



Low thermal and high electrical conductivity in hollow glass microspheres covered with carbon nanofiber–polymer composites



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ABSTRACT

To take advantage of both the low density and thermal conductivity of hollow glass microspheres, and the high mechanical and electrical conductivity of carbon-based nanofillers, micro- and nanosized fillers can be combined into a single composite material. Here we prepared composite materials from hollow glass microspheres (HGMs) and from the same microspheres surrounded by carbon nanofibers (CNFs). By adding 10% wt. of HGM-CNFs to a high-temperature resin we can obtain a low density (0.8 g/cm^3), low thermally (0.17 W/mK) and high electrically conductive ($7 \pm 3 \times 10^{-4} \text{ S/m}$) composite. This novel method demonstrates the possibility to achieve an unusual combination of properties such as low thermal and high electrical conductivity which, along with their light weight and thermal stability, makes these materials promising for aerospace applications or thermoelectric devices.

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1. Introduction

There is a need for high-performance polymers with high electrical and low thermal conductivity for aerospace, marine and energy applications. However, this combination of properties is really hard to obtain in a single material.

By adding conducting fillers [1–4] to a polymer matrix, the thermal and electrical conductivity of the resulting composite can be increased. Once these fillers form a conductive network within the polymeric matrix, the electrons can flow through the composite, increasing the thermal and electrical conductivity of the composite. In general, when electrically insulating fillers are added to a polymer [5–8] the thermal conductivity of the composite is modified but not the electrical conductivity.

Opposed effects on the thermal and electrical conductivity can also be obtained by combining insulating and conducting fillers. By adding carbon-based nanomaterials and electrically insulating fillers to a polymer matrix; composites with improved thermal conductivity and high electrical resistivity are obtained [9–11]. This approach, based on the combination of fillers has been followed in

the present work using hollow glass microspheres (HGMs) and carbon nanofibers.

Composites containing hollow glass microspheres are very attractive due to their light weight, high thermal stability, and low thermal conductivity [12–15]. Depending on the density (wall thickness) of the HGMs, stiffer composites can be obtained. However, as the interaction between the matrix and HGMs is generally poor, the resultant composites suffer reduced strength, compared with the raw matrix [16,17]. On the other hand, the addition of HGMs to a polymer, e.g., epoxy resin, results in a material with the same electrically insulating behaviour as the matrix but with reduced thermal conductivity [8,12].

Carbon-based nanostructures, such as graphene, graphite nanoplates, graphite oxide, carbon nanofibers (CNFs) and nanotubes are being extensively studied due to their outstanding mechanical, thermal and electrical properties, which make these nanosized structures ideal as nanofillers for aerospace or high-performance composites. To take advantage of both the low density and thermal conductivity of HGMs and the high mechanical and electrical conductivity of carbon-based nanofillers, both micro- and nano-sized fillers can be combined in a single composite material; for example, when 0.3 vol.% of CNFs is added to an epoxy composite with 50 vol.% of HGMs (0.46 g/cm^3), the tensile modulus and strength are increased by 10 and 29%, respectively, compared to the unmodified HGM composite [18]. For an epoxy composite with

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10 wt.% of CNFs and 15 vol.% of HGMs (0.22 g/cm³) the electrical resistance is reduced by 85% while the dielectric constant is increased by four orders of magnitude, compared to the neat resin [19]. The effect of CNFs on the viscoelastic properties [20], as well as on the degradation due to moisture exposure [21] or thermal expansion [22], were also studied.

Several groups have directly grown CNTs on micron-diameter fibres [23–25] and solid particles of different sizes and materials, such as alumina/iron oxide nanoparticles [26], ceramic spheres [27], alumina microparticles [28,29] or silica microparticles [30,31]. However, to our knowledge, there is scarce literature on the growth of carbon nanotubes or nanofibers on micron-scaled hollow glass spheres [32] and only the mechanical (compression) and thermo-mechanical (dynamic mechanical analysis) properties of the produced composites were characterized.

Here we present a method to develop a hybrid composite material with an unusual combination of properties such as improved electrical conductivity and low thermal conductivity. We tailored the composite properties by using a hybrid filler based on carbon nanofibers that were directly synthesized by chemical vapour deposition on micron-sized hollow glass spheres. We also compared our experimental results with analytical models and found a good correlation between the results obtained from both approaches.

2. Methods

2.1. Synthesis of hybrid HGM-CNF particles

Carbon nanofibers were synthesized on the surface of hollow glass microspheres (K20 Glass bubbles, 3M) by means of a chemical vapour deposition process. The catalyst precursor for the growth of carbon nanofibers was iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O) (Sigma-Aldrich, >98% purity). To coat the surface with the catalyst precursor [24], the microspheres were added to a solution of 50 mM iron nitrate in isopropanol and mechanically mixed for 2 h. Then, the mixture was filtered for overnight and dried at 150 °C for 3 h. After this process, the catalyst precursor-coated HGMs were stored until they were used as substrate for the growth of CNFs.

The treated microspheres were placed in an alumina boat, which was positioned in the middle of a quartz tube and heated by a mobile horizontal tube furnace that allows fast heating and cooling rates. A detailed explanation of the CVD system can be found elsewhere [33]. For the conditioning of the catalyst, the furnace was heated to 600 °C and a flow of 100 sccm of H₂ and 400 sccm of Ar was passed through the quartz tube for 20 min. Afterwards, for the carbon nanofibers growth, the temperature was maintained at 600 °C and a flow of 100 sccm of H₂, 400 sccm of Ar and 200 sccm of C₂H₄ was maintained for 20 min. After this process, the furnace was cooled down under a flow of 1000 sccm of Ar.

2.2. Composite preparation

The resin used as matrix for the preparation of composites was a high-temperature urethane acrylate resin (Crestapol 1234, Scott Bader Company Ltd.). Methyl-ethyl-ketone peroxide solution in diisobutyl phthalate (Butanox LPT) was used as catalyst (2% by weight of resin) and a solution of cobalt octoate in styrene (Accelerator G) was used as accelerator (2% by weight of resin).

Composites containing 0, 2, 5 and 10 wt.% of HGM and the hybrid material, obtained by the CVD process (HGMs-CNFs), were produced. Resin, catalyst and accelerator were hand-mixed and degassed for 1 min. Then, the appropriate amount of filler was

added to the resin and stirred by hand. Finally, the resulting mixture was cast in a silicone mould and cured at room temperature for 48 h, followed by a post-curing cycle of 5 h at 80 °C and 3 h at 195 °C.

2.3. Characterization

2.3.1. Morphology and Raman spectroscopy

The morphologies of the as-received HGMs and the synthesized HGM-CNF particles were analysed by scanning (SEM equipped with an energy-dispersive spectrometer, EVO MA15, Zeiss) and transmission electron microscopy (TEM, JEOL JEM 3000F). The elemental composition of the as-received HGMs was analysed by energy-dispersive spectroscopy (EDS). For SEM and EDS, the particles were lightly pressed onto an adhesive carbon tape and for TEM, a small amount of the hybrid material was dispersed in isopropanol by means of an ultrasonic probe. A drop of the resulting solution was carefully deposited on a TEM carbon-coated Cu grid (LC300-Cu, EMS).

The morphology of the resulting composites was assessed by analysing the fracture surfaces of the manually fractured specimens by light microscopy and scanning electron microscopy (Helios NanoLab 600i, FEI). For SEM, the surfaces of the samples were sputter-coated with a thin layer of gold to avoid electrostatic charge of the sample during the analysis.

The as-received HGMs and the synthesized hybrid fillers were placed on top of thin aluminium foils and analysed by Raman spectroscopy (Micro-Raman spectrometer Renishaw PLC), using a DPSS Nd:YAG green laser (532 nm wavelength). Three measurements were performed per sample. Spectra were obtained for an exposure of 15 s, 5 accumulations, in the range of 200–3500 cm⁻¹, applying a laser power of 5%.

2.3.2. Thermogravimetric analysis and density measurement

The thermal stability of HGMs and the carbon content of the HGMs-CNFs, as well as the thermal stability of the resulting composites, were analysed by using a thermogravimetric analysis (Q50 TA Instruments), during which the samples were heated under air, at a heating rate of 10 °C/min, from room temperature to 800 °C. The residue obtained after the thermogravimetric analysis was used to calculate the actual amount of HGMs and HGMs-CNFs added to the composites. The procedure followed is explained in the [Supplementary Information](#).

The density of the resulting composites was measured by following the ASTM D792-13 standard [34], through the application of the Archimedes' principle. At least three cylindrical samples for each filler content, were first weighted in air and then in distilled water at 24 °C. The theoretical density of composites was also obtained, by applying the rule of mixtures, to compare the experimentally measured densities of the composites with their theoretical densities. The HGM and HGM-CNF weight fractions used to calculate the theoretical densities were those obtained by TGA, as mentioned above. The equations used for the calculation of the filler volume fraction and the theoretical density are available in the [Supplementary Information](#).

2.3.3. Thermal conductivity analysis

The thermal conductivity, thermal diffusivity, and the volumetric heat capacity of the resulting composites were measured at room temperature by applying a transient plane source technique (TPS 2500 S, Hot Disk AB). A thin heater/sensor, with a radius of 2.001 mm, was placed between two identical samples (30 mm diameter and 3 mm thick). The heater/sensor element was first

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