Epoxy, the underestimated success factor in filament winding of type 4 pressure vessels


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Often underestimated but deeply interconnected, the properties and correct processing of the epoxy matrix in filament winding of composite pressure vessels are critical factors in driving fibre content optimisation, curing times and scrap rates.

When reviewing the pressure vessel certification tests prescribed by the applicable norms, many of the tests are significantly influenced by the properties and proper processing of the epoxy matrix used in the composite, as it represents 30 to 40% of the weight of the shell.

Epoxy: a key enabler of R134 compliance

Numerous tests are required for the certification of a hydrogen pressure vessel (see Table 1 next page), under Regulation R134 of the United Nations Economic Commission for Europe.
According to Olin's internal assessment, 16 of the 17 listed tests are heavily affected by the matrix behaviour, given the extreme focus that the norm addresses at dynamic loads (easily detectable analysing Figure 1: verification tests for performance durability prescribed by R134).

Epoxy and dynamic loads

While static parameters like burst pressure are mostly driven by the composite reinforcement, whenever the stress (mechanical or thermal) becomes cyclical, the matrix becomes a critical-to-success factor. As an example, Figure 2 shows the effect of 2 different epoxy systems on the retained burst pressure of a vessel after an impact at parity of other conditions. Within the tested conditions, an epoxy system toughened with Olin proprietary toughening technology has enabled a 24% increase in the retained burst pressure.

The root cause of this improvement is linked to the fracture behaviour of the composite when subject to an impact. The impact creates structural damage to the composite material. It results in a reduced burst pressure, in comparison to an undamaged pressure vessel. Toughening of the matrix has 2 effects: reducing the size of the impact damage, which results in a higher retention

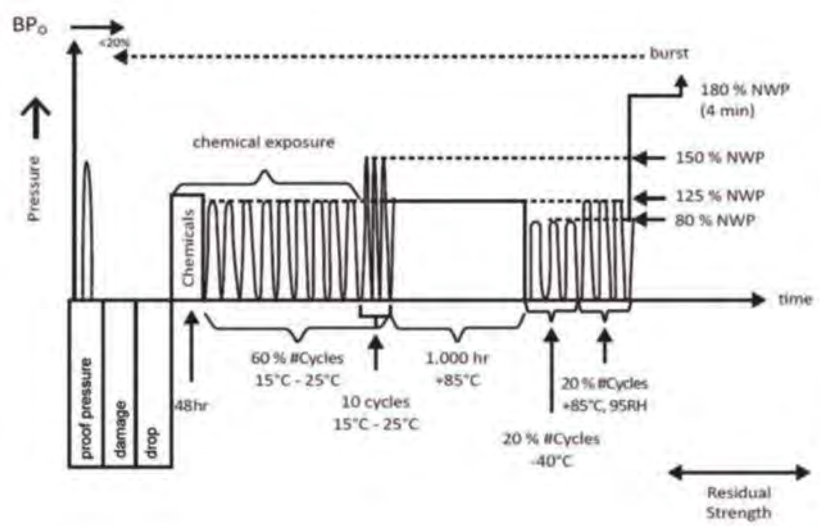

Fig. 1: Verification tests for performance durability prescribed by Regulation R134 of the United Nations Economic Commission for Europe

Tab. 1: Tests required for the certification of a hydrogen pressure vessel under Regulation R134 of the United Nations Economic Commission for Europe
5.1. Verification tests for baseline metrics
5.1.1. Baseline initial burst pressure
5.1.2. Baseline initial pressure cycle life L 129/48 EN Official Journal of the European Union 17.5.2019
5.2. Verification test for performance durability (sequential hydraulic tests)
5.2.1. Proof pressure test
5.2.2. Drop (impact) test
5.2.3. Surface damage
5.2.4. Chemical exposure and ambient temperature pressure cycling tests
5.2.5. High temperature static pressure test
5.2.6. Extreme temperature pressure cycling
5.2.7. Residual proof pressure test
5.2.8. Residual strength burst test
5.3. Verification test for expected on-road performance (sequential pneumatic tests)
5.3.1. Proof pressure test
5.3.2. Ambient and extreme temperature gas pressure cycling test (pneumatic)
5.3.3. Extreme temperature static gas pressure leak/permeation test (pneumatic)
5.3.4. Residual proof pressure test
5.3.5. Residual strength burst test (hydraulic)
5.4. Verification test for service terminating performance in fire
5.5. Requirements for primary closure devices

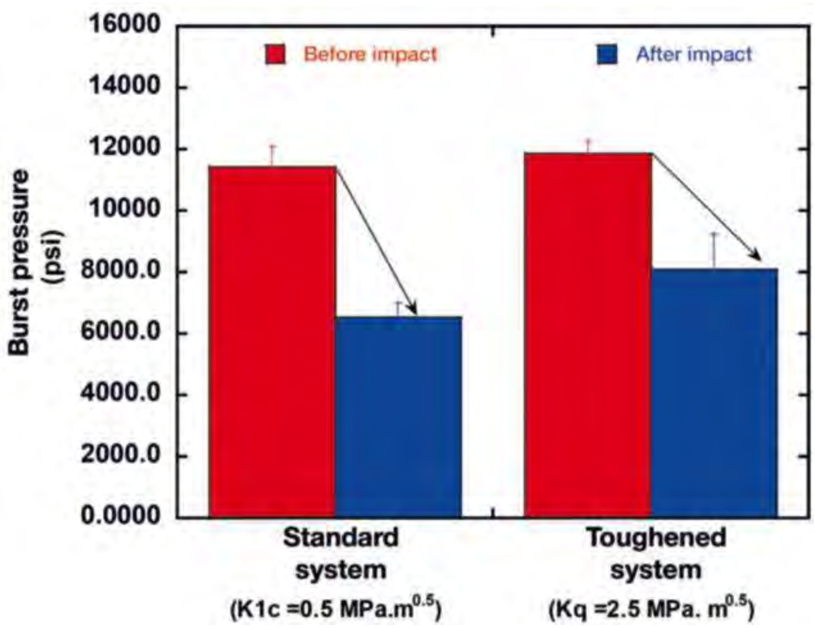

Fig. 2: Effect of 2 different epoxy systems on the retained burst pressure of a vessel after an impact – at parity of other conditions

of burst pressure, and reducing the propagation of the damage, which again has a positive impact on the residual burst pressure.

Another important aspect is how advanced toughening can inhibit crack propagation in a clear cast of epoxy resin subjected to thermal cycling (Figure 3) – 10 cycles from -20°C to 80°C.

These are just 2 tangible examples of how an optimally designed epoxy system can materially affect the dynamic performance of a composite pressure vessel.

Fibre optimisation potential

Considering the regulatory trend that sees safety factors shrinking, property retention after dynamic loads is gaining relevance in the dimensioning of the cylinder thickness and fibre content. The fibre optimisation potential of an advanced epoxy toughening solution is therefore getting more and more actual. Olin's LITESTONE® systems for filament winding incorporate advanced toughening technology with no compromise to viscosity, pot life, reactivity or thermal properties.

Cryogenic conditions

Composite pressure vessels may also need to withstand cryogenic conditions which also place severe residual stress on the epoxy matrix due to the mismatch in the coefficient of thermal expansion with the fibre reinforcement. A toughened epoxy system (Figure 4) may enable improved burst pressure even at cryogenic conditions, which could come into play as a potential solution for efficient hydrogen storage and delivery.

From paper to reality: correct processing

Mechanical properties listed on the Epoxy Resin Technical Datasheet, however, are not the only factor to consider. The complex process through which 2 liquid chemicals are transformed into the solid, fully cured matrix

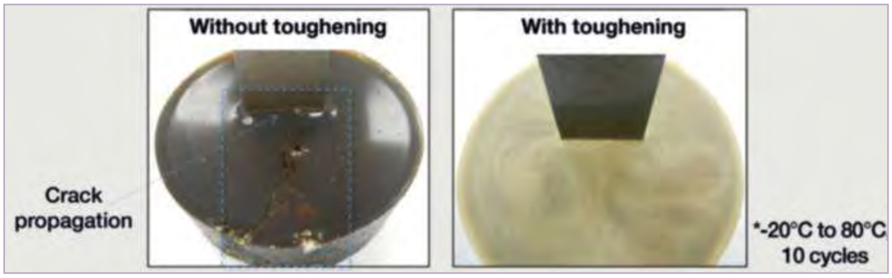

Fig. 3: Crack propagation in a clear cast of epoxy resin subjected to thermal cycling

of a thick composite element after being wound over a liner at high speed plays a pivotal role in transforming the numbers on a datasheet into reality.

In the next paragraph we will therefore analyse the filament winding process under a matrix perspective showing, from the processing angle, how critical the matrix role is to the ultimate performance of a pressure vessel.

In addition to the material properties themselves, the performance of the tank depends on good fibre wetting and well-defined positioning of the fibre tows. Furthermore, the production process must be robust enough to enable serial production under stable conditions.

Dissecting filament winding under matrix perspective

The filament winding process can be split into 5 main steps. Each process step has specific material requirements which, to some extent, are conflicting (Table 2).
The main conflictive resin requirement is the reactivity of the system. In the bath impregnation process, a long pot life and therewith low reactivity are required. In the following steps, higher reactivity is an advantage to control resin flow and minimise the overall production cycle. Also, exothermic behaviour must be considered as it is mainly limited by the liner temperature resistance. Thus, an optimised setup must be developed for every process configuration to balance requirements.

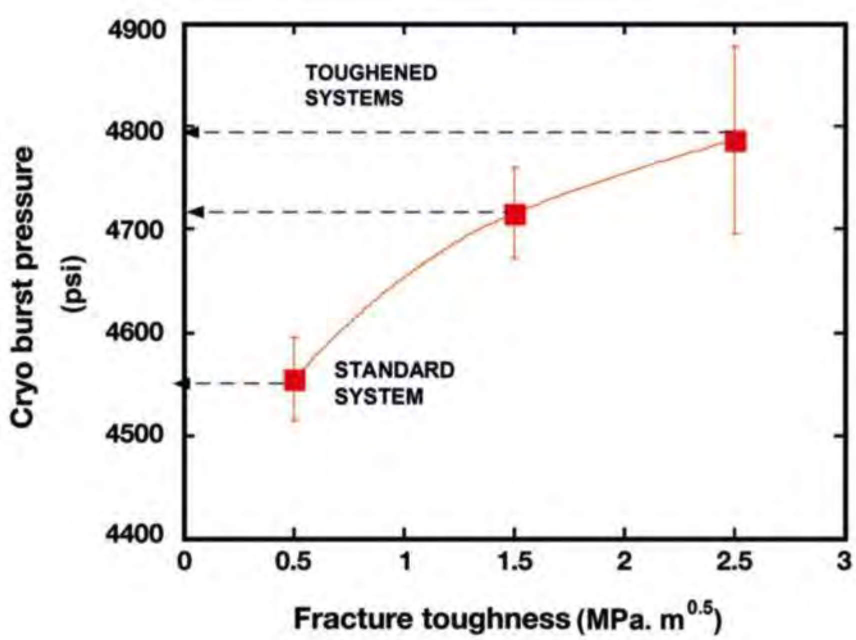

Fig. 4: Effect of toughening on the burst pressure of a Type 4 pressure vessel subject to cryogenic conditions

System viscosity development explained

The key resin parameter in the filament winding process is the viscosity development in the different steps. It is a function of start viscosity, reactivity and process temperatures (Figure 5). In the impregnation step, key parameters are:
- start viscosity;
- pot life.

For the impregnation, a low viscosity is helpful as fibre wetting is simplified. Additionally, due to the fibre movement through the bath – especially at high line speeds – air is entrapped. Low viscosity enables faster degassing and minimises foam creation.
For a stable process, the viscosity should be as consistent as possible to ensure a good wetting and reproducible resin flow in the following process steps.

During winding, however, a too low viscosity can result in resin dripping and unwanted fibre movement as a tack is not sufficient to fix roving. This has a negative impact on the performance of the tank. As the winding is done – usually at temperatures above 50°C – viscosity decreases at the beginning of the process and reaches at one point a minimum viscosity. By adjusting reactivity and process temperatures, this point can be affected to optimise the process. The minimum viscosity is an indicator to evaluate the resin flow behaviour during the winding.

In the initial cure phase, viscosity is built up until the gelation point to enable a free-standing post-curing. A high reactivity is helpful here to shorten this time and accelerate the process cycle. The final cure occurs in the post-curing step. To define an optimised cure temperature profile, the following parameters must be considered:
- the resin reactivity;
- the fibre heat conductivity;
- the maximum acceptable exothermic peak;
- the wall thickness.

Conclusion

Besides the process itself, the design of the tank has a significant impact on the resin requirements. With thicker walls, the cure kinetics are more important to manage the exothermic peak. Also, tack behaviour might be adjusted to minimise the movement of the fibre. Every process has its specific requirements, strongly depending on the design of the tank and the setup of the process. For this reason, an adapted system is required to optimise performance and processability.

Olin addresses this need by offering the LITESTONE 2000 series – a powerful toolbox designed to match different needs.

Olin's global technical service team is available to support customers in selecting the epoxy system matching the exact requirements of the specific application.

LITESTONE 2000 is part of the Olin epoxy LITESTONE systems portfolio for composites. The LITESTONE portfolio provides solutions for most epoxy composites applications (including filament winding of pressure vessels) at the quality, scale and supply reliability that only Olin can deliver. □

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Tab.2: List of the key processes and resulting resin requirements

Process step	Process requirement	Resin requirement
Fibre handling/ Guiding	• Optimised fibre guiding/ spreading to enable good wetting and maximise performance	• No specific requirements
Fibre impregnation	• Provide excellent and flawless fibre wetting • Avoid air entrapment • Provide stable processing over a long time	• Low viscosity • Long pot life/Low reactivity
Winding	• Sufficient tack to ensure good fibre placement • No resin dripping • Avoid air entrapments • Avoid high exotherm to protect liner material	• Medium to high viscosity to control resin flow • Controlled exothermic reaction to avoid temperature peaks
Gelation/Initial cure	• Fast viscosity built up/ vitrification • No resin dripping • Avoid high exotherm to protect liner material	• High reactivity at initial cure condition • Controlled exothermic reaction to avoid temperature peaks
Post-curing	• Fast T_g-build/High degree of cure • Avoid high exotherm to protect liner material • Maximum Temperature	• High reactivity to post-curing condition • Controlled exothermic reaction to avoid temperature peaks

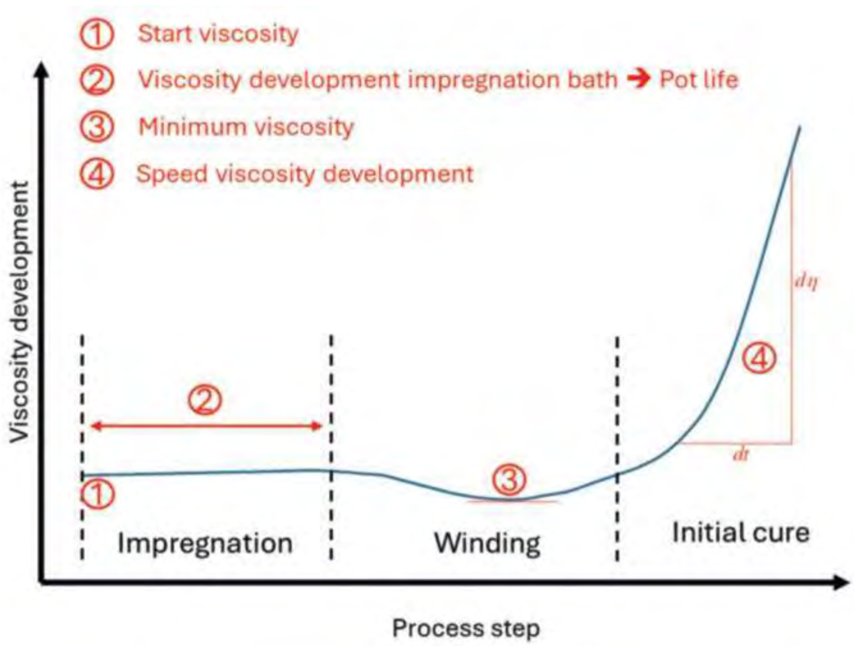

Fig. 5: The viscosity development in the process and the key resin characteristics impacting processability and part quality