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Multi-Wall Carbon Nanotubes Obtained by Fluidized Bed Pyrolysis of Virgin or Recycled Plastics

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MULTI-WALL CARBON NANOTUBES OBTAINED BY FLUIDIZED BED PYROLYSIS OF VIRGIN OR RECYCLED PLASTICS

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ABSTRACT

A new technique for a continuous, mass production of high-quality multi-wall carbon nanotubes (MWCNTs), based on fluidized bed pyrolysis of polymers (virgin or recycled polyolefins and recycled polyethylene terephtalate), is described in detail. The study investigates the role of interactions between the bed material and the polymer particles injected into the reactor as well as that of the reactor temperature. Results are reported in terms of yield and quality of obtained MWCNTs, all characterized by thermogravimetrical analysis and SEM microscopy. The production of MWCNTs, in a relatively large quantity and at a low cost, is demonstrated as technically feasible.

INTRODUCTION AND SCOPE

Present methods for production of carbon nanotubes (CNTs) utilize graphite, carbon monoxide or hydrocarbons for the construction of the carbon skeleton of CNT, and different kinds of metals as catalysts. Moreover, all these methods usually require critical operating conditions that are very expensive, and then strongly restrict the fields of applications of these nanostructures (1, 2): there is a general accordance that as new techniques to fabricate CNTs on a large scale emerge, they will find their way in a relevant number of applications (3).

A number of procedures to obtain MWCNTs has been recently proposed. In particular, some Authors (4-6) claim the possibility to obtain carbon nanotubes by means of different high-temperature thermolysis processes, generally carried out under reducing atmosphere, and applied to carbonaceous substrates (as bulk polymers) that fill metallic templates. The catalytic chemical vapor deposition carried out by feeding gaseous hydrocarbons in a continuous bench scale fluidized bed reactor has been also proposed (7, 8) as a process that could potentially give mass production of MWCNTs at reasonable costs, even though the problem of keeping both catalysts and CNT product within the reactor appears not yet solved.

This study refers to a new method for MWCNT production by means of a continuous fluidized bed pyrolysis process of virgin or recycled polymers, which has been recently proposed by the authors (9, 10). The technique produces, in a relatively large quantity and at low cost, carbon nanotubes having quality similar to MWCNTs available on the market even when the starting materials were polymers coming from post-consumers waste collection and recycling. Polyethylene, polypropylene and polyethylene terephtalate have been successfully fed to an atmospheric bubbling

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fluidized bed pyrolyser, to obtain MWCNTs. The yield and quality of the obtained nanostructures depend on the type of starting polymer and on operating conditions used (mainly, reactor temperature, gas residence time, bed material properties). Aim of this study is to investigate the influence of the polymer type and reactor temperature on the efficiency of the proposed process.

EXPERIMENTAL APPARATUS AND DIAGNOSTICS

The reactor used is an atmospheric bubbling fluidized bed (BFB), 102mm ID, made of high-temperature austenitic stainless steel, which is schematically described in Figure 1. Compared to other gas-solids contacting systems, fluidized beds have some rather unusual and useful properties: the very high heat and mass transfer between gas and particles allows short residence times at relatively low temperatures; the good quality of contact between gas and solids reactants increases their fractional conversions; the rapid and good mixing of solids leads to almost uniform isothermal conditions throughout the reactor, so allowing a reliable process control (10-12).

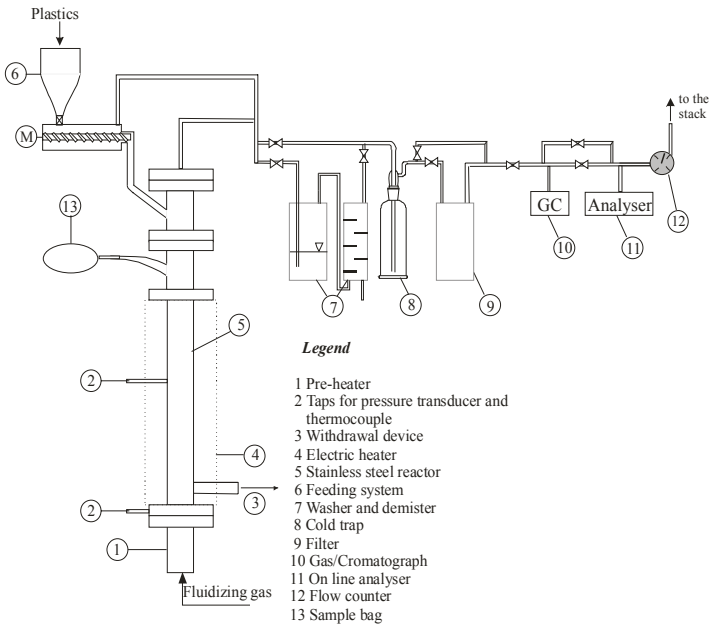

Figure 1. The bubbling fluidized bed reactor used for carrying out all the experiments.

The reactor was equipped with: a continuous plastics feeder located at the reactor top; pressure and temperature transducers located at the bed bottom and along the reactor; a conditioning line that addresses the produced gas to the on-line analyzers. Nitrogen was used to fluidize the bed. The measured 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. The pyrolysis gas was sent to the conditioning line connected to the on-line analysers: some samples were occasionally collected by means of a Tedlar bag. Solid phase was recovered from different areas: the internal reactor wall, the external tubes connecting the reactor exit with the conditioning line and the washer used to clean the pyrolysis gas from a part of heavy hydrocarbons and solid phases. In particular, since the total solids amount and the specific MWCNT yield found in the external tubes were much higher than those obtained from internal wall of the reactor, the tubes upstream the conditioning line were disassembled after each experiment in order to collect the solids and to re-establish a clean condition. The samples of solid phase were then purified and the quality of obtained MWCNTs was determined by using thermogravimetrical analysis (TG), Raman spectroscopy, SEM and TEM microscopy (9). In particular, TG-DTG allowed to verify the thermal stability of the samples under inert and oxidizing conditions in the temperature range 50-900°C.

The feeding materials tested in this study were virgin and recycled polymers, polyethylene (PE), polypropylene (PP) and polyethylene terephtalate (PET), even though similar results were obtained in tests with a packaging derived fuel (PDF) obtained as a mixture of these three polymers.

EXPERIMENTAL RESULTS AND DISCUSSION

Phenomenology of particle interactions inside the bed

The peculiar interaction between polymer and bed materials was already studied by the authors (13, 14) and indicated as the phenomenon that promotes a very fast thermal cracking of polymer chain with a contemporaneous production of light hydrocarbons, aromatics, waxes and carbon nanotubes. Just after the injection into the hot fluidized bed, a very fast heat transfer mechanism leads the polymer pellet external surface up to the softening temperature. Several bed particles stick therefore on the plastic surface, forming an aggregate that has the external shell made of bed particles and the internal core made of polymer not yet molten. When the temperature further increases, the surface of the pellet reaches the melting temperature and the polymer flows throughout the bed particles of the external shell, so forming a uniform coating over and between them. The described progress of heating leads to the cracking of the carbon–carbon bonds of the polymer chain, i.e. to the beginning of a fast pyrolysis process, that starts when the polymer has already covered the bed particles. Therefore, it is not related to the whole molten pellet, but to a layer of polymer which coats and adheres on the external surfaces of single bed particles (10).

The microphotographs reported in Figures 2 and 3 show a detail of the polymer layer that covers the bed particle surface: it is completely strewn by nanostructures (Figs. 2A and 3A) that sometimes form agglomerates (Figs. 2B and 3B). Investigation carried out with other techniques (TEM, X-Ray, Raman) demonstrated that these nanostructures can be classified as nanotubes and nanofibers having diameters between 10 and 150nm (9). The pictures are related to particles collected

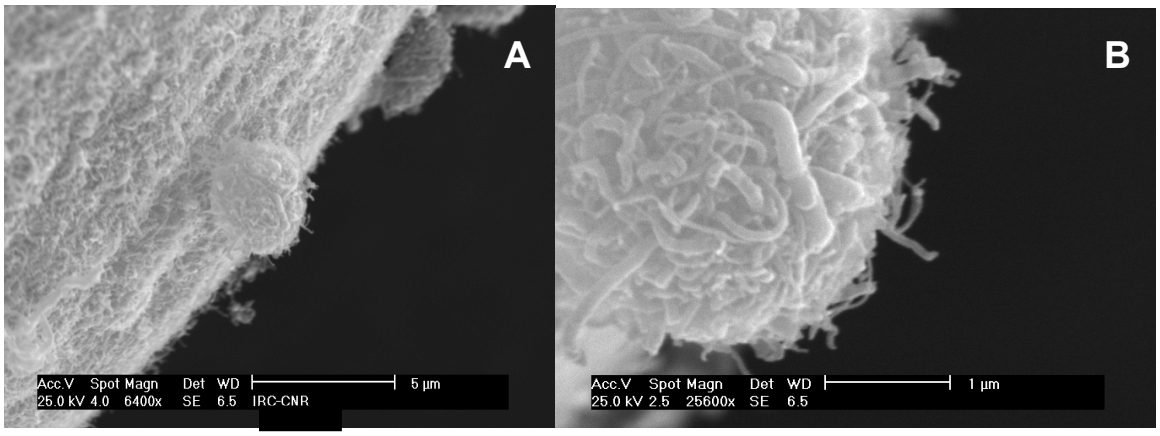

Figure 2 MWCNT agglomerates formed on the surface of bed particles in tests with PP in a bed of quartz sand (A) and a detail of one of these agglomerates (B).

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from the bed during a test carried out with a virgin polypropylene in a bed made of quartz sand or alumina, respectively.
The microphotographs are very similar to those obtained with PE, PET or PDF mixture and suggest that the MWCNTs form on the bed particle surface, and then moved towards other areas of the bed or towards the reactor walls as a consequence of the attrition phenomenon (15). In other words, the mechanical abrasion of the bed materials (connected to the continuous rubbing that bed particles operate each other as a consequence of their uninterrupted movement in the fluidlike state of the bed) detaches from the particle surface these nanostructures, which are then entrained out of the reactor together with flue gases.

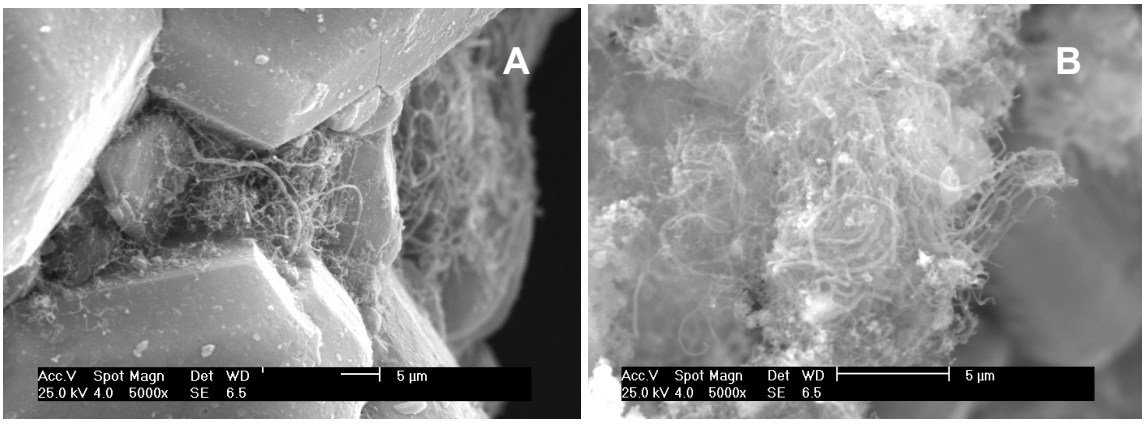

Figure 3 MWCNT agglomerates formed on the surface of bed particles in tests with PP in a bed of alumina (A) and a detail of one of these agglomerates (B).

Operating conditions of experimental runs

A series of experiments were carried out with PP, PE and PET in the described bubbling fluidized bed reactor, by keeping fluidizing velocity at a value able to provide a gentle fluidization. The base case was considered that of pyrolysis of PP in a bed of quartz sand particles at a temperature of 600°C. The effect of the polymer type was investigated by feeding PE and PET in the same reactor operated under the same conditions of the base case. The temperature ranged between 500 and 900°C, in order to take into account that temperatures lower than 500°C could lead to defluidization of the bed with consequent shut down of the reactor (13, 14) and that temperatures higher than 900°C require more thermal energy without any advantages in terms of yields.

Effect of main operating parameters

The base case. For all the experimental conditions tested, the collected solid phase was made of nanostructured materials (carbon black, MWCNTs or fullerenes) and of some impurities, like amorphous carbon and condensed heavy hydrocarbons. The presence of nanostructured material was detected by TG-DTG curves as well as SEM and TEM microphotograph observations. The presence of amorphous carbon impurities was detected by analysis of TG-DTG curves under oxidizing conditions, according to Pepka (16). The progressive release of heavy hydrocarbons was instead showed by TG-DTG curves under inert conditions. These latter are not reported here for reasons of space limitation, but indicated a weight loss of about 20% (from a minimum of 17% to a maximum of 30%) for all the operating conditions tested.

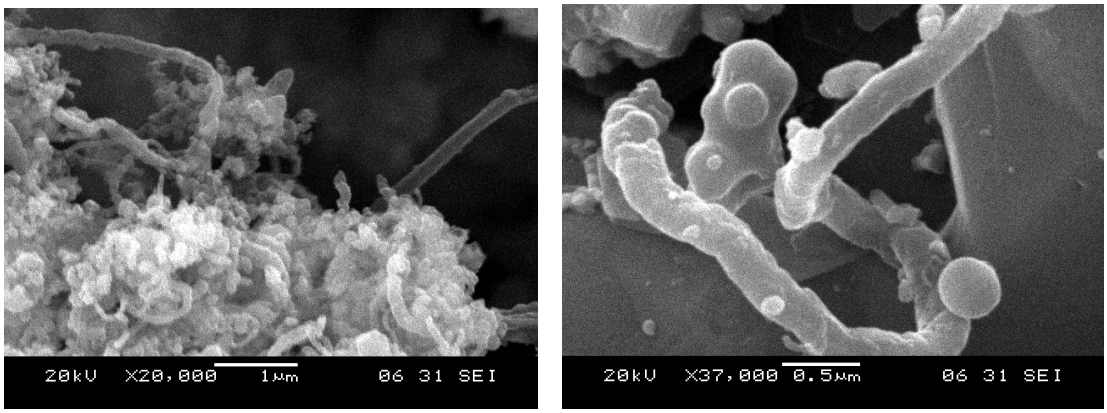

Figure 4 SEM pictures of MWCNTs as obtained in tests with PP at 600°C, with two levels of magnification.

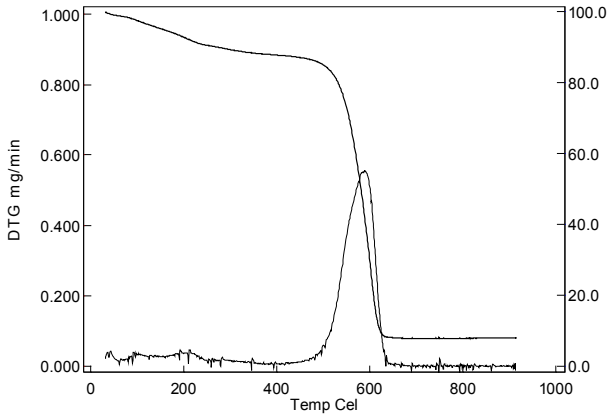

Figure 5 DT-DTG curves obtained under oxidizing conditions for sample obtained by the base case test with PP.

Under the operating conditions of the base case, the fluidized bed pyrolysis of PP produced a relevant amount of MWCNTs that can be estimated to be about 0.11g of MWCNTs for each gram of injected polymer. This value is obtained by multiplying the solids yield (i.e. the ratio between the amount of total solids collected at the end of each test and the amount of polymer fed during the test) by the purified solids yield (i.e. the ratio between the amount of solids obtained by the purification process and the total amount of solids collected during each test). Some SEM microphotographs of the obtained nanostructured material

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were already reported elsewhere (9, 10) and more are shown in Figure 4 at two levels of magnification. The relative TEM images confirm the quality of obtained carbon nanotubes, as well as other diagnostic systems like Raman spectroscopy and X-ray diffraction (9). Figure 5 reports TG-DTG curves under oxidizing conditions of the solid phase collected under the base case test. The material appears stable up to about 590°C while the limited material loss observed at lower temperatures indicates very little if any amorphous impurity (16).

The effect of polymer type. These results were confirmed in experiments with PE and in those with PET. These latter experiments allowed to obtain yield as high as 0.19g of MWCNTs for each gram of injected polyethylenterephtalate. Figure 6 shows some microphotographs of these nanotubes, again at different magnifications.

The effect of operating temperature. The influence of reactor temperature was analyzed starting from the base case. At a temperature of 500°C the fluidized bed

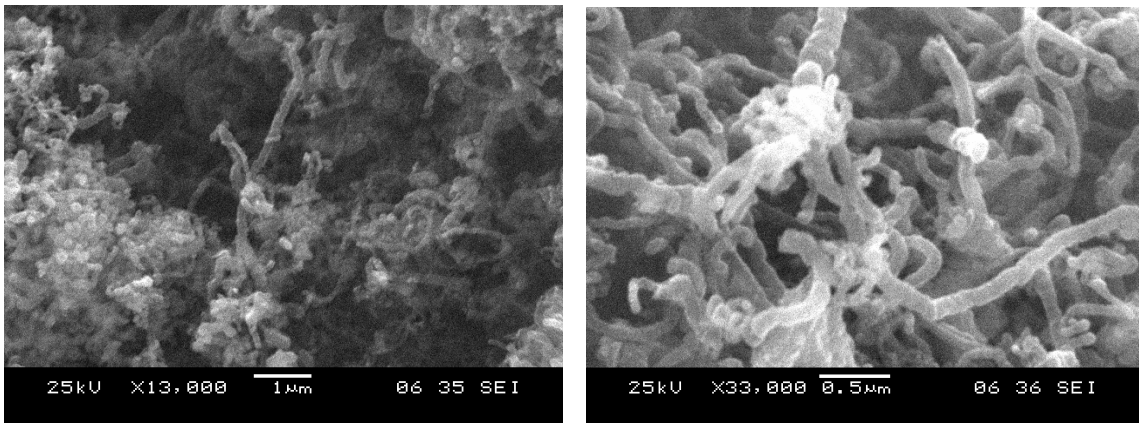

Figure 6 SEM pictures of MWCNTs as obtained in tests with PET at 600°C, with two levels of magnification.

pyrolysis of PP produced a lower amount of MWCNTs (about 0.07g/g of injected polymer), but however of a fairly good quality (Figure 7). TG-DTG curves obtained by oxidizing the solid sample of this test (Figure 8A) show that different structures are present since four peaks can be detected between 200 and 600°C. TG-DTG curves related to the test obtained at 700°C (Figure 8B) present a faster decreasing just after a peak at 600°C. SEM observations of the sample obtained in this test at 700°C (Figure 9) indicate a presence of nanospheres together with MWCNTs of good quality. The same result was obtained at a temperature of 850°C (Figure 10). The contemporaneous presence of MWCNTs and nanospheres was also detected in experiments with PE at 900°C (Figure 11).

CONCLUSIONS

The reported results demonstrate that the proposed process allows the production of high-quality MWCNTs, in a relatively large quantity and at low cost by means of bubbling fluidized bed pyrolysis of polymers.

A phenomenology of the MWCNT growth starting from a thin layer of polymer which covers the surface of bed particles has been proposed and supported by SEM images.

The experiments demonstrated that a mass production of MWCNTs can be obtained with all the three polymers tested.

The effect of temperature was investigated by carrying out experiments with polypropylene at temperatures from 500 to 850°C. The maximum MWCNT yield was obtained by performing experiments at 600°C. At temperatures as high as 700 and 850°C the presence of other nanostructures together with MWCNTs was detected.

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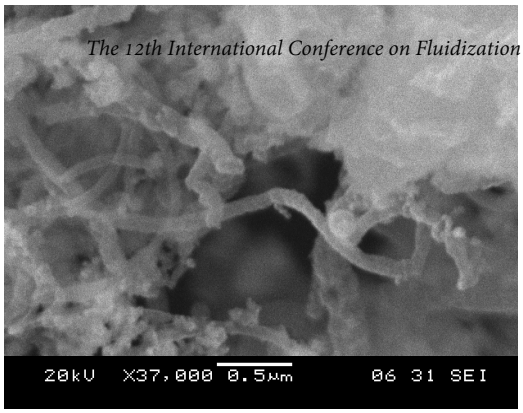

Figure 7 SEM picture of MWCNTs as obtained in tests with PP at 500°C.

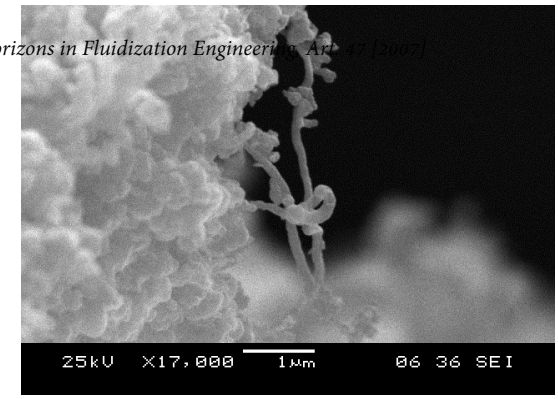

Figure 9 SEM pictures of MWCNTs and other nanostructures as obtained in tests with PP at 700°C

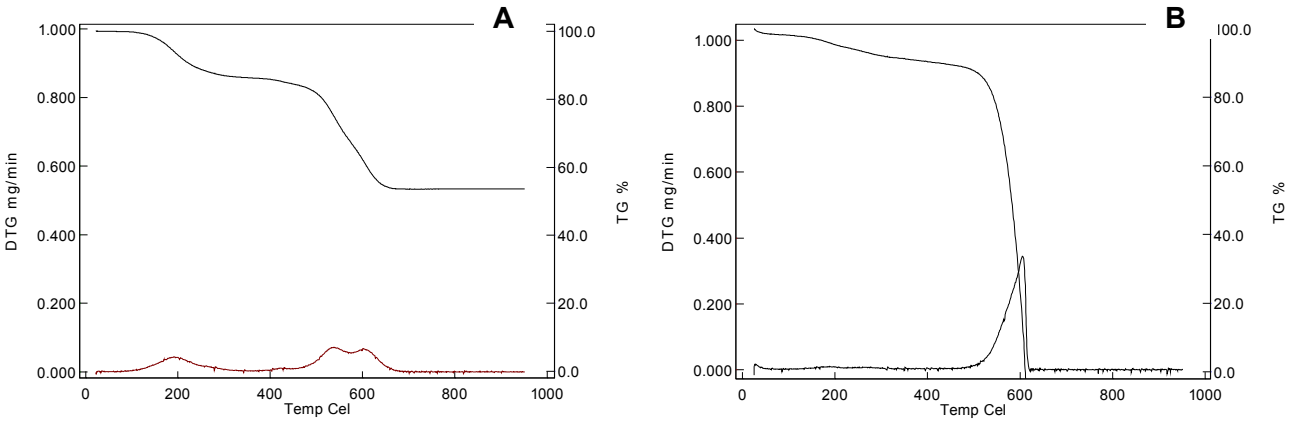

Figure 8 TG-DTG curves obtained under oxidizing conditions for samples obtained from tests with PP at 500°C (A) and at 700°C (B).

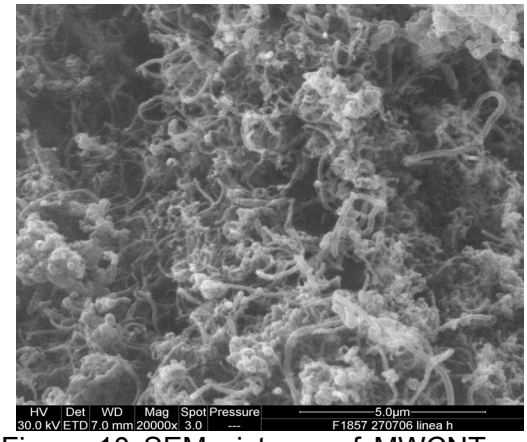

Figure 10 SEM pictures of MWCNTs and other nanostructures as obtained in tests with PP at 850°C

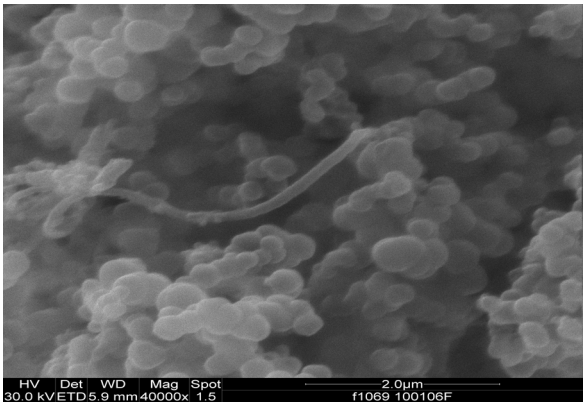

Figure 11 SEM pictures of nanostructures obtained in tests with PE at 900°C