Marine Composites

Webb Institute
Senior Elective

Environmental Degradation

Eric Greene, Naval Architect
EGAssoc@aol.com
410.703.3025 (cell)
http://ericgreeneassociates.com/webbinstitute.html

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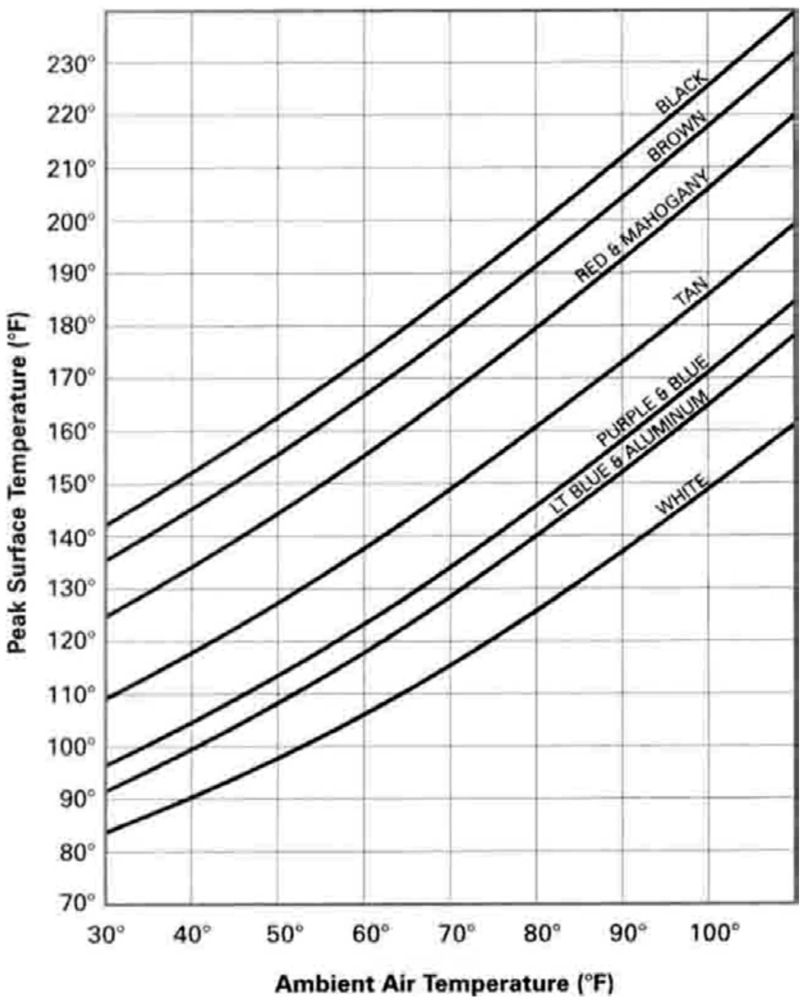
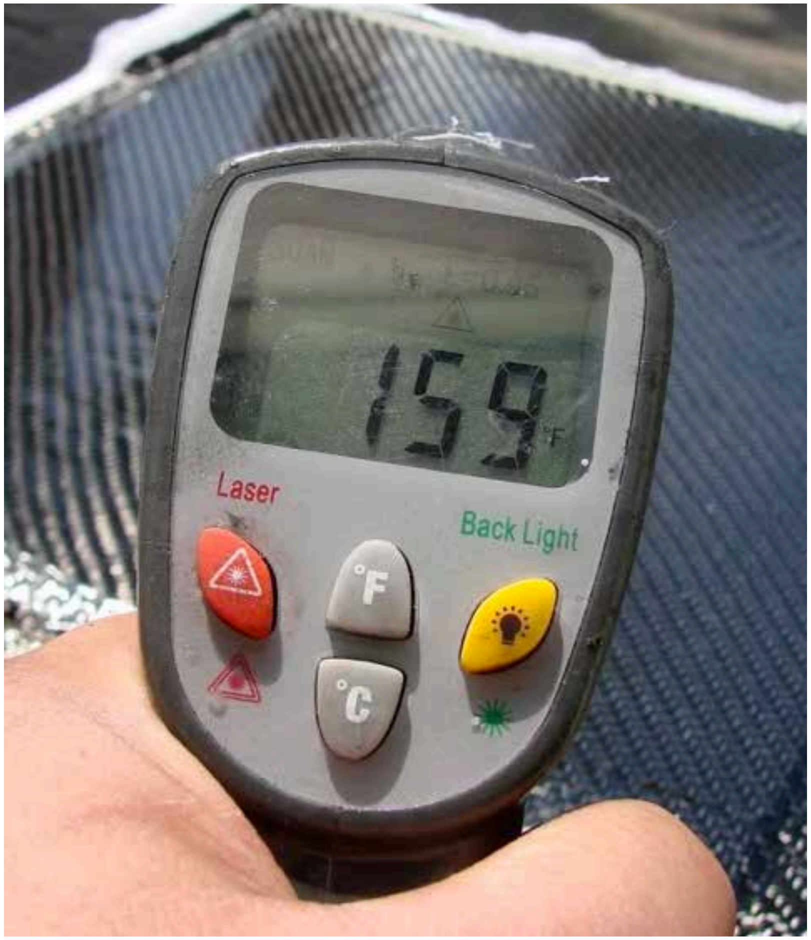
Surface Temperature

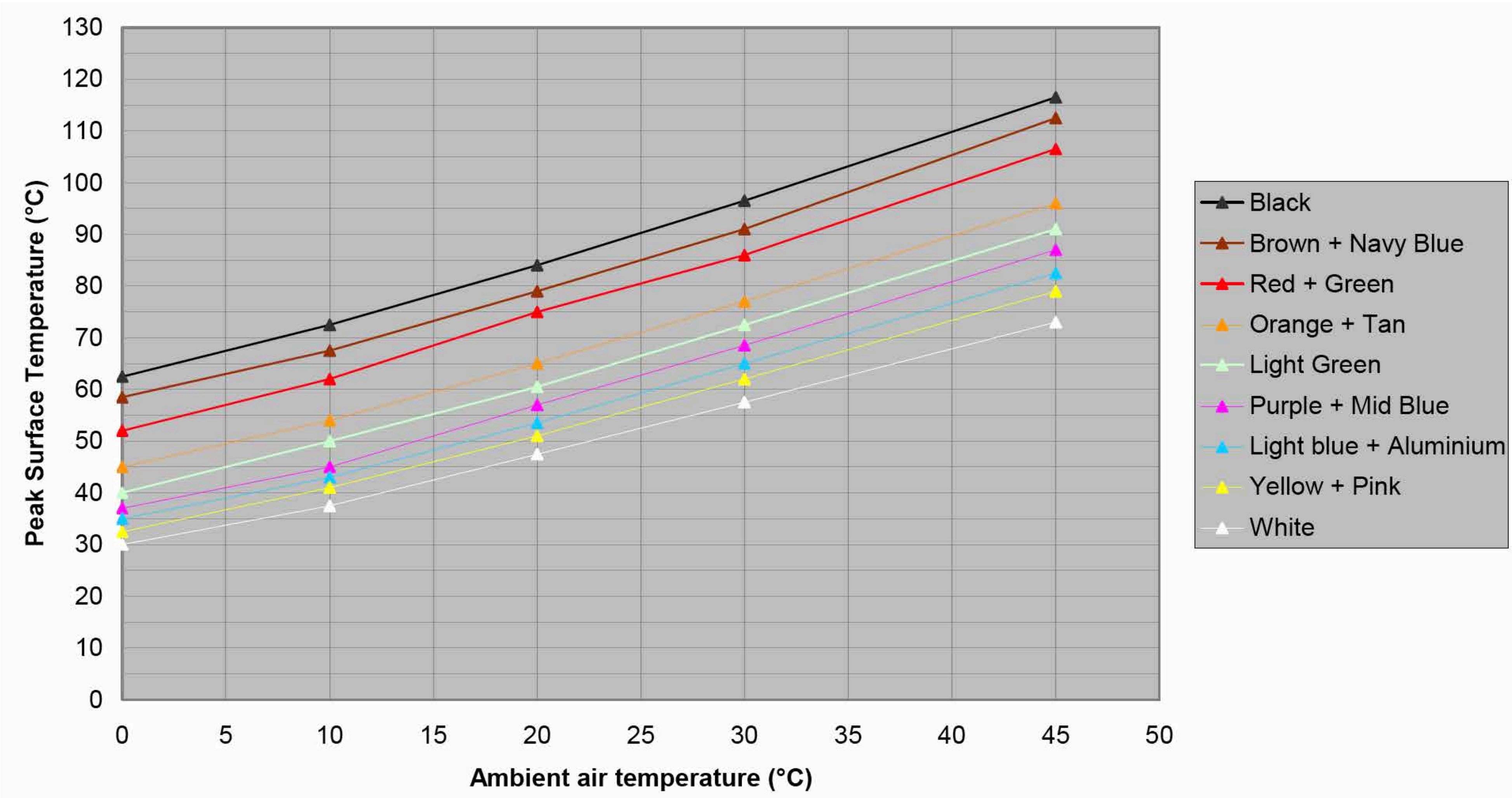
Anticipated Surface Temperature as a Function of Color and Ambient Temperature



Surface temperature of curing laminate after 4 hours



Color and Surface Temperature

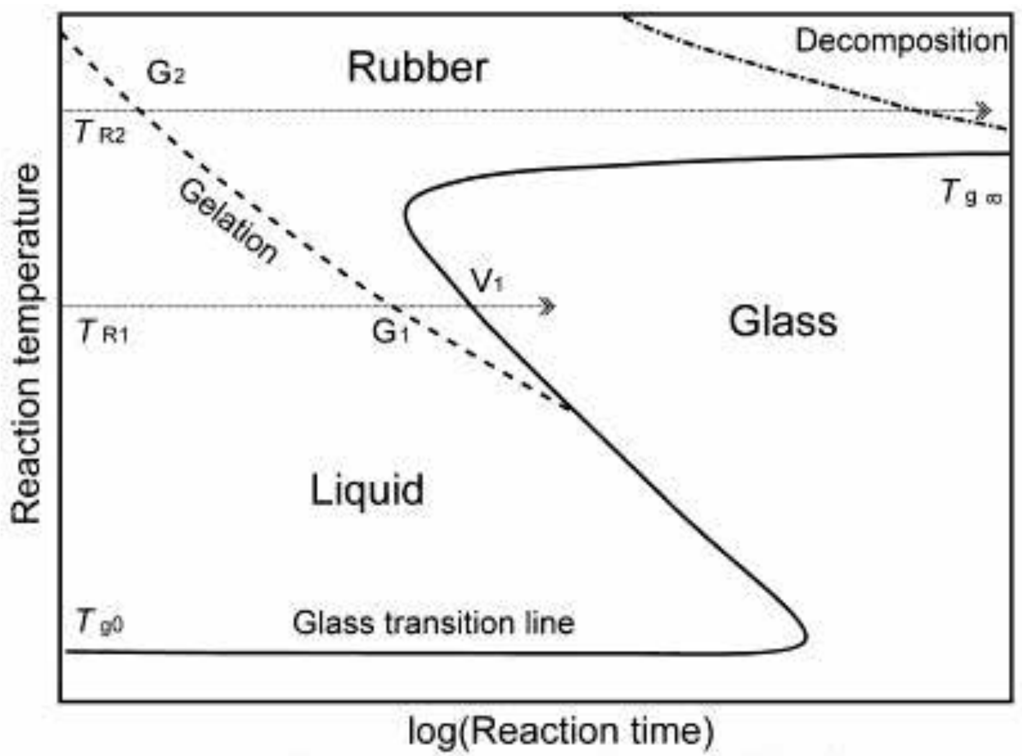


John Howard and Matt Searle, "Surface print on marine structures," SP Systems, May 2005

Glass Transition Temperature, Tg

The glass transition temperature (Tg) of a non-crystalline material is the critical temperature at which the material changes its behavior from being 'glassy' to being 'rubbery'. 'Glassy' in this context means hard and brittle (and therefore relatively easy to break), while 'rubbery' means elastic and flexible.

Time-temperature-transformation cure diagram

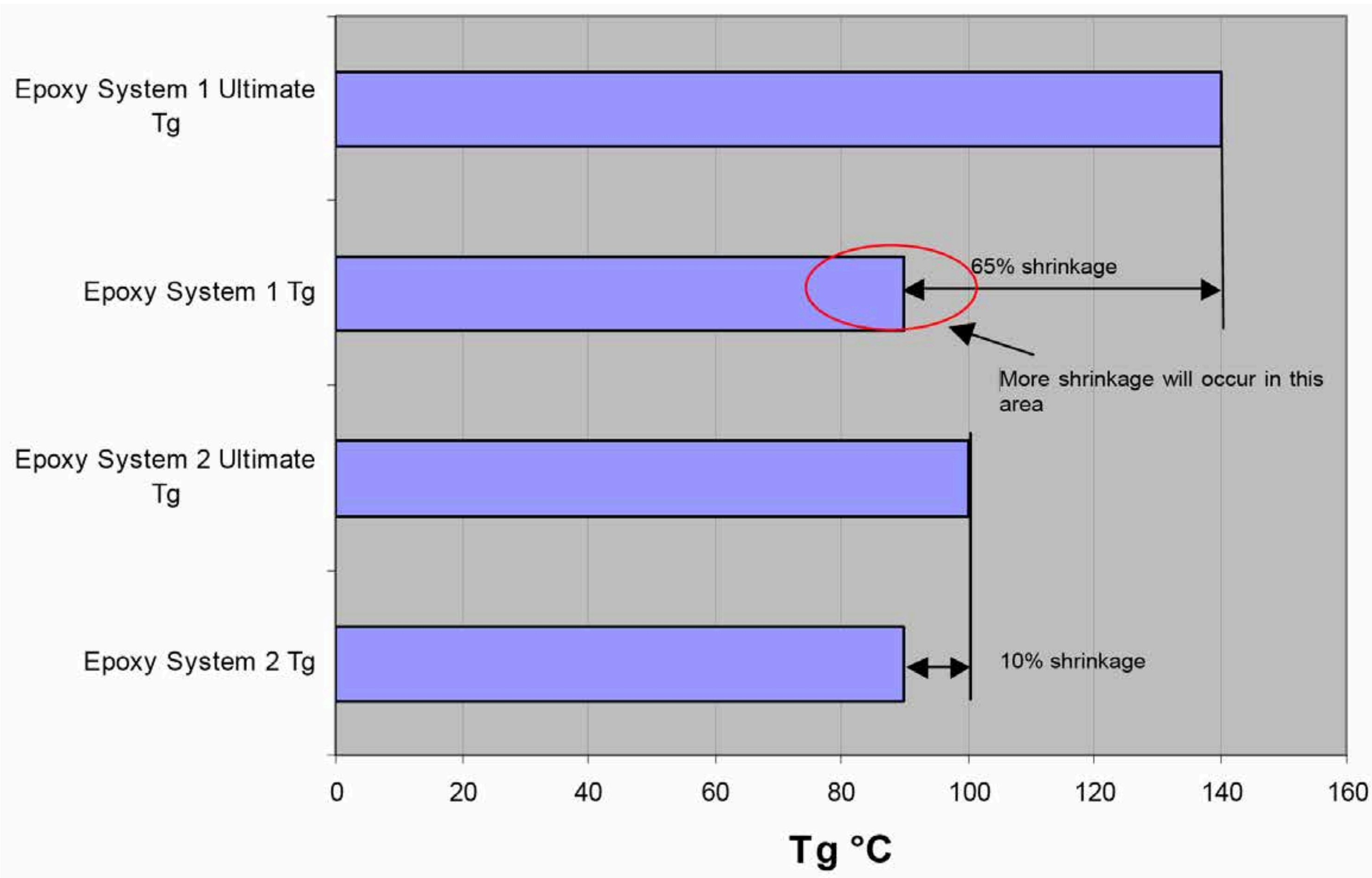


At a curing temperature T_{R2}, the gelation line (dashed line) is reached after a relatively short time, the material gels (gel point G_2) and is transformed to the rubbery state, and cross-linking continues until curing is complete. The curing temperature is thus always higher than the maximum possible glass transition temperature $T_{g\infty}$. Below T_{g0}, the resin is in the glassy state and the reaction is practically blocked.

Steve Sauerbrunn and Rudolf Riesen, "Thermosets: How to Avoid Incomplete Curing," www.americanlaboratory.com, Jan, 2010.

Resin Ultimate Tg and Shrinkage

If epoxy system 1 is exposed to temperatures just over 90°C a higher level of shrinkage will occur compared to epoxy system 2. This is because 90% of the cure as taken place, as cure has an exponential relationship less physical shrinkage will occur in the last 10% of cure.



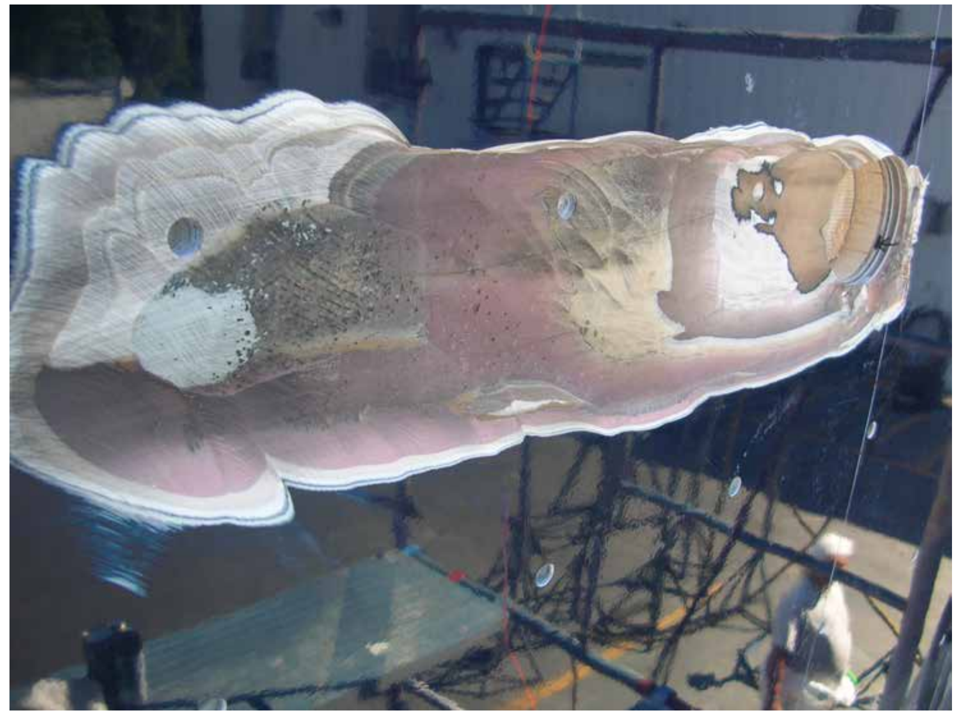
Epoxy system 1 has an ultimate Tg 140°C and epoxy system 2 has an ultimate Tg 100°C, both systems have been post cured to gain a Tg of 90°C.

John Howard and Matt Searle, "Surface print on marine structures," SP Systems, May 2005

Post Cure Print-Through

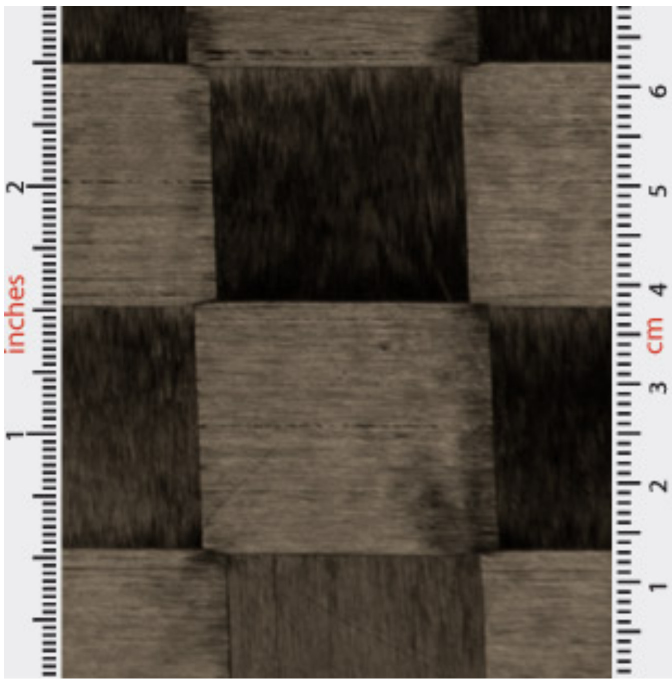
Typical reinforcement print-through problem when dark laminate "post cures"

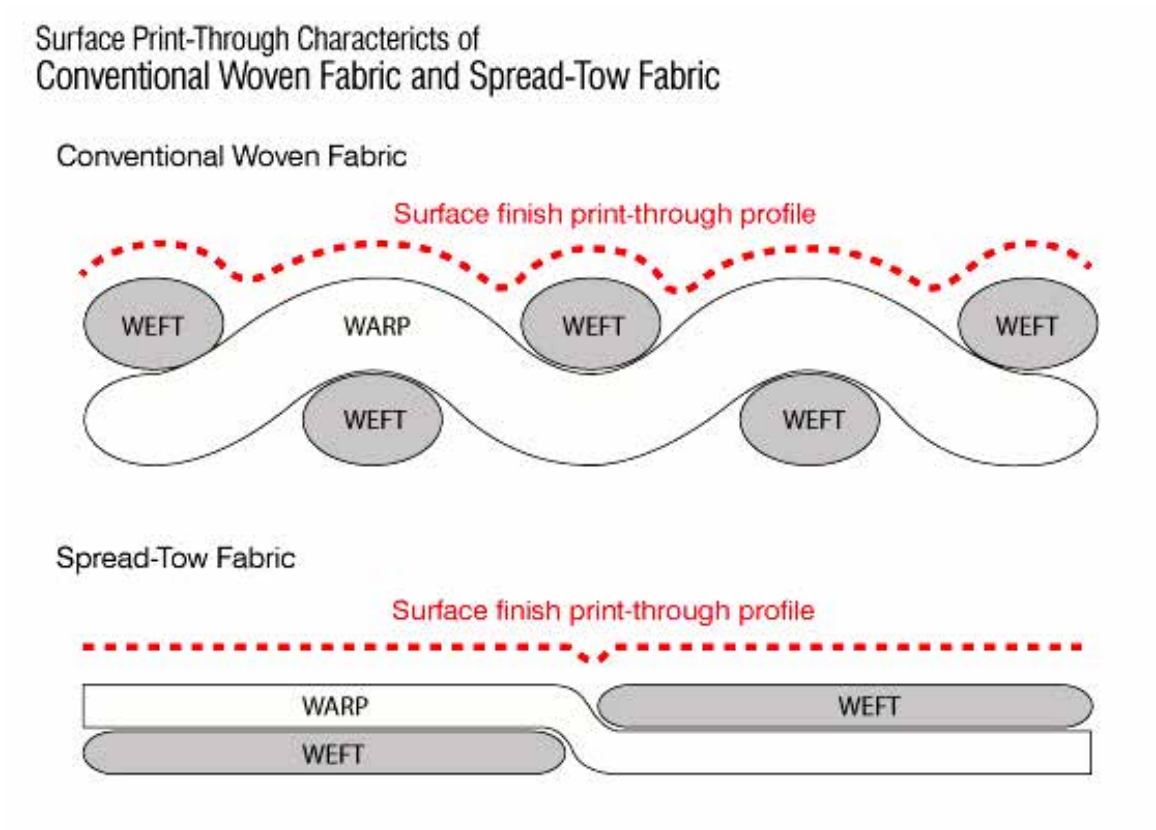
Porous fillers can create surface defects



Fiber Influences Print-Through

"Spread tow" is a new development in carbon fiber reinforcement whereby a sophisticated production process spreads out each tow (bundle) of carbon fibers making them significantly flatter and wider than they would be in a conventional woven fabric.

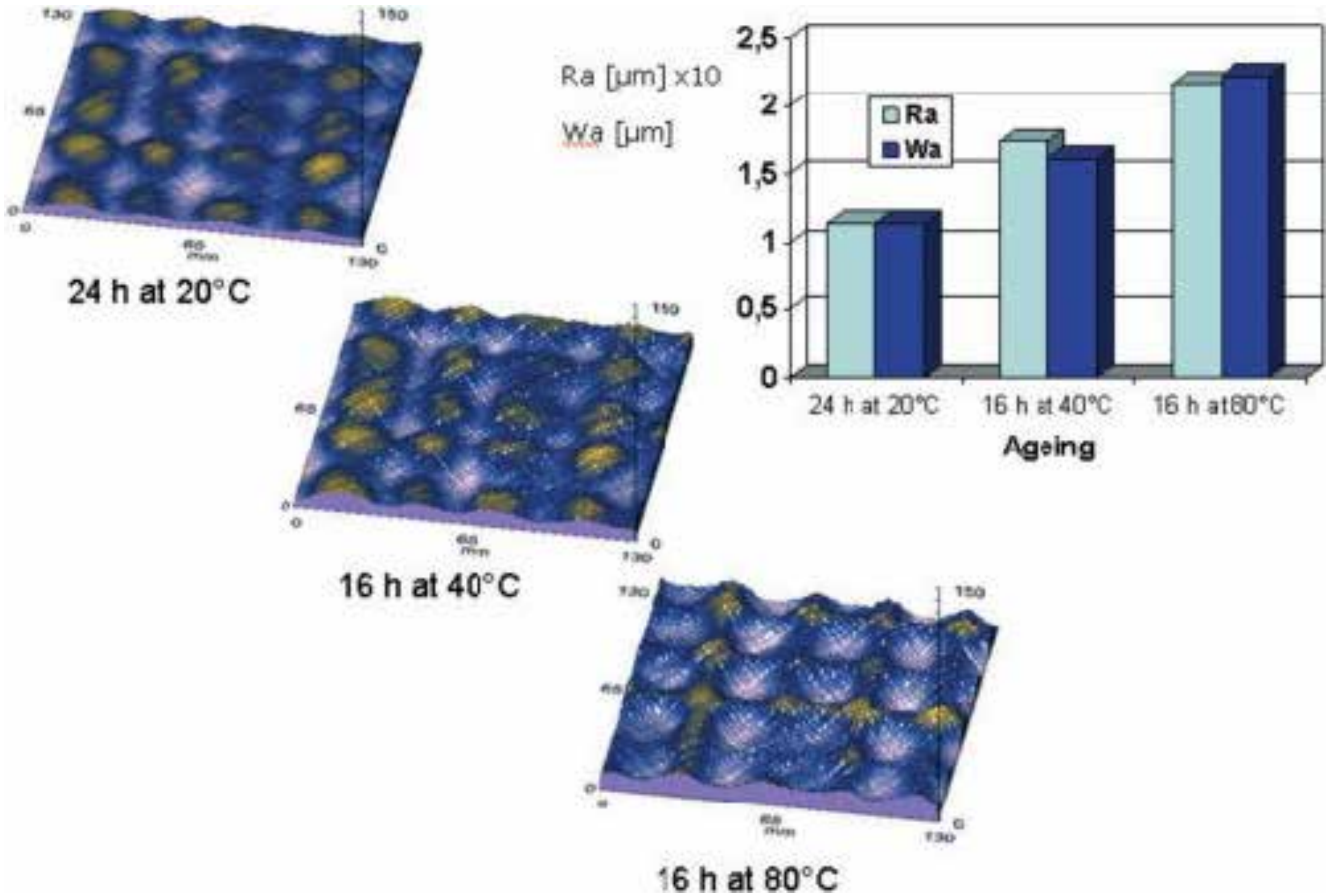




http://www.easycomposites.co.uk/products/carbon-fibre-cloth-fabric/carbon-fibre-spread-tow-20mm-very-large-pattern-plain-weave-SAMPLE.aspx

Quantifying Print-Through

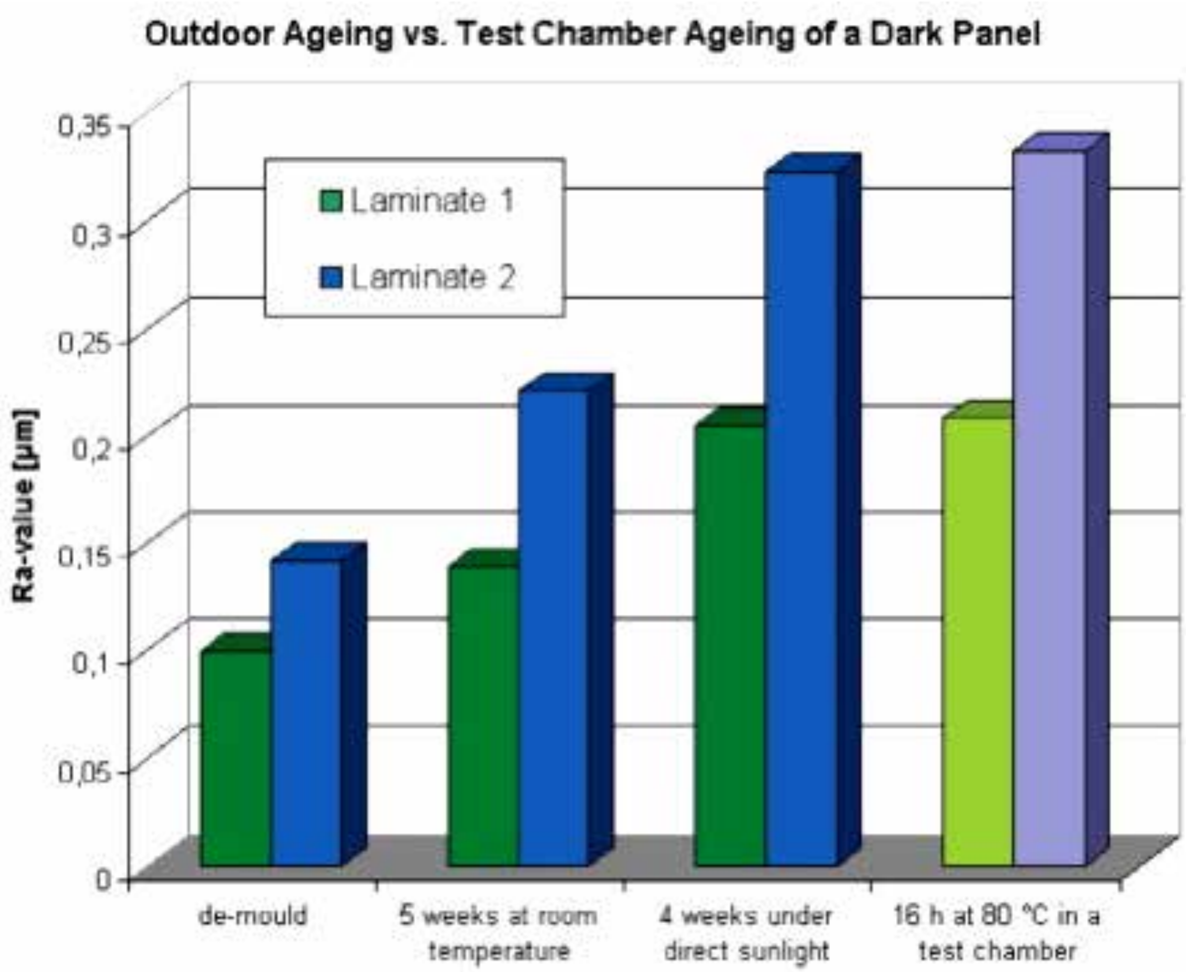
Exaggerated 3D-views from the same surface area after different ageing steps. Corresponding Ra (roughness average) and Wa (waviness average) values are displayed on the right. The size of the measured area was 130 by 130 mm.



Rainer Bergström, Olli Piiroinen and Antti Ylhäinen, “Improving surface quality in vacuum infused parts,” *Reinforced Plastics*, March 2008

Post Cure Print-Through Influence

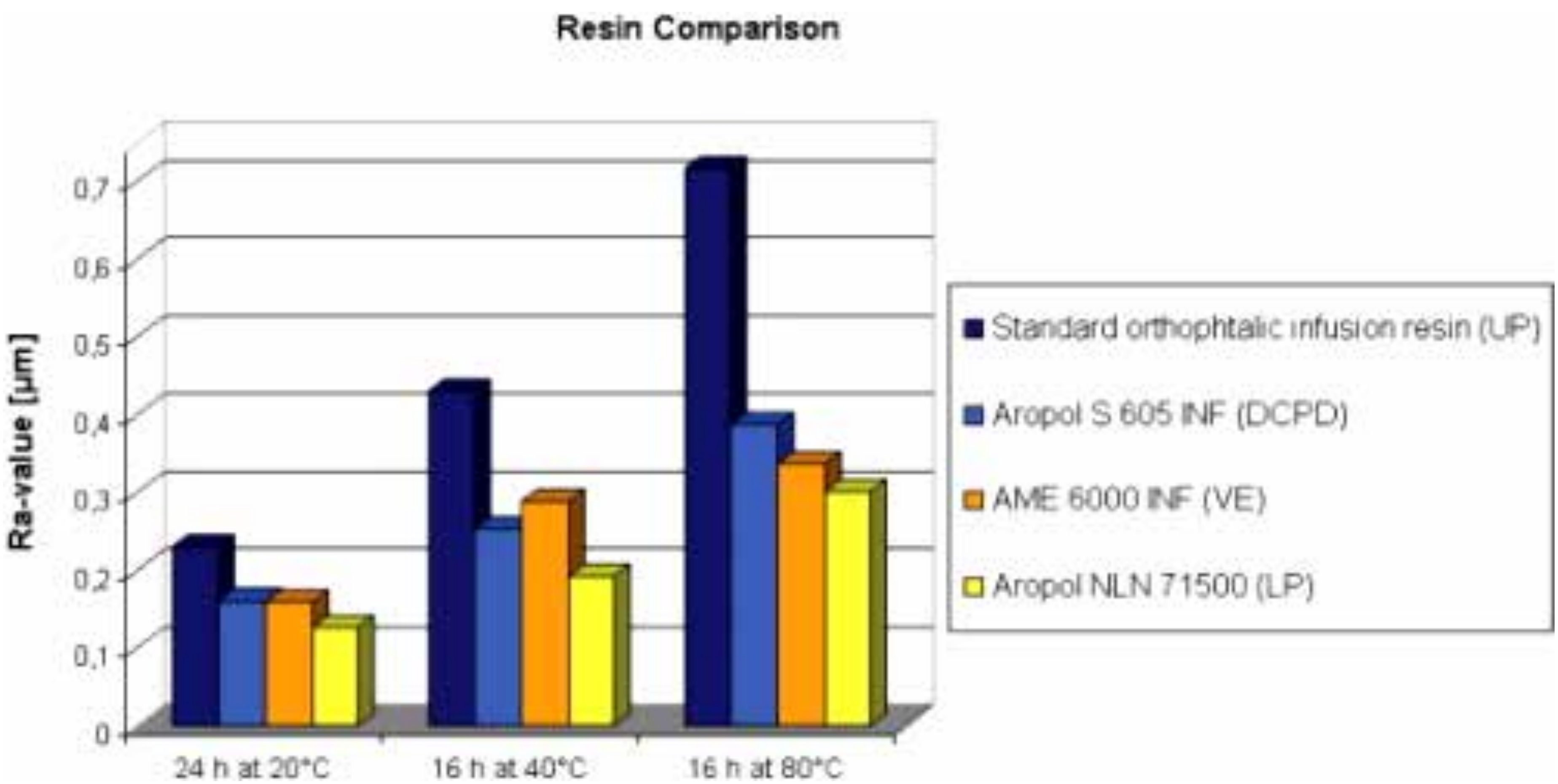
Comparison between outdoor and test chamber ageing. Two different laminates showed similar change in Ra-value with both ageing methods.



Rainer Bergström, Olli Piiroinen and Antti Ylhäinen, “Improving surface quality in vacuum infused parts,” *Reinforced Plastics*, March 2008

Resin Print-Through Influence

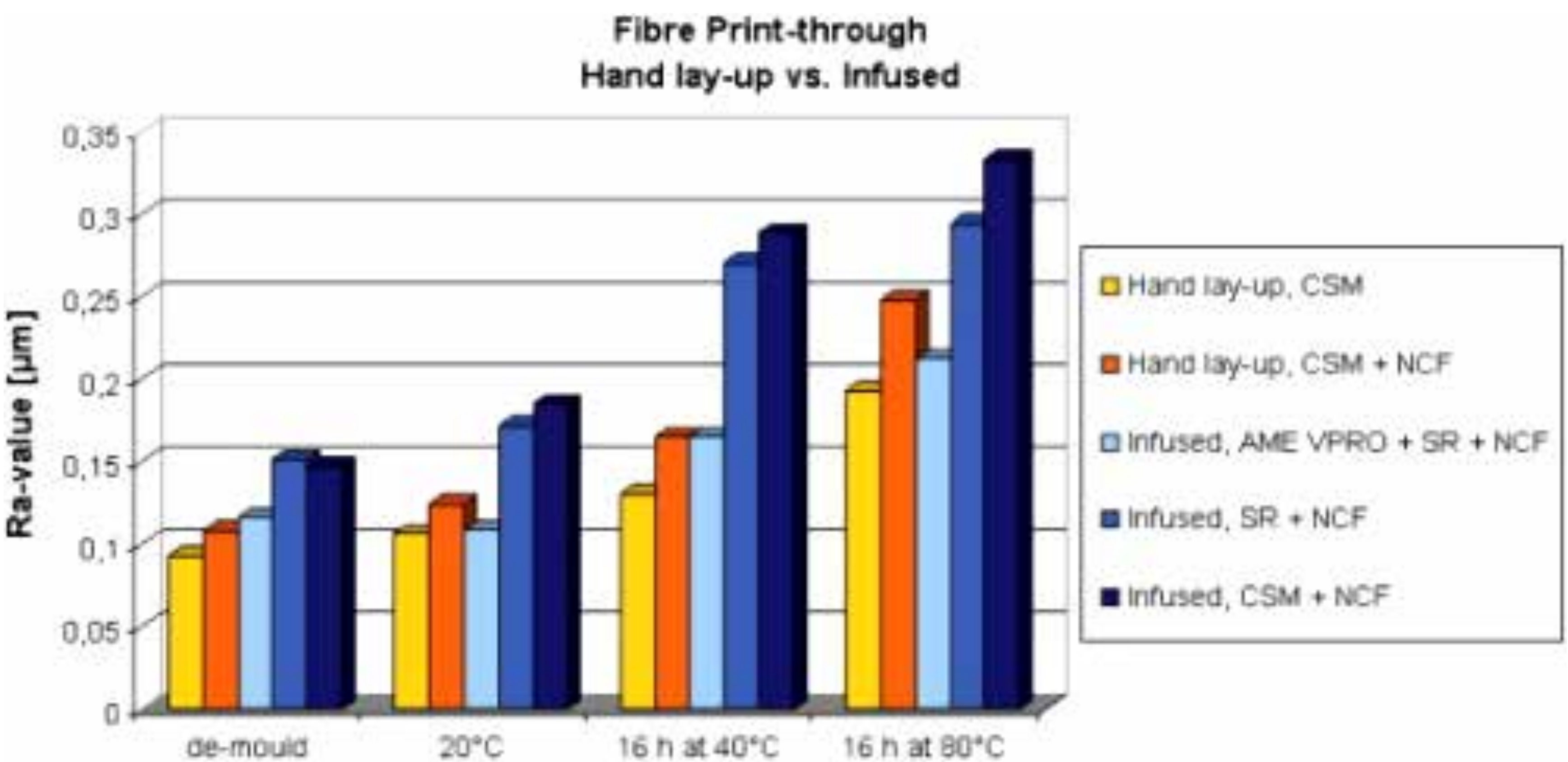
Different resins showed different surface quality properties. Note, in resin comparison all laminates were made without using a surface improving layer (skin or barrier coat).



Rainer Bergström, Olli Piiroinen and Antti Ylhäinen, "Improving surface quality in vacuum infused parts," *Reinforced Plastics*, March 2008

Infusion and Print-Through

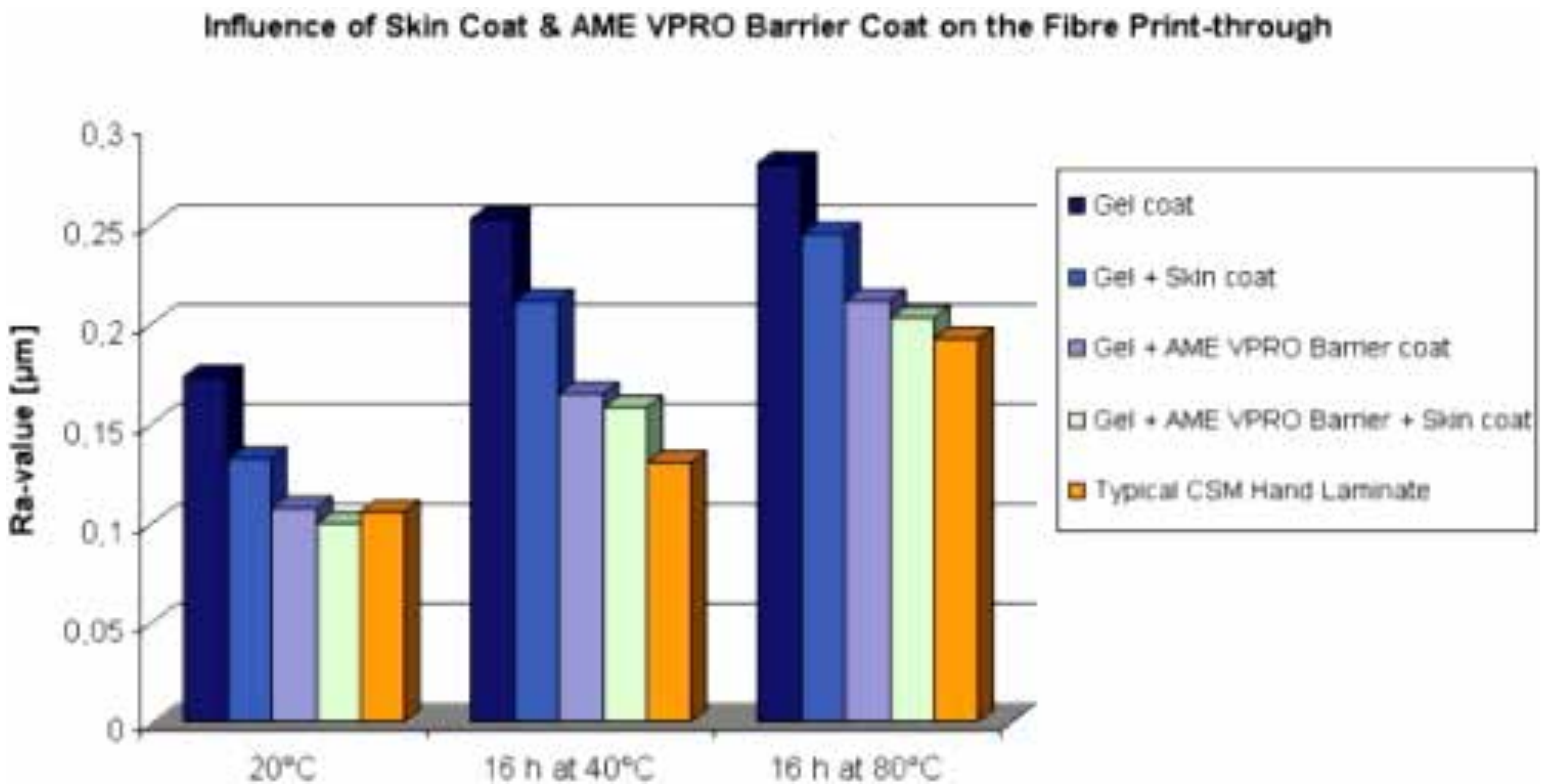
Influence of various reinforcement types and lamination methods on surface quality. Note that 2nd and 5th column consist of similar reinforcements.



Rainer Bergström, Olli Piiroinen and Antti Ylhäinen, "Improving surface quality in vacuum infused parts," *Reinforced Plastics*, March 2008

Print-Through Barrier Layers

Both skin and barrier coats lowered the fiber print-through. The surface quality of AME VPRO barrier laminate was eventually close to a typical CSM hand laminate level.



Rainer Bergström, Olli Piiroinen and Antti Ylhäinen, "Improving surface quality in vacuum infused parts," *Reinforced Plastics*, March 2008

Typical Material Property Temperature Reduction Factors

Temperature	Infused E-Glass/ Vinylester	End Grain Balsa	Foam Cores	'H' Type Foam Cores	'HT' Type Foam Cores
23°C (74°F)	1.0	1.0	1.0	1.0	1.0
52°C (125°F)	0.85	1.0	0.9	0.70	0.90
63°C (145°F)	0.84	1.0	0.7	0.60	0.80
79°C (175°F)	0.72	1.0	0.5	0.40	0.70
88°C (190°F)	0.60	1.0	0.3	0.30	0.60

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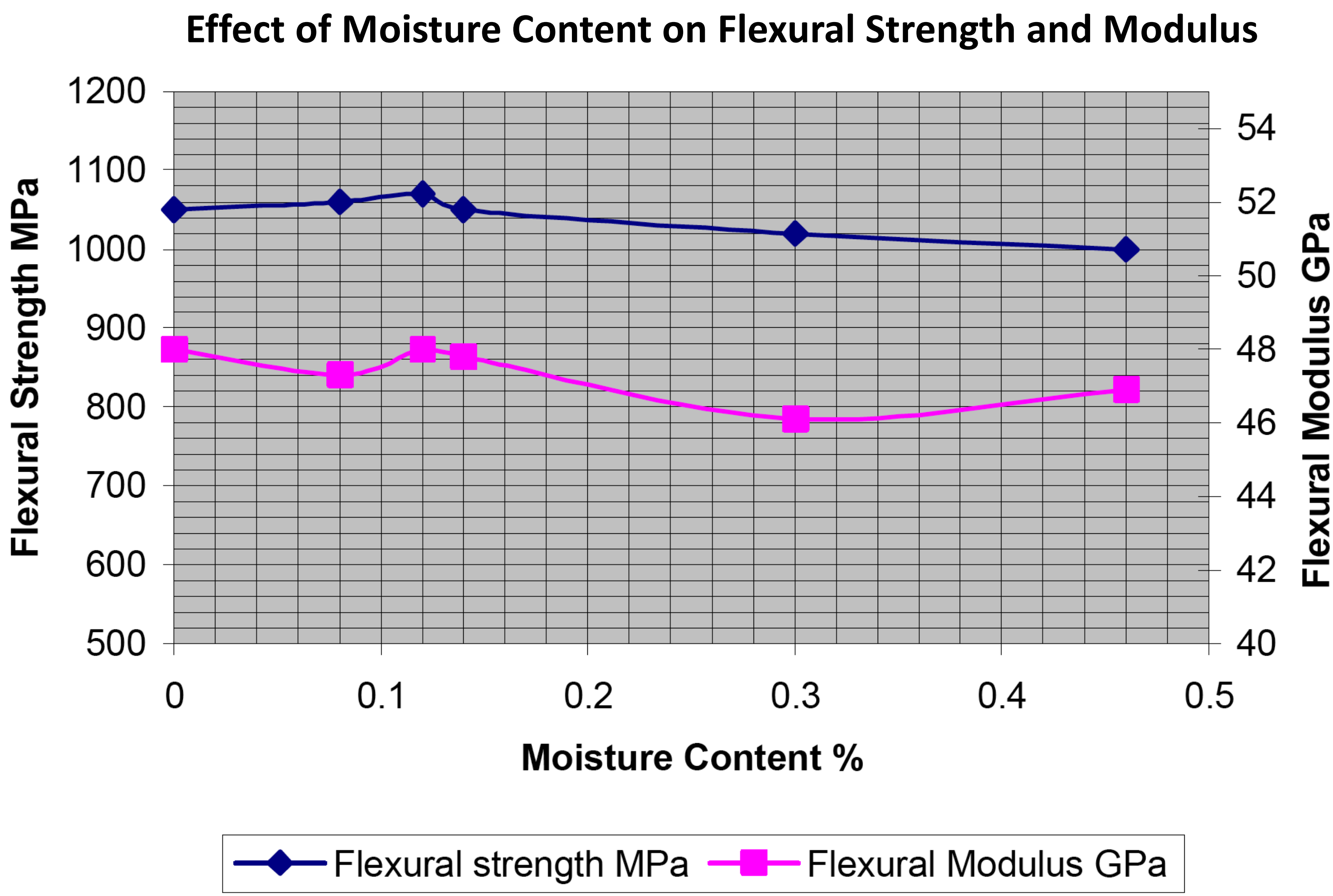
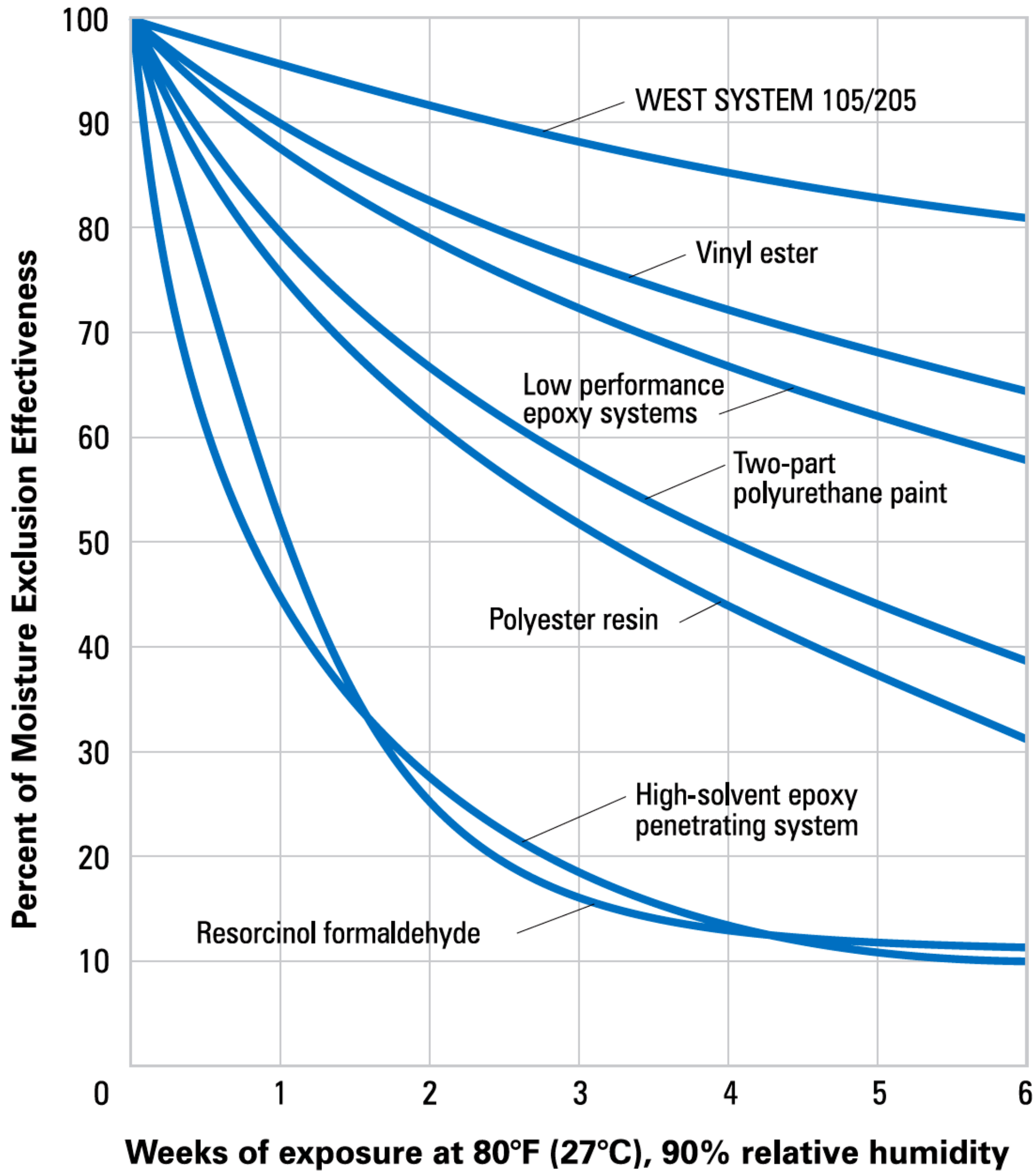
Moisture Effects



J. A. Quinn, "Composites – Design Manual," 3rd Edition, Liverpool, England, 2002.

Moisture Exclusion



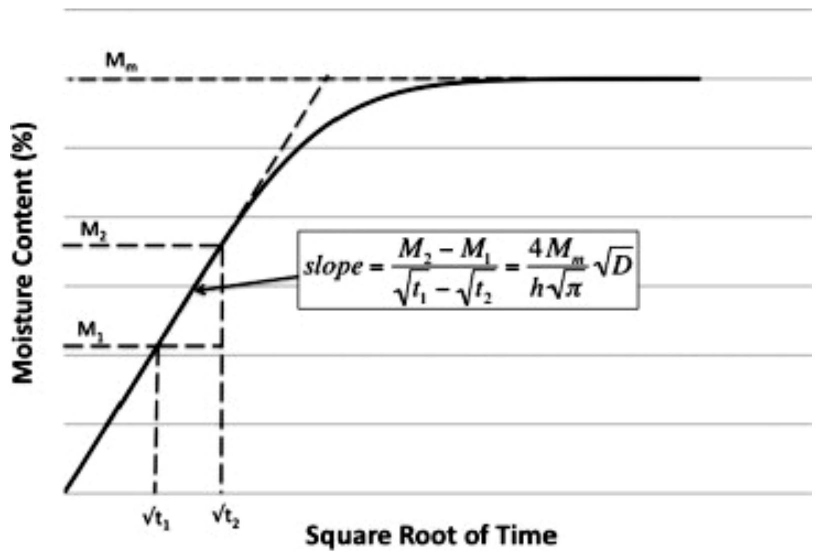
Moisture exclusion effectiveness (MEE) of various marine materials. Comparison of three coats of each material.

Gougeon Brothers, Inc., "The Problem of Gelcoat Blisters in Fiberglass Boats," 9th Edition, June 2007

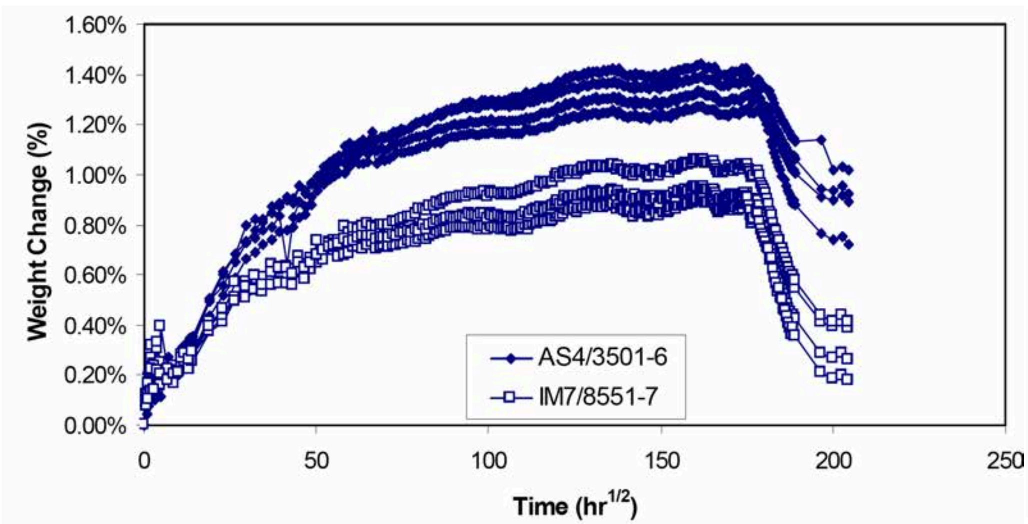
Fickian Diffusion

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \text{ in one dimension.}$$

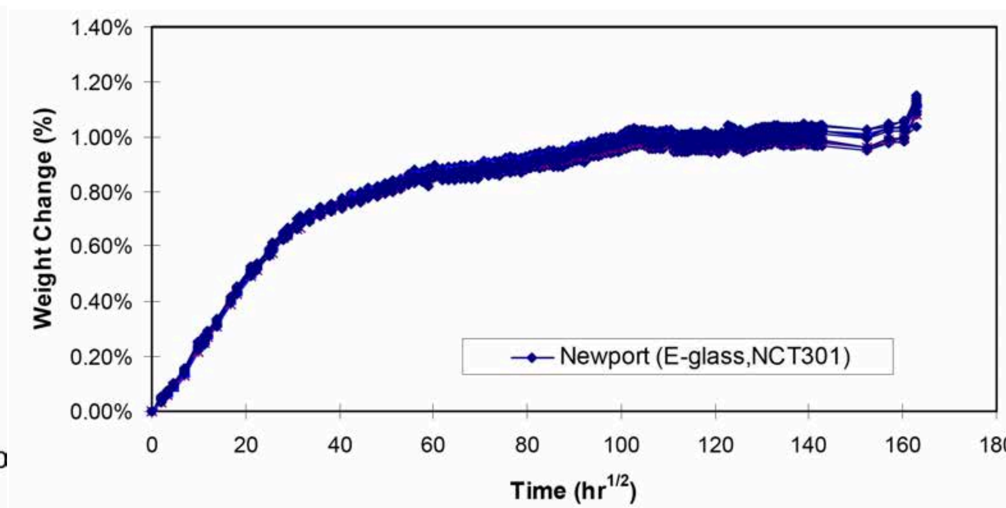
$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) \text{ in three dimensions.}$$



Five year sorption data for AS4/3501-6 and IM7/8551-7 coupons immersed in simulated seawater at 34 °C.

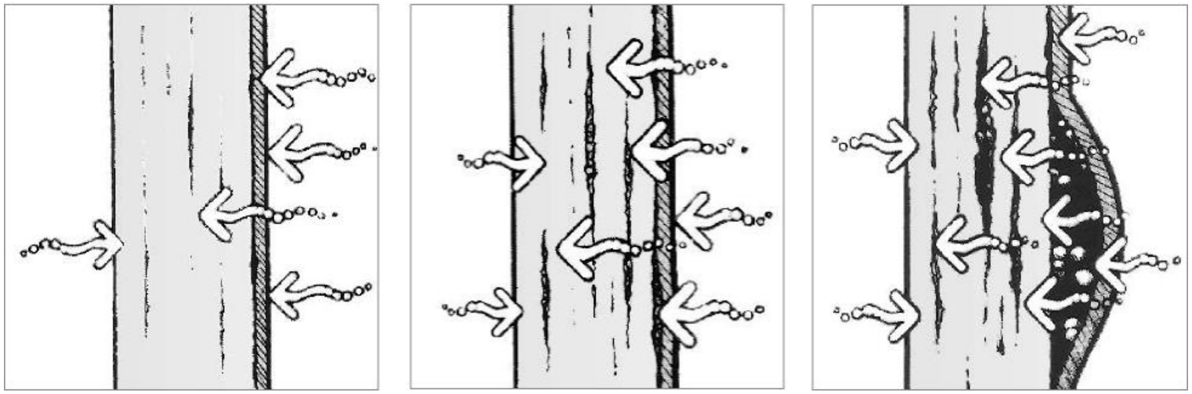


Four years weight-gain data for E-glass/NCT301 coupons immersed in simulated seawater



Y. J. Weitsman, "Composites in the Sea: Sorption, Strength and Fatigue," University of Tennessee for Office of Naval Research, Oct. 1999.

Osmotic Blistering



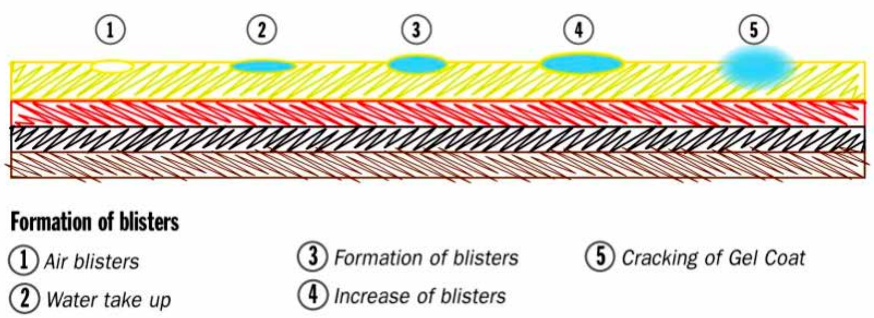
Polyester resins and gelcoats allow water molecules to migrate into the laminate and dissolve soluble materials within the laminate.

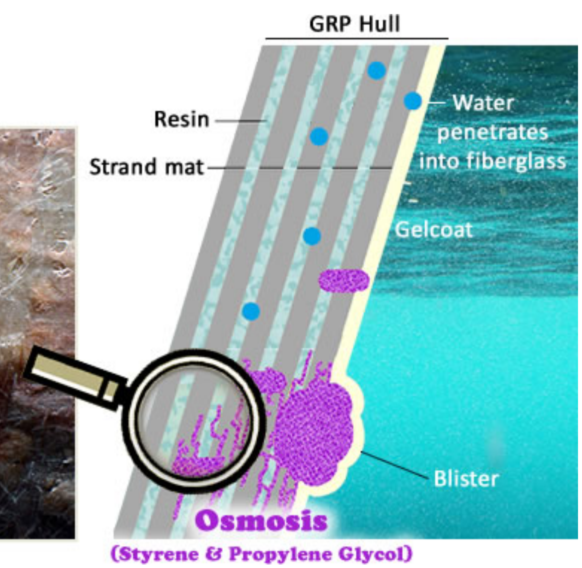
More water molecules are attracted to the voids to dilute the concentration of solutes in the blister fluid solution.

Accumulating fluid creates enough hydraulic pressure in the voids between the gelcoat and laminate to result in a gelcoat blister.

Gougeon Brothers, Inc., Bay City, MI

Tony Guild





Blistered Hulls

Contamination Sources for Blister

Liquid Contaminate Sources During Spray-Up That Can Cause Blistering

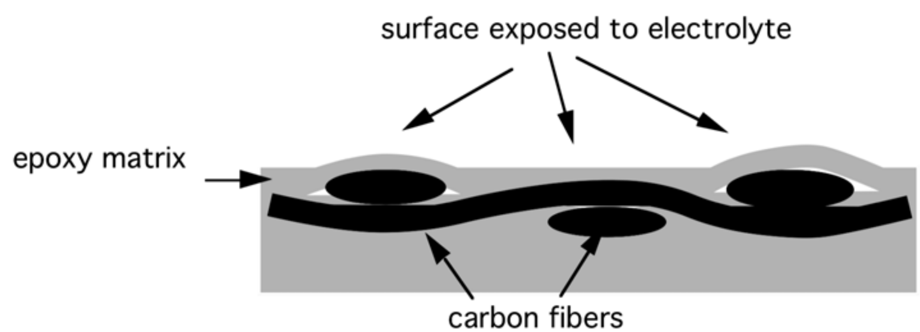
Liquid	Common Source	Distinguishing Characteristics
Catalyst	Overspray, drips due to leaks of malfunctioning valves.	Usually when punctured, the blister has a vinegar-like odor; the area around it, if in the laminate, is browner or burnt color. If the part is less than 24 hours old, wet starch iodine test paper will turn blue.
Water	Air lines, improperly stored material, perspiration.	No real odor when punctured; area around blister is whitish or milky.
Solvents	Leaky solvent flush system, overspray, carried by wet rollers.	Odor; area sometimes white in color.
Oil	Compressor seals leaking.	Very little odor; fluid feels slick and will not evaporate.
Uncatalyzed Resin	Malfunctioning gun or ran out of catalyst.	Styrene odor and sticky.

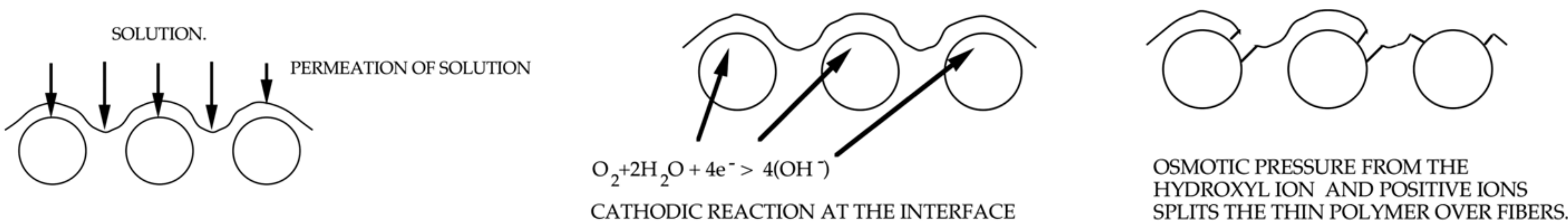
Cook, Polycor Polyester Gel Coats and Resins

Galvanic Cathodic Blistering

A portion of a carbon fiber mast is shown with metal couplings attached to it

Schematic diagram of carbon/epoxy composite





If the polymer layer over the location of osmotic pressure build up is thin, then the film will rupture. As a result, the solution will be directly exposed to carbon fibers with no intervening polymer layer. If the polymer layer is thick, The polymer can creep and slowly form a blister on the surface

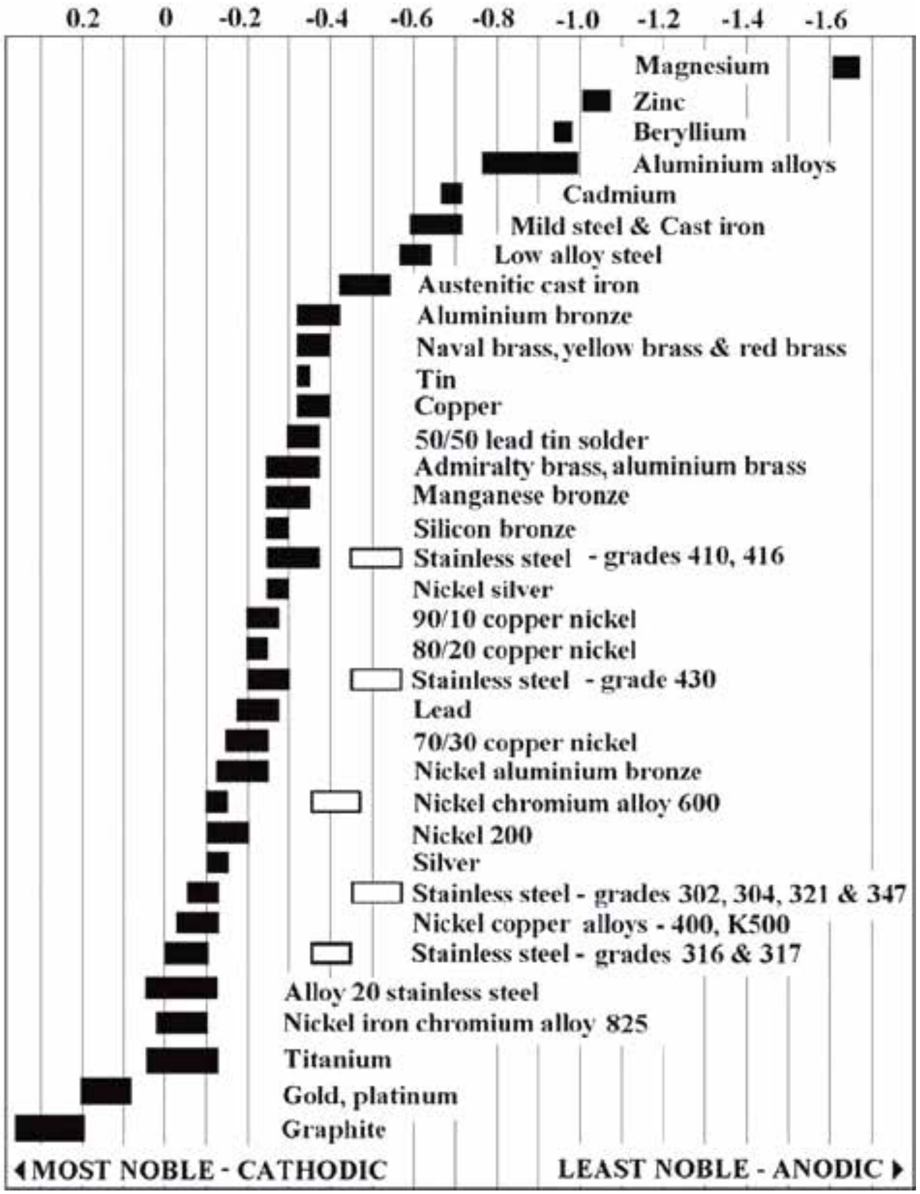
Richard Brown, "Galvanic blistering in carbon fiber polymer composites," University of Rhode Island, 2010.

Galvanic Activity

- Carbon fibers, unlike glass fibers, will conduct electricity. The carbon fiber's conductivity permits electrochemical activity - corrosion - to occur
- The cathodic activity at the carbon fibers can generate blistering
- Damage is usually limited to the surface, but this may initiate early fatigue failure and reduce impact resistance
- Long-term experience with large, carbon fiber marine structures is limited
- The phenomenon of galvanic blisters in carbon laminates has only recently been discovered
- Carbon fiber galvanic blisters require a microscope to observe - the problem is usually first observed in metal components that are in contact with the carbon fibers

Tucker & Brown, "Galvanic" Blisters in Carbon Fiber Composites, Professional Boatbuilder # 57

Galvanic Scale



- The material that is closest to the anodic end of the galvanic scale will be corroded in preference to the one that is closest to the cathodic end of the scale.
- As the distance between materials on the galvanic scale increases, a corresponding rise occurs in the rate and the extent of the corrosion.
- Corrosion will increase the saltier the water is. Increasing temperature will also increase the conductivity of water and the resulting corrosion. The corrosion rate doubles with every 10 degrees Celsius (18 degrees Fahrenheit) increase in temperature.

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Polymer Degradation

- Ultra Violet exposure – embrittles polymer, these days use clear coats which stop the process.
- Water uptake – polymers such as vinyl esters absorb 1.5% by weight of water.
- Water uptake can also cause polymer swelling and delamination.
- Dissolution – chemical attack, from imides in alkaline environment.

Richard Brown, "Degradation of Materials," University of Rhode Island, Nov. 2007

Ultra Violet Degradation

UV damaged (left) and restored gel coat (right)

Typical whitening of colored gel coat

Scott Bader Crystic marine gel-coat claims improved color stability and UV weather resistance

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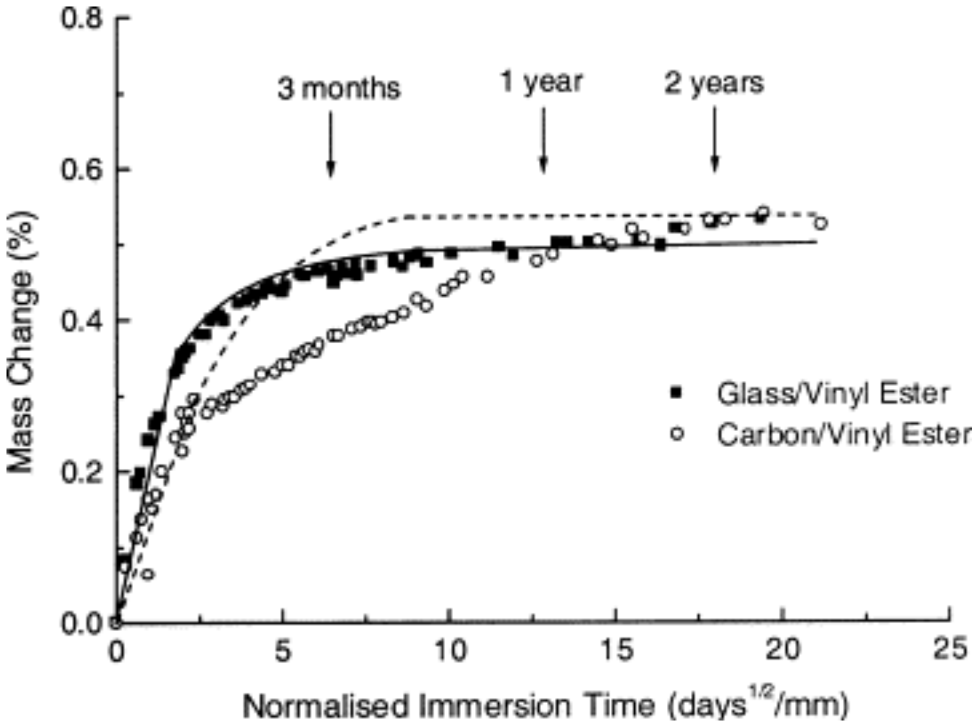
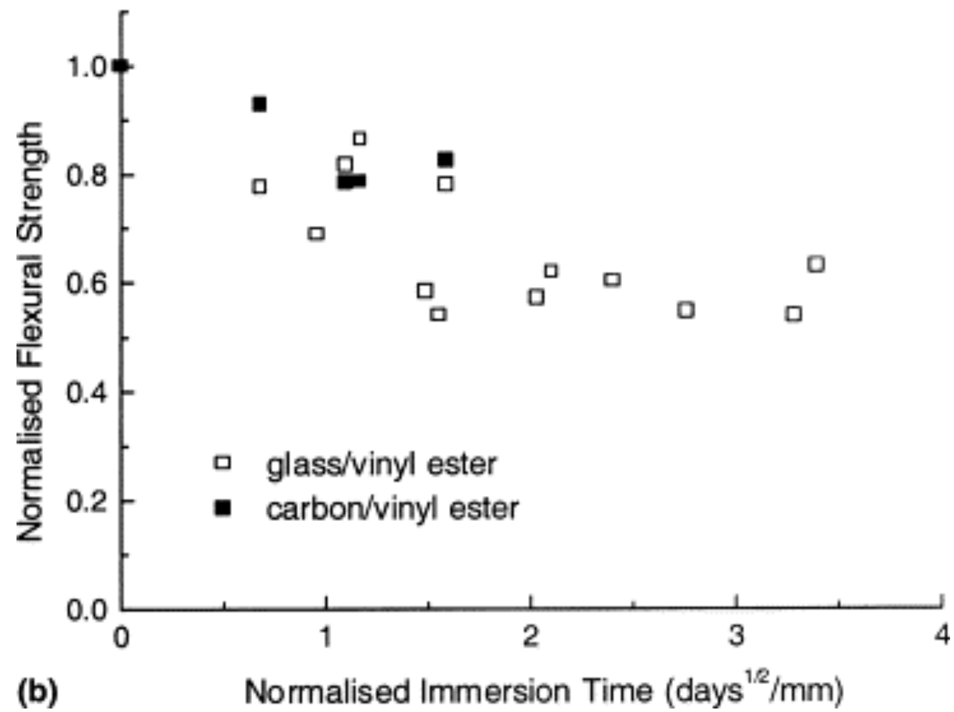
Water Uptake

Water uptake curves for the vinyl ester-based composites



Effect of seawater immersion time on the normalized on flexural strength of the vinyl ester-based composites



A. Kootsookos and A.P. Mouritz, "Seawater durability of glass- and carbon-polymer composites," *Composites Science and Technology*, Volume 64, August 2004.

Resistance to Chemical Attack

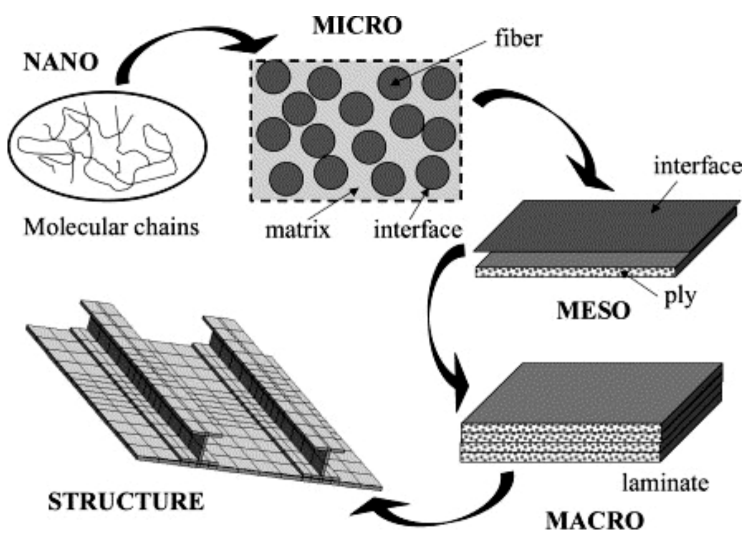
Petroleum Service Product Case Histories

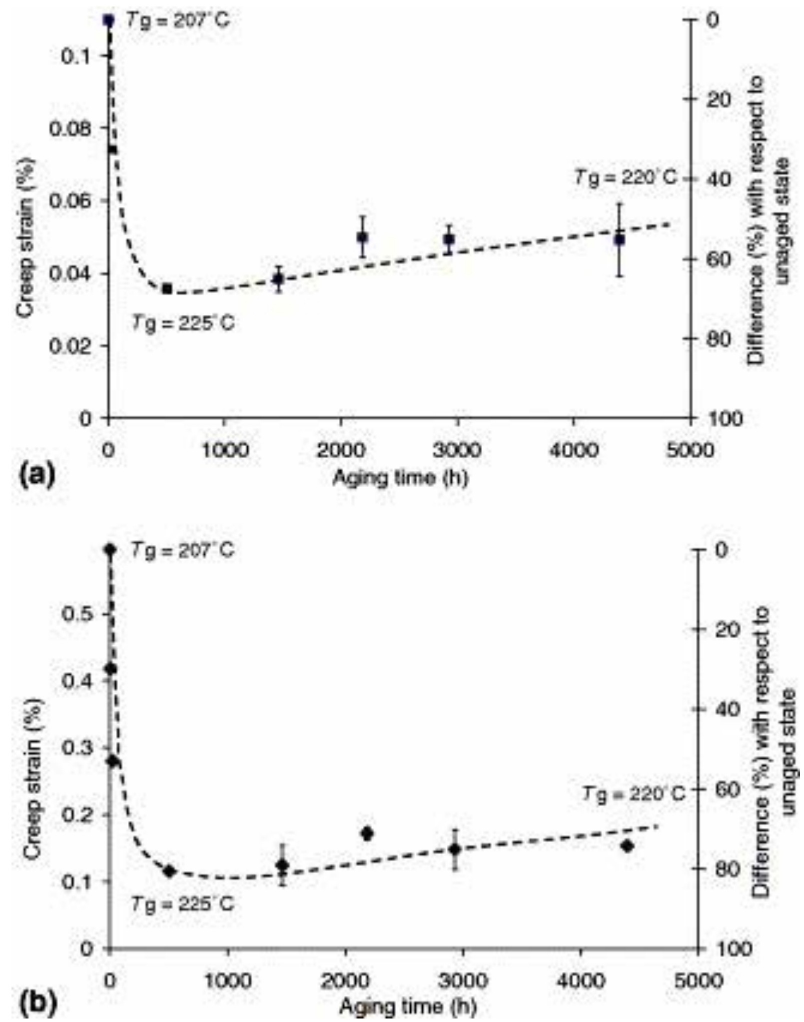
APPLICATION	ENVIRONMENT	RESIN	SERVICE TEMP ºC	YEAR INSTALLED	FABRICATOR	SERVICE LOCATION	Comments
Tank Lining	Diesel Fuel	DION® 6631	Ambient	Various	Standard Oil	Standard Oil of California	Tank life 11-15 years
Tank Lining	Crude oil	DION® 6631	Ambient			Conoco/Standard Oil of California	
Tank lining	Heavy fuel oil	DION® 6694	-	1973		Standard Oil of California	
Steek tank overwrap	Motor fuels	DION® 6631	Ambient	1971	Plasteel International, inc licensees	International	Single wall and double wall UL listed tanks
Settling tank	Kerosene/5% Sodium hypochlorite	DION® 6694	-	1969	Standard Oil	Standard Oil of California	Mild caustic and kerosene separation. Replaced epoxy tank which failed
Storage tank	Naphtha, aromatics & H_2S	DION® 6694	50°C	1969	Standard Oil	Standard Oil of California	Removal and containment of aromatics entrained in hydrogen sulfate
Tank Lining	Perco sweeteners	DION® 6631	Ambient	1962	Standard Oil	Conoco/Standard Oil of California	Straight run gasoline percolated through 2m x 6.1 m steel FRP l columns Ned

DION® Polyester Resins, Reichold Chemical Company, Research Triangle Park, North Carolina, Sep 2010

Thermal Aging Affects

Schematic representation of composite structure scales





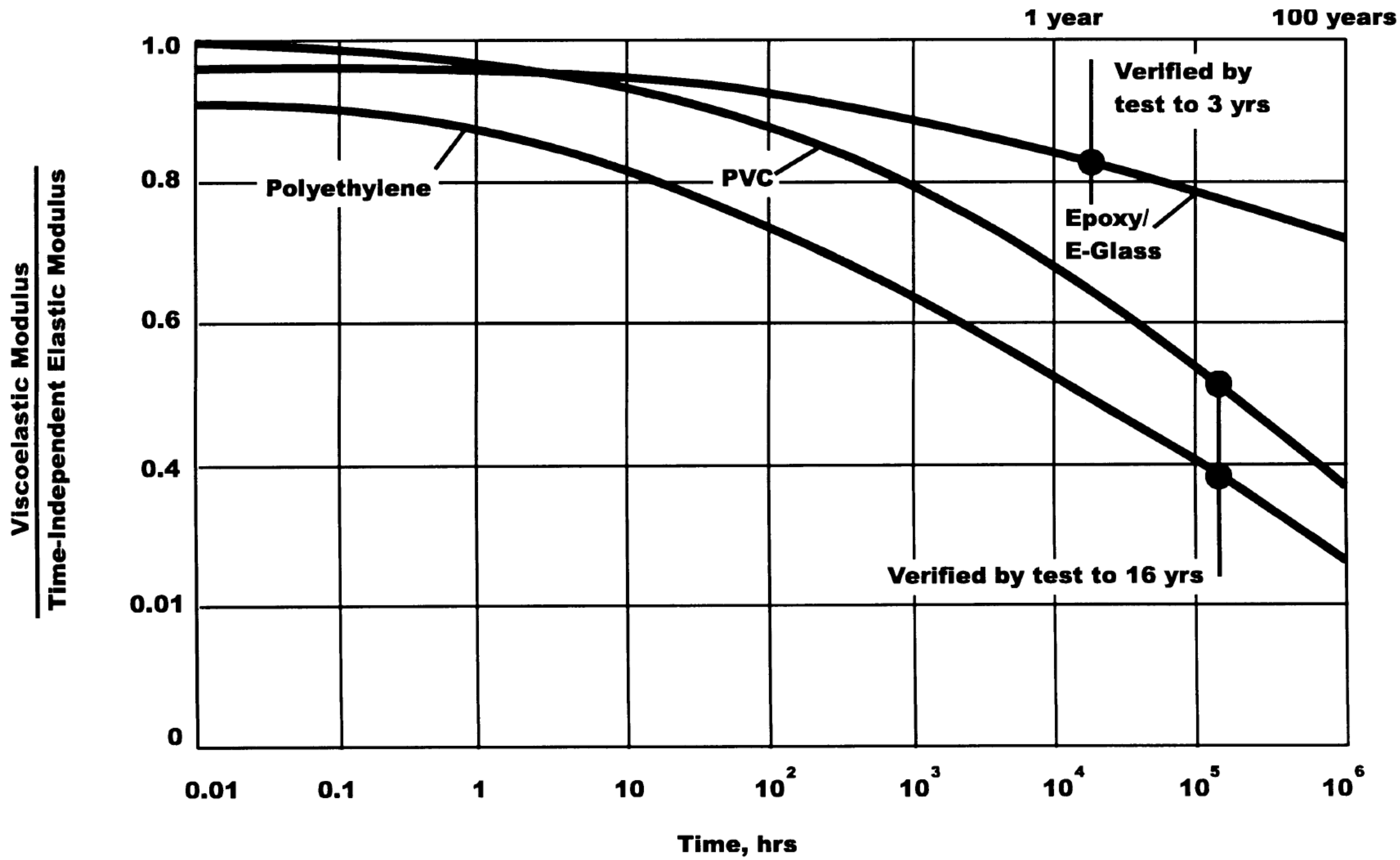
Creep tests on $[\pm 45]_{4s}$ laminate: creep strain after 1000 s versus aging time at 180°C: (a) creep tests at 40 MPa; (b) creep tests at 60 MPa.

Viscoelastic behavior, thermo-mechanical damage and degrading resulting from physical and chemical aging can be analyzed in a multi-scale model.

David Lévêquea, Anne Schieffera, and Anne Mavela, Jean-François Maireb, "Analysis of how thermal aging affects the long-term mechanical behavior and strength of polymer–matrix composites," *Composites Science and Technology*, March 2005.

Long-Term Stiffness Degradation

Variation in Viscoelastic Modulus with Time [Structural Plastics Design Manual published by the American Society of Civil Engineers]



Lightning

Chances of boats being struck by lightning

Type	Chances per 1,000	$ Severity (10 = highest)
Multihull - Sail	9.1	10
Auxiliary Sail	4.5	6
Cruiser	.86	6
Sail Only	.73	3
Trawler	.18	5
Bass Boat	.18	1
Runabout	.12	2
Houseboat	.11	3
Pontoon	.03	8
Personal Watercraft	.003	1

BoatUS Marine Insurance Claim Files

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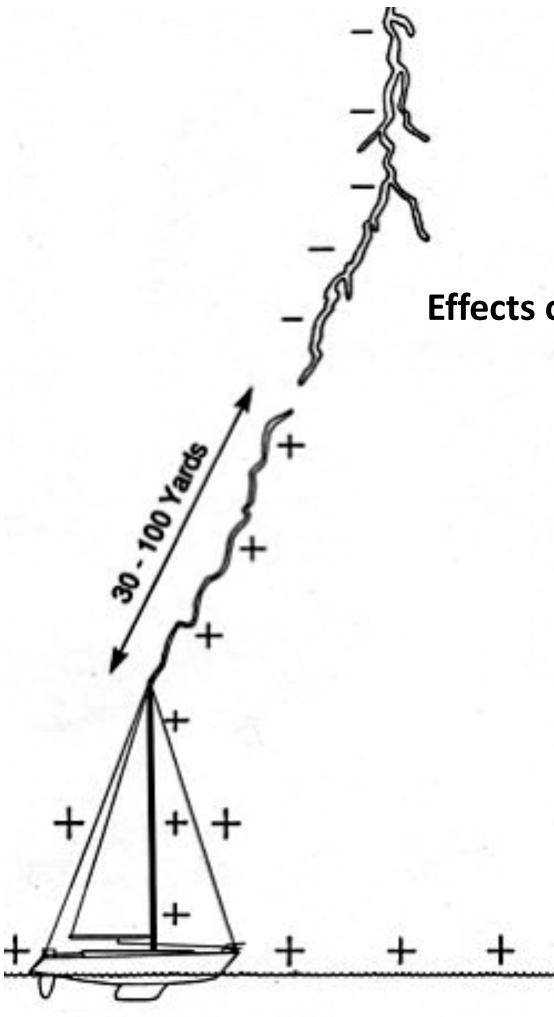
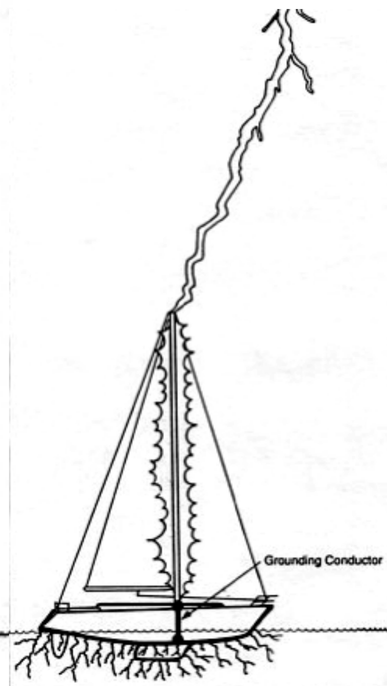
Lightning and Sailboats

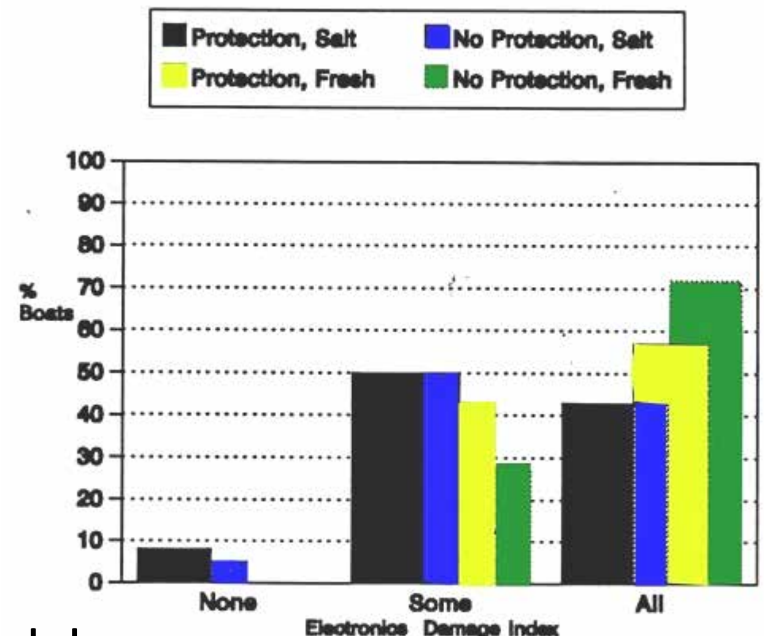
Lightning attachment to a sailboat



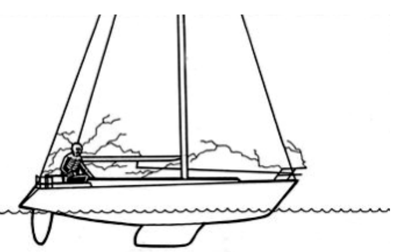
Effects of lightning strike to grounded boat



Proportion of boats struck by lightning suffering electronics damage of varying degrees



Effect to helmsman



Ewen M Thompson, “Lightning and Boats,” University of Florida Sea Grant, 1992.

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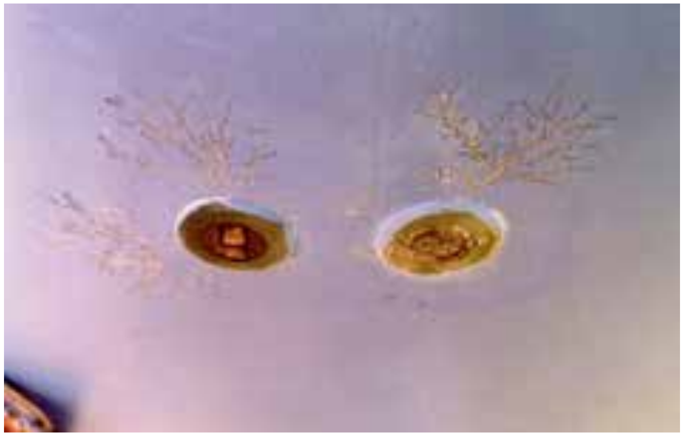
Typical Lightning Damage



Eric Sponberg

HWH Electronics,
St Pete Beach, FL