

Rheology and processability of multi-walled carbon nanotubes—ABSE polycarbosilazane composites

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Available online 25 October 2007

Abstract

An inexpensive method has been found to produce ceramic SiCN-fibres via the precursor route consisting of five processing steps: synthesis of the polymer, preparation of the spinning mass, melt-spinning, curing via electron beam and subsequent pyrolysis at 1100 °C in a nitrogen atmosphere. A special solid and meltable fibre polymer, the so-called polycarbosilazane ABSE, has been developed in the last decade for this purpose. Due to its low molecular weight, an adequate catalytic and thermal aftertreatment was necessary to guarantee a stable melt-spinning process. This article discusses an alternative way to tailor the rheology of the spinning mass, i.e. the addition of multi-walled carbon nanotubes (MWCNTs) to the ABSE melt. Measuring the viscoelastic properties of the prepared compounds as well as their behaviour during the melt-spinning process demonstrates the strong interaction between the MWCNTs and the precursor melt. Even 1 wt.% of the MWCNTs shows a significant positive influence on the rheological behaviour and thus an improvement in the spinnability of the ABSE crude precursor. The influence of the addition of a dispersing agent is investigated as well. In using a dispersing agent, the level of homogeneous dispersion of the MWCNTs increases, whereas the interactions between the MWCNTs and the precursor melt decrease. Thus, the addition of MWCNTs represents a new way to modify the ABSE precursor for the melt-spinning process.

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Keywords: SiCN-precursor; Carbon nanotube; Ceramic fibres; Rheology

1. Introduction

Particles with dimensions of less than 100 nm have a high surface to volume ratio. This can lead to a strong reaction with surrounding matrix materials. Such a significant influence of the particle size on the physical and chemical properties of materials is very well known from nature in nacre, for example.¹ But nanoscale particles such as carbon nanotubes (CNTs)² are also becoming increasingly interesting in the designing of new materials with improved or completely new properties as well. The strong interaction between the surface of CNTs with different kinds of polymers has been applied, for example, to adjust the rheology of polymer melts.^{3–5}

The precursor ABSE, which has been synthesised for the manufacturing of ceramic SiCN-fibres, possesses a low molec-

ular weight directly following synthesis that is unsuitable for the melt-spinning process. Thermal and catalytic aftertreatment is necessary to increase the molecular weight of the ABSE precursor and to improve the rheological properties of the melt with regard to viscoelasticity. With greater molecular weight, the viscosity increases and the elastic response of the melt to shear deformation intensifies.^{6–15} Furthermore, the non-Newtonian behaviour of the polymer melt (shear thinning) enables a stable, continuous melt-spinning process^{16,17} and leads to green fibres with improved mechanical properties. However, the thermally induced cross-linking of the ABSE precursor allows only the aftertreatment of small amounts of precursors. Whereas the crude precursor can be synthesised on a pilot plant scale of up to 4 kg, the aftertreatment is only possible on a laboratory scale of less than 200 g. Only by using this small amount of precursor, a homogeneous temperature distribution during the aftertreatment, as well as an equal state of cross-linking, is guaranteed; otherwise, the quality of the precursor varies from batch to batch. Although the crude ABSE precursor is available in sufficient

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amounts, a continuous and repeatable production of ceramic SiCN-fibres on a larger scale was not possible until now.

The aim of this work was to tailor the rheology of the crude ABSE precursor by adding MWCNTs, to improve the melt-spinning process, the mechanical properties of the green fibres, and the reproducibility of the spinning mass properties. Furthermore, for the processing of ceramic SiCN-fibres, it was important to investigate the effect of MWCNT addition on fibre curing and pyrolysis.

It is known that silazanes display a good affinity and compatibility to carbon.¹⁸ Also, the resulting SiCN ceramics show no significant problems (e.g. oxidation stability) if nano-sized free carbon (up to 30 wt.%) is included in the nanostructure. CNTs have a high length to diameter ratio. If the alignment of the CNTs is parallel to the fibre's longitudinal direction, they should act as a reinforcement to improve the mechanical properties of the green and ceramic fibre. Single-walled carbon nanotubes (SWCNTs) have a higher specific surface area and display greater interaction with the matrix than MWCNTs. But MWCNTs are not expensive and display a telescope-like behaviour during tensile deformation. The strong interaction between the outer shell of the MWCNT with the ceramic SiCN matrix and the relatively weak interaction between the other carbon shells should lead to an adjustable MWCNT/SiCN interface.¹⁹ For this reason, we used MWCNTs for our investigations.

2. Experimental

2.1. Materials and sample preparation

Non-purified CVD-made MWCNTs with a length up to 50 μm and a diameter between 20 and 50 nm were used for the experiments. To prevent agglomerates from forming and to cut the length for better dispersion, the MWCNTs were ball-milled for 24 h in toluene with Si_3N_4 balls of 7 mm in diameter. This produces MWCNTs with lengths of approximately 10 μm that are well dispersed in toluene.

To avoid integration of oxygen into the ABSE precursor, all manufacturing steps and experiments – except melt-spinning – were performed in an inert nitrogen atmosphere or by applying the Schlenk method.

The molecular weight of the reference spin masses without MWCNT was increased by applying conventional, i.e. thermal and catalytic, methods. Thus, 100 g crude ABSE precursor and 0.1 g vanadium(III) chloride were dissolved in toluene. After removing the solvent from the mixture via distillation at a temperature of about 80 °C and with reduced pressure, the remaining mixture of ABSE and catalyst was heat-treated at 190–210 °C for 18 h in order to purify the precursor of oligomers. The molecular weight of the resulting precursor increased to about 30,000 g/mol.

For the preparation of the spinning masses modified with MWCNTs, only a thermal aftertreatment for 24 h at 185 °C and under reduced pressure is needed to purify the precursor from oligomers. The ABSE precursor pre-treated in this way was dissolved in toluene, mixed with the MWCNT/toluene suspension and homogenised for 1 h in an ultrasonic bath. In some samples,

the dispersing agent (Byk 2070) was added (1:1 in relation to MWCNTs) in order to improve the level of dispersion. After removing the solvent via distillation under reduced pressure, the resulting black ABSE compounds contained a 1–5 wt.% MWCNTs.

2.2. Rheological measurements

All rheological measurements were conducted using a Modular Compact Rheometer MCR500 (Anton Paar GmbH, Germany). The rheometer was equipped with an electrically heated thermal chamber CTD600. The measurements were carried out in a nitrogen atmosphere with a coaxial parallel plate geometry having a diameter of 50 mm. The gap was adjusted to 0.5 mm. The rheometer was carefully calibrated with a Newtonian calibration liquid in consideration of the known fact that a change in the gap (from the standard width of 1–0.5 mm) influences the viscosity measurement, especially for gaps of less than 1 mm.^{20–22} A preheating period of at least 30 min was necessary in order to avoid changes of the gap during the measurements caused by thermal expansion of the upper part of the measuring geometry.

Prior to performing the measurements, the appropriate amount of the granular sample was taken from the nitrogen-filled containers and brought up to the lower plate. After closing the thermal chamber and adjusting the gap to the chosen value, a preheating period of 15 min was necessary in order to guarantee a stable thermal regime within the thermal chamber as well as to completely melt the sample.

Due to the squeeze flow during the gap setting, an outward flow of the melted sample occurs which leads to a preferred orientation of the MWCNTs in the suspension in radial direction, i.e. perpendicular to the shear direction. Furthermore, residual normal stresses may occur in the sample. The residual normal stresses may influence the results of the following rheological measurements. In order to reduce these effects, the samples were pre-sheared using an oscillatory shear flow with an angular frequency of 10 rad/s and a shear strain amplitude of 10% for 180 s.²³ A subsequent rest time of 60 s has been determined to be sufficient for relaxation of pre-shear-induced stresses. This procedure prior to all measurements was necessary in order to guarantee a unique mechanical pre-history of all samples.

The measurements were performed in the oscillatory mode of the rheometer. The amplitudes of the shear strain were chosen small enough to ensure that the samples are sheared in the linear-viscoelastic region (for details see e.g. Macosko).²⁴ From the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$, the complex viscosity and the loss factor were calculated according to $|\eta^*(\omega)| = (G'^2(\omega) + G''^2(\omega))^{1/2}/\omega$ and $\tan \delta(\omega) = G''(\omega)/G'(\omega)$, respectively, where ω is the angular frequency.

2.3. Melt spinning of the ABSE/MWCNT composite

Fig. 1 shows a schematic of the self-made spin equipment. The used spin masses are solid and were crushed into a crude

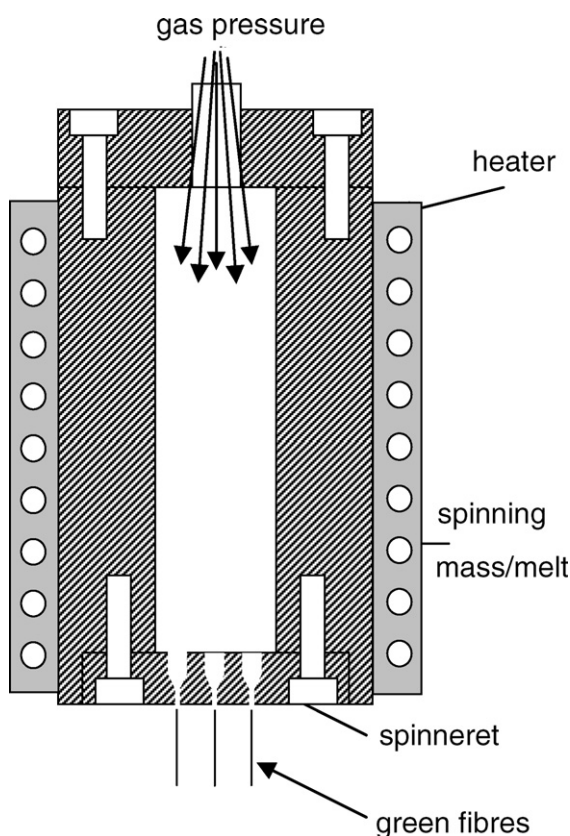


Fig. 1. Schematic of the spin equipment.

powder before the melt-spinning process. Approximately 8 g of the spinning mass was filled, evacuated several times and flushed with gaseous nitrogen to avoid contamination of the precursor with oxygen. The spinning mass was melted under reduced pressure at temperatures between 120 and 160 °C (depending on the mass used) in order to remove bubbles and to reach the optimal spinning viscosity. After this homogenisation and tempering process, a nitrogen overpressure was used to press the melt through the spinneret. Seven uniform green fibres were simultaneously formed and wound to a coil. The diameter of the green fibres was adjusted from 80 to 50 μm by varying the gas pressure and the pull-off speed. Gas pressures between 2×10^5 and 4×10^5 Pa and pull-off speeds between 100 and 200 mm/s were applied for the melt-spinning experiments.

2.4. Morphological characterisation

A scanning electron microscope (SEM–Zeiss model 1540 EsB) in mixed secondary electron (SE) and Inlense-SE mode was used for the characterisation of the milled MWCNTs, the resulting spinning masses and green fibres. The impact energy was set between 1 and 2 keV.

Of particular interest were the morphology of the MWCNTs, their dimension, entanglement and the absence of defects after milling. The kind of dispersion and orientation of the MWCNTs were examined in the spin masses and the green fibres. Owing to the very low electrical conductivity of the ABSE precursor, all samples were spattered with gold.

3. Experimental results and discussion

3.1. Rheological properties of the MWCNT/ABSE melt

The aim of the rheological measurements was to carry out a comprehensive investigation of the influence of the MWCNTs on the ABSE melt flow behaviour. In addition, the optimal fraction of MWCNTs in the ABSE matrix necessary to maintain adequate melt behaviour for the spinning process was investigated. Thus, in a first test series, the effect of 0.5, 1, 2 and 5 wt.% MWCNTs was studied without the addition of a dispersing agent to the ABSE matrix.

Fig. 2 shows the correlation between the complex viscosity, the fraction of MWCNTs and temperature at an angular frequency of 10 rad/s, measured in the linear-viscoelastic range.

On the one hand, the complex viscosity of the precursor melt depends on the adjusted temperature, i.e. the higher the temperature, the lower the complex viscosity. This is simply caused by increased motion and mobility of the polymer macromolecules of the matrix. On the other hand, the complex viscosity clearly increases already with the addition of 0.5 wt.% MWCNTs, and even greater with higher MWCNT fractions. Due to higher shear forces between matrix and particle at lower temperatures, the effect of a certain increment in the MWCNT fraction to the complex viscosity is higher than at elevated temperatures. Moreover, at 110 °C the complex viscosity reaches saturation at 1 wt.% MWCNTs, whereas this is not the case at higher temperatures. This suggests that the optimal addition of MWCNTs to the ABSE matrix for best spinnability is 1 wt.%.

Spinning masses with 5 wt.% MWCNTs cannot be measured in the coaxial plate-plate rheometer since the compound was not meltable even at much higher temperatures. The mass remains rubber-like, even at temperatures above 160 °C. Thus, the powerful influence of low amounts of MWCNTs on the rheology of the ABSE precursor is obvious. These effects, which appear to be much stronger than previously found by other authors,^{4,5} are explained by the high affinity of ABSE polycarbosilazane to carbon and thus by the strong interactions between matrix and MWCNTs particles.

In Fig. 3 the complex viscosity is shown as a function of the fraction of MWCNTs and the angular frequency at 120 °C. At this temperature the viscosity of compounds with 1–2 wt.%

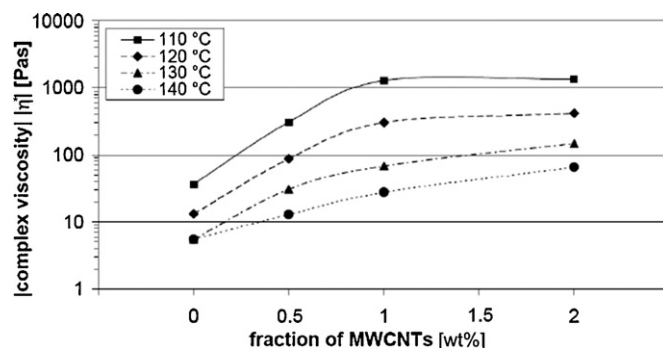


Fig. 2. Complex viscosity at an angular frequency of 10 rad/s as a function of the fraction of MWCNTs and temperature.

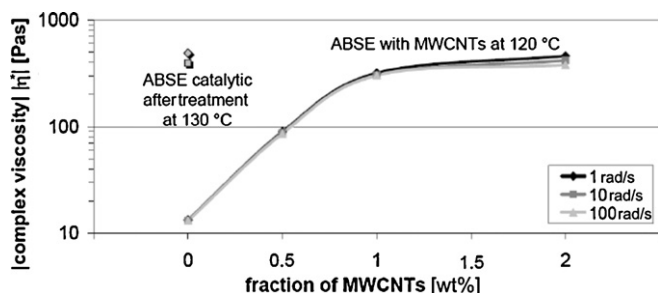


Fig. 3. Complex viscosity of the melt as a function of the fraction of MWCNTs and angular frequency. The complex viscosity of catalytically aftertreated ABSE is shown as a benchmark.

MWCNTs is approximately the same as for MWCNT-free, but catalytically aftertreated ABSE measured at 130 °C. The values between 300 and 400 Pa s observed for both types of spinning masses have been found to be optimum in preliminary tests in the applied spinning equipment.

For the determination of the dependency of complex viscosity on the angular frequency, tests at a constant temperature of 110 °C were performed. At first an ABSE spinning mass with 1 wt.% MWCNTs was examined. In the next step 1 wt.% dispersing agent was added to the ABSE/MWCNT mixture. As known from literature the homogeneous dispersion of the CNTs can be improved by using a dispersing agent.²⁵ But these organic additives can also influence the rheology of the precursor melt. To get information about possible effects on the rheological behaviour depending on the dispersing agent a reference spinning mass composed of only ABSE and 1 wt.% dispersing agent was investigated. Fig. 4 highlights the non-Newtonian flow behaviour of the MWCNT-added ABSE melt, which is considered to be beneficial for the melt-spinning process. The complex viscosity of the ABSE–MWCNT compounds decreases with higher shear velocities, whereas the complex viscosity of the pure precursor is independent of the angular frequency. With the further addition of 1 wt.% dispersing agent, the non-Newtonian flow behaviour disappears; however, the effect of increased complex viscosity compared to pure ABSE is maintained. This can be understood as a result of two contrary processes: on the one hand, the dispersing agent weakens the interaction between matrix and MWCNTs, theoretically leading to a viscosity drop; on the other, the dispersing agent increases the viscosity of the pure ABSE matrix (Fig. 4) through a chemical reaction, which, on the whole,

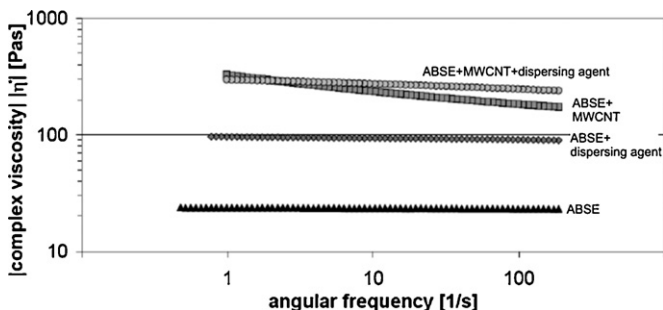


Fig. 4. Complex viscosity of ABSE with and without addition of MWCNTs and dispersing agent as a function of the angular frequency, measured at 110 °C.

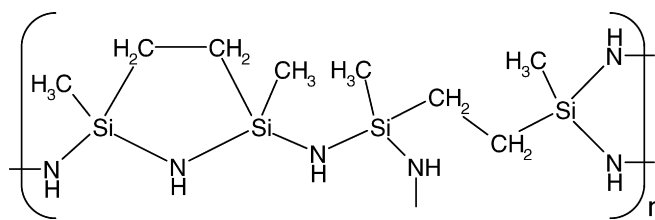


Fig. 5. Basic structural units of the ABSE polycarbosilazane.

obviously compensates the reduced interaction between matrix and MWCNTs in terms of viscosity.

The used dispersing agent Disperbyk 2070 consists mainly of phosphorus ester, 2-methoxy-1-methylethylacetate salt and *n*-butylacetate.²⁶ Especially the acetate function can react on different ways with the Si–NH groups of the ABSE polycarbosilazane (Fig. 5), which leads to higher average molecular weights and thus to an increase in viscosity.

Maintenance of the Newtonian flow behaviour upon addition of the dispersing agent is confirmed by Fig. 6. The loss factor $\tan \delta$ embodies the relation between loss modulus and storage modulus, i.e. between viscous and elastic fractions of the flow behaviour of a melt.²⁴ The higher $\tan \delta$, the closer the behaviour of a melt to a purely viscous fluid. The ABSE–MWCNT compound displays the lowest loss factor and thus the least prevalent viscous flow behaviour amongst the tested materials. In this particular case the deviation from Newtonian flow behaviour increases with decreased angular frequency. In contrast, the sample materials containing the dispersing agent display higher loss factors and thus more viscous flow behaviour.

In conclusion, the viscosity can also be set to a desired value of about 300 Pa s by adding a comparatively inexpensive dispersing agent to the pure ABSE. However, the dispersing agent prevents interaction between ABSE matrix and MWCNTs, leading to a clear Newtonian and viscous-dominated flow behaviour.

In terms of viscosity and elastic behaviour, an ABSE spinning mass with an amount of 1 wt.% MWCNTs displays the best properties.

3.2. Spinnability of the MWCNT/ABSE composite

The conventional, catalytically aftertreated spinning masses can easily be spun to regular green fibres at a temperature of 130 °C and 3 bar gas pressure.

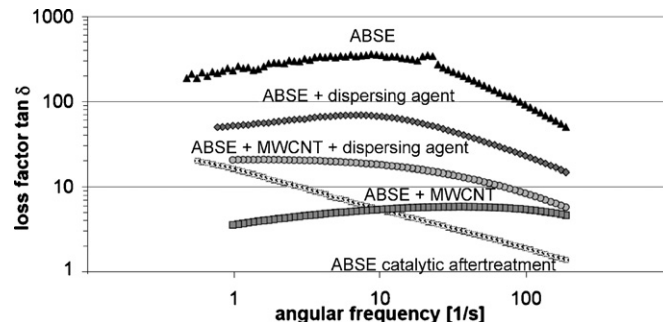


Fig. 6. Loss factor $\tan \delta$ of ABSE with and without addition of MWCNTs and dispersing agent as a function of angular frequency, measured at 110 °C.

Table 1

Optimised spinning parameters for spinning masses modified with different amounts of MWCNTs, without the addition of a dispersing agent

MWCNT fraction (wt.%)	Spinning temperature (°C)	Gas pressure (bar)	Comment
0.5	110–115	2	Irregular fibre diameter
1	120	3	Irregular fibre diameter
2	125	3	Irregular fibre diameter
5	–	–	Not meltable even at 160 °C

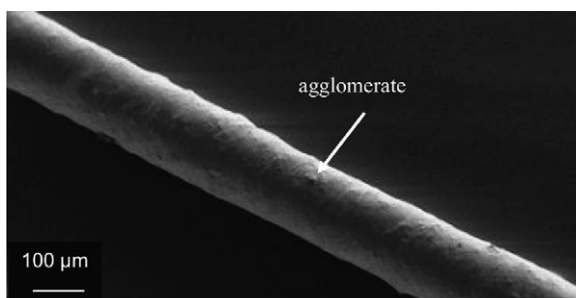


Fig. 7. SEM-micrograph of a green fibre with 2 wt.% MWCNTs.

ABSE-based spinning masses modified with 0.5, 1, 2 and 5 wt.% MWCNTs, respectively, were spun without the addition of dispersing agent. For the spinning process, a temperature was chosen at which the necessary viscosity of the melt is present (Table 1). These spinning experiments confirm the increase of the viscosity of the melt with the addition of larger amounts of MWCNTs previously found in the rheological measurements. The sample with 5 wt.% MWCNTs was not spinnable.

The diameter of the green fibre was observed to fluctuate in a wide range already during the spinning of the masses with up to 2 wt.% MWCNTs. The irregular diameter and coarse surface of the fibre was noticeable by running the fingers over it. In Fig. 7, the MWCNT agglomerates are easily visible that are responsible for the irregularities in fibre thickness.

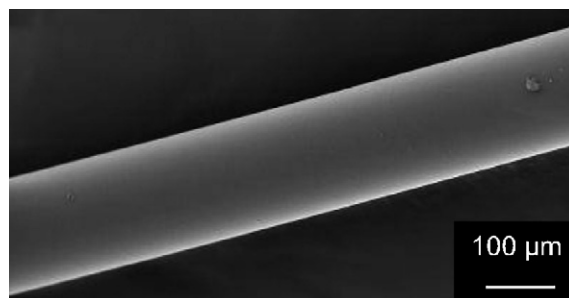


Fig. 9. SEM-micrograph of a green fibre with less than 1 wt.% MWCNTs and 1 wt.% dispersing agent.

The agglomerates contained in the green fibre are visible in the fractured surface (Fig. 8) as well. In Fig. 8a, regions with isolated and homogeneously dispersed MWCNTs can be found as well as regions with agglomerates (2–5 μm). Due to strong mechanical entanglements inside the agglomerates, the MWCNTs cannot be orientated along the fibre axis by streaming through the 400 μm wide opening of the spinneret and with the following stretching. Fig. 8b shows the fracture surface at a higher magnification. Here individual MWCNTs and ones partly protruding out of the fractured surface are shown, both of which indicate a good connection to the ABSE matrix without any pores or cracks at the interface. Furthermore, pullouts of single MWCNTs reveal the close bonding of the MWCNTs to the polymer matrix. So it is possible to transfer applied stress from the polymer matrix into the MWCNTs and thus to reach a high tensile strength for the whole compound.

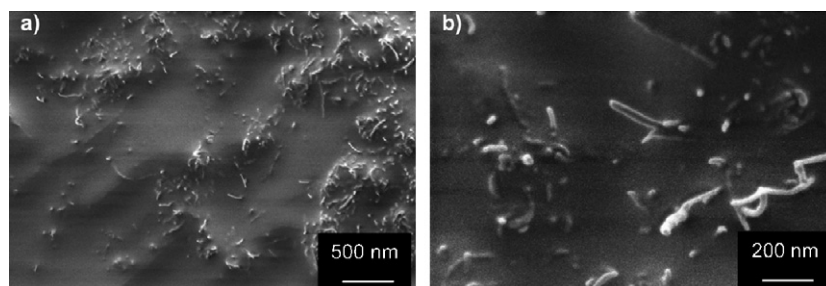


Fig. 8. SEM-micrograph of the fractured surface of a green fibre with 2 wt.% MWCNTs: (a) agglomerates in the dimension of 2–5 μm; (b) pullout of single MWCNTs.

Table 2

Tensile strength at room temperature of uncured green fibres depending on the fraction of MWCNTs in the spinning mass

Spinning mass	Average molecular weight (g/mol)	Tensile strength (MPa)
ABSE (catalytic aftertreatment)	24810	10–15
ABSE + 0.5 wt.% MWCNTs	3700	22.1 ± 11.5
ABSE + 1 wt.% MWCNTs	3500	29.6 ± 5.5

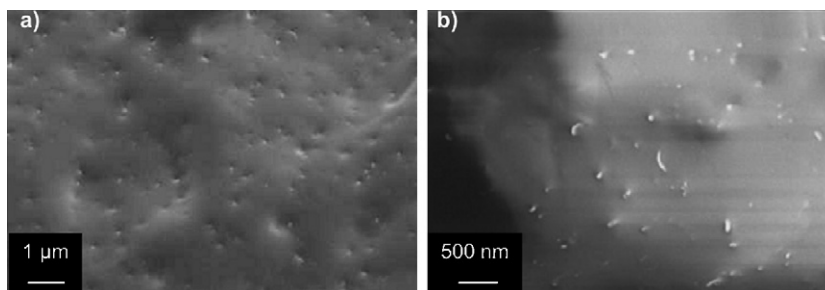


Fig. 10. SEM-micrograph of the fractured surface of a green fibre with a MWCNT fraction of less than 1 wt.% and a dispersing agent fraction of 1 wt.%. (a) isolated and homogeneously dispersed MWCNTs; (b) orientation of the MWCNTs along the fibre axis and pullouts of the MWCNTs.

The increase in tensile strength of the green fibres with higher fractions of MWCNTs confirms the efficiency of the fibre-reinforcement (Table 2).

The increase of tensile strength beyond that of the pure matrix is caused by the reinforcement with MWCNTs, which is also verified in other systems of polymer fibres.^{1,27–30} It must be pointed out that this strength increase appears despite the fact that (a) the MWCNT agglomerates prevent a consequent orientation of the MWCNTs along the fibre axis and (b) the reinforced ABSE precursor displays a much lower molecular weight than the conventional ABSE with catalytic aftertreatment. Usually one would expect the fibre strength to increase with the length of the macromolecules, i.e. the molecular weight. Through the improved strength of the green fibre, its handling and finishing into a ceramic fibre is greatly facilitated.

Spinning masses with the addition of a dispersing agent were also test-spun. Two spinning masses were applied in which residual agglomerates were eliminated by sedimentation. Following sedimentation, the spinning masses contained <0.5 and <1 wt.% MWCNTs, respectively. For the spinning experiments, a temperature of 90 °C, a gas pressure of 2 bar and a haul-off speed of 125 mm/min turned out to be most suitable. The spinning temperature is much lower compared to spinning masses without the addition of a dispersing agent. This fact confirms the influence of the organic additive on the rheological behaviour of the spinning mass. The dispersing agent reduces the interactions between the ABSE and the MWCNTs so that the polymer melt keeps its Newtonian flow behaviour. However, also these spinning masses are spinnable. Due to the absence of agglomerates, the spinning process is more stable than in the experiments using masses without a dispersing agent, and thus no irregularities in the fibre diameter were observed. In Fig. 9 the smooth surface of such a green fibre with regular diameter is shown.

No agglomerates can be found in the fractured surface either. Fig. 10a shows isolated and homogeneously dispersed MWCNTs. At a higher magnification (Fig. 10b), the entanglement of the MWCNTs along the fibre axis, i.e. parallel to the stress direction, becomes obvious. Despite the presence of a dispersing agent, the MWCNTs are well wetted by the ABSE matrix. Furthermore, pullouts were also observed, which suggests that a good connection between matrix and MWCNTs is present.

4. Conclusion

The production of ceramic SiCN-fibres via the precursor route is a very complex process that reacts sensitively to modifications in the processing and to the applied materials. Therefore, it was very interesting investigating the possibility of preparing the spinning masses using MWCNTs, the influence of the MWCNTs on the rheological behaviour of the compounds and the melt spinning process as well. Adequate dispersion of the MWCNTs in the ABSE matrix can be achieved in three steps: milling the MWCNTs, ultrasonic mixing of a MWCNT–ABSE–toluene suspension and distillation of the solvent. The spinning masses produced in such a way contain uniformly distributed residual agglomerates of MWCNTs in the dimensions of 2–5 µm. Through the addition of a dispersing agent, the agglomerates can be avoided entirely. The morphology of green fibres depends strongly on the level of dispersion. If residual agglomerates remain in the spinning mass, inhomogeneities will be present in the green fibre as well which are represented by irregular fibre diameters and a rough surface. The spinning process is not stable because of the agglomerates. Spinning masses without any agglomerates lead to regular and smooth green fibres. The melt spinning is more stable compared to the dispersing agent-free spinning tests. During this, the dispersing agent has a positive influence on the homogeneity of the spinning process and the morphology of green fibres; however, the interaction between ABSE matrix and MWCNTs was reduced. This effect is clearly indicated by the rheological behaviour of the different spinning masses. As hoped for through the addition of MWCNTs, the viscosity as well as elastic ratio of the melt is obviously higher compared to the pure ABSE. This effect is much lower when using a dispersing agent. Furthermore, the Newtonian flow behaviour of the basic ABSE is maintained. In contrast, the spinning masses without any dispersing agent possess non-Newtonian flow behaviour, which enhances the stability of the melt spinning process. For this reason, all spinning masses are processable through melt spinning, whereas the process parameters depend strongly on the chosen masses. Finally, it should be noted that the ABSE precursor possesses a high affinity to carbon so that even low fractions (1 wt.%) of MWCNTs display a remarkable influence on the rheological behaviour of the precursor melt. Processing in this way also represents an inexpensive method of modifying spinning masses as well.

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