Supporting Information

Lignin-based Adaptable Covalently Cross-linked Fabric for Flexible Sensors

Xiaozhen Ma[a,b], Xiaolin Wang[b], Honglong Zhao[a,b], Minghui Cui[b], Xiaobo Xu[b], Fangfang Kong[a,b], Peng Chen[b,*], Ning Yan[c,*], Jin Zhu[b], Jing Chen[b,*]

[a] University of Chinese Academy of Sciences, Beijing 100049, P. R. China.
[b] Key Laboratory of Bio-Based Polymeric Materials Technology and Application of Zhejiang Province, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, P. R. China.
[c] Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, ON M5S 3E5, Canada.

*Corresponding contributor. E-mail: pchen@nimte.ac.cn; chenjing@nimte.ac.cn; ning.yan@utoronto.ca.

Experimental

Materials

The lignin (LIG-II) was procured form Shandong LongLi Biotechnology Co., Ltd., China, and used without any treatment. Polytetrahydrofuran glycol (PTMG 2000), Zinc chloride ($ZnCl_2$), dimethyl sulfoxide (DMSO), hexamethylene diisocyanate (HDI), deuterated chloroform, pyridine, cyclohexanol, and chromium (III) acetylacetonate were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd., China. 2-Chloro-4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaphospholane (TMDP, 95%) was purchased from Sigma-Aldrich. Ethanol, Trichloromethane (CH_3Cl), Acetone. Hydrochloric Acid (HCl), Sodium Hydroxide (NaOH), Tetrahydrofuran (THF), N,N-Dimethylformamide（DMF）were supported by Sinopharm Chemical Reagent Co., Ltd., China.

Preparation of lignin-based polyurethane fabric (LPUF).

Lignin-based polyurethane Zn^{2+} coordination elastomers (LPUE) were synthesized according to our previous study [ref]. After degradation in ethanol at 60 ℃ for 2h, the lignin-based polyurethane degradation suspension (LPUS) was obtained. By adjusting the viscosity through ethanol volatilization, and the addition of varying quantities of graphene, a spinning solution was obtained that was suitable for electrospinning. Finally, LPUF with different graphene contents were prepared under specific conditions: voltage of 20 kV, roller speed of 120 rad/min, roller-nozzle distance of 15 cm, and injection speed of 2 ml/h.

Characterization

For quantifying the hydroxyl value of lignin, quantitative ^{31}P nuclear magnetic resonance (^{31}P NMR) spectrum was carried on a Bruker Avance III spectrometer at 400 MHz instrument (AVANCE III 400MHz, Bruker, Switzerland), using 500 μL of deuterated chloroform and anhydrous pyridine (1:1.6, v/v) as the solvent, 10 mg cyclohexanol as the internal standard, 100 μL of chromium (III) acetylacetonate solution (5.0 mg/mL in deuterated chloroform and anhydrous pyridine) as the relaxation reagent, 70 μL of (2-chloro-4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaphospholane) (TMDP) as the phosphitylation agent. Fourier transform infrared (FT-IR) spectra were performed on a Micro-FTIR Cary 660 spectrometer (Cary660+620, Agilent, America). Mechanical properties were recorded using a universal mechanical testing machine (Z1.0, Zwick Instrument, Germany). The samples, using strip splines with dimensions of 30 mm (length) × 10 mm (width) × 0.1 mm (thickness), were measured at a speed of 20 mm/min. The cyclic tensile test used a strip splines with dimensions of 30 mm (length) × 10 mm (width) × 0.1 mm (thickness), with a tensile rate of 10mm/min and a strain of 30%, and 20 times. The elastomer sample, using dumbbell splines with dimensions of 30 mm (length) × 2 mm (width) × 0.5 mm (thickness), was measured at a speed of 20 mm/min. And each sample was tested in five replicates. All samples were cut into blocks of 30mm ×20 mm, and were then placed in a glass bottle to be submerged for 72 hours. Light microscopy (BX51, OLYMPUS, Japan) was used to observe the dispersion of graphene in lignin-based polyurethane degradation suspension. The electrochemical workstation (chi660e, CH Instruments, China) was used to monitor the change of electrical signal during LPUF deformation, and it was used in conjunction with the universal mechanical testing machine to measure the value change of LPUF resistance with stress or deformation. The electrical signal was tested by the electrochemical workstation (chi660e, CH Instruments, China), using 2-wire mode, current-time curve (I-t) test method. Then, the sample was connected to the circuit as part of the circuit. And the relative current with time variation curve (voltage 1V) was obtained by stretching to make a change of resistance.

Table S1. Mechanical properties of LPUE and LPUF

	Strength (MPa)	**Elongation at break (%)**	**Toughness (MJ/m^3)**
LPUE	30.3±3.2	863±33	130±2.3
LPUF-0	29.1±1.6	653±67	103±3.8
LPUF-1	18.4±3.5	520±21	84±2.4
LPUF-5	13.9±4.1	576±38	53±4.3
LPUF-10	10.1±2.8	202±13	13±2.6
LPUF-20	2.8±0.4	64±6	4±0.9

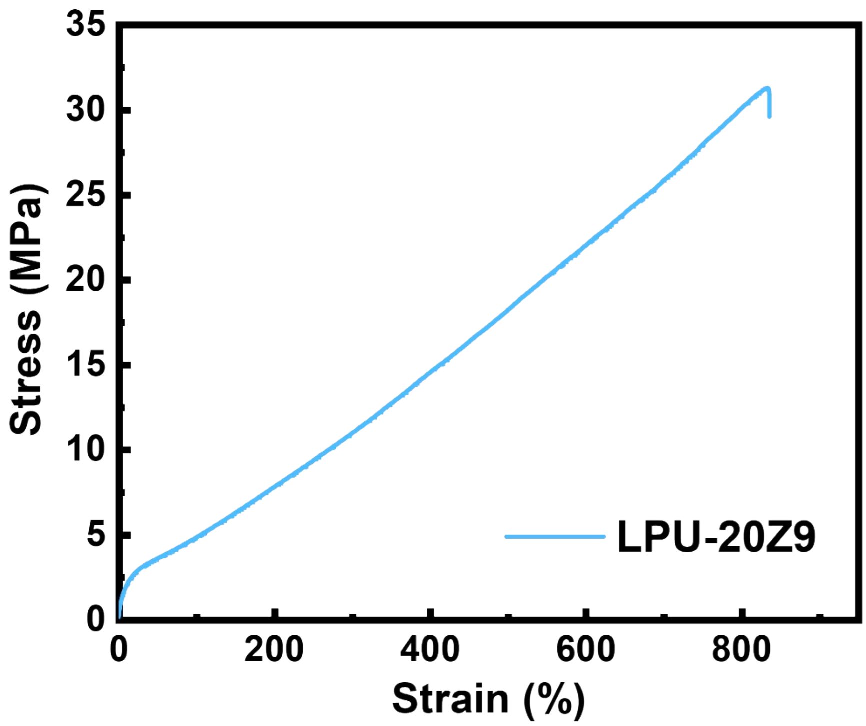

Figure S1. Representative stress-strain curves of LPUE.

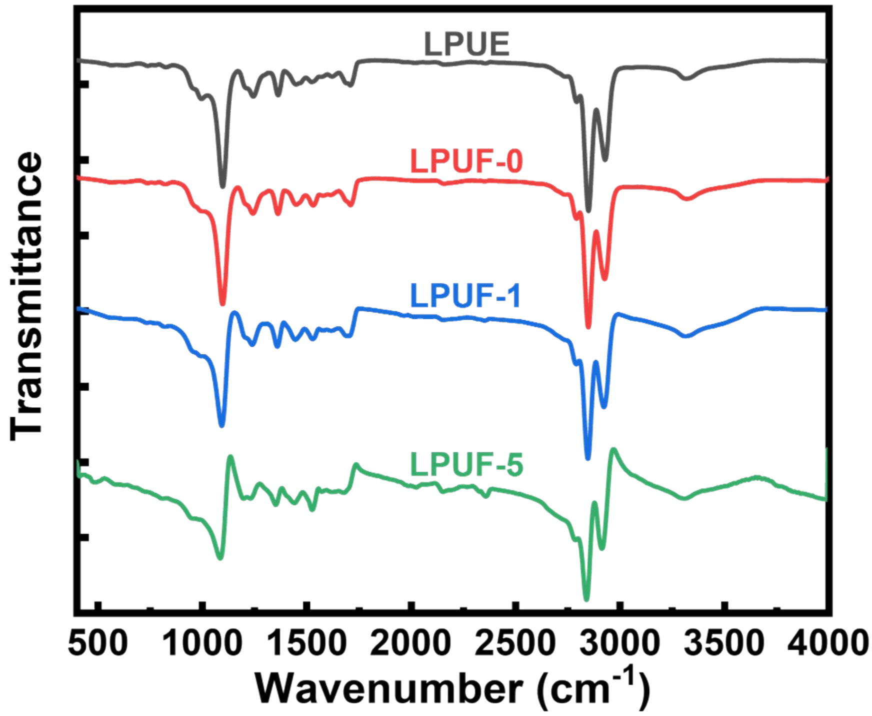

Figure S2. FTIR spectra of the LPUE and LPUF.

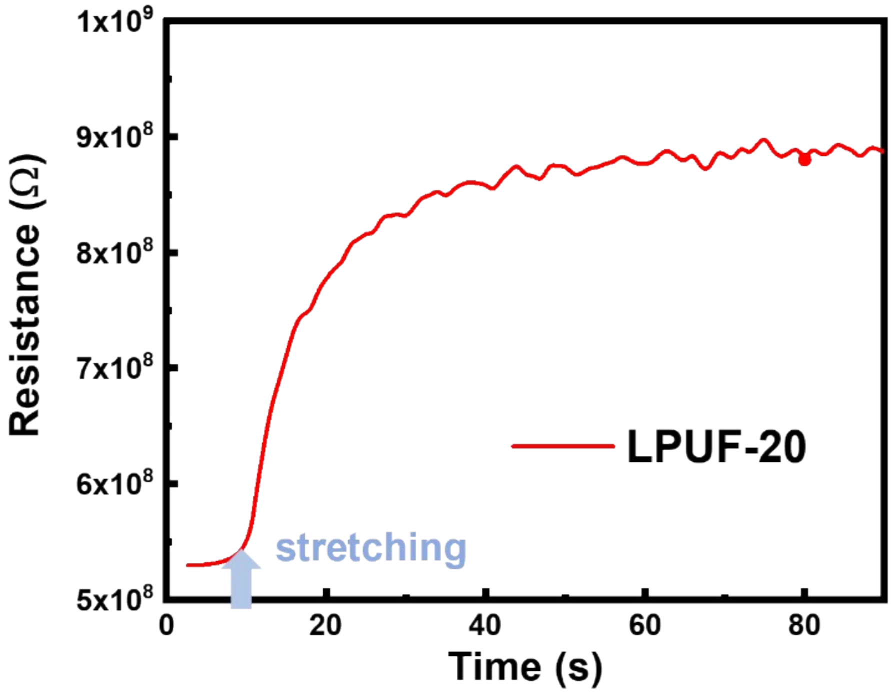

Figure S3. LPUF-20 resistance curve during the test.

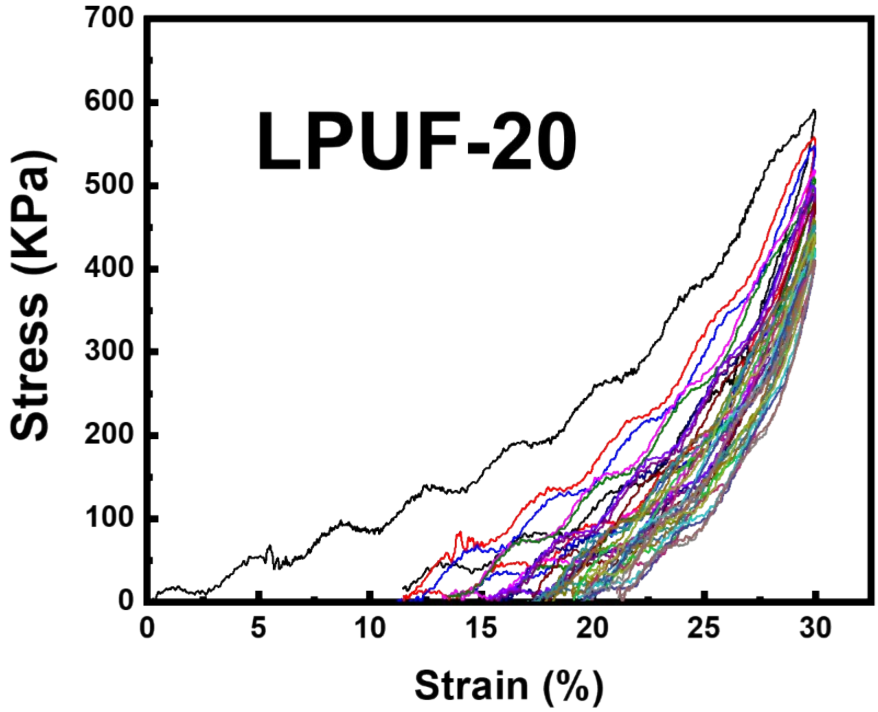

Figure S4. Cyclic stress-strain curve of LPUF-20

$$R = \frac{\Delta R/R_0}{\varepsilon} \quad \text{(EQ S1)}$$

$$S = \frac{\Delta R/R_0}{\sigma} \quad \text{(EQ S2)}$$

Where ΔR represents the change in resistance, R_0 is the original resistance, ε denotes deformation, and σ (MPa) signifies stress.

Table S2. The comparison data of maximal GF value. (Sort from highest to lowest)

References	Maximal GF value
Rf 28	2.24
Rf 31	3.93
This work	4.87
Rf 27	6.25
Rf 30	6.67