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Ultra-high performance fibre-reinforced cementitious composite with steel microfibres functionalized with silane

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HIGHLIGHTS

- Silane film of TEOS is formed over the fibre after functionalization.
- Increase of silane content in functionalization leads to higher pullout bond strength.
- Functionalization with TEOS enhance fibre-matrix interfacial properties.
- The Si/Ca ratio in the fibre-matrix interface is increased when the TEOS functionalization is applied.

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ABSTRACT

This paper explores the effect of fibre functionalization with tetraethoxysilane (TEOS) in the microstructure and mechanical property of ultra-high performance cement composites with steel fibres. Fibres treated with three concentrations of TEOS were evaluated by pullout tests and SEM/EDS analysis. Mixes with treated fibres showed up to 35.6% increase in bond strength and up to 49.5% reduction in the crack opening at the peak pullout load in comparison with reference mixes containing untreated fibres. The Si/Ca ratios in the fibre-matrix transition zone increases with the increment of the concentration of TEOS in the treatment of the fibre. This indicates an increase of C-S-H at the interface that justifies the enhanced mechanical performance.

1. Introduction

Introduced in the 80's, Ultra-High Performance Fibre Reinforced Concrete (UHPFRC) [1,2] has very high compressive strength (more than 150 MPa at 28 days [3,4]) and enhanced durability [5]. This is achieved by combining high content of binders, low water-to-binder ratios (typically smaller than 0.20 by weight) and ultrafine mineral admixtures. In most structural applications, mixes incorporate straight metallic microfibres to compensate for the brittle behaviour of the cementitious matrix and to achieve higher ductility and toughness in tension [6,7].

Pullout tests of UHPFRC, performed in specimens with aligned straight steel fibres embedded in cementitious concrete matrix, reveal a three-stage mechanical response [8–11]. An elastic stage takes place for small displacements as fibre and matrix show compatible deformation and the integrity of the fibre-matrix interface is maintained. As the load increases, tangential stresses in the fibre-matrix interface induce micro-cracks along the length of the fibre, initiating the debonding stage. Once the tangential stress reaches the bond strength along a critical length, the integrity of the interface is fully compromised and the strain compatibility between fibre and matrix cease to exist. The sliding stage follows, characterized by the relative displacement between fibre and matrix. The restriction to this movement is the result of friction at the fibre-matrix interface.

Since the tensile failure of UHPFRC is governed by the bond between fibre and matrix, attempts to enhance the mechanical performance of the material in tension often focus on improving the interfacial properties through modifications of the matrix composition or of the fibre geometry [12–14]. Few studies have addressed this issue by means of surface treatments applied to the surface of metallic fibres, prior to their mixing with concrete.

In several industrial applications, silane films are used as surface coatings to improve corrosion resistance [15,16] and as a primer to improve the adhesion of other polymeric coatings to metal plates [17,18]. Silanes are molecules of general formula $R'_y(CH_2)_nSi$

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$(OR)_{4-y}$, in which R' is an organofunctional group and R is a hydrolysable alkoxy group [19]. Studies with silane coupling agents showed the possibility of producing sheets of hybrid calcium silicate hydrate from the reaction of hydrolysed silanes in calcium hydroxide solution at room temperature [20–22]. Other studies revealed the potential use of silanes to improve properties in cement-based materials, such as workability or durability [23–28].

Research on modification of fibre surface with silanes to improve the performance of interfaces with cement-based matrices is still limited. [29] and [30] evaluated the mechanical properties of non-metallic fibres treated with silane and embedded in conventional cement matrixes. Pullout tests indicated an increase of up to 150% in the average bond strength and of up to 300% in the toughness. Similarly, [31] performed surface modification of polymeric fibres with silane for reinforcement of concrete. The authors found that the increase of mechanical properties resulted from the formation of high amount of calcium silicates hydrates (C-S-H) at the surface of the fibre.

However, the application of silane surface treatments to improve the performance of metallic fibres in UHPFRC is still unexplored. The objective of this study is to investigate the influence of steel fibres functionalization with silane on the pullout behaviour and on the characteristics of the fibre-matrix interface in UHPFRC.

2. Experimental program

2.1. Fibre treatment

Brass covered straight steel microfibre, with 13 mm of length, 0.16 mm of diameter and tensile strength of 2000 MPa was used in this study. This fibre has been extensively used in UHPFRC. The surface treatment used tetraethoxysilane ($C_8H_{20}O_4Si$) – a silane also known as TEOS with purity higher than 98% and specific gravity of 0.9935 g/cm^3. TEOS is among the most commonly used silanes in industrial functionalization of metals due to its controllable hydrolysis velocity and high degree of crosslink [32].

For effective functionalization with TEOS, all four methoxy groups have to be hydrolysed to release hydroxyls radicals (silanol) able to react with the base surfaces (metallic surface, in this case). Fig. 1 shows the representation of the procedure of hydrolyse of the TEOS, based on [24,33,34]. Since TEOS is not miscible in water, a 1:1 solution by volume of ethanol (C_2H_6O with purity higher than 96%) in water was used to disperse the silane. Then, acetic acid was added to ensure a solution with pH of 5 ± 0.2. After that, the solution was constantly homogenized in a magnetic stirrer at 25 °C. The optimum hydrolysis time was determined by infrared analysis (FT-IR). The transmittance of the wavenumber in the interval of approximately 960 cm^{-1} indicates the Si-OH (silanol) formation. Lower index at 960 cm^{-1} bands indicates a larger concentration of silanol groups produced by hydrolysis. The lowest wavenumber index was observed after 60 min of hydrolysis.

Silane concentrations of 1.0% by volume are typically used for industrial functionalization of metallic plates with amino, ureido and epoxysilanes [35–37]. For the functionalization of synthetic fibres, [29] and [30] used concentrations of 0.5%, 0.75% and 1.0% by volume of vinylsilane. Based on that, solutions with 0.1%, 0.5% and 1.0% of TEOS by volume were prepared in the present study (T_0.1%, T_0.5% and T_1.0%, respectively).

Fig. 2 summarizes the steps for the functionalization of the steel fibres, which was adapted from the work by [33]. Fibres were first submerged during 2 min in 1:0.25 solution of acetone (C_3H_6O with purity higher than 96%) in water to remove dust or grease off their surface and, then, dried during 12 h in a ventilated oven at 100 °C.

Next, the surface of the fibres was activated by the deposition of hydroxyl groups (OH^-) that might react with TEOS. Fibres were submerged in a 0.625 M aqueous solution of NaOH (97% purity) at 25 °C under constant agitation for 10 min, rinsed with distilled water and dried in an oven at 50 °C for 12 h. At this stage of the process, the surface of the fibres composed of a thin layer of brass oxidizes superficially, resulting in a darker finishing. This surface oxidation does not damage the steel of the fibre or affect the efficiency of the functionalization process. After that, the functionalization of the surface with TEOS was conducted following a sol-gel dip coating process. Fibres were submerged in the solution with the hydrolysed TEOS produced according with Fig. 1, in a proportion of 300 g/L. The components were constantly agitated in a mechanical stirrer during 10 min at 25 °C, rinsed in distilled water and cured for 30 min in an oven at 150 °C.

Fibres were then submerged in a 0.1 M aqueous solution of Ca $(OH)_2$ (purity higher than 95%), which was agitated for 30 min at 25 °C to remove loose TEOS from the surface. The removal of loose TEOS film prevented undesirable change in the composition of

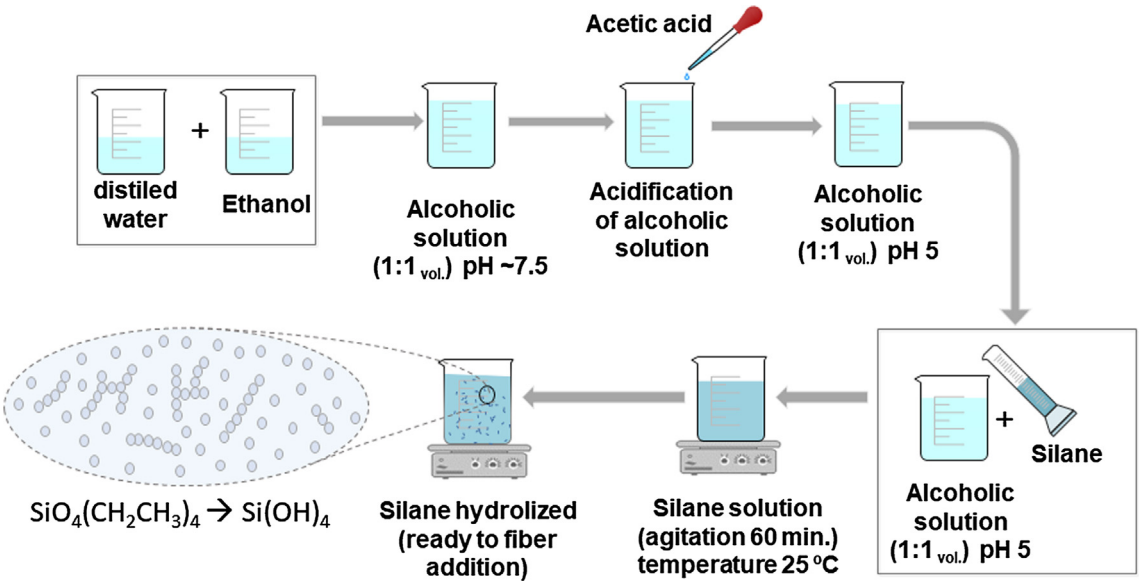

Fig. 1. Representation of the TEOS hydrolysis procedures.