J Mater Sci (2009) 44:2097–2100
DOI 10.1007/s10853-008-3174-0

Fabricated carbon from minimally processed coke and coal tar pitch as a carbon-sequestering construction material

Arman Wiratmoko · John W. Halloran

Received: 23 July 2008 / Accepted: 9 December 2008 / Published online: 26 February 2009

Abstract We report the mechanical fracture strength and physical properties of fabricated carbons made from pulverized metallurgical coke bonded with coal tar pitch, followed by pyrolysis. Tensile strength from diametral compression of discs ranged from 9.7 ± 1.3 MPa for materials bonded with 13 wt% pitch to 63 ± 7.1 MPa for materials bonded with 40 wt% pitch. Materials made by dry mixing pulverized pitch with coke were comparable with materials made by mixing coke powder with a solution of pitch in toluene. Strength increased with pyrolysis temperature. Pyrolyzed pitch-bonded coke was significantly stronger and lighter than ordinary Portland cement concrete.

Introduction

Recently we suggested that fossil hydrocarbons (CH_x) could be used as fuels without producing carbon dioxide if only the hydrogen was burned, with the carbon left as a solid sequesterant [1]. This implies foregoing the value of the carbon as a fuel, so requires an alternative use for the carbon. Since solid carbon is a material with excellent properties, we suggested that carbon could be used as a large-scale construction material in the place of ordinary concrete and masonry [2]. To serve as a useful construction material, the solid carbons must be as good as or better than concrete. An ordinary Portland cement concrete (OPC) has a tensile strength ranging from 3 to 5 MPa with a density of 2.8 g/cm^3 [3], so these values serve as a benchmark for carbon-based structural materials. This article concerns a prototype carbon structural material made from minimally processed metallurgical coke byproducts, and explores the processing and properties of fabricated carbons made from mixtures of pulverized coke and coal tar pitch (CTP).

We consider coal because it is the most abundant fossil hydrocarbon and is considered the "dirtiest" of the fossil fuels in terms of carbon dioxide production. But coal is in fact a quite rich "hydrogen ore", with a nominal atomic ratio of $CH_{0.7}$. If the carbon has a non-fuel value, coal is also the richest "carbon ore" for materials use. Coal is commonly pyrolyzed in a coke oven for metallurgical coke [4, 5]. When heated to 900–1200 °C in the absence of oxygen, coal produces coke oven gases which consists about 55 vol.% of hydrogen. Pyrolysis of coal also produces coke, a foamy cellular solid carbon, and byproducts such as CTP and liquids such as toluene, benzene, and xylene. About 90% of the coal mass will be converted to the solid products after pyrolysis. One way to make use of the carbon solid products is to manufacture carbon-based construction materials from coke and CTP. Mixture of coke and CTP can be heated to allow the carbonization of the CTP, producing a carbon-bonded carbon. Coke is a strong material by itself. Using coke and CTP as binder will produce an even stronger carbon-bonded carbon material.

These carbons are made from minimally processed coke oven products. They are similar to conventional fabricated carbons and graphites, which are commonly made from petroleum coke and petroleum pitch to produce a high-purity product with appropriate properties for applications such as electrodes or refractories [6]. However, purity is not important for ambient temperature construction products and graphitization is not required, so pyrolysis temperatures can be relatively low. As we are considering

---

A. Wiratmoko · J. W. Halloran (✉)
Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, USA
e-mail: john_halloran@umich.edu

these materials as co-products with hydrogen in a combined hydrogen fuel and carbon materials scheme, we consider the processing and properties of fabricated carbons produced exclusively from coal pyrolysis products.

Experimental methods

Our materials consist of coke aggregate and CTP binder from a metallurgical coke plant (donated by EES Coke Battery in Detroit by DTE Energy Services). The coke is particulate coke, consisting of irregular porous particles about 1–3 mm in size with a foamy texture having 100–300 μm pores. The coke particles were sieved using 2 mm sieve opening and then milled using wet ball mill with water for 24 h. The final coke particle size after milling had a broad particle size distribution ranging from d_{10} of 1 μm, with median d_{50} of 7 μm, and d_{90} of 35 μm, as measured by Particle Technology Labs (Downers Grove, IL) using a Malvern Mastersizer Laser diffractor. The specific surface area for the coke powder was 2.6 m^2/g after milling. After milling, the *c*. 1–35 μm particles are smaller than the pore sizes in the original coke, so that the particles are mostly solid.

CTP with softening point at about 110 °C was donated by Koppers Inc. Thermogravimetric analysis of the CTP showed a carbon residue about 50% after pyrolysis, which is typical for CTP [7]. The solid CTP was pulverized with a mortar and pestle. For the solvent-mix method, the pulverized coke was mixed with toluene, which is a component of coke oven “light oil” byproducts.

Two methods of fabrication were used: dry mixing and solvent mixing. For the dry powder mix method, fine coke powder and pulverized CTP were combined at proportions of 13 and 23 wt% CTP. The powders were mixed and milled in water using wet ball milling. The water was evaporated to recover the mixed fine powder.

For the solvent-mix method, the pulverized CTP was mixed with toluene to produce a fluid suspension consisting of undissolved colloidal residue suspended in a brown solution of the soluble pitch fraction. The CTP–toluene suspension was blended with the coke powder to produce a homogeneous paste. The toluene was evaporated.

The coke–CTP mixtures were formed into 12-mm-diameter discs, 6-mm thick, by compaction in a steel pellet die at 130 MPa. Pyrolysis was conducted at 800–1200 °C in flowing nitrogen in a tube furnace. This has the dual purpose of liberating hydrogen-rich pyrolysis gas from the pitch and converting the coke–CTP discs into hard carbon-bonded carbon specimens.

Tensile strength was measured using the indirect tensile technique using diametral compression test [8]. Samples were loaded along their diameter between steel platens at a crosshead speed of 2 mm/min using Instron 4502 Universal Testing machine until they fractured down the vertical diameter. Fracture strength σ_t is reported as the resolved tensile stress along the diameter, calculated from

$$\sigma_t = \frac{2P}{\pi d t},$$

where P is the load at fracture for a disc of diameter d and thickness t.

Results

There is minimal shrinkage or dimensional change during pyrolysis. The density, determined by Archimedes method using water immersion, varies from about 1 g/cm^3 for the dry mix to about 1.14–1.24 g/cm^3 for the solvent-mix method, apparently reflecting better compaction for the solvent-mixed powders. Note that the density is much lower than Portland cement concrete, which is about 2.8 g/cm^3. The microstructures appear in Fig. 1, showing fracture surfaces of two samples varying in CTP content and mixing methods. The microstructures are roughly similar, with angular coke particles bonded with a fine carbon residue from the pyrolyzed pitch.

The indirect tensile strength data are reported in Table 1. Strength varied from about 10 MPa for both dry

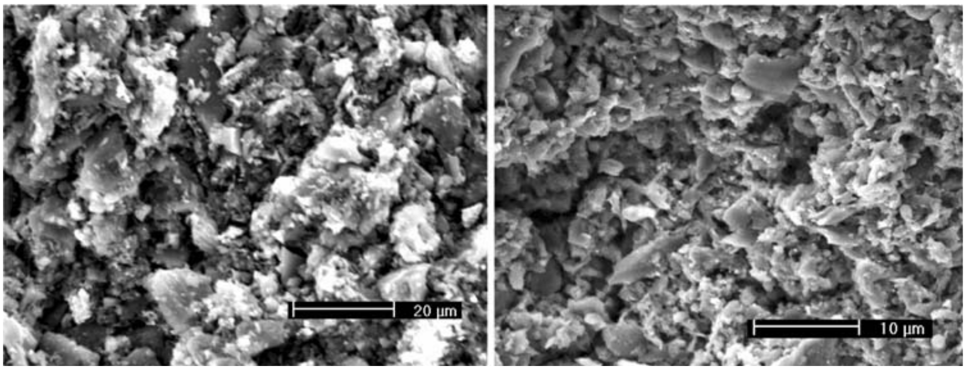

Fig. 1 Fracture surfaces imaged with backscattered electrons by SEM. (*Left*) Coke with 13 wt% CTP from the dry mix method, pyrolyzed at 1200 °C. (*Right*) Coke with 40 wt% CTP from the solvent-mix method, pyrolyzed at 1200 °C

Table 1 Tensile strengths and densities of fabricated carbon materials pyrolyzed at 1200 °C at various CTP compositions and concrete

Fabrication method	CTP (wt%)	Density (g/cm^3)	Strength (MPa)	Strength/density ratio (MPa cm^3/g)
Solvent mix	13	1.14	9.73 ± 1.27	8.55
	23	1.22	24.0 ± 1.19	19.7
	30	1.17	35.1 ± 6.12	29.9
	40	1.24	63.2 ± 7.10	51.1
Dry mix	13	1.06	9.10 ± 1.27	8.57
	23	1.01	29.5 ± 1.19	29.3
OPC concrete	–	2.3	3	1.30

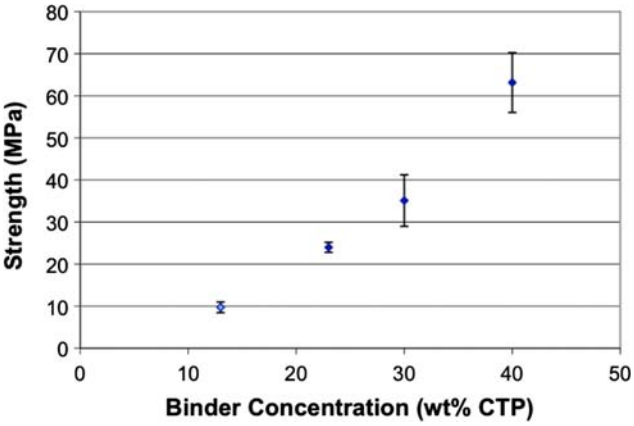

Fig. 2 Tensile strength of fabricated carbon versus CTP binder content for the solvent-mix method pyrolyzed at 1200 °C

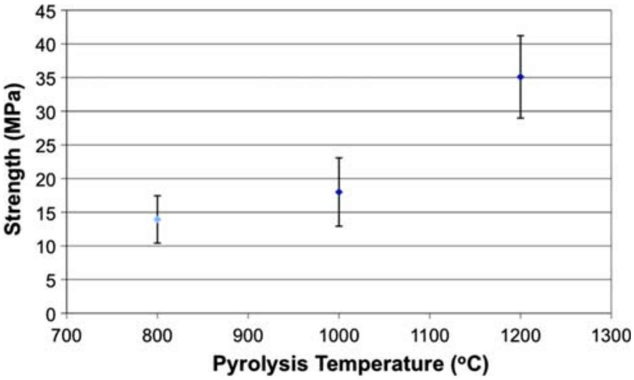

Fig. 3 Tensile strength of solvent-mix fabricated carbon with 30 wt% CTP binder at various pyrolysis temperatures

and solvent-mixed samples with 13 wt% CTP up to about 60 MPa for the solvent-mixed sample with 40 wt% CTP. Dry mixed and solvent-mixed material had similar strength. Figure 2 shows how the strength of the solvent-mixed samples pyrolyzed at 1200 °C increases with the amount of CTP binder, as expected for this range of binder content [9]. Lower temperature pyrolysis resulted in lower strength, as shown in Fig. 3 for solvent-mixed samples with 30 wt% CTP. We compare strength and density in Fig. 4. As expected, the tensile strength generally increases with density as the porosity diminishes.

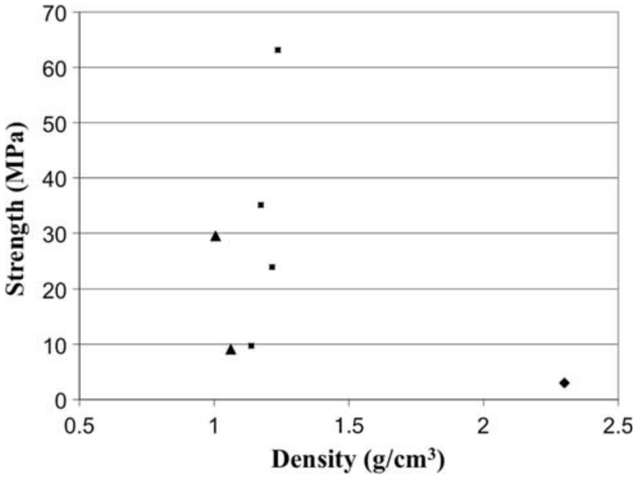

Fig. 4 Strength of fabricated carbons versus density for dry mix (*triangles*), solvent mix (*squares*), compared with OPC concrete (*diamond*)

Discussion

These fabricated carbons are stronger than metallurgical coke, where the indirect tensile strength of samples core-drilled from lumps of coke is about 5 MPa [10, 11]. This is possibly because the fabrication has eliminated macroscopic cracks and broken the cell walls of the pores, as the strength of metallurgical coke depends upon porosity and pore size [12].

As we contemplate the application of these carbons as construction materials in the form of masonry blocks or bricks, it is useful to compare the strength and density of the coke-derived carbons with cement and bricks. The indirect tensile strength of OPC is typically between 3 and 5 MPa [3]. Tensile strength values up to 7 MPa are reported for high-performance concretes [13, 14]. Thus, these carbons from coke and CTP have strength values several times larger than OPC. Concrete is also much denser, about 2.3 g/cm^3 or about twice the density of these carbon. The strength/weight ratio, listed in Table 1, is around 1.30 MPa cm^3/g for OPC. The strength/weight ratio of the coke–CTP derived carbons ranges from about 8.5 to as high as 51 MPa cm^3/g, suggesting that it could in fact be a more favorable material than ordinary concrete. As these coke–CTP materials have by fired during pyrolysis, they might also be compared to fired structural clay products. Commercial clay bricks [15] typically have a density ranging from 1.65 to 2.08 g/cm^3 with a modulus of rupture ranging from 5 to 28 MPa. These coke–CTP materials thus have mechanical properties comparable to clay bricks.

As these coke–CTP materials meet or exceed the structural properties of conventional masonry materials, it supports the concept of carbon materials as a valuable byproduct of hydrogen production by coal pyrolysis. It may be possible to obtain hydrogen fuel from coal without generating carbon dioxide. The carbon component would be sequestered as solid carbon and put to valuable use for building in the place of OPC. Pyrolyzed carbons are relatively inert and corrosion-resistant, so should be durable in service. Of course, carbon can burn, but this may not be a serious limitation. The ignition temperature of coke [16] is much higher than wood [17], and the oxidation of carbon composites can be greatly inhibited with small additions of phosphate [18, 19] or borate [20].

Conclusions

Carbon-bonded carbon material from minimally processed coke and CTP have indirect tensile strengths ranging from 10 to 60 MPa depending on composition, with densities of about 1.1 g/cm^3. The material is stronger and lighter than OPC and many clay masonry bricks, suggesting that they could serve as construction materials.

Acknowledgements We thank Dr. Frank T. Jere of DTE Energy Systems for donating the coke. The University of Michigan through the A.H. White Collegiate Professorship funded this research.

References

1. Halloran JW (2007) Energy Policy 35:4839
2. Halloran JW (2008) Int J Hydrogen Energy 33:2218
3. Mindess S, Young JF (1981) Concrete. Prentice-Hall Publishers, New Jersey, p 339
4. Sundholm JL, Valia HS, Kiesling FJ, Richardson J, Buss WE, Worberg R, Schwarz U, Baer H, Claderon A, DiNitto RG (1999) Making shaping and treating of steel. AISI Foundation, Pittsburgh, PA
5. Ertem M, Ozdabak A (2005) Appl Therm Eng 25:423
6. Petrova B, Budinova T, Eknici E, Petrov N, Yardim F (2007) Carbon 45:704
7. Wallouch RW, Murty HN, Heintz EA (1972) Carbon 10:79
8. Bhatia B, Aggarwal RK (1979) J Mater Sci 14:1103. doi:10.1007/BF00561293
9. Fahad MK (1996) J Mater Sci 31:3723. doi:10.1007/BF00352786
10. Sato H, Patrick JW, Walker A (1998) Fuel 77:1203
11. Patrick JW, Walker A (1987) J Mater Sci 22:3589. doi:10.1007/BF01161464
12. Patrick JW, Sims MJ, Stacey AE (1980) J Phys D Appl Phys 13:937
13. Rashid MA, Mansur MA, Asce M, Paramasivam P (2002) J Mater Civ Eng May/June:230
14. Zain MF, Mahmud HB, Ilham A, Faizal M (2002) Cement Concrete Res 32:1251
15. Robinson GC (1991) Engineered materials handbook vol 4: ceramics and glass. ASM International, Pittsburgh, PA
16. Herbig C, Jess A (2002) Fuel 81:2387
17. Babrauskas V (2002) J Fire Prot Eng 12:163
18. Lu W, Chung DDL (2002) Carbon 40:1249
19. Wu XX, Radovic LR (2006) Carbon 44:141
20. McKee DW, Spiro CL, Lamby EJ (1984) Carbon 22:507