



# Marine Composites

Webb Institute  
Senior Elective

## Reinforcements and Resin Systems

Eric Greene, Naval Architect

EGAssoc@aol.com

410.703.3025 (cell)

<http://ericgreeneassociates.com/webbinstitute.html>





# Reinforcement Fibers

*E-glass* - Glass fibers account for over 90% of the fibers used in reinforced plastics because they are inexpensive to produce and have relatively good strength to weight characteristics. Continuous glass fibers are formed by extruding molten glass to filament diameters between 5 and 25 micrometers. Individual filaments are coated with a sizing that acts as a coupling agent during resin impregnation.

*Polymer Fibers* - These range from aramids, such as Kevlar® with very high strength to polyester and nylon thermoplastic fibers, with very high elongation.

*Carbon Fiber* -The terms “carbon” and “graphite” fibers are typically used interchangeably. Carbon fibers offer the highest strength and stiffness of all commonly used reinforcement fibers.



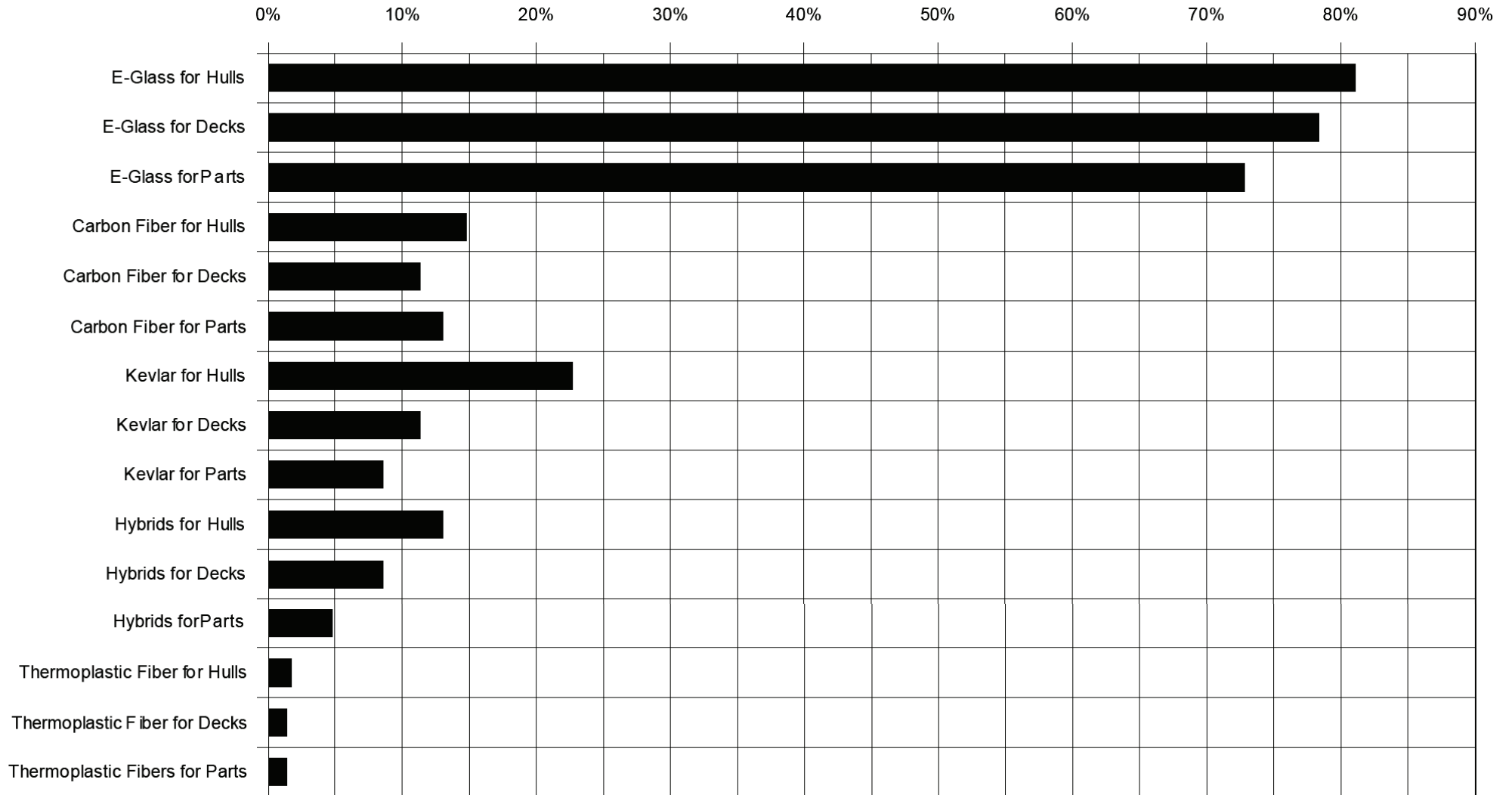
# Fiber Mechanical Properties

	Density gm/cm <sup>3</sup>	Strength MPa	Modulus GPa	Specific Strength MPa*	Specific Modulus GPa*
E-glass	2.60	3450	72	1327	28
S-glass	2.49	4589	87	1843	35
Aramid	1.44	3623	124	2516	86
Carbon (commercial)	1.76	2415	227	1372	129
Carbon (high performance)	1.76	4830	393	2744	223
Polyethylene	0.97	3000	170	3093	175
Basalt	2.66	2950	90	1109	34
HT steel	7.86	750	210	95	27
Aluminum	2.66	310	75	117	28

\* Strength or stiffness divided by density



# Boatbuilder Reinforcement Types

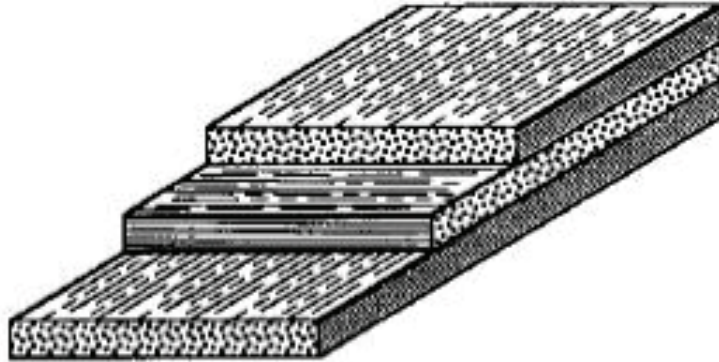


data from Eric Greene Associates 1995 survey

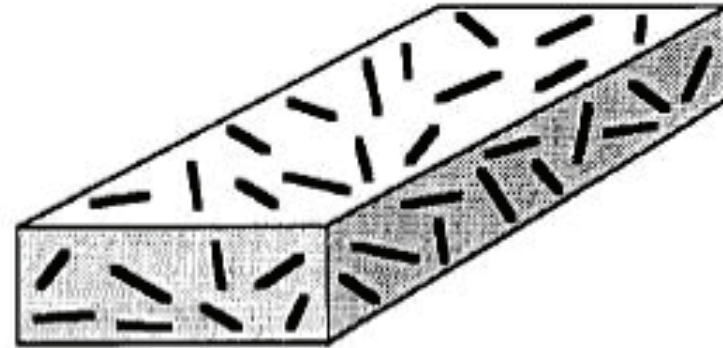


# Reinforcement Types

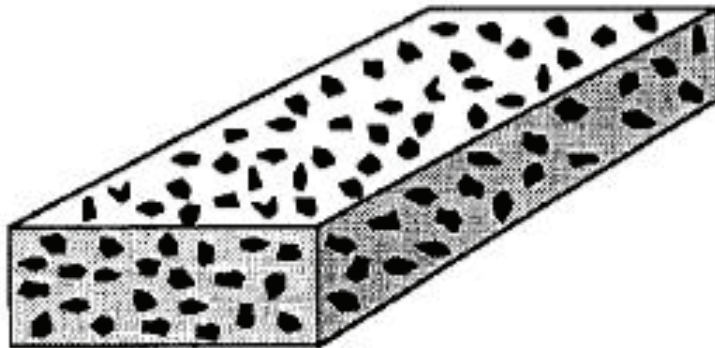
Continuous Fibers



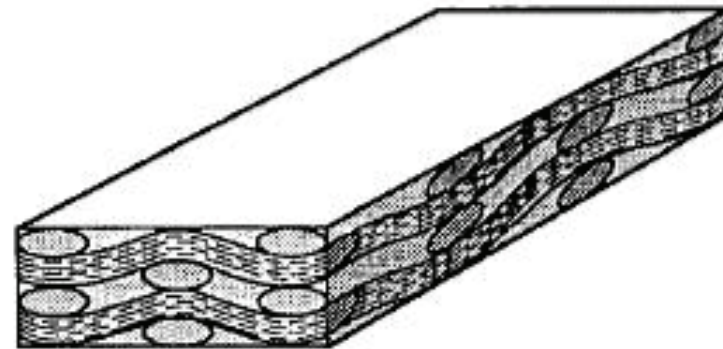
Discontinuous Fibers, Whiskers



Particles



Fabric, Braid, Etc.





## Reinforcement Architectures

*Filaments* - Fibers as initially drawn

*Continuous Strands* - Basic filaments bundled together

*Yarns* - Twisted strands (treated with after-finish)

*Chopped Strands* - Strands chopped 5 to 50 mm

*Rovings* - Strands bundled together like rope but not twisted

*Milled Fibers* - Continuous strands hammermilled into short lengths 0.8 mm to 3 mm long

*Reinforcing Mats* - Nonwoven random matting consisting of continuous or chopped strands

*Woven Fabric* - Cloth woven from yarns

*Woven Roving* - Strands woven like fabric but coarser and heavier

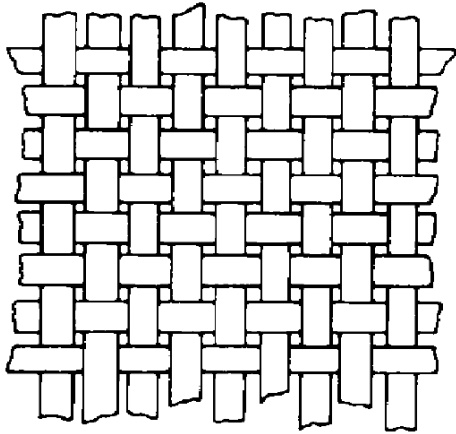
*Spun Roving* - Continuous single strand looped on itself many times and held with a twist

*Nonwoven Fabrics* - Similar to matting but made with unidirectional rovings in sheet form

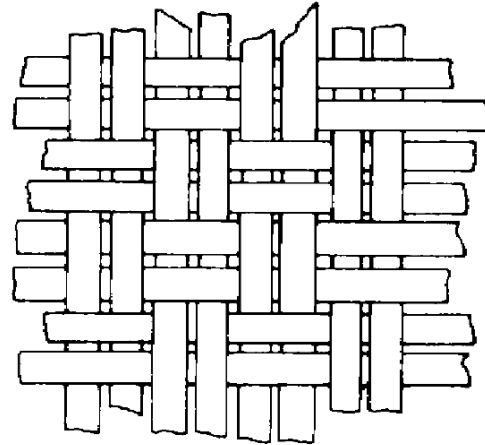
*Surfacing Mats* - Random mat of monofilaments



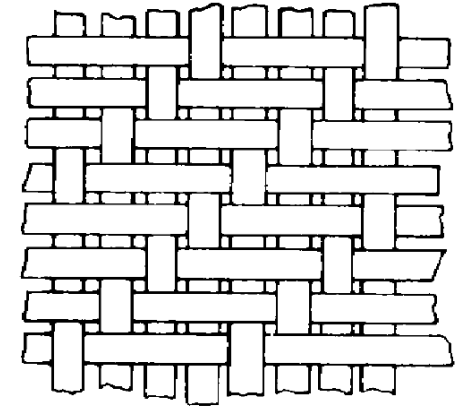
# Woven Reinforcement Styles



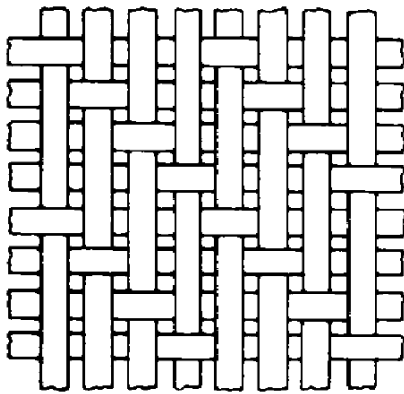
Plain weave



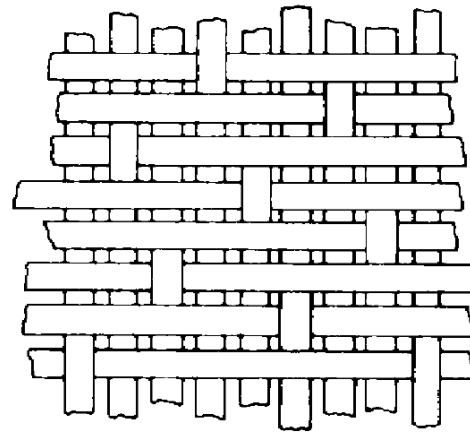
Basket weave



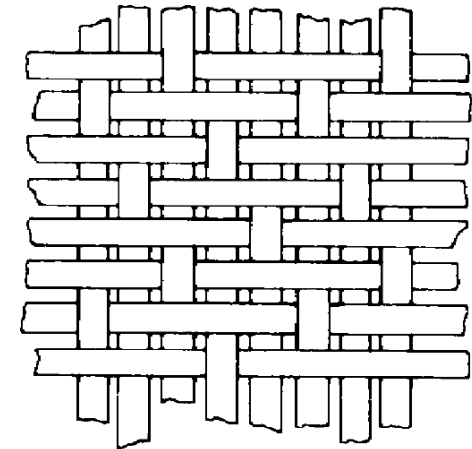
Twill



Crowfoot satin



8 harness satin

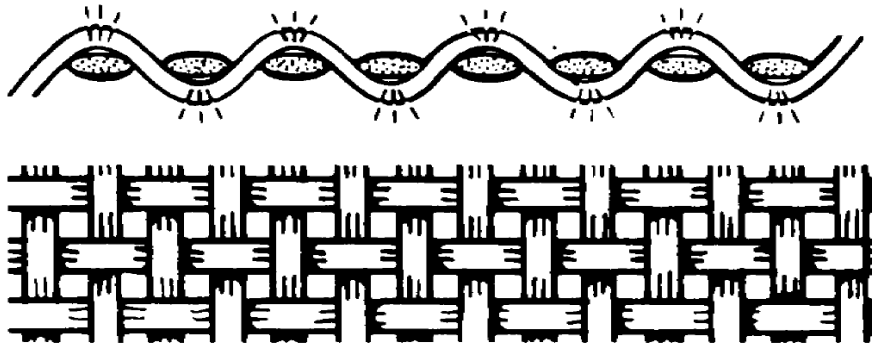


5 harness satin

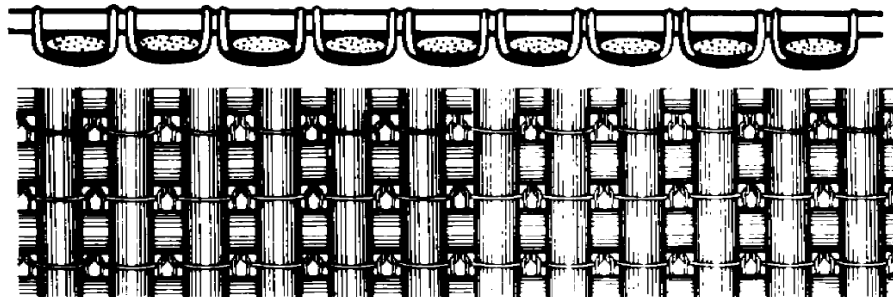


# Woven and Knit Reinforcements

Woven such as Woven  
Roving or Cloth



*Better damage  
resistance and good for  
building up single skin  
thickness*



*Better in-plane properties  
- best used with sandwich  
construction*

Knit or non-woven fabric

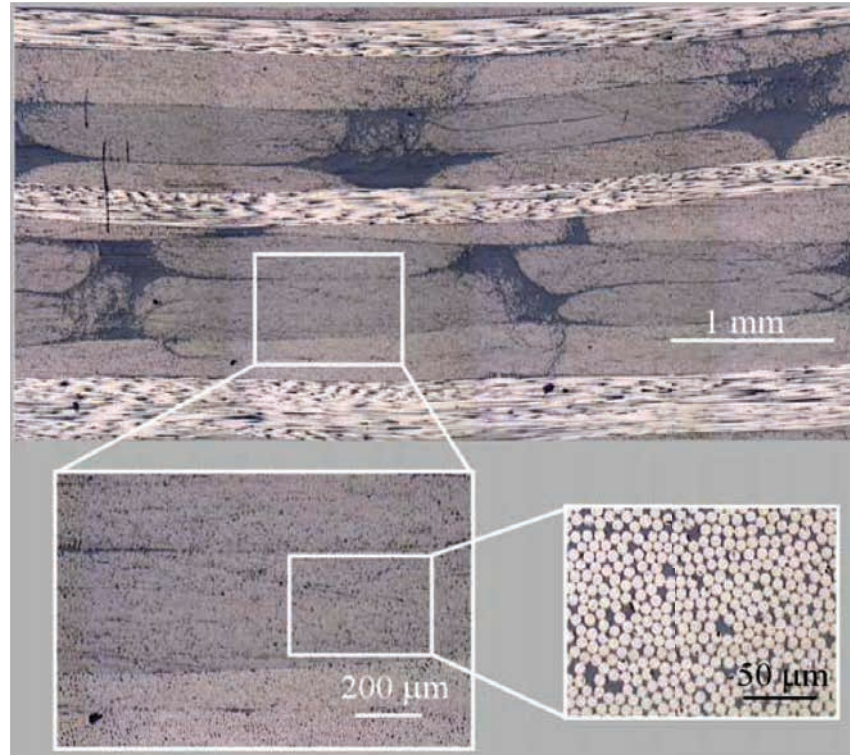




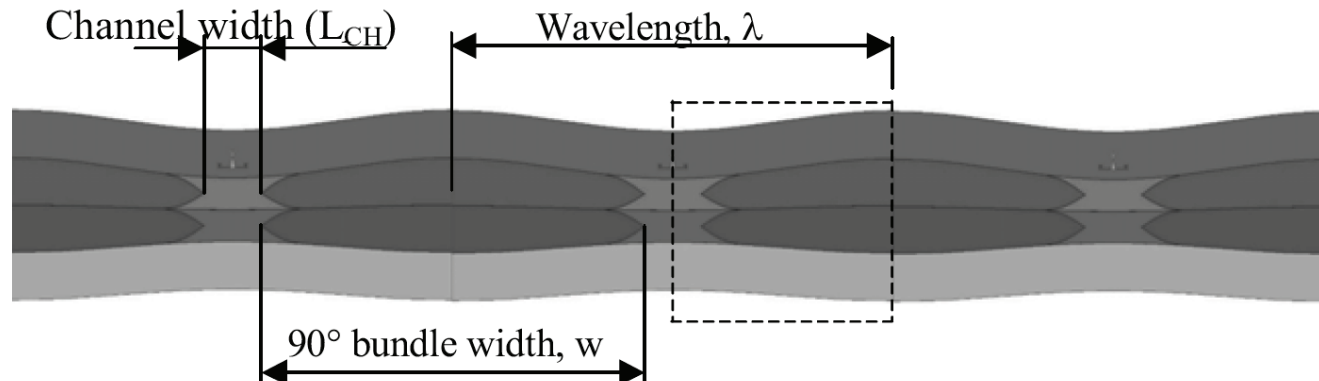
# Knit Reinforcement Architecture

## Structure of the knit reinforcement composites

David Mattsson, "Mechanical performance of NCF composites," , Luleå University of Technology, Luleå, Sweden, 2005



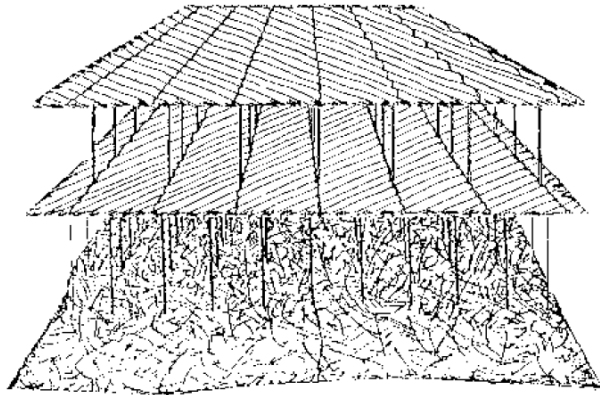
## Schematic picture of the out-of-plane misalignment of the 0° bundle



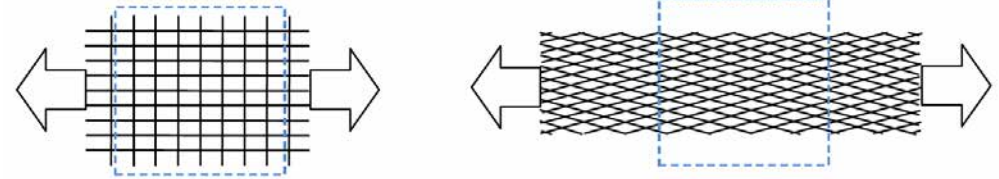


# Double Bias ( $\pm 45^\circ$ ) Reinforcement

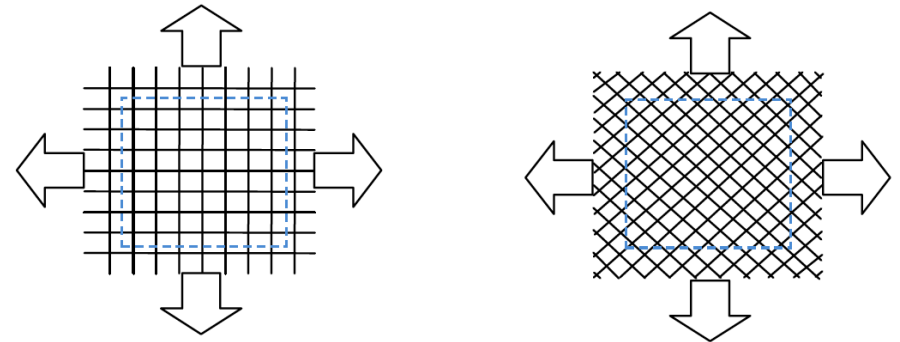
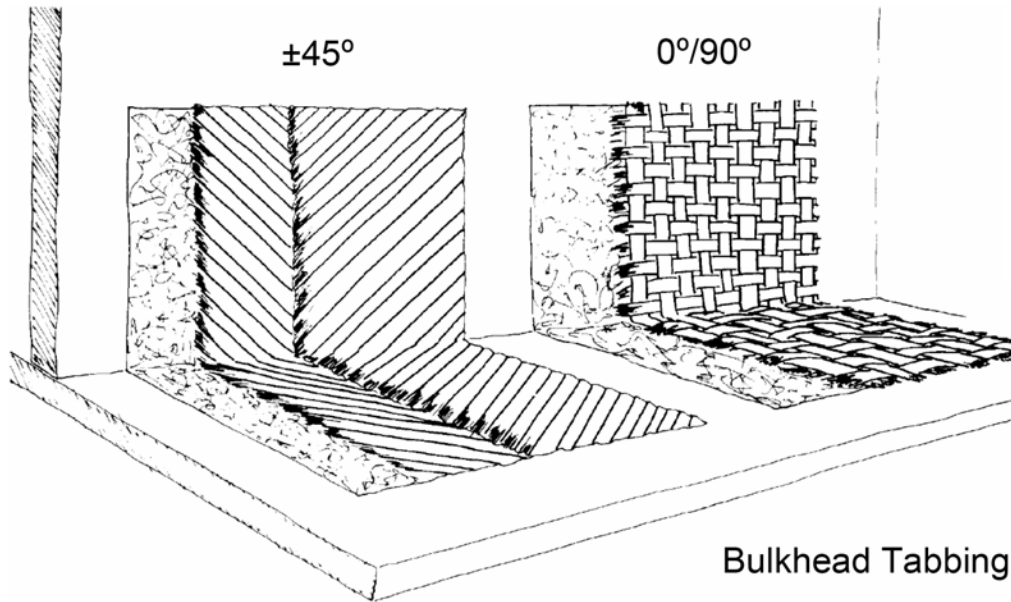
## Stitched Double Bias and Mat



Resists Membrane Tension  
better than In-Plane Loads



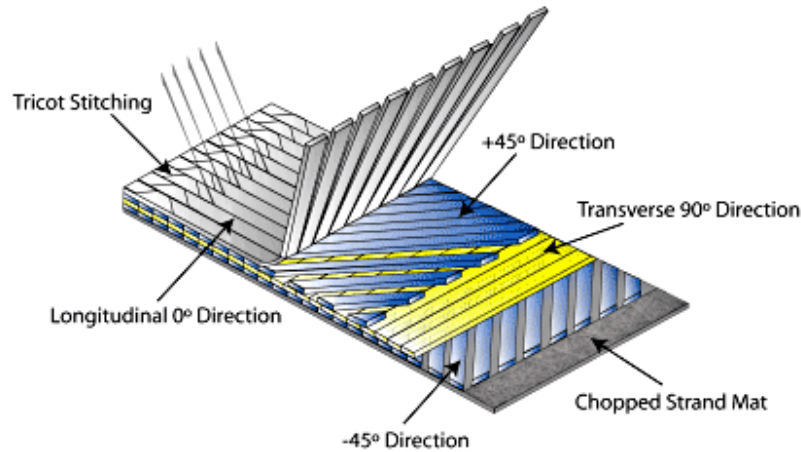
## Conformity and Shear Strength





# Multi-axial Reinforcements

## Multi-Axial Architecture



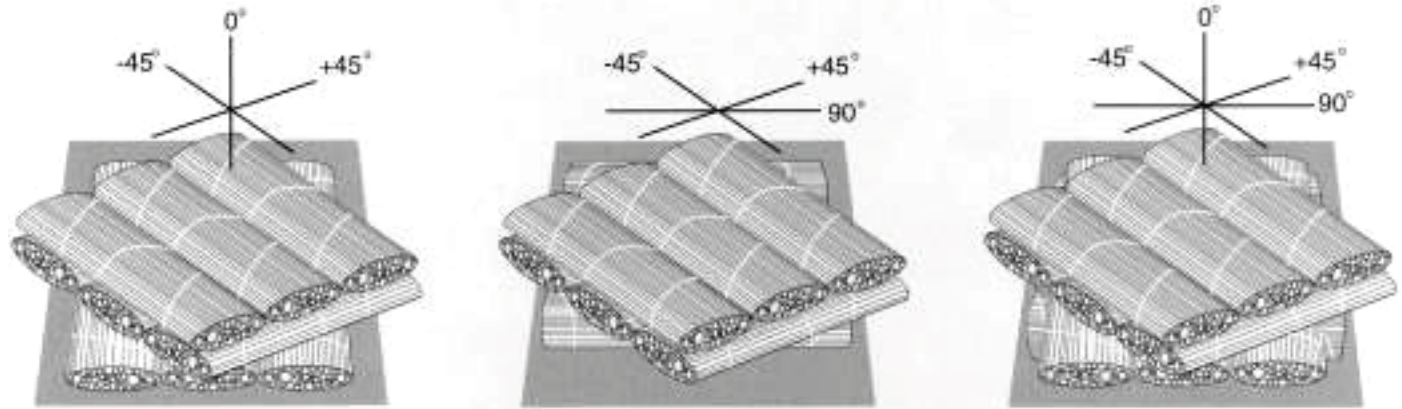
Stitch bonded example-Quadraxial. Typical quadraxial ply stack includes  $0^\circ$ ,  $90^\circ$ ,  $\pm 45^\circ$  plies. In this case quads are designed with more  $90^\circ$  fiber than the other axis. [Vectorply Corporation]

## Potential Fiber Waviness



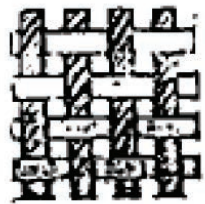
Detail image of stitched reinforcement shows fiber waviness as a potential manufacturing artifact

Diagram of Stitched Triaxial and Quadraxial Fabrics

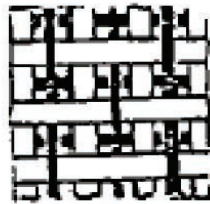




# Additional Reinforcement Styles



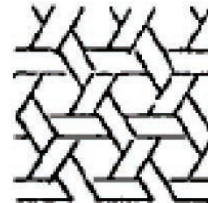
Biaxial Woven



High Modulus Woven



Multilayer Woven



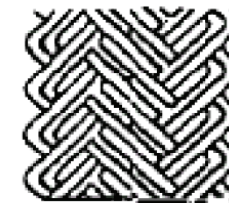
Triaxial Woven



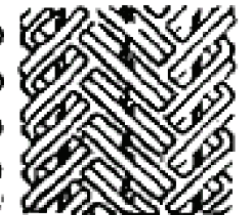
Tubular Braid



Tubular Braid Laid in Warp



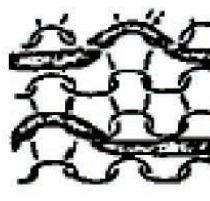
Flat Braid



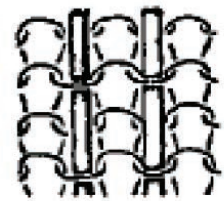
Flat Braid Laid in Warp



Weft Knit



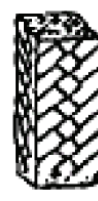
Weft Knit Laid in Weft



Weft Knit Laid in Warp



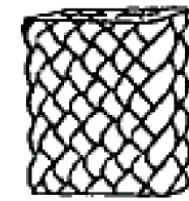
Weft Knit Laid in Warp Laid in Weft



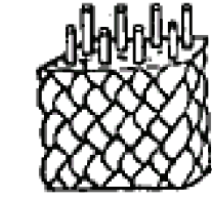
Square Braid



Square Braid Laid in Warp



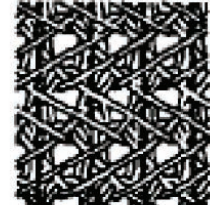
3-D Braid



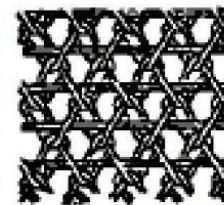
3-D Braid Laid in Warp



Warp Knit



Warp Knit Laid in Warp



Weft Inserted Warp Knit



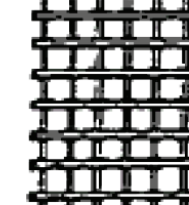
Weft Inserted Warp Knit Laid in Warp



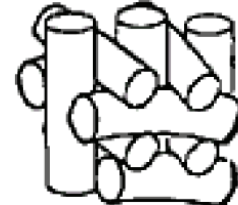
Fiber Mat



Stichbonded Laid in Warp



Biaxial Bonded



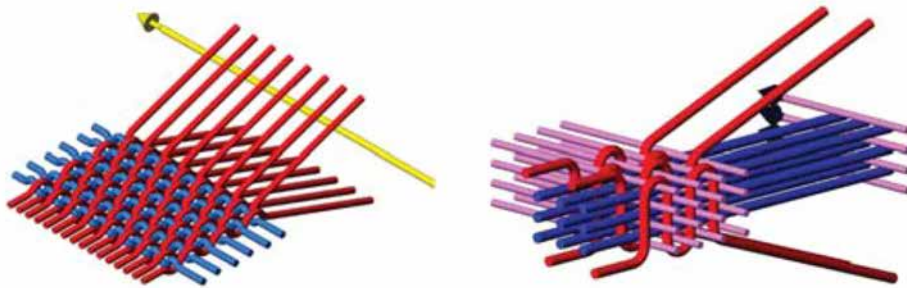
XYZ Laid in System



# Braided Reinforcements



Schematic of 2-D weaving (left) and 3-D weaving (right) [3TEX Inc]





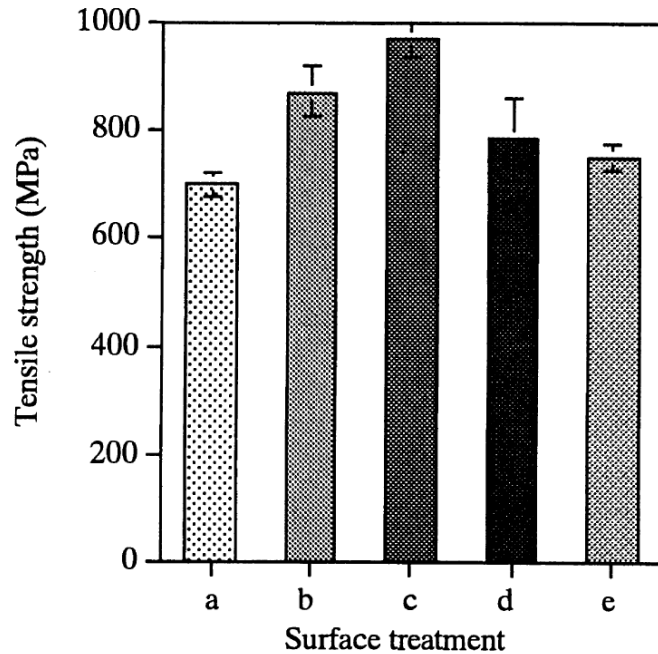
# Mat Reinforcements






- Mat reinforcements can be applied during hand lay-up as prefabricated mat or via the spray-up process as chopped strand mat.
- Chopped strand mat consists of randomly oriented glass fiber strands that are held together with a soluble resinous binder.
- Both hand lay-up and spray-up methods produce plies with equal properties along the x and y axes and good interlaminar shear strength.
- This is a very economical way to build up thickness, especially with complex molds. This is why most small parts are made with mat.
- Mechanical properties are less than other reinforcements.
- The weight by area of fiberglass mat is expressed as ounces/ft<sup>2</sup> or grams/meter<sup>2</sup>.



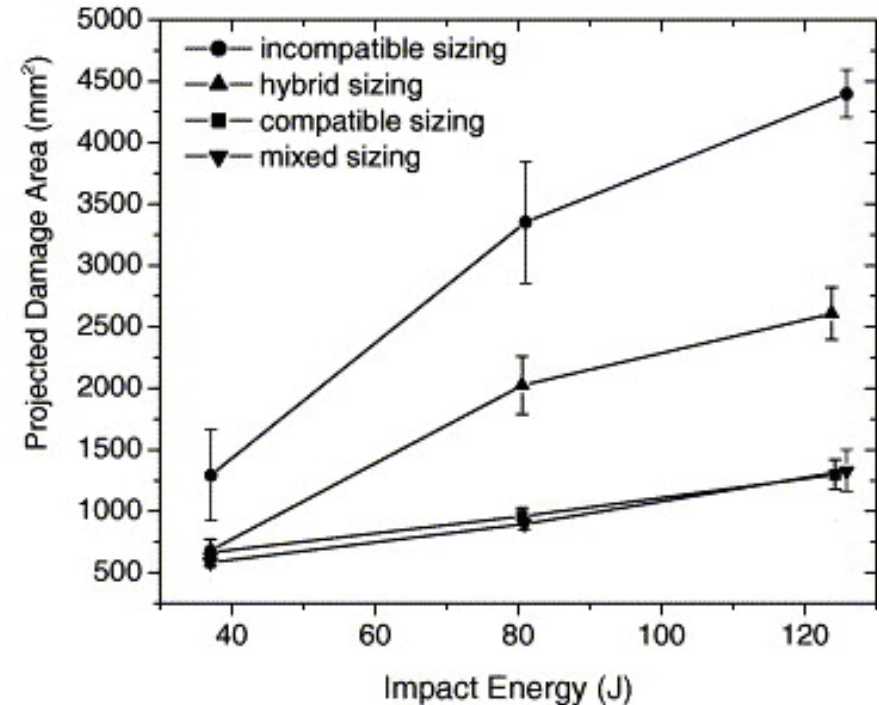
# Fiber Surface Treatment

### Strength of Carbon Fiber Laminates based on Surface Treatment



-  (a) Water-sized
-  (b) Epoxy-silane
-  (c) Methacryl-silane
-  (d) Mixture
-  (e) Urethane-sized

### Damage area vs. impact energy plots for composite panels with E-glass fibers treated with hybrid, compatible, mixed, and incompatible fiber sizings

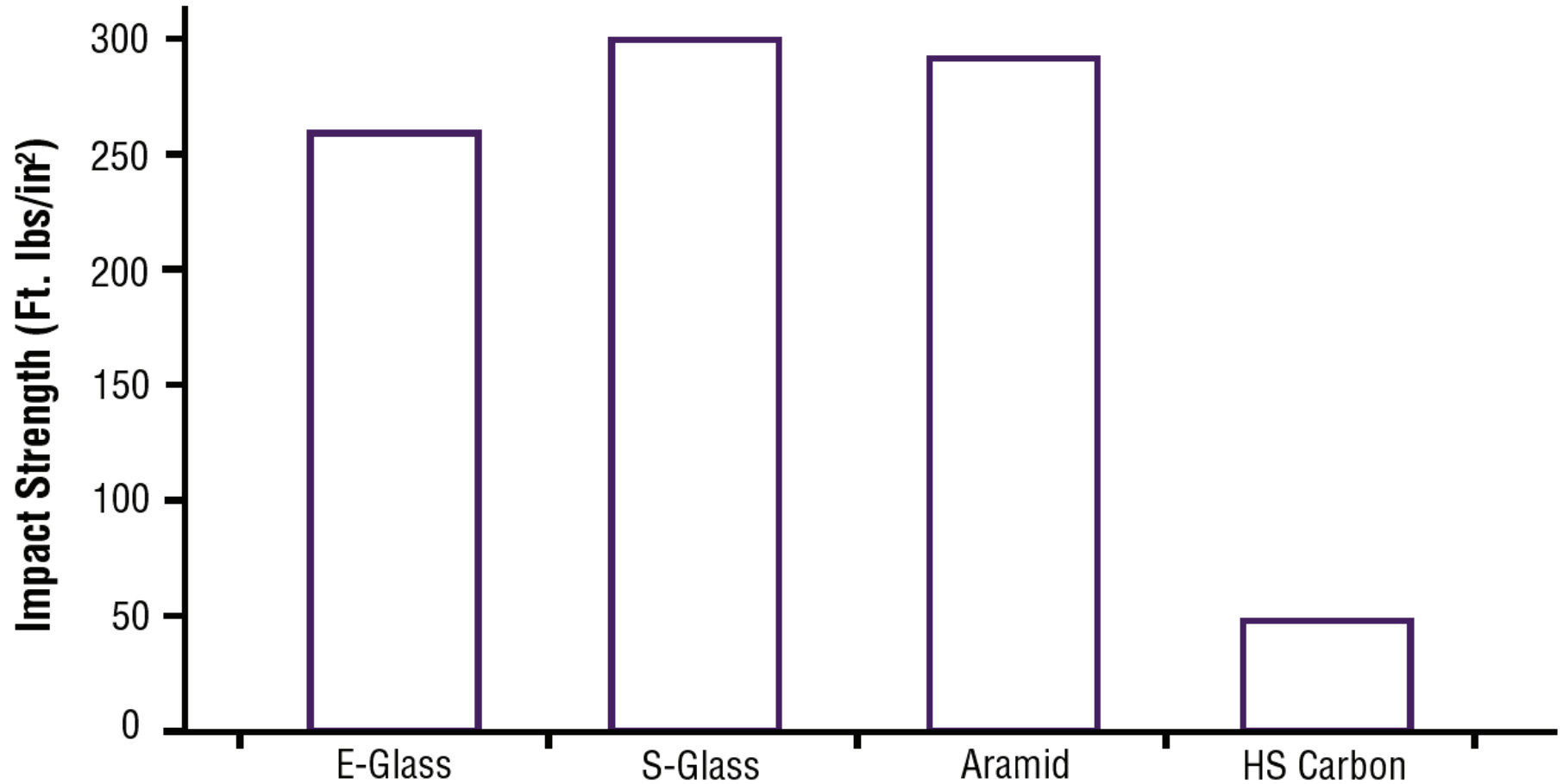


R.E. Jensen and S.H. McKnight, "Inorganic-organic fiber sizings for enhanced energy absorption in glass fiber-reinforced composites intended for structural applications," *Composites Science and Technology*, March 2006



# Impact Strength

## Comparison of Laminate Impact Strength

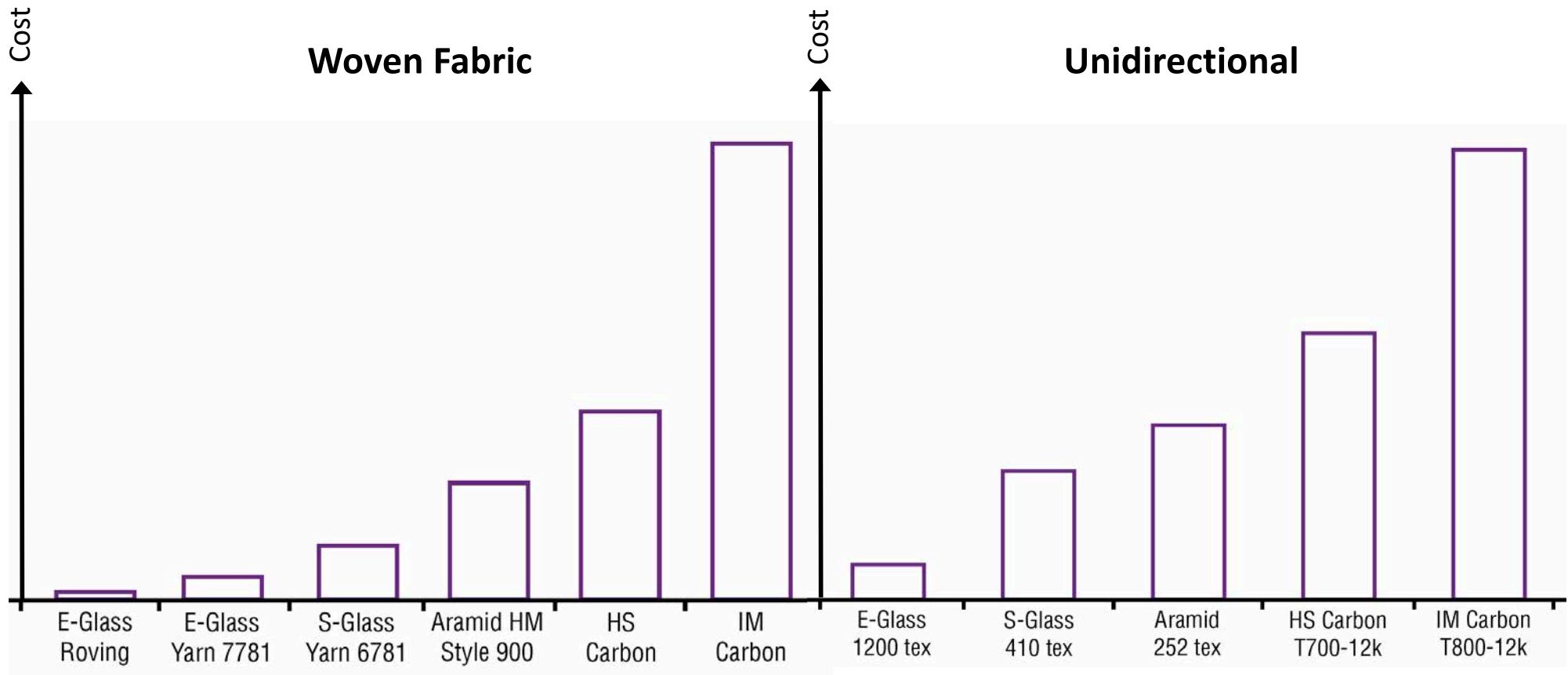


SP Systems, Guide to Composites," GTC-1-1098





# Comparative Fiber Costs



SP Systems, Guide to Composites," GTC-1-1098



# Carbon Fiber Data

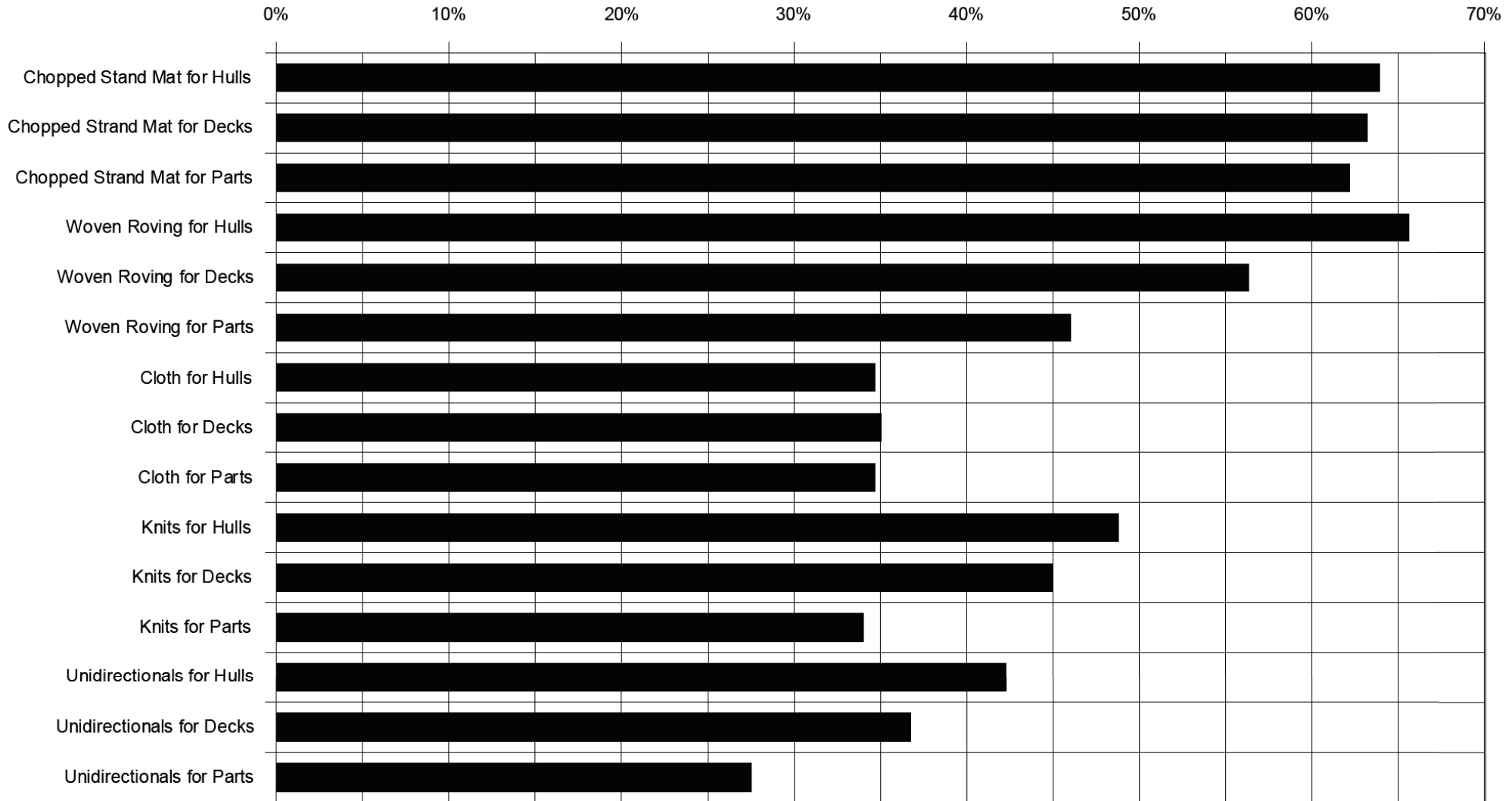
## Strength and Modulus Figures for Commercial PAN-based Carbon Fibers

Grade	Tensile Modulus (GPa)	Tensile Strength (GPa)	Country of Manufacture	Grade	Tensile Modulus (GPa)	Tensile Strength (GPa)	Country of Manufacture
<b>Standard Modulus (&lt;265GPa) (also known as 'High Strength')</b>				<b>High Modulus (320-440GPa)</b>			
T300	230	3.53	France/Japan	M40	392	2.74	Japan
T700	235	5.3	Japan	M40J	377	4.41	France/Japan
HTA	238	3.95	Germany	HMA	358	3.0	Japan
UTS	240	4.8	Japan	UMS2526	395	4.56	Japan
34-700	234	4.5	Japan/USA	MS40	340	4.8	Japan
AS4	241	4.0	USA	HR40	381	4.8	Japan
T650-35	241	4.55	USA	<b>Ultra High Modulus (~440GPa)</b>			
Panex 33	228	3.6	USA/Hungary	M46J	436	4.21	Japan
F3C	228	3.8	USA	UMS3536	435	4.5	Japan
TR50S	235	4.83	Japan	HS40	441	4.4	Japan
TR30S	234	4.41	Japan	UHMS	441	3.45	USA
<b>Intermediate Modulus (265-320GPa)</b>							
T800	294	5.94	France/Japan				
M30S	294	5.49	France				
IMS	295	4.12/5.5	Japan				
MR40/MR50	289	4.4/5.1	Japan				
IM6/IM7	303	5.1/5.3	USA				
IM9	310	5.3	USA				
T650-42	290	4.82	USA				
T40	290	5.65	USA				

SP Systems, Guide to Composites," GTC-1-1098



# Boatbuilder Reinforcement Architectures



data from Eric Greene Associates 1995 survey



# Resin Chemistry

- *Thermoset* resins are characterized by a non-reversible, chemical reaction (cross-linking) during cure that gives off heat (exothermic)
- *Catalysts*, such as MEKP, are mixed in quantities of 1% to 2.5% with the resin just prior to use
- *Inhibitors* are used to slow the rate of cross-linking, which increases the working time of the resin
- *Accelerators*, such as Cobalt, are used to help speed the crosslinking but only work in the presence of initiator. Accelerator and initiator should never come in direct contact or stored together (explosive hazard).
- If a resin is draining down a vertical surface, the “*thixotropic index*” can be increased with an additive, such as silicon dioxide
- The typical shelf life of un-catalyzed polyester resin is 90 days when stored in a controlled temperature environment protected from fire



# Thermoset Resins

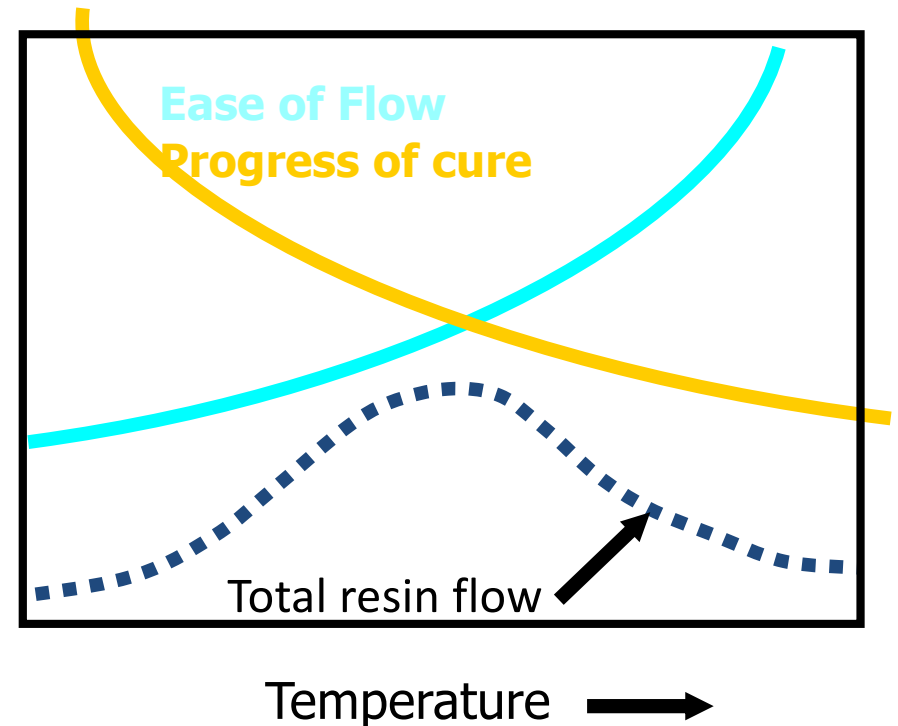
- Generally supplied as a liquid
- Cross-linked (cured) by chemicals (and heat)
  - heat reduces the instantaneous viscosity
  - heat increases the rate of cure
  - cure decreases the viscosity over time
- Product is a 3D molecular network whereas a thermoplastic is usually a 2D chain

## Stages of Cure

A-stage: soluble and fusible

B-stage: may be swollen but not dissolved by a variety of solvents

C-stage: rigid, hard, insoluble, infusible



John Summerscales, University of Plymouth, Jan., 2013



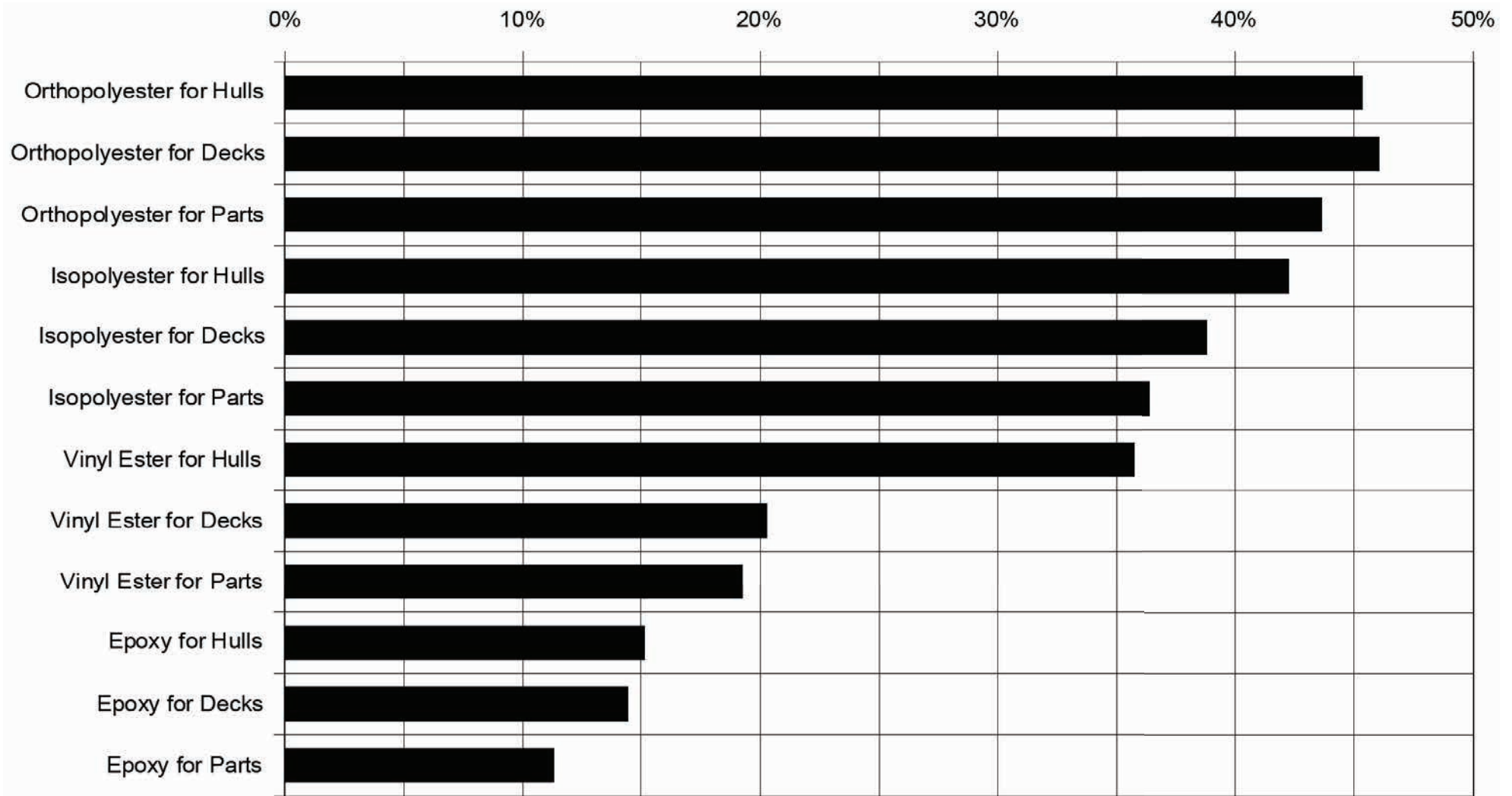
# Resin System Mechanical Properties

Property	Ortho Polyester	Iso Polyester	Vinylester	Laminating Epoxy	Multi-Purpose Epoxy
Tensile Strength (Mpa)	41	61	79	83	50
Tensile Modulus (Mpa)	3480	3380	3380	3650	3170
Tensile Elongation	1.2%	1.6%	5.0%	9.0%	10.0%
Heat Distortion Temperature (°C)	65	97*	105-120*	110*	54
Shrinkage	9.00%	8.20%	7.80%	0.75%	0.80%

\* Post-cured property [ATL Composites Pty Ltd]



# Boatbuilder Resin Use



data from Eric Greene Associates 1995 survey



# Resin System Comparison

## Polyester

Polyester resins are the simplest, most economical resin systems that are easiest to use and show good chemical resistance.

- *Orthophthalic (ortho)* resins were the original group of polyesters developed and are still in widespread use. They have somewhat limited thermal stability, chemical resistance, and processability characteristics.
- *Isophthalic (iso)* resins generally have better mechanical properties and show better chemical resistance.
- *Low-profile resins (DCPD)* are blends designed to minimize reinforcement print-through. Typically, ultimate elongation values are reduced for these types of resins.

## Vinyl Ester

The handling and performance characteristics of vinyl esters are similar to polyesters. Some advantages of the vinyl esters, which may justify their higher cost, include:

- Superior corrosion resistance
- Hydrolytic stability (blister resistance)
- Better secondary bonding properties
- Excellent physical properties, such as impact and fatigue resistance.

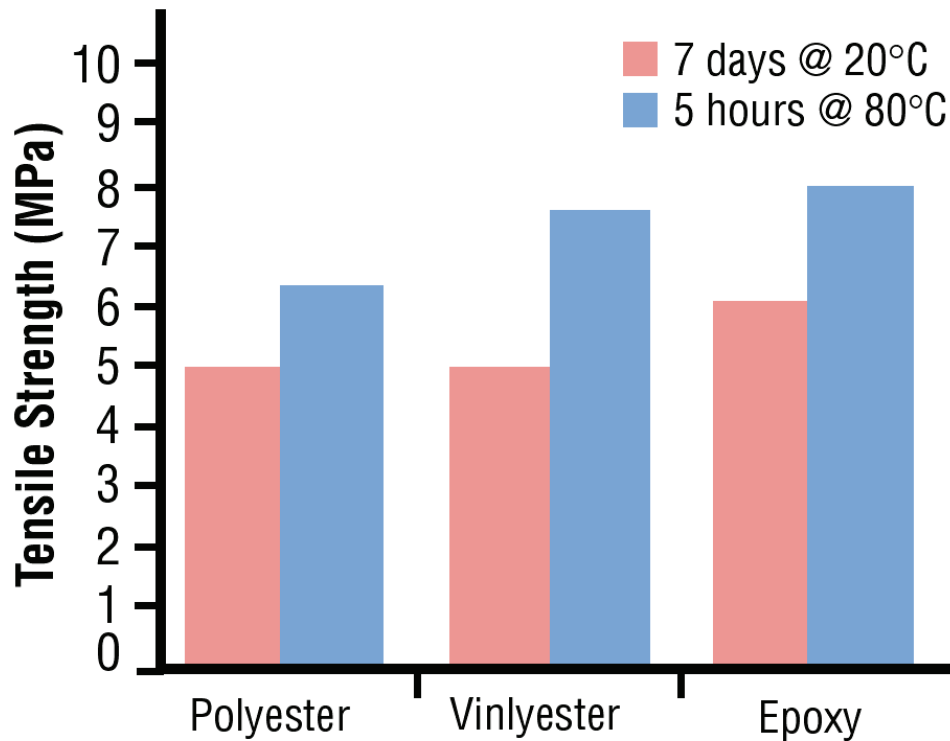
## Epoxy

- Epoxy resins show the best performance characteristics of all the resins used in the marine industry.
- Aerospace applications use epoxy almost exclusively, except when high temperature performance is critical.
- The high cost of epoxies and handling difficulties have limited their use for large marine structures to date.
- Epoxies are considered environmentally-friendly because styrene isn't released into the atmosphere during fabrication.

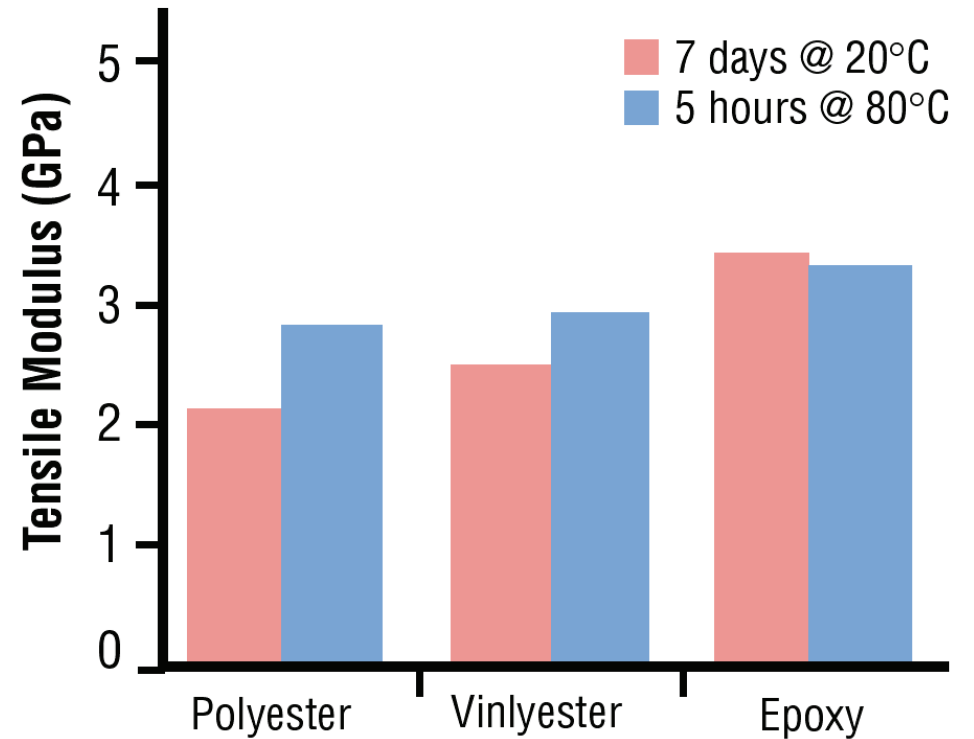




# Compare Resin Properties



Comparative Tensile Strength of Resins

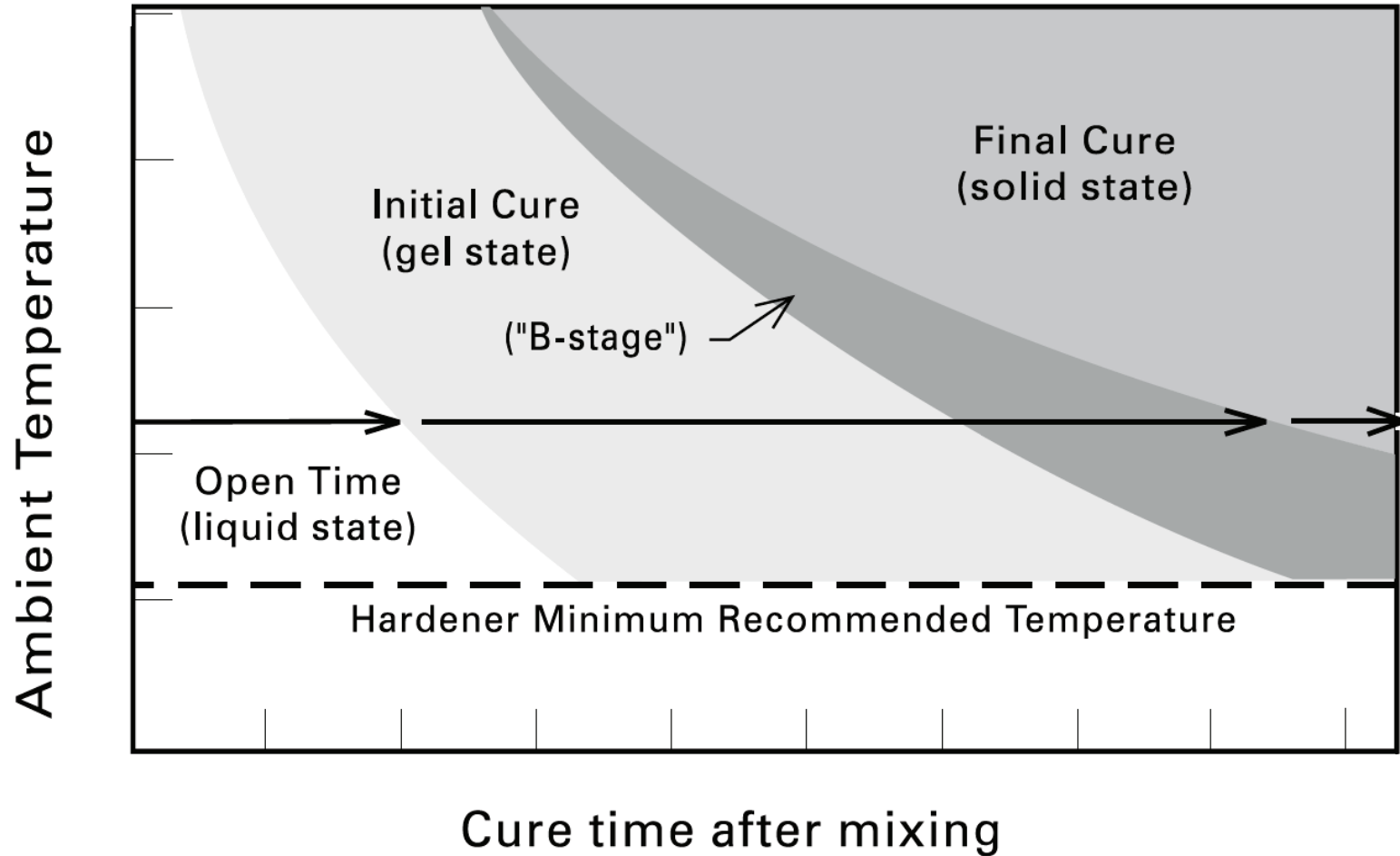


Comparative Stiffness of Resins

SP Systems, Guide to Composites," GTC-1-1098



# Epoxy Curing Stages

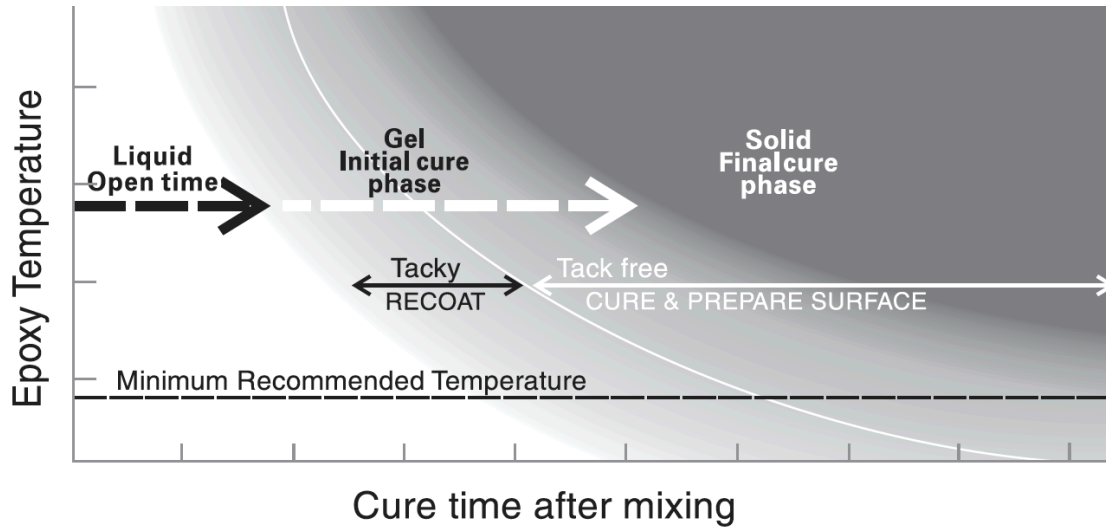


Pro-Set Epoxy Handling Guide, Pro-Set, Inc., Aug 2005



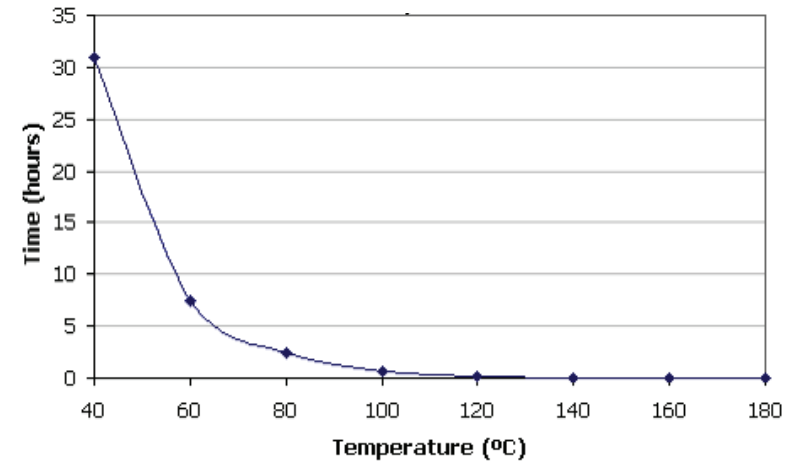
# Epoxy Cure Profile

## Typical cure characteristics of epoxy resin systems



Gougeon Brothers Inc., "WEST System Fiberglass Boat Repair & Maintenance," 15th Edition, April 2011

## Typical gel time of epoxy resin systems



John Summerscales, University of Plymouth, Jan., 2013

## Epoxy Cure Temperatures

- Low temperature - ambient to 60°C (140°F)
- Medium temperature - up to 120°C (250°F)
- High temperature - up to 180°C (360°F)



# Phenolic Resin

- Generally brittle due to moisture released during curing
- Exceptional Fire, Smoke & Toxicity (FST) properties when burning:
  - Low flame spread
  - Low smoke production
  - Low smoke toxicity - only CO<sub>2</sub> and H<sub>2</sub>O released
- Key markets:
  - underground railways
  - mining
  - Submarines
- First truly synthetic resins to be exploited - Baekeland (1907) controlled and modified the reaction to produce useful products (Bakelite)

John Summerscales, University of Plymouth, Jan., 2013



## Gel Coat

- Gel coat is a specially formulated resin system designed to be on the surface of the laminate and cure as a thin layer. In the U.S., it is typically applied using an atomized spray gun
- Gel coat typically consists of an unsaturated polyester resin (polyester) base, pigment, and various other additives. Styrene added to gel coat increases its workability but can lead to cracking and yellowing problems.
- Gelcoat is used to enhance cosmetic appearance, reduce water absorption, and protect laminate from the environment. Additives help fine-tune a gelcoat's properties. Pigment develops the quality and color of gelcoat. Fillers change viscosity, adhesiveness, and/or cured properties.



# Volatile Organic Compounds

Resin System	Volatile % (by weight)	VOC Content (g/L)	VOC Emissions (g/m <sup>2</sup> )
Multi-purpose epoxy resin (A)	1.5	17.7	11.2
Multi-purpose epoxy resin (B)	2.1	25.0	15.9
Multi-purpose epoxy resin (C)	1.6	18.2	11.6
Multi-purpose epoxy resin (D)	1.6	18.0	11.5
High perf. laminating epoxy (A)	0.5	5.9	3.8
High perf. laminating epoxy (B)	0.5	6.0	3.9
High perf. laminating epoxy (C)	0.5	5.3	3.3
High perf. laminating epoxy (D)	0.6	6.9	4.4
iso-NPG Gelcoat	5.6	196.0	124.5
Gelcoat Patch additive	19.0	196.0	124.1
Vinylester Resin	35.0	367.0	233.2
Polyester Laminating Resin	15.7	174.0	110.7

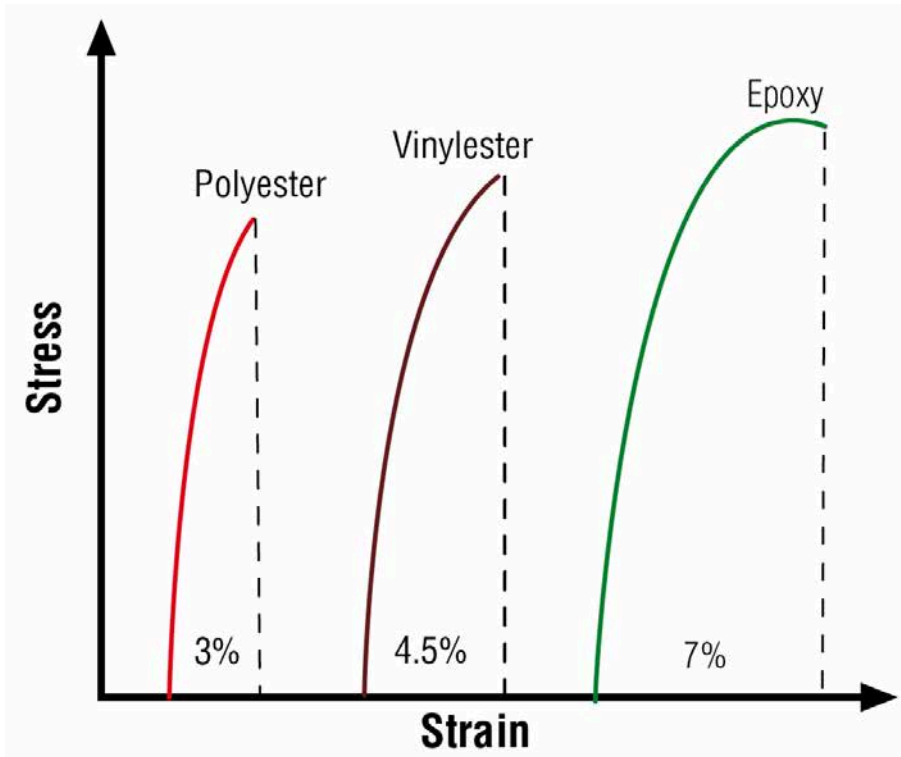
ATL Composites, Australia

According to the EPA, “volatile organic compounds (VOCs) are emitted as gases from certain solids or liquids. VOCs include a variety of chemicals, some of which may have short- and long-term adverse health effects.”

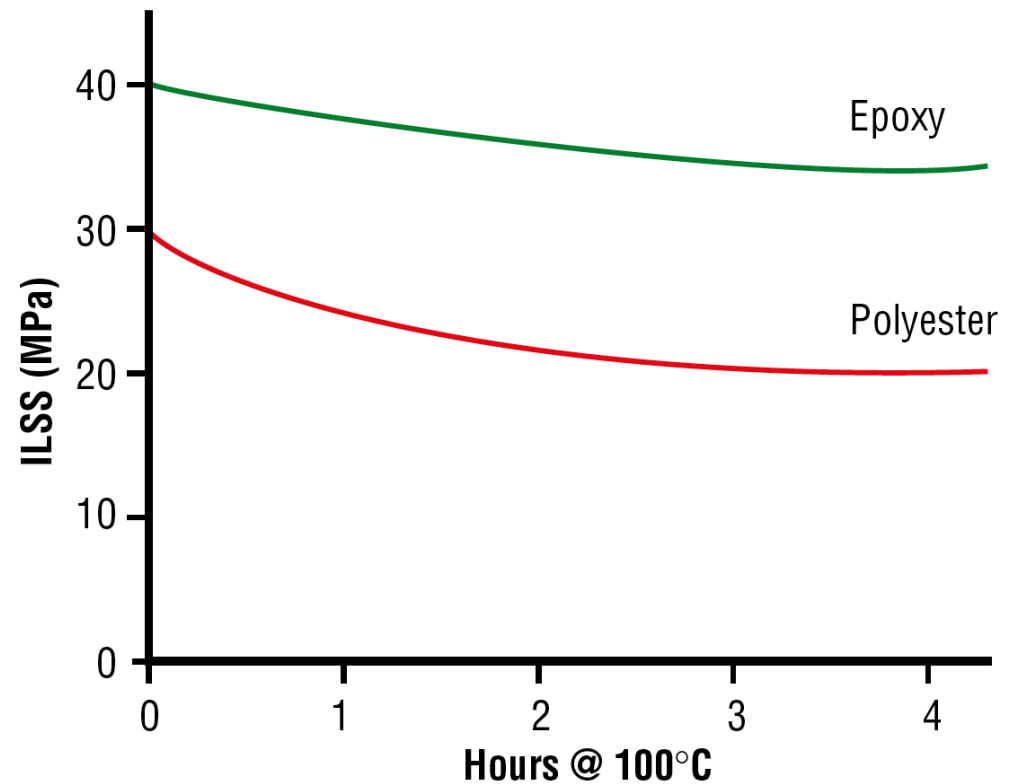


# Compare Strain and Moisture Effects

### Typical Resin Stress/Strain Curves (Post-Cured for 5 hrs @ 80°C)



### Effect of Periods of Water Soak at 100°C on Resin Inter-Laminar Shear Strength



SP Systems, Guide to Composites," GTC-1-1098