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SEPTEMBER 21-24
2020
A VIRTUAL EXPERIENCE

Research Tutorial on Thermoplastic Composite Technology

Dr. Robert G. Bryant
Senior Materials Engineer
NASA Langley Research Center

Composites because "It Is About the Matrix Resin"

In-Service Thermoset Composite Parts

Aircraft Component	Total Components		Start of Flight Service	Cumulative Flight Hours	
				High Time Aircraft	Total Component
L-1011 Fairing Panels	18	(15)	January 1973	52,610	742,430
737 Spoiler	108	(33)	July 1973	45,260	2,747,760
C-130 Center Wing Box	2	(2)	October 1974	10,920	21,520
DC-10 Aft Pylon Skin	3	(2)	August 1975	45,640	107,840
DC-10 Upper Aft Rudder	15	(10)	April 1975	58,340	519,430
727 Elevator	10	(8)	March 1980	40,930	336,610
L-1011 Aileron	8	(8)	March 1982	31,720	249,480
737 Horizonal Stabilizer	10	(8)	March 1984	19,620	189,800
DC-10 Vertical Stabilizer	1	(1)	January 1987	17,580	17,580
S-76 Tail Rotor and Horizontal Stabilizer	14	(0)	February 1979	5,860	53,150
206L Fairing, Doors, and Vertical Fin	160	(51)	March 1981	11,325	440,000
CH-53 Cargo Ramp Skin	1	(1)	May 1981	5,000	5,000
Grand Total	350	(139)			5,377,650

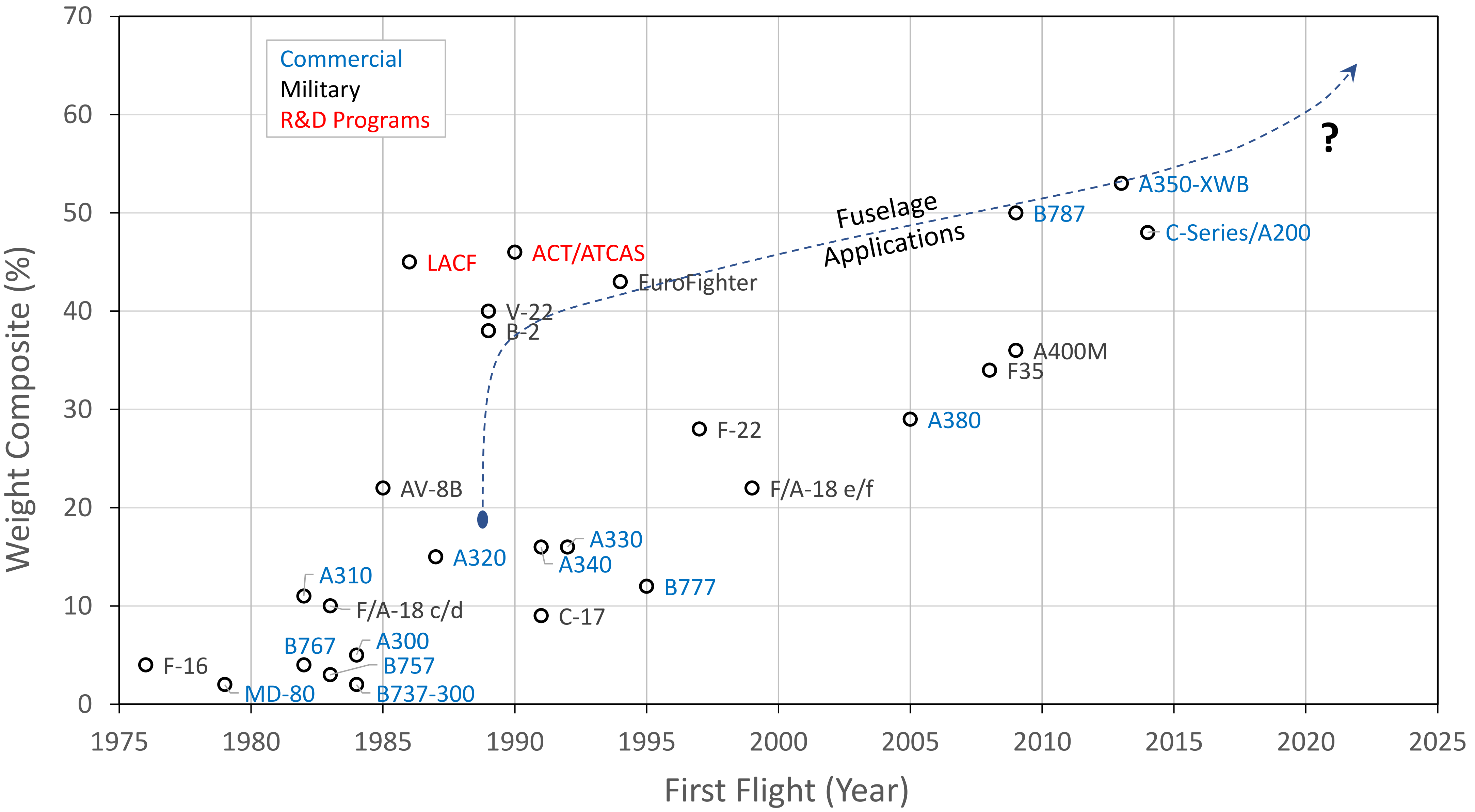
() = Still in service as of June 1991.

Improved Toughened Epoxies coupled with corrosion resistance demonstrated that composite parts were more durable and had increased service life than metallic counterparts.

H. B. Dexter and D. J. Baker, "Flight Service Environmental Effects on Composite Materials and Structures", Advanced Performance Materials, 1(1), (1994) pp 51-85.

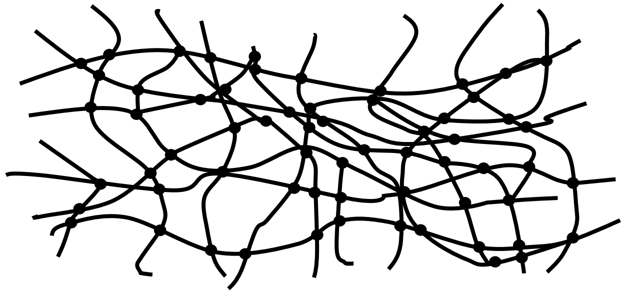
D. R. Tenney, J. G. Davis, Jr, R. B. Pipes, and N. Johnston, "NASA Composite Materials Development: Lessons Learned and Future Challenges", NATO Research and Technology Agency (RTA), AVT-164, Fall 2009.

Carbon Fiber Composites Usage on Commercial and Military Aircraft

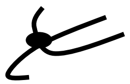


Thermoset
Thermoplastic

Macrostructure Overview

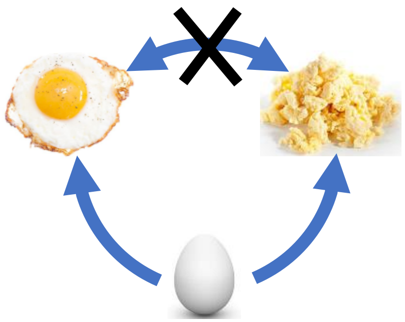


Thermosets

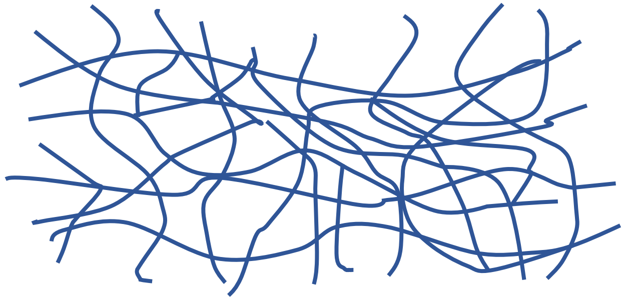


Chemical Crosslink

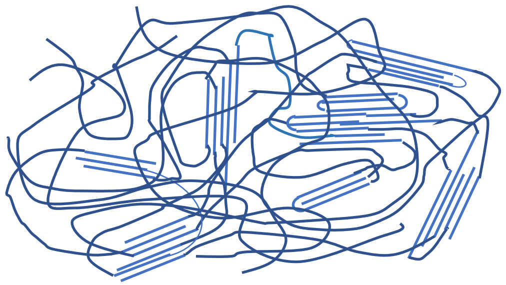
A polymer chain is chemically connected by at least two points to other polymer chains.



Thermoplastics



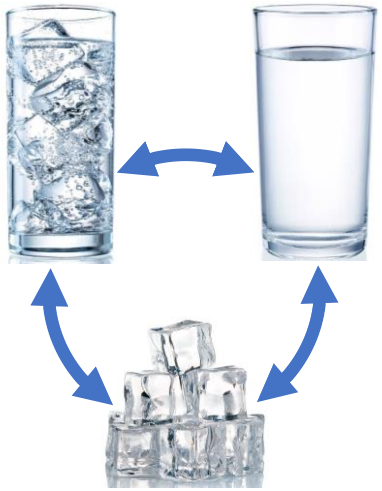
Amorphous

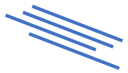


Semicrystalline

Entanglement

Minimal entanglement for bulk physical properties per chain is between "3 and 4 points average."





*3-D Crystalline Regions

A semicrystalline polymer has amorphous and crystalline regions; the latter serve as physical crosslinks

*2-D and 1-D crystalline mesophases are classed as liquid crystalline and referred to as nematic and smectic.

Courtesy of Stock Photo.com Royalty Free Images.

Aerospace Thermoset versus Thermoplastic : SOA

Relative Properties	Thermoset	Thermoplastic
Viscosity (slightly above RT)	Low	High
Toughness	*Moderate	High
Chemical Resistance	High	Moderate/**High
Shelf life	Low/Moderate	Infinite
Reusability (Thermoformable)	Low	High

*Thermoplastic additives.

**Semicrystalline resins.

Thermosets:

Advantages are:

- Initial low viscosity allows for low pressure consolidation prior to cure set.
- Crosslinking provides resistance to environmental intrusion.
- Legacy

Disadvantages are:

- Storage requirements.
- Cure parameters.
- Cannot be melt processed.
- Cannot be used near or above Tg.

Thermoplastics:

Advantages are:

- Increased toughness over thermosets, with added durability.
- Reusability and shelf life reduce scrap.
- Melt processing is inherently bonding.
- Can be used near or slightly above Tg.**

Disadvantages are:

- Percent crystallinity and creep resistance may change during processing.
- High viscosity limits resin injection processing methods.
- Currently higher cost than thermosets

N.H. Nash, T.M. Young, P.T.McGrail, W.F. Stanley, "Inclusion of a thermoplastic phase to improve impact and post-impact performances of carbon fibre reinforced thermosetting composites – A review", Materials and Design, 85(15), (2015) pp 582-597.

Commercial Thermoplastics : Resins and Preforms

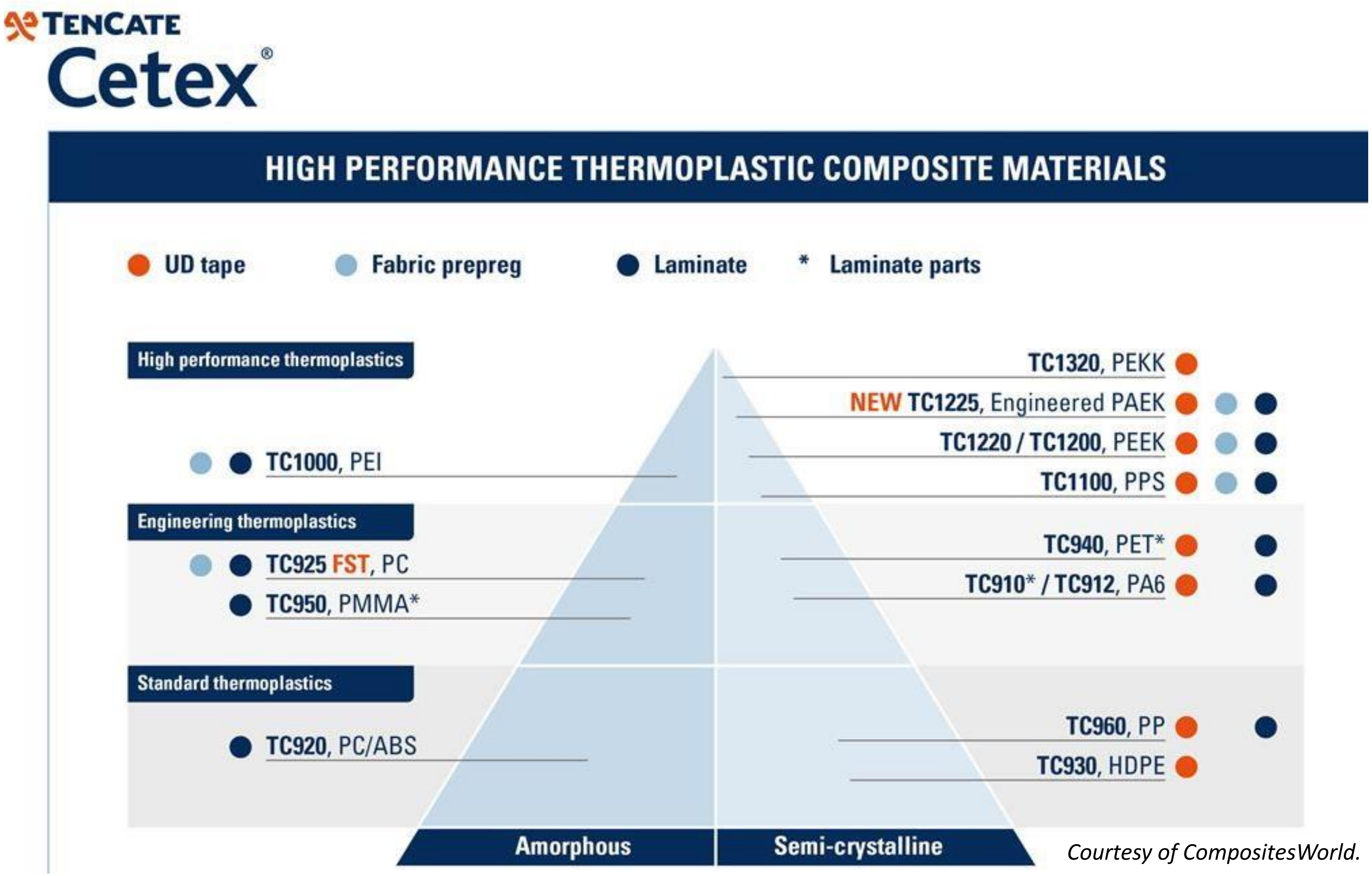
Thermoplastic Resins and Generalized Properties			
Amorphous		Semicrystalline	
Performance	Polymer Class	Polymer Class	Performance
Advanced Engineering Plastics			
Steam Resistant Thermoformable Transparent/translucent	PBI, PEI, PSU	PI, PAI, PEEK* PEKK*, PAEK* PPS, PTFE	High Temperature Good Chemical Resistance Good wear resistance
Engineering Plastics			
General purpose Thermoformable Bondable	PC, Acrylic	Nylon (PA) Acetal (POM) PET, PBT	Good Chemical Resistance General Mechanical Parts
Standard Plastics			
Non-critical applications	ABS, PVC, HiPS	HDPE, PP	Non-critical applications

PBI = Polybenzimidazole
PEI = Polyetherimide
PSU = Polysulfone
PI = Polyimide
PAI = Polyamide-imide
PEEK = Polyether-ether-ketone
PEKK = Polyether-ketone-ketone
PAEK = Polyarylether Ketone
PPS = Polyphenylene sulfide
PTFE = Polytetrafluoroethylene

PC = Polycarbonate
Acrylic = vinyl-type polymers.
PA = Polyamide
POM = Polyoxymethylene
PET = Polyethylene terephthalate (polyester)
PBT = Polybutylene terephthalate (polyester)

PP = Polypropylene
HPDE = High density Polyethylene
ABS = Acrylic-Butidiene-Styrene blends
PVC = Polyvinylchloride
HiPS = High impact polystyrene

Example of a COTS Product Line

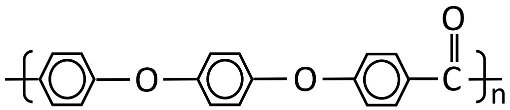
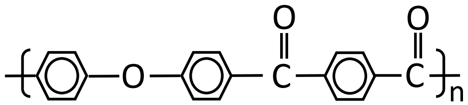
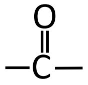
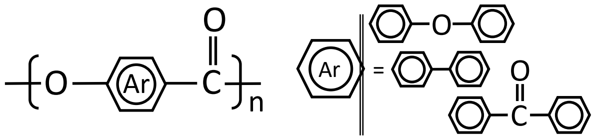
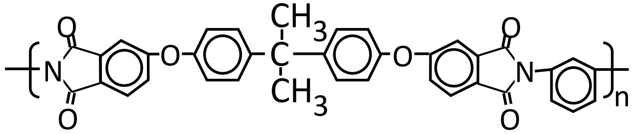
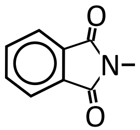
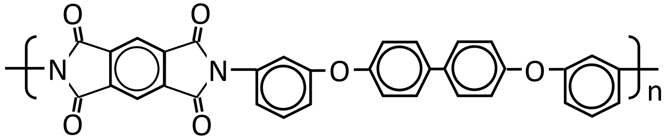
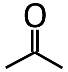
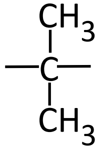
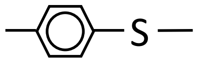


Courtesy of CompositesWorld.

https://www.compositesworld.com/blog/post/proving-out-lm-paek-welding-for-multifunctional-fuselage-demonstrator

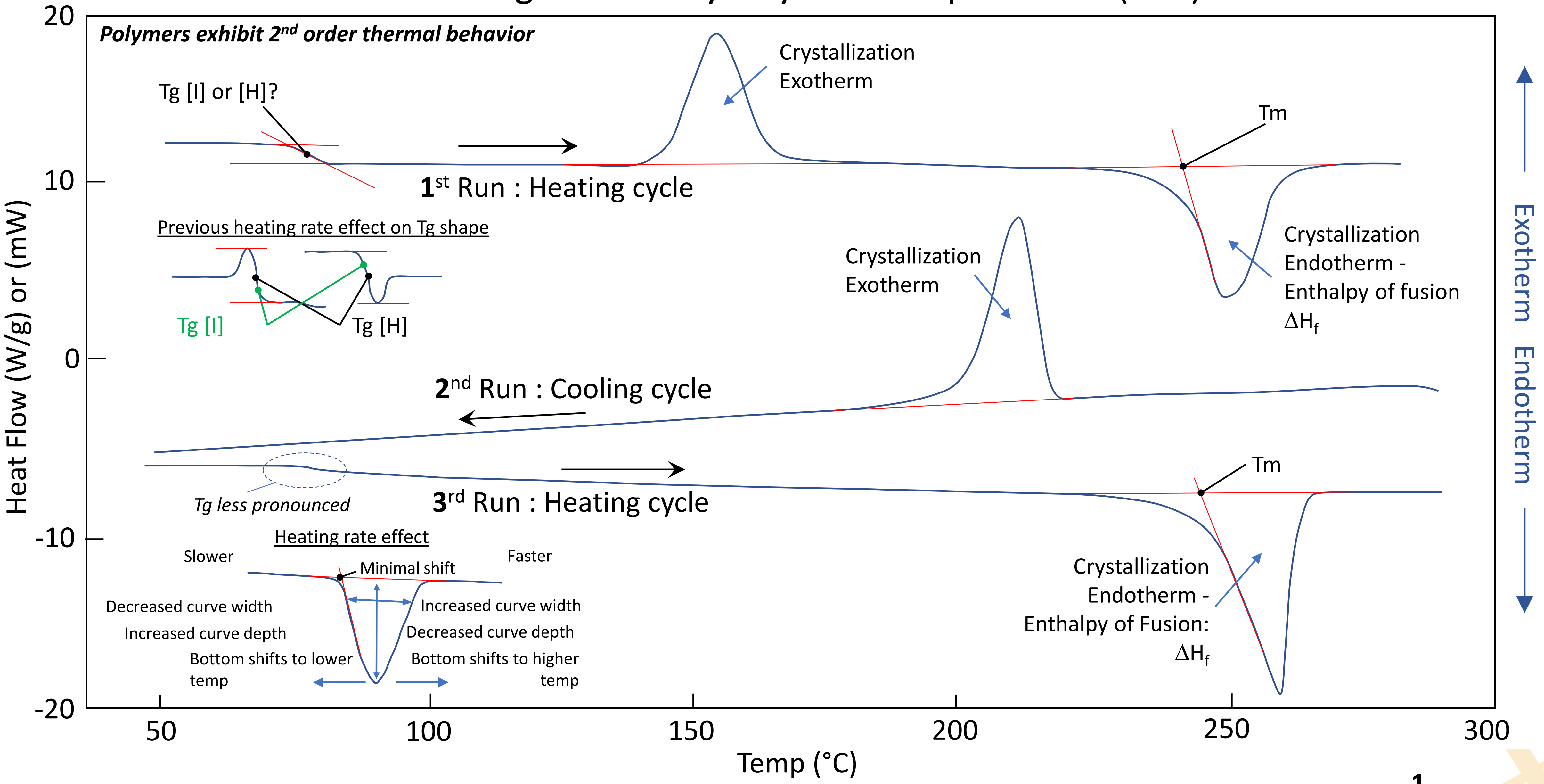
Advanced Engineering Thermoplastics

Microstructure

Abbr.	Polyarylene Ether	~ Tg / Tm (°C)	Chemical Group		Mechanical Analog
PEEK		144 / 344		Aryl, Phenyl, Benz	
PEKK		165 / 384-391		Ketone	
*PAEK		PAE: 163 / 361 *147 / 305	—O—	Ether	
	Polyether Imide	**~ Tg / Tm (°C)**	**Chemical Group**		**Mechanical Analog**
PEI		217 / N.A.		Imide	
Aurum		250 / - -	 	Imide ketone; Isopropylidine	
	Polyphenylene Sulfide	**~ Tg / Tm (°C)**	**Chemical Group**		**Mechanical Analog**
PPS		95 / 280	—S—	Sulfide	

*Copolymer

Interpreting a Differential Scanning Calorimeter (DSC) Thermogram of Polyethylene Terephthalate (PET)



http://www.tainstruments.com/pdf/literature/TA352%20PET%20Analysis%20by%20Rapid%20Heat-Cool%20DSC.pdf

TPC Thermal Properties as Related to Use Temperature

For load bearing applications, epoxy systems estimate max use ~25°C below Tg. This is due to the large modulus drop in amorphous epoxy systems prior to Tg. For semicrystalline thermoplastics, heat deflection measurements are emphasized over Tg as the modulus drop is less.

Polymer Name	Min Value (°C)	Max Value (°C)	Tg (°C)	Tm (°C)
PEEK	154	260	143	343
PET	80	140	69	255
PPS	200	220	126	279
PBT	80	140	40	223
PA	80	120	50	220

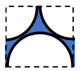
For semicrystalline (and some amorphous) thermoplastic composite systems, the heat deflection temperatures (Min and Max Values) show use temperatures above the Tg.

1. PPS composites have been used on the leading edge of the A340 and A380 where temperatures have exceeded 100°C.
2. Water uptake for these thermoplastic composites is ~0.1% versus 1-2% for thermosetting epoxies mitigating water-based plasticization. Thus, Hot-Wet performance knockdown is lower than for current SOA thermosetting composites.

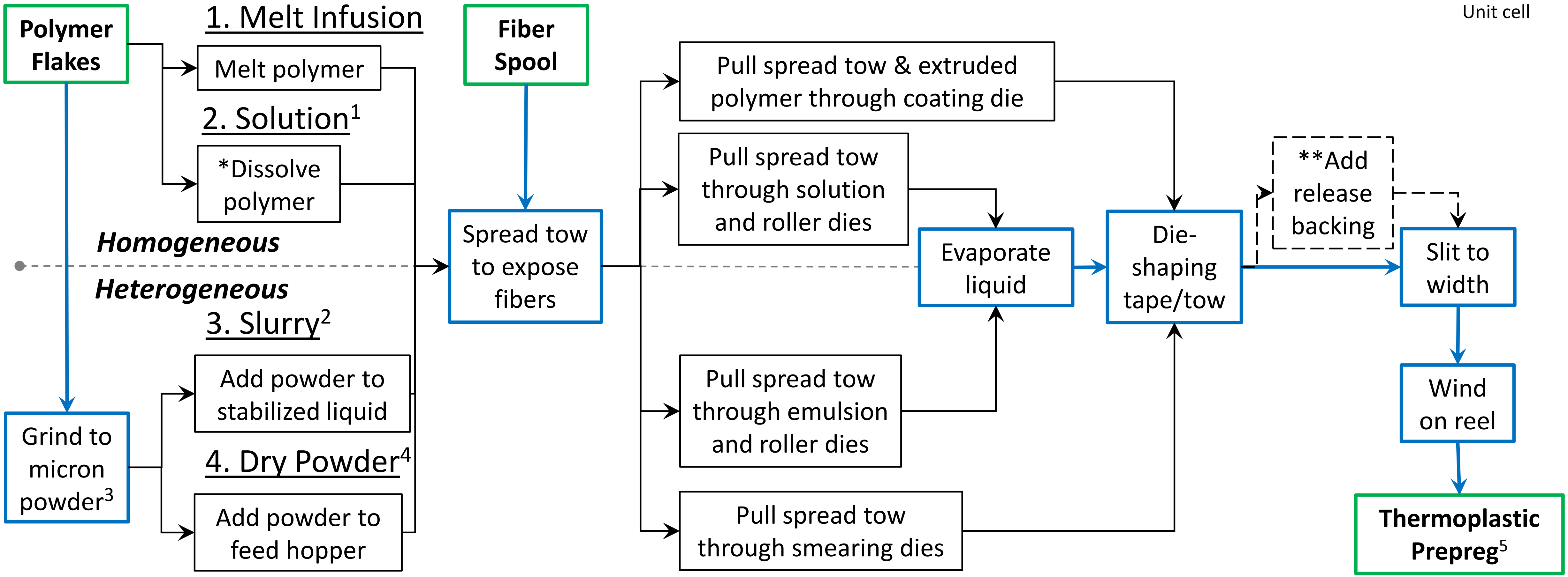
"Continuous Service Temperature of Plastics", Copyright © SpecialChem (2020).

Methods for Creating Thermoplastic Prepreg Tape

Objective is to minimally coat each fiber creating a void free composite ~33% by volume thermoplastic



Fiber/resin Unit cell



*If polymer remains soluble in reactor, can use directly after filtration.

**Used if prepreg is tacky.

1. Wilkinson, S.P., Marchello, J.M., Dixon, D., and Johnston, N.J. "A New LaRC Multi-purpose Prepregging Unit", 38th Intern. SAMPE Symp. May 10-13, (1993).
2. https://www.calitzler.com/prepreg-systems/thermoplastic-prepreg-systems/
3. Parquette, B., Giri, A., O'Brian, D.J., Brennan, S., Cho, K., and Tzeng, J., "Cryomilling of Thermoplastic Powder for Prepreg Applications", ARL-TR-6591, Sept. (2013) pp 24.
4. Baucom, R.M. and Marchello, J.M., "LaRC Dry Powder Towpreg System", NASA TM 102648, April (1990) pp 54.
5. https://www.compositesworld.com/articles/measuring-thermoplastic-prepreg-tape-quality-for-part-process-control

Methods of TPC Manufacture

Stamping

Continuous Compression Molding

In-Situ Filament Winding

Inflatable Mandrel

Automated Tape Placement

Assembly

Stamping

Part Configuration:

- Small, moderate complexity

Fabrication Technique:

- Pre-heat sheet in oven (e.g. IR)
- Transfer hot blank to stamping press
- Single sided tooling + rubber block
- Tooling ambient or 'warm'

Raw Material Form:

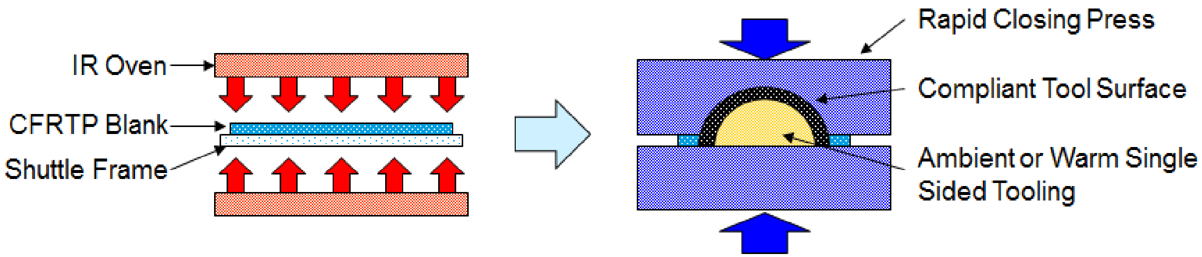
- Fully consolidated sheet

Process Variants:

- Tooling variations

Advantages / Disadvantages:

- Rapid cycle time
- – Limited in size and complexity of parts



SOLVAY

Images Courtesy of Solvay

https://www.solvay.com/en/chemical-categories/our-composite-materials-solutions/thermoplastic-composites

Continuous Compression Molding

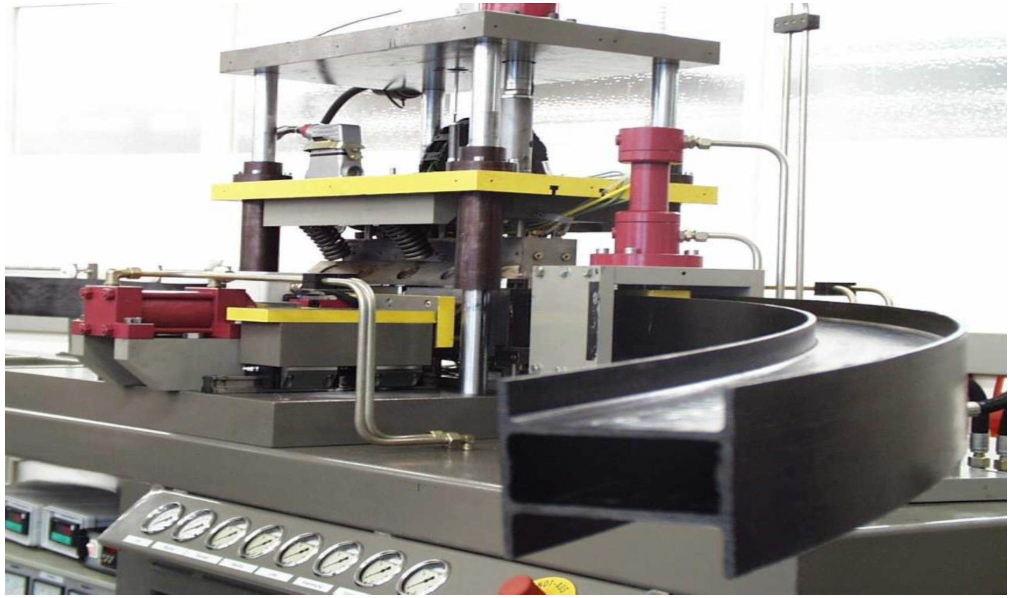
Part Configuration:
- Sheet, constant section profiles

Technique:
- Incremental Compression Molding Process

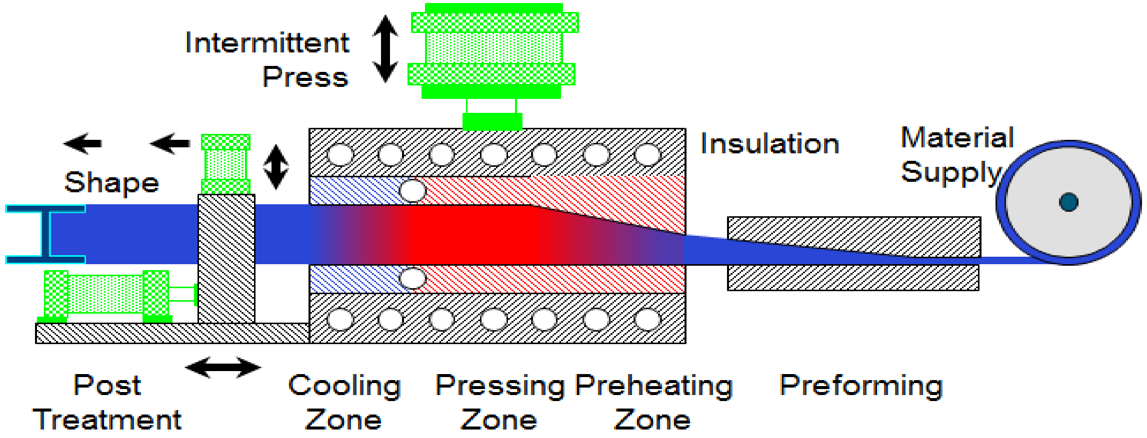
Raw Material Form:
- Fully impregnated prepreg

Process Variants:
- Flat sheet and stamping die

Advantages/Disadvantages
- Inexpensive route for sheet and simple shapes
- Specialized equipment



Advanced Composites and Machines



SOLVAY

Images Courtesy of Solvay

https://www.solvay.com/en/chemical-categories/our-composite-materials-solutions/thermoplastic-composites

In-Situ Filament Winding

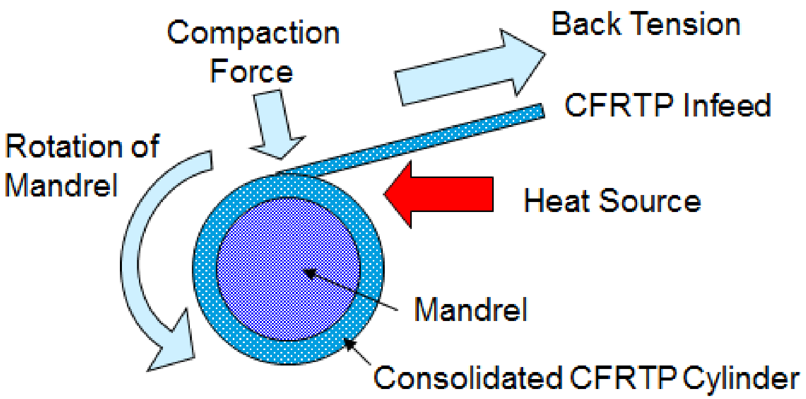
Part Configuration:
- Cylinders

Fabrication Technique:
- Tows consolidated in situ as mandrel rotates

Raw Material Form:
- Towpreg, narrow tape
- Finished part quality depends on material quality

Process Variants:
- Heat source, control technology

Advantages/Disadvantages
- Inexpensive route for cylinders
- Limitation on ply orientations



SOLVAY

Images Courtesy of Solvay

https://www.solvay.com/en/chemical-categories/our-composite-materials-solutions/thermoplastic-composites

Reusable Inflatable Pressure Mandrel

Part Configuration:
- Complex tubing

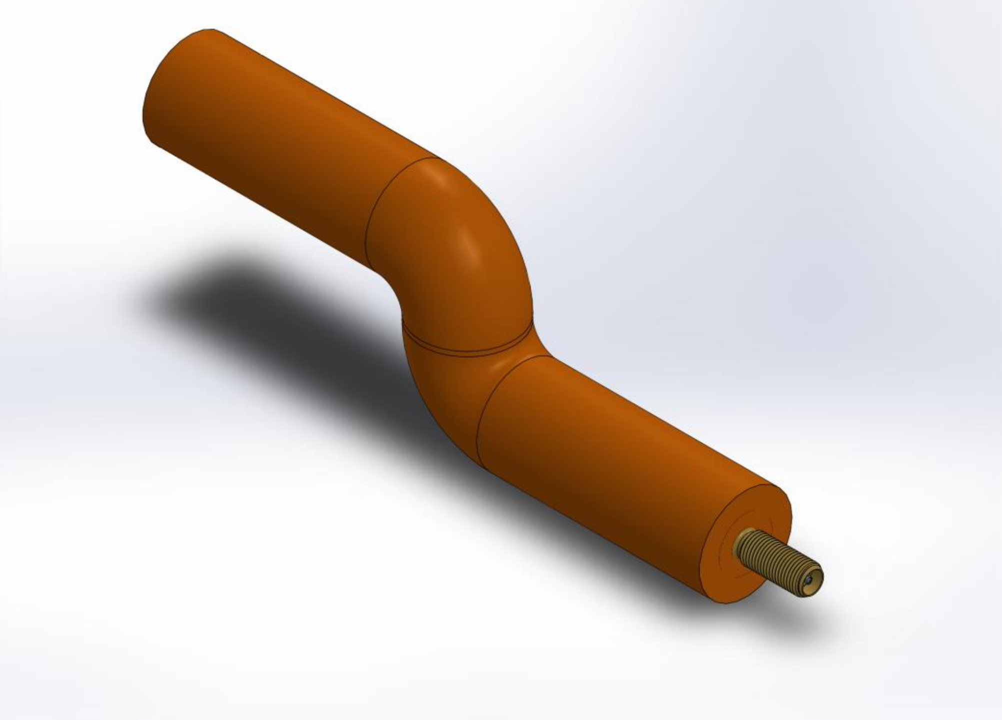
Fabrication Technique:
- Tows/preform forced against inner wall of mold by inflating mandrel

Raw Material Form:
- Towpreg, narrow tape, fabric
- Finished part quality depends on mold surfaces

Process Variants:
- Heat source, pressure

Advantages/Disadvantages
- Inexpensive route for cylinders
- Mandrel can be removed/reused
- OOA process

Rishon Inflatable mandrel used for thermoplastic molding.



- High temperature range -170 to +850 F
- Long life
- Light weight
- Insulation
- Electrically conductive or
- Approved for space use
- Impervious to salt spray,
- fungus, humidity, UV rays
- Fireproof
- Low outgassing
- non-conductive

TECHNOLOGIES

Images Courtesy of RCF Technologies

https://www.rcftechnologies.com/

Automated Tape Placement

Part Configuration:
- Sheet, closed structures, integrally stiffened structure

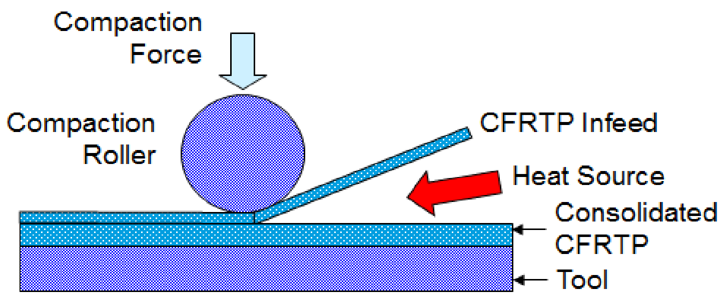
Technique:
- Tapes consolidated in-situ

Raw Material Form:
- Narrow tape, towpreg
- Finished part quality depends on material quality

Process Variants:
- Heat source, compaction device

Advantages/Disadvantages
- Can manufacture very complex parts
- Integrate welding of stiffeners etc
- Specialized equipment

Automated Dynamics Corp



Images Courtesy of Solvay

https://www.solvay.com/en/chemical-categories/our-composite-materials-solutions/thermoplastic-composites

AFP/ATP Process Variables

Application of Time, Temperature, Pressure

Prepreg Tape:

1. Fed or Pulled
2. Width
3. Surface Treaded
4. Resin
5. Preheated tape?

Layup:

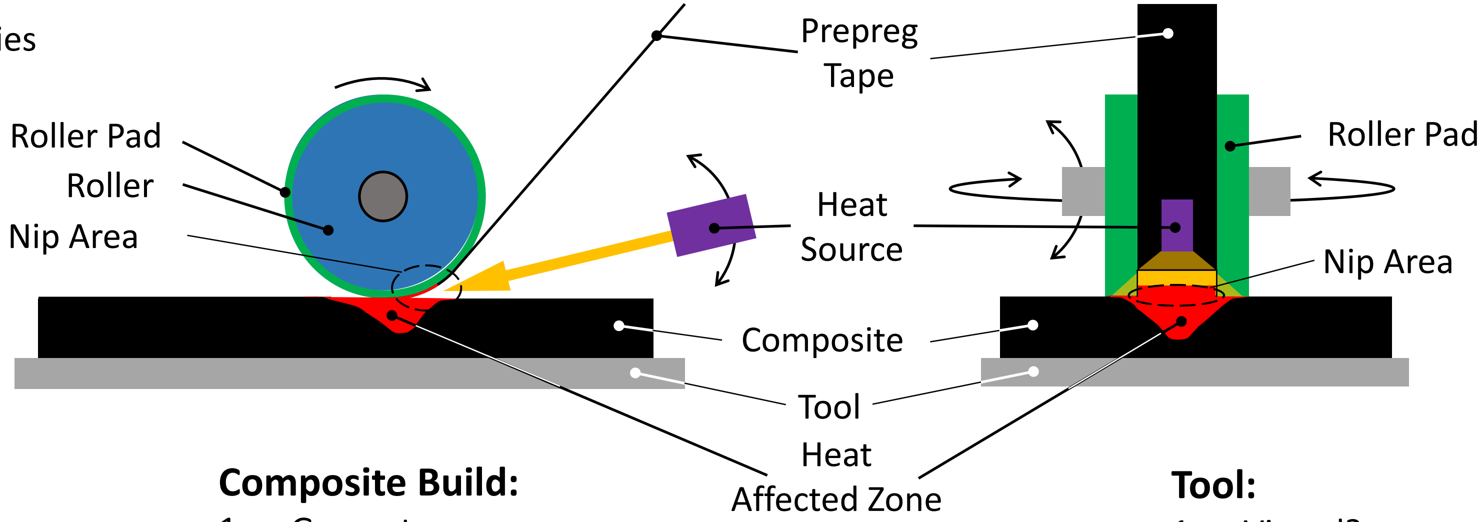
1. Speed
2. Pressure
3. Contouring

Heat Source:

1. Laser, Xe light, Ultrasound, IR…
2. Angle and Distance
3. Hot Area Coverage
4. Heat Affected Zone

Roller Pad:

1. Yes/No?
2. Soft/Hard
3. Thermal properties
4. Cleaning?



Roller:

1. Driven or Free
2. Width
3. Heated?
4. Tilt for turns?

Composite Build:

1. Geometry
2. Thermal profile
3. Thermal conductivity

Nip Area:

1. Atmosphere
2. Thermal geometry
3. Surface temperatures

Tool:

1. Virtual?
2. Material
3. Heated or Cooled

Clarkson, E., "Medium Toughness PAEK thermoplastics Toray (Formerly TenCate) Cetex® TC1225 (LM PAEK) T700GC 12K T1E Unidirectional Tape 145 gsm 34% RC Material Allowables Statistical Analysis Report", NCP-RP-2019-011 Rev N/c, Feb., 12 (2020).

Childers, C.H. "Determination of Thermoplastic Crystallization Process Limits for Dynamic and Isothermal Cooling Processes", Boeing Innovation Quarterly, (2019).

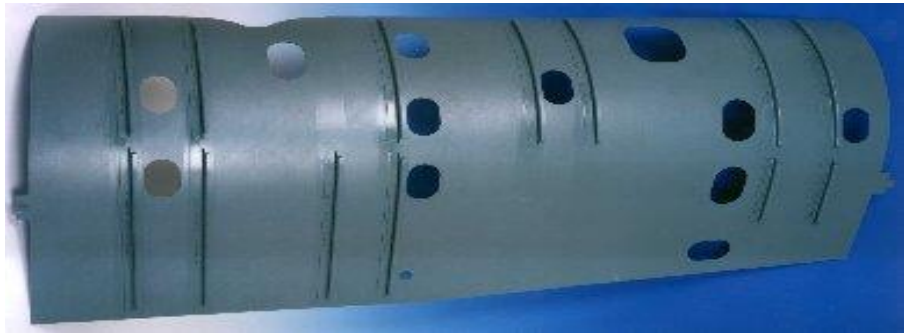
Assembly

Assembly Techniques:

- Fusion Bonding
- Co-consolidation
- Welding
- Dual resin bonding ‘Thermobond’
- In-situ consolidation

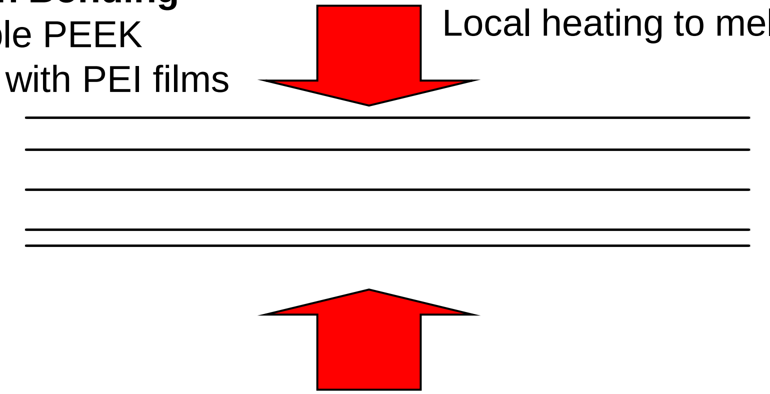
Welding:

- Convection
- Resistance
- Ultrasonic
- Induction



Dassault Rafale Engine Tunnel
Stiffeners Welded to Skin APC-2/AS4

Dual Resin Bonding
For example PEEK composite with PEI films



Local heating to melt film but not substrates

Lower melting point TP co-molded with CFRTP

Additional layer of lower melting point film

SOLVAY

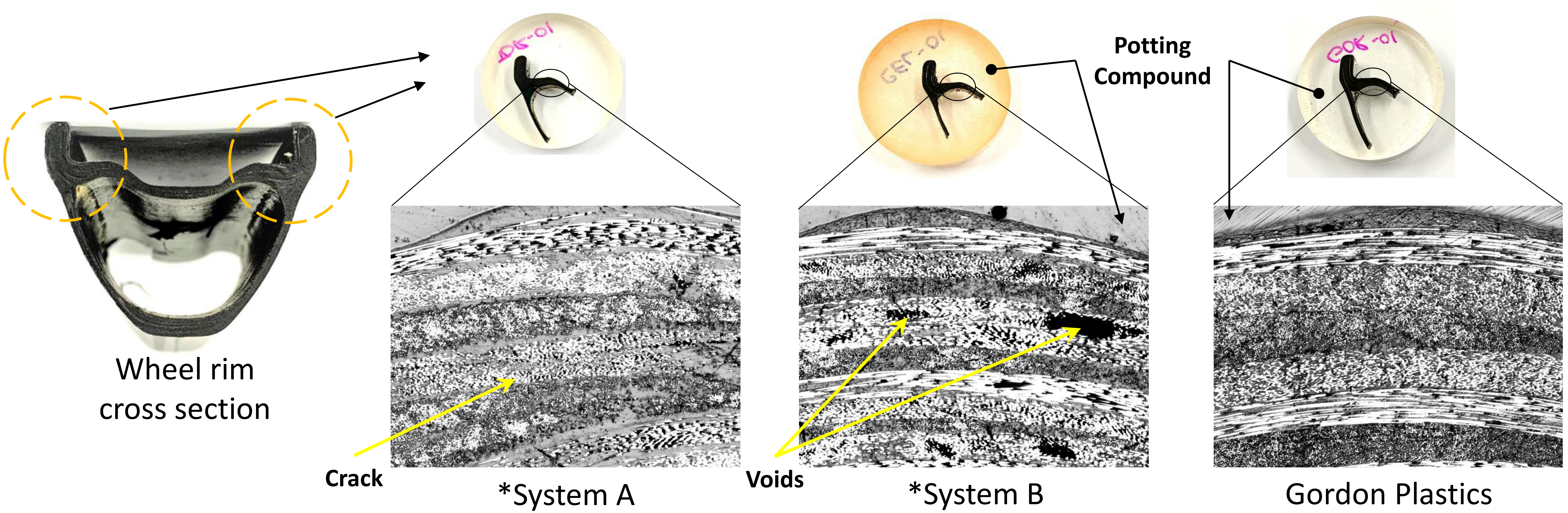
Images Courtesy of Solvay and their Partners

https://www.solvay.com/en/chemical-categories/our-composite-materials-solutions/thermoplastic-composites

A Case Study

The Importance of Selecting Both Process and Prepreg

TPC bike wheel rim made using Thermoplastic Prepregs



Optical micrographs 5X mag

System = Supplier Prepreg, Manufacturing Method, Process Cycle.

Notice the fiber directions between layers. Some have cracks and voids which are distinguishable from scratches and pullouts that occur during the polishing process.

Gordon Plastics

https://www.gordonplastics.com/

Images Courtesy of Gordon Plastics

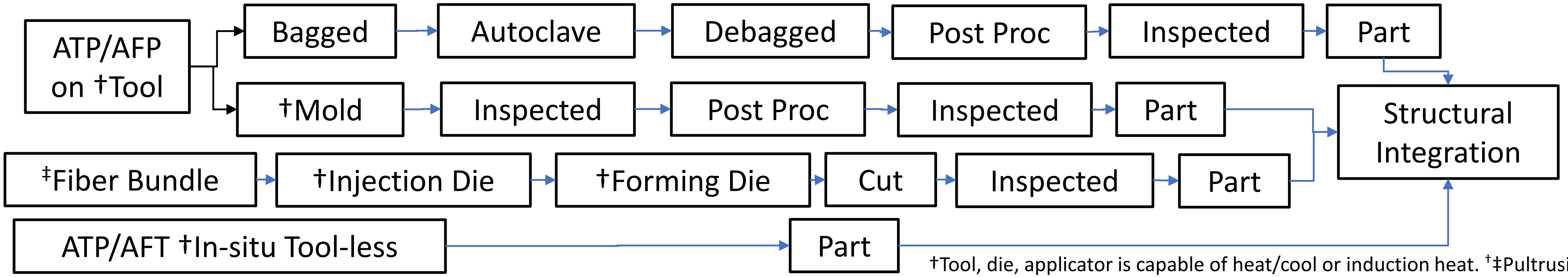
https://www.compositesworld.com/articles/measuring-thermoplastic-prepreg-tape-quality-for-part-process-control

Generalized Processing Methods

*Manufacturing & Cost Comparison	Thermoset	**Thermoplastic	Size Limited
Neat Resin Injection-based	Complex	Simplistic	Yes
Compression-based	Complex	Moderate	Yes
In-Situ Build (ATP/AFP)	Nonexistent	Demonstrated	No
Secondary Processing of ATP/AFP layup	Required	If needed	Yes / No
Single Process Unitization Potential	Poor	Good	No
Potential for Overall Cost Savings/Part	Low	High	Non-Applicable

*Time/Temperature/Pressure. **Most Out of the Autoclave (OOA) Process are Technical Readiness Level (TRL) 3-7. see also CompositesWorld.

Rapid Fabrication of Continuous Fiber Thermoplastic Composite Parts



†Tool, die, applicator is capable of heat/cool or induction heat. †‡Pultrusion.

"When you look at the amount of time it takes to make a thermoset part today and compare it with the amount of time it takes to make a thermoplastic composite part, [thermoplastic] is **about 10 times faster,"** - CompositesWorld.

"There are cost savings to be found in in-situ lamination and out-of-autoclave (OOA) post-consolidation. Plus, taking the autoclave out of the equation allows for the development **of larger structures**." - CompositesWorld.

"…using ATP robots and three-hour autoclave co-consolidation cycles (vs. seven to nine hours for cocured epoxies). In this case, the TPC approach reduced overall hours, resulting in a **25 percent cost reduction**." - CompositesWorld.

Applications for TPC Parts

Aerospace

Automotive

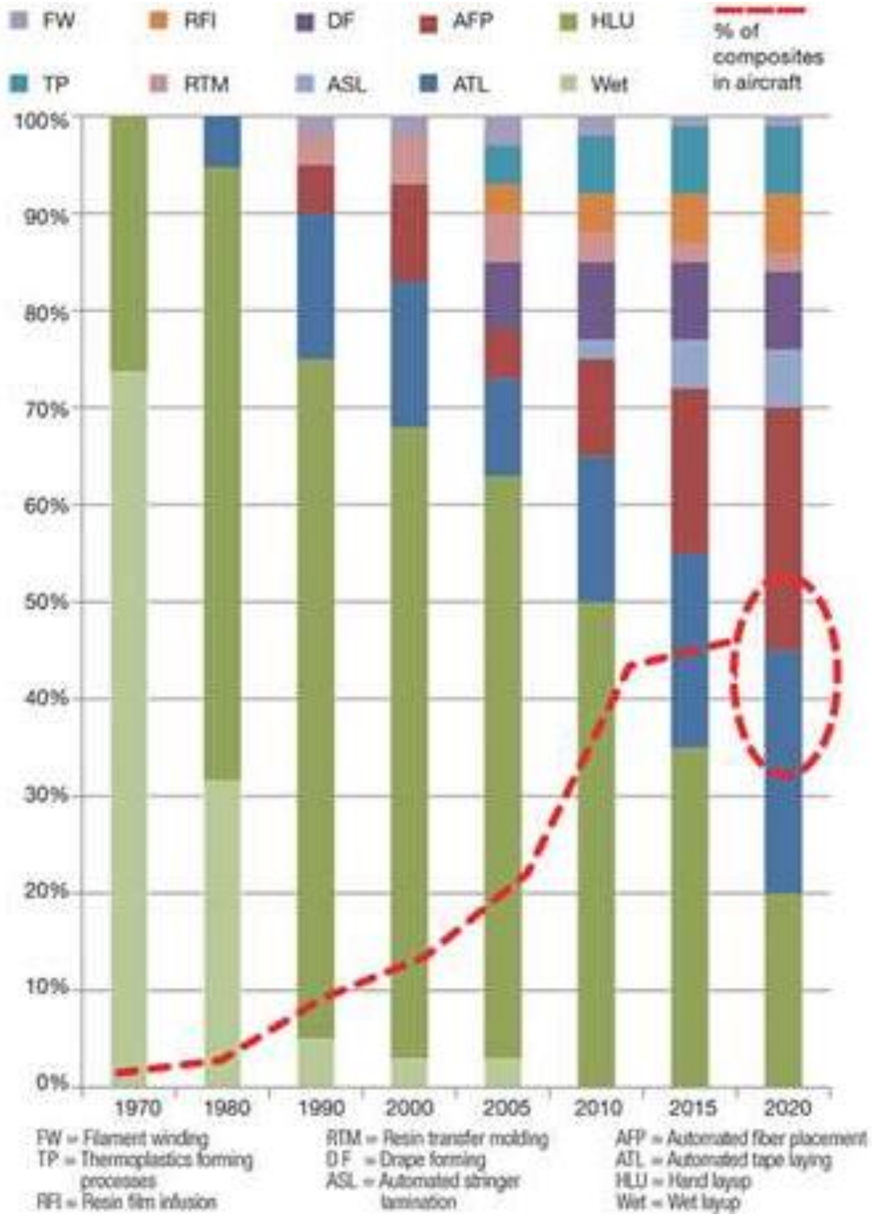
Sporting

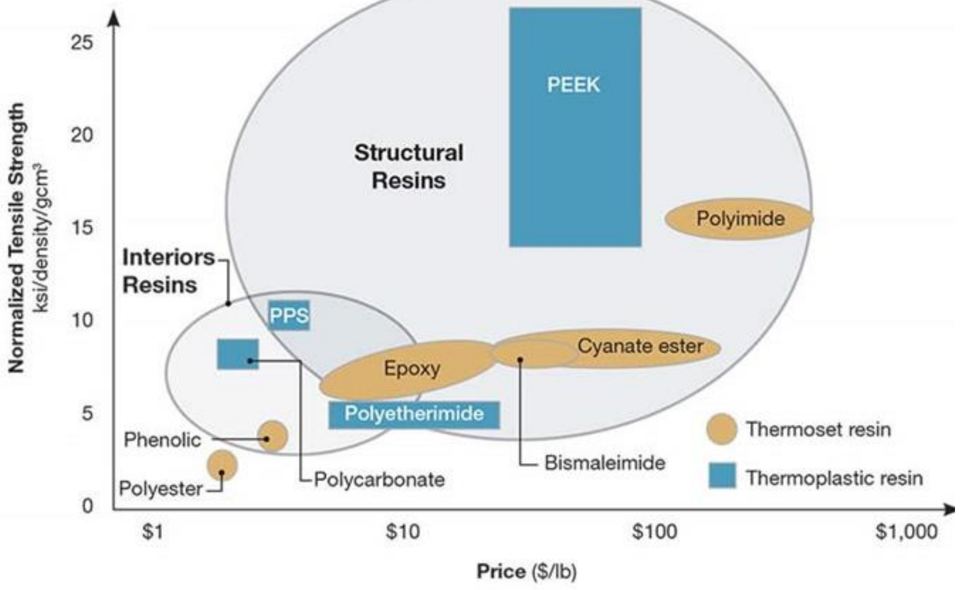
Energy/Civil

<u>Advantages</u>

- *Reduction in part count*
- *Increased durability*
- *Directional stiffness*
- *Light weighting*
- *Unitization*
- *Faster cycle times*
- *More manufacturing choices*
- *Lower manufacturing costs*
- *Reuse/Recycle*
- *Product formats beyond TPCs*

Increased Use of Thermoplastics





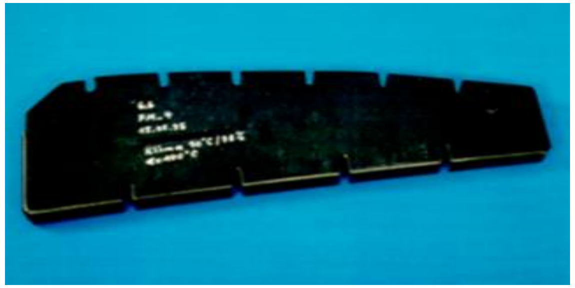
Double curvature. The thermoplastic composite fuselage panel accommodates the complex geometry of a Gulfstream business jet aft fuselage with fiber-steered AFP layup of the skin and co-consolidation of the orthogrid. Note the circumferential blade stringers, which are later welded to the frame. *Image Courtesy of Fokker GKN.*

Images Courtesy of CompositesWorld.

https://www.compositesworld.com/articles/the-outlook-for-thermoplastics-in-aerospace-composites-2014-2023

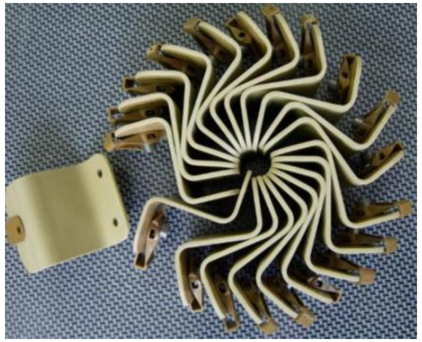
Aerospace

Airbus A320



Product: APC-2/AS4
Product Supplier: Solvay (Cytec)
Application: Ribs, Stiffeners
Manufacturer: Airbus Germany
Features: Rapid pre-heat and stamping

Boeing 787 Clips and Brackets



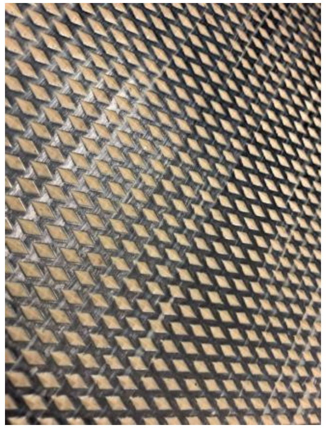
Product: APC(PEKK-FC)/AS4D & PEKK/Glass Fabric
Product Supplier: Solvay (Cytec)
Application: Clips & Brackets
Fabricator: ATC Manufacturing Inc
Features: CCM and stamp forming

Airbus A400M

Product: APC-2/AS4
Product Supplier: Solvay (Cytec)
Application: Cockpit Floor
Manufacturer: Daher-Socata Nantes Plant
Features: OOA consolidation

Aerospace

Leonardo (AgustaWestland) EH101 Helicopter



Product: APC-2/AS4
Product Supplier: Solvay (Cytec)
Application: Floor Panels
Fabricator: Leonardo (AgustaWestland)
Features: Textured surface molded onto upper panels

F-22 Weapons Bay Doors

Product: APC-2/IM7
Product Supplier: Solvay (Cytec)
Application: Weapons Bay Doors
Manufacturer: Marion Composites (for LM)
Features: Stiffened Skin Structure

Expansion of Aerospace Thermoplastic Composites

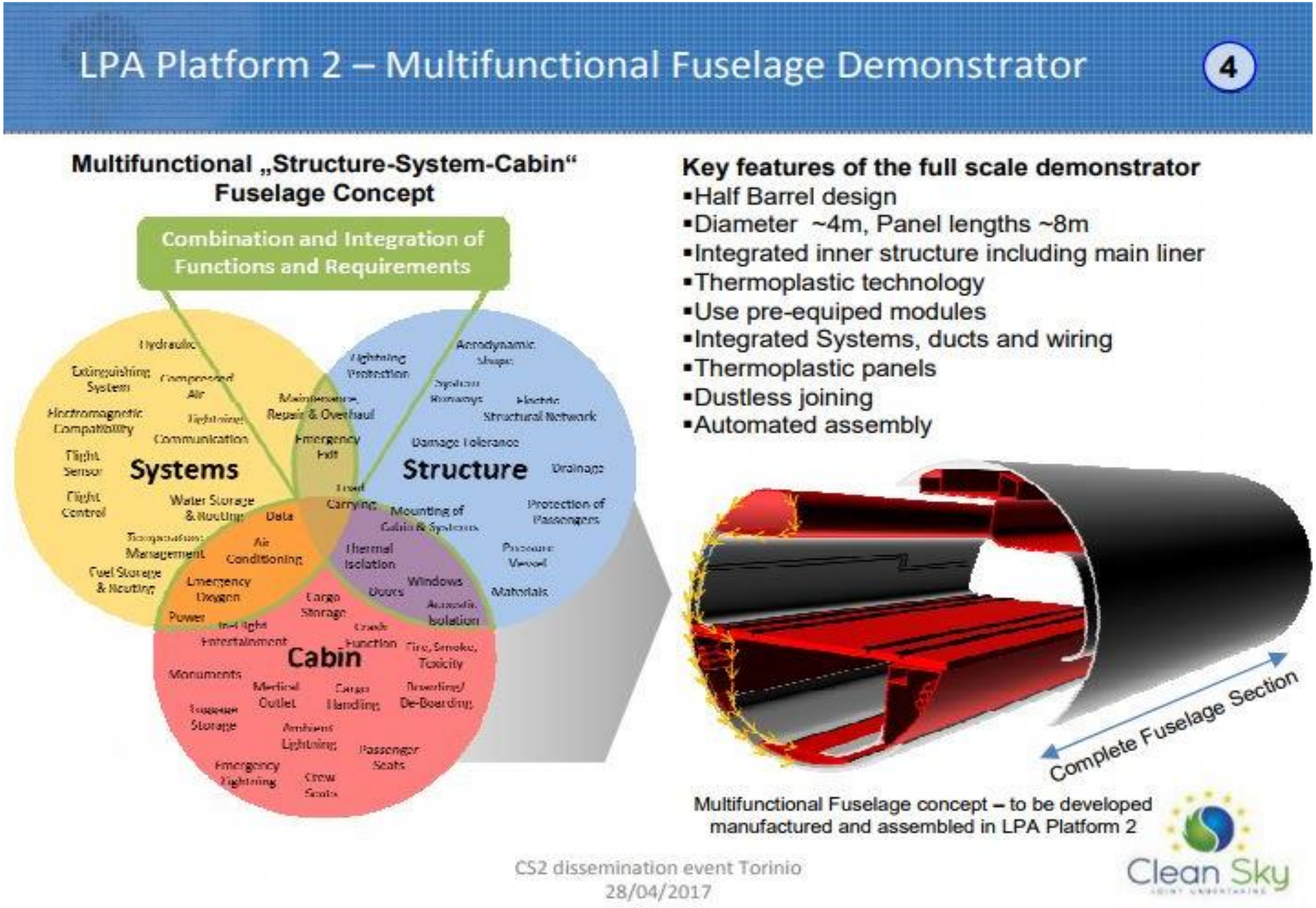
Current

- Clips and Brackets
- Galleys
- Leading Edges
- Vertical Stabilizers
- Environmental Control System Components
- Window Frames
- Aircraft Seats
- Riblets
- Wing Tips
- Stow Bin Latch Covers

Future

- Fuselage
- Wing Skins
- Floor Beams
- Radomes

See Slide 2, The same progression as thermoset composites!



https://www.cleansky.eu/the-next-generation-multifunctional-fuselage-demonstrator-leveraging-thermoplastics-for-cleaner

https://www.cleansky.eu/

Automotive

Door: Acura MDX (*future*)

Panel Covers

Oil Pan

Wheel

TPC-Metal Hybrid structures

Underbody Panel

Wheel well Liner

Interior Door Panel Development

https://www.compositesworld.com/articles/thermoplastic-door-a-first-for-automotive-composites

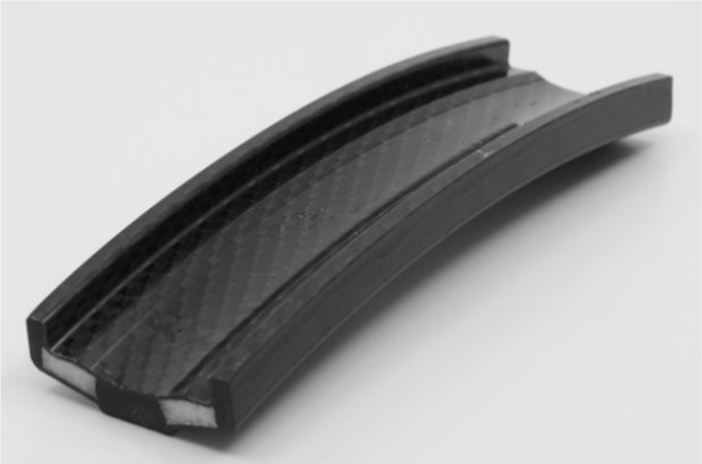
Images Courtesy of CompositesWorld

Sporting Equipment

Ski boot holder

Bicycle crankarm

Kayak



Bicycle wheel rim

Electric Bicycle

https://www.compositesworld.com/search?q=Sports%20%2B%20thermoplastic

Energy/Civil

Deep-water oil and gas pipes

Hydrogen storage tanks

https://www.compositesworld.com/search?q=Energy%20thermoplastics

Challenges Implementing Thermoplastic Composites

- 20 year material maturation rule still applies.
- Perfecting OOA process technology is the challenge to realize production of complex large thermoplastic parts.
- Must integrate current manufacturing methods to create thermoplastic parts to reduce capital reinvestment.
- Process-based residual thermal stress analysis to determine final part shape and internal stress.
- In-situ build quality assessment with corrective error mitigation to fully automate the manufacturing process.

R. Slayton, and G. Spinardi "Radical Innovation in Scaling Up: Boeing's Dreamliner and the Challenge of Socio-technical Transitions" Technovation, 47, (2016), pp 47-58.

Thank you, Contributors!

American Composites Manufacturers Association
https://acmanet.org/

CompositesWorld
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Toray
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Solvay
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PCF Technologies
https://www.rcftechnologies.com/

Gordon Plastics
https://www.gordonplastics.com/

Clean Sky
https://cleansky.eu/

Visit their websites to learn more!

A NEW CAMX
FOR A NEW TIME

Images Courtesy of Contributors

THANK YOU
FOR WATCHING

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THE COMPOSITES AND ADVANCED MATERIALS EXPO

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2020

Appendix

Future Areas For Thermoplastic Composite Research

Activity	Outcome
Develop amorphous systems with the same property advantages as semicrystalline resins.	• Eliminates process changes to crystalline morphology and percent. • Lower processing temps as Tm/% crystallinity does not have to be achieved.
Integrate metallic parts, shims and filaments into thermoplastics to create lightened hybrid structures beyond *ARALL and GLARE.	• In-situ electromagnetic emission (EME), discharge, and conductive pathways. • Metallics offer thermal pathways which may speed process heating and cooling. • Opportunity to go beyond flat laminates to change structural load paths and geometry.
In-situ robotic prepreg surface prep technology.	• Increase tack and bond strength/durability between plys during build.
Develop real-time closed loop build assessment technology.	• Flaw detection, repair, and in-situ process changes (TTP) based on part type.
Build directly onto other components to demonstrate unitization, overmolding, and tool elimination.	• Allows the use of other components to serve as a tool surface for unitization during build. • Build in other material parts as hardpoints and secondary support anchors.
Research tool-less technology.	• Increase build rates using multiple robots. • Eliminates tooling costs. • No size restriction (within reason). • On-site manufacturing (portable system)
Model bonding time-temp-pressure (TTP) to see the effects on bond integrity.	• Decrease void formation. • Prevents internal delamination. • Processing aid (TTP).
Integrate thermoplastic composites with thermoplastic film	• Create thermoplastic composites with in-situ liner systems for fluid transport and storage.
Thermoplastic resins with faster bond strength development.	• Increased processing rates at temperature.
Model and verify differences in thermoplastic/hybrid structures versus current thermoset composite structures.	• Develop more efficient (less material, lighter weight) load bearing structures.

ARALL = Aramid aluminum laminate.
GLARE = Glass laminated aluminum reinforced epoxy.

*Vogelesang, L.B., Gunnink, J.W., "ARALL: A materials challenge for the next generation of aircraft", Materials & Design, 7(8), (1986), pp 287-300.