TENCATE EXPERIENCE & APPLICATION GUIDANCE FOR OUT-OF-AUTOCLAVE COMPOSITE PREPREGS

Author: Barry Meyers, VP Technology, Edited by Michael Cichon Director of Marketing

TenCate Advanced Composites USA, Inc.

I. Introduction:

TenCate Advanced Composites USA (TCAC) has a long and extensive history of providing composite prepreg products for aerospace applications using “out-of-autoclave” (OOA) or “vacuum bag pressure” only (VBO) processing dating back to the origin of the company (1990 Bryte Technologies). TCAC is the prepreg supplier with perhaps the most volume of composite materials currently fielded on general aviation aircraft, satellites and unmanned aerial vehicles (UAVs). TenCate currently supplies out of autoclave prepregs to:

- Cirrus Aircraft for their line of general aviation aircraft,
- General Atomics for use on unmanned aerial systems
- Kestrel and Icon for general aviation & sport aircraft
- SpaceX for launch structures,
- Lockheed Martin for use on the Orion heat shield, and on a variety of satellite and radome applications.

The highly popular Cirrus SR-22 series of aircraft features both fuselage and wing structure manufactured in out of autoclave vacuum cure pressure conditions.

General Atomics Aeronautical Systems utilizes prepregs from TenCate in low pressure curing processes for Reaper and Predator programs.

TenCate Advanced Composites provides epoxy-based resin systems, and cyanate ester-based resin systems used for OOA and VBO cure processing. TenCate features systems that cure at under 250°F/121°C, as well as others that cure at higher temperatures for greater hot/wet service capabilities. Sometimes lower cure temperatures are valued because it allows the use of lower cost tooling, but lower cure temperatures also minimize thermal stresses which are important on dimensionally stable structure.

In addition to a variety of resins, TenCate has worked with OOA resin systems on a variety of standard, intermediate and high modulus fibers and fabrics, including pitch-based materials. In addition, TenCate has flight experience with glass and quartz based materials for aircraft structures and radomes with out of autoclave resin systems.

In the last several years, there has been a great deal of technical presentations and papers describing OOA composites and the use of vacuum bag only pressure for part processing. Many of these papers describe the processing conditions and resin databases created which rival traditional autoclave cure processes. In addition, a fair amount of technical study has been undertaken by large OEM's and government entities to validate the performance of these resin systems in a variety of configurations.

Lockheed Martin Denver Orion Heat Shield utilizes TenCate prepregs in a low pressure out of autoclave cure process.

II. TenCate History & Background

TenCate Advanced Composites has throughout its history produced hot melt impregnated composite prepregs for applications under either vacuum bag or autoclave cure processing. The part quality rivals that of the same resins cured in autoclave when applied to the right configuration of parts with appropriate process engineering and production workmanship. Although many technical papers emphasize that the layup methods and techniques are similar to lay ups and part processing for autoclaves, OOA processing requires inherently more process control and greater manufacturing controls over layup, debulking, cure and inspection to ensure good part quality with low void contents.

Additionally depending upon the structure's size, thickness, heat up rate and layup configuration, simple laminate fabrication process may not, and often do not scale directly to large thick and complicated structure. Further, on critical load carrying structure one must be able to reliably inspect the part.

Ultimately, the customer must determine the overall cost benefit of the overall process engineering and technical production resources to make quality parts that rival autoclave grade. Some users decide to use pressures above and beyond vacuum bag on critical strength parts like landing gear; spars and structural beams to mitigate the added cost and time from inspection, and multiple debulk cycles. However, there are many large parts where the cost of an autoclave makes vacuum bag processing the preferable and sometimes the best option. One example of such structure is the Orion heat shield, a 21 foot (6.4 meter) diameter structure manufactured by Lockheed Martin - Denver.

III. Processing

Most critical in large and thick structure are precise process controls and NDI inspection methodologies to assure that the structural part has the quality and long term durability of a part cured under high pressure in an autoclave. By its nature, an autoclave provides the pressure and temperature control which allows for production of lower void content parts without some of the necessary challenges found in non-autoclave vacuum pressure cure only parts. Debulk schedules, air path methods, breather types; layup materials and resin rheology, time and temperature and ramp rates require consideration when fabricating thick structural load carrying parts.

I. Prepreg Technology: The key to effective OOA parts production is to prevent and eliminate voids, principally in the form of air within the plies and between plies from the parts prior to resin gelation. Resin rheology characteristics are critical in developing a prepreg system that will be optimal for low pressure cure with the minimum of voids. Hot melt systems inherently are favored (vs. solvent systems) as they minimize volatiles and outgassing in the prepreg. Additionally, resins that have a cure mechanism that is inhibited to allow for a longer time before final cure better allow an air path for evacuation of intra and inter ply air and volatiles. Also, it is important that the prepreg resin does not cold flow as this may also close air paths during the layup and debulking process. TenCate has over twenty years of in developing proprietary prepreg resins and technologies to produce OOA materials that perform at the highest levels.

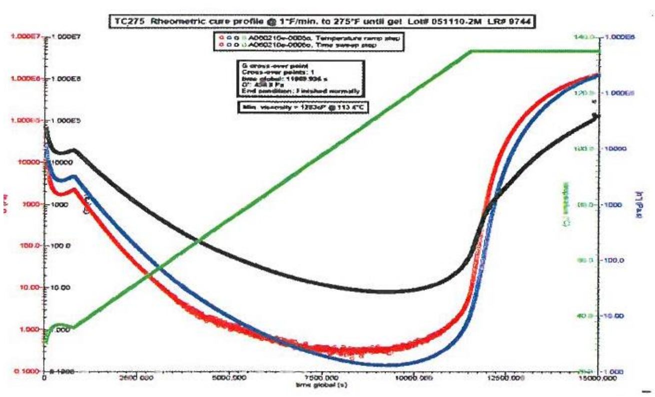


Figure 3.1 Dynamic curve of TC275

An example of an optimal viscosity profile which shows a gradual decrease in viscosity of the resin which then stabilizes during the temperature at cure before beginning to increase during final cure.

II. Debulk Schedules – As a general rule, debulk schedules are necessary for low void content structure. One of the lessons learned in out of autoclave processing is that the resin system must be adapted for debulks. Resin rheology must allow for debulks to consolidate plies without trapping air through resin flow. One might expect that hot debulks would result in the optimal de-bulk process, but hot debulks May close off some of the necessary air paths required during final cure. Ultimately, it is up to the prepreg supplier and the user to decide optimum debulk schedules, and to also determine if it is beneficial to integrate fabric prepreg plies with unitape layups or to insert some thin dry glass plies to aid in air evacuation.

III. Layup Considerations – Composite layups between autoclave and out of autoclave parts share may common features however with out of autoclave low cure pressures, it is critical that all tools be used to improve the ability to consolidate the plies and remove entrapped air. This is done through the use of dry roving's, light weight glass scrims, utilizing good vacuum pumps, having systematic vacuum port locations and minimizing areas where resins can block off air paths. Careful consideration to these techniques becomes more critical as the part size and thickness of the part increases.

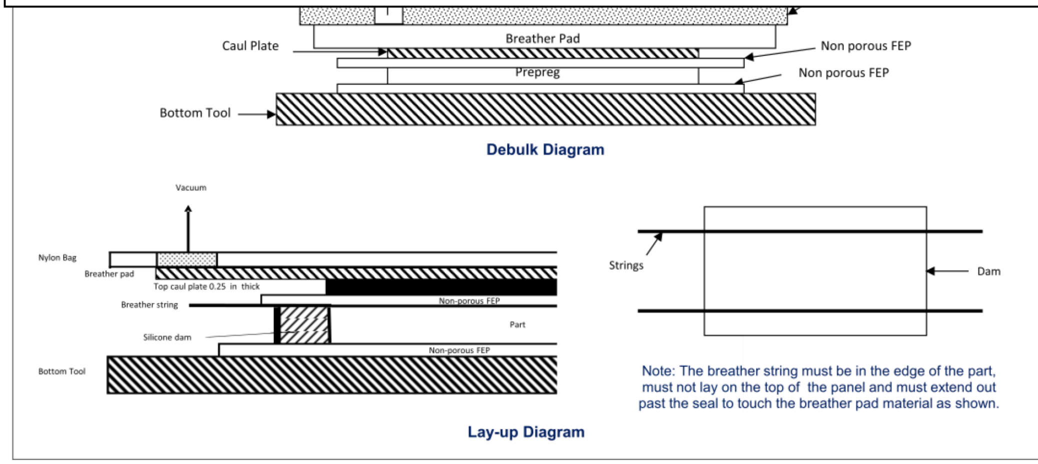
IV. Alternative Pressure Intensifiers – Thick complex parts carrying structural loads sometimes benefit from using secondary positive sources of pressure. While it is not the topic of this white paper, a variety of effective methods have been used for many years. These secondary methods utilize pressure intensifiers such as bladders, caul plates, solid closed mold tooling, shrink, hydrostatic pressure, closed mold processing, fluid pressure (i.e. SQRTM from Radius), double bag techniques to use vacuum for positive pressures etc.

V. Secondary Materials – Bonding films, peel plies, surfacing films and syntactics aid the manufacture of low void content parts if they are designed to function under both low pressure and under vacuum conditions. Please note the difference between low positive pressures vs. vacuum pressure. One observation is that very high molecular materials commonly used in highly toughened film adhesives sometimes exhibit cure porosity under vacuum conditions because of micro-entrapped air that is liberated during vacuum processing.

Also as a general rule, the more time a resin or adhesive can remain at a stable low viscosity the better the process ability of the system in removing volatiles and entrapped air. If one utilizes an adhesive or secondary material that cures or polymerizes during this long cure window, then it can inadvertently cut off a viable and necessary air path for the composite layers.

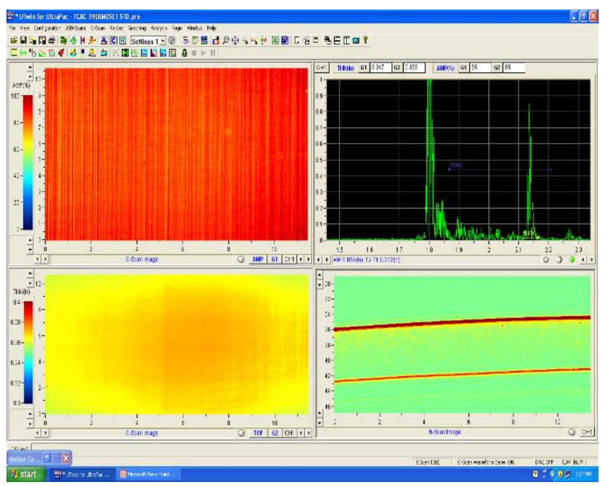
VI. Other Considerations – Honeycomb and foam structure should be dried before cure and if stored in a desiccated environment to minimize volatiles. Ply drop offs are areas where focus should be given for both inspection and air paths. Repair methods for voids found in thick parts should be documented and followed.

A common lay up example used in the lay up of out of autoclave cured laminates.



VII. Prepreg Selection:

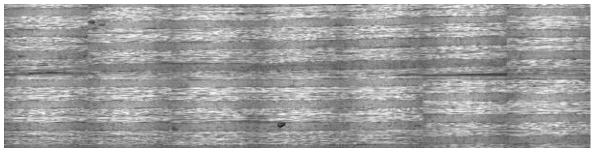
The selection of traditional autoclave cured materials in a particular part application is dictated by the critical permissible level of voids and the strength knockdown associated with that void level as well as the inspection expectations, part geometry (thickness and edge:area ratio), cost and part yield anticipated. Today, out of autoclave processing and prepreg system designed for low pressure processing offer the user the ability to compete with autoclaved cured systems.



Typical NDI results showing low porosity and good backwall, confirmed with cross section microscopy.

In general, curing in an autoclave under positive pressure is a better engineering solution for large thick composite parts production in load critical applications. Autoclave curing yields high quality and more consistent part quality because the increased cure pressure (>30 psi vs. the ~14.7 psi (1 atm)) collapses any air and volatiles within and between plies. Autoclave cured parts have traditionally had better matrix fiber interfacial properties, are more dense, have had fewer voids, and therefore are stronger, stiffer, and more inspectable by non-destructive techniques (NDI, C-scan). However, when a part size, cost constraints, or a process truly necessitates not using an autoclave, there are still an array of techniques a user can rely upon in out of autoclave processing by adding localized pressure through bladders, expanding plugs, mechanical means, resin injection, shrink wrap, double bag techniques. Viable matched mold hard tooling techniques also exists to provide process latitude to fabricate low void parts for thick primary load carrying structure.

TenCate has found the most success with customers when working together during prepreg selection or before qualification by optimizing the resin, impregnation level and lay up methods and techniques. This is done to ensure the best possible process and material for to yield parts that compare to autoclave cured parts.



VIII. Composite Laminate Fabrication:

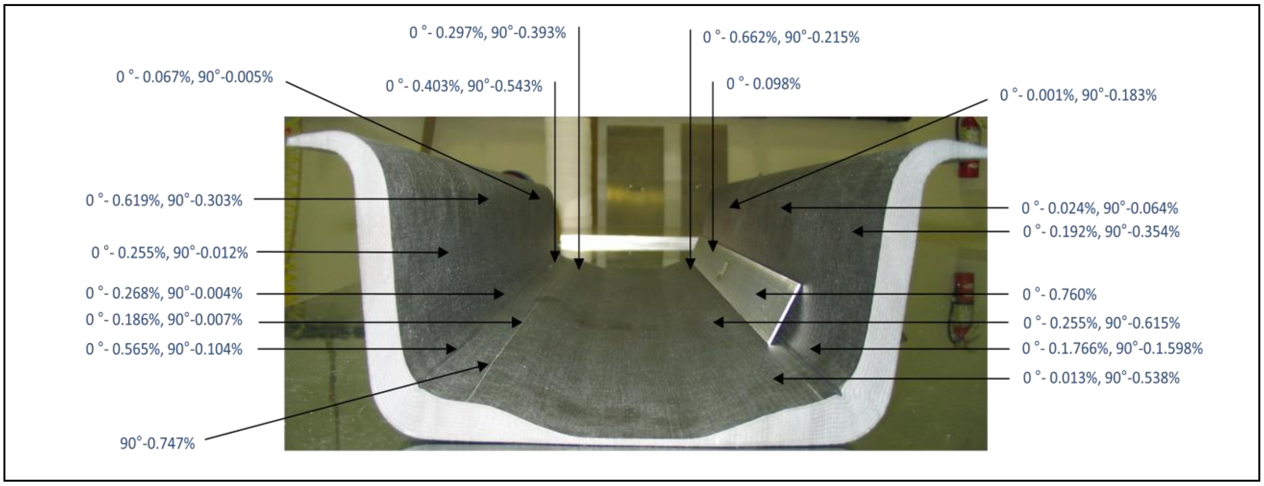
Craftsmanship in OOA part layup is critical because the added pressure that an autoclave imparts is not available, and therefore air and volatile release follows a slower more complex path through fibers, semi impregnated fabrics and breathers. Users of prepregs typically allow for specific debulk schedules (both time and number of plies) and rely on slow ramp rate/slow gel times to give the part time to allow air/volatiles to be liberated under these low pressure environments. Cold flow and hot debulks which remove ply to ply air may actually impede final part void contents in that remaining cure volatiles or air is trapped because all available air paths have been filled by resin.

Demonstration parts fabricated both in autoclave and out of autoclave to confirm processing equivalency.

In autoclave part fabrication, the care that a technician takes during ply lay down may be less critical than when using an OOA process. Some of the ongoing efforts in out of autoclave processing involve looking at ATL and AFP methods to ensure high quality layer to layer part build up to minimize gross air entrapment between plies. In OOA processing, it is important that in the lay down of each ply, that each layer must be smoothed to prevent and eliminate inter-ply air entrapment. In addition, frequent and sometimes lengthy vacuum debulk compaction is often required to reduce the risk of voids in a large part. Autoclave cured parts are likely to require less labor skill and time than OOA cured parts. OOA cured parts are therefore more likely to fail void content, NDI, quality and structural criteria than autoclave cured parts due to lay-up complexity and increased need for technician skill. Autoclaves, however, are expensive when compared to the required equipment for OOA processing, a vacuum and heat source. OOA tooling is also much less expensive since it is not required to withstand the additional forces of the positive cure pressure in the autoclave. The use of lower temperature tooling materials may also help reduce costs and depending upon the service temperature of the structure. Prepregs may be selected which either are fully cured at temperatures of 121°C or lower or utilize a free standing post cure. Free standing post cure capable prepregs may allow greater efficiency and life span of production rate tooling by allowing the final higher temperature oven cure for Tg purposes to be without the tool. These are the reasons that many TCAC customers originally and have continued to use OOA prepregs for parts production.

<u>IX.</u> <u>Part Quality Inspection</u>:

When comparing part quality between autoclave cured parts and OOA, the primary focus is on voids and delamination’s. These can be inspected by destructive techniques of the part or a



TenCate’s TC350-1 90+ ply carbon fiber spar (0.8 inches/2 cm) section illustrating a good example of how to conducting measurement of void content throughout the part to correlate with NDI inspection results.

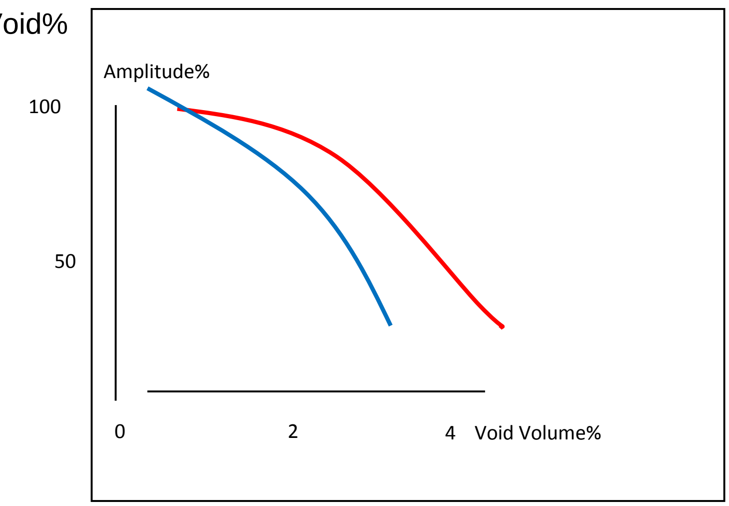
witness panel by microscopic cross sectioning and matrix acid digestion. Non-destructive inspection (NDI) may include ultrasonic C-scan, acoustic emission, thermography and other methods. TCAC has extensive experience in the sensitivities of parts inspection using C-scan techniques. OOA part inspectability has presented a myriad of challenges to the incorporation of OOA production at some customers. Not all parts or OOA materials requiring NDI are easily amenable to OOA fabrication and cure.

In addition to the type of C-scan technique used to inspect a part, such as pulse-echo (P/R) or through transmission (TTU), the sound frequency and equipment can influence which OOA parts are deemed by a customer as inspectable or not inspectable. The most common part void content criteria applied by customer part specifications is a void volume of <2% for both autoclave and OOA cured parts. Factors that contribute to the inspection challenge are the molecular chain lengths of the OOA resins, the tougheners added to the resins to enhance certain properties (CAI, $G^{1}c$, $G^{2}c$, etc.), the part thickness, part surface quality (bag side) and customer inspection method limitations.

Long chain molecules and tougheners which absorb and arrest crack growth energy may also absorb sound energy passed through the part during C-scanning. Even certain fibers and weave styles may influence the sonic energy propagation (crystallinity, geometry). These sound absorbers, like voids, decrease the sound energy amplitude that passes or reflects back through the part which is critical to this inspection technique. The thicker the part, more irregular the fabric or bag side texture (acting like a sound diffuser) the more difficult it may become to distinguish a good from a bad part. The pulse echo (P/R) C-scan mode of inspection is more sensitive to this signal loss than through transmission technique (TTU) because the sound must travel twice the distance, reflecting off the back wall prior to returning to the sensor. The loss of sensor amplitude or back wall may render the part uninspectable because the inspector cannot discern if the amplitude loss is due to a void, a delamination or an inclusion.

Figure 1 illustrates typical the effect of thickness on amplitude (baseline 80%) for autoclave and OOA laminates, while Figure 2 shows the relative effect of void volume. TenCate has found with toughened resins that laminates with void contents between 0.7 and 2% can result in returned signal amplitude loss of 50%. More loss occurs with greater laminate thickness, laminates > 0.25 inch may lose back wall signal if a suitable OOA material is not being used.

Figure 1 Typical C-scan Amplitude vs. Void%



Pulse echo inspection is popular with part producers. It can be performed on the parts on the line or in the field, is reasonably inexpensive, can be done manually and with wide phased area inspection probes can be done rapidly. Typically, the frequency of 5 MHz is used which is capable of distinguishing defects at a size of around 0.1 inch. By decreasing the frequency used (i.e. 1 to 2.5 MHz) more power can be passed through the part improving the back wall at the sacrifice of defect size resolution. The power or gain may also be increased which results in more inter-ply interface noise that makes C-scan quality interpretation more difficult in the absence of an inspection standard part. An inspection standard is a part made of the same cured prepreg materials and lay-up sequence with known defect inclusions, known void content (either ~0% or closer to the threshold), similar surface texture and representative thicknesses that is used to form the basis of the inspectors judgment of part quality. If the C-scan frequency is changed or amplitude increased to get a solid back wall signal, the inspector can compare the image to the standard to determine if the internal indications are normal or actual defects.

TTU inspection allows more sound energy to pass through the part due to the single direction of travel of the energy from the sender to the receiver on the other side of the part. The challenge of TTU inspection is that it typically requires a water tank or squirter system as the sound coupling agent and the sender/sensor must remain normal to the surface of the part to yield a good signal. This requirement in turn decreases the inspection speed, while driving the complexity and cost of TTU inspection up. Robotic multi-axis TTU probe end effectors and part geometry following computer controls must be set-up for each part. The TTU inspection at 5 MHz is, however, the defacto standard of inspection used by CHM-17 and NCAMP programs for grading the flat laminates used during materials qualification. And sometimes a good low void flat laminate inspected by TTU may not yield a C-scan inspectable part of similar thickness in a complex shape.

Lockheed Martin's Orion Heat Shield is 21 feet in diameter solid laminate structure, made with TenCate TC420 out of autoclave system. This new composite design replaced a titanium heat shield. NDI inspection was done via thermography.

Lockheed Martin has made one of the largest ever made space re-entry heat shields using TenCate's prepreg resin systems cured OOA, and uses thermography as the principal part quality assessment.

Additional Comments

NCAMP (NASA AGATE) – Over the past 5-10 years, FAA conformed databases have provided users with an initial design allowable database. One benefit of having such a database is the more equitable comparison between prepreg systems under consistent hot/wet conditioning. Also, having the initial database allows a new user to bridge their process with the three batch data developed under the NCAMP protocols. However, as always there is a trade off in that the prepreg resin once qualified to an NCAMP protocol may not be adjusted for a user's needs and must be adapted from the same qualified material. This may limit tailoring of a resin system for a specific program or application. Also, an NCAMP database is typically the first material characterization step, and many other more specific properties may need to be generated with certain types of fasteners, joints and special load conditions like cyclic fatigue.

Next Steps

While not part of this white paper, the next evaluations of out of autoclave cure processing involve looking at automation for ATL and AFP processes to insure that these automated lay down process yield low void content parts.

RESOURCES –

- *Non Autoclave (Prepreg) Manufacturing Technology for Primary Aerospace Structures*, Gail Hahn and Gary Bond, SAMPE Journal, Volume 47, No 1, Jan/Feb 2011.
- *Non-Autoclave Prepreg Manufacturing Technology for Primary Aerospace Structure,* Gail Hahn and Gary Bond. 42nd annual ISTC Salt Lake City UT October 2010
- *Advanced Composite Cargo Aircraft*, John D. Russell, Barth Shenk, Mike Swanson, Peter Neumeier, High Performance Composites Magazine, January 2010
- *Advanced Composite Cargo Aircraft,* J.*D. Russell, B. Shenk, and R. Holzwarth, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH; M. Swanson, D. Paige, M. Tresnak, and S. Ames, Lockheed Martin Aeronautics Company, Palmdale, CA; P. Neumeier, Lockheed Martin Aeronautics Company, Marietta, GA 2009 Fall Technical SAMPE.*
- *Designing with Composites: Suggested "Best Practice" Rules*, Dr. Scott Beckwith, SAMPE Journal, Volume 45, No. 1, Jan/Feb 2009.
- *Air Removal in VBO Prepreg Laminates: Effects of Breathe-Out Distance and Direction*, Lessa Grunenfelder, Steven Nutt, SAMPE Paper 43rd ISTC - Ft. Worth, TX - October 17-20, 2011
- *Advancement of Out of Autoclave Technology* at TenCate Advanced Composites USA, Frank Lee, Henry Villareal, Scott Unger. Baltimore Spring SAMPE, May 2012
- "*Part Quality Inspection*" section from Barry Meyers, VP of Technology, TenCate Advanced Composites.
- *Out of Autoclave prepregs: Hype or revolution?* Ginger Gardiner, January 2011 High Performance Composites.

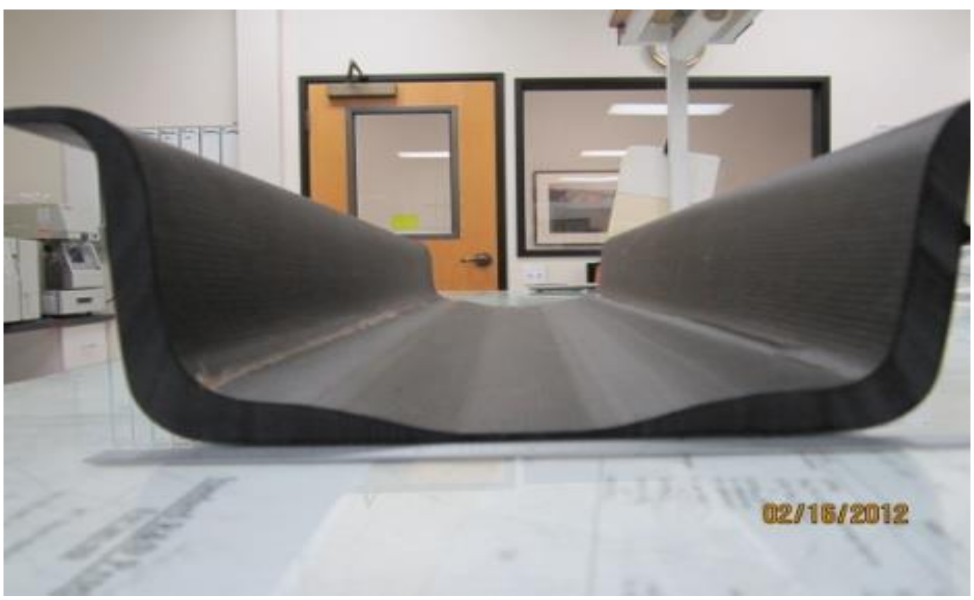


Table 1: Tencate Out of Autoclave Applied Resin Systems

BT250E-1- Industry standard out of autoclave prepreg resin used on over 5,000 Cirrus aircraft and hundreds of large scale unmanned vehicle systems.

BT250E-6 – Developed for high fatigue and fracture critical structure like helicopter rotor blades.

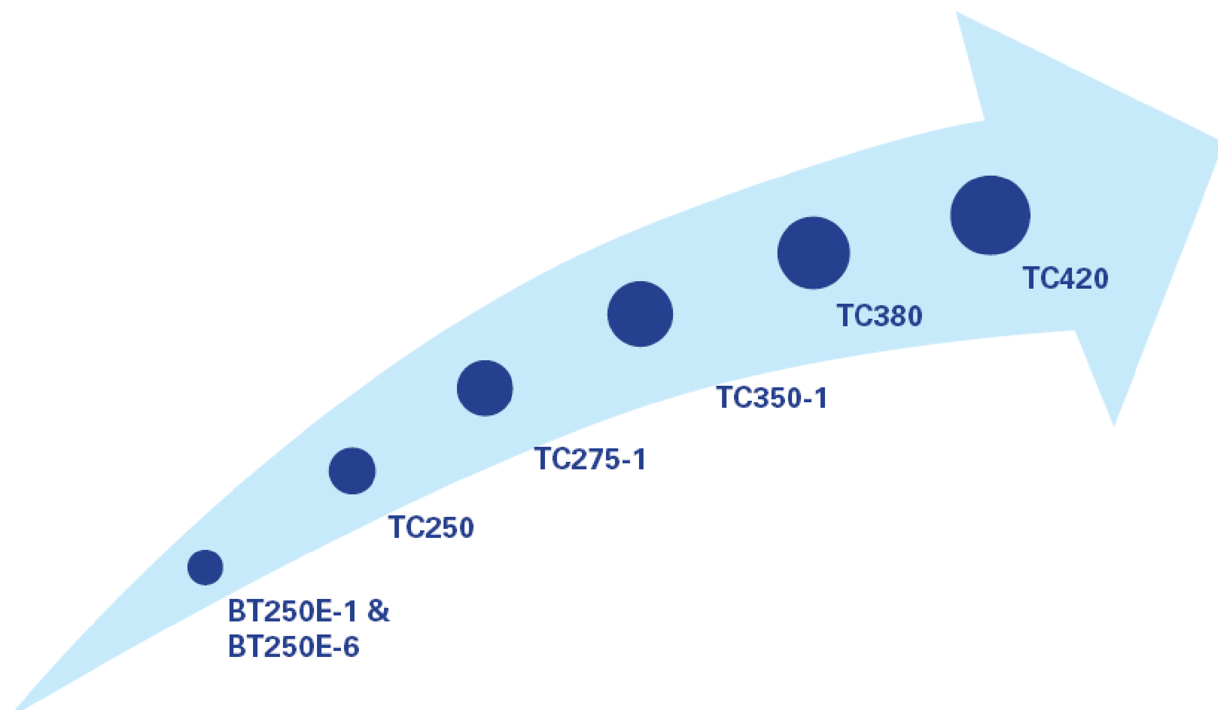
TC250 – Second generation improved toughness and higher temperature performance system.

TC275-1 - Third generation system with high degrees of inspectability, ability to cure at 135°C (275°F) and excellent resistance in hot/wet conditioning. TC275-1 features a longer outtime over TC275.

TC350-1 – High toughness third generation system with 45+ days outtime and capable of curing at 135°C (275°F) with a required 177°C (350°F) postcure.

TC380 – TenCate's toughness epoxy prepreg system with high CAI. OHC strength and 28 day outlife.

TC420 – Developed for high temperature applications with an operating temperature of up to 316°C (600°F).



TenCate's Progression of Out-of-Autoclave Prepreg/VBO Systems