Supporting Information

for

Melt-Reprocessing of Mixed Polyurethanes Thermosets

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Contents of the SI

1. Materials and Methods
2. Characterization
3. Synthetic Procedures
4. Scheme and Figures (S1-S11)
1. Materials and Methods:

**Materials**: 1,6-Hexanediol (Sigma Aldrich), 1,1,1-Tris(hydroxymethyl)propane (Sigma Aldrich), hexamethylene diisocyanate trimer (HDIT, UH80, from Sherwin-Williams), Hexamethylene diisocyanate (Sigma Aldrich), Tolylene-2,4-diisocyanate (Sigma Aldrich), Zn(II) 2-ethylhexanoate (STREM Chemicals Inc), Zn(II) acetate (Sigma Aldrich).

All the chemicals were of analytical reagent grade and purchased from the above suppliers. These chemicals were used without further purification.

**Methods**

i) **Grinding of PU Samples**
Cured PU samples were placed into the liquid nitrogen, followed by its initial crushing with a hammer. Next, these granules were crushed to their powder using “Eberbach E3300 Mini Cutting Mill.”

ii) **Extrusion and Sample preparation**
First, the mixture of PU ground PU samples and 1,6-hexanediol were fed in three increments along with the simultaneous additions of Zn (II) 2-ethylhexanoate in an extruder over about 20 seconds at a temperature of 170°C. After the addition of all ingredients, the mixture was compounded for 25 minutes. Specimens were prepared in dumbbell shapes by injecting the melt into a mold at a temperature of 50°C.

iii) **Testing**:
Tensile properties of prepared samples were evaluated using a computer-controlled Universal testing machine (Instron 5565) according to ASTM D-638. The samples were tested at a crosshead speed of 10mm/min.

2. Instruments and Characterizations:

i) **Extruder**
The extrusion was performed using DSM Xplore 15cc Micro Extruder equipped with co-rotating conical twin-screws, while samples were molded using a 3.5cc injection molder.

ii) **FTIR Analysis**
IRAffinity-1S spectrometer of Shimadzu technology was employed to record all the ATR-FTIR spectra of the synthesized and reprocessed polyurethanes samples at 22°C using 64 scans.

iii) **Differential scanning calorimetry (DSC) Analysis**
DSC (Differential scanning calorimetry) thermograms for the synthesized and reprocessed polyurethanes were obtained by using a TA Instruments DSC-Q100. The selected samples were heated in the range between 0 °C to 210 °C at a rate of 10 °C/min.

iv) **NMR Analysis**
A 500/54 Premium Shielded NMR instrument of Agilent Technologies was used to record the 1H and 13C NMR spectra. Chemical shifts δ were recorded in ppm. DMSO-d6 was used as a solvent, which was also used as internal references.

v) **Microscopic Analysis**
An olympus SZX12 Stereozoom microscope of the Olympus corporation was used to record the microscopic images of the coated surfaces of the glass slide obtained after the melting of the reprocessed polyurethanes.

i) General procedure for the preparation of PU1
A 20 mL vial was charged with, 1,6-Hexanediol (1.89 g, 16.0 mmol, 0.8 equiv.), 1,1,1-Tris(hydroxymethyl)propane (0.54 g, 4.0 mmol, 0.2 equiv.) and hexamethylene diisocyanate (3.36 g, 20.0 mmol, 1.0 equiv.). The reaction mixture was stirred for 2 min at 60-70 °C and next casted on the Teflon sheet. After 2 h the Teflon sheet along with uncured polyurethane was placed for curing at 130 °C for 3 h.

ii) General procedure for the preparation of PU2
A 20 mL vial was charged with, 1,6-Hexanediol (2.36 g, 20.0 mmol, 1.0 equiv.), 1,1,1-HDIT (2.02 g, 4.0 mmol, 0.2 equiv.) and hexamethylene diisocyanate (2.69 g, 16.0 mmol, 0.8 equiv.). The reaction mixture was stirred for 2 min at 60-70 °C and next cast on the Teflon sheet, which was subsequently kept at room temperature for 3-4 h to remove all of the visible solvents of the HDIT and then heated at 130 °C for 3 h to enable curing prior to evaluation and testing.

iii) General procedure for the preparation of PU3
A 20 mL vial was charged with, 1,6-Hexanediol (1.89 g, 16.0 mmol, 0.8 equiv.), 1,1,1-Tris(hydroxymethyl)propane (0.54 g, 4.00 mmol, 0.2 equiv.) and Tolylene-2,4-diisocyanate (3.48 g, 20.0 mmol, 1.0 equiv.). The reaction mixture was stirred for 2 min at 60-70 °C and next cast on the Teflon sheet. After 2 hours, the Teflon sheet along with uncured polyurethane was placed for curing at 130 °C for 3 h.

iv) General procedure for the preparation of PU4
A 20 mL vial was charged with, 1,6-Hexanediol (2.36 g, 20.0 mmol, 1.0 equiv.), 1,1,1-HDIT (2.02 g, 4.0 mmol, 0.2 equiv.) and Tolylene-2,4-diisocyanate (2.78 g, 16.0 mmol, 0.8 equiv.). The reaction mixture was stirred for 2 min at 60-70 °C and next cast on the Teflon sheet, which was subsequently kept at room temperature for 3-4 h to remove all of the visible solvents of the HDIT and then heated at 130 °C for 3 h to enable curing prior to evaluation and testing.

v) General Procedure for the Melt-Reprocessing.
A 20 mL vial was charged with 4.0 mmol ground PU followed by the addition of diol (0.3-0.5 equiv) and Zn (II) 2-ethyl hexanoate or Zn (II) acetate. Next, it was placed at 165-170 °C for 40 min and recorded the physical properties of the reaction mixture like
- Melting
- Color change; and
- Repeating melting
4. Schemes and Figures (S1-S7).

**Scheme 1.** Chemistry of Polyurethane (Pus).

**Scheme 2.**

Figure S1 Melt-reprocessing phenomenon for PU1, PU2, PU3 and PU4 and their corresponding mixtures PU_{MIX1} and PU_{MIX2} without catalyst at 170 °C or 1 hour.
**Scheme 3.**

**Melt Processing of PUs using Catalyst Zn(II)**

Figure S2 Melt-reprocessing phenomenon for PU1, PU2, PU3 and PU4 and their corresponding mixtures PU\(_{MIX1}\) and PU\(_{MIX2}\), using 1% w/w Zn (II) 2-ethyl hexanoate or Zn (II) acetate at 170 °C or 1 hour.

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**Scheme 4**

**Melt Processing of PUs using only Diol**

Figure S3 Melt-reprocessing phenomenon for PU1, PU2, PU3 and PU4 and their corresponding mixtures PU\(_{MIX1}\) and PU\(_{MIX2}\), using 0.5 equiv diol (1,6, hexanediol) at 170 °C or 1 hour.

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Zinc ethyl hexanoate or Zinc acetate
Polyurethanes (grinded) 170 °C at 1 hour Not melted

0.5 equiv Diol
Polyurethanes (grinded) 170 °C at 40 min Not melted
Figure S4. Melt processing of PU\textsubscript{MIX2} using different concentrations of 1,6 hexanediol.

Figure S5. Melt processing of PU\textsubscript{MIX2} after alternative cooling and melting at 120 °C.
Figure S6. A) DSC-thermograms for the virgin aliphatic polyurethane (PU2). B) DSC-thermograms for the reprocessed or melted aliphatic polyurethane (PU2).

The 1st heating (started from 0 °C to 210 °C) is denoted in red, while the cooling process is indicated in blue and 2nd heating is shown in green. \( T_g \) denotes glass transition temperature, \( T_m \) denotes melting temperature, and \( T_c \) denotes crystallization temperature.
Figure S7. A) DSC thermograms for the virgin aromatic polyurethane (PU4). B) DSC-thermograms for the reprocessed or melted aromatic polyurethane (PU4).
The 1st heating (started from 0 °C to 210 °C) is denoted in red, while the cooling process is indicated in blue and 2nd heating is shown in green. $T_g$ denotes glass transition temperature, $T_m$ denotes melting temperature, and $T_c$ denotes crystallization temperature.

**Figure S8.** Comparison of differential scanning data for the mixed sample (PU1+PU3 or PU_{MIX1}) in the blue, aromatic sample (PU3) in the green, and aliphatic sample (PU1) in red after reprocessing were carried out.
Figure S9. Extruded and re-melted sample (coin-shaped) of the mix-PU (PU\textsubscript{MIX2}) after 5 min at 120 °C.

The GPC analysis were performed as below. First, 2 mg of PU sample (PU\textsubscript{MIX2}) was dissolved in 1 mL of THF. The filtered PU solution (100 μL) was injected, followed by analysis in a total run time of 50 min (flow rate of 1 mL/min). The molecular weight distribution (MWD) curve for PU sample was obtained by analyzing the raw data from Waters Breeze™ 2 Software.

Figure S10. GPC analysis of the PU\textsubscript{MIX2}. GPC analysis was not possible for the aromatic and aliphatic PUs because of their partial solubility.
Figure S11. Molecular Weight Determination by GPC analysis of the PU_{MIX2}. 