

Dispersion of carbon nanotubes in polysilazanes for the preparation of reinforced Si-C-N composites

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Abstract: The present contribution reports two different approaches to achieve a good dispersion of single-walled carbon nanotubes (SWCNTs) in a precursor-derived Si-C-N matrix, which represents an important prerequisite for attaining a high-performance material. The first approach involves the use of SWCNTs covalently functionalized by disilazane groups, aiming at enhanced interfacial interaction between the nanotube surface and the matrix. Within the second approach, the effect of an electrical field applied in the cross-linking step during the nanocomposite synthesis was studied toward the task of dispersing and simultaneously aligning the SWCNTs in the Si-C-N matrix.

Introduction

Since their discovery [1], single-walled carbon nanotubes (SWCNTs) have attracted intense attention. Their exceptional mechanical, electrical and thermal properties make them excellent candidates as fillers in nanocomposites that are not only light and strong but also tough. [2,3]

The adhesion between the reinforcing elements and the matrix materials in composites determines the extent to which the mechanical performance can be enhanced. Due to the large surface-to-volume ratio of SWCNTs, appropriately tailored interfacial interactions are particularly important for achieving ultimate performance of the composite. Another relevant factor influencing the properties of CNT-reinforced composites is the dispersion degree of the CNTs. Efficient nanotube dispersion in the matrix is difficult to obtain because of the high intertube cohesive force [4] that lead to the formation of bundles and agglomerated structures. Hence, to be able to fully exploit the favourable mechanical properties of carbon nanotubes, they have to be homogeneously distributed into the matrix, and a properly balanced interfacial bonding is needed to ensure efficient load transfer between the matrix and the nanotube network. These requirements are difficult to fulfil with conventional powder-based ceramic processing techniques. Polymer-derived ceramics (PDCs) synthesized by direct thermal decomposition of polymeric precursors [5] offer advantages in this respect, including a lower processing temperature as well as the possibility to tailor their composition and microstructure [6,7]. Furthermore, the polymeric precursors can be utilized in various forms (e.g., liquid, melt, or within organic solution) that render the desired dispersion more easily.

One effective way to strengthen the interfacial bonding is the chemical modification of SWCNTs [8,9]. In particular, covalent functionalization of SWCNTs enables the disintegration of bundles into individual nanotubes and simultaneously provides anchors for the matrix. The type of processing techniques is also important for achieving a good dispersion of the carbon nanotubes in the matrix. One useful method for this purpose is shear-intensive mechanical stirring [10]. Moreover, through application of an electric field during the synthesis procedure, electrically conductive nanocomposites incorporating well-dispersed and aligned nanotubes can be obtained [11]. The ability to orient and move the CNTs originates from their high electrical polarizability [12].

Results and Discussion

In this section, we present first results obtained from the two different synthesis approaches to SWCNT-reinforced Si-C-N ceramics.

First approach: Chemical functionalization of the SWCNTs. To reinforce organosilicon polymer-derived ceramics, carbon nanotubes modified with organosilicon derivatives may be more compatible than SWCNTs modified with other functional groups. For example, organosilicon chemicals with a similar structure to that of the precursors will not introduce new elements in the final ceramic material. For this purpose SWCNTs were chemically modified by a radical reaction with 1,3-divinyltetramethyldisilazane ($\text{ViMe}_2\text{SiNHSiMe}_2\text{Vi}$) as follows. Pristine nanotubes (36 mg) were suspended in dry benzene (45ml) under argon atmosphere and sonicated for 30 min. $\text{ViMe}_2\text{SiNHSiMe}_2\text{Vi}$ (9 mmol) and benzoyl peroxide (3 mmol) were added and the mixture was magnetically stirred at 78°C for 30h. After cooling down to room temperature, the suspension was filtered through a $0.2\mu\text{m}$ PTFE membrane, washed with ethanol and THF for several times, and then dried in vacuum overnight at 80°C . Fourier transform infrared (FT-IR) spectroscopy, UV and Raman spectroscopy as well as thermogravimetric analysis provided evidence for chemical attachment of the silazane onto the nanotube surface.

For the preparation of the nanocomposites, 1wt.% SWCNTs have been ultrasonically dispersed into liquid poly(ureamethylvinyl)silazane (Ceraset, KION, USA), followed by casting, pressure-less cross-linking and thermolysis at 1000°C , as previously reported [13].

Although the sonication treatment of SWCNTs in THF can greatly debundle and deagglomerate SWCNTs improving their distribution in the matrix, it is found that some transparent pinholes appear in the cross-linked SWCNT/Ceraset composites. Apparently, the debundled and deagglomerated SWCNTs obtained by sonication at the beginning of the synthesis tend to reaggregate in the cross-linking step, where the temperature increases till 360°C . In this step the mixture, which initially was a thick paste, becomes more and more liquid while increasing the temperature. This phenomenon allows the nanotubes to reorganize themselves in the matrix, forming bundles and agglomerates again. According to these results, we can conclude that the defects of the cross-linked composites largely depend on the viscosity of their corresponding SWCNT/Ceraset mixtures.

Consequently, a proper chemical modification of nanotubes could provide a better interface compatibility of the nanotubes with the matrix and/or weaken the high intermolecular cohesive force between individual tubes, reducing their tendency to form bundles. In this context, SWCNTs covalently attached by silazanes or polysilazanes should be also a good choice. However, the distribution of divinylmethylsilazane-modified nanotubes in the matrix does not lead to an improvement compared to that of pristine SWCNTs (Fig. 1). Probably both of the vinyl groups belonging to the ligand used for the synthesis reacted covalently with the nanotubes, yielding bigger bundles or agglomerates, and therefore less homogeneous materials.



Figure 1: Cross-linked discs of a) SWCNT/Ceraset and b) ($\text{ViMe}_2\text{SiNHSiMe}_2\text{Vi}$)-SWCNT/Ceraset

Second approach: Electrical field applied during cross-linking. Applying electric fields after an intensive mechanical stirring during the synthesis of nanocomposites results in the formation of well-dispersed aligned nanotube networks. The sample preparation was carried out following a similar method to the one described above, with the difference that the cross-linking has been divided in two steps. In the first one, the sample was kept for 2 hours at 130°C in a field of 400 V/cm (0.5% dicumyl peroxide was added as initiator). Afterwards the sample was cross-linked at

360°C for 6 hours in the same way described earlier [13]. Samples needed for comparative experiments, where no electrical field has been applied, were prepared in the same manner.

In our experiments, the application of electric fields during the cross-linking step led to changes in the specific resistance with the time. Samples containing different SWCNTs amounts (0.05, 0.1,

0.5 and 1 wt.%) exhibited a similar behaviour. After the initial decrease in the specific resistance, all samples showed plateau behaviour, indicating that the network is stabilised. However, it was observed that the composites containing a higher percentage of nanotubes, and therefore a higher probability of nanotube contact, presented in lower values of the resistance, which agrees with the results found in the literature for composites with an organic polymer matrix [14].

As mentioned before, the debundled and deagglomerated SWCNTs obtained by sonication at the beginning of the synthesis tend to reagglomerate in the cross-linking step, where the temperature increases and the viscosity of the mixture decreases. The quality of the nanotube dispersion of cross-linked samples synthesized with and without electrical field was investigated by SEM (scanning electron microscopy), operated in the charge contrast imaging mode (Fig. 2). In the image of the sample where no electrical field has been applied (left) the agglomeration of the nanotubes is clearly demonstrated. In the other case (right) the application of an electrical field lead to the formation of a nanotube network and conductive pathways instead of the formation of nanotube agglomerates is significantly reduced.

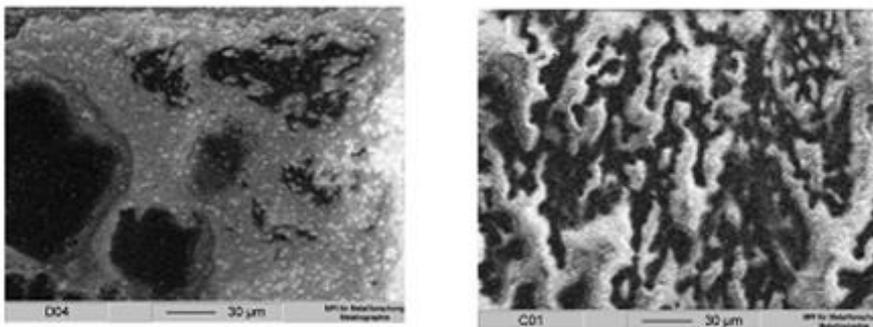


Figure 2: SEM images operated in charge contrast imaging mode. Cross-linked samples (containing 0.1 wt% of SWCNTs) synthesized without (left) and with (right) the application of an electrical field.

Experimental

Poly(ureamethylvinyl)silazan Ceraset was purchased from Kion (USA). Dicumylperoxide 989% was obtained from Aldrich (Germany). Single-walled carbon nanotubes were obtained from Carboxol (USA). Tetrahydrofuran was purified by distillation from potassium. Branson Sonifier 450 was used for ultrasonification.

An AC power supply Trek model PZD 700 and a function generator Wavetec model 95 were applied to control the electric field conditions.

A Jeol 6300F scanning electron microscope was used for charge contrast imaging.

All processes were carried out in a purified argon atmosphere using Schlenk techniques. Ceraset and 0.1% SWCNT was solved in the eightfold volume of THF by stirring 15 minutes. The mixture was cooled down in an ice-bath and ultrasonicated for 1 hour. Then, 0.5% Dicumylperoxide (related to Ceraset) was added and solved. The THF was removed in vacuum subsequently. This viscous solution was transferred into a mould, 1 x 5 x 10 mm in size (Figure 3). The mould was made of Teflon, encapsulated in steel. Two electrodes, 1 x 10 mm, were in direct contact to the solution on two sides.

An electrical AC field was applied with a field strength of 400V/cm as a step function by a frequency of 1 kHz. The mould was then heated to 130°C and kept 2 hours at this temperature while the field was



Figure 3. Steel encapsulated Teflon mould

being applied. The solidified sample was taken out of the mould and cross-linked 6 hours at 360°C. The so obtained green-body was characterised by SEM in charge contrast mode¹.

Summary and Conclusions

In order to improve the dispersion of the SWCNTs in ceramic Si-C-N matrices, composites were synthesized following two different methods. First, disilazane-functionalized carbon nanotubes have been used to synthesize such composites, with the aim of reaching a homogeneous dispersion as well as a good interaction between the matrix and the tubes. In the case of the chemically functionalized tubes, their dispersion was not improved compared to the composites containing pristine SWCNTs. Probably both vinyl groups present in the ligand reacted covalently with the nanotubes, creating bigger and stronger agglomerates, which could not be separated during the composite preparation. In the second part of our study, composites containing pristine carbon nanotubes were synthesized. An electrical field was applied during the cross-linking step in order to align the nanotubes and also to avoid their reagglomeration. According to SEM investigations a positive influence of the electrical field applied in the cross-linked samples was observed. In this case a more organized nanotube network was obtained. Future work will deal with the investigation of the structure of the ceramic samples as well as their electrical conductivity.

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SiAlONs and Non-oxides

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