Supporting Information

A Facile Strategy for High Performance Recyclable Polymer Systems via Dynamic Metal Ionic Crosslinking

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Section 1. Synthesis and characterization of waterborne polyurethane vitrimer (WPU-V)

1. Materials

Polytetramethylene glycol (PTMG, Mn = 2000 g/mol, Mitsubishi Chemical Industries, Ltd., Japan) and 2,2-bis(hydroxymethyl)propanoic acid (DMPA, Shanghai Titan Scientific Co. Ltd., China) were dried under vacuum at 90 °C for 2 h before used. Isophorone diisocyanate (IPDI, 99.5 wt% purity, Aladdin Reagents Co., Ltd.), dibutyltin dilaurate (DBTDL, Chengdu Kelong Chemical Reagent Co. Ltd., China), N,N-dimethylformamide (DMF, Chengdu Kelong Chemical Reagent Co. Ltd., China), trimethylamine (TEA, Chengdu Kelong Chemical Reagent Co. Ltd., China), ethylenediamine (EDA, Chengdu Kelong Chemical Reagent Co. Ltd., China), zinc acetate (Zn(OAc)2, Adamas Reagent Co. Ltd., China), zinc methacrylate (Adamas Reagent Co. Ltd., China) and ammonia solution (Chengdu Kelong Chemical Reagent Co. Ltd., China) were used as received.

2. Synthesis of WPU emulsion

Dried PTMG (50 g, 0.025 mol) was added into three necks round bottom flask at 60 °C. Once PTMG melted, DMPA (21.46 g, 0.160 mol) and DMF (50 g) was added and stirred at 250 rpm. Subsequently IPDI (45.90 g, 0.206 mol) and DBTDL (0.05 g) was put and stirred for 20 min. Then the temperature was increased to 80 °C and the system was stirred for 3 h to obtain prepolymer. The standard N-dibutylamine back titration method was adopted to determine the endpoint of this procedure. After that, the temperature was decreased to 50 °C and screw speed was kept at 500 rpm. TEA (14.57 g) was added and stirred for 15 min to neutralize the carboxy groups on the backbone of prepolymer. The temperature was further decreased to 30 °C and kept constant in the following steps. Distilled water (240 g) was put under stirring at 500 rpm for 5 min to emulsify the prepolymer. After that, EDA (1.26 g, 0.021 mol) dissolved in distilled water (30 g) was added dropwise in 30 min for chain extension. Then the system was stirred for another 1 h to obtain transparent WPU emulsion.
Figure S2. Pristine WPU emulsion.

3. Crosslinking of WPU

Zn(OAc)$_2$ (14.625 g) was dissolved in ammonia solution (32.52 g) to obtain Zn(OAc)$_2$ solution. The mixture of Zn(OAc)$_2$, ammonia solution (1.84 g), distilled water (25 g) and WPU emulsion (25 g) was mixed and ultrasound-treated for 3 min (27840 Hz, 800 W). Pristine WPU emulsion without Zn(OAc)$_2$ ammonia solution was adopted as control group. Then the mixture was poured into polytetrafluoroethylene (PTFE) mold and evaporated at ambient temperature. Finally, the cured sample was vacuum dried at 120 °C to remove residual H$_2$O, DMF and acetic acid. The obtained crosslinked WPU via ionic interactions was marked as WPU-V (the Zn$^{2+}$/COOH 1:2 stoichiometry).

4. Structural characterization

The structure of WPU and WPU-v was investigated at ambient temperature (Figure S4) by FTIR spectrometer (Nicolet-560 infrared spectrophotometer, USA) fitted with an ATR cell. Temperature-dependent FTIR spectroscopy of WPU-V was performed on a Nicolet iS50 Fourier transform spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. The structural variation of WPU-V was explored by at 35 °C to 175 °C. The absorption peaks at 3323 cm$^{-1}$, 1699 cm$^{-1}$ and 954 cm$^{-1}$ are assigned to the O-H stretching vibration, C=O stretching vibration and O-H bending vibration of –COOH, respectively. The absorption peaks at 2945 cm$^{-1}$ and 2856 cm$^{-1}$ represents C-H stretching vibration. The absorption peaks at 1238 cm$^{-1}$ and 1107 cm$^{-1}$ are assigned to C-O-C asymmetrical stretching vibration and symmetrical stretching vibration, respectively. The peak at 1539 cm$^{-1}$ is assigned to amide II. The obvious difference appears from 1675 cm$^{-1}$ to 1596 cm$^{-1}$. The absorption peak at 1630 cm$^{-1}$ of WPU-V suggests the formation of COO-Zn interactions.

Figure S3. FTIR spectroscopy of pristine WPU and crosslinked WPU-V.
5. Solubility and Swelling characterization

The WPU sample (4 mm × 20 mm × 0.5 mm) and WPU-V sample (4 mm × 20 mm × 0.2 mm) were immersed in tetrahydrofuran (THF) (5 mL) at 60 °C for 10 h, respectively.

6. Thermal and thermo-mechanical characterization

Dynamic mechanical analyses (DMA) were performed on a DMA Q800 machine (TA instruments). Tensile conditions and Multi Frequency–Strain/Temperature Ramp mode were adopted at 1 Hz, 15 μm oscillation amplitude. The heating rate was set at 5 °C /min.
Thermal stability was measured by a thermal gravimetric analyzer (SDTQ600, USA) under nitrogen atmosphere. The thermal gravimetric profiles were recorded from room temperature to 800 °C at a heating rate of 10 °C/min.

Mechanical characterization

The tensile properties of PU were tested with a strain rate of 50 mm/min under universal testing machine Instron 5567. Dumbbell-shaped sample was adopted. Five specimens were examined for each sample.

Rheological Characterization

Stress relaxation behavior were investigated with the DMA machine under Strain Rate conditions. The strain was set at 1.5%.

Gel content tests

Weighted dried WPU-V samples (~0.5 g) sealed in filter paper were put in a Soxhlet extractor with tetrahydrofuran (THF) reflux for 10 h. Subsequently, samples were washed with fresh THF and dried in vacuum oven at 100 °C until the weight unchanged. The gel content was calculated as the weight ratio of WPU-V sample after and before extraction.

Ion bond exchange reaction of model compounds

The dynamic nature of ion bonds was demonstrated by exchange reaction of Zn(OAc)₂ and zinc methacrylate. The mixture of Zn(OAc)₂ and zinc methacrylate with 1:1 stoichiometry was prepared. The mixture was ground in silica mortar and heated at 125 °C.
for 5h. Then the product (0.2284g) was dissolved in THF (5 mg) and analyzed by high performance liquid chromatography (Essentia LC-16, Shimadzu Co. Ltd.). THF was chosen as eluent and ultraviolet with 300 nm wavelength was taken to detect the samples. The retention time was recorded to 15 min at ambient temperature. The compound with stronger polarity was preferentially eluted in the reversed phase column.

**Figure S8.** High efficiency liquid chromatography traces of the model compounds before (cyan) and after (magenta) exchange.

### 11. Recyclability of WPU-V

**Hot-press recyclability:** Crosslinked WPU-V fragments were pressed at 170 °C for 5 min. Then WPU-V was solidified under pressure at ambient temperature to gain recycled WPU-V samples.

**Solution recyclability:** WPU-V fragments (Figure S10a) were added into acetic acid at ambient temperature (Figure S10b). The exchange reaction between carboxylic zinc and acetic acid could endow the solubility of WPU-V in acetic acid. After 1 h, the WPU-V fragments were dissolved completely (Figure S10c). The obtained WPU-V/acetic acid was poured into PTFE mold to evaporate the acetic acid (Figure S10d). Finally, the recycled WPU-V was gained after the evaporation of acetic acid and exchange reaction of carboxylic zinc (Figure S10e). The recycled WPU-V vitrimer could be reclaimed by the same procedure.

**Figure S9.** Solution recycle process of WPU-V.
Section 2. Synthesis and characterization of crosslinked HDPE

1. Materials

High density polyethylene (HDPE, PE P4406C) was supplied by Sinopec Maoming Petrochemical Company, China. Zinc acetate anhydrous (Zn(OAc)$_2$) was purchased from Adams Reagent Co. Ltd., China. Maleic anhydride, ammonia solution and dicumyl peroxide were purchased from Chengdu Kelong Chemical Reagent Co. Ltd., China. All of the reagents were used as received.

2. Synthesis of crosslinked HDPE-V

The crosslinked HDPE-V was synthesized in Haake Rheomix 600 QC internal mixer by reactive processing. Firstly HDPE (43 g), dicumyl peroxide (0.02 g) and maleic anhydride (2.15 g) were added into internal mixer at 50rpm and 170 °C for 10 min. Subsequently Zn(OAc)$_2$ ammonia solution (6.49g, prepared by 14.625 g Zn(OAc)$_2$ dissolved in 32.52 g ammonia solution) was added stepwise and mixed at 50rpm and 170 °C for another 5 min. As a contrast, pristine HDPE and the mixture of HDPE (43 g), initiator dicumyl peroxide (0.02 g) and maleic anhydride (2.15 g) were mixed at same condition for 15 min, respectively.

3. Structural characterization

The structure of HDPE-V was investigated at ambient temperature by FTIR spectrometer (Nicolet-560 infrared spectrophotometer, USA) fitted with an ATR cell (Figure S11).

![Figure S10. FTIR spectroscopy of HDPE, HDPE-M and HDPE-V.](image)

4. Solubility and Swelling characterization

HDPE sample (0.2 g) was added in toluene (10 g) at 95 °C for 12 h and xylene (10 g) at 95 °C for 7 h and 125 °C for another 5 h, respectively. As Figure S12-13 shows, virgin HDPE can be dissolved in toluene and xylene completely. HDPE-M and HDPE-V were partially dissolved.
Figure S11. Solubility and swelling of HDPE, HDPE-M and HDPE-V in toluene at 95 °C.

Figure S12. Solubility and swelling of HDPE, HDPE-M and HDPE-V in xylene at 95 °C and 125 °C.
5. Gel content tests

Weighted dried HDPE samples (~0.5 g) sealed in filter paper were put in a Soxhlet extractor with toluene reflux for 24 h. Subsequently, samples were washed with fresh toluene and dried in vacuum oven at 120 °C until the weight unchanged. The gel content was calculated as the weight ratio of WPU-V sample after and before extraction.

6. Thermal and thermo-mechanical characterization

Dynamic mechanical analyses (DMA) were performed on tensile conditions and Multi Frequency–Strain/Temperature Ramp mode at 1 Hz, 10 μm oscillation amplitude. The heating rate was set at 10 °C/min.

![Figure S13. Thermo-mechanical characterization of HDPE-V.](image)

Thermal stability was measured by a thermal gravimetric analyzer (SDTQ600, USA) under a nitrogen atmosphere. The thermal gravimetric profiles were recorded from room temperature to 700 °C at a heating rate of 10 °C/min.

![Figure S14. TG and DTG curves of PU.](image)

7. Rheological Characterization

The creep behavior was investigated by DMA on tensile conditions and Strain Rate mode at 30 °C. The creep curves can be obtained by applying and removing a constant stress of 1MPa. The melt flow index (MFI) was tested in a melt flow indexer (KEMI-AP, Dongguan Kunlun Experiment Equipment Co. Ltd.). The outlet diameter of melt flow indexer is 2.095 mm. 10010 g weight was adopted to extrude the melt. The outflow melt during 10 min was collected and weighed. Six specimens was tested for HDPE-V and two for HDPE. The average MFI of HDPE was 1.66 g/10 min, while that of HDPE-V was 0.17 ± 0.02 g/10 min. The average diameter of the extrudate was about 3.25 mm for HDPE and 2.6 mm for HDPE-V. The extrudate swell ratio was 1.55 for HDPE and 1.24 for HDPE-V, respectively.
8. Mechanical characterization

The tensile properties of PU were tested with a strain rate of 50 mm/min under universal testing machine Instron 5567. Dumb bell shaped sample was adopted. Five specimens were examined for each sample.

9. Recycle of HDPE-V

The HDPE-V fragments was compressed at 170 °C for 5 min. Then HDPE-V was solidified under pressure at ambient temperature to gain recycled HDPE-V samples.

References