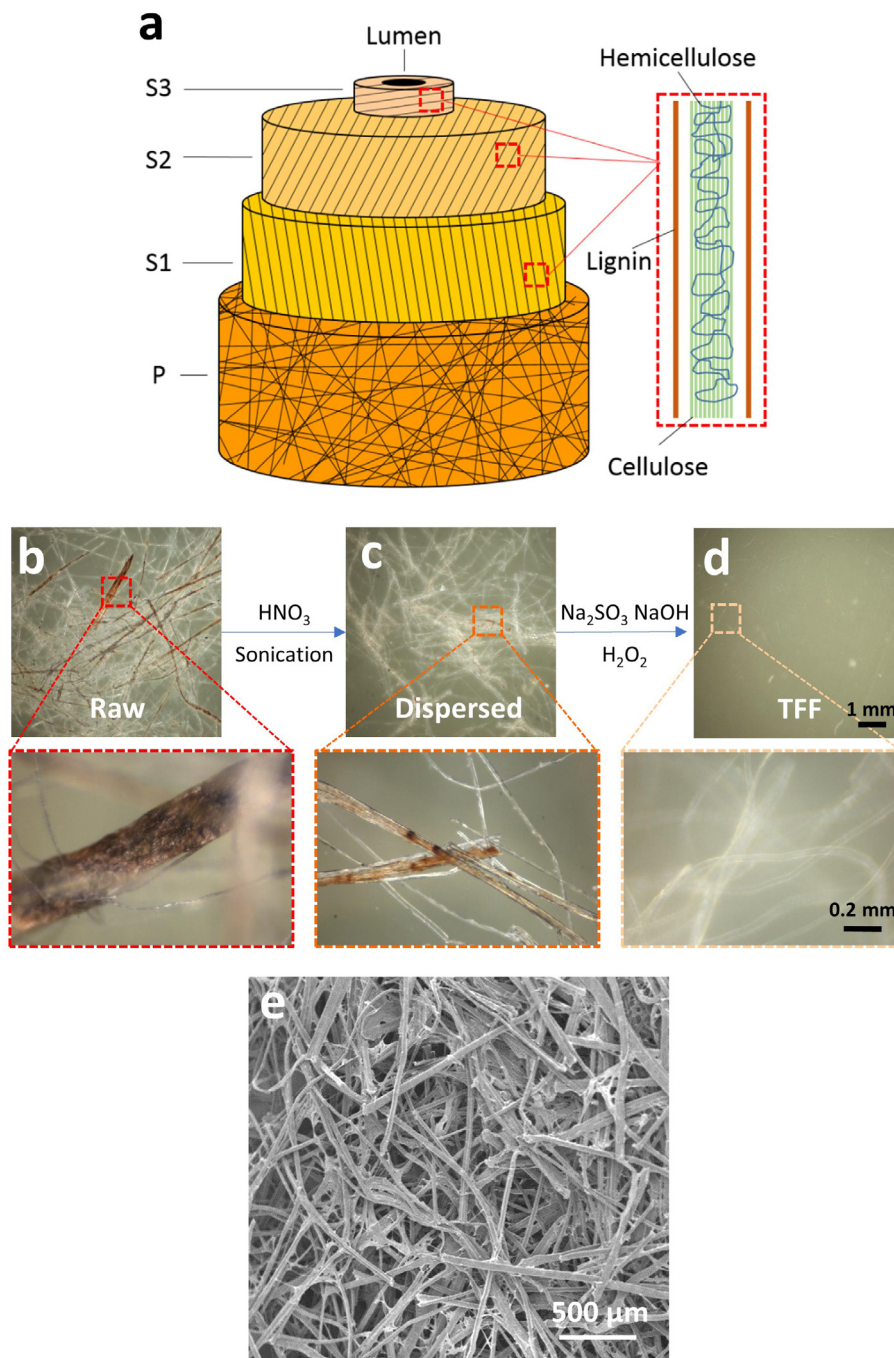


Fig. 1. (a) Natural flax fiber structure. (b) Raw flax fiber. (c) Dispersed flax fiber after acid-treatment and sonication process. (d) Lignin-removed flax fiber. (e) SEM image of TFFs.

(DI) water to remove residual acids. The obtained fibers were then immersed in DI water for a 30 min probe sonicating process (450-Watt, 12 mm probe diameter) [6]. The sonicating process detached the primary wall of the fiber, leaving well-dispersed repeatable fibers without agglomeration, which are appropriate to further improve the composite printability (Fig. 1c).

In the secondary wall structure of flax fibers, despite cellulose and hemicelluloses are optically colorless, lignin exhibits a significantly complicated structure with dark brown color [9]. Therefore, natural fibers always appear nontransparent. To remove the dark-colored lignin content, chemicals and processes utilized in conventional paper pulping techniques were used in this study [9]. Briefly, acid-treated flax fibers were soaked in 2.5 mol/L NaOH and

0.4 mol/L Na₂SO₃ in DI water at 90 °C for 6 h (Process I) to partially dissolve the lignin content. Then the fibers were transferred into 2.5 mol/L H₂O₂ in DI water at room temperature for another 72 h (Process II) to remove the remaining lignin. The as-obtained TFFs were preserved in ethanol. As expected, the fiber color becomes lighter as lignin was gradually removed and eventually the fibers become transparent, as shown in Fig. 1d. Subsequently, we observed the microstructure of TFFs using SEM (JOEL JSM-6320F FESEM). TFFs were coated by a 6 nm layer of platinum particles before observations. According to the SEM image (Fig. 1e), the estimated aspect ratio of TFFs ranges from 50 to 150.

To prepare the TFF composite, Dow Sylgard 184 silicone elastomer (PDMS) was purchased and used as received. It is a two-

component (base and curing agent, mix weight ratio 10:1), room temperature curing polymer. In this study, we prepared TFF composites with loading fractions ranging from 1 to 10 wt%. TFFs were first mixed with the elastomer base at 2000 rpm for 30 min and degassed (AR-100, Thinky) for 2 min. Afterward, they were blended with the curing agent at 2000 rpm for 3 min before loading into a customized aluminum mold with a corresponding specimen dimension of 50 mm × 20 mm × 1.5 mm. The TFF composites were heated at 100 °C for 30 min to thoroughly solidify for further optical and mechanical characterization.

3. Results and discussion

3.1. Optical properties

To investigate the influence of treatment time in both processes I and II of removing lignin, we quantified the removed lignin content in the flax fibers using the standard methods for lignin determination (Technical Association of Pulp and Paper Industry Standard Method T 222-om-83). Briefly, fully dried flax fibers (1.0 g, the mass denoted by m_0) were measured and extracted with ethanol for 6 h, which was then slowly stirred with cold 72% H_2SO_4 for 2 h. The mixtures were then transferred to a beaker and diluted to 3% by adding DI water and boiled for 4 h. After cooling down, they were filtered and washed using DI water. The insoluble materials were dried and weighed (the mass denoted by m_1). The lignin content was calculated as m_1/m_0 . As shown in Fig. 2a, the lignin was removed rapidly within the first 3 h in Process I, with an up

to 45% removal. Afterward the remaining lignin was further removed in Process II (Fig. 2b). Because lignin is colored, while cellulose and hemicellulose are colorless, the color of the fiber indicates the amount of lignin left. As expected, the color becomes lighter as more lignin is removed.

Fig. 2c depicts the measured regular light transmittance of the prepared flax-fiber composite samples at different processing stages. The tested fibers were stored in the elastomer at the 10 wt% fiber loading. The light transmittance of the composites was measured by a spectrophotometer in the 350 to 1000 nm wavelength range. The results revealed that samples after both Process I and Process II demonstrated a significant improvement in light transmission. Specifically, the flax fibers after process II (TFFs) exhibited superior optical properties and the prepared composites revealed an up to 95% regular transmittance. In addition, we found that by separating large fiber bundles, the light transmittance of sonicated fibers increased up to 90% compared with raw flax fibers. Afterward, we prepared TFF composites using the aforementioned mold with various TFF loadings and tested them under sunlight (Fig. 2d). As expected, although a lower TFF loading exhibits a slightly higher light transmittance, all the specimens with typical fiber loadings revealed superior performance.

3.2. Mechanical properties

The tensile strengths of TFF composites with different fiber loadings are presented in Fig. 3a. The measurements were conducted using an Instron 2710-205 tensile tester. The measured

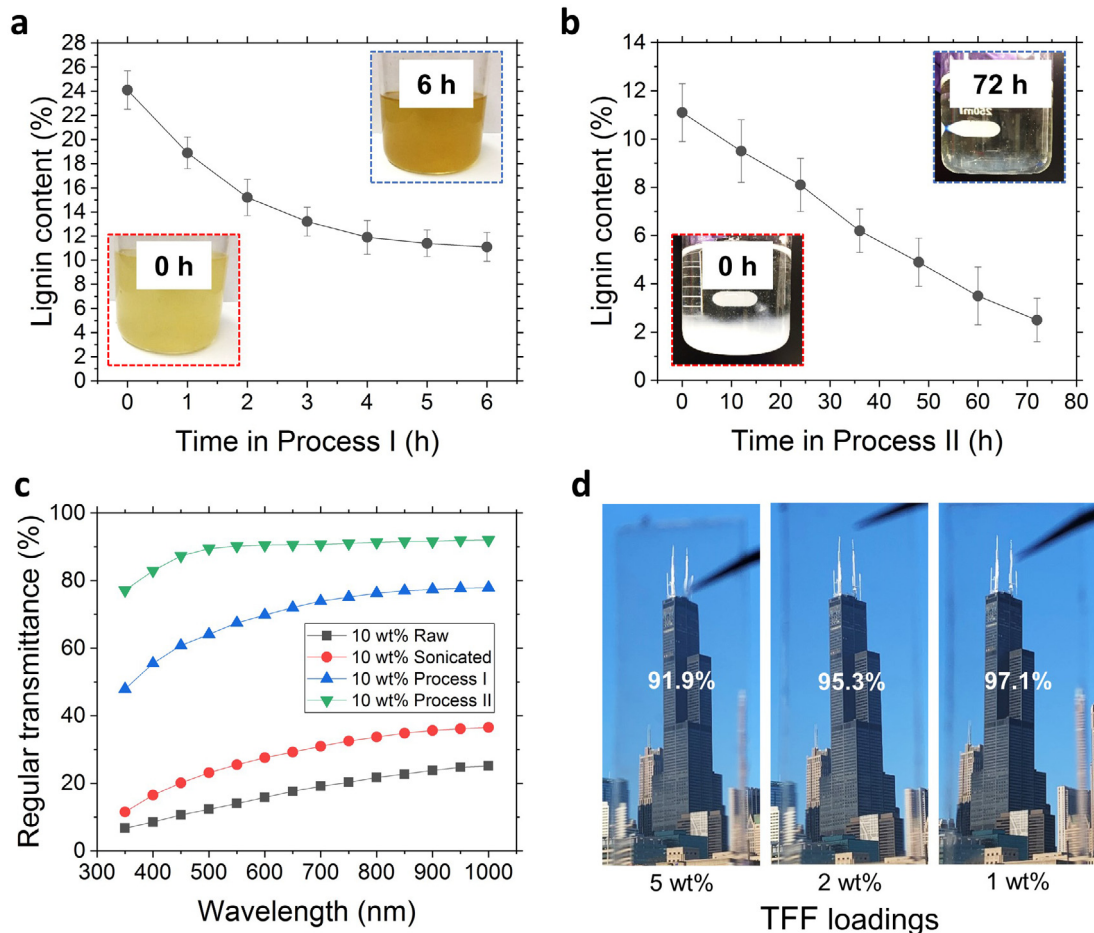


Fig. 2. (a) Time-dependent lignin content in Process I, 95% CI. (b) Time-dependent lignin content in Process II, 95% CI. (c) Light transmittance characterizations. (d) Demonstration of TFF composites under sunlight with different TFF loadings, light transmittance characterized at 700 nm wavelength.

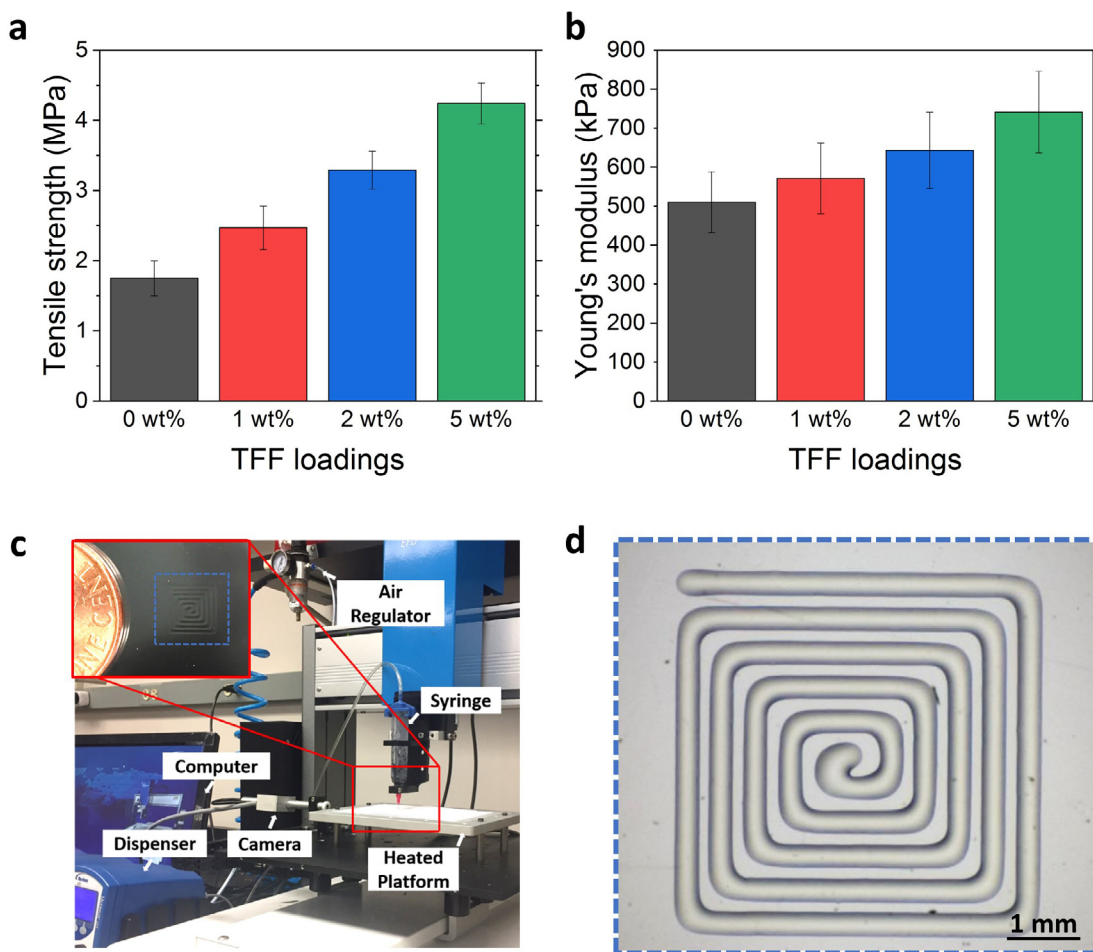


Fig. 3. (a) Tensile strength of TFF composites, 95% CI. (b) Young's modulus of TFF composites, 95% CI. (c) Extrusion-based additive manufacturing system. (d) Printed "loop" pattern, 5 wt% TFF/elastomer composites.

tensile strength increased from 2.5 to 4.2 MPa when the fiber loading increased from 1 to 5 wt%. Compared with pure elastomer, the 1 wt%, 2 wt%, and 5 wt% specimens revealed approximately 41%, 88%, and 142% increases in tensile strength, respectively. On the other hand, the measured Young's modulus with different fiber loading fractions are presented in Fig. 3b. Young's modulus characterizing stiffness was increased by 12%, 26%, and 46% after adding 1 wt%, 2 wt%, and 5 wt% TFFs into the elastomer, respectively. The findings related to both tensile strength and Young's modulus indicated a typical trend in non-transparent natural fiber-reinforced composites [10]. By removing the lignin content, the concentration of cellulose can be increased. Since cellulose has the actual fiber structure, while lignin only serves as binders to conglutinate fiber cells [1], the method of flax fiber treatment proposed in this study is beneficial for improving the overall mechanical reinforcement in composite structures. It should also be noted that the present transparent natural-fiber composites are competitive to many synthetic-fiber reinforced elastomer composites [11,12].

3.3. Printability

The printability of the prepared TFF composites was tested by printing TFF/elastomer composites (5 wt% fiber loading) using an extrusion-based additive manufacturing system to fabricate a 5 mm × 5 mm "loop" pattern. As shown in Fig. 3c, the system was developed by modifying a dispensing robot (E3V, Nordson

EFD). The experimental setup consisted of a camera for visual detection of the standoff distance (0.15 mm) between the platform and the dispensing tip. Printing was implemented by extruding the composite material through a dispensing tip (0.25 mm inner diameter, McMaster-Carr) onto a moving (5 mm/s) temperature-controlled platform (100 °C) in a trace-by-trace way. A dispenser (Ultimus II, Nordson EFD) provided the extruding air pressure (5.0 psi). As demonstrated in Fig. 3d, the width of the printed traces in the "loop" pattern is approximately $275 \pm 15 \mu\text{m}$, and the printing is free of any fiber agglomeration/inhomogeneity related defects, which confirms the excellent printability of the developed TFF composites in modern AM systems.

4. Conclusions

In summary, we reported the preparation of printable highly transparent flax fiber-reinforced composites. The prepared composites exhibited superior optical properties (>90% light transmittance), and their tensile performance was competitive to synthetic fiber-based composites. Their excellent printability in additive manufacturing processes allowed the fabrication of composite structures using plant-based materials. The findings of this study indicate a novel and sustainable method to engineer transparent composites with excellent mechanical and processing characteristics for functional devices, such as wearable electronics and soft robotics in multiplex geometries.

CRedit authorship contribution statement

Yizhou Jiang: Writing - original draft, Conceptualization, Methodology, Visualization, Investigation, Data curation. **Alexander L. Yarin:** Supervision, Validation, Writing - review & editing. **Yayue Pan:** Supervision, Validation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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