

FABRICATION OF AUTOMOTIVE BRAKE COMPOSITES FROM UNBURNED CARBON

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ABSTRACT

In pursuit of our goal of finding additional uses for those fly ashes that are rich in unburned carbon, we evaluated how fly ash, bottom ash, sulfate-rich flue gas desulfurization (FGD) scrubber sludge, and unburned carbon affected the frictional properties of composites. We extracted unburned carbon-rich fractions from a fly ash, which was known to have a high carbon content. The unburned carbons were characterized by scanning electron microscopy (SEM), and their oxidative resistance was probed at $30^{\circ}\text{C} < T < 710^{\circ}\text{C}$ using differential scanning calorimetry (DSC) technique. The frictional composites formulated from coal combustion by-products, containing 38-volume percent by-product concentration, were evaluated using Friction Assessment and Screening Test (FAST). Our results suggested that the unburned carbon, being highly porous and resistant to oxidation, had the traits of being an excellent additive for automotive brakes. The composites formed from unburned carbon gave stable frictional behavior and reduced wear and noise.

INTRODUCTION

A substantial portion of the electric power generated in the USA comes from burning coal. However, coal burning by the power plants brings about a huge production of solid residues, mainly fly ash and bottom ash. In an effort to meet the environmental concerns of coal burning, various technologies are employed by electric power utilities, which further add to the solid materials formed, e.g., fluidized bed combustion (FBC) spent bed ash and flue gas desulfurization (FGD) scrubber sludge. It is estimated that about 90 million tons of these solid residues, typically known as coal combustion by-products (CCBs), are produced annually in the USA. Presently, only about 25% of the CCBs generated are utilized [1], with the rest going to landfill or surface impoundments. Most of the CCBs have been largely used in the construction industry, though many additional uses have been proposed [1-4], e.g., ultra-lightweight aggregates for the insulation industry, Portland cement-based FBC mixes, highway and street construction, construction bricks, roofing or paving tiles, pipe construction, artificial reefs for marine wildlife habitat, and aluminum-fly ash composite materials.

In an effort to further mitigate the environmental concerns of coal burning, many utilities have or are installing low- NO_x burner systems [5]. Unfortunately, the fly ash produced by the low- NO_x burner systems has substantially larger unburned carbon in it [5,6]. The higher concentration of unburned carbon in ash stream has a deleterious effect on the utilization of fly ash, especially in the concrete industry. Therefore, intense research is underway by various groups to seek alternative uses of unburned carbon.

The frictional materials used in automobile brake linings are complex composite materials, which generally contain a large number of ingredients, i.e., both organic and inorganic [7]. Typically, brake linings are either organic pads or semi-metallic pads. More than twenty components have been reported for certain brake formulations, though the five major constituents are organic resin as a binder, fibrous reinforcement, filler materials, sliding materials, and friction modifiers. The fillers added into automotive brakes are low cost materials like barytes (BaSO_4), char, and clays. The sliding materials have a hexagonal crystal structure and are incorporated into the frictional materials to alter their lubrication by forming debris on the frictional materials' surface. Asbestos fibers because of their thermal and structural characteristics were frequently used in the recent past as a preferred fibrous support for brake pads. However, they no longer are used due to environmental and health considerations. Slag, mineral, kevlar, or carbon fibers are now used in automotive brakes, depending on the targeted market. Frictional modifiers and abrasives are typically metal oxides. It was felt from our characterization measurements [3,8-9] on CCBs and certain types of carbon extracted from CCBs that the combustion by-products could act as friction modifiers and fillers for automotive brake composites. Moreover, certain fractions of CCBs might help in controlling the thermal properties of brake composites. Therefore, we formed frictional composites from PCC fly ash,

PCC bottom ash, FGD scrubber sludge, and unburned carbon, which was extracted from a high LOI fly ash. These materials' structural, thermal, mechanical, and frictional behaviors were evaluated to probe the suitability of these materials for automotive brake composites.

EXPERIMENTAL TECHNIQUES

The CCBs, i.e., PCC fly ash (Baldwin Unit #3), high LOI PCC fly ash (Southern Illinois Power Co. IL (SIPC)), PCC bottom ash (City Water, Light and Power, Springfield, IL), and sulfate-rich FGD scrubber sludge (City Water, Light and Power, Springfield, IL), samples were obtained from the coal combustion by-product bank maintained in the Mining Engineering department of Southern Illinois University at Carbondale. We used the centrifugation and flotation approach to extract unburned carbon from the high LOI fly ash. Unburned carbon was extracted from two different batches of fly ash obtained from the same power plant, and henceforth, these fractions are called unburned carbon-1 and unburned carbon-2. We blended various CCBs or unburned carbon with polymer binder, slag fibers, and sulfate-rich scrubber sludge to form our composites (see table 1) using a high shear mixer. To minimize the effect of binder on the evaluation of frictional behavior of CCBs, we chose a binder, which is typically used for commercial brake formulations. The blended powders were hot-pressed at 170°C in a 5.72 cm diameter stainless steel die for 1 hour. The hot-pressed composites were further post-cured in air for 8 hours in an oven whose temperature was ramped to 170°C from room temperature at a rate of 3°C/min.

Table 1
Fractions used to form friction composites.

Composite ID	Polymer Binder (volume %)	Slag Fibers (volume %)	Scrubber Sludge (volume %)	By-Product (volume %)
Basic Matrix	45	22	33	
Fly Ash	42	20	30	8 (fly ash)
Bottom Ash	42	20	30	8 (bottom ash)
Carbon-1	42	20	30	8 (unburned carbon-1)
Carbon-2	42	20	30	8 (unburned carbon-2)

Microscopic measurements were undertaken on the as-received fly ash as well as on the unburned carbon fractions by acquiring their SEM microphotographs. The SEM images were obtained using a Hitachi S-570 scanning electron microscope. To record the SEM pictures, a thin layer of fly ash or unburned carbon was sprinkled on a SEM high resolution stub. The samples were then heated at 60°C for 24 hours. These steps were necessary to ensure that ash particles would not detach from the stubs when under electron beam and also would not decompose when under electron bombardment. The fly ash particles were sputter coated with a 40 nm thin layer of gold to reduce sample charging. Generally, the SEM microphotographs were collected using an accelerating voltage of 20 kV. The working distance used was in the range of 8 mm to 12 mm.

The resistance to oxidation of unburned carbon was an important parameter in controlling the oxidative wear of the brake lining formed from CCBs. Therefore, we evaluated the oxidation potential of the unburned carbon by conducting DSC measurements at 30°C < T < 720°C under flowing oxygen conditions. The DSC data were acquired on a Perkin-Elmer DSC7 system, interfaced with a PC 486 computer using a UNIX operating system. The DSC was calibrated for temperature and enthalpy [10,11]. The accuracy in temperature between 30°C and 420°C, based on our calibration procedure, was estimated to be ± 1°C. The conditions under which the instrument calibration were performed exactly matched the experimental run conditions, namely the scan rate of 20°C/min, oxygen gas purge at 30 psi pressure.

The frictional behavior of our composites, as well as of a commercial automotive brake pad, was obtained with the help of a FAST machine (see Fig. 1). The main elements of the FAST machine are the drive motor and friction cast iron rotor disk, the pivot and load arm, the clamping assembly, and the control valve assembly. FAST test samples of dimensions 12.7 mm X 12.7 mm X 4 mm were placed in contact with a rotor disk. The motor rotated the rotor disk at a constant speed of 875 rpm. A constant frictional force of 0.61 MPa was maintained on the sample as it rotated against the rotor disk throughout the FAST test.

RESULTS AND DISCUSSION

Figure 2 reproduces the SEM microphotograph of the as-received high LOI fly ash sample. As can be seen from this figure, the physical structure of this fly ash had a typical appearance of

PCC fly ashes, i.e., spherical particles of various sizes. Our attempts to locate and probe the physical structure of unburned carbon particles in as-received high LOI fly ash were not successful since no distinct carbon particles could be recognized in Fig. 2. The FTIR

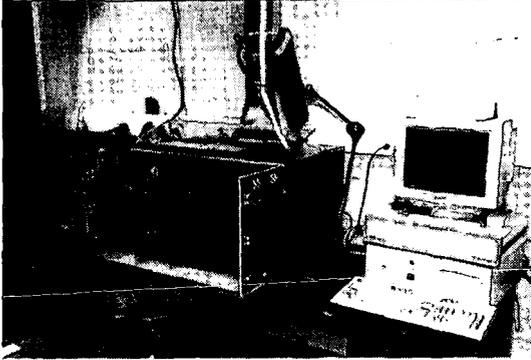
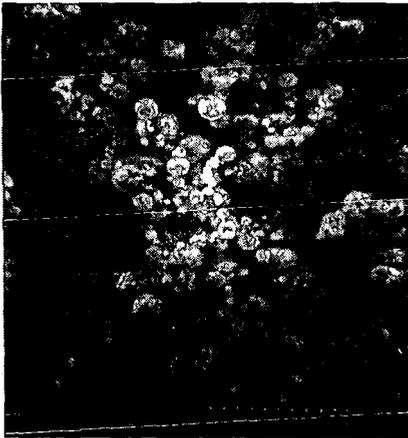


Figure 1. This figure shows the Friction Analysis and Screening Test (FAST) machine used to acquire frictional behavior of our composites.

measurements on as-received fly ash were not helpful either in identifying unburned carbon. Perhaps there were no functional groups in the unburned carbon. It is generally believed that the density of

the unburned carbon particles is lower than the spherical fly ash particles. Therefore, we attempted to separate the high carbon particles from as-received fly ash by centrifugation and flotation. Figure 3 shows the SEM microphotograph of the fraction which floated. It has been suggested that the nature of the unburned carbon in fly ash could be different depending upon the utilities which produce them and the initial structure of coal which undergoes combustion. In fact, Graham et al. [12] proposed that the unburned carbon in fly ashes was actually composed of three petrographically fractions, i.e., inertinite, isotropic coke, and anisotropic coke. The



inertinite fraction in the unburned carbon represents that part of coal which remained unchanged on combustion. The isotropic and anisotropic fractions of unburned

Figure 2. SEM microphotograph of as-received, high LOI PCC fly ash sample. It should be noted that it is difficult to discern the carbon particles in the fly ash.

carbon were those fractions of coal which underwent melting, devolatilization, swelling, and re-solidification during combustion. The isotropic carbon is that carbon which had a high degree of microscopic disorder in its structure, while anisotropic carbon displayed a higher degree of molecular alignment. It is clear from Figure 3 that it is difficult, if not



Figure 3. SEM microphotograph of the particles which were recovered from high LOI fly ash by centrifugation and flotation.

impossible, to distinguish these fractions in the unburned carbon. However, our SEM results did suggest that the unburned carbon in the high LOI fly ash was highly porous and had rough-textured spherical particles. Therefore, unburned carbon particles in frictional composites would facilitate breathing of the material especially under frictional application when the overall brake temperature could be as high as 400°C. The easier escape of the gases, which would be produced at $T > 200^{\circ}\text{C}$ in frictional materials due to the decomposition of organic fractions, could

reduce the thermal wear of the frictional materials.

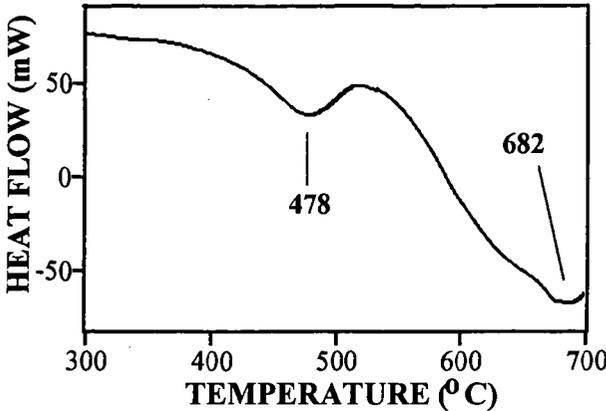
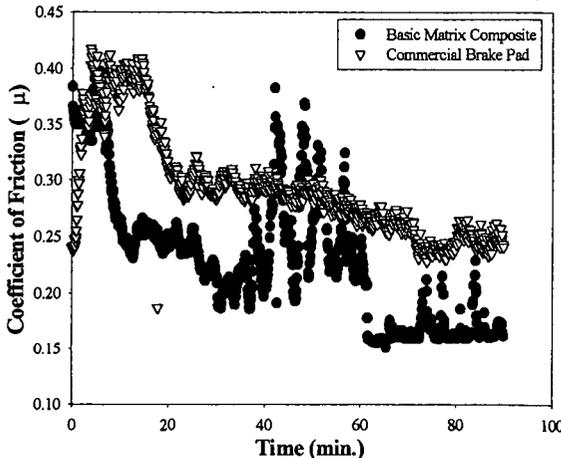


Figure 4: This figure shows the DSC thermograph observed for unburned carbon extracted from high LOI PCC fly ash. The DSC data were collected under flowing oxygen gas conditions.

An important consideration for using unburned carbon in frictional materials would be its resistance to oxidative degradation, especially at temperatures attained by automotive brakes during braking, i.e., $T > 250^{\circ}\text{C}$. Our DSC measurements, conducted under oxygen gas environment, showed no exothermic reactions at $T < 300^{\circ}\text{C}$. In the second batch of runs, we first heated the ash samples to 275°C under nitrogen gas purge environment to ensure the samples were free of water. After soaking the samples at 275°C for 10 minutes, the purge gas was switched to oxygen and the sample's temperature was ramped at the aforementioned heating rate. The typical DSC curve observed from extracted unburned carbon is depicted in Fig. 4. The unburned carbon concentrates, extracted from SIPC fly ash, showed four distinct exothermic reactions, i.e., at 478°C , 610°C , 640°C , and 682°C . The exothermic peaks of 610°C and 640°C overlapped between themselves as well as with the main exothermic peak located at 682°C . At present, it is difficult to assign the exact mechanism of the 478°C exothermic peak. Comparative DSC measurements on other fly ashes suggested that the peak at 478°C originated due to the oxidation of unburned carbon. Since the exothermic reaction of the unburned carbon did not begin until at around 380°C , it appeared that carbon concentrates extracted from fly ashes might be useful additives for automotive brakes.

FAST test results observed for our Basic Matrix composite as well as for a commercial aftermarket automotive brake composite are reproduced in Fig. 5. Generally, unused brake composites show strong variation in the coefficient of friction (μ) in the initial phases of the friction test as material breaks in and its surfaces align with that of the cast iron rotor. Therefore, the variation in μ -value observed in Fig. 5 at time < 10 minutes was attributed to the break in phase. It should be noted that the commercial brake composite μ -value stabilized around 0.3 though it continued to slightly decrease as FAST test time increased. However, this was not the case for our Basic Matrix composite which showed strong variations in the μ -value. The spikes observed in the μ -value could be attributed to the generation of chips from the surface of Basic



Matrix composite. The μ -value decreased to about 0.15 towards the end of the FAST run for Basic Matrix.

Figure 5. FAST test results obtained from a commercial automotive brake and our Basic Matrix composite.

How the incorporation of 8 volume percent of PCC fly ash, PCC bottom ash, or unburned carbon affected the

frictional behavior of our Basic matrix composite is shown in Fig. 6. After the break in period, the μ -value of composites containing fly ash or bottom ash increased to 0.7. As the time of the test increased beyond 60 minutes, the coefficient of friction decreased for both fly ash and

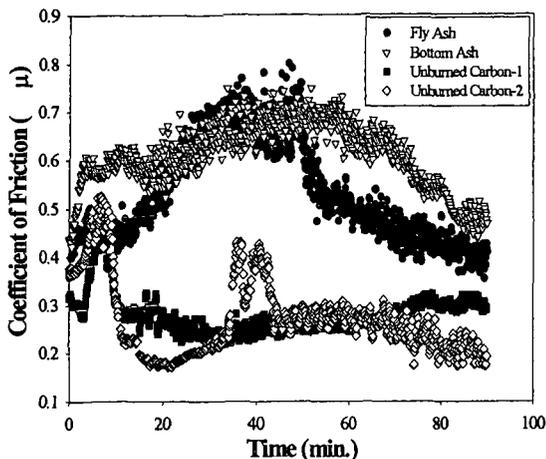


Figure 6. This figure shows how the incorporation of fly ash, bottom ash, or unburned carbon affected the frictional behavior of our composites.

bottom ash containing brake composites. It is important to note that no fade was observed from either of these composites even after 90 minutes of FAST test. The unburned carbon gave much lower μ -value than

those observed from fly ash or bottom ash composite. However, the unburned carbon concentrates not only induced considerable stability in the frictional behavior of our composites but also substantially reduced the noise and wear of the brake composites formulated from CCBs.

CONCLUSIONS

The following was concluded: (a) Our SEM experiments on unburned carbon, extracted from a high LOI PCC fly ash, suggested that the unburned carbon from this ash was highly porous and had rough-textured spherical particles. (b) The unburned carbon was resistant to substantial oxidation at $T < 380^{\circ}\text{C}$, with the major oxidation occurring around 480°C . The porous nature and oxidation resistant traits of unburned carbon made them excellent candidates for automotive brake composites. (c) The incorporation of fly ash, bottom ash, or unburned carbon had a strong effect on the frictional behavior of composites formed from coal combustion by-products. The unburned carbon composites gave desired frictional stability and considerably reduced noise.

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