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Pullout behavior of polypropylene macro-synthetic fibers treated with nano-silica

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HIGHLIGHTS

- Nano-silica treatment on macro PP fibers embedded in a cement matrix is proposed.
- We compared the pullout behavior by testing treated and untreated fibers.
- Abrasion phenomena on the fiber surface increase the frictional shear stress.
- An increase in maximum load and energy required for fiber extraction is observed.
- The nano-treatment can improve the engineering performance of structural components.

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ABSTRACT

A study of the effects of nano-silica treatment on the bonding properties of macro synthetic polypropylene fibers embedded in a cement matrix is provided in the present paper as a step to improve interfacial properties of the fiber reinforced cementitious composites (FRCC). Polypropylene fibers were treated by sol–gel technique, allowing to obtain a nano-silica coating. Scanning electron microscopy was used to observe the morphological features of PP fibers surfaces before and after the pullout test. The effects of the treatment were investigated by comparative pullout tests on treated and untreated fibers. An increase in maximum load and energy necessary for the complete extraction of the fiber was observed, as a consequence of the improvement of the interface properties due to the nano-silica hydration activity. These two parameters control the crack-resistance and ductility properties of FRCC and are deeply influenced by bonding and friction phenomena. The hydration products act as chemical and physical anchors, thus producing a densification of the interface transition zone (ITZ). The abrasion phenomena occurring on the fiber surface during the pullout test are responsible of hardening behavior, consisting in the increase in the frictional shear stress with the fiber slip and thus in the energy required for fiber extraction.

1. Introduction

Nowadays, fiber reinforced concrete is widely used in the many civil engineering applications (e.g. industrial pavements, tunnel linings, marine structures, earthquake-resistant structures, etc). Due to the addition of fibers, plain concrete can be transformed from brittle into a ductile material, thus improving the resistance to crack formation and propagation. In particular, fiber-reinforced cementitious composites (FRCC) have been widely used, although the use of macro synthetic fibers made of polymeric materials has been proposed only recently for structural purposes [1]. For instance, the use of polypropylene-based fiber reinforced concrete (PFRC) has been encouraged for the design of road pavement in order to prevent micro- and macro-cracking due to drying shrinkage and fatigue phenomena [2]. Moreover, experimental tests performed by Lanzoni et al. [3] show that the addition of polypropylene-based draw-wired fibers significantly improves the crack resistance of the concrete mixture, thus enhancing toughness and durability of FRC structural components. At the same time, such improvement is attained without significantly affecting the workability of the mixture.

It is well known that the ductility and flexural strength of FRCC are determined by energy-dissipation mechanisms related to the

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pullout of the fibers, which depends on the bonding properties between fiber and matrix [4,5]. However, with respect to other kinds of fibers, polypropylene (PP) macro synthetic fibers have the limitation of poor adhesion to the surrounding cement matrix due to their chemical inertness. The aim of the present work is to propose an innovative methodology for the improvement of the interfacial characteristics between PP macro synthetic fibers and cementitious matrices, validated by the results of pullout tests on single fiber.

The quality of the interface transition zone (ITZ) between the fiber and the matrix, and hence the bond strength, strongly depends on the extent of porosity in this area. Several studies have shown that microfillers e.g. microsilica (shotcrete application) added to cementitious composites may be employed to promote hydration and to decrease porosity [6]. The present study is inspired by the idea of implanting these densification agents directly on the surface of the PP macro synthetic fibers through a sol–gel treatment [7]. A surface nano-treatment has been proposed first in [7] for PP microfibers that can be employed mainly for reducing drying shrinkage in concrete. In the present work, a similar nano-treatment is proposed for macrofibers that can be added to the concrete mixture also for structural applications of FRC.

The sol–gel process, a chemical technique to synthesize inorganic materials, was initially employed to prepare high purity inorganic networks such as glasses and ceramic materials [8,9]. This method is characterized by mild conditions, which become a strategic point when organic materials are involved into the process permitting to avoid their thermal degradation. Typical precursors are metal (or non metal) alkoxides, which react with water in the presence of an adequate basic catalyst and allow appearance to nanoparticles having narrow grain size distribution with dimensions ranging between 5 and 100 nm. The aqueous sol–gel reaction is generally divided into two steps: the first one named hydrolysis, when hydroxyl groups are produced, and the second one named condensation, when the polycondensation of hydroxyl groups and residual alkoxyl groups to form a three-dimensional network are involved as follows:

Hydrolysis	$M(OR)_x + n\ H_2O \rightarrow M(OR)_{x-n}(OH)_n + n\ ROH$
Condensation:	$\equiv M\text{-}OH + HO\text{-}M\equiv \rightarrow \equiv M{-}O{-}M\equiv + H_2O$ (by water elimination)
and/or	$\equiv M\text{-}OR + HO\text{-}M\equiv \rightarrow \equiv M{-}O{-}M\equiv + ROH$ (by alcohol elimination)

Tetraethyl orthosilicate (TEOS) is a well studied alkoxide with chemical formula $Si(OR)_4$, where $R = C_2H_5$ is the alkyl group. The mechanisms of hydrolysis and condensation reactions of silicon alkoxides involve bimolecular nucleophilic substitution reactions that can occur under either acid- or base-catalyzed conditions. Under acid-catalyzed conditions, the rate of hydrolysis is slow compared to the rate of condensation, which leads to longer polymer chains in the sol that continue to grow and entangle, occasionally cross-linking, until the gelation point is reached. In contrast, under base-catalyzed conditions, hydrolysis occurs rapidly, resulting in more highly branched clusters that do not readily interpenetrate and thus behave as discrete nano-structured species [10–12].

In this study, silica nanoparticles were deposited on PP fibers by sol–gel synthesis using ammonia as the basic catalyzer. The consequent interfacial bond enhancement was then investigated by performing pullout tests on single fiber, which provided the load–displacement relationship for a single fiber pulled out from the matrix. The behavior of treated and untreated macro synthetic fibers was then compared by considering the maximum load and the pullout energy absorbed. Both parameters can be extracted from the results of the tests.

2. Materials and methods

2.1. Fibers and treatment methods

The macro synthetic fibers consist of PP monofilaments with a diameter of 0.78 mm (Fig. 1) and length ranging from 30 to 60 mm. The main properties of the used PP fibers are reported in Table 1.

The materials used for the sol–gel treatment are ethanol (EtOH), ammonium hydroxide solution (NH_4OH, ≈28 wt%) and tetraethyl-orthosilicate (TEOS). All materials are high purity reactants (Sigma–Aldrich) and have been used without any purification.

The chemical deposition has been obtained as follows. PP macro synthetic fibers were dipped in a 250 ml flask containing EtOH (120 g), distilled water (12 g) and NH_4OH (18 g) maintained at 60 °C. After 10 min, TEOS (24 g) was added into solution under magnetic stirring. After 2 h, PP macro synthetic fibers were removed, washed with clean water and dried at room temperature.

2.2. Cement matrix

Cement mortar with a mix proportion by weight of cement, sand and water C:S:W = 1:1.5:0.5 has been used for the experiment. The used cement was Portland Cement type CEM II/B – LL 32.5 R; the river sand with specific gravity of 2.69 Mg/m^3 had a particle size of 0–0.6 mm. The specimens were casted in plastic cylindrical molds and put to ripen at room temperature for 28 days.

2.3. Fiber and FRCC characterization

In order to evaluate the morphology and distribution of SiO_2 nanoparticles on PP macro synthetic fibers surface, scanning electron microscopy (SEM) characterizations were performed with Nova NanoSEM 450 SEMFEG (FEI Company, USA). All images were acquired on the PP macro synthetic fibers surface in high vacuum with an In-lens SE detector (Through Lens Detector – Secondary electron mode, TLD-SE) and an accelerating voltage of 2 kV. Chemical elemental analysis was carried out with an X-EDS QUANTAX-200 energy-dispersive X-ray spectroscopy system (Bruker, Germany).

To evaluate the interfacial bond enhancement due to the sol–gel treatment, pullout tests were performed on FRCC specimens. The test configuration (shown in Fig. 2) includes a single-side cement specimen. In order not to damage the fiber and to grip the fiber on the free side easier, the full length wire was used. One end of the wire was dipped in the cement sample for a length L_e, the other end of the wire was dipped in a resin capsule for a length much greater than L_e. In addition, in the latter part, two knots were practiced in order to avoid slip between wire and resin [13,14]. The cement specimen has cylindrical shape with both diameter and length of 80 mm. The diameter of the ring hole is 60 mm, so that no compressive stresses is

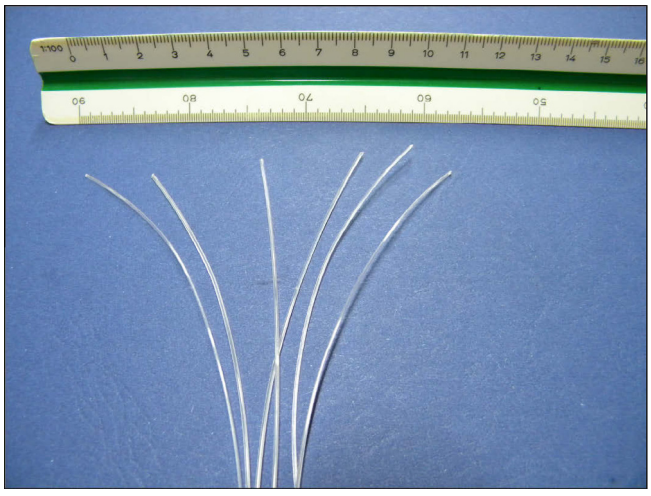

Fig. 1. PP fibers.

Table 1
Characteristcs of PP fibers.

Diameter (mm)	0.78
Length (mm)	30–60
Tensile Strength (MPa)	500
Elastic modulus (GPa)	4