

Carbon Nanostructures Incorporated to C₃S- and Cement-based Binders

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ABSTRACT

Carbon Nanotubes (CNTs) are well known for their unparalleled mechanical properties. Additionally their very high aspect ratio and low specific weight make them a very promising reinforcement material for composites. Recently carbon nanotubes were incorporated to plain cement pastes and normal concretes [1,2], ultra-high performance concretes [3] and C₃S-model systems [4] leading to improved mechanical properties. Also different carbon nanostructures like multi-walled carbon nanotubes (MWNTs) and carbon nano-coils (CNCs) were used and their influence on the hydration of C₃S and the mechanical properties of the composite were examined. *In situ* x-ray powder diffraction (XRPD) and differential heat-flow calorimetry (DCA) were used to get information about how the nanostructures influence the hydration. Also their effect on the microstructure had been observed [4]. The results show that the carbon nanostructures (CNSs) influence the hydration as well as the microstructure and are leading to improved mechanical properties of the composite. In this work we dispersed MWNTs by sonification and the use of sodium dodecyl sulfate (SDS) and incorporated them into pressure compacted prisms. The influence of the SDS and the MWNTs on the hydration, microstructure and the mechanical properties were examined.

1. INTRODUCTION

To achieve better mechanical properties of the nano-composites the dispersion of the CNSs and the linkage between the CNSs and the binder matrix has to be optimized. But also detailed information about the influence of the CNSs on the hydration of the binder is necessary to further improve the composite.

One group used plain cement pastes to incorporate MWNTs and SWNTs leading to an increase in the compressive strength of 30 % in case of the MWNTs and 6 % when using the SWNTs [1]. A use of MWNTs within a cement-based binder containing coarse aggregates led only to minor improvements in the compressive strength of the samples (Table 1).

Although the use of MWNTs modified by oxidation with an increased number of surface defects [1] and an improved anchoring should lead to improved mechanical properties deterioration had been found as shown in Table 2 [2,3].

Table 1. Compressive strength of non-compacted samples containing coarse particles

After 7 d		After 14 d	
Reference	0.5 ma.% MWNTs	Reference	0.5 ma.% MWNTs
142 N/mm ²	153 N/mm ² + 11 N/mm ² (8%)	149 N/mm ²	169 N/mm ² + 20 N/mm ² (14 %)

The investigation of the microstructure showed that the losses in the mechanical properties of the samples with the exohedral functionalized nanotubes were caused by an agglomeration of the MWNTs within the cavities between coarse particles. The MWNTs contained in the cavities were not completely bound into the matrix and led in this case to decreased mechanical properties.

Table 2. Compressive strength test after 7 d of compacted samples containing coarse particles

Reference	0.5 ma.% untreated MWNTs	0.5 ma.% HNO ₃ -oxidized MWNTs	0.5 ma.% H ₂ SO ₄ -oxidized MWNTs
214 N/mm ²	239 N/mm ² + 25 N/mm ² (12%)	184 N/mm ² - - 30 N/mm ² (-14%)	216 N/mm ² + 2 N/mm ² (1%)

The agglomeration of the MWNTs could be minimized by the use of finer particles. To additionally show the influence of different carbon nanostructures (CNSs) on the hydration of C₃S, they were used in a C₃S-water-superplasticizer-system with a grain size between 3 and 4 μm [4]. In these optimized binder systems the oxidized MWNTs showed the best improvement in the mechanical properties. We also used special carbon nanostructures, the so called carbon nano-coils, to improve the mechanical linkage between the reinforcement and the matrix. These showed without additional treatment good mechanical improvements. Especially the flexural strength values showed a remarkable improvement of 45 % when the oxidized nanotubes were used and 31 % in the case of the unmodified CNCs (Table 3).

Table 3. Mechanical tests after 7 d of compacted C₃S-samples without coarse particles

	Reference	0.5 ma.% untreated MWNTs	0.5 ma.% HNO ₃ -oxidized MWNTs	0.5 ma.% CNCs
Compressive Strength	238 N/mm ²	250 N/mm ² + 12 N/mm ² (8%)	263 N/mm ² + 25 N/mm ² (10%)	259 N/mm ² + 21 N/mm ² (9%)
Flexural Strength	17 N/mm ²	20 N/mm ² + 3 N/mm ² (18%)	25 N/mm ² + 8 N/mm ² (45%)	22 N/mm ² + 5 N/mm ² (31%)

In situ XRPD and DCA investigations gave us information about the influence of the MWNTs on the reaction kinetics of the hydration.

Statements about the influence on the reaction kinetics and the phase formation were thus possible. In this model-system a great influence on the crystallization of the portlandite could be observed, showing less and smaller crystals compared to a sample without MWNTs. The DCA measurements showed an acceleration of the hydration by the MWNTs so that the effect was not due to a retarding effect [4]. The found influence on the portlandite crystallization shows that the used MWNTs have a clear influence on the hydration of C_3S and showed an accelerated reaction with very fine portlandite. The effect of getting finer crystallisation products when using MWNTs could also be seen by SEM-investigations. Another team [5] mentioned a reaction of the COOH-groups at CNTs surface with the solution so that chemical link between the hydration products and the CNTs is possible. This means that the functional groups can act as crystal seeds resulting in an increased number of finer hydration products, this correlates very well with the results mentioned above.

2. EXPERIMENTAL PART

To distinguish if SDS which is used as a pore stabilizer could be used for stabilizing the CNTs-dispersions by forming micelle structures and thus preventing aggregation the following experiments had been done. Within pressure-compacted samples consisting of cement, water and a superplasticizer (SP) we used SDS-stabilized MWNTs and compared the influence on the hydration, mechanical properties and microstructure to systems without SDS.

2.1 Sample Preparation

The MWNTs (1 ma.% by cement content) were dispersed by sonification for 10 minutes within the mixing water than the SDS was added and the dispersion sonifacted for additional 18 minutes. At the end of the sonification the SP was added. As binder we used a CEM I 52.5 R and the water to cement ratio was 0.22. After the mixing process the pastes were moulded into prism-shaped forms and compacted by applying a pressure of 125 N/mm^2 for 30 minutes. The prisms were demoulded after 1 day of storage at a relative humidity of $>90 \%$ and $20 \text{ }^\circ\text{C}$. Afterwards the prisms were cured 6 d under water at $20 \text{ }^\circ\text{C}$ until the mechanical strength tests took place. For each test 3 prisms were made and used for the flexural strength examination. The resulting 6 halves of the prisms were used for the compressive strength tests.

The *in situ* x-ray powder diffraction experiments and the observation by the ultrasonic method were done on the same samples which were prepared for the prisms. A Panalytical X'Pert Pro diffractometer with Cu-K_α radiation equipped with an X'Celerator detector had been used for the

time dependent observation of solution and crystallization processes. The diffraction patterns were collected every 30 minutes over a period of 24 h. To prevent the sample from drying during the hydration process the pastes were measured in a special fluid cell where the sample had been covered by a Kapton[®]-foil.

2.2 Reaction kinetics

The influence of MWNTs on the hydration of the samples was observed by *in situ* XRPD and by the ultrasound method (UM). As an indicator for the hydration of the pastes during the XRPD-experiments the (001)-reflex of the hydration product $\text{Ca}(\text{OH})_2$ can be taken. Figure 1 to Figure 4 show the evolution of the ettringite ($9,1^\circ$) and portlandite-peak (18.066°) during the first 24 h of hydration. For better clearness only the 2-theta ranges from 7° to 22° are shown. The Intensities are scaled by colorization (blue: low intensities, red: high intensities).

The data of the samples without SDS (Figure 1 and Figure 2) can be compared with the data from the samples with SDS (Figure 3 and Figure 4) to show the influence of the SDS. Figure 1 shows the *in situ* XRPD measurements of the reference sample consisting only of cement, water and SP. The ettringite reflexion can be observed from the first measurement on and is growing during the hydration process. The first portlandite reflexion could be observed after 3 h. If we compare the measurement with the sample containing the MWNTs we can see that the first portlandite crystals could be detected after 4.5 h.

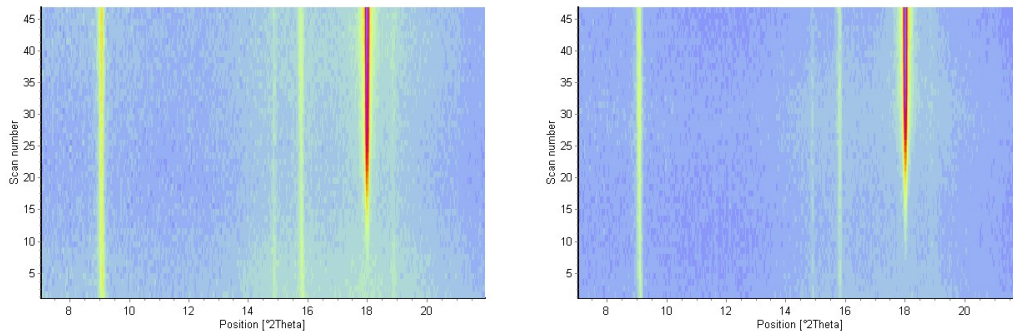


Figure 1. *in situ* XRPD of the reference sample Figure 2. *in situ* XRPD with MWNTs

When using SDS the crystallization of the portlandite seems to be inhibited (Figure 3 and Figure 4) while the ettringite formation is not so strongly affected. The ettringite and portlandite crystallization of the sample containing SDS and MWNTs is slightly retarded.

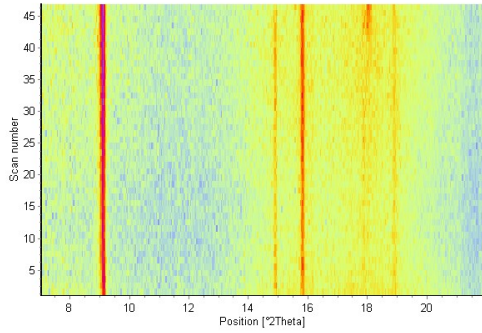


Figure 3. *in situ* XRPD with SDS

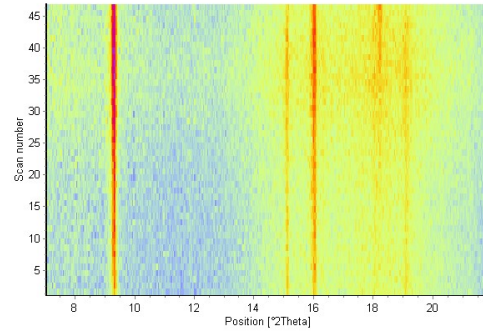


Figure 4. *in situ* XRPD with SDS and MWNTs

The UM uses ultrasound to observe the setting of binders. The ultrasound is produced and detected by a piezoelectric emitter-receiver pair. By measuring the time the ultrasound needs to pass through the sample the velocity of the waves can be plotted versus the hydration time.

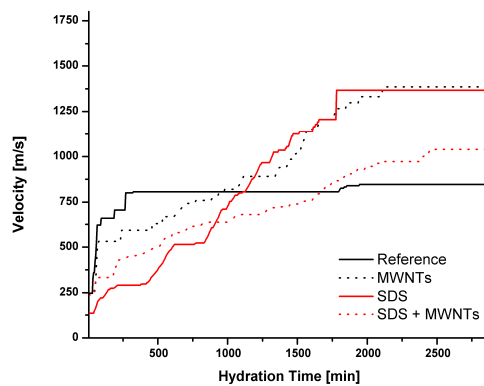


Figure 5. Velocity vs. hydration time results of the UM-measurements

In Figure 5 the results of the samples observed by the UM for 48 h are shown. Comparing the samples without SDS it can be seen that the hardening process of the sample containing the MWNTs is slower up to 250 minutes but constantly evolving up to 2000 minutes. The sample MWNTs had the highest value after 48 h which is pointing to a dense material. The samples with SDS are both showing a delay in the hardening process compared to the samples without SDS. The sample SDS + MWNTs showed the slowest hardening and it seems that after 48 h the maximum velocity isn't reached.

2.3 Microstructure

The microstructural investigations were done by SEM on fragments of the prisms from the mechanical tests and by AFM on polished specimens.

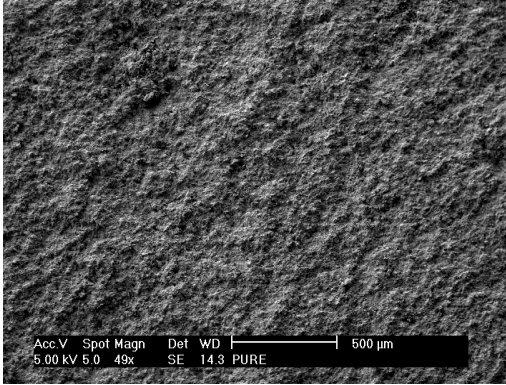


Figure 6. Microstructure of the reference, SEM

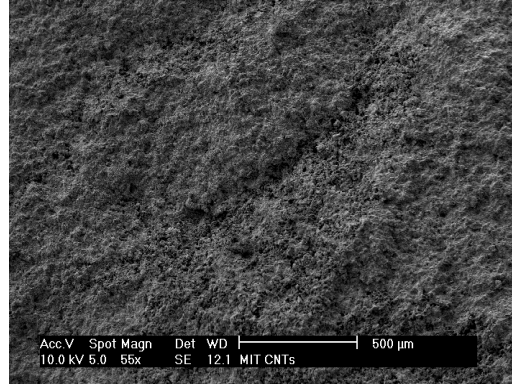


Figure 7. Microstructure with MWNTs, SEM

Figure 6 to Figure 9 show the influence of the MWNTs on the microstructure of the samples without SDS. A denser matrix could be found when using the MWNTs. In the center of the right micrograph (Figure 7) one of the few pores with agglomerated MWNTs can be seen. These pores had been found in earlier works [4], too, especially when coarse particles were present.

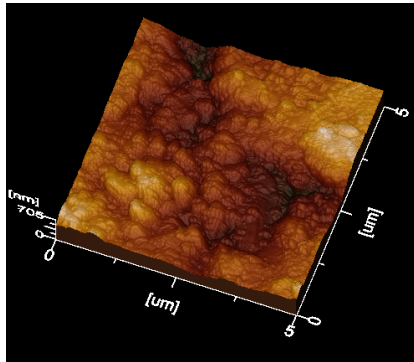


Figure 8. Microstructure of the reference, AFM

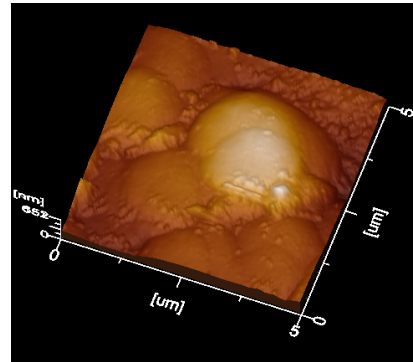


Figure 9. Microstructure with MWNTs, AFM

The topography of the two samples with and without MWNTs are depicted in Figure 8 and Figure 9 showing the more homogeneous and finer matrix of the hydration products when the MWNTs were used.

The microstructure of the samples with SDS (Figure 10 to Figure 13) are denser compared to the samples without SDS and no pores could be detected. The sample with SDS and MWNTs is more homogeneous than the sample without SDS and showing no large pores with agglomerated MWNTs. Furthermore many micro cracks and some small fragments still sticking to the surface can be seen.

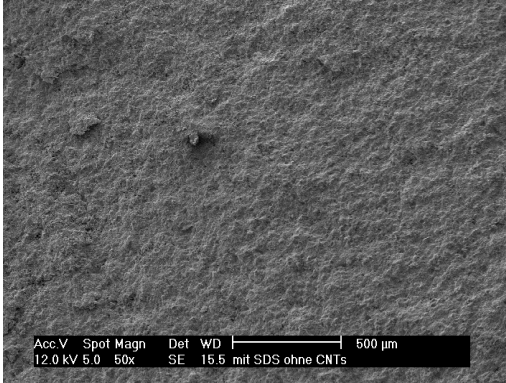


Figure 10. Microstructure with SDS, SEM

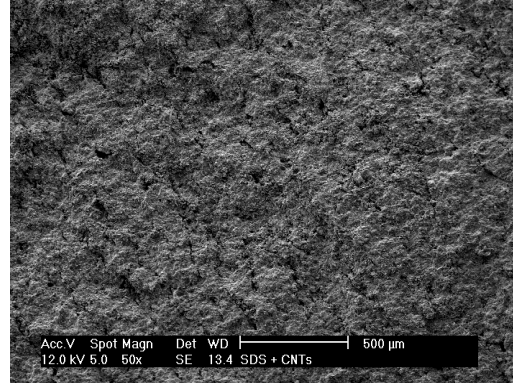


Figure 11. Microstructure with SDS+MWNTs, SEM

The topographical investigations by AFM of the two samples where SDS was used are depicted in Figure 12 and Figure 13 showing the more homogeneous microstructure compared to the samples without SDS. The sample with SDS and MWNTs had the most homogenous and finest matrix.

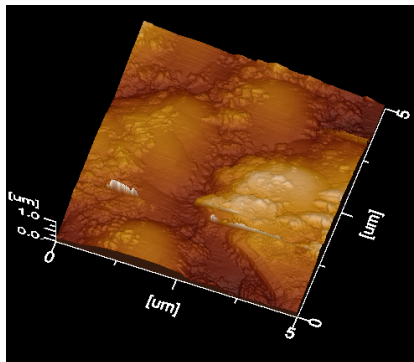


Figure 12. Microstructure with SDS, AFM

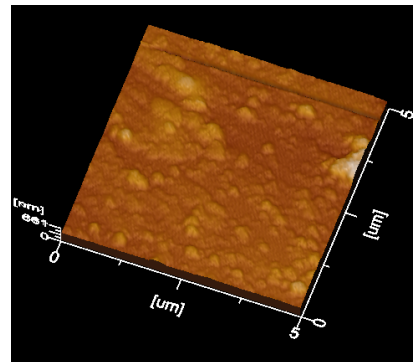


Figure 13. Microstructure with SDS+MWNTs, AFM

2.4 Mechanical Properties

The incorporation of MWNTs into the samples without SDS led to an improvement in the compressive strength after 7 d from 196 N/mm² to 202 N/mm². The SDS-sample's compressive strength could be improved from 197 N/mm² to 209 N/mm² (Figure 14).

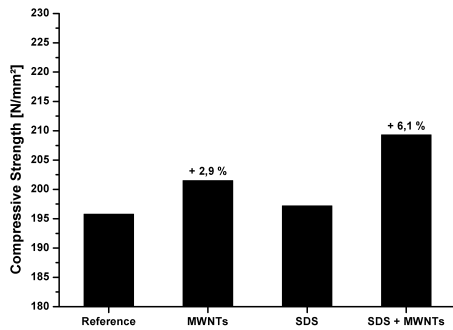


Figure 14. compressive strength 7 d

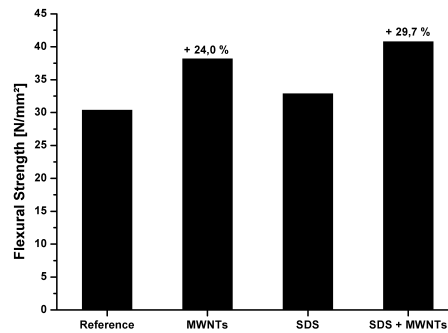


Figure 15. flexural strength after 7 d

The influence of the MWNTs on the flexural strength was more distinct. So the samples without SDS showed an increase from 30 N/mm² to 38 N/mm² and the samples with SDS from 33 N/mm² to 41 N/mm² (Figure 15).

3. RESULTS AND CONCLUSIONS

In this work the possible application of SDS for the stabilization of MWNTs in water and their use in pressure compacted prisms was tested. For this purpose the *in situ* XRPD and the UM were used in parallel to investigate the influence on the hydration with respect to phase and strength developments. Microstructural and mechanical experiments were additionally done.

The experiments showed an inhibited crystallisation of ettringite and especially portlandite. The shift to later hydration times of the crystalline portlandite had also been found in C₃S-water-systems but there it was more pronounced [4]. When SDS was used only a small amount of portlandite could be detected by XRPD after 24 h.

The UM showed, that both the MWNTs and the SDS led to a slower strength development. After 250 minutes there was nearly no increase in the velocity of the ultrasound when the sample without MWNTs and SDS had been observed. The sample with MWNTs and the sample with only SDS showed after 48 h the highest velocities. This indicates that they have the best strength and the densest microstructure within 48 h. It seems that the evolution of the velocity of sample MWNTs + SDS isn't completed within 48 h. These results are in good agreement with the microstructural investigations. The samples with the MWNTs are showing a denser microstructure which is even more densified when the SDS had been used. The numerous microcracks which could be found in the sample MWNTs + SDS point to a more regular distribution of the mechanical load in the sample. The mechanical properties were enhanced

by the use of the MWNTs. In the case of the SDS-stabilized MWNTs the best improvement in the flexural strength could be found.

The results show that the use of SDS for the stabilization of the MWNTs within the mixing water lead to improved mechanical properties of the composite when used in pressure compacted samples.

REFERENCES

- [1] Campillo, I., J.S. Dolado, A.Porro, High-Performance Nanostructured Materials For Construction, in: Proceedings of the 1st International Symposium on Nanotechnology in Construction, Paisley, 2003, pp. 110-121
- [2] T. Kowald, R. Trettin, Kohlenstoffbasierte Nanostrukturen in modernen anorganischen Bindemitteln, in: Tagung Bauchemie, GDCh-Fachgruppe Bauchemie, 2004, pp. 162-165
- [3] T. Kowald, R.H.F. Trettin, Influence of surface-modified Carbon Nanotubes on Ultra-High Performance Concrete, in: Proceedings of the International Symposium on Ultra High Performance Concrete, kassel university press GmbH, 2004, pp. 195-202
- [4] X. Jiang, T.L. Kowald, T. Staedler, R.H.F. Trettin, Carbon Nanotubes As A new Reinforcement Material For Modern Cement-Based Materials, in: Proceedings of the 2nd International Symposium on Nanotechnology in Construction, RILEM Publications s.a.r.l, 2005, p. 26
- [5] G.Y. Li, P.M. Wang, X. Zhao, Mechanical behaviour and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes, Carbon (43) (2005) 1239-1245