

Supplementary Information

Efficient Conversion of Poly (butylene adipate-co-terephthalate) into Covalent Adaptable networks via Chain Breaking-Crosslinking Strategy

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Methods and Materials

Materials. Poly (butyleneadipate-co-terephthalate) (PBAT) was purchased from Xinjiang Blue Ridge Tunhe Sci.&Tech. Co., Ltd. The antioxidant (Irganox 1010), dipentaerythritol (Di-PE, 90%), isophorone diisocyanate (IPDI, 99%), N, N-dimethylformamide (DMF), tetrahydrofuran (THF), toluene, chloroform, methanol, ethanol, DMF, and acetone were bought from Aladdin. PBAT pellets, Di-PE, Irganox 1010 were dried in vacuum oven at 60 °C for 12 h before use, and IPDI was used as received.

Preparation of PBAT-CANs. To avoid the impact of water, all materials (PBAT pellets, Di-PE, and Irganox 1010) were dried in a 60 °C vacuum oven for 12 h until the vacuum level did not change. As a representative example, 15 g of PBAT pellets, 0.06 g of Irganox 1010 and 0.45 g of Di-PE were mixed evenly in a plastic bag. Later, the mixture was added into a micro twin-screw extruder (SJZS-7A) bought from Wuhan Ruiming Co., Ltd through a hopper. Under nitrogen protection, the screw speed was set to 40 rpm and the four temperature ranges were set to 30, 150, 170 and 180 °C. After the mixture was completely added, it was subjected to cyclic extrusion for 5 min to get chain-breaking PBAT (B-PBAT) for testing. Adding 1.39 g of IPDI to the feeding port and cycling for 5 min to obtain PBAT-CANs. Before each use of the micro twin-screw extruder, it was cleaned with PBAT pellets for 3-4 times.

Characterization.

Gel content and Swelling Tests: The gel content of PBAT-CANs was characterized by Soxhlet extraction. About 0.1 g of sample was wrapped with filter paper. The THF was used as the extraction solution and reflux for 24 h. Later, the samples were dried at 60 °C for 24 h in a vacuum oven. The gel content was calculated by m_1/m_0 , where m_0 is the initial mass and m_1 is the final mass after drying. After soaking in ordinary solvents (tetrahydrofuran, toluene, chloroform, methanol, ethanol, DMF, acetone, and water) at 25 °C for 12 h, the solvent resistance was verified by observing the integrity of the sample and calculating the swelling ratio. The swelling ratio was calculated by m_1/m_0 , where m_0 is the initial mass and m_1 is the final mass after swelling.

Dynamic Thermomechanical Analysis (DMA) Measurement: Compression-molded PBAT-

CANs with dimensions of 100 mm (length) × 5 mm (width) × 0.2 mm (thickness) were measured on a Q800 DMA (TA Instruments, America) in a tension mode. A temperature swept from -50 to 180 °C was performed at a heating rate of 10 °C min⁻¹ and a frequency of 1 Hz. A force track of 125 %, an amplitude of 2 μm, and a preload force of 0.01 N were used. The storage modulus and loss modulus were recorded as a function of temperature. Stress relaxation test was conducted via the Q800 DMA using a stress relaxation mode. The samples were examined between 160 °C and 190 °C by applying a constant strain of 10%. Before the tests, all the samples were held at the test temperatures for 5 min to achieve thermal equilibrium and preloaded a 1×10^{-3} N force to prevent the samples from bending. Creep experiments were performed on the Q800 DMA. The samples were exposed to a constant stress of 1 MPa for 30 min at the test temperature, after which the tension was removed and a 30-min-recovery period was conducted. The strain of the sample was recorded throughout this process. Thermal Analysis: Thermogravimetric analysis (TGA) was examined on a Mettler-Toledo TGA/DSC1 thermogravimetric analyzer (METTLER TOLEDO, Switzerland) to evaluate the thermal stability. Each sample (around 5 mg) was heated from 50 to 800 °C at a heating rate of 20 °C min⁻¹ under nitrogen atmosphere.

Mechanical Property: The samples were compression-molded at 10 MPa and 170 °C for 5 min. The tensile properties of the PBAT-CANs were measured using an Instron 5567 Electric Universal Testing Machine (Instron, America) at room temperature. A gauge length of 20 cm, a preload force of 0.1 N, and a cross-head speed of 100 mm min⁻¹ was used. Each sample with dimensions of around 400 mm (length) × 5 mm (width) × 0.2 mm (thickness) was measured at least five times for accuracy.

Rheological Behavior: B-PBAT was hot pressed at 170 °C for 1 min using flat-panel vulcanizer XLB-D produced by Huzhou Shunli Machinery Co., Ltd. to prepare circular plates for rheological test. The rheological behavior of B-PBAT was examined using a Discovery HR-3 Rheometer (TA Instrument, America) operated with a 25 mm diameter parallel plate geometry. Frequency sweep experiments were performed at 190 °C with a strain of 1 %. The variations of the complex viscosity, storage modulus, and loss modulus were monitored as a function of frequency.

Fourier transform infrared characterization: The B-PBAT samples were first dissolved in THF

and then precipitated in water to wash away free polyols, and dried in a vacuum oven at 80 °C for 24 h. Infrared spectroscopy (FTIR-ATR) was recorded on an Agilent Micro-FTIR Cary660 with a scanning range of 4000-400 cm^{-1} and 32 scans.

Processability: The processability of the PBAT-CANs was verified by extrusion twice in micro twin-screw extruder. Under nitrogen protection, the screw speed was set to 40 rpm and the four temperature ranges were set to 30, 150, 170 and 180 °C. Compression molding was performed on a flat-panel vulcanizer XLB-D produced by Huzhou Shunli Machinery Co., Ltd. The extruded sample was compression-molded at 10 MPa and 170 °C for 2 min.

Degradation testing: Degradation experiment of PBAT-CANs: Firstly, PBAT-CANs film with a thickness of 0.2 mm was prepared by molding. Then, it was cut into a size of 25 mm \times 15 mm \times 0.2 mm. PBAT was hydrolyzed in deionized water at 23 °C, phosphate buffered saline solution (PBS, pH=7.40) at 37 °C, and 0.1mg/mL CALB/PBS solution at 37 °C. The solution is updated every seven days and the weight of the sample is measured accordingly. After 28 days, the degradation solution was dried by rotary evaporation and characterized by nuclear magnetic resonance (^1H NMR) spectroscopy using deuterated chloroform as the solvent. The surface morphology of degraded samples was observed by Thermo Scientific Verios G4 UC Scanning electron microscope (SEM, USA). Before observation, all samples are sprayed with a layer of gold to ensure conductivity.

Gas barrier testing: Based on GB/T 1038-2000, the gas barrier performance of PBAT-CANs against O_2 and CO_2 was evaluated on a Labthink VAC-V2 gas permeability tester (China) at 23 °C and 50 % humidity. The testing range was 0.05 ~ 50,000 $\text{cm}^3/\text{m}^2 \cdot 24 \text{ h} \cdot 0.1 \text{ MPa}$.

Supplementary Figures

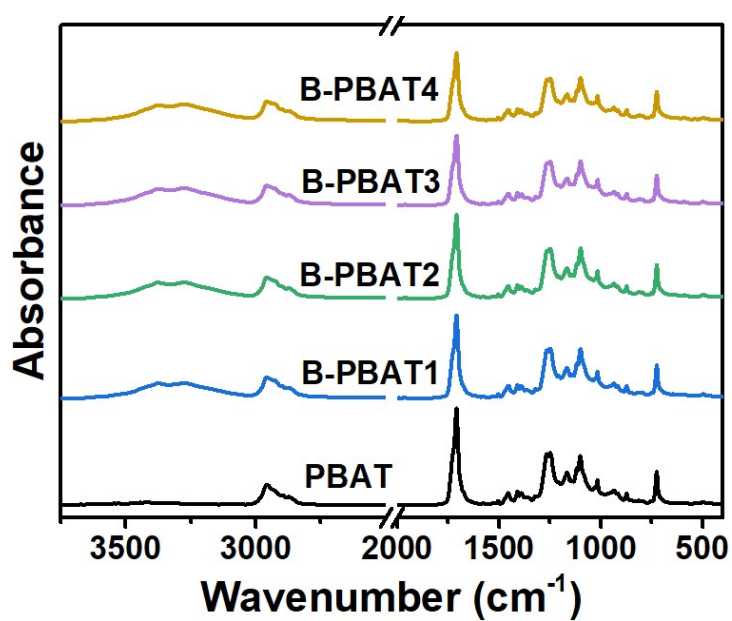


Figure S1. FTIR spectra of B-PBAT.

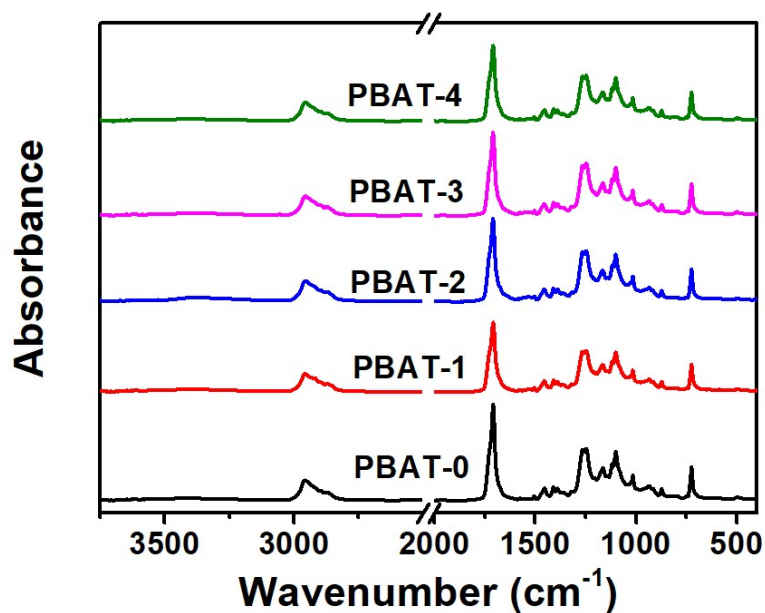


Figure S2. FTIR spectra of PBAT-CANs.

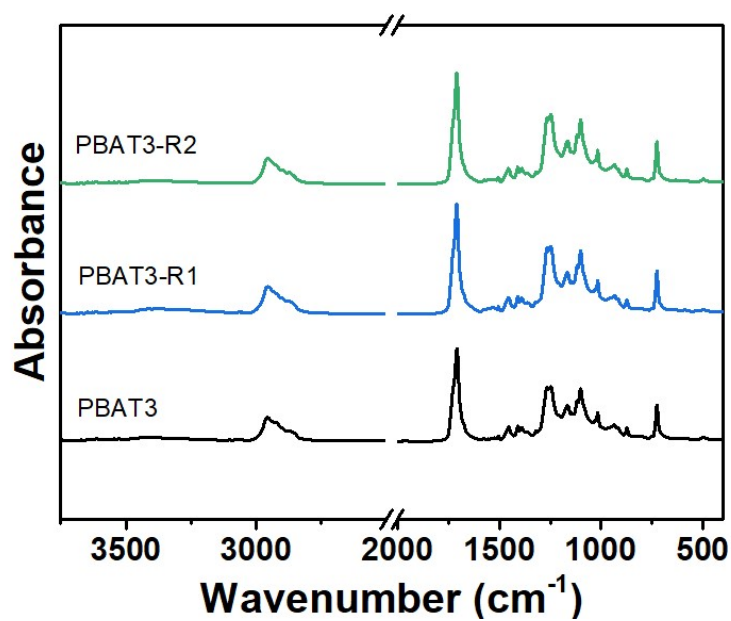


Figure S3. FTIR spectra of PBAT3 after one or two extrusion and hot-press recycling cycles.

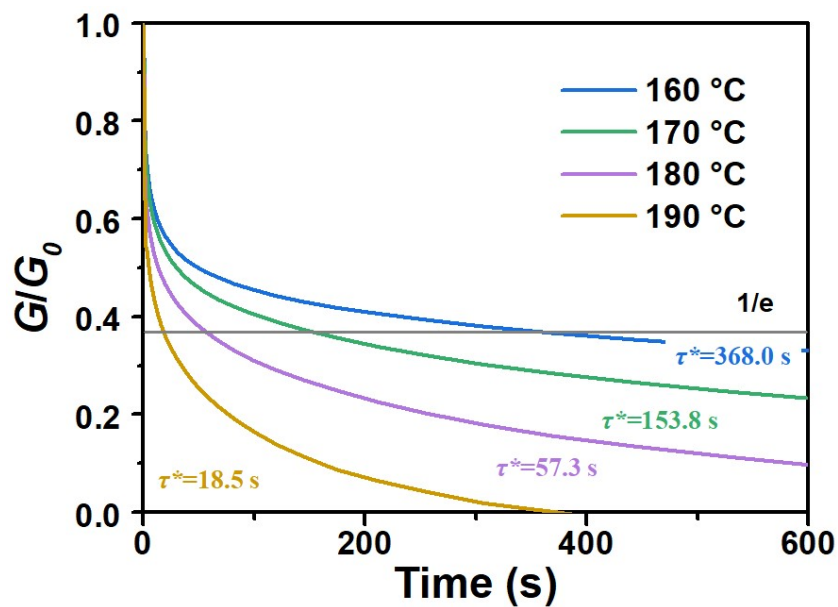


Figure S4. Stress relaxation curves of PBAT4.

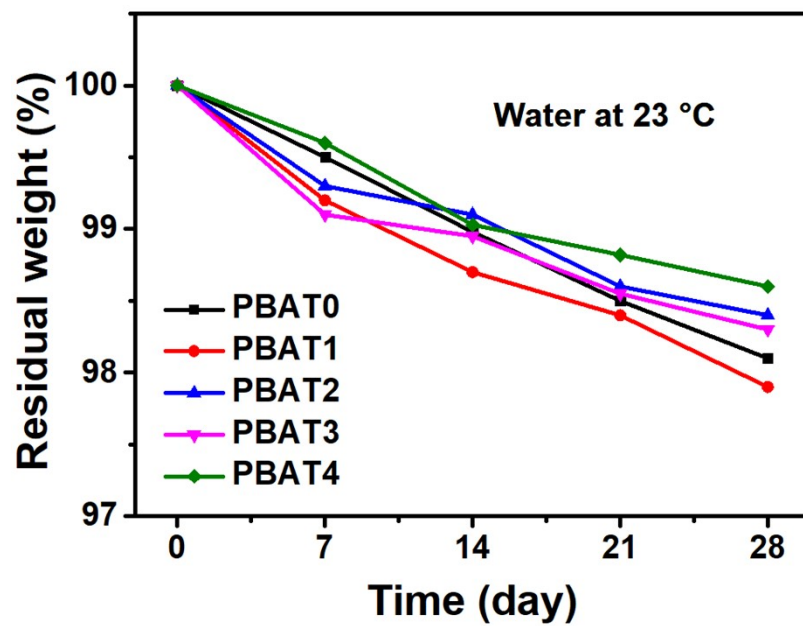


Figure S5. Residual weight curves of PBAT and PBAT-CANs hydrolysis in water.

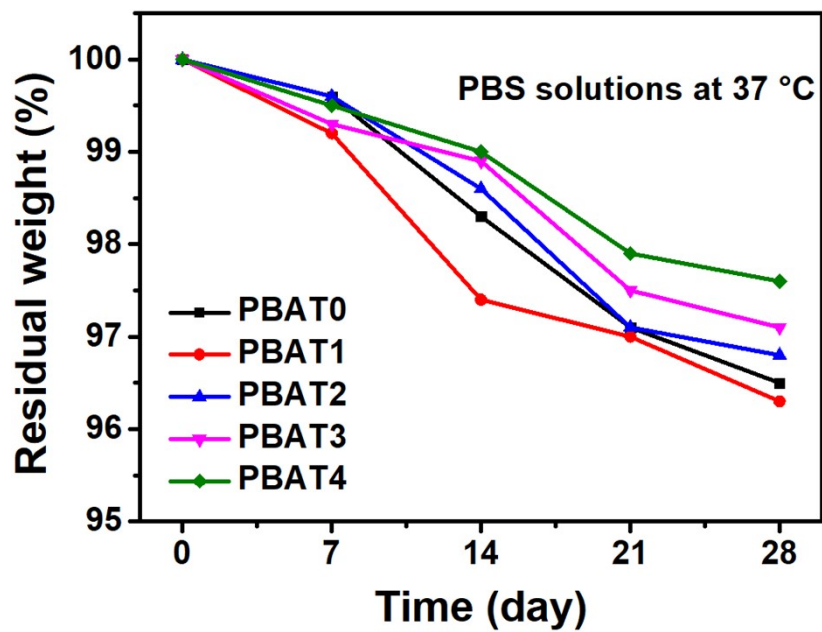


Figure S6. Residual weight curves of PBAT and PBAT-CANs hydrolysis in PBS solvent.

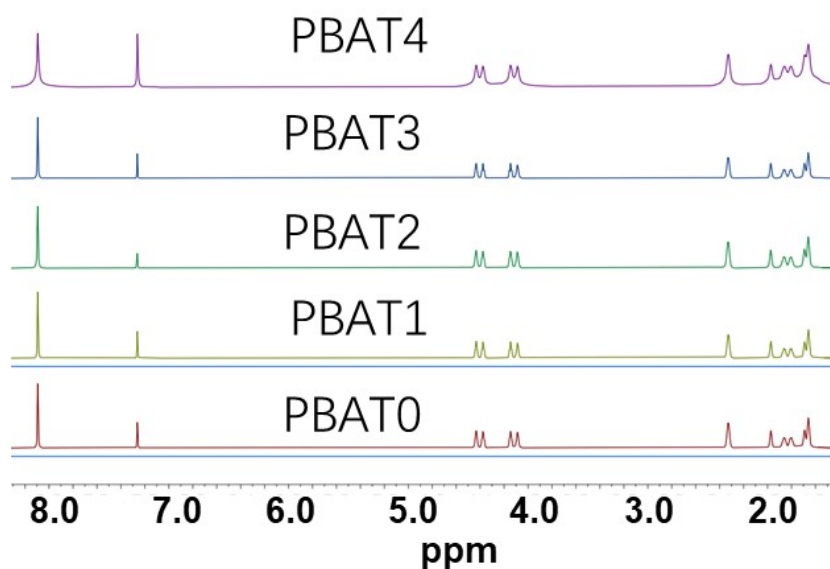


Figure S7. ¹H NMR spectra of PBAT and PBAT-CANs degradation solution after 28 days of hydrolysis in water.

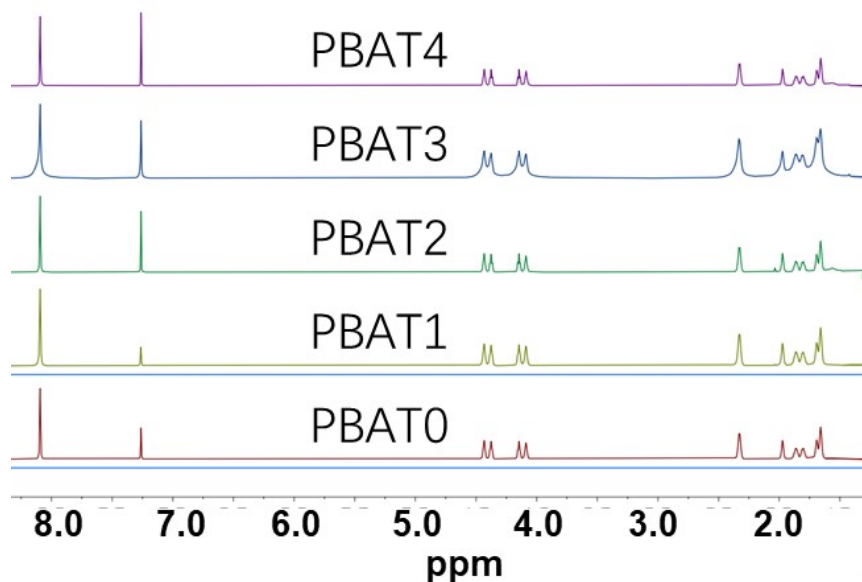


Figure S8. ¹H NMR spectra of PBAT and PBAT-CANs degradation solution after 28 days of hydrolysis in PBS solvent.

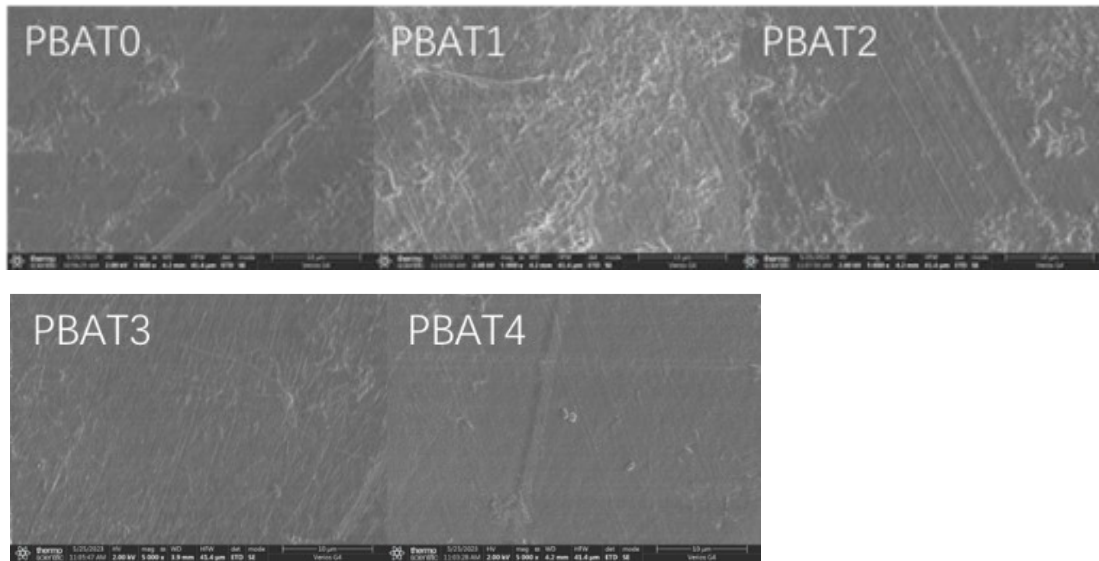


Figure S9. SEM photos of PBAT and PBAT-CANs after 28 days of hydrolysis in water.

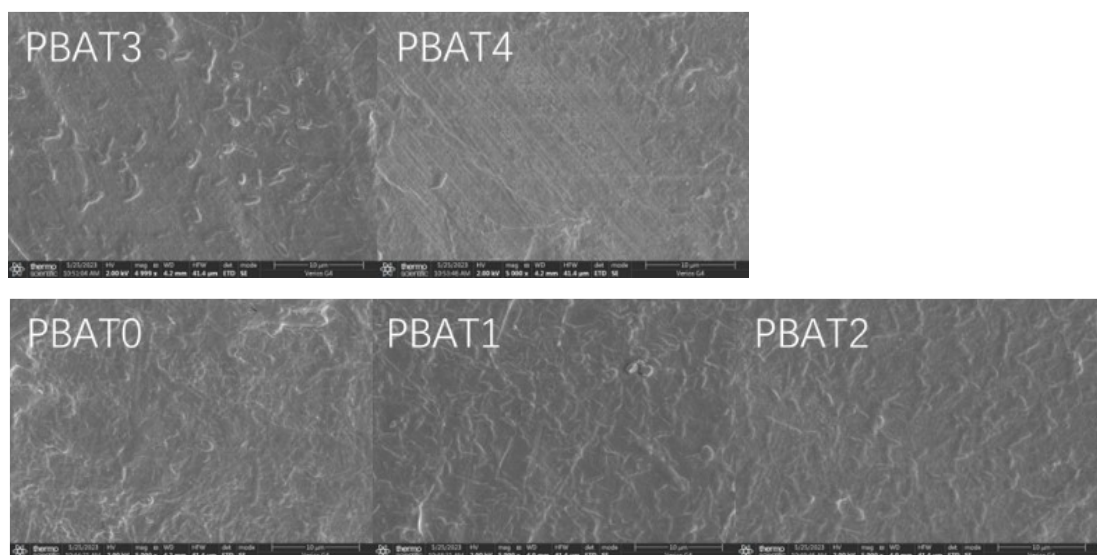


Figure S10. SEM photos of PBAT and PBAT-CANs after 28 days of hydrolysis in PBS solvent.

Supplementary Table

Table S1 Mechanical properties of reprocessed PBAT-3

Sample	E (MPa)	σ_m (MPa)	ϵ_b (%)
PBAT3-R1	93±8	30.9±6.5	932±46
PBAT3-R2	93±5	29.8±5.5	905±30

