Environmentally friendly polyurethane (PU) materials for space applications

ESA-ESTEC

TOSEDA s.r.o.
Ariane Group GmbH
Latvian State Institute of Wood Chemistry

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
- No solvent content in the target product.
- EU market availability / ITAR free.

Previous activity:

- Development of (H)NIPU conformal coating, potting and rigid foam
- ESA program: TRP
- Duration: 2017-2019
- ESA Contract: 4000119685/17/NL/KML
- TRL: 3-4

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. (CZ)

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

ArianeGroup GmbH (DE)

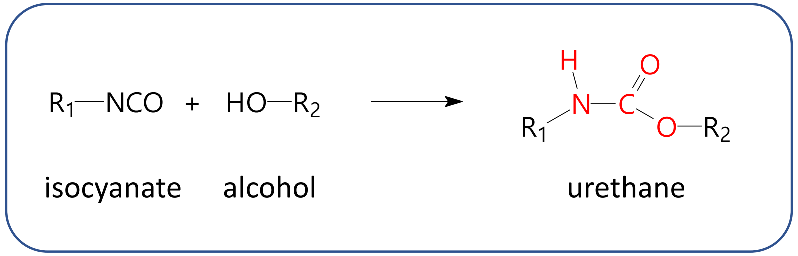
- Large Systems Integrator (LSI)
- Sub-Contractor
- Definition of industrial requirements and evaluation of HNIPU materials

CCN1:

- Extension towards applications as conformal coatings and as potting material
- Duration: 2020-2022
- TRL: 4-5

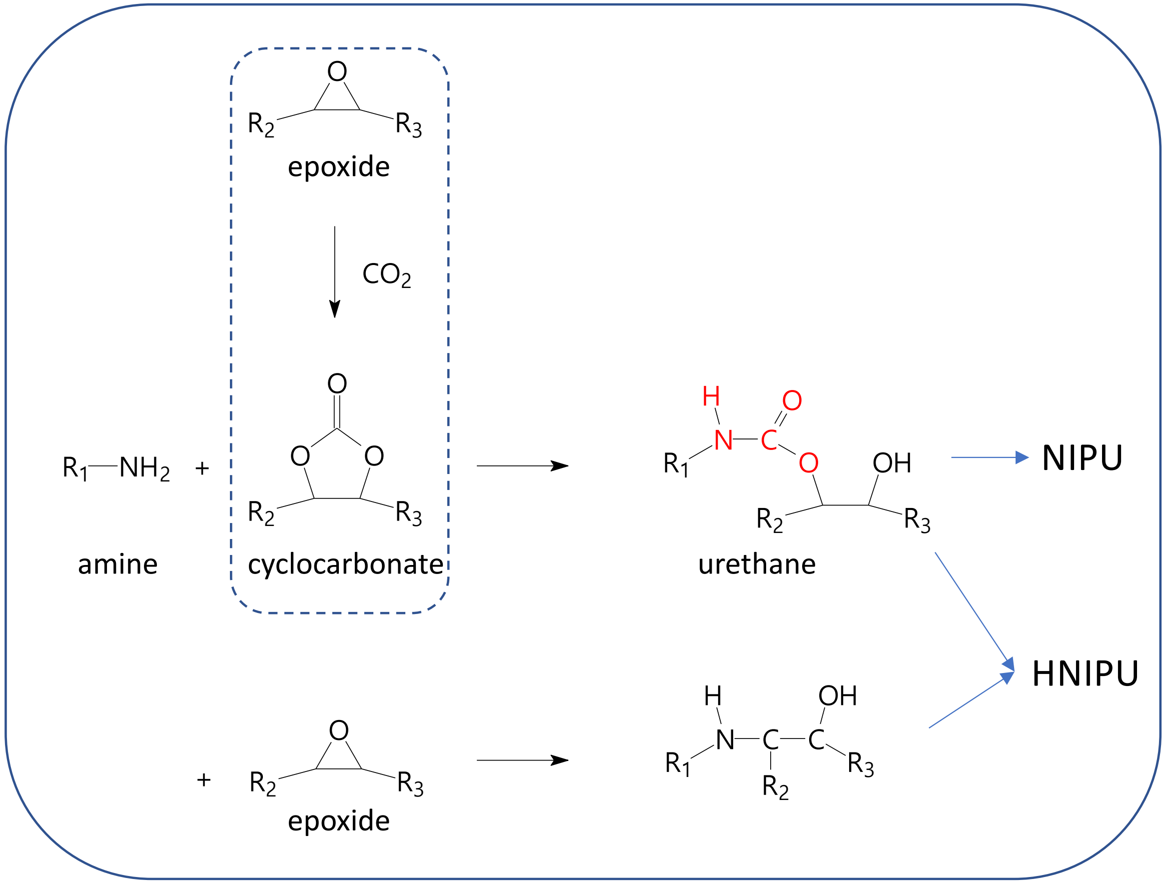
Approach

Traditional polyurethane synthesis

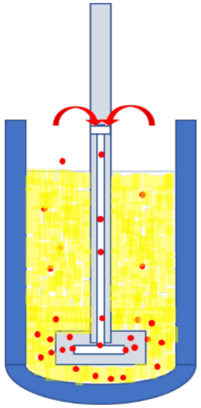


vs.

Non-isocyanate polyurethane synthesis



Synthesis of cyclocarbonates



300 g batch

TOSEDA's laboratory pressure reactor set-up.

- Starting raw materials: epoxy compounds based on renewables
- Pressure: 40 bars (CO_2 inlet)
- Temperature: 110 °C (inside of the reactor)
- Mixing: mechanic stirrer
- Capacity: 500 mL
- Catalyst: Quaternary ammonium salt
- Reaction time: ca 10 - 72 h (epoxy groups content ≤ 0.05 mol/kg)

Synthesis of cyclocarbonates

Cyclocarbonate	Viscosity @ 25 °C [Pa.s]		Epoxy group content [mol/kg]		Theoretical conversion [%]
	before	after	before	after	
	cyclocarbonation				
CC1	0.14	0.94*	6.07	0.03	99.5
CC2	0.40	2.76	5.17	0.03	99.4

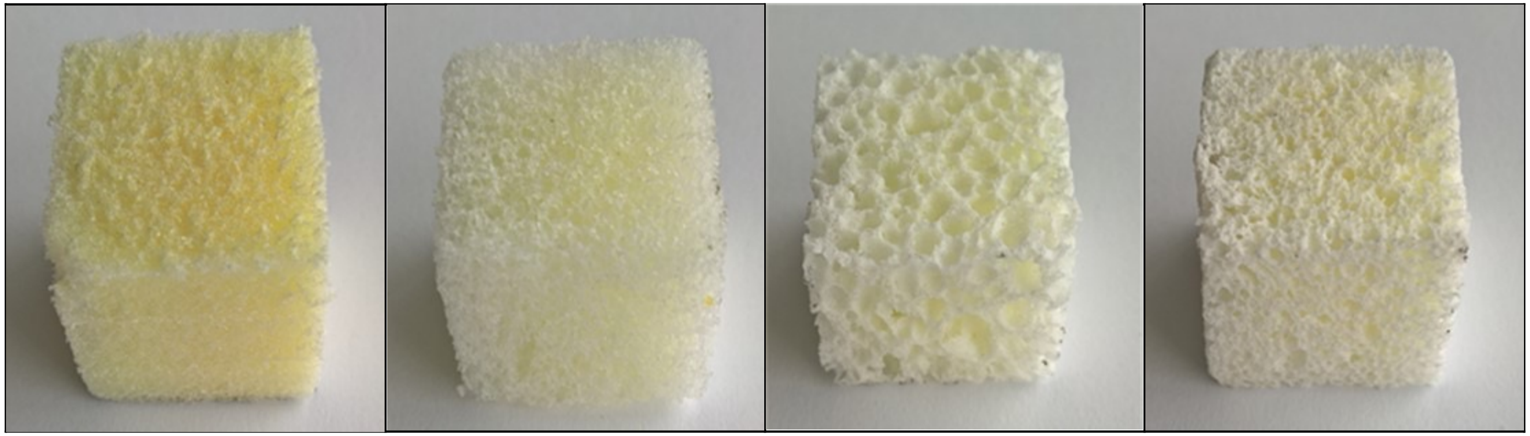
Previous activity

Application	Reference systems	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

Application	Non-isocyanate system	Bio-sourced mass content [wt. %]	Hydroxy urethane bond mass per total bond mass [%]
Rigid insulation foam	HNIPU	48.2	37.6
Conformal coating	HNIPU	51.3	42.8
Potting system	NIPU	56.7	100.0

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

Laboratory preparation in paper cup

- 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

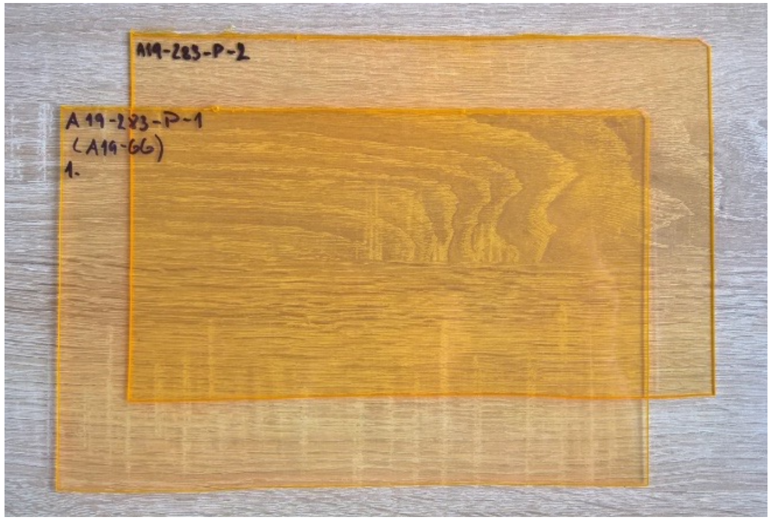
- A = 0.67 Pa.s (25 °C)
- B = 0.86 Pa.s (80 °C)

Scale-up

HNIPU rigid thermoinsulation foams

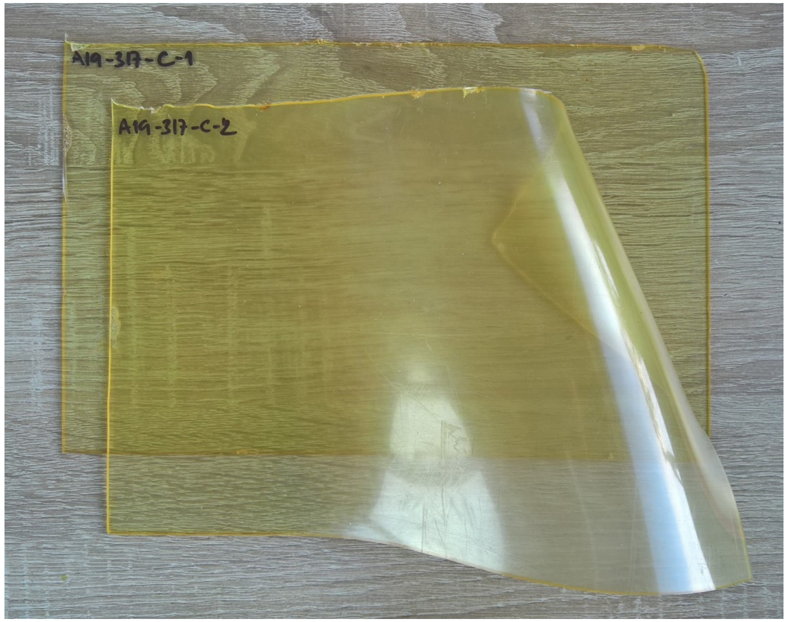
Parameter	Requirement	Results	Compliancy
Thermal conductivity	< 0.035 [W/m.K] at RT	0.039 W/m.K (26,1°C)	Y
Compressive strength load (externally applied insulation)	> 0.45 MPa (ETI); > 1.05 MPa (ITI)	0.09 MPa (RT) 0.37 MPa (-60°C)	N
Thermal efficiency [defined as 1 / density / thermal conductivity]	as 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

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

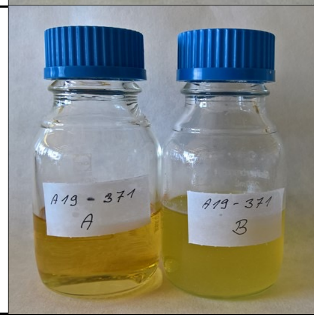
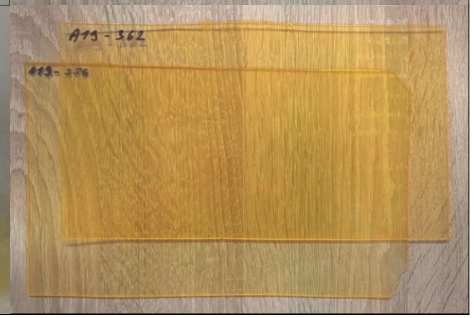
Parameter	Requirement	Results	Compliancy
Outgassing *	RML < 1.0%, CVCM < 0.1%	0.53 % RML	Y
Glass transition temperature **	≤ 50 °C	47 °C	Y
Surface hardness **	≥ 70 Shore D	84 Shore D	Y
Surface resistivity **	≥ 6.1 x 10^{10} Ω	1.7 x10^{13} Ω	Y
Volume resistivity **	≥ 3.2 x 10^{12} Ω.m	1.8 x10^{13} Ω.m	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)

Application	Dimensions of delivered HW	Appearance of the HW	
Rigid insulation foam	3 x 3 x 12 cm blocks (2 pcs)		
Conformal coating	250 ml of the uncured materials Recommended curing: 3h @ 50 °C + 11 h @ 70 °C + 3 h @ 110 °C 25 x 15 cm cured plates, thickness 2 mm (2 pcs)		
Potting system	250 ml of the uncured materials Recommended curing: 3h @ 50 °C + 11 h @ 70 °C + 3 h @ 110 °C 25 x 15 cm cured plates, thickness 2 mm (2 pcs)		

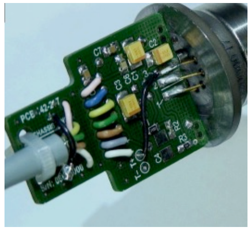
Conclusions - previous study

- 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	Hydroxy urethane bond mass per total bond mass [wt. %]	Content of renewables based components [wt. %]
NIPU potting	100	58
HNIPU conformal coating	43	51
HNIPU foams	38	48

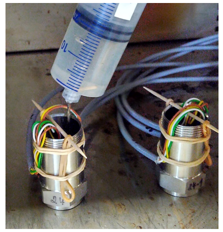
- The pre-developer HNIPU rigid foam has high potential to be implemented as external thermal insulation on existing and future Launch Vehicles by spraying without use of hazardous blowing agents
- The pre-developed (H)NIPU resins are suitable candidates for application in space vehicles electronics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

CCN1



Studied systems:

- Conformally coated printed circuit boards
  - 2 component system
  - 1 component system - UV curable (back-up system)
- Pressure sensors encapsulated by potting system


Target:

- Adjustment of key parameters - rheology, curing conditions, Tg, tensile properties, thermal conductivity, and electrical resistance according to the selected target applications.
- TRL: 4-5

The optimization:

- Verification of reproducibility of cyclocarbonates synthesis
- Optimization of formulations of the predeveloped (H)HNIPU systems

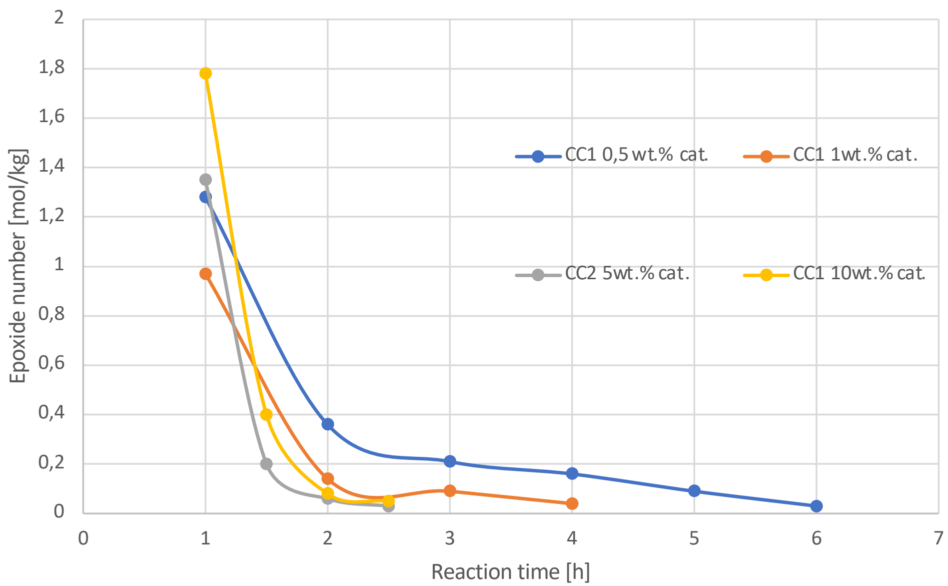
Synthesis of cyclocarbonates - optimization

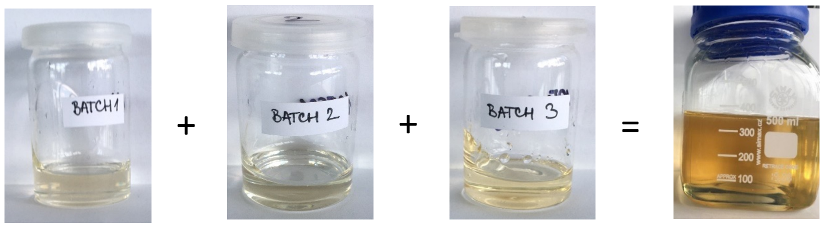
- Synthesis
  - ➢ Newly 4 types of cyclocarbonates (3 derivatives of renewables)

- Catalysts concentration
  - ➢ The most optimal TBABr catalyst concentration is 0.5-1.0 wt. % when the constant conversion ≥ 99% is reached after ca 6h.
  - ➢ Chemical structure confirmed by NMR.

- Catalysts regeneration
  - ➢ Possible by extraction, however with limited purity and yield.
  - ➢ Recycling extra technological step requiring solvents waste management – economically/ecologically ineffective.

- Synthesis reproducibility - scale up
  - ➢ Semi scale lab pressure reactor - 300 g of cyclocarbonate per batch with conversion over 99 %.
  - ➢ However, increase batch volume from 100 to 300 g reflected in 3x increase of the synthesis time.





Conformal coatings - updated requirements

- Outgassing (required as per ECSS-Q-ST-70-02C: RML < 1.0%, CVCM < 0.1%).
- Viscosity ≤ 8 Pa.s. at RT.
- Working time: 60 - 90 min (Pot life min 1 h).
- Curing time ≤ 7 days @ RT (preferably ≤ 24 h @ 60 °C) for two components system and preferably less than 1 hour @ RT for one component system.
- Operation temperature preferably -60°C to 120°C.
- Glass transition temperature ≤ 1 °C.
- Surface hardness ≥ 70 Shore A.
- Volume resistivity ≥ 5,7 x 10^{11} Ω.m.
- Tensile strength ≥ 2,5 MPa at RT and ≥ 45 MPa at -60 °C.
- Elongation at break ≥ 90 % at RT and ≥ 20 % at -60 °C.
- Resistance to common cleaning agents, such as isopropyl alcohol.
- Film quality inspection: Coating thickness and Uniformity of coating on selected surfaces.
- Ease of repair (e.g. by mechanical stripping).
- Linear thermal expansion coefficient (CTE) < 2 x 10^{-4} 1/°C.
- Thermal conductivity ≥ 0.35 W/m.K.
- Thermal cycling (10 cycles between LN2 and +120 °C at atm. pressure).
- Pull of strength before TC ≥ 3 MPa (Al substrate) and after TC ≥ 2.65 MPa (Al substrate).
- High temperature moisture absorption ≤ 3 %.
- Resistance to common cleaning agent such as isopropylalcohol.

Potting system - updated requirements

- Outgassing (required as per ECSS-Q-ST-70-02C: RML < 1.0%, CVCM < 0.1%).
- Viscosity ≤ 10 Pa.s.
- Working time at RT: 1-3 h (Pot life min 1 h).
- Curing time ≤7 days @ 25 °C (preferably ≤ 24 h @ 60 °C).
- Operational temperature -20°C to +80°C (preferably -60°C to +120°C).
- Glass transition temperature ≤ 50 °C.
- Surface hardness ≥ 70 Shore D.
- Volume resistivity ≥ 1 GΩ.m.
- Temperature range min from - 20 °C to 80 °C, preferably from -40 °C to 120 °C.
- Tensile strength ≥ 5 MPa @ 80 °C.
- Tensile strength ≥ 7 MPa @ RT.
- Elongation at break ≥ 8 % @ RT.
- Elongation at break ≥ 3 % @ -20 °C.
- Linear thermal expansion coefficient (CTE) < 2×10^{-4} 1/°C.
- Thermal conductivity ≥ 0.35 W/(K.m).
- Thermal cycling (10 cycles between LN2 and +120 °C at atm. pressure).
- Pull of strength before thermal cycling ≥ 3 MPa (Al substrate) and after thermal cycling ≥ 2.65 MPa (Al substrate).
- High temperature moisture absorption ≤ 3 %.

Conformal coatings - optimization

- Optimization of the formulation composition
- Modification by selected nanoadditives
- Viscosity reduction by reactive solvents

Sample ID	Tg [°C]	Surface hardness [Shore A]	Thermal conductivity [W/m.K]	Volume resistivity [Ω.m]	Tensile strength at RT [MPa]	Elongation at break at RT [%]	Hydroxy urethane bond mass per total bond mass [%]	Content of renewable based components [wt. %]
Requirements	≤ 1	≥ 70	≥ 0.35	≥ 5.7 e11	2.5	90	-	-
19E-83-MIX-1	4.2	74	0.33	4.2 e7	1.2	71	42,8	51,3
19E-101	**1.1**	**83**	**0.62**	5.3 e6	**2.3**	**93**	42,9	49,3
19E-100	**-1.8**	**80**	**0.45**	3.7 e7	**4.8**	**122**	44,9	30,5

Conclusions – CCN1

- Optimization of cyclocarbonation
  - Synthesis of 4 types of cyclocarbonates (catalyst content optimized to 0,5 wt. %)
  - Scale-up (300 g batch) and reproducibility – successful
  - Recycling of catalyst – economically and ecologically ineffective

- Optimization of formulations of the predeveloped NIPU conformal coating and potting materials according to the selected target industrial application (*TRL 4*).
  - In progress

- Validation of industrial applicability - testing of breadboard demonstrator (pressure sensor) in a collaboration of the industrial partner (*TRL 5*).
  - Next steps