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Degradation of recycled PET fibers in Portland cement-based materials

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Abstract

In order to investigate the durability of recycled PET fibers embedded in cement-based materials, fiber-reinforced mortar specimens were tested until 164 days after mixing. Compressive, tensile, and flexural strengths, elasticity modulus, and toughness of the specimens were determined. The mortars were also analyzed by SEM. The results have shown that PET fibers have no significant influence on mortars strengths and elasticity modulus. However, the toughness indexes I_5, I_{10}, and I_{20} decreased with time due to the degradation of PET fibers by alkaline hydrolysis when embedded in the cement matrix. Fourier transform infrared spectroscopy (FT-IR) and SEM analysis of PET fibers immersed and kept for 150 days in alkaline solutions supported the conclusions.

Keywords: PET fiber reinforcement; Degradation; Portland cement; SEM; FTIR

1. Introduction

Fiber-reinforced mortars (FRM) and concretes (FRC) have been studied for many years, specially after the banning of asbestos fibers, because the addition of fibers to mortars and concretes can modify many of their properties, such as tensile strength, elasticity modulus, and toughness.

The addition of small volume fractions of synthetic fibers (up to 2%) to the mixture can improve the toughness of mortars and concretes [1]. Many synthetic fibers are currently used to produce FRMs and FRCs, such as polypropylene (PP), polyethylene (PE), nylon, aramid, and polyesters. The poly(ethylene-terephthalate) fibers (PET) belong to the polyester group, and can be obtained from the recycling of PET bottles, which take more than 100 years to completely degrade. Thus, the use of PET fiber-reinforced cement-based materials is an effective contribution for environment preservation. They are normally used in the monofilament form, are hydrophobic, and do not have any effects on the hydration of Portland cement [2].

In order to improve mortars and concretes behavior, the fibers: i) must be easily dispersed in the mixture; ii) must have suitable mechanical properties; and iii) must be durable in the highly alkaline cement matrix [1]. However, there is no agreement about the durability of PET fibers in Portland cement matrix. According to some researchers [3–5], polyester fibers degrade when embedded in Portland cement matrix. On the other hand, Wang et al. [3] and the ACI 544.IR-96 [2] reported good performance of PET fiber-reinforced mortars and concretes.

The main purpose of this research is to investigate the durability of recycled PET fibers embedded in Portland cement-based materials. To achieve this goal, the behavior of mortar specimens was evaluated after 164 days through physical and mechanical tests, such as compressive and flexural strengths, elasticity modulus, and flexural toughness. Scanning electron microscopy allowed the authors to visualize the degradation of the fibers. Moreover, chemical studies on the fibers through Fourier transform infrared spectroscopy were also performed after exposition to aggressive solutions.

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2. Experimental procedure

Two distinct experimental procedures were adopted to investigate the degradation of the fibers in cement-based materials. In the first one, the fibers were analyzed by infrared spectroscopy and scanning electron microscopy (SEM) after their exposition to alkaline solutions, partially following the experimental procedure suggested by [6]. In the second procedure, specimens of fiber-reinforced mortar were produced and tested to determine some mechanical properties, such as compressive strength, tensile strength, flexural strength, elasticity modulus, and toughness. SEM was used to analyse the fibers inside the mortars 164 days after their production.

The PET fibers used in this research are a subproduct of a factory that recycles PET bottles to produce ropes. The fibers were added to the mortars mixtures as monofilaments with around 26 μm diameter and 20 mm length (aspect ratio=769). Table 1 presents the characteristics of the PET fibers investigated in this research, and Fig. 1 shows a fiber in a magnification of 1500 times.

In order to investigate the durability of the fibers in alkaline environments, they were immersed into the following solutions for 150 days at 5, 25, and 50 °C: $Ca(OH)_2$ saturated solution (pH=12.3), 0.1 M NaOH (pH=13), and Lawrence solution (0.48 g/l $Ca(OH)_2$+3.45 g/l KOH+0.88 g/l NaOH, pH=12.9). The latter solution is an estimation of the pore water composition of a fully hydrated cement paste, according to [4].

A Fourier transform infrared spectrometer Perkin-Elmer 16PC was used to analyse the fibers after the exposition to the alkaline solutions. To enable the analysis in pellets, the fibers were finely cut and mixed to KBr. The spectra were traced in the range 4000–400 cm^{-1} (wave number), and the band intensities were expressed in transmittance (% T).

The microscopy was performed in a Philips SEM XL-30 microscope equipped with an energy-dispersive X-ray analyser (EDXA). To obtain a conductive surface for the analysis, a thin gold layer was deposited on the fibers surface.

Table 2 presents information on the materials used for mortar production. Portland cement and medium-grade quartz sand (2.4 mm maximum diameter) were used.

Table 1
Characteristics of PET fibers

Physical properties determined by DSC[a]	Melting temperature (°C)	252.8
	Crystallization temperature (°C)	95.0
Mechanical properties determined in accordance with ASTM D 3822-96	Tensile strength (MPa)	323.5
	Total elongation (%)	70.7
	Yield stress σ_y (MPa)	196.4
	Elongation at σ_y (%)	7.18
	Elasticity modulus (MPa)	41.8
	Toughness (MPa)	17279.0

[a] Differential scanning calorimetry, heating rate 10 °C/min, 50 ml/min N_2.

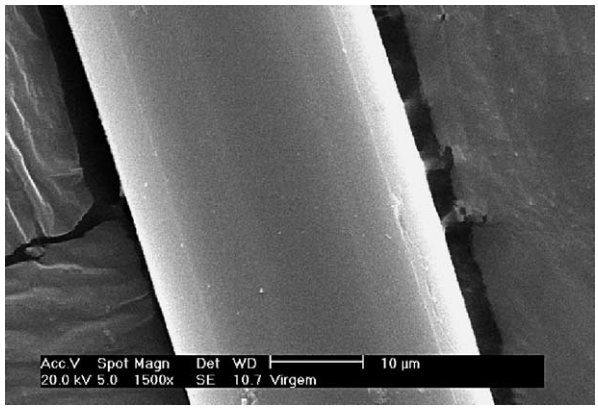


Fig. 1. Aspect of the recycled PET fiber observed in SEM.

The mixing proportions were 1:3 (cement:sand, in weight basis), and the water/cement ratio was kept constant at 0.61. Deionized water was used to produce the mortars.

The mortar specimens were moulded and kept in lime water for 14 days before the exposition to the laboratory environment. At the ages 42, 104, and 164 days old, the mortar specimens were tested in compression and tension (split tensile test) according to the Brazilian standards (specimens are cylinders 50 mm diameter and 100 mm height) [7,8], and in flexure according to the standard ISO/DIS 679 method [9] for the determination of the flexural strength, the elasticity modulus, and the toughness of the specimens. According to this method, the flexural strength (σ, MPa) is determined using Eq. (1), where P is the applied load (N), L is the span between the supports (mm), b is the

Table 2
Details on materials and proportions for the production of the fiber-reinforced mortars

Cement type	Mortar 1	Mortar 2
	CPV ARI[a]	CPII F 32[b]
Content of fibers (%vol.)	0.4	0.8
Geometry of specimens	Cylindrical, 50 mm diameter, 100 mm height	Prismatic, 20×40×160 mm
Tests	Compression and splitting tensile tests	Flexural load deflection test
Results	Compressive strength and splitting tensile strength	Tensile strength in flexural Toughness Elasticity modulus
Time of curing in lime water after mixing	14 days	14 days
Time of curing at ambient conditions (T=±23 °C, 85% RH)	28, 90, and 150 days	28 and 90 days

[a] CPV ARI is a high early-strength Brazilian cement in accordance to the Brazilian standard NBR 5733/91, and is equivalent to ASTM cement type III.

[b] CPII F is an ordinary Portland cement with up to 15% of ground limestone in accordance to the Brazilian standard NBR 11578/91.

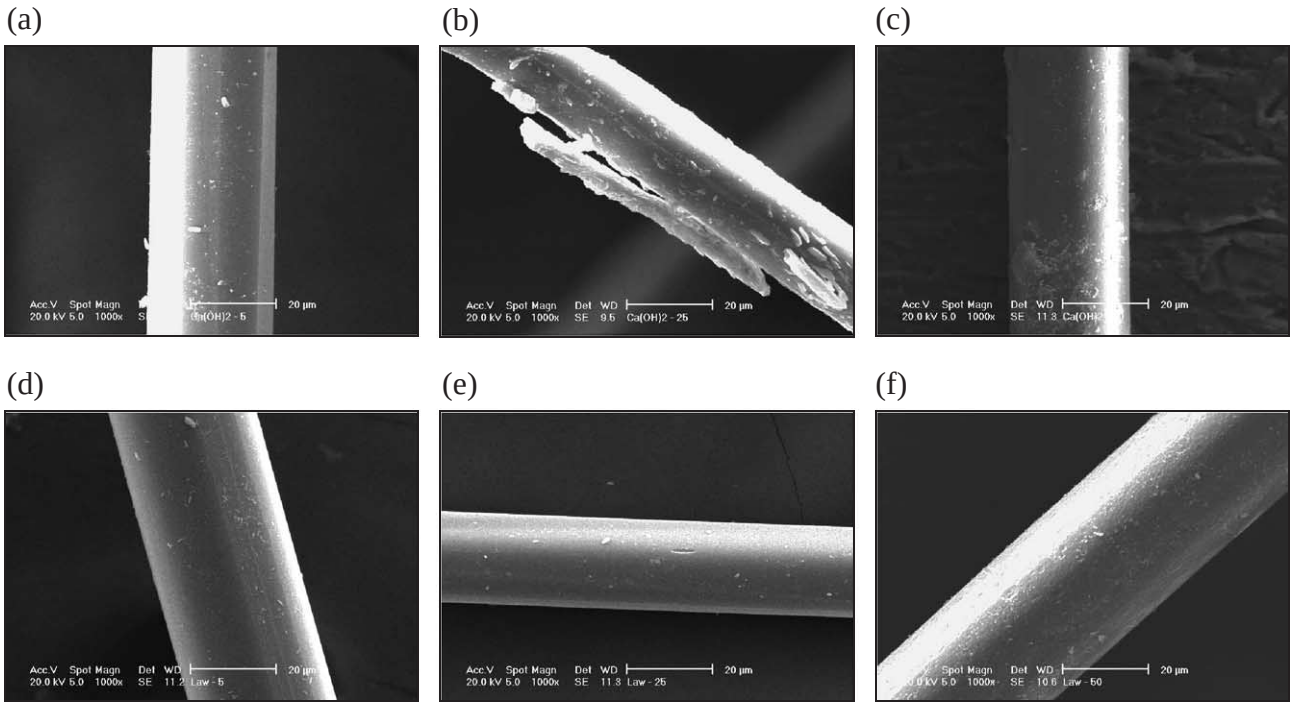


Fig. 2. Micrographs showing the aspect of the PET fibers after 150 days of immersion in $Ca(OH)_2$ solution at (a) 5 °C, (b) 25 °C, and (c) 50 °C, and in Lawrence solution at (d) 5 °C, (e) 25 °C, and (f) 50 °C.

largest cross-section dimension (mm), and h is the height of the specimen (mm).

$$\sigma = \frac{1.5PL}{bh^2} \quad (1)$$

Eq. (2) was adopted to determine the elasticity modulus (E, MPa) of the specimens, whose value was obtained from the declivity of the secant line at 5% and 30% of the ultimate strength on the graph stress (σ, MPa)×strain (ε, mm/mm) [10]. The elastic–linear behavior was consider for the calculus.

$$E = \frac{(\sigma_{30} - \sigma_5)}{(\varepsilon_{30} - \varepsilon_5)} \quad (2)$$

Toughness indexes were calculated from the stress×strain curves according ASTM C 1018/94 [11] (i.e., I_5, I_{10}, and I_{20} indexes, which are the numbers obtained by dividing the integrated area up to a deflection of, respectively, 3.0, 5.5, and 10.5 times the first-crack deflection by the integrated area up to first crack).

The fracture surfaces of mortar fragments obtained from the flexural test were analyzed by scanning electron microscopy (SEM), in order to detect any evidence of degradation of the fibers inside the cement matrix. The fragments were dried over silica gel under vacuum and coated with a thin gold layer to improve the surface conductivity.

Three or four specimens of each mortar were tested in compression, tensile, and flexural tests, and the results were statistically analyzed by the analysis of variance method (ANOVA).

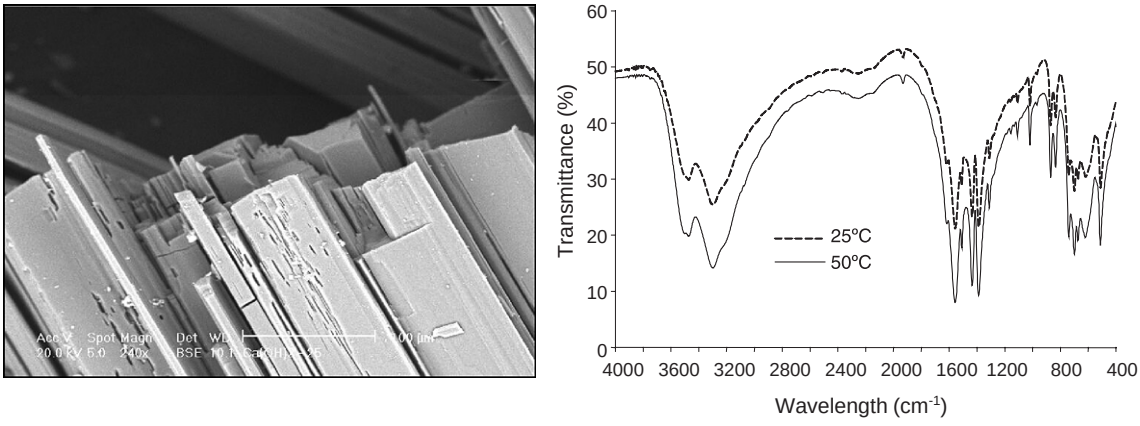


Fig. 3. Micrograph and infrared spectrum of the precipitated phase in $Ca(OH)_2$ solution after immersion of PET fibers for 150 days at 25 and 50 °C.

3. Results and discussion

Infrared spectroscopy and scanning electron microscopy did not allow the identification of any degradation process of PET fibers immersed in 0.1 M NaOH, regardless the temperature of the solution. However, in both Lawrence and $Ca(OH)_2$-saturated solutions, some particles precipitated in the bottom of the recipients during the 150 days of fibers immersion. There were few evidences of degradation of the fibers, as can be seen in the micrographs shown in Fig. 2. The infrared spectra and SEM micrographs of the precipitated phases are presented in Figs. 3 and 4.

The spectra shown in Figs. 3 and 4 have quasi-identical same bands and intensities, which could lead to the conclusion that the precipitated phases in $Ca(OH)_2$ and Lawrence solutions are the same (i.e., Ca-bearing phases) even though the morphology is different.

Comparing the infrared spectrum of the fiber before the immersion in the solutions (Fig. 5) with the spectra shown in Figs. 3 and 4, it is possible to observe that many bands from PET are present in the spectra from the precipitated phases (1930, 1508, 1018, 870, and 696 cm^{-1}), which are assigned to the aromatic ring of the polymer. Besides such bands, new bands at 3462, 3286, 2228, 1554, 1434, 1386, 834, 738, and 606 cm^{-1} appeared, indicating some interactions between PET and the alkaline solution.

The spectra shown in Figs. 3 and 4 are typical Ca, Na, or K terephthalate spectra. According to Ref. [4], the mechanism of chemical degradation of PET fibers consists in a depolymerization reaction that breaks the polymer chain. The ions Ca^{2+}, Na^{+}, K^{+}, and OH^{-} attack the C—O bonds of PET and split the polymer in two groups: the group of the aromatical ring and the group of aliphatic ester. Alkali ions and hydroxyls fix themselves to those groups, respectively. The products of such interaction are Ca, Na, and/or K-terephthalates and ethylene glycol.

The results from compressive and tension tests were statistically analyzed through the analysis of variance. The presence of fibers practically had no influence on the compressive and tensile strengths of the mortars. These

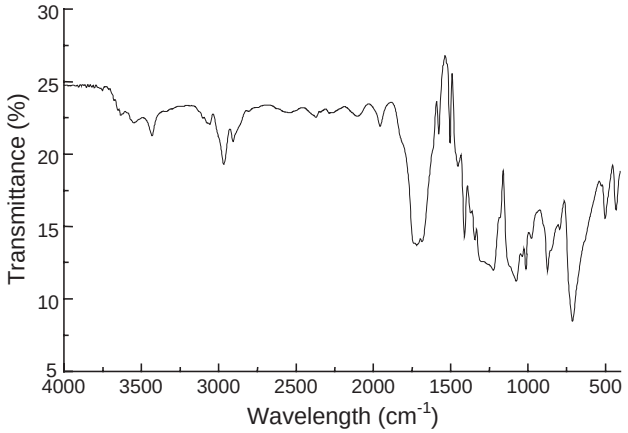


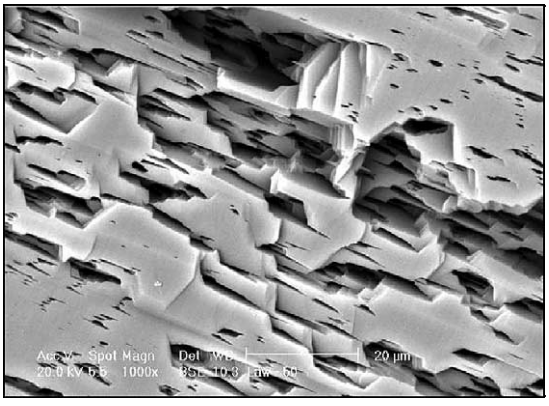
Fig. 5. Infrared spectrum of unattacked PET fiber.

results are in accordance with previous findings developed on low-volume PET fiber-reinforced cement-based materials [4,12]. The main factor that has significant effects on the results is the age of the specimens, as shown in Fig. 6.

The analysis of variance (ANOVA) showed that the fibers do not influence the tensile strength and the elasticity modulus of the mortars in flexural test, since the strength of the composite to the first crack usually is close to the resistance of the material without fiber reinforcement.

Analysis of variance of the area under the stress×strain curves was carried out in order to evaluate the effect of the fibers on the toughness of the mortars. Therefore, the effect of the fibers on the toughness up to the first crack and on I_5, I_{10}, and I_{20} indexes could be evaluated. As expected, the fibers had no influence on the toughness of the mortars up to the first crack, since they do not affect both the ultimate strength and the elasticity modulus. On the other hand, the toughness indexes could not be measured in non-reinforced mortars since they failed in a fragile way as soon as the first crack appeared.

Fig. 7 illustrates the effect of age on the toughness indexes of the mortars. For a conventional mortar, an increase of the toughness would be expected due to the



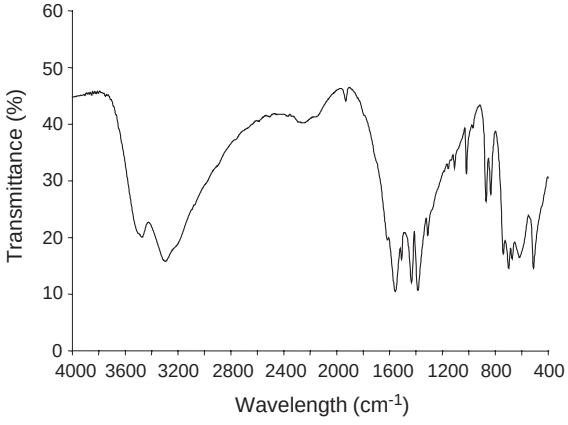


Fig. 4. Micrograph and infrared spectrum of particles precipitated in Lawrence solution after exposition of PET fibers for 150 days at 50 °C.

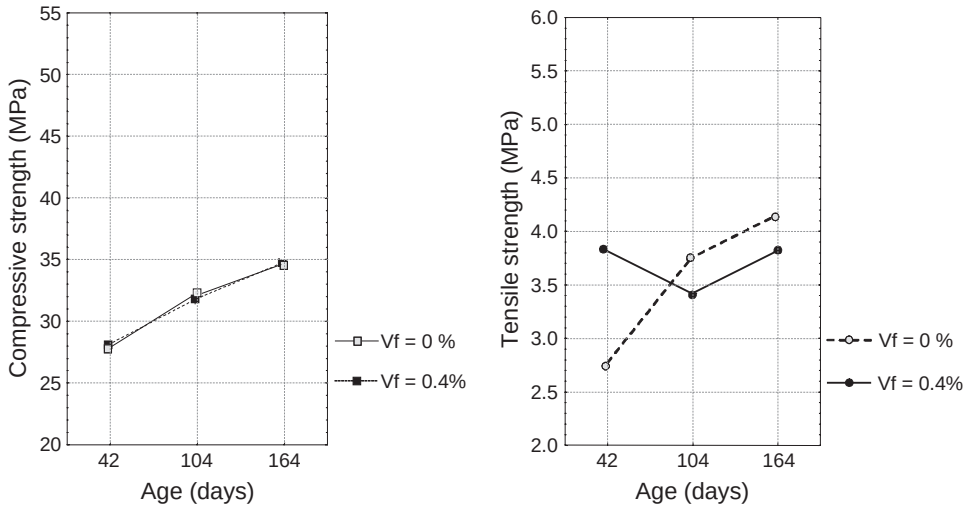


Fig. 6. Compressive and splitting tensile strengths of PET fiber-reinforced mortars.

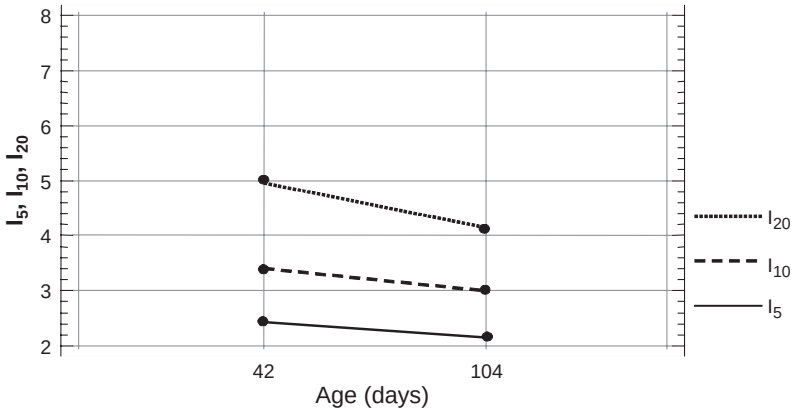


Fig. 7. Effect of age on toughness indexes of PET fiber-reinforced mortars.

higher hydration degree of the cement with elapsed time. However, the toughness of the PET fiber-reinforced mortars decreases with the age, as can be seen in the figure. This overall effect is attributed to the degradation of the fibers inside the mortars.

The results shown herein are in accordance with other researches who carried out accelerated tests of durability in alkaline environment with some types of fibers and concluded that the toughness of polyester fibers decreases with time [13]. Pelisser [12] worked with different contents

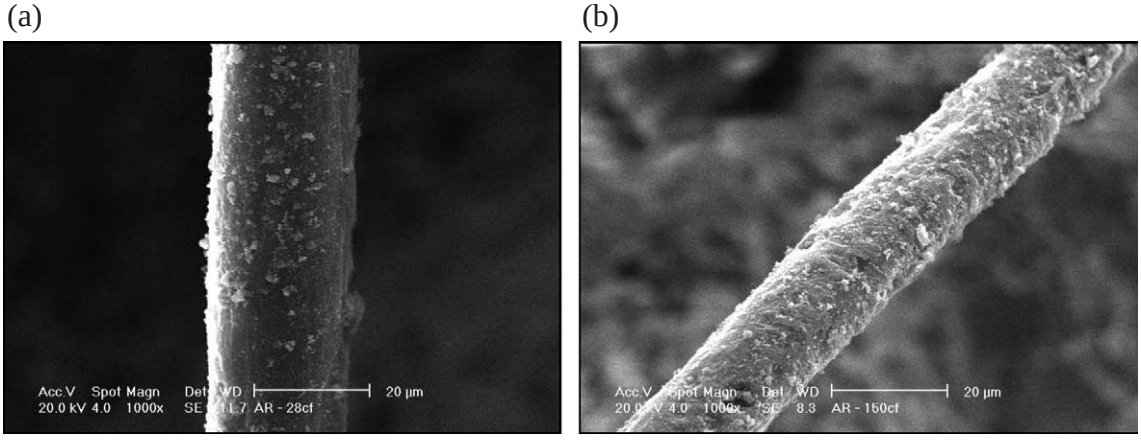


Fig. 8. Aspect of the PET fiber mortar after 42 (a) and 164 (b) days of hydration.

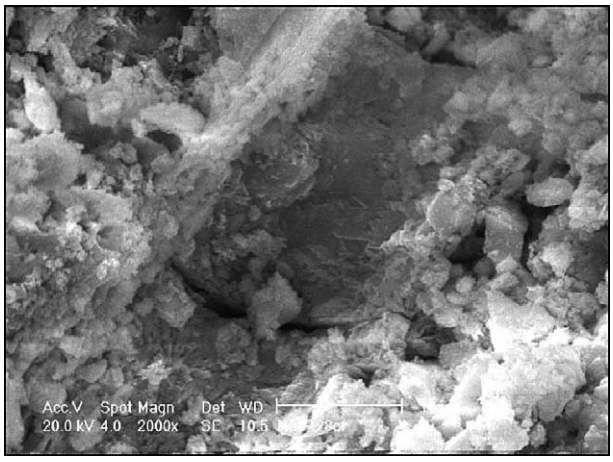


Fig. 9. Fiber bed in mortar.

of PET fibers in concrete and got the highest toughness for a concrete 35 days old, compared to others up to 150 days old.

Fig. 8 shows micrographs of the fibers inside the mortars after 164 days. As can be seen, the surfaces of the fibers appear quite rough, indicating that the fibers suffered some attack from the cement paste matrix. In some regions of the specimens, only the spaces previously occupied by the fibers could be observed (Fig. 9), due to their total degradation or pull-out during the tests.

4. Conclusions

From the infrared and microscopic analysis performed on PET fibers and from the mechanical tests on PET fiber-reinforced mortars, it was possible to conclude that:

(a) Recycled PET fibers interact with $Ca(OH)_2$ and Lawrence solutions. Their surface becomes rough and there is the precipitation of phases identified as alkaline terephthalates.
(b) The tested amount of PET fibers (0.4 and 0.8% vol.) has no effect on compressive, tensile, and flexural strength of mortars, as well as their degradation inside the composite.
(c) The elasticity modulus of mortars is not affected by the amount of PET fibers investigated in this research (0.8% vol.), as expected.
(d) The toughness of mortars in flexural tests increases when fibers are present. However, due to the degradation of fibers inside the mortars, the toughness decreases with time.
(e) SEM micrographs allowed the observation of the degradation degree of fibers inside the mortars after up to 164 days. All the fibers analyzed have shown some degradation observed by the surface roughness. In some regions, the complete degradation of the fibers can occur.

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