Supporting Information

Highly Tough, Degradable, and Water-Resistant Bio-based Supramolecular Plastics Comprised of Cellulose and Tannic Acid

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1. Experimental Section

1.1. Materials: Cellulose (absorbent cotton) was purchased from Aladdin. The viscosity-average molecular weight of the absorbent cotton was determined to be 1.30×10^5 according to the Mark−Houwink equation $[\eta] = 1.33 \times 10^{-4} (M)^{0.905}$ by using an Ubbelohde viscometer at 25 °C. Therefore, the degree of polymerization (DP) of the cellulose was calculated to be ~810. Tannic acid was purchased from Sigma-Aldrich. LiCl was purchased from Alfa Aesar.

1.2. Characterizations: The stress-strain curves were measured using a universal testing machine (Shimadzu AG-I 2 kN) with the stretching speed of 10 $mm \cdot min^{-1}$ at room temperature. The thermogravimetric analysis was determined on a TA Instruments Q500 Thermogravimetric Analyzer. Each sample (~5 mg) was heated from 25 to 800 °C with a rate of 10 $°C \cdot min^{-1}$ under the nitrogen atmosphere. Dynamic mechanical analysis (DMA) of C-TA plastics was performed on a DMA^+450 (01dB-Metravib, Inc.) using tension film mode with a frequency of 1 Hz and strain amplitude of 1%. FT-IR spectra were obtained by a Bruker VERTEX 70 FTIR spectrometer. UV−vis transmission spectra were recorded using a Shimadzu UV-2550 spectrophotometer. X-ray diffraction (XRD) measurements were performed at room temperature on a Rigaku D/max 2550 diffractometer with Cu Kα radiation (λ = 1.5418 Å), running at 50 kV and 200 mA. Cross-sectional scanning electron microscopy (SEM) images of PVA−Nafion films were recorded using a Hitachi SU8020 scanning electron microscope under vacuum. Samples were coated with a thin layer of gold (2−3 nm) before SEM imaging. Water contact angle measurements were performed using a

DSA-30 drop shape analysis system (Krüess, Hamburg, Germany) under ambient conditions. Water contact angles on the samples were measured at three different spots on each film within 1 s of contact with water droplets.

1.3. Welding Process of C-TA$_{0.15}$ Plastics: The C-TA$_{0.15}$ plastic sheet was cut into two halves with a blade. The ends of the two separate halves were then immersed into 1% C-TA$_{0.15}$ solution of DMAc/LiCl. Then, the ends of the two separate halves were overlapped and then compressed between two pieces of glass slides under a pressure of ca. 15 kPa. After standing for 30 min, these two halves of sheets were glued together, which were subsequently immersed into deionized water for another 10 min to remove the residual LiCl in the welded region. Finally, the glued sheets were compressed by two pieces of glass slides under a pressure of ca. 15 kPa for another ~4 h to obtain the welded C-TA$_{0.15}$ plastic.

1.4. Biocompatibility Tests: The LO2 (normal human hepatocytes) cell lines were purchased from the Institute of Basic Medical Sciences at the Chinese Academy of Medical Sciences. All cells were cultured in Dulbecco's modified Eagle's medium (DMEM) supplemented with 10% fetal bovine serum (FBS; Life Technology) at 37 °C in a humidified incubator with 5% CO_2. A cell counting kit-8 (CCK8, Dojindo Molecular Technologies) was used to investigate the cytotoxicity of the C-TA plastics, and Calcein-AM and propidium iodide (PI) co-staining were used to assess cell viability. The C-TA plastics were first cut into tiny pieces and sterilized by immersed in 75% (v/v) ethanol solution for 1 h, followed by washing with sterile PBS (pH 7.4) for 5 times to remove the residual ethanol. The resultant C-TA$_{0.15}$ plastics were added into DMEM for cell culture. The cells were grown in 24-well plates at a density of 1×10^4 cells per well in the presence of C-TA plastics and cellulose plastics for 2 and 7 days. Then, the cells were washed twice with cold PBS, resuspended in a live/dead double staining kit (Dojindo Molecular Technologies), and incubated at 37 °C for 15 min. The resultant cells were stained with green fluorescence of Calcein-AM (for live cells) and red fluorescence of PI (for dead cells), respectively, and observed under a Nikon confocal fluorescence microscope. The absorbance was measured by a microplate reader (BioTek Epoch) at 450 nm. All of the experiments were performed

in triplicate. Female Balb/c mice (18–20 g, Liaoning Changsheng Biotechnology) were used in this experiment. The C-$TA_{0.15}$ plastic sheets and cellulose plastic sheets were implanted into subcutaneous region of mice, denoted as experimental mice, and control mice, respectively. Before the implantation, C-$TA_{0.15}$ plastics and cellulose plastics were washed three times with autoclaved water, immersed in physiological saline solution for 3 days with daily buffer substitution, and autoclaved. The surgery was performed under isoflurane anesthesia. Specifically, a ~3 cm incision was made with a scalpel on the mouse skin, and a piece of respective plastic sheet (2.0 × 2.0 cm) was implanted. The organs were resected, followed with formalin-fixation for 3 days. For histological examination, the tissues were stained with hematoxylin and eosin (H&E) and evaluated by pathologists microscopically. All animal procedures were carried out in strict accordance with the National Institutes of Health Guide for the Care and Use of Laboratory Animals and were approved by the University Committee on the Use and Care of Animals of Jilin University of China.

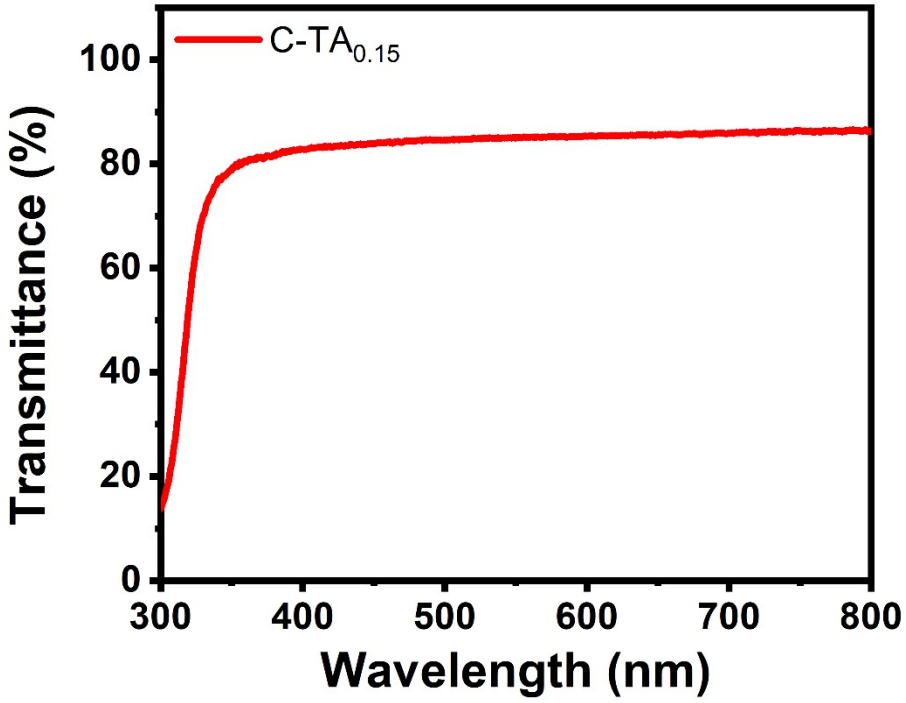

Figure S1. UV-vis transmission spectra of the C-$TA_{0.15}$ plastic sheet with a thickness of ~50 μm.

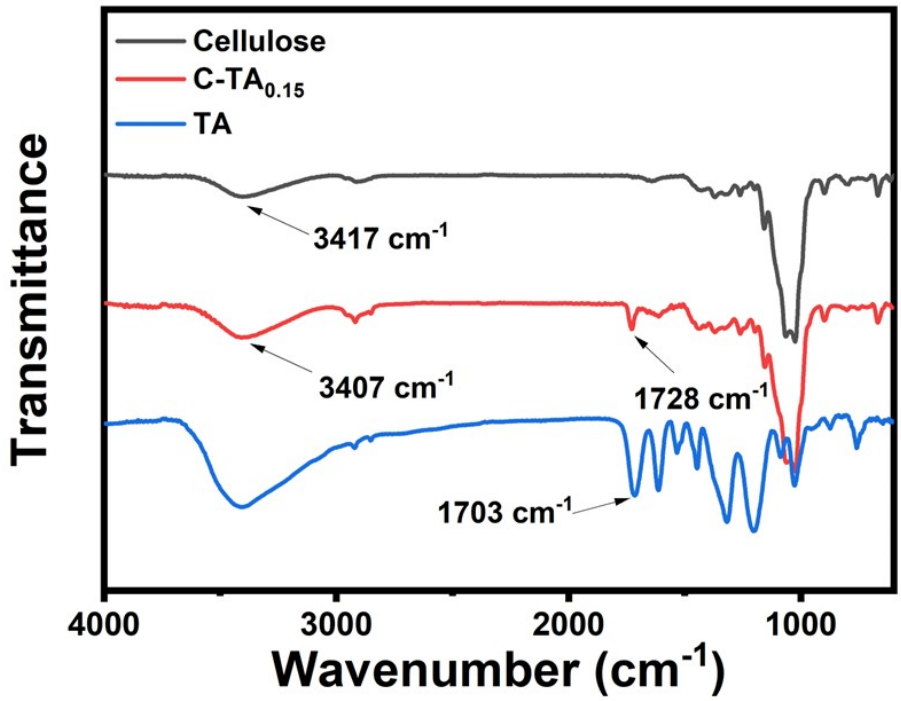

Figure S2. FT-IR spectra of cellulose plastic, TA, and C-$TA_{0.15}$ plastic.

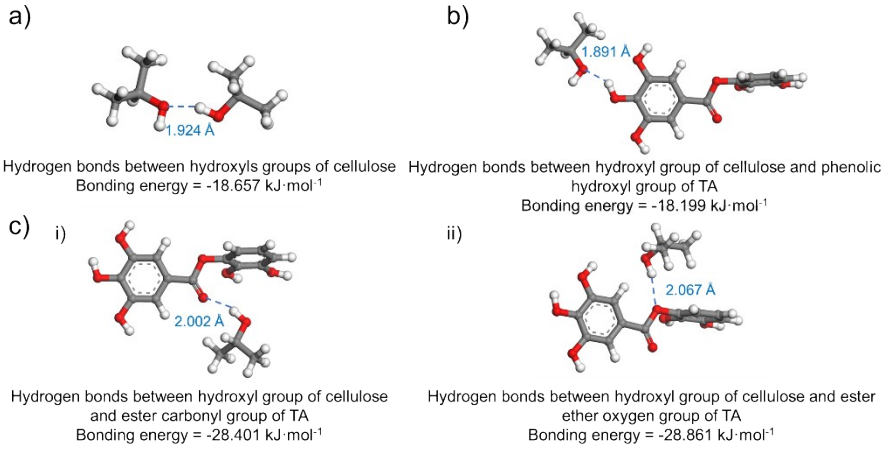

Figure S3. Binding energies and lengths of the hydrogen bonds in the C-TA plastic.

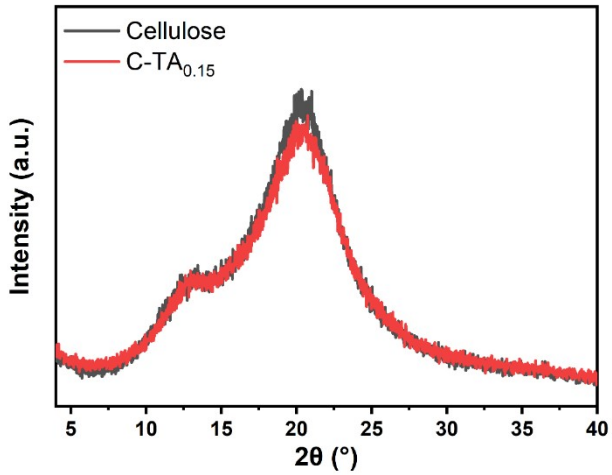

Figure S4. XRD patterns of the cellulose and C-$TA_{0.15}$ plastics.

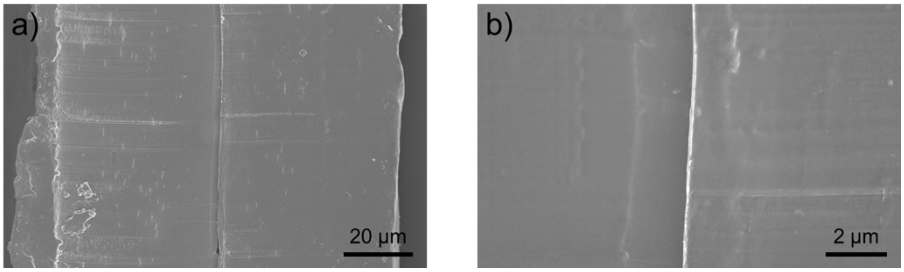

Figure S5. SEM analysis of overlapped interface.

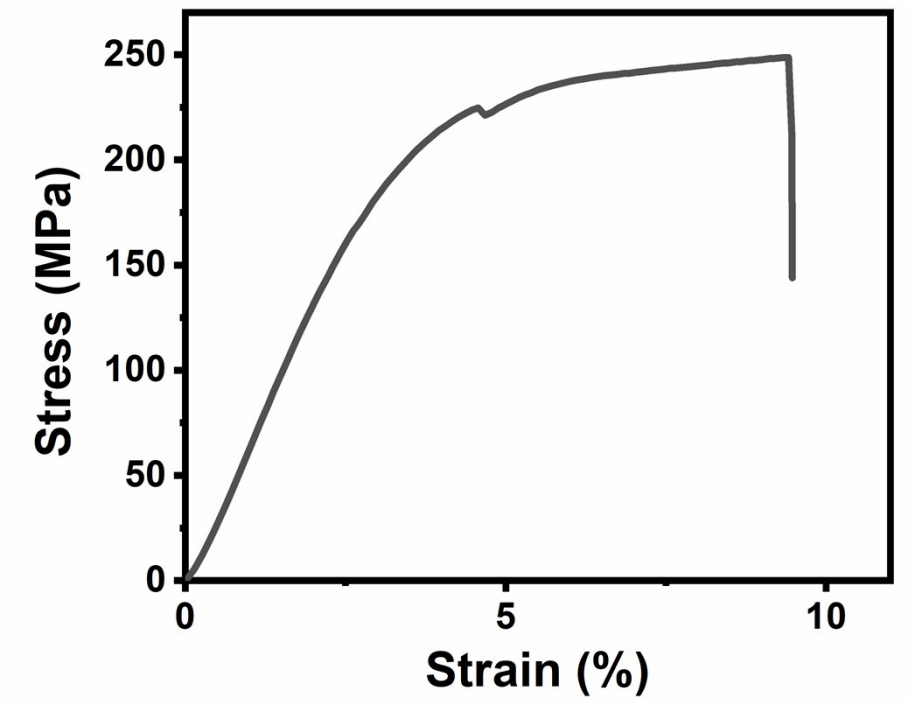

Figure S6. Stress-strain curve of the welded C-$TA_{0.15}$ plastic strip that was previously cut into two halves. The appearance of a sharp drop in the stress-strain curve of the

welded C-$TA_{0.15}$ plastic strip at a strain of ~5% can be attributed to the inevitably formed defects in the welded region. These defects weaken the integrity of the plastic and lead to stress concentration in the welded region, causing the observed decrease in stress during the stretching process.

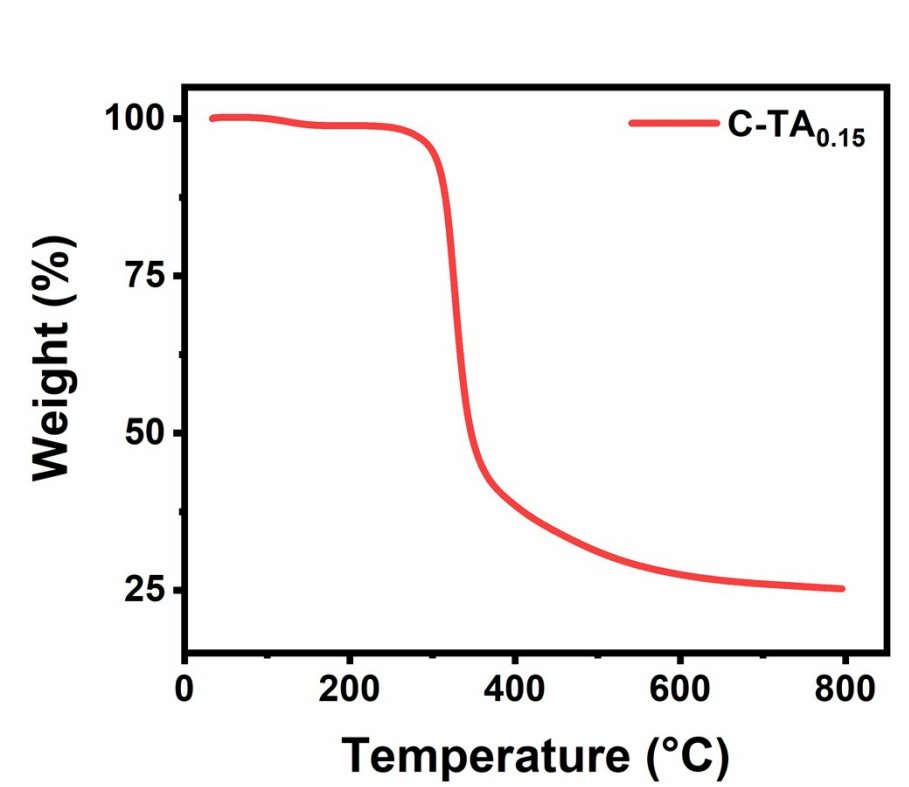

Figure S7. TGA curve of the C-$TA_{0.15}$ plastic.

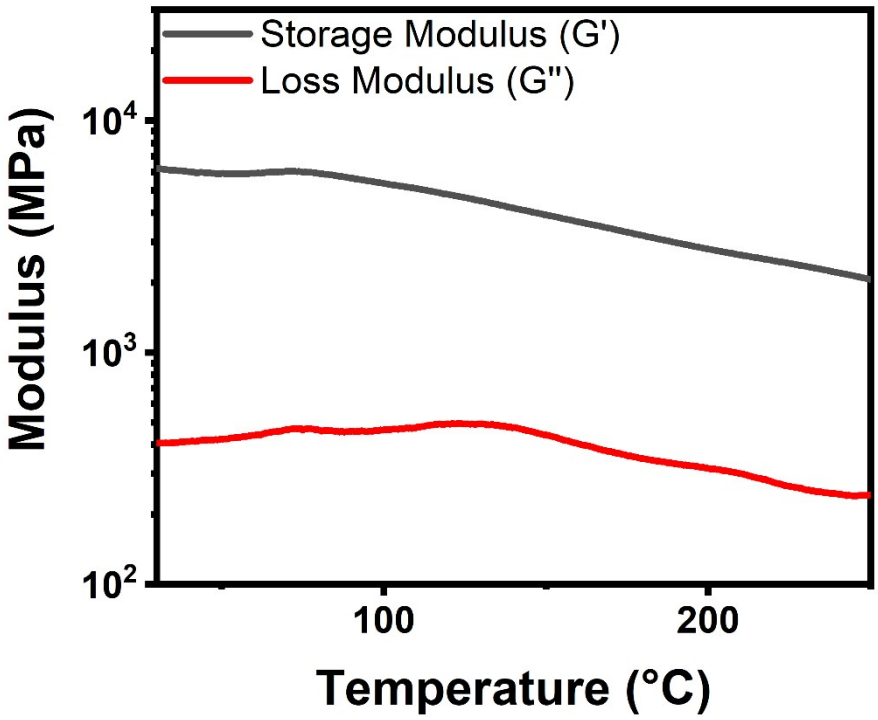

Figure S8. DMA curves of cellulose plastics. The storage modulus and loss modulus of the cellulose plastics show nearly constant in the temperature range of 25 to 100 °C. As the temperature increases, the storage modulus and the loss modulus slowly decrease in the temperature range of 100 to 250 °C. This result suggests the high thermal stability of the cellulose plastics.

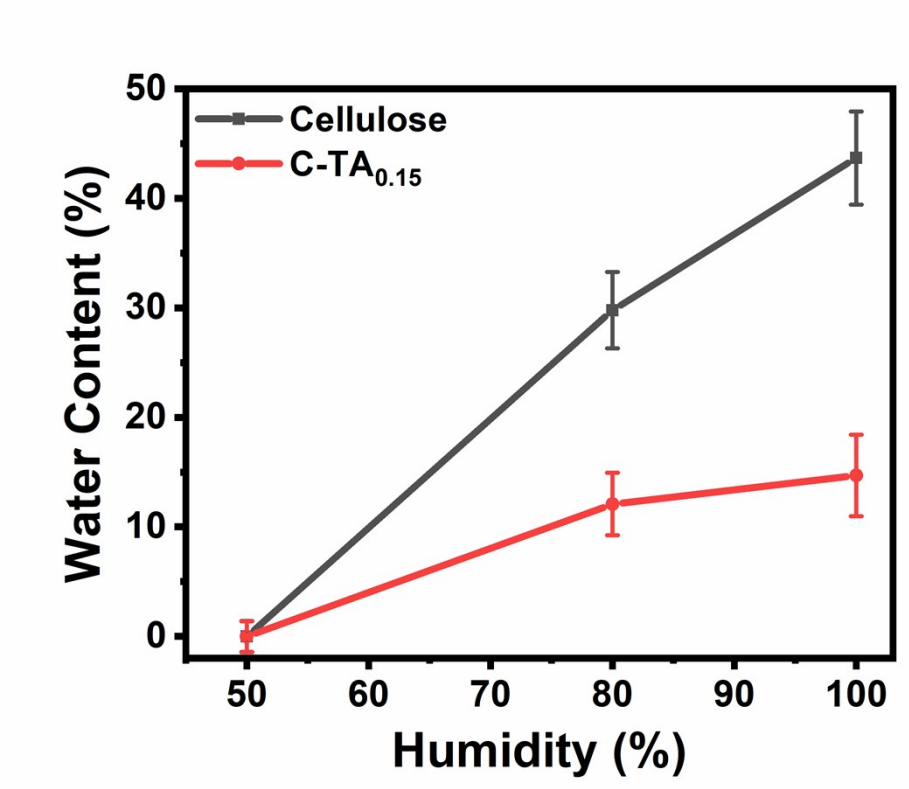

Figure S9. Water content of the cellulose and the C-$TA_{0.15}$ plastic. The water content of the cellulose and the C-$TA_{0.15}$ plastic were measured in a sealed box whose relative humidity (RH) was controlled with water and aqueous H_2SO_4 solutions of different concentrations. Aqueous H_2SO_4 solutions of 43.4 wt% (50% RH), 26.2 wt% (80% RH), and deionized water (100% RH) were used. The plastic samples were placed in the sealed box and equilibrated for two weeks to absorb water. The plastic sample was placed in the sealed box with a fixed RH and equilibrated for two weeks and its mass was measured and referred as m_0. After drying the sample in a vacuum oven at 50 °C for 2 days, the mass of samples was referred as m_1. The water content (C_{water}) of the plastics was calculated by the following equation:

$$c_{water} = \frac{m_0 - m_1}{m_0}$$

Table S1. Fracture strength, Young's modulus, strain at break, and toughness of cellulose and various C-TA_x plastics.

Sample	Fracture strength (MPa)	Young's modulus (GPa)	Strain at break (%)	Toughness ($MJ \cdot m^{-3}$)
C-$TA_{0.25}$	231±13	7.09±0.27	24.2±0.4	39.1±0.7
C-$TA_{0.15}$	265±17	7.64±0.38	31.9±4.8	55.2±3.9
C-$TA_{0.10}$	206±14	6.34±0.54	31.4±2.2	43.8±8.8
Cellulose	196±2	6.24±0.36	23.4±0.9	31.9±0.7

Table S2. Fracture strength, Young's modulus, strain at break, and toughness of cellulose and C-$TA_{0.15}$ plastics measured at 80% and 100% RH.

Sample	Fracture strength (MPa)	Young's modulus (GPa)	Strain at break (%)	Toughness ($MJ \cdot m^{-3}$)
Cellulose 80% RH	99±11	4.62±0.71	10.0±0.4	7.23±0.59
Cellulose 100% RH	56±8	2.64±0.42	10.6±1.9	4.39±0.7
C-$TA_{0.15}$ 80% RH	166±14	6.67±0.50	18.7±3.0	21.8±1.0
C-$TA_{0.15}$ 100% RH	98±5	3.20±0.48	21.3±1.7	13.8±1.8