

Insertion of Supramolecular Segments into Covalently Crosslinked Polyurethane Networks towards the Fabrication of Recyclable Elastomers

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Electronic Supplementary Information

Abstract Thermoset plastics have become one of the most important chemical products in the world. The consequent problem is that although the thermosets possess excellent performance in mechanical strength, they cannot be reprocessed because of the internal permanent network structures. Optimizing the molecular design of thermosets is one of the most feasible ways to improve their recyclability. Here we present a facile and robust strategy to engineer the reprocessability of thermoset polyurethanes without compromising their mechanical toughness and chemical resistance *via* adding supramolecular additives during the polymer synthesis process. By using a multiple hydrogen bonding moiety as the model supramolecular additive, we demonstrate that the mechanical properties, recyclability, and chemical resistance of the crosslinked polyurethanes can be precisely controlled by adjusting the contents of the supramolecular additive. Systematic studies on the relations between molecular design and material properties are performed, and the optimized polyurethane network with a moderate amount of the supramolecular additive achieves the right balance between the robustness and recyclability. This work provides a cost-effective and practical way to chemically engineer thermoset plastics, aiming to enable the recycling of mechanically tough and chemically stable polymer materials.

Keywords Thermoset plastics; Recyclability; Polyurethane; Supramolecular additives; Chemical resistance

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INTRODUCTION

Benefited by the superior mechanical properties, dimensional stability and chemical resistance, thermosets are of great interest in applications with high requirements of performance, such as aerospace, military and building materials.^[1–5] 65 million tons of thermosets are produced annually worldwide.^[6] However, most of them will be incinerated or landfilled inevitably after completing their missions, resulting in polluted environments, wasted resources and economic losses.^[3,7–10] The internal reason is that the networks of thermosets are crosslinked by covalent bonds permanently, once formed, hardly changed.^[1,3] Therefore, they are allowed to have excellent performance at the expense of reducing reprocessing ability. Some strategies are proposed to tackle this problem, for examples, acid and alkali treatments, high voltage discharge, biodegradation, and the use of strong acid catalysts.^[8,11–14]

However, the ways above are not satisfactory in either effect or cost, so they are hard to be accepted broadly in the industrial community. In fact, appropriate molecular designing can empower the crosslinked polymer networks with dynamism, thus making the thermosets have reprocessing ability.^[15–17] Moreover, this way does not increase the cost significantly, which has been one of the most feasible methods to enable the reprocessing of thermoset plastics.

The commonly used and effective methods are replacing the permanent covalently crosslinked structures with dynamic covalent or supramolecular networks, so that the molecular chains can achieve crosslinking and decrosslinking reversibly under certain conditions, making the networks rearrange possibly. Introducing reversible covalent bonds into thermoset plastics can balance both the robustness and reprocessing ability of polymer networks,^[7,18–26] but the chemical reactions may need catalysts, and the generation of reactive species may bring potential risks on the stability and recyclability of materials.^[27] Due to the weak binding forces, despite the introduction of supramolecular interactions enables the thermoset plastics to fracture and reform easily

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without catalysts,^[28–37] it may inevitably compromise the strength and stability of materials. In terms of thermoplastic elastomers, Liu and coworkers reported that the multiple supramolecular interactions significantly contributed to the improvement of the mechanical properties of polymer materials, yielding healable and recyclable elastomers with record-high mechanical robustness.^[38] Recently, Zhang and colleagues found that the incorporation of multiple hydrogen bonds into the main-chains of polyurea networks could permit the crosslinked supramolecular polyureas to have reprocessing ability without sacrificing their mechanical strength.^[39] Based on previous achievements, we assume a possibility of modifying thermosets by adding supramolecular functionalities as additives in polymer synthesis processes. The adjustment of material properties by adding different amounts of supramolecular additives is highly anticipated to balance the mechanical strength, chemical resistance and reprocessing ability. Most importantly, it will neither change the original synthesis process nor increase the cost significantly because of the low-content addition. Therefore, this method has the ideal feasibility in terms of both technique and cost, and it could be accepted broadly by the industrial world easily. To testify our hypothesis, in this study we choose cross-linked polyurethane networks and ureidopyrimidinone (UPy) functionalities as model thermoset plastics and supramolecular additives, respectively, to discuss the influence of the amount of supramolecular additives on material properties. We find that the recyclability of materials increases with increasing contents of supramolecular additives, while the solvent-resistance has an opposite tendency (Scheme 1a). The optimized sample determined by the orthogonal tests possesses not only excellent mechanical performance and remarkable solvent resistance but also multi-recyclability, suggesting that our strategy is efficient for chemically engineering the thermoset plastics.

EXPERIMENTAL

Materials

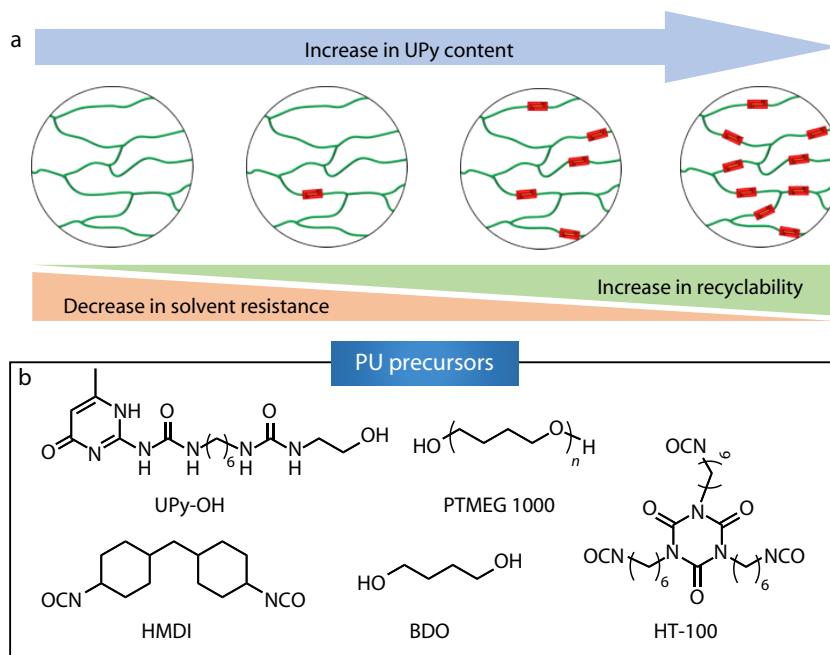
Poly(tetramethylene ether glycol) (PTMEG, $M_n=1000$ g/mol), dicyclohexylmethane 4,4'-diisocyanate (HMDI), isophorone-diamine (IPDI), 1,4-butanediol (BDO), hexamethylene diisocyanate (HDI) were purchased from Aladdin Biochemical Technology Co., Ltd. Dibutyltin dilaurate (DBTDL) was purchased from J&K Chemicals. HDI trimer (HT-100) was supplied by Wanhua Chemical Group Co., Ltd. 2-Amino-4-hydroxy-6-methylpyrimidine (AHM) was obtained from Accela ChemBio Co., Ltd. Ethanolamine was supplied by Tianjin Damao Co., Ltd. All materials and reagents mentioned above were used as received.

Synthesis of 2-(6-Isocyanato-hexylamino)-6-methyl-4[1H]-pyrimidinone (UPy-NCO)

AHM (5.00 g, 40 mmol) and 6 equiv. of HDI (40.45 g, 240 mmol) were mixed in a 100 mL three necked flask, and the mixture reacted in a N_2 environment for 24 h under moderate stirring. The crude products were then washed by *n*-hexane (*n*-Hex) for three times to fully remove the excessive HDI. Finally, the resulting products were dried at 50 °C under vacuum for 24 h to obtain white powders. The chemical structure of UPy-NCO was confirmed via proton nuclear magnetic resonance (^1H -NMR).

Synthesis of Hydroxyl Terminated Ureidopyrimidinone (UPy-OH)

UPy-NCO (5.86 g, 20 mmol) and ethanolamine (1.83 g, 30 mmol) were mixed in 180 mL of dry *N,N*-dimethylformamide (DMF), and the mixture was stirred at 100 °C for 2 h under N_2 atmosphere. Filtration was carried out when the mixture solution was still hot, then the filtrate was collected and precipitated in a mixed solvent of *n*-Hex and ethyl acetate (*V/V*=1/1) to obtain the crude product. Next, the crude product was washed with acetone for three times. Finally, the resulting product was dried at 60 °C under vacuum for 48 h to obtain



Scheme 1 (a) The influence of UPy contents on polymer properties; (b) Chemical structures of the involved PU precursors.

white powders. The chemical structure of UPy-OH was confirmed by $^1\text{H-NMR}$, mass spectrometry (MS), and Fourier transform infrared (FTIR) spectroscopy.

Preparation of HMPU-Ux Networks

The polyurethane samples were named as HMPU-U x , where x represented the weight percent of UPy-OH ($x=0, 1, 5$, or 9) in all raw materials. Taking HMPU-U5 as an example, UPy-OH and 10 mL of DMF were added into a 100 mL three necked flask and stirred for 30 min at 120 °C under N_2 atmosphere until the white powders were fully dissolved in DMF. After lowering the temperature to 80 °C, HMDI (2.63 g, 10 mmol), PTMEG (5 g, 5 mmol), and DBTDL (200 μL) were added into the flask and the reaction was conducted for 2 h to get the linear prepolymer. The prepolymer was then cooled to room temperature, and the chain extender BDO (0.53 g, 5.92 mmol) and crosslinker HT-100 (0.51 g, 1.44 mmol) were added into the flask with stirring to obtain a homogeneous solution. The solution was placed in a vacuum environment at room temperature for 5 min to remove bubbles in the polyurethane solution. Finally, the mixture solution was poured into a rectangular silicone mold (80 mm $\times$ 50 mm $\times$ 25 mm) and fully reacted in an oven at around 90 °C for 24 h. The system was then dried in a vacuum oven at 80 °C for 24 h to remove the residual DMF, and a transparent polyurethane film was obtained.

Characterizations

$^1\text{H-NMR}$ spectra were recorded on a Bruker AVANCE III HD spectrometer, CDCl_3 and DMSO-d_6 were used as the solvents. The mass spectrum was recorded on a Bruker Impact II ESI-MS spectrometer. FTIR spectra were collected on a Bruker Tensor II spectrometer in ATR mode with a resolution of 4 cm^{-1} and 16 scans. The dynamic reversibility of hydrogen bonds in polyurethane networks was determined by using a Nicolet iS50 spectrometer in ATR mode from 30 °C to 120 °C with the heating rate of 5 °C/min. Mechanical tensile test was performed on an INSTRON 3344 universal material testing machine. Rectangle-shaped polyurethane samples (25 mm $\times$ 5 mm $\times$ 0.6 mm) were prepared, and each sample was measured for 3 times with a stretching speed of 50 mm/min. Young's moduli of the samples were calculated by the slope of the stress-strain curve in the initial region within a strain of 2%. The toughness (T) was defined as the area surrounded by stress (σ)-strain (ϵ) curve, which was calculated by the following equation:

$$T = \int_0^{\epsilon_{\max}} \sigma d\epsilon \quad (1)$$

Dynamic mechanical analysis (DMA) of polyurethane networks was performed on a TA instrument Discovery 850 system. The rectangular samples were stretched at a constant frequency of 1 Hz in a temperature range from -50 °C to 125 °C with a heating rate of 3 °C/min. Stress-relaxation experiments were performed on a TA instrument Discovery 850 system, in which the samples were stretched under a deformation of 5% at 150 °C. Thermal stability analysis experiments were conducted on a TA instrument SDT 650 Thermogravimetric Analyzer. Samples (10–15 mg) were heated from 30 °C to 600 °C with the heating rate of 10 °C/min under a N_2 environment. To study the reprocessing behavior of polyurethane, samples were cut into small pieces and put into a polytetra-

fluoroethylene mould. They were then hot-pressed under 3 MPa at 150 °C for 30 min. The reprocessed polyurethane film was cooled to room temperature and cut into rectangular shape samples (25 mm $\times$ 5 mm $\times$ 0.6 mm) for further characterizations. Solvent resistance experiments were performed by soaking the rectangular samples (their mass was noted as m_0) into different solvents, including n -Hex, H_2O , dichloromethane (DCM), tetrahydrofuran (THF), toluene (TOL), DMF, dimethyl sulfoxide (DMSO), ethanol (EtOH), and chloroform (TCM) at room temperature for 24 h. The mass of the swollen samples was noted as m_1 . The samples were then transferred to vacuum oven for 24 h at 100 °C to remove the residual solvent, and the mass of the samples after fully dried was recorded as m_2 . The residual weight and swelling ratio of the samples were calculated according to the following equations:

$$\text{Residual weight (\%)} = \frac{m_2}{m_0} \times 100\% \quad (2)$$

$$\text{Swelling ratio (\%)} = \frac{m_1 - m_0}{m_0} \times 100\% \quad (3)$$

RESULTS AND DISCUSSION

As a pyrimidine derivative, UPy can produce quadruple hydrogen bonds when two UPy units assemble to form a UPy dimer. Due to high thermodynamic stability ($\Delta G_{\text{dim}} \approx -44$ kJ/mol) and dynamic reversibility ($K_{\text{off}} \approx 8.5 \text{ s}^{-1}$), the UPy dimers hold great promise for fabricating healable and recyclable supramolecular elastomers.^[40–44] Here a hydroxyl terminated UPy derivative (UPy-OH) was synthesized (the synthesis route and characterization data can be found in Figs. S1–S5 in the electronic supplementary information, ESI) and used as the supramolecular additive. As a kind of block copolymer with easily tunable and two-phased structure, the polyurethane possesses excellent adjustable properties which allow it to meet various performance demands. In this study, UPy-OH, PTMEG 1000, HT-100, and BDO were selected as the supramolecular additive, soft segment, crosslinker, and chain extender, respectively (Scheme 1b). The thermoset polyurethanes were further optimized by varying the hard segments. Under a constant feeding ratio of the supramolecular additive, IPDI, HDI and HMDI functionalities (their chemical structures can be found in Fig. S6a in ESI) were employed as hard segments for polyurethane synthesis. We found that the HMDI-containing polyurethane exhibited the overall best mechanical performance when comparing with the other two samples (Figs. S6b–S6f in ESI), and thus HMDI was selected as the optimal hard segment for polyurethane synthesis.

The HMDI-containing polyurethanes with different contents of UPy functionalities were noted as HMPU-U x , where x represented the weight percent of UPy-OH in polyurethane precursors ($x=0, 1, 5$, or 9). To confirm the successful introduction of multiple hydrogen bonds into HMPU-U x , FTIR was applied to observe the stretching vibration of carbonyl groups (C=O) at 1600–1750 cm^{-1} and the stretching vibration of N-H in urea groups near 3327 cm^{-1} in the spectra for HMPU-U x samples with different UPy contents (Fig. 1a). The absorption band for N-H shifted to lower wavenumbers as the UPy content increased, indicating gradually strengthened hydrogen bonding between molecular chains. By using Gauss peak

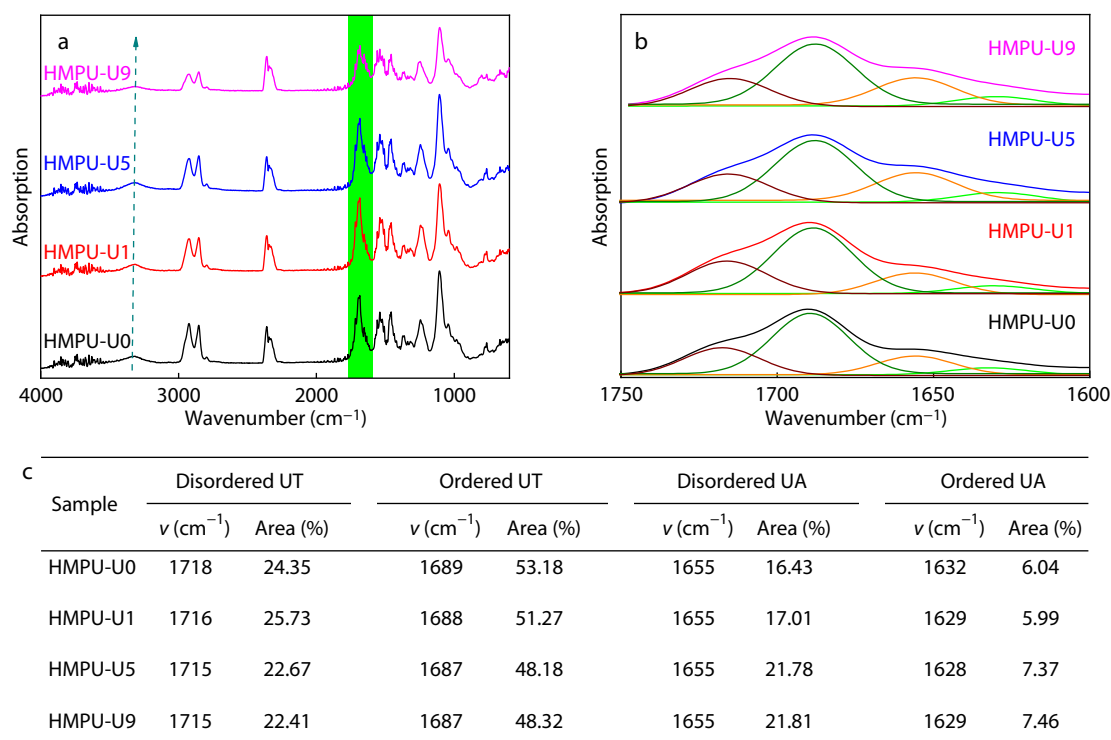


Fig. 1 (a) FTIR spectra of HMPU-Ux samples; (b) Peak fitting curves of C=O stretching vibration within the region of 1600–1750 cm⁻¹; (c) A table summarizing the ratios of C=O in different chemical environments.

fitting, the band for C=O groups was divided into four bands, including Disordered UT for disordered H-bonded C=O in the urethane groups, Ordered UT for ordered H-bonded C=O in the urethane groups, Disordered UA for disordered H-bonded C=O in the urea groups, and Ordered UA for ordered H-bonded C=O in the urea groups (Fig. 1b).^[45] The divided band positions were recorded, and the peak areas were calculated. These data were summarized in Fig. 1(c). The area of Disordered UA increased with increasing UPy content, demonstrating the existence of UPy in the form of dimer. These results also implied that the multiple hydrogen bonds had combined with the polymer chains successfully.

The photographs in Fig. 2(a) indicated that the HMPU-Ux samples with a thickness of 0.6 mm have satisfactory transparency and wholeness. To investigate the influence of UPy amounts on the mechanical properties of thermoset polyurethanes, we conducted a series of tensile tests on HMPU-Ux specimens, and the typical tensile stress-strain curves were shown in Fig. 2(b). We found that the toughness of HMPU-Ux increased from 37.2 MJ/m³ to 46.8 MJ/m³ upon the increase in UPy content from 0% to 5%. However, when the UPy content increased to 9%, the toughness of polymers decreased to 26.2 MJ/m³ (Fig. 2c). These facts suggested that the incorporation of moderate amounts of multiple hydrogen bonding moieties into the covalently crosslinked polyurethane networks would enable the materials to dissipate energy and redistribute stress fully, while too many UPy moieties in the polymer main-chains could weaken the covalently crosslinked networks, thus resulting in the decrease of material toughness. The insertion of UPy moieties into the polyurethane networks slightly decreased the breaking stress (Fig. 2d),

while the elongations at break had a similar changing trend with the toughness result (Fig. 2e). By contrast, the Young's moduli significantly increased with increasing UPy contents (Fig. 2f), which was attributed to the increase in H-bond density.

To investigate the energy dissipation of the dynamic multiple hydrogen bonds in HMPU-Ux, cyclic tensile tests were carried out. The HMPU-Ux samples were stretched to 250% strain, and then released back to 0% stress. The variation trends of the cyclic loading-unloading tests for HMPU-Ux samples with different UPy contents were generally the same: After the first cycle, significant hysteresis loop could be found in the loading-unloading curves, and from the 2nd to the 10th cycles, the hysteresis loops were smaller and approximately similar (Figs. 3a–3d). The hysteresis areas of the samples were quantitatively analyzed, and the data are summarized in Fig. 3(e). The results indicated that the introduction of UPy units enhanced the hysteresis areas of the polyurethanes. It could be ascribed to the effective disassociation of abundant multiple H-bonding between the molecular chains during the stretching which could not recovery soon.^[46] After standing at room temperature for 5 h, the samples were stretched again. The complete restoration of hysteresis areas in Fig. 3(f) suggested the recovery of multiple hydrogen bonds in the polyurethanes, in accordance with the work by Liu and colleagues.^[38,47]

To deeply elucidate the role of multiple hydrogen bonds in energy dissipation, the multiple consecutive incremental loading-unloading tests on HMPU-Ux samples were performed, and the curves are presented in Figs. 4(a)–4(d). The hysteresis areas were calculated and plotted against the max-

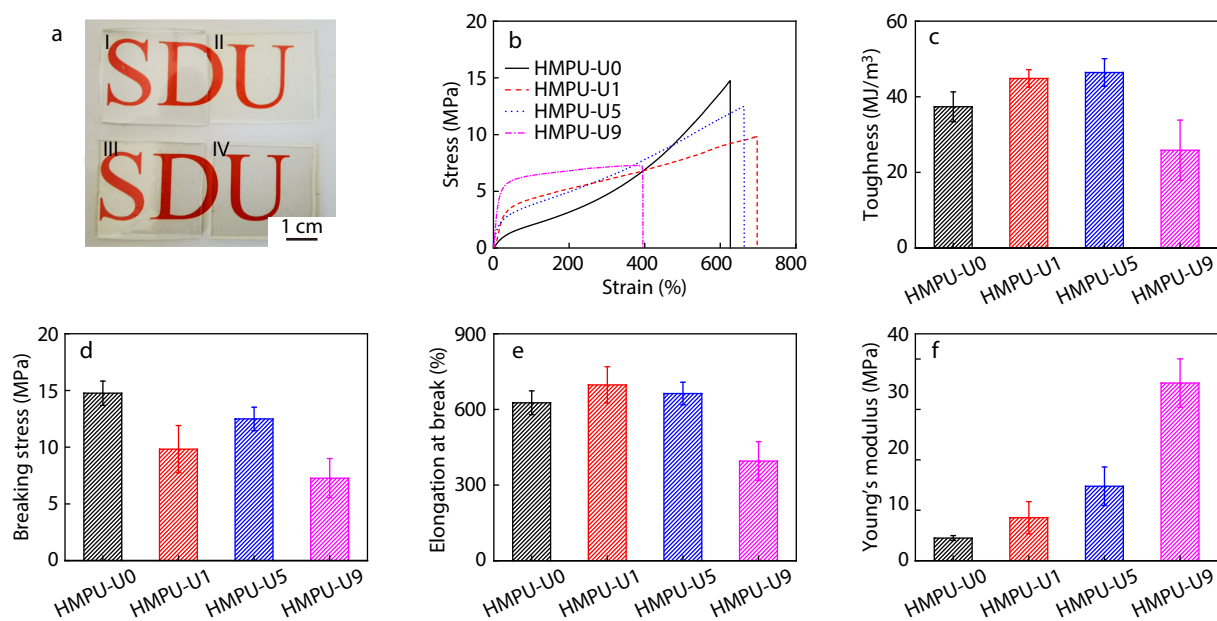


Fig. 2 (a) Digital photos of HMPU-Ux samples (I, II, III, and IV for HMPU-U0, HMPU-U1, HMPU-U5, and HMPU-U9, respectively); (b–f) Stress-strain curves (b), toughness (c), breaking stress (d), elongation at break (e), and Young's modulus (f) of HMPU-Ux samples.

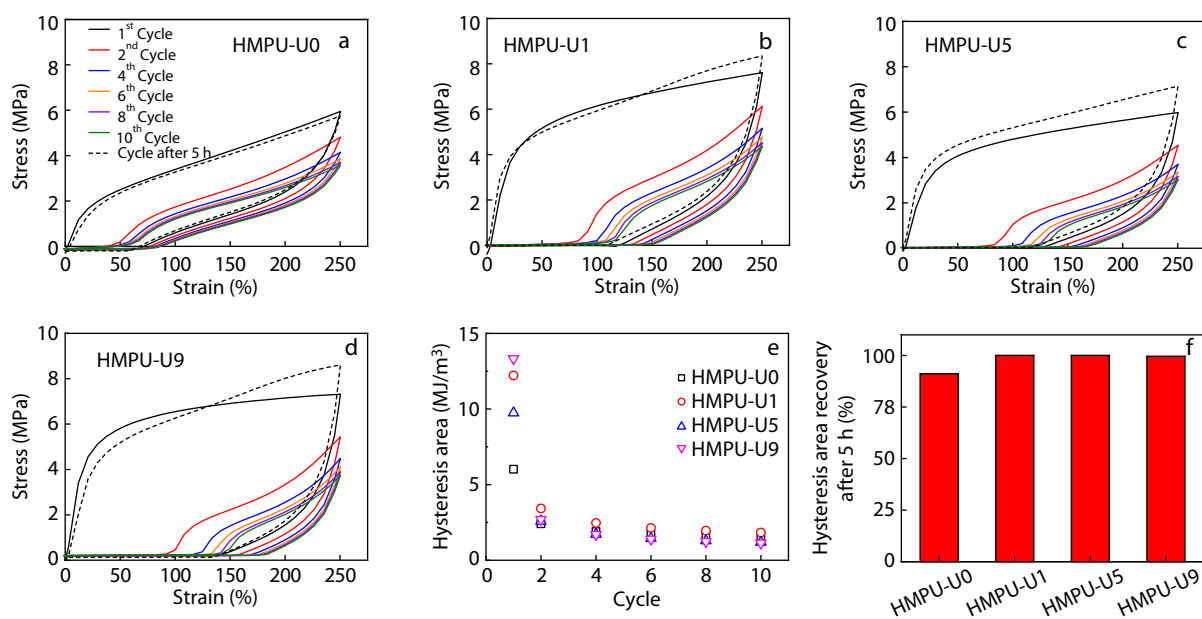


Fig. 3 (a–d) Cyclic tensile tests of HMPU-U0 (a), HMPU-U1 (b), HMPU-U5 (c), and HMPU-U9 (d) specimens in successive loading-unloading cycles and after 5 h at a strain of 250%; (e) Dissipated energy during ten successive loading-unloading processes of four specimens at a strain of 250%; (f) Hysteresis area recovery after 5 h for four specimens.

imum strains. Fig. 4(e) shows that the hysteresis energy increased with increasing incremental strains, and the slope for each curve generally maintained constant, indicating that the multiple hydrogen bonds located in the main-chains could dissipate energy homogeneously. Additionally, the slopes for HMPU-Ux samples increased steadily with increasing UPy contents. It demonstrated that the higher H-bond density, the longer time the hydrogen bonds took to recover after disassociation, along with the more obvious hysteresis phenomenon having a larger residual strain. Furthermore, under a small

strain (approximately 50%), the distinction of hysteresis areas in different HMPU-Ux samples was tiny. It could be explained by the hierarchical energy dissipation mechanism suggested by Xie and coworkers, which was caused by the friction between molecular chains.^[48] When the strain became large, the multi-dissipative mechanism included both the friction of molecular chains and the multiple H-bonding interactions played an important role in the tensile tests, resulting in the relatively large differences in hysteresis areas between different samples.

For demonstrating the dynamic properties of the multiple hydrogen bonds in the thermoset polyurethanes, DMA studies were performed. The temperature-dependent loss factors ($\tan\delta$) are presented in Fig. 5(a). The glass-transition temperatures for the four polyurethanes increased with increasing

UPy mass fractions in the polymers, which were 16.4, 31.4, 40.5, and 55.1 °C, respectively, and along with the widening peaks. This phenomenon was attributed to the increased density of multiple hydrogen bonds in the polymers. The temperature-dependent storage moduli (E') and loss moduli

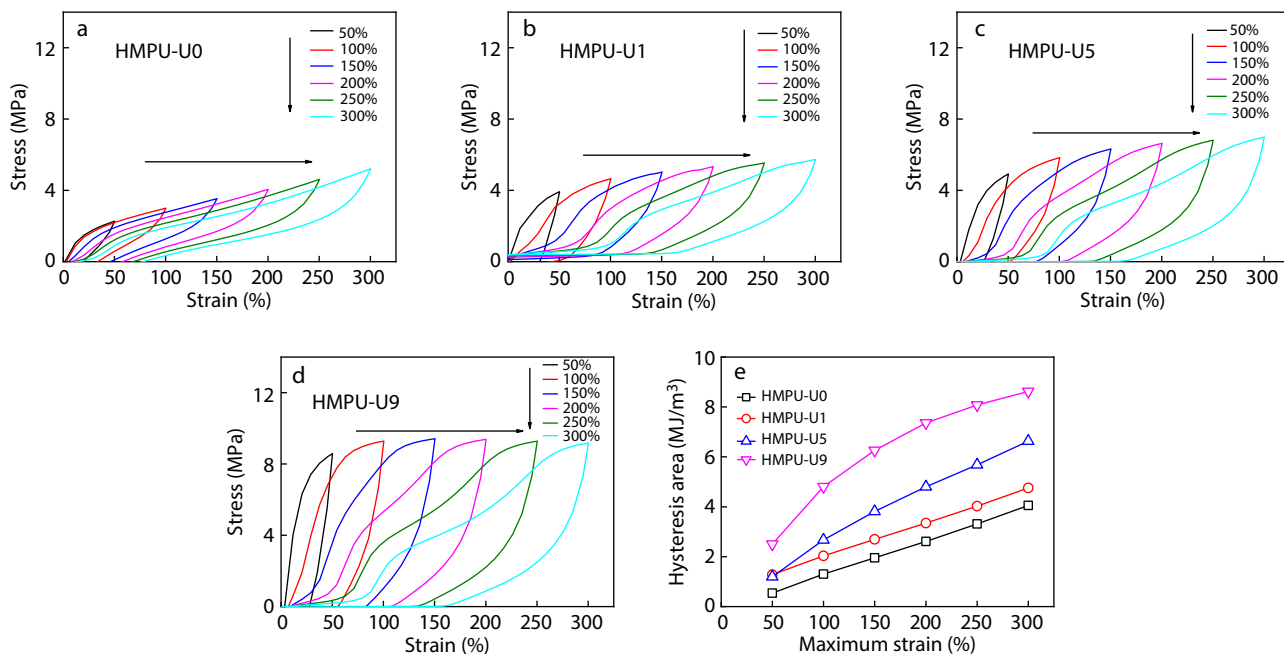


Fig. 4 (a–d) Loading-unloading curves of HMPU-U0 (a), HMPU-U1 (b), HMPU-U5 (c), and HMPU-U9 (d) specimens at different tensile strains; (e) Hysteresis area of four specimens during loading-unloading cycles at different tensile strains.

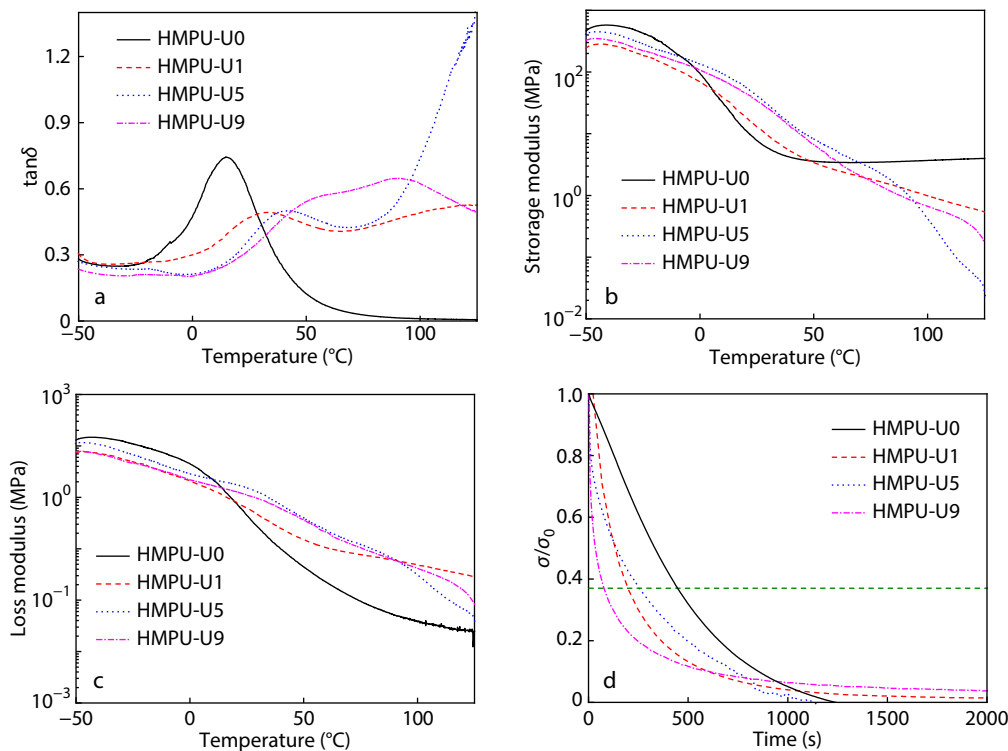


Fig. 5 (a–c) Temperature-dependent $\tan\delta$ (a), storage modulus (b), and loss modulus (c) for different polymers; (d) Stress relaxation curves of different polymers at 150 °C.

(E'') are shown in Figs. 5(b) and 5(c). Both the E' and E'' decreased with increasing temperature. For the UPy-containing samples, a decline of 3~4 orders of magnitude in storage moduli in the tested temperature range could be observed. When the temperature was above 80 °C, the E' of UPy-containing polymers dramatically decreased with temperature increasing. It could be attributed to the massive dissociation of multiple hydrogen bonds, which resulted in the intense movement of the polymer chains. At the same time, the E' of HMPU-U0 maintained a platform up to 125 °C due to the lack of hydrogen bonds.^[49] The comparison of dynamic characteristics of polyurethanes was also carried out by stress relaxation experiments with a constant strain at 150 °C (Fig. 5d). The relaxation time for HMPU-U0 was larger than the other three samples. It is evidently demonstrated that the insertion of supramolecular segments into the polymers enhanced the dynamism of polyurethane molecular chains.

The recycling and reprocessing of thermoset polyurethanes are highly demanded. Fig. S7 (in ESI) shows that our HMPU-Ux samples have high thermal stability below 190 °C. Therefore, the reprocessing temperature for our samples was set up as 150 °C, much lower than the decomposition temper-

ature. The recycling property of the thermoset polyurethanes with UPy functionalities was studied by comparing the mechanical properties of the samples before and after reprocessing. A series of pre-experiments were conducted to optimize the reprocessing condition (Fig. S8 in ESI), which was finally determined to be hot-press in mould at 150 °C for 30 min under a stress of 3 MPa. By using this condition, the thermoset polyurethane without UPy can be recycled because of the transesterification reaction catalyzed by DBTDL under high temperature,^[50] but the toughness is lower than 20% of the original value after 3 cycles of recycling (Figs. 6a–6d). The UPy-containing thermoset polyurethanes exhibit better recyclability, and the reprocessing ability of the samples are generally enhanced with increasing UPy contents in the polymers (Figs. 6e–6p). After 3 cycles of reprocessing, the toughness of HMPU-U9 was 16.0 MJ/m³, achieving 60.9% of the original sample. Though HMPU-U9 had the overall best reprocessing ability, HMPU-U5 held the highest toughness after 3 cycles of reprocessing, which was 20.0 MJ/m³. These results testified to the importance of multiple hydrogen bonds for improving the recyclability of thermoset plastics. After 3 cycles of reprocessing, the thermal stability of the polymer

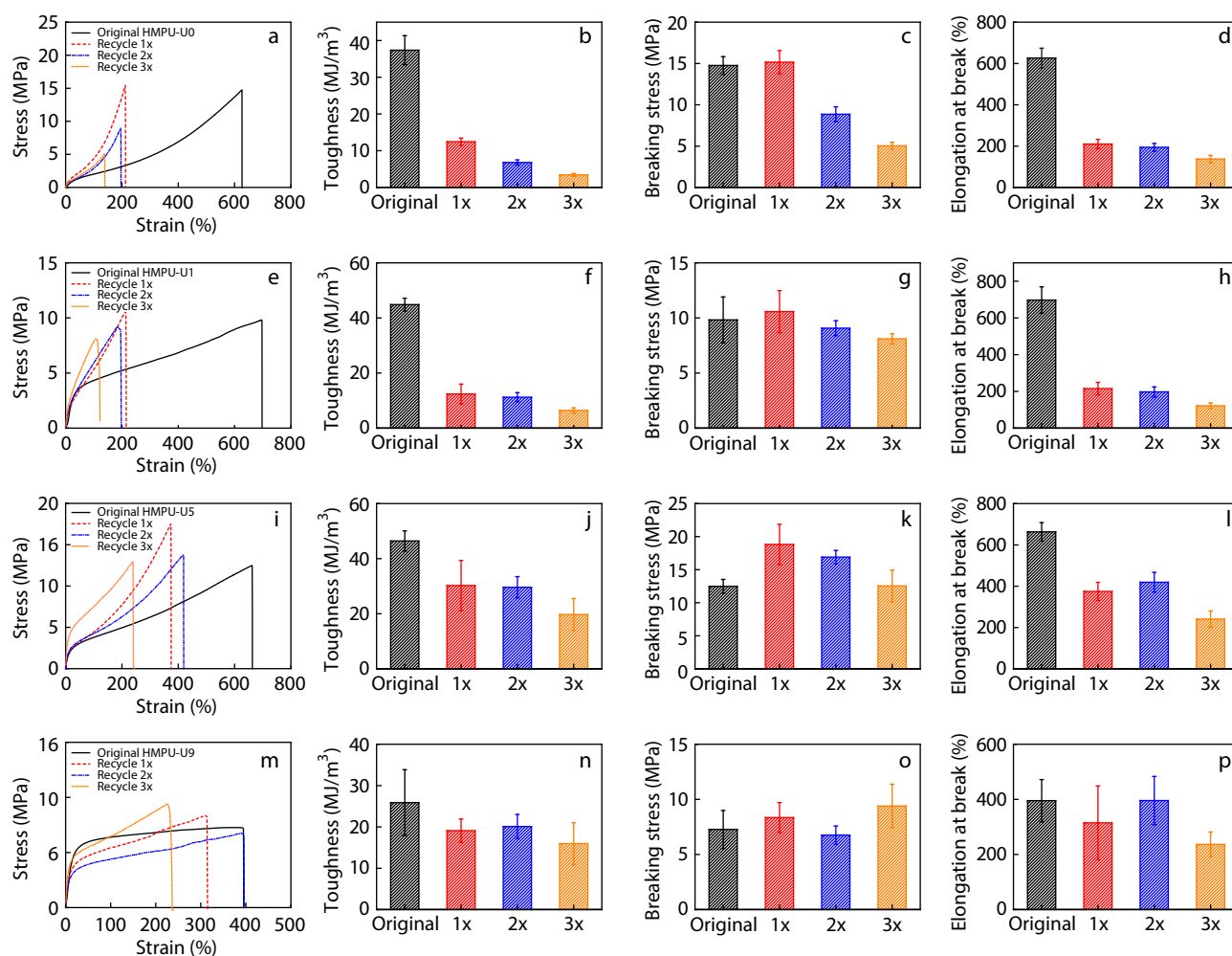


Fig. 6 Stress-strain curves (a, e, i, m), toughness (b, f, j, n), breaking stress (c, g, k, o), and elongation at break (d, h, l, p) for HMPU-U0 (a–d), HMPU-U1 (e–h), HMPU-U5 (i–l), and HMPU-U9 (m–p) before and after reprocessing for different time.

networks slightly decreased (Fig. S9 in ESI), implying the breaking of a small portion of covalent bonds in the polymer networks by the repeated cutting.

Chemical resistance is an inherent property of thermoset plastics, and theoretically the addition of dynamic units can compromise this excellent performance to some extent. To testify this assumption, dissolution experiments of HMPU-Ux were performed by immersing the specimens in different solvents including *n*-Hex, H₂O, DCM, THF, TOL, DMF, DMSO, EtOH, and TCM for 24 h at ambient conditions and then drying. The swelling ratios and residual weights of different samples in different solvents are shown in Fig. 7. HMPU-U9 exhibited apparent dissolution in most solvents except *n*-Hex and H₂O (Fig. 7d) due to the high UPy content. By contrast,

the chemical resistance for HMPU-U1 and HMPU-U5 was close to the crosslinked polyurethane without UPy (Figs. 7a–7c). In fact, HMPU-U5 had good chemical resistance against *n*-Hex, H₂O, DMSO, and EtOH in both residual weights and swelling ratios (Fig. 7c). It suggested that the insertion of a small amount of supramolecular additives would not significantly reduce the chemical resistance of covalently crosslinked polyurethane networks. Among the HMPU-Ux samples, HMPU-U5 had the highest toughness before and after recycling, as well as the satisfied chemical resistance, and it was, therefore, chosen as the optimal sample for further studies.

HMPU-U5 was further studied by variable temperature FTIR characterization to study the dynamic behavior of hydrogen bonds, and the whole spectra were shown in Fig. 8(a). The

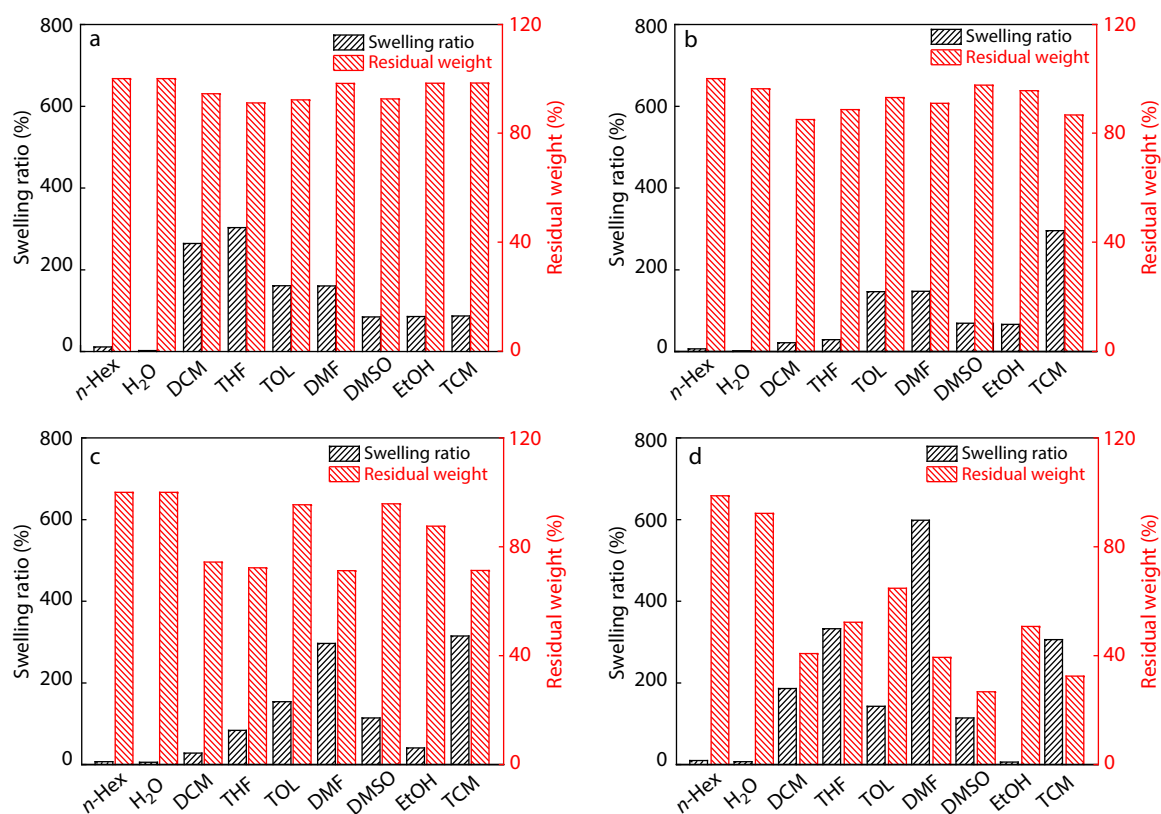


Fig. 7 Swelling ratios and residue weights of HMPU-U0 (a), HMPU-U1 (b), HMPU-U5 (c) and HMPU-U9 (d) after soaking in different solvents for 24 h.

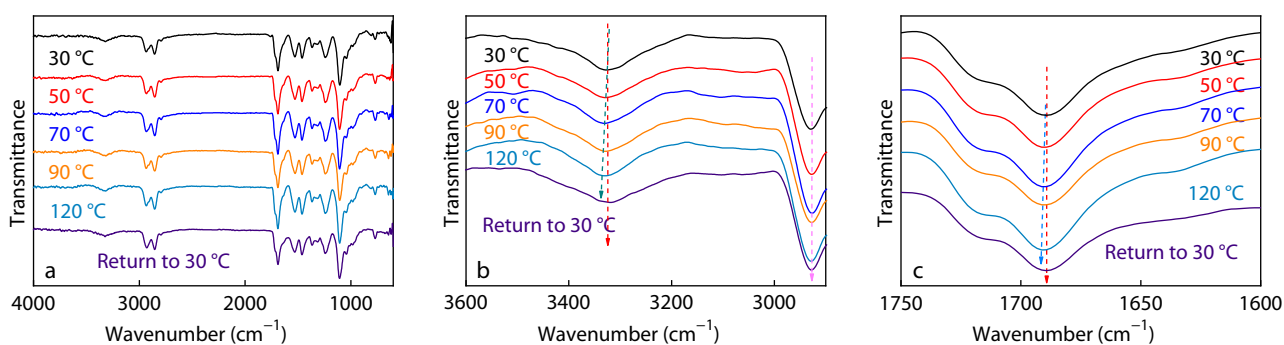


Fig. 8 *In situ* variable-temperature infrared spectra of HMPU-U5 with the wavenumber ranges of (a) 4000–500 cm^{−1}, (b) 3600–2900 cm^{−1} and (c) 1750–1600 cm^{−1}.

band assigned to the stretching vibration of C—H lied in 2930 cm^{-1} was set as a reference, and the band attributed to the stretching vibration of N—H at 3326 cm^{-1} shifted to 3336 cm^{-1} with temperature increasing from $30\text{ }^{\circ}\text{C}$ to $120\text{ }^{\circ}\text{C}$ (Fig. 8b). Similarly, the band ascribed to the stretching vibration of C=O shifted to higher wavenumbers gradually with increased temperature (Fig. 8c). These facts revealed the fracture of H-bonds in the polyurethanes following the temperature increase. When the temperature decreased back to $30\text{ }^{\circ}\text{C}$, the recovery of the bands for N—H and C=O bonds to the original positions was observed, which demonstrated the thermal reversibility of the hydrogen bonds in the thermoset polyurethanes. This was critical for reprocessing of the thermoset polyurethanes.

CONCLUSIONS

In this study, we introduce a concept of supramolecular additives for chemically engineering the covalently crosslinked polymer networks. A series of characterizations on material mechanical performance, dynamic property, recyclability and chemical resistance are performed to study the design-structure-property relationships in the supramolecular additive-containing covalently crosslinked polyurethane networks, thus verifying the feasibility to use supramolecular additives for the modification of thermoset plastics. It should be emphasized that our work focuses on the establishment of a robust and practical strategy to enable the thermoset plastics recyclable without sacrificing their mechanical toughness and chemical resistance, other than inventing new polymer materials with high performance. It is highly anticipated that this strategy can improve the properties of thermoset plastics on the premise of preserving the existing synthesis process and cost, by adding a small amount of supramolecular additives, so as to develop a suitable way for industrial production of reprocessable thermoset plastics.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2651-2>.

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