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An innovative process for mass production of multi-wall carbon nanotubes by means of low-cost pyrolysis of polyolefins

Umberto Arena [a,*], Maria Laura Mastellone [a], Giovanni Camino [b], Enrico Boccaleri [c]

[a] Department of Environmental Sciences – Second University of Naples, 81100 Caserta, Italy
[b] Centre for the Engineering of Plastic Materials – Turin Politechnic, Alessandria, Italy
[c] DISTA, Eastern Piedmont University, Alessandria, Italy

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Abstract

An innovative process for a mass production of multi-wall carbon nanotubes (MWCNTs) by means of pyrolysis of virgin or recycled polyolefins is described. The technique uses solid–gas fluidised bed reactors, continuously operated under conditions which allow high heating rates of the polymers, high heat and material exchange coefficients and a reliable control of residence times in the reactor. The obtained MWCNTs have been characterized by TGA, SEM and TEM microscopy as well as X-ray diffractometry and Raman spectroscopy. The results demonstrate that the proposed process allows the production of MWCNTs compatible with most of the already known applications, in large quantities and at low cost. This makes extremely wider the field of possible applications of these nanostructured materials.

Keywords: Carbon nanotubes; Pyrolysis; Plastic wastes; Polyolefins

1. Introduction

Nanotechnology involves the design, characterization, production and application of structures with at least one dimension in the nanometer length scale, i.e. between 1 and 100 nm. At the nanoscale, the ratio between surface area and volume raises causing materials to defy their conventional properties, instead exhibiting unique and often unparalleled characteristics [1–3]. Recently, a great effort has been devoted to the synthesis methodology and the production technology of carbon nanotubes (CNTs), since their very high aspect ratio and extraordinary mechanical, electrical and thermal properties can be extremely useful for several applications. The main fields of use for carbon nanotubes are [4]: materials, for the manufacture of ultra-strong fibres to be inserted into various matrices; mechanics, for the production of nanocomposites; electronics, for the production of transmitters and transistors; nanoelectronics, for the production of nanocables; biological chemistry, for the production of membranes to be used for molecular sieving; biomedicine, for the creation of optical biosensors and other applications; energy and environment, for gas capture.

Currently, the high cost of producing carbon nanotubes limits their use in the industrial market, but as new techniques to fabricate CNTs on a large scale emerge, it is expected that they will find their way into a relevant number of applications [3,5]. Present methods for production of CNTs utilize graphite, carbon monoxide

* Corresponding author. Tel.: +39 0823 274414; fax: +39 0823 274592.
E-mail address: umberto.arena@unina2.it (U. Arena).

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or hydrocarbons for the construction of the carbon skeleton of CNT. Some of them promote thermolysis of hydrocarbons and carbonaceous substrates by involving a metallic catalytic centre: in this way the metal-catalysed genesis and growth of the carbon frames can be controlled by means of some experimental parameters [1,3]. Anyway, all these methods usually require critical operating conditions that are very expensive, and then strongly restrict the fields of applications of these nanostructures [3,4].

This paper refers to an innovative process [6], for the mass production of carbon nanotubes by means of pyrolysis of polyolefins. The technique uses solid–gas reactors, continuously operated under conditions which allow high heating rates of the polymers, high heat and material exchange coefficients and a reliable control of gas and solids residence time in the various parts of reactor. The process allows obtaining carbon nanotubes, in large quantities and at low cost, which present a degree of purity compatible with most of the applications already known for this type of nanostructured material. Moreover, taking into consideration the possibility of large scale production of CNTs at significantly lower costs, the proposed process can be interesting for the development of new technological applications with lower added-value and large manufacturing volumes. The chemical structure of the starting polymeric material, its molecular weight and the possibility to utilize mixture of different polyolefins could also be used to obtain nanotubes variously functionalised. As a consequence, the proposed production process could allow utilization of the enormous wealth of knowledge that is today available in the field of polymer chemistry and technology, in order to design and realize tubular nanostructures of carbon characterized by a great structural versatility and a low cost. These features largely extend the potential market of CNT in a number of applications, as, for instance, those of composite materials [7,8].

This paper describes the first results related to the production of multi-wall carbon nanotubes by means of fluidised bed pyrolysis of virgin or recycled polypropylene, carried out accordingly with the cited innovative procedure.

2. Experimental

The experimental apparatus is a bubbling fluidised bed reactor 110 mm ID, made of high-temperature austenitic stainless steel, which is schematically described in Fig. 1. The reactor was equipped with a continuous plastics feeder located at the reactor top; a pressure transducer located at the bed bottom; a sampling line by means of which the produced gases were transferred to the online analysers; and a device able to withdraw part of the bed solid material. A series of experiments were performed by varying the bed temperature in the range 450–850 °C and the gas fluidisation velocity in the range 0.05–0.4 m/s. Nitrogen was used to fluidise the bed, which was made of quartz-rich sand or alumina. Throughout the duration of the experiment the online gas analysers allowed the identification and measurement of the hydrocarbon concentrations in the gas phase. The composition of produced gas as well as the temperature and pressure inside the reactor were continuously monitored and recorded during the test by a data acquisition unit [9,10]. Part of the pyrolysis gas was sent to the hood via a preferential route, and part to the sampling line connected to the reactor. Solid phase was continuously withdrawn from the bed while a same flow rate of bed material was fed into the reactor: this allows us to analyse and purify the solid phase and, at the same time, to keep constant bed height as well as residence times of gas and solid phases in the reactor [9].

3. Diagnostics, results and discussion

The collected solids were analysed by different techniques, which allowed their complete characterization and indicated a large content of MWCNTs.

The thermogravimetric analyses of collected carbonaceous products were carried out in air (60 cm^3/min) in a Q500 TA Instruments thermobalance, heating from 50 to 900 °C at 10 °C/min. The results showed a high stability to thermal oxidation in air: the main decomposition appeared to occur at about 690–700 °C. A purity of the raw material of about 85–90% wt was also estimated. The residue was essentially made of bed materials and traces of metals (essentially iron). A purification made using sonication in a 1:1 mixture of aqueous hydrofluoric and nitric acids [11] results in a purity of about 90–95% wt.

The collected material was observed by means of a Scanning Electron Microscope and of a JEOL 2010 High Resolution Transmission Electron Microscope operating at 200 kV. For SEM images, a small amount of sample was fixed on the microscope sample holder by adhesive tape; for TEM images, specimens were prepared through the dispersion of the sample by ultrasonication in isopropanol and deposition of drops of the suspension on carbon-coated grids. SEM images (Fig. 2) clearly evidence the presence of distributed nanodimensional tubular structures in the collected solid phase. HRTEM micrographs are much clearer for this structural aspect, as shown in Fig. 3: diameters can range from 15 to 40 nm, while small amounts of larger diameters could suggest that, tuning the process conditions, a size control towards MWCNTs or tubular nanofibres can be obtained. Both the morphology (coiled and straight tubes) and the mean length of the structures are comparable to those found in MWCNT commercial samples [12].