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Scientific paper

The Effect of Carbon Nano- and Microfibers on Strength and Residual Cumulative Strain of Mortars Subjected to Freeze-Thaw Cycles

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Abstract

The strength and development of residual strain of normal strength mortars subjected to freeze-thaw cycles incorporating carbon nanotubes (CNTs) and carbon microfibers (CMF) were studied. The workability was influenced by the fiber type, the dispersion method, and the amount of fibers. The obtained results showed that the measured flexural strength increased only in the case of mortars incorporating CMFs. The compressive strength remained unchanged in the case of mortars containing CMFs and was slightly lower when CNTs were present. The residual strain due to freeze-thaw cycles was lowered in comparison with reference mortar only when incorporating CMFs. The obtained results confirmed that in order to utilize the outstanding mechanical properties of CNTs the binder matrix must be very homogenous to provide sufficient contact area for stress transfer. The used water to binder ratio was sufficiently low only for long CMFs, which were able to bridge numerous weak inclusions present on the binder matrix.

1. Introduction

The frost durability of Portland cement based concretes has been one of the major research topics over the last decades. A significant number of theories were developed. The most known certainly include works done by Powers (1945, 1947, 1948, 1947, 1949), Everett (1961), Fagerlund (1975, 1977), Litvan (1972, 1997), Setzer (1997, 1999) and Penttala (1998, 1998a, 2002). There are many chemical and physical phenomena contributing to the deterioration processes. Damage can be manifested as internal cracking of the binder matrix or as surface scaling. Internal damage is usually related to frost attack, where pure water is the aggressive medium, while surface scaling occurs mainly in specimens being subjected to a combination of freeze-thaw cycles and de-icing salts. A combination of these two forms of deterioration is also possible. As Powers (1947) showed, the frost durability can be enhanced by incorporation of a system of fine air voids. Although, the actual function of the air voids is still a point of dispute, most agree that the internal stresses created during freeze-thaw cycles are decreased due to the shorter distance the water has to travel through the binder matrix between the air voids, in which the ice can grow. Other factors such as the microstructure of the binder matrix, its capillary porosity, (Penttala 1998, 1998a, 2002), or the Interfacial Transition Zone (ITZ), (Cwirzen 2005b), also affect the

extent and rate of deterioration. The development of high and more recently ultrahigh strength concretes enabled the production of binder matrices having low and very low porosity as well as a very homogenous microstructure. As a result, the frost durability of these concretes was in most cases improved; mainly due to a lower water uptake during freeze-thaw cycles, (Cwirzen 2005a, 2005b, Schmidt 2006). The newest studies concerning ultrahigh and high strength concretes containing large amounts of silica fume revealed a tendency of rapid “explosion”-like internal damage after a certain number of freeze-thaw cycles, (Cwirzen 2008, Cwirzen 2005b). This form of deterioration was attributed to large internal stresses developing during freeze-thaw cycles, due to either a movement of solution (Penttala 1998a) or a gradient of relative humidity (Cwirzen 2008) within a very dense and nearly impermeable microstructure of the binder matrix. This behaviour was related to the high brittleness of the binder matrix. To overcome those problems steel fibres having a diameter of 0.2 mm and a length of 12 mm were incorporated to the binder matrix. The results showed a significant delay of the internal damage as well as smaller deterioration rate which reminiscent normal strength concretes. SEM studies clearly showed a bridging effect of the fibres, which did not prevent formation of the microcracks but limited their propagation. Furthermore, sliding of the fibres under stress provided some degree of ductility, which counteracted the explosive nature of the damage. Other studies showed that the post-crack behaviour of UHSC increased even further by the addition of a mixture of fibres having different lengths, diameters, and type of material used for their production, (Schmidt 2006).

The frost durability is usually assessed by measurements of the surface scaling and of the internal damage.

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Determination of the surface scaling includes collection and weighting of the scaled off material. The internal damage appears as progressive cracking of the binder matrix and sometimes also of aggregates during freeze-thaw cycles. The most common ways to assess the internal damage is to measure the ultrasonic transit time (CEN/TC 51 N772, (2003)), fundamental transverse frequency (ASTM C 215) and relative dynamic modulus of elasticity (ASTM C666 and also CEN/TC 51 N772, (2003)). In addition a number of studies were done on a strain-temperature behavior of concrete in freeze-thaw cycles and which could be also used in assessment of frost damage, Penttala (1998, 1998a, 2002), Hassan *et al.* (2004), Muneo and Hidenori (1998), Kaufmann (2002). These results validated for example the theory of the critical degree of saturation of the pore system which is reached at some point during freeze-thaw cycles. After that point accumulation of the residual expansion takes place due to progressing disintegration of the binder matrix. The residual expansion can be recorded by strain gauges which method is also used in the presented paper.

Recent advances of research, focusing on the development of carbon nanotubes and carbon nanofibers, enabled their industrial-scale production and thus significantly lowered their price, which begin to create economical bases for their use in construction materials. Carbon nanotubes (CNTs) attract a lot of attention within the scientific community due to their superior mechanical and physical properties, (Treacy 2000, Treacy 1996, Treacy 2000, Smith 2004, Kong 1999, Arnason 1999). Extensive research on the CNTs was initiated by Iijima in 1991, (Iijima 1991). The CNTs were incorporated into various matrixes made for instance from ceramics, polymers or metals. The incorporation of the CNTs had two main objectives either to enhance the mechanical or the physical properties. A number of studies have also focused on the incorporation of the CNTs into a Portland cement based matrixes, (Cwirzen 2008, Kowlad 2004). The main problems regarding the usage of the CNTs in any type of matrix are their uniform dispersion, sufficient mechanical bond with the matrix material, as well as incorporation of a sufficient amount of nanotubes or nanofibers. In the case of Portland cement the most common way is to prepare a stabile suspension of the CNTs in water. The weak bond between the CNTs and the binder matrix can be enhanced by surface functionalization, or oxidation attaching for instance COOH or OH groups, or by polymer wrapping, (Ebbesen 1996). Functional groups are believed to chemically bond to the matrix. The main drawback of this method is the high agglomeration of the functionalized CNTs and their relatively short length in the range of, usually, 1-2 μm . Unfortunately, no research has been done to verify the effect of CNTs on the frost durability of normal strength mortars and concretes.

Microfibers were studied and applied as additions to cement based matrixes for some time now. Tests were

done on microfibers produced from steel, polyvinyl alcohol (PVA) and carbon etc. Extensive research done by Batterman (Batterman 1995) showed that PVA fibres can enhance the tensile strength of the cement binder matrix. The failure mechanism showed that the fibres are pulled out of the matrix in tension, which proved the weak bonding between these two materials. The recorded maximum pull-out loads were higher in comparison with steel fibres. A number of studies showed a dependence of the tensile properties and fibre dimensions, (Batterman 1995). The results showed that if only large fibres are used there is no improvement of tensile strength. The authors attributed this to the initiation of micro cracking at the micro level where large fibres are simply too far apart to be able to arrest the crack formation. Incorporation of smaller fibres could result in better crack arresting just after its initiation. Some tests on the effect of fibres on the frost durability were done by Pigeon *et al* (Pigeon 2002, 1996). They tested pastes and mortars incorporating either steel or carbon fibres. Their results showed an enhancement of the durability in freeze-thaw cycles, when water or de-icing salts were used as freezing medium. The fibres did not prevent the frost damage to occur but delayed the deterioration process.

The main objective of the study described in the present paper was to evaluate the effect of CNTs and CMFs on the mechanical properties and cumulative strains due to freeze-thaw cycles of mortars based on Portland cement. The study focused on mixes having higher water to binder ratio of 0.5 in order to verify a possibility to decrease the internal damage of normal strength concretes by application of nano and microfibers.

2. Materials and experimental setup

The proportions of six mortar mixes are given in **Table 1**. All mixes contained sulphate resistant Portland cement type CEM I 42.5 N (SR) produced by Finnsementti Oy. This type of cement was chosen, as it is known for showing a limited interaction with polycarboxylate-based superplasticizers. This cement consisted of 68% of C_2S , 13% of C_3S , 1% of C_4AF and 13% of C_3A . The specific surface area was $360 \text{ m}^2/\text{kg}$ and the density was 3100 kg/m^3 . The amounts of added sand, water and superplasticizer were constant. Two types of fibers were used in this study. The first type was carbon micro fibers produced by Applied Sciences Inc under the trade name Pyrograf I. Their diameters varied between 3 and $20 \mu\text{m}$ while the lengths were up to a few millimeters long. The density of these microfibers was 1.8 g/cm^3 and the tensile strength around 400 GPa.

The second type consisted of multi-walled functionalized CNTs, produced via a catalytic carbon vapor deposition (CVD) process, by Nanocyl (Belgium). After purification to 95% the CNTs were functionalized with COOH groups (CNT-COOH). The functionalization process involved a treatment of the nanotubes with cer-

Table 1 Mix proportions and fresh mortar properties (partly adapted from Cwirzen 2009).

Mix name	W/C ratio	Superplasticizer [wt% of cement]	Carbon fiber type	Fiber amount [wt% of cement]	Sonication intensity	Slump flow [mm]
REF	0.5	0.01	No fiber	0	-	30
PI1.4	0.5	0.01	Pyrograf I	1.4	No sonication	28
PI2.9	0.5	0.01	Pyrograf I	2.9	No sonication	27
CNT023L	0.5	0.01	CNT-COOH	0.23	Low intensity	30
CNT023H	0.5	0.01	CNT-COOH	0.23	High intensity	22.5
CNT05H	0.5	0.01	CNT-COOH	0.5	High intensity	0

tain acids at high temperatures. The average diameter of the CNTs was 10 nm and their lengths were 2-4 μm . The functionalized CNT-COOHs were highly agglomerated and an additional sonication was required to obtain a uniform dispersion in water, **Fig. 1**. In this study, medium and high intensity sonication in the presence of polymers was applied, see **Table 1**. Sonication was done using Ultra Sonicator Probe type ULM2 from Bekman Coulter. Two power setting were used: 45W and 70W which corresponded to medium and high intensity sonication respectively. Duration of sonication was 5 minutes in all cases.

The polymers originated from a polycarboxylate-based superplasticizer. The mixing procedure of the mortar batch in the case of the nanofibers included the preparation of a water suspension, containing the superplasticizer and the nanofibers, by using sonication. In the next step the obtained dispersion was added to dry premixed cement and sand. Mixing of the mortars was done in a small vacuum mixer for 3 minutes. The vacuum mixer was used in order to enhance the homogeneity of the produced mixes by removal of entrapped air. This procedure was required due to the small size of the produced specimens.

Fresh-state properties of the produced mixes were determined using an in-house made mini slump flow table test. The mold-cone having a height of 10 mm and upper and lower diameters of 13 and 20 mm respectively, was filled with mortar without any compaction in only one layer. After removal of the mold-cone the horizontal spread of the mortar was measured in two perpendicular directions and an average value was calculated.

Test beams having dimensions of 10x10x60 mm³ were produced to determine the flexural and compressive strengths while beams of 20x20x50 mm³ were used for freeze-thaw testing. All moulds were made from teflon to avoid contamination by the release oil. The specimens were stored in water until the compressive and flexural strengths were measured after 28 days. The test procedure consisted of the bending test followed by the compression test. The compression test was done on specimens, which beam-half's were obtained from the previous bending testing. The used testing apparatus was Roell+Korthaus type, the used load rate was 0.35mm/min for both bending and compressive strength measurements.

The freeze-thaw tests were performed using standard

Fig. 1 Aggregation of CNT-COOH before sonication, SEM image.

equipment for CDF/CIF tests, (CEN/TC 51 N772, 2003). Each freeze-thaw cycle 20°C to -20°C to 20°C was 12 hours. The used specimens had smaller dimensions in comparison, 20x20x50 mm³ instead of standardized 75x100x15 mm³. The preparation procedure has followed the standard. The elongation of the specimens due to internal damage was determined by strain measurements instead of using ultrasonic transit time measurements as required by the standard. For each mix three specimens were made, and each had two strain gauges bonded to its sides with epoxy resin. The specimens were water-insulated on their sides allowing water uptake only from the bottom of the specimens. The tests were continued for a 20 days period, which corresponded to 40 freeze-thaw cycles.

Microstructure was characterized using Environmental Scanning Electron Microscope (ESEM) type Electroscan E3, and low voltage scanning electron microscope type Hitachi S-4700. Studies involving ESEM included analysis of the back scattered electron images (BSE) and secondary electron images (SE). All measurements were done on 28 days old specimens and additionally after freeze-thaw cycles. Two types of specimens were studied, fractured and polished. Preparation procedure for polished specimens included cutting of samples using diamond saw and alcohol as a lubricant. In order to remove capillary water all specimens were stored for 24 hours in alcohol, followed by vacuum

resin impregnation. In the final stage samples were grinded and polished using diamond pads (125 and 25 μm) and diamond spray (6, 3, 1 and 0.25 μm). The fractured specimens were studied without any additional treatment.

The BSE and SE images were taken using magnifications of 500 – 1000 times, acceleration voltage of 20 keV, vacuum pressure of 1.8 Torr and working distance of 13.3 mm. BSE images were taken with SEM and no additional conductive coating was applied.

3. Test results

3.1 Fresh mortar properties

The fresh-state properties of the studied mortars are shown in **Table 1**. Mix CNT023L which contained 0.23 wt% of functionalized CNT-COOH calculated by cement weight percentage dispersed in water by low intensity sonication did not decrease the measured slump flow values. On the other hand in the case of mix CNT023H which contained the same amount of CNT-COOH but dispersed by a high intensity sonication decreased the slump flow from 30 to 22.5 mm. The intensity of sonication appeared to affect strongly the obtained workability of the test mortars. This effect can be directly related to a better dispersion of the CNT-COOH when high intensity was used and worst dispersion at low intensity sonication. Better dispersed CNT especially when functionalized with COOH groups tend to adsorb more superplasticizer on their surfaces, (Cwirzen *et al.* 2008). Higher addition of CNT-COOH, 0.5 wt% of cement weight, as in the case of mix CNT05H, caused a total loss of workability. The last mix had to be intensively vibrated to fill the molds. In the case of mixes PI1.4 and PI2.9 which contained carbon microfibers Pyrograf I workability was nearly the same as in the case of the reference mix Ref., see **Table 1**.

3.2 Mechanical properties

The mechanical properties of the studied mortars were determined based on the 28-day compressive and flexural strength measurements. The results shown in **Fig. 2** revealed that mortars containing functionalized nanotubes CNT-COOH (CNT023L, CNT023H and CNT05H) had, in general, slightly lower compressive strength values in comparison with the reference mortar. Intensified sonication resulted in generally smaller scatter of the obtained results. Incorporation of the carbon microfibers (CMF) also did not alter the ultimate 28-day compressive strength independently on the incorporated amount.

Addition of the Pyrograf I microfibers increased the measured flexural strength, **Fig. 3**. The results showed an increase from 12.5 MPa as measured for the reference mortar, to 16 and 15 MPa in the case of mixes PI1.4 and PI2.9 respectively. In contrary, incorporation of CNT-COOH caused a decrease of the 28-day flexural strength values.

The lowest flexural strength value was recorded in the case of the mix CNT05H, which contained 0.5 wt % of the functionalized CNTs, dispersed by using intensive sonication.

3.3 Residual cumulative strain due to freeze-thaw cycles

The cumulative strain values recorded during freeze-thaw cycles are shown in **Fig. 4**. The test results showed that CNT-COOH incorporated in the cement matrix as water dispersion by using high intensity sonication increased the cumulative strain of the studied mortars, mixes CNT023H and CNT05H. In contrary, mortar incorporating CNT-COOH added as dispersed in water by using a low intensity sonication showed an approximately 15% decrease of the cumulative permanent strain in comparison with the reference mortar. The decreased permanent elongation of the specimens was especially pronounced during the initial cycles. After 40 freeze-thaw cycles the elongation was very close to the reference mix. The most significant decrease of the cumulative permanent strain during 40 freeze-thaw cycles was measured in the case of mix PI2.9, which contained CMFs. The total strain decreased by 75% and by 87% in the case of mixes PI1.4 and PI2.9, respectively in comparison with the reference mix. Furthermore, in the case

Fig. 2 28-day average compressive strength values, adapted from Cwirzen (2009).

Fig. 3 28-day average flexural strength values, adapted from Cwirzen (2009).

Fig. 4 Strain values recorded during freeze-thaw cycles: a) as recorded during the entire test, b) as recorded during first 10 days. Partly adapted from Cwirzen (2009).

of the mixes PI1.4 and PI2.9 the strain values measured during one freeze-thaw cycle were significantly lower and had a constant value throughout the entire duration of the test duration. In the case of the remaining mixes, the measured 1-cycle strain value increased gradually with increasing number of freeze-thaw cycles. No signs of surface scaling were visible in any of the test specimens until the recorded strain values were substantial.

Due to the arrangement of the tests which included small specimens (20x20x50mm) with a number of attached electrical cables enabling continuous monitoring of the strain values the weight of the specimens was not measured. However, a visual observation of the specimens after the freeze-thaw cycles revealed penetration of water to the top of the specimens.

3.4 Microstructure

The SEM studies were performed on specimens after 28 of curing in water and on specimens subjected additionally to 40 freeze-thaw cycles. Some of the specimens were impregnated under vacuum with epoxy resin and were subsequently polished by using diamond spray. The preparation techniques did not involve any type of heat treatment to remove water but instead the alcohol exchange method was applied. As a result, no micro-cracking of the binder matrix, due to the impregnation processes, was observed. Some of the specimens were investigated as fractured without any additional treatments. Sample images are shown in Figs. 5-10. Studies on the micro porosity were done using both types of specimens. As shown in Figs. 5, 6 and 9 a significant amount of micro pores was present throughout the binder matrix. Interfacial transition zones were also visible around larger sand particles. Figure 10 shows the fractured specimen PI2.9 prior to the freeze-thaw cycles. The uniform dispersion of the CMFs within the binder matrix is clearly visible. ESEM study of samples subjected to freeze-thaw cycles were done on both types of specimens fractured and resin impregnated and polished. The studies showed that the reference mortar and mortars incorporating CNTs were severely damaged after 40 freeze-thaw cycles. Figures 7 and 8 show frac-

Fig. 5 ESEM image of specimen PI2.9 incorporating CMF after 40-freeze-thaw cycles.

Fig. 6 ESEM image of specimen PI1.4 incorporating CMF after 40-freeze-thaw cycles..

tured specimens of made from mixes CNT023L and CNT05H after 40 freeze-thaw cycles. Cracks with bridging CNTs and some agglomerated CNTs are visible. In contrary mixes with CMFs had no cracks when 2.9 wt% of CMFs were present and minor cracking at 1.4 wt% of CMFs addition, Figs. 5 and 6.

Fig. 7 Fractured specimen CNT023L.

Fig. 8 Agglomerate of CNT-COOH, mix CNT05H.

4. Discussion

Additions of CNTs and CMFs can have a significant effect on the workability of Portland cement-based mortars. As shown in **Table 1**, the actual measured slump flow depended on the type of the added fibers and on the degree of their dispersion.

The addition of CMFs, independently of the added amount worsened the workability only slightly. This positive effect can be related to a negligible water-uptake by the microfibers, caused by their significantly smaller surface area. Furthermore, the high flexibility of the fibers could prevent interlocking of the fibers, which is commonly observed in the case of e.g. stiff steel fibers. Additionally, although not measured, the CMFs could absorb less SP polymers in comparison with CNTs. In contrary, addition of functionalized carbon nanotubes (CNT-COOH) worsened the slump flow of the studied mortars. In this case, two factors appeared to contribute to the ultimate effect, the amount of the nanotubes and their degree of dispersion. As shown in **Table 1** the increasing amount of CNT-COOHs decreased the slump flow. The sonication intensity influenced the degree of dispersion of the CNT-COOHs in the mixture of water and surfactant. In the case of high intensity sonication a “gel-like” consistency of the solution was obtained while low intensity sonication produced a “thick”

Fig. 9 Large amount of airvoids visible as black areas throughout the binder matrix of mix CNT023L.

Fig. 10 ESEM-SE image of fractured hydrated mix PI2.9. Visible CMF evenly distributed in the binder matrix.

solution with clearly visible agglomerates. An earlier study, (Cwirzen 2008), has clearly shown that it is possible to obtain a high degree of dispersion of CNTs in water mixed with superplasticizers even by using sonicating bath, which is known to be less effective in comparison with the sonication finger used in this study. Consequently, taking into account the visual observation as well as the study, mentioned above, it can be assumed that especially in the case of mortars CNT023H and CNT05H a good distribution of the CNTs within the hydrated binder matrix was obtained. The main effect of the higher degree of dispersion is certainly based on the interaction between the functional COOH groups attached to CNTs and the superplasticizer. The possible interactions could have been of physical or chemical origin. The physical interaction could include wrapping of the polymers around the CNTs or/and bonding to the CNTs due to van der Waals forces. The chemical interaction could be related to covalent bonding between the functional groups and the superplasticizers. The chemical bond between the superplasticizer and CNTs could be also formed in any place where CNTs had defects or/and at their ends.

As shown in **Fig. 2** addition of CNT-COOH did not affect the compressive strength values. These results comply with earlier observations, (Cwirzen 2008,

Kowald 2004), which showed that in order to enhance the mechanical properties of Portland cement-based matrixes, by the incorporation of a certain amount of CNTs, a sufficient bond between the binder matrix and CNTs surfaces must be ensured. Better bonding can be obtained by surface functionalization of the CNTs. Additionally, the CNTs should be uniformly dispersed throughout the binder matrix. Although, the dispersion of CNTs in the hardened mortars was not quantified in this study it can be assumed that the better dispersion of CNTs in water/superplasticizers mix also led to a better dispersion within the hydrated binder matrix. The ESEM study of the fractured specimens showed that the CNTs were present in all micro cracks formed during freeze-thaw cycles. A clear bridging effect was observed, even in the case of specimens CNT023L, which utilized dispersion produced by using low intensity sonication. In all specimens incorporating CNTs some nanotubes agglomerates were still present within the hydrated binder matrix. As shown in **Fig. 8** even the high intensity sonication used for CNT05H did not fully break the agglomerates. In the case of this particular sample a higher amount of CNTs could additionally contribute to a worse ultimate dispersion.

The ESEM studies showed also a rather inhomogeneous macrostructure of the hydrated binder matrix, which can be additionally attributed to the high water to cement ratio of 0.5 for all mixes. A high amount of voids with diameters up to 10 μm is clearly visible for example in **Fig. 9**, which shows the polished specimen CNT023L prior to the freeze-thaw cycles. Furthermore, an interfacial transition zone appeared to be present between larger sand particles and cement matrix. It can be identified by its higher porosity, see **Fig. 5**. The formation of voids in the bulk binder matrix and of locally porous ITZ is can be related to the high water to cement ratio. The small size of the specimens in connection with high porosity resulted in presumably high degree of saturation already after initial capillary water uptake and before start of the freeze-thaw cycles. The voids present in the binder matrix had small contribution in protection of the frost damage due to their not uniform distribution within the binder matrix as well as due to presumably high saturation degree.

As a result, there was an insufficient transfer of stresses between the binder matrix and CNTs despite their functionalization, which should enhance bond between CNTs and binder matrix.

This was due to the length of the fibers, being too short to transfer the load efficiently a better homogeneity, a lower porosity, and a narrower Interfacial Transition Zone (ITZ) can be obtained by lowering the water to binder ratio. As shown in earlier studies, (Cwirzen 2008), improvement of the compressive strength by 50% due to the incorporation of CNTs was observed in the case of cement pastes having water to binder ratio of 0.3. There was no enhancement at higher ratios. Similar trends were observed by Kowald *et al.* (Kowald 2004)

where cement paste specimens were additionally compacted, by application of high pressure, to increase the density of the binder matrix.

The lack of enhancement of the mechanical properties by incorporation of CNTs into a porous matrix which was produced by a high water to cement ratio comply with the results obtained for mixes incorporating CMFs. In this case their greater length bridging of inhomogeneity such as micro pores and weaker phases. These fibers acted also similar to regular fibers and enhanced only the flexural strength and ductility while the compressive strength remained unchanged. The ESEM study of the fractured specimens incorporating CMFs, showed their good dispersion within the hardened binder matrix. **Figure 10** shows well distributed CMFs as observed in specimen PI2.9. A later investigation of samples produced using this mix but subjected to freeze-thaw cycles showed a bridging of micro cracks that developed within the binder matrix by CMFs as shown in **Fig. 11**.

The performance of sample mortars during the freeze-thaw cycles was evaluated based on the cumulative strain values, measured after 40 freeze-thaw cycles, and on the deterioration rate, which corresponded to a permanent strain recorded at each cycle. The lowest value of the ultimate strain, thus the least extensive internal microcracking, was measured for mortar specimens incorporating the highest amount of CMFs, 2.9 wt%. This result complies with the measured mechanical properties of the hardened specimens, which revealed a higher flexural strength in comparison with specimens incorporating CNTs and with the reference mortar. Surprisingly, the maximum flexural strength was measured for specimens incorporating 1.4 wt% of CMFs. These specimens showed a slightly higher strain values in comparison with specimens incorporating 2.9 w% of CMF. Presumably, this can be attributed to a less homogenous binder matrix structures resulting from a worse workability in comparison with specimens PI1.4.

These results corresponded well to the measured me-

Fig. 11 ESEM-SE image of fractured hydrated mix PI2.9. Visible anchoring effect by the CNF of developing micro-crack.

chanical properties as lower compressive and flexural strengths resulted in higher cumulative strain values and thus more extensive microcracking of the binder matrix. It is a further confirmation of the conclusions formulated on the basis of the mechanical properties. The CNTs even despite the surface functionalization, which as shown in previous studies, (Cwirzen 2008, Kowald 2004) enhances the bond strength with the matrix, did not improve the overall mechanical performance of the binder matrix. The increased amount of the CNTs, in this case a maximum of 0.5 wt% of the cement weight, in combination with a very intensive sonication, which has proven earlier to ensure a very good dispersion of the CNTs, also did not alter the strength.

5. Conclusions

The development of cumulative strain due to freeze-thaw cycles and mechanical properties of normal strength mortars incorporating various types of carbon nano- and microfibers were studied. The test mortars had water to binder ratio of 0.5 and contained from 0 to 2.9 wt% of nano- or microfibers. The incorporated nanofibers were multiwalled carbon nanotubes dispersed in the mixing water by means of high and low intensity sonication in the presence of superplasticizers. The microfibers were added as delivered directly into the dry mix. The cumulative elongation due to freeze-thaw cycles was determined by strain measurements and the results were compared with the reference mortar which did not contain any fibers.

The obtained results showed that the workability of the studied mortars depended on the type and amount of added fibers as well as the type of used processing. Additions of well dispersed functionalized CNTs caused a full loss of flow ability of the fresh mortars. Slightly worse dispersed CNTs, which were obtained by low intensity sonication, resulted in a better workability. The flow-ability depended also on the amount of the present CNTs. As expected with a higher addition the loss of the flow-ability was more pronounced. The measured mechanical properties revealed that the flexural strength increased only in the case of mortars incorporating CMFs. The compressive strength was not enhanced in any of the studied mortars. The cumulative measured strain revealed significantly lower values only in the case of mortars incorporating CMFs. Higher CMFs amounts resulted in lower ultimate strain values and thus in less extensive internal damage. Mortars incorporating functionalized CNTs (CNT-COOH) showed an only slight decrease of the cumulative strain, in comparison with reference mortar, only when a mix of CNTs dispersed by low intensity sonication was used.

All obtained results, supported additionally by earlier studies, showed that in order to utilize the outstanding mechanical properties of CNTs the binder matrix must be very homogenous to provide sufficiently low contact area for stress transfer. The used water to binder ratio of

0.5 appeared to be sufficient only for long CMFs, which were able to bridge numerous weak inclusions such as weaker hydration phases and/or micro pores. The application CNTs appears to be ineffective to counteract the crack formation in the binder matrix due to freeze-thaw cycles. As shown in this and an earlier study the binder matrix would have to have a very low water to binder ratio and perhaps also additions of micro- and nanofillers to densify the matrix. In this case, however, the resulting very low water permeability could decrease the extent of the internal damage more than the presence of CNTs. On the other hand ultra-high strength mortars have an extremely low porosity and an explosive type of frost damage mechanism. In that case, the presence of the CNTs could delay the damage and perhaps weaken its explosive character.

Certainly, further study on the effect of CNTs and CMFs on the frost damage and also on the mechanical properties of very low water to binder mortar should be made. Furthermore the effect of coarse aggregates which are present in concrete should be evaluated as well.

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