Abstract

PhD Thesis: Non-Isocyanate Polyurethanes Based on Epoxidized Vegetable Oils

The aim of this doctoral research was to develop an effective method for synthesizing polyhydroxyurethane (PHU) materials based on epoxidized vegetable oils. The research also focused on creating products such as non-isocyanate polyurethane (NIPU) foams and adhesives, as well as establishing assumptions for their production technology. These efforts aim to integrate these products into the offerings of the Łukasiewicz-Institute of Heavy Organic Synthesis "Blachownia" and facilitate their potential implementation in industrial practice.

In the initial phase, research was conducted on the epoxidation of cardoon, safflower, and linseed oils in the presence of hydrogen peroxide and formic acid. This work was preceded by an analysis of the composition and determination of the physicochemical properties of the oils. The reaction conditions and the quantities of epoxidizing agents were then optimized based on the degree of unsaturation of each oil.

In the subsequent stage, the epoxidized oils were carbonated via reaction with carbon dioxide to produce the desired cyclic carbonates. The research aimed to minimize the synthesis time and produce highly reactive products for reactions with polyamine compounds. A comprehensive review of catalysts was conducted, focusing particularly on quaternary ammonium and phosphonium salts, organometallic and inorganic catalysts, and various ionic liquids. The reaction conditions were optimized through infrared spectroscopy (IR) monitoring and analysis of the decrease in the epoxide number. The resulting products were characterized using mass spectrometry (MS) and nuclear magnetic resonance (^{1}H NMR).

Polyhydroxyurethane materials were synthesized from the cyclic carbonates and a variety of aliphatic, cycloaliphatic, and aromatic polyamines. To enhance mechanical properties, oligoamide adducts synthesized using polyamine compounds and a dimer acid were employed as cross-linking agents. Efforts were also made to modify the NIPUs using plasticizers and fillers. Gelation times were determined for selected systems, and thermogravimetric analyses were conducted. Preliminary mechanical tests of the synthesized products were performed to assess their functional properties. These PHU materials were subsequently used to develop foams and hot-melt adhesives. Foam compositions were formulated by selecting cyclic carbonates with suitable reactivity and an appropriate foaming agent, and the optimal foaming conditions were established. Industrial-scale trials of NIPU foam production were attempted to confirm the feasibility of large-scale synthesis, and a series of tests explored the potential of using NIPUs as hot-melt adhesives. Based on the findings, technical design assumptions and guidelines for necessary operations were developed.