Chiral augmentation of self-repair in thiourea-based polymers

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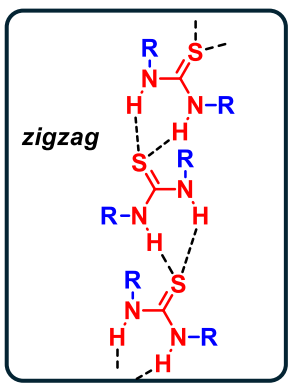
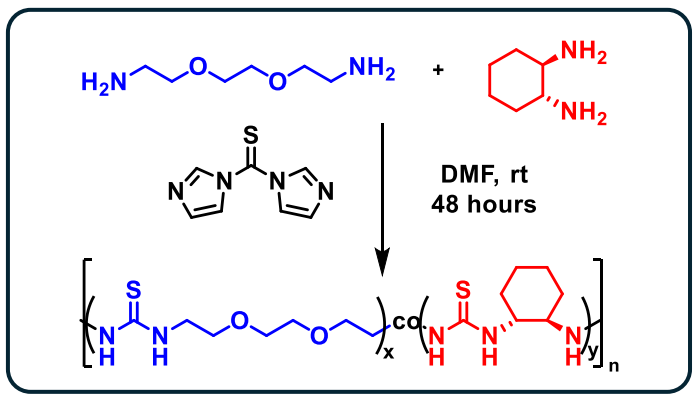
Introduction



Incorporating hydrophobic domains into thiourea–ethylene glycol backbones enables robust, self-healing materials through flexible hydrogen bonding and domain formation. Unlike classical ureas, thioureas form more adaptable, zigzag H-bond arrays that support healing as demonstrated before by Aida et al [1,2].

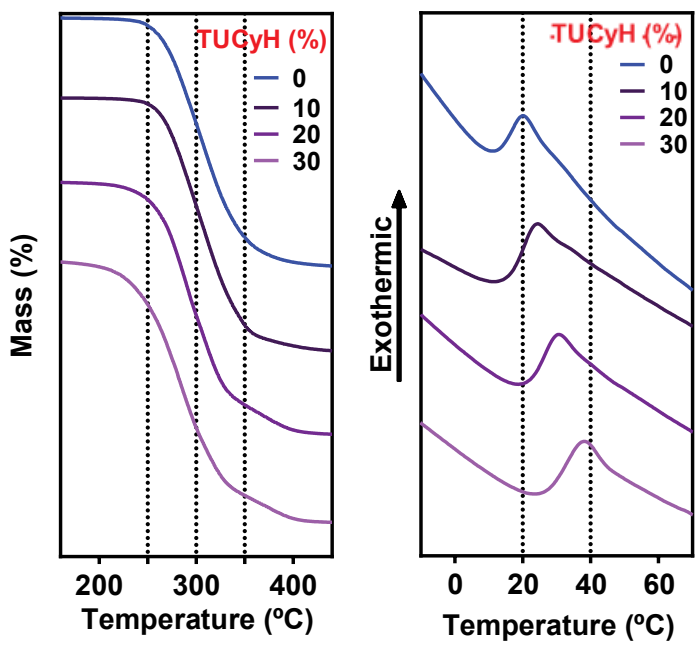
Here, we explore the effect of chirality on supramolecular organization by embedding enantioenriched 1,2-disubstituted cyclohexyl thioureas (**TUCyH**) into poly(**TUEG$_3$**). Copolymers with 10–30 mol % **TUCyH** were synthesized to probe hierarchical self-assembly and mechanical reinforcement.

Synthesis and compositions



Compound name	TUCyH %	Degree of polymerization
Poly(TUEG$_3$)	0	58
Poly(TUEG$_3$^{90}-(1R,2R)TUCyH^{10})	10	67
Poly(TUEG$_3$^{80}-(1R,2R)TUCyH^{20})	20	57
Poly(TUEG$_3$^{70}-(1R,2R)TUCyH^{30})	30	55

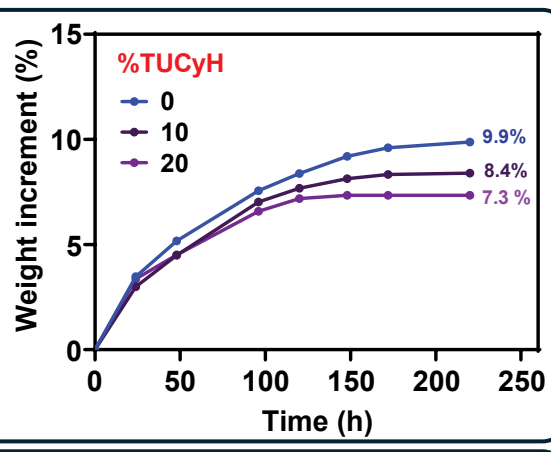
Thermal and Mechanical Properties



TGA: all copolymers showed thermal stability up to 250 °C.

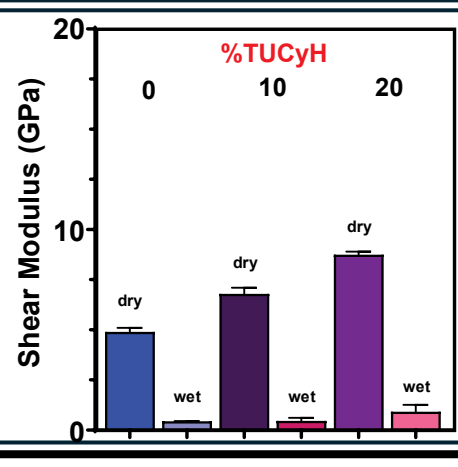
DSC: Tg increases with a higher % **TUCyH**.

Exposure to high humidity:
Water intake is lower for sample specimens with higher **TUCyH** content.



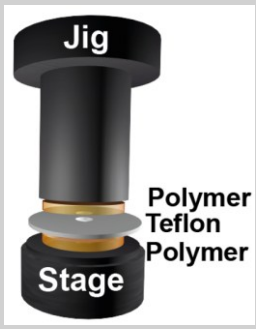
Shear moduli(G'):
G' increases linearly with % of **TUCyH**

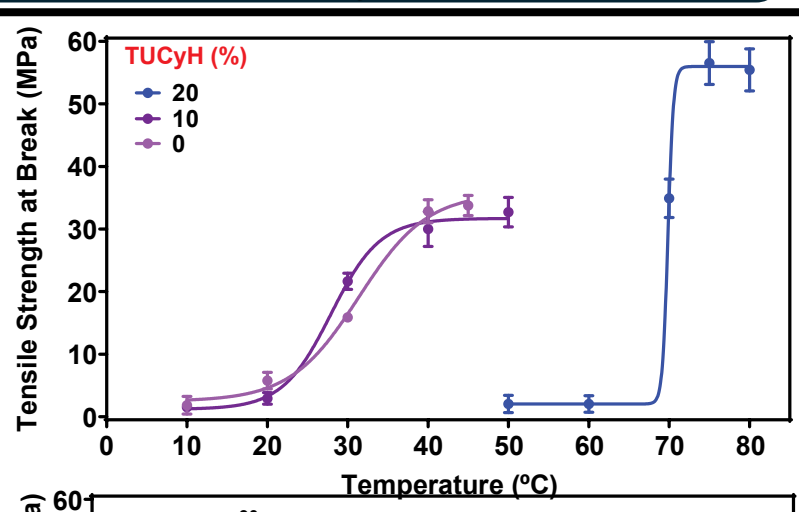
G' decreases significantly for samples after water absorption.

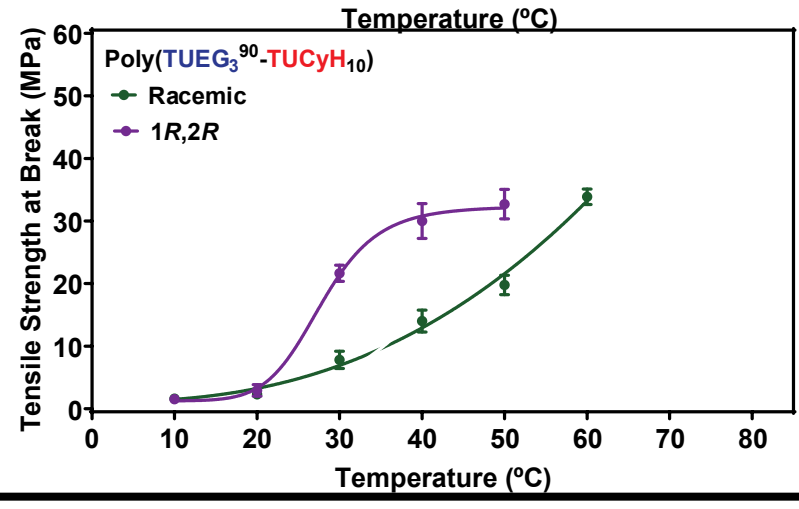


Self-Healing study

Method: Two sample discs are melted and joined through a hole in a PTFE sheet, then pulled apart to fracture. After healing at various temperatures, they are re-broken to measure tensile strength at break.







Results: The healing curve of 10% **TUCyH** copolymer is nearly indistinguishable from pure **TUEG3**.

When 20% of **TUCyH** is incorporated the healing curve is shifted to higher temperatures and the healing ability of the material is increased.

The racemic mixture of 10**%** **TUCyH** shows different healing behavior with respect to the enantiopure material.

Conclusions

- Incorporation of **TUCyH** in **TUEG3** polymers allows:
  - Improvement of thermal stability and increment of T_g
  - Increased storage moduli (G')
  - Shifting of healing to higher temperatures
- The 10% **TUCyH** enantiopure copolymer healing is distinct from the racemic analog.

References:

(1) Yanagisawa, Y. et. al, Mechanically robust, readily repairable polymers via tailored noncovalent crosslinking. *Science* **2018**, *359*, 72-76

(2) Fujisawa, Y. et. al, Mechanically Robust, Self-Healable Polymers Usable under High Humidity: Humidity-Tolerant Noncovalent Cross-Linking Strategy. *J. Am. Chem. Soc.* **2021**, *143*, 15279−15285;

Fundings:

TED2021-130285B-I00 and NWO