Recyclable-by-design thermosets

Degradable Polyurethane by Acylhydrazone Dynamic Covalent Bond

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Dynamic covalent bonds enable debonding and rebonding on demand, as well as facilitating end-of-life recycling [1,2]. Acylhydrazone chemistry offers a material with high stability under neutral and basic conditions making it a promising candidate for materials research, though the material is susceptible to acid degradation which then can be exploited, making it widely applicable in self-healing with potential for reprocessing and recycling.

Proof of concept design (linear PU)

The acylhydrazone chemistry was incorporated into the linear polyurethane by synthesising a series of monomers. The cured polyurethane showed exchange reaction on addition of a ketone (acetone) and in the presence of acid (glacial acetic acid). The linear PU could be readily dissolved in the solvent mixtures, enabling degradability of the polymer (Figure 1a).

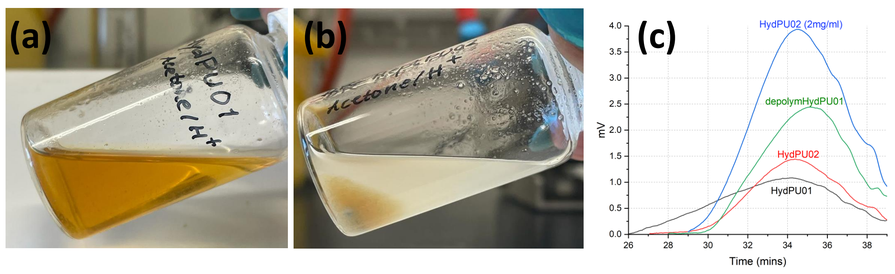

Figure 1: Degradation test of linear (a) acylhydrazone PU, and (b) control PU, in acetone in the presence of acetic acid, and (c) GPC result of the linear acyl hydrazone PU.

The degradation (the exchange reaction) was not occurred in the control sample with diol without acylhydrazone linkage, proving the concept design in the linear polymer (Figure 1b).

3D Network crosslinked PU synthesis and test

The concept of incorporation of acylhydrazone linkage into the polymer backbone was developed into the 3D network polyurethane (TriHydPU) by synthesising the preinstalled acylhydrazone diol followed by the reaction with isocyanate trimer with index of 110. The network PU showed degradation upon addition of acetone in the presence of acid (Figure 2a, b). The degradation (the exchange reaction) was not occurred in the control sample with diol without acylhydrazone linkage (Figure 2c, d). TriHydPU also demonstrated sol-gel-sol transition due to the bond exchange reaction with hydrazine monohydrate (Figure 2e-h).

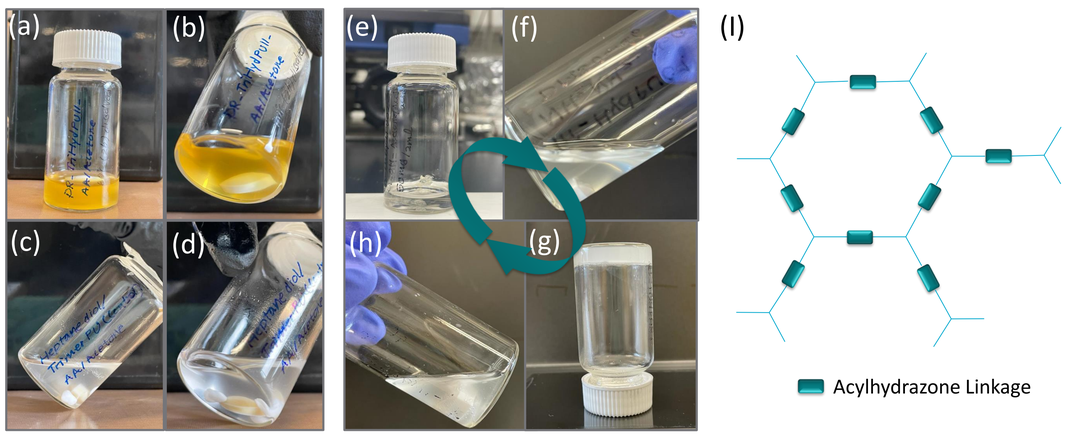

Figure 2: (a, b): TriHydPU sample dissolved in acetone and in the acidic medium, (c, d): TriPU-control not dissolved under the same conditions, (e, f, g, h): sol-gel-sol transition of TriHydPU with $NH_2NH_2.H_2O$ due to the bond exchange reaction, (f) schematic of TriHyPU 3D network.

Properties of Thermoset PU

Dynamic materials feature intrinsically dynamic functions, such as self-healing and reprocessing capabilities, however, in most cases, being a trade-off with mechanical robustness [3-5]. We performed dynamic mechanical analysis (DMA) and rheological analysis (Figure 3a and b) to understand the temperature dependency of their mechanical properties.

- **Mechanical Properties**: Tensile tests of TriHydPU showed identical stress and strain at break and very high young modulus in respect to the TriPU-control (Table 1).
- **Thermal properties**: DMA tests of TriHydPU demonstrated higher T_g and therefore thermal stability compared to that of TriPU-control.
- **Rheological properties**: Shear storage and loss moduli showed dependency to the angular frequency due to the dynamic bond.
- **Self-healing properties**: TriHydPU also showed self-healing properties (Figure 4).

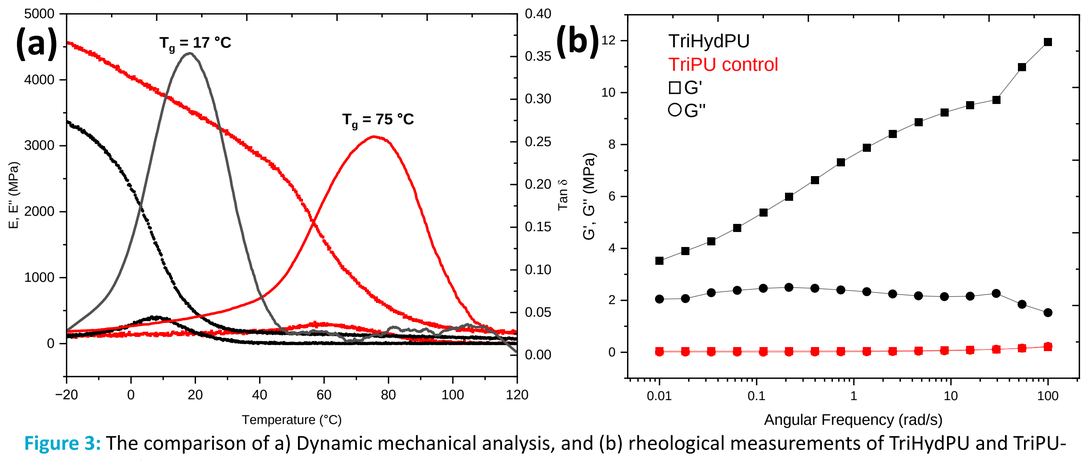

Figure 3: The comparison of a) Dynamic mechanical analysis, and (b) rheological measurements of TriHydPU and TriPU-control samples.

Table 1: Results from stress-strain tests on 3D network acylhydrazone PU (TriHydPU) in different polymer concentrations (TriHydPU05, 13, and 20) compared to that of control polymer with no acylhydrazone (TriPU-control).

SAMPLE	POLYMER CONCENTRATION (%)	FILM FORMATION	STRESS AT BREAK (MPA)	STRAIN AT BREAK (%)	YOUNG MODULUS (MPA)
TriHydPU05	5%	✗	-	-	-
TriHydPU13	13%	✓	17.30	38	794.15
TriHydPU20	20%	✓	24.60	44	1784.84
TriPU-control	20%	✓	20.07	42	398.14

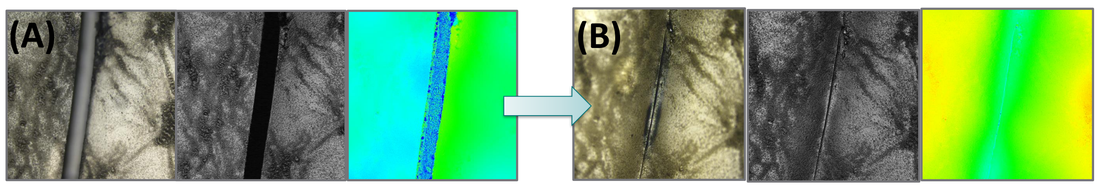

Figure 4: The self-healing properties of TrihydPU13 sample. A) A deep cut of 180 µm reduced to B) 40 µm after a drop of acetic acid dripped on it and heated at 60 °C for overnight (photos taken by laser optical microscope LEXT Olympus, objective lens, 3D optical image and heigh image, respectively).

FOR FURTHER INFORMATION

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