Cement and Concrete Composites 67 (2016) 20–29

Contents lists available at ScienceDirect

Cement and Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Characterization of a sustainable sulfur polymer concrete using activated fillers

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ARTICLE INFO

Article history:
Received 27 January 2015
Received in revised form
21 October 2015
Accepted 26 December 2015
Available online 2 January 2016

Keywords:
Sulfur
Fly ash
Polymer
Hydrocarbon
Alternative binder
X-ray absorption spectroscopy

ABSTRACT

Sulfur polymer concrete (SPC) is a thermoplastic composite concrete consisting of chemically modified sulfur polymer and aggregates. This study focused on the characterization of a new SPC that has been developed as a sustainable construction material. It is made from industrial by-product sulfur that is modified with activated fillers of fly ash, petroleum refinery residual oil, and sand. Unlike conventional sulfur polymer cements made using dicyclopentadiene as a chemical modifier, the use of inexpensive industrial by-products enables the new SPC to cost-effectively produce sustainable, low-carbon, thermoplastic binder that can compete with conventional hydraulic cement concretes. A series of characterization analyses was conducted including thermal analysis, X-ray diffraction, and spatially-resolved X-ray absorption spectroscopy to confirm the polymerization of sulfur induced from the presence of the oil. In addition, mechanical testing, internal pore structure analysis, and scanning electron microscope studies evaluate the performance of this new SPC as a sustainable construction material with a reduced environmental impact.

1. Introduction

Portland cement requires the heating of limestone in kilns at temperatures of more than 1400 °C for hours to form clinker materials. Because of the fossil fuel burned to power the kilns and the stoichiometric carbon dioxide emission from the conversion of limestone to calcium oxide, the process generates about one ton of carbon dioxide per each ton of cement and accounts for 5% of the global anthropogenic generation of CO_2 [1,2]. In contrast to traditional cement manufacturing, the production of sulfur based cement does not rely on heavy energy input or direct carbon dioxide emission [3–5]. In addition, sulfur is in net surplus on a global basis. Sulfur is the third most abundant chemical element in petroleum at concentration of over 10 wt.% and its recovery from petroleum and gas processing is mandated under environmental restrictions [6]. Thus, large quantities of sulfur are available as by-products of these processes [3]. Moreover, since sulfur itself is an industrial by-product, significant amount of carbon dioxide emission can be reduced by using sulfur based concrete.

Sulfur based concrete is a thermoplastic composite of mineral aggregates and sulfur. Early studies using elemental sulfur revealed that it has serious durability problems such as under repetitive cycles of freezing and thawing [7–10]. When sulfur and aggregate are hot-mixed and cooled to cast sulfur concrete products, the liquid sulfur binder initially crystallizes to monoclinic sulfur (S_β). As it continues to cool, the material goes through a solid phase transition to orthorhombic sulfur (S_α), which causes the material to shrink in volume. This reduction in volume creates internal stress and causes durability problems, especially when exposed to freeze-thaw cycling. Therefore, chemical modifiers that polymerize the sulfur to reduce or eliminate the solid phase transition and thus enhance the durability of sulfur based concrete have been previously studied [3,11,12]. This modified sulfur concrete is called sulfur polymer concrete (SPC). It has been used as a construction material due to its superior resistance to acid and salt environments. This binder is also known to effectively stabilize/solidify contaminated soils [13,14] or nuclear waste [4,15,16]. Unlike conventional hydraulic cement concretes, the SPC needs no water and can achieve full strength in several days, compared with up to 28 days for conventional portland cement based concretes.

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http://dx.doi.org/10.1016/j.cemconcomp.2015.12.002
0958-9465/Published by Elsevier Ltd.

Several organic chemical modifiers have been developed to effectively polymerize sulfur. The commonly used modifiers are dicyclopentadiene (DCPD), a combination of DCPD, cyclopentadiene and dipentene [10,17,18], olefinic polysulfide [9,19], and 5-ethylidene-2-norbornene (ENB) and/or 5-vinyl-2-norbornenen (VNB) [3]. When processed with molten sulfur, unsaturated hydrocarbons in the organic modifiers break up liquid S_8 rings and react to form long chain polymers. The polymerized linear sulfur chains improve durability. Although the modified concrete is environmentally sustainable and durable, the high cost for these organic modifiers has prevented it from being widely used in the construction industry [11].

This paper describes the development and characterization of a new modified SPC based on a patented process developed at Brookhaven National Laboratory (BNL) [20]. Instead of the expensive organic modifier, the process uses an industrial by-product of petroleum distillation (i.e., light catalytic cracking oil) as a sulfur modifier. Along with this modifier, another waste product, fly ash, (e.g., from coal power plants) and sand are used to provide reactive surface area and as physical filler materials in the SPC. Since most of the main ingredients for the new SPC are industrial by-products (i.e., sulfur, fly ash, and petroleum distillate), this low-cost solution is expected to expand the use of SPCs and significantly reduce the environmental impact in the construction sector. This study has focused on material characterization of the new SPC. Mechanical and thermal testing, crystallographic analysis, and microscopic analysis have been performed to evaluate the feasibility of using the material for construction applications. In addition, spatially-resolved X-ray absorption spectroscopy was firstly applied to identify heterogeneously distributed modified sulfur in the developed SPC.

2. Experimental method

2.1. Characterization of light catalytic cracking oil

Characterization of the light catalytic cracking oil was conducted by an independent laboratory according to ASTM Method D5554-15 which is to determine the number of unsaturated hydrocarbons available for reaction with sulfur to confirm the potential for polymerization [21]. The iodine value is a measure of the unsaturation of fats and oils and is expressed in terms of the number of centigrams of iodine absorbed per gram of sample as a result of the procedure, i.e., the amount of iodine that completely reacts with 100 g of the fat/oil [21]. Analysis of two replicates each, for four samples was conducted resulting in a mean iodine value of 51.9 ± 4.7. Furthermore, initial, final, and fractional distillation point temperatures were measured according to ASTM D86-12 [22] and summarized in Table 1.

Table 1
ASTM D86 characterization of used light catalytic cracking oil.

Parameter	Temperature, °F
Initial boiling point	335.4
5% Recovery	433.3
10% Recovery	453.1
20% Recovery	482
30% Recovery	495.8
40% Recovery	507
50% Recovery	520.1
60% Recovery	534.8
70% Recovery	553.1
80% Recovery	576.6
90% Recovery	612.2
95% Recovery	641
Final boiling point	660.6

2.2. Material synthesis

SPC fabrication includes pre-treatment of the filler materials (Type F fly ash from a coal-fired power plant and fine quartz aggregate) with the light catalytic cracking oil followed by processing with elemental sulfur to form the polymerized sulfur mortar. A mix design proportion of 54 wt.% sand, 18 wt.% fly ash, 26 wt.% sulfur, and 2 wt.% organic modifier was selected (Table 2). While fly ash is used in ordinary cement concrete for its pozzolanic reaction which allows a reduction in the product's carbon footprint, the fly ash in SPC (along with sand) is used to provide potential reaction sites for polymerization and as a filler component in the composite material. It has been also reported that the addition of fly ash in SPC is beneficial for increasing the consistency and workability of the mixture due to its round shape and appropriate size as a filler material [11,23]. Fig. 1 shows scanning electron microscope (SEM) images of the elemental sulfur and fly ash particles, depicting irregular shapes of ground elemental sulfur particles and the size (about 5 microns or smaller in diameter) and spherical shapes of the fly ash particles. For the pre-treatment stage, the filler materials and organic modifier were mixed and heated to a temperature of 170–180 °C for 12 h. The materials were combined with elemental sulfur and processed through a cross-beater mill with a mesh size of 1 mm to reduce particle size. The mixture was then heated and mixed in a molten condition at 135–145 °C for 4–6 h and poured into molds for cooling. The average density of the mortar specimens was 2282 (±41) kg/m^3.

2.3. Mechanical and thermal experiments

Mechanical and thermal experiments were performed to verify sulfur polymerization and to ensure the integrity of the product for construction applications. To evaluate the mechanical performance, compressive and three-points flexural tests were performed on $160 \times 40 \times 40$ mm samples. The mechanical strength of the samples was determined under two conditions of 20 °C and 50 °C. For each strength measurement, six samples were tested for a statistical assessment. The results are summarized in Table 3.

Thermal properties of elemental sulfur and SPC were measured using differential scanning calorimetry (DSC, PerkinElmer DSC 6000). To perform this test, a 30 mg sample was loaded in an Al crucible and heated at a rate of 5 °C/min in a controlled environment with flowing inert nitrogen gas. A temperature range from 25 to 200 °C was selected. Since there were no major temperature fluctuations below 90 °C, a temperature range of 90–180 °C in both samples was used as shown in the DSC thermogram in Fig. 2.

The chemical composition of SPC and raw material of fly ash was analyzed by X-ray fluorescence (XRF, Rigaku NEX CG EDXRF Analyzer). Finely ground SPC was combined with a spectroblend binder and mixed with a mixer mill for a period of 5 min to ensure a homogenous mixture. An analytical pellet was formed by pressing the powder for 1 min. A total measurement time of 20 min was selected to get a stable XRF signal from the samples. The measured elemental composition of SPC and fly ash is summarized in Table 4.

2.4. Microstructural characterization

A series of microstructural characterization studies was

Table 2
Mixture proportion of sulfur polymer concrete.

Oxide	Sulfur	Sand	Fly ash	Organic modifier	Total
wt.%	26	54	18	2	100