Cement and Concrete Research 95 (2017) 247–256

Contents lists available at ScienceDirect

Cement and Concrete Research

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

Effect of nano-SiO_2 particles and curing time on development of fiber-matrix bond properties and microstructure of ultra-high strength concrete

Zemei Wu [a,b], Kamal Henri Khayat [a,b,*], Caijun Shi [a,**]

[a] College of Civil Engineering, Hunan University, Changsha 410082, Hunan, PR China
[b] Department of Civil, Architectural and Environmental Engineering, Missouri University of Science and Technology, Rolla 65409, MO, USA

ARTICLE INFO

Article history:
Received 4 December 2016
Received in revised form 23 February 2017
Accepted 28 February 2017
Available online xxxx

Keywords:
Bond strength
Microstructural analysis
Nano-SiO_2
Pullout energy
Statistical model
Steel fiber
UHSC

ABSTRACT

Bond properties between fibers and cementitious matrix have significant effect on the mechanical behavior of composite materials. In this study, the development of steel fiber-matrix interfacial bond properties in ultra-high strength concrete (UHSC) proportioned with nano-SiO_2 varying between 0 and 2%, by mass of cementitious materials, was investigated. A statistical model relating either bond strength or pullout energy to curing time and nano-SiO_2 content was proposed by using the response surface methodology. Mercury intrusion porosimetry (MIP) and backscatter scanning electron microscopy (BSEM) were used to characterize the microstructure of the matrix and the fiber-matrix interface, respectively. Micro-hardness around the embedded fiber and hydration products of the matrix were evaluated as well. Test results indicated that the optimal nano-SiO_2 dosage was 1% in terms of the bond properties and the microstructure. The proposed quadratic model efficiently predicted the bond strength and pullout energy with consideration of curing time and nano-SiO_2 content. The improvement in bond properties associated with nano-silica was correlated with denser matrix and/or interface and stronger bond and greater strength of hydration products based on microstructural analysis.

Published by Elsevier Ltd.

1. Introduction

Ultra-high performance concrete (UHPC) is an advanced composite material typically made with very low water-to-binder ratio of 0.20 ± 0.02 and contains high content of binder, high efficiency superplasticizer, and high strength fibers [1]. As an intrinsically heterogeneous material, its mechanical properties are governed by the quality of the matrix, the characteristic of the fiber, and the quality of the interfacial transition zone (ITZ) between the fiber or aggregate and the matrix [2–4]. The bond properties of fiber-matrix interface play a predominant role in the mechanical properties of composite materials because of stress transferring at this interface, which can make an intrinsically brittle material into a ductile one [5,6]. The microstructure of UHPC is denser and more homogenous than that of ordinary concrete [7,8]. However, as the fiber-matrix interface bridging different phases with various stiffnesses, it is a special component and still the most important yet least understood part in UHPC. Therefore, optimization of the properties at the fiber-matrix interface is necessary for improving the overall mechanical behavior of composite materials.

With the advance and development of nanotechnology, the efficiency of using nano-SiO_2 in cement-based materials has been investigated. These include the effect on microstructure [9,10], heat of hydration [10,11], workability and rheological properties [12–15], mechanical properties [9,16], dimensional stability [17], and durability [18,19]. Because of its extremely small size and highly pozzolanic activity, it can act as nuclei or filler in cement paste to accelerate the heat of hydration [11], densify the microstructure [9,10], and hence enhance the homogeneity and improve the early-age mechanical properties and durability [16,17]. So far, no information focuses on the contribution of nano-particles on the interfacial bond properties between fibers and ultra-high strength concrete (UHSC).

This study aims at investigating the influence of different nano-SiO_2 contents, varying from 0 to 2%, by mass of cementitious material, on the fiber-matrix bond and microstructure of UHSC. A simple and effective doubled-sided pullout testing was conducted to evaluate the interfacial bond properties, which include pullout load-slip relationship, bond strength, and pullout energy. Mercury intrusion porosimetry (MIP), backscatter scanning electron microscopy (BSEM), micro-hardness measurement, and X-ray diffraction (XRD) analysis were employed to evaluate the microstructural features associated with the matrix and/

* Corresponding author at: College of Civil Engineering, Hunan University, Changsha 410082, Hunan, PR China.
** Corresponding author.
E-mail addresses: khayatk@mst.edu (K.H. Khayat), cshi@hnu.edu.cn (C. Shi).

http://dx.doi.org/10.1016/j.cemconres.2017.02.031
0008-8846/Published by Elsevier Ltd.

or interface. It seeks to develop a statistical model to evaluate the couple effect of curing time and nano-SiO_2 content on bond properties and clarify the reinforcing and toughening mechanisms of fiber-matrix bond associated with nano-SiO_2.

2. Materials and experiment program

2.1. Materials

A type P·I 42.5 Portland cement conforming to Chinese Standard was used. Powder silica fume (SF) with particle sizes in the range of 0.02 to 0.28 μm and SiO_2 content of 93.9% was used. Powder nano-SiO_2 with an average particle size of 20 nm and SiO_2 content of 99.8% was employed. The main chemical composition and physical properties of the cement, silica fume (SF), and nano-SiO_2 are summarized in Table 1.

Natural river sand with a maximum particle size of 2.36 mm and a fineness modulus of 3.0 was used. A polycarboxylate-based superplasticizer (SP) with good fluidity retention and solid content of approximately 20% was used. Straight brass-coated steel fibers with a diameter of 0.2 mm and a length of 13 mm were used.

2.2. UHSC mixture proportioning and sample preparation

Five mixtures incorporating 0, 0.5%, 1.0%, 1.5%, and 2.0% of nano-SiO_2, by mass of cementitious material, were prepared. These were designated as NS0, NS0.5, NS1.0, NS1.5, and NS2.0, respectively. Table 2 presents the mixture proportioning of these materials. According to the previous study [20], a water-to-cementitious materials ratio (W/CM) of 0.18 was adopted to ensure high mechanical properties. The dosage of SP was set at 2%, by mass of cementitious materials. This dosage corresponds to a well-dispersed system for the reference mixture made without any nano-material [10].

The dry ingredients were mixed at a low speed for 3 min. Water and SP were then slowly introduced and the materials were mixed for approximately 6 min at a low speed and for 1 min at a high speed. The mixture was then sampled for workability testing. Cubic samples with size of 40 × 40 × 40 mm for compressive strength testing and dog-bone samples for pullout testing were casted and consolidated for approximately 20 s by using a vibrating table. The samples were demolded after 24 h standard curing and then cured in lime-saturated water until 3, 7, 28, and 91 d.

Table 1
Chemical composition and physical properties of cementitious materials.

Materials		Cement	Silica fume	Nano-SiO_2
SiO_2 (%)		21.18	93.9	99.8
Al_2O_3 (%)		4.73	–	–
Fe_2O_3 (%)		3.41	0.59	–
SO_3 (%)		2.83	–	–
CaO (%)		62.49	1.85	–
MgO (%)		2.53	0.27	–
Na_2O (%)		–	0.17	–
K_2O (%)		–	0.86	–
Loss on ignition (%)		1.20	0.30	–
Blain surface area (m^2/kg)		350	–	–
BET surface area (m^2/kg)		–	18,500	160,000
Specific gravity (kg/m^3)		3140	2200	–
Average particle size (nm)		36,700	150	20
Setting time (min)	Initial	172	–	–
	Final	222	–	–
Compressive strength (MPa)	3 d	28.3	–	–
Flexural strength (MPa)	3 d	5.6	–	–

2.3. Experimental methods

2.3.1. Fiber pullout testing

According to the methods of applying force and fiber embedment, pullout testing can be divided into a single-sided and a double-sided one [21]. In view of the fibers are fully embedded in a real composite material, the double-sided pullout testing approach was adopted in this research. Dog-bone shaped specimens were used to measure the pullout behavior of four embedded fibers within the UHSC matrix according to the Chinese Standard CECS13-2009 [22]. The sample was divided into a pullout half and a fixed half from the center by using a plastic clip with four fibers that are firmly fixed to the clip. In order to ensure that the fibers can be pulled out from the pullout section, the embedded lengths of the fibers in the two sections were different. Detailed information on fiber fixing and sample casting can be found in Ref. [21]. According to the standard [22], the embedded length of fiber (l_{em}) at the pullout section should meet the following requirements:

$$l_{em} \le 0.4 l_f \tag{1}$$

$$l_{em} > f_t \cdot d_{eq} / f_m \tag{2}$$

where l_{em} (mm) is the embedded fiber length at the pullout half; l_f (mm) is the total length of steel fiber; f_t (MPa) is the tensile strength of steel fiber; d_{eq} (mm) is the diameter of steel fiber; and f_m (MPa) is the compressive strength of UHSC matrix.

Through calculation, the fiber length in the pullout section was set to 5 mm compared to 8 mm in the fixed section. An MTS testing machine with 20 kN load cell was used to conduct pullout testing under a loading rate of 1 mm/min. For each matrix, five specimens were tested. To ensure the reliability of results, only the results of those specimens with all the four fibers pulled out from the pullout half (short embedment length) were used. The bond strength can be calculated as follows:

$$\tau_{max} = \frac{P_{max}}{n\pi dl} \tag{3}$$

where τ_{max} (MPa) is the bond strength of the embedded fibers based on the maximum pullout load; P_{max} (N) is the maximum pullout load; d (mm) is the diameter of a single fiber, 0.2 mm; l (mm) is the embedment length of the fiber in the pullout half of the dog-bone sample, 5 mm; n is the number of fibers embedded in a dog-bone specimen, 4.

2.3.2. Pore structure measurement

Matrix samples with size of 3.5 to 5.0 mm from the inside of the dog-bone samples at given age were taken to evaluate pore size distribution using mercury intrusion porosimetry (MIP). The samples were soaked in acetone to stop further hydration and then dried at 60 °C in an oven for 24 h before examination. The MIP experiments were sequential carried out under low and high pressures of 0.2758 and 414 MPa, respectively. Glass tube with the mortar specimen and mercury was placed in low and high pressure analysis ports. Full-scan auto mode was selected with contact angle and surface tension of 140° and 480 mN/m, respectively. The intrusion mercury volume was recorded at each pressure point.

2.3.3. BSEM observation

Small samples measuring 15 × 15 × 15 mm with an embedded fiber at the fixed half of the dog-bone shaped sample were taken by cutting the dog-bone shaped specimens shortly after the pullout testing. They were soaked and dried as MIP samples did and then grinded and polished with high smooth surface quality. The polished samples were coated with gold and examined using a Hetachi S4700-SEM with the back-scattered detector. Images with a resolution of 2560 × 1920 were taken at 250 magnifications.