UNIVERSITÀ DEGLI STUDI DI PADOVA

Polymer Engineering Group

INDUSTRIAL ENGINEERING DEPARTMENT

Il riciclo chimico di sistemi poliuretanici e poliisocianurati nell'ottica dell'economia circolare

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ROME, 10th October 2019

Polyurethane industry

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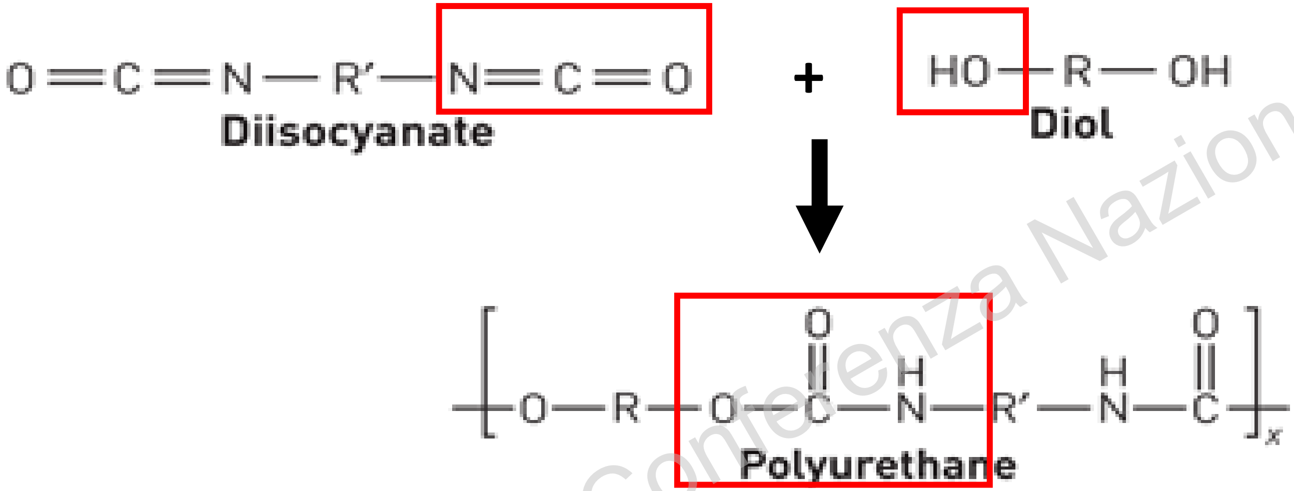
PU is a very versatile polymer family







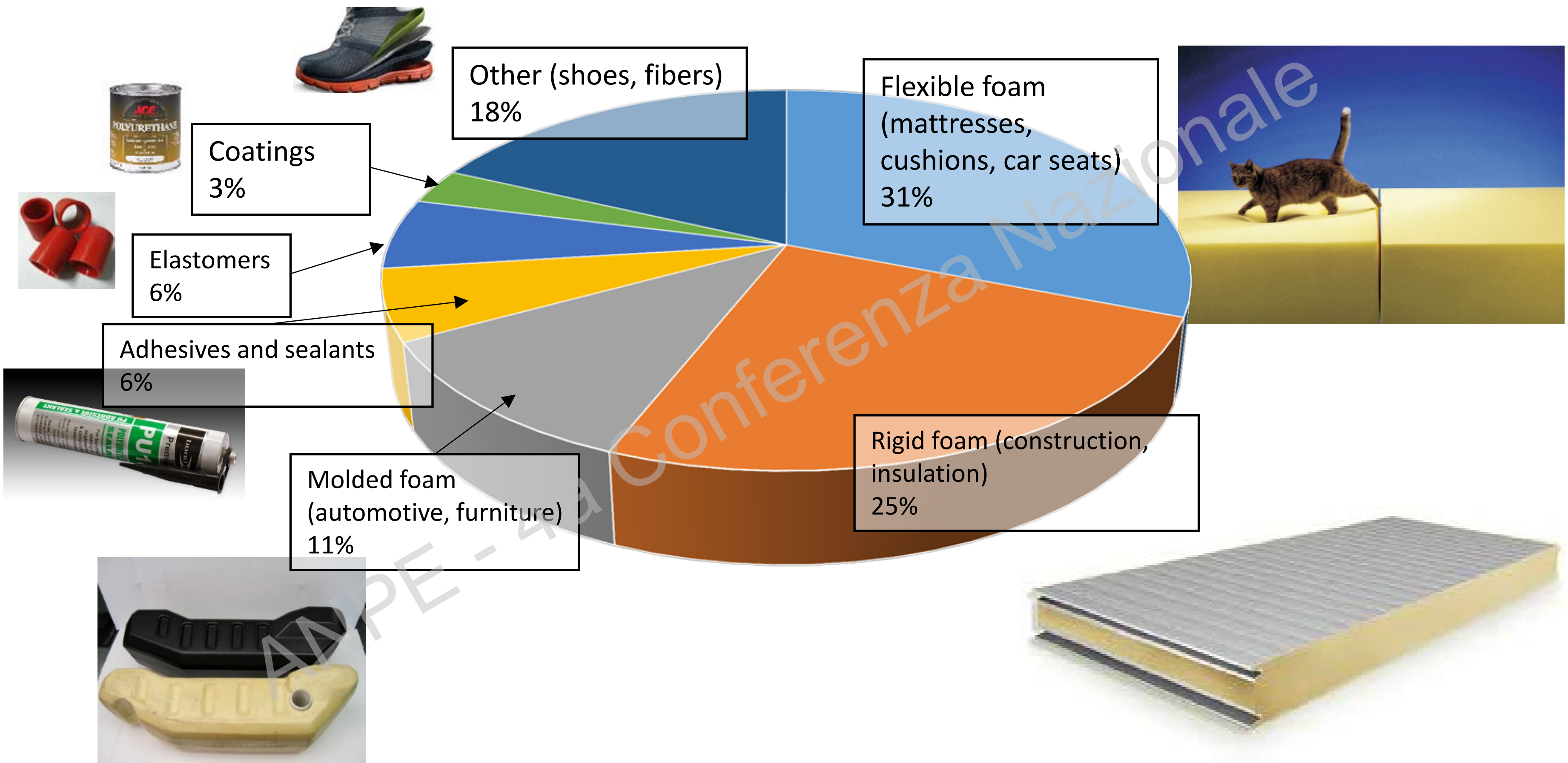


Polyurethane industry

World Consumption $Mton/y$	1990	2016	2021e	Annual growth 2016 – 2021e
PE-LD, PE-LLD	18.8	48.4	57.7	3.6%
PE-HD	11.9	42.4	50.1	3.4%
PP	12.9	64.3	78.2	4.0%
PVC	17.7	43.7	52.6	3.8%
PS	7.2	12.4	13.2	1.3%
PET	1.7	20.7	26.2	4.9%
PUR	5.0	18.4	23.3	4.8%
Other thermoplastics	2.8	10.2	12.3	3.8%
Total	**83.6**	**280**	**338**	**3.8%**

Source: PlasticsEurope Market Research Group (PEMRG) / Consultic Marketing & Industrieberatung GmbH

PU market


Other (shoes, fibers)
18%
Flexible foam (mattresses, cushions, car seats)
31%
Coatings
3%
Elastomers
6%
Adhesives and sealants
6%
Molded foam (automotive, furniture)
11%
Rigid foam (construction, insulation)
25%

PU wastes

More than 3.5 million tonnes of polyurethane are used in Europe each year. About 20% of this material ends up as waste, the vast majority of which (c. 460.000 tonnes per year) goes to landfill.

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The pyramid of sustainability

- Disposal of polyurethane waste is nowadays a problem
- European Union directive allows to landfill only 10 % of waste by 2035
- Europe purpose is to obtain a circular economy

LINEAR ECONOMY

CIRCULAR ECONOMY

Recycling strategies

RECYCLING OF POLYURETHANES

Physical recycling

Direct reuse of grinded material:

- Rebonding
- Regrinding / Powdering
- Compression Moulding
- Adhesive Pressing

Chemical recycling

Recovery of new raw material

- **glycolysis**,
- hydrolysis,
- aminolysis,
- phosphorolysis

Waste-to-energy plants

Energy recovery:

- Low energy recovery compared to the production energy demand
- Material is lost.

Chemical recycling: Glycolysis process

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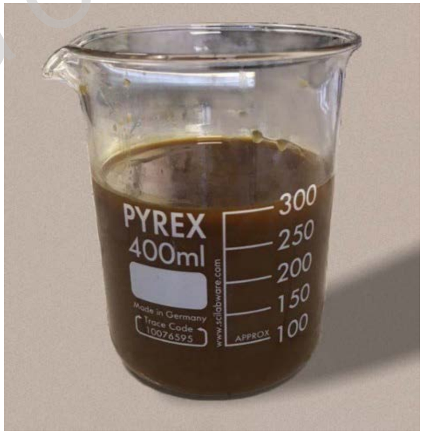
PU and PIR rigid foams scraps and wastes

cutting stage

PU powder waste

Glycol
+ catalyst
+ T
+ mixing

glycolysis reactor



recycled polyol

synthesis

new *PU* rigid foams

Glycolizable materials


Flexible foams

Thermoplastic TPU polymers

Polyurethane rigid blocks

Polyisocyanurate rigid foams

Glycolysis is a versatile process that can be extended to **different classes of polyurethanes** :

Elastomeric polyurethane

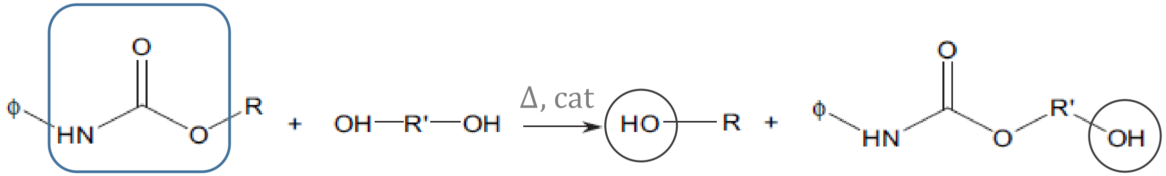
Rigid polyurethanic foams (building, insulation, refrigeration)



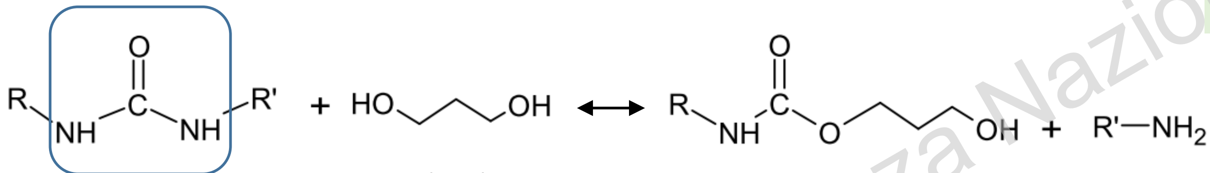
Reinforced injection molding (RIM) polyurethane or polyurea

Glycolysis reaction

Main reaction: **TRANSESTERIFICATION** through a glycol



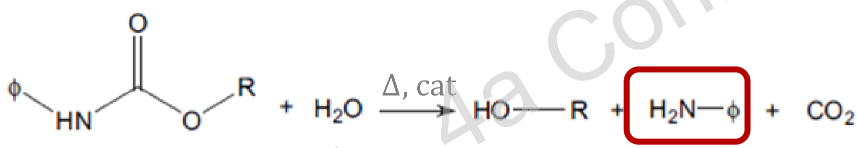
polyurethane glycol polyol Carbammate



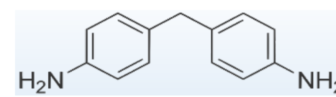
Urea Glycol Amine

All these reactions lead to the formation of products with end groups reactive with isocyanate

Side reaction: **HYDROLYSIS**, due to the humidity of reactants and environment



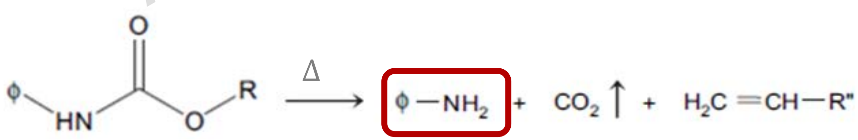
Urethane Water Polyol Amine Carbon dioxide



4,4'-methylene dianiline (MDA)

considered suspected carcinogen by NIOSH and ECHA

Side reaction: **PYROLYSIS**, due to the high temperature



Urethane Amine Carbon dioxide Unsaturated polyol

Kinetic study

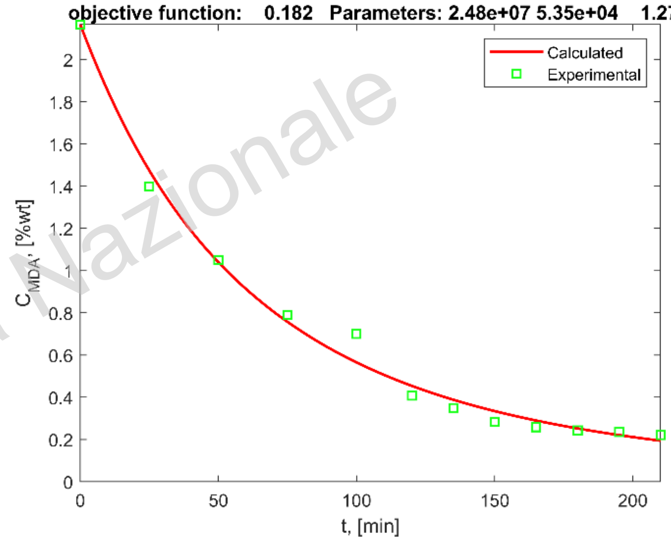
Large excess of deaminating agent such that $MDA \rightarrow products$:

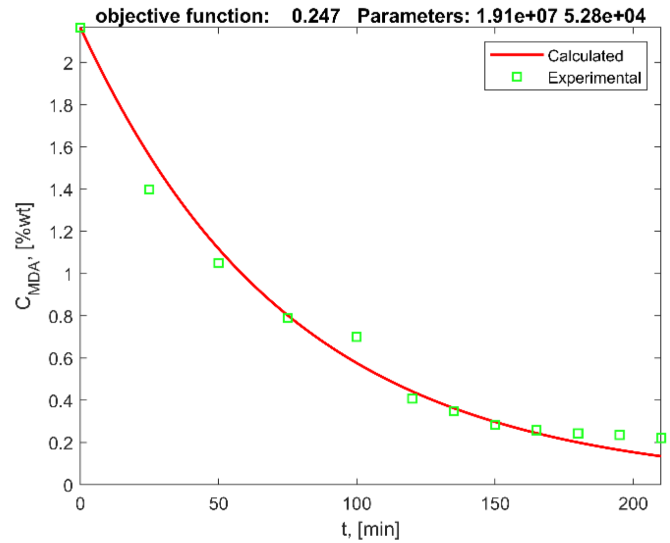
$$MB_{MDA}: \quad \frac{dc_{MDA}}{dt} = -Ae^{-E_a/R_gT} \cdot c_{MDA}^{\alpha}$$

Deamination tests at 28, 40, 105 and 120 $°C$

Test	Elementary reaction	
	$A, [s^{-1}]$	$E_a, [kJ/mol]$
Run 1, $90\ °C$	$1.70 \cdot 10^7$	58.7
Run 2, $107\ °C$	$1.71 \cdot 10^7$	60.8
Run 3, $40\ °C$	$1.85 \cdot 10^7$	54.5
Run 4, $28\ °C$	$1.91 \cdot 10^7$	52.8
Run 5, $28\ °C$	$1.98 \cdot 10^7$	50.8
Average	$\mathbf{1.83 \cdot 10^7}$	$\mathbf{55.5}$

Test	Non-elementary reaction		
	$A, [s^{-1} \cdot (\%wt)^{1-\alpha}]$	$E_a, [kJ/mol]$	$\alpha, [-]$
Run 1, $90\ °C$	$1.76 \cdot 10^7$	58.8	1.50
Run 2, $107\ °C$	$2.37 \cdot 10^7$	61.9	0.82
Run 3, $40\ °C$	$1.99 \cdot 10^7$	54.6	1.24
Run 4, $28\ °C$	$2.48 \cdot 10^7$	53.5	1.27
Run 5, $28\ °C$	$0.16 \cdot 10^7$	46.1	3.25
Average	$\mathbf{1.75 \cdot 10^7}$	$\mathbf{55.0}$	$\mathbf{1.17}$





Glycolysis process

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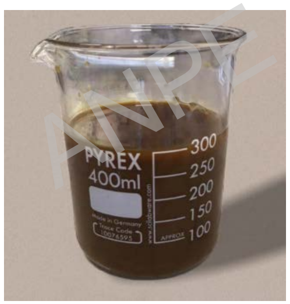
PROCESS PARAMETERS

- Glycol type
- Catalyst type
- Glycol/polimer waste ratio
- Catalyst/polimer ratio
- Temperature

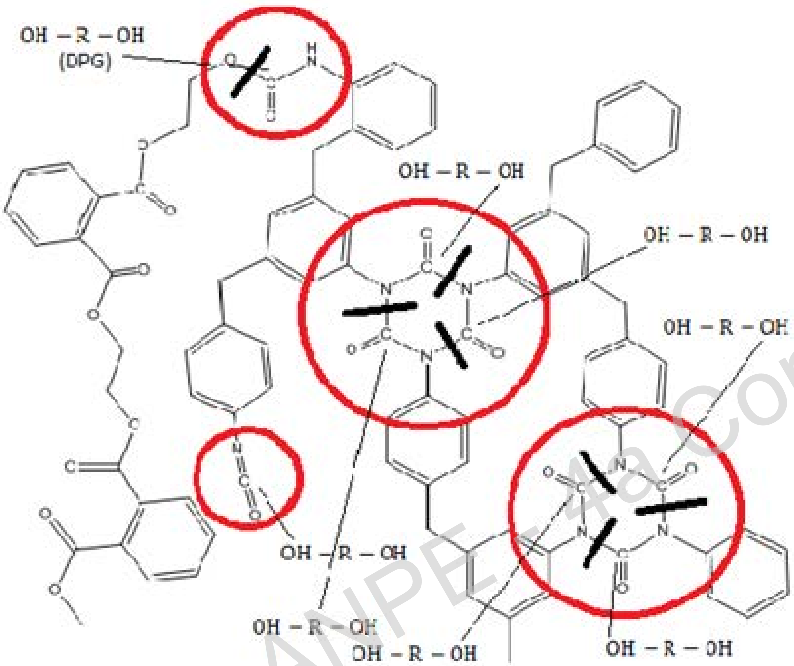
PRODUCT PROPERTIES

- Viscosity
- Hydroxyl Number
- Amine content HPLC
- Molecular weight GPC

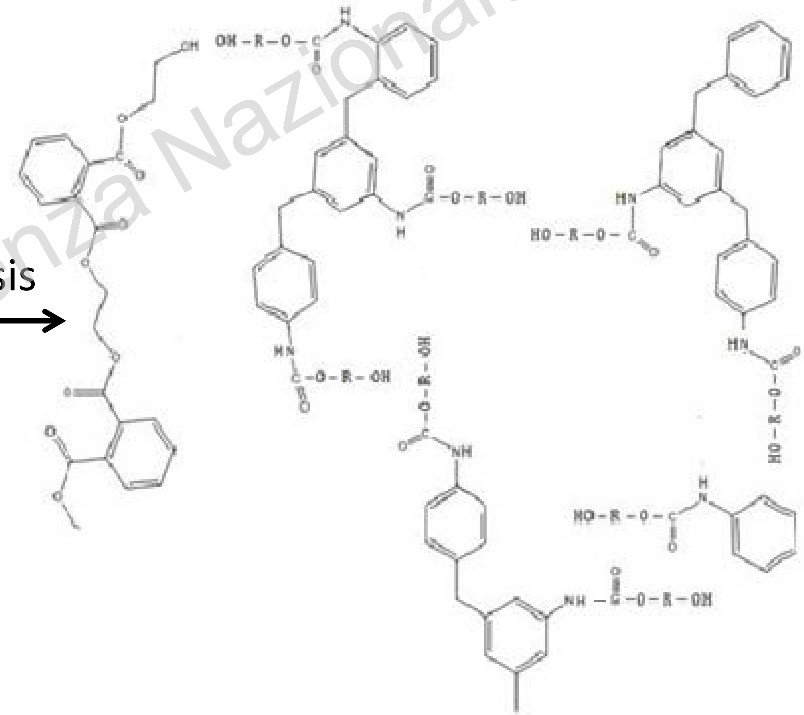


Glycolysis of PIR foams

Highly cross-linked structure of the early rigid polyisocyanurate foam → Glycolysis → **Liquid product made up of highly branched oligomers**

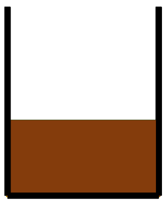


Glycolysis →

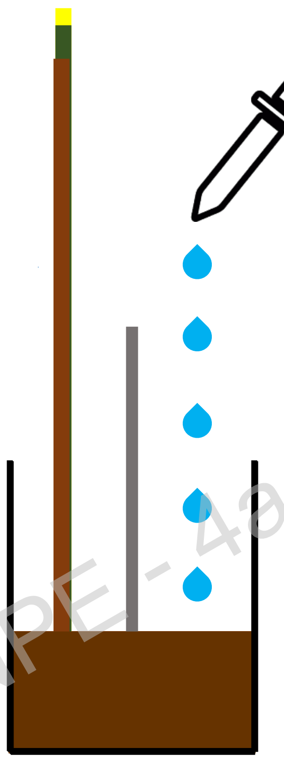


→ **Highly branched oligomers** — Synthesis of a new foam → **Highly cross-linked and rigid structure of the deriving foam**

New foams synthesis



Virgin polyol
Isocyanate
Recycled polyol



Mechanical mixing

Foam formation

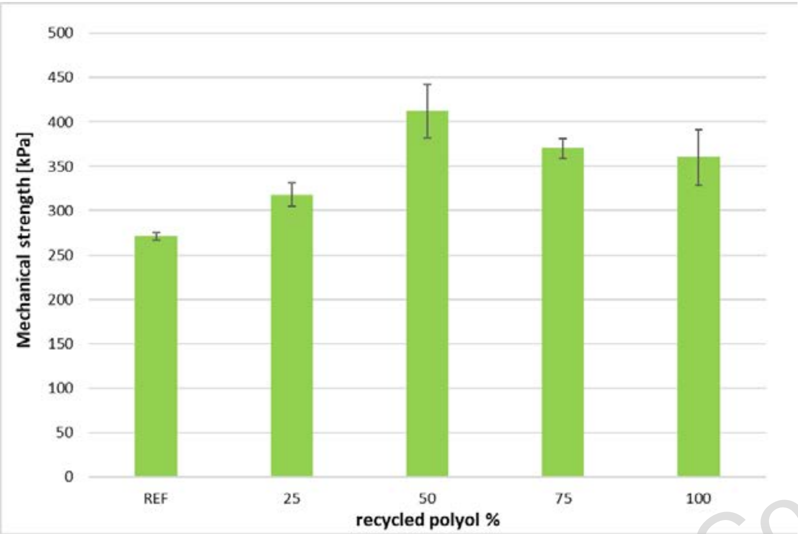
New foams characterization

Glycolysis of rigid foams:
FOAMS/Glycol = 60/40 w/w; Viscosity =5800 cP OH number =456

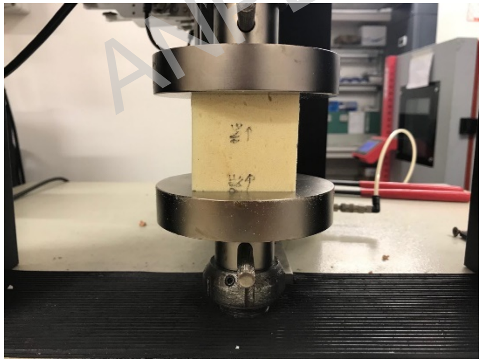
Glycolysis	Percentage of recycled polyol	Density [Kg/m^3]	Thermal conductivity [W/(m K)]	Compressive strength [kPa]
Reference	0 %	45.4	0.0242	271.0
3	25 %	48.9	0.0237	318.2
3	50 %	36.8	0.0241	412.4
3	75 %	34.5	0.0236	370.0
3	100 %	39.1	0.0231	360.0

New foams characterization

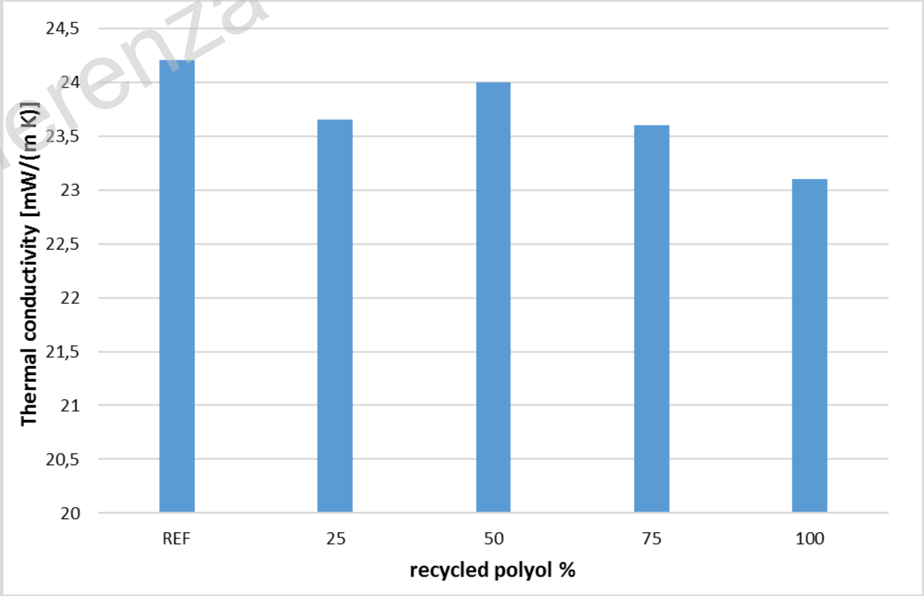
Compressive strength test



Density ≈ 40 kg/m^3



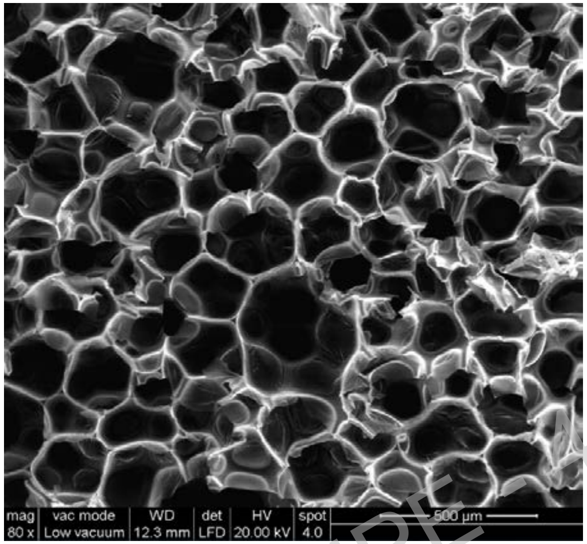
Thermal conductivity



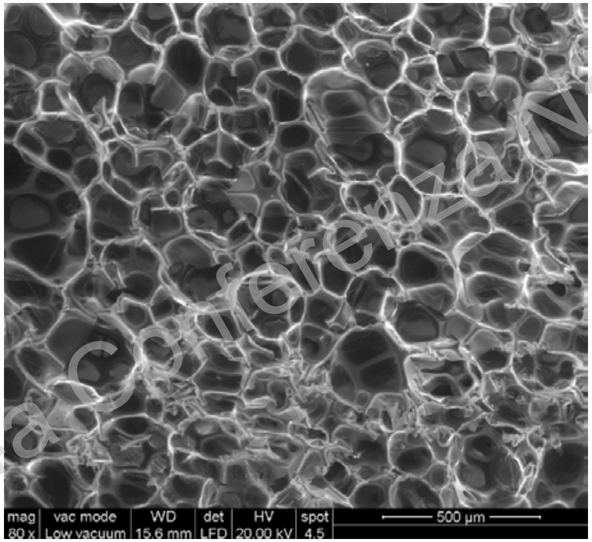
New foams morphology

Glycolysis product in the polyol blend:

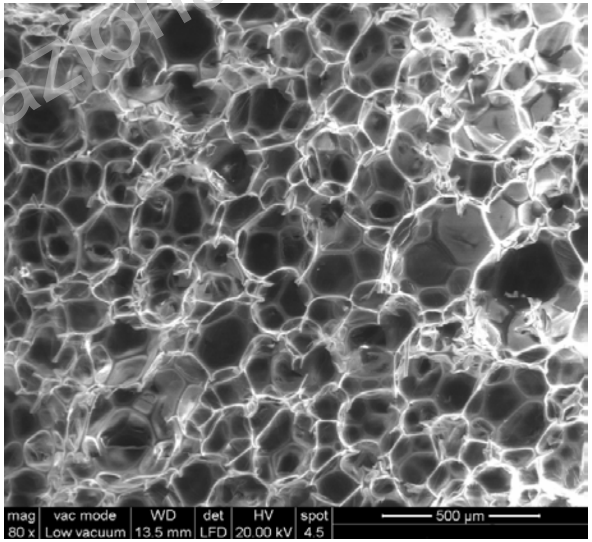
0 % R

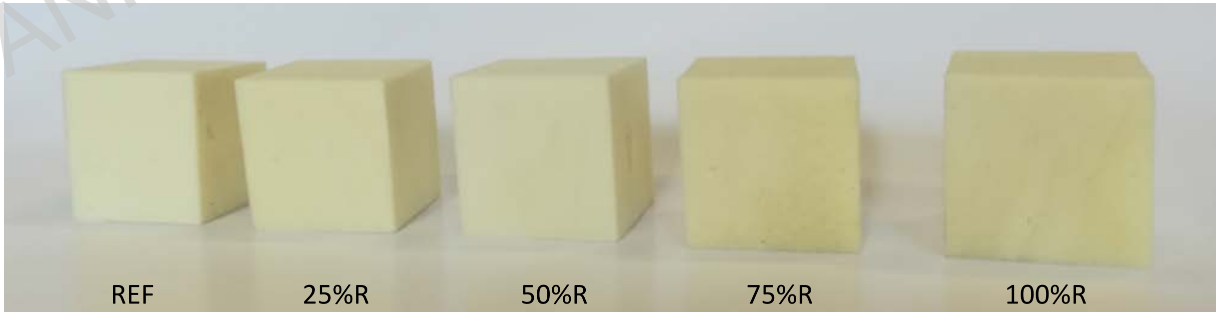


50% R



100% R





New foams performances

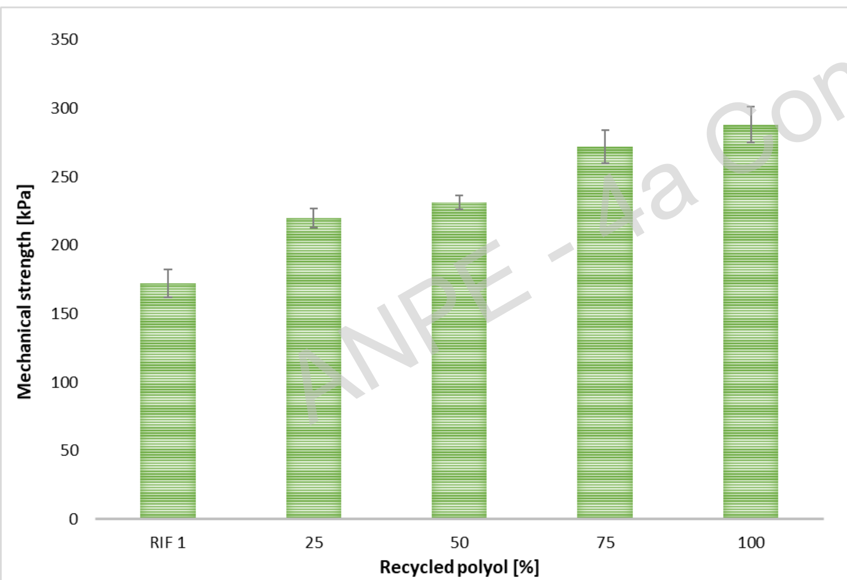
Glycolysis product from reinforced injection molding (RIM) polyurethane or polyurea

Glycol/RIM	Viscosity [cP]	nOH [mgKOH/g]
60/40	650	520

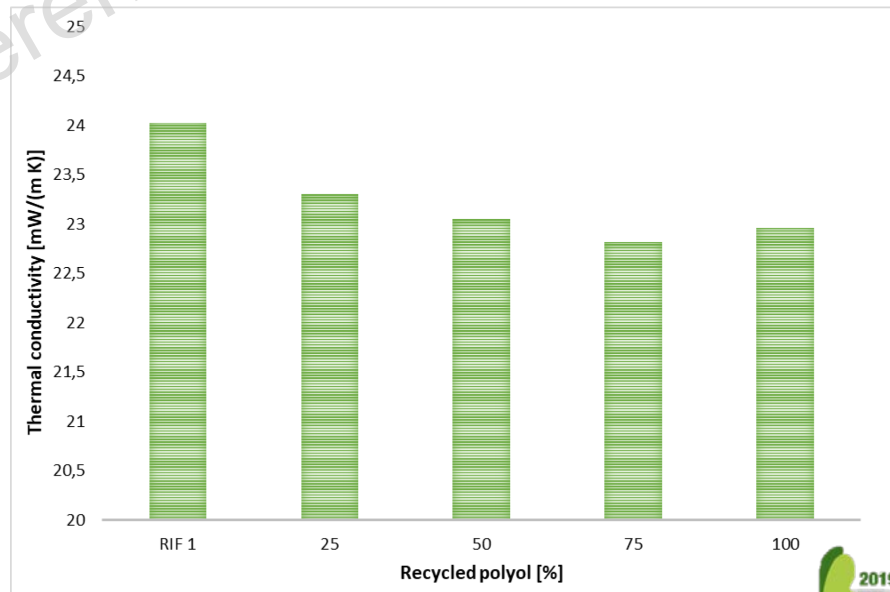
Density 38 kg/m^3

REF 25%R 50%R 75%R 100%R

Mechanical properties



Thermal properties



Glycolysis pilot plant

Glycolysis today

2014/2020 POR
FESR / REGIONE DEL VENETO
UNIONE EUROPEA
REGIONE DEL VENETO

2019 PU

Glycolysis in the past

Photograph of the plant for the chemical recycling of rigid PU foam using glycolysis. The ground PU scrap stored in silos is conveyed by means of a screw feeder to the glycolysis reactor containing an agitated mixture at 200°C

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Thank you for your attention

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