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(Article begins on next page)

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Use of Polypropylene Fibers Coated with Nano-Silica Particles into a Cementitious Mortar

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Abstract. Fiber reinforced cementitious composite (FRCC) materials have been widely used during last decades in order to overcome some of traditional cementitious materials issues: brittle behaviour, fire resistance, cover spalling, impact strength. For composite materials, fiber/matrix bond plays an important role because by increasing fiber/matrix interactions is possible to increase the behaviour of the entire material. In this study, in order to improve fiber to matrix adhesion, two chemical treatments of polypropylene fibers were investigated: alkaline hydrolysis and nano-silica sol-gel particles deposition. Treatmtents effect on fibers morphology and mechanical properties was investigated by scanning electron microscopy (SEM) and tensile tests. SEM investigations report the presence of spherical nano-silica particles on fiber surface, in the case of sol-gel process, while alkaline hydrolysis leads to an increase of fibers roughness. Both treatments have negligible influence on fibers mechanical properties confirming the possibility of their use in a cementitious mortar. Pullout tests were carried out considering three embedded length of fibers in mortar samples (10, 20 and 30 mm, respectively) showing an increase of pullout energy for treated fibers. The influence on fiber reinforced mortar mechanical properties was investigated by three-point flexural tests on prismatic specimens considering two fibers length (15 and 30 mm) and two fibers volume fractions (0.50 and 1.00 %). A general increase of flexural strength over the reference mix was achieved and an overall better behaviour is recognizable for mortars containing treated fibers.

INTRODUCTION

Brittle materials are reinforced since ancient times using fibers, resulting in a composite material. Generally, when the matrix is a cementitious material (cement paste, mortar or concrete) the composite is referred as fiber reinforced cementitious composite (FRCC). Different fibers (glass, steel, carbon, aramid, nylon, polyethylene and polypropylene) have been used according to the aim of the composite. High strength fibers are generally used for structural purposes (toughness increase) while low modulus synthetic fibers are used to avoid shrinkage cracking, concrete spalling and improve impact resistance [1-3].

The composite behaviour is greatly affected by the fiber/matrix bond and the effectiveness of fibers bridging across cracks strictly depends on it. However, synthetic fibers, particularly polypropylene (PP) fibers, are chemically inert into a cementitious matrix. On the one hand, due to chemical inertness, PP fibers are durable in the alkaline environment of a cementitious composite, but on the other hand their poor wettability implies a weak fiber/matrix bond.

The improvement of the fiber/matrix interactions can prevent the fiber/matrix debonding under load. To this aim, several approaches have been studied during last decades. Among them, the interfacial transition zone (ITZ) densification and the physical modification of fibers surface were demonstrated particularly effective. The ITZ densification, especially around fibers, is commonly obtained using low w/c ratios and nanosized additives such as silica fume. It is largely demonstrated, in fact, that nanoparticles are effective in reducing the porosity of cementitious materials [4, 5]. The physical modification of fibers consists in changing the shape of the fibers that can be twisted, crimped, hooked and fibrillated [6, 7]. Fibers mechanical deformation increases fiber/matrix contact area improving friction and thus pull-out resistance. More recently, fibers chemical treatments, oxygen plasma, graft copolymerization of acrylic acid [8], alkaline hydrolysis [9, 14] and nano-silica deposition [10] are attracting growing research interest. Nevertheless, only few authors studied the behaviour of cementitious materials containing such treated fibers and more studies are necessary.

Taking into account the poor adhesion between polypropylene fibers and cement matrix, the aim of this work was to compare two different fibers treatments: alkaline hydrolysis and sol-gel deposition of nano-silica. The effects of the investigated procedures were evaluated by scanning electron microscopy (SEM), single fiber pull-out tests and flexural test on fiber reinforced mortar. Moreover, the influence of chemical treatments on fiber mechanical properties were estimated by fibers tensile tests.

MATERIALS AND METHODS

Fibers and Treatment Methods

Fibers Production

Fibers were produced starting from a polypropylene strand produced by a laboratory scale extruder (BRABENDER DO-CORDER E330, L/D = 24, capillary die of 1 mm). A commercial polypropylene (MOPLEN V79S, Montell Polyolefins) was processed at the following barrel temperature profile: 180°C-220°C-180°C. The extruded filament was cooled into water, drawn and collected by a winder. In this way, polypropylene fibers of two different lengths (l_f, 15 and 30 mm) with an average radius (r) of 0.38 mm were produced. Fibers characteristics and nomenclature are summarized in Table 1.

Alkaline Hydrolysis

A solution with 40 g of NaOH (Sigma-Aldrich) and 100 g of distilled water was prepared. Fibers were maintained in the solution at 95 °C for 2 h and then left for 12 h at room temperature. Elapsed this time, fibers were washed with distilled water (till any alkalinity trace was removed) and dried at room temperature.

Sol-Gel Deposition of Nano-Silica

The sol-gel process involves the synthesis of colloidal suspension of solid particles (sol) in a liquid (gel). The chemical reaction can be divided in two following steps: a precursor reacts with water producing an hydroxyl ion (hydrolysis) then hydrolysed molecules can link together in a condensation reaction, liberating water or alcohol. As this reaction goes on, large molecules containing silicon are created by a process of polymerization. Metal alkolxides are popular precursors and the most used is tetraethyl orthosilicate (TEOS) which chemical formula is $Si(OC_2H_5)_4$. The chemicals used for the sol-gel reaction were: TEOS (99 %, Sigma-Aldrich), ammonium hydroxide solution (28 % NH_3 in H_2O, Sigma-Aldrich), absolute ethanol (Jt Baker) and distilled water. According to the procedure used by Yang et al. [10] fibers were dipped in a mixture of absolute ethanol (200 g), deionized water (20 g) and ammonia water (30 g). Fibers and the mixture were maintained for 10 min at 60 °C and then TEOS (40 g) was gradually added into solution. After 1 h of continuous magnetic stirring, fibers were filtered and dried at room temperature.

Cement and Aggregates

Mortar samples were prepared mixing a Portland cement (CEM II/A-LL 42.5 R) with calcareous sand (particle size 0-2 mm) and water. The mixing procedure and constituents proportion (1:3:0.5, cement sand and water respectively) were chosen according to UNI EN 196-1 [11].

Fibers and Fiber Reinforced Mortar Characterization

Fibers mechanical properties were determined by tensile tests using a universal testing machine (SANS CMT 6000) equipped with a load cell of 1 kN. The tests were carried out at two cross-head speeds: 4 mm/min for determining elastic modulus (E) and 40 mm/min to evaluate tensile strength and strain at failure (σ_b and ε_b). In both cases gauge length was 40 mm. Fibers diameter was evaluated by an optical microscope (Zeiss Axioskop 40) before tensile test. Fibers mechanical properties are reported in Table 2.

The mechanical properties of fiber reinforced mortars were determined by three-point flexural tests according to UNI EN 196-1 [11], three specimens for each mix were tested. Nomenclature of investigated samples is reported in Table 4.

The assessment of the sol-gel treatment effect was achieved by FTIR (Fourier Transform Infrared Spectroscopy); measurements were carried out on pristine and nano-silica coated PP fiber samples in the range of 4000-600 cm^{-1}, using a Nexus ThermoNicolet spectrometer equipped with a SmartPerformer accessory for ATR analysis.

The bond between fibers (treated and untreated) and mortar was analysed using single fiber pull-out tests. In particular, the test configuration consists of single fiber embedded in a 50 mm cubic mortar specimen (Fig. 5). Three embedded lengths of fibers were investigated (10, 20 and 30 mm). Tests were performed by a universal

testing machine (Instron 4301) equipped with a 1 kN load cell at a constant displacement rate of 1 mm/min. Performed pullout tests and results are reported in Table 3.

In order to evaluate nano-silica (SiO_2) morphology and distribution on fibers surface, SEM images were taken. Moreover, using SEM images was possible to assess fiber/matrix ITZ and thus adhesion.

RESULTS AND DISCUSSION

Fibers Characterization

Physico-Mechanical Properties

As reported in Table 1, chemical treatments were not influent on fibers radius while the sol-gel deposition slightly affects fibers density. For PP T2 a negligible increase of density, ρ, (from 0.91 to 0.93 g/cm^3) is recognizable.

TABLE 1. Nomenclature, density (ρ) and radius (r) of fibers

Fiber	Chemical Treatment	ρ (g/cm^3)	r (mm)
PP	-	0.91	0.38
PP T1	Alkalyne hydrolysis	0.91	0.38
PP T2	Sol-Gel process	0.93	0.38

Before to use treated fibers as dispersed phase to produce a cementitious composite, the influence of chemical treatments on fibers mechanical properties was assessed. As reported in Table 2, tensile strength of fibers was not affected by chemical treatments while a low decrease of strain at failure (about 15 %) for PP T1 fibers is recognizable. The slight decrease of ductility is due to material removal from PP T1 fibers surface during alkaline hydrolysis (Fig. 1b). Also fibers elastic modulus is approximatively constant, thus was possible to assess that chemical treatments have no influence on mechanical properties of the fibers.

TABLE 2. Fiber mechanical properties: modulus (E), stress at break (σ_b), elongation at break (ε_b)

Fiber	E (MPa)	σ_b (MPa)	ε_b (%)
PP	895	39	1345
PP T1	1036	45	1173
PP T2	1082	37	1330

Morphology of Fiber Surface

Fiber surface texture and its chemical reactivity with cement paste are the key parameters to have a good fiber/matrix bond. Figure 1a shows the smooth surface of a non-treated PP fiber while Fig. 1b reports the effects of the alkaline hydrolysis. The high aggressiveness of the performed chemical treatment results in the subtraction of fiber surface portions (Fig. 1b). The presence of a superficial roughness contributes at increasing the fiber/matrix interactions offering interlocking positions for cement paste. Whit regard to the sol-gel treatment, Fig. 2a shows the distribution of nano-silica particles on the fiber surface which appear as a powder (which can be well recognizable at naked eye); at higher magnification (Fig. 2b) the spherical shape and low diameter dispersion (with a mean value of 300 nm) of particles is evident.
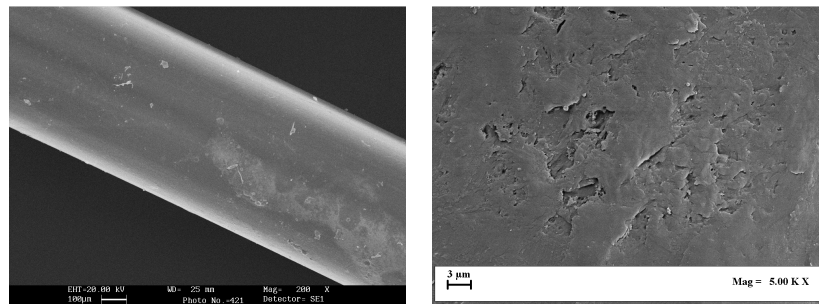

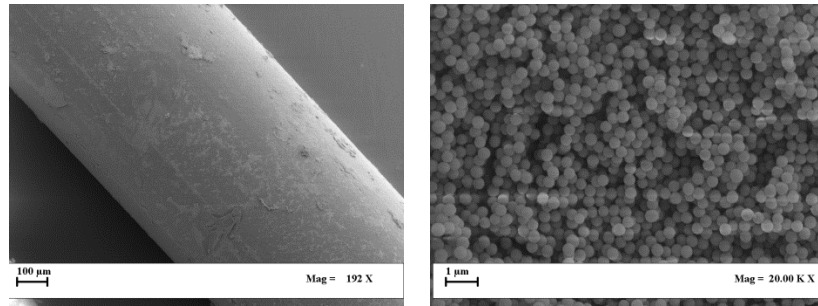**FIGURE 1. (**a) PP fiber and (b) PP T1 fiber surface

FIGURE 2. (a) PP T2 fiber and (b) detail of nano-silica particles on fiber surface

FTIR spectroscopy was performed on PP and PP T2 fibers and the obtained infrared spectra are reported in Fig. 3. The three main absorption peaks characteristic of silica groups appear at 1096 cm^{-1} (asymmetric vibration of Si-O), 948 cm^{-1} (asymmetric vibration of Si-OH) and 808 cm^{-1} (symmetric vibration of Si-O) [12, 13].
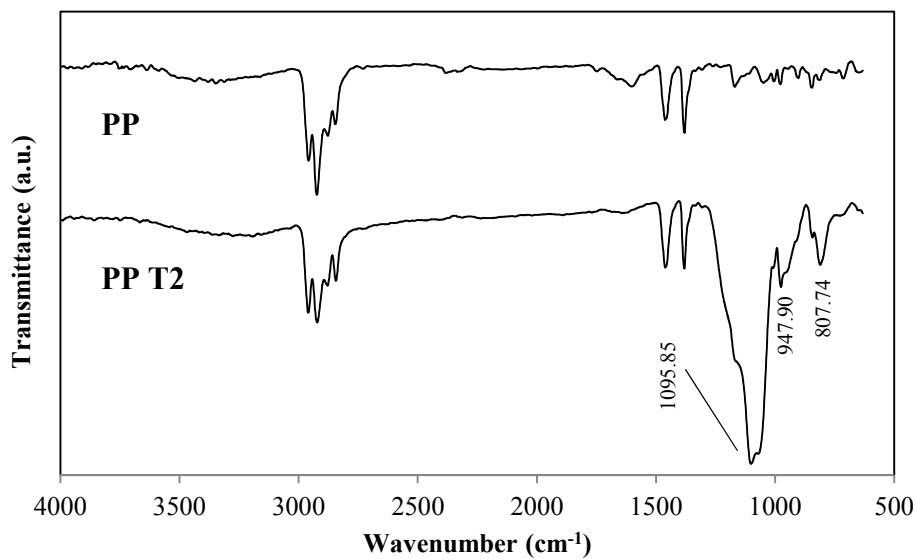

FIGURE 3. Infrared spectra of PP and PP T2 fiber

Fiber/Matrix Interaction

Fiber-Matrix ITZ

SEM is a valid methodology to investigate fiber/matrix interaction and particularly ITZ. The different ways the fibers can interact with the cementitious matrix can be recognized from Fig. 4. The low wettability of pristine PP fibers (Fig. 4a) results in a poor adhesion with the cement paste and the formation of a high porous ITZ [14]. The presence of interlocking positions onto PP T1 fibers (Fig. 1b) contributes to have a less porous ITZ but fiber surface (as in the case of pristine PP fibers) shows a limited presence of hydration products (Fig. 4b). In the case of PP T2 fibers, not only a dense ITZ is recognizable but also the high presence of hydration products on the fiber surface (Fig. 4c) is evident due to the well-known chemical reactivity of silica particles into a cementitious matrix [15, 16].
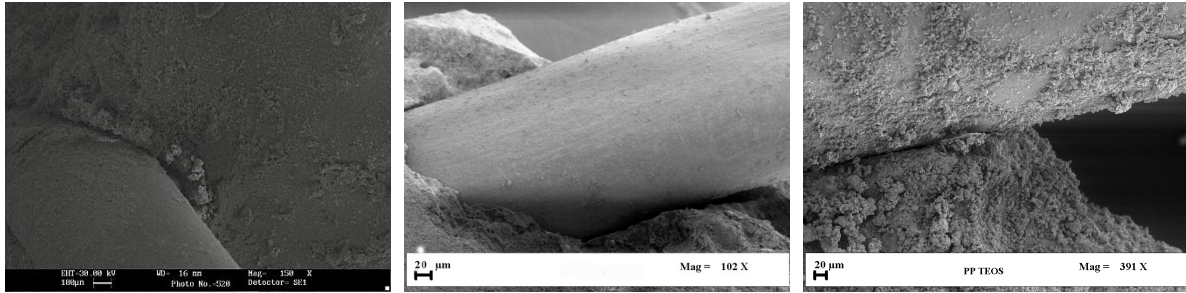
FIGURE 4. Fiber/matrix interfacial transition zone (ITZ) of: **(a)** PP; (b) PP T1 and (c) PP T2, respectively

Pull-Out Test

Pullout tests confirmed the weak interactions between untreated polypropylene fibers and cementitious matrix. Figure 5 shows the complete debonding of a smooth polypropylene fiber while Figs. 6-7 report load vs. displacement curves recorded during pullout tests considering the three investigated embedded lengths: 10, 20 and 30 mm, respectively. The mechanism of fiber pullout consists in two different steps: first, fiber debonding and then fiber slipping. Thus, after the initial linear load/displacement relationship up to a peak load value (clearly recognizable in Figs. 6-7), two potential behaviours are possible: slip-hardening and slip-softening. In the first case, the complete fiber pullout takes places and friction influence is quite negligible; in the second case, after fiber debonding, the slipping resistance contribution is high. At increasing fiber embedded length an increase of friction is achieved. The slip-hardening behaviour corresponds to an increase of pullout energy, i.e. the energy absorbed during pullout, that is the area under pullout curve.
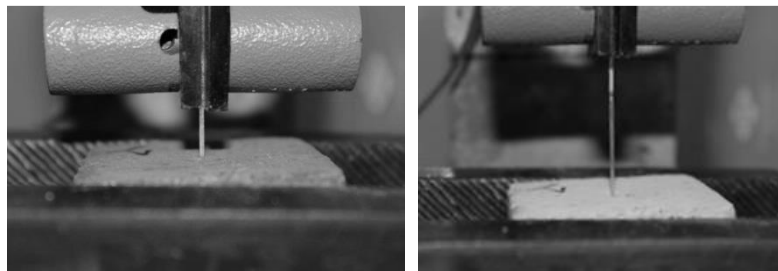

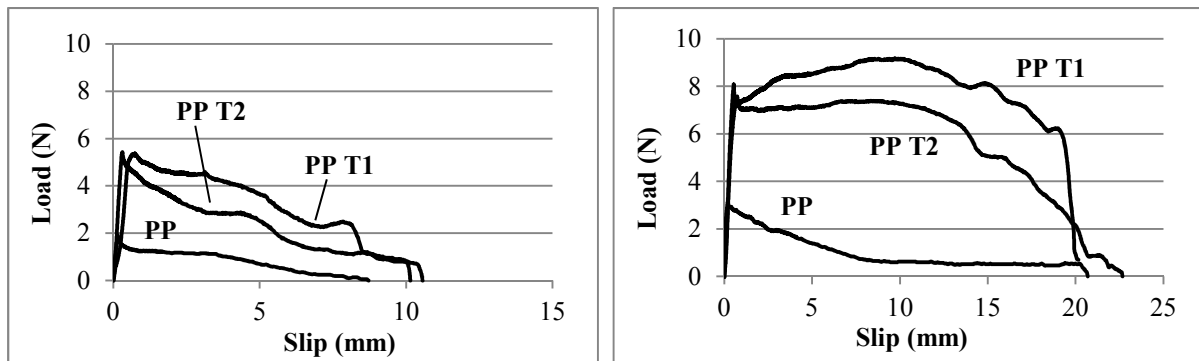**FIGURE 5.** Pullout setup and PP fiber debonding during the test

FIGURE 6. Pullout curves for PP, PP T1 and PP T2: (a) 10 mm and (b) 20 mm of embedment length, respectively
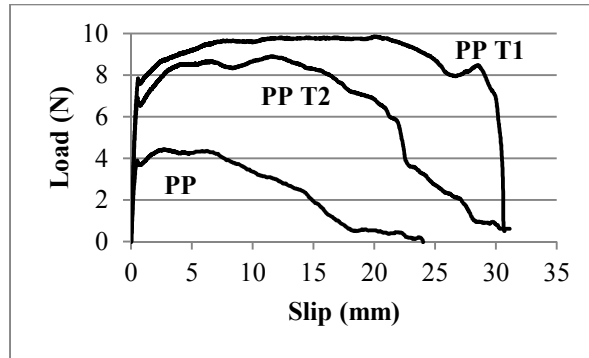
FIGURE 7. Pullout curves for PP, PP T1 and PP T2 (embedment length 30 mm)

The mean values of the pullout peak load (F_{max}), i.e. the load after elastic behaviour, obtained from the pullout test, are reported in Table 3. Both T1 and T2 lead to an increase of F_{max}, having a slight higher value for fibers treated by alkaline hydrolysis. Moreover, also for an embedded length of 20 mm a slip-hardening behaviour is recognizable while PP fibers show a slip-softening mode.

TABLE 3: Maximum pullout load varying fibers and embedded length

Fiber	Embedded length (mm)	F_{max} (N)
	10	1.92 ± 0.15
PP	20	3.57 ± 0.39
	30	3.93 ± 0.75
	10	5.34 ± 0.08
PP T1	20	7.40 ± 0.44
	30	7.54 ± 0.51
	10	4.91 ± 0.33
PP T2	20	6.19 ± 0.40
	30	6.67 ± 0.75

In order to better highlight the influence of the embedded length if the fibers on the pullout peak load, the data of Table 3 are also plotted in Fig. 8. A sharp increase of load is recognizable from 10 to 20 mm (85, 39 and 26 % for PP, PP T1 and PP T2 fibers, respectively). On the contrary, a mild increase of pullout peak load was registered for 30 mm of embedment length. An explanation of this phenomena derives on what stated before: at increasing fiber embedded length a greater friction during pullout is achieved. For an embedded length of 10 mm a slip-softening behaviour occurs (Fig. 6a) while for an embedded length of 20 and 30 mm a slip-hardening behaviour is achieved (Fig. 6b and Fig. 7).
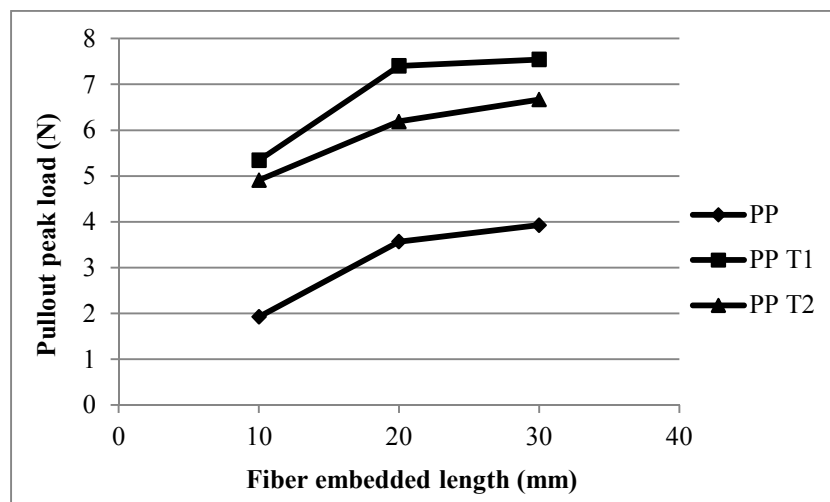

FIGURE 8. Maximum pullout load vs. embedment length

Fiber Reinforced Mortar Flexural Test

In order to investigate the effect of fiber length (l_f), volume fraction (V_f) and chemical treatment on the strength of a FRCC, the different compositions were submitted to flexural tests. The nomenclature and composition of the investigated systems are reported in Table 4, together with the values of the flexural strength R_f. The same R_f values are also reported in graph in Fig. 9, to better compare the flexural behaviour of the mixes.

TABLE 4. Mix nomenclature, composition and flexural strength (R_f)

Mix	Fiber	Fiber Length (mm)	V_f (%)	R_f (MPa)
Reference	-	-	-	7.09 ± 0.33
PP-FRMA15	PP	15	0.50	8.36 ± 0.70
PP-FRMB15		15	1.00	8.57 ± 0.86
PP-FRMA30		30	0.50	9.04 ± 0.16
PP-FRMB30		30	1.00	9.17 ± 0.08
PPT1-FRMA15	PP T1	15	0.50	7.69 ± 0.33
PPT1-FRMB15		15	1.00	9.45 ± 0.42
PPT1-FRMA30		30	0.50	9.52 ± 0.46
PPT1-FRMB30		30	1.00	9.56 ± 0.29
PPT2-FRMA15	PP T2	15	0.50	9.88 ± 0.24
PPT2-FRMB15		15	1.00	9.20 ± 0.54
PPT2-FRMA30		30	0.50	9.09 ± 0.70
PPT2-FRMB30		30	1.00	9.74 ± 0.77

As shown in Fig. 9, a general increase of flexural strength (R_f) over the reference mix was achieved. As expected, at increasing fiber volume fraction higher flexural strengths were obtained. On the contrary, fiber length was not particularly influent. As mentioned before, fiber chemical treatments improve fiber/matrix adhesion resulting in an increase of flexural strength for mix containing treated fibers compared to mix containing untreated fibers. Moreover, slight higher values of flexural strength were reported for mortars containing PP T2 fibers respect mixes with PP T1 fibers. Thus, the presence of nano-silica particles on fibers surface strengthens fiber/matrix bond resulting in a better transmission of stresses among matrix and fibers.
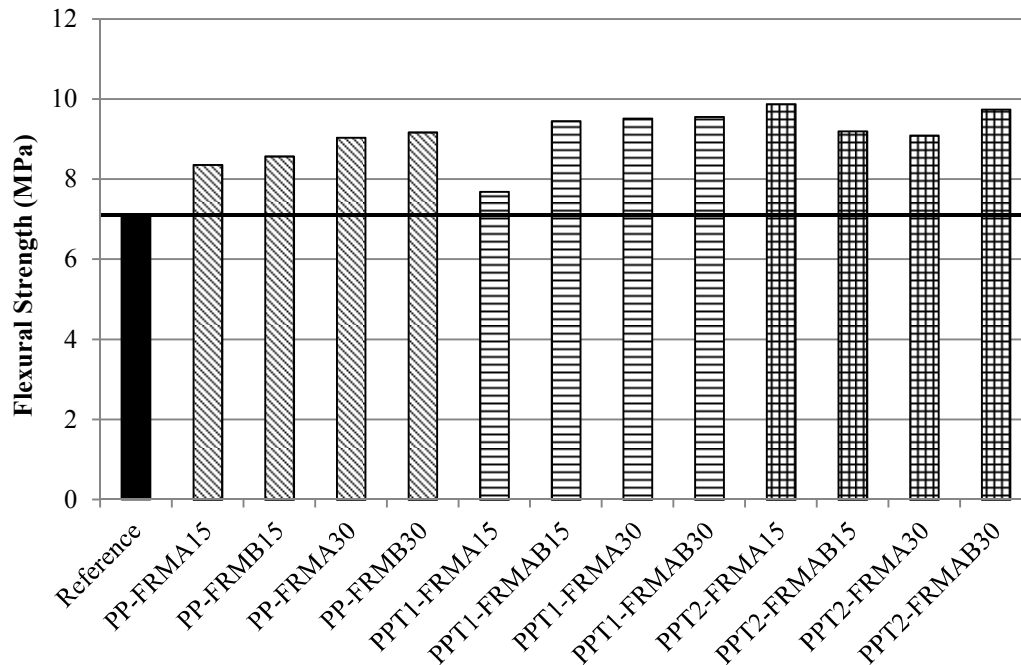

FIGURE 9. Comparison of fiber reinforced mortars flexural strengths

CONCLUSIONS

The aim of this work was to improve the adhesion between polypropylene fibers and cementitious mortar. The poor wettability of PP fibers results in a weak bond with the cement paste and thus mechanical or chemical treatments are necessary to improve fiber bridging ability in stress transfer.

In this study, two chemical treatments have been investigated: alkaline hydrolysis and nano-silica sol-gel particles deposition. SEM images revealed that alkaline hydrolysis increases fibers roughness while tensile tests reported a slight decrease of fibers ductility. On the contrary, sol-gel process produces nano-silica spheres particles on fibers surface and mechanical properties are not affected.

SEM pictures of ITZ reveal a poor adhesion between PP fibers and cement paste, a very porous ITZ and the absence of hydration products on fiber surface. Also for PP T1 fibers the surface is quite free of hydration products but the presence of interlocking positions contributes to have a less porous ITZ. In the case of PP T2 fibers, not only a dense ITZ is recognizable but also the high presence of hydration products on the fiber surface.

Pullout tests confirm the better performances of treated fibers: an higher pullout peak load is achieved and an increase of pullout energy is clear considering the slip-hardening behaviour showed by PP T1 and PP T2 fibers. Also bending tests report an increase of fiber reinforced mortar over the unreinforced mortar. Slight higher values of flexural strength were reported for mortars containing PP T2 fibers respect mixes with PP T1 fibers.

Thus, the interesting results confirm the promising application of nano-silica treated fibers for improving fiber/matrix interactions. The presence of nano-silica particles not only reduces the ITZ porosity, as shown by SEM analysis, thus giving beneficial effects on mortar durability, but also improves the fiber/matrix bond increasing the stress transfer, i.e. the fiber reinforced mortar strength.

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