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Cementitious composites reinforced with continuous carbon fibres for strengthening of concrete structures

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Abstract

"Continuous fibre wrapping technique" is becoming a common repair and strengthening technique for concrete structures. In this method continuous fibre sheets are bonded to the surface of a concrete structure using organic resins. The main disadvantages of this method are: (i) the use of resins (organic compounds) which are hazardous for the manual worker, and (ii) the low permeability of this type of organic materials. These problems could be solved if a cement-based matrix is used instead of epoxy matrix. In the current development stage one of the limiting parameter in a cementitious carbon fibre composite is the bond between the fibres and the cementitious matrix.

The main objective of the study presented in this paper was to improve the bond between the carbon fibres and the cementitious matrix. Two possible methods were studied: (i) the design of a complex binder based on Portland cement with polymer and silica fume additions and (ii) surface treatment of the carbon fibres prior to their casting in the cementitious composite.

Keywords: Strengthening; Bond properties; Carbon fibres; Polymer modified cement; Surface treatment of carbon fibres

1. Introduction

One of the most successful strengthening methods is the use of continuous carbon fibres in epoxy matrix bonded to structural concrete. This method is a relatively new retrofitting method, developed first in Japan [1], where the first research in this area was carried out in 1979. Still this method presents some important disadvantages like the use of resins (especially epoxies) which are hazardous for the operator (manual worker) and have a low permeability. These problems could be solved if a cement-based matrix is used instead of epoxy matrix.

The literature information concerning the use of a cementitious matrix instead of an organic one is very limited. A research program on this topic is currently conducted at the Royal Institute of Technology, Stockholm, Sweden [2]. The results obtained so far in the framework of this program show that the cementitious strengthening system reaches 65% of the short time load carrying capacity of an epoxy system containing the same amount of fibres. In the current development stage one of the limiting parameter in a cementitious carbon fibre composite is the bond between the fibres and the cementitious matrix.

The fibre–matrix interfacial properties are important in controlling the macroscopic properties of composite material. Cementitious composites are characterised by a transition zone in the vicinity of fibres, in which the microstructure of the paste matrix is considerably different from that of the bulk paste [3]. The microstructure of the transition zone between monofilament fibres and cement matrix in mature composites, is rich in $Ca(OH)_2$ crystals (with a preferential orientation and usually in direct contact with the fibre) and is also rather porous [4,5]. When silica fume and a plasticizer admixture are used as additions to normal Portland cement, the porosity of the transition zone decreases and the microstructure is changed [6,7]. This fact is explained by

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the increase in the density of the cement grain packing and to the consumption of $Ca(OH)_2$ through the pozzolanic reaction [8–10]. If the bond is assumed to be mainly of friction nature the densification of the matrix should improve the fibre–matrix interfacial zone, thus leading to a better bond.

The surface treatment of pitch carbon fibres was also reported to be an effective method for the improvement of the carbon fibres–cement matrix bond (mainly adhesive) [11,12].

The main objective of the study presented in this paper was to improve the bond between the carbon fibres and the cementitious matrix. Two possible methods were investigated:

(i) the design of a complex binder based on Portland cement with polymer and silica fume additions;
(ii) surface treatment of the carbon fibres prior to their casting in the cementitious composite.

2. Experimental

2.1. Materials

The materials used for the cement matrix were:

- Portland cement—CEM II/A-L 42, 5 R supplied by CEMENTA AB;
- Silica fume powder—with 85% SiO_2—supplied by ELKEM Company from Norway;
- Organic polymer—copolymer based on *n*-butyl acetate and styrene—ARCONAL S 430 P (redispersable powder) supplied by BASF AB;
- Antifoaming agent—Agitan P 830 from Munzing Chemie GmbH;
- Superplasticizer based on sulphonated melamine polycondensate and sulphonate naphtalene polycondensate—HPM supplied by CEMENTA AB;
- Aggregate—"minifiller" supplied by CEMENTA AB; minifiller is a mixture of slag, limestone and silica fume which according to the producer has no hydraulic properties together with Portland cement.
- Commercially available polymer mortar—BETOFLEX, was considered as reference.
- The carbon fibre (Grafil 34-700) were tows with 12 K (12000 filaments), with the following characteristics: fibre diameter—6.9 μm; modulus of elasticity—234 GPa; tensile strength of 4500 MPa; elongation at break—1.9%; density—1800kg/m^3; cross-section carbon fibre tow area—0.444 mm^2.

The particle size distribution of cement and minifiller is plotted in Fig. 1.

The composition of the studied binders is presented in Table 1.

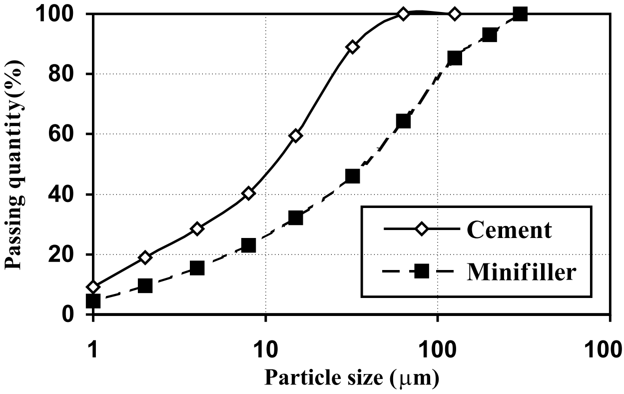

Fig. 1. Particle size distribution for the cement and minifiller.

2.2. Experimental methods

Mortars with a binder/aggregate ratio 1:1 and different water to binder ratios (see Table 1) were prepared. All ingredients were mixed in a rotary mixer with flat beater by

(1) mixing aggregate + cement + organic polymer at low speed for 2 min;
(2) dissolving the antifoaming agent in water, adding the superplasticizer and silica fume and mixing at low speed for 2 min;
(3) adding the solid mixture to the liquid components and mixing at low speed for 2 min and high speed for 3 min.

The workability of fresh mortars was determined by the flow table method according to the European Standard EN 1015-3:1999.

The fresh mortars were cast into moulds (see Fig. 2a) and kept in humid atmosphere the first 24 h. The samples were demoulded and then cured in two different conditions:

(1) in air for the next 13 days;
(2) first 6 days in fog room (air with 100% relative humidity) and in air for the next 7 days.

The pull-out test was performed on a MTS-machine (Fig. 3) with a cross-head speed of 0.01 mm/s. The applied load and the deformation were recorded. The final value of the maximum pull out force represents the average of three values.

Samples similar to those prepared for the pull-out tests were dried at 50 °C up to constant weight and sawn in 5 mm slices (Fig. 2b). The sawing of the samples stopped at approximately 3 mm before the matrix–fibre tow interface. The remaining part was fractured and the resulting samples were coated with carbon. A Philips 505 scanning electron microscope (SEM) was used to

Table 1
Composition and workability of different binder matrices

No	Sample	Composition (%)				Water/ binder[a]	Workability D (mm)
		PC	SF	Polymer (ARCONAL S 430 P)	HPM		
1	R	Betoflex (commercially available polymer cement)				0.65[b]	200
2	S	90	10	–	–	0.65	90
3						0.7	100
4	Sp1.4	90	10	–	1.4	0.6	90
5						0.8	230
6	Sp2.5	90	10	–	2.5	0.6	104
7	Sp2.75	90	10	–	2.75	0.6	115
8	Sp3.5	90	10	–	3.5	0.6	200
9	SL20	90	10	20	–	0.5	200
10	SL20-p1.5	90	10	20	1.5	0.45	220
11						0.4	150
12	SL20p3	90	10	20	3	0.4	200
13	SL30	90	10	30	–	0.35	197
14	SL50	90	10	50	–	0.4	250
15						0.35	200
16						0.3	195
17	St[c]	90	10	–	–	0.55	90
18						0.6	100
19						0.65	110
20	Stp3.5	90	10	–	3.5	0.55	220
21	StL30	90	10	30	–	0.3	150
22						0.35	210

In all sample the (PC + SF)/filler ratio was 1:1.

In all samples with polymer, antifoaming agent (AGITAN P803) was used—2.4% as a proportion of the polymer.

[a] binder = Portland cement (PC) + silica fume (SF) + polymer.

[b] Water/Portland cement ratio—specification obtained from product data.

[c] St—samples with silane treated silica fume.

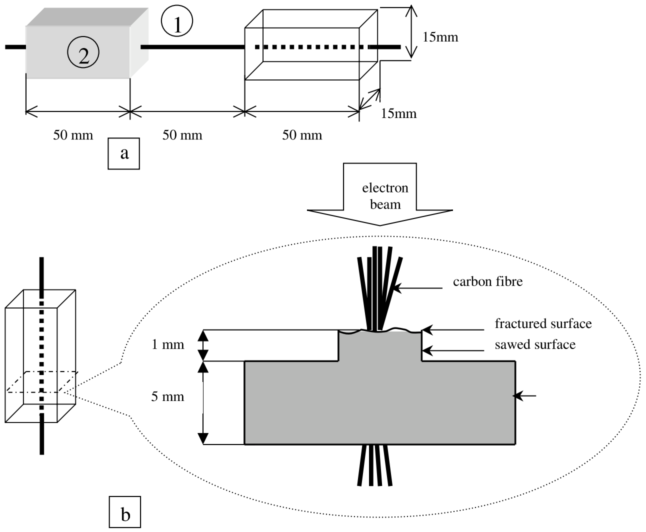

Fig. 2. Samples used for: (a) the pull-out test—(1) fibre tow, (2) mortar matrix; (b) SEM analysis.

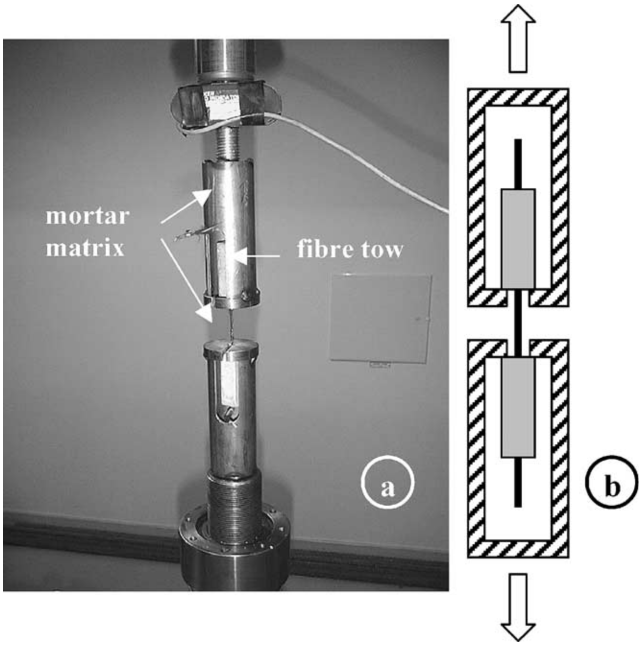

Fig. 3. The pull-out test: (a) MTS machine during the test; (b) sample loading in MTS machine during the pull-out test.

study the carbon filaments and the surrounding cement matrix. For qualitative analysis of different phases energy dispersive X-ray spectroscopy (EDS) analysis was performed.

The silane treatment [12] was performed by immersion of carbon fibres (or silica fume) in a silane solution. The solution is a mixture of two silane coupling agents: Z-6020-($H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH)_3)_3$ and Z-6040-($OCH_2CHCH_2OCH_2CH_2CH_2Si(OCH)_3)_3$ supplied by Dow Corning Corp. (USA). The solution containing the immersed tows was heated to 75 °C and held for 1 h at this temperature. After that the fibres where dried. When silica fume was treated the suspension was stirred for 1 h during the treatment at 75 °C.

3. Results and discussion

3.1. Workability of fresh mortars

The workability was estimated considering the diameter (*D*) of a fresh mortar sample using the flow table. As reference we considered the value obtained for the commercial available product BETOFLEX—200 mm. In Table 1 the workability values (*D*) obtained for the investigated mortars, prepared with different water/binder ratios are presented.

The substitution of Portland cement with 10% silica fume results in a reduction of the workability due to the high fineness of this material (Fig. 4). Even for very high water/binder ratio (0.7) the workability is very low as compared with reference (R). Therefore the addition of superplasticizer is absolutely necessary in order to obtain a good workability.

Increased superplasticizer addition causes an increase of workability. However, to achieve the reference workability, quite a high amount of superplasticizer (3.5%) was required even for high values of water/binder ratio (0.6). Such a high dosage of superplasticizer (the maximum HPM addition is 3%—producer recommendations) can cause an increase of the setting time of binder and can lead to lower values of compressive strengths at early hardening ages.

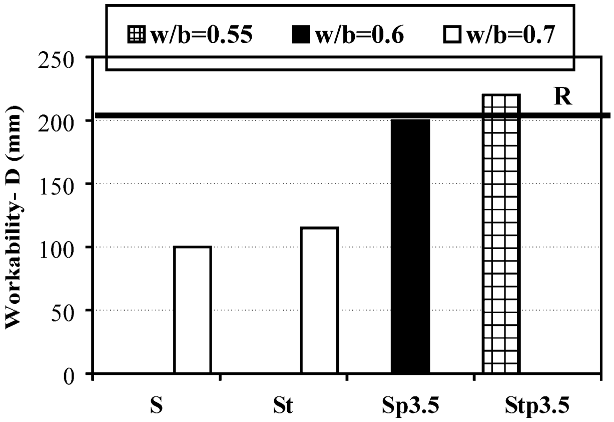

Fig. 5. Workability of fresh mortars with as-received silica fume (S and Sp3.5) and silane treated silica fume (St and Stp3.5) vs. water to binder ratio.

The silane treatment of silica fume improves the workability of fresh mortars (Fig. 5). Xu and Chung [13,14] also obtained an improvement of the workability for cement pastes with silane treated silica fume. They explained this behaviour by the improvement of the wettability of silica fume by water after silane treatment.

In our case, even if the workability was improved after silane treatment of silica fume, it was still necessary to use a superplasticizer, in order to obtain the desired value for the workability, but the water to binder ratio was decreased from 0.6 to 0.55.

Increased polymer additions cause an increase of the fresh mortar workability i.e. the water to binder ratio necessary to achieve the reference workability ($D = 200$ mm) decreases (Fig. 6). This results are in accordance with the conclusion from Ohama's work [15] concerning

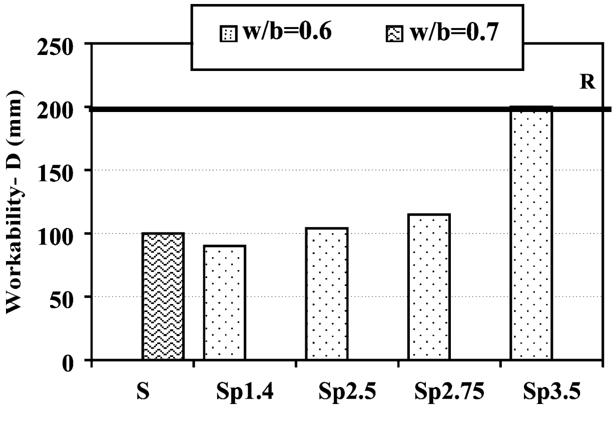

Fig. 4. Workability of mortars with 10% silica fume and different amounts of superplasticizer vs. water to binder ratio (R—reference workability).

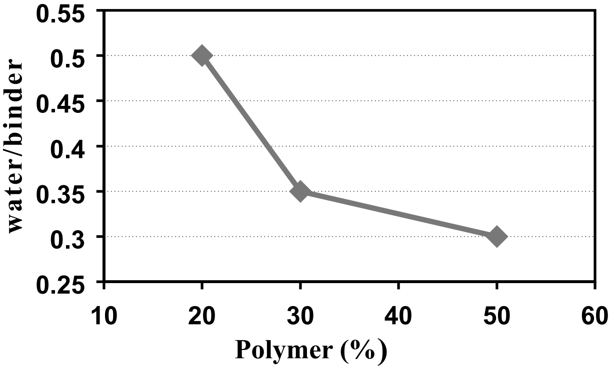

Fig. 6. The water to binder ratio necessary to achieve the reference workability ($D = 200$ mm) vs. polymer content.

the workability of cements with different polymer based admixtures.

For 20% polymer addition a good workability was achieved without the use of superplasticizer, for a water to binder ratio of 0.5.

The increase of the polymer addition (30% and 50%) further increases the workability of fresh mortar. This permits the reduction of the water to binder ratio to 0.35 respectively 0.3 without the use of superplasticizer admixtures.

3.2. The pull-out test

To evaluate the bond properties between fibres and cementitious matrices different tests where proposed.

For the assessment of the bond properties in small and brittle filaments or fibre bundles Bartos and coworkers [16–18] used the “pull-in” test and the “micro-indentation method”. These methods allow the bond properties at both the matrix–fibre interface and fibre–fibre interface within the glass fibre strand/bundle to be determined.

A non-destructive method based on the correlation between the bond strength and fibre–cement contact electrical resistivity was also used for the study of pitch carbon fibres in cement matrices [19–21].

One of the most used methods in the attempt to assess the bond properties in cement matrices of a wide range of fibres, is the pull-out test [6,22–24].

In the present work, the author’s intentions were to compare the bond strengths between bundled carbon filaments and different cement matrices and to evaluate the efficiency of the silane treatment of carbon fibres. For this purpose a simple pull-out test has been used.

The pull-out test was carried out on samples cured for 14 days. The values obtained at this age can be considered relevant for the strengths of the composites, because these values represent more than 80% of the compressive strength obtained by the cement matrix with silica fume/polymer admixture after 28 days of curing [25].

The bonding depends essentially on the structure of the fibre–matrix interface as well as the penetration of the cement matrix in the centre of the fibre tow. The development of the microstructure in the transition zone in the case of bundled fibres is different and also more complicated from the case of monofilament fibres separated one from an other.

In Fig. 7 the load–displacement curve recorded for the cementitious matrix without polymer addition is presented. This shape of the load–displacement curve was observed for almost all the investigated matrices (with/without polymer). As can be seen the load reaches a peak after a short pull-out displacement, followed by a severe drop probably due to the debonding and slip of the fibres in the centre of the tow, which were not very well bonded by the cement matrix. In our test we noticed the presence of a “curly tail” (see Fig. 8) on the opposite side of the mortar samples after the pull-out test. This behaviour seems to be due to the difference in bond strength of outer and inner carbon filaments from the carbon fibre tow. The filaments from the exterior of the tow (outer filaments) are broken and the filament from the interior of the tow (inner filaments) slip without any apparent damage. This type of failure known as “telescopic pull-out” has been reported first in GRC composites [18].

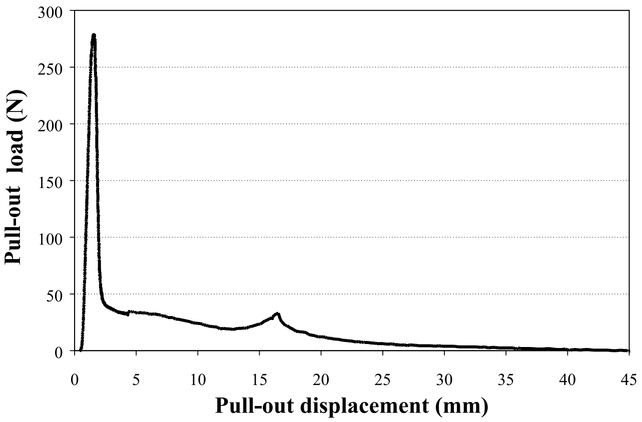

Fig. 7. The load–displacement curve for sample with Sp3.5 matrix (with 10% silica fume and without polymer addition), cured 14 days in air.

For the assessment of the bond properties of carbon fibres (silane treated or as received) in different types of cementitious matrices, the average value (for three samples) of the first peak load was considered.

The silane treatment of the fibre tows, leads to a significant improvement of the bond between fibres and reference matrix—BETOFLEX (Fig. 9). The pull-out load increases with 368% for samples cured in air and by 140% for the samples cured first in a fog room

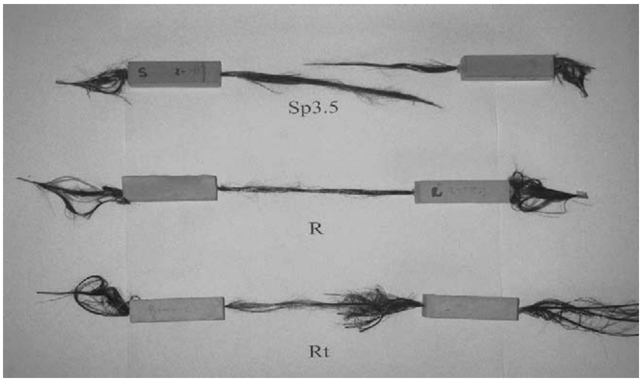

Fig. 8. Samples with different cementitious matrices after the pull-out test.

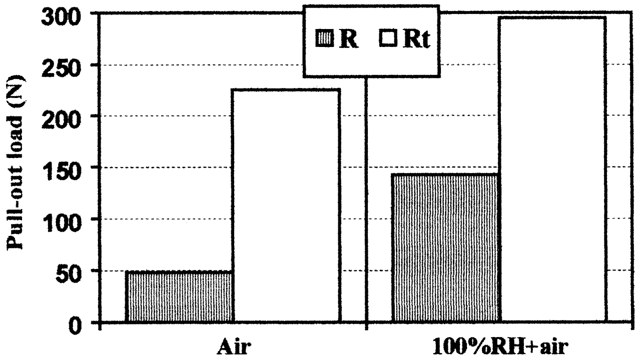

Fig. 9. Pull-out load for reference with non-treated carbon fibres (R) and silane treated carbon fibres (Rt), cured 14 days in air, respectively 6 days in fog room (100% R.H.) and 8 days in air. Cement matrix was betoflex (reference—R).

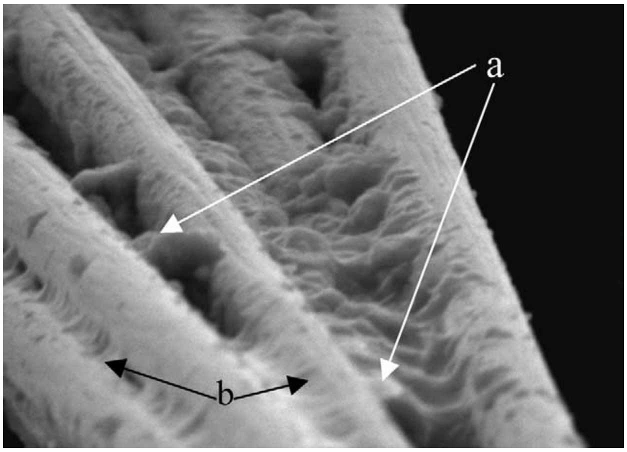

Fig. 11. Carbon fibres coated with hydrates (a) and bonded by polymer (b) in SL50 sample (x 2662).

(100% R.H.) followed by air curing, when the fibres were first subjected to silane treatment.

The influence of the cementitious matrix composition on the bond properties of as received carbon fibres, is presented in Fig. 10. The increase of the polymer content (from 20%—SL20p3 to 50%—SL50) resulted in increase of the pull-out load values, especially for dry curing conditions. This increase can be attributed to the supplementary adhesive bond at the fibres–binder matrix and fibre–fibre interfaces induced by the high amount of polymer (Fig. 11).

For the samples with a small amount of polymer (SL20p3) an increase of the bond strength is achieved when the samples are first cured under humid conditions, probably due to the improvement of the Portland cement hydration process.

For high amounts of polymer (SL50), the humid curing conditions seem to have a negative effect. This is in accordance with the literature data [15,26] which suggest that the best mechanical strengths of polymer modified mortars are obtained in dry curing conditions.

A very high value of the pull-out load was obtained for the sample without polymer (Sp3.5). The SEM investigation of this sample suggested a very good penetration of the mortar matrix into the carbon fibre tow. After 14 days of curing in air, even the filaments from the centre of the tow are covered with cement hydrates (Fig. 12).

On the contrary, in the sample with 50% polymer (SL50), only the carbon filaments from the exterior of the tow where covered with hydrates, which means that the penetration of this type of binder matrix in the centre of the carbon fibre tow was very poor (Fig. 13).

The use of silane treated fibres in combination with SL30 binder, leads to more than 30% increase of the pull out load (see Fig. 14).

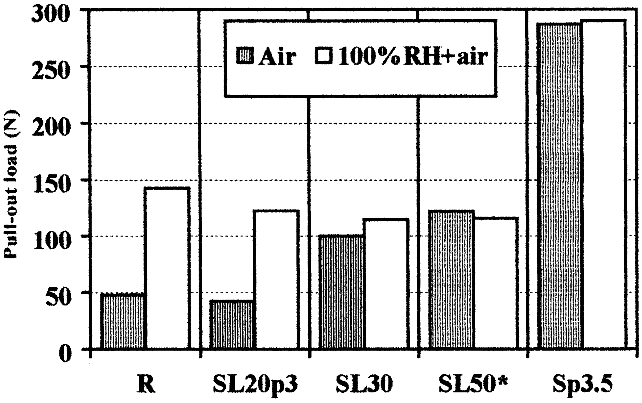

Fig. 10. Pull-out load obtained for samples with different types of binder matrices, hardened 14 days in air, and 6 days in 100% R.H. plus 8 days in air respectively. (*) Due to the very low mechanical strength after 1 day, the SL50 samples where demolded after 3 days of curing in air.

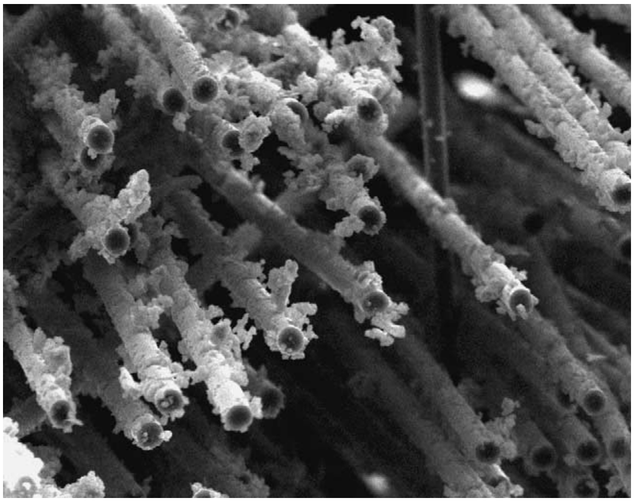

Fig. 12. Carbon filaments covered with hydrates pulled out from the Sp3.5 binder matrix (x 680).

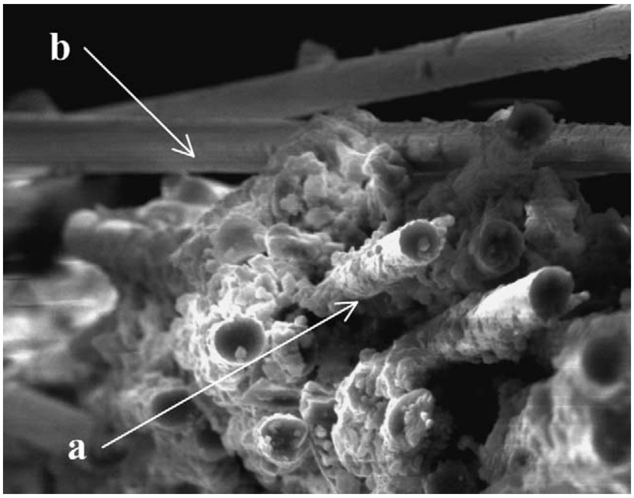

Fig. 13. Carbon filaments pulled out from the matrix with 50% polymer (SL50): (a) carbon filaments covered with hydrates; (b) "clean" carbon filaments from the centre of the tow (x 1310).

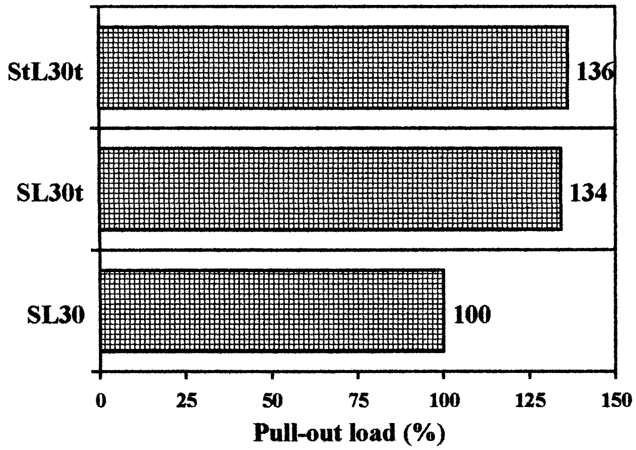

Fig. 14. Relative* pull-out load in samples: SL30—10% as-received silica fume and 30% polymer with non-treated carbon fibres; SL30t—10% as-received silica fume and 30% polymer with silane treated carbon fibres; StL30t—10% silane treated silica fume and 30% polymer with treated carbon fibres. (*) The reference value was the pull-out load of SL30 sample.

The silane treatment of silica fume previous to its mixing in the mortar, in combination with silane treated fibres, did not lead to a marked increase of the maximum pullout load.

4. Conclusions

Based on the results obtained in this research, the following conclusions can be drawn:

- As expected, the addition of polymer (ARCONAL S 430 P) increases the workability of fresh mortars for same (even smaller) values of water to binder ratios. Based on this effect, fresh mortars with adequate workability could be prepared using very low water to binder ratios (0.35–0.3) and 30–50% polymer additions, without any superplasticizer additions.
- In pull-out tests, an improvement of the bond properties of carbon fibres was observed in cementitious matrices containing silica fume and high amounts of polymer. The silane treatment of the carbon fibres prior to their casting in the cementitious matrix also lead to a major improvement of the bond properties. The highest bond was obtained with a cement matrix with 10% silica fume and without polymer (Sp3.5). One of possible explanations could be a good penetration of this type of matrix in the centre of the carbon fibre tow.
- The curing conditions also have an important influence on the bond properties of carbon fibres in polymer modified cement matrices. The samples with a small amount of polymer (20%) develop good bond properties when they are first cured in humid conditions, probably due to the improvement of the Portland cement hydration and hardening processes. On the contrary, for the samples with high amounts of polymer (50%) the best bond properties were obtained when the curing was made in air.
- The load capacity of the cementitious carbon fibre composite (studied in this is research) is influenced by the included amount of fibres (within the tow). If the cementitious matrix can penetrate in the interior of the carbon fibre tow, a higher number of filaments will be "active" during the composite loading and this will lead to the increase of the load carrying capacity.

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