

# Pyrolysis

Subjects: Polymer Science

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Pyrolysis: Thermochemical decomposition of organic materials in the absence of oxygen.

Polymer-derived carbon: Carbon obtained by heat-treatment (pyrolysis followed by carbon-carbon bond formation and rearrangement) of natural or synthetic polymers. In addition to the supplied heat, surrounding gaseous environment, presence of magnetic field and applied pressure influence pyrolysis.

Keywords: Pyrolysis ; polymer-derived carbon ; glassy carbon ; non-graphitizing carbon ; charring ; chemical vapor deposition

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## 1. Introduction

The term pyrolysis describes the decomposition of polymers (e.g. resins, cellulose), gaseous hydrocarbons (e.g. acetylene), hydrocarbon-rich oils and various other organic materials such as petroleum byproducts, induced solely by heat. Gas-phase pyrolysis (i.e., thermal cracking of hydrocarbons) followed by carbon deposition is generally referred to as the Chemical Vapor Deposition (CVD) of carbonaceous materials in the contemporary literature. Another well-known application of pyrolysis is in the treatment of waste polymers (both synthetic and natural) for biofuel and biogas production. Here, the heat treatment temperatures can be below 900 °C, and occasionally the environment may even contain oxygen depending on what is expected as the end-product. Pyrolysis is also used in the context of metallurgy (e.g., in pyrometallurgy), where the desirable end-product is usually not carbon.

When an organic polymer is heated above its degradation temperature, carbon-heteroatom bonds start to cleave, which is followed by the formation of the new carbon-carbon bonds. During the early pyrolysis stages, various hydrocarbon radicals are generated with their highest concentration around 600 °C. After 800 °C, a network of graphene fragments; containing a large fraction of defects as well as chemical impurities, starts to develop. Further heat allows for the annealing of the defects and an increase in the graphene crystallite size ( $L_a$ ) and stack thickness ( $L_c$ ). The absence of oxygen minimizes the CO<sub>2</sub> and CO formation (i.e., burning) however, if there is any (bonded) oxygen in the polymer itself, some oxides are generated. Other pyrolysis products such as CH<sub>4</sub> and small hydrocarbons are volatile that are released in the form of bubbles.

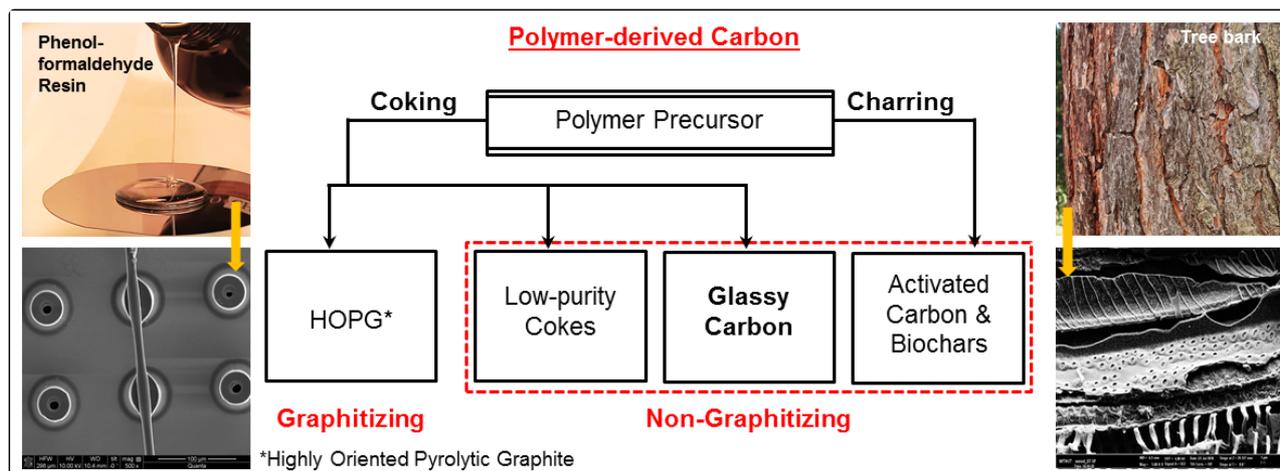
Various theories exist on the mechanism of the formation of elemental carbon from a decomposed polymer. Post-decomposition, the polymer fragments feature a variety of shapes and sizes, which are mobile during the initial pyrolysis stages (500-800 °C), and constantly try to attain a thermodynamically stable arrangement by separating from, and merging into each other. Different polymers display distinct disintegration patterns and fragment mobility. For example, pyrolysis mechanism of cellulose is quite different from that of the resins. Various polyimides, polyvinyl chloride, pyridine etc. have their own characteristic pyrolysis products and reaction kinetics. Major factors that influence the nature of the resulting carbon include the chemical composition of the precursor, structure size, heating conditions, forces applied during processing (if any), and in the case of epoxy resins, the extent of crosslinking.

Further details on the classification and applications of pyrolytic carbons can be found here [\[1\]](#).

Theoretical (computational) investigations of the pyrolysis process indicate that the primary fragments formed after the decomposition of a polymers contain atoms from the neighboring chains in addition to the parent molecule. This finding supports the idea that there are no specific patterns or well-defined nucleation points during the initial pyrolysis and carbon-carbon bond formation stages. Nonetheless, it has been confirmed by both theoretical and experimental investigation that the chemical composition of the polymer plays the most important role in determining the nature of the resulting carbon. Therefore, polymer-derived carbons can be segregated to a first approximation based on the nature of the precursor.

## 2. Polymer-derived carbon

A classification of polymer-derived carbon based on the precursors is shown in Figure 1, followed by a brief explanation of the terminology.



**Figure 1.** Classification of carbon materials obtained by pyrolysis of polymers. SEM images: Bottom-left: pyrolyzed SU-8 micropillars with a suspended SU-8 fiber [65] showing coking, and Bottom-right: part of a tree bark carbonized via charring. Both precursors are pyrolyzed at 900 °C at a temperature ramp rate of 5 °C/ minute in nitrogen environment.

### 2.1. Coking and Charring

If the pyrolysis product (mixture of all intermediate materials at any given temperature) goes through a semi-solid (rubbery) phase owing to the fact that its  $T_g$  falls just below the process temperature, this phenomenon is known as coking. The Scanning Electron Microscope (SEM) image in the bottom-left of Figure 1 represents a carbonized structure where a fiber was intentionally suspended onto an array of hollow micropillars. It can be observed that the pillars attached to the fiber are deformed because of the tensile stretching in the fiber during pyrolysis. Other pillars shrink uniformly, indicating that the  $T_g$  of the pyrolysis mixture was only slightly below the set temperature. As this gap increases, the patterned structures partially deform, and when it is significantly large, mostly oil-like materials are obtained. The semi-solid intermediate material is responsible for a smooth surface of the resulting carbon, as it tries to minimize its surface energy. Examples of coking polymers are phenol-formaldehyde resins (yield non-graphitizing carbon) and anthracene (yields graphitizing carbon).

Charring refers to a direct conversion of the rigid polymer structure into carbon, where the shape is preserved both macro- and microscopically. Wood and other cellulosic polymers are good examples of charring (see the bottom-right SEM image in Figure 1). The major and most studied intermediate formed during cellulose pyrolysis is known as levoglucosan, which further disintegrates via different pathways leading to the formation of tars (oil-like materials), volatiles and solid carbon. These phases generally coexist and remain distinct throughout the process. The solid carbon backbone is replicated in the final char, and the oils and volatiles are collected and distilled if so desired. Cellulosic materials do encounter some softening in the 230 – 255 °C region, but it is not directly correlated with either  $T_g$  or the melting point. Chars are predominantly non-graphitizing, and due to their porosity and surface chemistry, often serve as activated carbons. Pyrolysis of natural wood and other plant residues is more complex due to the presence of lignin and hemicellulose.

Carbonaceous residues obtained from biodegradable natural polymers at temperatures < 900 °C are often called biochars. The term char may also occasionally signify the solid carbon formation from polymers, even after initial coking. Importantly, the nomenclature of carbon materials is already full of ambiguities because of the existence of numerous carbon forms (including those with mixed hybridization), precursors and manufacturing processes. Any terminology that contributes to such confusions should therefore be avoided.

### 2.2. Graphitizing and non-graphitizing carbon

Graphitizing carbons are those polymer-derived carbons which can potentially be converted into polycrystalline graphite upon heat treatment, catalytic processes, stress or any other method. Graphite features an ABABA crystal arrangement with a layer separation of 3.354 Å along the c-axis. During initial pyrolysis stages, certain semi-crystalline polymers such as PVC convert into a carbonaceous material that resembles stacked graphene fragments. Although initially these fragments contain impurities and have a turbostratic arrangement (randomly rotated basal planes), their progressive

ordering at higher temperatures leads towards graphite formation. Pyrolytic graphite can be post-processed to yield Highly Oriented Pyrolytic Graphite (HOPG). HOPG can also be obtained using other methods such as recrystallization from the iron melts (commercially known as Kish graphite), or thermal compression of chemically deposited graphene.

Non-graphitizing carbons, by definition, cannot be converted into crystalline graphite, as they contain various structural defects, and randomly oriented graphene fragments exhibiting a strong 3D bonding. These turbostratic graphene fragments feature a Gaussian distribution in terms of size and shape, C-C bond-length and valance angles, and have an inter-layer separation  $> 0.335$  nm. The presence of defects causes these fragments to curl and fold, and form fullerene-like structures, and occasionally, completely closed buckminsterfullerenes. The curved structures coexist with the larger, stacked graphene sheets. Non-graphitizing carbons exhibit a lower electrical conductivity but an improved hardness compared to graphite, and are also called hard carbons. PF resins, cellulose, poly(vinylidene chloride) and certain polyimides yield non-graphitizing carbon on pyrolysis.

### **2.3. Glassy (glass-like) and activated carbon**

Non-graphitizing carbon with a high purity that has experienced at least some coking during pyrolysis is known as glassy carbon. In the case of large (millimeter)-scale structures, glassy carbon is obtained at  $> 2000$  °C, since the pyrolysis intermediates may display a poor thermal conductivity causing a thermal gradient across the sample. In order to systematically anneal out the volatiles and ensure purity all the way to the center of the structure, these elevated temperatures are essential. In some industrial processes, the preparation of glassy carbon is shown to take place at  $1000$  °C with modified pyrolysis conditions for  $\leq 3$  mm structural dimensions. It has been confirmed by several studies that in the case of micro/ nano scale structures, the properties of glassy carbon can be achieved at lower temperatures such as  $900$  °C, likely with some oxygen impurities.

Activated carbons are non-graphitizing carbons formed by direct charring that contain surface radicals and open pores. They have heteroatoms and more defects compared to glassy carbon, and their electrical conductivity and mechanical strength is typically lower. Owing to an active surface chemistry they are often used as adsorbants and catalytic beds.

### **2.4. Carbon fibers**

Micro and nano scale fibers prepared by pyrolysis of cellulose, polyacrylonitrile (PAN) or other polymer fibers were traditionally not classified as glassy or activated based on the precursor chemistry. The annealing pattern in fibers is significantly different from the bulk due to a high surface-to-volume ratio. Surface treatment, fabrication parameters, and in the case of PAN, pre-pyrolysis oxidation can strongly influence their properties. It has been reported that fibers tend to become more ordered (graphitic) if the fabrication process (typically electrospinning) is modified, additives are incorporated or stress is introduced.

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## **References**

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