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Microstructural analysis of the bond mechanism between polyolefin fibers and cement pastes

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Abstract

This paper presents an investigation of polyolefin bond mechanisms in shotcrete. Polyolefin fibers were characterized in terms of their mechanical properties and microstructure. Effects of hydration reaction and of the mixing of fibers on the bond between the fiber and the paste were investigated in both the concrete mixture and its pore solution. Three cement types commonly used in the field were tested. Test results using scanning electron microscopy (SEM) analysis showed that the morphology of the fiber changes with cement hydration and mixing.

Keywords: Fiber reinforcement; SEM; Transition zone; Microstructure; Polyolefin fiber

1. Introduction

To improve certain concrete properties, such as toughness and tensile strength, fibers are introduced in the concrete mixture [1–3]. The property investigated to obtain good mechanical behaviour is the bond between fibers and cement paste. Different types of fibers are generally used, such as steel or organic materials. Fibers differ according to shape, length, superficial roughness, etc.

Polyolefin fibers present a cylindrical shape with a smooth surface. Because of this smoothness, bond with the paste seems to be more difficult to achieve than with steel fibers [4]. Despite this phenomenon, concrete-containing polyolefin fibers display a good toughness and tensile strength, which is of great interest for shotcrete applications. The latter is a concrete or mortar that is pneumatically projected at a sufficient velocity to achieve proper in-place compaction. Polyolefin fibers have a much higher impact/static strength ratio and toughness factor than do steel fibers [5,6].

A dock in the Port of Montreal was repaired using two shotcrete mix designs: one with polyolefin fibers and another with steel fibers (Table 1) [7]. During preliminary tests, a tensile strength of 5.5 MPa, determined from a flexural test (ASTM C1018) after 7 days of hydration, was obtained for a shotcrete reinforced with polyolefin fibers. In the mix design, 11.4 kg/m^3 of fibers was used, which corresponds to 2% of total volume. On site, this concrete showed flexural results similar to those obtained for the same reinforced concrete, but with 60 kg/m^3 of steel fibers (Table 2) [7]. Nevertheless, at 28 days, polyolefin fibers present a lower toughness than do steel fiber, although it becomes equal at 180 days [7].

The aim of this research is to understand the bond mechanism between polyolefin fibers and cement paste. The evolution of the microstructural and morphological structure of fiber surfaces was characterized using conventional scanning electron microscopy (SEM). Various types of cement were used in this study. The polyolefin fiber was kept in the pore solution extracted from the cement paste at different hydration periods. This solution corresponds to the pore solution in the concrete. Moreover, the effect of mixing on the superficial roughness of the fiber was also evaluated.

2. Materials and method

2.1. Description of polyolefin fibers and mixture proportion

Polyolefin fiber is a polymer obtained from polypropylene ($CH_3CH=CH_2$) and polyethylene ($H\text{-}CH_2-\ldots-$

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Table 1
Mix design

Materials and characteristics	Unit	Polyolefin fibers	Steel fibers
Cement Type HSF	kg/m^3	430	430
Silica fume	kg/m^3	30	30
Sand	kg/m^3	1170	1170
Coarse aggregate	kg/m^3	390	390
Water	l	180	180
Superplasticizer	l	5.5	5.5
Polyolefin fibers (Type 3M)	kg/m^3	11.4	
Steel fibers (Dramix)	kg/m^3		60
Water/cementitious material ratio (W/CM)		0.40	0.40
Coarse aggregate/ total aggregate		0.25	0.25
Specific gravity		2.21	2.21

Table 2
Mechanical results

Flexural strength (MPa)	Concrete with steel fibers	Concrete with polyolefin fibers
28 days	5.2	5.8
91 days	6.6	6.2
180 days	6.8	7.4

CH_2-H). The characteristics of polyolefin are given in Table 3. The diameter and length of the fiber are 0.38 and 25 mm, respectively. The scanning electron micrograph presented in Fig. 1 shows the typical surface of a polyolefin fiber. The surface is smooth and does not present any roughness.

Three types of cement were selected for this study: Canadian Type 10, Type 30 and Type 10SF (incorporating 7% silica fume). The chemical and phase compositions of these different cements are given in Table 4. For these cements, a paste with a water/binder ratio equal to 0.4 was made with 2% polyolefin fiber (compared with total paste volume). Fibers were extracted from the paste after 5 min and after 2 h of cement hydration. A second series of samples was prepared in a nitrogen atmosphere to avoid carbonation. Thus, the only way to create $CaCO_3$ is through a reaction between the lime contained in the cement and the carbon in the fiber.

Table 3
Fiber characteristics

Characteristics	Unit	Value
Density		0.91
Tensile strength	MPa	257
Elastic modulus (E)	GPa	2.6
Strain failure (lengthening)	%	15
Inflammation point	°C	593
Plasticizing point	°C	160

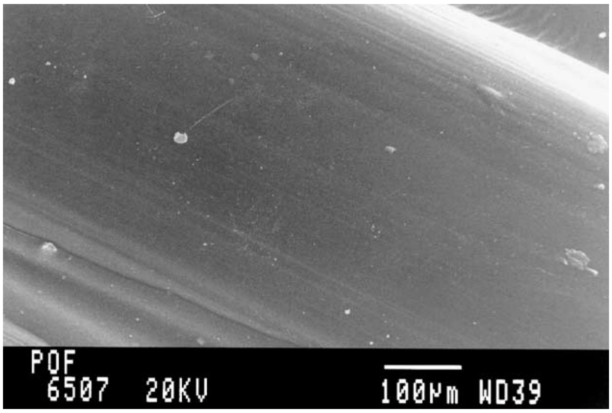

Fig. 1. SEM micrograph of a polyolefin fiber's surface.

2.2. Pore solution and the lime-saturated solution

The pore solution is obtained by filtering the different cement pastes (described previously) with the help of a vacuum pump and a filter paper. The pore solution is extracted after 5 min (Solution A) and 2 h (Solution B) of hydration. Fibers are then submerged in the two solutions and kept in a sealed glass tube for 72 h to avoid contact between the air (CO_2) and the lime. When fibers are removed from Solutions A and B, they are first rinsed by dipping them in distilled water for a few seconds. Afterwards, the fibers are dried at 60 °C for 24 h and gold–palladium coated for SEM analysis.

To show the effect of lime concentration on the surface of the fiber, a lime-saturated solution was prepared. Fibers were submerged in this solution for 5 min and for 2 h. The same procedure was maintained for the SEM analysis.

2.3. Mixing of the fibers in the concrete

To evaluate the effect of mixing on the surface of the fiber, 60 kg of concrete was made with 2% of fibers (compared with total concrete volume) in a concrete mixer. Table 1 presents the concrete mix design. The maximum

Table 4
Chemical and phase composition of the cements

	Cements	T 10	T 30	10 SF
Chemical composition (%)	SiO_2	20.3	20.8	26.7
	Al_2O_3	4.4	4.8	4.5
	Fe_2O_3	2.9	2.1	1.9
	CaO	62.1	63.6	58.7
	MgO	2.7	2.9	2.5
	SO_3	3.2	3.6	2.6
	$Na_2O_{equ.}$	1.07	0.81	0.67
Blaine fineness (m^2/kg)		410	500	560
Phase composition (Bogue) %	C_3S	55.6	55.2	N/A
	C_2S	16.1	18.0	N/A
	C_3A	6.7	9.2	N/A
	C_4AF	9.1	6.4	N/A

N/A—not applicable.

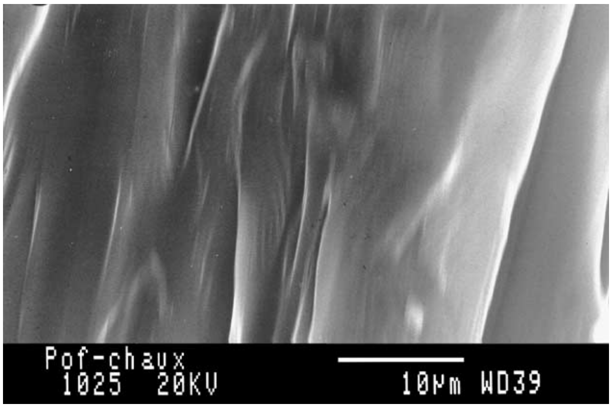

Fig. 2. Surface of a fiber submerged in a lime-saturated solution for 5 min.

size of the coarse aggregate was 20 mm. Silica fume was used as partial replacement, at 7 wt.% of cement. The total quantity of silica fume in the mixture (quantity added and contained in the cement) is relatively large (about 14% of cement mass). This silica fume concentration allows for improvement of concrete stiffness by increasing viscosity and bond conditions of the shotcrete during projection on the substructure.

To separate the chemical and mechanical effects of cement grains on the fiber's surface during mixing, another mixture was performed in which cement was substituted with limestone filler, with and without silica fume. Mixing was performed for 5 min, with two 30-s breaks. The fibers were then extracted from the concrete and characterized using SEM analysis.

3. Results

3.1. Polyolefin fibers in a lime-saturated solution

When the fiber is submerged for 5 min in a lime-saturated solution, the surface is slightly etched (Fig. 2). After 2 h of immersion in the solution, the damage is a little more important than after 5 min (Fig. 3). However, the reaction between the fiber and the lime is very small so that fibers used can be considered inert in a lime-saturated water medium.

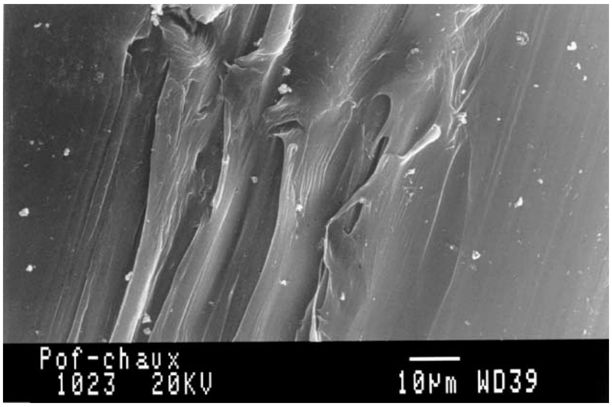

Fig. 3. Surface of a fiber submerged in a lime-saturated solution for 2 h.

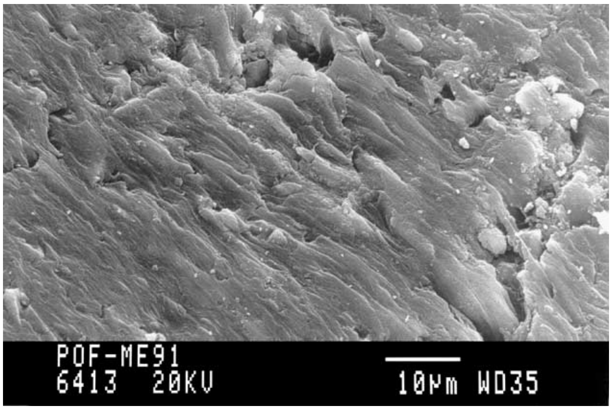

Fig. 4. Surface of a polyolefin fiber taken from Solution A.

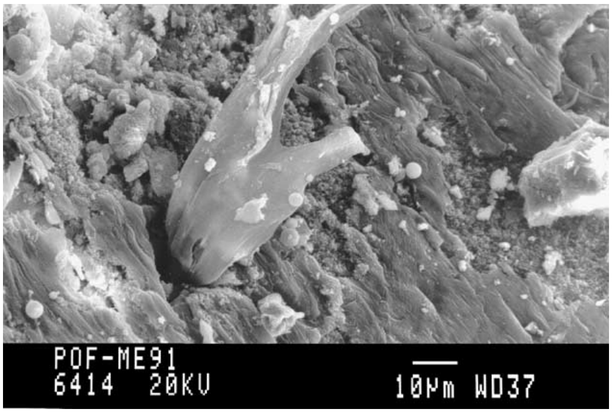

Fig. 5. Surface of a polyolefin fiber taken from Solution B.

3.2. Reaction between polyolefin fibers and the pore solution

For all tests conducted with the pore solution, several $Ca(OH)_2$ and $CaCO_3$ crystals are precipitated onto the

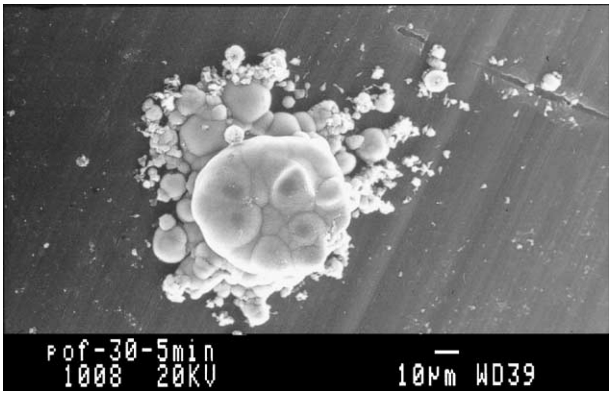

Fig. 6. $CaCO_3$ formed on a surface of a fiber taken from Solution A (Type 30 cement).

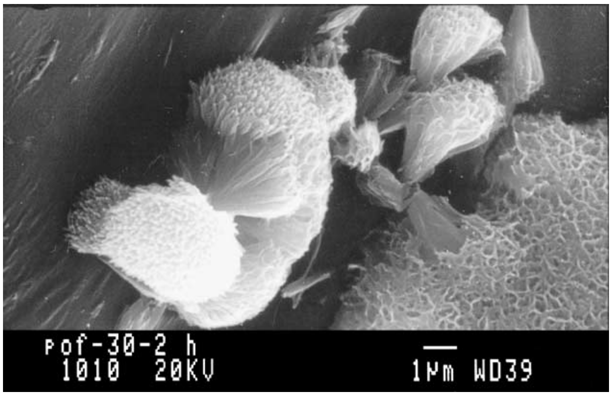

Fig. 7. $CaCO_3$ formed on a surface of a fiber taken from Solution B (Type 30 cement).

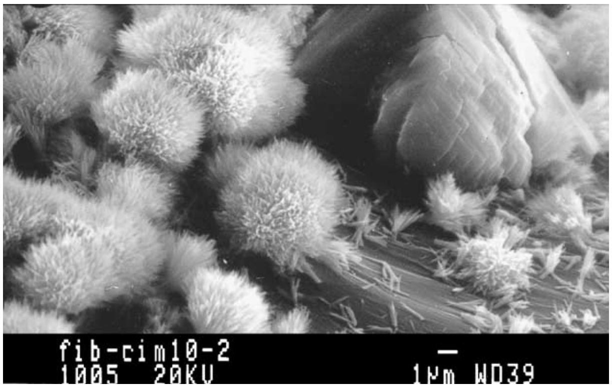

Fig. 9. Surface of a fiber submerged in Solution B for 2 h (Type 10 cement).

surface of the fiber. Even after cleaning of the fibers with distilled water, these crystals are still linked to the fibers. Because of the nucleation of crystals, the size of the $Ca(OH)_2$ and the $CaCO_3$ crystals is smaller for the cement with silica fume than for the other cement.

Fibers from Solution A present a marring of the surface (Fig. 4). In the case of Solution B, the surface of fibers presents more marring than Solution A does, and more crystals are linked to the fiber (Fig. 5). The superficial layer of the fiber is more damaged, and some parts are unstuck. This observation is the same for all three cement types.

The $CaCO_3$ crystals have different structures. The $CaCO_3$ formed on the surface of the fiber immersed in Solution A is in the shape of a bubble, with an average diameter of 10 μm (Fig. 6), while those formed from Solution B present a rose-like shape (Fig. 7). This transformation is the consequence of carbonation because this type of $CaCO_3$ was not observed when the experiment was conducted in a nitrogen atmosphere (Fig. 8a and b). The carbonation of the concrete is defined as the chemical reaction between atmospheric carbon dioxide and $Ca(OH)_2$ [8].

However, the surface morphology is slightly different in the case of a cement Type 10 or 30 (Figs. 7 and 9). Unlike the lime-saturated solution, pore Solution A precipitated onto the surface of the fiber and participated in surface damage during mixing. Moreover, results obtained in the cement paste show that the incorporation of fibers does not modify the pH values between 5 min and 7 h. The pH value of the pore solution with and without fibers is presented in Table 5. An excess of fibers was placed in the solution extracted from the cement paste after 2 h of hydration. For each type of cement, the evolution of the pH is similar. The pH according to time (between 2 h and 28 days) remains constant (12.6 ± 0.1).

3.3. Exothermic effect of the hydration reaction on the surface of the fiber

During cement hydration, the exothermic effect causes localized damage to the fiber's surface. The hardness of the superficial layer decreases, which allows the insertion of crystals. In the sites thus formed, the $Ca(OH)_2$ precipitates preferentially (Fig. 10). Consequently, at the microstructural level, the surface of polyolefin fibers behaves like a porous material. The transition zone between such porous material (Fig. 11) and cement paste becomes less porous compared with the transition zone between nonporous material such as steel fibers and cement paste (Fig. 12).

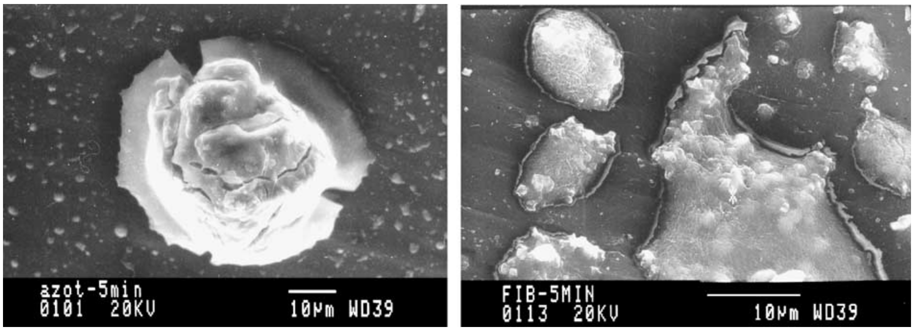

Fig. 8. SEM micrograph of a fiber in nitrogen atmosphere.

Table 5
Hydrogen ion concentration of solutions extracted from the paste with and without polyolefin fibers

Time	pH: Paste with fibers	pH: Paste without fibers
5 min	12.70	12.59
1 h	12.60	12.57
2 h	12.55	12.57
4 h	12.58	12.34
5 h	12.70	12.71
6 h	12.67	12.65
7 h	12.65	12.59

3.4. Effect of mixing on the surface of polyolefin fibers

During mixing, filler grains cause grooves and stripping (Fig. 13). Fiber roughness increases and allows a better adherence to the paste. Moreover, anchoring wires appear that also contribute to increase bond of the fiber in the paste (Fig. 14).

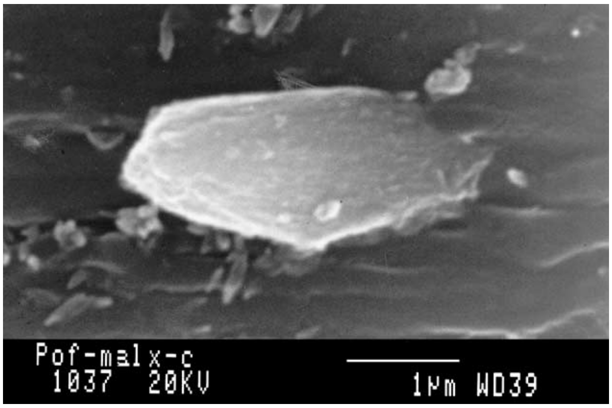

Fig. 10. Structural platelet inserted in the superficial layer of a fiber.

The same test was carried out with concrete containing Type 10 SF cement. A polyolefin fiber was extracted from the mixture and observed using the SEM 2 h after mixing. The SEM micrograph presented in Fig. 15 shows the same grooves and stripes, but in this case, the fiber also presents a transformation of the surface morphology. This transformation is the same as that created by the pore solution.

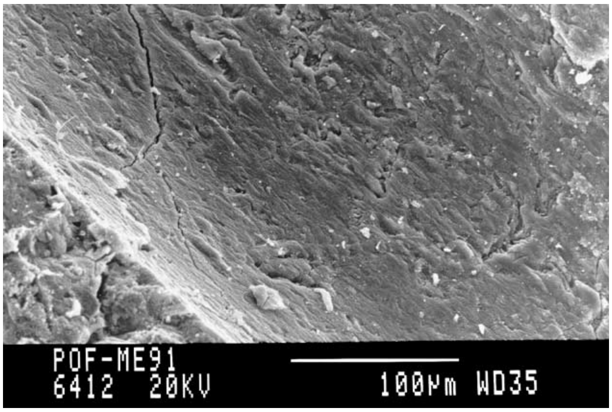

Fig. 11. Transition zone around a polyolefin fiber.

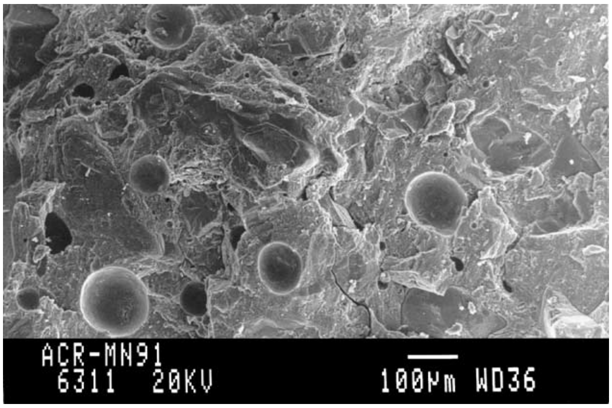

Fig. 12. Creation of a duplex film with a porous layer around a steel fiber.

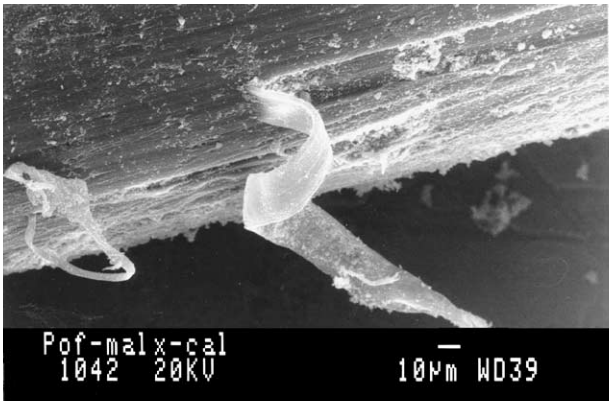

Fig. 13. Grooves stripping of a polyolefin fiber due to mixing with limestone filler.

After concrete mixing, during the drying period, the concentration of ions dissolved in water is higher in the damaged area. Consequently, the precipitation of new crys-

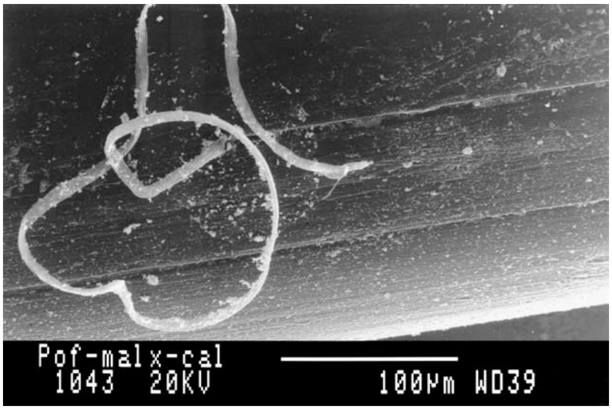

Fig. 14. Anchoring wires at the fiber's surface due to mixing with limestone filler.

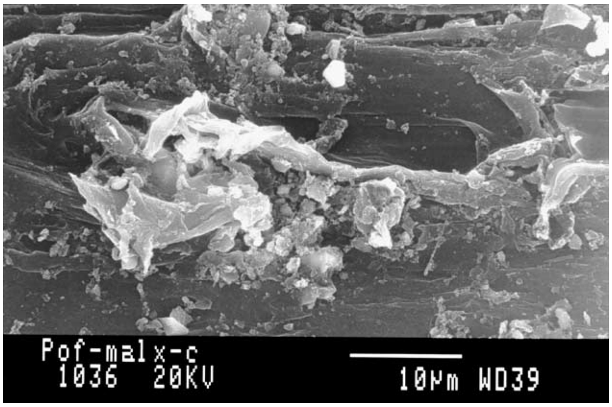

Fig. 15. Polyolefin fiber mixed in a concrete with Type 10 SF cement.

tals in this zone is preferential (Fig. 16). The crack is covered by an abundance of hexagonal crystals, of approximately 1 to 2 μm equivalent diameters.

4. Discussion

Microstructural observations show the evolution of bond between cement paste and polyolefin fibers. SEM analysis shows that the bond between fiber and concrete is mainly mechanical [9,10]. The different parameters tested in this study show that bond also depends on the heat of hydration, pore solution composition in the mixture, and effect of mixing. Moreover, the low superficial hardness of polyolefin fibers, compared with steel fibers, allows a change of fiber roughness during mixing. The effects of the pore solution in the concrete change the morphology of the fiber. Despite a plasticizing point of 160 °C, the possible explanation for a change in morphology is a higher temporary temperature in cement grains hydration near the fiber.

Interfacial structures between a steel (porous layer) and a polyolefin fiber (hydration products grow onto fibers) are very different [11]. Fig. 17 shows the transition zone in a paste (cement Type 10 SF) with a steel fiber. It appears as a duplex film with a porous layer and a random calcium hydroxide layer.

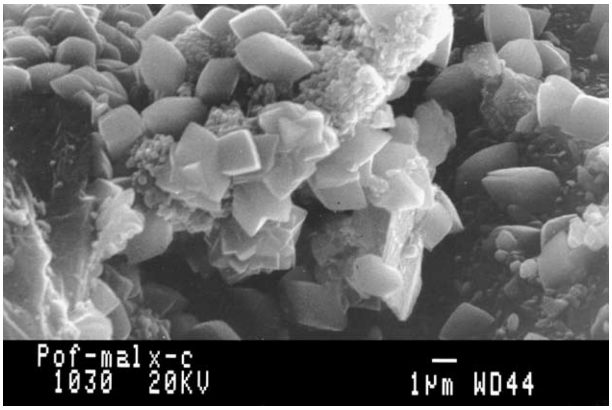

Fig. 16. Precipitation of hexagonal crystals on the surface.

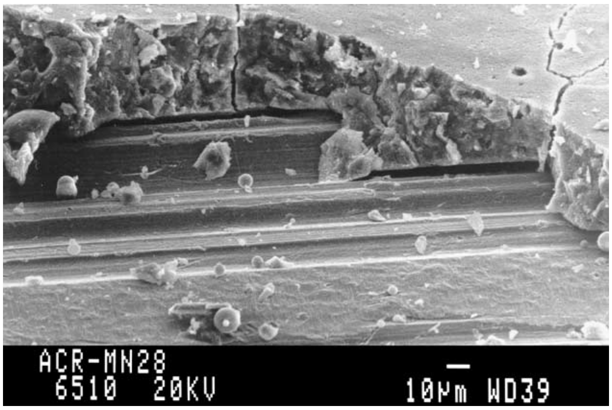

Fig. 17. Interface between a hydrated Type 10 SF cement paste and a steel fiber.

If there is no such interfacial roughness and a compact interface in the case of a polyolefin fiber, a slipping between the fiber and the paste will take place when shear stress is greater than bond strength [12]. During mixing, cracks appear, in which hydrates can form. The bond between the fiber and the cement matrix then increases.

Moreover, with mixing, fiber monofilaments remain anchored to the fiber and the paste. In short time spans, it is significant to wait for hydration of the different phases to increase bond. With vibration or other external solicitation, a fracture could appear and restrain the bond between the paste and the fiber. In this case, it is possible that the roughness and the shape are not sufficient to slow down crack propagation compared with steel fibers. The toughness of polyolefin showed an increase, over hydration time, superior to that of steel fibers. The hydration of cement could be a factor in this evolution.

5. Conclusions

The low superficial hardness of polyolefin fibers, compared with steel fibers, allows it to change its morphology and increase bond with the paste. Hydrate infiltration in the superficial layer of the fiber increases the bond between paste and fiber. This bond is improved with an increase of the fibers' superficial roughness. This observation is the consequence of several phenomena, such as impact between grains and fibers during mixing, which mechanically damages the surface of the fiber and produces filaments. Moreover, the exothermic nature of the hydration reaction generates a partial penetration of hydrates into the fiber, and bond quality increases according to hydration time.

The bond mechanism between polyolefin fiber and paste is similar to that of a porous material in contact with cement paste. A densification of the paste in the cavities increases the mechanical performance of the bond.

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