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Influence of surface-modification, length and volume fraction of carbon short fibers on the mechanical properties of calcium aluminate cement systems

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1. Introduction

As already known from literature, the compressive strength of cementitious systems is many times higher than the corresponding bending tensile strength. In order to use cementitious systems for the construction of load-bearing structures, it is necessary to overcome this inherent property. A common method in the construction industry is to use reinforcement steel [1]. This so-called composite material (concrete + steel) has significantly increased the bending tensile strength but also the weight. The corrosion sensitivity of steel is an additional disadvantage.

For this reason many studies have evaluated a large number of different materials to replace or partially replace reinforcement steel. Here, one of the most extensively studied materials are carbon fibers due

to their extremely high tensile strength and low material density. Because of the pre-eminence of Ordinary Portland cement (OPC) in the construction industry, almost all of these studies were carried out with this cementitious binder system [2–12]. In addition to this widespread OPC there are some cements for special applications about which not much is yet known [13,14] regarding the effect of carbon fibers on the strength and other properties of the hydrated cement stone.

Calcium aluminate cement (CAC) is the type of special cement in which the influence of short carbon fibers should be investigated more closely. At this point it must be mentioned that the hydration of calcium aluminate cement is completely different to that of OPC [15]. Additionally, an effect known as "conversion" is known in calcium aluminate cement chemistry. This effect indicates the increase of the porosity of hardened CAC with time, which leads to a decrease in strength. The

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reason for this effect is that some of the occurring CAC hydrates (C_2AH_8 and CAH_{10}) are thermodynamic instable at room temperature and change to hydrate phases which have a lower porosity (AH_3 and C_3AH_6) [16–18]. Depending on the production process (sintering or fusing), CAC can basically consist of three different phases [19,20]. These are $CaAl_2O_4$ (CA), $12 CaO \cdot 7Al_2O_3$ ($C_{12}A_7$) and $CaO \cdot 2Al_2O_3$ (CA_2). Of these three phases, monocalcium aluminate (CA) and mayenite ($C_{12}A_7$) are the hydraulically most active ones [21]. For this reason and due to the fact that commercial products – for example, Ternal White [22] from Kerneos – mainly consist of monocalcium aluminate (CA) ($C_{12}A_7/CA < 0.03$), the effect of carbon short fibers on the mechanic properties of hydrated CA (commercial product Ternal White) should be examined in greater detail. According to our knowledge, studies have not yet been carried out regarding the influence of surface-modified carbon short fibers on the mechanical properties of calcium aluminate-dominated systems. Thus, the studies carried out contribute to a deeper understanding of the optimization of special cements which are not OPC dominated. A critical point for all fiber containing materials is the quality of adhesion between the fiber and the surrounding matrix. The stronger this, in the following called cement – fiber connection is, the higher the mechanical characteristics are. For this reason the influence of surface treatment of carbon short fibers on the cement – fiber connection was evaluated over the achievable bending tensile strength and ESEM pictures. After that the effect of carbon short fibers with a length of 0.1 mm up to 6 mm in a different volume content (0.5 up to 3 %) on the bending tensile strength has been measured after 1 day and 1 week. The compressive strengths were also determined for the selected systems.

2. Material and methods

2.1. Materials

In order to determine the influence of surface modified carbon short fibers on the bending- tensile and compressive strength of the hydration products of the hydraulic active phase CA, we used the commercial cement Ternal White, from the French company Kerneos. Table 1 shows the composition of Ternal White and the material properties of the carbon short fibers from Procotex.

A water / cement ratio of 0.3 and a different cement / filler ratio were chosen for the preparation of the samples. The filler used is calcite (commercial name Ulmer Weiß MHM [24]) with an average particle size

Table 1
Chemical and mineralogical composition of Ternal White [22], and the material properties of carbon fibers from Procotex [23].

Ternal White (Kerneos)		Carbon fibers (Procotex)	Properties
Al_2O_3 (%)	68.7–70.5	Carbon content	94 % (> 92 %)
CaO (%)	28.5–30.5	Sizing level	1.4 % +/- 0.6
SiO_2 (%)	0.2 – 0.6	Density (continuous fiber)	$1.7 < d < 2.0$
Fe_2O_3 (%)	0.1 – 0.2	Mono filament diameter	7 +/- 2 μm
Mineralogical composition		Volume resistivity	15 $\mu\Omega m$ (20 maxi)
		Young's modulus (tensile)	230 GPa
Principal phase	CA and CA_2 ($C_{12}A_7$ / $CA < 0.03$)		
Secondary phases	$C_{12}A_7$ and $A\alpha$	Elongation at break	1.5 %
		Tensile strength	3.5 Gpa
		Mean length	Xx mm +/- 0.2
		Mass distribution	90 % +/- 5
		Bulk density	0.4 kg/dm ³ +/- 0.06
		Metal contamination	< 0.05 g/1000 g

of 21 μm . In order to regulate the setting time und viscosity of the mixture, it is necessary to use tempering water with a low proportion of lithium salts, organic acids [25–31] and a superplasticizer (required to ensure a homogeneous dispersion of the fibers). The exact composition of the mixed water in percent per weight is: 77 % tempered water, 15 % Li_2SO_4 and 8 % Visco Crete 2520 (polycarboxylate ether). The hydration process takes place at approx. 25 °C (room temperature) and a humidity of approx. 100 % (necessary to prevent evaporation and, consequently to stop the hydration process).

2.2. Methods

The bending tensile and compressive strengths were determined by Zwick/Roell Zwicki-Line Z0.5, with a 5 kN / 50 kN load cell. By measuring the maximum force F_{max} (breaking load), it is possible – with reference to DIN EN 196 [32] – to determine the bending tensile strength and compressive strengths. The sample dimensions are $50 \times 14 \times 6$ mm for the bending tensile and 15 mm cubes for the compressive strength test – determined before the measurement with an accuracy of 0.01 mm. In order to get a reliable result, it is necessary to measure each system 6 times and to determine the average and the standard deviation. The optical inspection of the fracture edge of the sample takes place by means of environmental scanning electron microscopy (ESEM). TG measurements on the carbon fibers are carried out with a LUX STA 409 PC, from Netzsch. The heating rate during the analysis is 10 °C/min up to 800 °C, under a constant flow of N_2 .

For the surface treatment of the carbon short fibers, a furnace (Modell RT 50–250/11 – manufactured by Nabatherm – oxidative treatment) and a low pressure plasma system (Femto with vacuum pump Trivac D16BCS with CFS Filter – produced by Diener Electronics GmbH – fiber coating with functional groups) were used. The specific parameters of the two systems during the process are given in the chapter results. Since a uniform dispersion of the carbon fibers in the cementitious system is required to compare the mechanical test results of different fiber length and contents the system is thoroughly homogenized for around 5 min by means of a spatula in a paper cup. The result of the homogenization is checked visually.

3. Results

3.1. Modification of the carbon fiber surface relating to the best fiber-matrix (calcium aluminate cement) connection

In addition to a high degree of dispersion of the carbon short fibers in the cementitious matrix, the fiber-matrix (CAC) connection is the determining factor for the enhancement of the bending tensile strength. For this reason, the influence of different carbon fiber surface treatment on the fiber-matrix (CAC) connection should be evaluated [7,33–39]. To test the connection behavior of hydrophilic and hydrophobic groups on the fiber surface to the cementitious matrix a washing-off, oxidation process and plasma treatment were carried out. Furthermore the oxidation process could lead to an improvement in fiber roughness which could probably strengthen the fiber-matrix (CAC) composite.

The carbon short fibers – supplied by Procotex (Table 1) – are coated with a water-soluble epoxy resin in order to simplify the cutting process. The first surface modification of the fibers is to wash them in a batch of 50 g each in a glass bowl under running water for approx. 5 min and allow them to dry at room temperature for two days. To ensure that the epoxy resin is completely washed off, the TG measurement of the carbon fibers is carried out before and after the washing process. As can be seen in Fig. 1, epoxy begins to burn at 300 °C, while carbon fibers begin to decompose at 600 °C. The washed carbon short fibers (supplied by Procotex) do not show weight loss until 600 °C, while the untreated fibers show a significant loss from 300 °C to approx. 600 °C. This mass loss can be attributed to the functionalization application on the carbon fibers made of epoxy resin and amounts to around 3.5 percent.

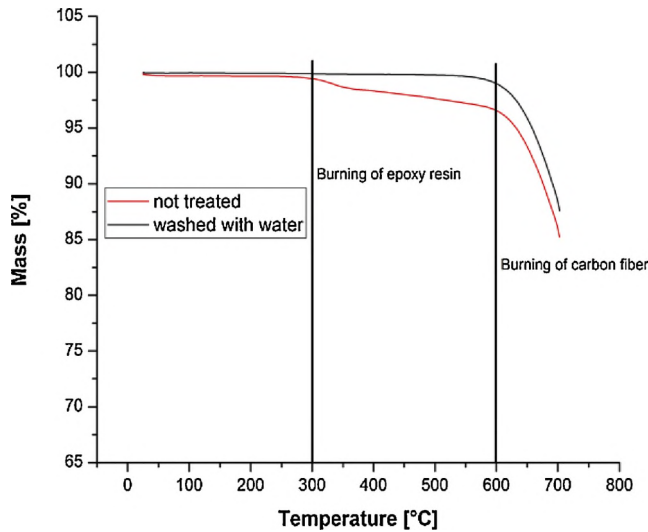


Fig. 1. TG-measurement of the weight loss of epoxy resin-coated and washed 3 mm carbon fibers.

The second surface treatment of the carbon short fibers is thermal oxidation. Here, the untreated, epoxy resin-coated carbon short fibers are oxidized in a batch of 50 g each in a porcelain crucible in a furnace under an oxygen atmosphere, at a heating rate of 50 °C/h. To determine the ideal oxidation temperature, 350 °C, 400 °C, 450 °C and 500 °C are rated. These temperatures are kept for 2 h and then cooled back to room temperature with also 50 °C/h.

The third modification of the carbon short fibers is a plasma treatment in a low-pressure plasma system, produced by Diener Electronics GmbH. To test the influence of nitrogenous groups on the fiber-matrix (CAC) interaction, ammonia gas is used in the plasma chamber. Determined by series of experiments, the parameters 300 W, 8 min – not pulsed – 13.56 MHz and 0.5 mbar are used. The presence of nitrogenous groups on the carbon fibers after the plasma treatment could be proven by XPS measurements.

To test the effectivity of the different carbon fiber surface treatments relating to an enhancement of the fiber-matrix connection, the bending tensile strengths of CAC-systems with 0.7 mm and 3 mm carbon fibers are tested. Fig. 2 shows the results of such tests with Ternal White (main phase: CA) as the binder, a carbon fiber content of 1-vol %, a water/

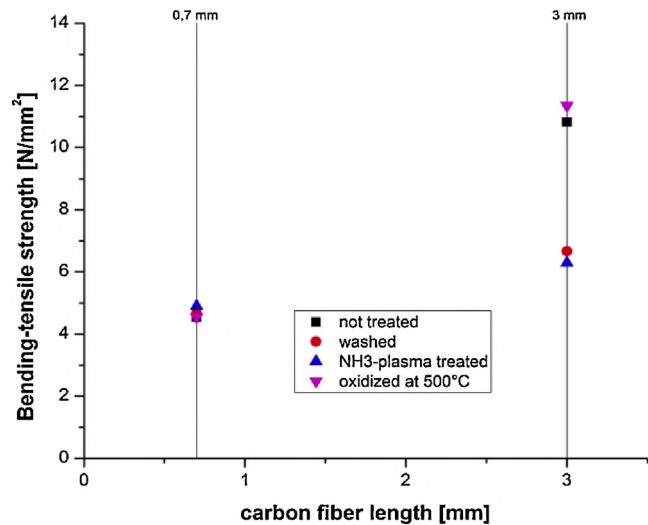


Fig. 2. Influence of the carbon fiber surface treatment on the bending tensile strength of CAC dominated systems (binder: Ternal White; 1-vol % 0.7 mm or 3 mm carbon fibers; water/cement – ratio of 0.5; cement/filler – ratio of 5).

cement-ratio of 0.5 and a cement/filler-ratio of 5. It can be seen that the addition of 0.7 mm carbon short fibers has – independently of the surface treatment – no positive effect on the bending tensile strength, whereas the oxidation process of the 3 mm carbon fibers at 500 °C leads to a slight increase (compared to the untreated fibers). The washing process and the creation of nitrogenous groups on the fiber surface results in a drastic decrease of approx. 40 %. Fig. 3 shows the effect of the carbon fiber oxidation temperature of 3 mm carbon fibers on the bending tensile strength. It can be seen that the bending-tensile strength decrease drastically below 400 °C compared to the untreated fibers. The highest bending tensile strengths were reached at an oxidation temperature of approx. 500 °C – which is slightly higher than that of the untreated fibers. In order to determine the ideal cement/filler and water/cement-ratio of a carbon short fiber containing CAC system with respect to the bending tensile strength, a large number of experiments were performed. Fig. 4 shows the influence of a variation of the cement/filler and the water/cement-ratio on the bending tensile strength of a system with 1 vol-% 0.7 mm and 3 mm carbon short fibers. At a cement/filler-ratio of 60, the water/cement-value is 0.4. As we increase the filler content of the system but still use the same amount of mixing water, the water/cement-value increases (from left to right in Fig. 4). Thus the values in Fig. 4 are only comparable at the same cement/filler-ratio. It can be seen that, at a cement/filler-ratio of 5 with 1 vol-%, 3 mm carbon short fibers leads to the highest bending tensile strength of the examined systems. For this reason, different water/cement-values of this and two other systems with similar cement/filler-ratios were tested (Fig. 5). Based on this, a cement/filler-ratio of 5, and a water/cement-ratio of 0.3 for the further investigations were selected. In addition to the drastic increase of the bending tensile strength through the addition of carbon short fibers with a length of 3 mm, we observed a significant reduction of the shrinkage during the hydration process. To determine the shrinkage of the CAC systems, the length of the bending tensile specimens after 1 day of hydration were measured and the percentage shrinkage was calculated based on the original lengths of the molds. Fig. 6 shows the shrinkage in systems containing carbon fiber plotted against the bending tensile strength. Because the only difference between these three systems is the presence of carbon short fibers with a different length, a direct comparison is possible. It was evident that an increase in the bending tensile strength was associated with an increase in the shrinkage over all three tested systems. In addition, shrinkage of the calcium aluminate cement systems decreases with the length of the carbon fibers used.

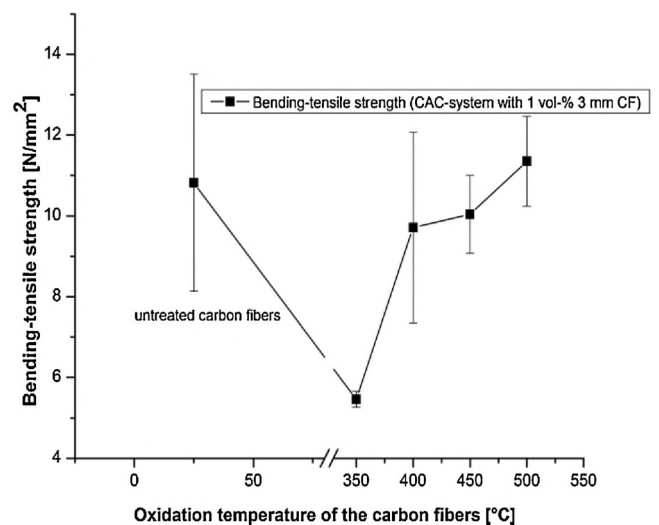


Fig. 3. Influence of the oxidation temperature of 3 mm carbon fibers on the bending-tensile strength of CAC dominated systems (binder: Ternal White; 1-vol % 3 mm carbon fibers; water/cement – ratio of 0.5; cement/filler – ratio of 5).

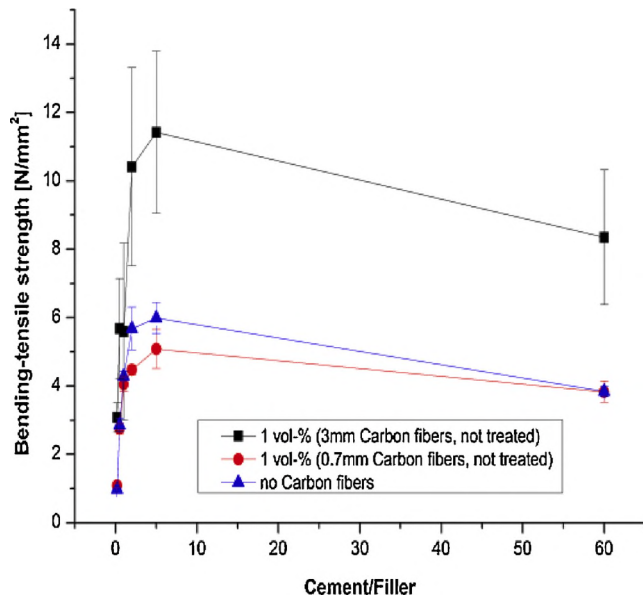


Fig. 4. Influence of the cement/filler -value of CAC dominated systems with carbon fibers on the bending-tensile strength (binder: Ternal White; 1 vol-% 0.7 mm and 3 mm carbon fibers, not treated).

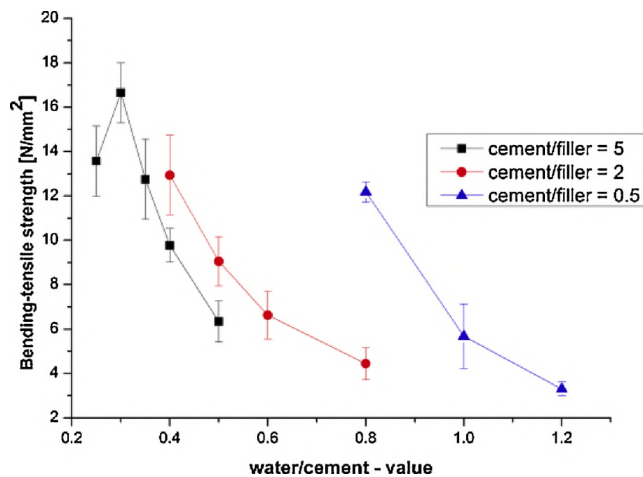


Fig. 5. Influence of the water/cement-value on the bending-tensile strength of a CAC system with 1 vol-% 3 mm not treated carbon fibers (binder: Ternal White).

3.2. Evaluation of the ideal carbon fiber lengths in respect to the bending tensile- and compressive strength

To determine the ideal carbon fiber lengths in terms of the bending tensile strength a CAC system with Ternal White as the binder, a water/cement-value of 0.3, a cement/filler-value of 5, and 1 vol-% of carbon short fibers with a length of 0.1 mm–6 mm, supplied and cut by Procotex were used. Based on the results of the preliminary tests, the carbon fibers have been oxidized for 2 h at 500 °C (specific parameter described in the chapter results). To ensure an optimal dispersion degree of the carbon fibers in the cementitious system through the mixing procedure, the opening time was increased by a modification of the mixing water (use of organic acid as retarder). Fig. 7 shows the relationship between the bending tensile strength and the length of carbon fiber used after 1 day and 1 week (1 week value in order to determine a possible postcuring). It can be seen that the length of the carbon fibers have a significant influence on the bending-tensile strength. Up to a length of 2.5 mm, the values increase constantly – while beyond this point, a decrease can be

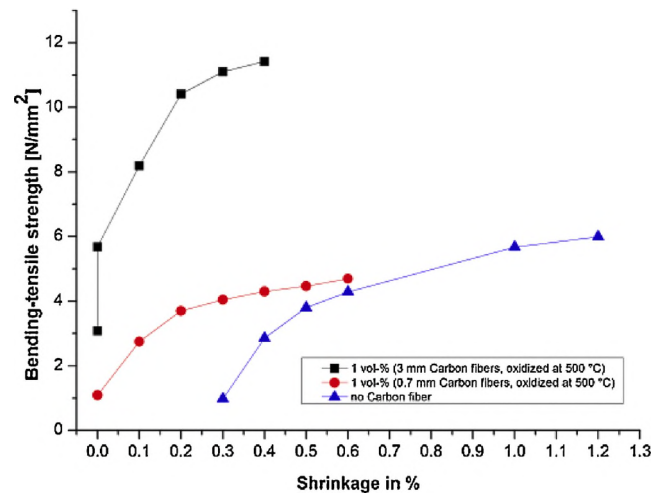


Fig. 6. Influence of the carbon fiber length on the shrinkage of CAC systems (binder: Ternal White; 1 vol-% 0.7 mm and 3 mm at 500 °C oxidized carbon fibers).

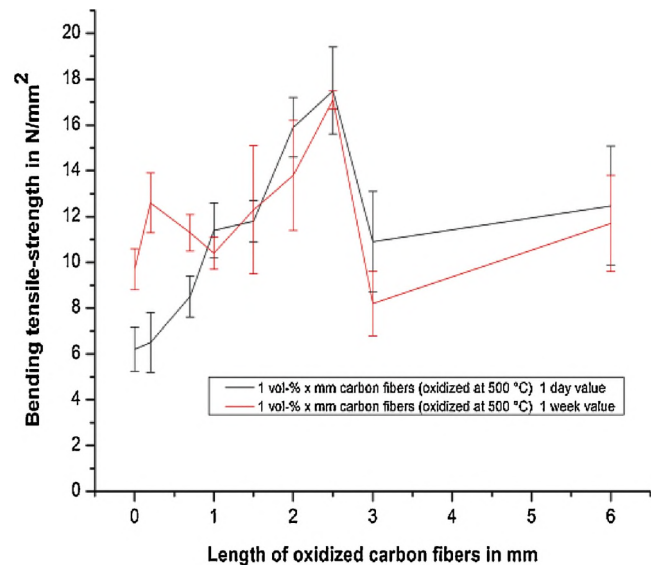


Fig. 7. Influence of the carbon fibers length on the bending-tensile strength of CAC systems after 1 day and 1 week (binder: Ternal White, 1 vol-% x mm carbon fibers, oxidized at 500 °C; water/cement-ratio of 0.3; cement/filler-ratio of 5).

observed. In order to estimate the influence of the vol-% of carbon short fibers on the bending tensile strength after 1 day and 1 week, the amount was increased from 0.5 vol-% to 3 vol-%.

In Fig. 8, it can be seen that the bending tensile strength of the CAC-system with different amounts of 2.5 mm carbon short fibers (oxidized at 500 °C) increases in percentage up to a volume content of 1 (vol-%) more than 200 % compared with the fiber free-system. Beyond this point, there is a drastic decrease in the 1-day values but a brief increase after 1-week.

In order to evaluate the influence of carbon short fibers on the compressive strength of CAC-systems mixtures with 0.5, 1 and 1.5 vol-% of oxidized 2.5 mm fibers (water/cement-value 0.3 and cement/filler-value 5) were also tested. The-1 day values for such systems are 44.3 ± 7.4 with 0 vol-% carbon fibers, 44.5 ± 6.5 with 0.5 vol-% 2.5 mm fibers, 46.4 ± 5.5 with 1 vol-% 2.5 mm fibers, and 47.5 ± 3.9 with 1.5 vol-% 2.5 mm fibers. Since all of these values lie in the same region, it can be said that the addition of carbon short fibers have no positive or

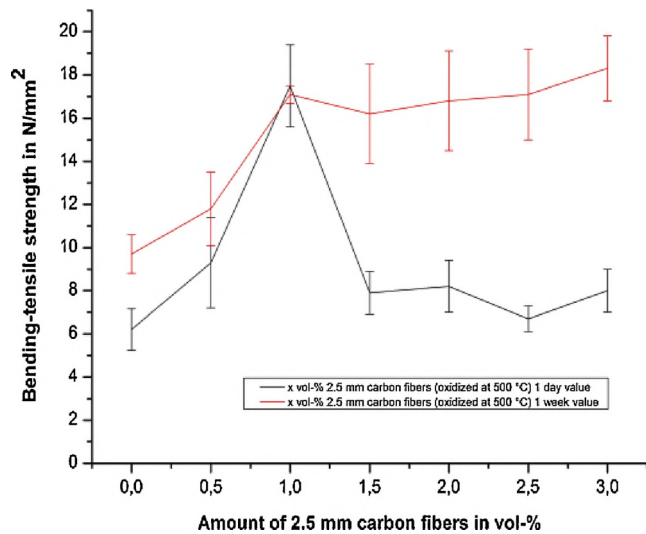


Fig. 8. Influence of the vol-% of carbon fibers with a length of 2.5 mm on the bending-tensile strength of CAC systems after 1 day and after 1 week (binder: Ternal White, x vol-% 2.5 mm carbon fibers, oxidized at 500 °C; water/cement-ratio of 0.3; cement/filler-ratio of 5).

negative influence on the compressive strength of CAC dominated systems (binder: Ternal White).

4. Discussion

4.1. Possible reasons for the influence of the carbon fiber treatment on the bending tensile strength of CAC containing systems

The interaction between carbon fiber and cement plays an important role in increasing the bending tensile strength of fiber reinforced cementitious materials. In general it can be said, that with an increase of the carbon fiber surface interaction with the surrounding cementitious material (matrix), the bending tensile strength also begins to increase. Thus an optimal interaction between carbon fiber/cement would result in a crack of the carbon fiber under tensile load. In this theoretical case, the cementitious material reaches a tensile load which corresponds to that of carbon fibers. In reality it is almost impossible to achieve such a strong adhesion. Fig. 9 shows an ESEM image of the broken edges of a 1 vol-% of 2.5 mm carbon fibers

reinforced CAC-system after a curing time of 1 day. It can be seen that some of the carbon fibers have been pulled out (holes) but others are still embedded in the cementitious matrix. It is hard to tell if these fibers were torn off or if they just ended at this point. With regard to the fiber-matrix interaction, we assume that the chemical groups on the fiber surface are the decisive factor. Due to the different surface modifications of the carbon fibers, it can be said that the oxidation process at a temperature of 500 °C leads to the strongest fiber-matrix connection, and therefore to the highest bending tensile strengths (Fig. 2). The reason for this could be that after the oxidation process the surface of the carbon fibers is combined with carbonyl- and hydroxyl groups, which leads to a hydrophilization of the – in their pure form (uncoated) – hydrophobic carbon fibers. Because cementitious systems are water based and, therefore, have a strong polar character, the fibers could be better embedded in them. In the ESEM images, this can be viewed as a significant decrease in the fiber-cement boundary (black area in the exposures) compared to the system with hydrophobic fibers (Fig. 10). Another reason for improving the bending tensile strength through oxidation of the carbon fibers could be that their roughness – and thus the surface available for interaction with the cementitious matrix – increases significantly.

In order to test the influence of other polar groups on the surface of the carbon fibers with regard to the fiber-matrix interaction, a plasma treatment with ammonia gas was carried out. From XPS-measurements after treatment, it can be said that the ammonia content on the fiber surface has increased significantly. Despite the presence of the polar nitrogen-containing groups, CAC-systems with this kind of surface-treated fiber as a reinforcing element, have only about half the bending tensile strength of the systems with oxidized carbon fibers (500 °C), and are in the same range as the uncoated, nonpolar. We assume that the reason for such a different behavior in the cementitious material could be that the carbonyl- and carboxy groups on the surface of the oxidized carbon fibers – and not its polar character are responsible for the improvement of the fiber-cement interaction. Fig. 11 shows this type of plasma-treated carbon fiber embedded in the CAC matrix after the bending tensile test. It can be seen that there is a large gap between the fibers and the cementitious matrix (approx. 1 µm). This is a strong indication that the fiber-matrix connection is quite poor. The rather poor bending tensile strength of such systems confirms our assumption. It should be stated that an ESEM picture provides information about a small area of the sample.

The surface modification of carbon fibers with the aim of strengthening the fiber / matrix bond can be done through chemical treatment in addition to plasma treatment. Two of these processes are described in more detail in [40,41]. The first publication describes the grafting of carbon fibers with cardanol, the second is the application of halloysite

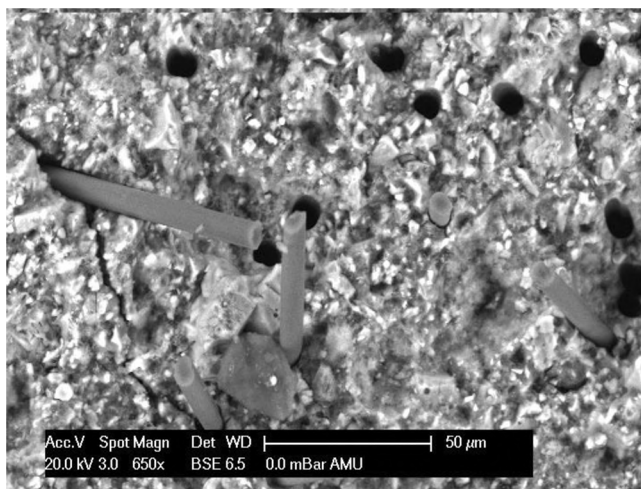


Fig. 9. ESEM picture (breaking edge) of 1 vol-% of 2.5 mm carbon fibers (oxidized at 500 °C) in a CAC-system after 1 day of curing (binder: Ternal White; water/cement-value = 0.3; cement/filler-value = 5) after bending-tensile test.

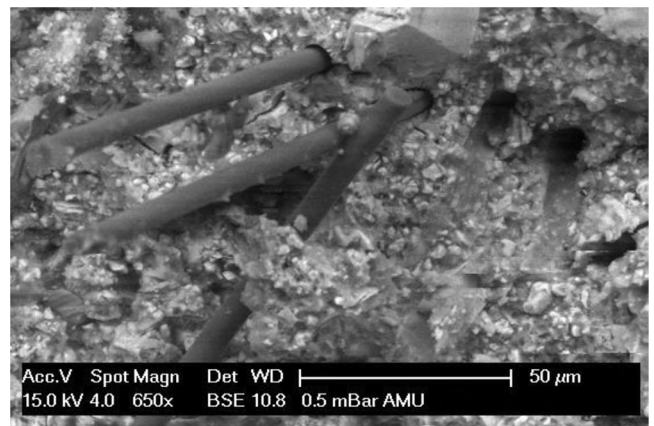


Fig. 10. ESEM picture (breaking edge) of 1 vol-% of 2.5 mm carbon fibers (untreated) in a CAC-system after 1 day of curing (binder: Ternal White; water/cement-value = 0.3; cement/filler-value = 5) after bending-tensile test.

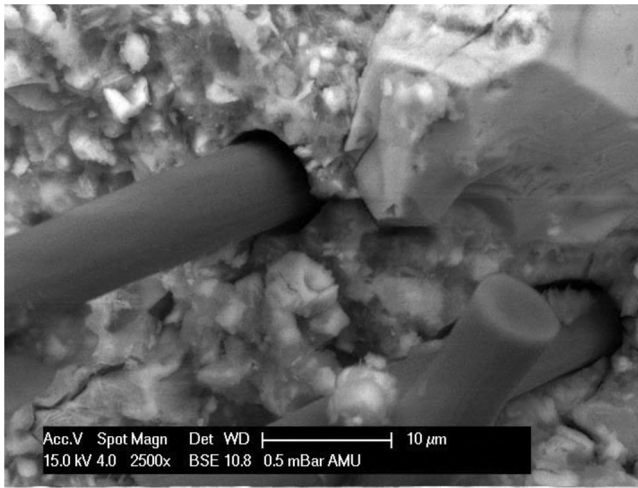


Fig. 11. ESEM picture (breaking edge) of 1 vol-% of 3 mm carbon fibers (treated in NH_3 plasma) in a CAC-system after 1 day of curing (binder: Ternal White; water/cement-value = 0.3; cement/filler-value = 5) after bending-tensile test.

nanotubes. The aim of these modifications is to increase fiber polarity, surface energy, and wettability. Although the carbon fiber modifications described have so far only been tested in polymer composites, they could also be suitable for reinforcing the CAC matrix. Investigating this influence more closely can be regarded as part of more extensive investigations.

Since different parameters such as water/cement, cement/filler-ratio, particle size of the filler, hydration degree have a big influence on the fiber-matrix interaction and are only partially controllable it is difficult to say whether the examination from a sample point is representative for the entire sample (e.g. pulling out or tearing of the carbon fibers). Nevertheless ESEM is a suitable method to get a first overview of the failure mechanism and the embedding of the different treated fibers in the cementitious matrix.

Fig. 3 shows the influence of the oxidation temperature of the carbon fibers on the resulting bending tensile strength after 1 day. The most important information in this diagram is that an oxidation temperature of approx. 350°C led to a drastic decrease in the bending tensile strength, whereas an oxidation temperature of ca. 500°C enhanced such value (compared to that of untreated fibers). We assume that the drastic decrease in the bending tensile strength at 350°C is due to the fact that the epoxy resin with which the carbon fibers are coated is only partly oxidized. The TG measurement of the carbon fibers used (Fig. 1) shows that the decomposition of the epoxy resin starts at about 300°C and ends at approx. 550°C . Therefore, oxidating the carbon fibers at 350°C for 2 h results in a significant amount of partly oxidized epoxy resin remaining on the surface. The bending tensile measurements (Fig. 3) show that this partially oxidized epoxy resin has no positive influence on the fiber-matrix (CAC) interaction.

The TG-measurement of the untreated carbon fibers (Fig. 1) show in the temperature range 300°C – 550°C a weight loss of 3.5 %. This weight loss can be attributed to the epoxy resin coating applied. As a result, the functionalization density of the carbon fibers used with epoxy resin is 3.5 percent (corresponds to the manufacturer's information). The functionalization with epoxy resin gives the non-polar fiber a polar character and an increased roughness. This can be seen as the main reason for the significantly higher bending-tensile strengths compared to the non-surface-modified fibers. The carried out oxidation process leads to a decrease in the degree of functionalization, which leads to a decreasing fiber / matrix connection and a significant decrease in the flexural strength.

Despite the fact that the bending tensile strengths of the epoxy-resin

coated carbon fibers (untreated) are only slightly higher than those of the fibers which had been oxidized at 500°C for 2 h, we used the oxidized (500°C) ones for the determination of the critical fiber length and volume content in CAC-systems. This was because the fibers oxidized at 500°C have a significantly lower tendency to agglomerate into fiber tufts than the untreated. This makes the homogenization process much easier, the distribution of the fibers more uniform, and therefore the results easier to reproduce.

4.2. Relation between carbon fiber length, volume fraction of fillers, w/z-value and time in relation to the bending tensile strength

The properties (e.g. final strength, viscosity, shrinkage, setting time, etc.) of a calcium aluminate cement (CAC) containing binder system depend on a large number of factors. The important ones for our system are the water/cement-ratio, the cement/filler-ratio, the type of filler, the composition of the mixing water (e.g. Li_2SO_4 , organic acids, superplasticizer, etc.), carbon fiber length and vol-%. These numerous parameters also interact and influence each other. A typical example is that a decrease in the water/cement-value leads – through the reduction of the capillary pore system – to an enhancement of strength. However, through the associated increase in the viscosity, a uniform homogenization is aggravated – this has a negative influence on the strength. Through the use of superplasticizer a uniform dispersion of carbon fibers in the cementitious system could be generated, but this also interacts with the hydration process, and thus has an influence on the strength development. Due to the extremely large number of parameters involved and the resulting unmanageable number of experiments, parameter studies are often carried out in the construction industry.

Because one of the aims of this study is to determine the ideal fiber length and volume content of carbon fibers in CAC (dominated) binder systems, as a first step the ideal cement/filler and water/cement-value of a system with 1 vol-% 3 mm carbon short fibers were determined. 1 vol-% of 3 mm carbon fibers was used because – in the preliminary tests – this combination was identified as the most suitable one, with regard to the bending tensile strength. As shown in Fig. 4, – the ideal cement/filler-ratio was estimated. The strategy chosen to determine the ideal value is to replace the binder (Ternal White) step by step with the calcite filler while the amount of mixing water remains constant (not the water/cement-ratio). Because the calcite filler used has a particle-size distribution which is comparable with that of binder, the viscosity of the whole system remains within the same range. As shown in Fig. 4, the ideal cement/filler-ratio (with regard to the bending tensile strength) is 5. The reason we have chosen calcite as a filler is, that after [42,43] the calcium aluminate phases react to the – in the presence of CaCO_3 – stable phase monocarboaluminate. Unlike other hydration products of calcium aluminate cement e.g. C_2AH_8 , monocarboaluminate does not undergo the conversion process [16,18,44]. Determination of the most suitable water/cement-value takes place at a cement/filler-ratio of 5 and, as a reference, also at 0.5 and 2 (Fig. 5). Here it is clear to see that, with a water/cement-ratio of 0.3 and a cement/filler-ratio of 5, the bending tensile strength reaches a maximum value of approx. 16 N/mm^2 after 1 day. The decrease of the bending tensile strength – at a water/cement-value of 0.25 – is probably due to the serious homogenization problems with this low amount of mixing water. This means that, due to the high viscosity, the mixing-water does not reach every grain of the cement → decrease of hydration degree → decrease of the bending tensile strength.

Fig. 7 shows the influence of carbon short fibers – at different lengths – on the bending tensile strength of CAC-dominated binder systems. It can be seen that up to a length of 2.5 mm the values increase considerably and that this enhancement in strength by up to 200 % is directly related to the fiber length used. The first significant increase of approx. 100 % takes place at a fiber length of 1.5 mm – when compared to the carbon fiber-free system. The second large step takes place at fiber lengths of 1.5 mm–2 mm (ca. 40 % increase). It can be assumed that the

drastic increase of the bending tensile strength through the use of carbon fibers of increasing length is due to the fact that longer fibers have a comparatively larger surface area for interaction with the cementitious matrix. The ESEM measurements show that most of the fibers are pulled out of the cementitious matrix during the bending tensile test. The reason can be seen clearly that shorter fibers – with a lower contact area – can be pulled out with considerably less force than longer fibers. This pull-out process is also responsible for the significant increase in deflection before component failure. Fig. 12 and 13 show the influence of different vol-% content and length of carbon fibers (oxidized at 500 °C) on the stress as a function of the deflection. It can be seen that an increase in the carbon fiber length leads to a significant enhancement of the deflection (about 10 times higher for 1 vol-% of 2,5 mm carbon fibers). The strength test of the carbon fiber reinforced samples show jagged progress after ca. 0.1 % of deflection. We assume that the reason for this is the pullout of the fibers. After the first crack which can be attributed to the cementitious matrix (CAC) and occurs for fiber-free and fiber-containing material at almost the same stress level. All of the subsequent jags show the pullout of fibers from the matrix. The dramatic increase of the tensile strength when using 1 vol-% of 2.5 mm carbon fibers can be assigned that here a critical value in concentration and length is reached. A further increase of the fiber content leads to a decrease of the strength because a homogeneous distribution is due to the high viscosity no longer possible.

The failure picture with a lot of jags is a strong sign that the fiber-matrix (CAC) connection is also very poor for carbon fibers, which have been oxidized at 500 °C. A system with reasonably good connections would show a much plainer progress without any jerks. Because the strength improvement for oxidized carbon fibers at 500 °C is not significant compared with the untreated fibers it can be concluded that an oxidation process for epoxide resin coated fibers is not suitable in order to improve the tensile strength. For uncoated carbon fibers the oxidation process at 500 °C is a necessary step in order to improve the connection and strength (Fig. 2).

When the strengths of the fiber containing systems are compared after 1 day and 1 week (Fig. 7 and 8) it can be seen that they are in most cases higher. The reason for this is the progress of the hydration process of CAC over time. This effect could be observed very clearly in systems where the carbon fibers have a length of only 0.2 mm or 0.7 mm because in these cases the 1-day levels are relatively low.

Mixing carbon fibers in a range of 0.5–1.5 vol-% has neither positive nor a negative effect on the compressive strength. It can be assumed that the reason for this is because the viscosity of CAC-systems with this amount of carbon fibers is low enough that there is no inclusion of larger

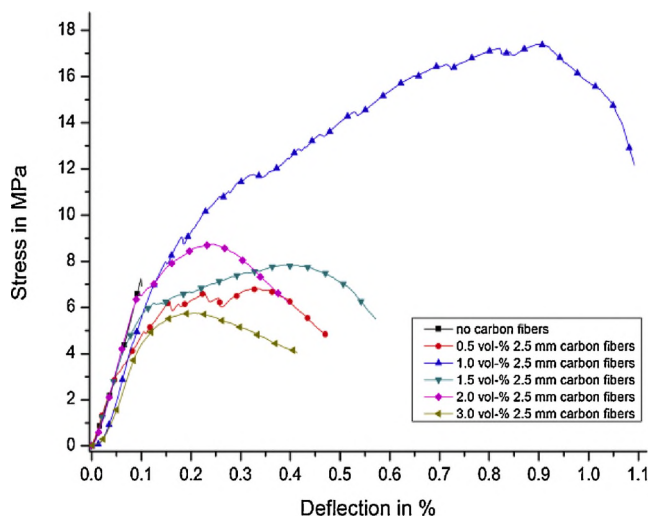


Fig. 12. Stress – Deflection plots of CAC-systems with different vol-% of 2.5 mm carbon short fibers (oxidized at 500 °C).

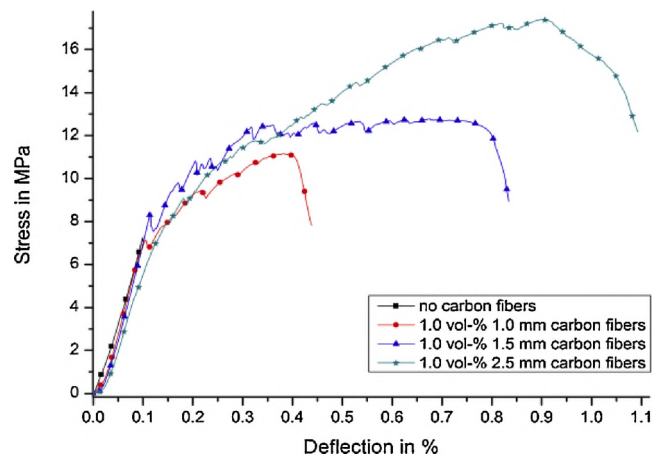


Fig. 13. Stress – Deflection plots of CAC-systems with 1 vol-% of vary in size carbon short fibers (oxidized at 500 °C).

air bubbles (which probably lead to a significant decrease in the compressive strength), etc.

5. Conclusion

As already known from OPC based systems, we showed in this work that, through the use of carbon short fibers, the bending tensile strength of CAC-based cementitious materials can also be greatly increased. Another important result of this study was that the mechanical properties and the setting time of CAC systems – especially those to which with calcite (filler) and carbon short fibers were added – depend on a large number of parameters, which also interact with each other. Because of this extremely large number of parameters (e.g. water/cement-ratio, cement/filler-ratio, amount/type/particle size distribution (PSD) of filler, lithium and citric/tartaric-acid content in the mixing water, length and surface treatment of the carbon fibers, etc.), continuous testing through a systematic variation of all parameters – with a reasonable effort – is almost impossible. For this reason, our starting mixture is, – especially with reference to the composition of the mixing-water (lithium salt, superplasticizer) – the result of a large amount of preliminary, empirical experiments. After evaluation of the cement/filler-value, water/cement-value and the, for our purpose, most suitable carbon-fiber treatment a readjustment of the mixing water with respect to the setting time is necessary (addition of organic acids). This is because the homogenization process of the carbon fibers, especially with an increased volume content and lower water/cement-value, takes a lot of time (homogeneous fiber dispersion necessary in order to compare the measured bending tensile strength). Modification of the mixing water, mainly through an enhancement of the citric-/ tartaric acid content has a significant influence on the resulting bending tensile strength after 1 day and 1 week. Therefore, the acquired strength values of systems prepared with a mixing water of different composition are not directly comparable.

With reference to the carbon fibers -matrix (CAC) connection we come to the conclusion that the interaction of all the surface modifications is rather poor in comparison to the interaction between carbon fibers -matrix (OPC)[12]. This is well shown by the fact that in the bending tensile tests the CAC-systems which were reinforced with carbon fibers show the first crack appearing at the same time as in fiber-free systems (after that the carbon fires are pulled out). The force which is necessary for this process depends mainly on the length of the carbon fibers used. In order to get the best possible fibers -matrix (CAC) connection an oxidation process at 500 °C or an epoxid resin on the fibers coating is recommended.

As a result of the examinations, we conclude that carbon short fibers are a suitable way to enhance the bending tensile strength of

cementitious systems with the binder CAC for a certain amount. The addition of carbon fibers could also be a way to decrease the volume shrinkage during the hardening process. It is worth mentioning that, because the strength of CAC based systems depends greatly on the additives in the mixing-water, for every modification in the water composition, the ideal carbon fibers length and its volume content should be determined separately.

The authors declare that they have no conflict of interest. The raw/processed data required to reproduce these findings cannot be shared at this time as the data are also part of an ongoing study.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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