Enhancement of Carbon Nanofibers Dispersion on Epoxy Resin Foams Leading to Remarkable Electrical Conductivity Improvement

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SUMMARY

A simple procedure to evaluate and improve the dispersion of carbon nanofibers is presented and validated, relating the observed dispersion of the nanofibers in an intermediate stage of the production process to the final macroscopic properties of the foams. Epoxy/carbon nanofiber foams with optimal nanofiber dispersion are produced taking advantage of this procedure using inexpensive industrial vapor grown carbon nanofibers. Furthermore, the main characteristics and the electrical resistivity of the foams with improved nanofibers dispersion have been determined and related to the presence of the carbon nanofibers, greatly enhancing the electrical conductivity of the epoxy/carbon nanofiber foams.

1. INTRODUCTION

Epoxy resins are relevant and well-known in material engineering due to their excellent performance in different applications [1, 2], as well as their exceptionally good electrical, thermal, and mechanical properties [3]. Epoxy resin-based materials are widely used as polymeric matrix for manufacturing

fiber reinforced materials, taking advantage of their great strength and high Young's modulus. Moreover, they are also commonly used as an adhesive, coating, or structural material [4, 5] in various industries such as electronics, automotive, aerospace, or for biotechnological applications [6, 7]. Despite these uses, epoxy resins have some drawbacks, such as low impact strength, poor resistance to crack initiation and their propagation [8], and low fracture toughness. Being the use of nanoparticles as fillers inside the epoxy matrix the usual approach to overcome these limitations [9].

In the last few years polymeric nanocomposites have attracted remarkable interest due to their enhanced properties compared with neat polymers [10]. The first study of polymeric nanocomposites was carried out in 1990 by the research group at Toyota. They synthesized nanocomposites based on nylon-6 and nanoclays, achieving a great improvement in the material properties [11]. Since then, production of composites reinforced with nanoparticles has been a prominent topic in recent research [12].

Polymer composites present two phases: the matrix and the filler, being the matrix the polymer phase in which the filler is embedded. In the particular case of nanocomposites the filler consists of particles with at least one of their dimensions below 100 nm [13]. It has been demonstrated that nanoparticles could present a better performance as a filler in polymers than other additives due to their large surface area relative to their volume [14]. In particular, the use of nanoparticles in epoxy resin matrices is aimed at improving the damage tolerance of the polymer, providing additional capacity to absorb energy [15].

Moreover, nanofillers present additional advantages on fine polymeric structures in which conventional fillers cannot be readily accommodated, such as polymer foams. Polymer nanocomposite foams present an additional gaseous phase leading into a cellular structure, which establishes a variety of attractive properties such as outstanding strength to weight ratio, resilience, as well as acoustic, thermal, and electrical insulation properties. Promising results have been obtained when studying nanocomposite foams with different nanofillers: nanoclays [16-27], graphene [28], and carbon nanotubes and nanofibers [29-32].

One of the industrial accessible nanoparticles with good performance as a filler is the vapor grown carbon nanofiber (CNFs), which presents high tensile strength, high modulus, and relatively low cost. These nanofibers can be synthesized from pyrolysis of hydrocarbons and carbon monoxide in the gaseous state in the presence of catalysts [33, 34]; and have recently been employed in several studies with the aim of modifying thermoplastics, such as polypropylene [35-37], polycarbonate [38], and nylon, and also thermostable polymers such as epoxy resins [39-41].

It is well known that one of the main problems when using of carbon nanofibers as fillers is their tendency to form agglomerates. However, optimal enhancement of the nanocomposite properties is reached when the fillers are well dispersed inside the polymer matrix. Therefore, an essential step required in the production process of polymer nanocomposites is the dispersion of the nanofibers from agglomerates to individual fibers, and their homogeneous distribution inside the polymer matrix [42-44].

There are two main approaches to achieve this dispersion: the modification of the filler surface by chemical methods (increasing the affinity between the filler and the polymer, allowing an easier dispersion of the filler inside the polymer) [45, 46], and the dispersion of the fibers by mechanical processes. Mechanical methods include ultrasonication using a bath or an ultrasonication probe [47, 48], shear mixing in a solvent [49], milling using a ball mill [50], and the combined use of several of these methods [44].

Ultrasonication has been identified as one of the more effective techniques to obtain a good dispersion of nanoparticles; being a simple technique that uses high-energy acoustic vibrations for mixing and dispersing materials. For instance, Suave et al. found that in systems with carbon nanotubes as fillers the tensile strength of the composite increased when short periods of sonication were used to improve the dispersion [51]. However, it should be considered that this process can cause damage and degrade the structure of nanofibers, generating properties loss [49].

Then, in this work it is presented a simple procedure to study the effects of the ultrasonication on carbon nanofibers, relating electron microscopy micrographs and macroscopic physical properties. Moreover, this procedure was employed to improve the dispersion of the carbon nanofibers on epoxy resin foams, leading to remarkable decrease of the foams electrical resistivity, of about eight orders of magnitude.

MATERIALS AND METHODS

Materials

The epoxy resin foaming system composed of resin (ref. PB250) and a hardener agent (ref. DM02) was provided by SICOMIN. This commercial formulation allows free-foamed epoxy resin foams to be obtained with densities of about 250 kg/m^3, being the density of the unfoamed resin of about 1350 kg/m^3. The foaming of the resin is triggered by the hardener agent, taking place during the beginning of the curing reaction.

Vapor grown carbon nanofibers (GANF, Grupo Antolin Carbon Nanofibers) supplied by Antolin Engineering Group Inc. were used as nanofillers. The manufacturer claims that GANF present surface areas of about 150-200 m^2/g, with a content of metal particles of about 6-8 wt%, average diameters between 20 and 80 nm, and fiber length over 1 μm. More information about these nanofibers provided by the supplier can be found in **Table 1**.

Table 1. Properties of Grupo Antolin carbon nanofibers (GANF)

Property	GANF
Fiber diameter [nm]	20-80
Fiber length [μm]	1-30
Bulk density [g/cm^3]	> 1.97
Apparent density [g/cm^3]	0.060
Specific surface area BET [m^2/g]	150-200
Surface energy [mJ/m^2]	≈ 100
Graphitization degree [%]	≈ 70
Electrical resistivity [Ω·m]	10^{-3}
Metallic particles content [%]	6-8
Young modulus (theoretic) [GPa]	230
Tensile strength (theoretic) [GPa]	2.7

The production route of these GANF, using the technique of floating catalyst, consists of a continuous process of gas phase decomposition of hydrocarbons (benzene, n-hexane, methane, and acetylene) in the presence of metallic catalytic particles (iron, nickel, cobalt, or alloys) at temperatures of about 1050-1100°C. It should be noticed that this technique (patented by Antolin Group Inc.) allows vapor grown carbon nanofibers to be produced on an industrial scale at a much lower cost than carbon nanotubes and other nanofibers.

Finally, acetone (density of 790 kg/m^3 and purity of 99.5 wt%, supplied by Scharlab Ltd.) was used as a solvent for the dispersion of the nanofibers.

Production Routes

Epoxy Foams

Cylindrical epoxy foams with dimensions of 10.2 cm in diameter and 0.6 cm in thickness were obtained using a steel mold. Each neat epoxy foam was produced as follows: about 41 grams of the epoxy foaming system with a constant resin/hardener ratio (100/36, provided by the supplier) were

mechanically mixed for 1 minute at 4000 rpm (AV-5 mixer, SBS); then 12.3 grams of the resin/hardener blend were placed into the mold (a higher quantity of resin than the one required for foam production is mixed in first place to obtain a good, reproducible mixing of the two components). After being closed hermetically, the mold was placed in a heated bath at 40°C for 6 hours to complete the hardening process of the resin.

Epoxy + GANF Foams

The production of nanocomposite foams consisted of three stages: dispersion of GANF, mixing of GANF and epoxy resin, and the foaming and hardening of the epoxy/GANF foam.

GANF were dispersed in acetone: three different amounts of GANF were employed (0.1/0.42/2.25 g, corresponding to concentrations of 0.2/1/5 wt% in the final epoxy foam). The ratio resin/solvent in volume was adjusted between 1:1 and 1:2 depending on the amount of GANF (no influence of the solvent amount was found in neat epoxy foams produced following this same procedure). Dispersion of GANF on the acetone was achieved by using an ultrasonic probe with 750 W of powder (VC 750, Sonic & Materials Inc.). The ultrasonication process was carried out during periods of between 1 and 30 minutes, at 40% of amplitude (below 30% no dispersion was found and over 50-60% the fibers began to break), and preferably using ON/OFF pulses of 30/20 seconds (determined as an optimal ratio to avoid undesired heating and evaporation of the solvent).

After the dispersion of the nanofibers, the acetone/GANF solution was mechanically mixed at 4000 rpm for 2 minutes (AV-5 mixer, SBS) with the uncured resin. Then, the solution/epoxy blends were placed in a vacuum oven (Vaciotem-TV, P Selecta) for 12 hours at 30°C and 20 mbar to evaporate the solvent. Once the solvent was removed the uncured resin/GANF blends were mixed with the hardener and foamed following the same procedure as in the case of neat epoxy foams; it was necessary to introduce a larger amount of the resin into the mold to fill it after foaming. Details of the different dispersion processes and epoxy foams produced can be found in **Table 2**.

Characterization Techniques

Foam densities (ρ_f) were determined geometrically from the constant volume of the samples and their weight. Relative density (ρ_r) was obtained using Equation (1), where ρ_s is the density of the unfoamed resin.

$$\rho_r = \frac{\rho_f}{\rho_s}$$

(1)

An emission scanning electron microscope (ESEM) model Quanta 200 FEG was used to observe the morphology of the carbon nanofibers after being dispersed in acetone or in the uncured resin; one drop of the acetone/GANF or uncured resin/GANF was placed into a sample holder and left to evaporate prior to being characterized. Also the cellular structure of the foams was characterized by using ESEM micrographs. The foams were frozen in liquid nitrogen and fractured to assure that the microstructure remained intact and then the exposed surfaces were coated with gold using a sputter coating equipment (model SCD 004, Balzers Union). The main cellular structure parameters, average cell size and cells density (number of cells per cubic centimeter of the foamed material), were obtained from the micrographs using a specific software [52].

Resistivity measurements of epoxy foams were performed using a Keithley Resistivity Adapter model 6105 according to ASTM D257-99 [53]. First, the surface of the samples was polished in a polisher LaboPol2-LaboForce3 (Struers) to ensure an appropriate contact. After polishing samples were first dried, and then conditioned at controlled temperature and humidity (23°C and 50% humidity) at least three days before being measured in order to avoid discrepancies in the measurements due to differences in temperature or humidity between the different samples. Then, samples were measured four times at +500 V, -500 V, + 500 V, -500 V. Time of electrification was 60 seconds, and the time of discharge before making a measurement with reversed voltage was over 4 minutes. Finally, electrical resistivity (*R*) was calculated using Equation (2), where *A* and *t* are the area and thickness of the sample respectively, *V* the voltage applied, and *I* the current intensity measured.

$$R = \frac{A \cdot V}{t \cdot I}$$

(2)

Graphical representation of the DC electrical resistivity results was done normalizing the resistivity values by the relative density of the porous materials, to be able to compare the results between samples with slightly different densities.

RESULTS AND DISCUSSION

Dispersion and Structural Integrity of GANF

The dispersion of GANF in acetone was performed by ultrasonication with fixed amplitude and different times from 1 to 30 minutes. Aggregation or dispersion of the fibers was evaluated by ESEM micrographs, taking as a reference the appearance of GANF fibers solved in acetone solely by mechanical means,

without ultrasonication. **Figure 1** shows the SEM micrographs corresponding
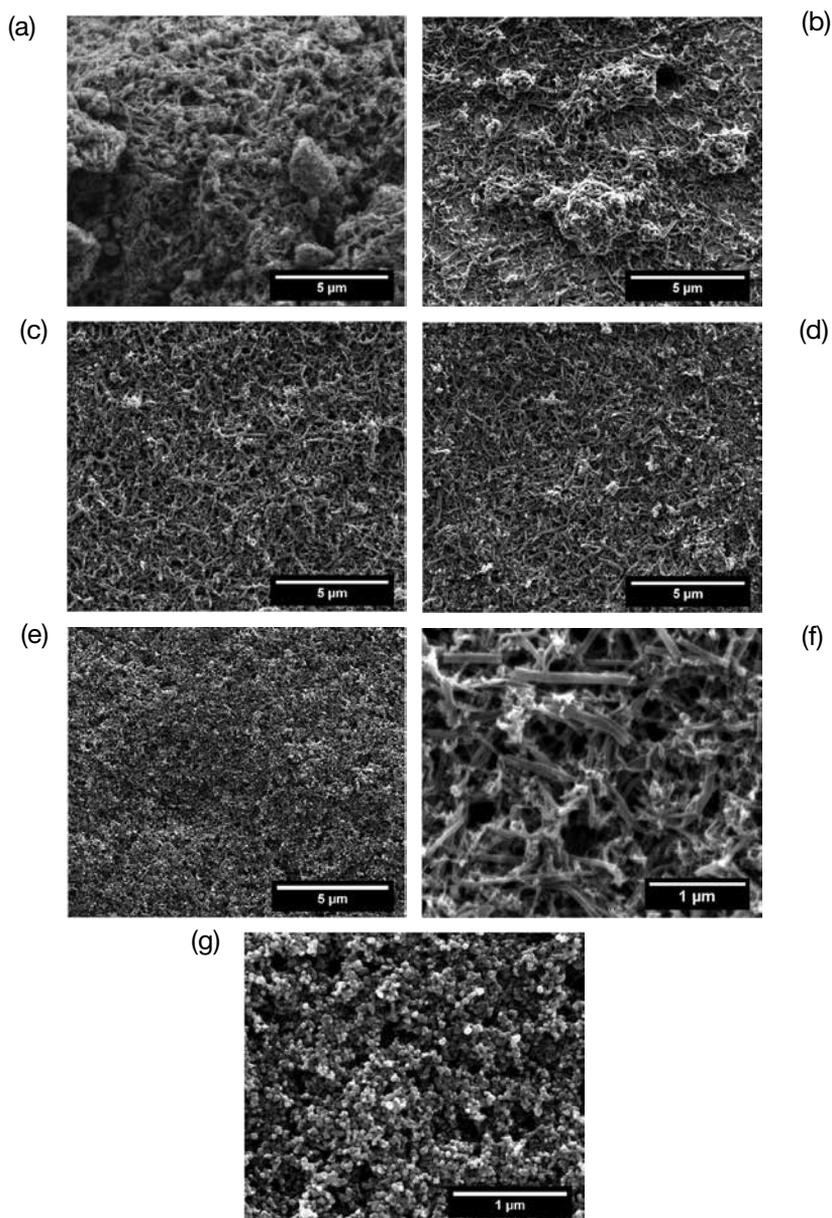to the different dispersion procedures.

Figure 1. *ESEM micrographs of fibers after dissolution in acetone: a) without
sonication, b) after 1 minute 20 seconds of sonication with pulses, c) after 10 minutes
of sonication with pulses, d) after 10 minutes of sonication without pulses, and e) after
30 minutes of sonication with pulses. Micrographs f) and g) show a detail of fibers
appearance after 10 and 30 minutes of sonication with pulses, respectively*

It is found a clear difference between the GANF dispersed in acetone solely by mechanical means and by ultrasonication. GANF which are dispersed mechanically are completely aggregated in bundles (**Figure 1a**), whereas the sonication process allows these GANF bundles to be dispersed. However, significant differences in the dispersion efficiency and structural integrity of the GANF are found depending on the ultrasonication time. The best results are obtained with times of about 10 minutes (**Figure 1c** and **Figure 1d**), as it is possible to identify the individual fibers (**Figure 1f**), without significant differences between performing the process with or without pulses (preferably with the use of pulses to avoid the evaporation of the solvent and to improve the reproducibility of the overall production process). Lower ultrasonication times (i.e. 1 minute 20 seconds, **Figure 1b**) seems to be insufficient time to disperse all the bundles; whereas higher times (i.e. 30 minutes, **Figure 1e**) lead to a significant degradation of the fiber structure, allowing just some short segments of the fibers and particles to be observed without a defined shape (**Figure 1g**).

Therefore, following this simple procedure by ESEM it is possible to define the ultrasonication parameters that provide an optimal dispersion of GANF in acetone without compromising their structural integrity. In the following sections the relationship between the dispersion of the GANF in acetone and the effects of the dispersion of GANF in the epoxy foams will be studied.

Influence of GANF on the Density and Cellular Structure of Epoxy Foams

Neat epoxy foams and epoxy/GANF foams were produced following the aforementioned production route. Epoxy/GANF foams were produced using the different ultrasonication processes studied in the previous section. Processing parameters and the main characteristics of the fabricated foams can be found in **Table 2**, and their cellular structure is shown in **Figure 2**.

Addition of GANF to the epoxy resin during the fabrication process hinders the expansion during the foaming process (probably due to an increase in the viscosity of the polymer), obtaining as a result higher densities than with the neat epoxy foam. Moreover, epoxy/GANF foams in general seem to present slightly lower average cell sizes, higher cell densities, and broader cell size distributions.

Further study of the evolution of the cellular structure related to the GANF content was carried out taking into account the cell size distribution of the foams with GANF amounts from 0 to 5 wt% obtained following the same fabrication procedure (10 minutes of sonication with pulses) (**Figure 3**).

Table 2. Fabricated foams and their characteristics

Fibers Content [wt%]	Sonication time [min]	Pulses	ρ_f [kg/m^3]	ρ_r	Cell size [µm]	Cells density [cells/cm^3]
0	-	-	250	0.19	215 ± 93	1.57E+05
0.2	1.33	30/20	295	0.22	160 ± 78	3.64E+05
0.2	10	30/20	303	0.22	199 ± 82	2.30E+05
0.2	10	NO	284	0.21	204 ± 92	1.78E+05
0.2	30	30/20	330	0.24	173 ± 85	2.79E+05
1	10	30/20	366	0.27	174 ± 100	2.66E+05
5	10	30/20	331	0.25	173 ± 113	2.78E+05

Figure 3 shows that the increase of the GANF content corresponds not only to an increase in the predominance of the smaller cells (about 100 µm) but also to the broadening of the cell size dispersion, with cell sizes higher than 500 µm in the samples with 1 and 5 wt% of GANF. Predominance of smaller cells can be induced by a nucleation effect of the GANF (more cells are nucleated in the same volume and therefore their size will be lower), or by the lower expansion ratio of the epoxy/GANF leading to a reduction of the cell coalescence. On the other hand, the broadening of the pore size distribution and the presence of bigger cells is an unexpected effect of the addition of GANF. A possible explanation for this behavior was found by studying the distribution of the dispersed GANF fibers on the uncured resin. **Figure 4** shows an ESEM micrograph of uncured resin/GANF with 1 wt% of fibers. No fibers aggregates were observed, confirming the good dispersion of the fibers achieved; however, the distribution of the fibers on the uncured resin does not seem completely homogeneous. This uneven nanofiber dispersion leads to many small cells (nucleated around the nanofibers) and a few large cells (nucleated in the areas without nanofibers).

Relationship Between the GANF Dispersion on Acetone and on the Epoxy Matrix

The dispersion of GANF on the epoxy matrix of the produced foams was studied indirectly by means of the measurement of the electrical resistivity of these materials. It is expected that the improvement of the GANF dispersion inside the epoxy matrix leads to a greater influence of the GANF on the electrical conductivity of the foamed nanocomposite. **Figure 5** shows the electrical resistivity, normalized by the relative density, of neat epoxy and epoxy/GANF foams with 0.2 wt% of GANF and different ultrasonication parameters.
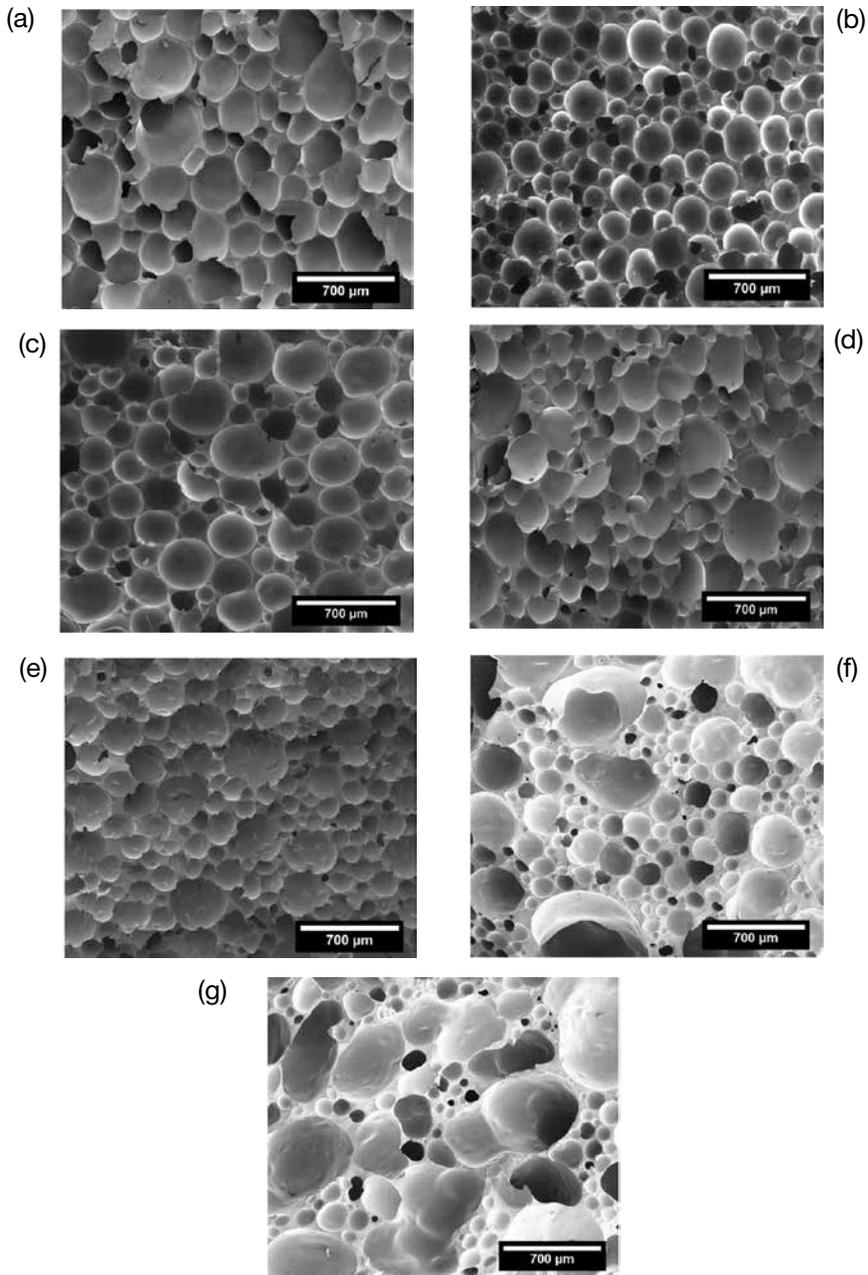
Figure 2. *ESEM micrographs of epoxy foams: a) without fibers, b) with 0.2 wt% of fibers and 1 minute 20 seconds of sonication with pulses, c) with 0.2 wt% of fibers and 10 minutes of sonication with pulses, d) with 0.2 wt% of fibers and 10 minutes of sonication without pulses, e) with 0.2 wt% of fibers and 30 minutes of sonication with pulses, f) with 1 wt% of fibers and 10 minutes of sonication with pulses, and g) with 5 wt% of fibers and 10 minutes of sonication with pulses*

All the epoxy/GANF foams present lower electrical resistivity than the neat epoxy foams, as can be expected due to the addition of GANF. And more importantly, it is found that the lower electrical resistivity of epoxy/GANF foams corresponds to the foams ultrasonicated using the parameters that were defined previously as optimum according to the dispersion degree of the
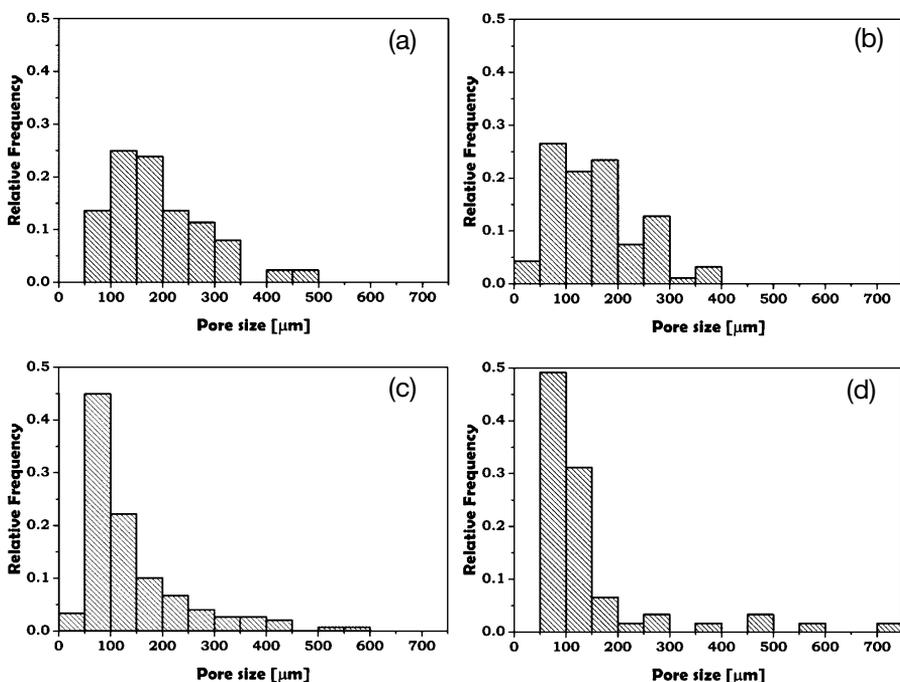

Figure 3. Cell size distribution histograms of epoxy foams: a) without fibers, b) with 0.2 wt% of fibers, c) with 1 wt% of fibers, and d) with 5 wt% of fibers
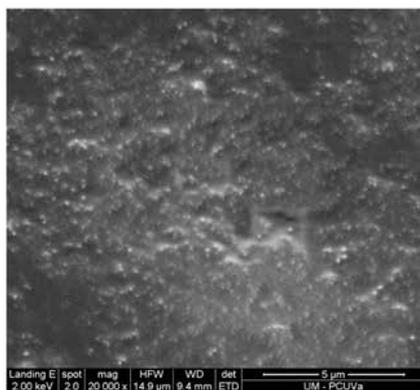

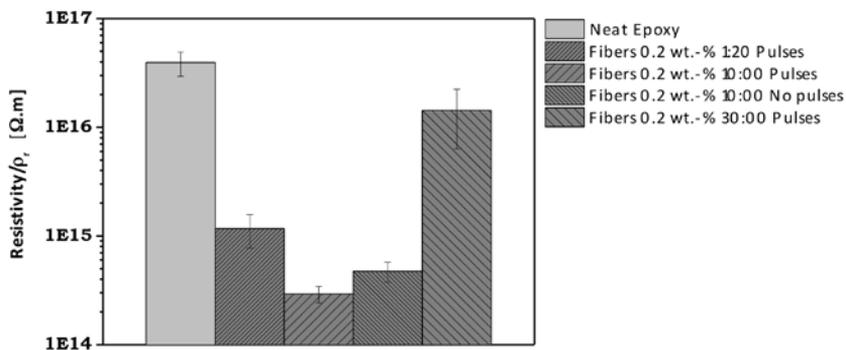*Figure 4. ESEM micrograph of the uncured resin/GANF (1 wt%)*

Figure 5. *Normalized resistivity of epoxy foams without fibers, and with 0.2 wt% of fibers produced using different sonication parameters*

GANF in the solvent. Moreover, foams produced with lower ultrasonication times (resulting in both dispersed fibers and bundles) also present also a significant reduction in their electrical resistivity; whereas foams produced with greater ultrasonication times (resulting in degraded fibers) present values near to those of the neat epoxy foams.

Thus, a direct relationship is found between the GANF dispersion degree in the solvent studied by SEM and the dispersion-related effects of the GANF in the properties of the epoxy foams. Therefore, these results confirm the possibility of estimating the dispersion degree of carbon nanofibers on the epoxy matrix just by studying the dispersion of the nanofibers in the solvent. In addition, it has been demonstrated that the expected loss of properties is produced by the degradation of the fibers. This degradation of the fibers is the result of an inappropriate dispersion process.

Evolution of the Electrical Resistivity Related to the GANF Content

Once the GANF dispersion procedure has been improved it is possible to study the influence of the GANF content on the electrical resistivity of these materials. **Figure 6** shows the evolution of the electrical resistivity of epoxy foams related to the GANF content.

As expected, it is found that the electrical resistivity of epoxy/GANF foams decreases with the amount of GANF, samples with GANF contents of 0.2 wt% and 1 wt% present a reduction of about two and three orders of magnitude, respectively. Moreover, epoxy/GANF foams with GANF content of 5 wt% present an remarkable improvement in their electrical conductivity, leading to a decrease in their electrical resistivity of eight orders of magnitude. Even
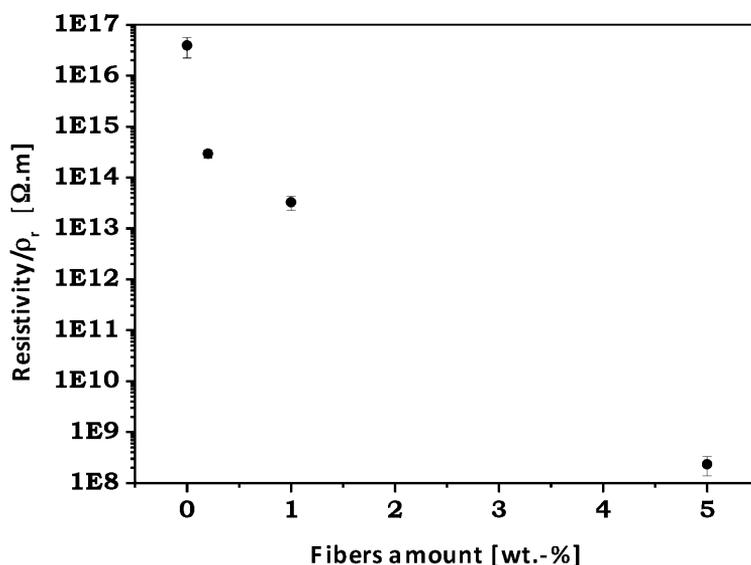
Figure 6. *Normalized resistivity of epoxy foams without fibers, and with 0.2, 1, and 5 wt% of fibers produced following the best dispersion process*

further studies are needed to determine the percolation threshold of these epoxy/GANF systems. These results demonstrate the potential of these industrial carbon nanofibers and the proposed methodology to be used in the industrial production of polymeric nanocomposites.

CONCLUSIONS

A simple procedure to evaluate the dispersion of carbon nanofibers in an epoxy matrix has been presented and validated. It has been demonstrated that the nanofibers dispersion in the solvent, used at an intermediate stage of the epoxy foam production process, is directly related to the dispersion of the nanofibers in the final epoxy foam.

Moreover, taking advantage of this procedure, the dispersion of GANF carbon nanofibers on epoxy foams have been improved, allowing the influence of well dispersed GANF on the properties of the resultant foams to be studied. It was found that the presence of GANF decreases the expansion ratio of the foam leading to slight increments of density. Also, a small influence of GANF has been found on the cellular structure, with a predominance of small cells and a broadening of the cell size distribution with a GANF content higher than 1 wt%.

The effects of the GANF dispersion on the final epoxy/GANF foams were studied on the electrical resistivity of nanocomposite foams, and a direct relationship between the dispersion degree of the GANF on the solvent and the reduction of the electrical resistivity of the foams was found.

Finally, a remarkable improvement of the electrical conductivity of the epoxy foams, of about eight orders of magnitude, was found by adding a 5 wt% of GANF and ensuring their optimal dispersion following the procedure presented in this work.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

ACKNOWLEDGEMENTS

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