Carbon nanofibers and nanotubes are promising to revolutionise several fields in material science and are suggested to open the way into nanotechnology. Further market development will depend on material availability at reasonable prices. We have achieved bulk production capacities of high purity carbon nanofibers (CNFs) at low cost by a catalytic chemical vapour deposition (CCVD) process. Reasonably low temperatures and yields of up to several g/m² min at more than 70% carbon gas-to-fiber conversion rates allow considerable cost reductions. Polymer composites have been prepared by dispersion of CNFs into polymer matrices applying intensive shear via extrusion. In polypropylene the application of less than 10 wt.% CNFs reduced the volume resistivity from >10¹³ Ω cm to a value of ~10⁵ Ω cm. Different sizing of fibers is normally used for nylon, polycarbonate and other high temperature applications. We are focussing on the development and volume production of a single carbon nanofiber type which can be used in the wide range of systems beyond, but not restricted to polymer composites.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Carbon nanotube; Carbon nanofiber; Polymer matrix composite; Metal matrix composite

1. Introduction

Since the revival of graphite whiskers as carbon nanofibers and nanotubes for composite applications, there has been increasing research and development into methods of dispersing and functionalising these materials to exploit their theoretical potential as superior functional additives and reinforcements. Especially the characterisation of fullerenes by Smalley and coworkers [1] and Kraetschmer et al. [2] and furtheron the discovery of carbon nanotubes by Iijima in 1991 [3] provided for insight into the huge potential of molecular sp² derived architectures of carbon. Such defined structures are suggested to boost both efficiency and capacity of electronic building blocks and result into novel functional materials specifically tuned on molecular basis. Though the academic knowledge how to beneficially use these materials practically is already quite mature and well described in the scientific literature [4–6]. In most cases wide practical application, in particular in the field of composites for electronics applications, is yet not possible due to lack of low cost materials in sufficient quantities. Synthesis procedures yielding high purity nanotubes of defined structure are still restricted to carbon arc discharge and pulsed laser ablation allowing gram per day rather than kilograms per day production quantities. Higher quantities can be manufactured by chemical vapour deposition processes having reasonable potential for extended industrial production but yielding materials with higher defect density. Bulk production and application of nanotubes is meanwhile realised in the field of electrically conductive nanotube–polymer composites requiring less narrow specifications in terms of tube diameter, length and structural perfection. However, to successfully compete with existing soot products in composite applications bulk amounts of nanotubes and nanofibers have to be produced at reasonable low costs without too much compromising on defects, thickness and lengths of the fibers. While each method used has it advantages in terms of physical control and process costs, the importance of understanding how to incorporate the fibers into a matrix of
polymer, metal or any other material has been underestimated for a long time. Good control over various mixing parameters are essential to obtain homogeneous composite materials. Bulk agglomerates of fibers up to several tens of microns in diameter act as macro-particle like centres of friction, unable to be compensated by regions exhibiting proper dispersion of fibers within the composite where physical properties are strongly enhanced. High contact resistance between fibers create percolation limits far above their theoretical limits. Therefore fiber surface effects have to be understood and measures taken so that electrical and thermal conductivity, but also mechanical adhesion between fiber and matrix as well is optimised.

The increasing amount of electronic hardware being used in automotive and aerospace applications has created a need for thermal conductive, light weight materials with tunable, well-defined coefficient of thermal expansion (CTE). Materials meeting these requirements will find wide use as heat sinks structural materials with improved thermal properties.

Traditional heat dissipating materials like copper and aluminum show CTE mismatch to silicon and insulating ceramics and cannot be used for direct device attachment without stress compensating interlayers. Alloys, such as FeNi and FeNiCo, however, exhibit suitable CTE, but poor thermal performance. Only CuMo and CuW composites combine good thermal properties and low CTE, but cannot be used in weight sensitive applications due to their high density.

Commonly used light weight matrix materials are aluminum and magnesium alloys combining low density and reasonable thermal conductivity. Only their CTE requires adjustment to lower values. Thus, composite materials, especially metal matrix composites, show the potential to fulfill the requirements. Careful control of reinforcing filler to matrix ratio in such composites allows good adjustment of physical and mechanical properties [7].

One technical mature example is silicon carbide infiltrated by aluminum. AlSiC offers already a set of outstanding properties required in high performance packaging such as high thermal conductivity, low coefficient of thermal expansion and low density.

Using new materials like carbon nanofibers exhibiting excellent physical properties within metal matrices like aluminum or magnesium alloys it should be possible to create novel composites with extraordinary thermal properties. The theoretical estimations of the thermal coefficient of expansion and the thermal conductivity shows the potential of this material.

Because the production costs are currently well above conventional graphite powders and soot products, presently only the combination of several improved property parameters justifies massive introduction of these relatively high cost materials into composite industry. However, nanoscaled additives, viz. carbon nanotubes and carbon nanofibers, having extremely large surface area and well-defined structure and morphology are deemed to be the key to novel composite materials with enhanced physical and chemical properties.

While academic research mainly focuses on single wall nanotubes (SWCNT) and multiwall nanotubes (MWCNT), many of the achievements can directly be transformed on vapour grown carbon fibers (VGCF). At least in the composite area VGCF are considered as relatively thick nanotubes without compromising on composite properties compared to SWNT and MWNT composites, especially with respect to realistic time to market scenarios.

The latter can be regarded as main reason why we are focusing on production and improvement of VGCF fillers for composite applications, however, not restricted to VGCF-polymer composites, but also on metal-matrix–VGCF and VGCF–carbon composites, respectively.

2. Experimental

Vapour grown carbon nanofibers (VGCF) were grown by catalytic chemical vapour deposition (CCVD) in a tube furnace equipped with appropriate gas feed unit and exhaust gas incineration. The process is operating in the batch mode, however, allowing productivity in the kg/day range. Nanofibers are grown by means of Ni based catalysts from diluted acetylene as the carbon feed stock at temperatures below 700 °C. Calculating the area of active catalyst the nanofiber growth rate can be formulated to be about 2.5 g/m² min yielding up to 70% conversion of the carbon precursor into fibers. After cooling to room temperature the fibers are collected as a black fluffy powder which undergoes subsequent polyaromatic hydrocarbon (PAH) stripping and to some extent post-graphitisation at 970 °C under reducing atmosphere. If desired the remaining catalyst can be removed by refluxing the crude fiber mass in aqueous nitric acid (1:1) for about 2 h prior to the thermal post-annealing procedure. SEM image investigation reveals the product to consist of curved and intertwined fibers having an average diameter of approximately 100 nm. The average fiber length is difficult to determine, but it can be concluded that substantial amounts exceed a length of 10 μm. Similar to other VGCF type fibers, as described in the literature, our carbon nanofibers reveal fishbone and platelet structure. As can be seen in the TEM inset in Fig. 1 the graphitic planes are arranged in an angle of around 20° towards the hollow inner channel of the fiber, which is typical for catalytically grown carbon nanofibers. Fig. 2 shows Electrovac nanofibers (ENF®) of 200 nm in diameter. For their average length we conclude similar as for the 100 nm fiber. However,
many of those fibers are spring like, helically curved what makes them appear as thick as 500 nm.

Polypropylene resin (PP), DM 55, was purchased from Borealis and Polycarbonate (PC), Lexan 121, was chosen from GE Plastics.

Polycarbonate–ENF/C226 composites were prepared by melt mixing using a DACA Microcompounder (DACA Instruments, Goleta, USA). The mixing chamber is equipped with two conical co-rotating screws and a bypass allowing the material to circulate for defined periods with a capacity of 4.5 cm³. Premixed, dried mixtures with different amounts of nanofibers were added to the extruder without addition of modifiers. The temperature was set to 260–310 °C, screw speeds of 50 and 150 rpm were applied for 5–30 min. ENF–polypropylene composite samples were produced applying a Brabender Lab Twin Screw Kneader designed to compound either 16 or 32 g of polymer. Masterbatches containing 30 wt.% ENF were produced in the first step at 190, 210 and 230 °C, respectively, and varying kneading times from 10 to 20 min. Appropriate addition of polypropylene resin to the masterbatch and 20 min kneading at 190 °C gave the desired composites of defined filling grade. The final composites obtained revealed fiber filling between 5 and 25 wt.%, respectively.

Aluminium matrix ENF/C226 composites were prepared applying a proprietary Al melt pressure infiltration process of a mechanically stable ENF/C226 preform. Such a preform is produced by coating the nanofibers with an organic binder by stirring the fibers in the binder containing solution. After removal of excess solvent and drying in air the coated fibers are pressure moulded in any desired shape. The dimension of sample preforms are 40×40×5 mm. The such obtained preform body is sintered in reducing atmosphere prior to Al infiltration.

For electrical measurements, sheets with a thickness of 350 μm and a diameter of 60 mm were pressed from the extruded strands. Electrical measurements were performed either using a Keithley electrometer Model 6517 with a 8009 Test Fixture measuring the volume resistance and a Tera Ohm Meter, Eltex 6206, suitable to measure both volume- and surface-resistivity.

For mechanical measurements tensile bars were produced with a Battenfeld BA 600 CDC. Destructive testing was done with a ZWICK 1435. Data were obtained following EN ISO 527-5-3.

Scanning electron microscopy (SEM) from materials and composite samples were taken using a LEO 435 VP scanning electron microscope and a Philips Fei XL 30 scanning electron microscope. Composites were cryo-fractured prior to SEM analysis. In some cases the fracture cross-section was sputter coated with a thin gold palladium layer.

3. Results and discussion

3.1. Polymer matrix composites

PP–ENF/C226 composites containing between 5 and 25 wt.% fiber load were produced by compounding appropriate amounts of masterbatch and pure resin as described above. The fibers were compounded into the resin as received from production. As found by SEM analysis they appear as interwoven bundles and aggregates of up to several tens of microns in diameter. However, applying shear onto these aggregates during the compounding process most of the aggregates became well dispersed as individual fibers as can be seen in Figs. 3 and 4. Of course, some aggregates up to 10 μm, not shown, were remaining randomly distributed through the composite, certainly reducing the mechanical properties. Mechanical testing was performed on PP–ENF/C226 200 nm samples. Composites containing 15 wt.% fiber filling showed an improvement of the Young’s modulus of about 90%, which means in figures
an increase from 410 N/mm² for the pure PP to 780 N/mm² for the nanofiber reinforced composite.

Electrical conductivity measurements were performed on both PP–ENF® and PC–ENF® composites as depicted in Fig. 5. Volume resistivity values for PP–ENF® 200 nm samples are similar to recently reported data obtained with Pyrograph III in Polyethylene (HDPE) giving $4 \times 10^6 \ \Omega \text{cm}$ with 18 wt.% fiber load [8]. PP–ENF® 100 nm composites are in the same conductivity range, however, already at 10 wt.% fiber load. Almost the same resistivity values for Pyrograf III PP composites were found by Gordeyev et al. [9].

Two orders of magnitude better values were reported by Kuriger et al. using treated Pyrograph III (PR-19-HT) fiber, which is heat treated at 3000 °C and therefore designed to exhibit enhanced thermal and electrical properties. These PP–VGCF samples gave 12.6 Ω cm at 9 vol.% (~18 wt.%) fiber load [10].

PC composites were just fabricated with ENF® 100 nm fibers, but showed surprisingly slightly lower conductivity values than PP at 7.5 and 10 wt.% VGCF loading between $3 \times 10^7$ and $10^6 \ \Omega \text{cm}$, respectively. However, for both PP– and PC–ENF® 100 nm composites the percolation threshold is between 5 and 10 wt.% fiber filling. SEM imaging of PC–nanofiber composites (Fig. 6) revealed a more or less homogeneous nanofiber distribution through the entire sample volume. In addition, in the extruded strands the nanofibers

Fig. 3. SEM image, cross-section of PP–ENF® 200 nm (15 wt.%) composite.

Fig. 4. SEM image, cross-section of PP–ENF® 100 nm (10 wt.%) composite.

gave 12.6 Ω cm at 9 vol.% (~18 wt.%) fiber load [10].

PC composites were just fabricated with ENF® 100 nm fibers, but showed surprisingly slightly lower conductivity values than PP at 7.5 and 10 wt.% VGCF

Fig. 5. DC volume resistivity of ENF® filled PP and PC.

Two orders of magnitude better values were reported by Kuriger et al. using treated Pyrograph III (PR-19-HT) fiber, which is heat treated at 3000 °C and therefore designed to exhibit enhanced thermal and electrical properties. These PP–VGCF samples gave 12.6 Ω cm at 9 vol.% (~18 wt.%) fiber load [10].

PC composites were just fabricated with ENF® 100 nm fibers, but showed surprisingly slightly lower conductivity values than PP at 7.5 and 10 wt.% VGCF

Fig. 6. SEM micrographs of cryo-fractured PC–ENF® 100 nm samples filled with 7.5 wt.% nanofibers prepared by melt mixing: (a) low magnification, and (b) high magnification.
are not preferentially oriented in extrusion (and strand) direction what we observed on PP samples as well. Surprisingly around most of the fibers holes and cavities are visible which indicates poor adhesion and fiber matrix interaction. Presumed that shock freezing down to liquid nitrogen temperature does not account for this phenomenon, it is quite understandable that just a fraction of all the fibers dispersed in the composite contribute to the conductive network within the polymer matrix.

The influence of kneading temperature and kneading time on conductivity of the resulting composite was investigated on PC–ENF® 100 nm samples containing 7.5 wt.% nanofibers. Unfortunately, no significant changes in conductivity could be determined and SEM images taken from fracture surfaces did not show changes in morphology as well. Polycarbonate Pyrograf III composites were assessed by Carneiro et al., however, only for their mechanical properties [11]. The SEM image depicted in this work reveals similar surface morphology features as our PC–ENF® samples.

To get a better understanding of the potential of ENF® as conductive filler in insulating matrices conductivity measurements of silicon oil ENF® 200 nm fibers were dispersed by vigorous mechanical stirring enhanced by the impact of ultrasound. Depending on the voltage applied $3 \times 10^{-4}$ S/m at 50 V and $5 \times 10^{-3}$ S/m at 1 kV were determined, respectively.

### 3.2. Metal matrix composites

By theory the resulting CTE of a composite can be predicted with the mathematical model of Turner [12]. Another algorithm applies for the thermal conductivity [13] which allows forecast on possible properties of composite material as depicted in Figs. 7 and 8.

Assuming fibers with a Young's modulus of 1500 Gpa and thermal conductivity of 1000 W/m K and isotropic arrangement of the fibers within preform fiber scaffold, very low CTEs and very high thermal conductivity can be expected.
VGCF based composites are allude reported in the literature, however, using unidirectional layered vapor grown carbon microfibers [14]. As an example one Al composite comprising 36.5 vol.% of those fibers gave a thermal conductivity of 642 W/m K along the direction of highest fiber placement. In contrast we focus on isotropic thermal properties of such metal composites. Thus, the Al gas pressure infiltration process is considered to be already highly elaborated [15], we regard the fiber preform manufacture as the crucial step. Fig. 9 shows a cross-section of such a compacted green ENF® preform.

Prerequisite on the preform is sufficient mechanical stability providing for high macro-porosity to allow the Al melt infiltrate homogeneously through all the pores within the nanofiber network. First results on Al ENF® composites are depicted in Fig. 10 showing a cross-sectional view of a cryo-fractured composite specimen. Note that ENF® 100 fibers are pore free embedded into the Al matrix. Examination by optical microscope reveals pore free surfaces as well.

4. Conclusion

Carbon nanofibers, though not that perfect in structure compared to other carbon nanotubes, are demonstrated to have positive impacts on properties of polymer composites and show potential to be reasonably used in metal matrix composites as well. Industrial production of these materials is obviously much more feasible than for single wall and thin multiwall carbon nanotubes with respect to volumes required in plastics and composite industry. Appropriate surface treatment of such fibers will result into improved fiber to matrix interaction. This in turn will enhance the dispersion and wetting properties of the nanofibers leading to further property improvement of composite materials; in some applications even at significantly reduced loads.

Acknowledgements

We wish to thank the Forschungs–Foerderungs–Fonds (FFF) der gewerblichen Wirtschaft, Austria, for supporting this work; Project no. 805180.

References