TRP ACHIEVEMENT

Title: Development of "Green" Polyurethane Materials for Use in Spacecraft and Launcher Applications

Estimated Start TRL: 2

Targeted TRL: 4

Achieved TRL: 4

Introduction

Polyurethanes (PUs) are versatile materials widely used also for space applications due to their stability under space environmental conditions. The traditional manufacturing process of polyurethanes involves the use of toxic isocyanates. Currently, more environmentally friendly methods for syntheses of conventional PUs are based on reaction of isocyanates with biobased polyols. However, these methods do not eliminate necessity of the use of hazardous isocyanate substances that may become subject to limitations imposed by the REACH regulation. Other and more challenging alternative ways for syntheses of eco-friendlier PUs include non-isocyanate chemistries based for instance on reaction of cyclic carbonates with amines leading to hydroxy-urethane bonds generation.
The main objective of the presented activity was to verify the possibility of implementing the most perspective non-isocyanate chemistry in the production of PU materials suitable for space applications. The activity was planned as generic but the specific launcher applications, including thermal insulation foam material, conformal coating and potting, were considered.

Objectives

The objective of this activity was to develop novel European polyurethane (PU) materials suitable for versatile space applications that can be manufactured via "environmentally friendly" procedure without the use of toxic isocyanates and/or employing sustainable materials sources. The following technical requirements were claimed:

The non-isocyanate PU shall be formulated preferably as systems applicable as:
- a/ potting systems (spacecrafts manufacturing),
- b/ conformal coating (spacecrafts manufacturing), and
- c/ thermal insulation foams (launchers manufacturing).

The new non-isocyanate PU materials should be formulated with the aim to reach basic

requirements defined for targeted application and/or maintain the properties of the existing commercial PU systems (low moisture absorption, suitable thermo-mechanical properties, high chemical resistance, high adhesion to various substrates even at cryogenic conditions, low outgassing etc.).
The manufacturing processes for the new non-isocyanate PU materials should be easily adaptable to conventional processes for the polyurethane systems application (coating, spraying, casting, foaming…).
Another surplus shall be implementation of sustainability aspects. That means to verify possibility to use renewable resources as starting raw materials for production of non-isocyanate PUs.

Achievements

The screening study confirmed possibility to manufacture polyurethane rigid thermo-insulating foam, conformal coating and potting system targeted for space applications without necessity to use toxic isocyanates. The non-isocyanate polyurethanes (NIPU) are effectively synthesized by reaction of cyclocarbonates with amines and eventually modified by epoxy compounds (hybrid types, HNIPU). The novel types of non-isocyanate materials were designed as environmentally friendly systems contributing to sustainability by using ca 50 wt. % of renewable resources for their synthesis. Their formulations do not contain any organic solvents and in case of foam no ozone depletant blowing agents (CFCs). The most promising results were obtained in case of HNIPU conformal coating and NIPU potting system providing properties comparable to selected reference space-qualified commercial polyurethane materials. HNIPU foam does not fulfill all key technical requirements for the intended application as external thermal insulation of tanks for liquid propellants of launchers. However, the foam is of a good quality and has potential to be applicable by requested spraying technique in industrial scale. Further investigation will be needed to improve the (H)NIPU materials properties and to adjust the processing parameter according to the targeted industrial application.

In accordance with the Statement of the Work (SoW) the activities foreseen to be performed within the Project included the following tasks:

Task 1: **Analysis of the market / literature on „green“ PUs and PUs for space applications with development of a technical specification**
Task 2: **Development plan (DP1) and test plan (TP1) for the „green“ PUs**
Task 3: **Preliminary development and testing of the „green“ PUs**
Task 4: **Development of a manufacture plan (MP2) and test plan (TP2) for „green“ PUs**
Task 4: **Manufacture and full testing of the „green“ PUs**
Task 4: **The final analysis and conclusions**

1 Literature and patent survey

The literature and patent survey confirmed that industrially most perspective route for synthesis of non-isocyanate polyurethanes (NIPU) is based on reaction of cyclocarbonates with amines.

The production of non-isocyanate polyurethanes included the following two perspective chemical routes (**Fig. 1**):

- Non-isocyanate polyurethanes (NIPU):
    - Cyclic carbonates cured by amine hardeners
- Hybrid epoxy - non-isocyanate polyurethanes (HNIPU):
    - Cyclic carbonates and epoxy compounds cured by amine hardeners

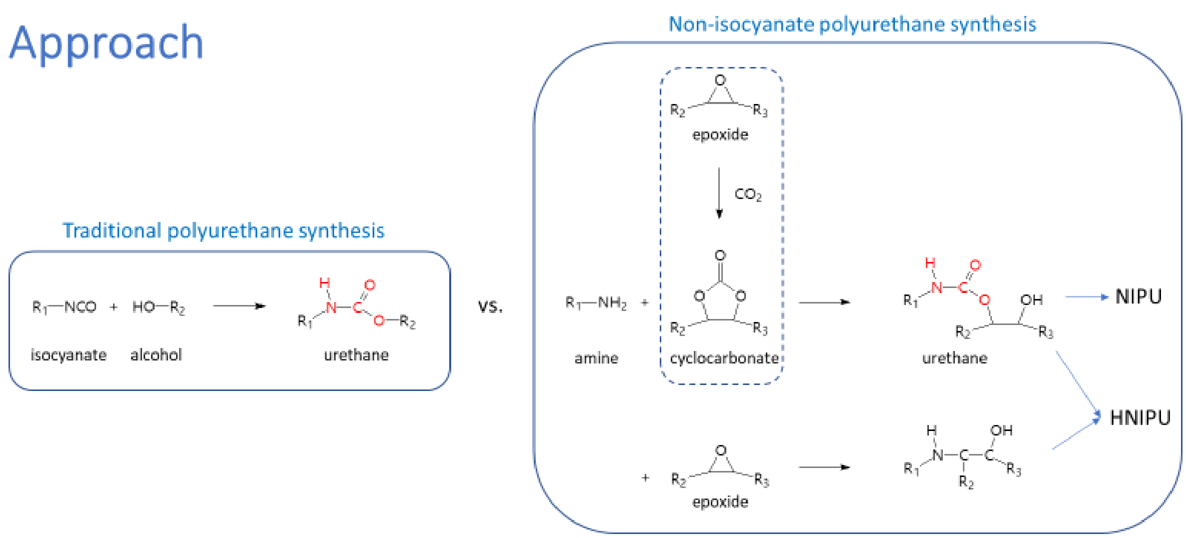


Fig. 1: Scheme of chemical synthesis routs leading to production of NIPU and HNIPU materials.

2 Development

The development works were conducted in two steps, where the first step was targeted to the preliminary development and testing and pre-selection of the best candidate system per each targeted formulation, and the second step was dedicated to the further optimization of the pre-selected systems followed by their scale-up verification and full testing (**Fig. 2**).

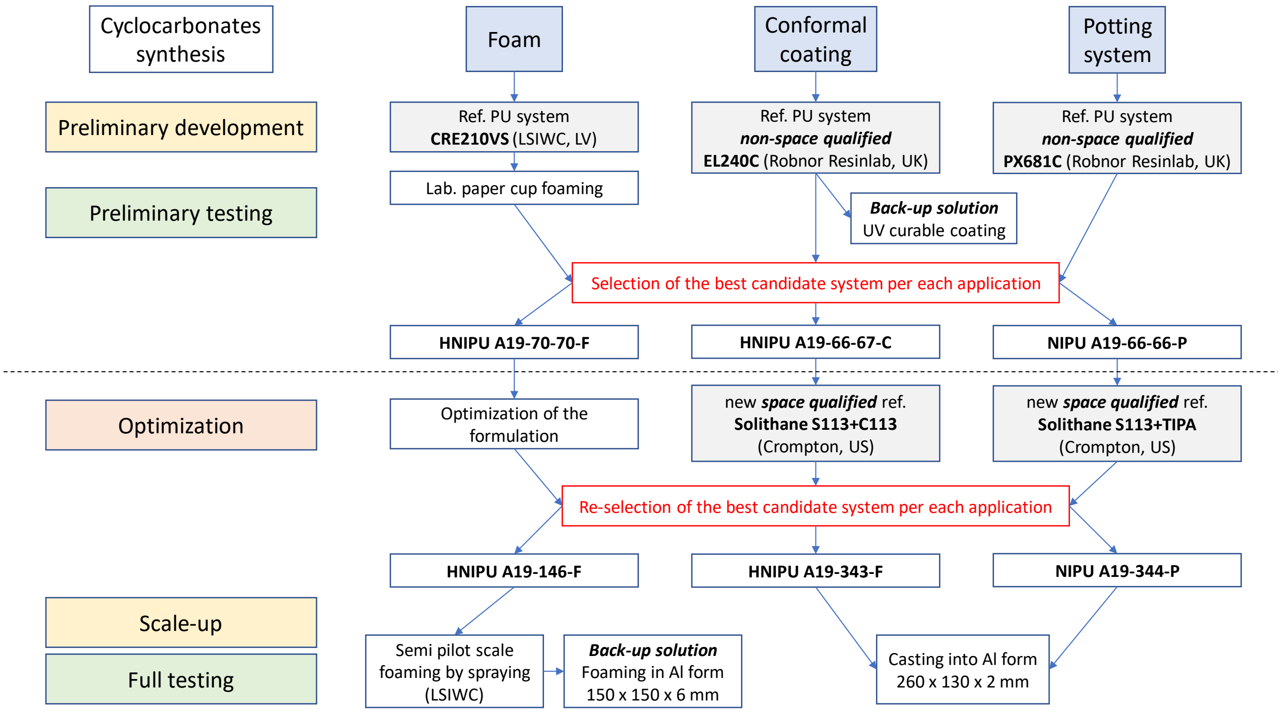


Fig. 2: Scheme of the performed development and scale-up activities.

1-1 Preliminary development and testing

TOSEDA confirmed possibility to synthesize different cyclocarbonated compounds in laboratory scale using a pressure reactor. In this way, TOSEDA synthesized 2 types of cyclocarbonated reactive solvents and 3 types of cyclocarbonated bio-based monomers. The reached conversion was over 98 %.

Drawback is that cyclocarbonization increases about 10x viscosity of starting epoxy compounds, what can be limiting factor for some applications.

The (H)NIPU materials were formulated with the aim to adjust properties of the developed materials to the selected reference systems that included rigid polyurethane foam CRE210VS (a product of LSIWC, LV) specially designed for insulation of tanks for liquid propellants of launchers, flexible two component polyurethane conformal coating EL240C (a product of Robnor Resin, UK), and rigid epoxy potting system PX681C (Robnor Resin, UK). The space non-qualified conformal coating and potting system were chosen as reference systems due to unavailability of space qualified products during the development activity.

The preliminary development study resulted in selection of the following NIPU/HNIPU rigid foam, conformal coating and potting systems, indicated as the most suitable candidates for up-scale and full testing.

Tab. 1: Basic characterization of the predeveloped NIPU/HNIPU systems.

Application	Non-isocyanate system	Sample ID	Bio-sourced mass content [%]	Hydroxy urethane bond mass per total bond mass [%]
Rigid insulation foam	HNIPU	A19-70-70	44.4	41.8
Conformal coating	HNIPU	A19-66-67	58.9	35.7
Potting system	NIPU	A19-66-66	56.7	100.0

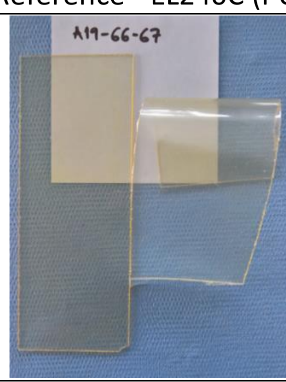
Rigid foam	Conformal coating	Potting system
		
Reference - CRE210VS	Reference - EL240C (PU)	Reference - PX681C (epoxy)
		
A19-70-70-F (HNIPU)	A19-66-67-C (HNIPU)	A19-66-66-P (NIPU)

Fig. 3: Appearance of pre-selected reference and preliminary developed (H)NIPU foams, conformal coatings and potting systems.

1-2 Manufacture and full testing

The manufacturing phase of the project consisted of the following steps:

- Optimization of the pre-developed (H)NIPU formulations
- Scale up

With agreement of the Agency there were selected new and space-qualified reference systems for conformal coating and potting system (**Tab. 2**).

Tab. 2: Updated reference systems for optimization of the predeveloped (H)NIPU systems.

Application	Composition	Supplier
Rigid insulation foam for launchers tanks	CRE210VS	LSIWC, LV
Conformal coating	Solithane S113 + Solithane C113-300	Crompton, US
Potting system	Solithane S113 + TIPA	Crompton, US

Therefore, the initial step of manufacturing was dedicated to the optimization of the pre-developed conformal coating and potting system formulations to adjust the properties to the newly used space-qualified reference samples. The optimization included also formulation of HNIPU rigid foam A19-70-70 with the aim to improve the material properties according to the requirements for the application technologies and processes and final product properties.

Two new types of biobased cyclocarbonates, CCECO and CCETP, were synthesized for preparation of down-selected formulations of (H)NIPU potting, conformal coating and foam systems. Cylocarbonation results in at least 10x increase of viscosity of the initial epoxy compounds, see **Fig. 4**.

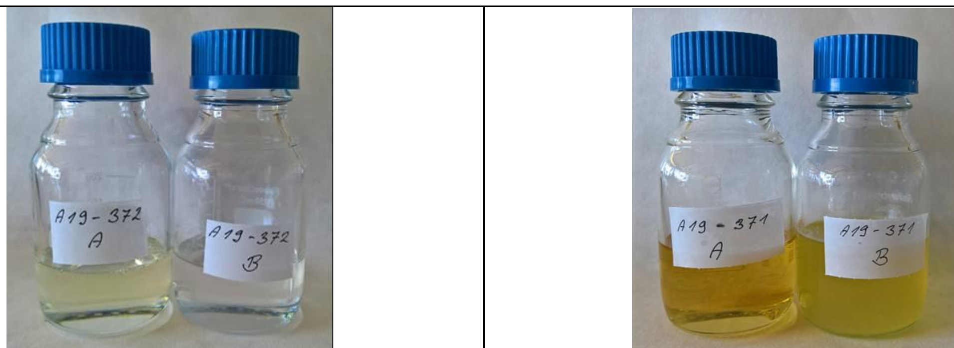
	
CCETP initial epoxy: 0.14 Pa.s (25 °C) Cyclocarbonate: 0.94 Pa.s (80 °C)	CCECO initial epoxy: 0.40 Pa.s (25 °C) Cyclocarbonate: 2.76 Pa.s (25 °C)

Fig. 4: Appearance of synthesized CCETP and CCECO cyclocarbonates.

TOSEDA selected the following best candidate non-isocyanate systems fulfilling requirements of each type of application given by Benchmark Targets and characterization of selected space-qualified reference systems (**Tab. 3**, **Fig. 5** and **6**).

Tab. 3: Down-selected best candidate (H)NIPU materials.

Application	Non-isocyanate system	Sample ID	Bio-sourced mass content [%]	Hydroxy urethane bond mass per total bond mass [%]
Rigid insulation foam	HNIPU	A19-146-F	48.2	37.6
Conformal coating	HNIPU	A19-300-C	51.3	42.8
Potting system	NIPU	A19-66-66-P	56.7	100.0



HNIPU conformal coating	NIPU potting system

Fig. 5: Appearance of the components A and B of the developed (H)NIPU systems.

HNIPU foam	HNIPU conformal coating	NIPU potting system

Fig. 6: Appearance of the best candidate (H)NIPU systems.

The results of full testing showing compliancy of the developed (H)NIPU foam, conformal coating and potting system with the key parameters are summarized in **Tab. 4**, **5** and **6**.

Tab. 4: Results of full testing of the developed **rigid HNIPU foam** system A19-146-F.

Parameter	Requirement	Results	Compliancy
Thermal conductivity *	< 0.035 [W/m.K] at RT	0.039 W/m.K (26 °C)[1]	N
		0.039 W/m.K (20 °C)[2]	N
		0.0382 ± 0.0004 W/m.K (25°C)[3]	N
Humidity absorption *	≤ 1% mass increase	348 ± 9 %	N
Dimension stability *	< 5% (dry; 80°C) < 10% (100% RH; 70°C) in 28 days	1.24 ± 0.03 % (dry; 80 °C) 0.80 ± 0.17 % (100 % RH; 70 °C)	Y Y
Tensile strength load (externally applied insulation) *	> 0.9 MPa	0.06 ± 0.02 MPa (RT) 0.40 ± 0.02 MPa (-30 °C)	N
Tensile strength load (internally applied insulation) *	> 1.13 MPa		N
Compressive strength load (externally applied insulation) *	> 0.45 MPa	0.10 ± 0.01 MPa (RT) 0.37± 0.04 MPa (-60 °C)	N
Compressive strength load (internally applied insulation) *	> 1.05 MPa		N
Max elongation at cryogenic temperatures *	> 2 %	24.48 ± 6.21 % (RT) 2.8 ± 0.34 % (-30 °C)	Y
Glass transition temperature	Not specified	52 °C (DSC)	-
Density	Not specified	0.078 ± 0.005 g/cm^3	-
Thermal efficiency [defined as 1 / density / thermal conductivity] *	as high as possible (0.72 as target)	0.33	N
Closed cell content *	as high as possible (90 % as target)	40.6 %	N
Permeability to GH_2 and LH_2 *, ***	as low as possible	Not evaluated*****	N
Chemical compatibility to LH_2, GH_2, GN_2 and He *, ***	Less than 20 % decrease of properties	0.07 ± 0.01 MPa (GH_2) 0.10 ± 0.01 MPa (GN_2) 0.11 ± 0.01 MPa (He)	N Y Y
Low mass gain and no mechanical failure induced by cryopumping effect *	Less than 20 % decrease of properties (Compressive strength)	0.09 ± 0.01 MPa	Y
Shelf-life of the installed foam insulation *	minimum of 5 years	Not evaluated******	N
Coefficient of thermal expansion (CTE) *	assumed 11x10^{-6} 1/°C at 20K, and < 50x10^{-6} at 25°C	56x10^{-6} 1/°C at -250 °C, and 158x10^{-6} 1/°C at 25 °C	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	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

* Benchmark target according to the SoW
** Reference polyurethane system CR S27 (a product of LSIWC)
*** According to the Minutes No.1 from the Negotiation meeting the permeability and chemical compatibility to LH2 requested in the Statement of the Work will be avoided.
**** Due to very low closed cell content (40.6 %) reflecting in very low barrier properties of the developed HNIPU foam it was decided to avoid permeability test the permeability.
***** The requested shelf life testing for the period of % years exceeds duration of the project and was avoided for very low closed cell content (40.6 %) reflecting in very low barrier properties of the developed HNIPU foam.
1,2,3 Test results observed by TCi Thermal Conductivity Analyzer, Linseis Heat flow Meter 200, and Transient hot wire technique.

Tab. 5: Results of full testing of the developed **conformal coating** A19-343-C (A19-300-C).

Parameter	Requirement	Results	Compliancy
Outgassing *	RML < 1.0%, CVCM < 0.1%	0.81 % RML	Y***
Pot life *	Min 2 hours	38 min (28 °C)	N
Curing time *	25 °C, max 7 days	80% conv. 5 days	Y
Operational temperature *	~ -60°C to 120°C	see tensile properties below	Y
Viscosity **	≤ 8 Pa.s (25 °C)	8 Pa.s (24 °C)	Y
Glass transition temperature **	≤ 1 °C	0 °C	Y
Surface hardness **	≥ 70 Shore A	75 ± 2 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 120 °C	-	0.81 ± 0.08 MPa	Y
Tensile strength at RT **	≥ 2.5 MPa	2.10 ± 0.21 MPa	N
Tensile strength at -60 °C **	≥ 45 MPa	53.2 ± 11.3 MPa	Y
Elongation at break at 120 °C	-	24 ± 3 %	Y
Elongation at break at RT **	≥ 90 %	92 ± 7 %	Y
Elongation at break at -60 °C **	≥ 20 %	3.3 ± 1.1 %	N
REACH and environmental requirements *	No solvent content in targeted product	No solvent	Y
	No use of isocyanates	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	42.8.0 %	Y

* Benchmark target according to the SoW. Simplified TOSEDA test method applied.
** Values derived from the ref. polyurethane system based on reaction of Solithane S113 and Solithane C113-300 (Crompton, US).
*** Partly compliant since CVCM not provided and not known.

Tab. 6: Results of full testing of the developed **potting** system A19-344-P (A19-66-66-P).

Parameter	Requirement	Results	Compliancy
Outgassing *	RML < 1.0%, CVCM < 0.1%	0.53 % RML	Y****
Pot life *	Min 2 hours	56 min (28 °C)	N***
Curing time *	25 °C, max 7 days	80% conv. 5 days	Y
Operational temperature *	~ -60°C to 120°C	see tensile properties	Y
Viscosity **	≤ 110 Pa.s (25 °C)	0.33 Pa.s (28 °C)	Y
Glass transition temperature **	≤ 50 °C	45 °C	Y
Surface hardness **	≥ 70 Shore D	86 ± 2 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 120 °C	-	0.62 ± 0.06 MPa	Y
Tensile strength at RT **	≥ 35 MPa	34.3 ± 3.3 MPa	Y
Tensile strength at -60 °C **	≥ 70 MPa	26.1 ± 10.1 MPa	N
Elongation at break at 120 °C	-	33 ± 3 %	Y
Elongation at break at RT **	≥ 15 %	4.9 ± 0.8 %	N
Elongation at break at -60 °C **	≥ 5 %	1.2 ± 0.4 %	N
REACH and environmental requirements *	No solvent content in targeted product	No solvent	Y
	No use of isocyanates	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

* Benchmark target according to the SoW. Simplified TOSEDA test method applied.
** Values derived from the reference polyurethane system based on reaction of Solithane S113 and TIPA (Crompton, US).
*** The viscosity increase after 2h is still acceptable for processing due to very low initial viscosity of reaction mixture.
**** Partly compliant since CVCM not provided and not known.

The screening study confirmed good potential for industrial use of all the developed non-isocyanate materials, i.e. HNIPU rigid foam, HNIPU conformal coating, and NIPU potting system.

The best results were obtained in case of HNIPU conformal coating and NIPU potting system. Also, these novel (H)NIPU materials did not show compliancy with all key parameters (see **Tab. 5** and **6**), particularly tensile properties and pot life, they provide properties comparable with properties of the selected space qualified reference commercial materials. With small adjustments, it can be predicted that the novel (H)NIPU conformal coating and potting systems can replace the traditional polyurethane materials in selected applications.

The developed HNIPU rigid foam did not fulfill majority of key parameters defined for external thermal protection of tanks for liquid propellants (see **Tab. 4**). On the other hand, the foam formulation should be possible to adjust to requested processing parameters needed for applicability by spraying.

The study further confirmed that these novel polyurethane materials can be formulated as environmentally friendly systems based on ca 50 wt. % of renewable resources and containing even up to 100 % of non-isocyanate urethane bonds generated by reaction of cyclocarbonates with amines.

Application

The developed 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.

Further Activities

Further development activities should be performed to optimize the formulations and application processes according to the targeted application and to reach industrial scale of manufacturing. The future activities should be focused on:

- Development and optimization of scale-up processes for synthesis of the used cyclocarbonates needed for production of the non-isocyanate materials.

- Development and optimization of the formulations/chemical composition of the HNIPU rigid foams, HNIPU conformal coatings, HNIPU UV curable conformal coatings and NIPU potting systems according to the selected application.
- Development and optimization of procedures for non-isocyanate materials manufacturing and application in industrial scale.

Due to already reached maturation (TRL 4) of the non-isocyanate polyurethane materials development, the future activities are foreseen to reach TRL 5, with roughly estimated budget 500 kEuro and in estimated time frame 24 months.

Non-Space Application

Reformulation of the developed (H)NIPU materials in accordance with technological requirements of the potential end-users will be possible and will allow broadening the applicability of this unique product also in other industries.

The novel type of HNIPU rigid foams can extend the portfolio of existing or replace traditional polyurethane foams applicable by spraying. They can be used as thermally insulating materials with reduced toxicity applicable in industries including aerospace, automotive, and construction.

The developed (H)NIPU resins can find utilization namely in electronic applications as eco friendlier potting resins for transformers and different sensors, or as a cost-effective one component UV curable conformal coating etc.

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