

THERMAL TRANSPORT PROPERTIES OF CARBONS DERIVED FROM MICROCRYSTALLINE CELLULOSE

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Abstract

Amorphous carbons were generated through the carbonization of microcrystalline cellulose at various heat treatment temperatures ranging from 250°C to 1000°C in argon atmosphere and their thermal transport properties including thermal diffusivity, specific heat, and thermal conductivity were measured via flash method. Thermal diffusivity was observed to increase linearly within four distinct regions as a function of increasing heat treatment temperature. These four regions were identified to be related to the micro-structural evolution of the organic precursor during carbonization. Specific heat values indicated the coexistence of polar and non-polar phases in both partially carbonized materials obtained at lower heat treatment temperatures and fully carbonized materials formed at higher heat treatment temperatures. For partially carbonized materials, the polar phase consists of residual hydroxyl and carboxyl groups; whereas for fully carbonized materials, the polar phase is believed to be composed of carbon clusters with delocalized sp^2 electrons. Such structural characteristics are well supported by FT-IR characterizations. Lastly, a linear relationship between testing temperature and thermal conductivity suggests phonon transport as the main mechanism for heat conduction, likely due to the absence or very low concentration of percolating electrons in these materials

Introduction

Electrical and thermal property studies of carbon and carbon-derived materials have become important in expanding the use of these materials in various applications. Carbon derived materials have been tested to act as fire retardants (Gupta et al. 2006), cooling thermal pastes (Leong and Chung 2004), and structural components in many aerospace and military uses (Redlands 1971). In this study, thermal measurements were conducted on micro-crystalline cellulose derived carbons, with a goal to provide a benchmark for such property measurements for all cellulose based carbons. Thermal diffusivity, specific heat, and thermal conductivity values were studied as a function of both testing temperature and final heat treatment temperature (HTT).

The conversion of organic materials to carbon and graphite materials under controlled thermal and atmospheric conditions has been extensively studied for many decades. Yet the atomic scale transformation mechanisms that come into play during carbonization are still poorly described in the literature. This study was undertaken in an effort to understand the structural changes that occur during this conversion process. For this study, microcrystalline cellulose was chosen as a model material due to its high purity. Cellulose is a major component of wood. Microcrystalline cellulose is a highly refined material used as an inert filler in many pharmaceutical products, and thus, does not have all the impurities found in most carbon precursor materials. This is an important consideration, since these impurities can alter the carbonization process.

Thermal transport of materials may be due to both electronic and lattice contributions (Castle 1956). Thus, both electrons and phonons may contribute to thermal conductivity and specific heat:

$$k = k_e + k_l \quad (1)$$

$$c_p = c_{p,e} + c_{p,l} \quad (2)$$

Where subscripts e and l denote electronic and lattice contributions, respectively. However, for non-metals, the electronic contribution may be neglected and heat transport is mainly due to lattice contributions. Numerous studies involving graphite (Jamieson and Mrozowski 1953), polycrystalline carbons (Castle 1956, Jamieson and Mrozowski 1953), baked carbons (Kelly 1969, Castle 1956) and glassy carbons (Vagh et al 1974, Mrozowski et al 1974) suggest that thermal transport is dominated by phonon scattering and is best described by Debye's relation:

$$K = \frac{1}{3} C_p v l \quad (3)$$

Thermal conductivity is thus a function of specific heat (C_p), speed of acoustic wave transporting heat (v), and the mean free path of acoustic waves (l).

Generally for graphite and polycrystalline carbons, thermal conductivity values reach a maximum at an intermediate testing temperature or at the Debye temperature, θ . A maximum in thermal conductivity is observed for such materials due to the effects of two different scattering mechanisms. At low temperatures ($T < \theta$), resistance to heat flow is mainly due to boundary scattering. The magnitude of mean free path is large and acoustic waves travel farther in this region. As temperature increases, boundary scattering is reduced leading to the increase of thermal conductivity. When testing temperatures increase beyond the Debye temperature ($T > \theta$), thermal conductivity decreases as the mean free path is reduced. Thermal resistance above the Debye temperature is mainly due to phonon-phonon scattering, where thermal conductivity is reduced as function of increasing temperature. When the effects of boundary scattering equal the effects of phonon-phonon scattering, a maximum in thermal conductivity is reached at the Debye temperature. Kelly (1969) and Castle (1953) have shown that peak thermal conductivity values were lowered and shifted to higher testing temperatures as crystalline size decreased. Jamieson and Mrozowski (1953) explained that such decrease and shift of maximum thermal conductivity was due to an added resistance that exists for disorganized carbon phase.

Materials and Methods

Sample Preparation:

Avicel microcrystalline powder was first mechanically pressed at 10 Tons. The sample disks were heat treated in an inconel-lined retort furnace under a constant argon flow. Final pyrolysis and carbonization heat treatment temperatures (HTT) were 250°C, 300°C, 350°C, 400°C, 450°C, 500°C, 550°C, 600°C, 650°C, 700°C, 750°C, 800°C, 900°C, and 1000°C. All samples were heat treated on graphite sheets to ensure uniform temperature distribution during heating. The heating schedule used for the pyrolysis and carbonization of samples was:

100°C/hr to 250°C
3 hr dwell
5°C/hr to 275°C
2 hr dwell
5°C/hr to 325°C
2 hr dwell
50°C/hr to 450°C
1 hr dwell
100°C/hr to final HTT such as 1000°C
12 hr dwell
100°C/hr to 25°C

Samples were then machined into disks with thickness of 0.125cm and diameter of 3.175cm to fit the sample holders of the Flashline equipment.

Sample Testing:

Thermal diffusivity, specific heat, and thermal conductivity values were measured as a function of testing temperature and final heat treatment temperature (HTT) using the laser flash technique described by Parker et al (1961). Anter's Flashline 3000 was used to record thermal diffusivity values, and to qualitatively measure specific heat using thermographite as the reference sample. All tests were conducted under nitrogen gas environment and were subjected up to testing temperatures that never exceeded the samples' final HTT. Thermal conductivity was then deduced from measured diffusivity and specific heat values according to the following relations:

$$\alpha = \frac{k}{\rho c_p} \quad (3)$$

$$k = \alpha \rho c_p \quad (4)$$

where k denotes the thermal conductivity, α is the thermal diffusivity, ρ is the measured bulk density, and c_p is the specific heat.

Results and Discussion

Thermal Diffusivity

Thermal diffusivity values were observed to increase as a function of HTT. Diffusivity results of samples with various HTTs at testing temperature 200°C are summarized in Figure 1. Four distinct linear regions were identified may be attributed to the evolution of micro-structure during carbonization. Confidence values for the linear regressions computed for these four regions were 99%, 96%, 97%, and 99% respectively, for regions I, II, III, and IV. These regions corresponded directly to the stages of decomposition and carbonization identified with our electrical studies.

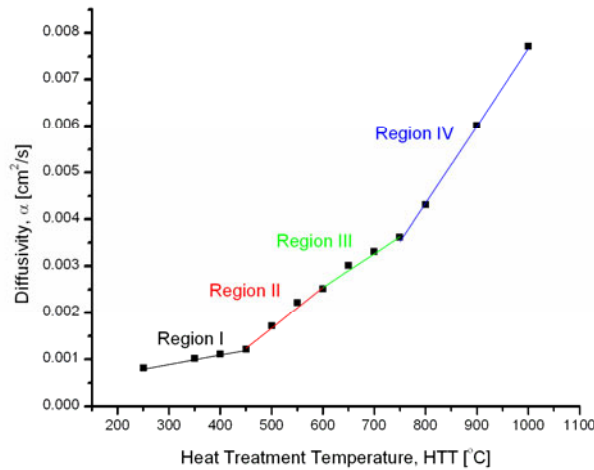


Figure 1. Thermal diffusivity, α , as a function of HTT, at testing temperature $T = 200^\circ\text{C}$.

In Region I, diffusivity increased as HTT increased from 250°C to 400°C. Electrical conductivity in the same HTT range was shown to decrease as organic polar groups were volatilized with increasing HTT. It is important to note that in this region, materials consist of highly amorphous non-conducting carbon and partially carbonized organic materials. Diffusivity values are greatly reduced compared to the other three regions, as the existence of volatile organic material increases thermal resistance. As HTT is increased from 400°C to 550°C, diffusivity values increase at a higher rate as conductive carbon nano-clusters begin to nucleate within the amorphous carbon matrix. The emergence of these clusters minimizes boundary scattering, and thus enhances thermal transport. In Region III, ranging from HTT 600°C to 700°C, thermal diffusivity is further increased as the nucleated clusters begin to grow in size. As a result, inter-particle distances of such conductive particles are reduced, further increasing the rate of thermal diffusivity growth. Finally, in region IV, as HTT is increased from 750°C to 1000°C, inter-particle distance is further reduced until conductive clusters begin to touch and merge. Overall, the

emergence and growth of such conductive sites with increasing HTT reduces the effects of boundary scattering and thermal resistance, and leads to thermal diffusivity increase.

Heat conduction in graphite is described to be strong along graphitic planes and weak perpendicularly (Castle 1953). Thus, heat in graphite and carbon flows through a path joined by graphitic planes and the presence of pores will disturb the total length of heat flow. In addition, pores will further reduce thermal transport as it adds the effects of possible cooling mechanisms via convection. For cellulose derived carbons, a decrease in macro-pore diameter with an increase in HTT was observed (Figure 2). As HTT increases, the macro-pore size distribution shifts to the left indicating smaller pores. As pore sizes were reduced as HTT increased, thermal diffusivity increased as the effects of porosity were minimized. Further studies involving similar tests under vacuum and neglecting porosity effects, will follow in the future.

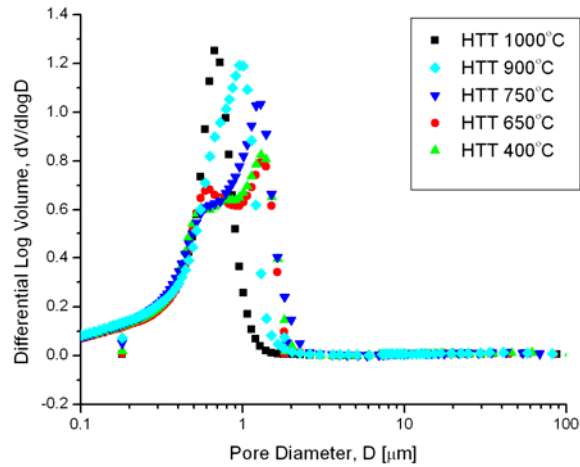


Figure 2. Macro-pore pore size distribution.

Specific Heat

Specific heat value characterizes the amount of heat needed to raise the temperature of a unit mass of a substance by one degree and is highly dependent on the chemical nature of the material. Specific heat values may be examined to indirectly support the presence of volatile materials at lower HTTs. Measured specific heat values as a function of testing temperature are summarized in Figure 3.

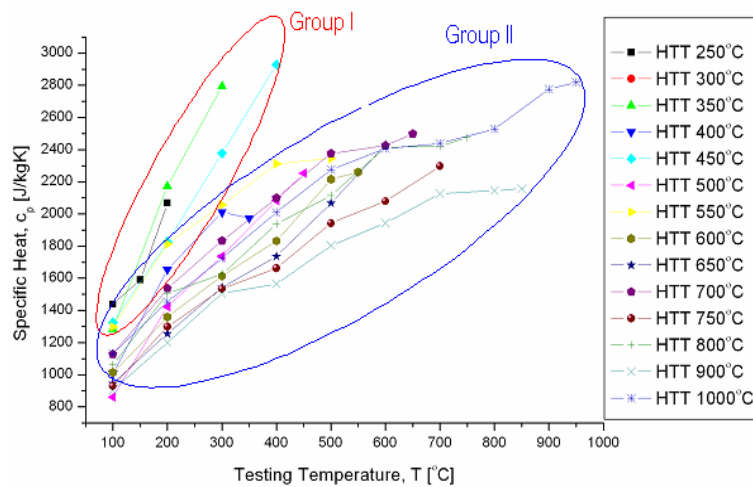


Figure 3. Specific heat, c_p , as a function of testing temperature, T .

It has been reported in several investigations (Gupta et al 2006, Suleiman 1999) that the heat capacity of wood is higher than that of charcoal. In Figure 3, two distinct groups may be identified. The first group (Group I) includes samples heat treated to temperatures from 250°C to 450°C with higher slopes; and the second group (Group II) includes samples heat treated to temperatures from 500°C to 1000°C with lower slopes. As shown in the figure, specific heat values decrease as HTT is increased. The decrease in specific heat is attributed to the chemical changes of the organic precursor during heat treatment. Higher specific values in Group I are due to the presence of volatile materials resembling the chemical structure in woods. As HTT increases and as organic polar groups are volatilized, specific heat values decrease and fall into Group II.

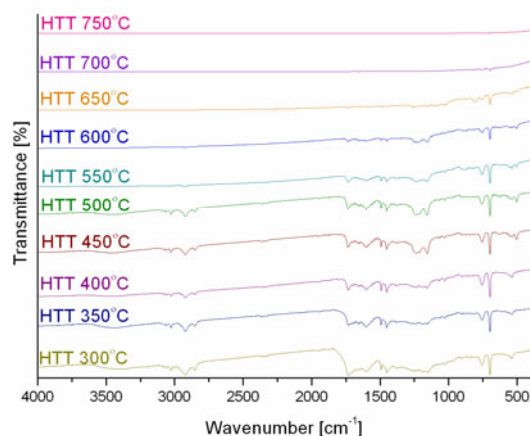


Figure 4. FT-IR Spectra of samples heat treated to temperature ranging from 300°C to 1000°C.

Changes in specific heat as a function of HTT are well supported by Fourier-transform infrared spectroscopy (FT-IR) studies. FT-IR studies were conducted as a function of HTT to observe chemical changes and the results are shown in Figure 4. Peaks in the range of wavenumbers of 3100 cm^{-1} to 2800 cm^{-1} and 800 cm^{-1} to 750 cm^{-1} indicate C-H stretching and C-H saturation, respectively (Silverstein et al 1991, Nishimiya et al 1998). The presences of such peaks are characteristic of C-H bond containing species. As HTT is increased, intensities of these peaks diminish as C-H bonds are broken to form new C-C bonds and the organic nature of the material is reduced. Peaks located at wavenumber of 3300 cm^{-1} and 1700 cm^{-1} correspond to O-H stretching (Silverstein et al 1991, Coates 2000) and C=O bonds, respectively. As expected, the strengths of all of these peaks diminish greatly as HTT is increased to and above 450°C when organic volatile materials are being driven off. Weakening of such peaks with increasing HTT as seen in our FT-IR spectra can be well related to the transition of specific heat values from Group I to Group II.

Thermal Conductivity

Calculated thermal conductivity values are summarized in Figure 5. Thermal conductivity values increased with increasing HTT and increased linearly with increasing testing temperature. As crystallite size is reduced, thermal conductivity peaks observed in carbon materials were depressed and shifted to higher testing temperatures (Kelly 1969, Castle 1953). For baked carbons, thermal conductivity values were reported to increase linearly with an increase in temperature and did not exhibit a maximum. The absence of a peak in thermal conductivity and increasing thermal conductivity values as a function of testing temperature, as shown in Figure 5, suggest that heat resistance is dominated by scattering of lattice defects and crystalline boundaries. Also based on previous results for baked carbons, the increase in overall thermal conductivity as a function of HTT may be related to the increase in crystallite size. Thus, an increase in predicted conductive cluster size with HTT attributes to the observed thermal conductivity increase. Since diffusivity values increase with a decrease in pore sizes, an increase in thermal conductivity due to the same phenomena may also be expected.

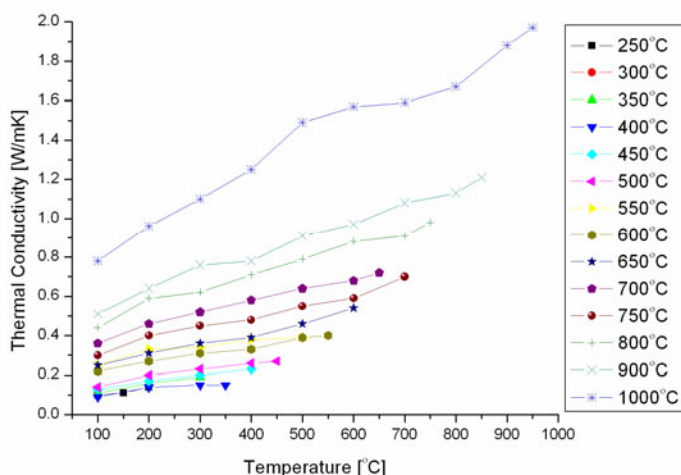


Figure 5. Thermal conductivity, k , as a function of testing temperature, T .

Conclusions

Thermal properties of carbon derived from micro-crystalline cellulose precursor were measured using the Flash method. Diffusivity, specific heat, and thermal conductivity were simultaneously measured as a function of HTT and testing temperature. Measured diffusivity values were closely related to pore-size and micro-structure evolution. As HTT increased, diffusivity was increased due to reduced macro-pore diameters and thus enhanced thermal transport by minimizing cooling due to convection within the pores. Diffusivity values were also shown to increase as a function of HTT, displaying four distinctive linear regions. These four regions were closely related to the micro-structural evolution of the precursor during carbonization.

Specific heat values of micro-crystalline cellulose derived carbons were shown to vary closely with changes in chemical structure. Two main groups were identified. Group I (HTT 250°C – 400°C) resembled specific heat values close to wood materials. As the HTT was increased, the slope of specific heat decreased resulting in higher heat treated samples into Group II. The presence of volatile polar groups in lower heat treated samples increased the specific heat. FT-IR measurements were used to closely examine the presence of such groups as a function of HTT. It was shown that the HTT region in which volatile groups disappeared in the FT-IR spectra correlated to the specific heat slope change. Therefore specific heat is highly dependent on chemical structure and is affected by the presence of volatile polar groups.

Thermal conductivity values exhibited strong affiliation to baked carbons. Thermal conductivity increased as a function of HTT and increased linearly with increasing testing temperature. Heat resistance in such materials was due to boundary scattering. More specifically, scattering was dominated by lattice defects and crystalline boundaries. The effects of phonon-phonon scattering were not suspected to contribute to heat conduction. Moreover, it was discussed that the nucleation and growth of conductive clusters did not only attribute to an increase in electrical conductivity, but also an increase in thermal conductivity by reducing scattering of cluster boundaries.

Acknowledgements

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