Polycaprolactone/multi-wall carbon nanotube nanocomposites prepared by in situ ring opening polymerization: Decomposition profiling using thermogravimetric analysis and analytical pyrolysis–gas chromatography/mass spectrometry

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ABSTRACT

Poly(ϵ-caprolactone) (PCL) was reinforced with amino-functionalized multi-walled carbon naonotubes (f-MWCNTs) by an in situ ring opening polymerization (ROP) procedure. Transmission electron microscopy (TEM) was initially utilized in order to observe the state of dispersion of MWCNTs in the matrix, which is known to affect heavily the physicochemical properties of the composite materials. Subsequently, a thorough investigation of the decomposition profiling of PCL and nanocomposites was performed by employing thermogravimetric analysis (TGA) and analytical pyrolysis–gas chromatography/mass spectroscopy (Py–GC/MS). The results from TGA revealed that the thermal stability of the matrix is not enhanced by f-MWCNTs, while the detailed study with Py–GC/MS showed that random chain scission via *cis*-elimination, intramolecular transesterification and unzipping reactions dominate the decomposition of PCL. It is noteworthy that the highest amount of filler was found to catalyze decomposition reactions without interfering with the detected mechanisms. In terms of the mechanical properties, the presence of f-MWCNTs improved the stiffness of the matrix, as evidenced through dynamic mechanical analysis (DMA).

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1. Introduction

Polycaprolactone (PCL) was one of the first linear aliphatic polyesters synthesized in 1932 by van Natta et al. [1]. It can be prepared by ring-opening polymerization (ROP) in the presence of catalysts, or by free radical ROP of 2-methylene-1-3-dioxepane [2]. PCL is known for its biodegrability, biocompatibility, ease of processing and uses in a variety of applications from degradable packing, to tissue engineering and drug delivery systems [3,4]. In terms of its physicochemical properties, it possesses superior viscoelastic and rheological properties, good solubility and blend-compatibility but also exhibits mediocre mechanical properties and low melting point and glass transition.

The introduction of inorganic fillers in the nanoscale has been proven an efficient way to improve significantly the properties of several polymeric matrices. PCL has not been unaffected by this emerging technology over the last decades and several PCL-based nanocomposites have been reported for use in various applications. Multi-walled carbon nanotubes are one of the most used fillers in this class of materials due to their unique mechanical, thermal and electrical properties [5–10]. Additionally, a number of studies have reported the formation of an interphase between the polymeric matrix and MWCNTs, which has been also identified as responsible for the increase of the properties of the composite material [11–15].

Several preparation routes have been reported toward the improvement of the dispersion of MWCNTs in the matrix, which is one of the most important factors for the enhancement of the physicochemical attributes of the composites. Some of the most used ones are melt mixing [16], electrospinning [17], solution blending [18,19], in situ polymerization [20] and others. In the present work, in situ polymerization was selected as a preparation procedure due to the fact that fillers in the nanoscale have been

proven to act effectively as initiators of the ring opening polymerization procedure [21–24] and it has also been observed that the specific technique can ensure a homogeneous dispersion and exfoliation of the layered-type filler in the matrix [25–29]. Furthermore, a functionalization of the filler with amino groups was performed prior to the introduction in the PCL matrix, in order to assist the formation of covalent bonds between *f*-MWCNTs and PCL and initiate also the polymerization of the matrix.

The catalytic and thermal degradation of plastics is an interesting subject of research and discussion and the continuous use of additives and nanofillers on commercial products can play a major role on the decomposition profiles of those materials [30–33]. The determination of the working temperatures of polymers and composites is vital for industrial purposes and should be studied thoroughly. It has already been reported that the presence of nanoparticles can affect the decomposition mechanism of certain polymers [34–38] and for this reason it is important to evaluate the specific characteristics in detail.

The main purpose of the current manuscript was to observe and report thoroughly the decomposition of PCL under the presence of *f*-MWCNTs. For this reason thermogravimetric analysis was initially employed in order to study the effect of *f*-MWCNTs on the thermal stability of the matrix and to select the proper temperatures for the pyrolysis tests. Pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) was also used for the analysis of the compounds during the decomposition and the representation of the detailed degradation mechanism of the samples. Fourier transform infrared spectroscopy (FTIR) was also used in an attempt to confirm the functionalization of the filler, while dynamic mechanical analysis (DMA) was applied to monitor the effect of MWCNTs on the mechanical properties of the samples.

2. Experimental

2.1. Materials

ϵ-Caprolactone (ϵ-CL) (purum 99%) and tetrabutyl titanate (TBT) catalyst of analytical grade, were purchased from Aldrich Chemical Co. (Stainheim, Germany). Amino functionalized multi-walled carbon nanotubes (*f*-MWCNTs) were kindly offered from GLONATECH S.A (Athens Greece, ONEX-MW 1004C2). The nanotubes have 5% $-NH_2$ content, average diameter of 15 ± 5 nm, length >5 μm and bulk density 0.2 g cm^3.

2.2. PCL synthesis and nanocomposites preparation

The detailed synthesis of PCL and its nanocomposites can be found in our previous work [39]. Briefly, the bulk polymerization of ϵ-CL was carried out in 250 mL round-bottom flask equipped with a mechanical stirrer and a vacuum apparatus using TBT as a catalyst. PCL nanocomposites containing 0.5, 1 and 2.5 wt.% *f*-MWCNTs were prepared by in situ polymerization following the same technique.

The prepared materials were afterwards hot pressed using an Otto Weber, Type PW 30 hydraulic press connected with an Omron E5AX Temperature Controller, at a temperature of $75 \pm 5\,^\circ$C, in order to prepare films of different thicknesses, therefore appropriate for each type of following measurements.

2.3. Characterization methods

2.3.1. Transmission electron microscopy (TEM)

Ultrathin film samples of the nanocomposites were prepared through cryomicrotoming at $-90\,^\circ$C with a DIATOME cryo -45° diamond knife by the ultramicrotome Leica EM FC7. Sections of the

thin films were placed on copper grids and studied using a JEOL HR-JEM 2100 electron transmission microscope operating at 200 kV.

2.3.2. FTIR spectroscopy

FTIR spectra were obtained using a PerkinElmer FTIR spectrometer, model Spectrum 1000. In order to collect the spectra of the studied materials thin films ($50 \pm 15\,\mu$m) were prepared in a hydraulic hot press at $75 \pm 5\,^\circ$C. The resolution for each spectrum was 2 cm^{-1} and the number of co-added scans was 64.

2.3.3. Dynamic mechanical analysis

Dynamic mechanical thermal analysis (DMA) for neat PCL and the nanocomposite samples (35 mm $\times$ 8 mm $\times$ 1 mm specimens) was performed in the tensile mode between -100 and $30\,^\circ$C using a DMA Q800 analyser (TA instruments). A heating rate of $3\,^\circ$C/min and a frequency of 1 Hz were employed.

2.3.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out with a Setaram Setsys TG-DTA 16/18. Samples (4.0 ± 0.2 mg) were placed in alumina crucibles. An empty alumina crucible was used as reference. All materials were heated from ambient temperature to $550\,^\circ$C in a 50 mL min^{-1} flow of nitrogen at heating rate of $20\,^\circ$C min^{-1}. Continuous recordings of sample temperature, weight, and heat flow were performed.

2.3.5. Pyrolysis–gas chromatography–mass spectroscopy (Py–GC/MS)

For pyrolysis–gas chromatography/mass spectroscopy (Py–GC/MS) analysis of PCL and its nanocomposites, a very small amount of each material was placed initially into the Multi-Shot EGA/PY-3030D Pyrolyzer (Frontier Laboratories Ltd., Fukushima, Japan). Each sample was placed into the sample cup which afterwards fell free into the Pyrolyzer furnace. The pre-selected pyrolysis temperatures were 370 and 400 $^\circ$C and the GC oven temperature was programmed from 50 to 300 $^\circ$C at 20 $^\circ$C/min. The sample vapors generated in the furnace were split (at a ratio of 1/50), a portion moved to the column at a flow rate of 1 mL/min and the remaining portion exited the system via the vent. The pyrolyzates were separated in the Ultra Alloy metal capillary column (UA^{+5}) and analyzed by the MS detector GC–MS-QP2010 Ultra (Shimadzu, Japan).

3. Results and discussion

3.1. Characterization of nanocomposites

In Fig. 1 TEM images of all PCL/*f*-MWCNTs nanocomposites are presented. Dispersed nanotubes as well as small aggregates were detected in the composites with lower filler amounts. Specifically, in PCL/0.5 wt.% *f*-MWCNTs individual nanotubes were found to be well dispersed in the matrix (Fig. 1a) while some small aggregates with dimensions less 200 nm were also observed (Fig. 1b). Similarly, in the PCL/1 wt.% *f*-MWCNTs composite, non-aggregated nanotubes could be observed (Fig. 1d) while larger arrays of MWCNTs were also found (Fig. 1c). On the other hand, the aggregates in the PCL/2.5 wt.% *f*-MWCNTs composite were significantly larger and no dispersed nanotubes could be observed (Fig. 1e and f). This is a result of the strong van der Waals interactions between the nanotubes, which make them form bundles and aggregates, especially at higher contents, which are very hard to break and which ultimately act as failure points during the testing of the nanocomposite materials (Fig. 2).

In order to evaluate the successful modification of MWCNTs with amino groups, FTIR was utilized. The functionalized MWCNTs were initially tested and the strong peak at 1640 cm^{-1} represents