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Closed-loop recyclable, biodegradable, shape-reconfigurable, water-weldable cotton-derived bioplastic

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Experimental section

Preparation of cotton-derived bioplastic

The chemical reagents used in this study include TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl, Sigma-Aldrich, ≥ 97.5% Purity), NaBr (Sinopharm Chemical Reagent Co. Ltd., ≥ 99% Purity), NaClO (Sinopharm Chemical Reagent Co. Ltd., chlorine concentration 8%), and NaOH (Sinopharm Chemical Reagent Co. Ltd., ≥ 96% Purity). TEMPO, NaBr, and NaOH were separately dissolved in deionized water with a magnetic stirrer (LKTC-M, 77-1A) to prepare 1 wt% TEMPO, 10 wt% NaBr, and 3 M NaOH aqueous solutions, respectively. Cotton was oxidized using a TEMPO-mediated system, which consists of TEMPO, NaBr and NaClO at a mol ratio of 1 : 15.2 : 84. In a typical procedure, 12 g cotton was combined with 20 ml 1 wt% TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) aqueous solution and 20 ml 10 wt% NaBr aqueous solution in 700 ml deionized water. The mixture was stirred thoroughly with an agitator (LICHEN, LC-OES-60) at 400 rpm for 30 min to obtain a homogeneous suspension. Subsequently, 100 g NaClO solution (chlorine concentration 8 %) was added gradually while maintaining the pH at 10.5 through continuous adjustment with 3 M NaOH. During the entire process, a pH meter (INESA, PHS-25) was continuously

immersed in the reaction solution to monitor the pH value in real time. Following completion of the oxidation reaction, the oxidized cotton fibers were thoroughly washed with deionized water and subjected to mechanical shearing with a powerful blender (Inkaxss, PJ02) to produce a cellulose nanofiber suspension. Finally, the suspension was processed into cotton-derived bioplastic using a vacuum filtration device (JOANLAB, VP-30L; BORO3.3).

Material characterizations

The sample morphology was analyzed by scanning electron microscopy (SEM; JSM-7001F, JEOL) and transmission electron microscopy (TEM; JEM-2100F, JEOL). Surface chemical modifications were characterized using Fourier transform infrared spectroscopy (FTIR; Bruker Vector-22). The tensile strength was tested by a universal testing machine (CMT6103). Crystal structures were analyzed using X-ray diffraction (XRD; Bruker D8-ADVANCE).

Figures and discussion

The oxidation mechanism of cotton using the TEMPO/NaBr/NaClO system is shown in Fig. S1. The reaction is initiated by adding NaClO to the aqueous suspension of cotton containing TEMPO and NaBr. It proceeds through four key steps[1-3]: (1) NaClO reacts with NaBr to form NaBrO; (2) the hypobromite ion (BrO-) oxidizes TEMPO to a nitrosonium-containing intermediate ($^{+}$N=O); (3) this intermediate then oxidizes the C6 hydroxyl group of cotton cellulose to a carboxyl group, while itself being reduced to a hydroxylamine species (N-OH); and (4) BrO- reoxidizes the hydroxylamine species back to the nitrosonium-containing intermediate, sustaining the catalytic turnover.

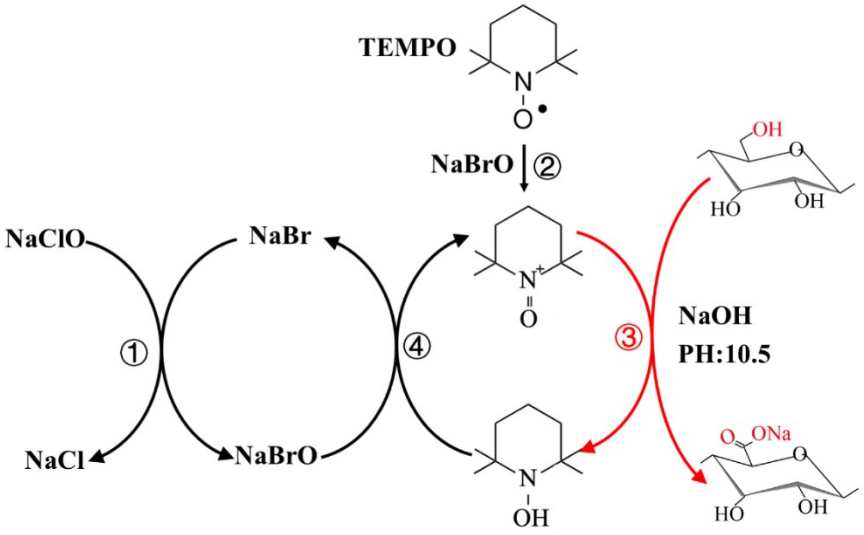

Fig.S1 Mechanism of TEMPO-mediated cellulose oxidation.

To gain deeper insights into the structural evolution, XRD analysis was performed on cotton before and after TEMPO-mediated oxidation (Fig. S2). The cellulose nanofibers derived from TEMPO-oxidized cotton preserve the characteristic diffraction peaks of native cellulose, indicating that the crystal structure remains largely intact without significant chain scission or ring opening reactions. This observation is consistent with the selective oxidation mechanism of the TEMPO/NaBr/NaClO system, which primarily converts C6-primary hydroxyl groups to carboxyl groups (-COO-). However, a detailed examination of the principal diffraction peak corresponding to the (002) plane reveals three quantitative changes that directly reflect the structural modifications induced by oxidation. First, a slight shift of the peak position from 22.8° to 22.6° indicates an increase in interplanar spacing after oxidation. This expansion results from the oxidation of C6-primary hydroxyl to carboxyl groups (-COO-), which disrupts the native interchain hydrogen-bonding and promotes the disintegration of cotton fiber into individualized cellulose nanofibers. This finding aligns with the FTIR results (Fig. 1e) and the morphological observations (Fig. 1a-b). Second, a decrease in peak intensity from 3439 to 2522, suggesting a reduction in crystallinity. This reduction reflects the partial loss of ordered molecular packing associated with the nanofibrillation process. Third, an increase in full width at half maximum (FWHM) from 1.75 to 1.86, reflecting a reduction in crystallite size. This observation aligns with the observed micro- to nano-scale morphological transition (Fig. 1a-b), further supporting the structural disintegration of cotton fiber resulting from TEMPO-mediated oxidation.

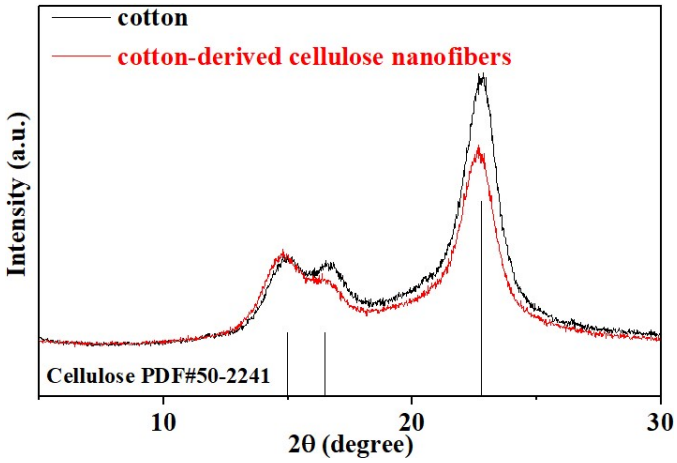

Fig.S2 XRD spectra of cotton and cotton-derived cellulose nanofibers.

The tensile strengths of the original and welded bioplastics are 151.2 MPa and 116.9 MPa, respectively (Fig. S3). Compared to the original bioplastic, the welded bioplastic still retains 77.3 % of the tensile strength.

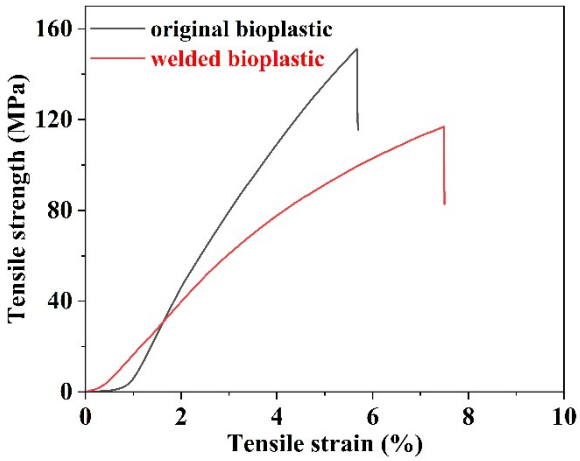

Fig. S3 Tensile stress-strain curves of original and welded cotton-derived bioplastics.

We further evaluated the mechanical performance of the bioplastic under varying moisture conditions. Controlled amounts of water are applied to the bioplastic specimens to achieve different moisture levels corresponding to 0.5, 1 and 2 times the original mass of the bioplastic. The tensile strengths under these conditions are 137.7, 110.9, and 96.7 MPa, respectively, retaining 91.1%, 73.3%, and 63.9% of the original tensile strength correspondingly (Fig. S4). These results demonstrate that the bioplastic maintains appreciable mechanical strength even under high moisture conditions.

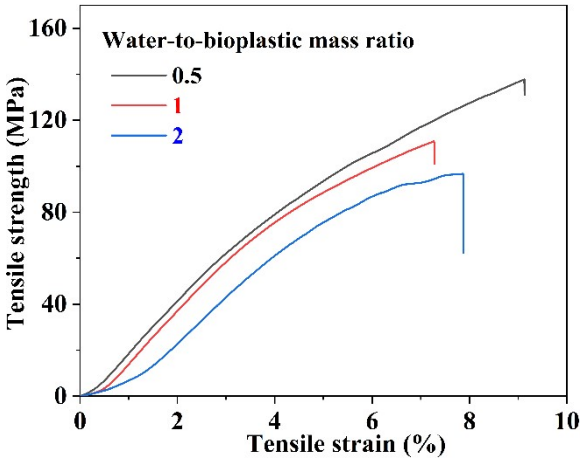

Fig. S4 Tensile stress-strain curves of cotton-derived bioplastics under varying moisture conditions.

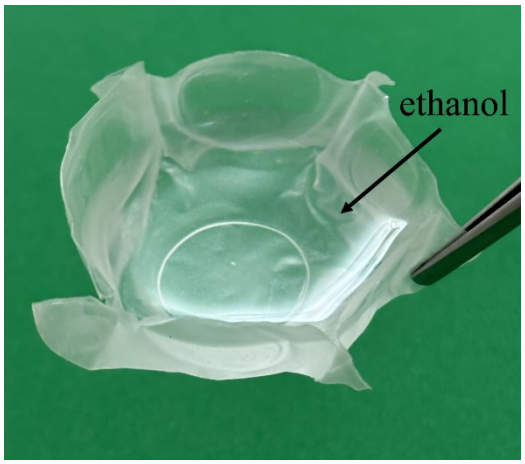

Fig. S5 Photos of container used for ethanol storage.

Notes and references

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