To: Undisclosed Recipients
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SBIR contract NNXXXXXX, Phase II activity
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CC: Undisclosed Recipients

I have prepared the following discussion to address some of the issues and concerns that were raised during our recent telecom meeting regarding the specific materials being used and manufacturing approaches under consideration for these prototype articles.

PreCeramic Polymers

All three semi-organic polymer systems referred to in Bulletin 11_1, that is, the polycarbosilanes, siloxanes and silazanes, contain vinyl or allyl side groups along the chains which provide for thermoset curing via free radical crosslinking with heat or by carefully incorporating the appropriate peroxide (which would allow for reduced temperature curing). Upon low firing (<~1200°C), all three of these precursors initially transform into glassy ceramics, and they all will ultimately transform (crystallize) into β-SiC when high fired – but they do not all share the same compositional and structural conversion pathways. During conversion into the glassy state, all three exhibit relatively minimal volume shrinkage and porosity formation. However, above about 1200°-1300°, significant changes begin occurring.

The carbosilanes, whose polymer structures consist of alternating carbon-silicon atoms along the main chains with terminal (protruding) allyl groups strategically placed along the end-branches, will convert directly into β-SiC. Because of the purely organic pendant groups, these deposits will always be a little carbon-rich depending on the level and type of groups incorporated. Due to the variety of polymer configurations now offered by Starfire, their different product classes contain pendant groups of varying levels and composition. Back in the early days (late 80's and early 90's), they had trouble incorporating crosslinking groups onto the polymer other than allyl ($\sim CH_2–CH=CH_2$), but over the years, they have learned to attach other crosslinking entities onto the chains which offer higher aromaticity or modified aliphatic behavior depending on the specific application.

Starfire's original product was allyl hydrido polycarbonsilane (AHPCS) which became the parent polymer system for all the other PCS products they offer today. That same polymer is now marketed by Starfire as SMP-10 and has been for several years. All this activity was headed up by Walt Sherwood who was the principal inventor of AHPCS and cofounder of Starfire. I spent much time experimenting with AHPCS and scaling up its use into production processes. As the material ages and/or is exposed to ever increasing temperatures, hydrogen is the main pyrolysis gas generated. However, a little silane and methane are also inadvertently emitted throughout pyrolysis. While hydrogen stripping is expected in all char and ceramic precursors, generation of silane and methane indicates undue polymer degradation. As you know, the green polymer resin is highly susceptible to damage from moisture in the air. Not only are the main chain silicon atoms vulnerable to protic intruders such as water but the pendant double bonds are also quite open to saturation. These reactions cleave the polymer chains and destroy the crosslinking capability.

Now, as the crosslinked polymer converts into glassy/amorphous SiC (which we can indicate by a-SiC), minimal-to-moderate volume shrinkage and porosity generation are incurred, say < 10%± and < 10%± respectively. However, above about 1400°-1500°C, the glassy structure begins to undergo significant changes. More H_2, SiH_4 and CH_4 are generated as the microstructure consolidates and substantial porosity is formed. Most of the porosity is *interconnected* as channels (or worm holes) are created by the pyrolysis gases which are expelled out of the system during dynamic structural conversion, but interconnectivity is not necessarily global as some pores are inadvertently closed off when the structure collapses around them.

The net volume shrinkage for Starfire polymers is known to be around 30-40% from the cured state to the fully crystallized β cubic form, and the net ceramic yield is somewhere in the 50-65% range. Note that the ranges given in Bulletin 11_1 from 73 to 86% represent the low fired (glassy) product. From a compositional and structural standpoint, a-SiC could be envisioned as a *partially* ceramicized form of this material as it is the precursor to β-SiC. Internal and external volumetric changes are overwhelmingly attributed to the high temperature (crystallization) portion of the firing process which fully converts the material into a true crystalline ceramic and the bulk of the pyrolysis gasses are emitted during structural crystallization and consolidation. Above around 2000°C, cubic β-SiC converts into the hexagonal α-SiC structure (coincidentially,both the β and α structural forms occupy about the same lattice volume). Finally, the α form sublimes or decomposes above about 2800°-3000°.

Most of the above description also applies to the carbosiloxanes, silazanes and ureasilazanes. These materials have their roots in Allied Signal's Blackglas (the original polysiloxane preceramic polymer) and Dupont's Lanxide and Ceraset products (silazanes and ureasilazanes). In its low-fired glassy form, polysiloxane is analogous to a ceramicized *silicone* (specifically, the family of cyclic silicones which have been formulated to undergo free radical crosslinking). In any case, all these materials convert into stable glassy ceramics, same as the carbosilanes with only moderate volume and porosity changes. However, in contrast to the carbosilanes, which contain only carbon, silicon and hydrogen, siloxane structures also include bound oxygen while the silazanes (and ureasilazanes) contain bound nitrogen. In all of these configurations, the oxygen and nitrogen are incorporated *directly* into the main chains of the polymers. Thus, the partially ceramicized (glassy) forms of these polymers contain oxygen and/or nitrogen in their low fired structures. They will ultimately decompose into β-SiC after high enough firing leading to substantial structural consolidation and advanced crosslinking (that is, *pyrolytic crosslinking*, which is quite different from organic crosslinking).

In general, pyrolytic crosslinking is one of the principal reactions taking place during high temperature thermal conversion/decomposition of thermosetting organics and semi-organics leading to char and ceramic formation. Indeed, these links are responsible for much of the volumetric shrinkage that occurs when networked polymer systems are pyrolyzed. Volume losses and porosity levels for these other PCP polymers are expected to be a little higher than the carbosilanes. Because of these compositional differences, the siloxanes, silazanes and ureasilazanes may sometimes be utilized more appropriately as 'low temperature' ceramics. This classification is particularly applicable to the siloxanes. Compared to the carbosilanes, *full* ceramicization yields for the siloxanes, silazanes and ureasilazanes may be even lower as more weight and volume losses are incurred due to expulsion of oxygen and nitrogen from the structures, a condition that the carbosilanes do not have to deal with. Recall that *main chain* degradation is required to ultimately purge these atoms out of the system. So the conversion process from glass to crystal may not always be as continuous or straightforward as that expected with the carbosilanes where carbon and silicon atoms have already been joined together in the initial polymer synthesis stage.

At the lower temperatures (<~1200°C), ceramicized polysiloxanes will provide better oxidation protection than an of the other polymer systems (since they already have oxygen in their structure). Indeed, this is their primary benefit and application – low temperature oxidation protection. But again, when exposed to high inert environments, the bound oxygen will be expelled from the polymer as the structure degrades (and substantially consolidates) into SiC. The siloxanes are essentially useless for high temperature oxidation protection. If SiC is the end-product that one seeks, siloxanes are not the best precursors. As previously noted, both the silazanes and ureasilazanes contain nitrogen in their pseudo-cyclic structures (actually, the ureasilazanes also include oxygen due to the presence of acyl groups joining nitrogen atoms). In either case, nitrogen (with its free electron pair) can provide enhanced reaction capabilities as a result of its basic character and potential to act as a strong reducing agent. If either of these materials are high fired in atmospheres containing N_2 or NH_3, near-stoichiometric Si_3N_4 (silicon nitride) can be produced. In an inert atmosphere, such as argon, hybrid Si_3N_4/SiC microstructures are formed. Hydrogen acts like a 'spoiler' gas as its reductive properties can be used to increase the levels of SiC in the conversion product. When high levels of H_2 are fed into the gas stream, near stoichiometric SiC can be produced. Heavy H_2 in Ar atmosphere is typical for the formation of glassy and β-SiC deposites. I have experimentally documented each of these situations using various precursor slurry formulations fired under numerous pyrolysis conditions (gas compositions, pressures, ramps, open, packed, etc…). For further information concerning the chemistry of preceramic polymers, please review Section VI given in the Addendum to this memo.

Thermomechanical Concepts

As you already know, the SiC matrix is essentially isotropic and the CTE for crystalline SiC runs in the 4-5 ppm/° range. However, PAN-based carbon fibers, their bundles and tow are highly anisotropic. Specifically, solution-spun PAN fibers are highly orthotropic. Across a wide temperature range, the *longitudinal* CTE for carbonized PAN fibers varies by only about ±0.5 ppm/°. That is, the longitudinal CTE for carbonized fibers is almost nil. On the other hand, the *transverse* CTE for carbon fibers can be anywhere from about 4 to 8 ppm/° (across the fiber diameter). Thus, as they heat up, the fibers and bundles get fatter while their lengths remain about the same. In an SiC matrix, expansion/contraction in the fiber diameter direction is not all that different than the surrounding matrix, so the transverse fiber CTE and the SiC matrix are essentially *compatible*, for the most part. Indeed, the primary CTE mismatch in C-C, C/SiC and C-C/SiC systems is along the fiber lengths as there is a ~0 to > 4 differential along these interfaces which often becomes the focal point for CTE-related delams, debonds and microcracks. The net CTE differential is intermediate in structures or regions comprised of angled plies or bundles. I have worked extensively in this area, investigating ways to mitigate this particular mismatch for many years, as so many others in the industry also have. Robust solutions are now at hand to make some astounding improvements in differential CTE mismatch issues for C-C and CMC systems without introducing new problems or degrading the existing benefits that these materials are so well known for.

There are several classes of carbonized PAN fibers available depending on the maximum heat treatments applied during fiber carbonization and post-carbonization processes. When the fibers are subjected to increasingly higher temperatures, their structures continue to consolidate as residual pyrolysis volatiles are released. Their strengths, modulii, densities, conductivity and CTE levels increase accordingly (especially when heated under tension as most PAN fibers are). High heat treatment (HHT) fibers (>~1500-1700°C) provide the highest strengths and stiffnesses of all the classes and are often used for ultra high temperature (UHT) carbon reinforcement applications requiring maximum tensile strengths. Structures derived from UHT C/C and CMC backbones often make use of PAN fibers and fabrics which have been post heat treated to temperatures as high as 2200-2300°C before prepregging operations, but this must often be supplemented with measures to mitigate the high thermal conductivity effects which also result. Low heat treatments (<~1200-1300°) can sometimes subdue these concerns as well as other adverse HHT effects such as brittleness or high CTE. However, low heat treatment (LHT) fibers are more appropriate for low temperature applications because undesirable consequences can often result when the fibers are exposed to higher temperatures (particularly after they are already embedded and fixed in a hardened composite matrix).

Recall that carbonized PAN fibers are comprised mainly of glassy carbons due to the pre-carb stabilization (thermosetting) step which makes carbonization of virgin organic fibers possible in the first place. Note that HHT fibers are often called 'graphite' fibers in the industry simply because they have been exposed to graphitization temperatures (>2200°C). However, while pitch fiber structures come the closest to actual graphitization, the rigid (crosslinked) graphene layers in 'hard' carbons such as stabilized PAN and rayon microstructures are not mobile enough to sufficiently index or line-up with adjacent layers to form true 3-D graphitic configurations. If such structures were not stabilized prior to carbonization, they would either melt away or would pass through mesophase around 400-500°, so pre-carb stabilization is a necessary step for traditional PAN fibers. However, next-generation PAN precursors are on the horizon which may permit melt-spinning synthesis and increased graphitization capabilities. Additionally, a number of polymeric carbon fiber precursors are currently under investigation which could offer some properties and attributes that PAN fibers do not.

At any rate, it is important to realize that when heated above their initial processing temperatures, LHT fiber microstructures will continue to consolidate, as one would expect. Clearly, subjecting substrates comprised of 1000° LHT reinforcements to 2000° PIP cycles is not a good thermomechanical design. Even though the rate of expansion/contraction is significant, physical transverse fiber volume shrinkage is also quite substantial. During high temperature PIP pyrolysis upramps, LHT fiber/bundle diameters continue to consolidate while the dynamically changing SiC matrix recesses simultaneously (due to volumetric shrinkage and microstructural consolidation as previously mentioned). At the least, these conditions build substantial fiber-to-matrix interface stresses during the upramp leading to highly weakened interfaces.

During cool down, the matrix contracts 4 to 5 times faster than the longitudinal fiber surfaces which only exacerbates the instantaneous mismatch as the two phases recede from each other. It would be no surprise to see debonds, delams and/or fractures occurring along the most highly stressed longitudinal fiber-to-matrix interfaces (and their angled projections to lesser degrees) in such configurations during the pyrolysis cool down of subsequent PIP cycles. In short, matrix interactions with longitudinal fiber surfaces represent the greatest CTE differentials in carbon fiber-reinforced C-C and CMC systems based on SiC or glassy carbon matrices. Glassy carbons derived from organic thermosets such as phenolic exhibit a CTE of about 3.5-4ppm/° which is compatible with SiC as well as transverse fiber movements. History has soundly proven that SiC conversion coated / phenolic-densified C-C systems are superior to most other C-C platforms in terms of differential CTE resiliency, thermal shock resistance, oxidation protection, manufacturability and almost all the mechanical properties of relevance.

Fiber-Matrix Binding Interactions

In fiber-reinforced composite systems, there are two important bonding mechanisms to consider along the fiber-to-matrix interfaces: chemical coupling and mechanical interlocking. Most PAN fibers are surface treated after carbonization to promote the formation of functional groups along the fiber surfaces (mainly carboxyl –COOH) which will effectively bind or couple with matrices containing hydroxyl (–OH) and nitrogen-based functional groups along the polymer chains. Such groups are abundant in most epoxy networks and so the entire PAN carbon industry is essentially built around epoxy matrix composites. However, it is important to note that in C-C and CMC systems, chemical binding along fiber-to-matrix interfaces is temporary and, in most applications, irrelevant.

Indeed, chemical bonding interactions are subject to thermal degradation at temperatures above about 350-400°C. Such temperature levels will destroy fiber-matrix chemical interactions rendering the composite almost completely dependent on the nature and degree of mechanical interactions which are established. Note that SiC matrix structures contain no functional groups to participate in fiber chemical bonding and so it is particularly important to provide the resources necessary for sufficient mechanical binding in SiC systems, including C/SiC, C-C/SiC and SiC/SiC configurations. But note that low-fired glassy siloxanes and silazanes *do* contain greater functionality than glassy SiC and are expected to exhibit higher levels of chemical interactions with PAN reinforcements. Both oxygen and nitrogen in the polymer chain offer the potential for increased dipole-dipole interactions and chemical coupling with fiber surface functional groups.

Now, mechanical interactions and interlocking effects can be influenced by (a) the specific fiber shape and surface morphologies (these features can be controlled during the fiber manufacturing process), (b) the weaving styles utilized to manufacture the fabric (ex.: protruding crimps, tow size and twist), (c) the initial composite molding process (there are specific techniques which can be applied during lay-up, autoclave cure and post-cure to promote interlaminar nesting and ply-to-ply intermingling), (d) the densification process (there are special techniques which can be incorporated during resin impregnation/cure to enhance permeation and wetting of the fiber surfaces deep within the composite core and into the hidden bundle porosities), (e) strategically incorporated 3-D reinforcement additives such as nanotubes, whiskers, needles, etc... In the early days, we were some of the first technologists to explore these concepts, now they are more widespread and documented. Such constituents, when properly incorporated, can provide substantial improvements in intrinsic mechanical interactions, interlaminar shear and flatwise tensile properties, improvements the industry desperately needs.

It is interesting to note that for most C-C and CMC systems, mechanical interlocking effects are constantly changing hysteretically along the interfaces as the material heats up and cools down. When the system is heated even higher, former mechanical bonds diminish and news ones form. Obviously, this dynamic condition of varying mechanical interactions is driven by expansion and contraction movements associated with heating and cooling events applied during the fabrication process and throughout the thermal lifetime of the article. Undoubtedly, these mechanisms are directly related to the toughness attributes associated with the composite. Note that any fiber-to-matrix *chemical* bonds which are formed during the initial molding process or subsequent impregnation/cure cycles are completely destroyed every time the material is heated up during pyrolysis as these links are degraded early in the cycle. In short, chemical binding is trivial in most C-C and CMC systems. If you are going to utilize high temperature PIP densifications or build structures for high temperature field applications, better make sure that ample mechanical interactions are provided for during the design stages and throughout the fabrication process. For cryogenic space structures, there may be manufacturing alternatives that completely bypass these issues providing for the presence (and benefits) of both chemical and mechanical binding scenarios along the fiber-to-matrix interfaces.

Densification Issues and Strategies

I have personally performed hundreds of polymer impregnation and pyrolysis (PIP) densifications on porous substrates and conducted numerous densification studies. At one time, I was considered the guru of densification processing (successive cycles of liquid polymer infusion/impregnation/cure followed by pyrolysis) as well as advanced porosity science and novel techniques for porosity measurement. Back in the early 1980's I developed several densification approaches and associated process characterization techniques specifically for C-C and CMC substrates. We may have been some of the industrial pioneers for refinement of this process (I believe Textron and FMI were early players in this technology as well). During my studies, I developed a fairly extensive densification model, if you will, to accurately monitor the densification process as it goes through each successive cycle relative to the critical property changes occurring as the composite substrate is gradually densified during each successive PIP cycle.

I have thoroughly documented the evolution of properties such as bulk density, true density, open porosity, total porosity, matrix content, fiber volume, matrix density, incremental and cumulative matrix weight gains, flexural strength, shear strength and interlaminar tensile strength across the entire densification process many times. These experimental studies allowed me to optimize the densification process, improving the effectiveness of resin infusion without generating undue porosity and developing a rapid inert pyrolysis approach to help streamline the process without the production of delams or weak planes. Results from these studies and model refinements have effectively facilitated the prediction of substrate physical and mechanical properties at any given point in the process, and they have enhanced efforts to develop the most optimal process needed to achieve a balance of thermomechanical attributes.

As you noted earlier, densification curves appear to be linear and during the first few cycles, this is essentially true. However, as the pores get smaller after each pyrolysis, the densification curve actually starts to level off, following what I experimentally surmised as a reverse exponential form, analogous to a $A(1 - e^{-x}) + \mathrm{C}$ or its negative counterpart, $-Ae^{-x} + \mathrm{C}$, both of which are ‘response’ type functions which asymptotically approach a theoretical limit or plateau. Excerpts from a few of my past studies illustrating some of these concepts are given in the Addendum to this report. Now, during each cycle, the resin permeates and fills the largest pores and tunnels first but then creates new (finer) porosity during the pyrolysis step. Each complete PIP cycle can be numbered and plotted along with measured property standards for each PIP state and corresponding intermediate bimatrix state. I am not sure how long some of the newer companies or research groups have been doing this sort of stuff but I characterized my first densification process in this manner back in 1982.

Now, if it were feasible for one to perform an infinite number of impregnation/pyrolysis cycles, the plateau could be reached, but this is not possible and thus, *it is physically impossible to densify a porous substrate to 0% porosity using traditional PIP methods*. From a practical perspective, there is a point of diminishing return and one will inevitably be left with 8-15% open porosity after 12-15 PIP cycles using any of these preceramic polymers (for phenolic-based C-C substrates, 3-6% porosity can be achieved after only 4 cycles; with modified pitch impregnations, even fewer cycles are possible, perhaps one or two). Each PIP cycle is expensive and adds time to the process, and there comes a point where so much more uncured resin is removed from the substrate surfaces during wipe-down than is actually deposited within the pores.

At the end of the PIP process, residual porosity must be sealed and coated via CVD/CVI, or by using low-fired glassy polymer impregnation coatings, a ceramic conversion coating concept or some other novel approach. Otherwise, the remnant porosity must be acceptable to the specific application conditions the article is intended for. Note that if carbon fibers are used in articles which are expected to see thermal oxidation environments during field use (>450-500°C), almost any level of open porosity is unacceptable, and an ingenious coating method must be developed. I have extensive experiences in high temperature coatings, gradient conversion processes and oxidation protection mechanisms, but we will not go there in this discussion.

Obviously, the very first pyrolysis or ceramic state (after the initial molding process) represents the highest porosity and the largest pores. After the first impregnation/cure, the matrix consists of previously deposited ceramic *plus* new preceramic polymer. I refer to this intermediate condition as a ‘bimatrix’ state. Pyrolysis from the first bimatrix state to the second ceramic state results in pores which are a little smaller and less intrusive than the first ceramic state. If the densification methodology is applied appropriately, the inner-most pores should be densified first while the finer peripheral pores are then filled. Inadvertently, there is often the likelihood that some of the inner pores will be closed off during the first couple of cycles and become completely inaccessible to subsequent impregnations. In well optimized processes, the fraction of sealed porosity and closed pores is small and may be neglected in many cases. Unfortunately, I have seen too many practices apparently utilizing improper impregnation techniques and/or pyrolysis approaches leading to deeply entrenched pore clusters which are permanently sealed and closed off during the first few cycles. It has been repeatedly demonstrated that such core defects usually become major contributors in catastrophic thermomechanical failures downline, either during subsequent processing or in the field.

Now the total porosity in a substrate is equal to the open porosity *plus* the closed porosity... period. However, the concept of porosity is *subjective* depending on the particular medium and technique used to measure it. Obviously, gases permeate deeper than liquids, but liquid polymers are the actual densifying agents used to process these substrates. The attribute known as ‘open porosity’ is conventionally based on ASTM standards (or modified ASTM techniques in my practices) in which a liquid, usually water or a solvent, is forced into the pores of a test sample (analogous to an impregnation), while suspended and saturated weights are accurately measured. I have experimented with and developed numerous porosity/density methods which utilize hot water intrusion, mercury intrusion (which I do not recommend) and water or fluid impregnation under vacuum and pressure (an original technique).

There are other similar methods which have been documented in the literature. For composite systems with negligible levels of fluid-impervious pores, the ‘closed’ pore fraction may actually be permeable to He atoms (less than a couple of Angstroms in diameter), which would make the total porosity approximately equal to that determined by helium pycnometry. In these cases, the ‘helium density’ and the ‘helium porosity’ may be regarded essentially as the true (skeletal) density and total porosity of the material (or the test sample). Then, the ‘open’ porosity fraction can be determined by one of the aforementioned liquid techniques (properly applied of course), and the complete density/porosity picture would be defined. In short, He pynometry *plus* one of the water intrusion methods will give the total porosity volume fraction (as well as the bulk and true densities) which can be used with confidence in calculations, rule of mixtures, models, etc... Note that He pycnometry *by itself* may give a false impression of the available porosity, because the open (liquid-permeable) porosity is still an unknown. If a choice had to be made selecting one method over the other, open porosity measurements are the most relevant to densification operations. He pycnometry is handy because it may provide an indication of the presence and level of closed porosity (closed to impregnating fluids, that is). Please consult the Addendum sections for application examples of Helium and open porosity concepts.

During a typical impregnation/infusion process, is often difficult to get the resin into the deepest and smallest pores but there are techniques to greatly enhance this process. One of the procedures I developed utilized a moderate vacuum (~0.1 torr) to draw the polymer into the pores of the substrate followed by venting and pressurization with N_2 gas (for phenolic resins, shop air is adequate, but not with these sensitive preceramics). This is where many CMC workers falter because of the requirement for a pressure vessel (rather than just a vacuum chamber). After vacuum impregnation, 100-120psi N2 is dumped on top of the impregnated articles and held for 30-60 minutes before venting and wiping the parts down. However, my experience teaches that vacuum/pressure impregnations followed by pressurized curing and ambient pyrolysis is not only an effective approach but is the most practical and affordable scenario for in-house processing of C-C and CMC substrates (of course, pressurized pyrolysis would be even better than ambient firing but this is not always feasible because of the additional cost and safety concerns, as it is with the pressure vessel). Nevertheless, some of these techniques are essential in reducing and possibly eliminating the fraction of closed pores. History has repeatedly shown us now that excessive porosity, closed pores and mismatched constituent interfaces are some of the primary reasons why so many C-C and CMC applications have problems.

When inert particles are blended into the resin and the resulting slurry is used as an impregnating agent, the fraction of closed pores in the substrate drastically increases giving the false impression that the densification process is more effective and fewer cycles are needed. It is a challenge, in and by itself, just to get the neat resin effectively infiltrated into the bottom of the porosity network. Attempting to force particles into the pores *in addition to* a viscous polymer resin is a self-defeating process. The particles already tend to agglomerate (or flocculate) during slurry mixing and preparation but when the vacuum forces attempt to suck these dispersed particles into the pore openings, interparticle interactions are magnified, ultimately leading to pore blockage at or near the pore openings.

Overwhelmingly, most of the particles in the slurry agglomerate and collect on the surfaces of the article and never even make into the pore channels. The few particles that manage to migrate a little deeper to the surface pores will eventually cause blockage at rather shallow pore depths. Once they become wedged in the pore channels and openings, they are there to stay, preventing access to the deeper pores, cavities and tunnels which are supposed to be densified with matrix polymer in the first place. During pyrolysis, these wedged-in particles and agglomerates will actually sinter into the pore walls and with themselves causing the blockage condition to become *permanent*. Clearly, blocked pore openings and passages decrease the effectiveness of resin infusion, particularly for the subsequent cycles.

It has already been shown that pore tunnels and openings which are clogged up with inert, nondissolving particles and their agglomerates remain constricted and impervious to subsequent resin impregnations and densification cycles. This is true even if high temperature pyrolysis treatments are applied between cycles, because such treatments will not dislodge, melt, react or ‘burn’ the particles away. Regardless of what some workers may claim, particle-filled infusion resins are not densification enhancers, they are densification spoilers as they lead to inferior densified product. This is a sure-fire way to create a bunch of permanently entrenched closed porosity in the composite.

Make no mistake about it however, I highly recommend the use of incorporated particles, fillers or 3-D constituents into advanced composites (nano, carbon black, SiC, silica, whiskers, needles, etc...). Without a doubt, such constituents are greatly needed for improved thermo-mechanical properties and I have dedicated much effort to the proper selection and incorporation of these important ingredients into composite materials for a number of years. But clearly, particulates and solid constituents should be added during or following the prepregging stage prior to the initial molding operation, not during the densification process. In recent years, Starfire has offered a couple of low viscosity CVD products based on the same PCS polymer as AHPCS (SMP-10). Personally, I would be looking at some of these polymer formulations as densification resins. Now the argument given above does not apply to the formulation of specialized *chemical* agents into the densifying resin as this opens up a new field of composite enhancements and modifications that need to be further explored, but that is topic for a another day.

An ideal PIP cycle might proceed according to the following scenario. The dry articles are placed in an empty vacuum chamber and held for 30 minutes (under moderate vacuum), after which the vacuum forces in the evacuated chamber are used to draw the resin deep into the pores. Keep in mind, an effective PI is a forced intrusion/impregnation process, not a passive dip and soak. After impregnation, the chamber is vented to ambient with N_2 in order to stabilize the intrusion (to maximize wetting and equilibrate capillary actions). In more robust processes, one should then apply 120 psi pressure for 30-60 minutes, re-vent, wipe the excess polymer resin off the surfaces, load them into a cure clave and then pressure-cure them under high N_2. As mentioned earlier, if it were then also possible to pressure-pyrolyze the articles, the best densification scenario is achieved. This is the more expensive approach but it is absolutely the best way to densify porous CMC and C-C substrates with thermosetting polymers and resins. Closed porosity is greatly minimized and densification is much more effective. One of the processes I developed in the past did everything above except the pressurized pyrolysis and this scenario was quite effective in and by itself. I would consider this procedure as a very close second. Remember, these are just comments and I am not suggesting you change anything.

It should be realized that *no further polymerization occurs during the curing of thermoset polymers* . . . only crosslinking takes place. This is true, not only for the preceramics, but also for most all other thermosetting polymeric densification precursors, including the phenolics, epoxies, esters, urethanes, cyanoacrylates, arylacetylenes, cyclopentadienes and most of the next-generation C-C/CMC densification resins on the horizon. Note that crosslinking in Starfire polymers occurs between neighboring molecules and end-branches as these are ‘star’ polymers, not linear chains. Pitch polymers are basically thermoplastics and can be designed to actually polymerize inside the pores. This is the ideal situation because it allows oligomers and prepolymers with much lower viscosity to permeate deeper into the fine pore tunnels before solidifying or crosslinking (however, other issues must be dealt with in pitch-densified systems).

In any case, such an approach is a much more effective densification concept as it minimizes the level of closed porosity incorporated into the substrate and reduces the number of densification cycles required. Indeed, low molecular weight prepolymers which could be designed to effectively undergo polymerization and crosslinking at the same time or in tandem after incorporation into their final resting places is one of the novel research ideas that needs to be exploited. Before Walt Sherwood and fellow founders (Herb Armstrong) were unfairly ousted from Starfire, they may have been working on such polymer modifications. The new Starfire entity is now a production-oriented company and the original innovators gone. Yes, I would highly recommend using current EEMS products and investigating their newer offerings as these guys will be the innovators for the next generation of preceramic polymers, and they will be the leading experts to consult when the tough problems come up.

Final Comments

Without a doubt, of all the preceramic polymers now available, the carbosilanes offer the most direct route to near-stoichiometric β-SiC. Those working with high temperature and ultra high temperature C-C/CMC forms must learn to deal with the porosity and volumetric changes as well as exacerbated CTE mismatches and fiber-to-matrix interface issues associated with the firing of these composites. But I wonder if these are the best material configurations for space telescope platforms. I personally do not know enough about your requirements to say one way or the other. However, I might offer some alternative ideas regarding the use of these polymers in their low-fired glassy forms. I know for a fact that the partially ceramicized amorphous preceramics, when compared to their crystallized forms, exhibit lower bulk densities, lower porosities, lower CTE values and lower conductivity, as one would expect with glass-type materials. Additionally, lower pyrolysis temperatures and fewer densification cycles would be required . . . and the use of the more flexible 1000° LHT fibers is back on the table.

It has been indicated that glassy a-SiC generated from Starfire precursors has a bulk density of about 2.5g/cc and a CTE of about 2.6ppm/° as compared to the fully crystallized cubic (β) polytrope with 3.1-3.2g/cc and 4-5ppm/°. Also, it would not surprise me if you were able to cut your densification requirements by 80-90% and essentially eliminate any major issues regarding the formation of excessive, localized or closed porosity. With this scenario, these lower modulus glassy structures would essentially densify, seal and coat from the inside out. Compared to crystallized surfaces, glassy surfaces could reduce the requirements for coating and finishing operations. Likewise, these forms are probably more machinable than their crystallized counterparts and would provide better thermal shock protection. There are other alternative processing scenarios which could be suggested here but that discussion will be postponed.

A hybrid approach might consider high heat treated core sections using high pyrolysis temperatures during the early part of the fabrication process which gradually transition into lower heat treatments and eventually to the glassy forms across the periphery of the structure. Intermediate microstructures would be a mixture of amorphous and crystalline forms which gradually transition from crystalline in the core to amorphous on the outside. This would provide for a low porosity seal coating across the surface of the article and a graded conversion between crystalline and amorphous phases.

However, this scenario would still require the use of HHT fibers and would probably introduce more CTE variation throughout the body (a more complex CTE configuration is not really desirable). Additionally, the possible formation of closed interior pore clusters would still be a concern. Personally, for your particular low temperature application, I would prefer the previous idea of using low fired glassy ceramics throughout the entire body and periphery. This approach solves most of the problems that the high temperature folks have to deal with every day. Keep in mind, my expertise with these materials is limited to high temperature processing and field conditions. I am not certain how they behave in ultra low temperature applications or whether their properties can be extrapolated or functionally surmised from high temperature data. It is suspected that property differentials and material behavior are less pronounced at low temperatures relative to high temperature environments.

Hopefully, the information in this memo has been helpful in your efforts. If you get the time, please take a few minutes to scan the Addendum which gives a few real life examples of some of these concepts. Admittedly, I slapped these comments together rather quickly. It would not surprise me to find that some of these statements are misstated or less than accurate. Please forgive those deficiencies. My understanding of the specific issues you face in conjunction with the materials and conditions you are employing may be lacking since I am on the outside looking in. Nevertheless, if you made it this far, it is hoped that you found this discussion enjoyable and beneficial. All comments and criticisms are most welcome...

Best Regards,

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