

MICROSTRUCTURE EVOLUTION OF WOOD DURING CARBONIZATION

Christopher Byrne

Mechanical Engineering
Western Kentucky University

1906 College Heights Blvd, Bowling Green, KY 42101-1082

Abstract

An extensive literature regarding structure in plant-based carbons has been assembled over many decades and is useful in optimizing material applications. This paper focuses on the carbon texture and its origin in cellulose molecular orientation. Structure development from nano- to micro-scale has suggested a preferred orientation exists in wood-based carbons that could be due to cellulose microfibril orientation. Different authors have presented various opinions on both the existence of texture and its origin. The published data regarding these observations is reviewed and assessed again to stimulate further discussions and research in this aspect of carbon science.

Introduction

The use of wood, and other plants, as a template for producing ceramic and composite materials has progressed significantly from when the technology originated in 1995 [1-3]. The natural microstructures lead to modern materials with properties that in many ways mimic those of the original plant. In one step of this emerging technology, wood is carbonized to form a porous char with structural integrity. Properties of the char depend upon precursor material and heat treatment processing. Thermal degradation of wood, cellulose and lignin (main constituents of wood) have been extensively studied for many decades [4].

Plants such as wood contain unique cellular structures that can be used to identify a particular species. Within the cell walls the constituents are arranged in a particular fashion as indicated in Fig. 1. The middle lamella (portion joining cells together) is mostly comprised of lignin whose molecules are arranged in a random manner but with varying concentration within the cross section. The first layer of the cell wall (primary layer) is thin, and connects the middle lamella to the cell secondary wall. The thickest portion of the secondary wall, S2 layer, is comprised of cellulose molecules arrange with a preferred orientation such that they are mainly aligned with the cell axis and contain enough order to form microcrystalline fibrils. These aligned microfibrils greatly influence the properties of the cell wall making it stiffer and stronger in the axial direction. That molecular structure, combined with the cellular structure of the wood species,

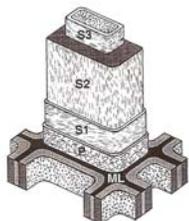


Fig. 1. Layers of cell.

results in a highly anisotropic bulk material. When carbonized, the wood constituents decompose to leave a solid carbon structure that retains the cellular features (micro-) but obviously alters any molecular (nano-) structures.

In order to obtain a non-graphitizable solid carbon with preferred orientation of basic structural units certain conditions must be in place. One is that carbonization and/or graphitization be done with an applied stress to produce an alignment of graphene layers. A second way is to begin with a precursor containing molecular order that serves as a template for the resulting graphene layers to align with. This second condition is relevant to the carbonization of wood.

The carbon fiber industry started with fibers made using rayon as a precursor. That polymer, made from regenerated cellulose, has been replaced by PAN or Pitch precursors. Nevertheless, early work by Bacon demonstrated the capability of having highly aligned cellulose molecules pyrolyze to produce carbon with a high degree of preferred orientation of the resulting graphene layers [5, 6].

Multiple authors over the past ~10 years have produced reports indicating how the micro- and nano-structures of wood is altered during carbonization and further heat treatment. The focus of this paper is to track the current status of the literature in how carbon texture is described, whether a preferred orientation exists, and what inherent features of wood leads to these conditions.

Review and Discussion

Pyrolysis of wood in a non-oxidizing environment has been studied to determine the temperatures at which the different constituents decompose. Unbound water is lost at 100°C, and then hemicellulose begins to decompose at 200°C. By 250°C cellulose begins to decompose such that by 290°C hemicellulose is gone and lignin decomposes significantly. Up to 360°C cellulose and lignin give the most rapid rate of decomposition. Lignin continues to decompose above 360°C and by 400°C the polymeric constituents are decomposed [2]. Additional structural rearrangement of the solid carbon occurs with higher heat-treatment temperatures.

Carbonized biomass has long been used to create activated carbons. The biomass (including wood) has the quality that when converted to solid carbon it has a nano-structure that contains a high proportion of molecular sized pores. Activation opens up these pores creating a very high specific surface area ideal for adsorbing undesired molecules from a fluid. This aspect of carbon science is well understood. Less well understood is the presence of any texture in the nano-structure that can be traced back to the precursor.

In a study of carbonization of wood at temperatures up to 2500°C Byrne and Nagle put forth the theory (microfibril dominance theory) that some preferred orientation of graphene layers exist in carbonized wood and has its origin in the cellulose microfibril of the secondary cell wall [3]. The supporting data included char dimensional changes, density measures, acoustic velocity changes, and x-ray diffraction.

Since then, some supporting and some dissenting studies have been reported.

In a study of activated maple wood Herzog, et.al., reported an increase in crystallization with increased temperature [7]. That effort using SAED and TEM seemed to provide mixed evidence for a preferred orientation in the carbon. Paris, et.al., looked at microstructure evolution of softwood pyrolysis at temperatures up to 1000°C and identified destruction of the polymer constituents and the subsequent formation of aromatic structures using a variety of data [8]. They identified a slight preferred orientation of graphene layers along the cell walls that appears supportive of the microfibril dominance theory. Using a variety of methods including EPR, acoustic, and physical properties Krzesinka, et.al., concluded carbonization and further heat treatment led to a preferred orientation of graphene layers along the cellular axis [9]. Increased temperatures gave increased order of the nano- structures. In a study of heating rates Xie, et.al., included electrical resistivity measurements to those of shrinkage, acoustics and XRD to find graphene layers aligned with the cell wall [10]. Use of nano- indentation on specific areas of pyrolyzed wood allowed Zickler, et.al., to follow mechanical properties up to 2000°C [11]. Indentations at certain locations in defined directions indicated a preferred orientation of graphene layers along the cell wall axis.

The tracking of electrical properties during pyrolysis and heat treatment has been performed by multiple laboratories. In a comprehensive look at XRD scans Kercher and Nagle tracked nano-structural evolution of medium density fiberboard [12]. Their results supported a model for electrical conductivity changes with heat treatment that can be modeled by a percolation theory. While this model at present does not contribute to an understanding of graphene layer texture, it does support the model of layer growth and rearrangement that accompanies solid carbon heat treatment. The percolation theory for electrical conductivity connects the changing microstructure to the properties of the char in a manner that illustrates the importance of graphene layer size and orientation.

Multiple studies have focused on the evolving molecular structures at pyrolysis temperatures up to 400°C. In a study evaluating the cell wall transitions Kwon, et.al., showed the cellulose crystalline structure disappeared above 350°C while cell wall layering also disappeared [13]. With their work going to 500°C it was not possible to evaluate graphene ordering or texture since this is not a sufficient temperature to achieve significant crystalline growth in solid carbons. In a different study Zollfrank and Fromm found the cell wall structure became amorphous at 300°C and microfibrils erased of structure [14]. They contend that later orientation of graphene layers may result from structural constraint within a cell wall as carbonization progresses. Their assertion is that any orientation of graphene layers is not connected to the cellulose orientation in microfibrils owing to the observations that all crystallinity is removed by thermal decomposition. Yet another study of wood carbonization was

conducted by Ishimaru, et.al. [15]. They used micro-Raman spectroscopy and TEM to follow cell wall microstructure. They interpret the data as showing no heterogeneity that originated from the original cell wall. Ordered regions detected were speculated to arise from a CVD mechanism.

Conclusions

The variety and extend of published work regarding carbonized wood microstructure and its' origin is substantial. While it is very clear that the resulting carbon is non-graphitizable (cellulose and lignin have long been know to be non-graphitizable), what is less clear is whether significant texture or preferred orientation exists even at heat treatment temperatures of 2500°C. However, when reviewing the entire body of published knowledge there is compelling evidence to support the presence of some nano- texture in carbonized wood. It is also highly likely that there exists some preferred orientation of graphene layers. This ancient form of manufactured material still has some elusive characteristics.

References

- [1] Byrne, C. and Nagle, D.C., Carbonized Wood – a Precursor for Advanced Ceramics, Proceedings of 22nd Biennial Conference for Carbon, 1995.
- [2] Byrne, C. and Nagle, D.C., Carbonization of Wood for Advanced Materials Applications, Carbon 1997; 35 (2): 259-266.
- [3] Byrne, C. and Nagle, D.C., Carbonized Wood Monoliths-Characterization, Carbon 1997; 35 (2): 267-272.
- [4] Antal, MJ and Gronli, M, The art, science, and technology of charcoal production, Industrial and Engineering Chemistry Research, 2003; Vol 42, no 8, 1619-1640.
- [5] Tang, M and Bacon, R., Carbon, Vol. 2, p. 211, 1964
- [6] Bacon, R. and Tang, M., Carbon, Vol. 2, p. 221, 1964
- [7] Herzog, A, et.al., Structural changes in activated wood-based carbons: correlation between specific surface area and localization of molecular sized pores, *Holzforschung*, Vol 60, issue 1, pp85-92, 2006
- [8] Oskar Paris, O., et.al., Decomposition and carbonisation of wood biopolymers—a microstructural study of softwood pyrolysis, Carbon, Volume 43, Issue 1, 2005, Pages 53-66.
- [9] Krzesińska, M., et.al., Physical characteristics of carbon materials derived from pyrolysed vascular plants, *Biomass and Bioenergy*, Volume 30, Issue 2, February 2006, Pages 166-176.
- [10] Xie, X., et.al., Significance of the heating rate on the physical properties of carbonized maple wood, *Holzforschung*, Vol 62, issue 5, pp 591-596, 2008.
- [11] Zickler, G., et.al., Mechanical Properties of Pyrolyzed Wood: A Nanoindentation Study, *Philosophical Magazine*, Vol. 86, No. 10, pp 1373-1386, 2006.
- [12] Kercher, A. and Nagle, D., Microstructural evolution during charcoal carbonization by X-ray diffraction analysis, Carbon, Volume 41, Issue 1, January 2003, pp. 15-27.
- [13] Kwon, S., et.al., An Investigation on the Transition Characteristics of the Wood Cell Walls During Carbonization, *Wood Science and Technology*, Vol 43, pp 487-498, 2009.
- [14] Zollfrank, C. and Fromm, J., Ultrastructural development of the softwood cell wall during pyrolysis, *Holzforschung*, Vol 63, no 2, pp 248-253, 2008.
- [15] Ishimaru, K., et.al., Microstructural Study of Carbonized Wood after Cell Wall Sectioning, *Journal of Materials Science*, vol 42, pp 2662-2668, 2007.