

Malleable and Recyclable Poly(urea-urethane) Thermosets bearing Hindered Urea Bonds

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Thermosets have excellent mechanical properties, solvent resistance, abrasion resistance, and load-bearing capacity, compared with thermoplastics, due to their covalently crosslinked structure. However, unlike thermoplastics that can be molded through injection or extrusion with the application of heat or solvent, most thermosets must be polymerized in the mold to set the desired shape, since they generally lack the ability to be reprocessed or recycled after curing.^[1] Recently, researchers have been trying to solve this problem by incorporating dynamic covalent bonds, which facilitate stress relaxation and reversible depolymerization through bond exchange.^[2–6] For example, Leibler and co-workers developed malleable thermosets based on polyester, in which metal catalysts were added to accelerate the transesterification reaction at high temperature.^[7,8] Guan and co-workers discovered that lightly crosslinked polybutadiene becomes malleable with the Grubb's catalyst, which promotes olefin metathesis.^[9–11] Hedrick and co-workers demonstrated that poly(hexahydrotriazine)s could be depolymerized by acid for recycling.^[12] However, most of them involve the use of catalysts, which add complexity to synthesis and recycling purification. To avoid this issue, Zhang and co-workers developed a catalyst-free malleable polymer network using imine chemistry.^[13] However, synthesis of imine produces water as the byproduct, which decreases the atom utilization and adds on another drying step in the material preparation. Other

reversible reactions, such as retro-Diels–Alder,^[14–17] reversible radical association–dissociation,^[18–20] reversible click chemistry,^[21] disulfide metathesis,^[22–24] transalkylation,^[25] boronic ester exchange,^[26] and transcarbamylation^[27] have also been reported in the design of malleable crosslinked polymeric materials. However, most of them are limited by the availability of commodity raw materials.

Crosslinked polyurethanes and polyureas that are synthesized from multifunctional isocyanates and alcohols or amines with 100% atomic conversion have been proven to qualify as high-performance polymeric materials with low cost. However, they also suffer from the lack of processing and recycling because of the extremely stable urethane or urea.^[27] Recently, we reported that by introducing bulky substituents on one of the nitrogen atoms of a urea bond, the resulting hindered urea bonds (HUB) show a dynamic nature under ambient/catalyst-free conditions.^[28,29] Hindered urea bond (HUB)-based soft organogels with low crosslinking density showed efficient self-healing properties. Here, we report a new class of hard poly(urea-urethane) thermosets based on HUB that behave like classic thermoset at ambient conditions yet can be reprocessed by application of heat and recycled from a mixture of traditional thermoplastics and thermosets.

The dynamic nature of HUB structures is related to the bulkiness of the substituents; 1-(*tert*-butyl)-1-ethylurea (TBEU), an HUB structure with both a high binding constant and dissociation rate ($K_{eq} = 7.9 \times 10^5 \text{ M}^{-1}$, $k_{-1} = 0.042 \text{ h}^{-1}$, data collected at room temperature), has been shown to be suitable for making dynamic polymers.^[28] Therefore, we first studied a crosslinked poly(urea-urethane) thermoset (PUU-TBAE) with the incorporation of the TBEU moiety (**Figure 1a**). PUU-TBAE was synthesized by curing two commercially available monomers: 2-(*tert*-butylamino)ethanol (TBAE) and a tri-functional homopolymer of hexamethylene diisocyanate (THDI) with aid from the catalysis of dibutyltin dilaurate (DBTDL), which serves to catalyze only the reaction between hydroxyl and isocyanate and makes little contribution to the dynamic nature of HUB (**Figure 1b**). The polymerization was complete after reaction at 60 °C for 12 h, which was confirmed by the disappearance of the isocyanate peak in infrared spectroscopy (**Figure S1**, Supporting Information). The resulting PUU-TBAE thermoset exhibits a high modulus (reduced modulus $\approx 3.5 \text{ GPa}$ by nanoindentation, Young's modulus $\approx 1.9 \text{ GPa}$ by tensile testing), high hardness ($\approx 250 \text{ MPa}$), and high breaking strength ($\approx 39.5 \text{ MPa}$), which are in the range of commercial, state-of-the-art, crosslinked thermosets. It has a good solvent resistance, and shows swelling rather than dissolution in organic solvents such as toluene, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), etc.

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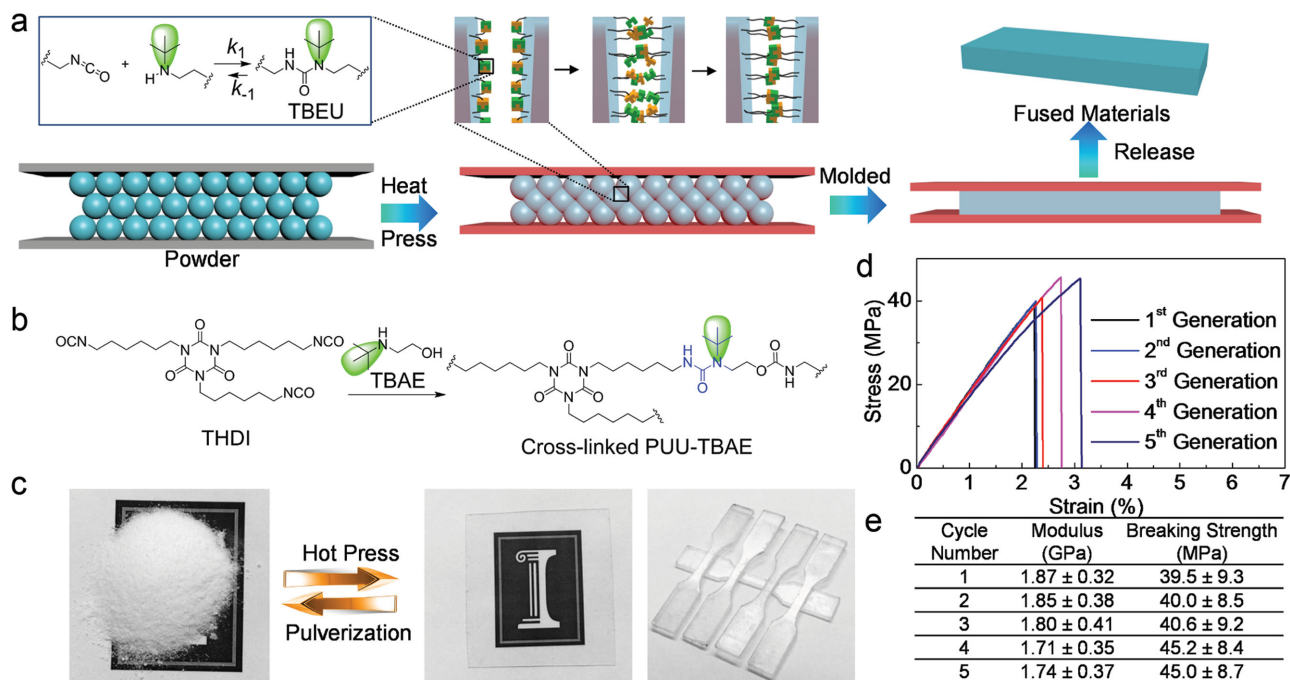


Figure 1. Malleable PUU thermoset design and characterization. a) Illustration of hot-press processing of crosslinked poly(urea-urethane) materials facilitated by dynamic exchange of the hindered urea bond (HUB). b) The chemical route for the preparation of malleable crosslinked poly(urea-urethane) (PUU-TBAE). c) Photographs showing molding of PUU-TBAE powders to transparent film and dog-bone-shaped specimens via hot pressing (100 °C, 300 kPa, 20 min). d) Stress–strain curves for the dog-bone-shaped PUU-TBAE sample shown in (c) through five generations of molding from powder to solid. e) Young's modulus and breaking strength of dog-bone-shaped PUU-TBAE specimens after different generations of molding.

We then investigated the malleability of the PUU-TBAE materials toward reprocessing from powder to bulk by the hot-pressing technique. Below the glass-transition temperature (glass-transition temperature (T_g) of PUU-TBAE ≈ 53 °C), the crosslinks and the network topology appear to be quenched because of their low chain mobility and the low dynamic nature of the HUBs. At high temperatures ($T > T_g$), the network shows fast bond exchange and behaves like a viscoelastic fluid (characteristic relaxation time $\tau^* = 32$ s at 100 °C, see Figure S2, Supporting Information). The bulk PUU-TBAE thermoset was ground into powder, and then treated with a pressure of 300 kPa for 20 min at 100 °C. Moisture was carefully avoided during the whole process to prevent the potential hydrolysis of the isocyanate intermediate. The polymer powder was molded into bulk samples (shapes determined by the molds shapes, Figure 1c and Figure S15, Supporting Information) with high mechanical stiffness, solvent resistance (Figure S6, Supporting Information), and transparency (over 70% transmittance from 400 to 800 nm wavelength for 200 μ m polymeric film, Figure S7, Supporting Information). To demonstrate that the malleability is from the dynamic exchange of the HUBs, we synthesized several poly(urea-urethane) (PUU) thermosets using the same isocyanate monomer but with less-bulky amine monomers: 2-(*iso*-propylamino)ethanol (IPAE) and 2-(*n*-butylamino)ethanol (NBAE) instead of TBAE as control groups. The resulting PUUs (PUU-IPAE and PUU-NBAE) contain similar HUB structures (1-isopropylethylurea (IPEU) and 1-*n*-butylethylurea (NBEU)) with a lower dynamic nature characterized by larger binding constants ($K_{eq} > 10^7$ M⁻¹) and smaller dissociation rates ($k_{-1} < 0.001$ h⁻¹) (Figure S3, Supporting Information). Both

PUU-IPAE and PUU-NBAE exhibited a comparable modulus (reduced modulus of ≈ 3.1 GPa for PUU-IPAE and ≈ 2.7 GPa for PUU-NBAE by nanoindentation). However, neither could be remolded to a shaped material with as high stiffness and transparency as PUU-TBAE with the same hot-press procedures from thermoset powders (Figure S5, Supporting Information), which is due to the lower dynamic nature of the IPEU and NBEU bonds. We also demonstrated that the PUU-TBAE thermoset could be remolded repeatedly. The shaped solids were re-ground to powders (Figure 1c) and then reprocessed by hot pressing using the same procedure multiple times. The tensile-test results showed that the recycled materials exhibit no major decrease of mechanical stiffness and strength even after the fifth generation of reprocessing (Figure 1d,e). In addition, solid-state ¹³C NMR spectra barely showed any signal change after the fifth reprocessing (Figure S8, Supporting Information), demonstrating that there was limited recycling fatigue during the whole process.

To further understand the role that TBEU exchange plays in the malleability of the bulk polymer, we investigated the bond exchange of TBEU-based small molecules at various temperatures by ¹H NMR spectrometry.^[13] We synthesized two TBEU dimers molecules, 1,1'-(ethane-1,2-diyl)bis(1-(*tert*-butyl)-3-butylurea) (AA) and 1,1'-(ethane-1,2-diyl)bis(3-benzyl-1-(*tert*-butyl)urea) (BB), by mixing corresponding isocyanate and *N,N'*-di-*tert*-butylethylene diamine in a 2:1 ratio without purification (Figure S9 and S10, Supporting Information). Subsequent to the mixing of the two parental model compounds, a new TBEU species (AB) was formed due to the bond exchange (Figure S11, Supporting Information), and its production rate

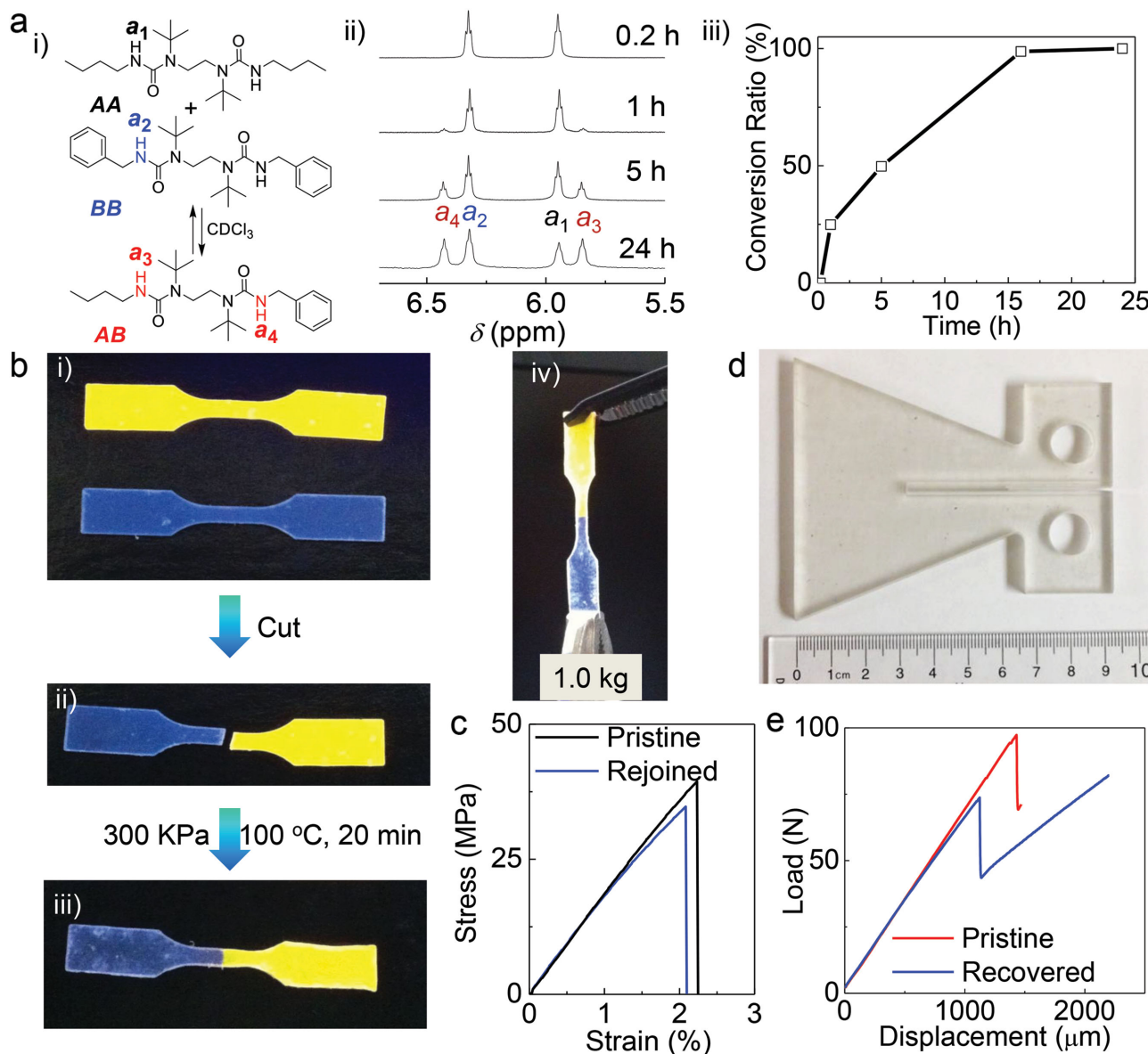


Figure 2. Interface fusion of PUU-TBAE thermoset through reversible bond exchange. a) Reversible exchange reaction between two TBEU model compounds. i) Chemical structures of model compounds (AA, BB, and AB). ii) ^1H NMR spectra showing the reaction progress over time (illustrated by reduction of a_1 , a_2 peaks and growth of the a_3 , a_4 peaks) at 60 °C. iii) Change of concentrations ratio: $[\text{AB}]/([\text{AA}]+[\text{BB}])$ over time as measured by the urea peaks integration of each species at 60 °C. Cease of ratio change indicates the reaching of chemical equilibrium. b) Interface rejoining of dog-bone-shaped PUU-TBAE thermoset. i) Two dog-bone-shaped solid materials with or without Rhodamine 6G staining; ii) two halves of samples cut from complete dog-bone materials with different colors; iii) rejoined sample with the exertion of heat (100 °C) and pressure (300 kPa) for 20 min. iv) The rejoined sample can sustain the weight of a 1.0 kg block. c) Stress–strain curves for the pristine and rejoined dog-bone-shaped PUU-TBAE samples. d) Tapered double-cantilever-beam (TDCB)-shaped PUU-TBAE materials molded by hot pressing. e) Representative curves of load versus displacement for pristine and recovered (cracked and healed at 37 °C for 5 d with the treatment of acetone) TDCB PUU-TBAE samples.

was monitored by NMR spectroscopy at different temperatures (Figure 2a). We observed that the reaction reached equilibrium within 16 h at 60 °C. Though the bond-exchange conditions in the bulk polymer would be different from those of small molecules in solution, the model study demonstrated the feasibility of utilizing TBEU exchange reactions as a temperature-dependent approach to achieve malleability of the polymer.

We next investigated the fusion of the thermoset interface during malleation. We prepared PUU-TBAE thermoset samples

with or without Rhodamine 6G staining using hot pressing with a dog-bone-shaped mold. Later, we cut the samples into two individual pieces (Figure 2b-i,ii), and then brought two pieces with different colors into contact inside the mold. They were treated at 100 °C with the exertion of 300 kPa pressure for 20 min, and the two different-colored pieces were perfectly rejoined (Figure 2b-iii,iv) with 95% of their strength recovered (Figure 2c). Although the bond exchange is still active at lower temperature, the interface fusion was much less efficient. This

is partially due to the lower dynamic nature of the TBEU structure, but more caused by the chain-mobility restriction at sub-glass-transition temperatures. To demonstrate this, we investigated whether the addition of solvent to the interface, which decreases the glass-transition temperature and increases the chain mobility, can facilitate the fusion process. We prepared tapered double-cantilever-beam (TDCB) specimens of PUU-TBAE (Figure 2d and Figure S16, Supporting Information) in the geometry described by Brown.^[30] Prior to testing, a small pre-crack was introduced into the center groove of the sample by lightly tapping a razor blade into the front of the fluted region. To test them, the samples were loaded in displacement control until the mid-plane crack propagated to the end of the crack-propagation region. Following testing, crack plane re-mending was facilitated by adding a drop of acetone to the fracture plane before incubating the specimen at 37 °C. Testing was then repeated after 5 d, with up to 75% recovery of fracture

toughness possible (Figure 2e). In control specimens where acetone was not added to the fracture surface, no recovery was observed. This result is consistent with our previous report of self-healing properties of a TBEU-based soft organogel, and illustrates the necessity of bringing the dynamic thermosets above T_g for processing.

The dynamic nature of the materials also facilitates the recycling of the thermoset, which otherwise causes issues of resources waste and environmental contamination.^[3,31] Recycling of conventional thermoset materials involves powder grinding as materials filler or backbone degradation in harsh conditions (e.g., high temperature, strong acid/base, etc.) followed by reuse of the monomers. Both methods sacrifice the virgin mechanical properties, involve tedious procedures, or consume a lot of energy. Some recent work has sought ways to improve recycling efficiency by incorporation of dynamic covalent chemistry. For example, Hedrick incorporated

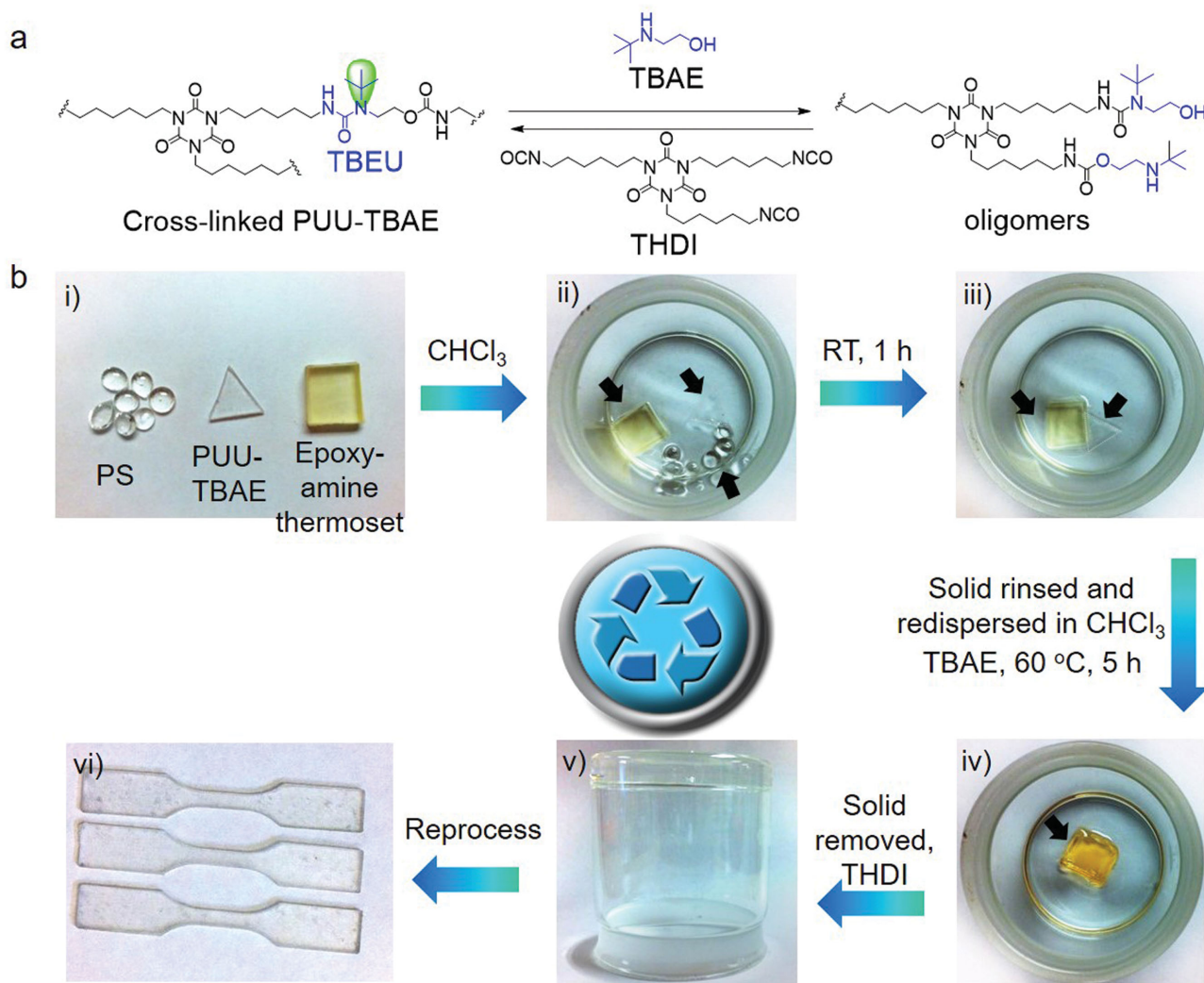


Figure 3. Recycling of PUU-TBAE thermoset. a) Degradation of the crosslinked network by excess TBAE and re-formation of the network by THDI. b) i) Sorting of PUU-TBAE thermoset from a mixture of traditional thermoplastic (PS) and thermoset (EAT); ii) PS, PUU-TBAE, and EAT were treated by chloroform; iii) After 1 h, PS was dissolved while the other two remained; the remaining solid was taken out, rinsed, and redispersed in chloroform with TBAE. iv) PUU-TBAE dissolved after 5 h with the incubation at 60 °C. v) The remaining solid was removed, organogel was re-formed with the addition of THDI; vi) Recycled dog-bone-shaped samples were prepared via hot pressing of dried powders from re-formed PUU-TBAE.

hexahydrotriazine into thermosets that could be fast depolymerized to monomers under mild conditions.^[12] However, the reuse of monomers still needs further purification. Here we demonstrate that the PUU-TBAE thermoset can easily switch between gel and solution states by tuning the monomer ratio, showing greatly improved efficiency for materials recycling and reuse. The PUU-TBAE thermoset only swells in an organic solvent, such as chloroform (Figure S12-i, Supporting Information), but it completely dissolves with the presence of excess TBAE (incubation at 60 °C for 12 h, with 3 equiv. excess TBAE, Figure 3a, Figure S12-i,ii and S13, Supporting Information). After that, the organogel could be reformed by the re-addition of the isocyanate monomer THDI with the same equivalence of functional groups as TBAE (Figure S12-iii, Supporting Information). The reformed organogel can be ground into powder, vacuum dried, and remolded into bulk samples with hot pressing, the same as described above, and has almost the same mechanical properties compared with the original solid materials (Figure S12-iv and S14, Supporting Information). Furthermore, the unique recycling procedures make it possible to separate the PUU-TBAE thermoset from a mixture of traditional polymers including thermoplastic (e.g., polystyrene (PS)) and a thermoset (e.g., epoxy-amine thermoset (EAT)). As shown in Figure 3b, we added a mixture of PUU-TBAE, PS, and EAT into chloroform. The PS dissolved quickly, while PUU-TBAE and EAT remained in solid form. These remaining solids were added into a solution of TBAE. Given enough time, PUU-TBAE dissolved due to the bond exchange, while EAT remained. After filtering the solid residue, the solution could be re-cured to PUU-TBAE with the addition of THDI and reprocessed as mentioned above. This property can significantly enhance the efficiency of classification during waste recycling.

In summary, a new class of PUU-TBAE with dynamic HUB was developed. This new thermoset has comparable mechanical properties and solvent resistance to conventional thermosets, but shows malleability under mild heating without the need of catalyst. Furthermore, the PUU-TBAE thermoset can be efficiently recycled, which avoids the use of energy-intensive degradation conditions and tedious monomer purification. Additionally, we showed that the PUU-TBAE thermoset can be easily sorted from a mixture of traditional thermoplastics and thermosets. Together with the green synthesis (100% atom economy) and wide availability of commodity monomers, HUBs show great potential as a new type of malleable crosslinked polymer of broad use.

Experimental Section

General: TBAE (Sigma–Aldrich) was purified by sublimation. IPAE and NBAE (Sigma–Aldrich) were purified by distillation. A tri-functional homopolymer of THDI (Desmodur N-3900) was purchased from Bayer MaterialScience (Pittsburgh, PA, USA) and used as received. DBTDL and other reagents and solvents were purchased from Sigma–Aldrich (St. Louis, MO, USA) and used as received unless otherwise specified. NMR spectra in solution were recorded on a Varian UI400 (400 MHz), UI500NB (500 MHz), U500 (500 MHz), or VXR-500 (500 MHz) spectrometer. NMR spectra of solid samples were recorded on a Varian UI300WB (300 MHz) spectrometer. The shaped solid materials were processed using a Tetrahedron MTP-14 laboratory hot press in specific shaped aluminum moulds. Tensile experiments were performed

on a custom-built, bidirectional screw-driven rail table assembled by IMAC Motion Control Group (Elgin, IL, USA) with a translation stage from Lintech (Monrovia, CA, USA), motor from Kollmorgen (Radford, VA, USA), and load cell from Honeywell Sensotech (Columbus, OH, USA). Nanoindentation measurements were performed using a Hysitron Triboindenter (TI-950) with a cube-corner probe of end radius ≈50 nm. Glass-transition temperatures were tested by differential scanning calorimetry (DSC) (TA instrument Q2000, New Castle, DE, USA). Films transmittance was tested using a Perkin Elma Lambda 25 UV–vis spectrometer. Infrared spectra were recorded on a Perkin Elmer 100 serial FTIR spectrophotometer equipped with universal attenuated total reflectance (ATR), which enables the analysis of polymer samples in powder form. The fracture toughness tests were performed using an Instron 8500 load frame (Grove City, PA, USA).

Synthesis of PUU-TBAE: TBAE (10.0 g, 85.5 mmol) and THDI (28.1 g, 55.9 mmol) were mixed in 50 mL centrifuge tube and heated up to 60 °C. After the dispersion turned into a homogeneous and viscous solution, DBTDL (100 μL, 0.17 mmol) was added into the mixture. Then the mixture was incubated at 60 °C for 12 h, and then cooled down to room temperature. The bulk materials were subsequently ground into fine powders by a pulverization machine (38.1 g, yield 100%).

Nanoindentation Experiments: The films were ≈2 mm thick and mounted with a cyanoacrylate glue (superglue) onto a stainless-steel substrate magnetically held on the sample stage. Prior to indenting into samples of interest, the probe was calibrated using a fused quartz sample 1 mm thick that was mounted similarly to the samples of interest. The probe-area function was fitted to the known modulus for fused quartz using three coefficients. Between indentations on the two samples, the probe was cleaned and recalibrated. Seven independent repeats of each load, separated by at least 10 μm in the X and Y dimensions, were performed to avoid any possibility of strain field coupling between indents. The reduced modulus was measured for each load, and an average modulus from at least three independent data points is reported as the film modulus.

Tensile Experiments: Tensile tests of PUU-TBAE dog-bone samples were conducted according to ASTM D638. Type-V dog-bone samples were prepared via hot pressing in the aluminum mold with the shape shown in Figure S15 (Supporting Information). Tensile experiments were performed on a custom built bi-directional-screw-driven rail table that allows tensile testing of samples with both grips translating simultaneously and in opposite directions, keeping the center of mass of the sample stationary. The samples were extended at the speed of 0.02 mm s⁻¹. The load was measured via a 220 N capacity load cell.

Dynamic Exchange of Small Molecular Model Compounds in Solution: In order to investigate the behavior of the dynamic urea bonds exchange reaction, compounds AA and BB were mixed in deuterated chloroform with 1:1 molar ratio (25 × 10⁻³ M), and the formation of AB was monitored by ¹H NMR spectroscopy over time at three different temperatures: 30, 45, and 60 °C.

Swelling of PUU-TBAE in Different Solvents: Square-shaped PUU-TBAE samples (0.5 g) were immersed in variant solvents (10 mL) in glass vials at room temperature. After 48 h, the samples were taken out, and the residual solvent on the surface was wiped. The weight increase percentage was calculated by Equation (1).

$$\text{Weight increase percentage} = 100 \times (M_t - M_0) / M_0 \quad (1)$$

where M_t is the mass of sample after swelling and M_0 is the mass of dry sample before swelling.

Interface Fusion Study of PUU-TBAE Thermoset under Heat and Pressure: Two dog-bone-shaped samples were prepared via hot pressing of ground powder with or without staining by Rhodamine 6G. They were cut by a blade into halves, and then pieces with different colors were put back into the original mold. A pressure of 300 kPa was applied at 100 °C for 20 min without the protection of inert gas. The resulting sample was subjected to stress–strain testing for the recovery of their breaking strength.

Solvent-Assisted Interface Fusion of PUU-TBAE Thermoset using the TDCB Method: TDCB-shaped samples of the PUU-TBAE thermoset

were fabricated via hot pressing with a TDBC-shaped aluminum mould (Figure S16, Supporting Information) for the fatigue-crack propagation behavior study. Fracture toughness testing was performed using a custom-built load frame with a 50 lb (223 N) load cell in displacement control at a rate of $5 \mu\text{m s}^{-1}$. After fracture was generated, acetone (0.3 mL) was added in the fracture area, and the sample was put in 37°C oven for 5 d. The fracture toughness of the recovered TDCB shape materials was retested by the load frame. For the TDCB geometry the recovery efficiency reduced to the ratio of critical fracture loads of the recovered and pristine tests:

$$\eta = \frac{P_c^{\text{recovered}}}{P_c^{\text{pristine}}} \quad (2)$$

where η is recovery efficiency, $P_c^{\text{recovered}}$ and P_c^{pristine} are the critical fracture loads of the recovered and pristine TDCB samples.

Recycling of PUU-TBAE Thermoset: A block of PUU-TBAE thermoset (1.0 g, 2.2 mmol of TBEU bonds) was immersed in chloroform (5 mL). TBAE (0.78 g, 6.6 mmol, 3 equiv. of TBEU bonds in the thermoset) was added into chloroform, and then the mixture was stirred at 60°C for 12 h, after which the solid was completely dissolved. The mixture was cooled down to room temperature, followed by the addition of THDI (2.2 g, 6.6 mmol). The solution became organogel after 10 min incubation at 60°C . After additional 12 h to drive the reaction to completion, the organogel was ground into the powder, and dried under vacuum at 60°C for 24 h. The powder was remolded into the shaped solid materials via hot-press processing (100°C , 20 min, 300 kPa).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Y.Z. and H.Y. contributed equally to this work. Y.Z. and H.Y. designed the research, performed the experiments, and wrote the paper. K.R.H. performed the TDCB tests and results interpretation. Y.W. and A.J.H. performed the polymer synthesis. A.M.C. performed polymer processing by hot press. K.Y. performed DCS tests. T.K. helped with the tensile tests. S.R.W., N.R.S., and J.C. supervised the overall experimental design and writing. All work was carried out at University of Illinois at Urbana-Champaign. The authors gratefully acknowledge the support from the NSF (CHE 1508710).

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[1] *Introduction to Polymer Viscoelasticity*, 3rd ed. (Eds: M. T. Shaw, W. J. MacKnight), Wiley, New York **2005**.

- [2] R. J. Wojtecki, M. A. Meador, S. J. Rowan, *Nat. Mater.* **2011**, *10*, 14.
 [3] Y. Zhang, A. A. Broekhuis, F. Picchioni, *Macromolecules* **2009**, *42*, 1906.
 [4] C. J. Kloxin, T. F. Scott, B. J. Adzima, C. N. Bowman, *Macromolecules* **2010**, *43*, 2643.
 [5] W. Denissen, J. M. Winne, F. E. Du Prez, *Chem. Sci.* **2016**, *7*, 30.
 [6] Z. Q. Pei, Y. Yang, Q. M. Chen, E. M. Terentjev, Y. Wei, Y. Ji, *Nat. Mater.* **2014**, *13*, 36.
 [7] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, *Science* **2011**, *334*, 965.
 [8] M. Capelot, D. Montarnal, F. Tournilhac, L. Leibler, *J. Am. Chem. Soc.* **2012**, *134*, 7664.
 [9] Y. X. Lu, F. Tournilhac, L. Leibler, Z. Guan, *J. Am. Chem. Soc.* **2012**, *134*, 8424.
 [10] Y. X. Lu, Z. Guan, *J. Am. Chem. Soc.* **2012**, *134*, 14226.
 [11] J. A. Neal, D. Mozhdghi, Z. Guan, *J. Am. Chem. Soc.* **2015**, *137*, 4846.
 [12] J. M. Garcia, G. O. Jones, K. Virwani, B. D. McCloskey, D. J. Boday, G. M. ter Huurne, H. W. Horn, D. J. Coady, A. M. Bintaleb, A. M. Alabdulrahman, F. Alsewaleim, H. A. Almegren, J. L. Hedrick, *Science* **2014**, *344*, 732.
 [13] P. Taynton, K. Yu, R. K. Shoemaker, Y. Jin, H. J. Qi, W. Zhang, *Adv. Mater.* **2014**, *26*, 3938.
 [14] X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. R. Nutt, K. Sheran, F. Wudl, *Science* **2002**, *295*, 1698.
 [15] E. Trovatti, T. M. Lacerda, A. J. Carvalho, A. Gandini, *Adv. Mater.* **2015**, *27*, 2242.
 [16] J. Bai, H. Li, Z. X. Shi, M. Tian, J. Yin, *RSC Adv.* **2015**, *5*, 45376.
 [17] Y. Heo, H. A. Sodano, *Adv. Funct. Mater.* **2014**, *24*, 5261.
 [18] T. F. Scott, A. D. Schneider, W. D. Cook, C. N. Bowman, *Science* **2005**, *308*, 1615.
 [19] Y. Amamoto, J. Kamada, H. Otsuka, A. Takahara, K. Matyjaszewski, *Angew. Chem., Int. Ed.* **2011**, *50*, 1660.
 [20] Y. Amamoto, H. Otsuka, A. Takahara, K. Matyjaszewski, *Adv. Mater.* **2012**, *24*, 3975.
 [21] S. Billiet, K. De Bruycker, F. Driessen, H. Goossens, V. Van Speybroeck, J. M. Winne, F. E. Du Prez, *Nat. Chem.* **2014**, *6*, 815.
 [22] J. J. Griebel, N. A. Nguyen, A. V. Astashkin, R. S. Glass, M. E. Mackay, K. Char, J. Pyun, *ACS Macro Lett.* **2014**, *3*, 1258.
 [23] A. Rekondo, R. Martin, A. R. de Luzuriaga, G. Cabanero, H. J. Grande, I. Odriozola, *Mater. Horiz.* **2014**, *1*, 237.
 [24] M. Pepels, I. Filot, B. Klumperman, H. Goossens, *Polym. Chem.* **2013**, *4*, 4955.
 [25] M. M. Obadia, B. P. Mudraboyina, A. Serghei, D. Montarnal, E. Drockenmuller, *J. Am. Chem. Soc.* **2015**, *137*, 6078.
 [26] O. R. Cromwell, J. Chung, Z. B. Guan, *J. Am. Chem. Soc.* **2015**, *137*, 6492.
 [27] D. J. Fortman, J. P. Brutman, C. J. Cramer, M. A. Hillmyer, W. R. Dichtel, *J. Am. Chem. Soc.* **2015**, *137*, 14019.
 [28] H. Ying, Y. Zhang, J. Cheng, *Nat. Commun.* **2014**, *5*, 3218.
 [29] H. Ying, J. Cheng, *J. Am. Chem. Soc.* **2014**, *136*, 16974.
 [30] E. N. Brown, *J. Strain Anal. Eng.* **2011**, *46*, 167.
 [31] S. J. Pickering, *Composites, Part A* **2006**, *37*, 1206.