Self-Blown Non-Isocyanate Polyurethane Foams with Disulfide-based Covalent Adaptable Networks: Enhanced Reprocessability And Adhesive Properties

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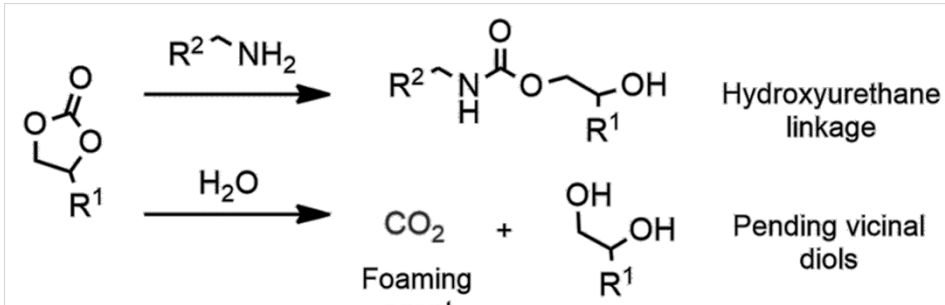
INTRODUCTION

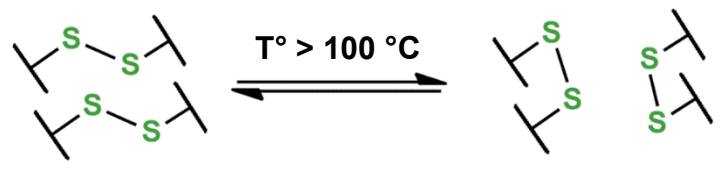
Polyurethane (PU) foams are widely used for insulation, comfort, or shock absorption purposes. Unfortunately, they are produced from toxic isocyanates and are difficult to recycle. Non-isocyanate PU foams such as polyhydroxyurethane (PHU) foams represent a promising alternative, with interesting dynamic hydroxyurethane linkages. However, their dynamicity is **slow** and requires **high temperatures** (160 °C), thus significantly degrading the material.

Reactions at play in water-induced self-blown PHU foams:



OBJECTIVES & STRATEGY

➢ Facilitate the reprocessing of the foams through the introduction of **disulfide bonds** in water-based PHU foams, as additional dynamic linkages



CHALLENGE

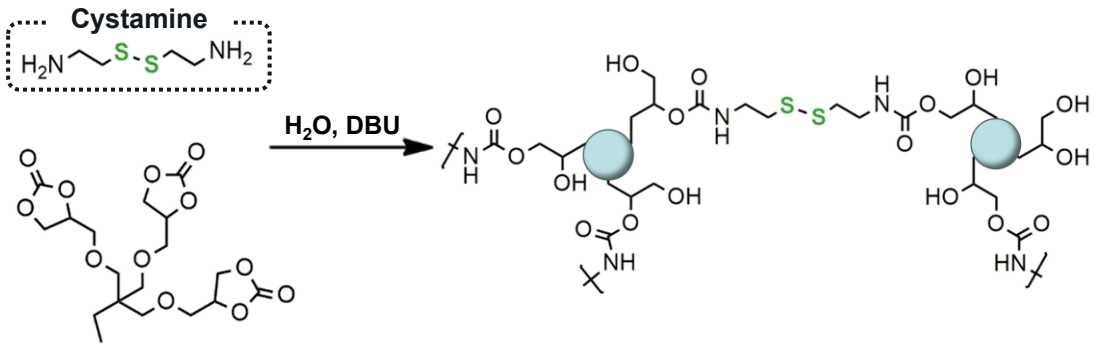
100 °C

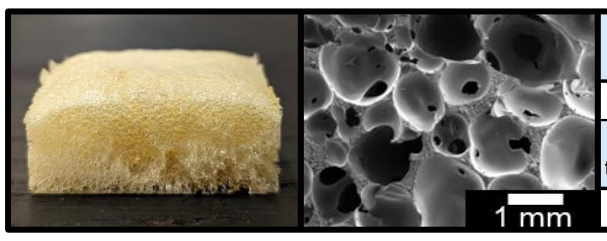
Competitive foam formation and disulfide bond dissociation

Will the foam collapse ?

RESULTS

CYSTAMINE-BASED WATER-INDUCED SELF-BLOWN PHU FOAM:





Gel content (%)	Density (kg/m³)	Cell size (mm)
95.6 ± 0.3	232 ± 19	0.88 ± 0.29
Glass transition temperature (°C)	Degradation temperature (°C)	
29.6	250	

Figure 1: Formulation, representation and characteristics of the cystamine-based PHU foam

APPLICATION OF THE REPROCESSED MATERIAL: A REUSABLE ADHESIVE

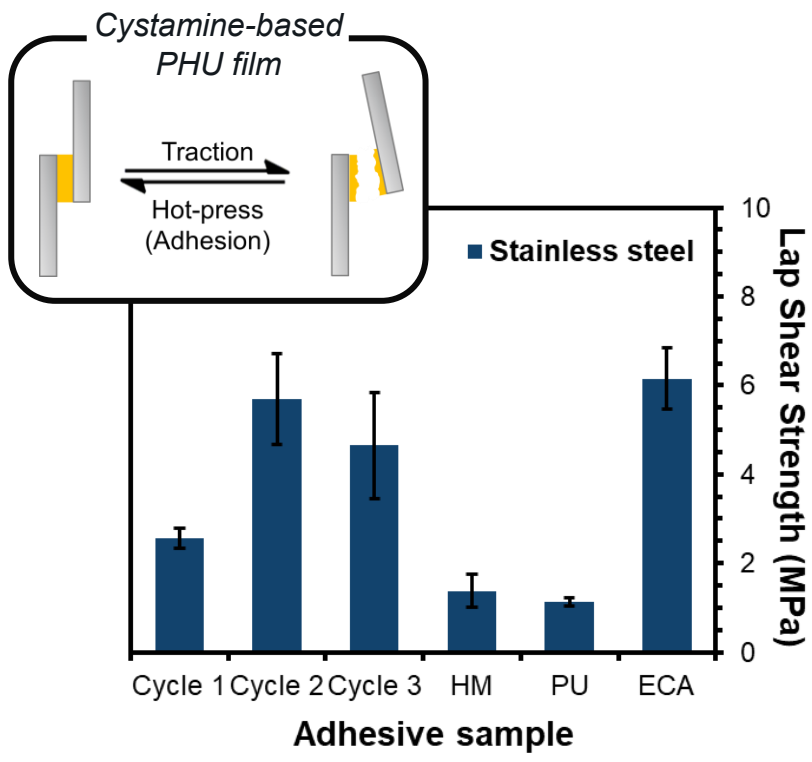


Figure 4: Lap shear strength tests conducted with stainless-steel substrates. Cycle 1, 2, 3 represent the tests conducted for 1 to 3 traction-adhesion cycles, and HM, PU and ECA represent commercial adhesives, respectively hot-melt ethylene-vinyl acetate, PU adhesive, and ethyl cyanoacrylate.

FOAM REPROCESSING AND RHEOLOGY STUDY:

➔ Crack-free, transparent and homogeneous film
➔ Milder reprocessing conditions (*vs* PHU foam without disulfide bonds: 170 °C, 5 tons, 2 h)

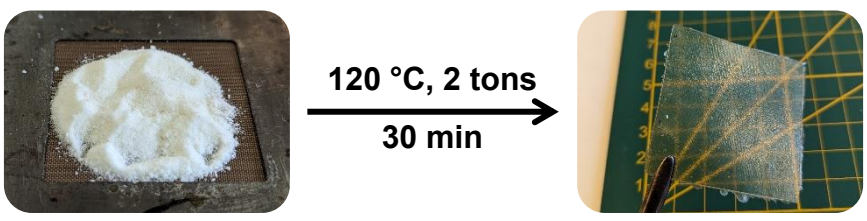


Figure 2: Hot-press reprocessing of the ground foam

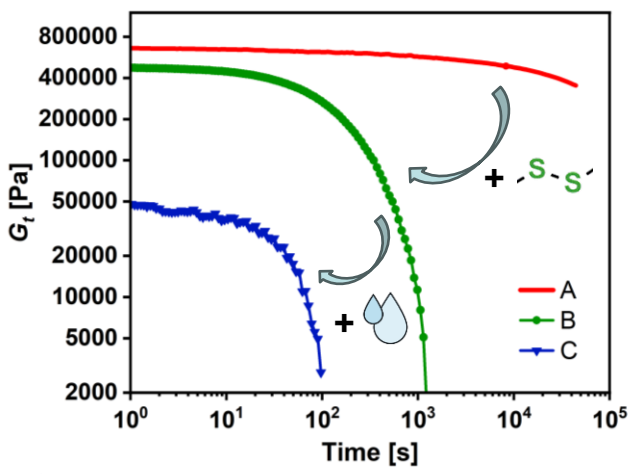


Figure 3: Stress-relaxation experiments conducted at 120 °C on: **A)** a dried PHU film without disulfide bonds; **B)** a dried PHU film with disulfide bonds; **C)** a humidified (80 %) PHU film with disulfide bonds.

CONCLUSIONS

➢ **Successful incorporation** of disulfide bonds within a water-based PHU foam
➢ **Enhanced reprocessability and relaxation**
→ less degradation
➢ Discovery of a water-dependency of the relaxation of cystamine-based samples
➢ Disulfide bonds confer **adhesive properties** to cystamine-based films, with the ability to compete with commercially available adhesives and a unique reusability after breakage

REFERENCES

Detrembleur et al. *Chem. Eng. J.* **2025**, *516, 163998*
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