Material Properties

Study of the thermal properties of polyester composites loaded with oriented carbon nanofibers using the front-face flash method

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In this work, we have prepared polyester resin based composites, loaded with carbon nanofibers decorated with magnetite nanoparticles (m-CNF) in several volumetric concentrations covering from 0 to 3.25% and oriented applying a constant magnetic field before polymerization. A study of the heat transfer along the direction of the alignment of the fibers was performed by measuring the in-depth thermal diffusivity and thermal effusivity using the laser flash method in the front-face configuration. For the maximum volumetric concentration of aligned nanofibers along the thickness of the sample, an improvement of 80% of the thermal conductivity above the thermal conductivity of the polyester resin was observed. In contrast, the increment of the thermal conductivity was only of 20% above the value of the matrix for samples with non-oriented carbon nanofibers. The effects of the m-CNF and their orientation on the effective thermal conductivity of the composites were analyzed using a simple theoretical model, which takes into account the thermal mismatch between the matrix and the fillers, as well as the aspect ratio of the embedded fibers.

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1. Introduction

During the last decades, improvement of the thermal conductivity of polymer composites has been a topic of great interest in the development of microelectronic heat sinks, heat exchangers, electric motors parts, aerospace industry applications, and it has generated a variety of studies using diverse techniques [1–4]. Orientation of the polymer nano and microstructure or addition of high conductivity particles, like carbon derived fillers, to the polymer have generated interesting results having wide range of applications [1,5–7].

Polymeric composites filled with multi walled carbon nanotubes (MWCNTs) have shown improvements up to 105% on the thermal conductivity of the polymeric matrix, using just 0.4% concentration in volume [2,8]. In the case of composite polymers with CNF loadings of 2% in weight, a thermal conductivity enhancement of about 115% has been found. It has also been reported that larger enhancements of the thermal conductivity can be reached (as high as 200%) in CNF-polymer composites, but at the expense of an extremely high concentration of CNF (40% in volume) [1,2,9–12]. This variability, found in the literature, can be understood taking into account that heat transport is strongly dependent on the coupling of the matrix with the filler as well as its dispersion and distribution.

However, it is important to develop methods to increase the thermal conductivity of a given composite, in which the filler content must be maintained below well-defined values even when the main characteristics of the fillers interactions with themselves and with the matrix cannot be controlled at enough extent. One of those methods, as mentioned above, consists in orienting individual polymeric units or fillers [5].

In this work, improvement of the thermal conductivity of a polymer using two mechanisms: filling the matrix with high...
conductivity carbon-derived particles and orienting them is presented. Alignment of this kind of fillers has been got using different techniques, such as mechanical stretching, external electric field or applying magnetic fields [11,13,14]. However, carbon nanofibers do not have a large magnetic moment. Due to this, very strong magnetic fields would be needed to achieve alignment in this kind of fibers. For this reason, we use a method by which nanoparticles of iron are attached to the fibers (m-CNf) and as a consequence, when applying a DC magnetic field of low intensity the nanofibers can be aligned along the field.

In order to measure the thermal diffusivity and thermal effusivity of the composite samples and to determine their thermal conductivity, in the direction along the oriented fibers, the non-invasive and non-contact technique known as front-face laser flash method was used. This technique consists in heating up the sample’s surface with a brief light pulse and record the temperature evolution of the heated surface with an infrared (IR) detector or IR camera. Nowadays, this technique has gained interest of scientists and engineers for its versatility in non-destructive testing of materials, since it only requires access to one surface of the component and engineers for its versatility in non-destructive testing of materials. Consequently, an alternative scheme has been used. This technique consists in heating up one surface of the component with an infrared (IR) detector or IR camera. Nowadays, this technique has gained interest of scientists and engineers for its versatility in non-destructive testing of materials, since it only requires access to one surface of the component and engineers for its versatility in non-destructive testing of materials.

2. Materials and methods

2.1. Materials

Carbon Nanofibers (Pyrograf CNF PR-19-XT-HHT) with nominal diameters of 100–200 nm and nominal lengths of 30–100 μm, have been used in this work for preparing the composites. Magnetic particles were obtained from a Ferrofluid (Ferrotec EMG900), which consists of iron nanoparticles with mean size of 10 nm and isoparaffin as solvent.

2.2. Oxidation of CNF

Carbon nanofibers were dispersed in toluene and then this mixture was vacuum filtered through a polyester nucleopore membrane with pore size of 0.1 μm. After that, the powder was rinsed with alcohol and filtered again by using a similar polyester membrane. Then, the filtrate was rinsed in water and then dried. Chemical oxidation of the CNF was carried out with nitric acid as follows: 1.0 g of CNF were pretreated by immersing them in a 25 ml solution of 70% nitric acid and 30% water using a three-neck flask and the resultant suspension was refluxed during 30 minutes at 130°C in slow agitation. Then, the oxidized CNF were filtered and washed with water until the filtrate was neutral.

2.3. Synthesis of CNF/Fe$_2$O$_4$

After drying the CNF, these fibers and the ferrofluid were mixed at 15% weight fraction. The solvent was evaporated at room temperature and the sample was rinsed with kerosene and filtered until the liquid was clear. After that, the filtrate was rinsed in alcohol. The sample was kept in vials and was allowed to dry. The magnetic response of these magnetic CNF was easily and quickly visualized, by the attraction of the nanofibers when a magnet is brought close to the sample.

2.4. Preparation of polyester resin composites loaded with magnetized carbon nanofibers

Composites of magnetic carbon nanofibers in a polyester resin matrix (RP RESINMEX) were prepared by dispersing the functionalized m-CNf in the polyester resin and mixing slowly for 30 min until a bubble-free homogeneous mixture was obtained. Then, the catalyst was added and was again mixed for two minutes. The mixture was poured onto an aluminum foil surface (placed on a glass plate) and it was covered with another aluminum foil and another glass plate was set above. The whole system was pressed with tweezers. In order to obtain samples with magnetic aligned CNF, the samples were placed for 15 min in the center of a pair of Helmholtz coils under the influence of a 600 G magnetic field. All samples were allowed to polymerize during 24 hours at room temperature. Finally, the samples were postcured at 80°C for 4 hours. The specimens obtained were composite plates of 3 cm × 2.5 cm × 1 mm, one set with randomly arranged fibers and the second with fibers aligned along the thickness of the plate (1 mm).

2.5. Scanning electron microscopy (SEM)

In order to analyze the orientation of the fibers in the polyester matrix, scanning electron microscopy (SEM) images were obtained on small sections of the samples. These sections were cut perpendicularly with respect to the lateral plane faces of the plates. Specimens of 1 mm × 3 mm surface area and 5 mm thickness were embedded vertically in an epoxy resin cylinder (in such a way that the surface of 3 mm$^2$ could be analyzed), which surface was polished and plasma cleaned during 6 min. Finally, the surface of the sample was covered with a 5 nm Cr layer using a sputtering unit (Bal-Tec SCD-004). A SEM system (JEOL JSM-6400) was used to perform the analysis.

3. Theory

The front-face flash method consists of heating up one surface of a slab using a uniform source during a short time interval. The temperature evolution of the heated surface is analyzed to retrieve
the thermal diffusivity or thermal effusivity of the material. In Fig. 1 we show a slab of thickness $L$, heated up by a uniform pulse of time duration $t$. The heat diffusion equation for this problem is easy to solve in the Laplace domain, where an analytical expression for the Laplace temperature at the front surface of the slab is given by Ref. [31].

$$\hat{T}(s) = \frac{Q}{\pi} \frac{\sqrt{s} + h'}{\sqrt{s} + \sqrt{\frac{(s + h^2)\tanh(x\sqrt{s})}{h}}} \frac{1}{\sqrt{s}}$$  \hspace{1cm} (1)

where $s$ is the Laplace variable, $x = L/\sqrt{D}$ and $h' = h/e$, being $e$ and $D$ the thermal effusivity and thermal diffusivity of the sample, respectively. $h$ is the heat transfer coefficient which takes into account the heat losses from both surfaces to the surroundings due to convection and radiation. $Q = \frac{Q}{\pi} \frac{\sqrt{s} + h'}{\sqrt{s} + \sqrt{\frac{(s + h^2)\tanh(x\sqrt{s})}{h}}} \frac{1}{\sqrt{s}}$.

According to these simulations, a curve fitting of the experimental data is used in order to retrieve the thermal diffusivity of the samples.

On the other hand, Fig. 2(b) shows numerical simulations for two materials of the same thermal diffusivity $D = 0.11 \text{ mm}^2 \text{s}^{-1}$, but different thermal effusivities $e = 580 \text{ Ws}^{1/2} \text{ m}^{-2} \text{ K}^{-1}$ (in black) and $e = 780 \text{ Ws}^{1/2} \text{ m}^{-2} \text{ K}^{-1}$ (in red). We have used the same thickness, power density, pulse duration and heat losses coefficient as in Fig. 2(a): $L = 1.0 \text{ mm}$, $P_0 = 5 \text{ W cm}^{-2}$, $t = 30 \text{ ms}$ and $h = 10 \text{ W m}^{-2} \text{ K}^{-1}$. As can be seen, in this case, a difference on thermal effusivities introduces a vertical shift on the temperature evolution graphs. Notice that the temperature rise of the material with higher thermal effusivity (red curve) is always smaller than that of the slab with lower thermal effusivity (black curve). This vertical shift, measured in the semi-infinite zone of the time evolution graph, gives the ratio of the thermal effusivities, when the same energy has been deposited on both slabs. Accordingly, the thermal effusivity of the samples can be obtained by comparison with a reference value.

4. Results

A diagram of the experimental setup used to study the thermal properties of our composite samples is shown in Fig. 3. A continuous wave diode laser (808 nm) with flat-top profile and adjustable power up to 60 W is employed as the heating source. It is
synchronized with a function generator in order to control the step pulse duration, which is fixed to 30 ms for all measurements. The beam is directed onto the sample surface by an optical fiber placed 20 cm away, to assure plane illumination. The infrared (IR) emission of the sample is collected with an IR camera (FLIR SC7500) in the 3–5 μm spectral range. A coated Ge window (3–12 μm) is used to protect the lens of the camera. The images (thermograms) are recorded at 200 Hz with 548 μs integration time in the full frame windowing mode (320 × 256 pixels). All samples are covered with a thin black paint layer (about 5 μm thick) in order to improve both the laser absorption and IR emissivity. Since the emissivity of the samples is unknown, the IR camera only collects data of an apparent temperature rise (ΔT) which is proportional to the actual temperature.

In order to reduce the noise level in the measured temperature, we have made an average over 7200 pixels in the thermograms obtained from the IR camera. With this procedure we keep the noise level below 5 mK in the measurements, which is one of the advantages of using an IR camera instead of a monolithic detector.

In Fig. 4, the time evolution graphs obtained from the measurements are presented. The experimental data is represented by dots, and continuous lines are used for the curve fittings to the model presented in Sec. III. The samples corresponds to: Polyester resin \((D = 0.102 \text{ mm}^2 \text{s}^{-1} \text{ and } e = 563.6 \text{ W m}^{-1/2} \text{ m}^{-2} \text{ K}^{-1}, \text{ in black})\), composite loaded with 3.25% of non-aligned m-CNF \((D = 0.141 \text{ mm}^2 \text{s}^{-1} \text{ and } e = 638.7 \text{ W m}^{-1/2} \text{ m}^{-2} \text{ K}^{-1}, \text{ in blue})\) and composite loaded with 3.25% aligned m-CNF \((D = 0.189 \text{ mm}^2 \text{s}^{-1} \text{ and } e = 738.8 \text{ W m}^{-1/2} \text{ m}^{-2} \text{ K}^{-1}, \text{ in red})\). Notice that, when the thermal diffusivity of the sample increases, the ‘elbow’ of the curves appears at shorter times (samples are of the same thickness, \(L = 1 \text{ mm}\)). On the other hand, the higher the thermal effusivity, the lower the temperature rise, as clearly seen in the linear zone (semi-infinite behavior). It is worth to mention that even when the same concentration is used, the alignment of the fibers changes both the thermal diffusivity and thermal effusivity as shown by the blue and red (in the web version) curves in Fig. 4.

A least squares procedure, based on the Levenberg–Marquardt algorithm [33], has been implemented to make the curve fitting of the experimental data with the inverse Laplace transform of Eq. (1). Three parameters \((Q, h’\text{ and } x)\) are retrieved from the fittings. In order to show the quality of the curve fittings, we have also plotted the residuals (crosses), \(\frac{T_{\text{exp}}(t) - T_{\text{fit}}(t)}{T_{\text{exp}}(t)}\times 100\), whose values are smaller than 2% in the whole time evolution graph.

The values obtained for thermal diffusivity are shown in Fig. 5(a) as a function of the particle concentration in volume \((\phi)\). Notice that, for aligned m-CNF (black) the enhancement on the thermal diffusivity of the composites is higher than for those non-aligned m-CNF (red), and this behavior is more remarkable for the highest values of the concentration of particles.

We have used the thermal effusivity of the polyester resin \((e = 545 \text{ W m}^{1/2} \text{ m}^{-2} \text{ K}^{-1})\) as a reference to obtain the thermal effusivities of the composites. Notice from Fig. 5(b), that for both kinds of samples, the enhancement on thermal effusivity of the composites is almost linear, and is better for the aligned m-CNF (black) than for non-aligned m-CNF (red). In both cases, the uncertainty on the measurement of thermal properties has been obtained from the standard deviation of five measurements and it is below ±5%.

5. Discussion

Fig. 6 shows the SEM images obtained for concentrations of 0.25%, 1.25%, 2.25% and 3.25% with non-aligned nanofibers from (a) to (d), respectively and aligned m-CNF, from (e) to (h). Also schematic pictures of the dispersed and aligned nanofibers on the sample’s thickness are shown in Fig. 6(a) and (e). Backscattered electron images have been used to show even the fibers buried near the surface of the specimens.

In Fig. 7 it is shown the thermal conductivity of the composites as a function of the m-CNF volume concentration. It was calculated using the well-known relation [34]: \(e = K/D\) and the uncertainties were obtained according to the error propagation theory [35]. Good enhancement of \(K\) is expected, due to the higher thermal conductivity of the carbon nanofibers with respect to that of the polymeric matrix. The enhancement in thermal conductivity is noticeable for concentrations higher than 1% in volume, in which a clear difference between the results obtained for the composites with aligned
m-CNF and the non-aligned ones is observed. The thermal conductivity of the composite loaded with 3.25% of aligned m-CNF in volume, is 1.8 times the one of the polyester resin. This is a good result considering the low loading percentage of nanofillers. In contrast, thermal conductivity of the composite only reaches 1.2 times for non-aligned nanofibers with respect to the resin matrix.

According to the interaction direct derivative (IDD) model, the normalized effective thermal conductivity ($K_{\text{norm}}$) of the composite with respect to the thermal conductivity of the matrix can be expressed as [26,30].

$$K_{\text{norm}} = 1 + \left[ 1 - \frac{1}{3} \left( \frac{K_{\text{dilm}}}{K_m} - 1 \right) \right]^{-1} \left( \frac{K_{\text{dilm}}}{K_m} - 1 \right).$$

(2)

where $K_{\text{dilm}}$ is the effective thermal conductivity in the dilute limit, also normalized by the thermal conductivity of the matrix ($K_m$). A good choice of the thermal conductivity in the dilute limit is the one obtained from the well-known effective medium approach [20].

$$K_{\text{dilm}} = \frac{1 + \frac{\eta \xi}{K_m} \left( 1 + \frac{2 R_{\text{th}} K_p}{\eta L} \right)}{\eta K_p} + H(p)$$

(3)

where $\phi$ is the volumetric fraction of the reinforcements, m-CNF in our case, $R_{\text{th}}$ is the thermal resistance between the m-CNF and the polyester matrix, $K_p$ is the thermal conductivity of the m-CNF, $\xi$ is a factor which takes into account if the reinforcements are dispersed in the matrix ($\xi = 1/3$) or they are aligned along the sample's thickness ($\xi = 1$) and $H(p)$ is a function which takes into account the depolarization factor (aspect ratio of the fillers).

$$H(p) = \frac{1}{p_2 - 1} \left[ \frac{p}{\sqrt{p^2 - 1}} \ln \left( p + \sqrt{p^2 - 1} \right) - 1 \right],$$

(4)

being $p = \eta l/d$. $d$ is the diameter of the m-CNF and $\eta$ is a correction factor introduced in the actual length ($l$) of the m-CNF due to entanglement effects. It takes into account the non-straightness of the fibers, which affects the thermal conductivity of a fiber in the longitudinal direction [26].
We have performed curve fittings of the experimental data using Eq. (2) with two free parameters ($R_0$ and $\eta$), as shown in Fig. 8. The thermal conductivity of the m-CNFS is 1550 W m$^{-1}$ K$^{-1}$ [36], and for the polyester resin it is 0.18 W m$^{-1}$ K$^{-1}$ [37]. Based on the scanning electronic microscopy images taken for the samples, the length of the fibers has been fixed to 30 $\mu$m and their diameter to 200 nm in the curve fittings. For non-aligned m-CNFS composites, we have obtained: $R_0$ = 4.6 $\times$ 10$^{-8}$ m$^2$ W$^{-1}$ K and $\eta$ = 0.28, and for aligned m-CNFS composites: $R_0$ = 7.5 $\times$ 10$^{-8}$ m$^2$ W$^{-1}$ K and $\eta$ = 0.27. The results obtained for the thermal mismatch are in good agreement with theoretical simulations and experimental studies reported in the literature [2, 25]. It is worth to mention that even though the value obtained for the thermal mismatch for aligned fibers is larger than the obtained for non-aligned ones, and that the correction factor is similar for both types of samples, the thermal conductivity of composites with 3.25% volume fraction of aligned m-CNFS is 1.4 times the thermal conductivity of composites with non-aligned fibers.

Our results show that the alignment of m-CNFS in polymeric composites, using external low intensity uniform magnetic fields, is a highly convenient methodology to enhance the heat transport in a given CNF composite.

6. Conclusions

It has been shown that the alignment of m-CNFS in the polymer matrix, with the help of a uniform low intensity magnetic field, enhances its thermal conductivity, along the direction of the alignment of the fibers, favoring the use of low concentrations of filler loadings. Accordingly, for a concentration of 3.25% in volume, an improvement of 80% in the thermal conductivity of the polyester resin was achieved by orienting the fibers. It is worth to mention that even under these conditions those samples show a higher thermal conductivity than samples with non-oriented fibers. However, more theoretical and experimental research should be done to device methods to reduce the thermal interface resistance in polymers with oriented m-CNFS. Additionally a broader range of concentrations and intensity of magnetic fields should be analyzed in order to develop a methodology to determine the optimal conditions to maximize the thermal conductivity of a given polymer.

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