

Abstract

Polyurethanes (PU) are indispensable materials in our everyday lives. PU foams account for more than half of PU materials, with flexible PU foams being an integral part of upholstered furniture, while hard PU foams are mainly used as thermal and sound insulation materials. The large-scale production and use of PU foams results in an increasing amount of waste that needs to be processed in accordance with European directives. A sustainable approach to dealing with PU foam waste is chemical recycling, which enables the recovery of recycled raw materials that can be reused for the synthesis of PU foams or other polymer products.

The aim of the doctoral thesis was to develop a method for the effective decomposition of waste based on flexible PU foam of different chemical composition. For this purpose, acidolysis and aminolysis were investigated as methods for the degradation of carbamate groups in the PU foam structure. Different reagents were used in different amounts and the degradation experiments were performed at different temperatures and times. The influence of the experimental conditions used for degradation of PU foams on the structural properties of the recycled polyether polyols and on the formation of side products was investigated. Conventional heating of the reaction mixtures was replaced by more energy-efficient microwave heating, which shortened the procedures from several hours to less than one hour. Acidolysis of PU foams with dicarboxylic acids is a promising chemical recycling method from the industry's point of view, as the degradation of PU foams takes place with smaller amounts of reagent than in the case of PU foam degradation by glycolysis. The reason for this is that the acidolysis of carbamate groups is an irreversible reaction, where carbon dioxide is released and a thermally stable amide bond is formed. In contrast to acidolysis, glycolysis as the most studied method for PU foam degradation is a reversible reaction, so the use of a large excess of glycolic reagents is required to drive the reaction towards product formation. The results of acidolysis of flexible PU foams show that, regardless of the experimental conditions chosen, we cannot obtain a fully hydroxyl-functionalized recycled polyether polyol that would be a perfect equivalent of the virgin polyol because, with small amounts of diacid used, the degradation of the carbamate groups is not complete, resulting in recycled polyols that are partially functionalized with aromatic amino end groups. With a sufficiently high amount of diacid reagent, a high degree of carbamate group degradation (> 98 mol%) can be achieved, but at the expense of a higher degree of esterification of the hydroxyl groups of the polyol with the diacid, resulting in partially carboxyl-terminated recycled polyols. The advantage of acidolysis over other methods is that the dicarboxylic acid also acts as an amine scavenger and prevents the formation of unwanted aromatic diamines during PU foam degradation. Aminolysis of flexible PU foams with a sufficiently large amount of the tris(2-aminoethyl)amine or polyethylenimine results in a high degree of degradation of the carbamate groups (~ 99 mol%), which is due to the catalytic effect of the tertiary amine group in the structure of the same reagent. For this reason, efficient aminolysis of PU foam can be performed with tris(2-aminoethyl)amine or polyethylenimine using small amounts of the reagent. The complete degradation of the carbamate groups in the PU foam structure was achieved with a two-step aminolysis, in which we used tris(2-aminoethyl)amine or cheaper hexamethylenediamine in the first step to degrade the flexible PU foam and isolate the recycled polyol partially functionalized with aromatic amino end groups, which was again subjected to an aminolysis process with tris(2-aminoethyl)amine.

Recycled polyols with different types and contents of end groups (aromatic amino, carboxyl and hydroxyl end groups) and hydroxyl-functionalized recycled polyol were then used in different amounts for the synthesis of new flexible PU foams. The results show that especially the carboxyl groups and to a lesser extent the aromatic amino end groups of the recycled polyols have a negative influence in the course of PU foam polymerization, which is due to unbalanced cross-linking and foaming reactions that affect the cell morphology and ultimately lead to a deterioration of the mechanical properties of the synthesized flexible PU foams. Suitable mechanical properties of the flexible PU foams were obtained with an unmodified catalytic system only by using purified hydroxyl-functionalized recycled polyol, regardless of how much of the original polyol was replaced by recycled in the PU formulation. This is a consequence of the comparable structural properties (molar mass, type of end groups) of recycled and original polyol and the absence of low-molar mass side products in the recycled polyol.

Key words: chemical recycling, flexible PU foams, microwave heating, acidolysis, aminolysis