

Supporting Information

An Unparalleled H-bonding and Ion-bonding Crosslinked Waterborne Polyurethane with Super Toughness and Unprecedented Fracture Energy

Yuan Yao, Bo Liu, Ziyang Xu, Jianhai Yang and Wenguang Liu**

Y. Yao, Prof. J. Yang, Prof. W. Liu.
School of Materials Science and Engineering
Tianjin Key Laboratory of Composite and Functional Materials
Tianjin University
Tianjin 300350, China
E-mail: jianhaiyang@tju.edu.cn; wgliu@tju.edu.cn

Table of Contents

Experimental Section

Supporting Figures

Supporting Tables

Supporting Movie

Supporting References

Experimental Section

Materials

Glycinamide hydrochloride (98%), acryloyl chloride (98%) and diethanolamine (99%, DEA) were supplied from Tokyo Chemical Industry Co. Ltd (Shanghai, China). Poly(ϵ -caprolactone) diol (PCL, $M_n = 2000 \text{ g mol}^{-1}$) and dimethylol propionic acid (DMPA, 97%) were purchased from Heowns Biochem Technologies Co. Ltd (Tianjin, China). Isophorone diisocyanate (99%, IPDI), dibutyltin dilaurate (DBTDL, 95%) and triethylamine (TEA, 99.5%) were purchased from Sigma-Aldrich (Shanghai, China). N,N-bis(2-hydroxyethyl)-3-amino propionyl glycinamide (OH-NAGA-OH) was synthesized according to our previous work.^[1] All other chemicals and solvents are analytical reagents and used as received without further purification.

Preparation of waterborne polyurethane

PCL (3.0 g, 1.5 mmol) was heated at 120 °C in a 100 mL three-necked glass flask under vacuum and mechanically stirred for 2 h to remove water. An appropriate amount of IPDI and one drop catalyst DBTDL were added into the melted PCL at 70 °C under a nitrogen atmosphere and further stirred for 3 h. Then the reaction mixture was cooled to 50 °C, and a stoichiometric amount of DMPA (0.2 g) dispersed in 1 mL acetone was added and further reacted for another 3 h at 70 °C. Moreover, a certain amount of chain extender OH-NAGA-OH in acetone (5 mL) were fed into the prepolymer solution and stirred at 50 °C for another 3 h until the chain extension reaction was completed. After that, triethylamine (0.2 mL) was added to neutralize the ionic centers of DMPA for 12 h, and the polymer was dispersed in deionized water under vigorous stirring (1200 rpm) for 30 min to obtain a semitransparent waterborne polyurethane emulsion with a solid content of about 20 wt%. The -NCO/-OH was fixed at 1.2. The polymers are denoted as WPU_x, whereas x means the molar ratio of OH-NAGA-OH to PCL. The polyurethane films were prepared by the solvent casting method on the clean polyethylene plates and then dried for 48 h to remove water.

Characterizations

The chemical structures of WPU were characterized by a nuclear magnetic resonance (NMR) spectrometer (AVANCE III, 400 MHz, Bruker, Germany) using CDCl_3 as the solvent, and an attenuated total reflection Fourier transform infrared spectrometer (ATR-FTIR, Nicolet 6700, Thermo Scientific, USA), respectively, and the splits of stretching vibration C=O bands in FTIR spectra of WPU were obtained by peak separation method. Variable temperature infrared (VT-IR) spectra were recorded on a Nicolet Magna iS50 spectrometer (Thermo Scientific, USA) over a temperature range from 30 to 120 °C to detect the dynamic reversibility of H-bonds in polyurethane. The molecular weight and molecular weight distribution of WPU were measured on a gel permeation chromatography (GPC, 1260 Infinity II, Agilent). The average particle size and zeta potential of WPU emulsions were recorded on a 90Plus PALS Zeta particle size analyzer (Brookhaven, USA). The morphology of WPU0 emulsion was characterized by a transmission electron microscope (TEM, JEM-2100, JEOL, Japan) at an accelerating voltage of 200.0 kV, and the crystal phases of WPU were analyzed via XRD (D8 Advanced, Bruker, Germany) using Cu K α radiation ($\lambda = 0.154$ nm) from 5° to 50°, with a scan speed of 4° min⁻¹.

The small-angle X-ray scattering (SAXS) measurement was recorded on a NanoSTAR system (Bruker, Germany). A film (10 mm × 5 mm × 1 mm) was first fixed on the clear aperture of the sample stage, and then exposed to capture images. The X-ray radiation wavelength was 1.54 Å, and the distance between the sample and detector was fixed at 1050 mm. In addition, the phase shift maps of WPU films were recorded on a CSPM5500A atomic force microscope (AFM, Being Nano-Instruments, China) with the tapping mode. Thermogravimetric analysis (TGA) was performed on a simultaneous thermal analyzer instrument (STA449F3, Netzsch, Germany), and each dry and weighed sample was heated from room temperature to 800 °C under N₂ atmosphere with a ramping rate of 20 °C min⁻¹. Differential scanning calorimetry (DSC) analysis was performed on a DSC instrument (200 F3, Netzsch, Germany) over a temperature range from -50 to 180 °C at a heating rate of 5 °C min⁻¹, and the test process was heated twice to eliminate heat history and remove the influence of other factors.

Mechanical Test

Mechanical tensile test was performed on an electromechanical dynamometer (Legend 2344, Instron, USA) at room temperature (25 °C) with a strain rate of 50 mm min⁻¹. Prior to the test, all the samples were cut into the dumbbell-shaped samples. At least three samples were analysed to obtain the average values. For fracture test, the notched and unnotched polyurethane films were tested with a strain rate of 3 mm min⁻¹, and the fracture energy was calculated from the Greensmith method.^[2] To evaluate the self-healing ability of WPU2 film, the samples were stained with methyl blue and cut completely in half in the air, and then two pudding samples were immediately spliced (not overlapped) and healed at 50 °C for a certain time. Finally, tensile tests with a strain rate of 50 mm min⁻¹ were performed on the healed samples. During the self-healing process, no solvents were added. The self-healing efficiency was calculated by the ratio of tensile strength of the pristine sample to that of healed sample

Dynamic Mechanical Analysis

The storage moduli and loss moduli of WPU films were measured on a dynamic mechanical analyzer (DMA, Q800, TA, USA). The samples were pulled at a dynamic strain of 0.1% and a constant frequency of 1 Hz in a temperature range from -80 to 90 °C with a heating rate of 5 °C min⁻¹.

Rheological Measurement

Rheological behaviors were investigated using a rheometer (MCR-302, Anton-Paar, Austria) with a 20 mm-diameter parallel steel plate. The disk-shaped WPU film with a thickness of 1 mm and diameter of 20 mm was pressed to the sandblasted parallel plate with a force of 5 N to avoid slippage. Temperature-sweep was performed on the sample from 25 to 180 °C (heating rate: 5 °C min⁻¹) at a strain amplitude of 1% (in the linear region) and a frequency of 1 Hz. Frequency sweeps were performed on the sample in a range of 0.1 to 100 Hz at different temperatures with a strain amplitude of 0.01%. Master curves of storage modulus G' and loss modulus G'' were obtained by time-temperature superposition shifts at a reference temperature of 50 °C. Based on the Arrhenius plot of temperature-dependent shift factors, apparent activation energy E_a was calculated from the slope of the curve. For shear rate sweep tests, shear viscosity

was recorded over a shear rate range of 0.01 to 1000 s⁻¹ at 140 °C. Cyclic temperature sweeps with an alternate alteration of 45 °C and 140 °C were performed at a fixed frequency (1Hz), and the measurement at each temperature was maintained for 100 s, and the retention time for each step was fixed at 400 s before test.

3D Printing of WPU

3D printing was carried out using a bio-architect 3D printer (Regenovo, China). A needle with an inner diameter of 0.4 mm was used as the printing nozzle, and the printing speed was 10 mm s⁻¹. The printhead temperature and the build platform temperature were set at 140 °C and 45 °C, respectively.

Electrospinning of WPU

WPU2 solution in CHCl₃/DMF (1:1 V/V) at a concentration of 10 mg mL⁻¹ was loaded into a plastic syringe and capped with a metal needle. The syringe was mounted onto a syringe pump, and a 13 kV positive voltage was applied to the needle tip. A thin metal rod was used as the collecting device, and a -2 kV voltage was applied. The rod was immersed in the molten PEG-800 at 90 °C. Then the PEG-coated rod was taken out and cooled down at room temperature. This process was repeated twice to form a thin PEG film on the rod. After electrospinning, the metal rod was soaked in water to dissolve the PEG layer. After being demolded, the electrospun tube was dried at room temperature. The distance between the needle tip and the collecting device ranged from 12 to 15 cm and the infusion rate was 0.8 mL h⁻¹. Nanofibers were continuously collected onto a rotating metal rod to obtain a WPU tube, and the tube morphology was observed on a scanning electron microscope (SU1510, HITACHI, Japan) after sputter coating with aurum for 30 s.

Supporting Figures

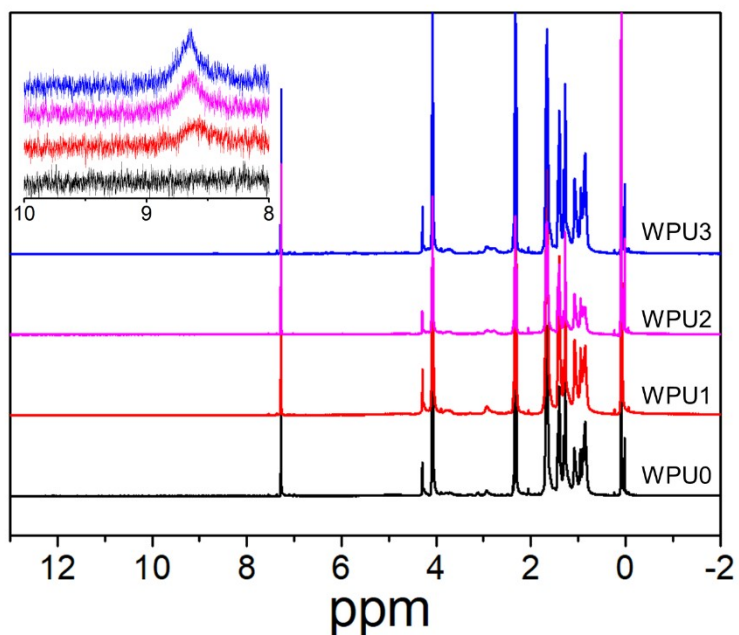


Figure S1. ¹H NMR spectra of WPU polymers in CDCl₃. The inset is an enlarged view of spectra ranging from 8 to 9 ppm. ¹H NMR spectrum of WPU (x=1, 2, 3) indicated that there were typical characteristic peaks of NAGA diol (8.66 ppm attributed to amide group), and PCL diol (1.29, 1.67, 2.33 and 4.10 ppm attributed to methylene).

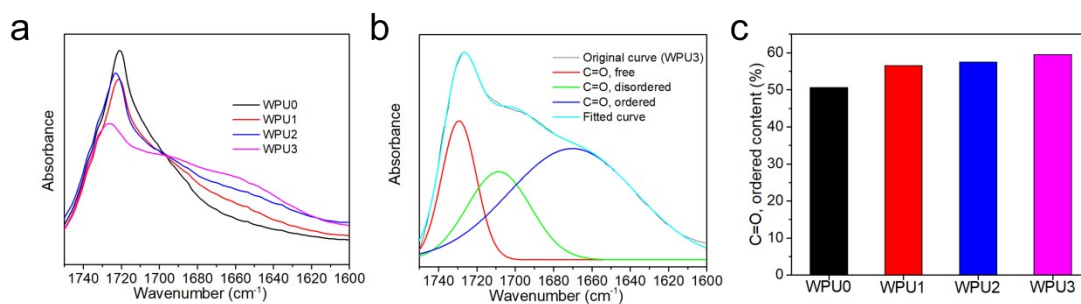


Figure S2. FTIR spectra of WPU films. a) FTIR Spectra of WPU in the range from 1600 to 1750 cm^{-1} . b) A split of stretching vibration C=O bands in the FTIR spectra of WPU3 via peak separation method. c) Proportion of ordered hydrogen bonded C=O bonds.

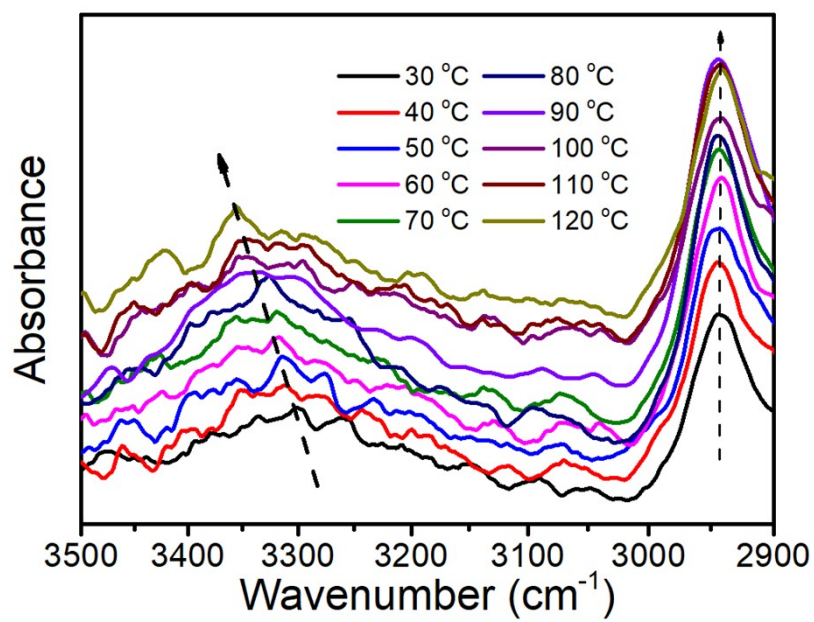


Figure S3. VT-FTIR spectra of WPU2 in a range from 30 to 120 °C.

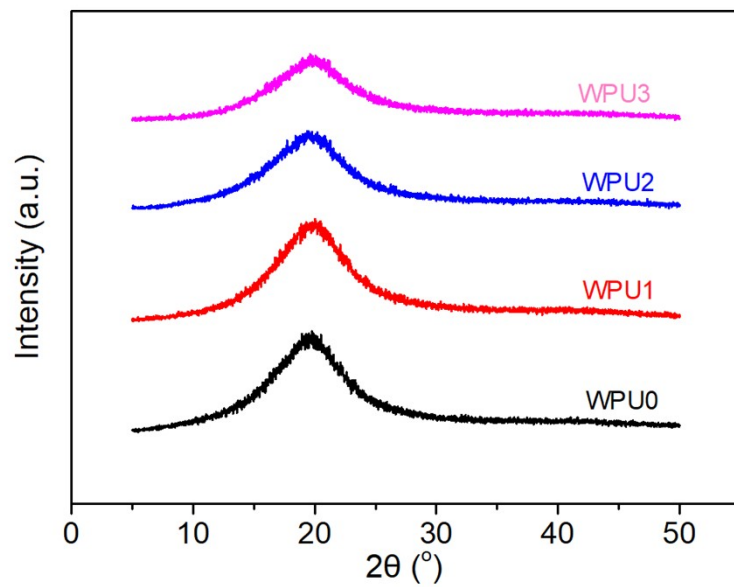


Figure S4. XRD patterns of WPUs



Figure S5. Digital photo of WPU2 film.

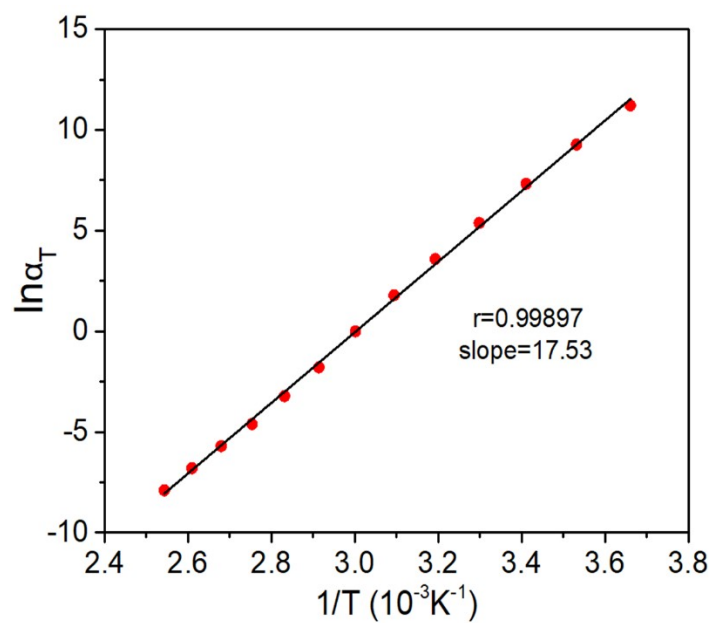


Figure S6. Arrhenius plot of the temperature-dependent shift factors α_T .

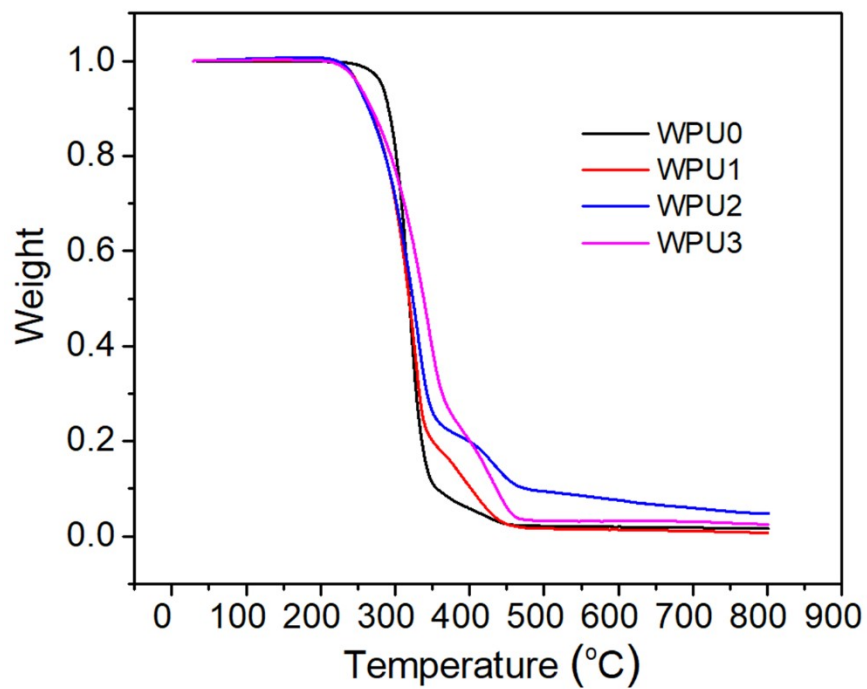


Figure S7. TGA curves of WPU.

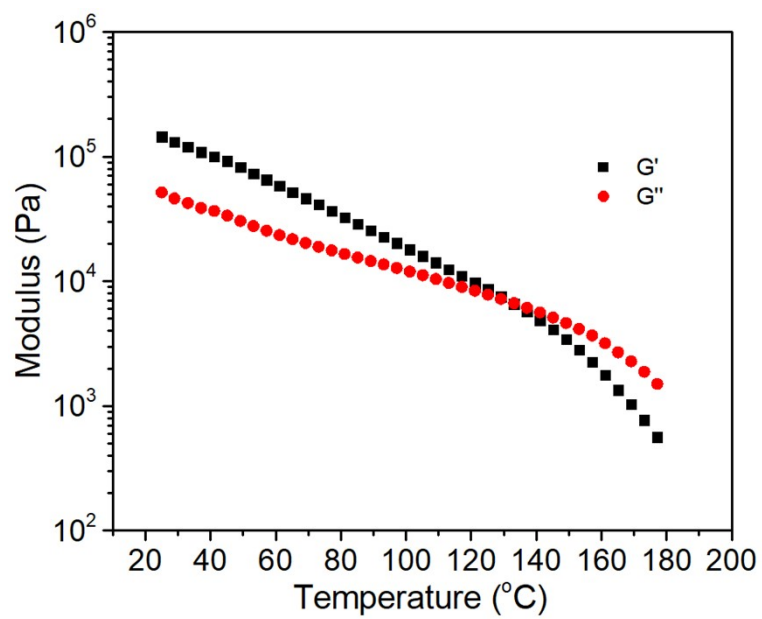


Figure S8. Storage shear modulus (G') and loss shear modulus (G'') of WPU2 at different temperatures.

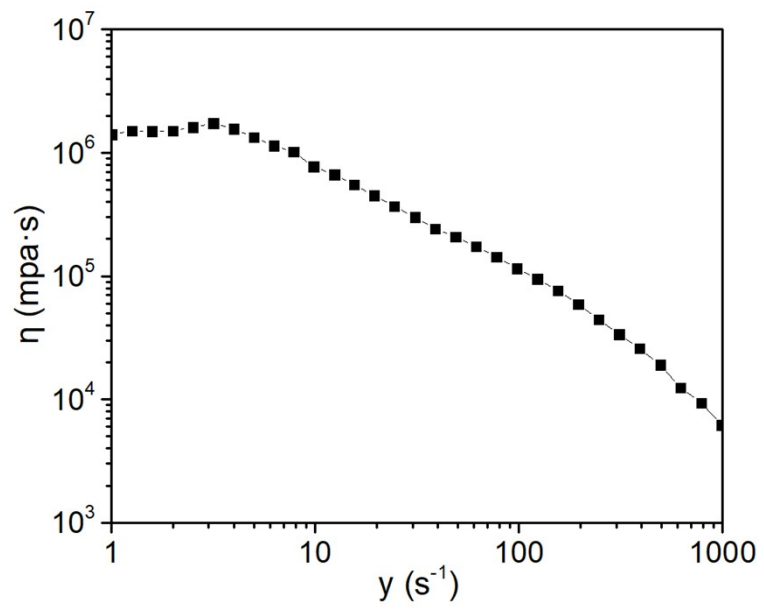


Figure S9. Viscosity of WPU2 in a shear rate sweep from 1 to 1000 s^{-1} at 140 °C.

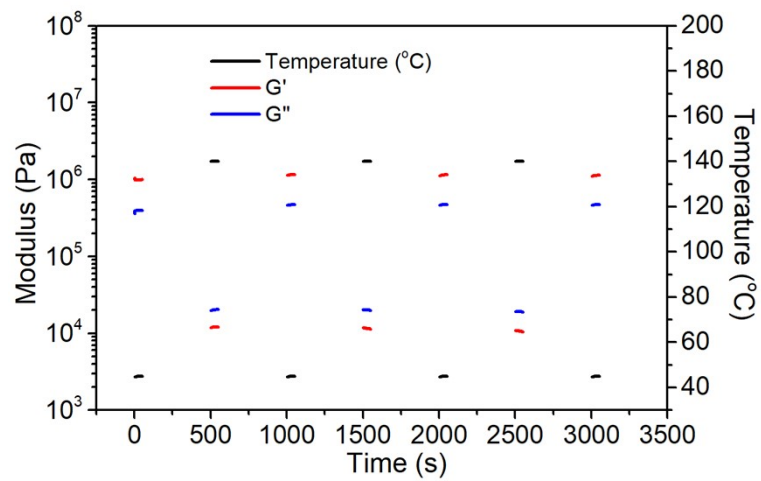


Figure S10. Cyclic temperature sweep curves of WPU2 with alternately being subjected to 45 °C and 145 °C variation.

Supporting Tables

Table S1. Particle size and Zeta potential of WPU emulsions.

Sample	Z-average size (nm)	PDI	Zeta potential (mV)
WPU0	36.4	0.164	-40.0
WPU1	45.1	0.160	-36.5
WPU2	72.4	0.128	-33.4
WPU3	158.3	0.128	-30.2

Table S2. Molecular weight and molecular distribution of WPU polymers.

Sample	Mn (g/mol)	Mw (g/mol)	PDI
WPU0	12200	19300	1.58
WPU1	7200	14900	2.05
WPU2	10300	23800	2.30
WPU3	16000	29600	1.85

Supporting Movie

Movie S1. Running water flows in the electrospun tube without occurrence of leakage.

Supporting References

- [1] Y. Yao, Z. Xu, B. Liu, M. Xiao, J. Yang, W. Liu, *Adv. Funct. Mater.* **2020**, *30*, 2006944.
- [2] H. W. Greensmith, *J. Appl. Polym. Sci.* **1963**, *7*, 993.