



Final report

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# POSSHYS

## Polymer Screening and Selection for Hydrogen Storage

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The author of this report bears the entire responsibility for the content and for the conclusions drawn therefrom

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# Part one

## Introduction

New Generation Tanks (NGT) develops hydrogen tanks for the transportation and aerospace industries. Its mission is to make fuel cell vehicles more competitive thanks to more efficient hydrogen tanks. NGT's innovative pressure tank concept and manufacturing process allow to make long and thin tanks that are easier to integrate into vehicles' chassis than current hydrogen tanks. Moreover, they are lightweight and recyclable, which makes them even more attractive.

Using the same material for the liner and the composite matrix is one of the manufacturing particularities that makes NGT efficient. The composite structure is made of pre-impregnated carbon fiber - polymer tape that is welded onto the polymer liner. This prevents durability issues such as liner collapse. The liner is used as a permeation barrier and preform for composite tape placement, while the composite, comprising fibers in the axial and hoop directions, ensures the tank's structural integrity. The tanks, being wrapped with 0° and 90° fibers, allow exploiting the full tensile strength potential of carbon fibers. In current type IV tanks, all "longitudinal" fibers are oriented with a certain angle from the axial direction such that in-plane shear strength becomes crucial, and the fibers do not deliver their full potential.

NGT's development has now reached a point where a materials selection must be completed. The goal of the POSSHYS project (Polymer Screening and Selection for Hydrogen Storage) is to come up with at least one high performance and one industrial, cheaper thermoplastic polymer, which are useable for NGT's concept. This first Work Package, *Literature Survey*, aims at collecting materials properties, identifying missing data and eliminating unsuitable polymers. The types of sources consulted are scientific articles, websites, manufacturers datasheets, books and test standards.

## Project planning

Project POSSHYS is split into the following Work Packages, organized in time as shown on the Gantt chart (Fig. 1).

- **WP1:** Literature survey, duration 2 month  
**Deliverables:** Database with polymer data from literature and identification of the knowledge gaps. (This document)
- **WP2:** Test methods definition & materials testing, duration 5 months
  - WP2.1: Test method definition and design
  - WP2.2: Experimental setup & calibration
  - WP2.3: Experimental campaign**Deliverables:** Review of test methods, definition of test protocol, design & implementation of the test setups, test results that fill the gaps identified in WP1. Deliver a completed material property database.
- **WP3:** Material selection & optimization, duration 2 months
  - WP3.1: Material ranking criteria & requirements
  - WP3.2: Selection & testing of optimized material candidates
  - WP3.3: Critical review of the results with respect to requirements**Deliverables:** material selection criteria derived from application requirements, define 1 or 2 best composite material(s) configurations for the manufacturing of thermoplastic composite pressure tanks, measure key material properties of those best candidates.

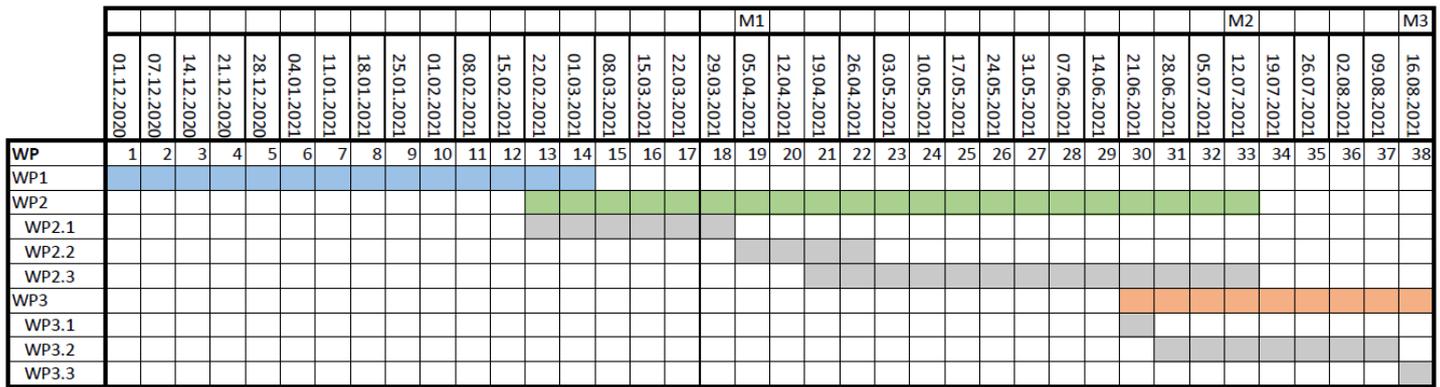


Figure 1: Gantt chart of the POSSHYS project

## Materials

The materials considered must be compatible with Automated Fiber Placement process (AFP) for the manufacturing of hydrogen tanks. Moreover, the composite unidirectional tape must be weldable to the liner and finally, the materials must be recyclable. It obviously leads our choice to thermoplastic polymers, in particular semi-crystalline thermoplastics, for most of them.

### Polyamides

- PA6, PA66, PA11, PA12
- PPA – Polyphthalamide

### Fluorinated polymers

- ECTFE – Ethylene Chlorotrifluoroethylene
- PVDF – Polyvinylidene Fluoride

### PAEKS (Polyaryletherketones)

- PEEK – Polyether Ether Ketone
- PEKK – Polyether Ketone Ketone

### Others

- HDPE – High Density Polyethylene
- PP – Polypropylene
- PPS – Polyphenylene Sulfide
- PC - Polycarbonate
- POM - Polyoxymethylene
- PBT – Polybutylene Terephthalate
- PET – Polyethylene Terephthalate
- PEI – Polyetherimide

## Evaluation criteria

To select the best candidates for the manufacturing of hydrogen pressure tanks according to NGT's technology, polymers listed above have been evaluated according to criteria. These criteria have been sorted into categories: processing, thermal, mechanical, hydrogen containment behavior, composite performance and other criteria. Some criteria are particularly critical. They are highlighted in bold in the table of criteria categories below:

### Processing

Property	Units	Test methods / standards
<b>Extrudability</b>		
<b>Compatibility with carbon fibers</b>		
Weldability		
Recyclability		

The most essential properties here, for NGT's concept, are the extrudability of polymers and their compatibility with carbon fibers. Most thermoplastics are theoretically extrudable but there may be some dimensional limitations for some of them. Furthermore, the processing temperature is crucial. The higher it is, the more complicated and expensive it is to process the material. The point here is mostly to identify polymers that may be harder to extrude from a qualitative point of view. As for their adherence with carbon fibers, this can be quantified by testing but the goal at work package 1 is to find out in the technical literature whether these polymers have ever been used as a matrix and if it was a good or bad option.

### Thermal properties

Property	Units	Test methods / standards
<b>Min service temperature</b>	°C	UL 746, ISO 974, ASTM D746
<b>Max service temperature</b>	°C	UL 746
<b>Glass transition temperature</b>	°C	DSC
<b>Melting temperature</b>	°C	ISO11357-3
<b>HDT – Heat Deflection Temperature (1.8 MPa)</b>	°C	ASTM D648, ISO75
Thermal conductivity	W/(m.K)	ASTM E1530

The minimal and maximal service temperatures are the temperatures beyond which a polymer degrades, or get its properties (thermal, mechanical) changed by a factor of 2 from room temperature. For instance, the glass transition temperature  $T_g$  may involve an abrupt decrease of Young's modulus. It affects the amorphous phase, which is brittle below  $T_g$  and rubbery above it. The range of operating temperatures of the tanks goes from -60°C to 95°C and having a glass transition in this range should be avoided.

Finally, the Heat Deflection Temperature (HDT) is given by a 3-point bending creep experiment with time-increasing temperature. The HDT is the temperature at which the specimen under a given stress has reached a deflection of a certain amount. In the test standards, two values of stress are used: 0.45 MPa or 1.8 MPa. The highest one is selected here. Indeed, it can be shown that in plane stress conditions, Von Mises equivalent stress in the liner can be expressed:

$$\sigma_{VM} = \frac{1}{\sqrt{2}} \frac{E}{1 - \nu^2} \sqrt{(1 + \nu^2)(\varepsilon_1^2 + \varepsilon_2^2) + 4\nu\varepsilon_1\varepsilon_2}$$

where  $E$  and  $\nu$  are the polymer Young's modulus and Poisson's ratio, and  $\varepsilon_1$  and  $\varepsilon_2$  are the deformations in the axial and in the hoop directions. If they are both equal to 2% (approximate carbon

fibers elongation at break) and  $\nu = 0.4$ , one obtains  $\sigma_{VM} \approx 30$  MPa for the most compliant materials (HDPE,  $E = 0.9$  GPa<sup>1</sup>) and  $\sigma_{VM} \approx 200$  MPa for the stiffest ones (PEI,  $E = 6$  GPa<sup>2</sup>). These values are obviously very high and making more relevant measurements at higher stress level will be necessary in the next Work Packages. Note that this calculation assumes linear elasticity. For each polymer, if the stress value obtained is larger than its yield stress, it is no longer applicable for accurate computation, though here it is sufficient for choosing the more relevant HDT testing condition as 1.8 MPa.

### Mechanical properties

Property	Units	Test methods / standards
<b>Yield stress</b>	MPa	ASTM D638-14, ISO 527
<b>Tensile strength</b>	MPa	ASTM D638-14, ISO 527
<b>Elongation at break</b>	%	ASTM D638, ISO 527
<b>Creep resistance</b>	-	ASTM D2990-01, ISO 899-1, DIN 53444
Impact resistance	J/m or J/m <sup>2</sup>	
Toughness	MPa.m <sup>1/2</sup>	

An essential mechanical property of the polymer alone is its elongation at break. As explained previously, the carbon fibers are used at their full potential and in a pure bi-axial stress state (in the cylindrical part). Hence the tank is expected to explode when the fibers reach their maximal elongation, around 2%. The polymer must be able to undergo such deformation, whether it has reached its yield stress or not.

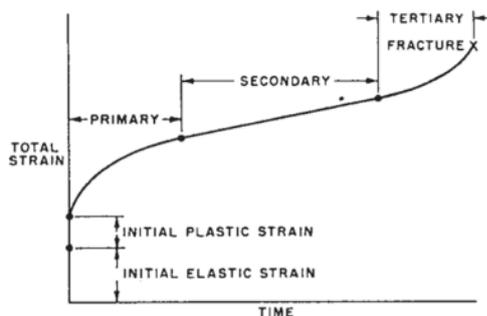


Figure 2: creep curve (ASTM D2990)

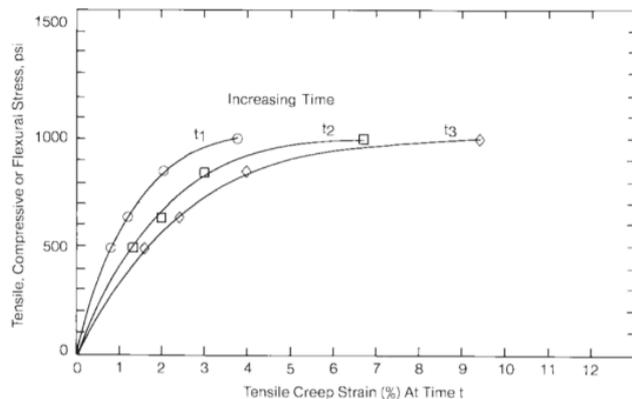


Figure 3: isochronous stress-strain curve

There are several ways to determine creep behavior of a polymer. In the literature, experiments are done at different temperatures and different stress levels, and various results may be available: creep curves like in figure 2, creep modulus or even isochronous stress-strain curves (figure 3). In order to quantify creep resistance of polymers with a single number, the value  $E_c(t = 1000h)/E_c(t = 1h)$  quantifies how much the creep modulus  $E_c$  decreases over time. The value should be as close as possible to 1.

### Hydrogen containment behavior

Property	Units	Test methods / standards
<b>Permeability (H<sub>2</sub>)</b>	mol/(MPa.s.m)	ASTM D1434, ISO 2556, DIN 53380
<b>RGD – Rapid Gas Decompression</b>	Ranking 0-5	NORSOK M-710, ISO 23936, NACE TM0297
Diffusivity (H <sub>2</sub> )	m <sup>2</sup> /s	

<sup>1</sup> <https://polymerdatabase.com/Commercial%20Polymers/HDPE.html>

<sup>2</sup> <https://designerdata.nl/materials/plastics/thermo-plastics/polyetherimide>

Solubility (H <sub>2</sub> )	mol/(m <sup>3</sup> .MPa)
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Hydrogen permeability measures the flow of hydrogen which passes through a film or a plate, multiplied by its thickness and divided by its area, per unit of pressure. It is also equal to the diffusivity times the solubility of hydrogen in the polymer. The maximal acceptable permeability can be estimated for a 3-liter tank, which was studied in a previous project (design and simulation project between Heig-VD and NGT). The surface area  $A$  of the tank is about 0.24 m<sup>2</sup>, its total thickness  $t$  is 4.75mm and its service pressure  $p$  is equal to 300 bar. The largest acceptable leak rate<sup>3</sup> is 6cm<sup>3</sup>/(L.h) at standard temperature and pressure conditions. For this tank, it is equivalent to  $6 \cdot 3/3600 = 0.005$  cm<sup>3</sup>/s. Using the ideal gas law, the largest acceptable flux of matter can be computed as

$$\dot{n} = \frac{p_{atm} \dot{V}}{RT} = \frac{1.013 \cdot 10^5 \cdot 0.005 \cdot 10^{-6}}{8.31 \cdot 293} \cong 2.08 \cdot 10^{-7} \text{ mol/s.}$$

As mentioned above, the flux of gas can be expressed  $\dot{n} = PpA/t$ ,  $P$  being the permeability, which can be directly calculated

$$P = \frac{\dot{n}t}{pA} = \frac{2.08 \cdot 10^{-7} \text{ mol/s} \cdot 4.75 \cdot 10^{-3} \text{ m}}{0.3 \text{ MPa} \cdot 0.24 \text{ m}^2} \cong 137 \cdot 10^{-10} \text{ mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{MPa}^{-1}.$$

Note that in this case the thickness of the liner is 3.2 mm but it can also be adjusted to satisfy this maximum leak rate condition. Moreover, the permeability of the composite is in principle lower than the one of the polymer alone, so the limit permeability value of the polymer<sup>3</sup> is likely to be higher than the value above.

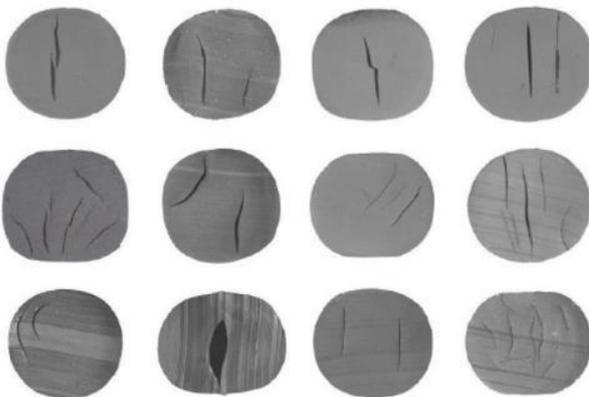


Figure 4 : RGD tested O-ring surfaces rated 3 according to ISO 23936-2<sup>4</sup>

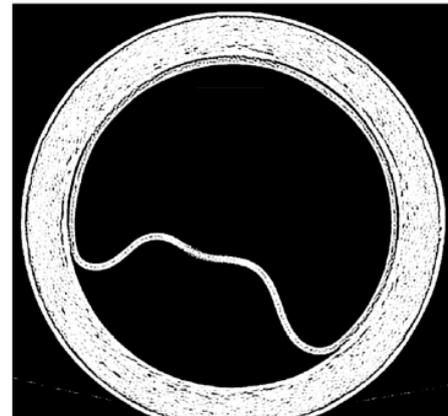


Figure 5: liner buckling after RGD<sup>5</sup>

Finally, Rapid Gas Decompression (RGD) may cause blistering of polymers or even liner buckling in the worst case. It is related to permeability. When hydrogen molecules have migrated into the liner, rapid decompression (that may occur in extreme pressure tank use conditions) causes them to expand too quickly and create blisters (figure 4). Liner buckling (figure 5) occurs if the adhesion between the liner and the composite structure is not good enough and hydrogen has migrated up to that point.

<sup>3</sup> Regulation (EC) No 79/2009, <https://eur-lex.europa.eu/legal-content/FR/TXT/PDF/?uri=OJ:L:2010:122:FULL&from=EN>

<sup>4</sup> <https://www.element.com/materials-testing-services/rapid-gas-decompression>

<sup>5</sup> BLANC-VANNET, Pierre, PAPIN, Philippe, WEBER, Mathilde, *et al.* Sample scale testing method to prevent collapse of plastic liners in composite pressure vessels. *International Journal of Hydrogen Energy*, 2019, vol. 44, no 17, p. 8682-8691.

Different norms propose a ranking which quantifies RGD resistance. Based on the number of cracks and their length after testing, a grade from 0 to 5 is established. On Figure 6 is an example of that ranking with respect to the NORSOK norm.

Description	Rating
No internal cracks, holes, or blisters of any size.	0
Less than 4 internal cracks, each shorter than 50% of the cross section, with a total crack length less than the cross section.	1
Less than 6 internal cracks, each shorter than 50% of the cross section, with a total crack length of less than 2.5 times the cross section.	2
Less than 9 internal cracks of which max. 2 cracks can have a length between 50% and 80% of the cross section.	3
More than 8 internal cracks, or one or more cracks longer than 80% of the cross section.	4
Crack(s) going through entire cross section or complete separation of the seal into fragments.	5

Figure 6 : ranking criteria according to NORSOK (2001) testing standard<sup>6</sup>

### Composite properties

Property	Units	Test methods / standards
<b>ILSS – Interlaminar Shear Strength</b>	MPa	ASTM D2344
<b>Tensile strength 90°</b>	MPa	ASTM D3039
<b>Elongation at break 90°</b>	%	ASTM D3039
<b>HDT – Heat Deflection Temperature (1.8 MPa)</b>	°C	ASTM D4648

Interlaminar Shear Strength (ILSS) is mostly important because the S-shaped tank extremity (where the diameter decreases) is subjected to shear. The transverse tensile properties of the composite are important as well, especially in the cylindrical part of the tank. Since carbon fibers are placed in the axial and hoop directions and the tank is designed such that all fibers reach their maximum deformation at burst pressure, all fibers approximately undergo the same deformation in both directions. This is why their transverse properties, which strongly depend on the fiber-matrix interface quality, are crucial.

The HDT of the composite is measured at 1.8 MPa of stress as well, according to the norm. This value is way below the stress levels in the composite part of the tank, so it will certainly be necessary to measure HDT at higher stress level. Nonetheless, any of the composites HDT at 1.8 MPa below 95°C will be eliminatory.

<sup>6</sup> SCHRITTESSER, B., PINTER, G., SCHWARZ, Th, *et al.* Rapid Gas Decompression Performance of elastomers—A study of influencing testing parameters. *Procedia Structural Integrity*, 2016, vol. 2, p. 1746-1754.

## Other properties

Property	Units	Test methods / standards
Density	g/cm <sup>3</sup>	ASTM D792-13, ISO1183
Crystallinity	%	DSC, Raman Spectroscopy
Water absorption (24h)	%	ASTM D570, ISO 62
Cost	€/kg	
Scalability / Cost improvement potential		
Fire resistance	Norm ranking	ASTM D635
Toxicity		
Chemical resistance		ASTM D4648

The remaining important properties are density, crystallinity, water absorption and cost. Crystallinity is not directly essential in the polymer selection process but it has a strong influence on many properties, so it is useful to know how crystalline each polymer can be. The crystalline phase of a thermoplastic generally acts as a gas permeation barrier. It also has better mechanical properties and is less affected by glass transition.

## Results

Alongside this report is delivered an Excel file, the first tab of which contains all collected data. Some polymers contain several data sources for some properties. The source of each value is referenced just next to it and additional information is sometimes indicated as well (test conditions for instance). This table being very large and difficult to read, it was condensed into a smaller table that summarizes/averages it. It is presented in figure 12. Finally, a OneNote file comprising other interesting information such as DMA (Dynamic Mechanical Analysis) curves is delivered as well.

## Data analysis

First of all, some criteria must be set to eliminate inappropriate polymers. One of them is that the glass transition temperature must be out of the range of pressure tanks operating temperature (-60°C to 95°C). The second one concerns the HDT, which must be above 95°C. Thus, the following polymers are disqualified: PA6, PA66, PA11, PA12, PVDF, ECTFE, HDPE, PP, PBT and PET. While some polymers, including most polyamides, are clearly not adapted for high temperature applications, some others deserve a deeper analysis and a chance of being preselected.

It is the case of HDPE for instance, which was eliminated only for its low HDT. All other properties are acceptable and it is one of the cheapest materials considered. PVDF as well, can be picked up because its  $T_g$  of -40°C is close to the lower bound. Its DMA curve (Dynamic Mechanical Analysis) on figure 7 shows a drop of storage modulus (“stiffness”) when passing by the  $T_g$ , that is not catastrophic compared to other polymers (such as PPA, figure 8).

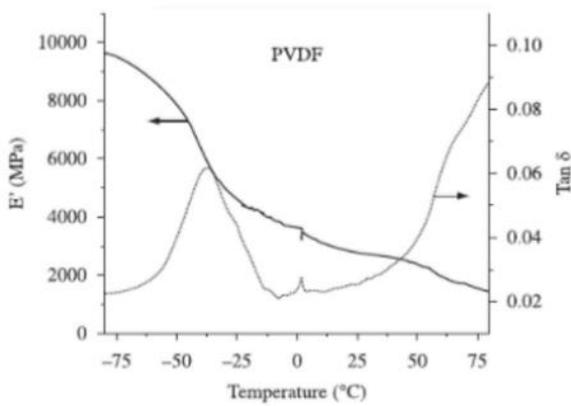


Figure 7: DMA curves of PVDF<sup>7</sup>

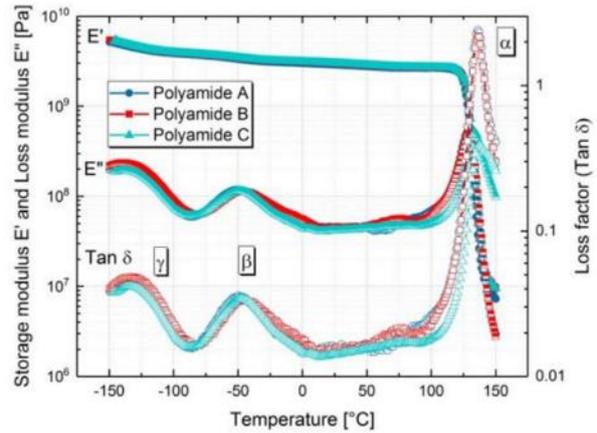


Figure 8: DMA curves of diverse PPAs<sup>8</sup>

To compare all polymers properties, rankings were attributed to each property for each polymer, from 1 to 5, 1 being very poor and 5 being excellent. An overview of these rankings, colored from red (ranking 1) to green (ranking 5), is shown in figure 12. For each polymer, the sum of all their grades were computed to help classifying them from “best” to “worst”. The resulting grades are displayed in figure 9. The polymer selection should of course not blindly follow this ranking. For example, PEEK and PEKK have outstanding properties but their price is high and choosing a “lower class” polymer would be a good idea as long as it fulfills NGT’s requirements. This leads to plotting the polymers global grades with respect to their cost ( figure 10).

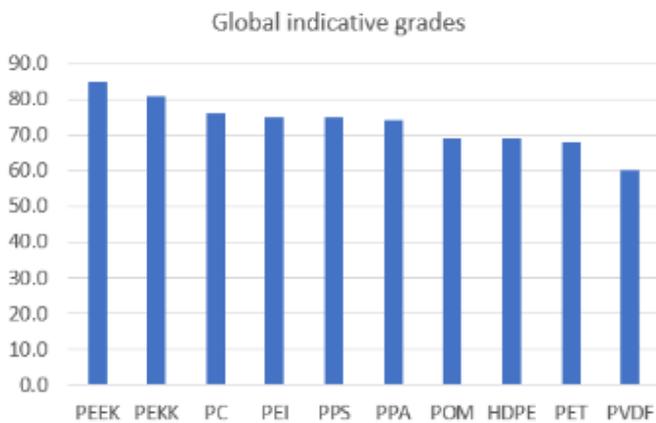


Figure 9 : polymers total indicative grade

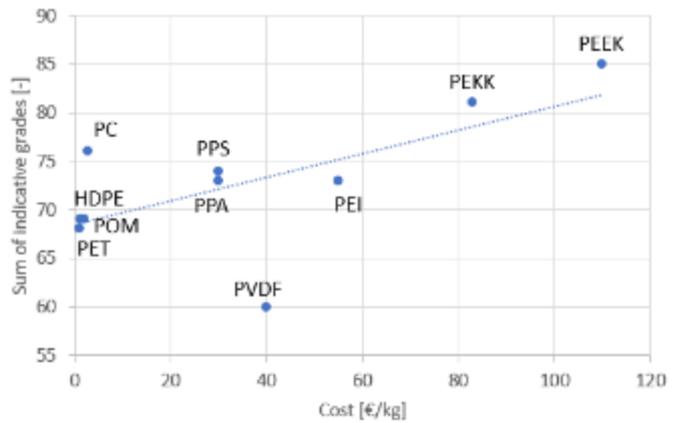


Figure 10 : relation between performance and cost

<sup>7</sup> MALMONGE, Luiz Francisco, LANGIANO, Simone do Carmo, CORDEIRO, João Manoel Marques, *et al.* Thermal and mechanical properties of PVDF/PANI blends. *Materials Research*, 2010, vol. 13, no 4, p. 465-470.

<sup>8</sup> DJUKIC, Stéphanie, BOCAHUT, Anthony, BIKARD, Jérôme, *et al.* Mechanical properties of amorphous and semi-crystalline semi-aromatic polyamides. *Heliyon*, 2020, vol. 6, no 4, p. e03857.

PROCESS	POLYAMIDES						FLUOROPOLYMERS		PAEKs		OTHERS							
	PAG	PA66	PA11	PA12	PPA	PPA	PVDF	ECTFE	PEKK	PEEK	HDPE	PP	PPS	PC	POM	PBT	PET	PEI
Compatible with extrusion process	Yes	Yes	Yes	Yes	Yes	Yes (spc)	Yes (//) adhe: Yes but really	Yes	Yes	Yes	Yes (//) pi Yes	Yes	Yes	Yes (//) pi Yes	Yes	Yes	Yes	Yes
	Yes	Yes	Yes	Yes	Yes	Yes	-40	-200	255	155-260	-70	-15	-30	-100	-50	-40	-40/-100	-60
Min service temperature (middle of range) (NGT : -60 ; 95°C)	-20	-70	-72	-70	-60	140	150	145	160	145	100	100	210	120	80-140	>100	100	170
Max service temperature (middle of range) (NGT : -60 ; 95°C)	100	120	100	100	80	130	-40	170	160	145	-110	-15	90	150	-75	60	75	215
Tg	62	56	40	40	40	85	170	240	315	343	125	164	278	240	170	225	255	380
Tm	216	255	190	180	180	260	240	141	155	155	50	58	105	160	120	50-80	65	195
HDt (1.8 Mpa)	58-80	65-105	48	50	50	74	>95 // \grade	65-90	107	107	25	35	62	67	70	60	40-60	73-110
Yield Strength Mpa	50-90	45-85	42	45	45	30	50	30	110	95	30	33	40-80	67	73	55	55	96
Ultimate tensile strength Mpa	36-95	50-95	55	65	40-89	22-50	46	46	>10	>12	>500	>150	>5	>15	>5	>30	>60	
Elongation at break	>50	>60	>50	>250	>2.6	>20	>20	>20	0.97 // 0.3: 0.97 // 0.3	0.84	0.65 (110°/0.93/150°/0.84	0.55	0.55	0.55	0.73	0.85	0.78 (50°	
Creep resistance (Ed(1000h) / Ed(1h) , 23°C)	0.68	0.53	0.48	0.48	0.53	0.53	5.2	25.8	6.2 - 12.4	8.2 - 38	31 - 138	(-3-6) = 36.4	6.7	0.3-1.8	20.8			
Hydrogen permeability	5.8	4.8	34.2 @55°C	18MPa	0.2-1.8	5.2												
Rapid gas decompression - Blistering after RGD	NORSC																	
Composite IJSS	MPa				44	85	7-50		33-100	35-83	61	25	30-97	51		35.8	40-85	
Composite transverse tensile strength	MPa	41		40	40	27			90	76		37				7-27		
Composite transverse tensile elongation	%			1.37-2.3					0.9 >0.6							>0.09%	210	
HDt (1.8 Mpa)	°C	235	252	142	1.01	1.12	1.8	1.7	360		135	280	143		214			
Density	g/cm3	1.15	1.15	1.05	1.01	1.12	1.8	1.7	1.27	1.32	0.95	0.9	1.25	1.2	1.4	1.31	1.35	
Crystallinity	%	35-45	35-45	25-40	25-55	0-17	35-70	50-60	0.28	19-35	60-90	50-80	60	0	65-80	35-50	0-40	
Water Absorption (24h)	%	1.6	1.3	1	1.3	0.55	0.03	0.1	0.15	0.25	0.008	0.05	0.02	0.2	0.25	0.15	0.1	
Material cost	€/kg	2.25	3.2	12	6	<30	<40	57	75-90	100-120	1.25	1.35	30	2.8	1.9	2.6	1	

Gap  
 Prohibitive  
 Poor / to be noted  
 Property to measure

PROCESS	POLYAMIDES						FLUOROPOLYMERS		PAEKs		OTHERS							
	PAG	PA66	PA11	PA12	PPA	PPA	PVDF	ECTFE	PEKK	PEEK	HDPE	PP	PPS	PC	POM	PBT	PET	PEI
Compatible with extrusion process	5	5	5	5	5	5	5	4	5	5	5	5	5	5	5	5	5	5
	5	5	5	5	5	5	3	3	5	5	3	5	5	4	5	5	5	5
Compatible with carbon fibres	2	5	5	4	5	5	3	5	5	5	5	1	2	3	3	3	4	4
Min service temperature (middle of range) (NGT : -60 ; 95°C)	4	5	5	5	5	5	5	5	5	5	4	5	5	5	5	5	5	5
Max service temperature (middle of range) (NGT : -60 ; 95°C)	1	1	1	1	1	1	3	1	5	5	5	1	4	5	5	5	5	5
Tg	2	3	2	2	3	3	2	3	4	4	2	2	3	3	3	3	3	3
Tm	1	2	1	1	1	1	4	1	5	5	1	1	4	5	4	1	4	4
HDt (1.8 Mpa)	3	3	2	2	3	3	2	1	5	5	1	1	3	3	3	3	4	4
Yield Strength Mpa	3	3	2	2	3	3	2	1	5	5	1	1	3	3	3	3	4	4
Ultimate tensile strength Mpa	3	3	2	2	3	3	1	2	5	4	1	1	3	3	3	2	2	4
Elongation at break	5	5	5	5	2	2	4	4	4	4	5	5	3	5	4	3	5	5
Creep resistance (Ed(1000h) / Ed(1h) , 23°C)	3	1	1	1	1	1	5	4	5	4	2	5	4	2	3	4	5	5
Hydrogen permeability	4	4	4	1	4	4	5	4	2	4	2	4	4	1	4	5	3	3
Rapid gas decompression - Blistering after RGD	NORSC																	
Composite IJSS	MPa	2	2	2	2	5	2	2	5	5	3	4	3	3	3	2	3	3
Composite transverse tensile strength	MPa	2	2	3	3	5	2	2	5	5	1	1	3	3	3	2	1	1
Composite transverse tensile elongation	%	4	4	2	5	5			3	3			3	3	3	3	3	3
HDt (1.8 Mpa)	°C	4	4	4	5	4	1	1	3	3	5	5	4	5	5	5	5	5
Density	g/cm3	4	4	4	5	4	1	1	3	3	5	5	5	5	5	5	5	5
Water Absorption (24h)	%	1	2	3	2	4	5	5	5	4	5	5	4	5	5	5	4	4
Material cost	€/kg	5	5	5	5	4	3	3	1	1	5	5	4	5	5	5	5	2
SUM		59	67	63	61	74	60	60	81	85	64	57	75	76	69	65	68	73

Figure 12 : properties rankings

Figure 11 : polymers properties ; condensed data

The graphic in figure 10 shows quite clearly the link between the cost and the performances of polymers and based on that, they can be divided in three classes regarding our criteria: 1<sup>st</sup> class polymers (PEEK, PEKK), 2<sup>nd</sup> class polymers (PPA, PEI, PPS, PPA) and 3<sup>rd</sup> class polymers (HDPE, POM, PET, PVDF). figure 13 shows the average grades of polymers by criteria categories, for the 3 classes.

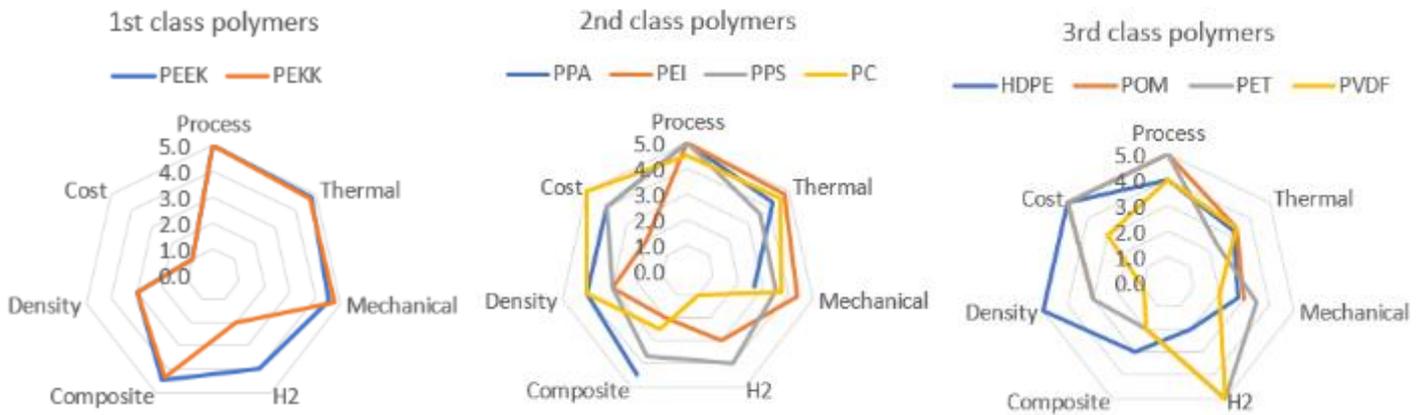


Figure 13 : polymers average grades with respect to each relevant category of properties

Given the maximal allowed permeability computed 4. Selection criteria

$$P \cong 137 \cdot 10^{-10} \text{ mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{MPa}^{-1},$$

all polymers a priori satisfy this relation and permeability is no longer an issue in this work package. Again, note that it was computed for a 3 liter, 300bar tank with liner thickness 3.2mm and total thickness 4.75mm. It shall be necessary to redo this computation later for different tanks. Among the 1<sup>st</sup> class polymers, PEEK and PEKK could both be chosen for high-end applications such as aerospace. As for the 2<sup>nd</sup> class polymers, all of them could potentially work as well, however PPA and PPS seem to be the most promising ones for industrial applications (cars, trucks & buses for instance). Below are listed 2<sup>nd</sup> class polymers main characteristics or issues.

- PPA is thermally stable through the whole service temperature range. It significantly cheaper than PEEK and PEKK. But its mechanical properties are suspected to decrease considerably once saturated in water (humid, tropical meteorological conditions). This should be investigated further.
- The price of PPS is reasonable as well. It is quite commonly used with carbon fibers. Its behavior at low temperature is not completely known, so its relatively low elongation at break at room temperature suggests it might become brittle. This is yet to be investigated.
- Most PEI's properties are very good, but its high price and very high processing temperature may lead to high costs.
- PC could be a suitable choice, though it is not commonly used with carbon fibers and it is difficult to process. Moreover, it is amorphous so its permeability is high and its resistance to creep is expected to be low.

Finally, PVDF should definitively be removed from the selection because of the potential release of HF (hydrogen Fluoride) when exposed to fire, and due to its bad adhesion to carbon fibers. HDPE, POM and PET could possibly be considered as a last, cheap "industrial" options if further experiments are carried out. Note that HDPE's main drawback is its low resistance to creep, and the  $T_g$  of PET is close to the upper bound of the service temperature range.

# Part two

## Introduction and summary of previous steps

New Generation Tanks (NGT) has developed a novel concept of hydrogen pressure tanks. The particularity of these tanks is that they are slendrer than those currently manufactured, which facilitate their integration in vehicles (in the floor, for example) and that they are based on thermoplastic composite to allow for efficient industrial manufacturing and recycling. To produce these new tanks, the choice of materials has to be made among the vast array of possibilities offered by contemporary thermoplastic materials namely: a thermoplastic matrix - carbon fiber composites for the envelope and a compatible thermoplastic polymer for the liner.

The POSSHYS project, supported by SFOE, aims at evaluating which thermoplastic polymers and composites are best suited for the manufacturing of such hydrogen storage tanks.

The POSSHYS project is split into the following Work Packages:

- **WP1:** Literature survey  
**Deliverable:** Database with polymer data from literature, and identification of the knowledge gaps.
- **WP2:** Test methods definition & materials testing
  - WP2.1: Test method definition and design
  - WP2.2: Experimental setup & calibration
  - WP2.3: Experimental campaign**Deliverable:** Review of test methods, definition of test protocol, design & implementation of the test setup, test results that fill the gaps identified in WP1. Deliver a completed material property database.
- **WP3:** Material selection & optimization
  - WP3.1: Material ranking criteria & requirements
  - WP3.2: Selection & testing of optimized material candidates
  - WP3.3: Critical review of the results with respect to requirements**Deliverable:** material selection criteria derived from application requirements, define 1 or 2 best composite material(s) configurations for the manufacturing of thermoplastic composite pressure tanks, measure key material properties of those best candidates.

The literature review carried out in WP1 helped narrowing down the material choices to a short list of potential polymers, namely PVDF, PEEK, PEKK, PPS, PPA, PC, POM, PEI. The main selection criteria and “knowledge gaps” with respect to available literature were :

1. The glass transition temperature  $T_g$  should be outside of the range of the service temperature [-60°C ; 95°C] to limit the variations of properties
2. The heat deflection / softening temperature (HDT) should be above 95°C to avoid risks of creep / visco plastic flow of the material over time.
3. The H<sub>2</sub> permeability criterion has been found to be not critical as all polymers in the short list should provide a sufficiently low diffusion rate for applications in vehicles.
4. Rapid gas decompression induced damages (cavitation or cracking) has been identified as potential risk that was not covered in literature

A multicriteria evaluation of the acceptable polymers was performed in Work Package 1 and led to the following ranking (Figure 14):

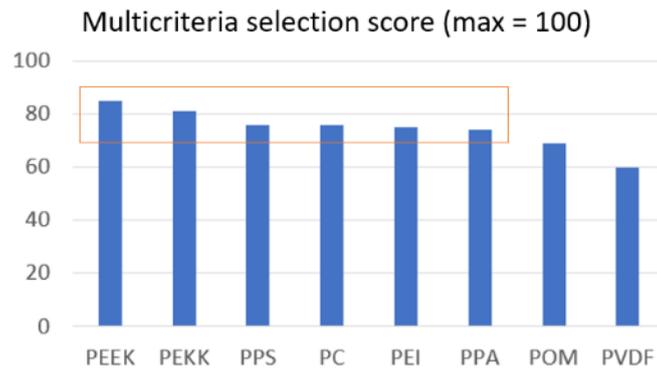


Figure 14: Multi-criteria ranking of possible polymers

At the end of this first screening process based on available literature, the following research activities were defined for WP2 and WP3:

### WP2

1. Evaluation of potential rapid gas decompression induced damages in the candidate (polymers & composites) to assess this risk: this required the development of a pressurized H<sub>2</sub> test cell and ad-hoc equipment to carry out this test
2. Finding suppliers and relevant products for the selected classes of polymers and composites and obtain sample materials: this task was led by NGT and resulted in many contacts with the main industrial actors in the field of thermoplastic polymers & composites (for example EMS, DSM, BASF, SOLVAY, DUPONT, TORAY, ARKEMA, KURARAY, CELANESE).
3. Define testing protocol and prepare samples from the available material for mechanical / physical testing. Provide a comparative performance evaluation of the tested materials.

### WP3

1. For the best candidates found in WP2, procure or produce composite laminates representative of the final application.
2. Carry out mechanical tests on the “representative” laminates to evaluate the mechanical performance of the shell of the H<sub>2</sub> tank: ultimate strength, first ply failure and onset of damage in tension
3. Identify best candidate and reference material properties for designing the pressure vessel

The present report covers the outcome of the experimental testing and material selection / optimization performed in WP2 & 3. It contains an overview of the test campaigns conducted and a review of the key results which led to the identification of the best candidate materials that can meet the mechanical, thermal, hydrogen compatibility and commercial requirements.

## Materials, Equipment and Installation

A list of different materials has been established after numerous contacts with various suppliers through NGT. The list of materials includes a neat PEEK and a PEEK-Carbon fiber composite that will serve as a reference for evaluating the performance of other materials. There were two other groups of polymer that were tested and referenced later as Polymer A and Polymer B. The list of materials provided is presented in figure 15.

Supplier	Index material	Code	Polymer Group	Description	Supplier Reference	POSSHYS Reference
SUPPLIER 1	1	Confidential	Polymer A	NEAT Resin - 3 plates 140x140x3	Confidential	Confidential
SUPPLIER 1	2	Confidential	Polymer A	NEAT Resin - 3 plates 140x140x3	Confidential	Confidential
SUPPLIER 2	3	Confidential	Polymer B	NEAT Resin - 15 plates 125x125x2	Confidential	Confidential
SUPPLIER 2	4	Confidential	PEEK	NEAT Resin - 15 plates 125x125x2	Confidential	Confidential
SUPPLIER 3	5	Confidential	Polymer A	NEAT Resin - 10 plates 100x100x2	Confidential	Confidential
SUPPLIER 4	6	Confidential	Polymer A	NEAT Resin - 5 plates 100x100x2	Confidential	Confidential
SUPPLIER 5	7	Confidential	Polymer A	NEAT Resin - 20 plates 110x110x2	Confidential	Confidential
SUPPLIER 5	8	Confidential	Polymer A	NEAT Resin Film - 20 plates 180x180x2	Confidential	Confidential
SUPPLIER 6	9	Confidential	Polymer A	NEAT Resin - plates	Confidential	Confidential
SUPPLIER 7	11	Confidential	Polymer B	NEAT Resin - plates 80x80x1	Confidential	Confidential
SUPPLIER 7	21	Confidential	Polymer B	NEAT Resin - plates 80x80x2	Confidential	Confidential
SUPPLIER 7	22	Confidential	Polymer B	NEAT Resin - plates 80x80x2	Confidential	Confidential
SUPPLIER 7	23	Confidential	Polymer A	NEAT Resin - plates 80x80x2	Confidential	Confidential
SUPPLIER 4	12,1	Confidential	Polymer A	COMPOSITE laminate	Confidential	Confidential
SUPPLIER 4	12,2	Confidential	Polymer A	COMPOSITE laminate	Confidential	Confidential
SUPPLIER 4	12,3	Confidential	Polymer A	COMPOSITE laminate	Confidential	Confidential
SUPPLIER 4	12,4	Confidential	Polymer A	COMPOSITE laminate	Confidential	Confidential
SUPPLIER 4	12,5	Confidential	Polymer A	COMPOSITE laminate	Confidential	Confidential
SUPPLIER 4	12,6	Confidential	Polymer A	COMPOSITE laminate	Confidential	Confidential
SUPPLIER 2	16	Confidential	Polymer B	COMPOSITE laminate	Confidential	Confidential
SUPPLIER 2	17	Confidential	PEEK	COMPOSITE laminate	Confidential	Confidential
SUPPLIER 8	18	Confidential	Polymer A	Prepreg tape - hot pressed into COMPOSITE laminates	Confidential	Confidential
SUPPLIER 8	19	Confidential	Polymer B	Prepreg tape - hot pressed into COMPOSITE laminates	Confidential	Confidential
SUPPLIER 9	20	Confidential	Polymer B	COMPOSITE laminate	Confidential	Confidential

Figure 15 : List of materials

## List of tests

To characterize the materials, several types of tests have been performed, based on standards. Some of these standards have been used as guidelines and some test parameters have been adjusted, for example the size of samples or test spans, to achieve the failure modes that need to be characterized.

Within the framework of the project, the materials must be evaluated mostly comparatively as the final design of the pressure vessel will be adapted to the design allowable of the material. The key element is to maximize the mechanical performance for a given mass. The tests have thus been performed by batch in the same method and setup for each material.

The tests that have been carried out are the following :

### On neat polymers :

*Relaxation test, ISO 6914.* The principle of this test is to place a tensile specimen under tension, with the help of a tensile testing machine, and to observe the relaxation of the stresses in the specimen. This relaxation mechanism is sensitive to temperature, which is why this test is performed at 95°, the limit temperature of use of the tanks. The relaxation test allows determining the behavior of the polymer at elevated service temperature and how the stress relaxation or creep deformation will develop. Indeed, if creep deformation develops in service, a differential stress may appear between the loading and unloading of the tank. Thus, relaxation or creep are important factors to select the best material for the application. The best material is thus the one with least creep deformation and thus with the lower the stress relaxation.

*Rapid gas decompression RGD, ISO 23936.* The principle of this test is to saturate the specimens with hydrogen at 300 bars to represent the fully acclimated state of the material, in equilibrium in terms of diffused hydrogen content. That preconditioning step was performed in external environment for safety reasons and took several weeks due to the relatively low ambient temperature. Finally, a fast purge over a few minutes is carried out to represent the fast decompression of a tank. The specimens are then observed under microscope to evaluate the presence of micro cavitation or cracking. the resistance of the specimens to the saturation in hydrogen and their survival. It's obvious but if the tank is filled with

hydrogen, the tank should survive, and it should survive at full purge. It's why the RGD test is realized.

### ***On composites:***

*Relaxation tests (ISO899-1) and RGD tests* are also performed with the particularity that the relaxation tests are performed on unidirectional composite specimens whose fibers are oriented at 90° to the stress as it is the most critical loading direction.

*Interlaminar shear strength, short beam bending test, ILSS, ISO 14130.* The purpose of this test is to cause a rupture by delamination of the specimens caused by interlaminar shear. With this information we can evaluate the risk of delamination of the laminate constituting the shell of the tank. In this test we encountered a difficulty to produce a clear interlaminar crack in the sample due to the plastic nature of some of the matrix polymers used. The test configuration was modified slightly by adjusting the span to increase the chance to produce an interlaminar crack.

*Heat deflection temperature HDT, ISO 75-3.* The HDT test is performed to evaluate the behavior of a composite under a constant load subjected to an increasing temperature ramp. The critical temperature where creep deformation become prevalent is considered as the critical heat deflection temperature, HDT. At such temperature, the cohesion between fiber and polymer will strongly decrease. The load level used in the test has been adapted compared to the standard to be more representative of a realistic stress level for a composite shell of a pressure tank.

*Tensile testing, 0° and 90°, ISO527-5.* Standard tensile tests are used to define longitudinal and transverse fracture strength. This defines the resistance of a composite when loading in the direction of the fibers ( 0° ) and transversally to the fibers (90°). These quantities are the most important to design the pressure tank.

*Tensile testing of cross-ply laminates with acoustic emission monitor test and free edge observation.* This tensile test, performed following the guidelines of ISO527-5, is complemented by video observation of the damages at the free edges of the specimen as well as acoustic emission monitoring via two acoustic sensors that can detect cracking and other types of damages insides of the sample. The samples were a specific design for corresponding to the skin of the future tank with a layup of [0°<sub>4</sub>/90°<sub>4</sub>/0<sub>4</sub>°] or [90°<sub>4</sub>/0°<sub>4</sub>/90°].

## Equipment

The following equipment of COMATEC institute / HEIG-VD was used to perform the tests.

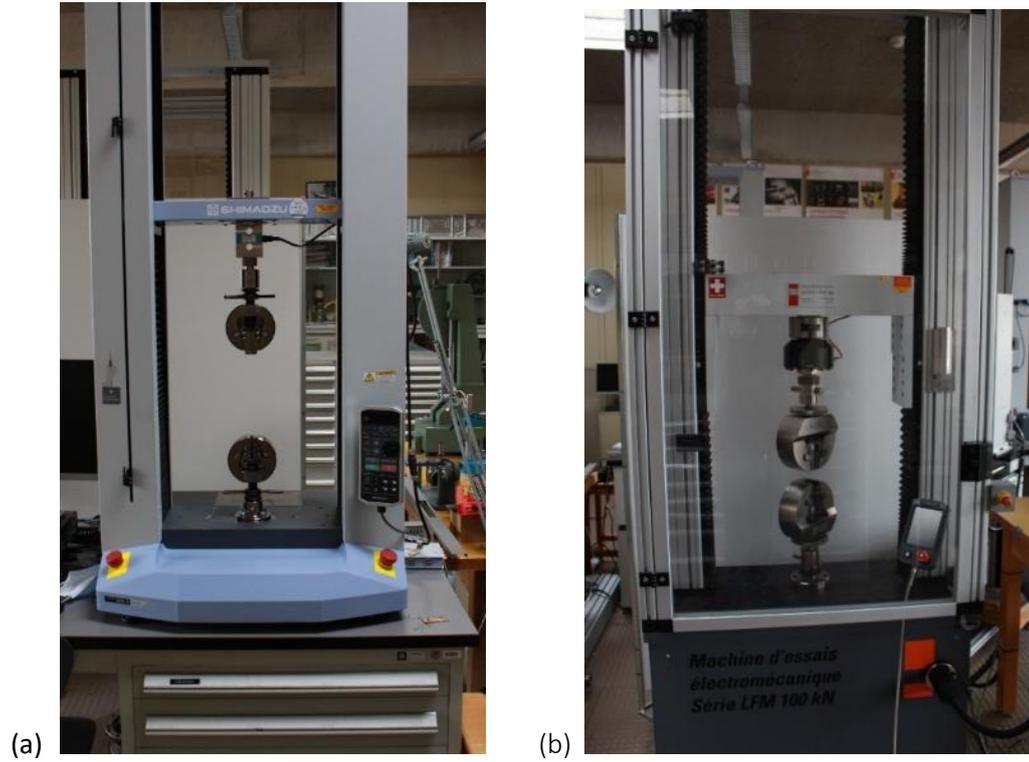
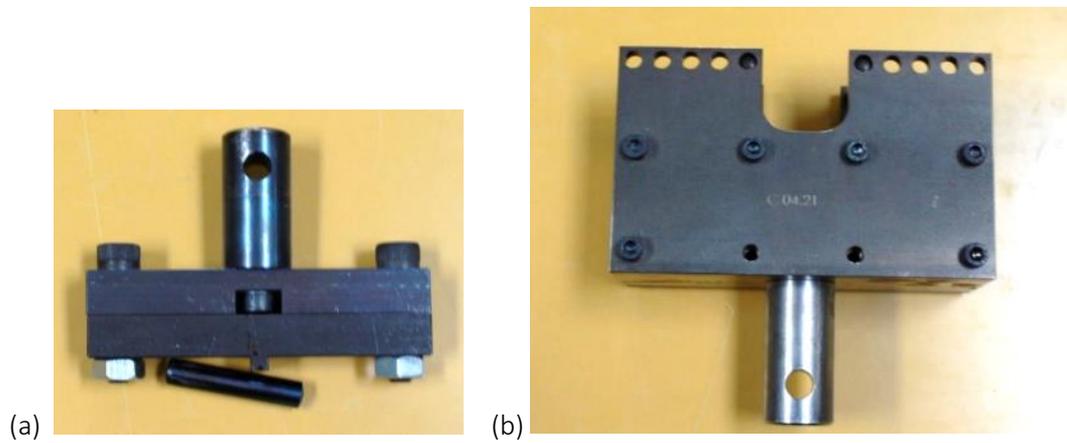
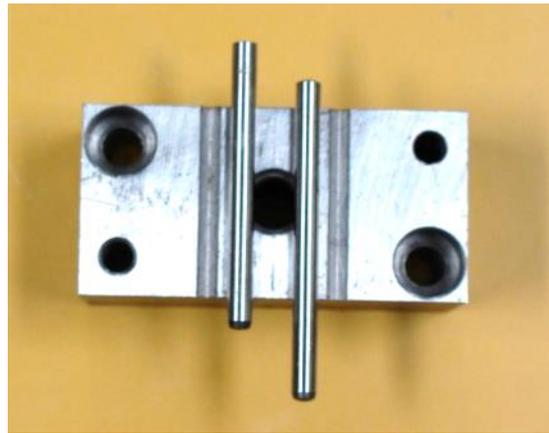


Figure 16 Tensile testing machines: (a) Shimadzu tensile machine 20 [kN] (b) Walter & Bai 100 [kN] (cross ply & 0° tests)





(c)

Figure 17: Three point bending and ILSS fixtures : (a) central pin & support for load introduction (b) three point bending support, (c) ILSS short beam bending supports

The RGD setup consists in a custom developed pressure chamber containing the specimens, which is supplied with H<sub>2</sub> at 300 bar, using an pressure regulator and a rack of high pressure H<sub>2</sub> tanks (Pan Gas, Switzerland):



(a)



(b)

Figure 18: RGD test setup (a) H<sub>2</sub> supply from rack of tanks (Pan Gas) and pressure regulator (300 bars) (b) RGD test cell with a single purge valve, and two intake valves (H<sub>2</sub> for testing and N<sub>2</sub> for purging).

## Sample production and machining

Mostly, already consolidated or injected plate were received, so sample preparation consistent in the most part in machining the samples with a CNC milling machine. Two cutting tool types were used: one single flute end-mill for polymers and another double helix “diamond cut” for composites. For tensile tests, fiber glass – epoxy tabs were glued to the specimens end with Gurit SA80 epoxy adhesive film and cured at 80°C.

Some prepreg was received in roll, so it was cut, dried in an oven and consolidated before machining the plate. The consolidation was made with a hot press and the process temperature of the two prepreps supplied by Supplier 8 were 280° (Material index 19) and 320° (Material index 18) . Due to a lack of appropriate release agent for the model, a thin (0.05 mm) copper foil was used as a skin for the plate (figure 19) which worked well as the Cu foil does not stick to the plate and can be remove when the plate is cold (but it is expensive and unsuitable for series production). Some excessive flow during

compaction was observed and several molding methods had to be tried. The final plate quality is potentially not yet optimal.



Figure 19 : Hot press setup to process plate

## Relaxation tests

### Method

The relaxation tests are performed as follows:

- 1) Heat the chamber and fixtures to 95°, with test specimen mounted
- 2) Perform a regular (constant speed) tensile test at 95° to produce a stress/strain curve.
- 3) Using the tensile test curve, define the force steps to be applied to cause the desired elongations: strain level targets set at 1%, 3%, 5% for neat polymers and 0.2% for composites
- 4) Establish a ramp loading protocol with the crosshead position maintained over time at set elongation targets. Hold time is set to 1600s and ramp time with a slop of 1N/s (figure 20).
- 5) Preheat the system and the specimens to 95°C.
- 6) Install the test sample in the system.
- 7) Wait 30 minutes to stabilize the temperature at 95°C.
- 8) Start the test protocol and record load-displacement vs time

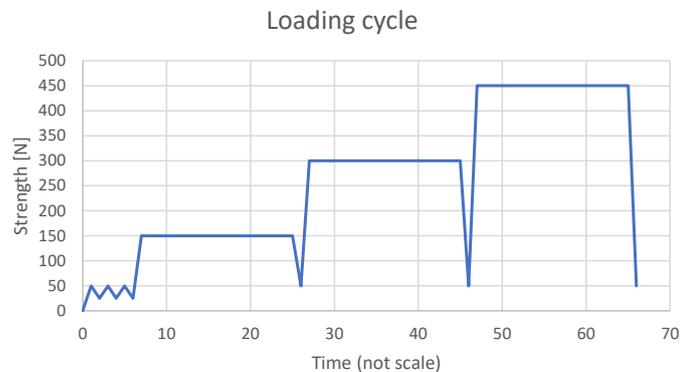


Figure 20 : Example of a loading cycle

To define the applied stress is defined simply as:

$$\sigma = \frac{F}{S}$$

With

$F$  : the force applied by the machine [N]

$S$  : the cross section [mm<sup>2</sup>] of the specimen tested

### Example of results and outcomes

The results obtained can be represented as in figure 21 in which the three typical elongations chosen (three "trapezoids"), can be clearly seen as well as the evolution of the stress over time (1600 [s] per step).

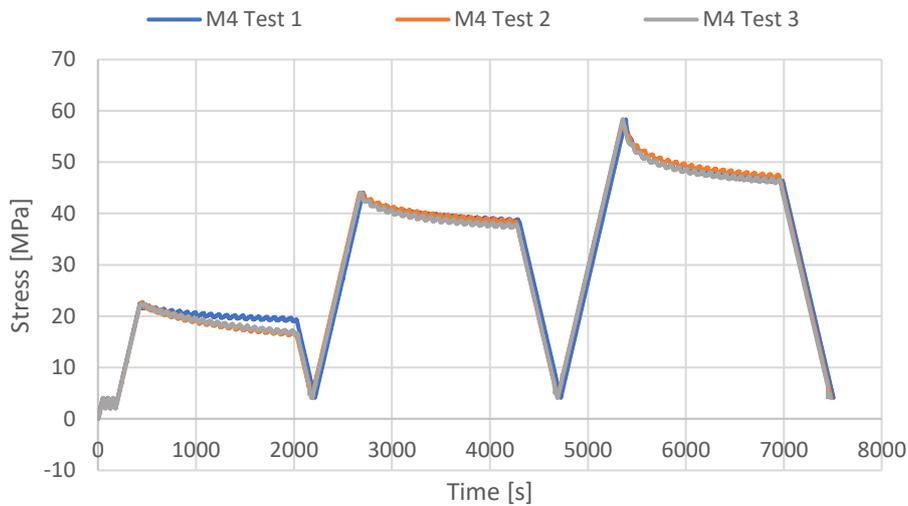


Figure 21 : Relaxation example

Once all the tests have been carried out, a common condition corresponding to an elongation of 3[%] at 95[°] was selected for comparison, which corresponds to the following graphs. The figure 22 shows the results in absolute terms, while Figure 23 shows the results normalized by those obtained for PEEK. To make this comparison, the following relative measure of relaxed stress with respect to PEEK has been defined:

$$K_{t_i} = \frac{\sigma_{mat_{t_i}}}{\sigma_{peek_{t_i}}}$$

Where  $t_i$  is the relaxation time considered in the comparison. By convention,  $t_0 = 0$  [s], is defined as the time when the target elongation is reached, while  $t_{400}=400$  [s] or  $t_{1600}=1600$  [s] correspond to relaxed states.

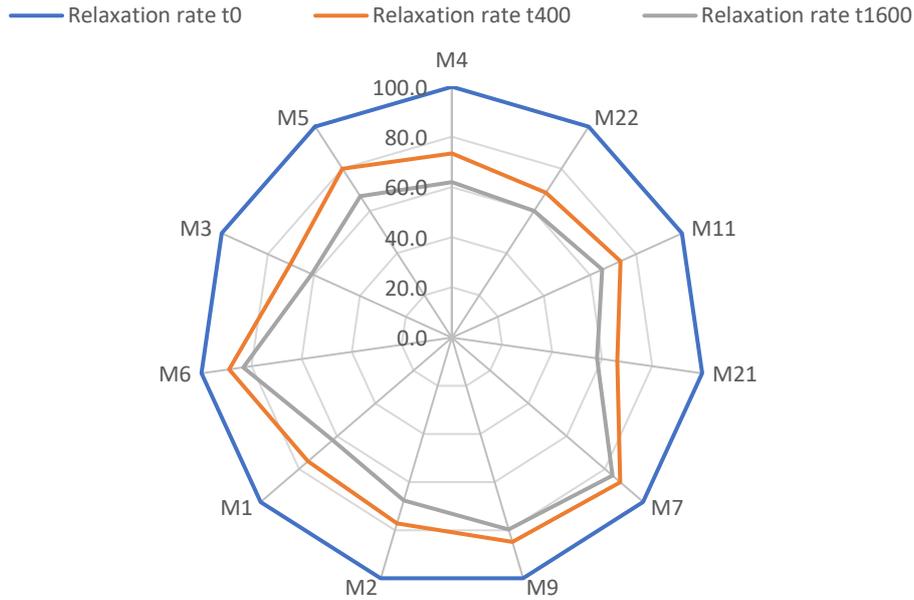


Figure 22 : Relaxation with initial stress as reference (in [%])

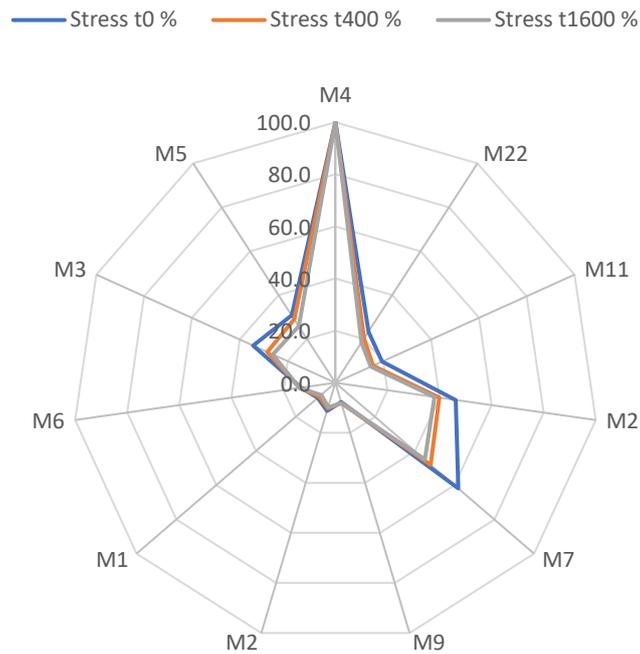


Figure 23 : Relaxation stresses with PEEK as reference (in [%])

What emerged from this first experience is that PEEK is indeed the material with the best possible mechanical performance, which confirms the choice to make it the test reference. It might be wise to mention that PEEK is far too expensive to be integrated into the product. Two materials are distinguished by their stability. The neat polymers referenced M7 (Polymer A) and M21 (Polymer B) which are able to keep 40[%] of the stress set in the PEEK while having a relaxation of up to 40[%] of their initial stress after 1600s at 95°C. These two materials seem thus good candidates for the liner of the tank in terms of relaxation at elevated temperature.

Applying the same method to the composites, it is possible to create the two graphs shown in figure 24 and figure 25. It is observed again that the composite with a PEEK based matrix dominates mechanically the other two grades but, also for price reasons, the PEEK based grade is only considered as a reference for mechanical performance. Figure 24 shows that PEEK and Polymer B are much more stable than Polymer A, which relaxes its stress by 40[%] over 1600 [s] with an elongation of 0.2[%]. On figure 7, it appears that Polymer A is only able to retain 37[%] of the stress of PEEK in relaxed state. However, it should be noted that the relaxation of the 90° ply in a cross-ply composite laminate does not affect much the stress in the fiber directions (0°) and thus a limited relaxation is not a critical as long as it does not create micro cracks or other types of damages (voids). Thus, the lower performance of Polymer A in this case is not considered critical.

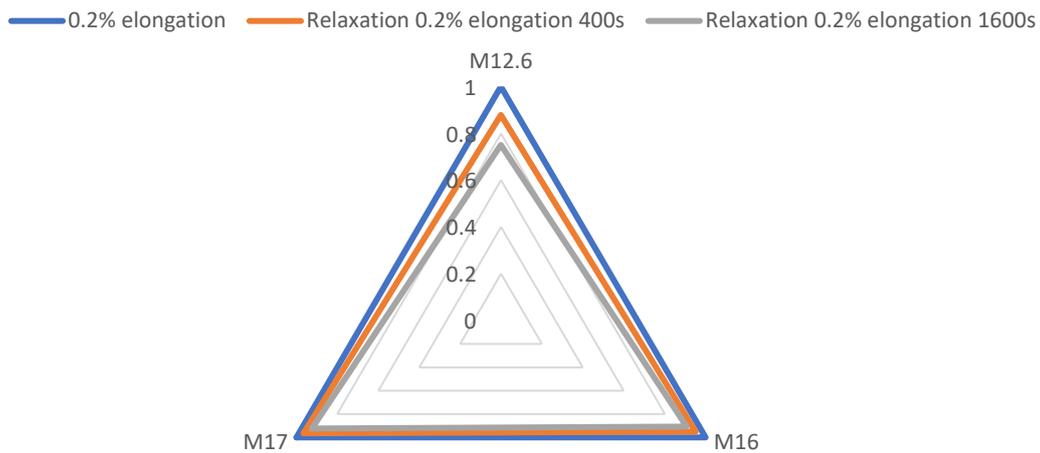


Figure 24 : Relaxation with initial stress as reference

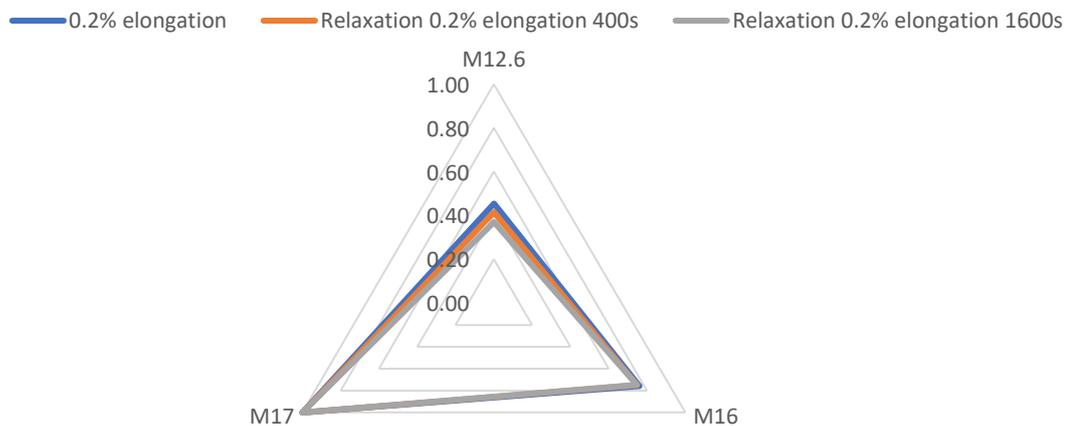


Figure 25 Relaxation with PEEK (M17) stress as reference (in [%]) compared to Polymer A (M12.6) and Polymer B (M16)

## ILSS

The objective of this test is to define the failure stress corresponding to transverse shear failure between the layers of a laminated composite. The ILSS delamination stress is established using a 3-point bending device as shown in figure 26. After some calibration tests, the test fixture was modified from the standard to achieve more consistent delamination fracture (instead of plastic buckling in compression). To induce the delamination failure in a more repeatable way, the support span was increased from 10

[mm] to 15 [mm]. This reduces the amount of “extra” material on the side (which is not bent). Since this material is outside the 15[mm] gap, it is not affected by the shear stress, but it prevents the crack from propagating to the edge of the specimen. Despite this change, not all specimens showed visible delamination. In some cases, the failure was more of a tensile failure of the lower fibers of the material or a compression failure under the punch.

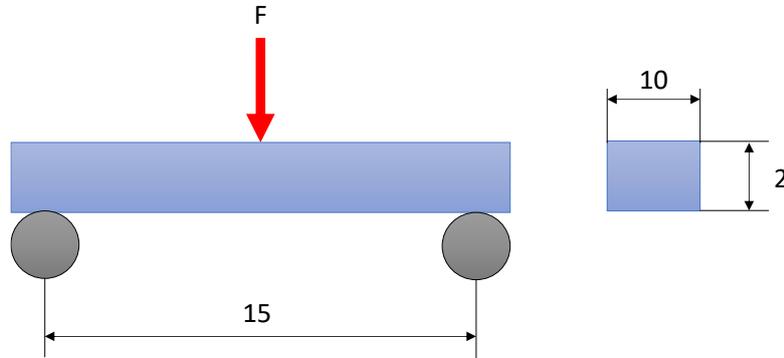


Figure 26 : 3-point bending diagram

The relationship that defines the shear stress can be found using the following method. Figure 27 shows the infinitesimal equilibrium diagram and it allows writing the following relation. Note that the coordinate system of the beam is taken at the neutral fibre, so the  $Y$  axis extends from  $-\frac{h}{2}$  to  $\frac{h}{2}$  and the  $Z$  axis extends from  $-\frac{b}{2}$  to  $\frac{b}{2}$ .

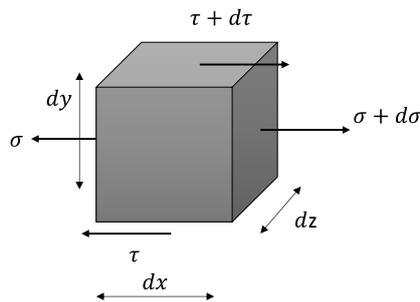


Figure 27 : Infinitesimal equilibrium diagram

$$d\tau \, dx \, dz = -d\sigma \, dz \, dy$$

$$d\tau = -\frac{d\sigma}{dx} \, dy$$

$$\frac{d\sigma}{dx} = \frac{dM_f}{dx I} y = \frac{F}{2 I} y$$

$$\tau = \int -\frac{F}{2 I} y \, dy$$

$$\tau = -\frac{F}{4I}(y^2 + c) = -\frac{12F}{4bh^3}(y^2 + c) = -\frac{3F}{bh^3}(y^2 + c)$$

The shear stress must be zero in the edges of the specimen which allows writing:

$$0 = -\frac{3F}{bh^3}\left(\frac{h^2}{4} + c\right)$$

Therefore.

$$c = -\frac{h^2}{4}$$

The shear expression takes the form:

$$\tau = -\frac{3F}{bh^3}\left(y^2 + -\frac{h^2}{4}\right)$$

This, when evaluated at the center of the beam at  $y=0$ , gives:

$$\tau_{dél} = \frac{3F}{4bh}$$

### Example of results and outcomes

Figure 28 shows a series of ILSS tests, the blue curve is the test carried out according to the standard (with the spacing of the supports at 10[mm]). It can be seen that the curve behaves in a similar way to all the others except after the delamination point where a shearing/crushing phenomenon occurs between the punch and the supports. Moreover, no cracks appear on the specimen (sudden drop in stress) unlike the other configuration with a 15[mm] spacing of the supports. What is still notable is that cracking appears in the transition zone of the configuration with 10[mm] which allows us to have confidence in these results, on the one hand, because the stress is independent of the distance between the supports and, on the other hand, because the curves are very similar in the "normal" working zone.

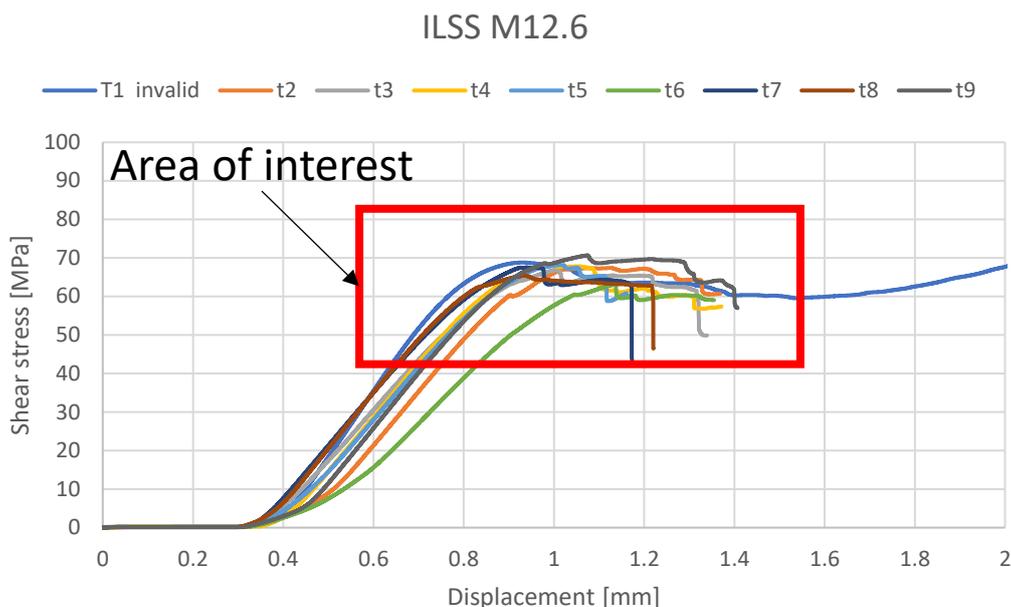


Figure 28 : ILSS example

The table presented in figure 29 summarizes the results obtained during the ILSS tests. The tests #1 were carried out according to the standard with the spacing of 10 [mm] and the mode of rupture observed was that of compression between the punch and the support points. These tests are therefore set aside for the calculation of the average and the deviation. Then all the others that have been marked in red are those where no visible crack has managed to propagate to the edge of the specimens. The value retained is therefore a value due to a failure mode, but the latter is rather a compression of the upper fibers and the traction of the lower fibers while in the case of tests in green, we see the propagation of a crack to the edge of the part as expected in an ILSS test.

Material	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Mean	Deviation
	[Mpa]	[Mpa]	[Mpa]								
M12.6	368.5	67.4	66.9	68.4	68.2	63.1	67.5	65.4	70.7	67.2	3.8
M16	317.7	70.4	66.3	73.9	81.2	65.2	74.2	71.8		71.9	8.0
M17	709.5	85.4	89.6	83.9						86.3	2.9

Figure 29 : ILSS results for PEEK (M17), Polymer A (M12.6) and Polymer B (M16)

## HDT

The principle of this test is to observe the critical temperature from which the material flows under a specific load. The loading level defined in the standard is normally defined for neat polymers, not for composites. Thus the loading level has been adapted to be more representative of a realistic load case. To set the target bending stress, a regular three point bending test was performed (figure 30) to determine two bounds: the lower bound corresponding to the minimum force needed to achieve a linear response of the setup (compensation of the play / contacts in the fixtures used) and the upper one being the failure load of the specimen. Finally, a level of bending stress of 310 [MPa] was chosen which is far enough from both bounds, well within range of linear response of the setup & specimen.

### Bending 3 points at 95° M12.6

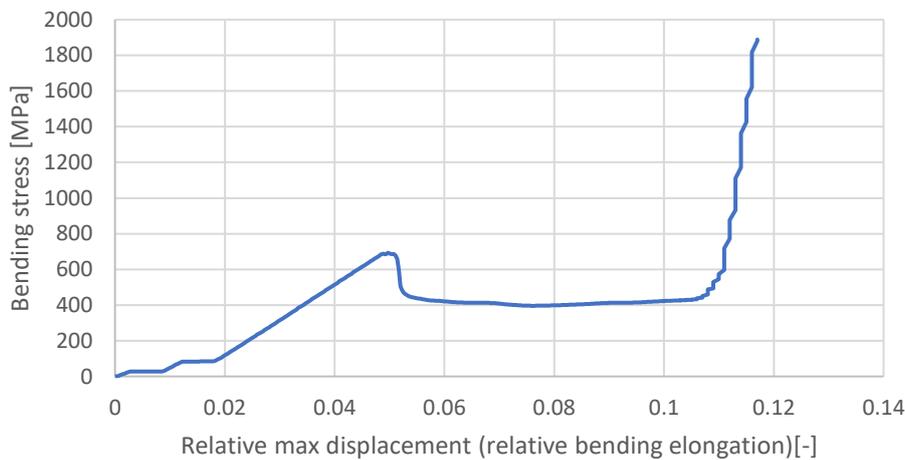


Figure 30 : 3-point bending 95°

### Example of results and outcomes

The climatic chamber cannot be controlled to follow a temperature ramp. Thus, the temperature was changed by hand on the controller of the chamber, step-by-step. The temperature value of the command is used as a reference. Figure 31 represents the evolution of the displacement of the specimens as a function of time as well as the evolution of the set temperature as a function of time. Figure 32 presents the displacement- set temperature relationship. It should be noted however that

the temperature steps limit the available resolution in the temperature scale and thus the HDT can only be determined as falling within a range of a +/- 7.5 degrees.

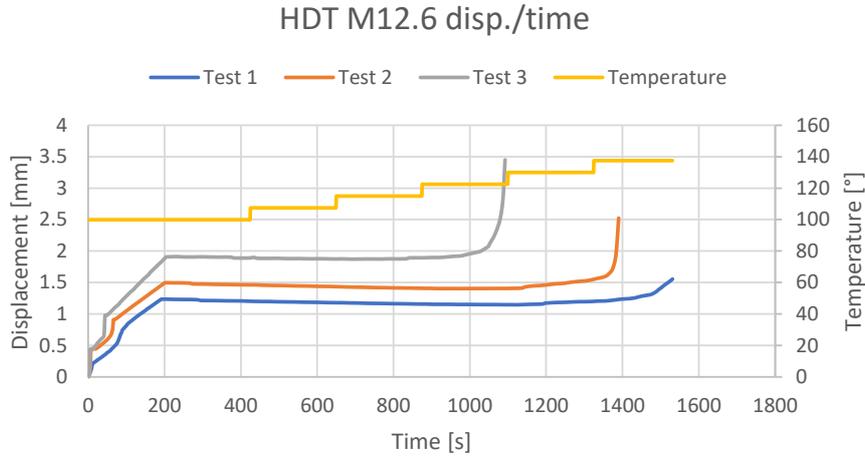


Figure 31 : HDT displacement-time

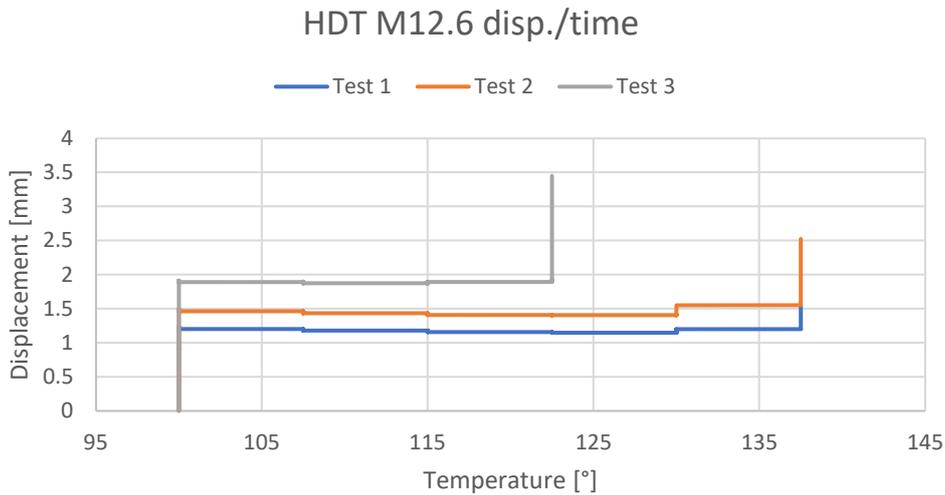


Figure 32 : HDT displacement-temperature

Figure 33 shows the results obtained during the HDT tests which are summarized graphically in Figure 34. It is observed that the critical heat deflection temperature (activation of the creep mechanism) are all above the maximum service temperature of 95°C. Therefore, both PPS and PPA tested here should not exhibit sudden creep due to the service temperature of the tank.

	T1 [°]	T2 [°]	T3 [°]	Mean [°]	Deviation [°]
M12.6	137.5	137.5	122.5	132.5	7.5
M16	237.5	222.5	222.5	227.5	7.5
M17	282.5	280	287.5	283.3	3.75

Figure 33 : HDT results for PEEK (M17), Polymer A (M12.6) and Polymer B (M16)

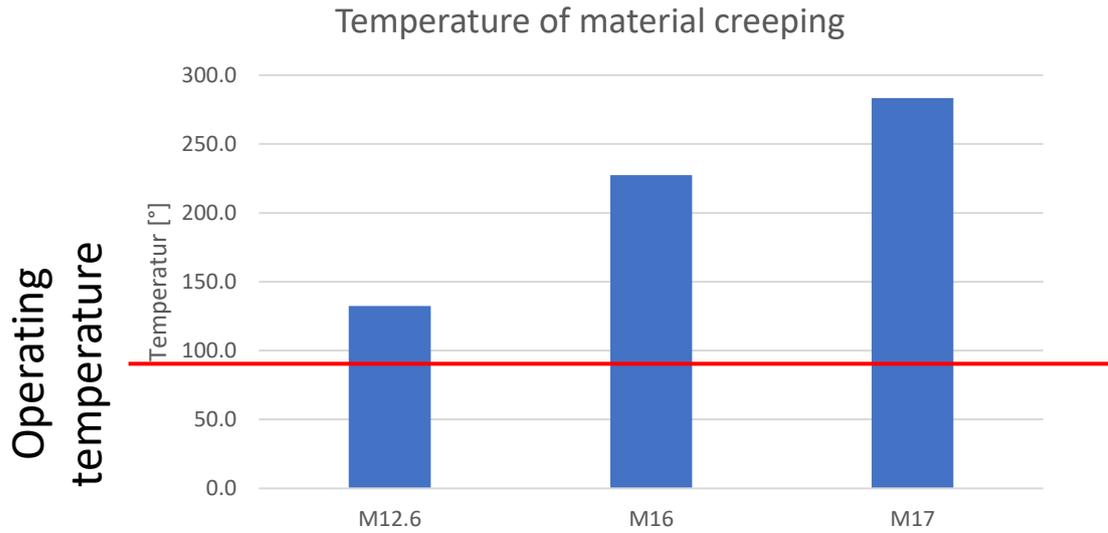


Figure 34 : HDT results for PEEK (M17), Polymer A (M12.6) and Polymer B (M16)

### Tensile 90°

The objective of this test is to characterize the resistance of the composites in the transverse direction of the fibers. In the quasi cross-ply layup considered in NGT tank concept, the first ply failure is expected to be the failure of the 90° ply in tension. Thus, the goal of this test is to give a limit value for the design of the laminate. Moreover, this test is known to be very sensitive to the matrix properties and its adhesion to the carbon fibers.

### Example of results and outcomes

Figure 35 shows a typical 90° degree tensile test.

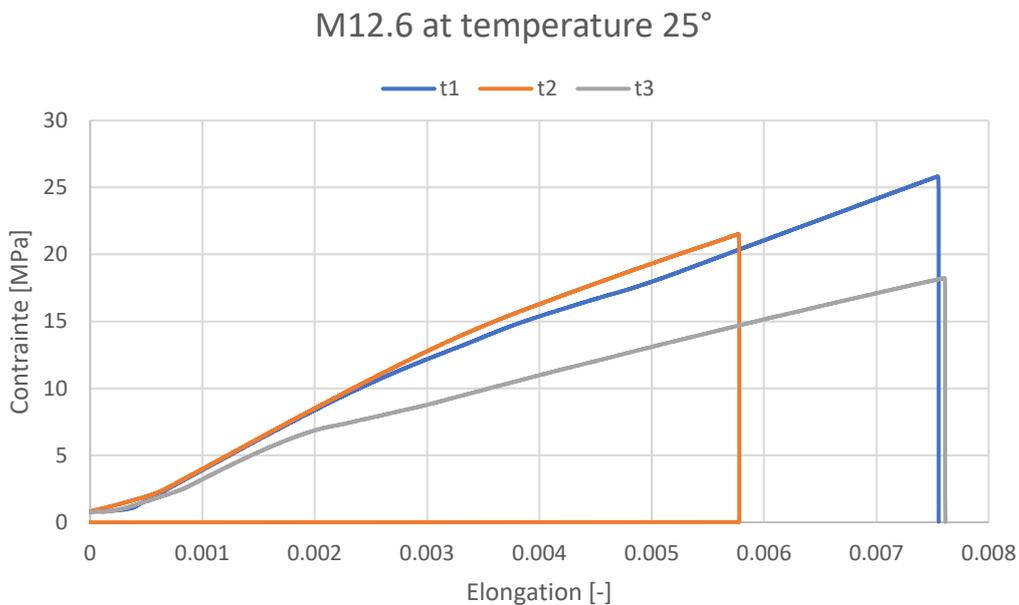


Figure 35 : Tensile 90° for Polymer A (M12.6)

Figure 36 presents a table that summarizes the results obtained. It can be seen again that PEEK has the best mechanical performance (reference) and is followed by Polymer B (M16) reaching 54[%] of the

reference while Polymer A (M12.6) failure stress reaches only 35[%]. However, for elongation, the opposite is observed, the Polymer A is able to elongate up to 64[%] of the elongation of the PEEK while the Polymer B can only go to 42[%]. Figure 37 summarizes the results of the table in graphical form. For the application considered, the stress in the 90° ply does not contribute much to the laminate performance. However, the 0° and 90° plies in the laminate will experience the same strain levels that can reach up to ~2% (fiber fracture). Thus, the maximum elongation in the 90° direction is a critical factor that defines the onset of damage / first ply failure. In that regard, Polymer A being more ductile would be preferable over Polymer B.

Material	Max stress [Mpa]	Stress deviation [Mpa]	Elongation [-]	Elongation deviation [-]
M12.6	21.8353	7.6739	0.0070	0.0018
M16	33.9101	5.1780	0.0045	0.000002
M17	62.3564	8.8491	0.0108	0.0019
M20	3.8670	4.2700	0.0020	0.0650
Peek reference				
M12.6	0.3502	0.8672	0.6428	0.9348
M16	0.5438	0.5851	0.4158	0.0011
M17	1.0000	1.0000	1.0000	1.0000
M20	0.0620	0.4825	0.1877	34.2105

Figure 36 : Tensile 90° results for PEEK (M17), Polymer A (M12.6) and Polymer B (M16 & M20)

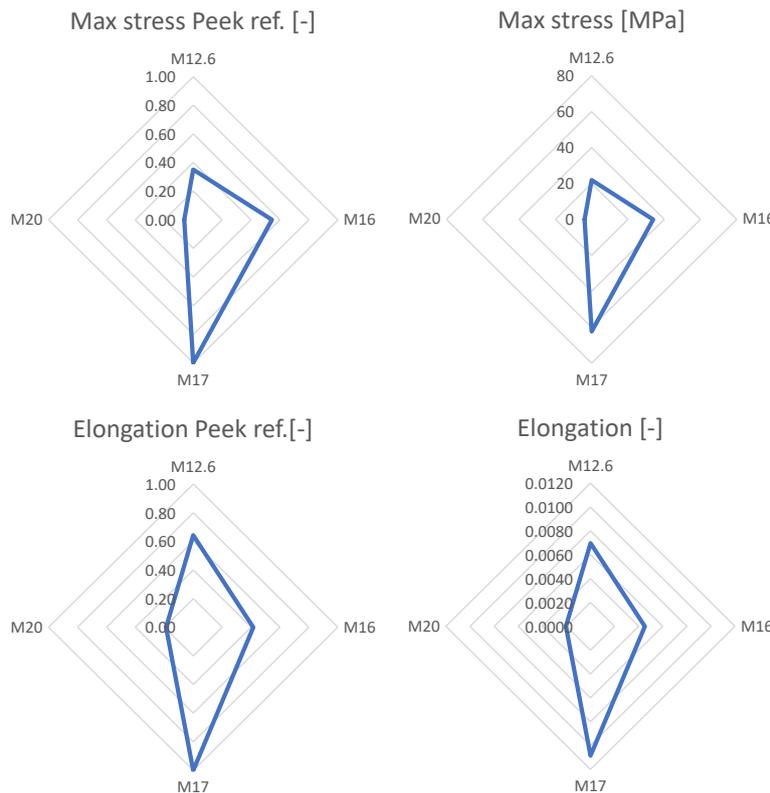


Figure 37 : Tensile 90° graphics for PEEK (M17), Polymer A (M12.6) and Polymer B (M16 & M20)

## Tensile 0°

The purpose of this test is to evaluate the composite performance in the longitudinal direction of the fibers. Figure 38 shows the results obtained through two series of tests. The results shown in red have

been removed from the analysis, because of bonding or initial damages & defects. Figure 39 represents the results obtained in graphical form, with the measurements taken out of the analysis in hatched filling. Finally, figure 40 presents the averaged results.

		S1T1	S1T2	S2T1	S2T2	S2T3	S2T4
M12.1 Load	[kN]	39.37	19.94	37.06	28.84	35.83	36.40
M12.1 Surface	[mm <sup>2</sup> ]	14.75	14.92	12.52	12.52	12.52	12.55
M12.1 Stress	[Mpa]	2669.37	1336.51	2960.91	2304.07	2862.40	2900.73
M12.1 Elongation	[%]	5.30	2.60	5.00	4.50	4.30	4.70
M12.2 Load	[kN]	28.91	32.82	27.75	35.61	26.36	12.48
M12.2 Surface	[mm <sup>2</sup> ]	14.90	14.90	14.84	16.41	13.96	11.25
M12.2 Stress	[Mpa]	1940.55	2202.93	1869.63	2169.50	1888.39	1109.72
M12.2 Elongation	[%]	3.50	4.00	4.80	4.90	3.60	3.00
M12.3 Load	[kN]	41.14	16.11	41.45	42.76	46.25	43.14
M12.3 Surface	[mm <sup>2</sup> ]	16.30	15.98	17.19	17.19	17.11	16.62
M12.3 Stress	[Mpa]	2523.36	1007.67	2411.01	2487.43	2703.31	2595.57
M12.3 Elongation	[%]	5.25	3.25	4.75	5.00	5.50	5.25
M12.4 Load	[kN]	15.49	22.53	43.18	38.40	37.34	41.18
M12.4 Surface	[mm <sup>2</sup> ]	11.84	17.12	16.58	17.90	16.92	17.53
M12.4 Stress	[Mpa]	1308.46	1315.62	2605.11	2144.52	2207.08	2348.42
M12.4 Elongation	[%]	3.25	2.75	4.05	4.25	4.25	4.50
M12.5 Load	[kN]	16.63	41.12	40.77	41.08	39.70	41.51
M12.5 Surface	[mm <sup>2</sup> ]	15.92	16.32	16.96	16.96	16.67	17.19
M12.5 Stress	[Mpa]	1044.78	2518.83	2403.15	2421.79	2382.02	2414.56
M12.5 Elongation	[%]	4.75	4.55	4.85	5.25	4.50	4.80
M16 Load	[kN]	22.84	23.59	25.17	23.60		
M16 Surface	[mm <sup>2</sup> ]	15.65	15.98	15.75	15.23		
M16 Stress	[Mpa]	1459.80	1475.94	1598.14	1550.36		
M16 Elongation	[%]	2.75	3.00	3.25	3.25		
M17 Load	[kN]	26.33	24.29	26.10	26.24		
M17 Surface	[mm <sup>2</sup> ]	15.69	14.56	14.30	14.50		
M17 Stress	[Mpa]	1678.13	1668.21	1824.96	1809.63		
M17 Elongation	[%]	3.40	3.10	3.30	3.00		
M20		T1	T2	T3	T4	T5	T6
M20 Load	[kN]	22.20	20.12	21.11	14.62	17.14	16.50
M20 Surface	[mm <sup>2</sup> ]	17.41	17.39	17.89	17.89	17.37	17.37
M20 Stress	[Mpa]	1275.00	1157.04	1179.98	817.10	986.44	949.58
M20 Elongation	[%]	4.30	4.50	3.85	not standard test	4.00	3.60

Figure 38 : Tensile 0° results for PEEK (M17), Polymer A (M12 series) and Polymer B (M16 & M20)

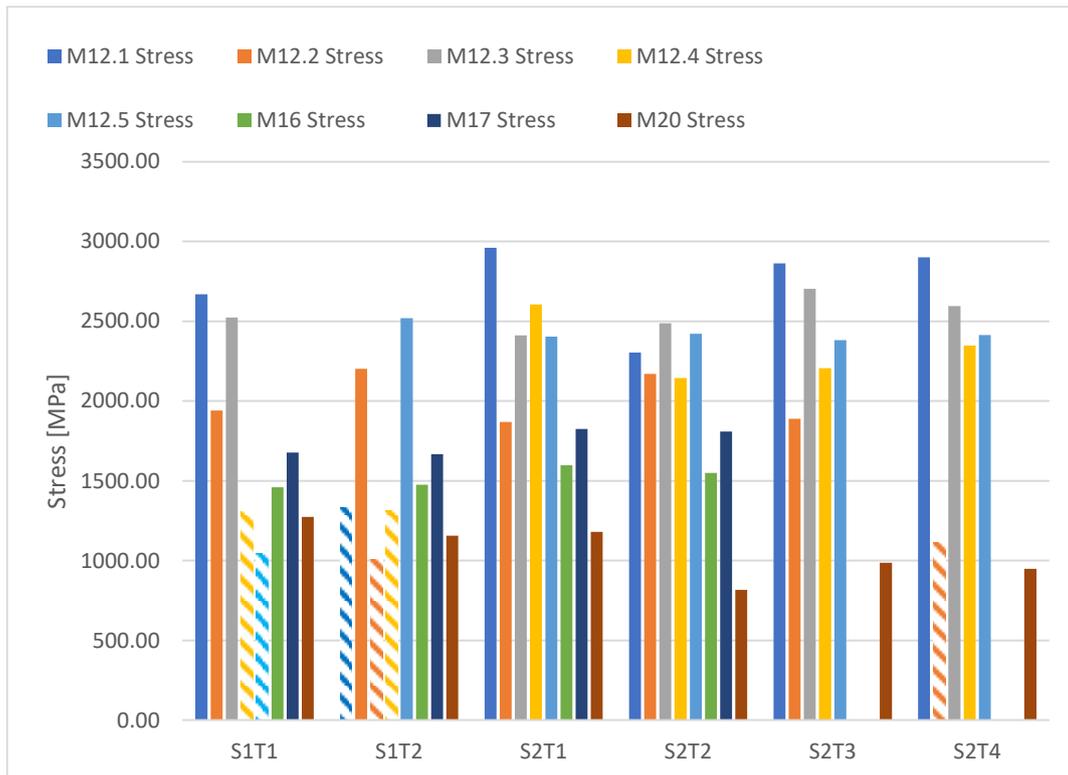


Figure 39 : Tensile 0° graph for PEEK (M17), Polymer A (M12 series) and Polymer B (M16 & M20)

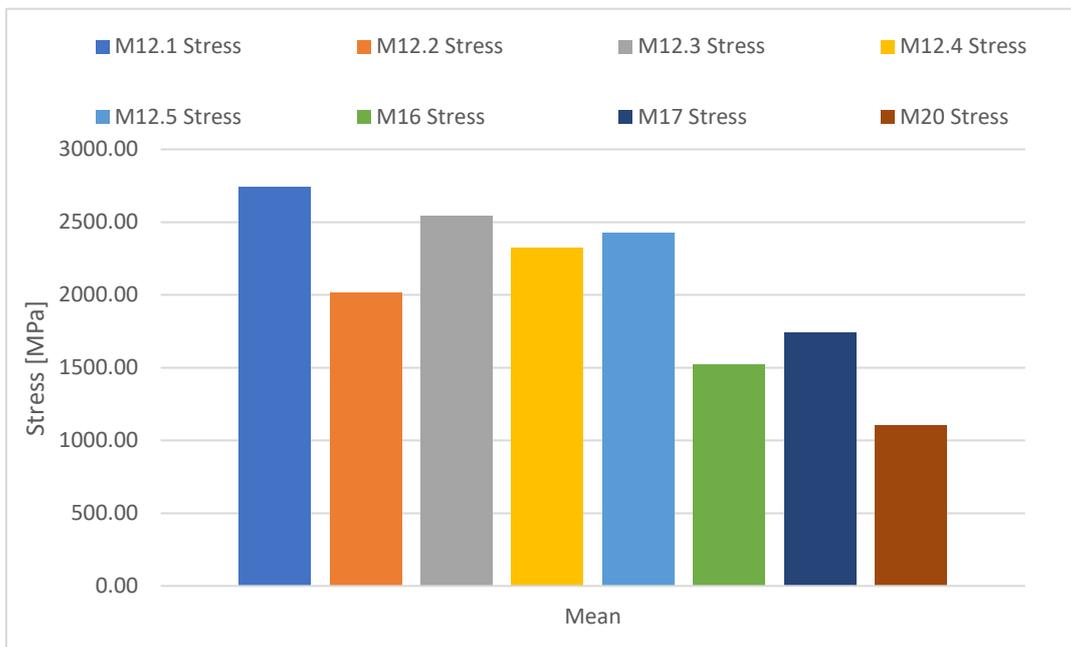


Figure 40 : Tensile 0° mean for PEEK (M17), Polymer A (M12 series) and Polymer B (M16 & M20)

Overall, except for the last material in the list, the measured tensile strength corresponds to the range expected. However, as the supplied materials used different types of fibers, the comparison can be slightly biased by the grade of fiber used by each manufacturer. The results obtained on the PEEK and Polymer B plates are slightly lower than expected which could be attributed in part to issues with the gluing of the tabs (parallelism of the faces not sufficiently good). Nevertheless, the results obtained for the Polymer A composites can be considered very good and thus validate the potential use of Polymer A for such application.

## RGD

This test was performed in external environment for safety reasons, and it was subject to the exterior temperature. The temperature ranged was  $-0.5[^\circ\text{C}]$  to  $10[^\circ\text{C}]$  with a mean in the order of  $5[^\circ\text{C}]$ . In fact, due to the relatively low temperature which reduces the diffusion rate, the test was extended up to three weeks to ensure that saturation is reached. At the end of this three weeks, the pressure was slowly released in four minutes. So, the depressurization rate is  $75[\text{bars}/\text{min}]$ . The samples are little disk of  $17[\text{mm}]$  of diameter, with a hole of  $3[\text{mm}]$  of diameter in center and a thickness of  $2[\text{mm}]$ .

No visible damage were observed immediately after pressure release and after that the sample were exposed to ambient atmosphere for three days. A detailed visual examination does not reveal any change of aspect, color, or surface appearance, no crack, no bubble or delamination. That conducted us to conclude that polymer used are not subject to visible damage during RGD. Figure 41 show the samples after RDG.

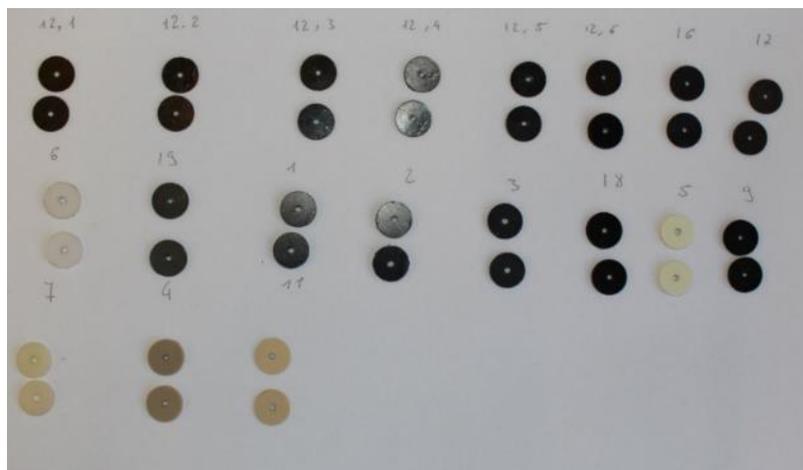


Figure 41 : Samples after exposition to hydrogen

We realized a microscopy for two materials. The first one is Polymer A material index M7 (Figure 42). Overall, despite a slightly different contrast in the pictures, no visible cracks or voids could be observed after RGD. Some particles or inclusions can be observed on both micrographs, but with more prevalence on the picture after RGD. These particles could be inclusions or reinforcements already present in the material or residues due to the polishing, but they are visibly not voids or cracks. As these are two different specimens, it might also be that the local content of reinforcements varies from place to place in the sample. Also, the contrast of the second image has been enhanced compared to the first observation which highlights those inclusions more clearly.

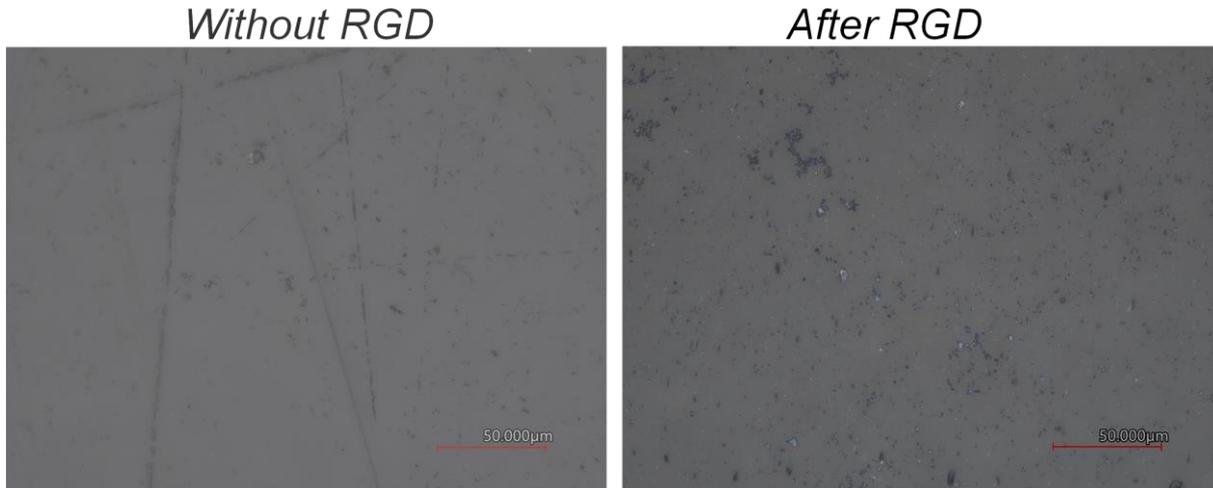


Figure 42 : Polymer A – M7 microscopy

The second material is references 12.1 in the Polymer A group. On the micrographs in figure 43, no significant difference can be seen before and after RGD. Due to the level of observation (optical microscopy only), we cannot completely rule out potential changes of the material during RGD or exposure to H<sub>2</sub> for a long time, but if a change in the material is induced, then it is very limited and at a much smaller scale than what could be observed here.

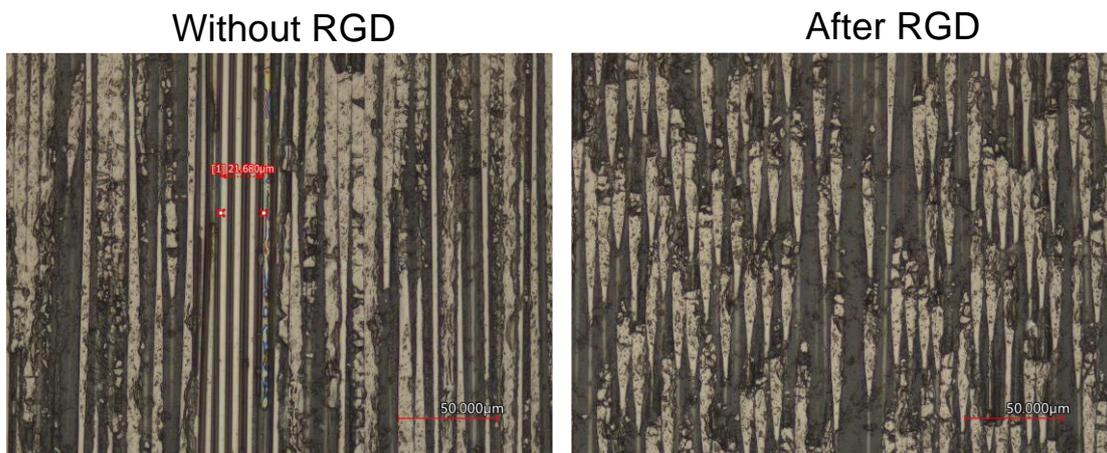


Figure 43 : Material 12.1 (Polymer A) composite microscopy before / after RGD

## Tensile tests with video & Acoustic Emission monitoring

The purpose of this test is to evaluate a composite laminate representative of the tank composite shell. Thus, the composite plates have four plies in the first direction (0°), then eight in the second direction (90°) and again four in the first direction. Two kinds of sample were cut from the master plate: [0°<sub>4</sub>/90°<sub>8</sub>/0°<sub>4</sub>] and [90°<sub>4</sub>/0°<sub>8</sub>/90°<sub>4</sub>]. Two suppliers provided materials either as a plate or prepreg. The plate provided by Supplier 9 (Polymer B, index M20) had many visible defects, and dry spots / porosity related probably to a non-optimal manufacturing. This material was thus not tested. The second material set was provided by Supplier 8 in the form of prepreg of Polymer A / CF and Polymer B / CF. Plates were produced internally using hot press consolidation. Due to limited material quantities, the manufacturing was not perfect either, with significant lateral flow of the some plies, but no voids or dry spots were present at least. The tensile tests have been carried out with an extensometer, a video camera for close up observation of the free edge and two acoustic monitoring sensors (Physical

Acoustics Corporation : NANO-30) . Acoustic emission was recorded and analyzed using a Vallen system & analysis software (AMSY-5). The basic concept of this setup (figure 44) is to capture the deformation under load and to detect the initiation and evolution of the micro failure inside of the laminate, while observing the visible cracking (transverse or delamination) at the free edge of the sample.

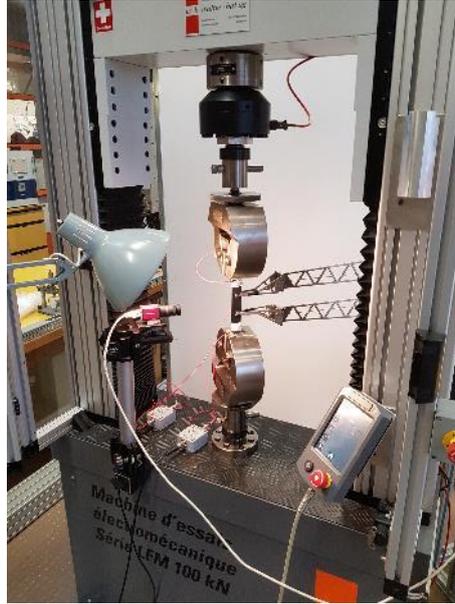


Figure 44 : Acoustic emission setup

## Result examples

Polymer A with fibres at 0/90/0°

The figure 45 shows the tensile test results where we can see some initial slipping during the test. In fact, the slipping of the sample is not a real problem because an extensometer was used to record the strain. In these results, the ultimate stress can be estimated ( ~370 MPa) from the cross section of the sample (95.25 mm<sup>2</sup> here). The figure 46 show the linear portion of the sample stress-strain response which is used to derive the Young's modulus (43 GPa).

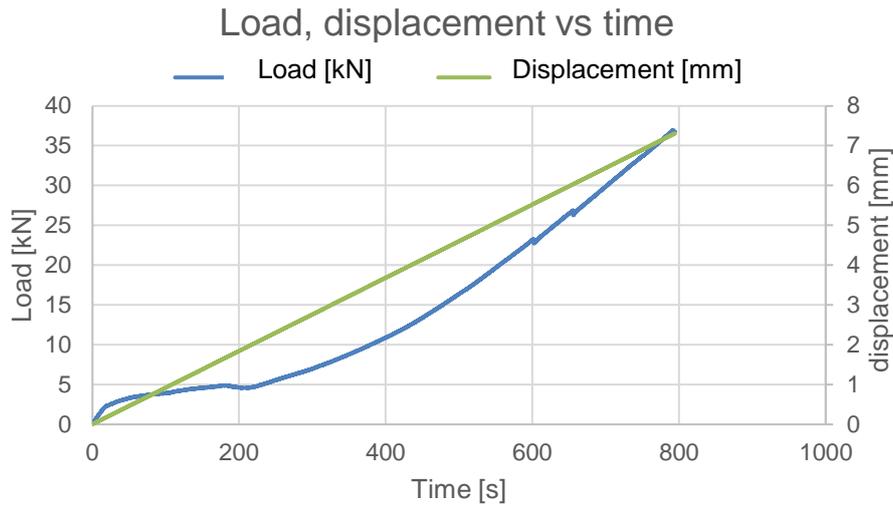


Figure 45 : Tensile test for Polymer A laminate (M18)

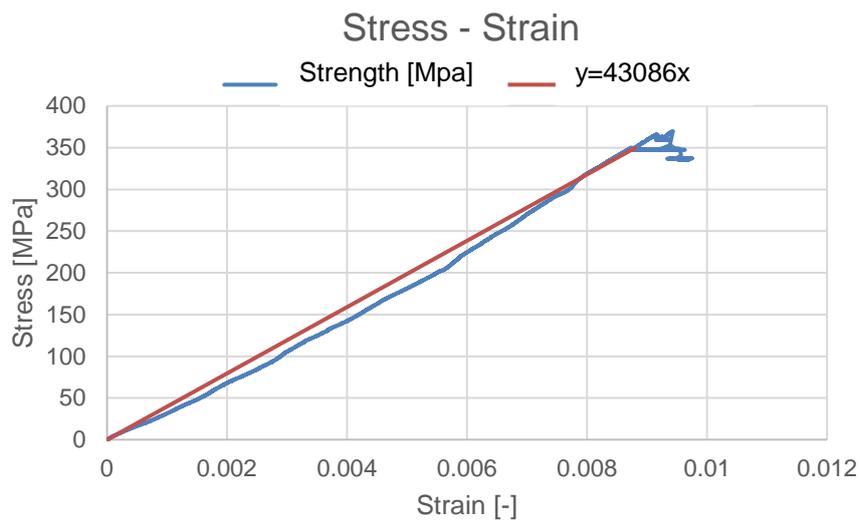


Figure 46 : Stress-elongation graph for Polymer A at 0/90/0° not to rupture

The correlation of the video monitoring with the acoustic emission helps us to understand what happens during the tensile test. The figure 47 show some key pictures of the test. The acoustic emission data and the related damage events are represented in figure 48.

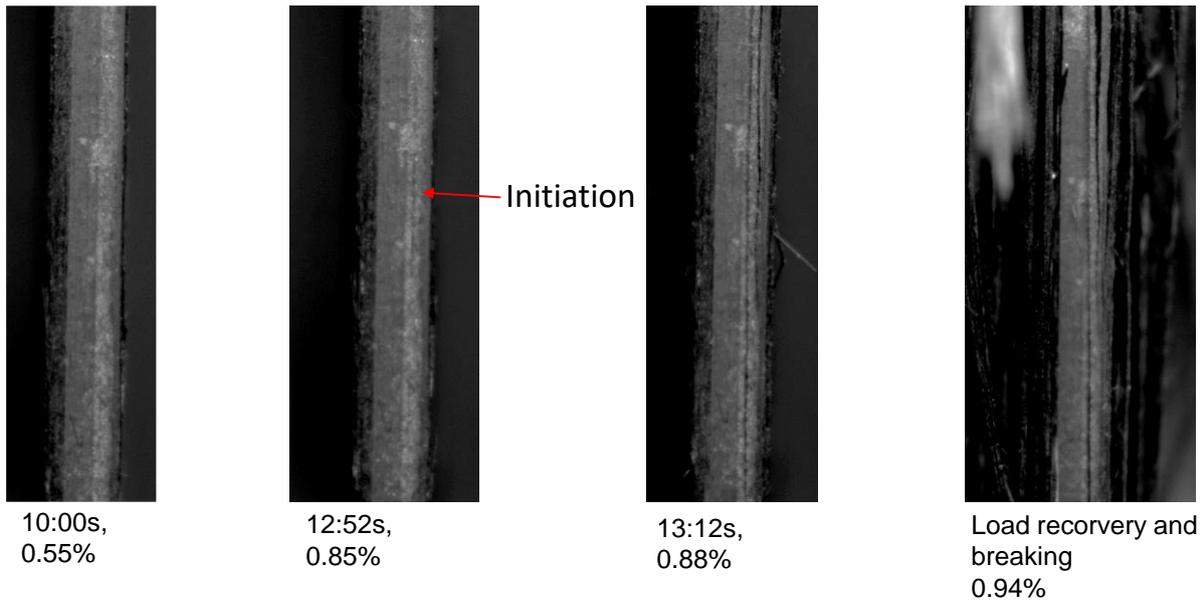


Figure 47 : Images during the tensile test

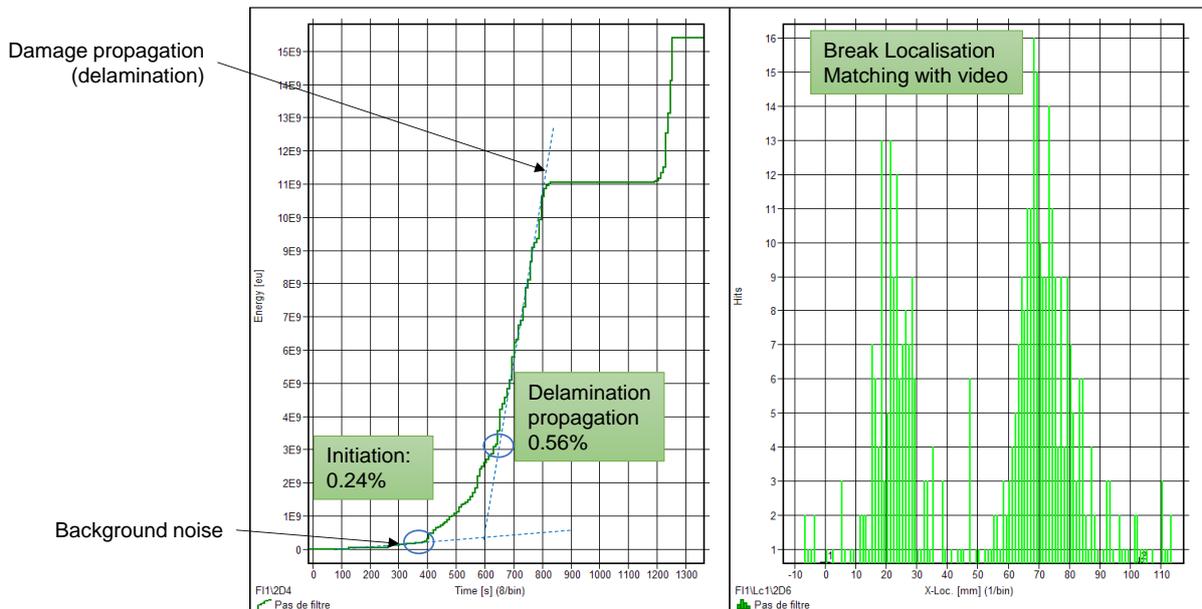


Figure 48 : Acoustic emission

From this data, several damage “thresholds” have been identified for each specimen. First, the acoustic emission events are filtered to retain only the events occurring in the gage length of the specimen and a cumulative AE energy is computed for that region. The slope of the cumulative energy curve represents indirectly the rate of damage development. In the early stages of the test, the recorded signals are mostly due to background noise and thus a baseline curve is drawn to represent that background effect. Then AE emission accelerates, which deviates from the background activity. This first deviation point has been defined as the “damage initiation” point where first acoustic activity occurs. This does not necessarily represent a significant damage of the material in terms of reduction of strength, but it represents the activation of some non-linear internal mechanisms. Then at higher stress, the AE energy rate becomes more or less constant (constant slope in cumulative energy diagram). This domain can be interpreted as steady damage development such as crack growth for example. The point

at which the steady state region starts is defined as the “damage propagation” point. Finally, the video observation allows to determine when and which type of macro damages occurs.

The figure 49 shows a synthesis of the results obtained with the tensile test with video and acoustic emission monitoring for the two laminate orientations 0/90/0 and 90/0/90 and two materials Polymer A & Polymer B. We observe that the ultimate strain and ultimate stress are always higher for Polymer A than for Polymer B. This trend was already observed for the 0° tensile tests. However, the failure mode observed in these cross-ply tensile tests are mostly related to delamination, not fiber fracture. Thus, the lower ultimate strength of Polymer B laminate could be interpreted as a lower resistance to delamination (lower interlaminar toughness) of Polymer B compared to Polymer A. The observed onset of cracking occurs at a higher stress level for Polymer B. The onset stress for the Polymer B is twice higher than for Polymer A and the strain is nearly twice the strain of Polymer A. For the onset strain the Polymer A and Polymer B are roughly equivalent in the 0/90/0 tests. However, the first crack appear relatively early at about 0.56% strain while the ultimate strain of the 0° ply is closer to 1.5%. Thus the early onset of damage in the 90° ply and subsequent delamination can be considered as the main limiting factor for the design of the pressure vessel and defines the maximum allowable pressure in service. Indeed, as first cracks appear, the damage accumulation during pressure cycles can become unstable and lead to premature failure. Thus, a material with higher onset of transverse cracking (higher ductility and toughness) would be ideal. Among the two materials tested, Polymer A is obviously more suited for the application in that regard. Also, a shallow helicoidal winding angle with alternate helix angles (+/- alpha) instead of pure 0° or pure 90° thick ply blocks could help to limit the crack growth and delay the onset of transverse cracking (ply thickness effect). Also as we can see in the table, when the 90° ply is outside, the damage onset stress is lower. A “simple” solution would be to add a thin 0° or shallow angle +/- alpha helical winding as a blocking ply on the outside.

Laminate Structure	0/90/0°		90/0/90°	
	M18	M19	M18	M19
Polymer				
Cross section	95.25 mm <sup>2</sup>	78.4mm <sup>2</sup>	96.9 mm <sup>2</sup>	80.8 mm <sup>2</sup>
Damage onset strain	0.24%	0.40%	0.22%	0.27%
Damage onset stress	104 MPa	199 MPa	71 MPa	84 Mpa
Damage propagation strain	0.56%	0.57%	0.48%	0.34%
Damage propagation stress	240 MPa	229 MPa	155 MPa	104 MPa
Ultimate strain	0.94%	0.82%	0.58%	0.38%
ultimate stress	370 Mpa	244 Mpa/278 Mpa	168 Mpa	107 Mpa
Failure mode	0° delamination	0° delamination +90° cracks	0° delamination +90° cracks	0° delamination +90° cracks

Figure 49 : Results synthesis for Polymer A (ref. M18) and Polymer B (Ref. M19)

## Conclusion

First, despite the perceived potential risk due to lack of literature concerning the Rapid Gas Decompression induced damage, our small test campaign showed that all the polymer considered in this study are not significantly affected by RGD and thus can be considered as good candidates for the application. However, more detailed observations using electron microscopy could be interesting to verify if small scale damages are present. The tensile test at 0° show that the Polymer A composite of has a very good performance while the Polymer B composite tested showed unexpectedly low performance in this test. This low performance might however be related to issues with the specimen preparation, even though the procedure was the same for all materials. In the tensile test at 90°, we observed that the Polymer A composite of Supplier 4 is not as good as the Polymer B (or PEEK) of

Supplier 2 in terms of ultimate strength, but it is more performant than the Polymer B of Supplier 9. However, in terms of elongation to failure at 90°, the Polymer A outperformed both Polymer B laminates while the PEEK composite was clearly the best. The Heat Deflection Temperature is the lowest for the Polymer A but remains higher than the service temperature of 95°C, so the Polymer A tested in this work can be considered for this application if the thermal management of the tank is well under control. In terms of Inter-Laminar Shear Strength, the Polymer A showed slightly lower performance compared to Polymer B or to PEEK but the differences are marginal and the ILSS value remains sufficient for the application.

Overall, we can conclude that a composite with Polymer A can be suitable for the application. Its performance is not the best in terms of Heat Deflection Temperature but it remains acceptable up to a service temperature of 95°C. Another potential advantage of the Polymer A could be its price which could be below Polymer B once it is fully industrialized. Polymer B composites showed also sufficiently good performance for the application but their inherent brittleness can be an issue in terms of cyclic behavior or resistance to impacts. PEEK / CF composite offers clearly the best performance but its price is out of reach for mass production of H2 tanks for vehicles. The acoustic emission test showed that the cross-ply laminates with Polymer A and Polymer B matrixes both exhibit early onset of damage and failure dominated by delamination. The relatively low onset of damage observed could be linked to non-optimal manufacturing quality, but it highlights the importance to use such tests on the final material and laminate sequence to determine the allowable strain in service from the damage onset strain recorded. Indeed, if damage initiates, the fatigue life of the pressure tank is significantly reduced and depends on the rate of damage accumulation at each pressure cycle. Both Polymer B and Polymer A composites exhibited damage onset at about 0.5% strain, thus the tank should be designed to have a strain level below that threshold under normal service conditions. In that regard, Polymer A showed slightly better performance than Polymer B in terms of ultimate strain of the laminate.

For the neat polymer (liner), we can see that the references 7 (Polymer A group) and M21 (Polymer B group) are both interesting. These two materials have a relative relaxation stress of ~50 [%] compared to PEEK at 95°C over 1600 [s]. Overall, both materials would have a good behavior in terms of creep / viscoelastic stresses inside of the tank during pressure & thermal cycling.

With these results we can conclude that the optimal choice to design a thermoplastic composite pressure tank for hydrogen storage using the NGT concept is with a liner in Polymer A like the material reference 7 and a shell of Polymer A and Carbon Fibre composite from supplier 4 (similar material M12.1). Both materials have good performances, could become affordable when industrialized and can be recycled. However, specific improvements to the laminate design have been proposed and further material research could be beneficial to further increase the ductility, ultimate transverse tensile strain and toughness of the Polymer A / Carbon Fibre composite to improve the onset of damage.

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