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Mechanical and microstructural properties of cement pastes with rice husk ash coated with carbon nanofibers using a natural polymer binder

Nima Farzadnia [a,*], Sayed Hessam Bahmani [b,*], Afshin Asadi [c,d], Soraya Hosseini [e]

[a] Key Laboratory for Green & Advanced Civil Engineering Materials and Application Technology of Hunan Province, College of Civil Engineering, Hunan University, Changsha 410082, China
[b] Department of Civil & Environmental Engineering, University of Auckland, New Zealand
[c] Center for Research and Innovation, International College of Auckland, Queen Street, Auckland, New Zealand
[d] Marie Sklodowska – Curie Actions – Research Fellow, School of Engineering, London, South Bank University, London, United Kingdom
[e] Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

HIGHLIGHTS

- The CNFs were uniformly distributed on the surface of RHA using a natural polymer.
- The modified RHA improved the mechanical properties of cement paste specimens.
- The coating process delayed the hydration process.
- The efficiency of modified RHA increased after 7 days of curing age.

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ABSTRACT

This study investigated a new approach to dispersion of carbon nanofibers (CNFs) in cement paste by coating rice husk ash (RHA) particles using a natural polymer binder. Light Chitosan with low molecular weight was used to provide bonding between CNFs and SiO_2 from the RHA substrate. Mechanical properties namely, compressive strength and flexural properties of paste specimens were assessed to evaluate the efficiency of the applied method. Microstructural analysis was carried out using FTIR, XRD, TGA, and SEM to investigate the effects of the coating process on the hydration products and to explain the mechanical properties of specimens with the modified RHA. The results showed that 15% and 5% modified RHA increased the compressive strength and flexural strength of paste specimens at 28 days by 53% and 187%, respectively. Microstructural analysis showed that the coating process delayed the hydration, however, the physical crosslinking effect of carbon nanofibers enhanced the mechanical properties at all ages.

1. Introduction

Cement composites are quasi-brittle and susceptible to cracking due to limited functional properties in tension. Recently, the effects of carbon nanofilaments such as carbon nanofibers (CNFs) and carbon nanotubes (CNTs) on flexural properties of cement composites were underscored in various studies due to their high tensile strength [1,2]. CNFs and multi-walled carbon nanotubes (MWCNTs) are nested arrays of graphene, whereas single-walled carbon nanotubes (SWCNTs) are composed of a single graphene sheet rolled into a long hollow cylinder. Experimental tests on CNFs/CNTs showed that they have Young's modulus as high as 400 GPa, with a tensile strength of 7 GPa [3]. CNFs/CNTs have very high aspect ratio, so they can be distributed widely and densely at the microscopic scale yet covering longer lengths [4]. This property helps to bridge the cracks within the cement matrix, and restrict them from increasing; and essentially can create a new generation of a crack-free material [3]. However, they are easy to agglomerate due to their high specific surface energy (van der Waals forces) [5,6]. Agglomeration of CNFs/CNTs causes two major defects in the cement matrix; degradation of the bridging effects and induction of their inert behavior which can cause crack growth inside cement composites. Therefore, effective dispersion methods are needed to disperse carbon nanofilaments into the cement-based materials in order to fully implement their enhancing effect. To solve the problem, researchers suggested some effective methods, such as physical dispersion methods (including high-speed shear and ultrasonic dispersion) [7,8], chemical dispersion methods

* Corresponding authors.
E-mail addresses: nima.farzadnia@hnu.edu.cn (N. Farzadnia), h.bahmani.eng@gmail.com (S.H. Bahmani).

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(surface covalent bond modification with strong acid treatment or non-covalent bond modification with surfactants) [9–11], or the combination of physical and chemical methods. However, it was found that these methods are neither cost effective nor feasible in process. They may also act as an air-entraining agent, generating entrapped pores in the cement matrix and ultimately degrading the mechanical properties of the cement composites.

Recently, research on the in-situ growth of CNFs/CNTs on the cement and mineral admixture such as silica fume and fly ash have been conducted to overcome the dispersion problem as well as to exploit pozzolanic behavior of mineral admixture [12]. Two methods, namely, chemical vapor deposition (CVD) and microwave irradiating conductive polymers method were implemented. In CVD method, CNFs/CNTs are produced on the substrate by passing gaseous hydrocarbon through a template containing catalyst particles under high temperature of up to 800 °C [13–15]. The other approach to in-situ growth of CNT/CNF on cement/mineral admixtures is microwave irradiating conductive polymer method which uses rapid heating in a short time. In this method, a conductive polymer, such as Polypyrrole, is used, which is able to absorb microwave irradiation to produce heat needed for the growth of nanocarbons. Polypyrrole is physically mixed with microwave poptube precursors such as ferrocene powders to produce temperatures up to 1100 °C upon microwave irradiation. This process leads to decomposition of ferrocene to an iron catalyst and cyclopentadienyl as a carbon source to initiate CNFs/CNTs growth [16–18]. Compared to the CVD approach, the microwave irradiating conductive polymer method does not need any inert gas protection and additional feed stock gases, however, both methods are rather complicated and energy intensive. Detailed information on the in-situ growth of CNFs/CNTs is available in [12] for further reference.

In this study, a new approach was used to disperse carbon nanofibers in the cement matrix by coating the surface of rice husk ash (RHA) with industrially produced CNFs using a natural polymer binder. Accordingly, light Chitosan with low molecular weight was applied to provide bonding between CNFs and SiO_2 from the substrate. Chitosan, a natural biopolymer, is a chemical derivative obtained by deacetylation of chitin, the second-most abundant biopolymer in nature next to cellulose. Chitosan is mostly used to form films in biomedical applications and tissue engineering. It is a biocompatible, biodegradable, non-toxic biopolymer, and cheaper comparing to synthesized binders. Therefore, the usage of Chitosan in concrete is environmentally friendly and available. Chitosan, as a binder for RHA and CNF, is used in very small amounts compared to RHA and CNF and does not change the concrete properties [19,20]. RHA is one of the agro-waste materials, recently introduced as a silicate source in the modern concrete technology [21,22]. The RHA mainly consists SiO_2, CaO and low content of Al_2O_3. In this study, 5, 10, 15, and 20% (by weight of cement) RHA modified with CNF (MRHA) and non-modified (NRHA) were used as cement replacement. The overarching purpose of this study is to investigate the effects of the modified RHA on the mechanical properties in compression and tension as well as microstructural and chemical phase changes of cement paste. Investigating the use of natural materials can lower the cost and energy consumption for CNFs dispersion; meanwhile can enhance mechanical properties of the cement-based materials.

2. Experimental study

2.1. Materials

In this study, Portland cement Type I was used in compliance with ASTM C150 [23]. Cement was stored in airtight plastic containers and sealed to avoid any likely reaction of air moisture with cement. The RHA was produced through uncontrolled incineration by a local supplier. The uncontrolled fired husk residue ash was black in color due to excessive amount of carbon content. The mill fired husk residue ash was further burnt in an industrial furnace at a temperature of 650 °C over a period of 1 h with heating rate of 200 °C per hour [24,25] to ensure the uniform amorphous property of the RHA particles. After a constant heating, the RHA was cooled down in an oven to reach room temperature. The RHA was then pulverized to a mean grain size of 20 μm. Fig. 1 shows the XRD pattern of NRHA. As seen, the hump at 2-theta of about 14 to 35 indicates the amorphous state of the applied RHA. The chemical composition and physical properties of the RHA and OPC are given in Table 1.

The CNFs used in this experiment were provided by Sigma-Aldrich, USA, under the commercial name Pyrograph PR-25-XT-HHT. CNFs were produced by heat-treating to temperatures up to 3000 °C, which graphitizes chemically vapor deposited carbon present on the surface of Pyrograf®. This high heat treatment creates the most graphitic carbon nanofiber and reduces the iron catalyst content to very low levels. Table 2 shows the physical properties of the CNFs used in this study.

Chitosan is the most abundant natural polysaccharide after cellulose. Chitosan is derived from the shells of arthropods such as crabs, shrimps, lobsters, and insects, fungi and brown algae. The supplied Chitosan was purchased from Sigma Aldrich with the molecular weight of 50,000–190,000 Da (based on viscosity). Viscosity is 20–300 cP (1 wt% in 1% acetic acid).

2.2. Coating process of CNFs on rice husk ash using a natural polymer binder

Coating process of CNFs on RHA was carried out using the following method: First, CNFs were soaked in an acid solution of

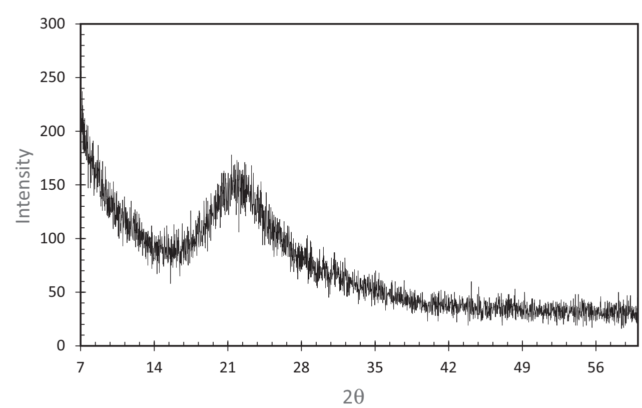

Fig. 1. The XRD pattern of NRHA.

Table 1
Chemical properties of Portland cement type I and RHA.

Component	PC%	RHA%
SiO_2	21.89	91
Fe_2O_3	3.34	0.41
Al_2O_3	5.3	0.35
CaO	53.27	1.3
MgO	6.45	0.81
SO_3	3.67	1.21
Na_2O	0.18	0.08
K_2O	0.98	1.16
P_2O_5	0.23	0.31
Specific gravity (g/cm^3)	3.14	2.06
Loss of ignition (LOI)	3.21	3.37