New solutions for hydrogen pressure vessel manufacturers

Huntsman Advanced Materials offers innovative solutions that support manufacturers in the design and production of composite pressure vessels for hydrogen storage and transportation. This includes high-performance resin systems complemented by extended material characterization, processing expertise, and process simulation.

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The 2020s will be a decade of change, with governments worldwide implementing ambitious hydrogen strategies to help meet emissions targets

All eyes on hydrogen

Hydrogen costs are expected to drop significantly as production capacity increases, enabling hydrogen-powered fuel cell vehicles (FCEV) to become a cost-competitive, zero-emission solution for applications requiring long range and fast charging times.

Beyond road vehicles, hydrogen is also generating interest in the aerospace, rail, and maritime sectors. Composite pressure vessels will play a key role in hydrogen storage, whether within vehicles or for transport and distribution, in order to build a cost-competitive hydrogen infrastructure.

Supporting manufacturers worldwide

Huntsman Advanced Materials is a leading global supplier of epoxy resin solutions for Type 3, Type 4, and even Type 5 filament-wound composite pressure vessels. With a comprehensive range of epoxy-based resin systems, the company's solutions are trusted worldwide for material performance, efficient manufacturing and increased productivity (Figure 1).

A tough regulatory landscape

The emergence of hydrogen storage has led to technical challenges, especially considering the increased pressure requirements that can range from 350-700 bar. Today, the Global Technical Regulation on Hydrogen and Fuel Cell Vehicles (GTR No. 13) demands not only pressure testing with high safety margins, but also impact resistance, chemical exposure, and numerous temperature- pressure cycling tests, as shown in Figure 2.

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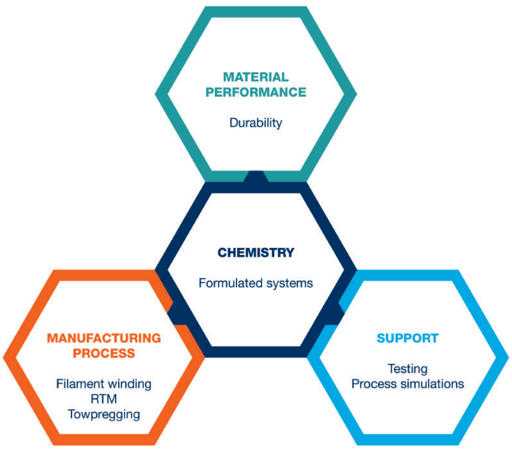

Fig. 1: Huntsman Advanced Materials offers a suite of products and services for pressure vessel manufacture

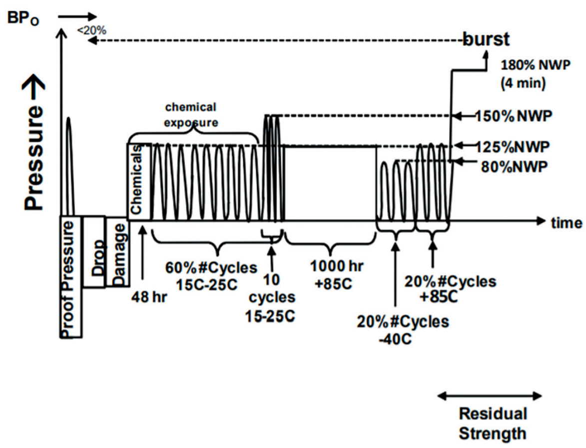

Fig. 2: Sequential hydraulic cycling tests. (source: https://unece.org/ – GTR 13)

Meeting stringent requirements

The pressure resistance of hydrogen vessels is mainly governed by the reinforcement fibres, but the resin matrix plays a key role in providing environmental exposure protection (thermal, chemical, impact) as well as fatigue/pressure-cycling resistance to withstand the filling and emptying cycles.

The severe pressure cycling test at 85°C, required by the GTR 13 standard means that, in practice, resin systems must have a glass transition temperature (Tg) of at least 115-120°C to avoid premature failure, even in hot/wet conditions.

Studies have shown that resin systems featuring high mechanical strength and high elongation at break can better support dimensional changes (strain) induced by pressure cycling, preventing crack initiation within the laminate even at maximum rated pressure.

In addition, a high fracture toughness can enhance fatigue performance and impact resistance by reducing damage initiation and crack propagation. Standard epoxy systems have fracture toughness (KIc) values around 0.7 to 0.9 MPa.m$^{1/2}$, whereas Huntsman's toughened epoxy systems can offer values as high as 1.7 MPa.m$^{1/2}$, significantly improving pressure cycle and impact performance.

Static, dynamic, and hot/wet performance of both the pure resin and composite parts can be fully characterized in the company's ISO 17025-accredited laboratories. The key properties of several toughened ARALDITE® systems for pressure vessel manufacture are shown in Table 1.

Tab. 1: Key properties of ARALDITE® resin systems

Resin system	ARALDITE® LY3608 ARADUR® 917-1 Accelerator 960-1	ARALDITE® LY3512 ARADUR® 1571 Accelerator 1573	ARALDITE® LY3508 ARADUR® 3478
Process	Wet filament winding	Towpreg	RTM
Cure cycle	2 hrs 80°C + 2 hrs 110°C	2 hrs 140°C	20 min 100°C + 2 hrs 130°C
Tg (°C) DSC Midpoint ISO 11357-2	120	130	115
Tensile strength (MPa) ISO 527	75	87	70
Fracture toughness KIc (MPa.m$^{1/2}$) ISO 13586	1.58	0.85	1.70

A range of manufacturing processes

Wet filament winding is a well-established manufacturing method, but increasingly resin injection (Resin Transfer Moulding, RTM) and towpreg winding are considered in order to meet the need for increased productivity and greater part consistency (Table 2).

The RTM process consists in forming a braided fibre preform over an inliner, followed by fast injection of a fast-cure resin system within a closed mould. While equipment investment and process complexity may be high, there can be advantages for the mass production of smaller pressure vessels.

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Tab. 2: Process features for composite pressure vessel manufacturing

	Wet filament winding	Towpreg	RTM
Main features	• Well-established technology and production equipment • Winding speed of 1-2 m/s max. Range of winding angles	• Clean process • Fast winding speed (> 5 m/s) • Controlled and consistent resin content • Variable winding speed (fast on hoops, slower on domes) • Range of winding angles • Optimized winding patterns • High reproducibility • Short cure times (down to 30 min) • Out life between 1 week and 1 month at room temperature	• Clean process • Fast injection versus filament winding operations • Fast cure in mold (20 min) • Ideal for small sized vessels • High laminate quality (low porosity content) • High investment (braiding, molds, press, dosing equipment) • Higher resin content than towpreg and FW

Towpreg filament winding (using a preimpregnated fibre tow) is gaining popularity for mass production of hydrogen tanks, mainly due to clean processing, improved part quality, fast winding speeds, and short cure cycles. Towpregs can be manufactured in-situ, with equipment available for speeds up to 100m/min, which is both cost effective and limits cold transportation and storage issues. Towpreg resin systems must offer low initial viscosity for fast impregnation, high storage stability at 23°C and the correct level of tack to enable bobbin unwinding and subsequent mandrel winding up to 5m/s without slippage. Curing can be via the classical oven process or by infrared exposure.

Prototypes have demonstrated that hydrogen vessels made with an ARALDITE® towpreg system can be cured as quickly as 30 minutes, while still providing the required toughness and hot/wet performance.

Faster, more robust processing

Achieving short cycle times while properly curing laminates up to 50 mm thick can be a real challenge. The exothermic curing reaction can lead to temperature overshoots, damaging thermoplastic liners and creating high internal stresses. The definition of cure cycles often requires a large number of experimental trials and may never be fully optimized.

Simulation provides a valuable tool to quickly assess the effects of changes to cure cycles, gaining insight into all areas of the simulated part. Providing that a detailed material data model is available, accurate predictions of exotherm temperature, degree of cure and Tg can be made. Figures 3 and 4 shows how simulation makes it possible to visualize the temperature evolution at any point during curing of the pressure vessel. Tg build-up and degree of cure can be visualized in a similar manner (Figure 5).

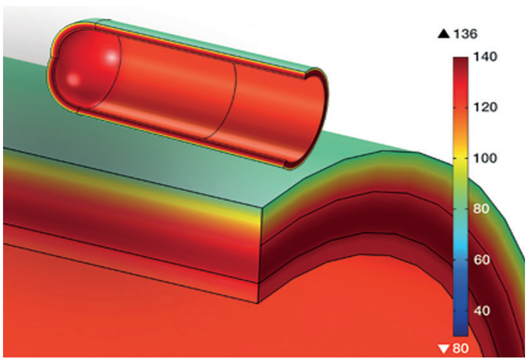

Fig. 3: Temperature prediction through thickness during curing

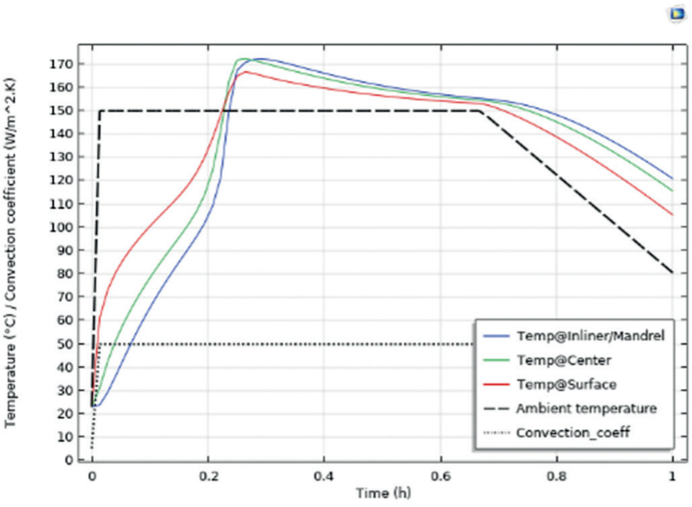

Fig. 4: Temperature prediction for a pressure vessel cured at 150°C

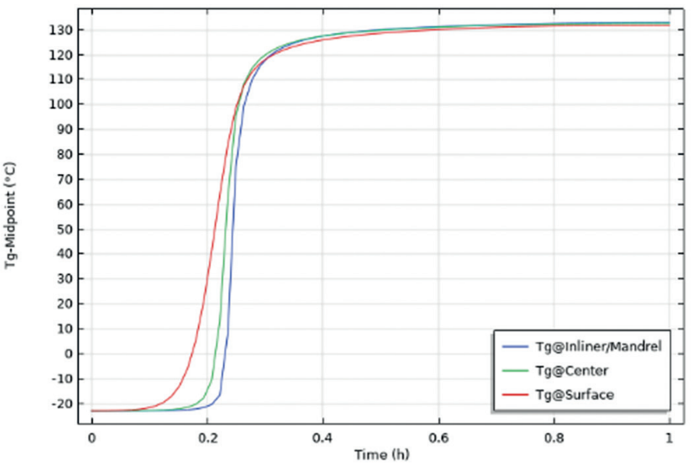

Fig. 5: Tg build-up prediction for a pressure vessel cured at 150°C

The company has developed in-house expertise not only in the complex material characterization needed to generate an accurate data model, but also in cure simulation of real customer parts, providing tailored guidance for process optimization.

An experienced partner

Building on strong experience in natural gas pressure vessel technology, Huntsman Advanced Materials can offer a comprehensive range of epoxy resin systems that address the emerging challenges and manufacturing requirements for hydrogen storage.

In addition, expertise in material characterization and process simulation offers a powerful tool to accelerate product development and optimize manufacturing, leading to increased part quality and minimum production cycle times.

Enabling energy transition while minimizing environmental impact

The solutions developed by Huntsman Advanced Materials empower customers to reach their targets, enable the rise of more sustainable technologies, and contribute to the development of a hydrogen-fueled economy. Creating innovative solutions is not the only way Huntsman is impacting the world for the better; the company also considers the environmental impact of its products and operations.

In addition to a continual effort to reduce energy consumption and waste generation at its manufacturing sites, for more than 10 years, Huntsman Advanced Materials has utilized bio-based feedstocks to manufacture several of its resins and hardeners. This has already had a positive impact, for instance, on their global warming potential (GWP: kg of CO_2 emitted to produce 1 kg of product). As part of its commitment to increase its efforts to further reduce its impact, Huntsman Advanced Materials has voluntarily committed to a certification process for its manufacturing sites and products. This certification, known as REDcert2, is based on the implementation of the Biomass Balance concept, which proposes that bio-feedstock can replace fossil raw materials at any step in the value chain and be digitally traced; at each transformation step, with an official certification body validating the sustainable character of the intermediates and the final product. Commercialization of the first REDcert2-certified products is expected early in 2023, with savings of up to 70% of CO_2 emissions.

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