Overview of Mesophase, Graphite, Soft Carbons and Glassy Carbon

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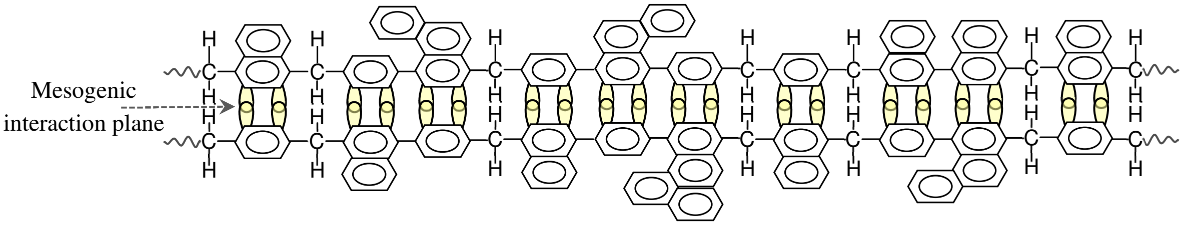
Carbonaceous Mesophase Residuals from Oil Extractions

During the cracking process of heavy oil or crude, isotropic mesophase residues are generated. Bulk petroleum mesophase pitch mixtures processed to yield complex blends of polyaromatic, naphthenic with aliphatic polymers/oligomers. At some point in the operation, these products must also be processed to remove a host of contaminates, including metals, unwanted components and inorganic side groups. Then the product may be heat processed (~1000°F) to yield an anisotropic carbonaceous mesophase pitch with high molecular weight and aromaticity vis dehydrogenative polymerization and the production of free radicals which promote polyaromatic ring formation.

Anisotropic mesophase pitch is a thermoplastic that exhibits mesogenic (liquid crystal) properties in which the planes of benzene rings (or groups of rings linked together through methylene groups) interact with one another via the aromatic π orbitals in each ring between adjacent planes. These interactions cause the layered mixture to bypass the traditional thermoplastic melting point and convert directly into an amorphous 'soft' carbon form when heated or pyrolyzed to around 1200°-1500° and can subsequently be graphitized upon firing to the 4000°-5000°F temperature range. The specific methods and techniques Poco uses for producing high purity true graphite as well as controlling properties such as '*d*' spacing distances within the graphitic structure as well as densities and porosities are proprietary.

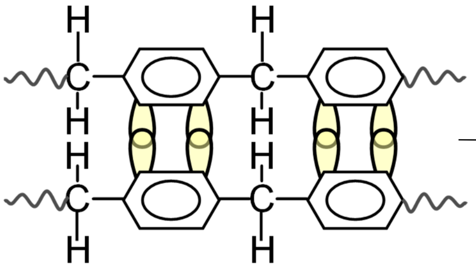


Example of a simplified carbonaceous mesophase structure showing π orbital electron cloud overlaps/interactions between two mesophase layers. The π orbital clouds associated with each ring are comprised of six *p* orbitals donated from each ring. Note that only two of the *p* orbitals from each ring are shown for each. This is only for visual clarity purposes as the two *p* orbitals actually represent the π clouds associated with ring.

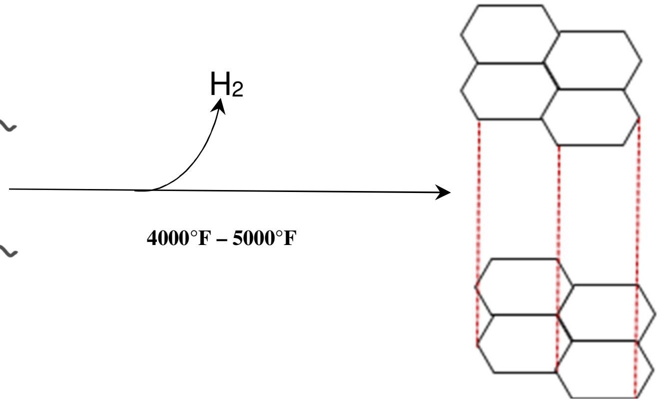
A Few Aspects of Graphite

The anisotropic, hexagonal close packed lamellar structure of true graphite includes characteristic interlayer '*d*' spacings that are responsible for many of its unique properties. These '*d*' spacings which index staggered planes of hexagonally bonded carbon rings by way of very weak, van der Waals-like forces as they permit slipping between the planes (hence, graphite's lubricating properties) and ultimately affect the thermal conductivity and thermal expansion characteristics quite differently than the other forms of carbon. Carbon atoms in these planes are covalently bonded to two other carbons via trigonal sp^2 hybrid orbitals in the form of six membered carbon hexagonal ring (analogous to the benzene precursor).

Also analogous to the benzene molecule, each carbon atom in a given ring donates a π electron to the delocalization pool responsible for graphite's high conductivity along these planes. However, during thermal conversion of the aromatic precursor, all organic character is lost as the material becomes ‘inorganic’ carbon. In order to produce graphite, the precursor material must exhibit a certain degree of mobility in order to facilitate the structural order of graphite. Anisotropic mesophase provides the required mobility to form lamellar layers of solid graphite planes separated by distances referred to *d* spacings whose exact distance varies according to the precursors and the processes used.



Carbonaceous Anisotropic Metaphase



Hexagonal, laminar graphite with
d spacings indicated in red

A Few Properties of Soft Carbons (Graphitizable Precursors)

Amorphous carbons forms are mostly joined to one another via tetrahedral sp^3 orbitals. These carbon forms may include carbon black, petroleum coke, ‘green’ cokes and the carbonized form of coal tar pitches. These more common amorphous allotropes are considered to be ‘soft’ carbons as they readily crystallize into the graphitic structure when heated to graphitizing temperatures (> 4000°F). During early heating cycles, soft carbons will go through a temporary semi-mesophase, similar to that discussed earlier somewhere in the range 800°-900°F. This is generally recognized as the earliest temperature range in which thermal pyrolysis or degradation begins. All graphitizable (soft) carbon forms must pass through a mesophase state before developing substantial hexagonal *sp*^{2} character. As the temperature continues to rise, mobile mesophase regions begin to facilitate the formation of graphitic lamellar planes (or graphene layers in some processes) leading to pre-graphite structures at around 1200°-1500°F. Upon continued heating, nucleating or condensing mesophase clusters grow as they are carbonized into larger aromatic molecules through condensation and dehydrogenation. Around graphitization temperatures (4000°-5000°), *sp*^{3} bonded layers increasingly convert into pseudo-aromatic *sp*^{2} planes as the network continues to become rich in *sp*^{2} orbitals and the mesophase eventually solidifies into graphite.

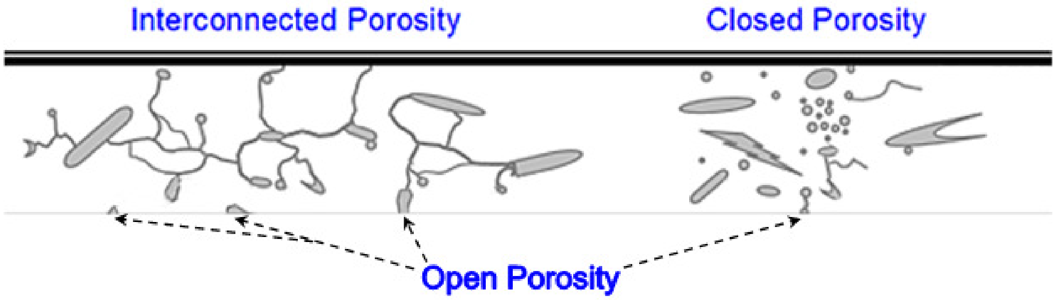
In some cases, oxidation pre-treatments are applied to the mesophase precursor which may create a few crosslinks and greatly thicken the liquid phase in order to simplify the graphitization step without the use of restraints or molds. This approach may require high pressure to be applied during the graphitization step in order to destroy the crosslinks and allow the graphitic structure to form effectively. This approach is often employed during the production of anisotropic pitch fibers.

A Few Properties of Hard Carbons (Non-Graphite Carbons)

Hard, non-graphitizing carbons are formed from substances containing less hydrogen and more oxygen than graphitizing carbons and are often derived from high density crosslinked polymer networks such as resins of phenolic, furfuryl alcohol and divinyl benzene precursors. There are many others. Non-graphitizing carbons may contain non-six-membered rings, whereas soft carbon precursors generally have an abundance of hexagonal rings. As mentioned earlier, soft graphitizing carbons can be easily transformed into crystalline graphite by heating to temperatures in the range 4000°-5500°F. In contrast, hard, non-graphitizing carbons cannot be transformed into crystalline graphite even at temperatures of 5000°F. There are an abundance of carbon forms which contain crystalline graphite-like regions or domains embedded within a glassy network and vice versa.

Glassy (vitreous) carbon forms essentially form amorphous structures when fired or heated to carbonization temperatures (1200°-1500°F). In order to convert the structure into true hexagonal graphite, the solid vitreous carbon must be fired to temperatures in the 4000°-5000°F range under very *high pressures*. The high pressure is required to break the crosslinks allowing the structure to crystallize. Glassy carbons are more inert to oxidization than soft, graphitizable carbons and are resistant to concentrated acids whereas soft carbon forms are degraded into powders. Pyrolyzed vitreous carbons consists entirely of *sp*^{3} bonded carbon atoms and the structure tends to resemble that of the amorphous crosslinked precursor rather than lamellar graphitic structures. Without applied pressure, glassy carbons can be taken to graphitizable temperature ranges (4500°-5500°F) with little or no signs of devitrification. The char remnants of densely crosslinked thermoset polymers are essentially fixed in space due to the heavily crosslinked and interconnecting network established during the thermosetting cure process. Not only do their pyrolyzed forms contain very high degrees of amorphism, they can develop fractured faces characteristic of glass and ceramic materials. Fibers: contrary to industry perceptions, crosslinked composite fibers based on PAN, rayon and most composite pitch-based fibers are more correctly referred to as ‘carbon’ fibers rather than ‘graphite’ fibers since it is essentially impossible to graphitize these crosslinked polymer networks.

Bulk permeability and porosity are often present due to pyrolytic recession of the internal microporosity network and the release of non-carbon volatiles created during the curing and carbonization processes of glassy precursors. As a result, solid bodies of glassy carbon often contain hermetic occlusions (closed porosity), but will usually also contain a network of interconnected and open porosity. This has been demonstrated with polymers that undergo condensation polymerization and crosslinking such as the phenolic and furfuryl alcohol thermosets. 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.



Graphical display of possible pores generated during a pyrolysis of crosslinked polymer thermosets. Note: in R&D roles previous to Poco, the author has experimentally conducted about 1000 tests estimating open porosity values on samples of cured phenolic resin, glassy carbon and carbon-base composites via water impregnation, mercury porosimeter, helium psychometry, and also developed an original test method for measuring open porosity of samples down to about 0.3nm size.

When carbon fiber-glassy phenolic matrix composites 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 along fiber-to-matrix interfaces due to differential expansion and 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. Graphitized interfaces in these composite systems can be detrimental in certain applications and beneficial in others. For phenolic matrix precursors within a PAN fibrous network (polyacrylonitrile), 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 Tg 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 runs around ~0 ± 0.5 ppm/°C, and ~4 – 10 ppm/°C for transverse fiber directions (out-of-plane or across the bundle diameters).

During heating cycles for crosslinked thermosets, pre-graphitic molecular movements are controlled by the density and strength of the crosslinks. In well-crosslinked structures, such movements are almost completely inhibited. Again, when processed properly, non-crosslinked soft polymers (thermoplastics or isotropic mesophase mixtures) will initially convert into a pre-graphitic green carbon structure during early pyrolysis and then transform into 3-D hexagonal graphite around 4000°F and above. However, crosslinked thermosets appear to attain and retain structural features which that resemble their virgin amorphous structures, even when processed to beyond graphitization temperatures at ambient pressures. For virgin polymers stabilized with high crosslink densities during the initial molding stages, migrations and movements of larger polymer segments and branches are restricted during graphitic heating as they tend to be ‘fixed’ in space, and crystallization becomes difficult thermodynamically.

In general, most thermoplastics will melt or flow long before they ever reach carbonization temperatures. Mesogenic (liquid crystal) thermoplastics are the exception. As noted previously, mesogenic polymers exhibit no Tg and no melting point but begin to char and solidify at early pyrolysis temperatures (950°-1050°F). In terms of their carbonization/graphitization aspects, mesogenic polymer networks could essentially be considered a new category of polymers outside of the traditional thermoplastic and thermoset families. Research by various entities is underway to developed more very high char yielding mesogenic thermoplastics as superior substitutes to typical glassy carbons. Newer, high char-yielding mesogenic polymers allow for high char values that far exceed phenolics and the like. The list continues to grow.

In terms of processing, common thermoplastic polymer networks are difficult to convert since they generally exhibit glass transition softening prior to their melting points. If not restrained somehow or heated in a container or a mold, some thermoplastic polymers or mixtures will boil or volatilize during the heating process. However, if a few crosslinks are incorporated into the structure, melting can often be bypassed. This is the principle behind the stabilization step applied to carbon fiber precursors prior to carbonization.

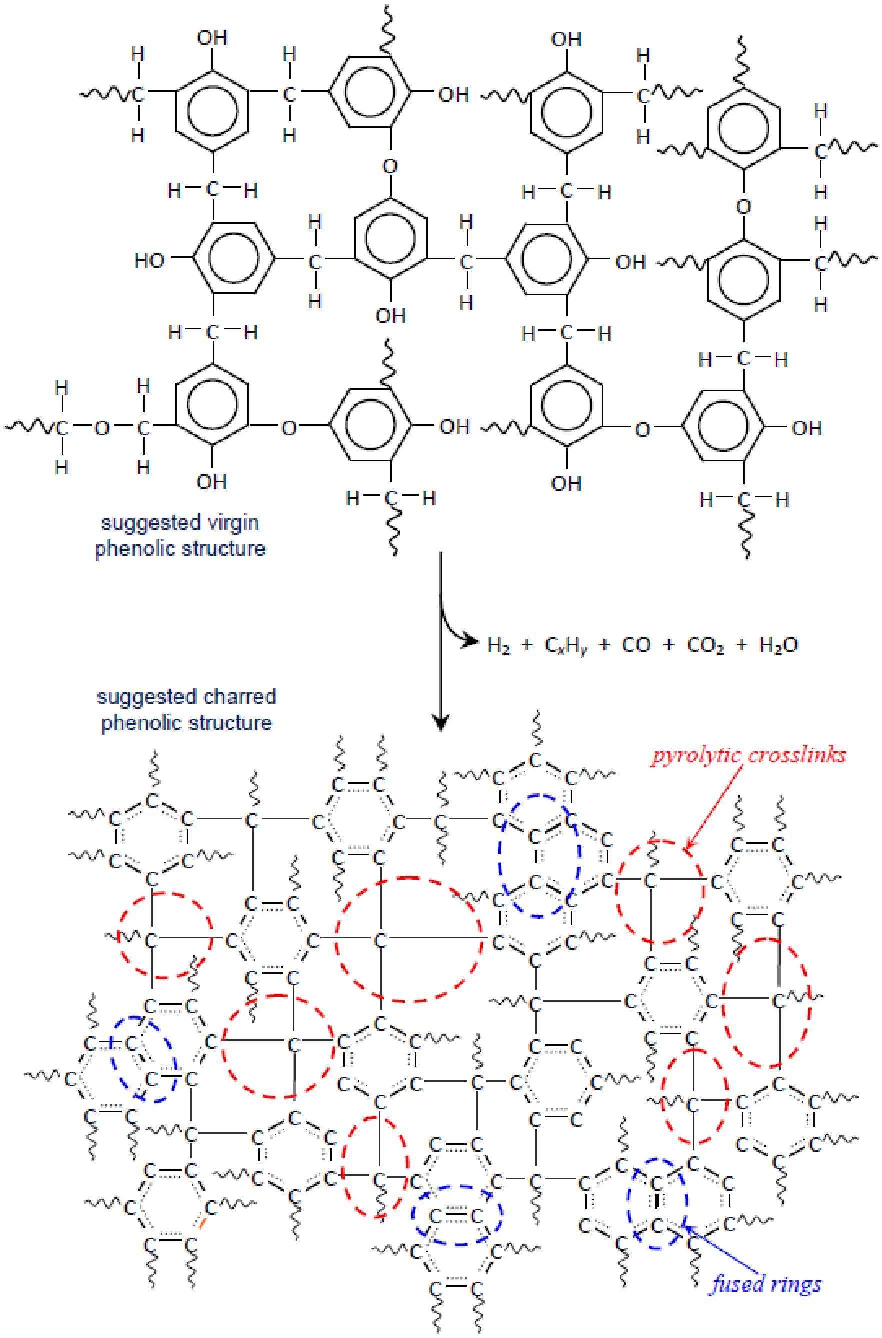
Polymers with non-homogeneous structures (i.e… those containing varying amounts of crystalline, amorphous and/or crosslinked segments) are not so easy to define. Such structural mixtures may be more representative of the majority of polymer systems we actually deal with in the real world. In any heterogeneous polymer structure, thermoplastic segments and branches which are successfully converted into green char early in the heating process and may undergo crystallization into 3-D graphite or at least attain a higher degree of structural order or graphite-like domains embedded within the mixture when taken above 4000°. Inadvertently, the semi-crystalline regions which have been rigidized with structural crosslinks may become inert to complete graphitization or crystal-like ordering. These crosslinked regions or domains usually carbonize into vitreous/glassy carbon arrangements in which amorphicity is permanently retained in the structure.

Aliphatic polymer networks which contain little or no aromatic rings consist of thermostructurally weak chain segments linked to one another. 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).

This specialized glass-ceramic-like carbon material is gaining increased use in a variety of high temperature applications such as ablators, semiconductors, electrodes, 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, furfuryl alcohol, polyaryl halides, divinyl benzenes and substituted polynuclear aromatics give high char yields of glassy carbon when pyrolyzed (~60-80%). Articles of homogeneous, monolithic glassy carbon are isotropic, amorphous and are generally hard, brittle and shiny (like glass). In the industry, one of the most well-known and utilized precursors for glassy carbon are those derived from cured phenol-formaldehyde (phenolic) resole resins.

For virgin polymer networks with high crosslink densities, the intermediary char structure will condense and form new crosslinks during the pyrolysis process. The author refers to these bonds as ‘pyrolytic crosslinks’ since they form during thermal transformation or degradation processes. They are the primary bonds created during pre-graphitic high temperature treatments of high density crosslinked polymer networks. Pyrolytic crosslinks differ from those formed during initial curing of a polymer as these advanced pure carbon-based links are driven by high temperature radical generation with interactions and couplings between dangling end-groups created throughout the carbonizing polymer structure during pyrolysis. In general however, a high density of crosslinks formed during the development and structural evolution of a cured polymer tend to favor high amorphous-like character within the structure.

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 disintegration 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 (4000°- 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 thermoplastic-based mesophase structures are entirely bonded via sp^2 hybridization, leaving the pool of π electrons free to influence material properties such as conductivity effects and graphitic transformation. 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

References: General library literature research, subject matter experts and pro-active involvement while at Poco Graphite, previous hands-on experiences in the field of carbon, ceramics, ablatives and carbon-carbon materials.

Note: All illustrations, reactions and technical descriptions are exclusively the handiwork and interpretation of the author except where noted.