ELECTRICAL AND THERMAL CONDUCTIVITY OF AEROGEL/EPOXY COMPOSITES

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Keywords: Aerographite, carbon aerogel, thermal conductivty, electrical conductivity, interpenetrating structure

Abstract

This study investigates the electrical and thermal characteristics of two novel carbon aerogel composites containing Aerographite (AG) and a CNT foam. Aerographite of densities between 3 to 16 mg/cm^3, and the CNT foam with densities of 17 and 31 mg/cm^3 were prepared in the CVD process. Both aerogels were infiltrated with epoxy resin using a vacuum assisted infiltration technique that preserves the interconnected structure.
The neat Aerographite showed a maximum electrical conductivity of 10.3 S/m while the CNT foam reached 1.7 S/m. In the epoxy composites the electrical conductivity of the neat materials is adopted, thus resulting in an enhancement of orders of magnitude when compared to neat epoxy.
Thermal conductivity was studied using a Xenon flash method. First results show an improvement of thermal conductivity of the composite by 33 % at the low filler content of only 0.26 wt.-% for the Aerographite and of 91 % for the CNT foam at 2.7 wt.-% filler content.

1 Introduction

Developing new thermally and electrically conductive polymer composites is of great interest for many industries (e.g. electronics and aerospace). Currently used composites often require high loadings of metallic fillers such as copper, which often has a negative effect on the mechanical properties and increases their density significantly [1]. Instead, composites are needed which can dissipate heat and prevent the build-up of static electric charge at low filler contents while preserving the mechanical properties. Carbon nanotubes have long been a promising conductive filler for this purpose, due to their impressive individual longitudinal thermal conductivity [2, 3] and their ability to form electrically conductive networks in the polymer matrix at low filler contents [4]. However, thermal conductivities of CNT composites have so far remained rather disappointing or could only be achieved using very high filler loadings of more than 30 % [5, 6].

Carbon based materials as well as epoxy resin conduct heat mainly in the form of phonons. Collision processes between phonons are therefore crucial for the heat conduction in a composite. Mainly three phonon interactions can be distinguished: phonon-phonon interactions (n- and u-processes), interactions with foreign atoms or impurities and interactions at interfaces. Phonon-phonon interactions become important in bulk graphite due to a dimensional crossover of phonons. The three phonon Umklapp-mechanism is the most important factor limiting the thermal conductivity. Therefore, in particle modified composites a high transfer resistance arises from the scattering of phonons at the surrounding epoxy interface [5]. Regarding the electrical properties an electron scattering at interfaces of the filler and the matrix has only minor influence on the overall electrical conductivity as electrons are able to tunnel through the material when two particles are separated by a sufficiently low distance. However,

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the tunnel resistance is orders of magnitude higher than the resistance of carbon based materials and therefore limiting the electrical conductivity.

A material class with potential to overcome this challenge are carbon aerogels which, due to their interconnected 3D structure, provide interpenetrating electrically and thermally conducting pathways. Carbon aerogels were first synthesised by Pekala et al. in 1990 [7]. While the application of carbon aerogels as electrodes in batteries [8], supercapacitors [9] or fuel cells [10] has been extensively studied, only few studies focused on carbon aerogel composites. Tang et al. [11] prepared an aerogel epoxy composite with an electrical conductivity of 4×10^{-2} S/m at 0.21 vol% filler content. Chen et al. [12] reached a conductivity as high as 1000 S/m graphene foam polydimethyl siloxane composite at 0.5 wt.-% filler content. Similar results were presented by Wang et al. [13] who obtained 100 S/m for an aerogel epoxy composite at 1.5 wt.-% filler content. Thermal conductivity was studied by Zhang et al. [14] and Zhao et al. [15] for graphene aerogel/PDMS composites with thermal conductivites of 0.59 and 0.55 W/mK, respectively.

The aim of this study is to investigate the electrical and thermal conductivity of carbon aerogel composites containing two novel aerogels – Aerographite [16], developed in a close cooperation between the Hamburg University of Technology (TUHH) and Kiel University, and a structure of entangled carbon nanotubes, coated with pyrolytic graphite (CNT foam) developed at TUHH, respectively. Their electrical and thermal properties will be discussed in terms of filler content, defects of the filler, filler geometry and surface of filler.

2 Materials and methods

2.1 Production and morphology of carbon aerogels

The Aerographite samples were synthesised via a two-step method: manufacture of a zinc oxide (ZnO) template followed by a Chemical Vapour Deposition (CVD) process using these templates. Each ZnO template is composed of a scaffold of individual ZnO tetrapods that were produced in a flame spray process [10]. These templates are placed in the maximum temperature zone of a CVD reactor. Toluene, acting as a carbon precursor, is then injected into the furnace at a predefined rate. It evaporates when entering the furnace, and is subsequently deposited onto the ZnO templates in the form of graphitic layers. In a subsequent pure hydrogen treatment without injection of toluene the ZnO is reduced and ejected through the exhaust system so that no etching of the template is required. The resulting Aerographite structure can be adjusted in morphology and density by the design of the template and by controlling the CVD parameters. This high tailorability combined with the innovative synthesis approach are the major advantages of Aerographite.

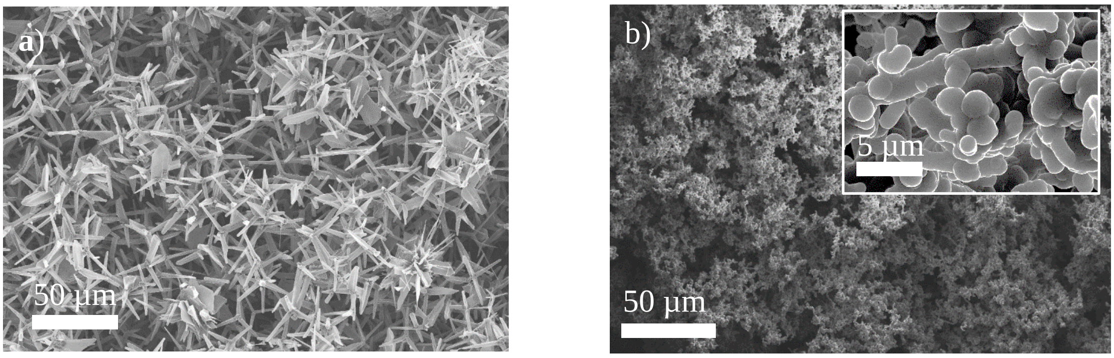

Figure 2.1: SEM images of a) Aerographite and b) CNT mat

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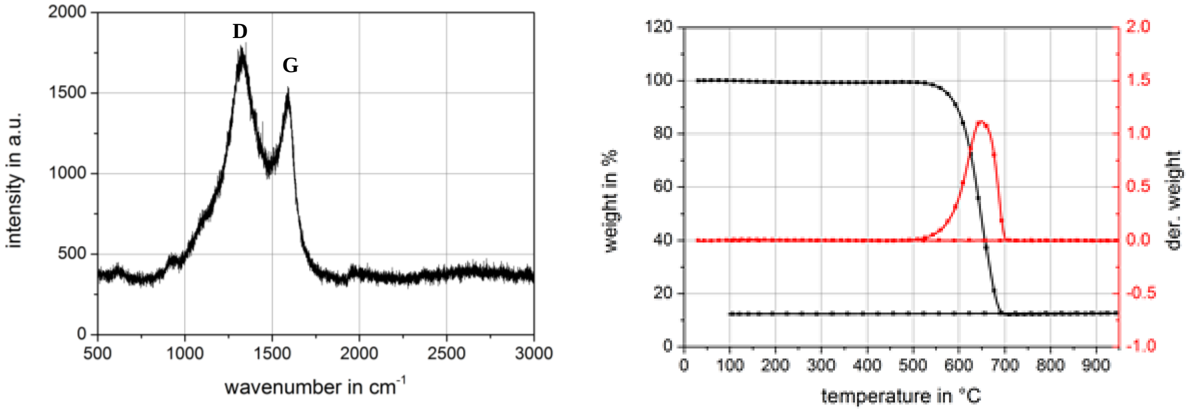
For the following research, toluene injection rates used were between 2 and 9 ml/hr/g_{ZnO} to produce Aerographite samples with densities between 3 and 14 mg/cm^3. Figure 2.1a shows exemplarily the morphology of an Aerographite sample with 13 mg/cm^3.

The CNT foam is a novel 3D interconnected, self-supporting graphitic material, produced in a similar CVD process to Aerographite, though no template is needed. A quartz glass plate is placed in the reactive zone of the CVD reactor. A mixture of 5 wt.-% ferrocene in toluene is used as a carbon precursor and is injected at a rate of 15 - 25 ml/h for 1 h at 1000 °C. After one hour a sheet of CNT foam of 2 mm height and 17 - 31 mg/cm^3 can be removed from the quartz glass plate. The morphology of the foam synthesised by this process can be seen in Figure 2.1b. The structure is a partly "woven" and partly interconnected network of thickwalled, graphite-coated CNTs. The template free synthesis is a very fast and easy process and basic tailorabilty in density and height of the foam is given by variation of synthesis time and injection rate.

The Raman spectra and TGA curves of both materials are presented in Figure 2.2. Both Raman spectra show a pronounced D peak. In contrast, in TGA observations in air atmosphere an excellent temperature stability can be observed which is an indicator for a good graphite quality. The high D peak is expected to exist due to a short crystalline length of the graphite sheets and thus the presence of a lot of edges.

Aerographite:



CNT foam:

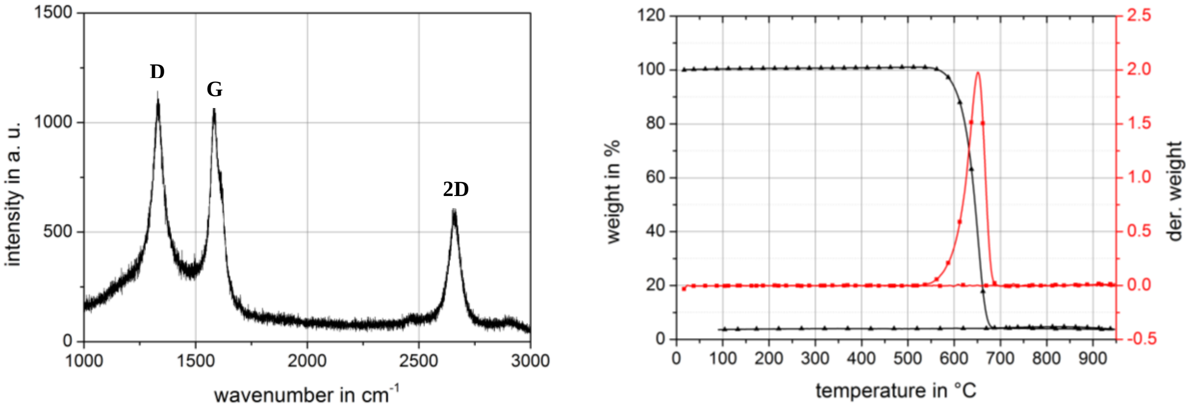


Figure 2.2: Raman spectra and TGA patterns of Aerographite and CNT mat

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From SEM, TEM and XRD (not shown here) the wall thickness in Aerographite can be estimated. It ranges from about 5 to 35 nanometers which corresponds to a number of layers of approximately 15 to 100. The CNT foam consists of thick-walled elements with a diameter between 0.3 µm and 2 µm that are not hollow which would correspond to 500 to 3000 layers. Therefore, both structures are supposed to have electronic and thermal transport properties of bulk graphite.

2.2 Composite preparation

All samples were infiltrated with epoxy using the same method. Epoxy resin RIMR 135 was mixed with hardener RIMH 137 (both from Hexion) according to a 10:3 mass ratio. The epoxy was then degassed at a pressure of 2 mbar and a temperature of 50 °C to make it less viscous, making the infiltration process easier and faster. The samples to be infiltrated are placed in a vacuum desiccator. The degassed epoxy is then added by a syringe and drawn into the mould by the vacuum, infiltrating the sample as required. After infiltration a standard curing cycle was carried out for 24 hr at room temperature (25 °C) followed by post-curing for 15 h at 80 °C. After curing the samples were cut into cubic samples of 20 x 20 mm size and about 1 mm height. For thermal conductivity measurements they were coated with a thin layer of graphite to prevent a reflection of the xenon lamp.

2.3 Characterisation, electrical and thermal conductivity measurement

Scanning electron microscopy observation was carried out on a Zeiss Supra 55 VP. DC electrical conductivity measurements were performed using a Keithley Source Meter 2602 in a four-wire configuration with an impressed current of 1 mA. For measurements on pristine Aerographite and CNT foam the material was electrically contacted by pressing two plate-shaped electrodes, one of which was translationally movable, against its surfaces.

Thermal conductivity measurements were carried out using a Linseis XFA 600 xenon flash device. Specific heat capacity was measured using differential scanning calorimetry on a NETZSCH DSC 204 F1 Phoenix. Thermal conductivity measurements were repeated at least 10 times to ensure accuracy.

3 Results and discussion

3.1 Electrical conductivity of carbon aerogels and their composites

The electrical conductivity of the aerogel composites is displayed in Figure 3.1. The two carbon aerogels used must be understood as random networks of conducting elements. In neat Aerographite for example a pathway can either be a direct interconnection of two tetrapods covalently bonded or a contact between two tetrapods touching each other. The overall resistance can be approximated as a parallel circuit of N pathways. For the composite a tunneling resistance of two tetrapods separated by a thin layer of epoxy, is added. The same applies for the CNT foam, with its thick walled, knobbly elements instead of tetrapods.

Conductivity values are located in the range of 1.6 and 10.1 S/m for the neat Aerographite, between 1.4 and 1.7 S/m for the neat carbon mat and between 2 and 13.6 S/m and 1.3 and 1.5 S/m for the composite, respectively (Figure 3.1). For all samples the conductivity of the composite resembles the conductivity of the as prepared aerogels, showing that the epoxy does not cause damage to the structures. These values are orders of magnitude higher than conductivities found in CNT composites [17, 18]. Thus, we can conclude that the proportion R_{tunnel} is negligible and the electrical conductivity is not influenced by the surrounding matrix. This means also that the conductivity is also independent of the surface area of

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the filler. Instead, electrical conductivity is a measure for the interconnection density of the filler. The CNT mat which shows a lower conductivity at higher filler content seems thus to contain less covalent bonds between the CNTs.

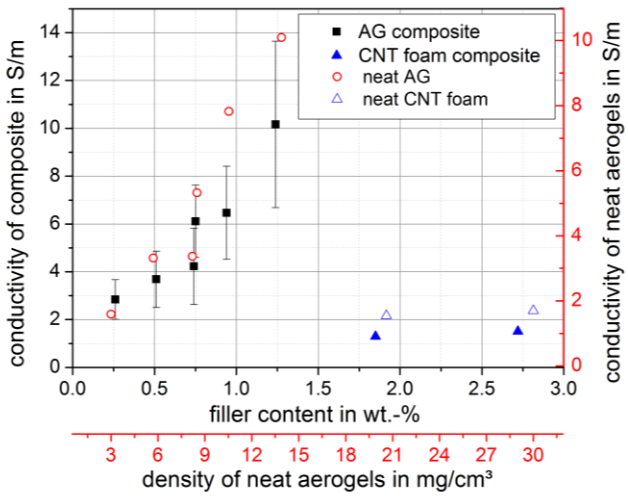

Figure 3.1: Electrical conductivites of neat aerogels and their composites

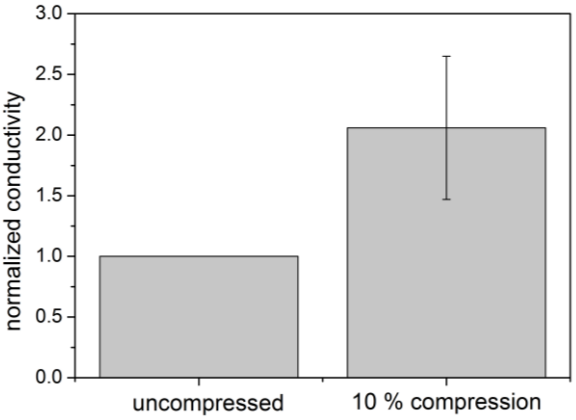

Figure 3.2: Improvement of conductivity of Aerographite composites with compressed Aerographite

The conductivity can easily be adjusted by simple compression of the filler. In Figure 3.2 this is exemplarily shown for an Aerographite composite. Its conductivity can be doubled with only 10 % compression of the Aerographite before infiltration. Especially for low compressions Aerographite exhibits a sensitive, piezoresistive behaviour due to the formation of many new nodes between the tetrapods.

The influence of a heat treatment of the filler is currently in the scope of further investigations. Due to the enlargement of the crystalline length of the graphitic sheets which will be determinded by Raman spectroscopy we expect the scattering of electrons on the edges of a graphitic layer to be reduced.

3.2 Thermal conductivity of carbon aerogel composites and comparison with electrical properties

In Figure 3.3 the thermal conductivity oft the aerogel composites is shown. A maximum improvement of 33 % can be perceived for the Aerographite and 91 % for the CNT mat. Different from electrical conductivity results no direct correlation between the filler content and the thermal conductivity can be perceived for the Aerographite.

In Figure 3.4 the thermal conductivity is displayed over the electrical conductivity of the aerogel composites. It is conspicuous that the CNT mat exhibits the highest thermal conductivity although they have relatively low electrical conductivity and thus a low amount of covalent bonds. More significant seems to be the surface area of the filler and the amount of graphitic layers that do not have an interface with surrounding matrix. While in Aerographite the tetrapods are filled with polymer from the inside, too, the CNT mat has solid building elements that are only covered with epoxy from the outside. Furthermore, Aerographite in contrast to the CNT foam has a lot of “dead ends” – tetrapod arms that are not connected to another arm so that a lattice vibration that is entering a tetrapod is redirected to where

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it cannot be transmitted to the next tetrapod. A more detailed investigation of the surface dependence of thermal conductivity will further be conducted via BET method.

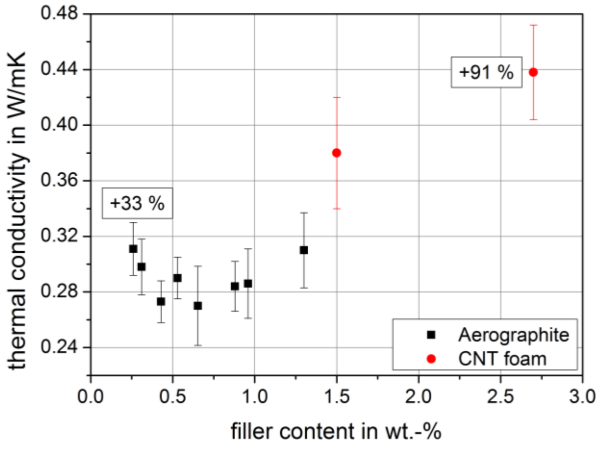

Figure 3.3: Thermal conductivity of aerogel composites as a function of filler content

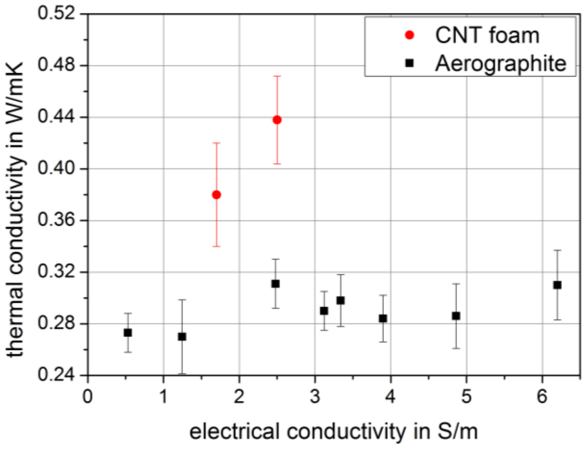

Figure 3.4: Thermal conductivity vs electrical conductivity of aerogel composites

In Figure 3.5 the thermal conductivties for two composites with Aerographite and the CNT mat as a filler, respectively, are compared to the thermal conductivity of the neat materials. It can be seen that the thermal conductivities of the neat fillers are similar with mean values of 0.62 W/mK for the Aerographite and 0.58 W/mK for the CNT foam. However, as a composite the Aerographite conductivity is reduced about 54 % whereas for the CNT mat the mean value of thermal conductivty decreases only by 24 %. This would as well confirm that the surface area is a crucial factor for thermal conductivity.

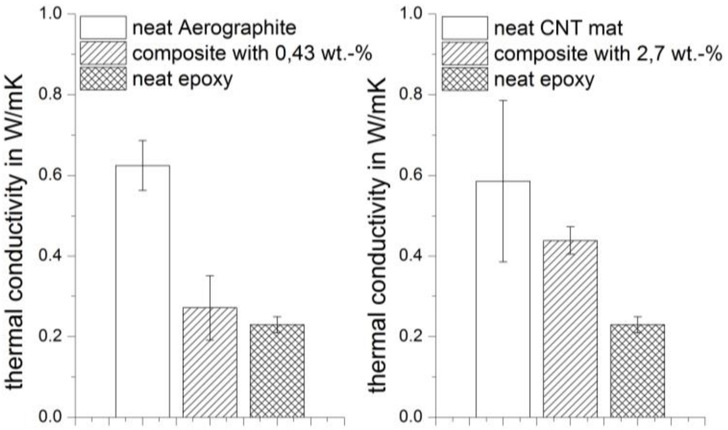

Figure 3.5: Thermal conductivity of neat fillers and its epoxy composites

Similar to the electrical conductivity it is expected that the thermal conductivity can be influenced by compression and a heat treatment of the filler as well. This topic is subject of ongoing research.

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4 Conclusions and outlook

We presented two different, novel approaches for manufacturing of carbon aerogels, their processing to an aerogel/epoxy composite and the composites´ electrical and thermal conductivties. It was demonstrated, that an infiltration with resin is possible while the interconnected structure of the aerogels is preserved. First results for electrical conductivity showed a significant increase in conductivity of several orders of magnitude compared to particle modified composites of similar filler content. Also their thermal conductivties exceed what was achieved for CNT or graphene based composites at similar filler contents.

However, a classification in existing literature shows that the results lie below what was achieved with other aerogel composites (e. g. [10-14]). Supplementary experiments to find out the influence of the filler surface and graphitisation are still ongoing and not yet included in this paper. As both synthesis approaches are very new these are preliminary results. With further improvement of the synthesis a higher amount of interconnections inside the aerogels will be possible. This will lead to further improvements of electrical and thermal conductivites.

5 Acknowledgements

The authors would like to acknowledge the European Union Seventh Framework Programme under grant agreement n°604391, Graphene Flagship and the German Research Foundation (DFG SFB-986) for financial support.

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