

Università degli Studi

Master's Degree Thesis in Chemical and Process Engineering Chemical Recycling by Glycolysis of Rigid Polyurethane and Polyisocyanurate Foams Candidate: Francesca Costantini Tutor: Prof. Michele Modesti

> 4° Conferenza Nazionale Poliuretano Espanso Rigido Roma, 10/10/2019

# Main purposes of the project



**Urethane group** 

- Carry out chemical recycling by glycolysis of rigid polyisocyanurate foams in order to obtain liquid products suitable for reuse
- Apply glycolysis products to the synthesis of new rigid foams

~ 60% w/w of isocyanate trimers





# Reaction conditions and equipment



Università degli Studi di Padova

- ✓ High reactivity, high lipophilicity and high boiling point glycol
- ✓ High activity alkaline catalyst
- ✓ High temperature
- ✓ Reaction time = 3 h







#### Characterization of the glycolysis products:

- ✓ Analysis of reaction trend and trimer conversion by FTIR
- ✓ Hydroxyl Number measurements
- ✓ Viscosity measurements
- ✓ MW measurements by GPC

Characterization of the new foams made by glycolysis products:

- ✓ Mechanical characterization by compressive strenght test
- ✓ Morphological characterization by SEM





Iniversită egli Stud i Padova



# Hypothesis on trimer reactions





### Tests with pure isocyanate trimer



Università degli Stud di Padova



## Analysis of reaction trend by FTIR





### Determination of trimer conversion







### Determination of trimer conversion





Catalyst/Foam Ratio has a strong influence on trimer reaction rate

## Effect of catalyst concentration



#### High catalyst concentration enhances secondary reactions



# Hydroxyl Number (nOH) measurements



Hydroxyl Number: concentration of reactive hydroxyl end-groups per unit mass [mgKOH/g]

Measured by an experimental method which employs a calibration curve





Università degli Stud di Padova



### MW measurements by GPC



- ✓ Qualitative chromatogram analysis by means of a calibration curve
- ✓ Quantitative chromatogram analysis by measurements of peaks areas



#### MW measurements by GPC





## Temperature effect on reaction rate



Viscosity trend with time for the reaction performed at 215°C:



Reaction time can be reduced by acting on temperature

### Compressive strenght tests of the new foams



NIVERSITÀ



# Compressive strenght tests of the new foams





# Limits on the percentage of glycolysis polyol







# Microphotographs of the cell structure of PIR foams



Università degli Studi di Padova



# 0 % glycolysis polyol



#### 50 % glycolysis polyol



75 % glycolysis polyol



#### 100 % glycolysis polyol



- ✓ The glycolysis process of polyisocyanurate foams with very high isocyanate index proved to be a feasible and promising solution to recover a "polyol-like" product suitable for the synthesis of new rigid foams.
- ✓ An alkaline catalyst and a catalyst/foam ratio of 10·10<sup>-3</sup> mol/100g turned out to be effective for adequate reactions enhancement.
- ✓ The glycol/foam ratio was identified as the process variable which is more conveniently manipulated in order to obtain the desired values of both the hydroxyl number and the viscosity. A massive ratio of 60:40 was defined as the optimal one.
- ✓ The recovered glycolysis products were employed successfully in the synthesis of new rigid foams. The mechanical properties and the morphologies of specimens based even on high amounts of glycolysis polyol turned out to be better or either very close to those of standard specimens based on only virgin polyol.



UNIVERSITÀ **DEGLI STUDI DI PADOVA** 

lazionale Francesca Costantini 🥆 Chemical Recycling gy Glycolysis of Rigid Polyurethane and Polyisocyanurate Foams

્ર (૦)

Com Thank you for your attention