Characterization of high-strength cement paste with pristine graphite and heptane-graphite emulsion

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Abstract: Heptane-graphite emulsion or pristine non-oxide graphite was incorporated into high-strength cement paste (HSC) using either a standard paddle mixer or a non-contact low-frequency acoustic resonance mixing technology by ResonantAcoustic® Mixing (RAM), Inc. Compression tests according to ASTM C109 and three-point bending tests were performed at 3 and 7 days as well as at equivalent 28 days by accelerated heat steam curing. A decrease in compressive and flexural strength with the heptane-graphite emulsion was found, while results were inconclusive for compressive strength. Additionally, pristine graphene results with the paddle mixer did not show any improvement either. However, when mixed with acoustic resonance mixing technology 7 day flexural results for pristine, non-oxide powdered graphite in high strength cement paste showed a 73% improvement in flexural strength compared to HSC.

Keywords: graphite, graphene, high strength cement paste, graphite – heptane emulsion, resonant acoustic mixing, harden state properties

1. Introduction

While non-fiber reinforced ultra-high performance concrete (UHPC) exhibits excellent durability and low permeability against chlorides, sulfates, carbon dioxide and other aggressors in comparison to conventional concrete it is an exceptionally brittle material (Wille and Boisvert-Cotulio 33-43). Fiber reinforcing steel has already been shown to improve UHPC's toughness and ductility on the macroscopic level (Naaman and Wille 3-16). Therefore, seeking a solution to improve tensile strength, flexural strength, and toughness of UHPC at the microstructure level is important to consider. Incorporation of nano-carbon particles such as carbon nanotubes and carbon nanofibers in cement paste, mortars, and concretes like UHPC are already showing it is possible to improve mechanical and transport properties on the microstructural level (Abu Al-Rub et al. 1-6; Metaxa, Konsta-Gdoutos, and Shah 25-32). Both steel and carbon fibers represent one-dimensional (1D) reinforcement (Chuah et al. 113-124). Recently, work has been published on how two-dimensional (2D) reinforcement, in the form of graphene oxide, improves or changes the properties of ordinary Portland cement (OPC) paste (Gong et al. A4014010; Lv et al. 231-239; Lv et al. 121-127; Lv et al. 1-9).

The promise of graphene for material applications comes from its highly advanced electrical, thermal, and mechanical properties. Thermal conductivities as high as ~5,000 W/mK, Young's modulus values of up to ~1.0 TPa, and breaking strengths of ~40 N/m have been reported (Oyer et al. 5018). Currently, the most commonly used graphene involves the oxidation of graphene to graphene oxide (GO). Graphene oxide is a 2D sheet of carbon with a mixture of oxygen, carboxyl, hydroxyl and epoxy functionalities that give it enough electrostatic repulsion to counter the van der Waals attractive forces between sheets as well as a hydrophilic nature allowing it to disperse in water (Pan et al. 140-147). It is the oxygen functionalities that have attracted initial investigations of GO in cement paste (Lv et al. 1-9; Mohammed et al. 341-347; Horszczaruk et al. 234-242). Lv et *al.* found that incorporating GO into cement paste changed the morphology of the cement hydration products into a more polygonal shape indicating that the oxygen sites of GO are interacting with cement particles and their hydration products. Gong et *al.* (Gong et al. A4014010) found that indeed enhanced production of hydrates, improvements to tensile and compressive strength, as well as a reduction in porosity occurred. This demonstrates that this type of 2D reinforcement has potential. However, given the need for cementitious materials to have large industrial scale applications the use of these 1D and 2D nano-reinforcements are limited. It is then of interest to explore more economically feasible nano-reinforcements.

The formation of graphene oxide is either done with chemical modification that can significantly damage the pristine graphene sheet and hinder its advantageous properties or chemical vapor deposition that requires high production costs (Woltornist et al. 7062-7066). It would be tremendously advantageous to use pristine graphene to lower the cost and boost film conductivity Recently, Woltornist et *al.* have developed a one-step technique to produce laterally macroscopic, transparent, and conductive films from pristine (untreated and unmodified) natural flake graphite with well-controlled thickness (Woltornist et al. 7062-7066; Woltornist et al. 687-693). This is accomplished by modest sonication of natural flake graphite in a water/heptane mixture to form continuous films at the interface between two immiscible liquids. It is estimated a savings of 95% is achieved with this emulsion method over graphene oxide production.

The study presented in this paper is a preliminary investigation on incorporating this unique graphene-heptane emulsion into high strength cement paste. Comparisons with powder pristine graphene and with normal strength cement paste are made. Two mixing methods are utilized and an assessment of flexural and compressive strengths are conducted to see if any change of mechanical properties arise.

2. Background

The formation of water-in-oil emulsions by graphite takes advantage of the surfactant character of graphene sheets recently described by (Woltornist et al. 687-693; Woltornist et al. 7062-7066). Graphite is found to spontaneously spread at high energy interfaces, exfoliating into graphene sheets that sit at the water-oil interface and lower the free energy of the system. This provides for the extensive exfoliation of graphite without the input of large amounts of mechanical energy or the use of aggressive oxidation methods (as in the formation of graphene oxide, or GO), both of which damage the graphene sheets and add to the cost of the material.

The thermodynamics of the graphene spreading have been investigated by computational methods, and the results show a steep increase in the energy of the system as the graphene sheets are moved from the oil-water interface. The kinetics of the system, however, are less well understood. It is clear that smaller graphene sheets sizes form emulsions much faster than do larger sheets. For this reason, graphite of a flake size centered at approximately 1 µm is used and in our experience it forms very stable emulsions.

3. Testing Methods

3.1. Materials

Type I white cement conforming to ASTM C150 (*ASTM C150 / C150M-15, Standard Specification for Portland Cement*) was used in all the mixtures. A commercially available high-range water reducer (HRWR) conforming to ASTM C494 (*ASTM C494 / C494M-15, Standard Specification for Chemical Admixtures for Concrete*) Type A & F polycarboxylate (PCE) superplasticizer (SP), with specific gravity 1.060 and solid content of 29%, was used at 0.2% by weight of cement (bwoc). Nano-24 grade graphite from Ashbury Carbons was chosen for its average flake size of 1 µm. The surface area is 350 m^2/g and lamella thickness index (LTI) is 7-8. The graphite to cement ratio was set to 0.005% bwoc.

3.2. Production of Graphene-Heptane emulsion

To prepare graphene films, a typical procedure is as follows: 1.4 mg of bulk pristine graphite for every ml of water was first put into a 20 mL glass scintillation vial. Then, n-heptane (Fisher Scientific, HPLC grade) was added at amounts of 7:4 water:heptane by volume, and then tip sonicated (Cole-Parmer 750 W Ultrasonic processor) for 15 min at 40% power to exfoliate the graphite and disperse it into the heptane. After the sonication, water was added and the system was bath sonicated again briefly to help move the graphene sheets to the interface. Several emulsions were made with HRWR incorporated, but it was found the stability of the emulsion did not change.

3.3. Mixing Methods

Five series of samples were prepared (Table 1) – normal strength paste (w/c 0.30) with and without pristine powdered graphite and high strength cement paste (w/c 0.25, 0.2% HRWR) with or without either pristine powdered graphite or heptane-graphite emulsion. Mixing was performed using either a three-speed Hobart laboratory bench mixer with a standard designated paddle or a LabRAM mixing device which utilizes ResonantAcoustic® Mixing (RAM) technology. RAM technology uses a non-contact mixing technology that subjects the media to a high intensity acoustic energy for rapid fluidization. More detailed information of this technology can be found in (Vandenberg and Wille).

For the HSC_NG samples, the HRWR was added to the water first, then it was added on top of the cement powder and mixed between 3 – 5 minutes. For the HSC_PG samples, results showed that there was no difference whether the powder was mixed first with the cement powder or with the water and HRWR. The HSC_HG samples, trial results found that first mixing the heptane-graphite emulsion with the cement, then adding the remaining water and HRWR produced the best results.

Table 1. Mix Proportions

Sample	Cement	Water	HRWR	Graphite	Heptane
NSC_NG	1	0.30	-	-	-
NSC_PG	1	0.30	-	0.0005	-
HSC_NG	1	0.25	0.002	-	-
HSC_PG	1	0.25	0.002	0.0005	-
HSC_HG	1	0.25	0.002	0.0005	0.0428

3.4. Mechanical Testing Procedure

ASTM C109- Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens) was followed for the compression testing. Specimens were cast in 2-in. (50-mm) cubic brass molds and vibrated for approximately 30s. The specimens were covered and placed in a controlled curing room for 24h at 20°C (68°F) before being demolded and placed in a lime-saturated water bath at the same temperature. 28 day strength samples were aged via a heat steam curing method for 48h at 95°C (68°F). Samples were tested at 3d, 7d, and 28d equivalent. The compressive strength was taken as maximum force divided by the average area of the load face surfaces.

Three-point bending testing was performed on specimens to obtain the maximum flexural strength at 3d, 7d and 28d equivalent. Beams with average dimensions of 16 in. × 1 in. × 0.5 in. (40.6 cm × 2.5 cm × 1.3 cm) were cast in a high-density polypropylene (HDPE) beam mold. They were demolded after 24h and then placed either in the curing water tank or the steam cure tank to obtain their respective strengths. To obtain a plane surface for the three points of contact, the specimens were subjected to grinding. The beams were then cut into three sections and each section was tested at least once to obtain an average flexural strength.

4. Results

Results for the compressive strength are shown below (Figure 1). Due to the limited amount of heptane-graphite emulsion, 3 day strengths were not tested for this series. At best 28d graphene and graphite emulsion specimens show marginal gains, but taking in consideration the error bars it appears that there is no difference in strength for the HSC specimens. The NSC specimens show a slight decrease in strength for pristine graphite specimens. The lack of improvement in strength could be not only due to improper dispersion of the graphite, but changes to porosity and/or rate of hydration, changes in hydration products, and mixing technique.

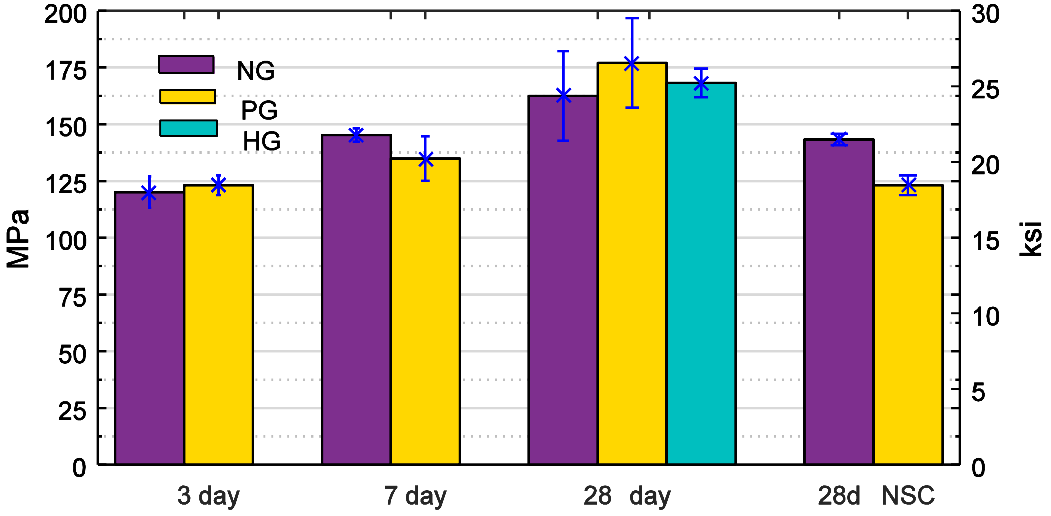

Figure 1. Compressive Strength Assessment of HSC and NSC specimens.

Results for the flexural strength are shown in Figure 2. Due to the limited amount of heptane-graphite emulsion, 3 day strengths were not tested for this series, as well. Results are similar to the compression strength tests in that there exists a lack of improvement in strength. The only exception is for the 7 day specimens mixed with the Resodyn labRAM mixer. For this series there is a considerable improvement in flexural strength for the HSC_PG series.

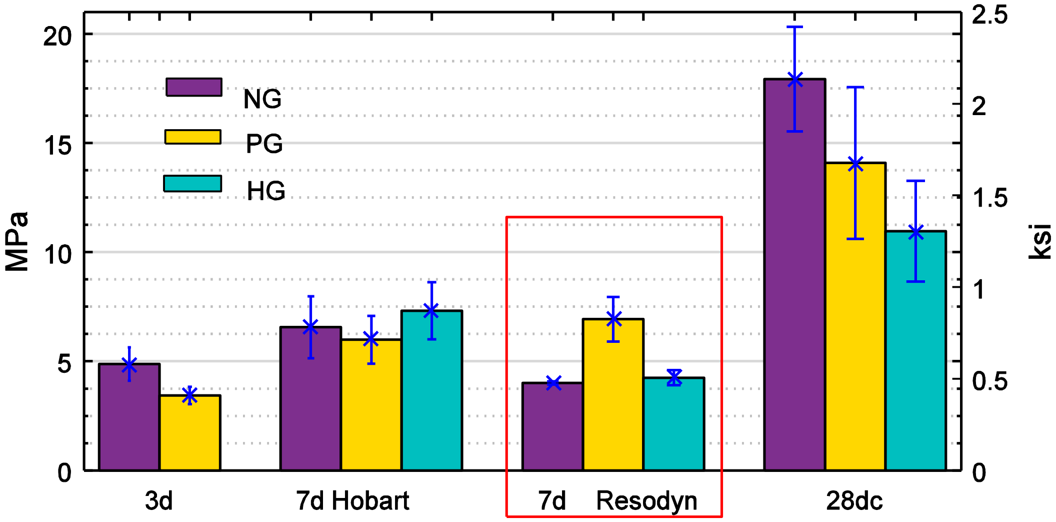

Figure 2. Flexural Strength Assessment of HSC specimens. NG is no graphite, PG is powder graphite, and HG is heptane-graphite emulsion.

5. Discussion

The lack of improvement in strength could be due to improper dispersion of the graphite, or to the impact graphite has on porosity, rate of hydration, morphology of hydration products, or to the mixing technique. In this study only the mixing technique was addressed. Tests on microstructural development are the next phase of this study.

The flexural strength of the 7d graphite specimens mixed with the Resodyn LabRAM, could indicate that the mixing energy is an important factor. There is on average a 73% improvement when powdered pristine graphite is added to high strength cement paste. This astonishing result could not be replicated with the Hobart Mixer. In fact, results show a decrease in strength on par with HSC. This decrease could be attributed to the fact that pristine graphite does not contain the compatible oxygen sites that graphene oxide has. It has been shown that compatibility from graphene oxide with cement arises from its oxygen sites (Lv et al. 3925-3932) which creates a stronger bond with the developing hydration products. Perhaps the lack of oxygen sites in pristine graphite make it less likely to bond with the matrix and cause other interactions.

It is hypothesized that when the heptane-graphite emulsion is introduced to the cement matrix its hydrophobic nature allows the heptane to travel through the pore structure to the top of the paste, where it evaporates at room temperature, inserting the graphite in the hydrating matrix. While mechanical results can only give an indirect assessment of this hypothesis, it is clear that the heptane-graphite emulsion has no effect or even a detrimental effect on these properties, indicating that perhaps it is not a suitable dispersing agent for cement. More in-depth analysis of the microstructure is needed to fully conclude this.

6. Conclusions

In this study pristine graphite and a heptane-graphite emulsion were introduced into high strength cement paste and normal strength cement paste. A focus on mixing technique and mechanical strength (flexural and compressive) were used as an indirect assessment tools to determine whether pristine, non-oxide form of graphite either in powder form or in an emulsion with heptane changed the properties of high strength cement paste. Of the two types of mixing devices used, a standard Hobart paddle mixer or ResonantAcoustic® Mixing, the ResonantAcoustic® mixer showed an average of 73% increase in flexural 7 day strength with pristine powdered graphite high strength cement. Results with the heptane-graphite emulsion showed no improvement or even a decrease in both compressive and flexural strength. Further investigations will need to be conducted to analyze the microstructure such as changes in porosity or hydration products, as well as understand how the mixing energy imparted into the mix affects the properties. While preliminary results indicate that heptane is probably not the most compatible dispersant in cement, finding a more suitable emulsion could still be of interest.

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