Original Concepts for Strengthening Interlaminar Properties in Polymer Matrix Composites

A Survey of New and Improved Techniques for Advancing the State-of the Art in Composite Design and Manufacturing

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Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Introduction

- Two of the top culprits responsible for poor shear properties in laminated composites are porosity, especially interface porosity, and weak interlaminar interactions. The two are often interrelated.
- Most advanced composites consist of a reinforcement phase (typically carbonized fibers and fabrics) and a matrix phase, which could consist of polymers, ceramics, carbon, metals or possibly a hybrid of these. Polymer matrix composites (PMC) are the most prevalent today.
- While the family of epoxy thermosets form the backbone of the advanced PMC industry, there are growing segments and needs for matrices derived from the vinyl esters, polyimides, phenolics, polyurethanes, siloxanes, nitriles and an expanding list of engineering thermoplastics.
- The matrix phase binds the reinforcement together while the reinforcement phase may consist of fibers and tow (yarns) that are continuous throughout the composite article or discontinuous (chopped, whiskers, staple) or a mixture of continuous and discontinuous fibers and tow.
- However, it should be realized that there is a third constituent in all composite platforms that is sometimes overlooked or poorly understood . . . the interphase zone, which is the thin boundary or transition region along all the fiber-matrix interfaces where chemical and mechanical bonding interactions occur, joining the two phases together. We might call this the ‘slip-and-grip’ zone.
- This region is of utmost importance and should be a major topic in any study of this type which seeks to improve the performance properties of fiber/fabric-reinforced polymers, ceramics, carbon or metal matrices. Interfacial chemical binding is extremely critical in PMC systems.
- There is a very long list of concepts and practices which have been introduced, pursued and attempted over the last three decades to address the industry-wide problems associated with ply-to-ply defects, interlaminar weaknesses and delaminations in PAN-based composite systems.

Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Introduction

- Since the advent of carbonized PAN (polyacrylonitrile) fiber/fabric-reinforced polymer matrix systems in the 1970's, perhaps the most prevalent issue topping the list of concerns revolves around low interlaminar shear (ILS) strengths and interlaminar tensile (ILT) strengths where countless dollars and R&D efforts have been expended, often with only limited improvements.

- The need to resolve, or at least substantially improve, these weaknesses is world-wide as laminated carbon fiber composites are finding more applications throughout industry everyday. This project effort will address some of these concerns with two primary objectives:

  (1) To enhance and advance the state-of-the-art by refining and improving current methodologies and developing new and alternative approaches to many of the interlaminar strengthening techniques which have already been attempted or are already in practice to varying degrees of success.

  (2) To explore new, alternative, novel and radical ways to improve *z*-directional ILS/ILT attributes and ply-to-ply interactions with no or minimal loss in 2-D mechanical properties. This opens the door to a host of emerging concepts which have yet to be tried. A briefing such as this can only touch on a few ideas and hope to spur the imagination of others.

- Admittedly, it is primarily the attractive longitudinal properties of carbonized PAN-reinforced composites that drove these systems into dominance over their carbonized rayon predecessors, but with the increases in tensile strength came the substandard interlaminar properties.

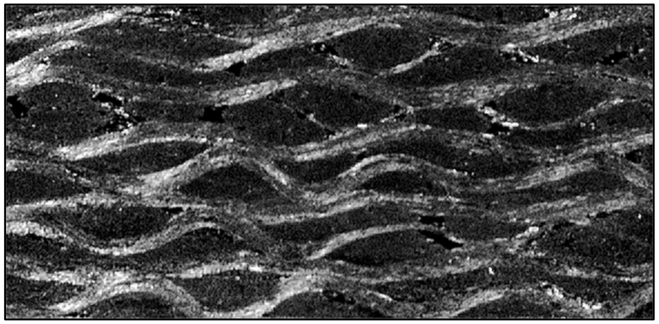
- It is well established, longitudinal tensile strengths for PAN composites are several orders of magnitude greater than those of their rayon counterparts. However . . . in rayon-based systems, ILS and ILT strengths are notably higher and the occurrence of delaminations is rare. Why?

Please note, the number of slides is limited and it is not the intention to addle this briefing with textbook concepts, formulas or details that the reader already knows or can look up. The objective is to present unique topics that compliment or extend the existing science and add value to the current knowledgebase.

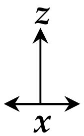
Fiber Shape Morphology

- Fiber shape morphology plays a direct role in ply-to-ply fiber intermingling and interlaminar nesting which influences *z*-directional properties by reducing Mode II and Mode I weaknesses.

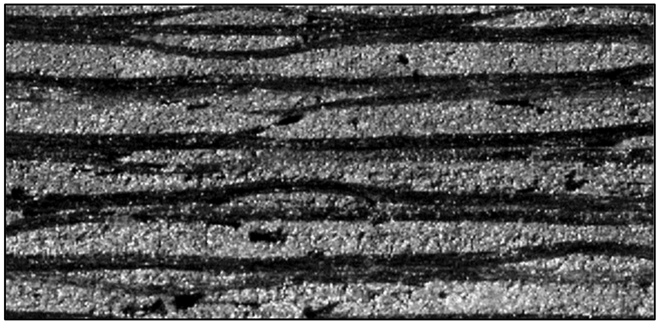
Rayon laminate . . . Natural ply-to-ply intermingling



Side view of carbonized rayon / phenolic matrix substrate (Lee, 1986)



PAN laminate . . . No ply-to-ply intermingling

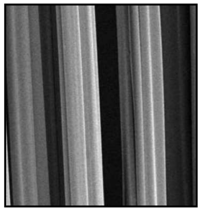


Side view of carbonized PAN / phenolic matrix substrate (Lee, 1986)

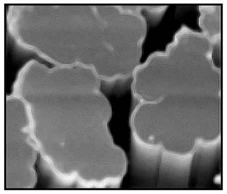
It is apparent which configuration possesses greater interlaminar interactions

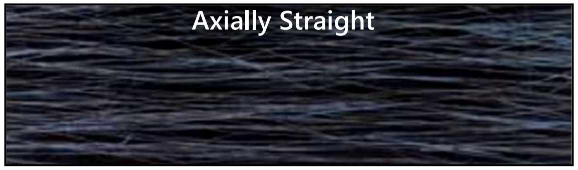
- Longitudinal and lateral features specific to the fibers/fabrics employed are key factors in mechanical bonding, interlocking and slippage effects along fiber-matrix interfaces as they facilitate ‘slip-and-grip’ toughness actions during expansion and contraction. Current state-of-the art PAN fibers are smooth, straight, non-interacting structures that exhibit minimal interlocking.

Carbonized rayon filaments (Lee, 1998)

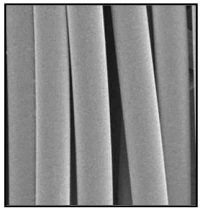


Laterally Crenulated

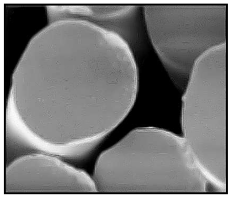




Carbonized PAN filaments (Lee, 1998)



Laterally Smooth



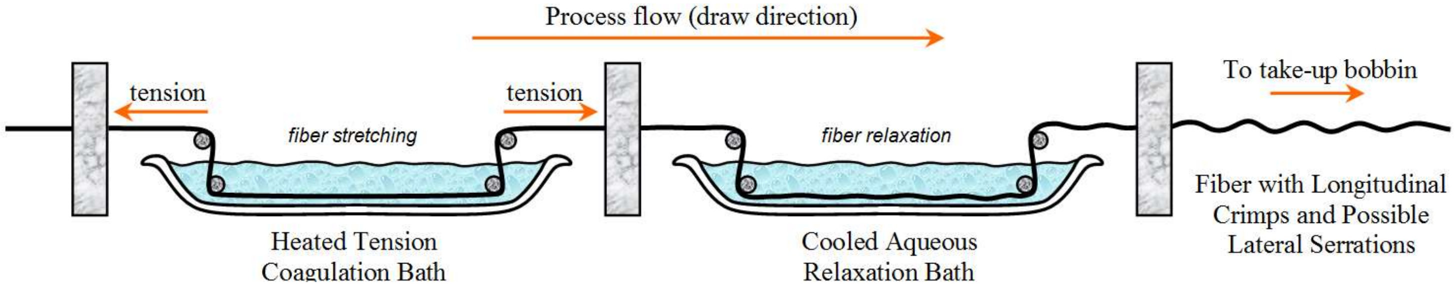
Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Fiber Shape Morphology

- Longitudinal and lateral fiber shape features are generally imparted during the fiber synthesis stage due to differential core and skin shrinkage effects. Obtaining natural crimps in PAN fibers is a challenge since diffusion and precipitation/coagulation are inherently slow processes, and polymerization is already complete when the spinning dope leaves the spinneret.

- By design, PAN fibers are processed via lower solution temps and diffusion rates which minimize core-skin gradients, while stretching of the fibers during virgin processing, stabilization and heat treatment increases crystal orientation with enhanced longitudinal properties. Even though this increases the ultimate tensile properties, it only leads to meager shape and surface features.

- Controlled variations in PAN fiber processing leading to axial z-directional features and/or lateral serrations have been demonstrated and it is believed this process can be optimized to provide reinforcement options exhibiting improved ILSS while maintaining impressive tensile properties.

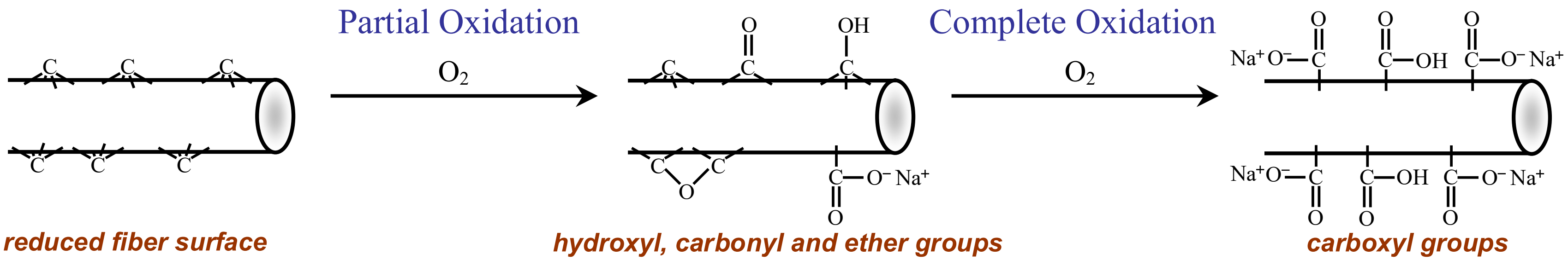


- Composite axial strengths are maximized when bundles are molded under slight tension or at least when all the slack is taken out prior to molding. Thus, laminates derived from crimped PAN fibers may exhibit slightly reduced longitudinal tensile strengths . . . but with significant improvements in ILS properties. In any event, both natural and weaving crimps may promote ply-to-ply nesting.

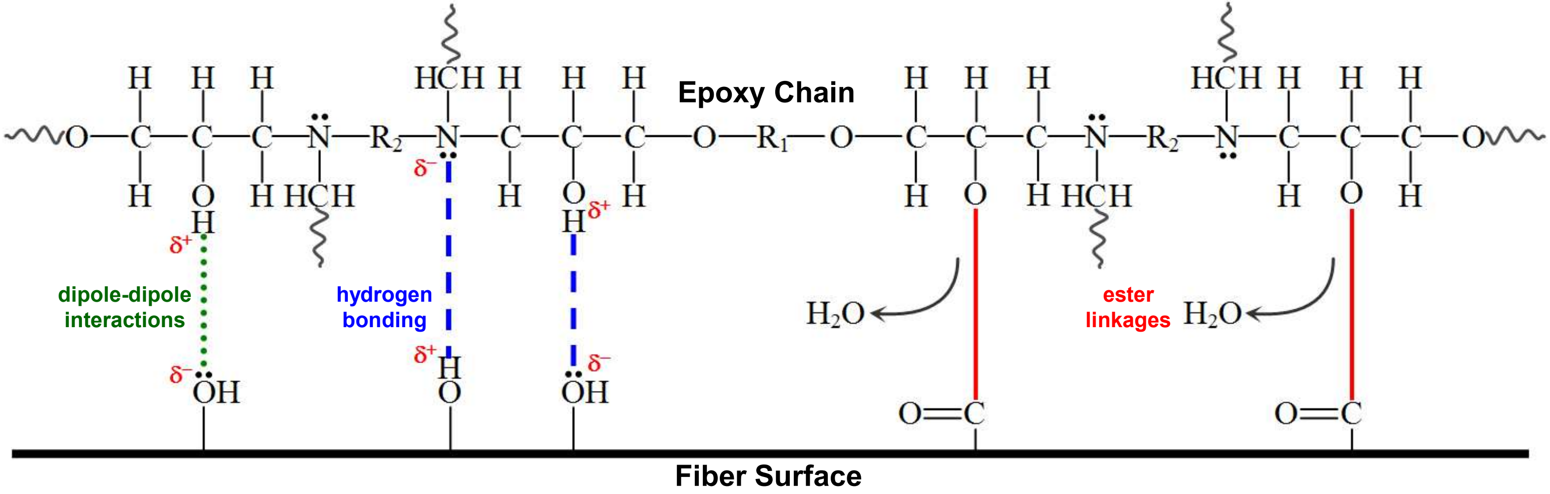
- Layer-to-layer fiber intermingling can also be enhanced by using fabrics derived from hybrid tows blended with straight, high tenacity filament cores wrapped in highly crimped filament sheaths.

Fiber Surface Chemistry

- After the carbonization step, many fiber manufacturers will subject the fibers to proprietary treatments that increase the surface activity (via surface functional group modification) in order to enhance interactions with polymer matrices, primarily those based on epoxies. Most of these methods involve some form of oxidation or nitration of the fiber surface.



- Possible interactions with epoxide functional groups include (a) dipole-dipole associations between carbonyl functionalities, (b) hydrogen bonding between hydroxyl groups and nitrogen groups, and (c) direct coupling with carboxyl groups (covalent bonding). In the ladder case, functional groups can connect to the polymer chain via (1) amide links with amino crosslinking groups, (2) ether linkages with epoxy end groups and (3) ester links with pendant hydroxyl groups.



Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

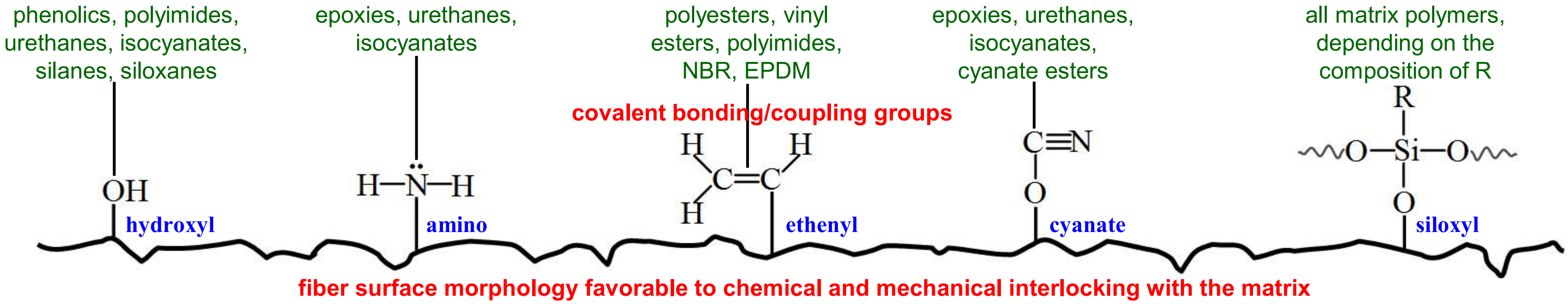
Fiber Surface Chemistry & Surface Morphology

- All these interactions are governed by differential surface energies (wetting effects), varying hydrophilic-hydrophobic regional balances, relative group reactivities, varying bond flexibilities, steric hindrance and bulk tertiary properties of the specific polymer chains, all of which impose undesirable limitations on bonding associations along fiber-to-matrix interfaces.

- There several ways these concepts can be improved upon at the fabric level that will substantially alter fiber surface hydrophilicity, increase surface energy and active surface area, and provide composite ILS and ILT values 2 to 3 times greater than the current state-of-the art.

- One example might utilize novel approaches to electrooxidation (polarization) of carbon fabrics via multi-step processes strategically exploiting voltage-driven etching and oxidation effects of various acids HNO_3, HX, H_2SO_4, RCOOH and/or bases NaOH, NH_4OH and amines $N_xH_yR_z$. Another might use a combination of electrooxidation and plasma to produce anhydrous surface groups.

- Such treatments can be tailored to emphasize unique functionalities with strong affinities specific to chosen binders (epoxies, polyimides, vinyl esters, urethanes, siloxanes, etc...) while also generating physical surface features that enhance mechanical bonding with minimal fiber damage.

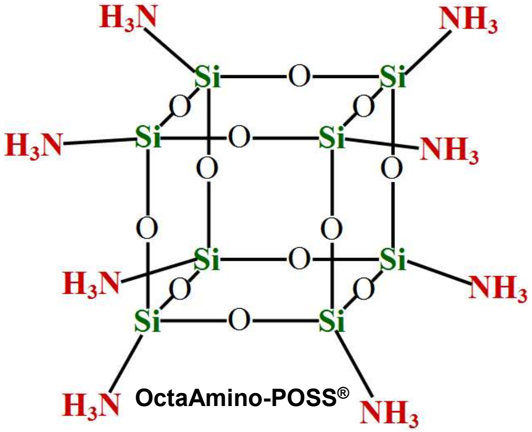


Concepts, mechanisms and illustrations are strictly the perception and handiwork of the author

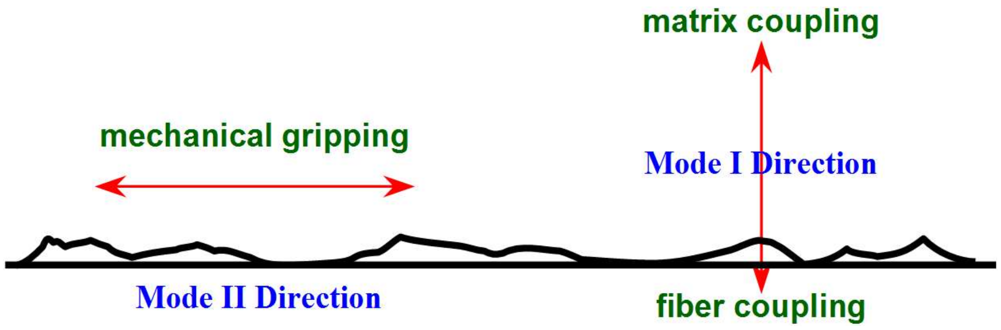
Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Fiber Surface Chemistry & Surface Morphology

- The last functional group depicted in the previous illustration represents a special case where silane/siloxane coupling agents are directly attached to the fiber surface prior to impregnation.
- The class of organo/inorganic silicon-based materials also includes the emerging family of POSS® compounds (polyhedral oligomeric silsesquioxanes) which lead to extraordinary bonding agents.
- Nanoparticles of these cubic, cage-like molecules have now been established to greatly improve ILS properties . . . and their functionality can be tailored to attach covalently to fiber surfaces and then couple with just about any matrix polymer of interest.



- They can be deposited as nano-slurries where they polymerize non-uniformly on fiber surfaces, forming scattered ‘islands’ of deposit with overall surface roughness and morphological features that facilitate both chemical and mechanical bonding as well as interlocking at the matrix interface.
- Utilizing 1^o and 2^o amine groups to create OctaAmino-POSS®, common carboxyl-heavy PAN fibers may be ideal for epoxy systems where POSS® coupling agents are covalently bound to the fiber surface on one side and covalently bonded to the matrix phase on the other end which also interacts mechanically with the reinforcement to reduce Mode II shearing effects.

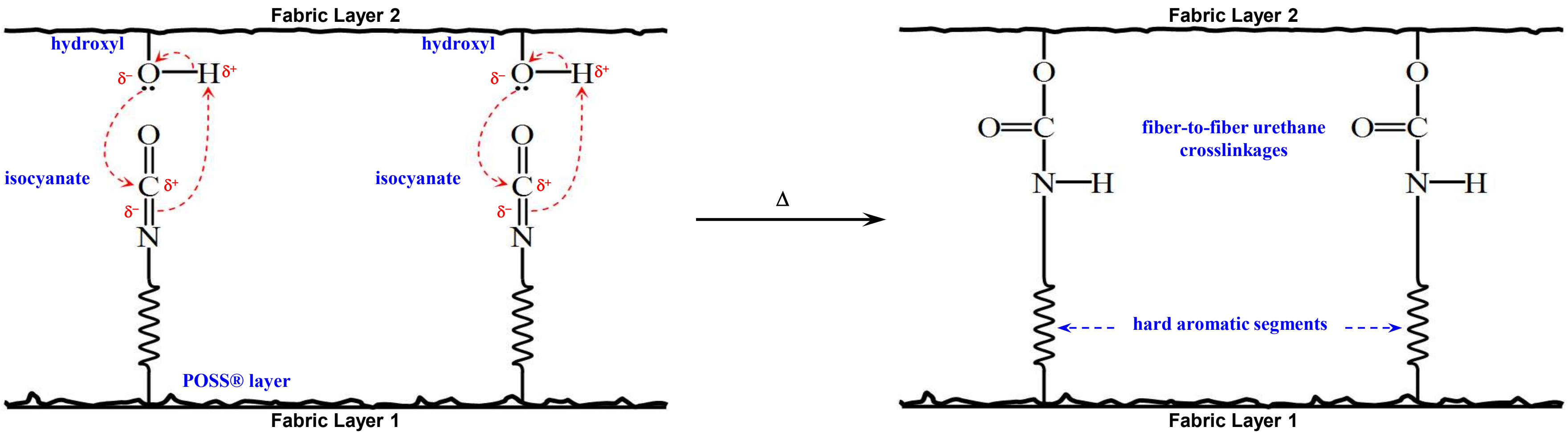


Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Fiber Surface Chemistry & Surface Morphology

- Another idea might consider the concept of ‘ply-to-ply crosslinking’ or ‘ply-to-ply coupling’ where alternating fabric layers are utilized, one layer being treated with POSS®-grafted, long-chain aromatic oligomers containing terminal isocyanate groups and the other fabric layer treated to contain high levels of hydroxyl (–OH) groups, resulting in strong inter fiber-to-fiber bonding.

- A fabrication scheme might be: (1) replace one of the pendant groups on an Amino-POSS® structure with a ‘hard’ hydroxy-terminated polyurethane (PU) segment (such as one based on diphenylmethylene diisocyanate; hard blocks will provide stiff, high strength fiber-to-fiber crosslinks), (2) coat the fabrics with the modified POSS® compound and cure (or dry), (3) attach isocyanate (IC) end caps to protruding PU segments, (4) saturate the treated fabrics with a suitable solvent, (5) assemble the wet lay-up and apply heated debulking which enhances mobility of PU-IC dendrites to neighboring fabric planes while providing the necessary reaction activation energy, and finally, (6) impregnate or infuse the bagged assembly with matrix resin, and then mold and cure the composite as usual. A possible scenario could be suggested and illustrated . . .



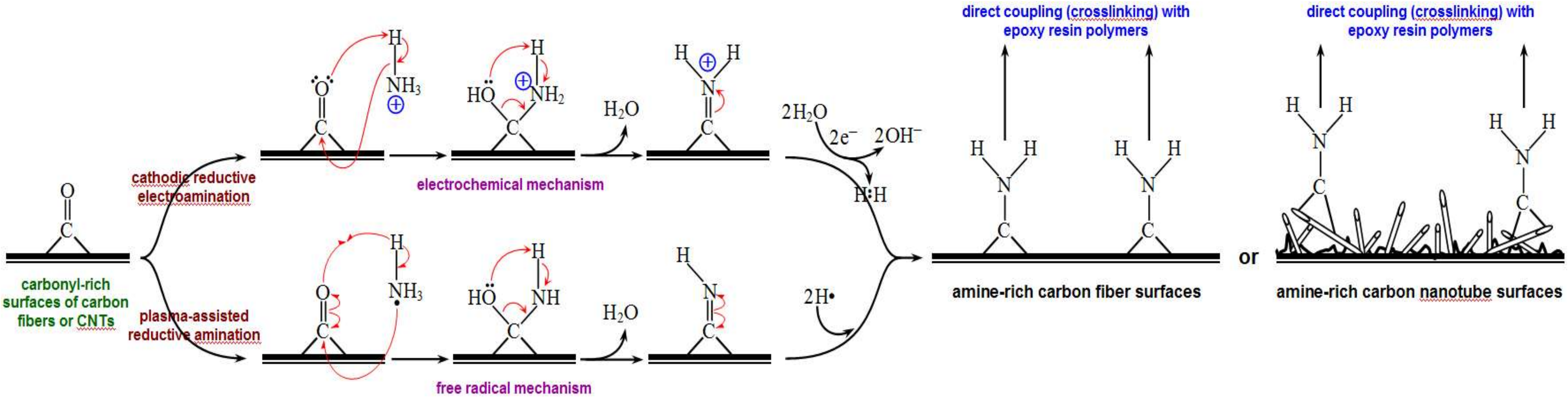
Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Fiber Surface Chemistry & Surface Morphology

- OctaAmino POSS® slurries can also be utilized to graft long, carboxyl-rich carbon nanotubes (CNT), carbon nanofilaments (CNF) or carbon whiskers (CW) directly to the reinforcement surfaces providing mechanical *z*-directional interactions between adjacent fabric planes.

- An extension of these concepts could establish a condition where the surfaces of carbonized PAN fibers or POSS®-grafted CNTs/CNFs/CWs would be rendered amine-rich and then inducing the epoxy polymers to 'crosslink' directly with treated carbon surfaces during cure. Since 1° amines are highly reactive with the epoxide groups in liquid epoxy resins, surfaces rich in amino functionality would become prime candidates for direct coupling with precured matrix polymers.

- Possible scenarios might utilize plasma or polarization techniques to deposit amine (–NH_2) groups on the desired surfaces, and then the dried reinforcement layers could be impregnated/infused with liquid resin precursor. During cure, amine groups along the reinforcement surfaces would interact directly with the matrix. Possible mechanisms could be suggested . . .

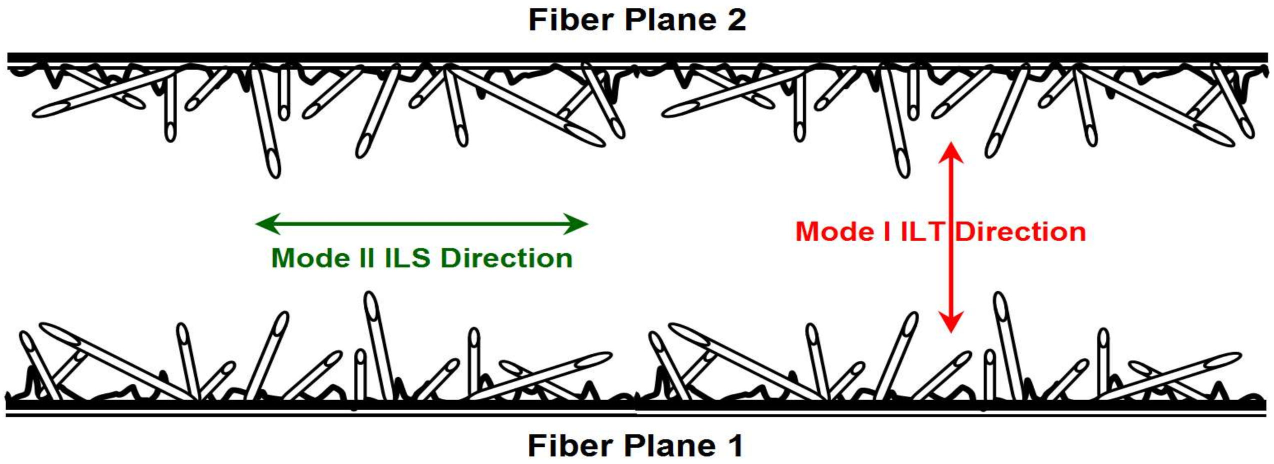


Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Mechanical Z-Directional Constituents and Concepts

- The preceding examples are just a few of the ideas involving fiber surface chemistry modifications. There are many more techniques and improvements which cannot be covered here. In all cases, characterization methods might include one or more of the following: SEM, contact angle/surface tension, Zeta potential, BET, XPS, ESCA, AFM, ILSS, ILTS and flexure.

- Acicular nanoparticles and functionalized nanoplatelets of CNT, CNF, CW and graphene/graphene oxide can be incorporated within a compatible resin vehicle and tactically applied during the lay-up sequence much like a laminating resin without negatively impacting the composite resin content, closed porosity or fiber volume fractions. When properly implemented, these reinforcement artifacts have been shown to increase ILS strengths some 20%-50% with moderate increases in ILT values as well. The mechanical benefits of carefully crafted nanocomposites are indisputable.



- As a side point, it is important to note that chemical bonding is insignificant in high temperature systems such as carbon-carbon (C-C) and ceramic composite (CMC) platforms since all the links are destroyed during pyrolysis. In these systems, toughening properties rely exclusively on strategically incorporated mechanical bonding, interlocking and slip-and-grip mechanisms.

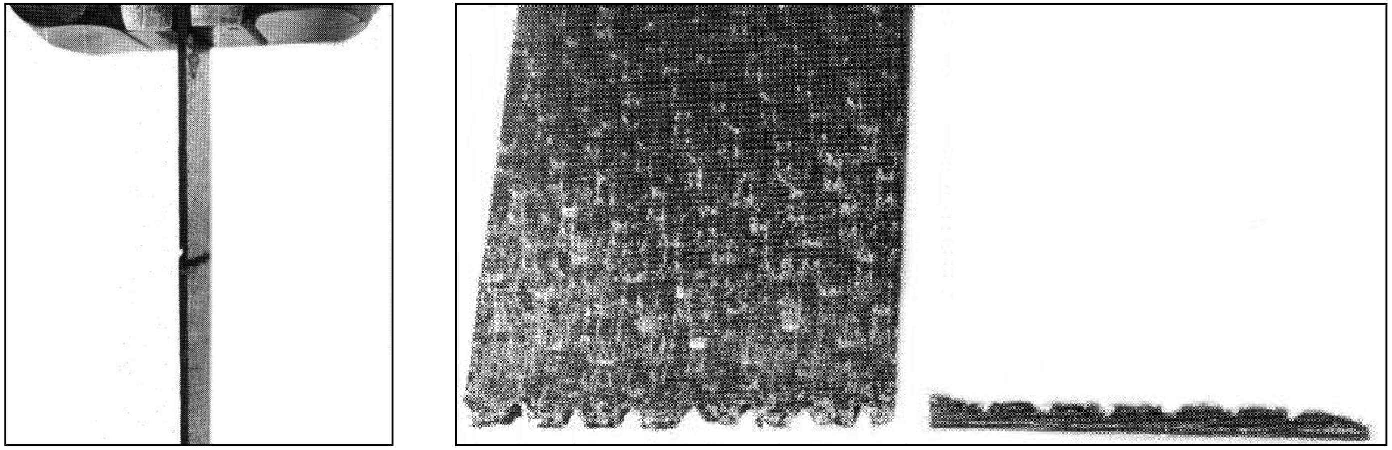
Concepts, mechanisms and illustrations are strictly the perception and handiwork of the author

Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Mechanical Z-Directional Constituents and Concepts

- Stitching of laminated lay-ups and preforms has been attempted by numerous workers over the years with less than desirable results. Machine stitching of carbon fiber yarns into T-300 PAN-based laminates was personally conducted and evaluated in the late 1980s with similar results.

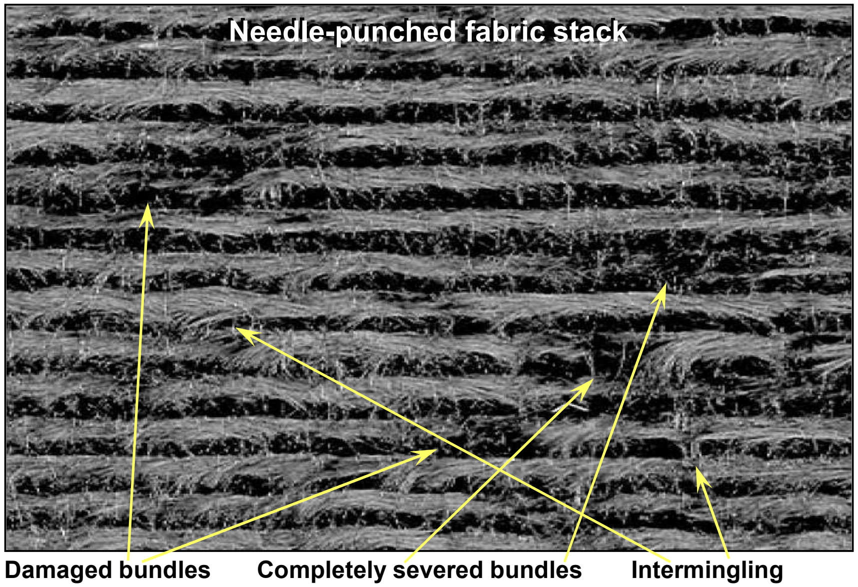
Machine stitched lay-up (Lee, 1987)



Lap shear test showing catastrophic failure at very low loading – right along the stitch line (Lee, 1987)

- ‘Needle punching’, ‘needling’ or simply ‘punching’ refer to the machine insertion and removal of barbed metal needles into the fabric stack in attempts to intermingle fibers across-ply each time the needle is removed.

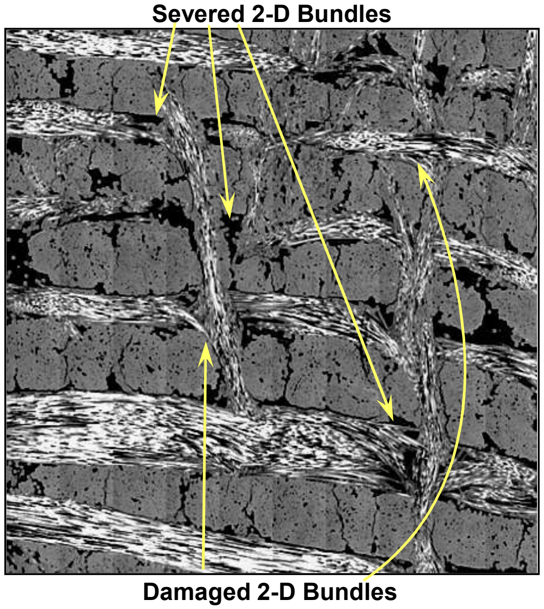
- While intermingling does indeed occur and slight increases in ILSS may be observed, this comes with great sacrifice as substantial damage to the 2-D network is undeniable.



Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Mechanical Z-Directional Constituents and Concepts

- The original *z*-pinning process was invented by Foster-Miller in the late 1980s. Different variations have been developed and practiced by numerous workers over the years.
- The concept uses ultrasonic forces to insert pre-fabricated (pultruded) needle-like carbon fiber 'pins' or 'nails' of specified length through a collapsible sponge into the lay-up and across several plies providing trans-laminar, thru-the-thickness reinforcement fibers at preselected depths and areal densities.
- It has been well established by this time that most *z*-pinning operations lead to in-plane material damage and degraded mechanical properties of the base 2-D network.



- It has also been discovered that the intruded pins often initiate crack growth in the surrounding polymer matrix as substantial cracking has been reported in many pinned articles after cure.
- Local matrix cracking is likely manifested during thermal expansion and contraction events because thru-the-thickness lateral (transverse) expansion rates of 2-D fiber bundles can be 4-8 times greater than those of the axially-oriented fibers comprising the pins, while lateral pin CTE movements are 4-8 times higher than the longitudinal bundles in the 2-D frame.
- Pinning processes should be used with caution and planning. They are more appropriate in systems which already possess abundances in 2-D longitudinal and lateral properties. Improvements are needed in applications requiring the full 2-D tensile properties offered by 2-D PAN networks.

Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

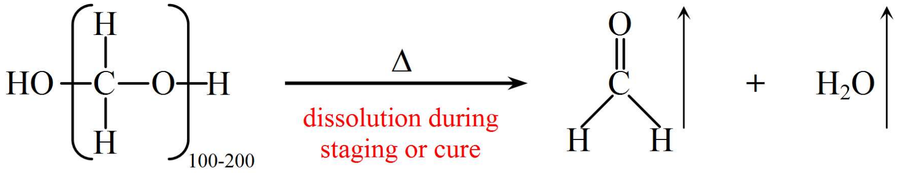
Mechanical Z-Directional Constituents and Concepts

- Prefabricated pins are usually comprised of fiber bundles saturated with epoxy resin, pultruded and cured. These typically have sharp points, much like nails. Damage to the underlying 2-D network can be minimized by utilizing a different approach in the design and fabrication of these pins.

- Fiber bundles could be encapsulated with a special low friction polymer that is hard/stiff, low T_m and compatible with epoxy polymers. Products such as Delrin® and Celcon® are high molecular weight (MW) polyoxymethylenes (POM) designed with these qualities – except that they are intentionally produced for thermal stability by the types of end groups attached to the polymers.

- Lower MW polymers with hydroxyl end groups could lead to dissolvable encapsulants made from modified POM which would provisionally maintain its stiff, low friction properties during the insertion process. After resin infusion and during cure of the dry pinned lay-up, the encapsulant depolymerizes to formaldehyde which volatilizes away and/or co-crosslinks with local amine groups. The dry interiors of bundled fiber pins become infused with fresh matrix resin and the entire *z*-reinforced system cures homogeneously. High compatibility via constructive interaction or noninterference with crosslinking epoxies, phenolics and many resin systems are expected.

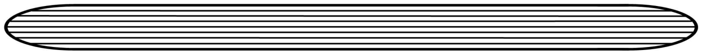
- Also, the pins could be cast or pultruded with soft, dome-shaped points which could be guided through the base weave, slipping around primary bundles during insertion. Sizings could be formulated for the base 2-D fibers emphasizing lubricity, perhaps a modified POM.



$$HO\!\left[\,CH_2-O\,\right]_{100\text{-}200}\!H \xrightarrow[\text{dissolution during staging or cure}]{\Delta} H_2C{=}O\uparrow \;+\; H_2O\uparrow$$

modified polyoxymethylene (polyformaldehyde)

volatization and removal from system during normal cure



possible pin configuration with soft tip points temporarily encapsulated in modified POM

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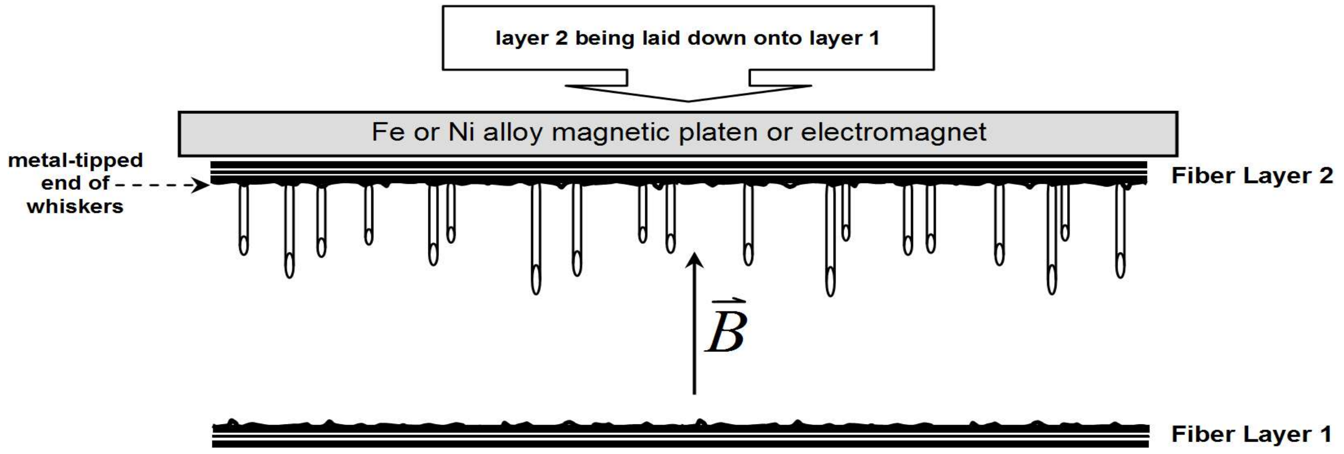
Mechanical Z-Directional Constituents and Concepts

- It should be noted, the amount of damage imparted during insertion of *z*-directional reinforcements into wet prepreg lay-ups is much greater than that experienced in dry fabric networks prior to impregnation/infusion. Such operations are most appropriate for dry fabric lay-ups and preforms.

- Production of CWs, CNTs and CNF via CVD techniques is common. The process may utilize catalyst-assisted thermal decomposition of hydrocarbons on substrates coated with transition metals such as Fe, Ni, Co and others. These three metals exhibit very strong ferromagnetic properties. From a quality perceptive, it is an undesirable to have remnants of the metal catalyst still attached to one of the ends of these micro/nano structures after production and collection.

- However, such ‘impure’ configurations could conceivably provide a possible mechanism for *z*-orientation of the structures during the composite fabrication process. Acicular metal-tipped CW/CNT/CNF particles could be distributed on a one fabric layer temporarily attached to a strong magnetic platen and then slowly applied to another (untreated) layer, allowing the *z*-oriented reinforcements to slide into the 2-D weaving pattern. A simplified diagram might be . . .



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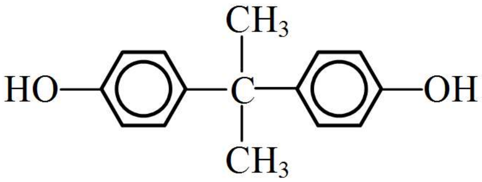
Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Polymer Modifications and Formulation Options

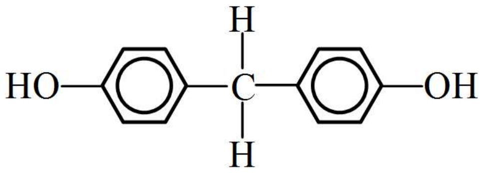
- The number of thermoplastic and thermoset polymer systems used in composite materials today is enormous, and the range of polymer modification techniques and formulation additives is limitless. This briefing is intended to focus on epoxy systems and only a few examples can be highlighted.

- Classical epoxy resins are synthesized from two compounds based on bisphenol-A (Bis-A) and a chloroepoxide to form a diglycidyl ether of Bis-A (DGEBA). This is well known, as is the baseline chemistry associated with almost all epoxy resins used in carbon fiber prepreg materials*.

- Bis-A is a diphenol which can also be used to make phenolic resins. A better diphenol is Bis-F which is one of the early products formed during the classical phenol-formadehyde reaction. If Bis-F (a diphenol methylene) is first reacted with formadehyde in an acidic environment to form a phenolic novolac resin oligomer or prepolymer, and then reacted with one of the chloroepoxides in an alkaline environment, a diglycidyl ether of Bis-F phenolic novolac (DGEBF) resin is produced.



Bis-A Co-Monomer for DGEBA



Bis-F Co-Monomer for DGEBF

- The DEGBA precursor molecule contains two steric methyl groups while DEGBF contains hydrogen atoms instead. The structures are very similar but their end properties are quite different.

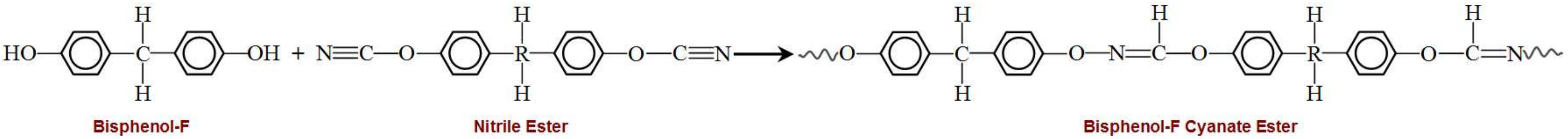
- Bis-F novolacs provide more crosslinking sites and lead to epoxy resins that are stronger with high temperature resistance and better adhesion to carbon fibers. Prepreg manufacturers may incorporate these resins upon request, or the end user can pre-impregnate their own fabrics with DGEBF.

* The number of slides is limited and it is not the intention to addle this briefing with textbook chemistry or reactions that the reader already knows or can look up. The objective is to present unique topics that compliment the existing science and add value to the current knowledgebase.

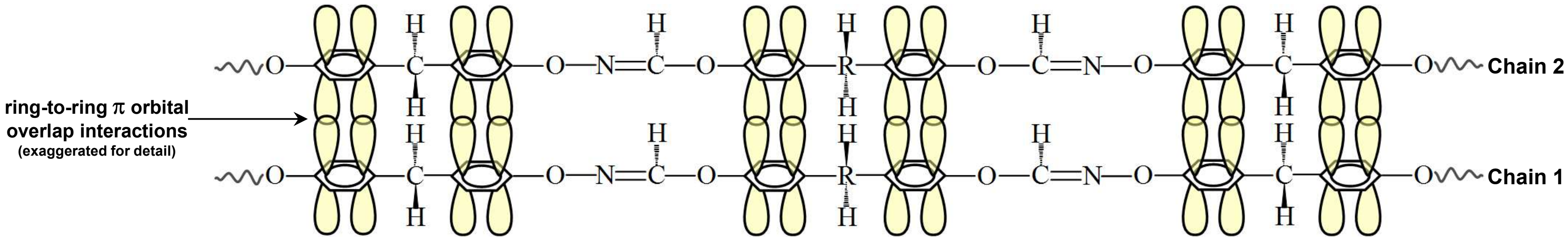
Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Polymer Modifications and Formulation Options

- Careful selection of monomers and strategic control of the reaction sequence can lead to some very interesting Bis-F-based thermoplastics with extraordinary properties. No need to crosslink these polymers as melting points can be almost as high as their decomposition temperatures (> 700°F). One example might use a nitrile ester in place of the epoxide monomer to form a cyanate ester:



- One of the primary reasons these types of resins exhibit such extreme properties is due to their mesogenic structure. Because of the planar nature of the chains, π orbital interactions or *p* orbital overlaps are established transversely between adjacent benzene rings which become indexed on top of one another, facilitating stacking of the electron clouds. The greater the density of aromatic rings along the polymer chain, the more extensive the mesogenic bonding effects . . .



- For extraordinary properties, strategic incorporation of a few vinyl groups along the chains of these polymers would permit free radical crosslinking without the requirement for an autoclave.

- Mesogenic interactions are influenced by the arrangement of biphenyl rings and bond flexibility between the adjoining segments. These types of intermolecular interactions form the foundation of a whole new class of materials . . . liquid crystal polymers and memory shape polymers.

Concepts, reactions and illustrations are strictly the perception and handiwork of the author

Polymer Modifications and Formulation Options

- The addition of solid particles, such as CWs, CNTs, carbon black and ceramics, into impregnating resins should be approached with great caution. Sometimes they can be incorporated – up to the percolating threshold, but many attempts have produced less than desirable results.

- While low CNT levels (1-5%) have been reported to provide moderate increases in ILS properties, higher loads will begin to reduce mechanical interactions and eventually lead to delaminations.

- Carbon particles have a notorious tendency to agglomerate or flocculate due to strong π-π orbital interactions between their carbon rings. Dispersing agents and ultrasonic techniques can sometimes facilitate deagglomeration, but pore opening congestion is still an issue that must be resolved.

- Also, with these types of particles, there is even a propensity for lateral π-π interactions between the particles and the fiber surfaces. When introduced into the network with flowing resin, CNTs will tend to orient themselves parallel to the fibers rather than perpendicular to the fabric planes.

- It has been established by many workers over the years that improperly applied resin-particle mixtures will lead to closed pores as they tend to block the necessary movement of resin throughout the interconnecting channels and bundle interstitials of a porous fiber/fabric network.

- Pore clustering in cured articles which are comprised of larger closed voids associated with bundle intersections has become a major culprit in composite weaknesses and failures, and these types of pore networks are prevalent in matrices containing even moderate levels of particles or powders.

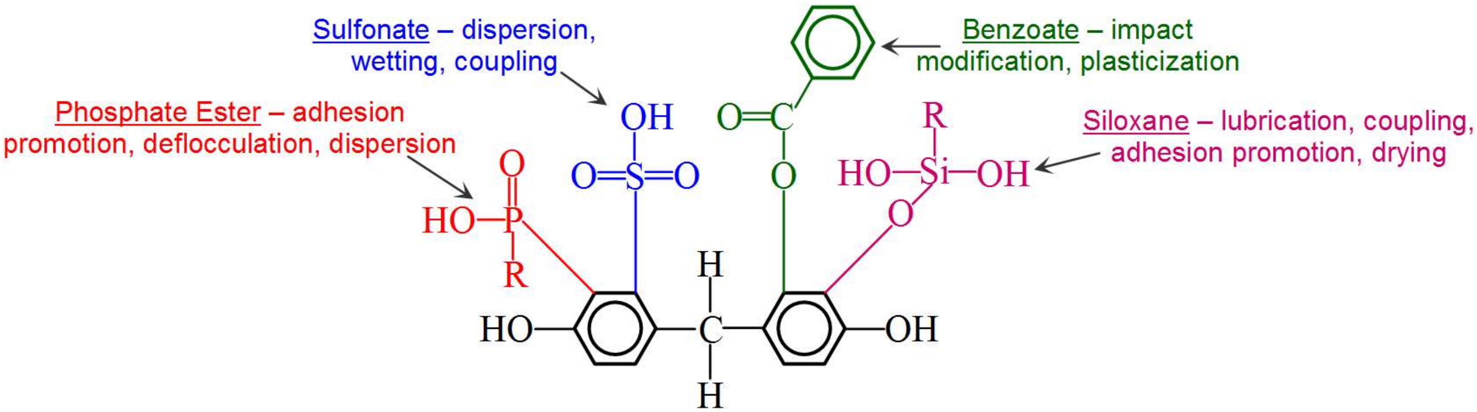
- Particle levels greater than about 5-10% are not recommended for composite impregnating resins. Graphene particles is an emerging carbon form whose effects need to be evaluated more decorously.

Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Polymer Modifications and Formulation Options

- Surfactants are generally linear-type molecules in which the two ends are immiscible with each other. One end may be polar, the other end nonpolar, or one end hydrophilic and the other hydrophobic. This is accomplished by attaching specific functional groups to one or both ends.

- While anionic or nonionic surfactants can be blended into resins, the epoxy chains themselves can also be chemically modified to acquire even greater property enhancements. Functionalized polymers may exhibit improvements in adhesion, dispersion and toughness. Custom resins can be purchased and demonstrated in-house. For epoxy systems, functionalization is best accomplished by incorporating strategic substituents onto ring positions in the diphenol monomer . . .



Bisphenol-F

- Epoxies typically use diamino compounds to crosslink the diepoxide polymer chains. Primary (1^{o}) amines provide the greatest crosslink capacity as each nitrogen atom can facilitate two separate crosslinking reactions connecting multiple chain segments and chains together. However . . .

- Amines are not the only agents that can form crosslinked networks with epoxy polymers. Anhydrides, isocyanates and other crosslinkers can be used. It is interesting to note that specially functionalized silanes and siloxanes can form some very unique crosslinked epoxy networks.

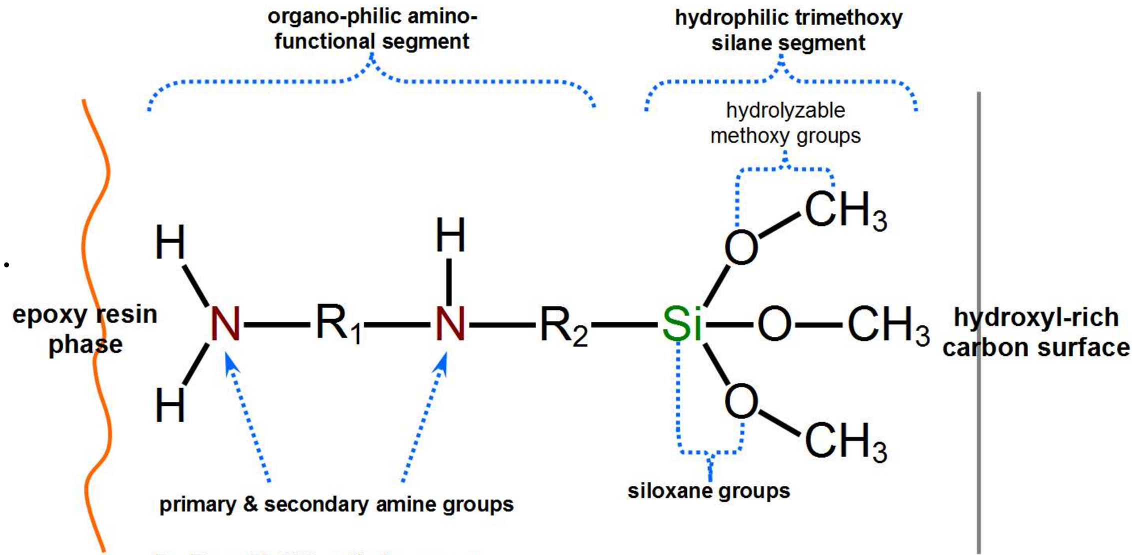
Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Polymer Modifications and Formulation Options

- One of the primary causes of weak ILS properties in laminated composites is the intrusion of excess moisture into the system and it usually accumulates right along the fiber-matrix interfaces.

- Amino-functional oligomers of silane/siloxane and organo-functional siloxanes can not only solve this problem but will impart increased resistance to elevated temperatures, provide a moisture barrier, enhance bonding (coupling) to hydroxyl-rich fibers and facilitate mechanical slip-and-grip effects.

- When blended in with the resin, these agents exhibit multifunctional benefits. They behave as wetting agents, surfactants and coupling agents combined. A properly designed siloxane agent can improve the performance properties of a composite system by 2 or 3 fold.



Possible structure of siloxane coupling oligomer for epoxy resin

- Standard industrial grade prepregging resins already contain a variety of agents and modifiers, but siloxane-type additives can be incorporated by the end-user prior to in-house pre-impregnation.

- Speaking of silanes/siloxanes, amino-functional POSS® compounds, such as OctaAmino-POSS® discussed earlier, can be utilized to impart even more advanced properties and extraordinary performance effects compared to the straight chain entities just covered. These leading-edge materials should definitely be investigated for both fiber treatments and resin modifiers.

Concepts, structures and illustrations are strictly the perception and handiwork of the author

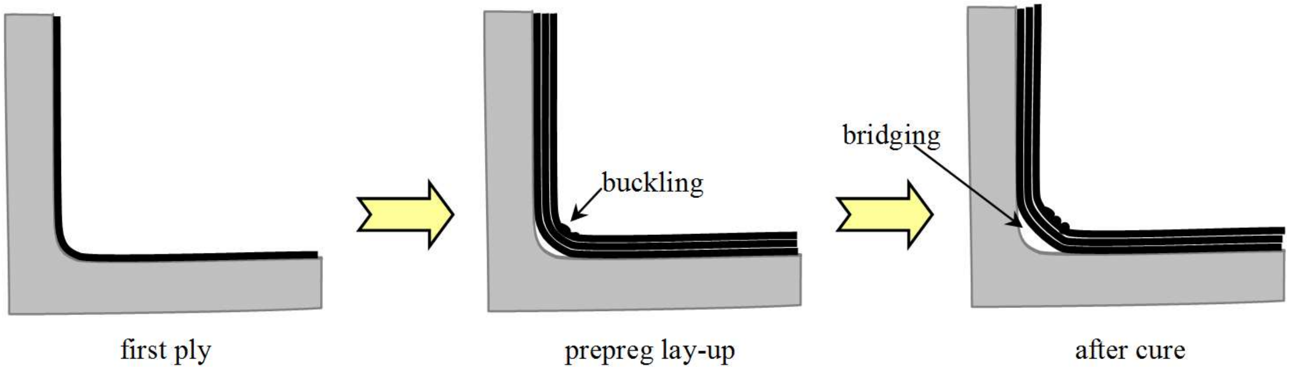
Fabrication, Molding and Curing Concepts

- A few of examples relating to flat *z*-reinforced laminate fabrication have been introduced. The number of options and parameters available is limitless and only a few ideas can be briefed here.
- Also, several references have been made regarding the use of resin infusion methodologies and these are excellent approaches for dry fabric lay-ups, certain preforms, resin transfer molding and solid porous substrates. Obviously, not all articles can be fabricated with this approach.
- As stated earlier, in order to maximize mechanical properties, the reinforcing bundles actually need to be under very slight tension or at least, have all the longitudinal slack removed prior to cure.
- Traditional fiber placement operations can orient the bundles in almost any direction imaginable, but all the fibers are generally in a relaxed state. This is analogous to non-woven n-D preforms. In tow-wound and tape-wound articles (nozzles and tanks), fiber tension can often be controlled.
- However . . . too much fiber tension in any composite system will exacerbate the effects of excessive residual stresses which become cast-in-place during cure, and it is well known that residual stresses often lead to weak interfaces, interlaminar fractures and composite failure.
- Indeed, residual stresses can be present in flat laminates due to over-tensioning, CTE effects and *z*-directional spring-back forces which are cast-in-place. In flat regions, out-of-plane stresses are driven by factors associated with the lateral compressive modulus of the fiber bundle assemblies.
- In contoured articles and female radial regions, out-of-plane spring-back forces are coupled with opposing in-plane compression and tensile forces which intensify the tendency of the prepreg stack to separate from the mold tool during the lay-up procedure and during cure.

Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Fabrication, Molding and Curing Concepts

- Consider the case of a simple female lay-up across a 90° angle mold. The 1st ply (the OML) lays down well, but as each successive ply is applied, the ILM radius is reduced. Longitudinal tension in the first ply forces the lay-up away from the apex, which leads to bridging of the prepreg stack.

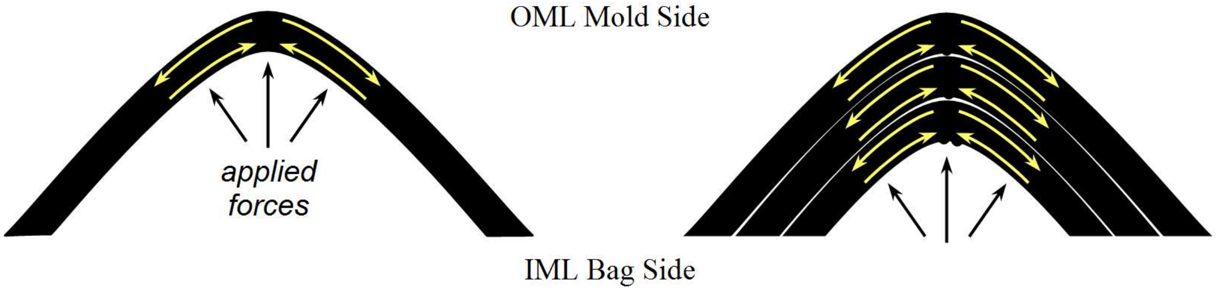


- Often, the full effect is not realized until *after* the cured article is de-bagged and removed from the mold tool. In many cases, the gap fills with resin and the OML edge becomes resin-rich.
- The effects are cumulative. After several plies are applied, a state of trans-laminar ply-to-ply interfacial shear is established across female contour regions throughout the article as a result of the interactions between compressive forces along IML ply faces and tensile forces along OML faces.
- Pre-molded rubber tooling aids, blocks and intensifiers are often applied during the bagging process to help mitigate these effects. In most cases, reduced ILS and ILT properties across radial thicknesses become the weak regions in a contoured laminated article after molding.
- These stresses are long range in nature and their in-plane effects often interact with lamina regions well away from the contour as fiber bundles are stretched and compressed into the acreage regions.

Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

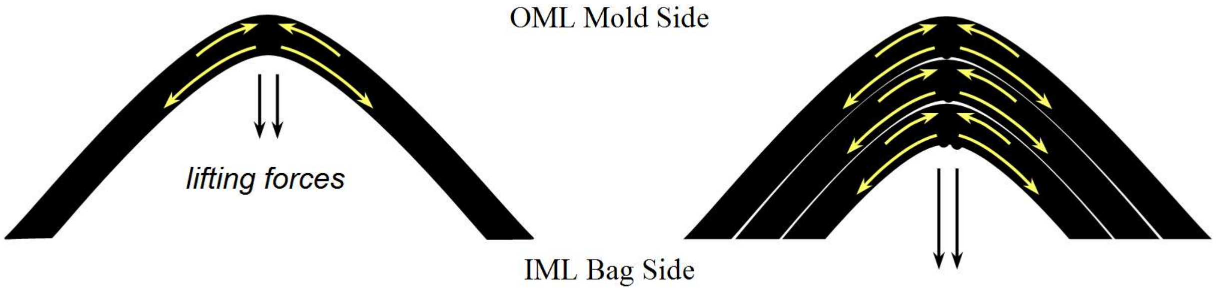
Fabrication, Molding and Curing Concepts

Forces acting on the prepreg *during* lay-up



The operator works the material into place, forcing it to conform to the female contour. Generated in-plane stresses are in yellow, operator-applied forces are in black. The effective radius gradually decreases as each ply is incorporated. Ultimately, in-plane compressive forces along the IML faces begin to buckle the plies. From the operator's IML perspective, these may look like wrinkles.

Forces acting on the prepreg *after* lay-up



In-plane reaction forces (yellow) are responsible for interlaminar shear weaknesses between plys. Tensile forces along OML faces dominate the condition as the material separates from the apex. The material attempts to relieve the in-plane stresses by trying to return to its original (flat) position. The operator may engage in a process of trying to keep the material down and the wrinkles ironed-out at the same time. In these cases, Mode II and Mode I forces are coupled as the Mode I condition is a direct result of the Mode II stresses. These stresses are permanently molded into the article. At some point, the energy may be released in the form of delaminations.

- If implemented effectively, *z*-pinning in these regions could help mitigate the separation forces, but if conducted improperly, damage to the 2-D network could make a bad situation worse. Fabrics treated with CWs, CNTs or CNF could have substantial benefits in ILS (Mode II) strengthening but improvements in out-of-arc ILT (Mode I) would need to be confirmed experimentally.

Concepts, mechanisms and illustrations are strictly the perception and handiwork of the author

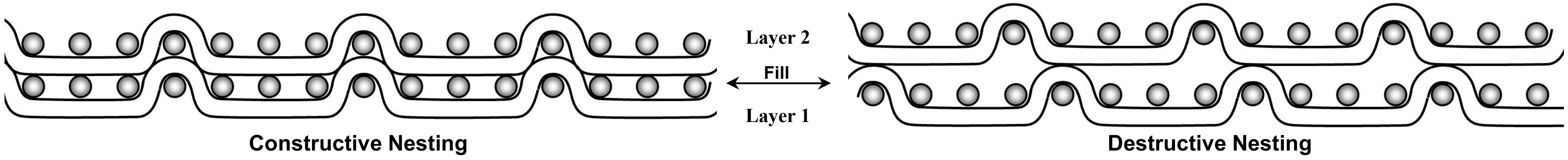
Fabrication, Molding and Curing Concepts

- Laminated composites laid up by hand are subject to human error and part-to-part inconsistencies. Disregarding the principle mechanical property aspects, the specific stacking sequences chosen play a substantial role in ply-to-ply nesting, interlocking and hence, interlaminar shear properties.

- For example, unidirectional (UD) tape lay-ups with all the layers oriented 0° have constructive nesting in the lateral, in-plane direction but none in the axial direction. All angle-ply UD lay-ups possess destructive nesting throughout and usually exhibit the lowest of ILS properties.

- Plain weaves and satin weaves stacked in angled-ply configurations may possess varying degrees of nesting but constructive interactions between weaving features will be highest for 0/0 and 0/90 satin weave lay-ups. Interactions are primarily between weaving crimp peaks and valleys.

Ply-To-Ply Nesting in a 0° 4-Harness Satin Lay-Up, Warp Side Up

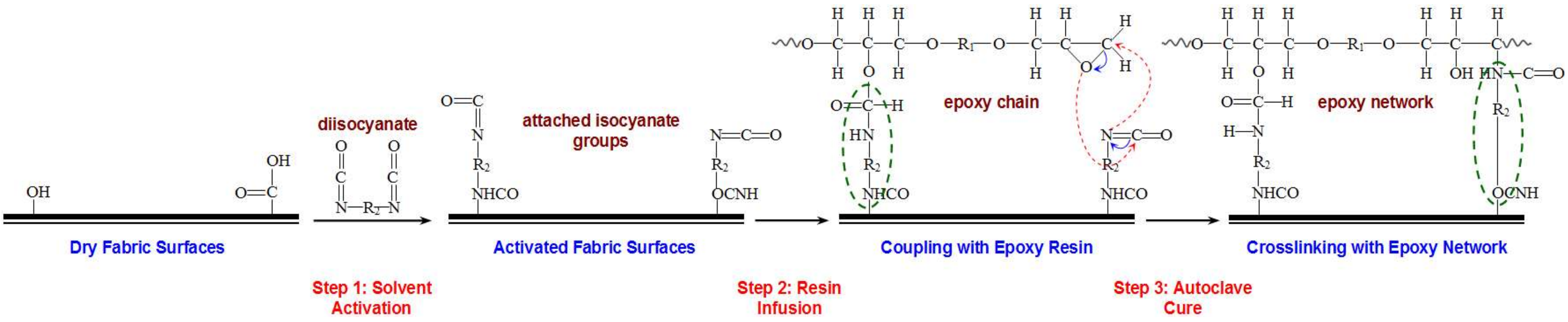


- Even for the best lay-up configurations, efforts to achieve exact placement of each layer for maximum nesting and interlocking are futile. Depending on tow size, varying degrees of constructive nesting and destructive nesting are prevalent across all interfaces in all composites. This alone could account for variations in ILS values from region-to-region in a single article.

- Too many crimps weaken the fabric, promote fiber breakage, decrease fabric pliability and they add to spring back effects. Due to the stiff and brittle nature of carbonized PAN fibers, the more pliable 4 and 8 harness satin weaves are most common and provide for moderate nesting.

Fabrication, Molding and Curing Concepts

- Introduction of the double bag resin infusion technique to the industry is attributed to workers at Lockheed Martin in the mid 1990s. Experiments studying parameters for single bag impregnation of dry fabrics and solid porous composites were personally conducted in the mid 1980s.
- With dry lay-ups, the double bag approach offers better resin distribution as the second bag applies pressure to help spread the resin into regions far away from the resin front. For articles with vertical contours, uniform distribution can be challenging, but multiple resin inlets and vacuum ports can be strategically positioned to facilitate movement of the resin against gravitational forces.
- In either approach, interactions between resin polymers and fiber surfaces can be improved by incorporating a step prior to resin infusion. The appropriate solvent can be infused through the system to modify fiber surface energies (wetting of the fibers) just prior to resin impregnation.
- Better yet, a reactive solvent can be utilized such as a diisocyanate which will interact with fiber carboxyl (–COOH) and hydroxyl (–OH) groups to incorporate active entities along the surfaces that will couple with liquid resin during infusion and crosslink with epoxy OH groups during cure.



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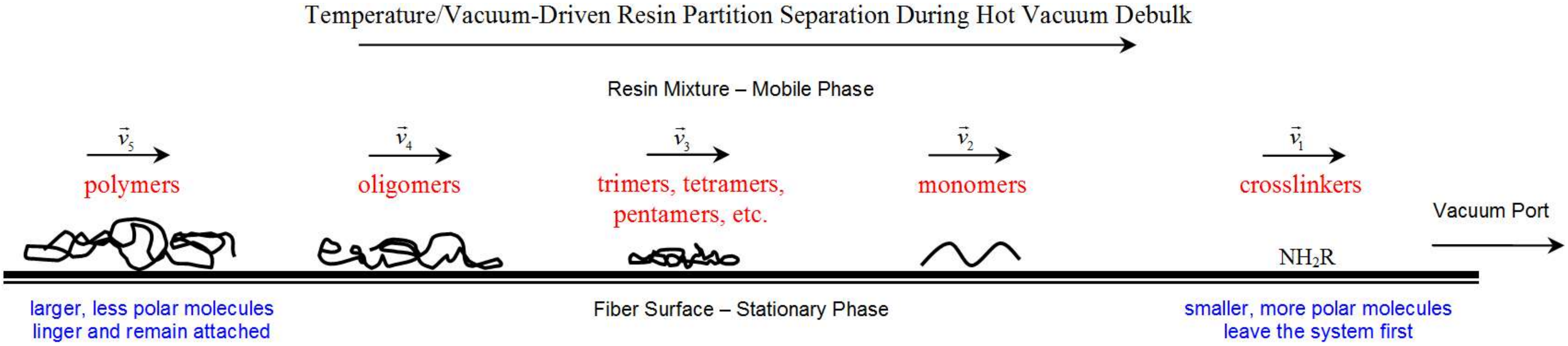
Fabrication, Molding and Curing Concepts

- Hot vacuum debulking is a technique that has been practiced by many composite manufacturers over the years. The intent is to stage the resin, remove air pockets and consolidate the prepreg stack at the same time. It sounds like a good concept. However . . .

- Resins are often mixtures of monomers, dimers, trimers, oligomers, additives, agents and crosslinkers. When heat is applied to a bagged prepreg stack under full vacuum, the components mobilize and begin to move toward the vacuum ports at different speeds . . . much like the partitioning effect in a chromatography process. As the resin mixture is dragged across relatively inactive fiber surfaces (the stationary phase), reverse phase separation tends to occur. Components leading the front may include volatile and semi-volatile solvents, monomers and crosslinkers.



Temperature/Vacuum-Driven Resin Partition Separation During Hot Vacuum Debulk

Resin Mixture – Mobile Phase

$\vec{v}_5$ polymers

$\vec{v}_4$ oligomers

$\vec{v}_3$ trimers, tetramers, pentamers, etc.

$\vec{v}_2$ monomers

$\vec{v}_1$ crosslinkers

NH_2R

Vacuum Port

Fiber Surface – Stationary Phase

larger, less polar molecules linger and remain attached

smaller, more polar molecules leave the system first

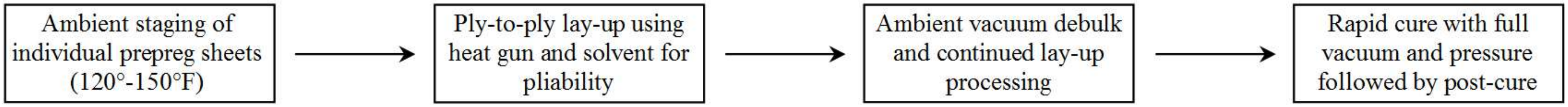
- With varying degrees of porosity and functional activity along the fiber surfaces, a combination of molecular size partitioning and differential polarity segregation may be at play. In any event, long periods of hot vacuum debulking can have damaging effects on resin composition and distribution throughout the entire laminate. After cure, the effects are often perceived as partially cured sections or resin-rich/resin-poor regions, but the results are the same . . . low ILS and low ILT.

Concepts, mechanisms and illustrations are strictly the perception and handiwork of the author

Fabrication, Molding and Curing Concepts

- When properly conducted, the greatest benefits of staging prepreg material before and during lay-up procedures is to control resin viscosity, handleability, resin distribution, degree-of-cure uniformity in the cross section, and to minimize losses in critical low MW components during the early part of the cure cycle – almost opposite to that achieved during hot vacuum debulking.

- Ideally, single layers of prepreg material should be staged individually without the influences of extraction forces or stacking pressures, thus allowing the mobilized resin components to remain evenly distributed on the fabric. Special in-process staging techniques can also be improvised to help facilitate resin distribution through the cross section, but these should be used with caution.



Ambient staging of individual prepreg sheets (120°-150°F) → Ply-to-ply lay-up using heat gun and solvent for pliability → Ambient vacuum debulk and continued lay-up processing → Rapid cure with full vacuum and pressure followed by post-cure

- Methods were developed and shown to minimize degree-of-cure variations across the thickness by differentially staging each ply as it was being applied. While this approach may be subject to variation and individual technique, once the process was optimized, the results were substantial.

- The primary initiation factors associated with weak interfaces and subsequent delaminations are established during the lay-up and molding stages and may include residual stresses, nonuniform resin distributions and compositions, excessive porosity, closed porosity and trapped volatiles.

- Cure cycle design is as much an art as it is a science. The right time/temperature/vacuum/pressure profile for a given configuration is usually determined by trial and error. This field is too vast to cover here but a few comments are in order. As an extension to staging, the goals of curing are to achieve high fiber volume and low porosity with a uniformly cured matrix distribution throughout.

Fabrication, Molding and Curing Concepts

- In conventional autoclaves, composite articles cure from the outside in. For thick parts, this usually means that the degree-of-cure for the interior plies is less than that for the outer plies which often results in over-cooking the outer plies and/or under-cooking the inner plies.

- Degree-of-cure (DOC) variations can be devastating for large structural parts as regions which are not fully cured can exhibit great losses in ILS and ILT. After the resin passes through the gelation process during cure, it undergoes vitrification as glassy hardening takes place due to the crosslinks.

- Unfortunately, for many large or thick articles, long cycles are required to ensure that the differential between leading and lagging thermocouples meets established quality standards.

- In general, long cure cycles are damaging for polymer matrix composites, particularly those with extended gel periods and cycles requiring long catch-up periods for lagging sections. While resin flow and wetting out of fiber surfaces are absolute requirements, excessive resin movement and component separation leads to large inconsistencies in resin content and . . . poor bonding to fibers.

- Resin Transfer Molding (RTM) is an example of an out-of-autoclave (OOA) closed molding process that has gained substantial ground in recent years for producing very consistent, high quality articles by rapid curing of the resin. Dry fabric stacks and prepreg lay-ups can both be processed via RTM. While there are numerous variations in RTM (vacuum-assisted, light RTM, SQRTM, etc.), tooling costs can be high and not all configurations are viable candidates.

- Microwave curing (MC) systems offer another option for OOA rapid curing of bagged articles with an age old consumer technology that is now becoming commercially viable for advanced composites and complex shapes. There are other rapid curing techniques on the horizon.

Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Fabrication, Molding and Curing Concepts

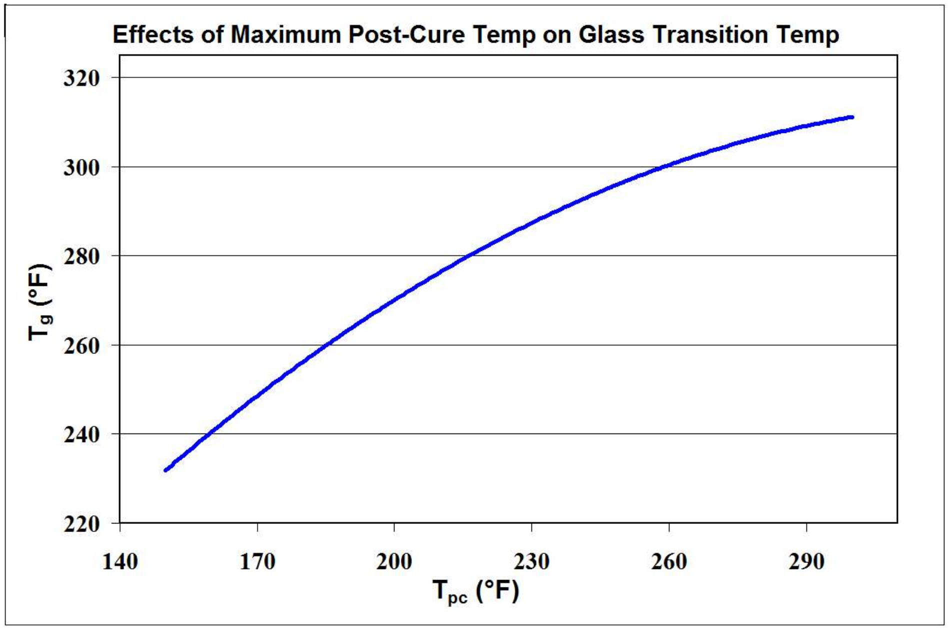
- One tried and proven approach to mitigate the effects of long cure cycles is to subject molded articles to a follow-up post cure treatment. The perception of post-curing within the industry is mixed as the full benefits, design criteria and implementation are not always straightforward.

- However, there is compelling historical evidence clearly showing that properly tailored post-cure processes will enhance interlaminar properties and minimize the propensity for delaminations in almost all thermoset-based composites. This is true regardless of the initial cure cycle applied.

- Crosslinking is a diffusion-controlled process, and the cured glass transition temperature (T_g) is determined by the maximum temperature (T_c) applied during the cure cycle. When T_c is increased, T_g increases correspondingly up to or slightly above T_c. Thus, T_g can be tailored.

- A well executed post-cure treatment will provide high crosslink densities with high DOCs throughout the structure. Such concepts were demonstrated for several thermoset resins including phenolic, Bis-A epoxy and Bis-F novolac.

- Under favorable conditions, it is proposed that a good overall curing approach is to apply a quick, initial cure at normal T_c followed by a time-extended post-cure to ~150°-200°F above T_c.



Data summary of post-cure experiments conducted on epoxy novolac samples which were initially cured to 150°F (Lee, 1984).

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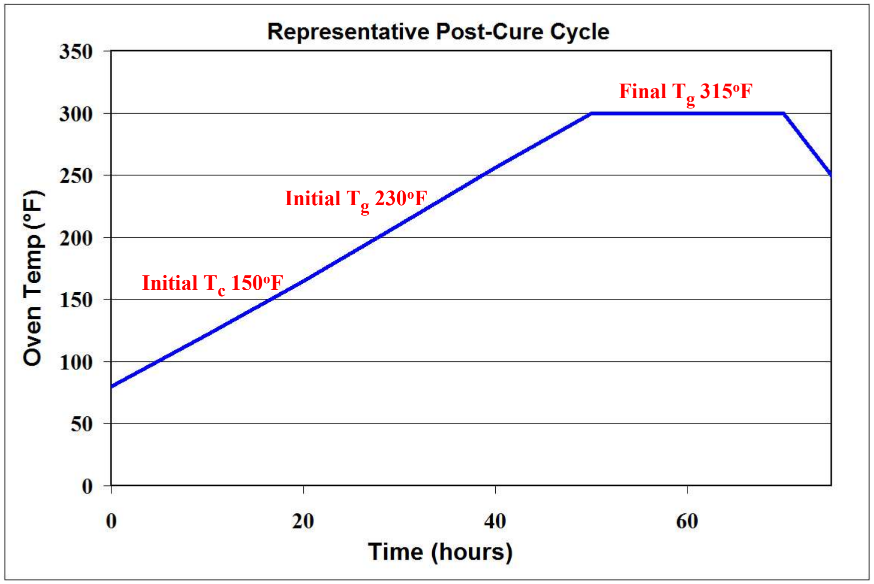
Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Fabrication, Molding and Curing Concepts



Example post-cure cycle applied to small samples of cured epoxy novolac. Larger articles require cycle times in the 7-10 day time frame (Lee, 1984).

- An effective post-cure cycle is a slow process. The temperature ramp should stay behind the gradually increasing T_g without overtaking it.
- When the article exceeds the initial T_g, advanced crosslinking takes place and the material properties increase. For the most part, T_g is directly related to the DOC and crosslink density.
- Such processes will (1) release trapped and residual volatiles (solvents, unreacted components, side products), (2) increase crosslink density, (3) advance and promote uniform crosslinking throughout the article, (4) raise the T_g of the matrix, and most importantly, (5) reduce cured-in residual stresses along the constituent interfaces, thus increasing ILS and ILT.
- Post-curing may have its greatest benefit in troublesome configurations exhibiting wide DOC variations. For cryogenic applications, ambient cure polymers with low post-curing treatments are best in order to minimize CTE differentials and maximize compatibility in cold environments.
- A novel approach to achieve maximum thermomechanical properties would be to flash cure using RTM or MC, de-bag and then post-cure restrained articles in an air-circulating oven for 7-10 days.
- The lesson is plain and simple here . . . the higher the designer/fabricator can raise the final T_g of the matrix, the higher the interlaminar properties and the more thermally stable the composite will be.

Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

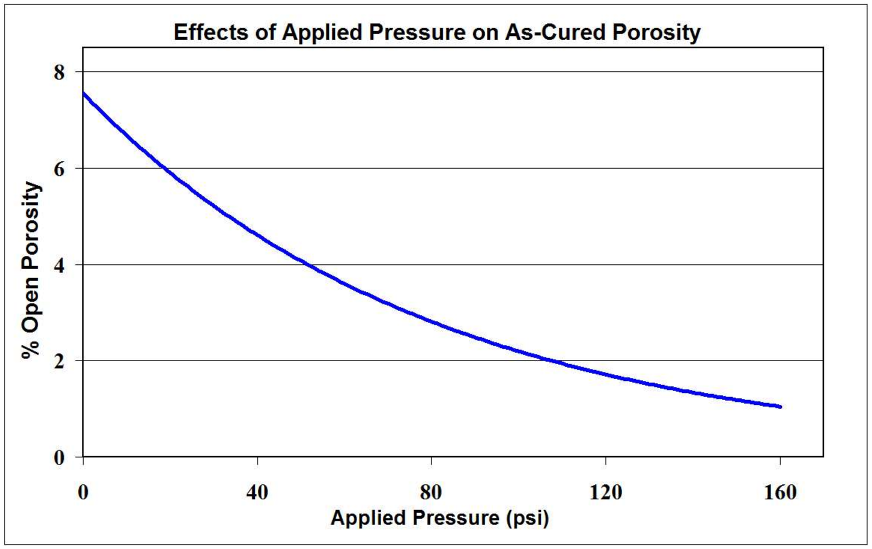
Fabrication, Molding and Curing Concepts

- Application of vacuum throughout the cure cycle has been proven to reduce voids and porosity in cured composites. In addition, applied pressure also reduces porosity, resulting in substantial increases in interlaminar strengths.

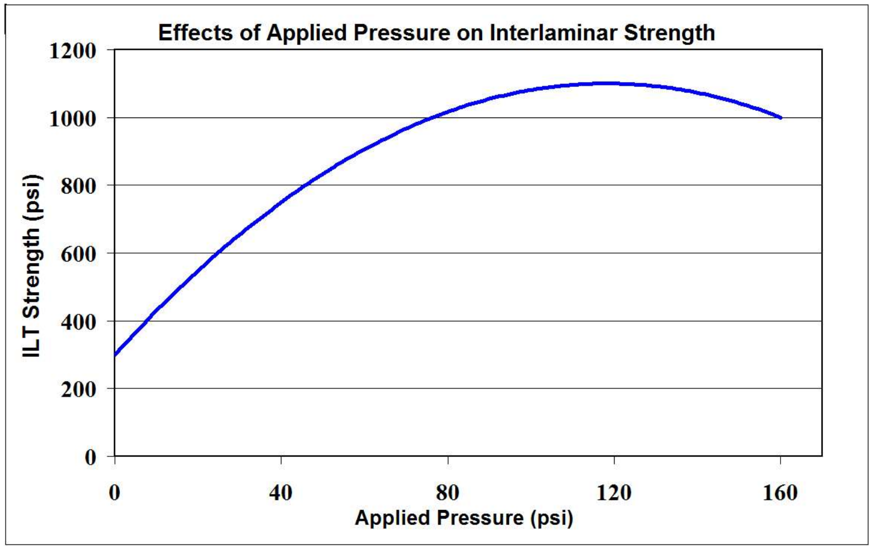
- However, there appears to be a threshold cure pressure after which ILS/ILT properties begin to decrease. Factors associated with excessive cure pressures resulting in weakened interlaminar strengths may be a combination of (1) bulk lateral fiber bundle compressibility, (2) transverse fiber modulus, (3) laminate spring back forces and (4) destructive interlaminar nesting.

- All these factors are pushing back as the laminate is compressed, creating increased levels of cured-in, out-of-plane stress along the fiber-matrix interfaces.

- Experiments evaluating the evolution of porosity and its effects on interlaminar strengths, indicated reduced ILT values when samples of 3K tow 8-harness phenolic/PAN laminates were cured with external pressures in excess of about 120-130 psi.



Data summary from curing trials conducted on T-300 8-harness 3K tow phenolic/PAN test panels; open porosity via ASTM C-20 (Lee, 1985).



Data summary from curing trials conducted on T-300 8-harness 3K tow phenolic/PAN test panels; ILT via in-house technique (Lee, 1985).

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Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Fabrication, Molding and Curing Concepts

- The negative effects of pores/voids on out-of-plane properties is much greater than that for in-plane properties. The magnitude of pressure applied during cure as well as when and how it is applied controls the level of pores and voids, their size and shape morphologies and . . . interconnectivity.

- Interconnected porosity can relieve volatiles and stresses throughout the lifetime of a composite but they can also exacerbate microcracking when extraneous or extreme forces are imparted. Hermetically closed pores and interface voids along fiber surfaces are the most damaging.

Microporosity < 2 nm	**Mesoporosity** 2 nm – 50 nm	**Macroporosity** 50 nm – 100 nm	**Metaporosity** > 100 nm	**Ultraporosity** > μ
water, solvents, unreacted crosslinkers, monomers, dimers, trimers, tetramers, straight chain non-branched oligomers and small linear polymers . . . but not necessarily their agglomerates	moderately branched high molecular weight polymers, folded high tertiary structure polymers, small adducts and some of their agglomerates	branched prepolymers, larger resin polymers and their conglomerates, small crosslinked segments and fragments, very low aspect nanoparticles may pass into pore openings before lodging	most particle fillers and moderate aspect nanoparticles, especially their agglomerates may pass into pore channels but will likely clog passages up to a micron and greater	voids, large pores, micro-cracks and pore clusters not driven by volatiles may represent dry areas with low resin content; primary spaces where particles and their agglomerates come to rest

- The total porosity fraction is the sum of the open and closed porosity fractions, but it should be realized that composite density and porosity are actually a function of the techniques used to measure them. Apparent or open porosity can be measured by infiltrating/intruding/impregnating specific liquids into the material. Special techniques have personally been developed in this area.

- Many test methods are available and most also provide the apparent or bulk density. Bulk density and porosity are two properties that go hand-in-hand. Nitrogen pycnometry can provide the total and skeletal volumes of a sample and hence the total porosity.

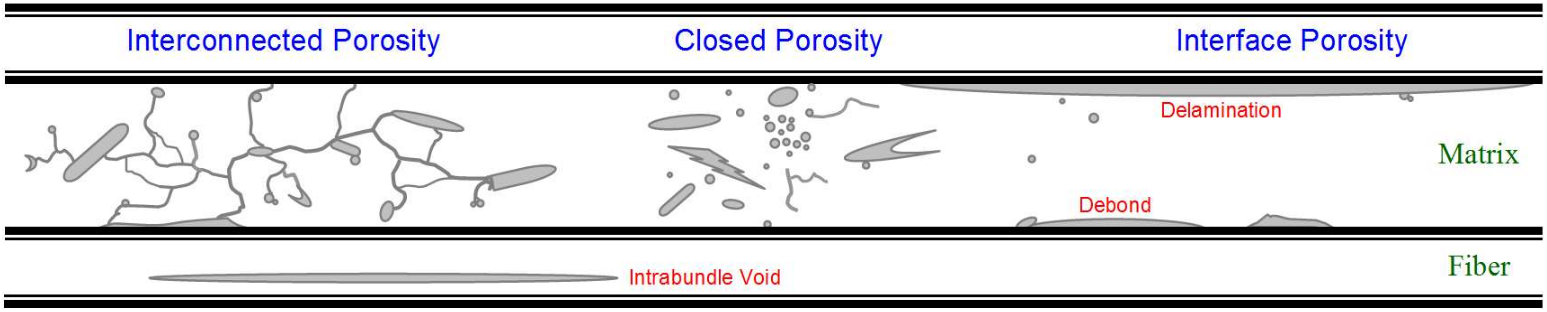
Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Fabrication, Molding and Curing Concepts

- Pores and voids are usually created during resin infusion/impregnation and during cure due to entrapped air and volatile release. When the void pressure exceeds the resin pressure, it continues to grow until the gel point is reached. However . . .

- The total porosity network in a cured article may also contain larger voids and pore clusters created by irregular resin content distributions and compositional inconsistencies as well as stresses and constituent movements manifested during pre-gel and early gelation stages leading to reinforcement distortions and interface separations which become fixed-in-place.

- If pressure is applied during the early phase of gelation, resin loss can be minimized, but if applied too late in the gelation process, the effects on void reduction become insignificant and residual stresses may be incorporated. Every article behaves a little differently than the next, and so-called ‘delayed pressure cures’ can have some undesirable consequences if not precisely controlled.



- The lesson here is that for any given configuration and platform, the maximum applied cure pressure and the time-pressure profile must be optimized. It is usually determined empirically. Just because a certain time-temperature-pressure profile works well for one reinforcement configuration and resin system does not mean it will produce the same results for a similar system.

Concepts, mechanisms and illustrations are strictly the perception and handiwork of the author

Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Fabrication, Molding and Curing Concepts

- Physical measurements of only two or three parameters permit characterization of composite densities, porosities, weight fractions and volume fractions with a given fabrication process. Greater precision requires additional testing and analysis which also provides more details such as closed porosity fractions, matrix density, mechanical strength and modulus correlations.

- Precision values for the fiber density ρ_f and the certified resin content r_w in a given batch of prepreg are generally provided by the vendor. Liquid and cured resin densities ρ_r' and ρ_r can be obtained easily in-house, as well as panel weights before cure and after cure *W'* and *W*.

- At any point during the fabrication (or lifetime) of a nonporous composite substrate, the bulk density ρ_b can be defined as the sum of the products of the fiber volume fraction f_v, its corresponding density ρ_f and the resin volume fraction r_v and its density ρ_r . . .

$$\rho_b = \frac{w_f + w_r}{V} = \frac{\rho_f v_f + \rho_r w_r}{V} = f_v \rho_f + r_v \rho_r$$

- With inclusion of the open porosity fraction p, the bulk density can be written in terms of component weight fractions . . .

$$\rho_b = \frac{W}{v_f + v_r + v_p} = \left(f_w \rho_f^{-1} + r_w \rho_r^{-1}\right)\left(1 - p\right) = \left(f_v \rho_b^{-1} + r_w \rho_r^{-1}\right)\left(1 - p\right)$$

where *w* and *v* are the actual weights of constituents as indicated by their subscripts and the relevant conversion factors are recognized . . . $f_v = f_w \rho_b / \rho_f$ and $r_v = r_w \rho_b / \rho_r$

A few concepts from an extensive composite fabrication model created and developed by the author in the early 1980's

Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Fabrication, Molding and Curing Concepts

- Precision values for the resin content can be analytically determined via several established test methods (such as acid digestion) which permits estimation of the fiber volume fraction . . .

$$f_v = (1 - r_w)\rho_b \rho_f^{-1}$$

- Several published test methods are also available for open and total porosity but if these are not convenient, approximations for the open porosity can be acquired from these expressions . . .

$$p = 1 - \rho_b\left[(1 - r_w)\rho_f^{-1} + r_w \rho_r^{-1}\right]$$

- For practical applications, the bulk density of the composite is taken relative to the open porosity which pertains to the pore fraction that is accessible to liquids such as the matrix resin. This is a reflection of the particular test methods used to measure ρ_b and p.

- The skeletal density is defined as the volume of material that is impervious to the intruding liquids and contains the ‘closed’ pore fraction. Thus, the skeletal density ρ_s and the bulk density are related through the open porosity fraction . . .

$$\rho_s = \frac{W}{v_f + v_p} = \frac{W}{V - v_p} = \rho_b (1 - p)^{-1}$$

- Disregarding small levels of diffusion into the solid material, pycnometry measurements permit approximations of the ‘true’ density and hermetically sealed porosity fraction which compliment open porosity measurements determined from one the Archimedes-type methods.

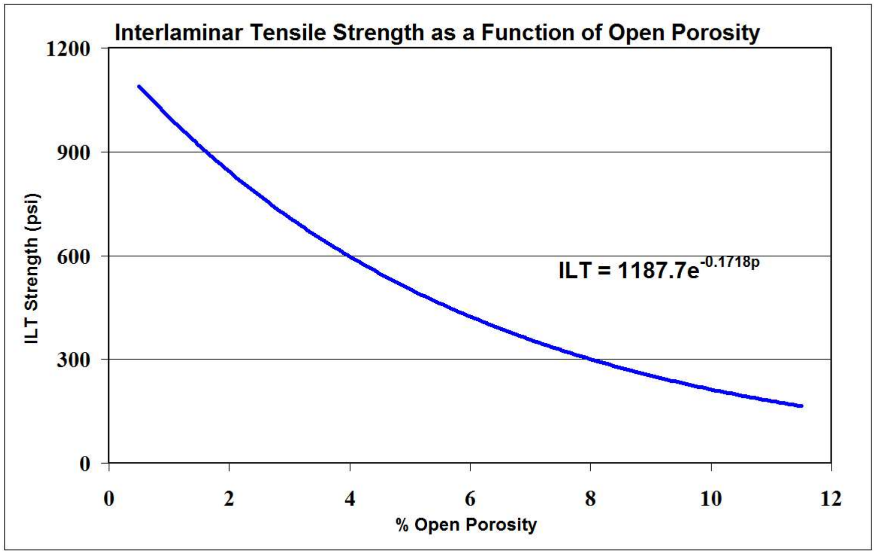
A few concepts from an extensive composite fabrication model created and developed by the author in the early 1980’s

Enhanced Techniques for Improving Z-Directional Properties in Laminated Composites

Fabrication, Molding and Curing Concepts

- As-cured ILT strengths are a function of the total porosity in a given composite with varying dependencies on the closed porosity fraction, the open fraction, the interface and reinforcement fractions (extent and types of voids and pores along the interfaces and within the reinforcement).

- It was shown that the relationship between measured ILT strengths and open porosity measurements is basically exponential in form, $ILT = A\mathrm{e}^{-kp}$ which permits estimated correlations for ILT from open porosity data. If porosity testing is not feasible, p can be approximated using measured values for composite bulk density and resin content data as indicated earlier.



Data summary from porosity studies conducted on phenolic/PAN samples (Lee, 1986).

- This is a sampling of special tools which have provided great benefits over the years for a variety of reinforced and particle filled binder/matrix systems. Analogous characterizations have also been developed for flexural strength, short beam shear, matrix content, matrix volume, co-matrix volume, fiber weight fraction, particle weight and particle volume fractions and other properties.

A few concepts from an extensive composite fabrication model created and developed by the author in the early 1980's

Author Biography, Background Skills and Expertise

- Hands-on involvement in wet composite lay-up, molding, forming, adhesive bonding, sealing, fill & fare, metal finishing, corrosion control, primers and paints since the early 1970's (family-owned business). Over 40 years scientific/engineering experience in leading edge technologies, experimental R&D, industrial processing and shop manufacturing including roles as Principal Investigator in applied R&D and corporate-sponsored IRAD in the areas of Composite Materials Science, Coatings Formulation, Polymer Chemistry, Surface Finishing and Electrochemistry.

- Principle Scientist/Engineer throughout the 1980s at LTV Aerospace & Defense for the design and fabrication of advanced aerospace composites. Chief Assistant to the inventor of Reinforced Carbon-Carbon (RCC) composite technology for the Space Shuttle program. Formulated, developed and characterized the original phenolic matrix / PAN fiber-reinforced, next-generation Advanced Carbon-Carbon (ACC) platform. Pioneered new approaches for 2-D/3-D composite design, composite fabrication, polymer densification, manufacturing science and process characterization. Improvised leading edge methodologies for thermoset and thermoplastic polymer infusion/impregnation, resin formulation and modification, porosity control, pore characterization, delamination remediation, enhanced curing/crosslinking mechanisms, unique molding techniques, incorporation of 3-D reinforcements, z-directional enhancements and special hybrid fiber/tow configurations, alternative weaving and reinforcement designs, fiber/fabric surface modifications via chemical and thermal treatment, and differential CTE mitigation between constituents. Formulated, investigated and/or characterized low CTE phenol-aldehyde resins, high T_g epoxies, mesogenic polyimides, cyanate esters, and polysiloxanes as pre-ceramic binders and coatings. Developed original methods for chemical, physical, mechanical and thermal characterization of porous and nonporous materials, carbon fibers and fabrics, thixotropic polymers, cured, partially cured and post-cured resins.

- Engineering experience also includes tenures at Lockheed Martin and Bell Helicopter Textron utilizing carbon and glass fiber-reinforced epoxies, polyimides and cyanate ester composite structures, plating and metal finishing on the V-22 Osprey, the F-22 and the F-35. Project Scientist at Poco Graphite studying the various forms carbon, graphite and oxide/nonoxide ceramics including amorphous carbon, pyrolytic carbon, CVD graphite, mesophase/petroleum pitch, SiC/Si_3N_4, polysiloxanes, ureasilazanes and organosilanes as precursors for polymer-derived ceramics. Chief Formulation Chemist at Graham Magnetics for experimental R&D into elastomeric adhesive coatings derived from both solvent-borne and latex-type water-based semi-thermoset formulations utilizing uniquely synthesized polyurethanes, functionalized vinyl esters, non-isocyanate crosslinkers, phenoxy-modified epoxies, siloxane-acrylates, silane-terminated polyethers, and numerous graft, block and hybrid copolymer systems as well as hundreds of surfactants, additives and modifying agents, nanoparticles, pigments, ball milling, sand milling and contemporary slurry processing methods from small experimental test trials to thousand pound master batches. Innovated, developed and scaled-up several original new coating products from bench level R&D through pilot line production. Independent Consultant for several composite companies investigating alternative polymer precursors, strategic reinforcement configurations and novel manufacturing methods for lay-up, spray-up, pultrusion, bonding/fastening, infusion/impregnation, densification, out-of-autoclave curing, high performance coatings and ceramicization of carbon substrates. Manager, Failure Analysis & Reliability at RF Monolithics. Developed original electroless plating formulations E-Ni, Cu, Ni-Cu, Ag, Au, Pd, Cr, SiC/E-Ni and PTFE/E-Ni for deposition onto metallic and nonmetallic substrates as Lead Plating Chemist at PVI. Materials Science Engineer for Jacobs Technology at NASA Marshall Space Flight Center since 2007 providing support in multiple areas involving leading edge metallic and nonmetallic materials for the design and manufacturing of next-generation space vehicles and launch platforms.

- Over the years, pioneered numerous innovations in advanced composites, protective coatings, ablatives, ceramics, corrosion technology, manufacturing development and mixed material systems. Scaled-up new products and processes from bench level R&D to semi-scale production. Established unparalleled expertise with a quintessential vision for the development of next-generation C-C materials (NCC, nomen novum), CMC platforms, polymer-impregnated ablatives, and reusable polymer matrix composites that can survive extreme environments. Acquired B.S in Chemistry at UTA in 1982 and completed graduate work as an M.S. candidate in Chemistry and Materials Science at UTA and UAH.

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