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Plastics Upcycling

Chemical Upcycling of Thermoplastics Towards Thermosets Based on Dynamic Dimethylglyoxime-Urethane Moiety

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Abstract: Huge annual consumption of thermoplastics results in the generation of large amounts of waste after their service life. Currently, the most popular recycling method based on mechanically melt-reprocessing deteriorates the material performance and is economically unattractive, which makes it unviable to be implemented in large scale. Herein, we present a chemical upcycling strategy that can transform dimethylglyoxime-urethane based thermoplastic waste into thermoset product with superior mechanical properties and higher economic values than the initial one. It is found that the dimethylglyoxime-urethane moiety has dynamic nature, endowing the material with open-loop upcycling ability. By removing the dimethylglyoxime segment via a simple sublimation process, the material structure is transformed from linear molecular into crosslinked network. More interestingly, the transformation is reversible, and the regenerated crosslinked network can be transformed back to linear molecule by returning the removed dimethylglyoxime segment to the material, which means the upcycled product can be recycled again after its service life. Our linear/crosslinked transformation strategy provide a new option for recycling thermoplastic waste.

Introduction

Synthetic polymers have been widely used in our daily life to meet various demands owing to their lightweight, flexible, tough, and inexpensive characteristics. As reported by "Plastics Europe", the world annual production of synthetic polymers in 2022 has reached 400 million tons.[1] Among them, thermoplastic polymers occupy the largest share (more than 80 %) of the market, and are particularly popular in packing, agriculture, architecture, transportation, medical treatment, electronics, aerospace, etc..[1,2] After their service life, a great deal of waste plastics are generated, thus causing the increasing environmental concern. In the past, the waste was usually disposed in landfill or incineration, but both of them will cause secondary pollution and resource wasting.[3] For ecological and economic benefits, many attempts have been made. Mechanical recycling that could be performed through melt-reprocessing is the most commonly used and simple method. However, the properties of the materials will be obviously degraded due to the molecular chain scission, degradation, and oxidation under the condition of high mechanical forces (e.g., grinding, hot-pressing, and/or extruding), high temperature, oxygen, moisture during melt-reprocessing.[4] Besides, during their service life, the long-time exposure to all kinds of factors (e.g., mechanical force, chemicals, heat, oxygen, moisture, microorganisms, and/or UV-radiation) in the environment usually also cause the destructive molecular events.[4] In principle, the mechanical properties could be improved by introducing stabilizers to alleviate the above side reactions.[5] However, this approach does not bring high economic value because the structure of polymer is typically a static and closed system after polymerization and the properties of the regenerated product is inferior to the initial one.[6]

Dynamic covalent bonds, which can undergo reversible dissociation and/or bond exchange, could serve as a "living center" to adjusting the polymer structure and enable it with dynamic and open ability.[6,7] Accordingly, the polymer can be endowed with self-healing,[8] self-growing,[9] mechanically programmable,[10] shape-shifting,[11] and/or chemical recycling abilities.[12] In terms of the recycling ability emphasized in this paper, there are two typical strategies: I. Recycling via bond exchange to make the crosslinked polymer waste reprocessible in the same fashion as the thermoplastic polymers. II. Recycling to obtain monomers/oligomers for preparing new products without deteriorated properties. The former one mainly focuses on addressing the problem of reprocessing the classical thermoset waste, but it does not allow upcycling.[12a,b] The latter one provides an opportunity for upcycling via innovating the polymer topological structure and enhancing its mechanical properties which has been recently confirmed by us.[12c] As thermosets with crosslinked network possess superior mechanical properties than the counterpart thermoplastics with linear molecule, recently, upcycling thermoplastics to thermosets is on the rise.[13] For example, Tomovic et al. depolymerized polycarbonate by employing vanillin derivative, and the resulting monomer was used for preparing crosslinked poly(imine-carbonate)s by reacting with amines.[13a] For another example, Beckham et al. depolymerized polyethylene terephthalate by using

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diol, and then reacted with unsaturated acid to prepare crosslinked and fiber-reinforce materials.[13b] These works are very meaningful and give us great inspiration. However, they typically require consuming a large amount of additional chemical reagents (e.g., degradation agent, catalyst, and/or curing agent). Furthermore, the current research is primarily focused on thermoplastics, with few reports on thermoplastic elastomers.

In this work, we develop a dynamic mechanism that can not only upcycle thermoplastic elastomer to thermoset elastomer with better properties but also be reagent-saving. Clearly, this innovative strategy will make the recycling more economic. We think it may be realized by introducing a switch based on dynamic moiety containing a "living segment" in the thermoplastic polymer network. By removing and recovering the "living segment", the switch is triggered to turn the linear molecule to crosslinked network. More importantly, the recovered "living segment" can not only be used as raw material for new products, but also turn the crosslinked network back to linear molecule. Hereafter, we present our successful effort in this direct with a dynamic dimethylglyoxime-urethane based thermoplastic polyurethane material.

Methods

Materials. Dimethylglyoxime, dimethyl sulfoxide (DMSO) and poly (tetramethylene glycol) ($M_n = 1000\ g{\cdot}mol^{-1}$) were purchased from Aladdin. Diphenylmethane diisocyanate (MDI) was purchased from Wanhua Chemical Group. Acetone was purchased from Huzhou Shuanglin chemical technology Co., Ltd. N-Methylpyrrolidone (NMP) was purchased from Energy Chemical. Anhydrous N, N-dimethylformamide (DMF), anhydrous diethyl ether and tetrahydrofuran (THF) were purchased from Sinopharm Chemical Reagent. Poly (tetramethylene glycol) was dried in vacuum for two hours before use. All other chemicals were used as received.

General measurements. ^{1}H-nuclear magnetic resonance (^{1}H NMR) spectra were recorded by Bruker Avance 500 NMR spectrometer. Chemical shifts (δ) were reported in ppm relative to residual solvent signals (DMSO-d6: 2.50 ppm, water in the deuterium reagent: 3.31 ppm). Fourier transform infrared (FTIR) spectra was performed on a Bruker VERTEX 70v spectrometer. The spectra were collected through 16 scans with a spectral resolution of 4 cm^{-1}. Gel permeation chromatography (GPC, Waters 1525) analysis was performed with tetrahydrofuran as the eluent at a flow rate of 1 $mL{\cdot}min^{-1}$ at 36 °C using polystyrene as the standard. Differential scanning calorimetry (DSC) was performed on a TA DSC Q2000 at a heating rate of 20 $°C{\cdot}min^{-1}$ under a nitrogen atmosphere. Thermal gravimetric analysis was performed on a Thermo Electron NICOLET 5700 at a heating rate of 10 $°C{\cdot}min^{-1}$ in nitrogen. Gel fraction test was conducted though solvent extraction in tetrahydrofuran for 24 h and vacuum-drying at 50 °C for 2 h. Tensile tests were performed on an electronic universal testing machine (SUNS) at a tensile rate of 20 $mm{\cdot}min^{-1}$.

Synthesis of dimethylglyoxime-urethane based thermoplastic polyurethane. Poly (tetramethylene glycol) (40 g, 0.04 mol) and dimethylglyoxime (4.64 g, 0.04 mol) were mixed in DMF (180 mL). Then diphenylmethane diisocyanate (20 g, 0.08 mol) was added and reacted at 70 °C for 6 hours. After precipitating with diethyl ether and drying at 50 °C for 24 hours in vacuum, dimethylglyoxime-urethane based thermoplastic polyurethane (TPU) was obtained. GPC analysis suggests that the prepared TPU has an averaged molecular weight of 46,106 $g{\cdot}mol^{-1}$ and a polydispersity index of 2.6.

Transformation of linear molecular to crosslinked network. The prepared TPU sample (500 mg) was added onto a Teflon sheet and placed in the reactor bottom. Then the reactor bottom was heated at predetermined temperature (110 °C, 140 °C, 170 °C, or 200 °C) for predetermined time (0 h, 1 h, 3 h, 5 h, 10 h, 15 h, or 20 h) in vacuum. After completion, white dimethylglyoxime powder appeared on the reactor cap, meanwhile yellowish solid with crosslinked network was obtained in the bottom. Then, both of them were collected, and characterized by FTIR and/or ^{1}H NMR. In addition, the solid sample was hot-pressed (30 MPa at 100 °C for 10 min) into a transparent film before tensile test.

Study on the thermal dissociation behavior of dimethylglyoxime-urethane moiety. The thermal dissociation behavior of dimethylglyoxime-urethane group was investigated by variable-temperature FTIR. The temperatures of the variable-temperature FTIR ranged from 25 °C to 140 °C and the soak time at each predetermined temperature was two minutes. The higher temperature (above 140 °C) was not studied due to the limitation of the instrument. The peak at around 2275 cm^{-1} corresponding to isocyanate group (-NCO) was monitored.

Study on vacuum sublimation behavior of dimethylglyoxime. Dimethylglyoxime (white powders, 100 mg) was added onto the bottom of a reactor. Afterwards, the reactor bottom was heated at 140 °C in vacuum, the white powders gradually sublimated from the bottom and then deposited onto the unheated reactor cap. The complete migration of the white dimethylglyoxime powers from the bottom to the cap took about 30 min.

Reverse transformation of crosslinked network back to linear molecular. The obtained crosslinked film and the recovered dimethylglyoxime were soaked in 8 times of DMF. After heating at 130 °C for 15 min, the crosslinked film was dissolved, yielding a transparent TPU solution. Then the solution was cast into Teflon dish. After drying at 50 °C for 8 hours followed by 100 °C for 8 hours, a transparent TPU film was regenerated again.

In addition, diphenylmethane diisocyanate (2 %, 4 %, 6 %, and 8 % weight of TPU) was added into the TPU solution. After drying at 50 °C for 8 hours followed by 100 °C for 8 hours, a series of isocyanate-reinforced TPU material were obtained.

Results and Discussion

Design Principle for Upcycling TPU

The thermoplastic polyurethane (TPU) is prepared through the reaction of diisocyanate with a dimethylglyoxime and a polyol (Figure 1a). Its structure was confirmed by ^{1}H NMR and FTIR analysis (Figures S1–2). Accordingly, two kinds of urethane moieties, a dimethylglyoxime-urethane and a common urethane, are generated (Figure 1a). For the former, it has excellent dynamic covalent nature upon heating, and will reach an equilibrium state with isocyanate and oxime.[12d,14] Normally, the equilibrium has favor to the associated state. However, upon removing the small molecule compound (oxime) in vacuum based on its vacuum-sublimation ability,[15] the equilibrium will be pushed towards to the dissociated state to release more isocyanate (Figure 1b). For the latter, its dynamic nature is negligible relative to the former,[12d,14] while it can react with isocyanate

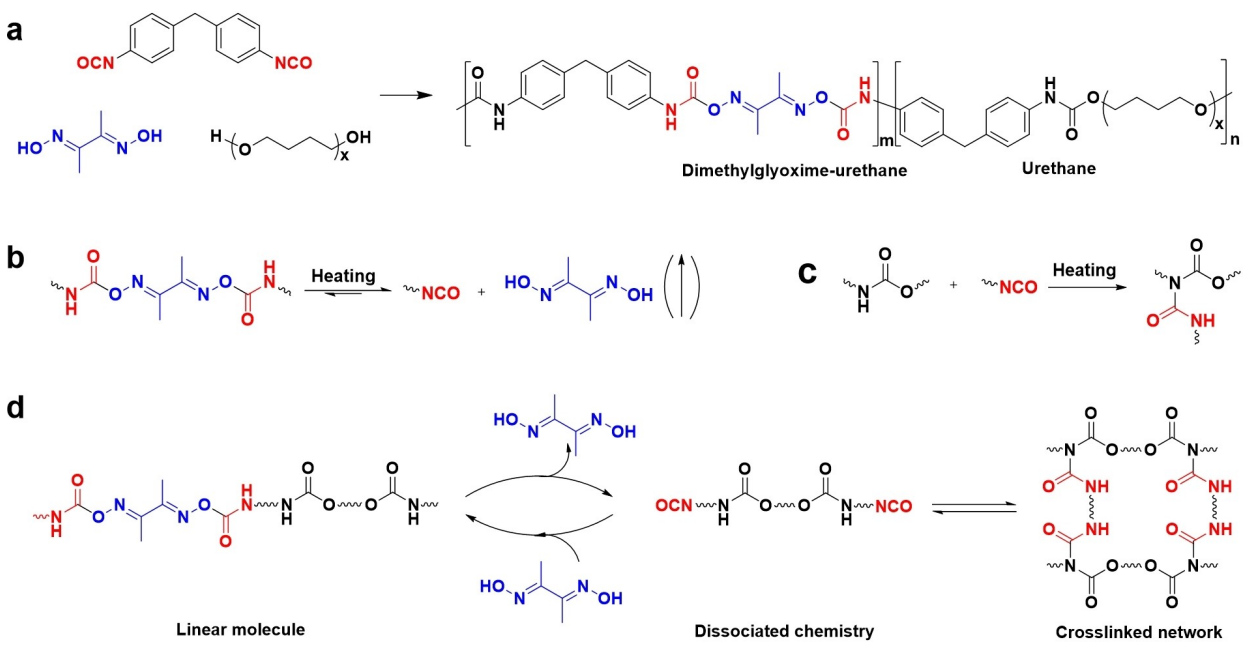

Figure 1. a) The chemistry for synthesis of TPU with dimethylglyoxime-urethane and common urethane moieties in the molecular chain. b) Shifting thermal equilibria of dynamic dimethylglyoxime-urethane to release isocyanate by removing and recovering dimethylglyoxime segment. c) The reaction of urethane with isocyanate to generate allophanate. d) The chemistry for upcycling TPU with linear molecule to CPU with crosslinked network by removing dimethylglyoxime (from left to right), and converting CPU back to TPU by returning the removed dimethylglyoxime (from right to left).

released from the reaction in Figure 1b to form allophanate at heated state (Figure 1c).[14,16] Based on the above reactions, upon heating in vacuum to remove and recover the dimethylglyoxime segment, the TPU structure will be converted from linear polyurethane molecule to crosslinked polyurethane network (CPU) (from left to right in Figure 1d). This conversion will yield a mechanical-reinforcing effect and make the material stronger than the initial one. More interestingly, the recovered dimethylglyoxime can not only serve as raw material for producing new TPU in the same fashion as shown in Figure 1a, but also convert the crosslinked network back to linear molecule (from right to left in Figure 1d) based on the fact that the relative reactivity of oxime is far more than urethane against isocyanate.[14] In this whole process, dimethylglyoxime is the only chemical reagent involved and can be recovered upon process completion.

Transformation of TPU Towards CPU

The transformation was conducted by heating the TPU sample in vacuum, accompanied by removing and recovering dimethylglyoxime segment from the sample. As shown in Figure 2a, the TPU sample was placed in the reactor bottom. Upon heating the reactor bottom, dimethylglyoxime would release from the TPU sample and deposit on the unheated reactor cap (see the inset in Figure 2a), meanwhile the TPU sample was converted to CPU material. With collecting and weighting, around 85 % of dimethylglyoxime are recovered, importantly with a high purity identical to the initial dimethylglyoxime as evidenced in their ^{1}H NMR and FTIR spectra (Figure 2b and Figure S3). The conversion of TPU to CPU was verified by dissolution experiment. As shown in Figures 2c and Figure S4, the initial TPU sample is completely dissolved in THF, acetone, DMSO, DMF and NMP due to the linear molecular structure. However, after heating at 140 °C for 5 hours in vacuum, the sample only swells but never dissolves in these solvents though they possess strong solvent powers for a wide range of solutes. This result confirms the successful conversion from linear molecule to crosslinked network. Gel fraction tests suggest the gel content of the sample increases with the heating time at 140 °C until reaching a plateau value of 88.7 % at around 10 hours (Figure 2d). This variation behavior is highly relevant to the removing ratio of dimethylglyoxime (Figure 2d), which confirms the key switch role of dimethylglyoxime for the TPU/CPU transformation. As decreasing the transformation temperature from 140 °C to 110 °C, the heating time will increase from 10 hours to more than 60 hours to reach the plateau value of gel content (Figure S5a). In contrast, change transformation temperature from 140 °C to 200 °C will shorten the time to 1 hour (Figure S5b–c), but usually will bring more side reactions. For efficiency purpose, we select 140 °C as the temperature for the TPU/CPU transformation unless otherwise noted.

Study on the TPU/CPU Transformation Mechanism

As described above in Figure 1, the TPU/CPU transformation mechanism mainly involves three steps: (1) the thermal

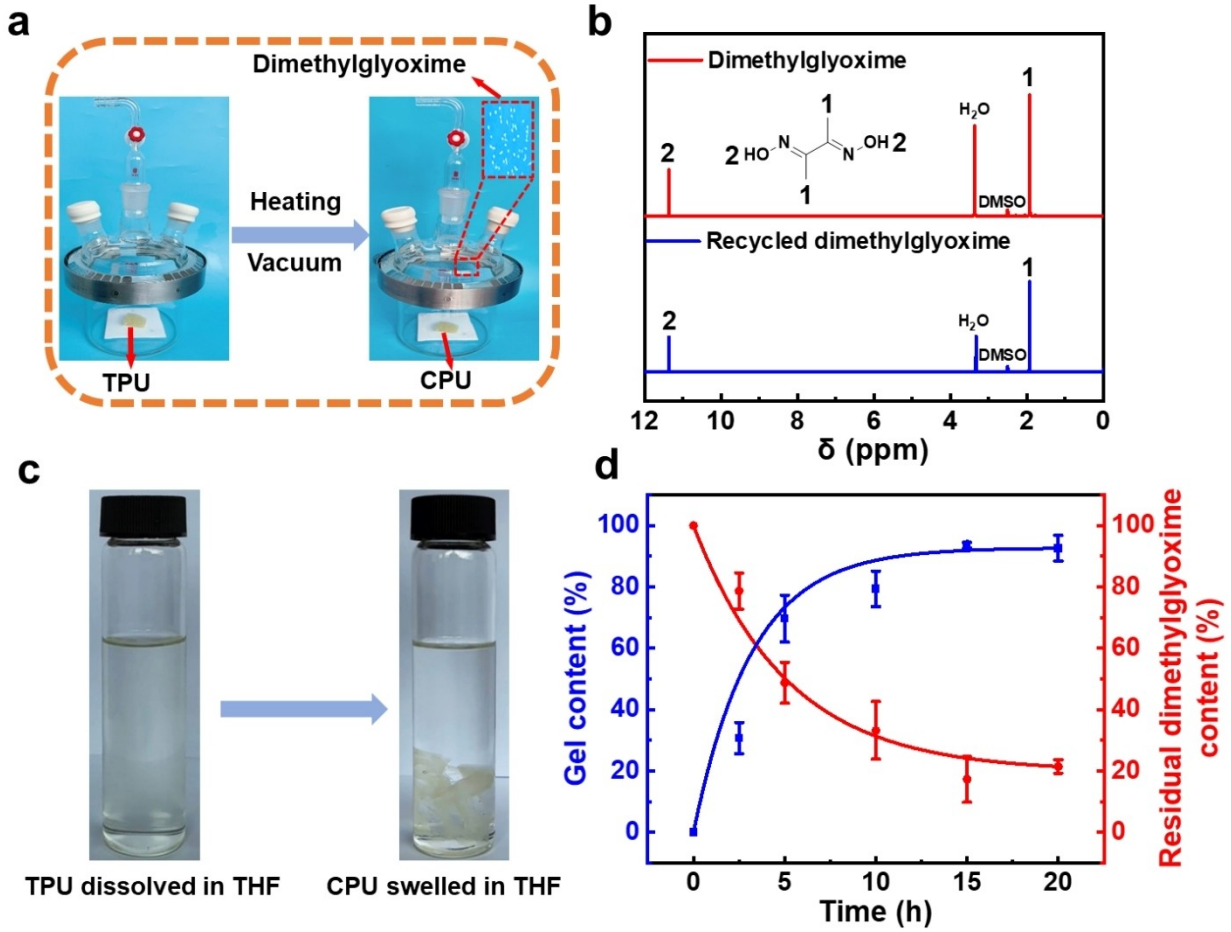

Figure 2. a) Transformation of TPU towards CPU via heating in vacuum, accompanied with the removing and recovering of dimethylglyoxime from the sample. b) ^{1}H NMR spectra of recovered and initial dimethylglyoxime. c) Photographs of the dissolution experiments, verifying the transformation of TPU to CPU. d) Evolution of the sample gel contents and residual dimethylglyoxime contents at 140 °C in vacuum with the time. The initial dimethylglyoxime content was set as 100 %.

dissociation of dimethylglyoxime-urethane moiety in TPU to generate isocyanate and dimethylglyoxime, (2) the removal of dimethylglyoxime from the sample, and (3) the reaction of urethane with the generated isocyanate to form crosslinking allophanate.

For the first step, the thermal dissociation reaction was investigated through monitoring the evolution of isocyanate (NCO) peak at around 2275 cm^{-1} by variable-temperature FTIR spectra (Figure 3a). The FTIR spectrum of the TPU sample shows no peak at around 2275 cm^{-1} at 25 °C. With raising the temperature, an NCO peak appears at 100 °C and become stronger at higher temperature, indicating the generation of isocyanate-terminated polyurethane from the dissociation reaction of dimethylglyoxime-urethane moiety (Figure 1d).

For the second step, the removal of dimethylglyoxime from TPU is based on the vacuum-sublimation behavior of dimethylglyoxime,[15] accompanied by the decrease of relevant molecular segment in the sample. For this reason, vacuum-sublimation experiment, thermal gravimetric and FTIR analyses were conducted. Vacuum-sublimation experiment was conducted using the same apparatus and condition with the TPU/CPU transformation experiment except that the initial TPU sample was replaced by dimethylglyoxime. As shown in Figure 3b, upon heating at 140 °C in vacuum, the white dimethylglyoxime powders migrate completely from the reactor bottom to the cap within 30 minutes, indicating the excellent vacuum-sublimation ability. Thermal gravimetric analysis curve of the initial TPU sample shows a weight loss in the temperature range from 180 °C to 225 °C (Figure 3c), which is ascribed to the decomposition of dimethylglyoxime segment (Figure S6). By comparison, the samples after heating in vacuum show little weight loss in this temperature range, which indicate the "removing" function of vacuum-sublimation process for dimethylglyoxime from the TPU samples. In addition, FTIR spectrum of the initial TPU sample shows a peak at around 1000 cm^{-1} corresponding to the dimethylglyoxime segment (Figure 3d). After undergoing the vacuum-sublimation process, the peak of the sample is weakened, which again confirms the removal of dimethylglyoxime from the TPU samples.

For the last step, the reaction of urethane with the generated isocyanate to form crosslinking allophanate was

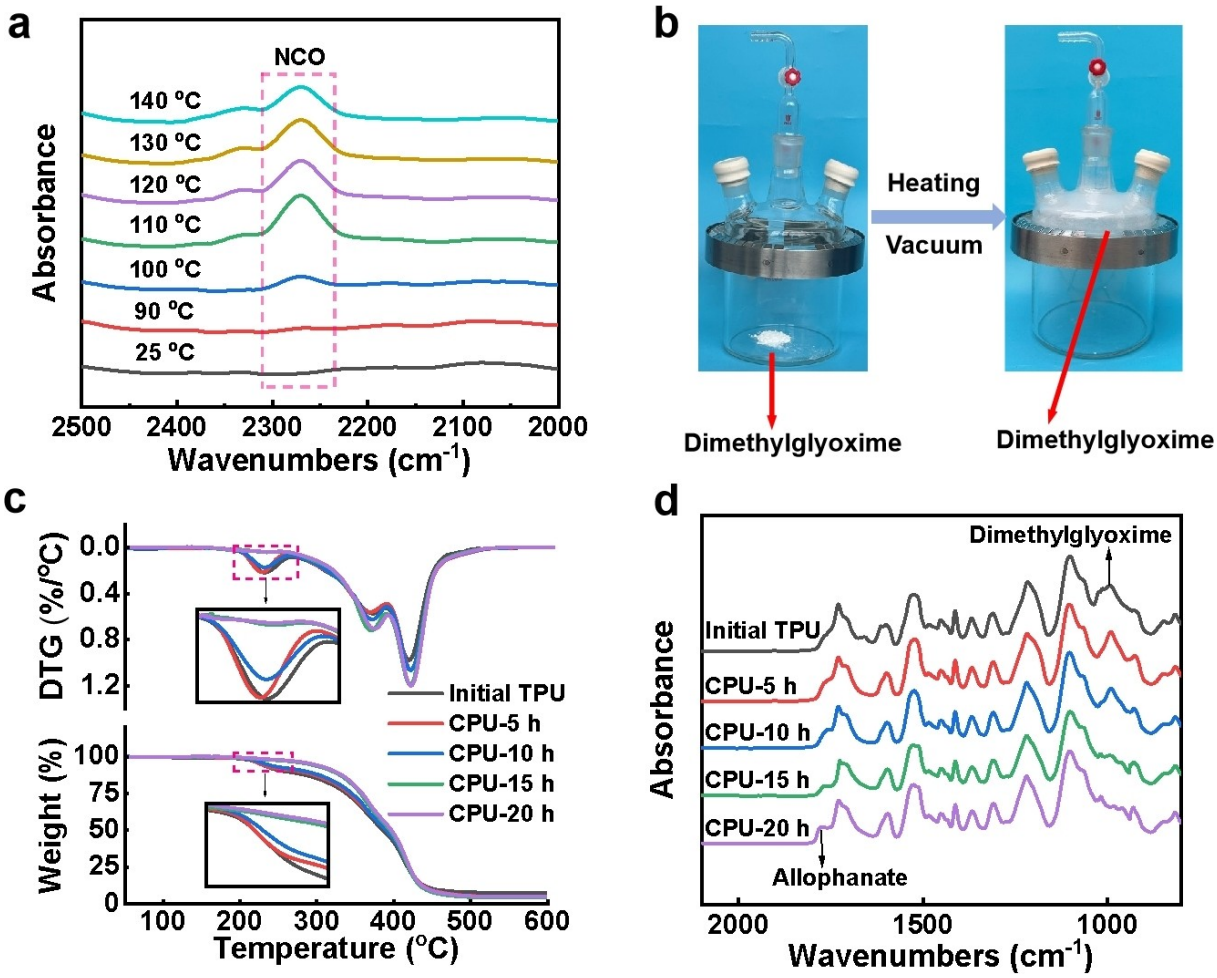

Figure 3. a) Variable-temperature FTIR spectra of TPU. b) Photographs of dimethylglyoxime in a reactor before and after heating the bottom at 140 °C in vacuum for 30 minutes. c)–d) Thermal gravimetric and FTIR analyses of the TPU samples before and after heating at 140 °C in vacuum for 5 h (CPU-5 h), 10 h (CPU-10 h), 15 h (CPU-15 h), and 20 h (CPU-20 h).

investigated by FTIR analysis. The FTIR spectrum of the initial TPU sample shows a combined peak with many shoulder peaks at around 1730 cm^{-1}, which are corresponded to the carbonyl bands of urethane bond and dimethylglyoxime-urethane in non-hydrogen bonded and/or hydrogen-bonded states (Figure 3d). After undergoing the vacuum-sublimation process, a sharp peak at around 1760 cm^{-1} occurs in the higher wavenumber direction of the spectrum, which indicates the formation of crosslinking allophanate.[16]

Enhancement of the Mechanical Properties

The TPU/CPU transformation induced by vacuum-sublimation process could significantly reinforce the polymer material based on the fact that the formed covalent crosslinked network in CPU is typically stronger than physical binding network in TPU. The stress-strain curves of the TPU samples before and after heating in vacuum at 140 °C are presented in Figure 4a. The initial TPU sample has a tensile strength of 1.6 MPa, modulus of 2.5 MPa, breaking elongation of 903 %, and toughness of 12 $MJ{\cdot}m^{-3}$, respectively (Figure 4a–e). As the thermally treatment proceeded, the mechanical properties are improved with the time. At the optimal treatment of 5 h, the tensile strength, modulus, and toughness are significantly increased to 4.5 MPa, 4.3 MPa, and 18 $MJ{\cdot}m^{-3}$, respectively, meanwhile the breaking elongation almost remain unchanged. Further prolonging the thermally treatment time (>5 h) to increase the crosslinking density, the tensile strength and breaking elongation are decreased instead of increased, which is ascribed to the molecular chain scission and degradation caused by the long-time thermally treatment. Nonetheless, the tensile strength, modulus, and toughness are consistently higher or comparable to the initial TPU. Based on the above results, we select 5 h as the treatment time for the TPU/CPU transformation.

To highlight the enhancement of mechanical properties based on our vacuum-sublimation process, a control experiment with conventional mechanical recycling method was conducted. Briefly, the TPU sample was cut into pieces and then mechanically reprocessed to obtain a new TPU film via hot-pressing (30 MPa at 100 °C for 10 min) in air. Unsurpris-

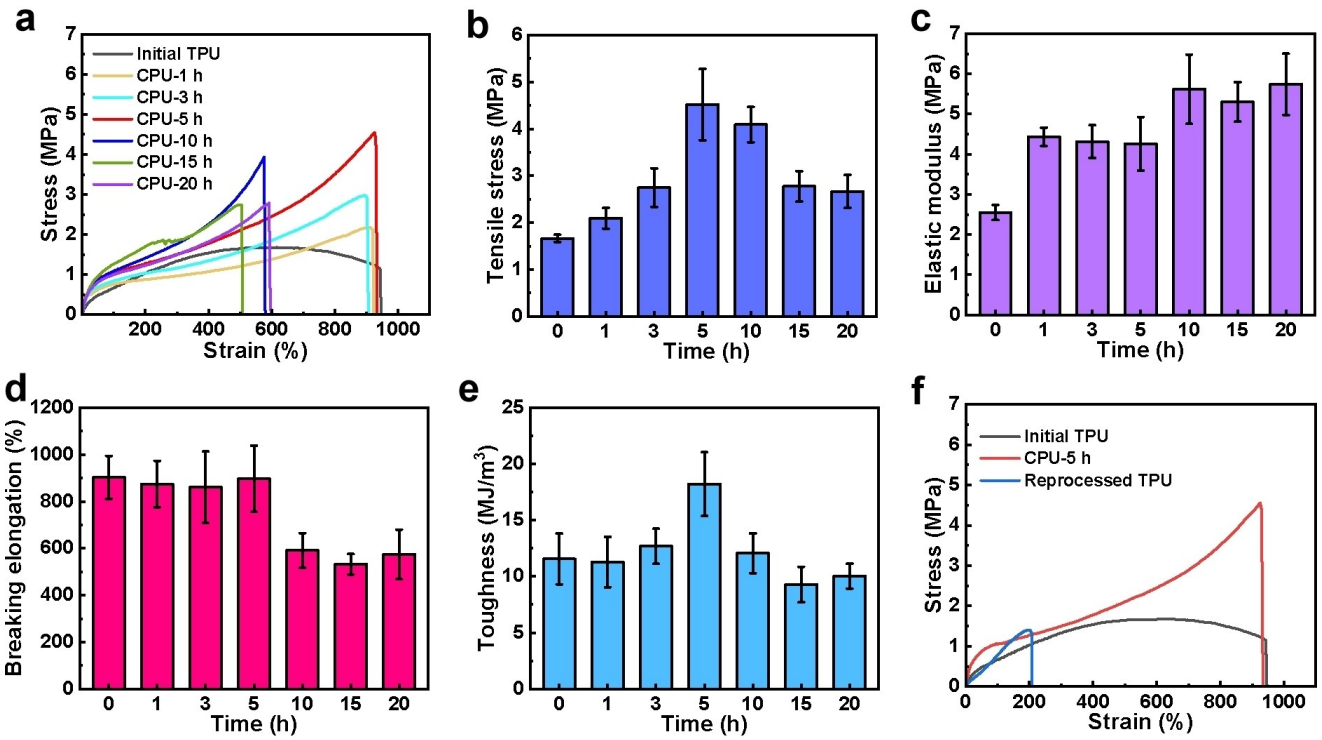

Figure 4. a) Stress-strain curves of the TPU samples before and after heating at 140 °C in vacuum for 1 h, 3 h, 5 h, 10 h, 15 h, and 20 h, and the corresponding b) tensile stress, c) elastic modulus, d) breaking elongation, and e) toughness. f) Stress-strain curves of the CPU-5 h and TPU samples before and after reprocessing via hot-pressing in air.

ingly, gel permeation chromatography analysis suggests that the molecular weight of the TPU sample significantly decreases from 46,106 g·mol^{-1} to 24,252 g·mol^{-1} after undergoing hot-pressing. The decrease is ascribed to the molecular chain scission, degradation, and oxidation under the condition of high mechanical forces, high temperature, oxygen, moisture during reprocessing.[4] Accordingly, the mechanical properties, especially the breaking elongation, of the TPU sample deteriorates significantly after mechanical reprocessing although the decrease of the tensile strength is not significantly (Figure 4f). Take this reprocessed TPU as reference, the tensile strength, breaking elongation, modulus, and toughness of the upcycled CPU are 3.2, 4.3, 3.0, and 10.6 times that of the reprocessed TPU respectively, indicating the significant upcycling effect.

Besides the mechanical properties, another key factor needs to be considered is the thermal properties. Differential scanning calorimetry (Figure S7) suggests that the CPU and the initial TPU samples have a low glass transition temperature at around −45 °C, which indicates the excellent low-temperature workability.

Reverse Transformation of CPU Back to TPU

Although the transformation of TPU to CPU could reinforce the material and realize upcycling of TPU, how to recycle the generated CPU after its service life become a new problem. Therefore, if the reverse transformation of CPU back to TPU could be realized, the lifetime of the material would be prolonged again. The reverse transformation was realized by returning the removed dimethylglyoxime to the sample. Briefly, the CPU sample and the recovered dimethylglyoxime were immersed in DMF. Upon heating at 130 °C, the sample completely dissolved within 15 min (Figure 5a), indicating the successful transformation of CPU back to TPU (Re-TPU). After removing DMF, a new TPU film was regenerated.

Compared with the initial TPU sample, the mechanical property of Re-TPU slightly deteriorates (Figure 5b) due to the fact that the inevitable side reactions at elevated temperature during the whole transformation cycle degrade the material (Figure 5c). However, the mechanical property can be improved significantly via adding a small amount of MDI (Figure 5b), a diisocyanate that can react with the terminal active hydrogen of Re-TPU and increase its molecular weight (Figure 5c). With the addition of 2 % MDI, the modulus, breaking elongation, and toughness of the regenerated TPU become better or comparable to the initial one, in spite of the lower tensile strength (Figure 5b). After increasing the dosage of MDI to 4 %, the improvement of the all-around mechanical properties is realized. Further increasing the MDI dosage could make the tensile strength and modulus higher, but result in the generation of crosslinked network and make the regenerated TPU insoluble, which is mainly ascribed to the reaction of the extra MDI with urethane/moisture to form crosslinking allophanate/biuret.

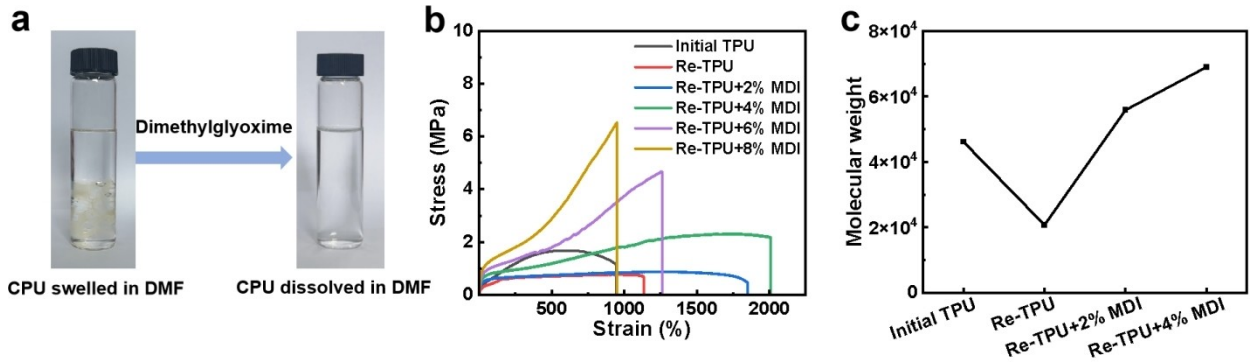

Figure 5. a) Photographs of the dissolution experiments, verifying the transformation of CPU back to TPU (Re-TPU). b) Stress-strain curves and c) molecular weights of the initial and regenerated TPU samples, and the regenerated TPU samples reinforced by MDI.

Conclusions

We demonstrate a chemical upcycling strategy for thermoplastics, especially for TPU, based on dynamic dimethylglyoxime-urethane moiety, which allows us to transform the thermoplastic waste into high-performance thermoset product. The introduction of the dimethylglyoxime-urethane moiety into the material can be readily realized via one-pot polymerization from commercially available and inexpensive reagents, making it easy to be implemented in large scale. The transformation of thermoplastic to thermoset can be readily realized by removing dimethylglyoxime via sublimation, which is also a common industrial practice. More important, the transformation is reversible, which means that the lifetime of the upcycled thermoset product can be prolonged again. Furthermore, this thermoplastics/thermosets transformation strategy can be extended beyond dimethylglyoxime-urethane chemistry and TPU material.

Supporting Information

Supporting Information is available for this paper. Correspondence and requests for materials should be addressed to Z. L. and Y. Z.

Author Contributions

Z. L. and Y. Z. conceived the concept and supervised the project. Q. S., L. L., J. Z, performed the experiments, with assistance from X.C and J.C. All authors participated in result analysis and discussion, and manuscript writing.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Upcycling · thermoplastic · thermoset · dynamic bond · dimethylglyoxime-urethane

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