

A new process scheme for 100% chemical recycling of polyurethanes

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Background

Polyurethanes (PUR) are a class of mostly thermoset polymers, produced by a condensation of di-(or poly)isocyanates with polyols (polyfunctional alcohols). Typically, the reaction of isocyanate groups with water is used for foaming, as a result of the CO₂ formed during that reaction. Depending on the type of diisocyanates and polyols, a multitude of material properties can be obtained, resulting in rigid foams, flexible or viscoelastic (memory) foams, or films. Global production rates are increasing, to currently about 18 million tonnes annually (Molero et al. 2010).

Almost in parallel with the breakthrough of PUR applications was the search for depolymerization methods (Behrendt and Naber 2009). At first, a hydrolysis (either base or acid catalyzed) can break the urethane bonds at temperatures above 200 °C and pressures above 16 bar (Simon et al. 2015). In theory, the products should be the constituting polyols, next to amines and CO₂ as derivatives of the original diisocyanate monomers. Similarly, soon thereafter, alcoholysis using e.g. methanol, glycol or glycerol, was explored, allowing the recovery of the constituting polyols after a transesterification similar to that for other condensation polymers (e.g. PET) (Wu et al. 2003). In theory, split-phase glycolysis of PUR should result in a pure polyol phase, a glycol phase and a diurethane molecule of the constituting starting diisocyanate with two glycol molecules (Herlinger 1970, Dai et al. 2002).

To date, despite several pilot-scale trials and larger scale projects, the chemolysis of PUR is primarily limited to industrial production losses, with high purity, where only the polyol constituents are (partially) recovered. However, many projects have failed on the heterogeneity of post-use waste materials, and failure to completely recycle the diisocyanate (or polyisocyanate) derivatives, which make up 10-40 % of the PUR mass, strongly hampers the commercial potential of this technology: a considerable part of the PUR should still be incinerated in such instance (Behrendt and Naber 2009).

New recycling route

In this study we propose a new recycling method for polyurethanes, whereby in a fully circular way both the polyol and diisocyanates can be completely recycled. Schematically, this technology is summarized in Figure 1.

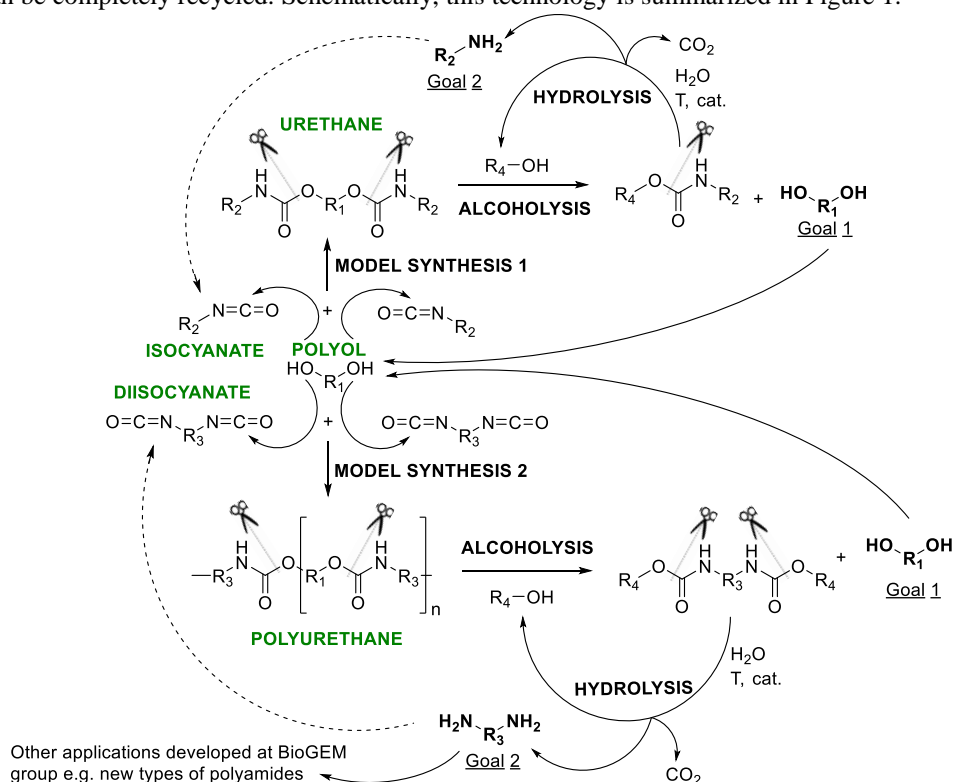


Figure 1 – Schematic representation of two-stage circular scheme for PUR (model synthesis 2), including the basic research demonstration that demonstrates the concept (model synthesis 1)

The new concept, shown as *model synthesis 2* in Figure 1, is a two-step chemolysis approach, whereby in the first step PUR is glycolyzed into a split polyol phase and a residual, usually solid, diurethane moiety. The diurethane is a derivative of the initial diisocyanate bonded to the glycol used as alcoholysis agent through urethane bonds. In a second step, this diurethane is hydrolyzed, giving thermally unstable carbamates, which immediately convert to diamides and carbon dioxide. The diamides are classical feedstock diisocyanate monomers, or can be used directly in a variety of high-end applications.

Given the complexity of these reactions, in which mass transfer and phase separations can be limited and increase the study's complexity, we demonstrated the feasibility of our new recycling scheme for synthesized model urethane molecules (*model synthesis 1* in Figure 1), starting from small alcohols (such as butanol) or polyols (such as glycol) and monofunctional isocyanates (such as phenyl isocyanate). This way, polymer formation is excluded, facilitating advanced spectroscopic analysis by FT-IR, ¹H-NMR, ¹³C-NMR, and chromatography. From a chemical point of view, the process was demonstrated with good yields of the various constituents. Subsequent research takes into account the complexity related to polymeric systems, and transfers the built knowledge to actual waste materials.

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