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Comparative study between the microwave heating efficiency of carbon nanotubes versus multilayer graphene in polypropylene nanocomposites

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ABSTRACT

Multiwall carbon nanotubes (MWCNT) and multilayer graphene (MLG) were studied as microwave susceptor additives for polymers. Different percentages of both nanoparticles were added to polypropylene by melt compounding in order to study the microwave absorption and the polymer heating. Polypropylene was selected as polymer matrix due to its unpolar nature to avoid the influence of polymer polarity and evaluate the influence of the nanoparticles. Electrochemical spectroscopy impedance measurements were carried out to evaluate the conductive and dielectric properties of nanocomposites. Results showed that nanocomposites with higher electrical conductivity have better capacity of absorbing microwave radiation. High values of permittivity and loss tangent also increases the microwave radiation absorption and the ability of the material to convert this electromagnetic radiation into heat. Carbon nanotubes showed better microwave susceptor behavior than graphene multilayer. Nanocomposites with 1% w/w of carbon nanotubes can be compared with the heating efficiency of a polypropylene filled with 10% w/w of multilayer graphene. The higher efficiency of carbon nanotubes it is explained by their higher electrical conductivity and optimal dielectric properties of the nanocomposites compared to multilayer graphene polymer systems.

1. Introduction

Microwave technology is an alternative to conventional heating methods with important advantages like penetrating radiation, controllable electric field distribution, rapid heating, selective heating of materials and self-limiting reactions [1]. Nevertheless, microwaves also present important disadvantages, mainly related to the lack of uniform and selective heating over a large volume and the transparency of most of the materials to microwaves. In order to improve the heating homogeneity it is necessary to understand the heating mechanism. The energy involved in the process is supplied by an electromagnetic field that interacts with the material. Two major effects are responsible of the material heating [2]:

- Dipolar polarization: the charged particles cannot move in the space. In that case, this limited displacement provokes the orientation of particle in the opposite region balancing the electric force. The result is a dipolar polarization in the material. Magnetic polarization can also contribute to heating effect in the case of materials with magnetic properties.
- Conduction: it happens when the charged particles are free to travel through the material. For example, electrons in carbonous substances. This movement induces a current that travel in phase with the electromagnetic field.

Therefore, material properties are of greatest importance in microwave processing, being the electrical conductivity and the dielectric properties very influencing properties on the heating behavior under microwave radiation. The complex relative permittivity $\varepsilon = \varepsilon'' - j\varepsilon''$ and the loss tangent, $\tan\delta = \varepsilon''/\varepsilon'$ are critical to study the interaction between the electric field and the

Abbreviations: MWCNT, Multiwall Carbon Nanotubes; MLG, Multilayer Graphene; CVD, carbon vapor deposition; PP, polypropylene; SEM, scanning electron microscopy; TEM, transmission electron microscopy; ISE, impedance spectroscopy electrochemical.

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dipoles of the material. The real part of the permittivity, ε', called the dielectric constant, mostly determines how much of the incident energy is used in the dipole rotation. The most important for a material is to look for a frequency where the absorption of energy will be high, ε', and the energy loss, ε''. This equilibrated frequency point is well defined by the loss tangent, tan δ, or dielectric loss, which predicts the ability of the material to convert the incoming energy into heat [3].

Most thermoplastics are transparent to microwaves. Polymers do not absorb microwaves to a sufficient extent to be heated as exhibit very low dielectric losses in the GHz region. Using specific fillers can increase the susceptibility of common polymers to microwave processing [4]. These additives are conductive, or have dielectric properties significantly different from the matrix polymer. The presence of these inclusions strongly influence on the interaction of composite material with the microwave radiation. Some examples of these conductive additives include carbon black [5,6], metal fibres [7], silicium carbide [8], titanium dioxide and others [9]. The effect of conductive additives on microwave heating depends on the size, shape, concentration, electrical conductivity and dielectric properties of the inclusions and their distribution in the matrix. Carbonise particles are excellent microwave susceptors showing high permittivity values (ε') and high values of loss tangent (tanδ) [10–12].

Several studies have been found regarding the use of carbon nanotubes as polymer microwave susceptor additive. P. Zhinhua et al. [13] incorporated MWCNT in polystyrene matrix. These authors found that 2.487% w/w of carbon nanotubes considerably increases the dielectric properties of polystyrene in a frequency range of 50 MHz–3 GHz. Z. Fan et al. [14] analyzed the influence of carbon nanotubes on the microwave radiation capacity of polypropylene, polyethylene and polyethyleneterephtalate. Loss tangent of nanocomposites in creased with the content of carbon nanotubes in all the polymer systems. The optimal content of carbon nanotubes was found to be 4% w/w. Polyethylene terephthalate showed higher microwave radiation absorbance than polyolefins due to its polarity. No study was found regarding the use of multilayer graphene as microwave susceptor additive for thermoplastic polymers.

The aim of the present work consists of studying the properties of carbon nanotubes and multilayer graphene nanoparticles as microwave susceptors. Dielectric properties of the nanocomposites are being studied to predict microwave absorption and heating effectiveness for this the heating effectiveness of both nanoparticles are being studied just to know the differences when they are compared. Polypropylene [15] was selected as matrix due its non-polar nature and microwave transparency and the nanocomposites were prepared by melt mixing procedure using a co-rotative twin-screw extruder. Multiwall carbon nanotubes (MWCNT) and multilayer graphene (MLG) were studied as microwave susceptor due to their high electrical properties.

2. Experimental

2.1. Materials

NC7000 multiwall carbon nanotubes (MWCNT) were purchased from the Belgium Company Nanocyl. These MWCNT are produced via catalytic carbon vapor deposition (CVD) process with an average diameter of 9.5 nm, length of 1.5 μm and carbon purity around 90%. Multilayer graphene (MLG) was purchased from XGScience. Grade M with a diameter of 5 μm was selected for the trials, which is claimed to have high thermal and electrical properties. Homopolymer polypropylene was selected as polymer matrix. The employed grade was PP DUCOR 1101S from DUCOR Petrochemicals. This material has a MFR (230 °C/2.16 kg) of 25 g/10 min, a tensile modulus of 1500 MPa and a melting point of 163 °C.

2.2. Sample preparation

Nanocomposites with different percentages of MWCNT and MLG were obtained in a co-rotative twin screw extruder COPERION W&P ZSK25. The extruder has a diameter of 25 mm and an L/D ratio of 40. MWCNT nanocomposites were produced with a nanoparticle loading of 0.5%, 1%, 3% and 5%. MLG nanocomposites were obtained with 0.5%, 1%, 3%, 5% and 10% of filler loading. Nanocomposites were produced with the same processing conditions. The nanoparticles were incorporated via masterbatch which was produced in a previous process. Two masterbatches with a MWCNT loading of 15% and a MLG loading of 15% were produced under the following conditions: highly dispersive screw configuration, 600 rpm and temperature profile 260 °C/220 °C/220 °C/210 °C/200 °C/190 °C. Masterbatch dilutions were processed with the same temperature profile and the screw as the masterbatch. The screw speed was increased up to 800 rpm to ensure the nanoparticles dispersion. Test bars were produced by compression moulding in a hot press (COLLIN model P200E) at 200 °C/15 bars during 15 min. Samples with dimensions of (10 × 1 × 0.4) cm were used in morphology characterization and electrical conductivity studies.

2.3. Characterization techniques

The dispersion of MWCNT and MLG in the nanocomposites was examined by optical microscope (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Dispersion analysis was carried out on the samples with 1% of nanoparticles as the matrix is not collapsed with nanoparticles and it is possible to analyse individual particle size and homogeneity.

Optical microscope analysis was done on samples with disc shape of 2.5 cm of diameter and 100 μm of thickness were prepared in a hot plate press at 210 °C for 3 min. The microscope employed was LEICA model DMRX equipped with software of image analysis (Leica Materials Workstation V 3.6.3). The parameters measured in the samples were mean particle size and agglomerates density. Agglomerate density makes reference to the area of the sample, which is occupied by aggregates in relation to the total area of the sample. It is calculated with the following formula [16]:

$$\textit{Agglomerates density} = \frac{A_x}{A_0} \times 100 \quad (1)$$

Where A_x is the area of the sample with CNT agglomerates and A_0 is the total area of the sample.

Scanning Electron Microscopy (SEM) studies were performed with a Phenom Pro X desktop microscope. The microscope works at multiple acceleration voltage (5, 10, 15 kV), reaching a resolution of less than 12 nm. The samples were prepared by cryogenic fracture of compression moulding test bars and subsequent coated with gold by sputter coating technology.

The dielectric properties of the nanocomposites with different percentages of MWCNT and MLG were measured by impedance spectroscopy at 20 °C, 30 °C, 40 °C, 50 °C and 60 °C of temperature, in the frequency range $10^{-1} < f < 3 \times 10^6$ Hz with 0.1 V amplitude, using a Novocontrol broadband dielectric Spectrometer (Hundsangen, Germany) integrated by a SR 830 lock-in amplifier with an Alpha dielectric interface. The temperature was controlled by nitrogen jet (QUATRO from Novocontrol) with a temperature error of ≈0.1 K during every single sweep in frequency. The measurements have been made using a dry procedure where the sample of interest was sandwiched between two gold circular electrodes coupled to