Char and Erosion Factors – with Reference to PBI/NBR and Phenolic Matrix Composites

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February 2011

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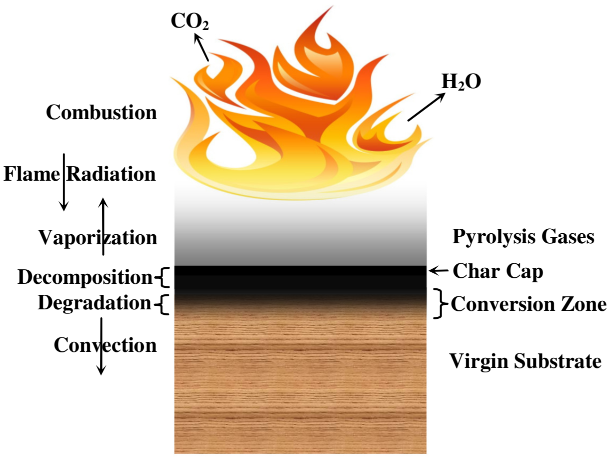
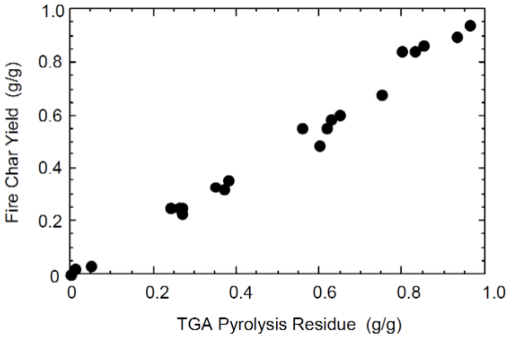
Burning and Pyrolysis of Thermosets and Thermoplastics

When common organic polymer-based materials undergo *static* flaming combustion, the heat delivered to the surface of the material degrades and pyrolyzes the polymer structure releasing gas molecules and volatile fragments which are highly flammable and combustible. As these vapors diffuse into the oxygen-rich atmosphere just above the surface of the polymer substrate, they act as fuel to the flame, undergoing thermal oxidation in reactions which are highly exothermic ultimately producing the primary products of complete combustion, H_2O and CO_2 . . . but they also feed heat flux (radiation) back into the charring substrate which permeates into the virgin phase via convection and continues the process. In some cases, migration of the conversion zone may follow the classical parabolic recession rate law but evolution of the charred phase is inherently a function of the pyrolytic affinity of the virgin material and its constituents. While energy transport into the substrate is relatively straightforward, the kinetic production and outward diffusion of the pyrolysis volatiles generated are expected to be the primary rate-controlling factors in these processes. In many situations, the process becomes self-sustaining. For static combustion (such as the simple burning of plastic or wood), the substrate itself does not undergo oxidation but rather the released gases do . . . while the substrate actually undergoes near anaerobic pyrolysis.



If there no oxygen present in the surrounding environment, the released gases do not undergo oxidation and the charring substrate tends to cool since no heat is delivered back into it. In this situation, pure anaerobic pyrolysis takes place, leading to a net burning process that is endothermic. During controlled materials processing operations, anaerobic pyrolysis can be accomplished by firing the substrate in an inert gas such as nitrogen or argon (above about 2800°F, molecular N_2 may become reactive so ultra high temperature treatments and processes typically use Ar). In purely anaerobic situations, the escaping gases retain their flammability as they volatilize away, and heat energy must continuously be supplied to the substrate to keep the conversion/decomposition process going. Thus, it should come as no great surprise that the char yields for static combustion and open flame burning are often very similar to those obtained for pure anaerobic pyrolysis, and in many cases, essentially identical. Such a correlation is depicted in the figure to the right for a wide variety of char-producing polymers [1]. However, an analogous correlation cannot be identified for firing processes involving *dynamic* combustion where the ambient environment and overlaying vapor phases are not static but are in rapid laminar and/or turbulent motion.



In dynamic burning events, the situation is drastically different than with static burning, particularly when thermal blasting, sacrificial ablation, physical and chemical erosion of the exposed materials are involved. During dynamic pyrolysis of an article, degradation is often pronounced along sharp edges, protruding features and polymer end groups as these features are most vulnerable to the blast forces. In addition, material degradation and damage that occurs during thermal blasting is influenced by the gases and particles within the blast stream since these constituents can lead to ablation via physical and physicochemical erosion. From another perspective, exposed surfaces of vehicles and objects entering the earth's atmosphere at subsonic speeds are degraded as collisions with hot air molecules induce frictional heating leading to ablation which leads to charring, erosion and direct oxidation of the substrate material. For leading edges entering the atmospheric at hypersonic speeds, heat is generated by the compression of air in front of the leading edge creating a very hot shock wave. In these situations, reactive oxygen ions and radicals may enter into the boundary zone along the material interface where ablation and erosion can occur as well as direct oxidation of the substrate. For substrates utilizing ablation-resistant ceramic coatings (such as the Shuttle's SiC conversion-coated RCC), it may still be possible for oxygen to enter through defects in the ceramic layer (which may include pinholes or craze cracks) and then migrate deeper into the material through inner pore channels where direct oxidation and loss of the carbon substrate can occur.

For flame-exposed materials comprising the liners, insulator panels and ablative nozzle structures in aluminum/perchlorate-based solid fuel rocket motors (SRM), most of the oxygen generated during decomposition of the oxidizing agent (perchlorate) in the fuel mixture is instantly consumed as the burning/blasting process progresses. In this reaction, elemental aluminum is oxidized to alumina as triplet oxygen radicals are generated and the organic binder in the reaction mixture (an NBR-like elastomer) is pyrolytically decomposed into smaller, combustible molecular fragments which themselves consume residual or excess oxygen generated in the reaction mixture. Additionally, radical chloride atoms are generated abundantly during the fuel reaction and these intermediaries act as scavengers to the more reactive radicals responsible for oxidative combustion. Thus, gas-phase oxidation is inhibited by the presence of chlorine entities within the system (fluorine constituents can provide even greater inhibition). However, it is possible that, rather than a drastic flame-killing effect as one might expect, the inhibition factor actually helps to regulate the flame providing a degree of stability to the burning process. An inherent, self-generated stabilizing agent such as gaseous halide could conceivably play a vital role in the consistency, uniformity and overall effectiveness of the burn process in these types of solid fuel systems.

When the burning fuel front reaches the insulator material surface, the interfacial environment is quite dynamic and turbulent, and the level of free oxygen available at the interface is expected to be relatively low. The liner material essentially undergoes near anaerobic pyrolysis and/or *partial* oxidation (incomplete combustion). Leading products in the partial oxidation of organic matter will always include high levels of H_2 and CO along with small molecular hydrocarbons such as methane, ethane and their radicals (benzene and methyl-substituted benzenes will be generated from aromatic substrates such as crosslinked epoxies, esters and phenolic networks). Intermediary products of partial combustion may also include formaldehyde ($H_2C{=}O$), hydrogen peroxide ($HO{-}OH$) and their radical forms (hydrocarbonyl and peroxy). Note that most of these intermediates are still flammable downline or in the main plume. Many can act as reducing agents (especially at elevated temperatures) as they undergo full oxidation to CO_2 and H_2O. In sulfur-vulcanized aliphatic elastomers, (such as SBR), smaller levels of SO and SO_2 will also be generated, and in nitrile rubbers (i.e... NBR), emissions of both SO_x and NO would be expected (both of which can act as reducing agents). In any kind of burning event, if appreciable levels of either H_2O or CO_2 happen to stagnate or make their way back to the flame interface, they will tend to extinguish to the flame. It is interesting to note, flaming combustion produces its own extinguishers and the burning process is sustained only as long as there is a mechanism in place that rapidly transports the extinguishing species away from the burn zone.

Further down and out of the burn zone within the nozzle exit cone cavity, there is even less available oxygen. Here, the vapor layers interfacing the ablating surfaces are essentially starved of oxygen since none is generated from local fuel reactions in this area and the majority of oxygen produced in the motor case section is consumed before entering the exit cone region. Considering the possible products and species generated during the overall burn process, the plume will likely contain a mixture of both oxidizing and reducing agents of varying strengths and concentration levels. So does the nozzle chamber become an oxidizing or reducing environment during a burn cycle?' The answer likely includes both. There may be localized regions where atoms/molecules comprising the ablating materials undergo oxidation (loss of electrons) and other areas where reduction predominates (gain of electrons). Overall, the burn environment in the nozzle section probably favors reduction while both processes may be occurring concurrently.

During an SRM burn cycle, perhaps this region of the motor could be effectively characterized as a *depleted* oxidation environment. Oxidation of the material will almost always lead to chemical erosion, but this is not necessarily the case for reduction reactions (in general, oxidation degrades or disintegrates the material while reduction is sometimes likened to a building process). Under *static* burn conditions, the data clearly indicates that oxidative chemical erosion of char-producing substrates is generally insignificant [1]. Consider the idea that within a typical SRM environment, the hot blasting forces are so intense, that even a very small level of weakly oxidizing species present within the high energy plume can result in substantial material losses. Overall, ablation in such systems might occur as a result of two major contributions: thermophysical abrasion due to high energy particle impingement and phyiscochemical erosion brought about as small, localized streams of weak-to-moderate oxidation agents are forced into and along the surface boundaries of exposed substrate materials.

Some Polymers Carbonize While Others Volatilized Away

Thermal degradation of a polymer structure involves bond-breaking and usually begins before the onset of thermochemical decomposition which leads to the production of char and volatiles. Under slow to moderate heating rates, thermal degradation begins around 550°- 650°F for most highly crosslinked aromatic thermosets, such as those within the phenolic, epoxy and polyester families. This is typically the temperature range at which the lowest energy bonds in the molecular structure weaken and begin to rupture. As degradation and decomposition begin to overlap, chemical links containing sigma-bonded oxygen, terminal carbons, protruding pendant groups, secondary and tertiary hydrogen atoms are often the first to break. The intermediary products are free radicals which react and combine which other species, ultimately releasing a mixture of gases (CO, CO_2, H_2O and methane CH_4) as the non-volatizing portion of the burning substrate consolidates into a carbonaceous char. It should be realized, even in anaerobic pyrolysis, varying degrees of oxidation take place, at least in the early burning stages, due partly to the presence of bound oxygen within the substrate, as well as the generation and presence of CO_2 and H_2O, both of which can act as weak-to-moderate oxidation agents at elevated temperatures.

Around 800°- 900°, the polymer structure starts to decompose pyrolytically as main chain scissions occur along with hydrogen stripping liberating hydrogen atoms $H\bullet$ (radicals) which are free to initiate and propagate a multitude of free radical chain reactions as the burning event progresses. Throughout the process, the solid charring structure undergoes bond cleavage, advanced (pyrolytic) crosslinking, rearrangement and consolidation. While CO is only moderately combustible, CH_4 and H_2 are highly flammable fuels, and during ordinary burning processes, the heat from their combustion is fed back into the charring substrate helping to sustain the pyrolysis process. As the temperature and/or hold time are increased, the production of more complex molecular fragments becomes inevitable as secondary and tertiary reactions lead to more complex combinations producing volatiles which may contain a variety of alkanes, alkenes, branched aliphatics, substituted benzenes, di- and tri-nuclear aromatic compounds and soot (polycyclic aromatic hydrocarbon particles). All of these products are highly combustible.

For many thermoplastics and lightly crosslinked elastomers (such as NBR and EPDM), the onset of thermal degradation may be as low as 400°- 500°F with pyrolytic decomposition beginning in the 600°-700° range. Non-crosslinked thermoplastics typically undergo hydrogen stripping, side group elimination, depolymerzation to monomers and finally, volatilization. On the other hand, polymer networks which incorporate extensive crosslinks in their structures during the initial molding process behave quite differently from thermoplastics. As the rigid virgin material is converted into solid carbon char, advanced crosslinking reactions facilitate the processes of cyclization, aromatization, branching and ring fusion while radicalized reaction sites along the degrading chains interact, and the bulk volume of the evolving char structure undergoes significant volumetric shrinkage.

It is worth noting that, under static conditions, highly crosslinked aromatic phenolic thermosets, which produce about 50% w/w char yield, lose about 40% of their original volume while most thermoplastics and all aliphatic rubbers such as NBR and EPDM are completely volatilized away. When thermosets are heated under a constant heating ramp, the extent of char conversion is about 85-90% complete upon reaching the 1100°-1150° range. However, if held at 950°-1000° long enough, it is possible to approach 85-90% conversion after several days, while hold times of about 24 to 48 hours at 1100°-1200° will almost always yield > 90% conversion or better. Pyrolysis cycles with > 8 hour holds in the 1400°-1600°F range are typical within the materials processing industries for yielding ~98-99% converted product. Keep in mind however, these temperatures are not anywhere near high enough to induce structural graphitization (crystallization) of the material, which does not even start until well above 4000°- 4200°F (in any event, crosslinked thermoset polymers do not typically undergo graphitization).

For virgin polymer networks with high crosslink densities, the intermediary char structure will condense and form new crosslinks during the pyrolysis process. Again, pyrolytic crosslinks are the primary bonds created during the char-forming process as the virgin polymer network is transformed into an inorganic carbon structure. Polymer systems in which the hydrogen content is relatively low tend to give higher char yields. That is, high carbon/hydrogen (C/H) ratios favor pyrolytic crosslinking and hence higher char yields, while high H/C ratios favor increased main chain cleavage and the release of higher levels of $H\bullet/H_2$ leading to increased formation of small molecules, hence more volatiles and less char. Pyrolytic crosslinks differ from those formed during initial curing of a polymer as these advanced links are driven by high temperature radical interactions and couplings between dangling end-groups created throughout the polymer structure during pyrolysis. In general however, all crosslinks formed during the development and structural evolution of a polymer tend to inhibit crystallization of the structure.

During heating cycles, pre-graphitic molecular movements are controlled by the density and strength of the crosslinks. In well-crosslinked structures, such movements are completely inhibited. It is interesting to note that while non-crosslinked polymers (thermoplastics) will initially convert into a pre-graphitic green carbon structure during early pyrolysis and then readily transform into 3-D hexagonal graphite above 4000°- 4500°F, crosslinked thermosets appear to attain and retain structural features which are reminiscent of their virgin amorphous structures to well beyond 5000°F. For virgin polymers stabilized with high crosslink densities during the initial molding stages, large migrations and movements of the polymer segments and branches during heating are prohibited as the structure is basically 'fixed' in space, and crystallization becomes disallowed thermodynamically. In many cases, the apparent structural texture of the fully charred residue often bears a striking semblance to the cured polymer.

In general, most ordinary thermoplastics will melt or flow long before they ever reach carbonization temperatures. They are difficult to convert in this respect. If constrained somehow or heated in a container, some thermoplastic polymers will boil or volatilize during the heating process. However, if a few crosslinks inadvertently form or are deliberately incorporated into the structure, melting can almost be bypassed. Certain thermoplastics with light-to-moderately crosslinks can sometimes be carbonized effectively without any melting at all. Indeed, this is the principle behind the stabilization step applied to carbon fiber precursors prior to carbonization (this includes rayon, PAN and pitch). Polymers with non-homogeneous structures (i.e… those containing varying amounts of crystalline, amorphous and/or crosslinked segments) are not so easy to define. However, such structural mixtures may be more representative of the majority of polymer systems we actually deal with everyday in the real world. In any heterogeneous polymer structure, thermoplastic segments and branches which are successfully converted into green char early in the heating process will typically undergo crystallization into 3-D graphite or at least attain a high degree of structural order when taken above 4000°-4500°F, while the regions which have been rigidized with structural crosslinks become *inert* to graphitization or crystal-like ordering. These crosslinked regions carbonize into vitreous carbon configurations in which amorphicity is permanently retained in the structure.

Even though crosslinked networks may not go through a distinctive melting point or range, they often exhibit a slight softening effect around their characteristic glass transition temperature T_g. Indeed, inter-chain crosslinks make it possible for these materials to remain exclusively in the solid state throughout the thermal conversion process. Ideal examples might include common thermosets which are pyrolyzed under slow, steady state conditions. In most cases, the T_g of a polymer network can be influenced systematically by applying the appropriate controls and techniques during the primary and secondary curing processes (T_g is usually adjusted upward). In general, the ultimate T_g of any thermoset material is established by the maximum temperature applied during the fabrication and post-processing stages. For instance, crosslinked phenolic resoles have been shown to exhibit a T_g some 20°- 40° above the maximum hold temperature applied during the cure process. For phenolic systems single cured to 315°F, the T_g may run in the 335°-355° range while the same systems effectively post-cured to ~500°F have been shown to possess softening points that occur very close to the onset of thermal degradation.

Clearly, this condition significantly enhances the stability of such composite systems during high temperature applications since low T_g values can lead to premature movements and undesirable ply shifts within the structure. Indeed, inadequately cured systems have been known to fail long before the onset of the thermal degradation stage. It is a foregone conclusion that the higher the T_g, the higher the char yield and the lower the erosion rate. Producers of high temperature polymer-based structures who are *not* rigorously trying to maximize the T_g and char yields of their materials, especially for components which are expected to generate char as part of their performance criteria, are delivering inferior products. Modification of the T_g has also been demonstrated for other thermosets, such as amine-cured epoxies, peroxide-crosslinked polyesters and crosslinked siloxanes. It could be surmised that the same principles are viable for lightly networked elastomers and rubbers including NBR, peroxide-cured EPDM and isocyanate-crosslinked urethanes whose T_g transitions occur over wider ranges.

Thermoplastic Chars Graphitize While Thermosets Do Not

In addition to high char yields, one of the more interesting properties of heavily crosslinked aromatic polymers is the fact that they convert directly into *glassy* (vitreous) carbon, a unique form of amorphous carbon which is akin to glassy ceramics. Glassy carbons are non-graphitizable under static, stress-free pyrolysis conditions. In contrast to other carbon forms, glassy carbons undergo no further phase transitions or structural rearrangements across the attainable temperature span, even when taken well above graphitization temperatures. In the industry, the most well known and utilized precursors for glassy carbon are those derived from cured phenol-formaldehyde (phenolic) resol resins. This specialized glass-ceramic-like carbon material is gaining increased use in a variety of high temperature applications such as ablators, semiconductors, machining tools and optics. Their structures contain a very high aromatic content in which the rings are joined by short methylene links providing very high char yields.

Well connected networks which contain high levels of regularly arranged aromatic rings such as those based on custom resorcinol-aldehyde resoles, polyaryl halides, divinyl benzenes and substituted polynuclear aromatics give high char yields of glassy carbon when pyrolyzed (~60-80%). Pressure cured articles of homogeneous, monolithic glassy carbon are isotropic, amorphous and are generally hard, brittle and shiny (like glass). While bulk permeability is often present due to pyrolytic recession of the internal microporosity network created during the curing/molding process, solid regions are generally hermetic (like glass) but may contain tiny hermetically sealed occlusions which have been shown to exist in glassy carbons derived from these polymers [2].

Under certain conditions, it *is* possible to induce graphite-like character into evolving glassy structures by applying the appropriate levels and forms of anisotropic stress or pressure during the conversion process. Interestingly, if composites comprised of carbon fiber / glassy carbon matrix (such as carbonized phenolic matrix carbon/carbon) are subjected to graphitization temperatures, the bulk of the glassy matrix throughout the composite does not graphitize, as expected. However, as localized regions or layers of the cured phenolic matrix directly interfacing the carbon fibers begin to undergo the transformation process into carbon, they may actually try to crystallize due to differential expansion/contraction along the fiber surfaces which can lead to *stress graphitization* of the carbon matrix at the fiber interfaces. Such effects have been demonstrated independently as well as by other workers in the field [3]. Graphitized interfaces in these composite systems can be detrimental in certain applications and beneficial in others (as covered in other papers). The effect is undoubtedly driven by the 4-to-0 CTE differential between the isotropic matrix phase and the longitudinal fiber surface.

Note: the isotropic CTE for cured phenolic resoles above their T_g runs around ~ 35 - 65 ppm/°C, while that for glassy phenolic char is about ~ 4.5 – 5.0 ppm/°C; longitudinal CTE for carbonized fibers of PAN, rayon or pitch run about ~ 0 ± 0.5 ppm/°C, and ~ 4 - 10 ppm/°C transverse CTE for the same).

On the other hand, sparsely crosslinked aliphatic elastomers and rubbers such as NBR and EPDM contain no aromatic rings since they are purely aliphatic in structure. Thus, the networks in these systems consist of crosslinks joining thermostructurally weak chain segments to one another, which may indeed be more stable and tougher than their non-crosslinked counterparts, but they are still quite vulnerable to the effects of heat degradation. During pyrolysis, the main chain C-C bonds are sequentially cleaved producing radical fragments which further react, ultimately leading to smaller radical volatiles that combine with available hydrogen atoms and other radicals within the pyrolysis layer. Whether in isolated form or as a binder/matrix within a multi-component composite formulation, these polymers will volatilize away during pyrolysis, perhaps leaving a few trace remnants of glassy char here and there (fragments containing residual crosslinks that happened to survive).

Special Thermoplastics That Do Not Melt or Volatilize

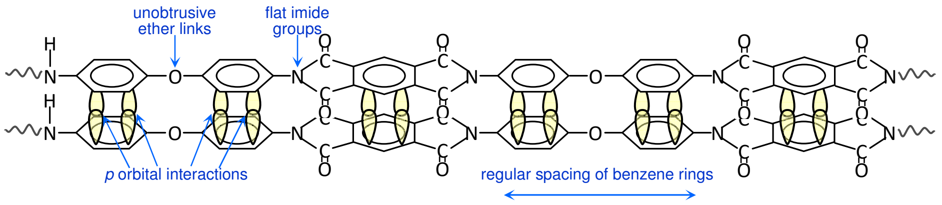
Now, there is a unique class of polymers which does not follow the normal pathways of the more traditional thermoplastics or thermosets, particularly in terms of their mechanical and thermal properties. Of interest here are the synthetic polymer systems exhibiting extraordinary properties due to their liquid crystal (mesogenic) effects. Some of the more prominent liquid crystal (LC) systems include PBI (polybenzimidazole), PBO (polybenzoxazole), the polyimides (e.g... Kapton®, PMR), the aramids (e.g... Kevlar®, Nomex®), polyphenyl ketones and ethers (e.g... PEK, PEEK and PEKK), polyamideimides (e.g... Torlon®), and custom LC polymers based on bisphenol phthalonitriles or certain methylene-linked cyanate esters. It is interesting to note here, these materials are all *thermoplastics* containing no thermosetting crosslinks . . . but they are a unique class of thermoplastics. In general, LC polymeric materials have extraordinarily high T_g's (~900°- 1000°F) and high degradation temperatures (~1000°-1100°) which pushes their capabilities well above the norm of traditional engineering polymers and high performance binder/matrices.

Some LC systems can be synthesized and tailored for crosslinking, but their thermoplastic properties are already superior to most other polymer systems including many thermosets. Unlike highly crosslinked polymers which are usually stiff and rigid, many cured LC polymers can be tailored to exhibit elastomeric properties characteristic of flexible thermoplastics. As one might expect, the higher the level of mesogenic activity within the network, the greater the thermal and mechanical properties of the material. On the other hand, high mesogenicity also results in polymers that are extremely difficult to process with higher stiffness and reduced elasticity.

Historically, within the industry, compromises have been sought between extreme and moderate mesogenic behavior by synthesizing specially tailored LC polymer structures in which the number of interacting ring systems along the chains is slightly reduced, providing considerable improvements in polymer solubility and processability without undue losses in the thermal and mechanical attributes desired.

For example, the para-aramids (ex. Kevlar®) exhibit straight chain structures with comprehensive ring overlaps along the chains which offer unbeatable performance properties, but are plagued with limited processing capabilities. On the other hand, the meta-aramids (ex. Nomex ®) have structures in which some of the rings along the chains are shifted so that indexing between polymer chains is reduced (along with mesogenic activity). Thermal and mechanical performance properties are not quite as high as those for Kevlar® but polymer processability is greatly improved. Para-substituted monomers enhance LC alignment while meta-substituted units introduce staggered ring orientations into the chains which disrupt ring-to-ring interactions between chains. Also, N-substituted PBI molecules have been shown to exhibit improved solubility over traditional PBI materials with no loss in thermal stability[4]. Of interest here is the Celazole® series of PBI products offered by PBI Performance Products as resin solutions and powders which appear to be melt-processable and can be utilized for film casting, fiber spinning, coating and impregnation. Due to the high level of solvents required in these systems (80-95%), the PBI phase usually foams up during cure which is extremely porous with low density.

Now, mesogenic LC activity is a unique condition established by having a high level of aromatic rings along the polymer chain which are joined together in a regular but specific repeating fashion by small linking groups, often a single atom or non-intrusive functional group such as an ether oxygen, a methylene group or an imide pattern (typical polymer families might include the biphenyl ethers, phenyl methylenes or imidazole-linked biphenyls). In these configurations, *p* orbital overlap interactions are established between the π systems in aromatic rings of adjacent chains as they become layered or stacked on top of one another with such strong interactions that the bulk material does not melt or flow (appreciably). This is the mesogenic effect and gives rise to LC behavior.



Such structures are will be anisotropic (orthotropic) since the inter-chain (transverse) properties are expected to be different that those along the chain direction. During the early synthesis stages, PBI polymers of high molecular weight (MW ~100,000) are almost impossible to process and must be dissolved in 100% hot sulfuric acid just to get a 10-15% solution (as you might imagine, 100% sulfuric is pretty nasty stuff, especially when it is boiling hot). However, if the MW of the initially synthesized polymer is lower (say around 50,000-60,000), processable solutions of PBI in other solvents becomes possible. Aprotic solvents such as N-methyl pyrrolidone (NMP), dimethyl acetamide (DMAc) and dimethyl formamide (DMF) are now widely used throughout the industry for these systems. Indeed, PBI Performance Products offers solution versions of Celazole® polymer in DMAc at concentrations > 25% which is the spinning dope used for producing their fibers of PBI. Controlled polymerization techniques during the spinning and coagulation steps allows for fibers with greatly enhanced anisotropic properties.

Again, these polymers have unusually high T_g's and thermal degradation temperatures T_d, but when degradation and decomposition finally do commence, the reaction sequences and mechanisms are probably not a whole lot different than those pertaining to crosslinked thermosets where the main chain network is essentially ‘protected’ while only the hydrogens, oxygens, nitrogens and sulfur atoms are pyrolytically extracted from the structure. For some LC polymers, the quantity of hydrogen and other groups is relatively low, leading to very high char yields, sometimes as high as ~90%. Deviations from these mechanisms might include the modification of pyrolytic crosslinks since the organic structures of most LC polymers are already well organized and compatible with the pre-carbonized structures that lead to the formation of green coke and ultimately to hexagonal graphite. Since these materials generate their own carbonaceous mesophase medium, they readily transform into green (semi-crystalline) carbon at the onset of pyrolysis. In general, polymers that char quickly and result in high char yields provide the greatest heat stability, the lowest heat release rate, the best flammability inhibition and most impressive high temperature properties since the char that quickly and abundantly forms on the surface protects the virgin material from the penetrating heat waves, prolonging the pyrolysis process and retarding the recession front.

Pyrolysis/Combustion Reactions and Mechanisms Simplified

There is ample information available detailing the reaction kinetics, mechanisms and thermodynamic factors for classical processes involving the thermal oxidation, combustion and pyrolysis of organic materials into CO_2 and H_2O. There is no reason to duplicate all those concepts here. However, it might be interesting to explore some of the partial oxidation aspects of these processes in greater depth. For starters, consider the anaerobic pyrolysis of simple hydrocarbon-based materials under static conditions (oxygen-free thermal cracking). A generalized (unbalanced) representation of the *overall* reaction might show a product mix containing carbonized substrate (solid char remnant), molecular hydrogen and small gaseous hydrocarbon molecules . . .

$$\underset{\substack{\text{hydrocarbon}\\\text{substrate}}}{C_aH_b\ (s)} \xrightarrow[\substack{\textit{cracking}\\\textit{(pyrolysis)}}]{\Delta} \underset{\substack{\text{carbon}\\\text{char}}}{C\ (s)} + \underset{\text{hydrogen}}{H_2\ (g)\uparrow} + \underset{\substack{\text{small aliphatic}\\\text{hydrocarbons}}}{C_fH_g\ (g)\uparrow}$$

For the majority of polymers used in industrial and everyday products, including elastomers and conventional binders used in adhesives, coatings and low tier composites, the chains and structures are easily disintegrated when exposed to pyrolytic temperatures, volatilizing into H_2 and small hydrocarbons (methane, ethane, ethene, etc...) with little residual char produced (that is, $[C] \sim 0$ in the above equation). Additionally, H_2O, CO_2 and CO are produced in quantities that are related to the amount of oxygen present in the flame environment (if any) *and* within the substrate as water previously absorbed from the environment and/or chemically bound within the polymer structure. In general, most of the common polymers are hygroscopic to varying degrees, containing appreciable levels of oxygen and water, both physically and chemically bound. Thus, even under anaerobic pyrolytic conditions, some oxidation of the material is unavoidable as the oxidizer can come from within the material. Lower levels of intrinsic oxygen imply burn processes where incomplete combustion is taking place, accompanied with the release of CO. In any event, the product gases will also include lower levels of CO_2 and H_2O, corresponding to instances or locations where full oxidation takes place. Overall, one could write . . .

$$\underset{\text{oxygenated substrate}}{C_aH_bO_c} \xrightarrow[\textit{pyrolysis}]{\Delta} C + H_2 + C_fH_g + CO + CO_2 + H_2O$$

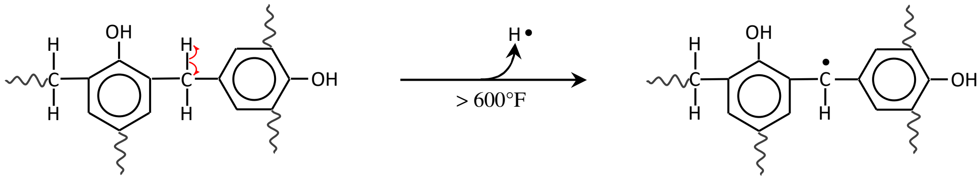
Polymers containing other entities such as nitrile groups and/or disulfide links (i.e... NBR, EPDM, etc...) can be represented in an analogous manner with the net reaction given by the generalized formula . . .

$$C_aH_bO_cN_dS_e \xrightarrow[\textit{pyrolysis}]{\Delta} C + H_2 + C_fH_g + CO + CO_2 + H_2O + NO + NO_2 + SO + SO_2$$

As it is with the carbon oxides, high oxidation events tend to favor formation of the dioxides of nitrogen and sulfur, while in starved oxidation scenarios, higher levels of the mono-oxides are always produced. It should be realized that nitrogen oxides and compounds are not even generated unless the flame or heating temperature surpasses ~2800°F. While particulate alumina is typically the primary media responsible for *physical* erosion (abrasion) of impacted surfaces in aluminum-based fuel mixtures, any and all gaseous products indicated in these equations, as well as their intermediary radical forms, could be considered as potential candidates for *chemical* erosion of the exposed materials (Note that above about 3700°-3800°F, Al_2O_3 particles will melt, altering the erosion patterns and depth accordingly; above ~5400°, alumina will vaporize where it's physical erosion properties vanish but it's ability to participate in chemical erosion could become feasible). In addition to H•, some of the more prominent gaseous radicals generated in these reactions which propagate the pyrolysis process include hydroxy HO•, formyl HOC•, peroxy HOO• and atomic oxygen •O•, a diradical. As with molecular dioxygen O_2, ground state oxygen atoms are triplet state paramagnetic diradicals which can be excited to metastable singlet states under certain conditions. For this study however, triplet state oxygen atoms are considered to be the principal culprit involved in the oxidation and erosion of materials in the SRM burn/blast environment.

It should be obvious at this point that, in general, the thermal conversion of organic matter into volatiles and carbon char is a *free radical-driven process* involving an array of possible chain reaction sequences, be it flaming combustion, pure anaerobic pyrolysis, static or dynamic oxidation. When heat degrades these materials, the chemical bonds joining adjacent atoms along the polymer chains are cleaved into segments while the pairs of bonding electrons are split homolytically between the separating atoms. For example, when the level of heat absorbed within a crosslinked phenolic network reaches the effective bond dissociation energy of a secondary methylene carbon-hydrogen bond, scission occurs in which one electron is retained by each fragment – the phenolic substrate and the released hydrogen atom (recall that a single hydrogen atom is a free radical). With numerous radical sites along the chains at any given time, the substrate becomes a very reactive paramagnetic radical with each lone electron occupying a singly occupied molecular orbital (SOMO) . . .

Abstraction of a secondary hydrogen

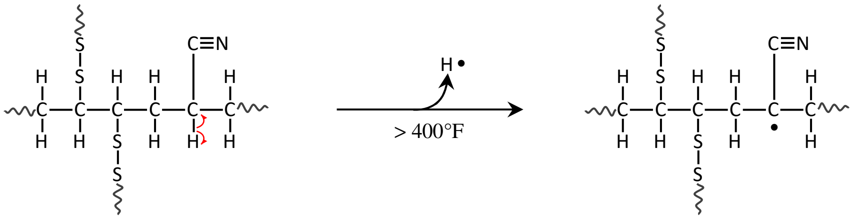


crosslinked phenolic segment

pre-carbonized intermediary (a secondary radical)

In branched structures (most polymer systems of interest), these unpaired radical electrons will almost always rearrange or shift around to other atoms along the structure resulting in radicals with greater stability, lower energy and increased reactivity. Tertiary and secondary hydrogens are often the first H-atoms generated during a burning event (they are easy to abstract and represent stable radicals). For example, during the early decomposition of crosslinked nitrile rubber (NBR) polymers, tertiary radicals could be the first intermediates produced . . .

Abstraction of a tertiary hydrogen



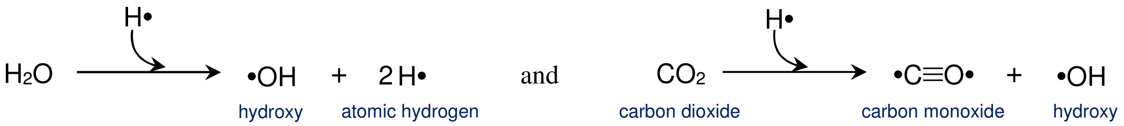
vulcanized NBR segment

pre-carbonized intermediary (a tertiary radical)

Pyrolysis Volatiles and the Agents of Chemical Erosion

In any and all cases, generated hydrogen radicals (free hydrogen atoms H•) can go on to instigate a rather large number of chain reactions as the decomposition process progresses. All of the chain-propagating reactions cannot be covered here. Keeping in mind that varying quantities of water and CO_2 are almost always present within and around the burning flame, hydrogen radicals can instigate the formation of radicals that are also quite reactive including hydroxy, triplet oxygen, hydroperoxy, formyl, singlet carbon monoxide (a diradical) and so on. A few examples representing some of the chain-propagating steps can be illustrated in a general fashion . . .

Radical-induced homolytic cleavage and one-electron redox of H_2O and CO_2 to generate hydroxy radicals, triplet state carbon monoxide and more hydrogen atoms...



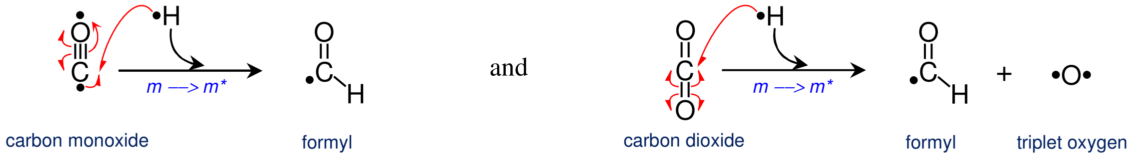
Above about 3500°- 3600°F, H_2O and CO_2 will undergo homolytic dissociation to give radicals of hydrogen, hydroxy, oxygen and carbon monoxide...

$$H_2O \longrightarrow H\bullet \;+\; \bullet OH \qquad \text{and} \qquad CO_2 \longrightarrow \bullet C{\equiv}O\bullet \;+\; \bullet O\bullet$$

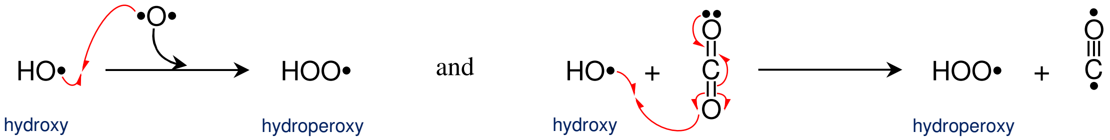
triplet oxygen atom

Note that while CO may undergo molecular conversions, chemical decomposition and coordination with metals, it's bond dissociation energy is the strongest known . . . it takes well over 6000°F to cleave the C≡O bond and so thermal decomposition of CO is not considered in this analysis. Additionally, considering the aggressive blasting/flame environment involved, the singlet ground state configuration of carbon monoxide $:C{\equiv}O:$ is presumed to become easily excited to the more reactive triplet state which is a *diradical* . . . $:\underset{\delta-}{C}{\equiv}\underset{\delta+}{O}: \longrightarrow \bullet C{\equiv}\underset{\cdot\cdot}{O}\bullet$. Here, the σ_3 non-bonding electron pair is homolyzed with one of the radical electrons entering a π^* anti-bonding orbital.

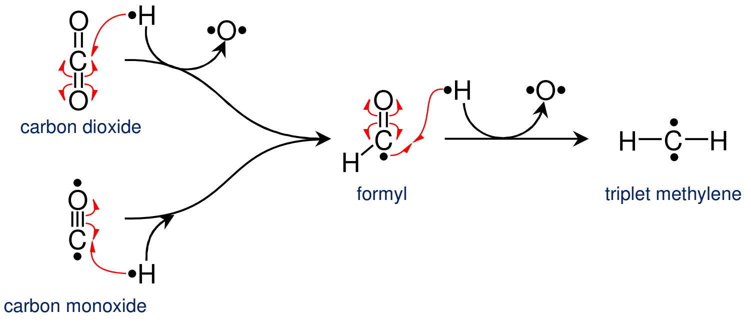
Radical-induced fragmentation of carbon monoxide and carbon dioxide via electronic excitation, energy transfer to an acceptor (m —> m) and decay to the formyl radical*



Formation of hydroperoxy radicals from hydroxy: (a) radical combination with triplet oxygen diradicals and (b) oxidation of hydroxy by carbon dioxide



Radical-induced formation of triplet state paramagnetic methylene diradicals from carbon dioxide and carbon monoxide

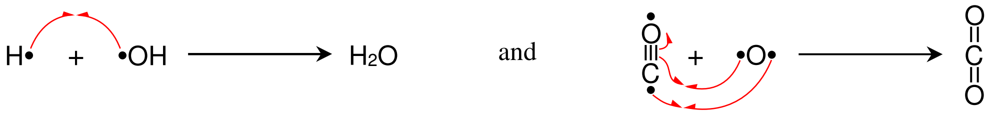


Note: Methylene is the precursor to *methane* and is the building block to larger carbenes, alkanes and alkenes that may form during pyrolysis.

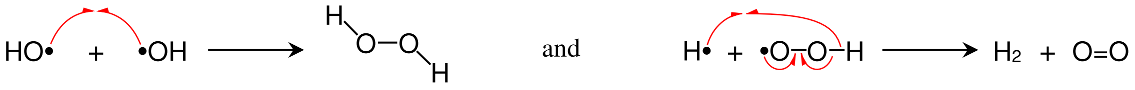
Again, there are literally hundreds of likely chain reaction steps occurring throughout the burn process, and even more for polymers containing nitrogen and sulfur groups. However, within cooler regions of the flame or plume as well as when the burn cycle begins to subside, a number of termination and recombination reactions are taking place which ultimately lead to the formation of the (non-radicalized) molecular species produced and detected during pyrolytic burning events. Some of the more relevant termination reactions might include . . .

Combination of hydrogen atoms to give molecular hydrogen and the combination of atomic oxygen to give triplet molecular oxygen

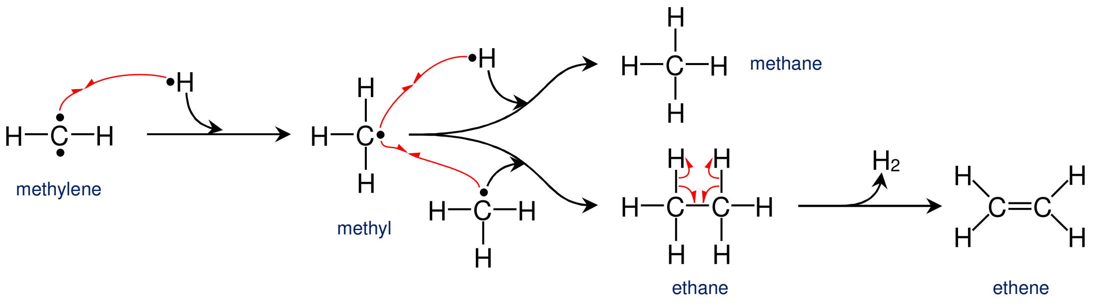
Combination of hydrogen with hydroxy to give water and the combination of carbon monoxide with atomic oxygen to give carbon dioxide



Combination of hydroperoxy to give hydrogen peroxide and the combination of hydrogen with hydroperoxy to give molecular hydrogen and molecular oxygen



Combination of hydrogen with methylene to give methane and the combination of methyl radicals to give ethane and ethylene



Note1 : It should also be realized that in perchlorate-based SRM fuel mixtures, free radical chlorine atoms are ever present to participate in reactions with other radical species, the most obvious being combination with hydrogen to form gaseous hydrogen chloride . . . $\mathrm{H}\bullet + \bullet\mathrm{Cl} \longrightarrow \mathrm{HCl}$.

Note 2: In cooler regions and when the burn process begins to subside, most of the triplet carbon monoxide $\bullet\mathrm{C{\equiv}O}\bullet$ will have a tendency to decay to it's non-radical singlet ground state $:\mathrm{C{\equiv}O}:$ perhaps by triplet-singlet inter-system crossing with phosfluorescence . . . $\bullet\mathrm{C}{\equiv}\underset{\bullet\bullet}{\mathrm{O}}\bullet \longrightarrow :\mathrm{C{\equiv}O}: + h\nu$.

Note 3: There is so much CO generated in these types of processes that a substantial portion does not even enter into any of the chemical reactions and is liberated throughout the process. Both triplet and singlet CO are expected to be released (at least initially) during an SRM burn cycle.

Note 4: In a typical Shuttle-type SRM chamber near the peak of a burn cycle (~5500°F, ~900psi), it could be surmised that $n_2/n_1 \sim P_2/T_2(P_1/T_1)^{-1} \sim 5$ which implies that there is a five-fold increase in the number of molecules (this of course neglects the volume change as the fuel is consumed).

All these products and intermediates become potential agents for the chemical erosion of liners and substrate materials which are exposed to the flame and blasting forces. The preceeding discussion explored some of the more prominent reactions associated with pyrolysis and conversion of organic matter into the volatile species which are known to be generated during partial oxidation burning events but has not considered any of the reactions taking place in the solid state phase . . . which involves the formation of inorganic carbonaceous char.

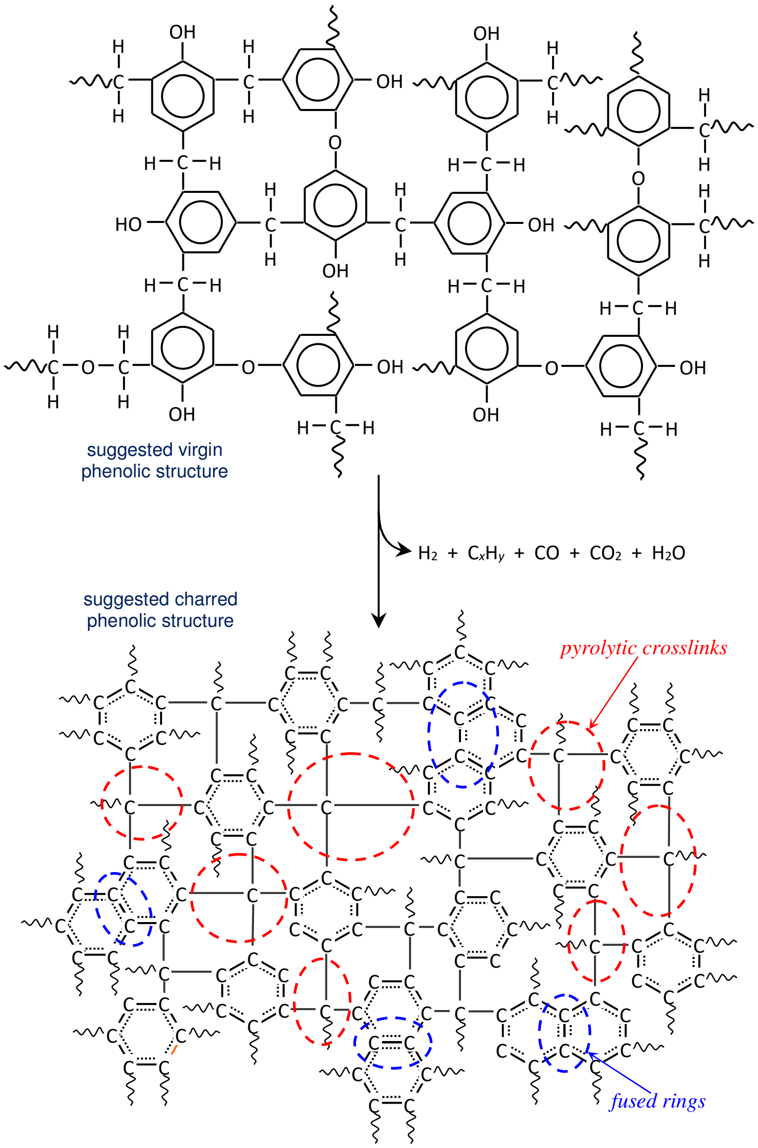
Production of Solid Pyrolytic Char and Char Yield

It is interesting to reiterate here that during static pyrolysis and combustion events, almost all thermoplastics and some of the thermoset materials we are familiar with produce very little char upon firing, often less than 10%. A surprising number of common polymers yield no char residue at all as the material is completely volatilized by the heat (oxygen and blasting forces not required). A few of the more well known polymers (non-crosslinked thermoplastics) which have been shown to yield 0% char upon pyrolysis include [5] polyethylene (LDPE), polypropylene (PP), polytetrafluoroethylene (PTFE – Tefon), polymethyl methacrylate (PMMA), polystyrene (PS), polycaprolactam (Nylon 6), styrene butadiene rubber (SBR), polyacrylonitrile butadience-styrene (ABS), and of course, nitrile butadiene rubber (NBR), but there are many more. Some of the familiar thermoplastics yielding > 0% but < 5% char remnant include polyvinyl alcohol (PVOH), polyvinyl acetate (PVAc), polyethlylene terephthalate (PET) and bisphenol-A epoxy (Dow DER-332). The halogentated analogs of some of these polymers can give > 10% char yield. Examples include polychloroprene (Neoprene), polyvinyl chloride (PVC) and chlorosulfonated polyethylene (Dupont's Hypalon®). In these systems, the pendant halogen atoms act as flame retardants which increase the char yield (. . . the higher the char yield, the lower the flammability).

Some of these thermoplastics can be tailored to incorporate crosslinks which are generated during a second stage curing process to give network polymers that are either (1) lightly crosslinked, (2) moderately crosslinked or (3) heavily crosslinked. Crosslinking will invariably increase their char yields. The NBR polymers of interest in our study fall into catagory (1) and are not really qualified to be called 'thermosets'. While a few fragments of the lightly vulcanized NBR may survive static pyrolysis, it is not realistic to consider this material a char-producer and certainly not an ablative as it is destined to be consumed during the burn process. In contrast, the highly crosslinked phenolic structure yields over 50% char and loses about the equivalent of all the hydrogens and hydroxy groups within the structure as the network of strong crosslinks retards main chain depolymerization and decomposition.

In further contrast, mesogenic structures and liquid crystal polymers often have minimal hydrogen and oxygen content within their structures and thus, many LC materials provide impressively high char yields. For example, PBI (polybenzimidazole) and PBO (polyphenylene benzobisoxazole) give around 70% char yield, Dupont's polyphenylene isophthalamide aramid 50% char yield, Ciba's F-10 cyanate ester 55%, GE's BPCPC bisphenol-C polycarbonate 50%, Amoco's polyamideimide (Torlon) 55%, Victrex's P22 polyetherketone (PEK) 53% and Madem's X-1000 polybenzoyl phenylene 65%. There are many more, and there are a number of similar LC research polymers which are on the brink of commercialization including UMASS' polyazomethine which yields ~78% char and the Navy's biphenol phthalonitrile at 79%. Though not well publicized, a couple of polymer classes, the polyarylacetylenes and polyalkynyl cyclopentadienes can yield > 85% char. These would be some interesting polymers to experiment with for potential development of advanced carbon fabric / polymer matrix rocket liners, polymer-impregnated ablators and next-generation carbon/carbon composites.

As inferred earlier, one of the key factors leading to high char yields is the formation of advanced *sp*^{2}–*sp*^{3} bonded pyrolytic crosslinks during the decomposition phase of the burn process. In addition, the char consolidation process is greatly facilitated, particularly in high aromatic structures, by the fusion of *sp*^{2}-bonded benzene rings. It is surmised that the original thermoset crosslinks 'hold' the polymer structure in place (preventing disintigation and volatilization) while facilitating the formation of high temperature pyrolytic links and fused rings which connect neighboring radical sites together. An illustration of this can be visualized by considering representative configurations of the virgin phenolic structure and it's fully charred conversion product * . . .



Ring fusion also occurs in aromatic thermoplastics as they pass from their mesophase state into green carbonaceous char where the absence of pyrolytic links permits easy transformation into the 3-D graphite structure later on (4200°- 4500°F). These high temperature crosslinks are the principal attribute responsible for the formation of non-graphitizable glassy carbons. There is much evidence that the green carbon forms derived from

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* All reactions, mechanisms, theories and representative chemical structures provided throughout this report are the perceptions and opinions of the author. No guarantee is made regarding their accuracy or correctness.

thermoplastic-based mesophase structures are entirely bonded via *sp*^{2} hybridization, leaving the pool of pi electrons free to influence material properties such as conductivity effects. In contrast, thermoset-derived glassy carbons are believed to contain a mixture of *sp*^{2} and *sp*^{3} bonding orbitals throughout the structure. This corresponds to the well documented attributes for glassy carbon of low conductivity with glassy/amorphous ceramic-like properties.

Physicochemical Erosion of Composites and Their Constituents

The kinetics of chemical erosion of nonmetallic nozzle materials has been well documented. It is not the intent here to duplicate any of those efforts but to expand or elaborate and propose some additional insight that may help account for the chemical loss of exposed materials and structures during the burn cycle of a typical SRM. For motors based on aluminum fuel, flame temperatures have been reported as high as ~5500°- 6000°F. During the burn cycle, aluminum oxide (alumina) is produced in abundance (Al_2O_3, m.p. ~3760°F, b.p. ~5400°). Also, certain flame-exposed insulator/ablative components and liner structures in the SRM systems of current interest (such as PBI/NBR composite) contain particles or fibers of silica (SiO_2, m.p. 2900°-3200°, b.p. > 4000°), and once this silica is dislodged from the composite material, it becomes part of the particle stream or slag. However, relative to the level of alumina, the quantity of silica in the flame is minuscule.

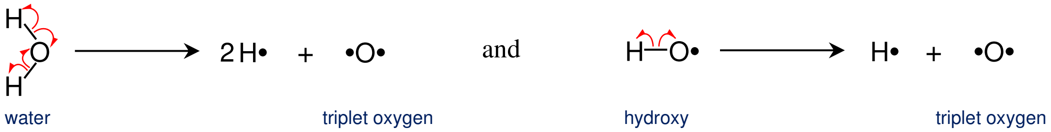
Thus, in these systems, physical erosion is due almost entirely to the ablative action of high energy impacting Al_2O_3 particles. However, in regions of the flame that surpass about 3800°-3900°F, the alumina particles are expected to be in the liquid state and their erosion properties are diminished accordingly. It is presumed that the melting points for these types of oxide ceramics (aluminas and silicas) are elevated under increased pressures in accordance with Simon's equation[7] . . . $a\left(P - P_{tp}\right) = \left(T_m - T_m^{1atm}\right)^b - 1$. Thus, in aluminum-fueled systems, physical erosion is expected to impart the greatest degree of material damage earlier in the burn cycle. It is feasible that chemical erosion could affect certain constituents anywhere above about 700°- 800°, but it is probably during the peak of the cycle when chemical erosion effects are maximum as the erosive agents are chemically energetic and physically driven onto/into the material surfaces by the hot blasting forces. It is also presumed that, at the lower temperatures, chemical erosion is kinetic-dominated but at the higher temperatures when the density of reaction products in the plume is highest, erosion reactions probably become more diffusion-controlled. Bear in mind that chemical and physical erosion are in addition to and may be coupled with the temperature-driven processes of pyrolytic char formation and volatilization since for much of the burn cycle, they occur simultaneously.

It may also be feasible to presume that charring, carbonization and/or volatilization of flame-exposed virgin material surfaces has already progressed to a significant extent before the degree of chemical erosion reactions become prononunced. Thus, char-producing polymer constituents (such as phenolic and PBI) are essentially in a pyrolyzed carbon state when erosive effects reach their most aggressive stage, while volatilizing constituents (NBR, EPDM, etc...) have all but vanished. This implies that, for the most part, chemical erosion reactions are essentially occurring on *carbonized* surfaces of the substrates. For example, exposed surfaces of carbon fiber / phenolic matrix composite structures may already be in a carbon-carbon state before the damage from chemical erosion reactions becomes substantial. Erosion of PBI/NBR structures is trivial since the primary binder (NBR) is volatilized and blown away during the early pyrolysis phase. However, protruding PBI fibers whose roots remain embedded in the virgin NBR phase will themselves produce high char yields and are also subject to chemical erosion forces. The effects and consequences associated with physical particulate erosion are topics for another study.

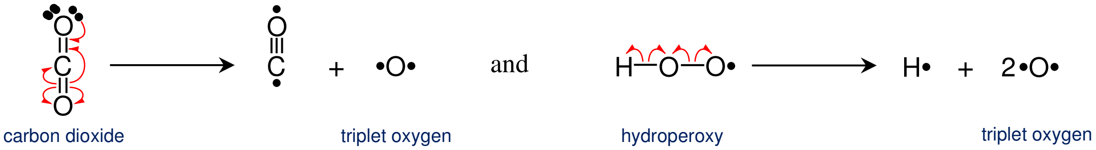
Now if chemical erosion is considered to be primarily an oxidation process, then even small levels of weak-to-moderately oxidizing species under the turbulent thermophysical action and high pressures of the plume can lead to substantial material losses through physicochemical ablation. The strongest oxidizers in this series might exhibit effective thermal oxidation strengths according to $\bullet O\bullet > HOO\bullet > HO\bullet > CO_2 > H_2O$. However, in terms of the relative concentration levels within the plume or flame, species likely to cause the greatest amount cumulative damage to the exposed materials and surfaces may be more on the order $H_2O > HO\bullet > CO_2 > HOO\bullet > \bullet O\bullet$. Generally, there are abundant levels of $H\bullet$ and $\bullet C{\equiv}O\bullet$ generated throughout the burn process, but these molecules will tend to act as reducing agents, having little effect on material degradation. Also, the relative redox power of methylene, the carbenes and alkyl radicals is considered to be weak and insignificant. Thus, the most likely culprits driving erosive degradation of susceptible materials comprising the liners and exposed structures of the combustion chamber would likely include water, hydroxy, carbon dioxide, hydroperoxy and oxygen.

Studies have indicated that reactions leading to the formation of carbon monoxide are the most damaging and that the weak-to-moderate oxidizers H_2O, $HO\bullet$ and CO_2 are the primary kinetic drivers for erosion of carbon substrates [6]. This approach can be expanded and further explored by suggesting that all the agents identified above play direct roles in the erosion process when considering the decomposition mechanisms of H_2O, $HO\bullet$, CO_2 and $HOO\bullet$ as these agents prepare to interact with the carbon substrate in a two step reaction scenario. . .

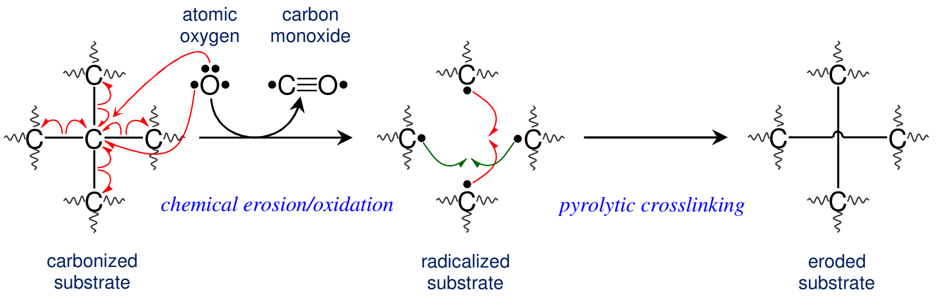
Decomposition of water and hydroxy to give triplet state atomic oxygen



Decomposition of carbon dioxide and hydroperoxy to give triplet atomic oxygen



Thus, in this approach, the first step (the rate-determining step) produces the fundamental oxidizing species which is ultimately involved in the erosive degradation process, triplet state atomic oxygen $\bullet O\bullet$, even though the kinetics scenario can be built around the overall reactions [6] . . . $C_s + H_2O \longrightarrow CO + H_2$, $C_s + CO_2 \longrightarrow 2CO$ and $C_s + OH \longrightarrow CO + H$. Now, it would be enlightening to explore how the fundamental oxidizing agent actually interacts with the carbonized substrate and then how the substrate might respond after the extraction of carbon atoms. In the second reaction step, it can be established that carbon monoxide is generated and released from the local surface as the erosion/extraction of carbon atoms from the substrate creates radicalized 'holes' in the microstructure. These reactive sites are then free to form pyrolytic crosslinks as the structure consolidates and the surface volume recesses exothermically. Consider the following simplified illustration . . .



Note: Triplet state oxygen exhibits three peaks on the ESR spectrum, a primary peak with two smaller peaks on either side, while singlet states produce a single peak. Multiple peaks (or states) are indicative of radicalized paramagnetic species containing uncompensated electron spins, and arise as a result of exchange interactions between the spins of the radical electrons in separate orbitals.

If erosion-driven pyrolytic links also form during the thermal conversion of PBI fibers, then glassy-like regions may develop in the periphery of these structures as well and these regions will tend to retard graphitization in the upper temperature regimes (after exposure to > 4000°F erosion, the fibers may contain regions that are both glassy-like and graphitized). The preceding illustrations and ideas are proposed only to indicate the basic reactions that might describe oxidation-based erosion of the concerned materials and are not intended to imply anything about the relative erosion rates. Obviously, carbon fibers, phenolic matrices and PBI phases exhibit much lower erosion rates than soft polymers such as NBR and EPDM which would erode very quickly if they survived the pyrolysis heat. It could be presumed here that the erosion reaction scenario tends to follow first order kinetics while the erosion recession process conforms to a first or second order parabolic law, but these are topics for another study.

A Few Notes on White Asbestos (AS) Fibers

White asbestos (chrysotile)[8] is basically a hydrated magnesium silicate glassy-type material ($Mg_3(Si_2O_5)(OH)_4 = (MgO)_3 \bullet (SiO_2)_2 \bullet 2H_2O$). It is highly crystalline and inert up to about 1000°-1100°F when the water is dehydrated from the structure. In this process, amorphicity increases and the anhydrous structure becomes more and more porous as the material loses its flame retardancy and insulative properties. For most commercial and industrial applications, this is the end of the useful life and thermal benefits of chrysotile-type asbestos materials. Thus, white asbestos only provides insulation properties up to about 1500°F and then the crystal structure starts to break down. It is probably not too long after this point when the hot blasting forces in the SRM chamber blow the remnants of this constituent out of the system. There is not much information available on the behavior and properties of chrysotile in the extreme temperature regimes. However, for the sake of curiosity, let us consider what might happen to this material in a static high temperature burning event as the fibers and their remnants are taken well beyond their normal and intended temperature ranges.

After dehydration (~1100°F), chrysoltile begins to lose it's identity as the anhydrous material increases in amorphous character and starts to segregate into rich Mg and Si dominated regions. Spacial distances between the Mg and Si rich domains increase as the bulk fiber structure becomes porous and discontinuous. Above about 1600°, the fiber remnants recrystallize and decompose several times with increasing amorphous silica character along with the co-existence of fosterite, $(MgO)_2 \bullet SiO_2$, estantite $(MgO)_2 \bullet (SiO_2)_2$ and other magnesia-silica compositions. These oxide mixtures essentially undergo decomposition as they melt (incongruent melting). The fiber structure begins to disintegrate and becomes more of a sintered powdery form. The decomposition/recrystallization process continues until well above 2400°- 2600°F. Around 3000°-3100°, the silica fraction melts, liquefies and begins to flow out of the fragmented remants. Above 4000°, any residual silica will completely vaporize, leaving sparsely-spaced, discontiguous particles of MgO as the last vestiges of the original asbestos fraction remaining (magnesia begins to melt somewhere above ~5000°). In short, the asbestos fibers start to become discontinuous (and insignificant) above about 1600° when they lose all their reinforcement and filler properties . . . and from that point on, they undergo a continual process of disintegration, ultimately ending up as nothing but scattered MgO powder remnants above 3000°- 3100°F. Note that in contrast to PBI and it's highly conductive carbonized forms, chrysotile is an insulator, as are all the SiO_2 and MgO polytypes that could possibly develop during the decomposition process.

A Few More Notes on Polybenzimidazole (PBI) Fibers

In PBI networks, the longitudinal direction is along the plane of the flattened ring-structured polymer while the transverse or lateral dimension pertains to the p-to-p π orbital overlap interactions between the flat mesogenic chains. The transverse interactions are a natural consequence of the liquid crystal (LC) effect and are quite intense. They impart extraordinary properties to the molecular network that are not present in other polymer systems.

Additionally, because of the regularly repeating ring configuration along the length of the chains, longitudinal anisotropy may be significant. When solutions of PBI polymers are spun into fibers and extruded through the spinnerets, an astounding level of anisotropy is achieved which establishes an extraordinary degree of thermal and mechanical properties associated with these polymer systems. Also, in contrast to more ordinary polymers, the pool of interacting π electrons in PBI networks is so pronounced that a small degree of electrical conductivity might be expected along these organic polymer chains under certain conditions. Polymers of PBI which have been passively precipitated from solution without the application of any forces or constraints will be anisotropic in and by themselves, but after spinning into fibers, anisotropy is increased several-fold in accordance with the mechanical and thermal properties. However, after conversion into inorganic carbon, LC polymers lose their flexiblity and organic mesogenic properties as they attain the attributes more reflective of a soft, green carbonaceous coke.

Since the LC forces between polymer chains facilitate the formation of their own in-situ mesophase medium and since there are no crosslinks links that form naturally in the network, PBI becomes an easy candidate precursor for graphitization. As it is with most carbon forms, low temperature carbonized PBI fibers are expected to be quite conductive, both electrically and thermally, and their conductivity properties only increase with temperature. It is well known that *sp^2* molecular orbital hybridization is characteristic of the graphene layers comprising most carbon forms while in contrast, the insulative diamond structure is purely *sp^3* hybridized. The polymer structures of PBI and other LC systems are composed heavily of *sp^2* bonding orbitals, and it is this configuration that stabilizes the pool of delocalized electrons responsible for the conductivity effects attributed to these materials. It is a foregone conclusion that graphitized PBI is a highly conductive material as all graphites are. In contrast to chrysotile, PBI becomes a highly conductive material above about 1200°F and the conductivity effects continually increase all the way through graphitization, while AS is a strong insulator at all temperatures until about 1500° when it begins to disintegrate and then all properties associated with the fiber are permanently lost.

Various forms of synthetic graphite can be hard, soft, chalky, brittle, dense or porous depending on the size of the initial particles or grains that the material is derived from and the conditions applied during the graphitization process. In its virgin state, a single organic PBI fiber will likely contain a few regions of amorphous character, but overall, the structure is expected to be dominated by semi-crystalline *sp^2* structures associated with the strong transverse mesogenic interactions. Static carbonization or pyrolysis of PBI fiber will likely yield a semi-crystalline carbonaceous monolith that is slightly soft (rather than hard and brittle like a ceramic) with a highly ordered green structure. Mesogenic activity is expected to vanish upon carbonization as the pre-graphitic structure undergoes ring fusion and the sheets of rings begin to loosely interact through their *p* orbitals via van der Waals forces. Static graphitization of the structure increases these interactions as the rings 'index' on top of one another at a spacing of about 3.5 Å resulting in a hexagonal structure that is relatively soft. Because of their easy transformation into the close-packed structure, graphitized PBI fibers are expected to yield a soft form of graphite (not hard and brittle). However, regions of the fiber that have developed pyrolytic links may tend to be glassy, harder and less ordered.

A Few Notes on Carbonized Polymer Fibers

Carbonized fibers of rayon, PAN and pitch are often assumed to remain unaltered throughout pyrolysis and non-oxidative burning events, and this is indeed the case . . . as long as the exposure temperature remains below the maximum process temperature applied to the fibers during their manufacture. These polymer precursors are thermoplastics which will melt or soften. So before they can be carbonized, they must first undergo an oxidative stabilization step where the virgin fibers or fabric are subjected to a 400°- 500°F treatment in air which creates crosslinks within the polymer network. This basically converts the thermoplastic fiber into a thermoset and prevents subsequent melting of the polymer. The step is sometimes called 'precarbonization' and results in a fiber structure that is composed essentially of glassy, non-graphitizable carbon. Thus, the term "graphite fiber", as used extensively throughout the composites industry, is not exactly accurate. Even after the fiber has been exposed to graphitizing temperatures (4000°- 4500°F) and the consolidated structure has become highly ordered, it cannot crystallize in regions where virgin crosslinks have been incorporated. To the carbon scientist, these are well documented facts in spite of the nomenclature that has been adopted in the shop.

As the stabilized polymer fiber undergoes the primary carbonization cycle, a substantial volume loss is incurred. Obviously, this is most pronounced during initial conversion from the crosslinked organic state to the green carbon state, and then volume reductions grow smaller as the structure continually consolidates over the remainder of the temperature ramp. While there may not be a linear relationship between process temperature and structural consolidation, the two parameters are intimately related to beyond the graphitization range when maximum structural order and consolidation are achieved. Some of the consequences associated with fibers and fabrics which have been processed through high heat treatment (HHT) temperatures (> 3600°- 3800°) include very high tensile strengths, higher modulus, increased bulk density and increased conductivity. In essence, these properties are established by the temperatures applied during the carbonization and post-treatment processing steps.

Composite systems based on ≥ 4000° HT carbonized polyacrylonitrile (PAN) fibers are quite attractive for high performance aerospace components used in very hot motors and extreme re-entry vehicles which require at least a certain degree of survival in ultra high temperature environments. As one can imagine, these fibers and fabrics are relatively expensive. On the other hand, intermediate heat treatment (IMT) carbon fibers (≥ 2700°- 2900°) and intermediate modulus (IM) fibers are the most prevalent type used throughout the aircraft and automotive industries as they provide a balance between cost and performance. Finally, carbon fibers with the lowest cost, lowest mechanical and thermal properties and the lowest conductivity properties are those which are processed only to > 1800°- 1900° and are classified as low heat treatment (LHT) fibers. While these acronyms were basically derived for the PAN carbon fiber industry, they also apply to carbonized rayons and pitch-based fibers.

Nanotubes, milled fibers, chopped fibers, continuous fibers/filaments, yarns, roving and tow (hundreds or thousands of filaments bundled together), chopped mats, woven fabrics, knitted fabrics, hybrid fabrics, three dimensional preforms, 3-D braids, and other advanced configurations are now available for designers to use in composite structures. The selection is based heavily on the structural needs, the particular service applications and end uses of the final product, as well as cost. In specialized carbon fiber-filled products such as sheet molding compounds, adhesive pastes and thermoplastic composites, chopped fiber filler/reinforcements of the LHT type are commonly used as these constituents impart greater benefits than S-type glass fibers but are not intended to provide the high performance properties required for continuous fiber-reinforced advanced composites. For CF/EPDM formulations used in SRM components, the chopped carbonized PAN fiber component is expected to be of the LHT or IHT type. When these composites are exposed to blast temperatures in excess of 3000°F, the fiber volume begins to contract as the fiber macrostructure continues to consolidate. Of course, this consolidation effect is probably irrelevant since the EPDM binder and other constituents are long gone by that temperature.

The phenolic structures utilized for flame-side Shuttle SRM nozzle liners are comprised of LHT carbonized rayon fabrics which have been processed to 2200°-2400°F (by design) in efforts to mitigate conductivity effects in these components. However, when exposure temperatures exceed 2200°-2400°F later on, the lateral fiber volumes in these articles are expected to shrink. This could instigate problems down line possibly related to fiber-matrix debonds or other performance problems. Even though high carbon assays have been reported for some of these fabric products by their vendors, it is likely the fiber microstructures will continue to consolidate upon further heat exposure, regardless of whether weight changes occur or not. Additionally, it is obvious that hot erosion forces of any kind will degrade these green fibers much faster than their HHT counterparts. The selection of LHT fibers in highly erosive, high temperature environments may not always be the best choice for optimal survivability.

A Few More Notes on Nitrile-Butadiene Rubber (NBR)

In some respects, cured acrylonitrile/butadiene elastomers (nitrile rubbers) contain the properties of both thermoplastics and thermosets, depending on the crosslink density achieved. Specifically, crosslinked density is affected by (a) the number of butadiene units incorporated into the structure, (b) the nature and level of crosslinker (peroxide vs sulfide) and (c) the specific cure/post-cure molding process applied, among other factors. Compared to non-crosslinked thermoplastics, elastomers with at least a few crosslinks exhibit higher mechanical strengths, thermal and solvent resistance than their pure thermoplastic counterparts, while higher crosslink densities increase these attributes even more. However, as the number of crosslinks are increased throughout the network, the elastomeric properties begin to diminish. Additionally, as the mechanical and thermal properties increase, flexibility decreases and the polymer material starts to become more rigid.

Synthesis procedures utilizing larger prepolymers of acrylonitrile joined together with mono-, di- and tri-monomers of butadiene (that is, high AN/Butadiene ratio), allow for the incorporation and control of localized thermoset crosslinks within the chain which are separated by long flexible thermoplastic segments. This configuration imparts a unique form of elasticity and resilient thermomechanical stability relative to other crosslinked networks. A rigid thermoset would result if equal portions of monomeric acrylonitrile and butadiene were reacted together and crosslinked to the fullest extent. Also, when aromatic rings are incorporated into a polymer structure, there is usually an accompanying increase in mechanical properties, thermal stability and polymer hardness – at the expense of the elastomeric properties. Of course, neither NBR nor EPDM contain benzene rings of any kind in their structures and there are certainly no mesogenic interactions. So NBR is a better elastomer than say, SBR (styrene butadiene rubber) while SBR is expected to have somewhat higher mechanical and thermal properties. In general, the presence of crosslinked regions in a polymer network will retard the tendency for the bulk material to melt or flow during re-heating events as they help to 'anchor' the softer thermoplastic segments. When heated to the thermal degradation range (400°- 500°F), unvulcanized regions along the NBR backbone will start to break down, and as the temperature passes into the decomposition regime (600°- 700°), these regions will tend to volatilize, leaving large holes in the structure which evolve into larger discontinuities that eventually affect the crosslinked regions, perhaps depositing a few residual char fragments in the end. Thus, the more crosslinked the virgin polymer network is, the higher the char yield and the more continuous the char structure is.

The NBR polymers to be used in PBI/NBR composite liner/insulators for the Ares SRM concept are produced by Zeon and are basically ordinary acrylonitrile-butadiene formulations but with higher than average nitrile contents (30-35%). Other versions of this copolymer are available. For example, there are carboxylated nitrile rubbers or carboxyl-terminated NBR such as the Hycar® line of latex COx-NBR products by Lubrizol which incorporate carboxyl side groups along the chains. There also similar analogs incorporating hydroxyl, amine and methacrylate-terminated NBR products. All of these end-branch modifications tend to impart improved properties such as abrasion and wear resistance, ozone protection, cryogenic flexibility and compatibility for blending with other thermoplastic polymers and thermoset resin systems for advanced applications.

A Few Notes Pertaining to the Composite Phase

It has been well recognized that many composite systems provide some of their mechanical and thermal properties in a synergistic way so that the end result is greater than the individual constituent contributions. Indeed, this concept is incorporated into the very definition and purpose of composite materials in general. However, the argument could be made that when it comes to charring, pyrolysis and erosion, degradation and decomposition of the matrix polymers proceeds unabated regardless of what fibers are formulated into the composite. Likewise, thermal and physical changes occurring to the fiber phase are unaffected by the presence of the matrix. There is no synergy or masking one phase from the other . . . when the appropriate temperatures are reached, the various phases decompose independently as though they were isolated entities. Ultimately, the differential charring, erosion and recession rates of the principal constituents comprising each composite system determine the net performance value for the system in terms of how well the overall structure holds up throughout the burning process or performance cycle. If the matrix burns up first, then the reinforcement provides no value, if the matrix yields no solid char residue, then the converted form of the composite has no binder and the pyrolyzed product is useless.

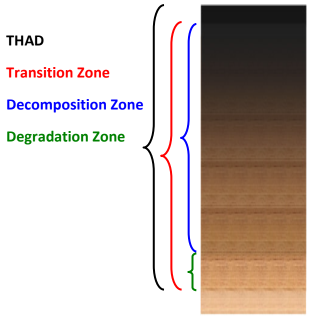
From another perspective, this argument may not be entirely valid when one considers the interactions associated with the interphase mediums and interface boundaries separating adjacent phases in the system. Bonding, adherence, repulsion, interlocking and/or coupling interactions are present in essentially all composite systems along the interfaces separating the matrix/binder phase from the fibers and particles embedded in it. These interactions are controlled, in large part, by the selection of constituent materials, their surface treatments and the process techniques used to fabricate the composite. There are two basic types of bonding: chemical and mechanical or physical. Chemical bonds between the matrix and solid phases are establish by the presence and deliberate incorporation of surface functional groups along the polymer chains and along the solid interfaces which interact to form chemical coupling links joining the two phases via ionic bonds, covalent bonds or van der Waals interactions. Interactive groups within the polymer network can be accomplished via polymer modification or custom synthesis techniques which incorporate or attach reactive pendant groups at certain points along the polymer chains or end-branches. Compatible functional groups can be generated along the solid surfaces of the fibers or particles or even the bonding substrate (in the case of coatings and adhesives) by specialized surface treatments and modifications such as etching via plasma, acid/base or redox, solvent treatment, application of coupling agents, specialized primers, etc...

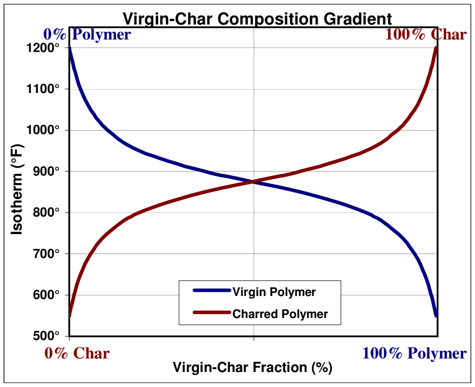
One of the problems encountered in these systems is the lack of compatibility between the two mating groups. Examples of compatible interfaces include pendant hydroxyl groups along the polymer chains which covalently react with protruding acid groups along the fiber or particle surfaces to form ester coupling links; dipole-dipole interactions between polar surface groups along the interfaces; and π–π orbital interactions between mating carbon phases which are rich in aromatic rings. Chemical interfacial bonding is established during (a) introduction of the liquid polymer into the fibrous reinforcement preform or fabric, or when the powder or chopped fibers are introduced into the polymer vehicle, and (b) the curing or molding process as coupling reactions take place that are influenced by the molding temperature and the curing profile applied, as well as the flowing motion of the polymer in which the functional groups are mobilized to facilitate proximal interactions with solid surface mating groups.

Mechanical interface interactions between the matrix phase and the fibers or particles are established during the cool down stage of the curing or molding process as the polymer recedes along the solid interfaces 'locking' into the irregularities and morphology features while it hardens. These are sometimes called mechanical interlocks. Mechanical interlocking effects are highly dependent on fiber surface irregularities as well as regular fiber surface features and shape morphologies. In polymer-densified carbon/carbon and ceramic matrix composites, mechanical interlocking also occurs during the cool down stages of applied firing and pyrolysis cycles. A third form of interaction which occurs in *laminated* composites involves the meshing or nesting of fabric layers with one another due to ply-to-ply intertwining and the physical interaction of weaving patterns which contain regular and symmetric protruding features such as weaving knuckles, weaving crimps, fiber crimps and fiber crenulations. These out-of-plane features play a direct role in establishing the interlaminar shear properties of the composite.

In general, the chemical interface links begin to weaken when the composite reaches the thermal degradation stage (550°- 600°F) and they continually degrade as the matrix undergoes thermal decomposition. By about 800°- 900°, most of the chemical links along the matrix-to-solid interfaces are destroyed and the system becomes entirely dependent on the mechanical interlocks. However, the mechanical interactions are also changing in accordance with the increasing temperature as differential CTE effects and the receding matrix volume alter the properties of these interactions. Sometimes, new mechanical interactions develop at the elevated temperatures providing high temperature mechanical interlocks which function during the pyrolysis stages. These interlocks are vital to the thermomechanical stability of carbon/carbon and ceramic matrix composites. Of the material systems under study here, the carbon fabric / phenolic matrix system is particularly important when it comes to high temperature behavior relative to the various chemical and mechanical interface bonding mechanisms.

When an article containing organic polymers is pyrolyzed or exposed to flame, the heat flux flows into the object from the periphery creating a conversion zone or transition region (sometimes called the pyrolysis zone) which separates the charred material from the virgin substrate. If the substrate or one of it's major components exhibits an appreciable char yield, a fully carbonized char cap may develop on top of the conversion zone. So then the total heat-affect depth (THAD) would consist of the fully charred layer (if it remains intact) followed by 'layers' of affected material which have undergone thermal degradation and decomposition to varying degrees from the outside inward to create a gradient transition zone. Levels of temperature exposure or 'isotherms' represent the degree of conversion or extent of partially carbonized material. Partially carbonized (partially charred) material fills the conversion zone where the degree of conversion from one isotherm to the next, when moving outward from the virgin side, is slightly more advanced. The term 'layer' is used to facilitate these descriptions but is not necessarily related to the visual appearance of layers or discrete levels that are seen in some material conversion zones. Unless stratification effects are caused by inherent properties of the material, the transition structure is usually smooth as it is bounded by fully charred material on the flame side and pure virgin (unaffected) material on the inside.





As one might expect, material properties also change across the conversion zone in a transitional manner. However, these properties do not necessarily track together nor are they necessarily proportional. Perhaps the two most important properties defining graded conversion zones are the *compositional* and *microstructural* gradients. A number of compositional/structural gradients have been characterized via EDX and XRD analyses, and they usually show a smooth transition as one material phase fades out and the other fades in[9],[10]. A good non-composite example is the conversion of virgin phenolic resin into carbonized/charred phenolic resin since a great deal of information is already (personally) known about these materials. A few comparative property examples that may be of interest for typical cured phenol-formaldehyde type phenolic resols can be given: (a) the true density of fully cured virgin phenolic resol at 68°F has been confirmed to be 1.24 - 1.26 g/cc while the same sample fully pyrolyzed to 1800° has a measured true density of 1.45 - 1.50 g/cc; (b) the CTE of cured virgin phenolic resol (above it's T_g) runs somewhere in the range 35 - 65 ppm/°C while pyrolyzed samples have been measured at around 4.5 - 5.0 ppm/°C (see the note on page 6 for additional CTE information); (c) the thermal conductivity of cured phenolic resin at 68°F runs in the 0 - 1 W/m-K range while pyrolyzed samples have been measured to be in the range 4 - 7 W/m-K. Even though functional descriptions of these properties are not known at this time, it can be presumed they follow analogous transitions from one phase extreme to the other.

Now let us explore how some of these materials behave in the SRM environment. At the end of a typical SRM burn/blast cycle, there should be very little left of the AS/NBR surface regions which are directly exposed to the flame, other than a thin, *partially* charred layer that gradually transitions into the virgin substrate material. The flame side AS/NBR composite is expected to have a relatively narrow transition region of partial charred material interfacing the virgin substrate as the flame-exposed virgin layer pyrolyzes and is blown away almost the instant the flame hits it, including all the polymer constituents, powders, sulfur links and asbestos remnants. And since the chrysotile fibers completely disintigate at relatively low temperatures, there should be no protruding fiber remnants sticking out of the partially charred AS/NBR layer as there undoubtedly are with PBI/NBR systems. The minute levels of dislodged silica and magnesia particles likely contribute very little to to the slag stream and their contribution to physical erosion processes downstream is probably insignificant.

As it is with the AS/NBRsystem, flame-exposed surface layers of PBI/NBR will have all the formulation components either dislodged, disintegrated and/or blown away . . . except for the PBI fibers. While the somewhat brittle carbonized forms of the PBI structures are subject to breakage and fragmentation under the action of the turbulent blasting forces, many fully carbonized and partially carbonized PBI fragments will remain embedded in the virgin matrix as they protrude through the partially charred layer. Thus, it is expected that one would see protruding fragments and features of carbonized (and perhaps even graphitized) PBI fibers sticking out of the thin partially charred layer at the end of the burn cycle. Embedded sections of these structures will add some toughness to the substrate remnant perhaps increasing the gradient transition region somewhat between the partially charred layer and the pure virgin material. Dislodged fragments of carbonized and graphitized PBI may be sucked into the slag stream, but compared to hardened alumina and silica particles, these carbon forms are relatively soft and their levels would also be quite insignificant compared to the amount of erosive alumina generated during the blast.

As it is with both the AS and PBI systems, the NBR binder/matrix phase that is directly exposed to the flame is quickly decomposed, volatilized and blown away during the burn cycle while the remaining partially carbonized PBI/NBR layer is in a weakened state. Some of this layer could be subsequently dislodged and washed away during post-fire clean-up processes. Just below that, layers of NBR which are only in the thermal degradation stage are more intact and better adhered to the virgin substrate. Most of this layer should survive high pressure washing as it is directly connected to the unaffected virgin material, and survival is enhanced with the tough PBI fibers when compared to the AS fibers which disintegrate into particles and fragments below 1500°F.

The preceding descriptions for PBI/NBR would also apply to CF/EPDM systems as the EPDM polymer phase will easily pyrolyze, volatilize and be blown away at relatively low temperatures, leaving protruding remnants of the carbonized PAN fibers sticking out of the partially charred layer. Compared to carbonized PBI fibers, the chopped PAN fibers are stiff and straight. Keep in mind that initially, the PBI fibers are organic and as they convert from the virgin state into carbon or graphite during the burn cycle, they are subject to microstructural consolidation and volatile losses as the temperature increases (albeit small). This effect could conceivably contribute to fiber-matrix debonding as the decomposition stage progresses. On the other hand, the chopped carbon fibers in CF/EPDM are already carbonized and may remain bonded to the EPDM matrix a little longer. However, this is probably irrelevant since both EPDM and NBR are volatilzed at relatively low temperatures regardless of the nature or content of the embedded fibers. During the burn cycle, the exposed PAN carbon fibers may experience marginal oxidation effects with some fracturing and fragmentation (of course, the carbonized PBI fibers are also subject to some of these effects as well). Even though the carbonized PAN fibers are comprised of the more abrasive glassy-type carbon (compared to softer cokes and graphites), the level of dislodged fiber fragments emitted into the slag stream is probably too low to contribute appreciably to any measureable physical erosion effects downstream.

For carbonized fabric-reinforced phenolic matrix structures throughout the SRM nozzle, the chemical interface bonding links joining the matrix and fiber phases begin to weaken around 600°F and then become insignificant by about 800° when the phenolic matrix is well into the pyrolytic decomposition stage. Some of the mechanical interlocks established during cure are partially retained while others are completely debonded. The thermal expansion rate of the isotropic phenolic matrix decreases (by > 90%) as it is transformed into isotropic glassy char, while the longitudinal expansion rate of the fibers remains relatively unchanged (see page 6, end of the second paragraph for the respective CTE values). Also, the bulk volume of matrix decreases (by ~40%) as it converts into char while the transverse fiber volumes (diameters) increase. During this process, the matrix content has decreased (by ~30%) and its binding power has also decreased accordingly since much of the matrix has receded from the fiber surfaces. However, a few high temperature mechanical bonds have been created by the stresses and expansion differences which will be good for a while longer during the temperature ramp as the carbonized phenolic continues to expand four times faster than the longitudinal fibers (however, CTE values for the transverse fiber and charred phenolic are comparable and compatible). Still higher, new mechanical interactions develop while former ones diminish. It should be realized however, the specific binding power of carbonized phenolic matrices in carbon fiber/fabric networks is quite impressive. At comparable matrix contents, the purely mechanical interfacial binding strength of fully charred phenolic is close to the combined chemical and mechanical bonding forces at work along the interfaces in as-molded virgin phenolic composites. Independent testing has confirmed this.

When the burn cycle is complete and the structures start cooling down, stresses develop across the conversion zone. These stresses are mitigated by the gradual transition between phases (one of the benefits of engineered gradient material systems). However, along the relatively thin transitional interface separating the fully carbonized char cap and the beginning of the conversion zone, the stresses are magnified as the interface is greatly weakened due to cool-down stresses and thermal shock effects (recall there is about a four-fold CTE differential between the char cap and the longitudinal component of the fibers or the ply angle). In regions where weakened interlaminar interactions exist below the char cap or have been generated during the burn cycle, it is conceivable the char cap could separate from the partially charred layer underneath during cool down. This effect might be influenced by low ply angles since the resultant lateral CTE differential between the charred matrix and fiber phase increases with decreasing fiber orientation or ply angle. It should also be realized that the fused, low porosity char cap formed during an SRM blast cycle is not exactly the same as the char layer created during static pyrolysis. It is well documented that thermoset polymers (and their composites) which are pyrolyzed under static conditions yield very porous char structures (recall there is a ~40% reduction in bulk volume when virgin phenolic is carbonized).

There are a couple of areas of concern regarding the design and fabrication of Shuttle/Ares nozzle hardware that would be appropriate to introduce here: (a) the LHT carbonized fabrics selected and used in these structures are thermally inert until about 2500° when they become subject to potential thermal and volumetric instabilities. Recall that, even though these fibers will not graphitize, consolidation of their microstructures (and transverse volumes) continues into the graphitization range (4200°- 4500°F); (b) it is apparent that the cure package selected for these components has not been fully optimized and does not include an effective elevated post-cure to stabilize their structures. Indeed, there are instances when simply re-heating some of these phenolic articles to their original cure temperature induces delaminations or fracturing. There is ample historical evidence indicating that phenolic materials bound for high temperature applications which have not been properly debulked, staged, cured *and* post-cured have increased risks of delaminations, microcracking and other ply separation phenomenon. Of the benefits derived from an effective cure/post-cure procedure, elevation of the phenolic matrix T_g and establishment of a 1-3% interconnected microporosity network throughout the structure are perhaps the most important attributes derived. Some of the strongest real-life experiences supporting these contentions have been witnessed first hand and their resolutions have already been proven out.

There have been several theories put forth pertaining to the root causes of the ply lifting effect which sometimes occurs in SRM nozzles during their burn cycles. A couple of factors which could possibly influence initiation and propagation of these short, side-by-side delaminations during the first few seconds of a typical SRM burn cycle could be given here. The lack of an optimized cure/post-cure package for these articles results in a relatively low T_g (only 20°- 40° above the standard 315°F cure temperature used for current Shuttle/Ares configurations), and ~0% porosity which prevents the subsequent release of trapped volatiles during re-heating events. When heat from the blast flame first rushes into the material periphery, the T_g is easily surpassed, the resin softens and fiber-to-resin mechanical interlocks are destroyed. This leads to 'weak planes' and reduced interlaminar interactions which continue to worsen above about the 400° isotherm as the material passes through the degradation stage (~600°) when chemical interactions diminish and into the decomposition phase (700°- 800°). Also, release of the largest pyrolysis molecules during this range (phenols, cresols and diphenols) as well as the massive out-flux of hydrogen, carbon monoxide and dioxide lead to abrupt pore pressure increases which only exacerbate the weakened interlaminar interactions. Above about 900°- 1000°, the receding matrix char rapidly loses it's binding power and fiber-to-matrix interface interactions quickly diminish facilitating Mode I ply separations or debonds as the ply lift event initiates. At about the same time, fiber-to-matrix interfaces in layers adjacent to the developing char cap, say near the 2500° isotherm, separate as the carbonizing matrix continues to recede and the fiber microstructures begin to consolidate. At this point, both the fiber and matrix are receding . . . away from each other.

As the instantaneous isotherms move inward, the region of ply separations expands and their heights increase coherently, to a point. As the THAD expands and the heat front continues to progress inward, the isotherm spacings spread out and heat distribution is somewhat improved permitting advanced curing and post-curing of the phenolic matrix ahead of the 600° isotherm. This raises the T_g and degradation temperature of the innermost material and stabilizes the height of the lift area as the ensemble of separations remains under the dynamic action of the lift forces throughout the remainder of the burn cycle. Upon cooling, the separations become static and permanently fixed in the structure under the forces of the partially carbonized phenolic binder. The use of low strength LHT fibers may also be a factor in pocketing and wedge-out effects as well, particularly in localized regions containing preexisting defects such as carbonization variations in the fabric, broken or severed fibers and/or degree-of-cure variations in the matrix phase. Obviously, many of the ideas presented in this section are unsubstantiated. At this point, the discussion just represents another hypothetical scenario to throw into the pool of theories.

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