Environmentally friendly polyurethane (PU) materials for space applications

Tomas Vlcek, **TOSEDA s.r.o.** (Czech Republic)
Ugis Cabulis, **Latvian State Institute of Wood Chemistry** (Latvia)
Arturs Jasjukevic, **Ariane Group GmbH** (Germany)
Malgorzata Holynska, **ESA-ESTEC** (The Netherlands)

General target

- Development of novel eco-friendly polyurethane materials avoiding use of toxic non-isocyanate based PU materials for versatile applicability in aerospace industry:
  - a/ potting systems (spacecrafts manufacturing),
  - b/ conformal coating (spacecrafts manufacturing), and
  - c/ thermal insulation foams (launchers manufacturing).

Requirements

- Elimination of toxic isocyanates used in traditional production of PU materials
- Minimization of health and ecological risks
- Sustainability aspect – use of renewable resources

Development of „Green“ Polyurethane Materials for Use in Spacecraft and Launcher Applications

ESA Contract No. 4000119685/17/NL/KML
2017 - 2019
Targeted TRL = 3-4

TOSEDA s.r.o. (CZ)

- SME
- Prime-Contractor
- Design, formulation, preparation and testing of HNIPU materials

ArianeGroup GmbH (DE)

- Large Systems Integrator (LSI)
- Sub-Contractor
- Definition of industrial requirements and evaluation of HNIPU materials

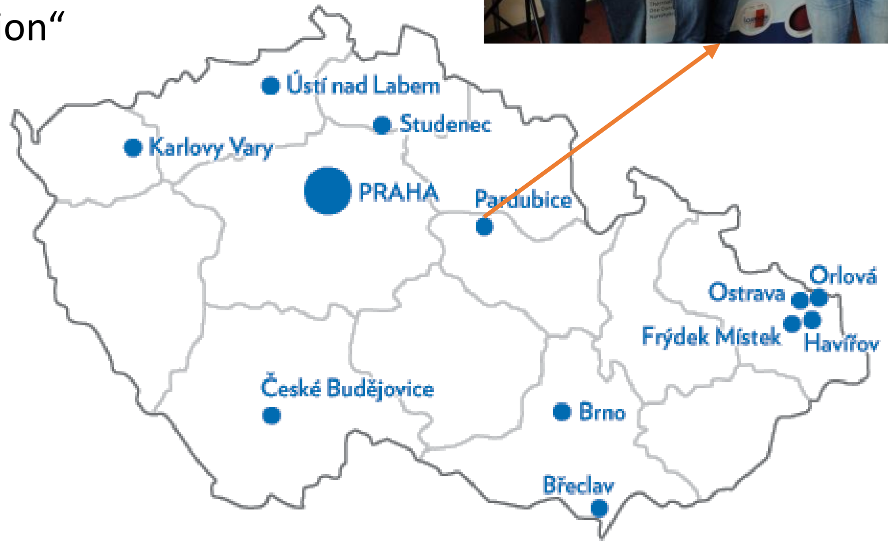
Latvian State Institute of Wood Chemistry (LV)

- Non-profit organization
- Sub-Contractor
- Semi scale of HNIPU foams by spraying and testing

TOSEDA s.r.o.

Who we are

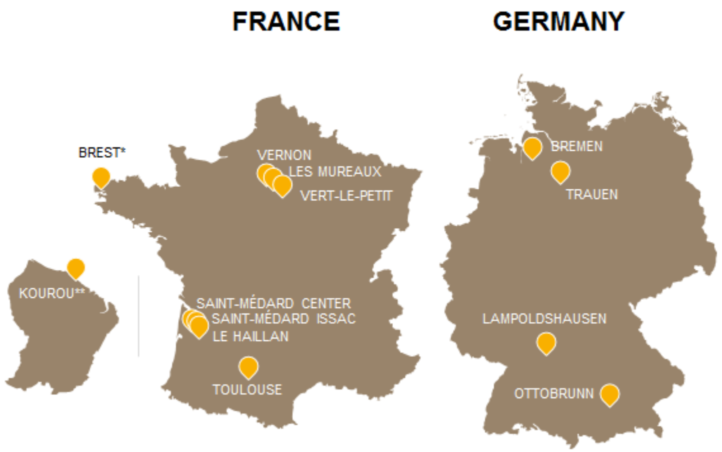
- Status: SME
- 2012: R&D company focused on “Research, development and small scale production“
- Ownership: Tomáš Vlček (50%), Jiří Zelenka (40%) and Markéta Zelenková (10%)
- Number of employees: 12
- 2012 registered at ESA
- 2013 membership at Czech Space Alliance



What we are doing

- Custom design, development and commercialization of polymeric and nanocomposite materials for hi-tech applications.
- Cooperation with key EU partners from the space industry (Airbus, Thales Alenia Space, MT Aerospace…).

ArianeGroup



- A world leader in access to space, serving institutional and commercial customers and supporting Europe’s strategic independence
- 9000 employees, 11 subsidiaries & main affiliates
- 50/50 joint company between Airbus & Safran
- Main projects:
  - Ariane 5
  - Launch Services
  - <u>Ariane 6</u>
- <u>Development and industrial application of the External Thermal Insulation (ETI) for the application on the Ariane 6 launch vehicle</u>
- In the frame of the “Green” PU project:
  - Providing LSI inputs, as well as support in testing

Latvian State Institute of Wood Chemistry

History

Present – cooperation with ESA and ArianeGroup

LS IWC mission is the development of knowledge-based, environment friendly low-waste technologies for obtaining competitive materials and products from wood and other plant biomass for sustainable utilisation of natural resources for economic, social and ecological benefits.

- Founded in 1946
- 118 employees;
- 38 Dr.

Cooperation with ArianeGroup (former Airbus DS; Airbus SL; ...) since 2004: development of ETI and IWTI

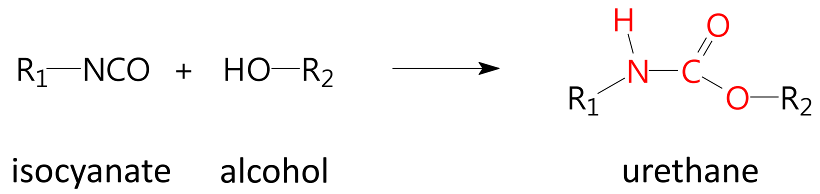
- Rigid Polyurethane Foams for External Tank Insulation for Launcher Upper Stages (**CRYOFOAMS**), 2015 – 2017
- Light Weight Polyurethane Insulation for the Bulkhead of Ariane Rocket, Produced with Next Generation Blowing Agents and Environmentally Friendly Catalysts (**CRYOFOAMS-LW**) 2018 - 2020

M-era.Net

Development of Biobased Cryogenic Insulation Modified with Nanocrystalline cellulose

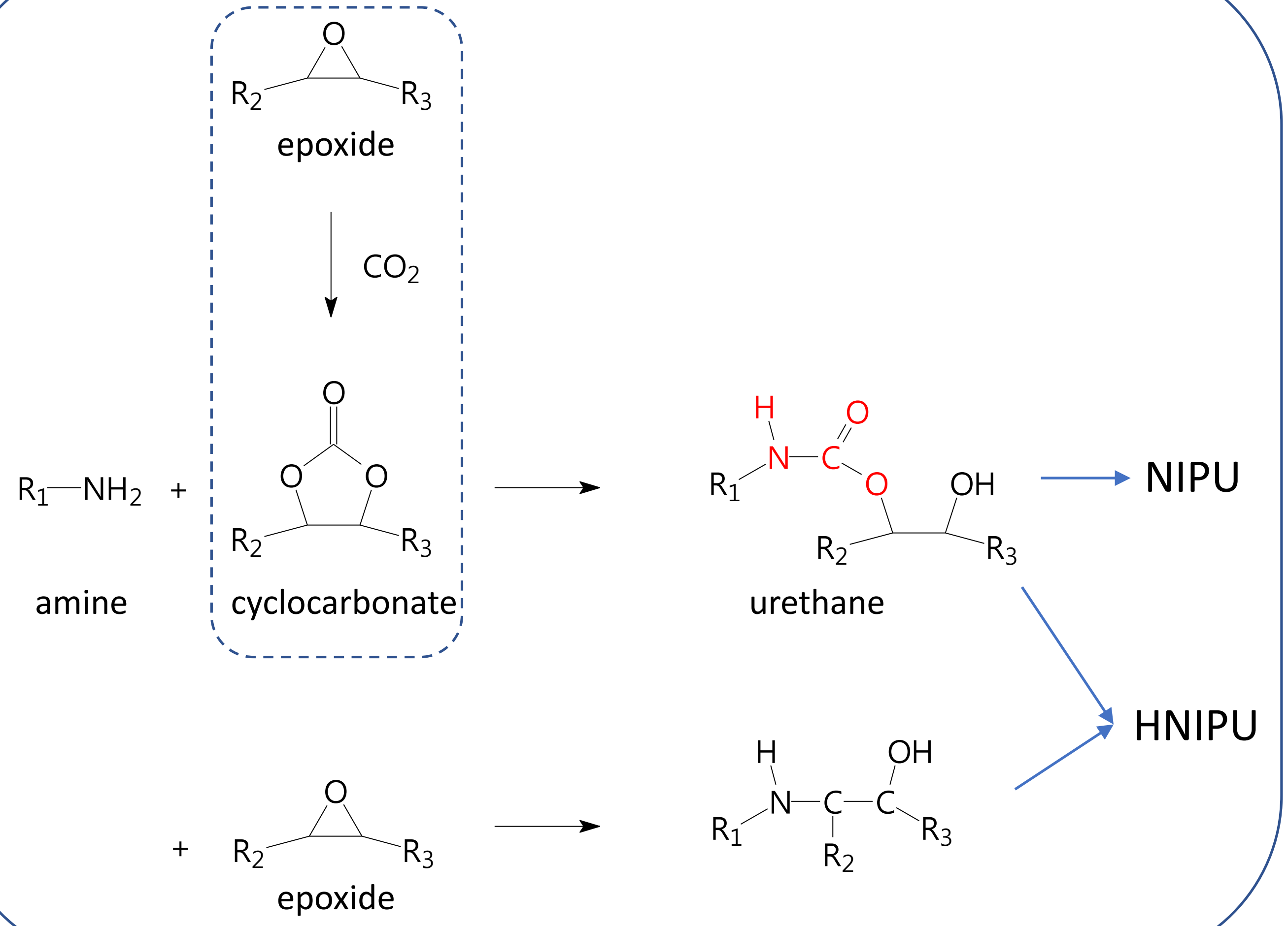
Approach

Traditional polyurethane synthesis



vs.

Non-isocyanate polyurethane synthesis



Synthesis of cyclocarbonates

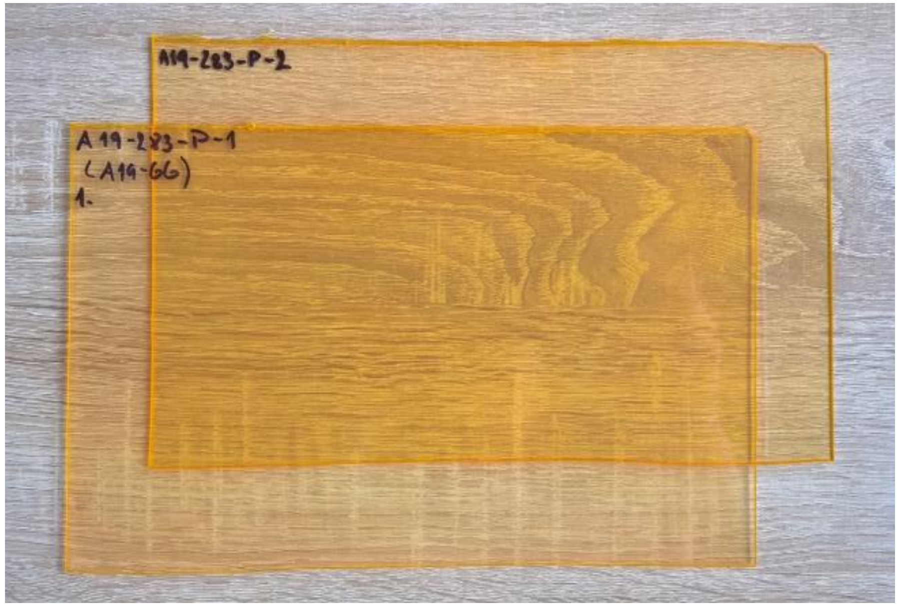
Photo of TOSEDA's laboratory pressure reactor set-up.

- Pressure: 40 bars (CO_2 inlet)
- Temperature: 110 °C (inside of the reactor)
- Mixing: mechanic stirrer
- Capacity: 500 mL
- Catalyst: Quaternary ammonium salt
- Co-catalyst: Catechol based hydrogen bond donor
- Reaction time: ca 10 - 72 h

E1 = 0.14 Pa.s (25 °C)
↓
CC1 = 0.94 Pa.s (80°C)

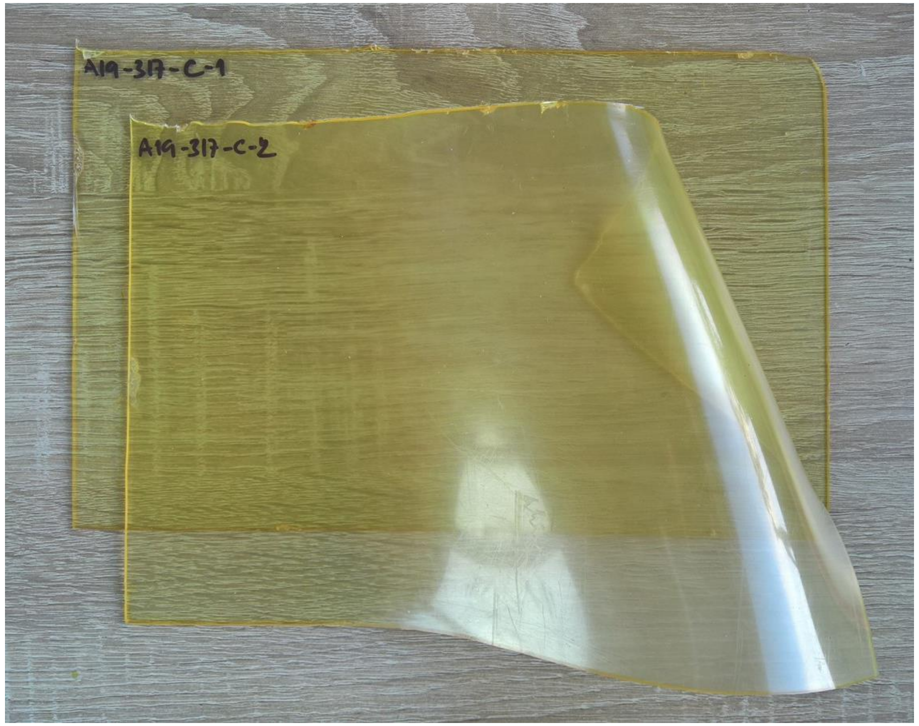
E2 = 0.40 Pa.s (25 °C)
↓
CC2 = 2.76 Pa.s (25 °C)

NIPU potting system



Renewables = 57,8 %
Non-isocyanates urethane bonds = 100 %

HNIPU conformal coating



Renewables = 51,3 %
Non-isocyanates urethane bonds = 42,9 %

NIPU potting system

Parameter	Requirement	Results	Compliancy
Outgassing *	RML < 1.0%, CVCM < 0.1%	0.53 % RML	Y
Glass transition temperature **	≤ 50 °C	47 °C	Y
Surface hardness **	≥ 70 Shore D	84 Shore D	Y
Surface resistivity **	≥ 6.1 x 10^{10} Ω	1.7 x10^{13} Ω	Y
Volume resistivity **	≥ 3.2 x 10^{12} Ω.m	1.8 x10^{13} Ω.m	Y
Tensile strength at RT **	≥ 35 MPa	35 MPa	Y
Tensile strength at -60 °C **	≥ 70 MPa	26 MPa	N
Elongation at break at RT **	≥ 15 %	5.1 %	N
Elongation at break at -60 °C **	≥ 5 %	1.2 %	N
REACH and environmental requirements *	No solvent content in targeted product	No solvent	Y
	No use of isocyanates in the synthetic route	No isocyanate	Y
	Possibly use of renewable sources	57.6 %	Y
Materials procurement *	EU market availability / ITAR free	Yes	Y
Thermal conductivity (26 °C) **	≥ 0.164 W/m.K	0.290 W/m.K	Y
Urethane related mass	As high as possible	100.0 %	Y

Note: * Benchmark target according to the SoW.
** Values derived from the reference polyurethane system based on reaction of Solithane S113 and TIPA (a product of Crompton, US)

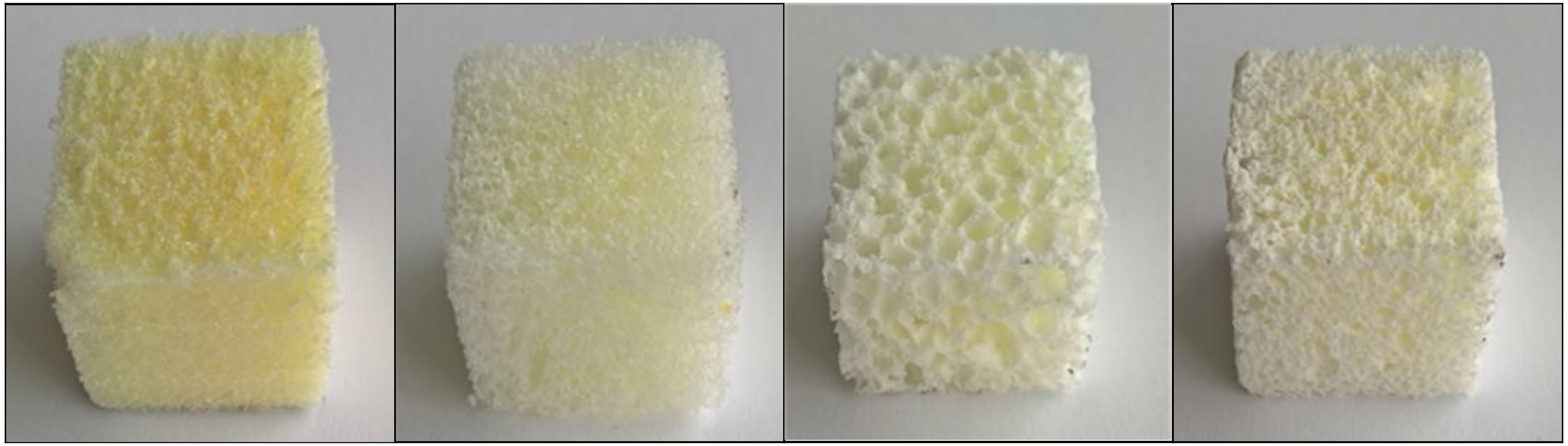
HNIPU conformal coating system

Parameter	Requirement	Results	Compliancy
Outgassing *	RML < 1.0%, CVCM < 0.1%	0.81 % RML	Y
Glass transition temperature **	≤ 1 °C	0 °C	Y
Surface hardness **	≥ 70 Shore A	75 Shore A	Y
Surface resistivity **	≥ 1.5 x 10^9 Ω	1.55 x 10^{11} Ω	Y
Volume resistivity **	≥ 5.7 x 10^{11} Ω.m	3.8 x 10^8 Ω.m	N
Tensile strength at RT **	≥ 2.5 MPa	2,1 MPa	N
Tensile strength at -60 °C **	≥ 45 MPa	53.2 MPa	Y
Elongation at break at RT **	≥ 90 %	92 %	Y
Elongation at break at -60 °C **	≥ 20 %	3.3 %	N
REACH and environmental requirements *	No solvent content in targeted product	No solvent	Y
	No use of isocyanates in the synthetic route	No isocyanate	Y
	Possibly use of renewable sources	51.3 %	Y
Materials procurement *	EU market availability / ITAR free	Yes	Y
Thermal conductivity (26 °C) **	≥ 0.251 W/m.K	0.292 W/m.K	Y
Urethane related mass	As high as possible	42.9 %	Y

Note: * Benchmark target according to the SoW.
** Values derived from the reference polyurethane system based on reaction of Solithane S113 and Solithane C113-300 (a product of Crompton, US)

HNIPU rigid thermoinsulation foams

Laboratory testing



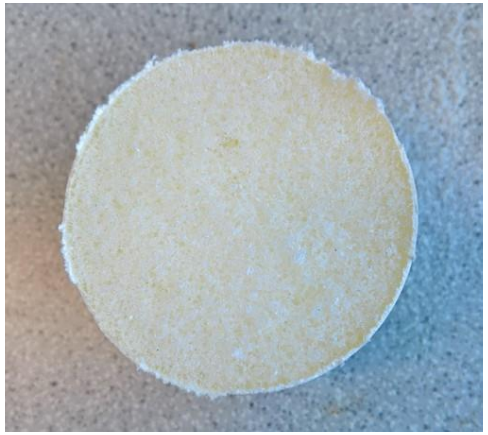
		PU CRS 127 reference	HNIPU F 1	HNIPU F 2	HNIPU F 3
Density [g/cm^3]	-	0.05	0.08	0.11	0.14
Compression strength at 10% deformation [MPa]	> 0.45*	0.16	0.09	0.35	0.48
Thermal conductivity [W/m.K]	< 0.035*	0.033	0.039	0.038	0.042

*Benchmark targets

HNIPU rigid thermoinsulation foams

- Best candidate HNIPU foam
- Non-isocyanates urethane bonds = 37,6 %
- Renewables = 48,2 %
- Density 0.075 g/cm^3
- CF free blowing agent
- Mixing ratio A/B = 1/1
- Applicable by spraying
- White color
- Fine cell structure
- No shrinkage

- A = 0.67 Pa.s (25 °C)
- B = 0.86 Pa.s (80 °C)



Laboratory preparation in paper cup

Scale-up

HNIPU rigid thermoinsulation foams

Parameter	Requirement	Results	Compliancy
Thermal conductivity	< 0.035 [W/m.K] at RT	0.039 W/m.K (26,1°C)	Y
Compressive strength load (externally applied insulation)	> 0.45 MPa (ETI); > 1.05 MPa (ITI)	0.09 MPa (RT) 0.37 MPa (-60°C)	N
Thermal efficiency [defined as 1 / density / thermal conductivity]	as high as possible (0.72 as target)	0.34	N
Closed cell content	as high as possible (90 % as target)	40.6 %	N
Chemical compatibility to GH_2, GN_2 and He	Less than 20 % decrease of properties (compression strength load at 10 % deformation)	0.07 MPa (GH_2) 0.10 MPa (GN_2) 0.11 MPa (He)	N Y Y
Low mass gain and no mech. failure induced by cryopump. effect	Less than 20 % decrease of properties	0.09 MPa	Y
REACH and environmental requirements	No solvent content in targeted product	No solvent	Y
	No use of isocyanates in the synthetic route	No isocyanate	Y
	Possibly use of renewable sources	48.2 %	Y
	No CFC foaming agents are to be used	Yes	Y
Materials procurement	EU market availability / ITAR free	Yes	Y
Urethane related mass	As high as possible	37.6 %	Y

Conclusions

- Hybrid non-isocyanates polyurethanes as new environmentally friendlier alternative to traditional PU materials
    - Up to 100 % replacement of toxic isocyanate hardeners
    - Up to ca 60 % renewable raw materials

SYSTEM	Non-isocyanate urethane bonds [%]	Renewables content [%]
NIPU potting	100	58
HNIPU conformal coating	43	51
HNIPU foams	38	48

- The pre-developer HNIPU rigid foam has high potential to be implemented as external thermal insulation on existing and future Launch Vehicles by spraying without use of hazardous blowing agents
- The pre-developed (H)NIPU resins are suitable candidates for application in space vehicles electronics such as potting and conformal coating materials
- Next steps: to increase maturity to TRL 5