



Compressive strength sensitivity of cement mortar using rice husk-derived graphene with a high specific surface area



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HIGHLIGHTS

- Graphene-like materials (GRH) with high SSA were synthesized from rice husks.
- GRH mortar, with a higher SSA, showed a better compressive strength.
- Large edges in GRH may provide a better bonding environment with cement molecules.

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ABSTRACT

Herein, we demonstrate improvements to the compressive strength of cementitious mortar by incorporating rice husk-derived graphenes (GRHs). Several manufacturing trials were undertaken to synthesize optimized GRHs using different dosages of rice husk ash and potassium hydroxide as well as a range of activation temperatures. The incorporation of GRHs into mortar exhibits a generally enhanced reinforcing effect compared to graphene nanoplatelets (GNPs) and multi-walled carbon nanotubes (MWNTs) because of its high specific surface area. SEM/TEM image analyses confirm that GRH has a corrugated graphene structure and clean edges at the atomic scale. GRH showed extremely high BET surface area (2274 m²/g) compared to those of multi-walled carbon nanotubes and GNPs (50–200 m²/g).

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1. Introduction

For many decades in civil engineering, cementitious materials have been widely used in constructing architectural structures. Traditionally, mortar or concrete structures have been composed of cement, fine/coarse aggregate, water, some inorganic additives, and chemical agents. Concrete structures, however, are brittle and have low tensile strength, and multiple crack formations develop under mechanical and environmental loads, limiting their durability and contributing to increased maintenance costs.

Ideally, these problems should be identified early to reduce failure risk or maintenance costs, which could be achieved if structures were able to send current information on their internal health status using embedded sensors via wireless networks. High thermal conductivity in cementitious materials is desirable under certain environmental conditions, e.g., areas that experience

heavy snowfall or structures used in critical infrastructure such as railways, bridges, airports, and harbors. Although this capability is some way off, this is an important issue for achieving “sustainable” management of cementitious material-based structures in the near future.

To achieve these aims, the electric and thermal conductivity of cementitious materials has become an important research subject. Recently, single/multi-walled carbon nanotubes (SWCNTs/MWCNTs), carbon nanofibers, and graphenes have been studied for creating a cementitious carbon nanomaterial composite, utilizing their exceptional mechanical, chemical, electrical, and thermal properties, and excellent performance as polymeric reinforcement materials [3,4,11,30]. Many studies have been carried out to establish the effect of carbon nanotube composites on the cement hydration process, as well as the resulting mechanical properties of the matrix [22–24]. Some durability studies on freeze–thaw capability have also been reported [23]. In contrast, to date, few studies on graphene-based mortar composites have been undertaken [13,25–27,30].

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Exfoliated graphene nanoplatelets (xGnPs) have the same chemical structure as CNTs, and their edges are easily chemically modified for enhanced dispersion in polymeric composites. Such nanoplatelets are typically less than 5 nm thick and can be synthesized with lateral dimensions ranging from <1 to 100 μm . The use of exfoliated xGnPs could open up many new applications in which electromagnetic shielding, electrical conductivity, high thermal conductivity, and high fracture toughness are required [6].

Graphene oxide (GO) is also widely used for similar research. The fundamental natures of SWCNT vs. GO and MWCNT vs. xGnP are similar to each other. SWCNTs and GO are expensive, but have desirable properties for synthesis with cementitious materials. MWCNTs and xGnPs are cheap and hence have been widely used in many studies, although these generally utilized stacks of carbon sheets in multiple layers [31,32]. MWCNTs can be visualized as concentrically nested multiple graphene sheets [31] and xGnPs (graphite nanoplatelets), produced by the mechanical and chemical exfoliation of natural graphite, consists of vertically stacked multiple graphene sheets having a platelet shape [32], in which the graphene layer number varies from 5 to 100 and interlayer distances are similar to those of graphite. In the long term, the use of high-quality carbon-based compounds in cementitious materials for macrostructures (e.g., concrete beams, columns, and tubes) requires high dosages, and thus cost reduction is essential if this technology is to be applied in the future, particularly in civil engineering.

The four major synthesis methods for producing graphene are chemical vapor deposition (CVD) on metallic films [9], epitaxial growth on silicon carbide (SiC) [1], liquid exfoliation of graphite crystals [8], and the chemical reduction of GO [5]. Even though graphene shows great potential in various fields, some obstacles still remain such as the complexity of the CVD process, the need for high temperatures (>1500 $^{\circ}\text{C}$), and expensive substrates in the case of epitaxial growth on SiC, in addition to the use of toxic chemical agents and complex processing requirements when using exfoliation or chemical reduction of GOs.

For civil engineering applications, the high cost of graphene is a potential obstacle for pursuit of graphene mortar and concrete research, with typical costs for GO being around \$220/g. However, cheap graphene-like products exist, such as graphene nanoplatelets (GNPs), which have multiple layers stacked together and a very low specific surface area (SSA). A cheap process using an abundant resource for reducing the price of graphene has been widely sought, and recently, green production methods using environmentally friendly biomass precursors (e.g., sugar, chitosan, alfalfa plants, and other foodstuffs) have been suggested [17,19,20,21]. Graphene obtained using these “green precursors” has not been systematically characterized, especially at the atomic level (edges, defect distribution) to establish intrinsic properties and applications.

Muramatsu et al. [29] proposed an alternative method for making graphene from rice husk. Their study, using ordinary synthetic apparatus and abundant agricultural waste, suggested that low-cost graphene materials could be easily and cheaply synthesized on an industrial scale. Annual global rice production is almost 700 hundred million tons, and waste from rice husks—the outer, protective covering of a rice kernel, which is about 20 wt% of the entire kernel, or roughly 120 million tons a year [18]—may be a significant resource as feed material for graphene production. Due to its abundance, rice husk has already received much attention as a starting material in generating high-value-added materials such as silica and porous carbon, and may now lead to a reduction in the cost of graphene to as low as \$10/g.

In this paper, we attempt to explore enhancement of the compressive strength of cementitious mortar using rice husk-derived graphene (GRH). To this end, a novel manufacturing process for

graphene using local agricultural waste—rice husks—is proposed. The study focuses on the enhanced effect of GRH on the mechanical properties of cement composites, by incorporating silica fume compared to commercially available GNPs and MWCNTs. Cement composites with fixed amounts of added nanomaterials (0.8% by weight of cement) were designed, and for each mixture, silica fume in amounts of 0%, 10%, and 30% by weight of cement was applied. A qualitative analysis using scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX) images was carried out to observe the surface morphology and microstructure of cement composites with different amounts of silica fume and GRH added.

2. Synthesis of rice husk-derived graphene

We demonstrate the feasibility of producing bulk amounts of a new type of graphene by activating agricultural waste using potassium hydroxide (KOH) at 550–700 $^{\circ}\text{C}$. In this study, we confirmed that the black sample we extracted from calcinated rice husk, termed rice husk ash (RHA), with simple KOH treatment, consisted of nano-sized crystalline graphene and corrugated graphene with atomically smooth surfaces and edges. For main characteristics of our graphene were summarized compared to commonly known activated carbons from the same precursor, rice husk [29]; (a) The graphene sample shows a corrugated paper-like texture with nanosized crystalline domains and also clean edges (see Fig. 4(a and b)). However, it is not possible to see the crystalline region from activated carbon under TEM. (b) low R value (I_D/I_G , the integrated intensity of the D band divided by the integrated intensity of the G band) from Raman spectra signifies the high crystallinity as compared with high R value of activated carbons, (c) An obviously observed D' band around 1620 cm^{-1} indicates the presence of edge sites in graphene sample and (d) a highly intensified G' band around 2650 cm^{-1} is a characteristic Raman peak of graphene sample. In case of activated carbon, the intensity of the G' band is low. This method produces GRH at temperatures significantly below those used by Muramatsu et al [29].

The synthetic conditions were varied by changing the quantity of KOH, activation temperature, and time, as shown in Table 1. The criteria for optimal manufacturing conditions for GRH was set to that which achieves the largest SSA, since a large specific area in graphene is expected to allow strong bonds with cementitious grains at micro- and nanoscales in the hydration process. Note that the bulk morphologies of the graphene samples prepared by activating RHA with KOH were largely different from previously reported activated carbons derived from rice husk [2,16].

Ten grams of raw rice husk (retrieved from Gwangju area, Korea) was thermally treated at various pretreatment temperatures in the range 500–700 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ to obtain RHA; the yield of RHA from raw rice husk is 30–35%. Then

Table 1
Trial conditions for the fabrication of GRH with large specific surface area.

Sample No.	KOH (g)	Heat ($^{\circ}\text{C}$)	RHA (g)	GRH (g)	SSA ^a (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	V_{total} (cm^3/g)
GRH-1	12.5	600	2.50	1.40	1052	0.50	0.48	0.71
GRH-2	12.5	600	2.50	0.93	1349	0.63	0.43	0.79
GRH-3	13.7	600	2.50	1.01	1168	0.54	0.49	0.76
GRH-4	15.0	600	2.50	0.92	1629	0.92	0.90	1.19
GRH-5	12.5	700	2.50	1.21	1099	0.49	0.31	0.64
GRH-6	16.2	600	2.50	1.02	1173	0.76	0.87	1.08
GRH-7	12.5	550	2.50	0.73	2274	1.37	1.11	1.60

^a SSA denotes specific surface area; V_{micro} , V_{meso} , and V_{total} are the volumes of micropores, mesopores, and total pores, respectively, using nitrogen gas adsorption isotherms. Note that the micropore is below 2 nm and the mesopore is in the range from 2 to 50 nm.

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