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Effect of Low Temperature Reactive Dye Reactive Red 2 on Dyeing and Tensile Properties of Twisted Bamboo Fibers

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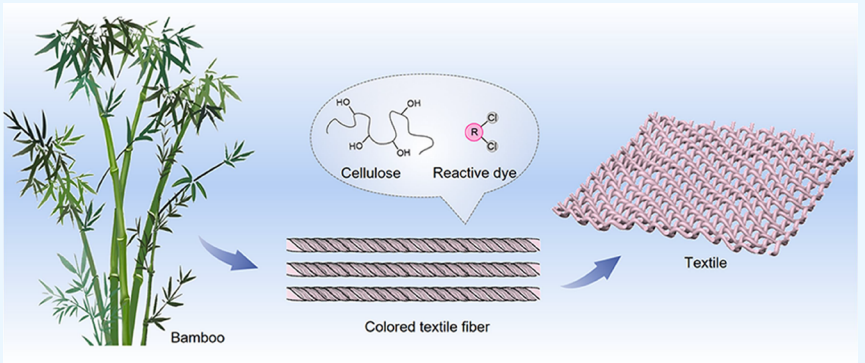

ABSTRACT: This study employed bamboo as the raw material and employed the sodium chlorite method to remove most of the chromogenic groups in bamboo. The low-temperature reactive dyes were then utilized as the dyeing agents in combination with the one-bath method to dye the decolorized bamboo bundles. The dyed bamboo bundles were subsequently twisted into bamboo fiber bundles with high flexibility. The effects of various factors, including dye concentration, dyeing promoter concentration, and fixing agent concentration, on the dyeing properties, mechanical properties, and other properties of the twisted bamboo bundles were investigated using a tensile test, dyeing rate test, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and scanning electron microscopy. The results indicate that the macroscopic bamboo fibers prepared by the top-down method have excellent dyeability. The dyeing treatment not only improves the aesthetics of bamboo fibers but also improves their mechanical properties to a certain extent. When the concentration of dye is 1.0% (o.w.f.), the concentration of dye promoter is 30 g/L, and the concentration of color fixing agent is 10 g/L, the comprehensive mechanical properties of the dyed bamboo fiber bundles are the best. At this time, the tensile strength is 95.1 MPa, 2.45 times that of undyed bamboo fiber bundles. XPS analysis results show that the relative content of C−O−C in the fiber is significantly increased compared with that before dyeing, which indicates that the formed dye fiber covalent bond can strengthen the cross-linking between fibers, thus improving its tensile performance. The covalent bond is stable, and the dyed fiber bundle can retain its mechanical strength even after high temperature soaping.

1. INTRODUCTION

Over the past century, the technical expertise of the modern textile industry has improved substantially. The advent and implementation of synthetic fibers have considerably facilitated people's lives. However, the limited availability of oil resources has significantly constrained the development of the textile industry.[1,2] In recent years, with the worldwide ecological environment in flux, people have become more attentive to environmental and energy issues, prompting the development and utilization of new green and sustainable textile fibers, such as bio-based new cellulose fibers,[3] bio-based synthetic fibers,[4] marine bio-based fibers,[5] and bio-protein fibers.[6] The preparation processes for these biological fibers are intricate and labor-intensive, requiring a significant amount of man-power and material resources, and exerting a major negative impact on the natural environment and ecology.

As a kind of natural biological material with abundant resources on the earth, the bamboo material has been widely used in furniture, textile, construction, and transportation.[7,8] Regenerated cellulose fibers extracted from bamboo have become a popular raw material in the textile industry, including bamboo fibers, bamboo viscose fibers, and bamboo charcoal fibers. Fabrics produced from regenerated bamboo fibers exhibit high hygroscopicity, air permeability, wear resistance,

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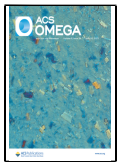

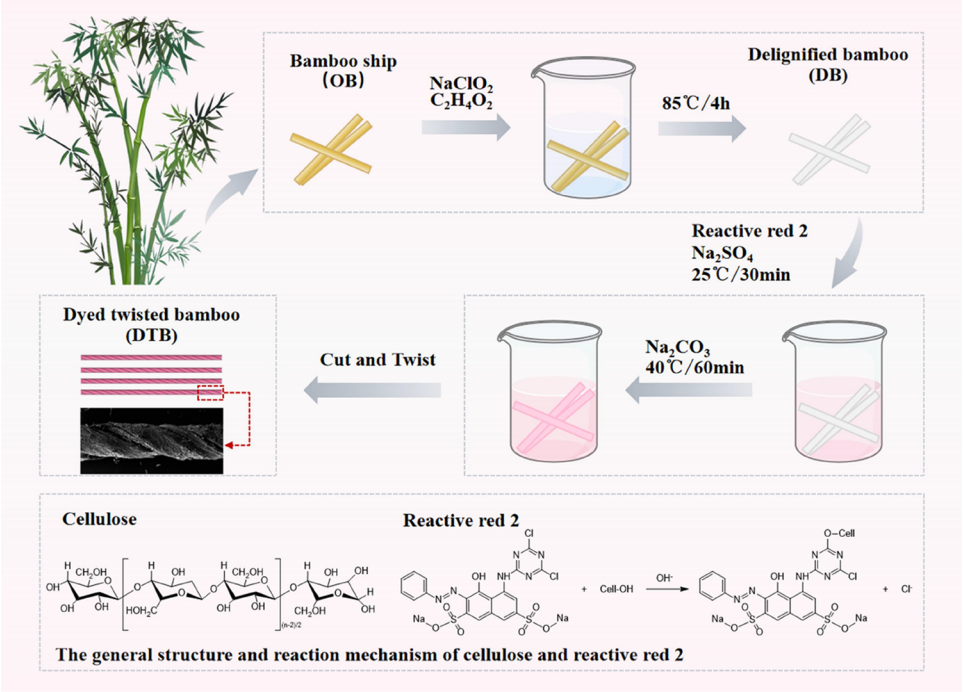

Figure 1. Preparation process and reaction mechanism of dyed twisted bamboo fibers.

and excellent antibacterial properties.[9,10] However, the process of crushing the raw materials to extract the cellulose fibers and purifying them through a series of refining and molding processes to prepare macroscopic textile fibers is complex and time-consuming. It also destroys the characteristics of bamboo raw materials to some extent and has a severe impact on the environment. Recently, a top-down method to prepare macroscopic textile fibers with spinnability was found by Jia et al.[11] This method retains the ordered cellulose structure within the wood, and the twisting treatment enhances elasticity, flexibility, and mechanical tensile properties. Bamboo and wood have similar structural components, but bamboo has a short growth cycle and high strength, converting it into a suitable alternative material for wood in preparing textile fibers. Wu et al.[12] processed the delignification of bamboo bundles by a twisting process to prepare bamboo textile fibers and studied the influence of the twisting process on the internal structure and tensile properties of bamboo fiber bundles. This study confirmed that twisted bamboo fibers hold significant application prospects in the textile industry. The dyeability of macromolecular fibers is essential to the practical application of twisted fibers in the textile industry. Therefore, this paper primarily discusses the dyeing process of twisted bamboo fibers.

Bamboo is rich in lignin, cellulose, and hemicellulose. The twisted bamboo fiber prepared from bamboo is a new type of cellulose fiber and contains rich hydroxyl groups.[13,14] Currently, the dyes commonly used in the dyeing of cellulose fiber fabrics on the market are direct dyes, reactive dyes, vat dyes, and so on, so this experiment uses reactive dyes that can form stable chemical bonds with bamboo fibers.[15] Due to the chromogenic and water-soluble groups contained in the parent structure of reactive dyes, they have excellent solubility and can achieve good color rendering properties when used in dyeing. In addition, because their molecular structure also contains one or two active groups that can form stable covalent bonds with the hydroxyl groups in cellulose, reactive dyes are widely welcomed in the dyeing of cellulose fiber fabrics.[16] Reactive dyes are mostly used in the dyeing of traditional fibers, such as cotton and hemp. However, there are currently relevant studies applying it to the dyeing of some new textile fibers.[17,18] Balakrishnan et al.[19] confirmed that the dyeing behavior of the banana fiber with reactive dyes is close to that of the cotton fiber and has excellent color rendering rate and washing fastness. Amin et al.[20] used different techniques to dye pineapple leaf fibers, which not only greatly improved the aesthetic value but also found that the pineapple leaf fibers prepared by infrared staining had better color effect and color fastness while saving time and energy consumption. Sun and co-workers[21] used polyvinylamine as an additive for salt-free dyeing of calcium alginate fibers, which enhanced the interaction between reactive dye molecules and fibers, and the obtained dyed fibers had higher tensile strength and color yield. There are also studies on the dyeing process and properties of bamboo fibers. For example, Larik et al.[22] used the ultrasonic method to dye bamboo fiber fabrics in batches. Compared with conventional dyeing methods, they improved the color yield while reducing the dyeing time and consumption of dyeing raw materials. However, there are few studies and reports on the dyeing process of twisted bamboo fibers.

In this study, the yellow part of 3−4-year-old moso bamboo was utilized as the raw material for modification. The original bamboo possesses a dense texture and high strength due to the presence of lignin in the molecular structure that contains a large number of Chromogenic and auxiliary color groups, which contributes to the yellow color of the bamboo. To improve the dyeing process, sodium chlorite was employed for pretreatment, resulting in decolorized bamboo with reduced chromogenic groups and increased fluid permeability, leading to improved color rendering and easier processing into bamboo textile fibers.[23,24] In the dyeing stage, reactive red 2

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ACS Omega 2023, 8, 21726−21735

is selected as the dye, and the-SO_3Na contained in its molecular structure makes the dye have good water solubility. Due to the high activity and reactivity of the dichlorotriazine group in the molecular structure, the fixation temperature required to bind to the fiber is low. In this experiment, the temperature is set to 40 °C, and the dyeing process can be carried out at room temperature. The dyeing method adopts one bath two-step method. First, the bleached bamboo bundle is immersed in the dye bath for a period of time, so that the dye molecules penetrate into the fiber bundle, and then the alkali agent is added to the same dye bath to make the dichlorotriazine group, and the cellulose molecule undergo a nucleophilic substitution reaction under the action of −OH to form a dye-fiber covalent bond, which not only shortens the dyeing time but also reduces energy consumption and wastewater discharge. The dyeing rate of the fibers was analyzed by adjusting the dye concentration, dyeing promoter concentration, and fixing agent concentration.[25] Dyeing bamboo fiber bundles (DDB) can be obtained from the pretreated decolored bamboo bundles (DB) after dyeing. The dyeing rate of the fibers was analyzed by adjusting the dye concentration, dyeing promoter concentration, and fixing agent concentration. DDB was treated by the twisting process to prepare dyed twisted bamboo fiber bundles (DTBs) and the tensile properties of each group were compared. The chemical composition and microstructure of dyed twisted bamboo fiber bundles (DTB) were characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) (Figure 1).

2. EXPERIMENTAL AND MATERIALS

2.1. Materials. The yellow part of 3−4 years old bamboo was selected as the original bamboo (OB) for the experiment. Sodium chlorite, purity 80%, was supplied by Shanghai MacLean Biochemical Technology Co., Ltd. Acetic acid, analytically pure, was purchased from Nanjing Chemical Reagents Co., Ltd. Active red 2 was purchased from Tianjin Baima Technology Co., Ltd. Sodium sulfate and sodium carbonate, analytically pure, were provided by Nanjing Chemical Reagents Co., Ltd. Standard soap tablets for textile tests were provided by the Shanghai Textile Industry Technical Supervision Institute. Deionized water for laboratory was homemade. The laboratory-grade ultrapure water machine model used was PLUS-E3-10TH, which was purchased from Nanjing Yipu Yida Technology Development Co., Ltd.

2.2. Experimental Methods. To begin, the dried bamboo chips were subjected to a decolorization process where lignin was removed using an acidic sodium chlorite solution. Reactive dyes were selected for the subsequent dyeing process, which involved a one-bath two-step method. The decolorized bamboo was then further processed by loosening it into bamboo fiber bundles, which were subsequently twisted.

2.2.1. Preparation of Decolored Bamboo Slices. The yellow portion of moso bamboo was utilized in this study and was cut into bamboo slices measuring 100 mm in length, 6 mm in width, and about 0.5 mm in thickness. These slices were then dried in a blast drying oven at 60 °C for 24 h. To decolorize the bamboo, a solution with a mass fraction of 4% sodium chlorite was prepared by dissolving 28 g of sodium chlorite in 672 mL of deionized water. The pH of the solution was then adjusted to 4.6 by adding acetic acid. The dried bamboo slices were immersed in the solution and heated in a water bath at 85 °C for 4−5 h. To further remove the residual chromophores, the delignified bamboo strips were bleached using a hydrogen peroxide solution with a mass fraction of 6%, which was prepared by diluting a 30% hydrogen peroxide solution. The strips were then rinsed with deionized water and air-dried at room temperature for 12 h.

2.2.2. Preparation of Dyed Bamboo Slices. In the pursuit of developing an effective dyeing process for twisted bamboo fibers, an X-type reactive dye, reactive red 2, was selected for its compatibility with fiber and fabric dip-dyeing applications. The active dichlorotriazine-type reactive group within the dye molecule facilitates dyeing and fixing at lower temperatures.

A dye solution containing 0.5−1.5% (o.w.f.) of reactive red 2 was prepared, and 5−15 g/L of sodium sulfate was added at 25 °C until completely dissolved. The decolorized bamboo chips were subsequently introduced to the dyeing bath at a 1:25 bath ratio and left to dye for 30 min. Following the dyeing stage, 5−15 g/L of sodium carbonate was added to the bath and the temperature was raised to 40 °C at a rate of 3 °C/min, fixing the dye for 60 min. The dyed bamboo fiber bundles were then washed thoroughly with deionized water until the washing solution became neutral.

2.2.3. Twisting of Dyed Bamboo Fiber Bundles. The decolored and dyed bamboo chips were meticulously cut into fine bamboo fiber bundles with a width of approximately 0.8 mm along the fiber direction using a blade. Thereafter, the bamboo fiber bundles were manually twisted by applying a force in the opposite direction at both ends to obtain the twisted bamboo fiber bundles.

3. CHARACTERIZATION METHOD

3.1. Dyeing Rate Test. The dye uptake is a critical parameter in the dyeing process and is defined as the ratio of the amount of dye absorbed by the fiber to the total amount of dye present in the initial dye bath, expressed as a percentage. The calculation formula is as follows:

$$\text{Dye uptake}\ (\%) = [1 - (A_i n_i)/(A_0 n_0)] \times 100\%$$

In this equation, A_0 is the absorbance of the initial dye solution diluted n_0 times, and A_i is the absorbance of the dyeing residue diluted n_i times. To determine the dye uptake, each group of dye baths was stained for 10, 20, 30, 40, 50, 60, 70, 80, and 90 min, and the dyeing residue was extracted by taking 0.1 mL at regular intervals and diluting it 100 times. The absorbance Ai was measured at λ_{max} using an ultraviolet spectrophotometer, and the dyeing percentage was calculated to draw the dyeing rate curve.

A U-3900 Spectrophotometer was used to measure the absorbance of the samples. The Abs mode was selected for the determination, and the spectral scanning range was set to 800−200 nm, with a scanning speed of 300 nm/min.

3.2. Tensile Strength Test. The tensile test was conducted using a universal mechanical testing machine controlled by a CMT4000 microcomputer. The sample was fixed with a fixture at both ends, and the gauge was set to 40 mm. Tensile strength, elastic modulus, and elongation at break of the sample were measured at a loading speed of 3 mm/min. The calculation formulas for each index are as follows:

$$\text{Tensile strength: } \sigma = F_b/\text{So}$$

where F_b is the maximum force when the specimen is broken in Newtons (N), and So is the original cross-sectional area of the sample in square millimeters (mm^2).

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Table 1. Comparative Analysis of the Dye Concentration, Salt Concentration, and Alkali Concentration Was Carried Out on Seven Sample Groups

species	DTB-1	DTB-2	DTB-3	DTB-4	DTB-5	DTB-6	DTB-7
reactive red 2 (o.w.f.)	0.5	1.0	1.5	1.0	1.0	1.0	1.0
Na_2SO_4 (g/L)	30	30	30	20	40	30	30
Na_2CO_3 (g/L)	10	10	10	10	10	5	15

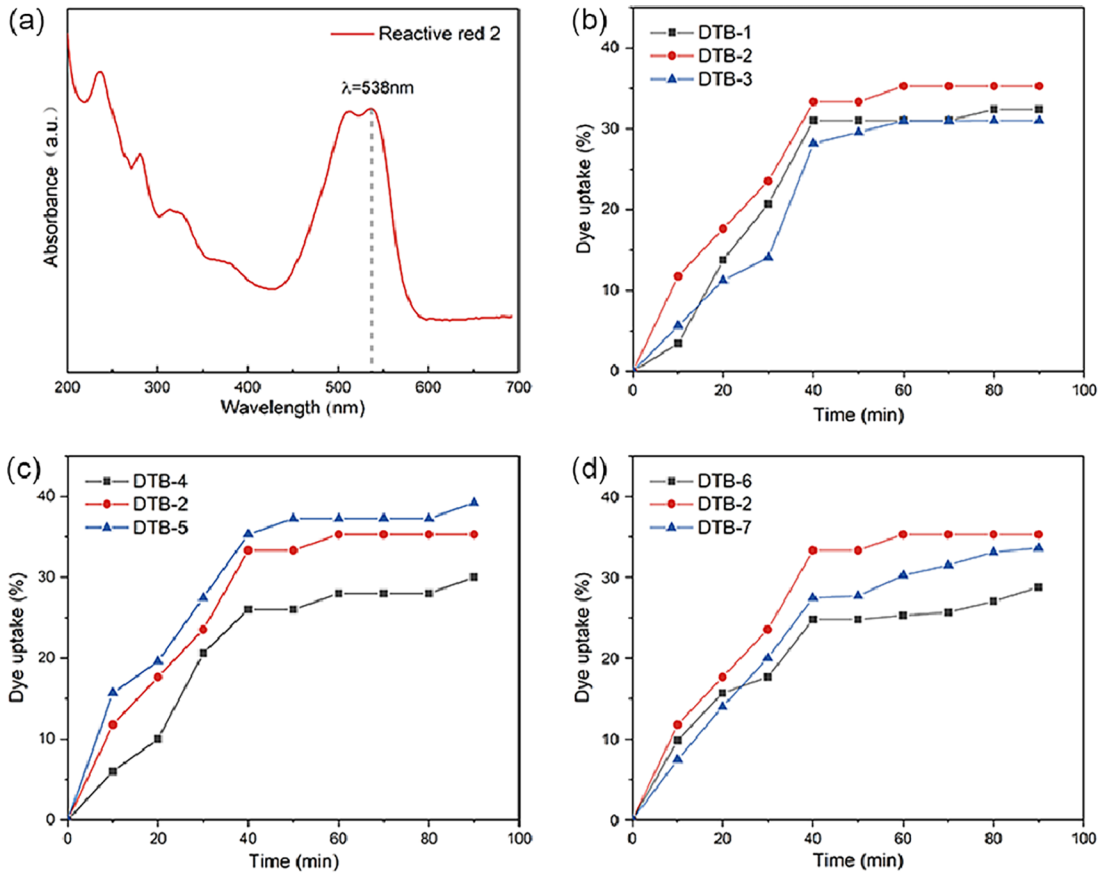

Figure 2. Dyeing rate of seven groups of samples: (a) UV absorption spectrum of reactive red 2 showed the maximum absorption wavelength at 538 nm. (b) Dyeing rate curve under different dye concentrations. (c) Dyeing rate curves under different salt concentrations. (d) Dyeing rate curves under different alkali concentrations.

Elastic modulus: $E = \sigma/\varepsilon$

where E is the elastic modulus, σ is stress, and ε is strain.

Elongation at break: $e = (L_a - L_0)/L_0$

where e is the elongation at break, L_0 is the initial length of the sample, and L_a is the length of the sample at break.

3.3. Fourier Transform Infrared Spectrum. Before testing, the samples were completely dried. The functional group changes of raw bamboo (OB), decolored bamboo (DB), and dyed bamboo (DDB-2) were measured using a VERTEX 80 V FTIR spectrometer. The infrared spectrometer was set to reflection mode during the test, and the scanning range was 4000−500 cm^{-1}.

3.4. Determination of Cellulose, Hemicellulose, and Lignin Content. The relative contents of lignin, cellulose, and hemicellulose in OB, DB, and DDB-2 samples were determined according to the National Renewable Energy Laboratory (NREL) method.

3.5. X-ray Photoelectron Spectroscopy. An AXIS UltraDLD X-ray photoelectron spectrometer (AXIS UltraDLD, Shimadzu, U.K.) was used to analyze the X-ray photoelectron spectroscopy of OB, DB, and DDB samples.

3.6. Environmental Scanning Electron Microscope Test. To observe the microstructure of the samples, ultra-thin slicing machine was used to cut the samples of OB, DB, and DDB-2 into 3 mm long fiber bundles. The gold spraying process was applied to the samples before they were observed under a FEI200 scanning electron microscope in both longitudinal and transverse sections. To determine the elemental composition, energy dispersive spectroscopy (EDS) was performed using an AztecX Max Extreme system, which was attached to the scanning electron microscope from Oxford Instruments (OIMS), UK.

4. RESULTS AND DISCUSSION

4.1. Analysis of Dyeing Rate Curve of Dyed Bamboo Fiber Bundles. To investigate the impact of various process parameters on the dye uptake, we prepared a total of seven dye baths (Table 1). The dye concentration ranged from 0.5 to 1.5% (o.w.f.), while the salt concentration ranged from 20 to 40 g/L, and the alkali concentration varied from 5 to 15 g/L.

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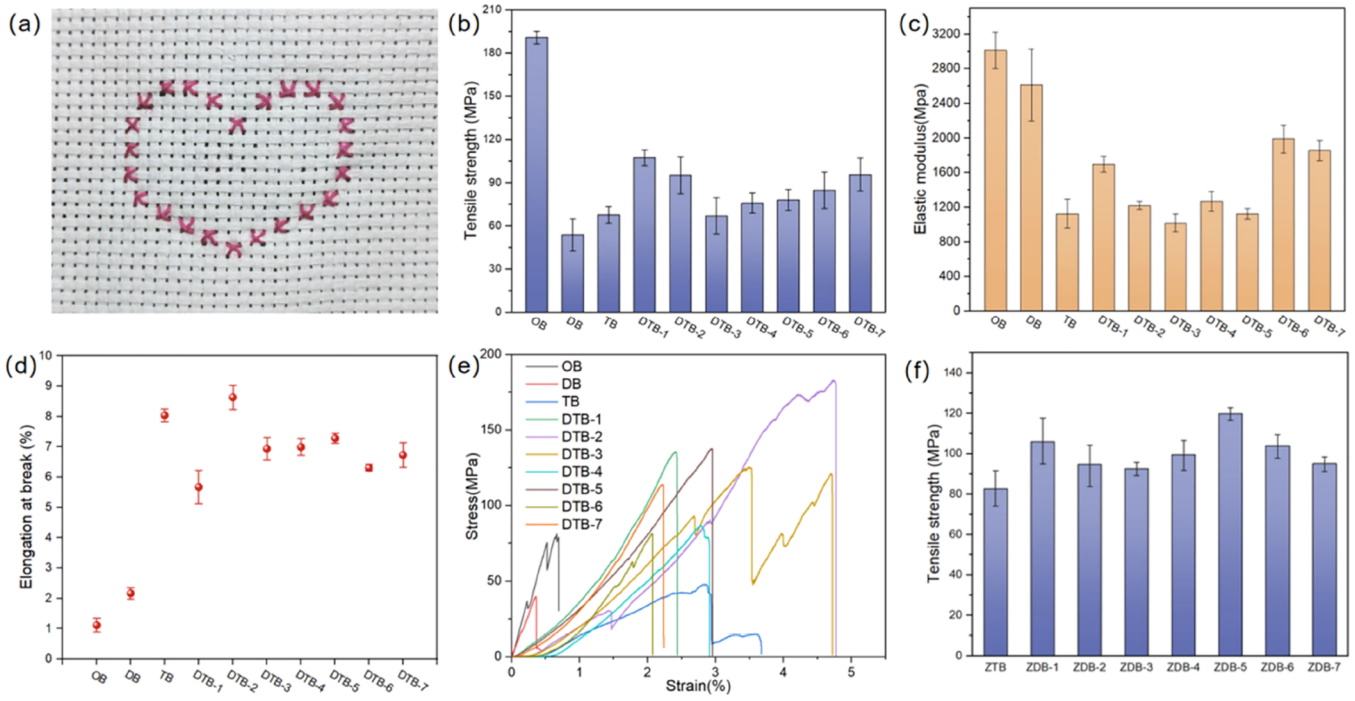

Figure 3. Pattern (a) of DDB-3 embroidered on the cross-stitch fabric and the mechanical properties of the samples: (b−e) Tensile strength, elastic modulus, elongation at break and stress−strain curves of OB, DB, TB, and DTB-1−7; (d) tensile strength of ZTB and ZDB-1−7, in which ZTB is soaped twisted bamboo fiber bundle and ZDB is soaped dyed twisted bamboo fiber bundle.

Additionally, we set the bath ratio at 1:25 to ensure consistency across all samples (Figure 2).

The dyeing of bamboo fibers involves two stages: dyeing and fixation. In the dyeing stage, comparing the initial dyeing slope of fiber dyeing in each dyeing bath, it can be seen that the dye concentration and salt dosage will affect the initial dyeing and diffusion rate of the dye. The electronegativity of bamboo cellulose in aqueous solution results in ionization, and cations with opposite charges in the solution form an adsorption layer and a diffusion layer on the surface and around the fiber. This is known as the electric double layer. The potential difference between the fiber and the dye molecule resulting from the electric double layer affects their mutual movement. In addition, the dye molecule is ionized and negatively charged in the solution, which causes Coulomb repulsion and van der Waals force between the negatively charged cellulose. The addition of neutral electrolyte to the dye bath introduces positive valence cations, which reduce the Coulomb repulsion and promote molecular movement in the solution. This improves the adsorption of dyes by cellulose fibers.[26,27]

The fixation stage begins after 30 min of dyeing, during which the fixing agent sodium carbonate is added to the dyeing system. This causes the hydroxyl groups on the surface of bamboo cellulose to dissociate, forming anions that provide reaction sites for nucleophilic substitution with dye molecules to form dye-fiber covalent bonds. Sudden dyeing occurs on the fiber, and the dyeing rate increases greatly and then levels off.

When the amount of salt is constant, the initial dyeing slope of the bamboo fiber bundle increases with the increase of dye concentration in the dye bath. However, during the continuous dyeing process, the dyeing rate of bamboo fibers in the dye bath with a dye concentration of 1.5% (o.w.f.) slows down due to the accumulation of excessive dye molecules on the fiber surface. This accumulation affects the diffusion and fixation of dye molecules into the fiber, resulting in a decrease in the dyeing rate. In the fixation stage, dye adsorption and diffusion occur with the fiber bonding reaction under the catalysis of the alkali agent. The dye molecule itself also undergoes a chemical bond cleavage leading to a hydrolysis reaction. Since the group of reactive red X-3B reacting with cellulose is the more active dichlorotriazine group, the hydrolysis reaction is more intense. Although the reactive dye can continue to adsorb and diffuse after hydrolysis, it loses the ability to bind to the fiber, leading to a decrease in the dyeing rate. Therefore, the suitable dye concentration for reactive red X-3B to dye bamboo fiber bundles in this experiment is about 1% (o.w.f.).

When the dosage of sodium sulfate is increased from 20 to 40 g/L, the initial dyeing slope and dye-uptake of reactive red X-3B increase with the increase of sodium sulfate dosage. Sodium sulfate acts as an accelerant by increasing the positive charge in the dyeing bath, promoting the diffusion of sodium ions to the fiber surface, shielding the negative ions on the fiber surface, reducing the energy barrier of the dye to the fiber surface, and promoting dyeing. In summary, the optimum dosage of sodium sulfate is about 40 g/L.

When varying the amount of fixing agent in the dye bath, the reaction conditions were kept constant for 30 min prior to dyeing in each of the three dye baths, resulting in similar trends in the dye-uptake rate curves. Upon adding the fixing agent, an increase in the dosage of sodium carbonate from 5 to 10 g/L raised the pH of the dye solution, significantly increasing the concentration of cellulose anions, and resulted in sudden dyeing of the fiber by the dye, causing a rapid increase in dye-uptake rate. However, as the dosage of sodium carbonate increased from 10 to 15 g/L, the hydrolysis of the dye intensified, causing the breakdown of some dye-fiber covalent bonds and leading to a decrease in the fixation effect and the final equilibrium dye uptake value. Taking into account the dyeing effect, the optimal dosage of sodium carbonate is approximately 10 g/L.

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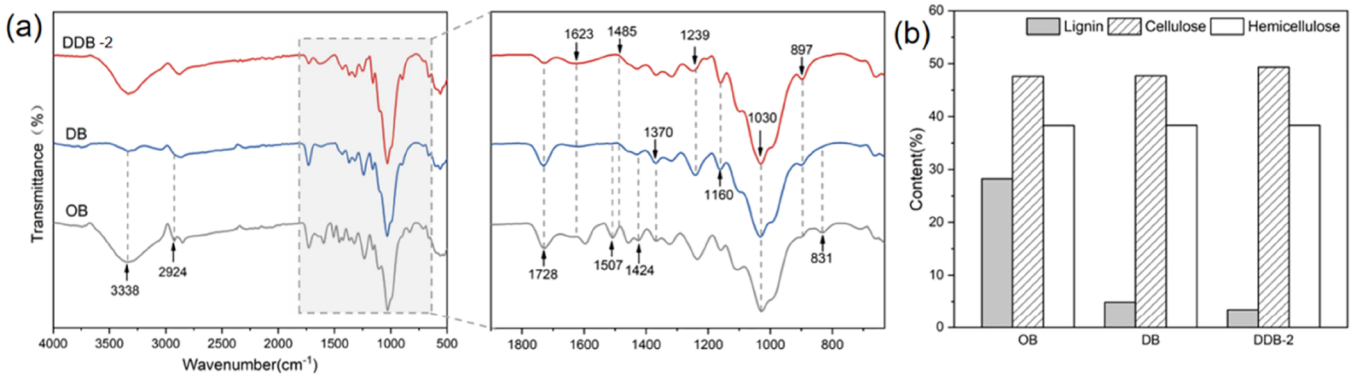

Figure 4. Chemical composition analysis of raw bamboo fiber bundles (OB), twisted bamboo fiber bundles (DB), and dyed twisted bamboo fiber bundles (DDB-2). (a) Fourier transform infrared spectroscopy; (b) relative content of lignin, cellulose, and hemicellulose.

4.2. Analysis of Mechanical Properties of Twisted Bamboo Fiber Bundles before and after Dyeing. According to Figure 3, natural bamboo has a hard texture and excellent tensile strength. As a chromogenic group in bamboo, it also exists between cellulose fibers to provide rigid substances. Lignin is largely removed in decolorization treatment, so the tensile properties of DB change significantly. The twisting treatment changed the arrangement of bamboo fibers in DB, made it twisted and tightly combined, improved flexibility and strength, and could better resist fiber breakage caused by stretching.

After dyeing bamboo fiber bundles, the dyed and twisted bamboo fiber bundles (DTB) showed a significant increase in tensile strength compared to undyed twisted bamboo fiber (TB), with an increase ranging from 55.9 to 155.79%, and an overall decrease in elongation at break. This is because during the dyeing process, the dichlorotriazine group in the dye reacts covalently with the hydroxyl groups in the cellulose molecules, and the resulting hydrogen bonds strengthen the cross-linking between the dye molecules and the cellulose molecules, thus limiting the slip of the cellulose macromolecular chains under external forces. As a result, the tensile strength of DTB is higher than that of TB that has not undergone dyeing.[28−30]

With an increase in dye concentration, the elastic modulus of the dyed bamboo yarn decreases, indicating that it is more prone to elastic deformation and has better flexibility. When the concentration is 1.0% (o.w.f.) and 1.5% (o.w.f.), the elastic modulus of the dyed bamboo yarn is similar to that of TB, and changes in salt concentration have little effect on the elastic modulus of the dyed bamboo fiber. However, when the alkaline concentration increases, the elastic modulus of DTB first increases and then decreases. This is because in an alkaline solution, cellulose undergoes limited swelling, exposing more hydrogen bonds as reaction sites for the dye molecules and cellulose molecules, which strengthens the cross-linking between the dye and cellulose. However, when the alkalinity is too strong, the cellulose with a low degree of polymerization in the amorphous region swells indefinitely, causing partial dissolution of the cellulose in the bamboo cell wall fiber. Meanwhile, the hydrolysis reaction of the reactive dye molecules intensifies, and the ability to bond with fibers decreases. As a result, some of the already generated covalent bonds between the dye and fiber also break as the dyeing time is prolonged, leading to an increase in the brittleness of the fiber. Based on the changes of elongation at break and stress−strain curves, it can be seen that the twisting process can give bamboo fiber bundles excellent flexibility, and the change of the dyeing process will also have a positive or negative impact on the elasticity and toughness of twisted bamboo fiber bundles, but in general, this change basically floats near the mechanical properties of TB.

Based on the above analysis, it can be concluded that reactive dyeing can optimize the tensile properties of bamboo spinning fiber bundles, providing better tensile strength while retaining the excellent elasticity and flexibility of the original bamboo spinning fiber. Different dyeing process parameters lead to different mechanical effects, and the optimal comprehensive mechanical properties of dyed bamboo spinning fiber bundles are achieved with dye, accelerating agent, and fixing agent concentrations of 1.0% (o.w.f.), 30 g/L, and 10 g/L, respectively.

4.3. Analysis of Mechanical Properties of Twisted Bamboo Fiber Bundles after Soaping. The soap washing process refers to the relevant regulations of GB/T 2931-2014 "Determination of Fixation Rate of Reactive Dyes". A soap solution was prepared using 2 g/L of standard textile test soap chips, and the dyed bamboo strips were immersed in the solution at a liquor ratio of 1:25, washed for 10 min at 92−95 °C, and then rinsed with cold and hot water alternately until the washing solution became neutral. The washed bamboo strips were air-dried at room temperature for 24 h before being subjected to twisting treatment.

The analysis of the tensile strength of the dyed bamboo fibers after soap washing showed that the mechanical properties of the dyed bamboo fibers were not greatly compromised by the high-temperature soap washing process. For the bamboo bundles in which the strength was significantly reduced due to the use of excessive amounts of salt and alkali during the dyeing process, the soap-washing treatment could improve their strength to a certain extent.

4.4. Fourier Infrared Spectrum Analysis. FTIR spectrum analysis can characterize the change of the internal chemical structure of the sample by analyzing the chemical composition. According to Figure 4a, compared with OB, the absorption peak of O−H stretching vibration (3338 cm^{-1}), C−H stretching vibration peak (2921 cm^{-1}), C═O stretching vibration (1728 cm^{-1}), lignin aromatic ring skeleton vibration (1507 cm^{-1}), C−H in-plane bending vibration of cellulose and hemicellulose (1370 cm^{-1}), lignin aromatic ring skeleton vibration, and C−H in-plane bending vibration of cellulose and hemicellulose (1424 cm^{-1}) in DB can be seen. The stretching vibration peak (1239 cm^{-1}) and aromatic ring C−H out-of-

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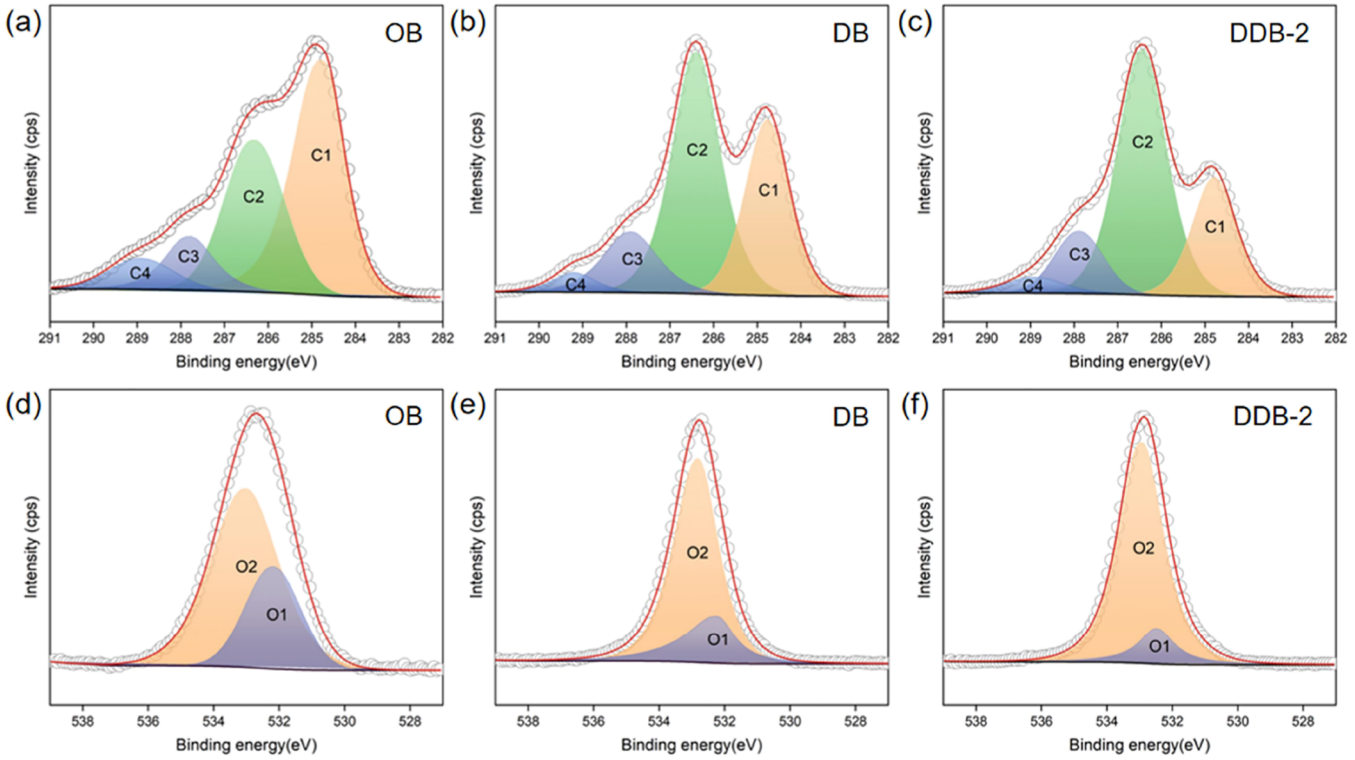

Figure 5. XPS high resolution (a–c) C1s and (d–f) O1s fitting spectra.

Table 2. Peak Separation Results of C1s and O1s and O/C Ratio

	C (%)				O (%)		
samples	C1	C2	C3	C4	O1	O2	O/C (%)
OB	48.19	33.53	10.96	7.33	30.60	69.40	41.62
DB	32.32	49.57	14.29	3.82	22.66	77.34	57.12
DDB-2	24.69	57.08	13.83	4.40	13.78	86.22	64.22

plane vibration peak (896 and 825 cm^{-1}) of the fatty acid group have different degrees of change.[31,32] These characteristic peaks correspond to cellulose, hemicellulose, and lignin in bamboo. The peak values of DB at 1508 and 1239 cm^{-1} decreased, which corresponded to the characteristic peaks of lignin, while the peaks of characteristic functional groups related to cellulose and hemicellulose did not change significantly. Combined with Figure 4c, it can be seen that sodium chlorite decolorization treatment can remove a large amount of lignin components in bamboo, and its content is lost by about 82.75%. This process is also accompanied by the reduction of some carbohydrates, which has little effect on the content of cellulose and hemicellulose.

After dyeing, the skeleton vibration of DDB-2 at 1623 cm^{-1} was strengthened, which corresponded to the *s*-triazine ring in the dye structure, and the stretching vibration of C−O−C at 1160 m^{-1} was strengthened, indicating that the dyed bamboo bundles contained reactive red 2 and may have dye-fiber covalent bonds. In addition, the absorption peaks of DDB-2 at 1728, 1239, and 1028 cm^{-1} changed, which indicated that the residual lignin in DB was further decomposed in the alkaline dyeing bath during the dyeing process. The three major test results also showed that the lignin content was further reduced by about 5.07% compared to OB.

4.5. X-ray Photoelectron Spectroscopy. The qualitative and quantitative analysis of elements and functional groups on the surface of fiber bundles by X-ray energy spectrum analysis (XPS) can further characterize the effects of decolorization and dyeing on the internal chemical composition and structure of bamboo cellulose. This study mainly evaluated the atomic connectivity related to carbon and oxygen in the sample, where C1 corresponds to C−C or C−H in lignin and extract, C2 corresponds to C−O in cellulose and hemicellulose, C3 corresponds to C═O or O−C−O in cellulose, C4 corresponds to O═C−O in hemicellulose and extract, O1 and O2 represent O−C═O and C−O, respectively. From Figure 5, it can be seen that C and O in OB, DB, and DDB show obvious differences in peak intensity and chemical shift at different binding energy levels.[33,34]

In the existing related research, it is found that the proportion of cellulose, hemicellulose, lignin, and extract in plant components can be judged by calculating the O/C value. Therefore, the content of C1−4 and O1, O2, and O/C values were calculated according to the fitting of C1s and O1s in the XPS spectrum (Table 2). After decolorization treatment, the content of C1 decreased from 48.19 to 32.32%, and the O/C value also increased from 41.62 to 57.12%. After the dyeing process treatment, it also showed a similar trend, indicating that lignin had different degrees of decomposition in these two processes. The latter removes a small amount of lignin while accompanied by the C−O−C bond formed by the dye molecules and cellulose. The decreasing and increasing trends

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ACS Omega 2023, 8, 21726−21735

of O1 and O2 were also consistent with the conclusions in the existing literature.[35] In the quantitative analysis results of XPS, the content of N and S in DDB-2 increased by 59.34 and 140%, respectively compared with DB (Table 3), which corresponded to the triazine group and water-soluble group-SO3Na in reactive red 2.

Table 3. Relative Content of C, O, N, and S in Fiber

	C (%)	O (%)	N (%)	S (%)
OB	72.50	22.65	4.65	0.21
DB	68.70	29.49	0.91	0.05
DDB-2	65.62	31.64	1.45	0.12

4.6. Environmental Scanning Electron Microscope Test. The SEM images of the bamboo fiber bundles revealed that the bamboo fibers and parenchyma cells were arranged at intervals. On the end surface, clear vascular bundles, parenchyma cells, and starch granules in some cells were observed (Figure 6a–c). Upon the removal of lignin, the impurities on the surface of the fiber bundle were effectively eliminated, and the fiber and cell morphology remained intact, while the cell wall became thinner, and the cell spacing became larger. From the end face of the fiber bundle, the vascular bundle with a complete cross-section and the thin wall tissue surrounding it could be observed (Figure 6d–f). However, after staining, the fiber and cell structure remained but were partially damaged. The cell wall was partially dissolved, the fiber became more brittle, and cracks were more easily generated inside the fiber bundle (Figure 6g–i and 7).

After dyeing, the decolorized bamboo fiber bundle displayed a vibrant color, and the bundle was further twisted. This operation applied an external force to the fiber bundle, causing plastic deformation and significantly improving its flexibility and bending properties, making it suitable for weaving. Microscopically, the cross sections of TDB and DTB exhibited a certain degree of distortion, and the end surface was approximately circular. The vascular bundles and cell tissues were tightly combined by extrusion, reducing the gaps and filling, and compacting the internal voids, which increased the fiber density and strength. Elemental analysis showed that the content of sulfur, the characteristic element, was higher in the dyed bamboo fiber bundle, second only to the carbon element. It was distributed in the bamboo fiber and parenchyma cells, and the distribution at the end face was also more uniform, indicating that the dye molecules had successfully penetrated the fiber bundle.

5. CONCLUSIONS

As a sustainable and eco-friendly material, the twisted bamboo fiber is expected to emerge as a novel textile fiber for future applications in the textile industry. It is of equal importance to enhance both the aesthetic and practical aspects of fiber products. In this study, dyed bamboo fibers were prepared through a one-bath method at a lower temperature, effectively demonstrating the dyeability of twisted bamboo fibers, while also investigating the impact of different dyeing process parameters on their properties. The augmentation of dye and accelerant concentrations accelerates the dyeing process and enhances the final dyeing rate. The optimal concentration of the fixing agent is 5–10 g/L, while the excessive usage of alkali

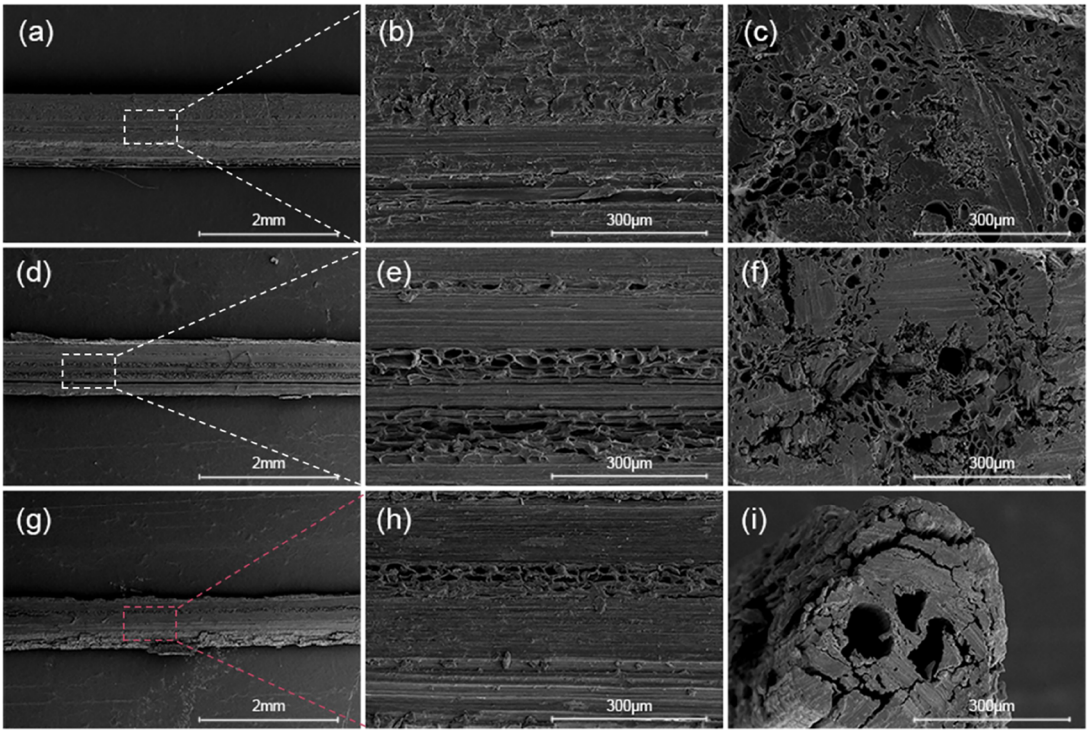

Figure 6. Scanning electron microscope images of raw bamboo, decolorized bamboo bundles, and dyed bamboo bundles. (a,b) SEM images of the cross-section of bamboo with parenchyma cells and bamboo fibers. (c) SEM images of the end face of bamboo with vascular bundles and dense parenchyma cells. (d,e) SEM images of the cross-section of the decolored bamboo bundles with parenchyma cells and bamboo fibers arranged in intervals. (f) SEM images of the end faces of the decolorized bamboo bundles with gaps. (g,h) SEM images of the cross-section of stained bamboo bundles partially dissolved in parenchyma cells. (i) SEM images of the ends of dyed bamboo bundles with gaps and vascular bundles.

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ACS Omega 2023, 8, 21726–21735

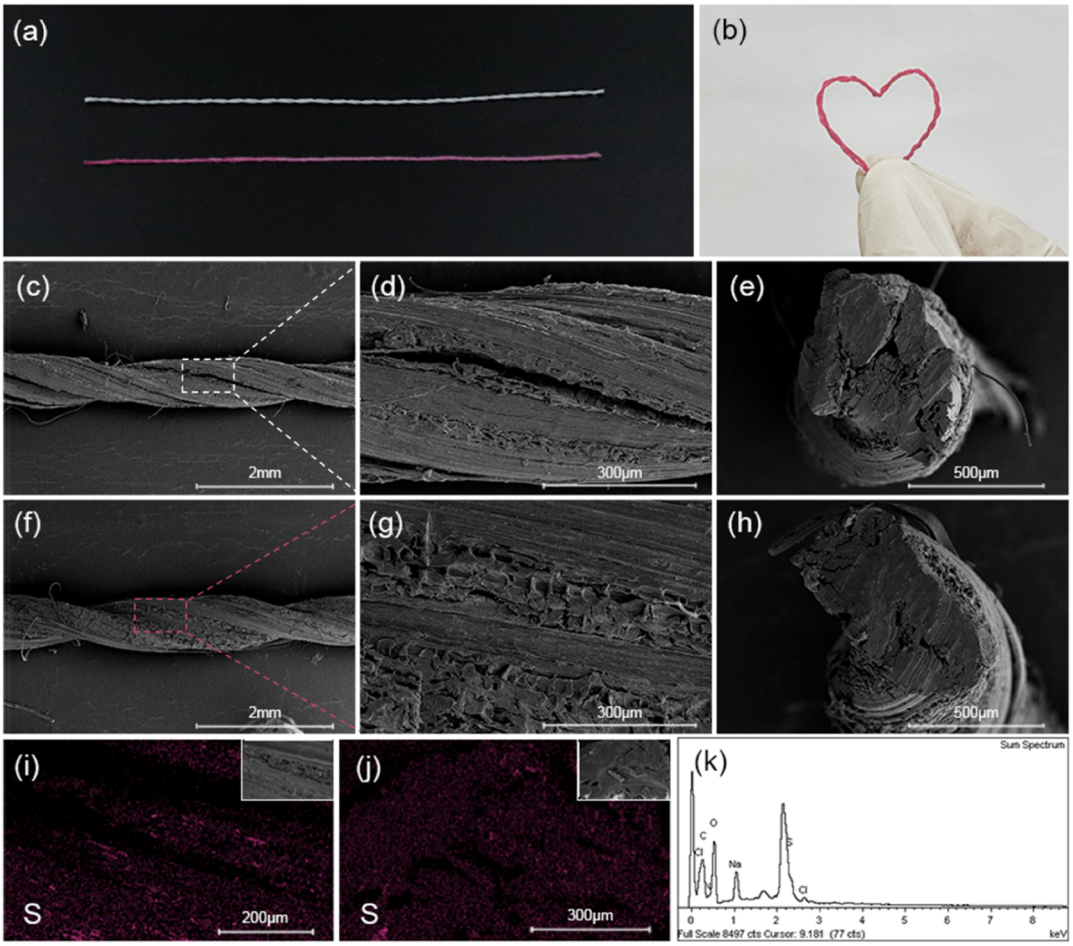

Figure 7. Scanning electron microscopy images of twisted decolored bamboo (TDB) and twisted dyed bamboo (DTB). (a) TDB and DTB naturally stretched state. (b) Three DTB woven images. (c,d) SEM image of TDB cross-section. (e) SEM images of TDB end face. SEM images of (f,g) DTB cross-section. (h) SEM images of DTB end face. (i) Element diagram of DTB cross-section. (j) Element diagram of DTB end face. (k) EDS images of DTB.

may impede the dyeing process. The results of tensile testing demonstrate that the dyeing treatment effectively enhances the tensile strength and flexibility of twisted bamboo fibers, with a maximum increase rate of 155.79% in fiber tensile strength. Consequently, the texture of the fibers becomes softer and enables weaving processes.

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ACS Omega 2023, 8, 21726−21735