

MULTIFUNCTIONAL HYBRID COMPOSITES FOR THERMAL BARRIER AND HIGH TEMPERATURE APPLICATIONS

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Keywords: Carbon nanofibers, Hollow glass microspheres, Polymer-matrix composites (PMCs); Thermal properties, Chemical vapour deposition (CVD)

Abstract

In the present work, we propose a method to develop a composite material which satisfies different requirements to make this material very attractive for high temperature aerospace applications. Our approach is to use a high-temperature resin matrix and as a reinforcement, a hybrid filler composed by hollow glass spheres with carbon nanofibers directly synthesized on their surface by a chemical vapour deposition process. The density, the storage modulus and the thermal and electrical behaviour of the composites have been studied to assess the effect of the HGMs on the matrix and the effect of the hybrid microspheres, compared with the as-received HGMs. Thus, we have obtained a lightweight composite material with low thermal conductivity, able to withstand high temperatures and, at the same time, a material that is electrically conductor.

1. Introduction

Carbon fibre reinforced polymers (CFRPs) can meet multiple-functional requirements at prolonged service temperatures. However, new aerospace vehicles have pushed sustained service temperatures into higher temperature ranges well beyond the capabilities of traditional CFRPs. When composite structures, such that located near engines in aircraft, are heated to temperatures greater than the glass transition temperature of the composite, weight loss, chemical reactions and mechanical properties losses due to thermal aging occurs.

In this work, we have developed a material able to withstand high temperatures and, at the same time, able to act as a thermal insulator to protect other sensitive structures. Our approach is based on the dispersion of hollow microspheres in a high-temperature resin in order to obtain a composite with a high air volume-fraction, providing a polymeric material with low thermal conductivity and low density. This approach has already been investigated, producing both thermoplastic and thermoset matrix composites [1,2]. Composites with a reduced thermal conductivity, light weight and improved specific mechanical properties have been produced [3,4].

Generally, there are some requirements really hard to find in traditional composite material. For example, due to the interdependence of the electrical and the thermal conductivity [5], it is complicated to improve one of these properties without increasing the other at the same time, which is necessary to increase the efficiency of thermoelectric materials [6]. In order to address this drawback, the addition of a second dispersed phase within the resin matrix, along with the hollow microparticles, can result in an effective solution to assess this drawback. Thus, in the present work, we also propose the addition of a hybrid microstructure composed by carbon nanofibers (CNFs) grown on the surface of the HGMs.

2. Experimental

2.1. Synthesis of hybrid microspheres and composites preparation

Hybrid microspheres were obtained by directly growing carbon nanofibers (CNFs) on the surface of hollow glass microspheres (K20 Glass bubbles, 3M), by chemical vapour deposition (CVD) process. The microspheres have a particle size distribution between 20 and 105 μm and a density of 0.2 kg/m^3 . The catalyst precursor for the CNF growth used in this work was iron nitrate. In order to coat the surface with the catalyst precursor [7], the microspheres were added to a solution of iron nitrate in isopropanol and mechanically mixed for 2 hours. Then, the mixture was filtered for overnight and dried at 150 $^{\circ}\text{C}$ for 3 hours.

The microspheres covered with the catalyst precursor were placed in the middle of the CVD furnace. A detailed explanation of the CVD system can be found in [8]. For the conditioning of the catalyst, the furnace was heated to 600 $^{\circ}\text{C}$ and a flow of 100 ml/min of H_2 and 400 m/min of Ar was passed through the quartz tube for 20 min. Afterwards, for the carbon nanotubes nanofibers growth, the temperature was maintained at 600 $^{\circ}\text{C}$ and a flow of 100 ml/min of H_2 , 400 m/min of Ar and 200 ml/min of C_2H_4 was settled for 20 min. After this process, the furnace was cooled down under a flow of 1000 ml/min of Ar.

The resin used in this work for the preparation of the composites was an urethane acrylate resin (Crestapol 1234, Scott Bader Company Ltd.). For curing at room temperature the resin requires the addition of a catalyst (methyl-ethyl-ketone peroxide solution in diisobutyl phthalate) and an accelerator (cobalt octoate dissolved in styrene), each of them added in 2% by weight of resin

Composites containing 0, 2, 5 and 10 wt.% of HGMs and the hybrid microspheres were produced. First, resin, catalyst and accelerator were mixed and degassed for 1 minute. Then, the appropriate amount of filler is added to the mixture and stirred by hand. Finally, the resulting mixture is poured in a mould and cured at room temperature for 48 hours, followed by a post-cure cycle of 5 hours at 80 $^{\circ}\text{C}$ and then 3 hours at 195 $^{\circ}\text{C}$.

2.3. Characterization

The as-received microspheres and microspheres after the CVD process were analysed by using a scanning electron microscope (SEM, EVO MA15, Carl Zeiss). The samples were sputter coated with a thin layer of gold prior SEM characterization.

Thermal stability and carbon content of the hybrid microspheres was analysed using a thermogravimetric analyser (Q50, TA Instruments) in a temperature range from room temperature to 800 $^{\circ}\text{C}$, with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in oxygen environment.

The density of composites was measured following the ASTM D792-13 standard [9], 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 $^{\circ}\text{C}$.

Differential scanning calorimetry (DSC) was performed on a DSC Q200 (TA Instruments). The samples were encapsulated in aluminium pans, and the lids were perforated to avoid internal pressure build-up. During the measurements, the samples were heated from 20 to 320 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere.

Dynamic mechanical analysis (DMA) was performed on a Q800 (TA Instruments) testing specimens with dimensions of 20 x11 x3 mm, in the temperature range between room temperature and 300 °C at a frequency of 1 Hz and a heating rate of 3 °C /min.

The thermal conductivity and diffusivity of the resulting composites with HGM and HGM-CNF was measured, at room temperature, using a hot disk thermal constants analyser TPS 2500 S (Hot Disk AB). The measurements were performed with cylindrical shaped samples, with a diameter of 30 mm and a thickness of 3 mm. For each filler content and neat resin at least three measurements were taken, with an output power of 0.01 W and a measuring time of 20 s. Detailed description of the transient plane source technique, as well as its theoretical background, can be found in [10,11].

The cooling behaviour of the composites with 10 wt.% of HGMs and HGMs-CNFs was qualitative analysed using an infrared camera (FLIR). The cylindrical samples, previously used for the thermal conductivity measurement, were placed on a heating plate that was heated up to 150 °C. Once that temperature is reached, the samples were taken from the heating plate and immediately placed on a Teflon plate at room temperature. Images were taken during the cooling-down process.

The electrical conductivity of the composites with the hybrid microspheres was measured from samples taken from the disc samples used for the measurement of the thermal conductivity. The surfaces of the samples were coated with silver paint to ensure good contact between the sample surface and the electrode, which was copper film and the electrical resistance was measured, at room temperature, using a digital multimeter (Agilent 34410A 6 1/2 Digit multimeter).

3. Results and discussion

The SEM images confirm that the as-received HGM have a size distribution between 20 and 100 µm, approximately. It can be observed that the microspheres are well dispersed, with no observable agglomerates, and that just a few of them are broken (Figure 1a). After being held at 600 °C during the CVD process, the hollow microspheres maintain their spherical shape (Figure 1b). This seems to indicate that the softening point of the particles has not been reached [12]. In Figure 1b can also be seen that the CNFs (Figure 1c) grown by the CVD process cover the surface of HGMs, although not completely.

The thermogravimetric analysis (Figure 1d) shows that the glass microspheres are thermally stable up to 800 °C. It has been obtained that the amount of carbon-based material of the total weight of the hybrid HGMs-CNFs corresponds to a 25 wt.%. By the TGA analysis is also determined that the synthesized CNFs have an oxidation temperature of ca. 570 °C.

From the DSC measurements (Figure 2a) it can be observed that the addition of HGMs to the resin has no significant effect on the glass transition temperature. The modification of the microspheres with the CNFs synthesized on their surface seems to have no significant effect on the glass transition temperature of the resulting composites, as it can be observed in Figure 2b.

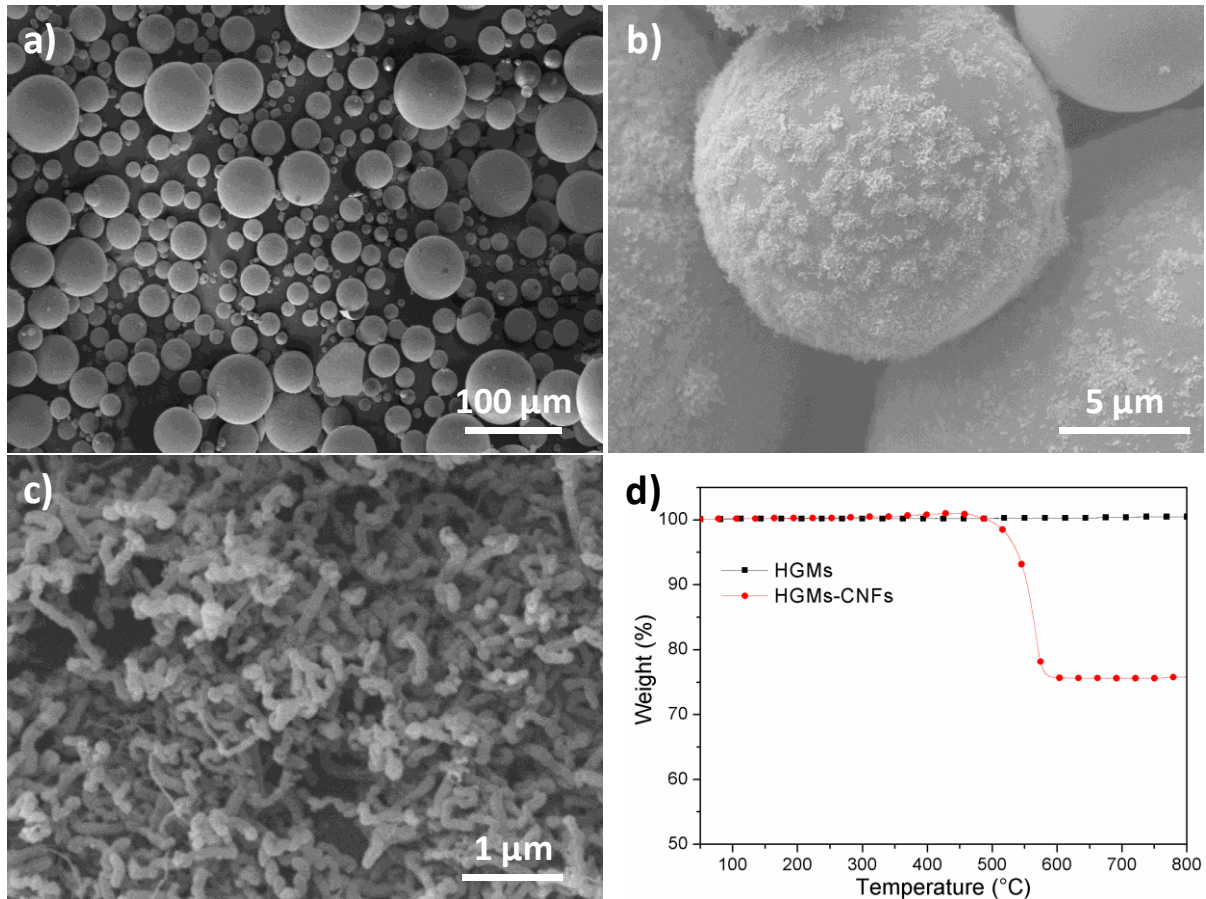


Figure 1. SEM images of a) the as-received microspheres, b) of the hybrid HGMs-CNFs that have been grown on the surface of the microspheres and partially covers it. A high magnification SEM image of the CNFs is shown in c). In d) are shown the weight change as a function of the temperature, of the HGMs and the HGMs-CNFs.

The storage modulus (Figure 2c) was obtained from the dynamic mechanical analysis [13]. It can be observed that at room temperature, the addition of HGMs or the hybrid microspheres results in a decrease in the storage modulus of the material. However, except for the 5 wt.% composite, the materials with HGMs-CNFs have slightly higher storage modulus than the samples with HGMs. At a temperature of 225°C, near the glass transition temperature of the materials, the storage modulus remains almost unaffected with the addition of the hybrid microspheres. In the case of the composites with HGMs, the behaviour is similar to the composites with HGMs-CNFs, except for the 5 wt.% HGM composite, which has an storage modulus a 20% higher than the 5 wt.% HGM-CNF composite.

The addition of HGMs and HGMs-CNFs to the polymeric matrix led to a decrease in the density of the material, as it was expected. The lowest densities were obtained for the 10 wt.% HGM and HGM-CNF composites, being a 35% and a 29%, respectively, lower than the density of neat matrix.

The thermal conductivity of neat resin was found to be 0.228 W(mK)^{-1} . The thermal conductivity of composites decreases with increasing the amount of HGMs added. The thermal conductivity can be reduced a 30% for the composite with 10 wt.% of HGMs. This was the expected behaviour taking into account the low thermal conductivity of HGMs, compared to that of the resin. The value of the thermal conductivity of the HGMs, provided by the manufacturer, was 0.07 W(mK)^{-1} .

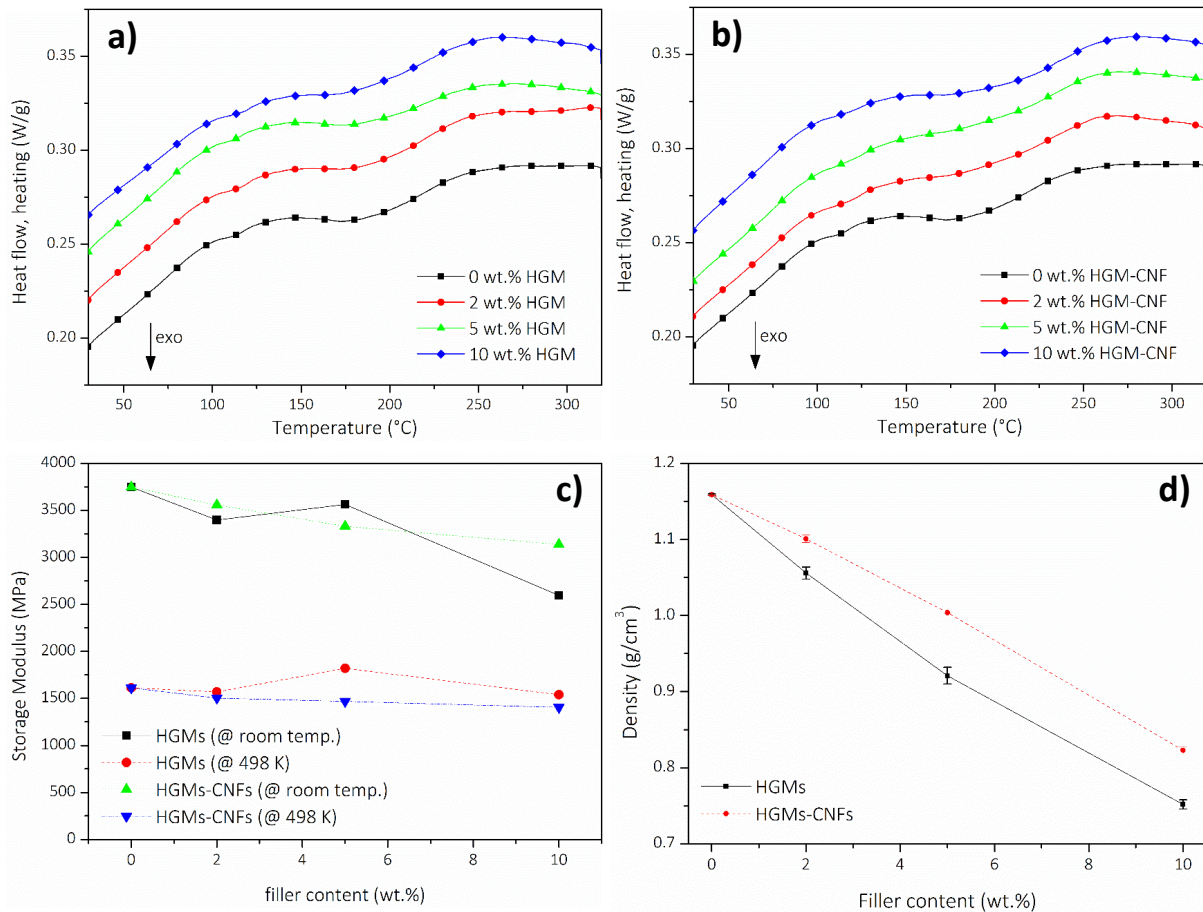


Figure 2. Differential scanning calorimetry thermograms showing the heating curves of the of a) HGM and b) HGM-CNF composites and c) value of the storage modulus, as a function of the filler content, measured at room temperature and at 498 K. d) Measured density of the neat resin and HGM and HGM-CNF composites.

In the case of the HGM-CNF composites, it was observed that the thermal conductivity of the resulting material decreases, compared to the resin, with increasing the amount of hybrid filler. Nevertheless, the reduction on the thermal conductivity upon the addition of HGMs-CNFs was lower, compared with the reduction that takes with the addition of HGMs. In this case, the thermal conductivity of the composite with 10 wt.% of HGMs-CNFs was a 25% lower than that of the neat resin. This behaviour could be explained as the result of combination of two effects. First, as the CNFs of the hybrid filler have higher thermal conductivity than the matrix and the HGMs [14], they counteract the dominant insulating effect of the HGMs. In the second place, for composites with the same wt.% of filler, the HGM-CNF composites have a 25% lower amount of HGMs than the HGM composites. This percentage accounts for the amount of CNFs grown on the HGMs by the CVD process.

The qualitative analysis of the thermal behaviour of the composites is performed by infrared thermography (Figure 3). In the first infrared image, obtained when the samples were taken from the heating plate ($t=0$ min), the neat resin have the highest temperature (126 °C), while the sample with HGMs and HGMs-CNFs composites had reached only 119 and 121 °C, respectively. One minute later, the sample with the hybrid microspheres is at 69 °C, while the HGM composite and neat resin are at higher temperature (71 and 81 °C, respectively). At the end of the cooling-down process, the HGM-CNF composite has reached the room temperature (23 °C), while the HGM composite and the neat resin are 1 and 3 °C above the room temperature.

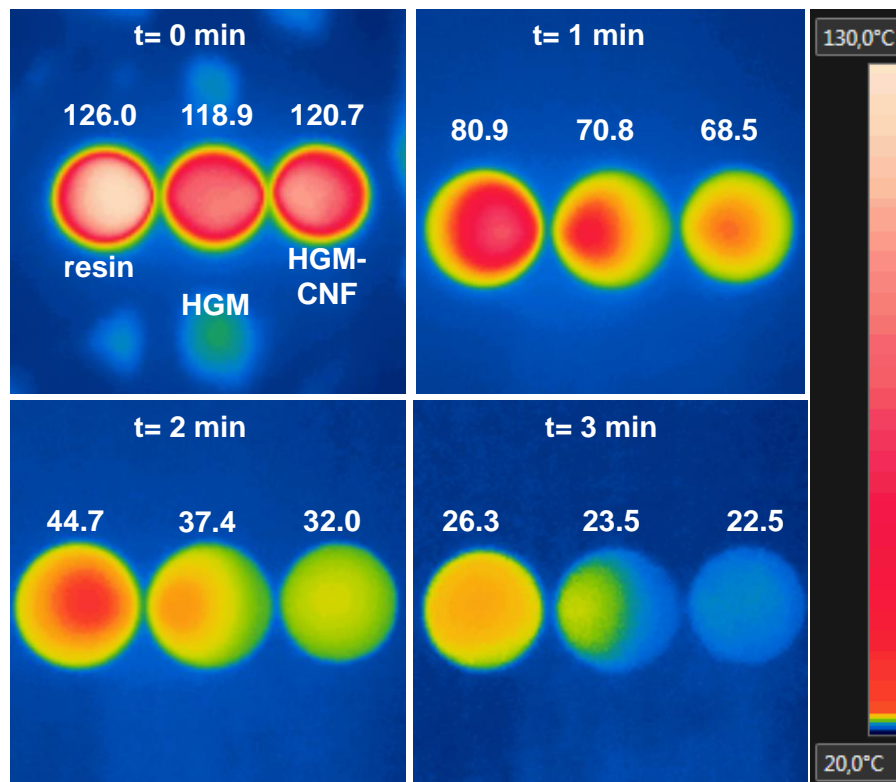


Figure 3. Cooling process of samples of resin and composites with 10 wt.% of HGMs and HGMs-CNFs observed with an infrared camera. It seems that CNFs grown on the surface of the HGMs increases the rate of heat evacuation, compared with the HGM composites.

It seems that the addition of HGMs to the resin improves the ability of the material to evacuate the heat, compared with the neat resin. The CNFs synthesised on the surface of the HGMs seems to further improve this ability of the material, as the sample of the composite with HGMs-CNFs have the highest cooling rate. This could be explained in terms of the thermal diffusivity of the material, which is a measurement of the speed of heat propagation within the material, due to a temperature change, over a period of time [15].

With respect to the HGM composites, as it was expected, no electrical conductivity was measured with the equipment used. In the case of the HGM-CNF composites, for the composite with 10 wt.% of HGMs-CNFs an average value for the electrical conductivity of $2.5 \pm 0.1 \times 10^{-5}$ S/cm was obtained. For the rest of the HGM-CNF composites, no measurable values of the electrical conductivity were obtained with the used equipment. Taking into account the results obtained from the TGA of the hybrid materials obtained by CVD, this result implies that the percolation threshold of the resulting HGM-CNFs composites is between a 1.25 and 2.5 wt.% of CNFs, which corresponds to the composites with 5 and 10 wt.% of HGMs-CNFs.

3. Conclusions

The synthesis of a hybrid material, consisting in carbon nanostructures grown on the surface of hollow glass microspheres, is reported here. Composites with as-received HGMs and HGMs-CNFs have been prepared. By the addition of HGMs, composites that are a 35% lighter and are more thermally insulating, compared to neat resin, have been obtained. The use of the hybrid microspheres allows us to produce composite materials that are a 29% lighter than neat resin. It can be said that, the storage

modulus, at room temperature, of the composites with hybrid microspheres is slightly higher than that of the composites with unmodified HGMs. The thermal conductivity can be reduced up to a 25%, compared to the neat resin. Further research will be focused in the quantitative measurement of the thermal diffusivity in order to validate the qualitative characterization done with the infrared camera. The dispersion of HGM-CNFs within the matrix, by hand mixing, additionally allow us to obtain materials with an electrical conductivity of $2.5 \pm 0.1 \times 10^{-5}$ S/cm. Thus, it has been shown that the appropriate combination of materials results in a material with the desired thermal and electrical properties.

Acknowledgments

This work was supported by the European Commission under the 7th Framework Program, NFRP project (PICIG12-GA-2012-33924). R. G. V. gratefully acknowledges the Spanish Ministry of Science and Innovation for financial funding through the Ramon y Cajal Fellowship. L. C. H-R acknowledges the support from the Spanish Ministry of Education through the FPU program (FPU014/06843). The authors would like to acknowledge 3M for providing the hollow glass microspheres and Scott Bader for providing the resin.

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