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# Micro- and nanoparticle mineral coating for enhanced properties of carbon multifilament yarn cement-based composites

Roey Nadiv [a], Alva Peled [b, *], Viktor Mechtcherine [c], Simone Hempel [c], Christof Schroefl [c]

[a] Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel
[b] Department of Structural Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel
[c] Technische Universität Dresden, Institute of Construction Materials, Dresden, Germany

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ABSTRACT

The reinforcing efficiency of Textile-Reinforced Concrete (TRC) is often limited by the low penetrability of the cement products into the inner fibers of the multifilament, leading to premature failure of the composite due to low bonding strength. Usually, polymer coatings are applied to carbon yarns to improve their bond properties. However, such coatings are sensitive to elevated temperatures and, in many cases, also to moist and alkaline environments (ageing) and, consequently, the composite material does not perform according to expectations. This paper presents an investigation aimed at improving control of the bonding of carbon multifilament yarn to a cement-based matrix by means of inorganic particle coatings. A carbon multifilament yarn was impregnated by micro- and nano-silica fillers and compared to conventional epoxy-polymer-coated yarns in terms of pullout behavior and microstructure morphology. The micro-silica filler coating proved to be the most efficient, enhancing both pullout strength and toughness, well beyond the effects induced by the nano-silica and epoxy coatings. The superior performance of the micro-silica coating is attributed to the high degree of impregnation of the inter-fiber space by the particles and to the pozzolanic reactions of the silica particles, promoting the formation of beneficial nanocrystalline products within the multifilament yarn. The nano-silica did not show the same effect due to extensive agglomeration and subsequent coating segmentation during the coating's drying process. Although the epoxy polymer effectively coated the fibers, the low penetration of cement hydration products into the yarn resulted in inferior bonding strength compared to that obtained by using the micro-silica coating. It may be concluded that the coating of multifilament yarns with mineral fillers offers an efficient option for improving the performance of TRC materials. As such, it is recommended to use pozzolan particles that disperse well and effectively impregnate the yarns, filling in the bundle spaces.



## 1. Introduction

Over the past two decades, textile-reinforced concrete (TRC) has been extensively studied [1–10]. The notion of reinforcing the cement matrix by means of hundreds of fibers, that can carry the very high stresses induced in the composite and are able to resist crack propagation, is indeed appealing. Many studies have reported the enhanced tensile strength and toughness of such composites [3,11]. However, the low penetrability of cement products into the interior of multifilament yarns hinders the full utilization of fiber strength and often leads to premature failure, due to low bonding both between the individual filaments in the yarn and between the yarn and the cement-based matrix. Subsequently, the stress transfer between a cement-based matrix and its textile reinforcement is often insufficient [12]. The bond quality between the multifilament yarn and the cement matrix is, therefore, a key aspect in manufacturing state-of-the-art TRCs [1,7,12–14].

To tackle this challenge, fiber interface modification by coating is usually employed [7,13,15,16]. For any interface, predominant hydrophobic surfaces should be avoided, in order to obtain the most beneficial interaction between the reinforcement and matrix constituents of the TRC. Polymer coating is a popular choice. It provides enhanced filament-to-filament and cement matrix-to-multifilament yarn bonding and subsequent, enhanced

* Corresponding author.
*E-mail address:* alvpeled@bgu.ac.il (A. Peled).

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mechanical performance [12,13,17]. However, polymer coatings do not perform well in elevated temperatures, especially in cases in which TRC is exposed to fire [17]. Coating the multifilament yarns with thermally-stable particles is, therefore, a promising route towards improving cement matrix-to-multifilament yarn bonding and, thus, the TRC's performance [12,18].

Naturally, nanomaterial coatings have received much attention due to their extraordinary properties and high surface areas [19]. Among the various coating candidates, one finds numerous types of nanomaterials that have already showed positive effects on cementitious systems, including carbon nanotubes [20–23], tungsten di-sulfide nanotubes [20,22], graphene oxide [24], nano-titanium di-oxide [25] and nano-silica [25–28]. Currently, nano-silica seems to be the most practical candidate, considering its availability and pozzolanic potential [19,26].

In this article, the authors study the influence of different coatings on the pullout behavior of carbon-fiber TRC. The physical and chemical properties of the surfaces of these carbon yarns were assessed by wettability and zeta potential measurements. Silica filler coatings in two different scales (sub-micro and nano) were used and their effects were compared to conventional epoxy-polymer coatings. A comprehensive electron microscopy study, supported by energy-dispersive X-ray spectroscopy (EDX), was conducted to assess the particles' dispersion, coating state and the penetrability of the cement products into the interior of the multifilament yarn. Finally, the postulated pozzolanic effect of these particles was evaluated by calorimetry.

## 2. Material and methods

### 2.1. Materials

A commercially-available sample of carbon multifilament yarn (Toho Tenax, yarn fineness 800 tex) was selected for this basic, mechanistic study of textile-reinforced cement-based materials and used as-obtained. A sub-micron-sized silica suspension (termed 'micro-silica'; Emsac 500 SE by Elkem, with a particle diameter of approximately 0.15 μm, according to the provider), a nano-sized silica suspension (termed 'nano-silica'; Dispercoll S 3030 by Bayer, with a particle diameter of approximately 9 nm, according to the provider) and an epoxy polymer (epoxy-ester polymer, developed at Technische Universität Dresden) were used as-received. The matrix was a fine-grained concrete of a mix composition presented in Table 1. The cement was a normal Portland cement, CEM I 42.5 R (Schwenk), according to EN 197-1. A quartz sand (H33 by Euroquartz) and a polycarboxylate-based superplasticizer (MC-PowerFlow 5104 aqueous solution, as obtained from MC Bauchemie) were also used.

### 2.2. Methods

#### 2.2.1. Wettability and zeta potential of the carbon yarns

Wettability and zeta potential were assessed to disclose the physical-chemical surface properties of the carbon yarns. Wettability measurements (Tensiometer K12, Krüss) should disclose the hydrophilic or hydrophobic nature of the yarns' surface. The data recorded from the diluted-cement pore solution (dilution factor 1:10, using deionized water) should shed light on the potential effects of the ionic characteristics in the cementitious environment. The zeta potential was measured in an electro-kinetic analyzer streaming potential device (EKA, Anton Paar) and the raw data were evaluated according to Smoluchowski's equation. The 0.001 mol/L KCl solution served as the electrolyte base. Titrations were conducted with 0.1 mol/L HCl or KOH, respectively, to cover the range from pH 3 to 10.5. Such an experiment discloses the isoelectric point, which indicates the prevailing presence of acidic, basic or uncharged functional groups at the solid-to-liquid interface, in this case, at the yarns' or filaments' surfaces. In addition, extracted cement-pore solution, diluted 1:10 with deionized water, was used to mimic the ionic properties of the construction material in the matrix (pH 11.8, conductivity 170 mS/m). Note that the wettability and zeta potential were not determined here for the coated products for experimental reasons. The inorganic particles would be stripped off and wiped away during such experiments.

**Table 1**
Fine-concrete mix composition.

| | kg/m$^3$ |
|---|---|
| CEM I 42.5R | 861 |
| Sand (0–1 mm) | 1148 |
| Superplactisizer | 9 |
| Water | 287 |

#### 2.2.2. Sample preparation

A filler slurry was prepared by diluting each filler with tap water (1:1 mass ratio). A 5 min sonication (Sonopuls 3100, Bandelin) was employed to ensure adequate filler dispersion. The multifilament yarn's coating process was initiated by immersing the bundle in the filler slurry for 5 min. Then, to allow the filler slurry to efficiently impregnate the interior of the multifilament yarn, the yarn was passed through a special set of rollers that squeeze the filler particles into the bundle and between filaments. The impregnated multifilament yarn was then dried for 24 h before the preparation of samples for the pullout tests, thus, it was in a dry condition when placed into the cement matrix.

At this point, the cement mixture was prepared using a Hobart mixer and mix proportions according to Table 1. First, the dry materials were mixed. Then, the water was gradually added, followed by the addition of the superplasticizer at the final stage, to achieve the proper workability.

Doubly-symmetrical narrowed-prism specimens with defined failure cross-section (by a notch of 1 mm depth) were prepared (see Fig. 1a). At the narrowest part, each specimen was only 5 mm thick, the thickness increasing to 10 mm at the ends. The width of the samples was 50 mm. In each specimen, one multifilament carbon yarn was located on the longitudinal axis of symmetry of the prism. Prior to concreting, the multifilament yarn (either impregnated or the reference sample) was fixed on a stretching frame, to enable its taut embedding into the matrix. Note that the yarn was not tensioned but only aligned. These specimens were manufactured using all-sides-closed molds to prevent unevenness in the quality of cementitious matrix surfaces, thus preventing asymmetric deformations due to drying shrinkage. The specimens were removed from their molds one day after fabrication and placed in a fog room at a temperature of 40 °C and relative humidity of nearly 100% for 4 days, followed by 2 days at constant room condition (23 °C, 60% RH), until tested in double-sided pullout condition on day 7. This curing procedure was performed to reflect on the efficiency of both the mineral and epoxy coatings.

A reference composite sample (Ref) containing non-coated multifilament yarn was also prepared for the sake of comparison.

#### 2.2.3. Pullout test procedure

The efficiency of the coating was estimated by measuring the force needed to pull out a multifilament yarn from a fine-grained concrete sample (see Fig. 1b). Before testing, both ends of the specimen were encapsulated by steel plates, glued by epoxy resin to the sample. By means of these steel plates, the specimens were clamped by steel grips arranged in the testing machine. This stiff