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Non-isocyanate polyurethanes (NIPU) based on plant oils

Authors: Damian Kiełkiewicz[1], Izabela Semeniuk[1], Simona Furgoł[1], Anna Chrobok[2], Agnieszka Siewniak[2]

Affiliation: [1] Lukasiewicz Research Network – Institute of Heavy Organic Synthesis "Blachownia", ul. Energetyków 9, 47-225 Kędzierzyn-Koźle, Poland,
[2] Silesian Technical University, Faculty of Chemistry, Department of Chemical Organic Technology and Petrochemistry, ul. Krzywoustego 4, 44-100 Gliwice, Poland
Telephone: +48 664718940, mail: damian.kielkiewicz@icso.lukasiewicz.gov.pl

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Introduction

Polyurethanes are polymers typically obtained through the polyaddition of organic aromatic or aliphatic isocyanates with compounds containing at least two hydroxyl groups (polyols) [1]. Approximately 90% of the global production of polyurethanes is based on two isocyanate compounds: methylenediphenyl-4,4'-diisocyanate (MDI) and 2,4-diisocyanatotoluene (TDI). Due to their high reactivity, MDI and TDI exhibit strong irritant and toxic effects, both during application and synthesis, which involves highly toxic phosgene as a raw material. For these reasons, in the near future, the use of isocyanates is expected to be more challenging due to legal and health-related concerns.
An alternative to conventional isocyanate-polyol based polyurethanes are non-isocyanate polyurethanes (NIPUs), which are obtained through the reaction of cyclic carbonates with polyamines containing primary amine groups. This process results in the formation of linear, crosslinked polyhydroxyurethane polymers (Fig. 1). The resulting materials exhibit strong adhesion to substrates due to the presence of hydroxyl groups in the polymer chain. Polyhydroxyurethanes have higher thermal resistance because they do not contain thermally unstable biuret or allophanate groups found in polyurethane chains and instead have urethane and hydroxyl groups that can form intermolecular hydrogen bonds. Instead, they contain urethane and hydroxyl groups capable of forming intermolecular hydrogen bonds. These bonds block the carbonyl carbon atom, increasing the resistance of the urethane group to hydrolysis. Furthermore, the chemical resistance of polyhydroxyurethanes can increase up to twice as much compared to compounds with similar structures but without intermolecular hydrogen bonds [2].

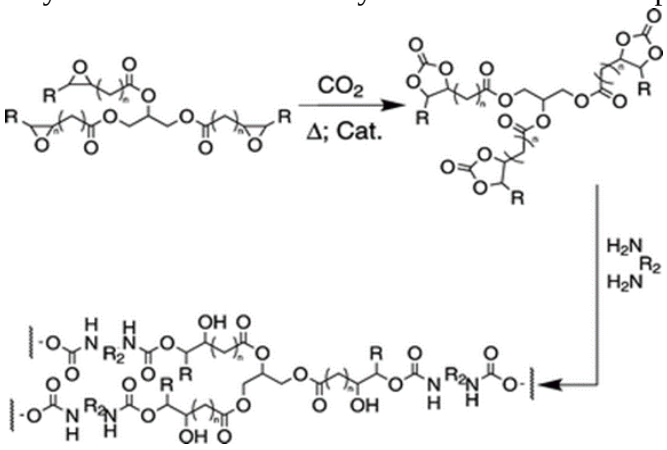

Figure 1. *Scheme of NIPU formation in the reaction of cyclic carbonate with polyamine.*

Experimental

NIPU synthesis is a two-step process:

- **the first step**: synthesis of cyclic carbonates by:
  - epoxidation of plant oils: cardoon and safflower oils were used in the researches
  - carbonization of epoxided oils in the reaction with CO_2 under elevated temperature and pressure
- **the second step**: synthesis of polyhydroxyurethane materials in reaction of cyclic carbonates with different biobased commercial polyamines.

Results and Discussion

Works on NIPU thermoplastic polymers and foams development comprised:

- determination of the suitability of different purity grades of cardoon and safflower oils for the synthesis of cyclic carbonates,
- research on the epoxidation of oils using hydrogen peroxide; reaction conditions were adjusted to the degree of unsaturation of raw materials,
- research on the carbonization of epoxidized oils in the reaction with CO_2; catalyst screening was performed and catalytic activity of compounds derived from the group of quaternary onium salts, ionic liquids, organometallic catalysts and inorganic compounds was determined. Reaction progress was monitored by measuring of epoxy value, viscosity and by FTIR technique.
- NIPU synthesis in the reaction of cyclic carbonates with selected polyamine compounds; improving of the products mechanical properties through chemical modification of the polymer structure and the use of selected plasticizers and fillers. The study of the properties of the obtained polymers included the determination of gelation times for various carbonate-amine systems, as well as thermogravimetric analyzes in order to determine the glass transition temperature of the obtained polyhydroxyurethanes. In the presence of selected polyamines, NIPU was synthesized on the basis of the tested oils, and their mechanical properties, such as tensile strength, elongation at break and Shore hardness were compared.

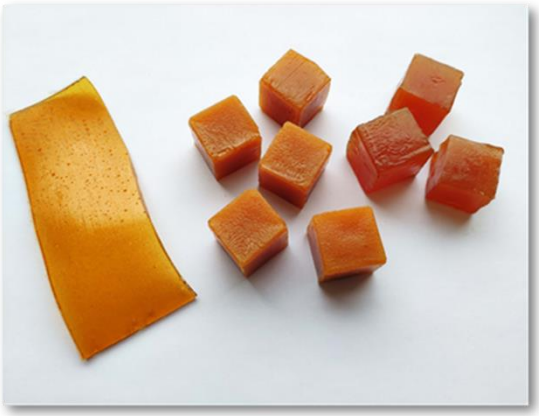

Figure 2. *Thermoplastic NIPU*

Conclusions

NIPU polyhydroxyurethanes, offering very high bio carbon content (80-90 %) are still new, but promising materials. The result of the work was the development of a method for the production of thermoplastic polyhydroxyurethane plastics. Compared to traditional polyurethanes, they have a number of advantages, such as the possibility of partial replacement of petroleum-derived raw materials with compounds of plant origin, the elimination of toxic isocyanates from the synthesis and the use of CO_2 as a raw material in the synthesis of cyclic carbonates.

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Biography

Damian Kiełkiewicz is the Leader of Advanced Materials Research Group at Institute of Heavy Organic Synthesis “Blachownia”, a member of Łukasiewicz Research Network. He was graduated at Opole University and completed postgraduate studies at Stanford University. His main research area comprises technologies of epoxy resins, phenolic resins and non-isocyanate polyurethanes. Co-author of 3 papers and 27 patents, mostly implemented into industrial practice.

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