Composites Science and Technology 86 (2013) 177–184

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Electrical and thermal conductivities of multiwalled carbon nanotubes-reinforced high performance polymer nanocomposites

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ARTICLE INFO

Article history:
Received 8 February 2013
Received in revised form 4 July 2013
Accepted 23 July 2013
Available online 31 July 2013

Keywords:
A. Carbon nanotubes
A. Polymers
B. Electrical properties
B. Thermal properties
E. Extrusion

ABSTRACT

Polyethersulfone (PES) and phenoxy based-nanocomposites filled with unmodified multi-walled carbon nanotubes (MWCNT) from 0.25 to 10 wt.% have been prepared by melt processing with a twin-screw extruder and a hot press. A morphology analysis is performed by transmission electron microscopy (TEM) in the extruded nanocomposites disclosing difference in state of dispersion despite a proper MWCNT scattering in both matrixes. The electrical conductivity measurements establish a percolation threshold $\Phi_c = 0.58$ wt.% and a critical exponent $t = 2.3$ for phenoxy against $\Phi_c = 0.89$ wt.% and $t = 1.89$ for PES-based composites by following a percolation scaling law of the form $\sigma = \sigma_0(\Phi - \Phi_c)t$. Thermal conductivity assessments as function of MWCNT concentration and temperature is then carried out by modulated temperature dynamic scanning calorimetry (MDSC) in both nanocomposites. In analogy with the electrical properties, no thermal percolation behaviour is pointed out despite noteworthy increases above 1 wt.% MWCNT incorporated in PES and phenoxy and temperature dependence below glass transition temperature. The effect of gas purge is also considered and reveals to be meaningful in relation with the thermal conductivity values of MWCNT-reinforced PES and phenoxy nanocomposites. Afterwards, a comparison of the DSC technique results byMDSC is performed with a thermal conductivity measurement using a Hot Disk transient technique showing significant discordance in experimental data, sometimes over the range of ±15%.

1. Introduction

The incorporation of nanoscale particles into polymers have been a great accelerator for scientific investigations for several years thanks to their high aspect ratio. The increase of the interfacial area between nanoparticles and the polymer matrix have enabled to offer improved properties to materials as flame retardancy [1], mechanical properties [2], electrical or thermal conductivity performance [3].

Carbon nanotubes (CNT) are one of these most promising nanoscale fillers and have received considerable interests by scientists since their first published report by Iijima [4]. This is especially attributed to their exceptional mechanical strength and superior electrical and thermal conductivities. The CNT addition within a polymer has exhibited in numerous studies electrical percolation at a low filler concentration [5,6] creating a CNT network, which allows a pathway from an insulating to a semiconductive or conductive materials. This phenomenon commonly named a percolation threshold can be explained by the electrical percolation theory [7], when a conductive pathways is formed at a critical filler concentration in an insulating material. Conversely, thermal conductivity data in CNT/polymercomposites do not reveal a percolation behavior as for electrical conductivity notably because of difference in the conduction mechanisms of electrons and phonons. Thermal conductivity values for CNT-based nanocomposites are often underneath theoretical expectations [8]. Indeed, the most theoretical models overestimate thermal conductivity value of CNT-based nanocomposites compared to experimental results despite the extraordinary intrinsic thermal conductivity of CNT [9]. The many investigations have also demonstrated that the electrical and thermal conductivities are strongly dependant of a wide range of parameters: synthesis method, structure and morphology of CNT as well as polymer type, nanocomposite processing method and dispersion, agglomeration or alignment of CNT in the polymer matrix [10–12]. On theother hand, different methods performed for thermal conductivity measurements can be found in literature: steady-state method, transient method as hot wire, hot disk or laser flash techniques, and Differential Scanning Calorimetry (DSC) which create a large scattering of experimental data [13,14] leading to different accuracy on thermal conductivity measurements.

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http://dx.doi.org/10.1016/j.compscitech.2013.07.017

In this paper, two high performance thermoplastics are filled with multiwalled carbon nanotubes (MWCNT): polyethersulfone (PES) and phenoxy resins. These both amorphous polymers have increasingly interests in the aeronautic industry especially for their miscibility with epoxy resins which results in the heat resistance and toughness enhancement of fiber-reinforced composite materials [15,16]. Their association with MWCNT enlarge their potential applications with aerospace composite materials particularly for electromagnetic (EMI) shielding and lightning strike protection.

This study aims at investigating the influence of MWCNT concentration on the electrical and thermal conductivities of PES and phenoxy-based nanocomposites prepared by melt blending. The determination of percolation threshold Φ_c and the conductivity exponent t will be determined from the curves $\sigma = f$ (MWCNT mass fraction). A correlation between dispersion and experimentally obtained results will be then discussed, as well as the comparison between two different methods for thermal conductivity and thermal diffusivity measurements: a non-steady state method by Hot Disk Technique and a DSC technique by modulated temperature dynamic scanning calorimetry (MDSC).

2. Experimental methods

2.1. Materials

Two high performance thermoplastics are used in this study: polyethersulfone (PES) and phenoxy resin. PES used is PES 4100G (Mw = 37,500) from Sumitomo Chemicals (Japan). This polymer is a high performance amorphous polymer with a glass transition around 226 °C and a density evaluated as $d = 1.37$ g/cm^3. Phenoxy used is PKHH (Mw = 52,000) from Inchem (Switzerland). This polymer is a high performance amorphous polymer with a glass transition around 90 °C and a density evaluated as $d = 1.18$ g/cm^3.

Multi-wall carbon nanotubes (MWCNT) are produced by catalytic vapor deposition (CVD) system and were supplied by Nanocyl (Belgium) under the reference NC7000®. MWCNT have a degree of purity equal to 90%. Their average diameter and length are respectively 9.5 nm and 1.5 μm with a surface area of 300 m^2/g.

2.2. Nanocomposites preparation

Before preparing the both nanocomposites, a drying in a vacuum oven at 80 °C during 16 h was made in order to remove absorbed water contained in PES and phenoxy. The MWNT incorporation into the both polymers with different weight percentages from 0 wt.% to 10 wt.% was realized by melt processing thanks to a co-rotating intermeshing twin-screw extruder from Thermo Haake ($L/D = 25$). For each blend, the rotational speed was 100 rpm. The five heating zones of the extruder was gradually fixed temperatures, ranged between 200 and 260 °C and 320 and 325 °C respectively for phenoxy and PES nanocomposites to have similar melt viscosities.

A part of rods obtained after extrusion process were used for the electrical measurements. The other part was pelletized to make by hot press the required samples for the MSDC and Hot DISK experiments. In view of thermal conductivity measurements by MDSC and Hot Disk Technique, table 1 lists the characteristics of the samples' form and size, and the experimental conditions used during the thermocompression process for material preparation. The pellets were introduced in aluminum moulds of different forms and thicknesses according to the method used (MDSC or Hot Disk). Two cylindrical moulds, with a diameter of 6.3 mm and respectively a thickness of 0.4 and 3 mm, were used to respect the procedure indicated in the standard ASTM E1952-98 [17] for thermal conductivity measurement by MDSC. For HotDisk methods, a 100 cm^2 rectangular mould with a thickness of 3 mm were used. In both cases, each mould was put between two aluminum slabs coated with Teflon adhesive tape to minimize irregularities on the surface of the nanocomposite slabs. The whole elements were then placed in a hot press system between two heated plates at 320 and 280 °C, for PES and phenoxy nanocomposites respectively. The nanocomposite pellets contained in the moulds were molten within 2 min without applying any pressure, and were then compressed for 10–15 min under 50 Bar. A cooling was performed before the removal from the moulds. Finally, all the samples were polished with a 600 grit emery paper to obtain samples with smooth and parallel end surfaces. This polishing was made in order to minimize thermal resistance contact during thermal conductivitymeasurements.

2.3. Transmission electron microscopy (TEM)

Transmission electron microscopic analyses of the PES and phenoxy nanocomposite rods were performed with a PHILIPS CM 120 device at low and high magnifications in order to study and compare the dispersion of MWCNT. Ultramicrotomy has been used to prepare TEM samples with a thickness of 70 nm. Nanocomposite specimens were directly microtomed in the cross section before TEM experiments.

2.4. Electrical conductivity measurements

The electrical conductivities of nanocomposite rods were measured using an Keithley 617 ammeter connected with electrodes. The electrodes consist of two clamps which are fixed on the rod and are separated by 5 cm. In order to provide stable values of sample conductivity, silver paste was coated onto the sample's surface in contact with the clamps to ensure a good electrical contact. Ten measurements were performed along each tested nanocomposite rod and the average calculated. The measurement device was interfaced with a computer to record and process data. A

Table 1
Characteristics and experimental conditions used to prepare nanocomposites specimens for MDSC and Hot Disk experiments.

Experimental conditions	MDSC		Hot Disk	
Polymer	PES	Phenoxy	PES	Phenoxy
Form	Cylindrical		Rectangular	
Thickness	1 × 0.4 mm + 1 × 3 mm		3 mm	
Diameter/surface	6.3 mm		100 cm^2	
Temperature (°C)	320	280	320	280
Pressure (Bar) + time (min)	0 bar – 2 min 50 Bar – 10 to 15 min			
Cooling	100 °C	70 °C	100 °C	70 °C
Finishing	Polishing of circular end surfaces with 600 grit emery paper			