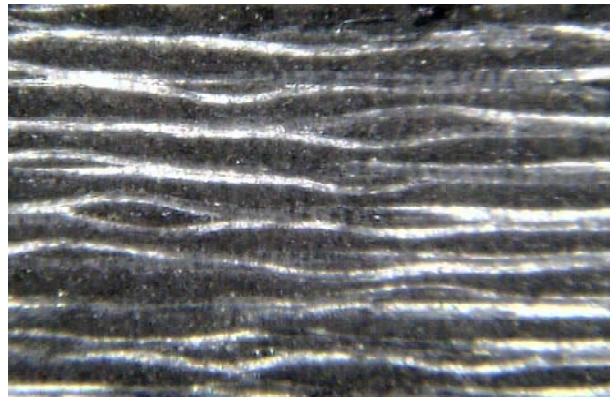


Interlaminar Factors in Rayon vs. PAN-Based Laminated Composites

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Cross-sectional thickness image of carbonized rayon fabric-reinforced / charred phenolic-matrix laminate



Cross-sectional thickness image of carbonized PAN fabric-reinforced / charred phenolic-matrix laminate

Longitudinal tensile strengths for carbonized PAN-reinforced laminates are 4 to 5 times greater than those which are reinforced with carbonized rayon fabric. In actuality, the tenacity of isolated PAN carbon fibers is only 2 or 3 times greater than rayon carbon filaments, but because rayon fibers are crimped along their lengths during the fiber manufacturing process, tensile strengths of their corresponding laminates are reduced accordingly. In addition, modulus values for carbonized PAN fibers can be 6 to 10 times higher than moduli for carbonized rayon fibers. In short, PAN-based laminates are significantly stronger and overwhelmingly stiffer than rayon-based laminates . . . in the x - y plane.

From these photos, it is apparent which of the two laminate systems exhibit the greatest ply-to-ply associations and *interlaminar nesting*. In fact, it is well documented that interlaminar properties for rayon-based laminates are 2 to 4 times greater than those for PAN laminates, particularly in terms of interlaminar shear (ILS) and interlaminar (flatwise) tensile (ILT). Not surprisingly, ILS failure modes for rayon laminates often include in-plane micro-buckling and out-of-plane flexural protrusion of the fiber bundles sometimes leading to brooming effects, while PAN laminates often undergo classical ply-to-ply interlayer shear due to bondline rupture along the affected fiber-to-matrix interfaces. Analogously, ILT failures often fibrillate the rayon fiber bundles while the stiffer, more tightly bound PAN bundles frequently generate clean interlaminar (bondline) separations with occasional out-of-plane transverse fractures through the adjoining fabric layers.

For these two samples, fiber processing temperatures are comparable so both contain similar fiber surface functional group compositions to participate in chemical bonding, but mechanical interlocking properties between the two are vastly different. This is due primarily to the morphology differences generated during the fiber polymerization/spinning process and partly to the specific fabric weaving styles utilized for each system. These differences result in composite laminates in which the rayon fabric layers are highly interacting while the PAN layers are not. For the samples above, the rayon laminate was molded from fabric of a plain (square) weave configuration while the PAN sample was fabricated using 8 harness satin weave fabric layers.

Thus, the rayon lamina are more interacting and intertwined, but overall, the end composite product is softer and weaker. While 2-D PAN-based laminated systems may fulfill the structural designer's mechanical requirements in many regards, it is an unavoidable fact that PAN layers are flat, smooth and non-interacting . . . and fiber-to-matrix mechanical interactions are relatively insignificant, which translates into poor z -directional (interlaminar) properties. This is one of the most challenging issues facing the advanced composites industry today, and has been for several decades. To date, an effective, universal solution to the interlaminar weakness problem in PAN-based composites worldwide has not been found or publicized.

Due to the widespread use of carbonized PAN fibrous reinforcements throughout the composites world, this issue is of utmost importance and often tops the list of research efforts under pursuit. One thing has become increasingly clear . . . inferior interlaminar properties in reinforced composites can almost always be attributed to the presence of 'weak planes' (or weak interfaces), that is, poor ply-to-ply interactions and weak interlaminar bonding. In general, all contoured laminated composite systems contain interlaminar weaknesses to some extent or another. This pertains to shaped articles with continuous woven fabric-reinforcements of glass, ceramic and carbon alike. It is even possible for the *flat* regions in highly contoured articles to contain interlaminar weaknesses which have transferred into the region from adjoining contoured sections. This is something that should be kept in mind when using flat control or witness panels to evaluate contoured articles.

Initiation and provocation of weak lamina interfaces can be associated with poor interlaminar ply-to-ply nesting and/or the effects of extraneous or intrinsic mechanical forces generated along the fabric layers often during the fabrication stage. Perhaps the latter of these conditions could be classified as *mechanically-induced* weak interfaces. Aside from some of the more modern alternatives to laminated configurations such as fiber placement, filament winding, z -pinning and 3-D preforms, classical laminated systems have long been and are still plagued by the effects of weak interfaces which may be regionally localized, widely scattered or pervasive. Undoubtedly, these weak bonding interactions are one of the leading culprits to inferior interlaminar properties. More importantly, they too often become the precursor to ply separations and delaminations which manifest themselves during subsequent processing steps or sometime during the article's service life.

It can now be stated with confidence that one of the principal factors leading to the formation of weak interfaces in laminated composite systems is the development of *residual stresses* which are incorporated into the composite during one or more of the steps applied in the fabrication process. At any given temperature, an array of varying residual stresses may be present within any of the composite constituent phases . . . or along their interfaces. Two types of stresses are of relevance here. Stresses associated with CTE differentials between the constituents which develop during thermal processing (cure cycles, heat treatments, pyrolysis, etc...), and those associated with constituent material properties, such as fiber/fabric moduli – as they interact with the contour of the mold tooling and the constraints of complex article geometries. Either of these stress forms may act at the constituent level, at the lamina level, at the bulk composite level, or simultaneously across all three levels, either independently or in a coupled/combined fashion where one exacerbates the other.

For composite materials, CTE-related stresses are expected to exhibit thermal hysteretic behavior and may be associated with a specific temperature value during heating and cooling cycles in which the stresses are near zero, the so-called 'stress free temperature'. Upon heating, the composite or its constituents do not return to their original positions when cooled. On the other hand, geometrically-induced stresses are purely mechanical in nature and exist as a result of material behavior during prepreg composite assembly and its response to the tooling geometry (effects such as fabric deformations, distortions and radial springback). It is thus temperature-independent. A certain degree of coupling between the two conditions is inevitable and essentially insures that thermal cycling (and CTE movements) will either relieve or intensify the mechanical stresses to some degree before they reciprocate in the second half of the cycle. Obviously, the long term effects of thermal cycling include material fatigue and weakening of the structure, particularly along the constituent interfaces. Inevitably, residual stresses initiated within the fiber phase will translate into stresses at the fiber-to-matrix interfaces which establishes the condition of mechanically-induced weak planes. Regions containing these weaknesses may eventually lead to the formation of interlaminar separations in and by themselves or when augmented with extraneous bifurcation forces which can be associated with thermal, structural or geometrical factors.

Interlaminar ply-to-ply nesting (or nestling) is characterized by the alignment and intertwining of protruding fabric features from one layer to the next. Obviously, precise alignment between every ply in a composite structure is impossible, regardless of how precise the lay-up equipment is or the skill level of the lay-up technician. Without a doubt, the quality and extent of nesting will vary throughout the article. The 2-D lateral weaving style of the reinforcement fabric determines the pattern and symmetry of potential meshing features across the x - y fabric plane along with the 3-D out-of-plane (z -directional) indentions and protruding features associated with the fabric layer, all of which play a major role in the nestling effect. Such features may typically be fiber bundle segments which bulge in and out of the fabric plane in accordance with the lateral weaving pattern (plain vs. satin) and the protruding crimping amplitudes generated during the weaving process as the fill yarns pass over and under the warp yarns. These features could perhaps be referred to as *weaving* crimps.

In the case of traditional composite grade rayon, the shape of the fiber becomes an important factor in its role as a reinforcement. Near the end of the fiber manufacturing process, *fiber* crimps or bends are generated along the length of the filaments which exhibit a zig-zag or sine wave like appearance. Additionally, during the coagulation step, typical rayon fibers will develop an inner core of unprecipitated viscose surrounded by a peripheral region (skin or corona) which is fully polymerized and solidified. In the process, the shrinking periphery forms a serrated pattern around the circumference of the fiber. These features are often referred to as *crenulations*. In the photo of the rayon sample given earlier, the longitudinal crimping pattern is apparent and can be seen collectively within the fiber bundles as depicted, but the crenulations cannot be seen unless the sample was rotated 90° and zoomed in on the cross-section of the individual filaments. Thus, conventional rayon fibers possess features of *shape morphology*, both longitudinally and laterally, that traditional PAN fibers do not exhibit, and these features become key attributes in the distinction between the two fiber systems in terms of interlaminar nesting, ILT and ILS . . . before the fabric weaving style is even selected.

In addition to fiber shape morphology and the attributes associated with the specific fabric weaving pattern, the particular lay-up configuration and laminating process chosen for the composite article can also influence the nature and degree of ply interactions. Obviously, not all ply-to-ply lay-up orientations produce the same results. Clearly, cross-ply plain weave configurations (0° - 90° or 45° - 45°) nestle quite well in the x - y plane, while cross-ply unidirectional tape lay-ups do not nestle at all, and pure 0° unidirectional lamina might exhibit exceptional nesting . . . in one dimension. One could speculate on the effective ply-to-ply nesting effects associated with crossply laminates formed from 4 and 8 harness satin weave configurations. An argument could be made that fewer z -directional features provide greater opportunities for more effective alignment and nestling between layers, while too many features distort or subdue the overall effect, but such an argument would be unfounded.

In any case, it is a foregone conclusion that poor ply nesting can facilitate the evolution of weak interfaces within any composite structure. Such a condition could be referred to as *nestling-induced* weak planes. Weak interfaces attributed to poor ply nesting are inherent conditions that many composite designers never fully realize. The absence of inadequate nesting interactions and ply meshing tend to limit the physical and mechanical interactions between interfacing ply bundles and can only lead to lower ILT/ILS properties. This is obvious. More importantly, the ever-presence of intrinsic residual stresses which exist in essentially all composite structures can only make a bad situation worse, and when poor nesting and residual stresses interact, the consequences can be disastrous. Unfortunately, both of these conditions are completely undetectable by current NDE methods. From a diagnostic perspective, they are invisible subtleties. Traditional forms of nondestructive energy attenuation (x-ray, ultra-sonic, IR, etc..) can only reveal separation-type anomalies well after the defect has already materialized and progressed to the point of physical detection. Ultimately, the coupling of residual stresses and inadequate nesting sets the stage for delaminations and ply separations that can make the failure analysts scratch their heads for years to come.

Ply-to-ply nesting can also be influenced by the fiber *surface morphology*, that is, fiber surface roughness and irregular micro-features which might include tiny protrusions, indentions, pores, holes, gaps and interstices. When combined with robust fabric weave nesting patterns, surface morphology features can enhance mechanical interlocking effects in two very important respects . . . (a) interlaminar (ply-to-ply) interactions as already discussed, and (b) physical/mechanical binding interactions between the fiber and the matrix phases. As a matter of course, intrusion of liquid matrix polymer into these pores and surface features is never complete. The degree of matrix penetration and interaction with the fiber morphology is dependent on several factors. A few of these might include . . . the molding conditions utilized (specific time/temperature/pressure curing profiles), fiber sizing formulation (fiber coatings may include coupling agents, surfactants and wetting agents among other ingredients), resin viscosity and resin solvent(s), resin distribution and local volume fractions, and the degree of hydrophobicity/hydrophilicity which is influenced heavily by the nature and density of chemical functional groups along the surfaces of the fibers (an abundance of compatible reaction sites across the fibers attracts resin into the surface aberrations).

Thus, some of the factors which can control or influence the degree of ply-to-ply nesting include (a) fabric weaving patterns and associated out-of-plane features, (b) longitudinal and transverse fiber shape morphology, (c) fiber surface morphology, (d) fiber bundle tow size and style including attributes such as filament count, twist, plying, etc..., and (e) fabrication parameters and molding conditions. Further elaboration of these factors might include the following comments. For (a) and (d), unidirectional, plain weave and satin weaves are the most prominent configurations used for laminated composites worldwide, but the respective 2-D weaving architectures and z-directional features do not necessarily produce the same results in a composite. Larger tow diameters may reduce the density of nesting sites but could also increase the intensity of mechanical interlocks. An ideal tow size and optimal weaving configuration exists for each composite system and must be determined.

For item (b), longitudinal crimps and lateral crenulations are unique to commercial rayon fibers, however, production of these features has been demonstrated, to varying degree, with fibers made from polyester, polyamide and even PAN. Apparently, in order to maintain the high strength properties PAN fibers are so well known for, PAN fiber manufacturers perceive these types of shape morphology features to be detrimental (after all, the crenulated corona layer surrounding the core is often split, weaken peripheral material while nonlinear longitudinal features, such as crimping, prevent the true tenacity of the fibers from being realized when embedded within a hardened composite matrix). For (c), glass fibers are brittle with pits, pores and irregularities, PAN fibers are brittle but stiff, straight and smooth, while rayon fibers are softer and more porous. Fiber surface features and aberrations can sometimes play a moderate role in interlaminar nesting effects, but they provide their greatest benefits at the fiber-to-matrix interface by enhancing mechanical bonding (interlocking) between the two phases (of course, these effects cannot be fully realized in the case of smooth fibers such as PAN).

For (e), the specific curing pressures as well as the overall time/temperature/pressure profile can influence the level of damage and shifting that occurs to the principal nesting features at the ply meshing interface. Obviously, a certain level of pressure is needed to effectively mate the nesting features together but clearly, excessively high curing pressures on soft rayon laminates can damage and shift the nesting contact points, degrading the interlocking effect. Indeed, high pressure cured laminates of both rayon and PAN have been independently documented to exhibit reduced interlaminar properties. Under the sustaining conditions of full vacuum bag pressure (14.7psi), it has been repeatedly demonstrated that supplemental autoclave pressures of less than about 80-100psi for both rayon and PAN-based laminates produce the most optimal mechanical properties and the highest ILT/ILS values. Nesting effects manifest their greatest benefits in laminated composites during ILS loading, while ILT is more dependent on the degree and quality of fiber-to-matrix bonding, but excessive pressures and extended autoclave ramp and hold times have been shown to have negative effects on both properties.

The chemistry and polymer science behind the formation of rayon (cellulose) and PAN (polyacrylonitrile) fibers is well documented throughout the literature. Likewise, manufacturing details associated with the fiber spinning processes for these two polymer systems can easily be referenced and documented from textbooks and publications. It is not the intent here to rehash or delve heavily into these topics since one can become enlightened from other readily available sources, but it would be most interesting to explore their relevance with respect to the unique fiber shape morphology

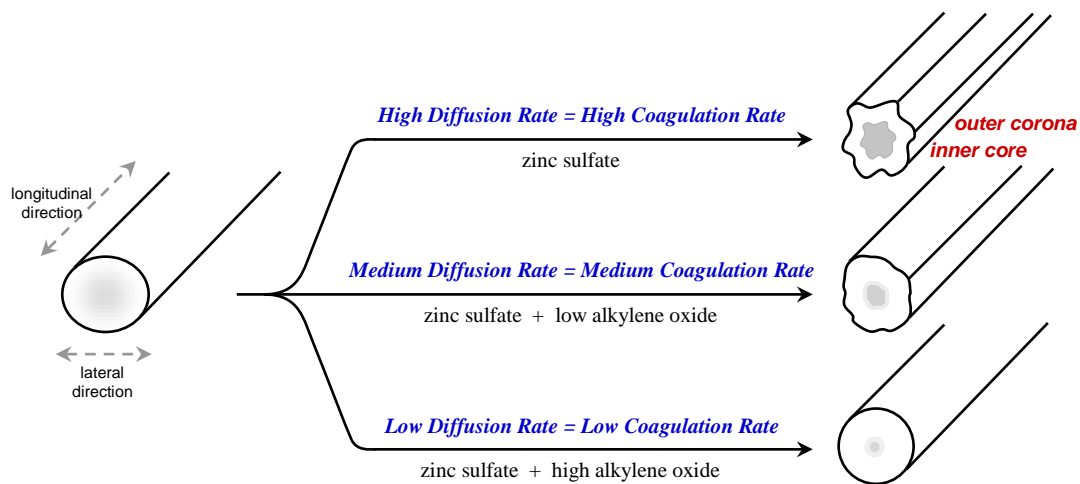
features which are of interest here . . . unfortunately, it is information concerning these particular morphological features that is not so easy to find. Thus, it seems appropriate here to offer a theory or plausible explanation regarding the likely factors that are believed to be responsible for influencing the formation (or the lack thereof) of lateral fiber crenulations and longitudinal bending crimps.

While the production of both rayon and PAN fibers traditionally utilizes a wet-spinning process, these materials can also be formed using dry spinning techniques and in some cases, melt spinning (other emerging approaches of potential prominence include gel spinning, reaction spinning and electro-spinning). In general, for wet (solution) spinning, the raw fiber precursor is dissolved in an appropriate solvent to form the 'doping' solution which is forced through a spinneret (a shower head) that is immersed and fixtured inside the coagulation bath. Polymerization and/or solidification (precipitation) of the fiber occurs during the coagulation process and the drawn fibers are sequentially subjected to weaker coagulating solutions as well as additional mechanical, thermal and rinsing treatments. A more recent approach for the formation of high performance fibers uses a combination between wet and dry spinning referred to as *dry-jet wet spinning*. Here, the doping liquid leaves an unimmersed spinneret and passes through an air gap before entering the coagulation bath. When effectively applied, this method has been shown to produce fibers with improved properties (such as increased crystallization and tenacity) and it is actively being considered for the formation of rayon, PAN, PBI, aramid, polyimide fibers and several others.

As is well known, traditional rayon fiber is a cellulose derivative and wood pulp is the most common starting material for cellulose fibers. The final fibrous product sold on the market is often called 'regenerated cellulose' because the original cellulose must be partially de-polymerized and converted into a salt that can be solution-processed (wet spun) before it is finally de-salinated and converted back into polymeric cellulose during the coagulation process. The doping solution contains the cellulose-salt which is drawn up through an acidified coagulation bath containing a zinc salt (or other transition metal compound which act as 'non-solvents') where it polymerizes and solidifies from the outside in. This results in a scalloped or crenulated cross-section because the outside periphery (the skin or corona) polymerizes first and is drawn more rapidly through the bath than the interior (core) of the fiber which remains in a less polymerized liquid (viscose) state.

In practice, the raw wood pulp is first dissolved in strong caustic solution (sodium hydroxide) and then reacted with carbon disulfide to form the corresponding xanthate salt whose higher polymers will remain in solution as they form. The initial xanthate solution is aged and oligomerization occurs which forms a viscous liquid sometimes referred to as 'viscose'. After the viscose is forced through the spinneret holes and drawn through the first coagulation bath, it is highly gelled and the outer regions (the corona) are polymerized as the regenerated fiber begins to form. It is then passed through several sequential coagulation baths with decreasing levels of sulfuric acid and metal salt which propagate the regeneration process. One or more of the baths are heated and the fiber is stretched as it passes through, increasing its tenacity. Eventually, the fibers go through an aqueous bath where *relaxation* occurs resulting in the formation of sine wave-like *crimps* along the length of the fiber (10 to 30 crimps per inch are common). These longitudinal crimps are permanent so that every time the fiber is stretched out, it naturally returns back to the crimped position under ambient (humidity) conditions.

In actuality, the regeneration/polymerization process that occurs during coagulation is a *diffusion* process in which the acid diffuses into the thickening viscose where neutralization takes place while the regeneration products (sodium salts of sulfide and sulfate) diffuse out as polymerization progresses and the viscose precipitates into a solid fiber. Thus, there is simultaneous diffusion into and out of the fiber. It might be surmised that the zinc compound acts as a catalyst in the polymerization process and facilitates these transfer reactions, thus increasing both the rates of coagulation and diffusion. High diffusion rates lead to the formation of a distinct inner core of liquid viscose surrounded by a skin or corona of polymerized product around the outer diameter of the fiber whose lateral morphology becomes serrated as the polymer solidifies. Lower coagulation/diffusion rates soften the crenulations and diffuse the skin-core boundary. Certain agents (based on alkylene oxide, glycols or amines) appear to retard this process, leading to the formation of smooth (non-crenulated) fibers. Thus, the rate of coagulation/diffusion is the primary factor that determines the formation and nature of lateral crenulations in rayon fibers in terms of shape, amplitude and frequency. These effects can be illustrated in a simplified fashion . . .

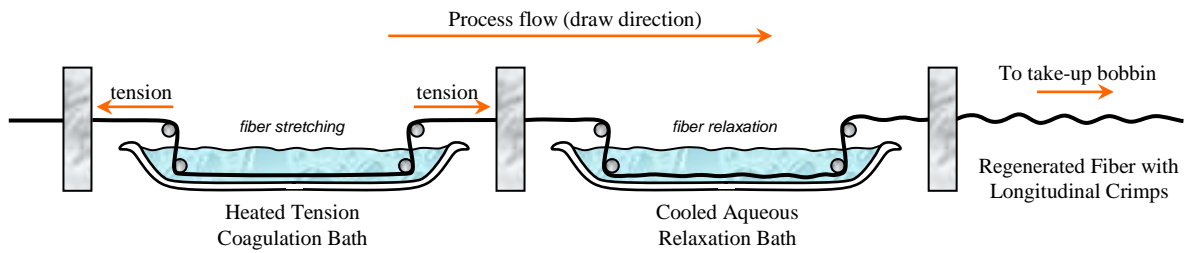


More recently, it has been found that cellulosic wood pulp can actually be dissolved in certain polar organic amine solvents leading to the formation of higher tenacity rayon fibers – *without* depolymerization or the production of undesirable caustic and sulfide waste products. Coagulation is accomplished by successive drawing of the fiber through increasingly dilute aqueous rinses (both rayon and PAN polymers are insoluble in water). The most well known cellulosic fiber product from this method is *Lyocell*. This has helped open the door to a family of polar *aprotic* amine solvents such as NMMO (N-methylmorpholine N-oxide), NMP (N-methyl pyrrolidone), DMF (dimethyl formamide), DMAc (dimethyl acetamide) and DMSO (dimethyl sulfoxide) which have impacted the high performance fiber industry in a big way. These next generation solvents have permitted the successful production of an array of advanced fibers including PBI, aramid, polyimide, PAN and . . . Lyocell. The key to their power is their action as *Lewis bases* in the dissolution process. Even more, they are environmentally friendly, can be recycled during the fiber manufacturing process and exhibit reduced safety concerns compared to the convention chemicals used. Other modern approaches have employed dissolution of the wood pulp in such Lewis bases followed by coagulation in *protic* organic solvents (like some of the lower aliphatic alcohols) to give completely smooth rayon fibers without any lateral surface features.

Both rayon and PAN fibers have traditionally been spun out of solution, usually at low polymer concentrations (< 10%) – the solvent must not only dissolve the monomeric reactants and the intermediary oligomer products, but also the high molecular weight polymers that are formed (the higher the molecular weight desired, the less soluble the polymer will be). Acrylonitrile is an unsaturated monomer which readily undergoes free radical polymerization to form the corresponding atactic polymer PAN. The urge to delve into the chemistry of this process is tempting but such an excursion would be out of the intended scope of this essay. Here, it is only relevant to highlight some of the more important facts associated with the process. First, a small amount of copolymer (such as methacrylate or a vinyl acetate) must be used to plasticize the PAN polymer and improve processability (by itself, PAN is too brittle and insoluble). Thus, common PAN fibers are actually copolymers. The PAN copolymer is then dissolved in one of the Lewis solvents listed above (again in concentrations less than about 9 or 10%) which also contains a non-solvent (a thiocyanate salt is common), and is spun into one or more sequential coagulating baths of increasing aqueous dilution until the fiber is fully precipitated. Again, low coagulation/diffusion rates, as well as reduced coagulation bath temperatures suppress formation of the skin-core structure. This is the preference of most PAN fiber manufacturers.

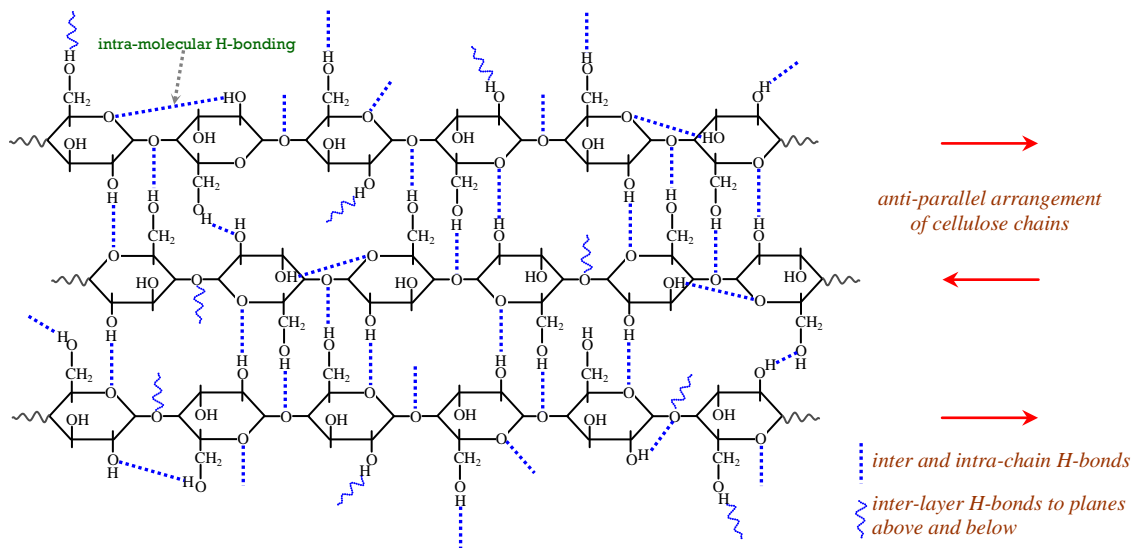
One of the major differences between rayon and PAN is that the initial PAN feedstock is already fully polymerized before the fiber spinning process even begins. If solution polymerization is employed, the final polymer reaction medium will typically act as the spinning dope (after unreacted monomer is extracted). In short, the monomer is polymerized, spun and precipitated. Of course, an array of thermal, mechanical and chemical treatment steps typically follow the initial coagulation bath. Since there is no aging involved, no viscose and no polymerization taking place during the coagulation process, uniform solidification of the fiber from the periphery to the core is more favorable. Actually, in traditional wet spinning production processes, formation of distinct skin-core structures in PAN fibers is rare. Thus, smooth lateral surfaces generally define the predominant morphology of PAN fibers throughout the industry. A similar corollary could be given regarding the formation of longitudinal morphologies occurring along the length of the fibers.

For rayon fibers, it can be postulated that the formation of longitudinal bending crimps is governed by differential shrinkage effects between the core and the corona during the relaxation process. This implies that both lateral crenulations *and* longitudinal crimps are a result of the skin-core effect which is unique to regenerated viscose rayon. Since the core material is likened to a viscose-like gel and the skin becomes a hardened polymer when the fiber undergoes stretching, it seems plausible to attribute the amplitudes and longitudinal frequency of these zig-zag bends to differences in the degree of regeneration and polymerization between the two regions. Substantial differences in the degree of polymerization from the periphery to the center of the fiber are expected even when the skin-core boundary or transition zone is indistinct and gradual. This implies that longitudinal crimps could be formed along fibers in which lateral crenulations are completely absent (. . . crimped smooth fibers). Thus, it is suggested that swelling and drying differentials between the lower molecular weight core and the precipitated outer corona induce buckling effects along the fiber length during the wet relaxation bath (after heated tensioning) which are manifested as repeating patterns of longitudinal crimps. A laboratory concept for a representative process illustrating these effects is given below . . .

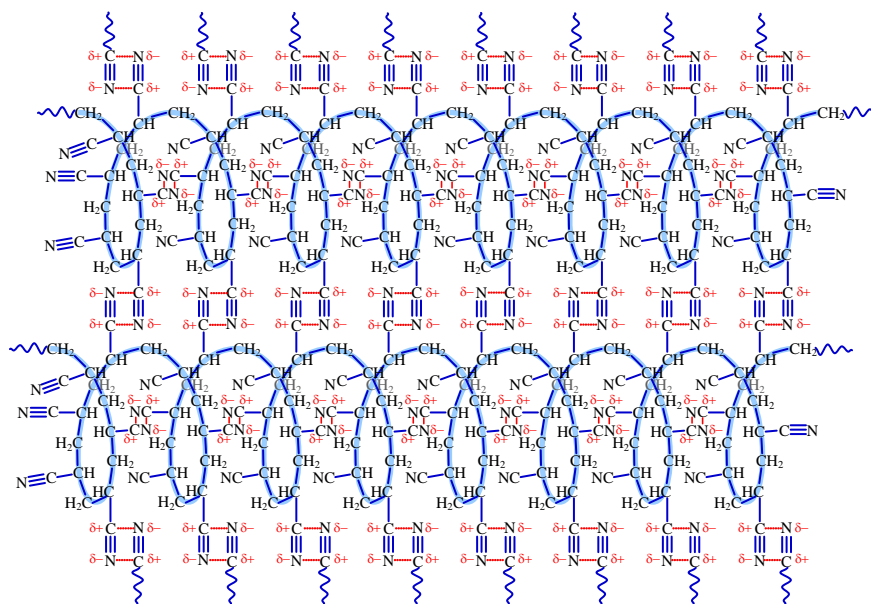


These lateral and longitudinal features are retained in the rayon filaments as they are woven into 2-D fabrics and throughout carbonization process. Longitudinal tensioning forces are generally applied to PAN fibers during carbonization . . . any minor axial features which might have formed during the coagulation process are stretched out of the fiber. Thus, due to the molecular nature of the starting materials entering the spinning process (viscose oligomer vs. solid polymer) and the particular methodology applied during the coagulation/precipitation steps, the relative morphologies of carbonized rayon and PAN fibers are quite different. Prior to carbonization however, these two polymer systems exhibit strong inter-molecular associations which give both macromolecules a high degree of order . . . the secondary structure in both polymer systems provides some unique reinforcement qualities due to the extent of inter and intra-molecular bonding interactions holding the polymer chains together laterally in three dimensions.

The two fundamental classes of polysaccharides include starch and cellulose. Both are comprised of glucose units but the bonding orientation of the 1-4 hydroxyl groups which link each glucose unit to the next for the two classes is different. For the α -glucose units that form starch polymers, both hydroxyl bonds are parallel, while they are anti-parallel in the β -glucose units that make up cellulose. This causes the secondary structure of most starches to assume helical forms while cellulose polymers tend to line up anti-parallel to each other which then assemble into flat rigid sheets or layers. Because of the availability of protruding hydroxyl groups along all the glucose units, this arrangement permits an abundance of hydrogen bonding between cellulose chains within each layer (and within the chains themselves – intra-molecular) and laterally between adjacent cellulose layers to give highly ordered structures in three dimensions as illustrated below (H-bonds in blue) . . .



In contrast, PAN polymers are characterized by linear carbon-carbon bonds and protruding nitrile groups on every other carbon which lead to stiffened secondary structures that are also highly ordered laterally in three dimensions. Since the $C\equiv N$ nitrile bond is moderately polar, substantial dipole interactions are established between PAN molecules (nitrile-nitrile interactions) leading to a stable secondary structure that assumes a coiled (helical) form. An idealized representation of the interactions between and within helix-shaped PAN polymers is given below (inter and intra-molecular dipole interaction attributes are indicated in red) . . .

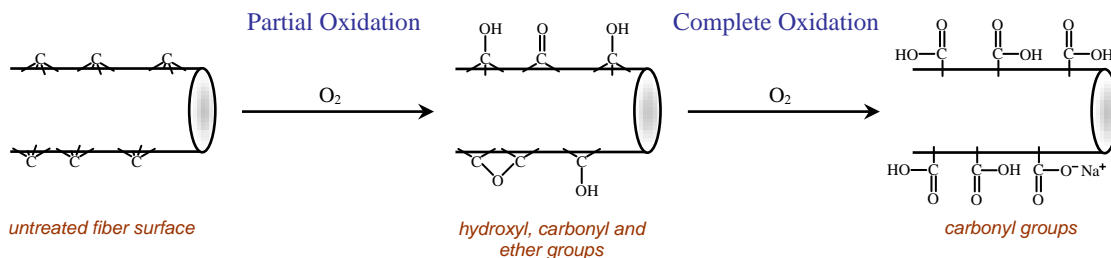


The hardened macrostructure of both polymer systems is known to contain amorphous regions separated by regions that are quasi-crystalline (in essence, rayon and PAN could be considered as quasi-crystalline polymers). While the crystal-like segments may outweigh the less ordered regions, local amorphous structures within a polymer network are the first regions attacked by the solvent during the dissolution process. Also, higher amorphous character in a polymer structure leads to greater flexibility and a lower T_g . Typical Lyocell polymers contain higher crystal-like order than conventional regenerated rayon . . and a higher corresponding tenacity. PAN structures are also expected to exhibit high order due to the extensive nitrile-nitrile interactions. Such order facilitates the slow diffusion/coagulation rate associated with PAN polymers and retards the tendency for skin-core formation.

For rayon, bundles (tow) of regenerated polymer fiber have traditionally been woven into 2-D plain and satin weave fabrics which are stabilized with oxygen at elevated temperatures and then carbonized at temperatures somewhere in the range 2200° to 4500°F depending on the end properties desired. On the other hand, PAN fibers are customarily spun, stabilized, carbonized, bundled into tow and then woven. To varying degrees, the carbonized macrostructure of both fiber systems contains glassy (amorphous) regions separated by regions that are quasi-crystalline (graphite-like), but neither rayon nor PAN undergo true graphitization . . . in the polymerization and stabilization processes, both polymers are converted into non-graphitizable pre-carbon forms due primarily to a network of thermosetting crosslinks which are established during the oxidative stabilization process.

Low temperature (LT) processed PAN fibers (2000°-2500°) exhibit low enough moduli to be woven in plain weave styles, but high modulus, high temperature (HT) fibers (4000°-5000°) are characteristically more stiff and brittle and must be woven in satin weaves in order to minimize crimping and fiber breakage. Prior to weaving, carbonized PAN fibers are usually subjected to chemical/physical surface treatments. Some of these steps could involve surface etching with reactive gases (such as air or CO₂) and/or strong acids (nitric, perchloric) which cause the formation of surface morphology features (roughness) along the fiber surfaces as described earlier. These agents not only etch the surface physically but result in the formation of active chemical (functional) groups which protrude laterally from the surface of the fiber and serve to establish the principal interface coupling mechanism for matrix-to-fiber chemical bonding within the composite system.

Of course, the specific functional groups created must not only be compatible with the chosen matrix polymer (hydrophile/hydrophobe compatibility), but they must actually bind with reactive sites along the polymer chains of the matrix. Thus, during the initial autoclave curing process and subsequent post-cure operation (if one is applied), matrix functional groups are directly coupled to the fiber through the surface groups generated during the oxidative etching process. For cases in which incomplete (partial) oxidation is performed, products along the fiber surface include hydroxyls –OH, ketones and aldehydes C=O (carbonyls) and ethers –O–. Partial oxidation can be influenced by using lower temperatures, lower oxygen concentrations, and/or shorter residence times (time the fiber spends in the oxidation furnace). Full oxidation of all such groups to carboxylic (acid) –COOH can be accomplished by extending these parameters. These ideas can be illustrated in a simple fashion as given below which shows a representative fiber surface as it undergoes treatment . . .



Ambient sodium may associate with some of the carboxylic groups forming ionic salts which can affect the surface potential of the fiber. Carboxyl groups (their acids and salts) are especially reactive with amine-crosslinked epoxy resins since they can form ester and ether links with available epoxide and hydroxyl groups along the polymer chains, as well as amide and urethane links with amine groups in the crosslinker phase. Since most of the PAN fibers manufactured worldwide are destined for use in epoxy-based composites, they are intentionally processed to contain mostly (and in some cases only) carboxyl groups. In general, carboxylic acids readily condensate with aliphatic alcohols to form esters but their reactivity towards *phenol* is minimal due to the acidity of the active hydroxyl hydrogen atom on phenol to preferentially undergo substitution. Additionally, the number and availability of phenol hydroxyls in a typical phenolic matrix are low, and reactivities of surface hydroxyls and carbonyls with phenolics are insignificant. Thus, fiber surface compositions comprised of by carboxyls, hydroxyls, ethers and carbonyl groups are not expected to show appreciable affinity for phenolic matrices.

Other carbon fiber etchants might contain nitrogen, chlorine, sulfur and phosphorous, or silane compounds to give the respective amine, chloride, sulfonyl, phosphoryl or siloxane fiber surface functional groups. Also, these groups can subsequently be subjected to partial oxidation or reduction to form the corresponding derivatives. Siloxane groups might be compatible with certain silicone, SiC ceramic or Si metal matrices exposed to moderate temperatures, while sulfonate or phosphate groups could enhance binding with matrix polymers such as urethane and polyester.

Primary and secondary amines may show a tendency to interact with phenol hydroxyls but then again, the small number of hydroxyl groups which might be present are often shielded or constrained by the bulk phenolic structure and/or consumed during the phenolic crosslinking process. This would also pertain to the amine-phenolic interactions associated with silane coupling agents as these interactions are much more relevant in epoxy and polyester matrices. In any event, fiber-to-matrix chemical bonding in carbon/phenolic composites is relatively insignificant. Additionally, none of these functional groups are very common in the PAN fiber industry since the majority of their customer base is centered around composite matrices comprised of epoxies, vinyl esters and cyanate esters all of which interact readily with surface carboxyl groups to form strong chemical binding links.

During the 1960s-1990s, when Union Carbide carbonized much of the rayon fabric bound for the advanced composites industry, post-carbonized versions of woven WCA, American Enka and Avtex rayon also received similar types of surface treatments, but the exact process flows for the more recent carbonization vendors (Hitco, NSP) are not clear. In any case, for high temperature composites, it almost becomes ironic since these coupling groups will begin to degrade as the penetrating thermal energy destroys the interface bonding links at temperatures above about 600°-700°F.

Ester and ether coupling links established along constituent interfaces can sometimes provide substantial binding effects in polymer matrix composites at moderately elevated temperatures . . . but as temperatures increase, these binding interfaces eventually become completely dominated by and reduced to the mechanical interactions and interlocks that exist. Thus, the importance of interlaminar nesting and reduced residual stresses along these interfaces becomes increasingly apparent. Traditional low temperature composite articles such as fiberglass tubs and phenolic counter tops are able to reap the full benefits of fiber-to-matrix chemical bonding . . . but high temperature laminated composites must be designed and fabricated to maximize mechanical bonding effects from as many angles as possible because the chemical bonds will eventually decompose as the material is heated up.

In summary, ply-to-ply meshing and nesting interactions can be influenced by the particular 2-D weaving configurations chosen for the reinforcement, by the use of spikes, pins, stitches, whiskers or other exotic 3-D approach, sometimes by advanced lay-up techniques or equipment utilized during fabric placement, tapering and debulking, or by the particular curing profile applied during the molding process. A few techniques which have proven beneficial in certain applications include tapered layering of prepreg plies, precise placement and configuration of doublers and filler strips, application of breather strips or barrier films in specific areas of the bagging assembly, special molding aids embedded within the bagging assembly to re-direct vacuum/pressure forces in the appropriate direction, more frequent debulking during prepreg lay-ups, say every fifth or tenth ply instead of after 40 or 50 plies.

It could be debated whether the application of cold CO₂ blasting on the prepreg material the instant it makes contact with the warm lay-up substrate facilitates nesting or not. Additionally, the gross separation of ply interfaces while the prepreg material is still in the uncured state will destroy any nesting interactions which may have been established during the initial lay-up step. This is obvious. Whether or not such separations are appropriately re-established during subsequent debulking and curing operations is debatable. More importantly, these gross separations are only an indication of the unseen weak planes that likely exist throughout much of the laminate . . . that is, any pre-cured article which exhibits random ply separations is probably laden with weak interfaces throughout. Such interlaminar weaknesses could definitely play a role in subsequent ply lifting phenomena or delamination events down stream. In general however, ply-to-ply nesting effects are often difficult to control and herein lies the challenge to the ILS/ILT issue facing the industry.

On the other hand, residual stresses are driven heavily by specific properties of the reinforcement and its interaction with the tooling contours, and by the particular lay-up or prepreg application techniques employed. While the use of HT materials may mitigate issues related to structural integrity at high temperatures, these higher modulus reinforcements often exhibit reduced drape and higher spring back effects during lay-up and handling of the material. Hybrid reinforcements may be key to maintaining physical/mechanical attributes while improving handlability factors. Optimized tooling configurations and mating restraint fixtures can often confine residual stresses or localize their pervasive effects to certain smaller (less critical) regions.

In general, all non-flat laminates contain residual stresses which are inevitably generated during the lay-up process and become permanently fixed within the laminate during the molding or hardening process. It is an unfortunate fact that each individual *curved* ply in a shaped composite article contains opposing stress conditions on the front and back faces of the ply, similar to a bending test specimen under stress . . . and the cumulative effects of thicker, multi-ply lay-ups creates an inherent net interlaminar stress condition throughout the laminate that cannot be debulked or cured away. This could be taken as a minimum stress scenario within any contoured composite laminate – there are likely other forces generated within the article which contribute to the overall stress picture. Herein lies a key factor to mechanically-induced residual stresses that many designers fail to realize.

From another perspective, the specific curing procedure applied to the article can have a huge impact on the condition of molded-in residual stresses. It has already been proven that phenolic laminates bound for high temperature applications require a two-stage curing process . . . an initial autoclave curing step to quickly harden the matrix while maintaining *pore interconnectivity* followed by an extended, elevated post-cure to complete the curing process. For this technique to be effective, the initial autoclave cure cycle must be optimized and tailored to complement the post-cure. This approach is known to drive down residual volatiles and reduce the inherent *residual stresses* imposed along the interfaces of the composite. Optimization of appropriate two-step curing approaches have been implemented in large scale production operations and documented to relieve internal pressures due to volatiles generated in trapped pores and to minimize the molded-in latent interface stresses which can eventually lead to interlaminar defects. Such stresses have been identified as primary culprits in the generation of weak planes and interfaces within laminated composite systems of every class.

Indeed, it is not unusual nowadays to find other fabricators implementing optimized cure/post-cure operations for a number of polymer systems including epoxies, polyesters, vinyl esters, cyanate esters and urethanes, as well as certain high performance thermoplastics. Benefits from such approaches have included slight but measurable improvements in product survivability, material performance and long term structural integrity. For instance, one attribute affected by the curing process is the glass transition temperature T_g , which is the temperature (region) encountered during re-heating of a polymer when the chain segments begin to move and the material softens (this is equivalent to the heat deflection temperature HDT). Most importantly, in composite systems, this softening effect can facilitate the separation of plies which are already under the influence of residual stresses. It can now be recognized that the T_g (or HDT) of a given polymer matrix is established some 20° to 30°F above the maximum cure temperature applied during the molding process. So there is little doubt that the specific curing profile and molding conditions applied to a given composite system can play a strikingly important role in the mitigation of residual and interlaminar stresses.

In many systems, direct or interconnecting relationships between interlaminar nesting effects and residual stresses becomes obvious. In other situations, their sources arise from completely unrelated factors, where bifurcations, combinations or couplings of the two phenomena often result in catastrophic effects. For carbonized rayon and PAN-reinforced systems, some of these differences are apparent, while others are subtle. In general however, carbonized PAN fibers are smooth, slick, hard and straight while rayon carbon fibers are rough, porous, soft and crimped. These are some of the not-so-subtle differences that determine the mechanical behavior differences between the two systems, and so the primary structural trade-off often becomes one of choosing between high longitudinal (in-plane) strengths or higher interlaminar (out-of-plane) strengths. Meanwhile, as the industry continues its quest to raise interlaminar properties in PAN systems to the next level, it is sometimes easy to forget where we have been relative to where we are today . . . for the time being, the interlaminar properties of PAN systems have a long way to go before they can even compete with those offered by rayon.

About the author . . .

Direct involvement with composite materials, adhesives, ceramics and polymer coatings since the early 1970's, including hands-on participation in the design, development, fabrication, machining, NDE, chemical, physical and mechanical characterization of numerous advanced composite systems and their constituents. Conducted extensive research investigations and performance evaluations for a myriad of reinforcements, particles, matrix binders and coatings, including glass, ceramic, carbon and organic fibers, fabrics and powders . . . along with polyester, epoxy, urethane, siloxane, imide/BMI, PEEK, phenolic, carbon, ceramic, cement, metal matrices and coatings. Improved a number of proprietary innovations at several major corporations in the aerospace, defense, electronics and private manufacturing sectors in various hands-on positions and professional leadership roles including composite shop fabricator (owner/operator), lead manufacturing engineer, process development engineer, chief formulation chemist, analytical chemist, senior materials scientist, senior quality engineer, root cause & corrective action engineer, lead failure analysis & reliability engineer, technical manager, and independent consultant.

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