

# MECHANICAL PROPERTIES OF CARBON FIBER COMPOSITES FOR ENVIRONMENTAL APPLICATIONS.

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## Abstract:

Activated carbon fiber composites show great promise as fixed-bed catalytic reactors for use in environmental applications such as flue gas clean-up and ground water decontamination. A novel manufacturing process produces low density composites from chopped carbon fibers and binders. These composites have high permeability, can be activated to have high surface area, and have many potential environmental applications. This paper reports the mechanical and flow properties of these low density composites. Three point flexural strength tests were used to measure composite yield strength and flexural moduli. Composites containing over 10 pph binder had an adequate yield strength of about 200 psi at activations up to 40% weight loss. The composites were anisotropic, having along-fiber to cross-fiber yield strength ratios between 1.2 and 2.0. The pressure drop of air through the composites correlated with the gas velocity, and showed a dependence on sample density.

## Introduction:

The use of activated carbons for waste stream clean up is well known. However, the costs of using beds of adsorptive carbons are prohibitive in many cases. The uptake of chemicals into beds of granular carbon can be slow, and the pumping cost for beds of powdered carbons can be prohibitively high. The carbon fiber composites studied here have the advantages of high mass transfer rates inside the fibers, good mechanical strength, and high permeability to liquids and gases.

The composites were manufactured using a novel process developed at the University of Kentucky. ACFC's are made from amorphous carbon fibers which are "glued" together using a variety of binder systems. The binder works by cementing together fibers at their points of intersection. Binder may also adhere to the fiber surface, and can be activated as well.

These materials, which can be described as a highly porous solids, can be machined or formed to fit in many existing systems, and will act as fixed bed catalytic reactors for chemical removal or adsorption. Specific applications of these materials will result in different static and dynamic loadings. The composite parts must be able to withstand the loads seen during installation as well as operation and exhibit low pressure drop characteristics.

## Mass Transfer Inside the Fibers

Reactants need to move from the bulk gas stream to the fiber surface, and then diffuse to reaction or sorption sites inside the fiber interior. One critical step in this sequence is the diffusion of the reactants inside the fibers. Because of the small diameter of the fiber, the rate at which this step takes place will be rapid compared to other factors in the process. The fibers have small pores through which gases and liquids can diffuse to the interior. The Fourier number for diffusion can be used with various unsteady state solutions to the cylindrical diffusion equation (Newman, 1931) in order to estimate the time needed to accomplish 90% of a step change in the gas phase concentration at the fiber surface. The diffusion coefficient of the solute is taken to be appropriate values for gas or liquid solutes, and the average fiber diameter was less than 25 microns. The Fourier numbers for the two types of carbons show that the diffusion time for a fiber is several orders of magnitude shorter than for a granular carbon particle (Table 1). The fibers used in the ACFC's studied here have intrinsically rapid uptake rates for both gas and liquid systems.

## Mechanical Strength

The activated carbon fiber composites would be used either as flat filters treating the entire gas flow, or as annular (candle) filters arranged in a bag house type system. In either case, the filter unit would require good flexural strength. It also must withstand installation, cyclic loading, and, for some applications, regeneration. These criteria have led us to evaluate the mechanical performance of the composites using flexural tests. In addition, some applications will require complex composite shapes which are expected to be anisotropic due to the nature of the forming operation. Therefore, measurements in the machine and transverse directions are compared.

## Permeability to Gases and Liquids

Activated carbon fiber composites (ACFCs) can be used in gas phase processes because of their low pressure drops and high internal mass transfer rates. Possible uses include low temperature removal of sulfur dioxide and nitrogen oxides from flue gas streams. The flue gas velocities are on the order of 3 meters per second, requiring high reaction rates, high mass transfer rates, and low pressure drop operation for economic treatment. The pressure drop for a fluid flowing through the composite can be compared to that of a fluid in a packed bed. The commonly used model for flow in a packed bed is the Ergun equation:

$$\frac{\Delta P}{L} = \frac{150\mu U}{D_p^2} \cdot \frac{(1-\epsilon)^2}{\epsilon^3} + \frac{1.75\rho U^2}{D_p} \cdot \frac{1-\epsilon}{\epsilon^3}$$

where ( $\Delta P/L$ ) is pressure drop per length,  $U$  is the superficial velocity,  $D_p$  is the effective fiber diameter,  $\mu$  is the fluid viscosity,  $\rho$  is the fluid density, and  $\epsilon$  is the composite void fraction. As the system studied does not follow the

assumptions necessary for use of the Ergun equation, a modified form of the equation was used in this study. This is equation is

$$\frac{\Delta P}{L} = K \cdot (U')^n,$$

with K being a parameter dependent on the fluid properties, and n is between one and two.  $U'$ , the corrected velocity, is defined by

$$U' = \frac{(1 - \varepsilon)^2}{\varepsilon^3} \cdot U.$$

## Objectives

This study measures the failure strength and the permeability of a novel activated carbon fiber composite. The mechanical properties of these materials were studied using modified ASTM flexural testing methods. Pressure drop was correlated with gas velocity and the density of the composite.

## Experimental:

The composites were tested to determine flexural strength at break, maximum strain, and the elastic modulus of the material. Samples were formed in 4 inch diameter cylinders, about 4 inches in height. ASTM standard C203-92 (3 point bend flexural testing of block type insulation) was followed. The samples were cut from the block in two directions. The cross direction is the plane parallel to the direction of composite formation. The along direction is the plane perpendicular to the direction of formation. The samples were tested using a three point apparatus on an Instron.

Scanning electron micrographs were taken of the fracture plane of the samples. SEM analyses were used to identify failure mechanisms and binder distribution in the samples. In most cases, the samples were sputtered with gold and then analyzed at 600x magnification.

Pressure drop measurements were made using an Omega DP41-E High Performance Process Indicator and 0 - 2 psi microtransducer. Nitrogen at controlled volumetric rates was passed through composite samples until a constant pressure drop was determined for each flow rate.

The variables effecting the flexural strength of the composites were: fiber length, binder content, thermal treatments, and preactivation of the fibers before formation. The binder used in composite formation is a phenolic thermoset. All fibers used were obtained from Ashland Chemical and have an average diameter of 17 microns. Samples were made which contained differing binder quantities: 5, 10, 20 and 40 parts per hundred. Each of these samples were also tested under all of the activation phases: cured, baked, and activated at 10%, 20% and 40% weight loss.

Several different thermal treatments were studied: curing, baking, and activation. During curing, the composite is held at 150 °C to completely cure the binder resin. The composite is baked in an inert atmosphere at > 650 °C. Activation is done by heating the composite at temperatures greater than 750 °C in a carbon dioxide or steam atmosphere.

## Results:

### Composite Morphology

The 5 pph binder composites were found to be too weak for practical application, and friable during handling for all thermal treatments. Because of this poor sample integrity, the 5 pph samples were difficult to test, and had low reproducibility. SEM analysis of these composites showed binder wicking at the fiber contact points during the curing process. Some of the fiber contact points were not wetted with binder, and the fiber surfaces were not been coated with binder.

The 10 pph binder composites exhibited much higher strength than the 5 pph samples. In the SEM analysis of the 10 pph binder composites, most of the fiber contact points are wetted with binder. Some of the excess binder wicks onto the fibers, completely covering the fibers in samples containing 20 pph binder. This wicking of binder to cover the fibers continues at the 40 pph binder content level and gives a thick coating.

### Mechanical Strength

The flexural strength at break of standard samples made with P400 fibers and cured only were compared in the cross- and along-fiber directions. These samples were found to exhibit anisotropy. The yield strengths of these samples are adequate in all samples except the 5 pph binder content sample. The yield strength increases with increasing binder weight fraction. The level of anisotropy is 1.1 to 2.0 based on cross- to along-fiber strengths. (Figure 1).

More thermal processing reduces yield strength and elastic modulus. This trend is true for samples with differing binder contents as well (Figure 2). The effect of thermal processing can also be seen in the SEM analysis. Composite samples containing 40 pph binder before curing were activated to 13, 19, and 35 % weight loss. At 13%, binder completely coats the fibers. At 19%, binder still coats the fibers, although not as thickly. At 35 % weight loss activation the fibers are no longer coated with binder. At each activation level, evidence of binder failure, fiber pullout, and flaking of the binder away from the fibers can be seen. This indicates a failure mechanism of fiber pullout, or, failure of the fiber binder interface.

Fiber length has a significant effect on composite strength. The shortest fibers, P200's with a length of 350 microns, result in the composite with the highest flexural strength at break. The longest fiber, at 10,000 microns, has the longest span between binder contact points, resulting in the weakest composite. See Table 2.

Composite mechanical properties decrease with increasing thermal processing. Cured composites are the strongest, have the highest modulus, and have the highest density. Baked samples have a lower density, but also have lower strength and modulus. Activated samples have the lowest strength, the lowest modulus, and the lowest density (Table 3). This could be a result of the binder coating acting to stiffen the fiber-binder piece. At higher stages of thermal processing, excess binder is burned away, and the strength of the composites decrease. This trend of decreasing modulus and strength with increasing thermal processing is seen in composites made from medium and long fibers as well.

Higher amounts of binder in the composite make it stronger, but increase the density. Normalized moduli ( $E/\rho$ ) increase directly with binder content, suggesting that the binder contributes directly to material strength (Table 4).

### **Composite Flow Characteristics**

Pressure drop per unit length increases with composite density, and with increasing fluid superficial velocity (Figure 3). The data is fitted by the modified Ergun equation:  $K$  equals 288 for nitrogen and  $n$  is 1.168 (Figure 4). Ninety-eight percent of the data fall within two standard deviations of this fit. Thermal processing has no significant effect on pressure drop. The composites are isotropic with respect to pressure drop.

### **Conclusions:**

Variables which effect the strength and modulus of activated carbon fiber composites are fiber length, binder content, and level of thermal processing. The composites show strength anisotropy, 1.1 to 2.0, between the cross- and along-fiber alignment directions.

SEM micrographs show that the failure mechanism for these composites is fiber pullout. Increasing binder content leads to thicker layers of wicked binder coating the fibers. Thermal processing burns away the binder, resulting in a weaker composite with lower density.

For most applications, the strength of composites with 10 parts per hundred binder and higher composites would have adequate strength for low pressure drop systems at activations up to 40% weight loss. This implies great flexibility in application and tailoring of the composite morphology for different catalytic systems.

The effect of fiber length was as expected. Composites made with shorter fibers have higher densities, higher yield strengths at break, higher elastic moduli, and a lower elongation at break. Thermal processing reduces the composite strength and moduli because the wicked binder is burned away.

The composite is highly permeable to gas flows, and has a low pressure drop at industrial flue gas velocities. The pressure drop in the composites can be accurately predicted using a modified form of the Ergun equation. Pressure drop is proportional to the corrected velocity to the 1.168 power, and  $K$ , the proportionality constant, is 288 for nitrogen.

Table 1: Time to accomplish 90% of a step change in the surface concentration.

Carbon Form	Length Scale, cm	Gas Phase (90%), s	Liquid Phase (90%), s
fiber	0.0025	0.000005	0.05
granule	0.10	0.032	320

Table 2: Effect of fiber length on strength.

Fiber	Length, microns	Strength, psi
P200	350	324
P400	700	215
P3200	10,000	8.5

Table 3: Effects of thermal processing on short (P200) fiber composites.

Thermal Stage	Dry Density, g/cc	Strength, psi	Modulus, psi
cured	0.330	324	39,000
baked	0.309	249	14,200
activated	0.261	157	9,870

Table 4: Effect of binder content on normalized modulus. P400 fibers.

Binder Content, part per hundred	Modulus, psi	Dry Density, g/cc	E/p
10	6,430	0.210	30,600
20	10,300	0.220	46,800
40	22,000	0.237	92,800

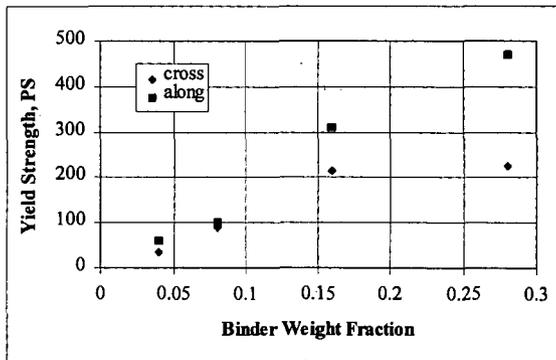


Figure 1. Effect of binder weight fraction on Yield Strength. P400 fibers, cured.

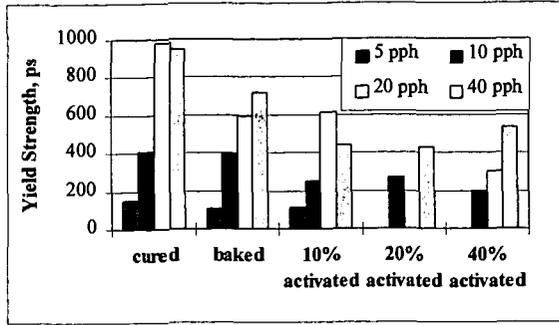


Figure 2. Yield strength over the processing lifecycle.

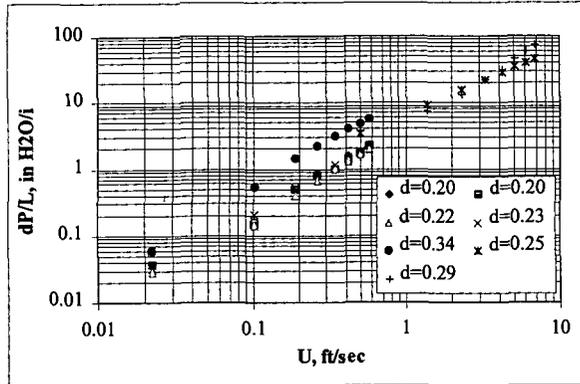


Figure 3. Pressure Drop versus Superficial Velocity.

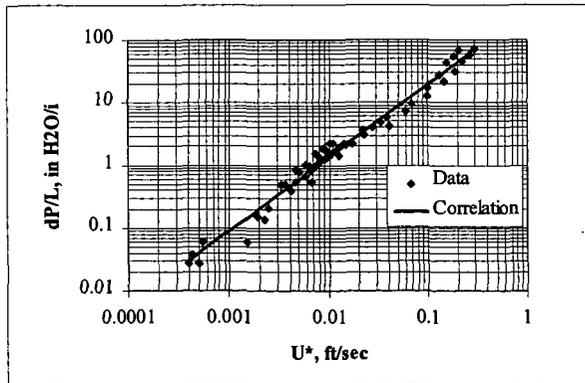


Figure 4. Pressure drop versus corrected velocity.  $K = 288$ ,  $n = 1.168$ .