The Structural and Property Evolution of Cellulose During Carbonization

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The understanding of the structure and related property evolution during carbonization is imperative in engineering carbon materials for specific functionalities. High-purity cellulose was used as a model precursor to help understand the conversion of organic compounds to hard carbons. Several characterization techniques were employed to follow the structural, compositional, and property changes during the thermal transformation of microcrystalline cellulose to carbon over the temperature range of 250°C to 2000°C.

The purpose of this study was to observe electrical and thermal properties and correlate them to microstructural evolution. These studies revealed several stages of thermal decomposition and microstructure evolution during carbonization supported by the observation of five distinct regions of electrical and thermal properties (Fig. 1). The "regions" here refer to the observed data, whereas "stages" correspond to the identified microstructural development during carbonization.

We therefore were able to identify the stages of carbonization by observing five different regions from electrical and thermal studies. In Region I, from 250°C to 400°C, depolymerization of cellulose molecules caused the evolution of volatile gases and a decrease in dipole polarization, which also led to the reduction of overall AC electrical conductivity and specific heat. In Region II, from 450°C to 500°C, the formation and growth of conducting sp^2 carbon clusters resulted in increases in overall AC electrical conductivity and thermal diffusivity with rising temperature. For heat-treatment temperatures (HTTs) of 550°C and 600°C, Region III, carbon clusters grew into aggregates of curved carbon layers leading to interfacial polarization and onset of percolation. AC electrical and thermal conductivities are enhanced because of electron hopping and improved phonon transport among carbon clusters. With temperatures rising from 650°C to 1000°C, Region IV, DC conductivity began to emerge and increased sharply along with thermal conductivity with further percolation of carbon clusters as lateral growth of carbon layers continued. Finally, from 1200°C to 2000°C, Region V, DC electrical conductivity remained constant because of a fully percolated system.

Microstructural studies also were conducted to understand these structure–property relations during carbonization. Electron energy loss spectroscopy (EELS), x-ray diffraction (XRD), Raman spectroscopy, and high-resolution transmission electron microscopy (HR-TEM) were used to identify carbon clusters and observe their evolution upon heat treatment (Fig. 2). HR-TEM imaging identified carbon clusters as aggregates of curved "onion-like" carbon structures similar to those observed in soot and referred as fullerenoids. EELS analyses showed the conversion of most of the sp^3 to sp^2 bonds with increasing HTTs. XRD and Raman analyses provided insights to the mechanisms of carbon cluster growth. Amorphous sp^3 and sp^2 phases were converted to crystalline phases during heat treatment. Increases in crystallinity along the lateral direction of carbon-layered structures occurred between 600°C and 1200°C, as both curva-

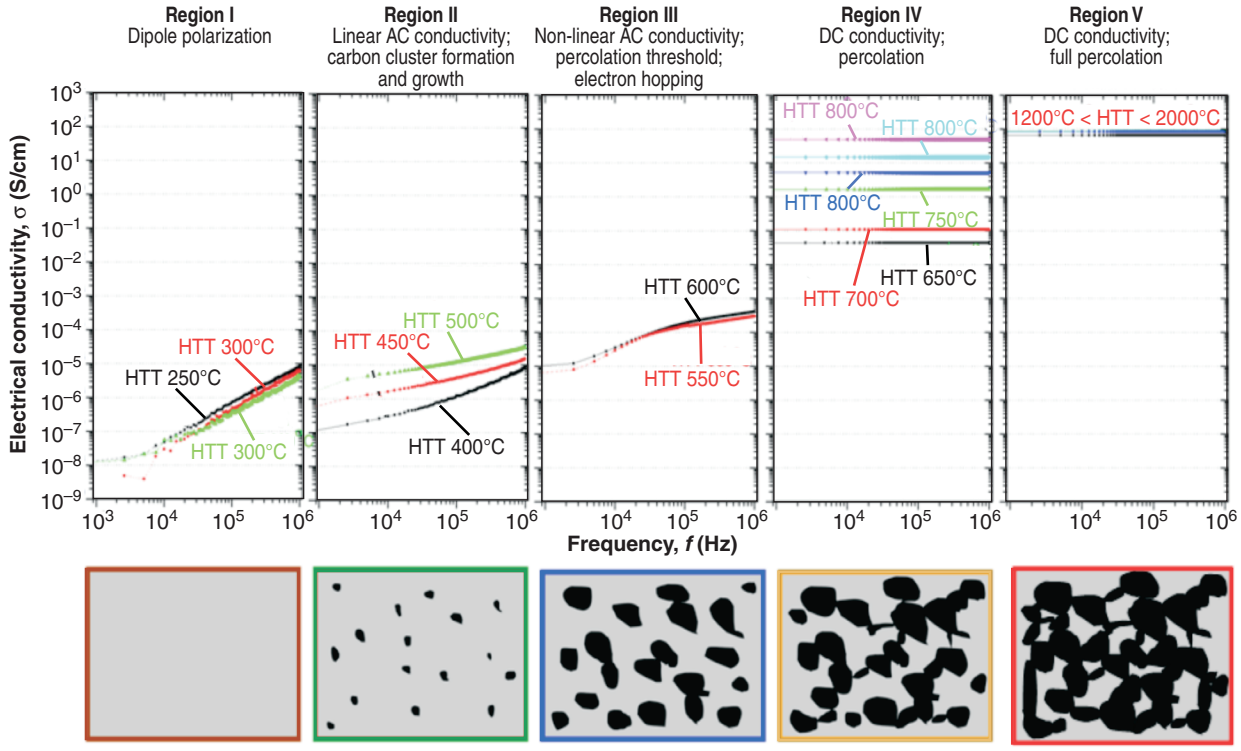

Figure 1. Five regions of electrical conductivity measurements and microstructure evolution originated from microcrystalline cellulose at final HTTs of 250°C to 2000°C. (Adapted from Ref. 1 © 2009, Elsevier.)

tures and lengths of these layers were shown to grow. At HTTs between 1200°C and 1500°C, a slight decrease in curvature was observed with no obvious changes in length. Carbon-layer length starts to increase again when the temperature is raised to 2000°C. The main cause of the increase in electrical and thermal conductivities is the growth of ordered carbon structures along the lateral direction, whereas the contributions from dimensional increases attributable to the stacking of carbon layers are insignificant.

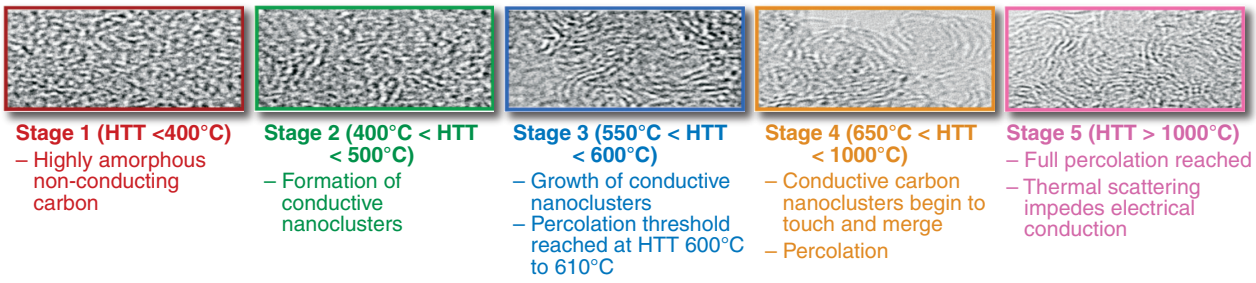

Figure 2. The stages of microstructure development during carbonization.

For further information on the work reported here, see the references below or contact yo-rhin.rhim@jhuapl.edu.

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