MWCNTs Production by means of Pyrolysis of Polyethylene-Terephtalate in a Bubbling Fluidized Bed

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ABSTRACT

A bubbling fluidized bed reactor 102mmID has been used as pyrolyser by feeding polyethylene-terephtalate at two different reactor temperatures. Experiments were carried out with the aim to quantify the yield and composition of gas, liquids and to characterize the solid phase. The solid phase has been characterized by means of different methods: TG-DTG allowed to obtain a preliminary indication about the nature of the different compounds present in the solid sample by means of determination of the thermal stability of their structures; SEM and TEM microscopy, coupled with EDAX analysis, allowed to investigate the morphology of solid structures and to recognize the presence of some specific elements. Different nanostructures, having different degradation temperatures, have been obtained at 600°C and at 800°C. Moreover, the effect of metals extracted by reactor walls on MWCNTs production and the activation/deactivation of this "in-situ" catalyst during pyrolysis of PET is described and supported by experimental evidences.

Keywords: bubbling fluidized bed, carbon nanotubes, polymers, pyrolysis

1 RESULTS AND DISCUSSION

1.1 Effect of reactor temperature: experiments at 600°C.

Pyrolysis of PET in BFB reactors at temperatures lower than 800°C presents some troubles due to risk of defluidization as a consequence of the accumulation on the bed particles of the solid-liquid products of polymer cracking [1]. In fact, even if the thermo gravimetrical studies demonstrated that the temperature for which there is the onset of PET degradation was about 370°C and that at 550°C degradation was totally completed, in the actual reaction conditions a high viscosity, very stable product formed and covered the bed particles so causing a "layering" process [2] that induced defluidization. This occurrence did not allow having stable operation for time longer than 1100s, as showed by Figure 1. During the steady-state regime the gas products have been measured. The composition in term of gas concentration (molar fraction) and in term of yields (mass of gas compound/mass of PET fed during the test) is reported in table 1. Gas composition obtained by PET pyrolysis is strongly related to the monomer structure of PET that contains two carbonyl groups, one aromatic ring and an oxidized ethylene radical. As expected the experimental results showed the presence of hydrogen, methane, ethylene, carbon monoxide, benzene, ethylene glycol and other heavier hydrocarbons. In particular, the GC-MS of a gas sample collected during a test at 600°C allowed to identify also acetaldehyde, methyl-benzene, naphthenol, phenil-naphtenol, and phenanthrene.

Once the feeder was turned off the accumulated residue in the reactor (bed, wall and connected lines) was retrieved in order to carry out TG-DTG analysis and SEM and TEM observations. The reactor wall appeared as completely

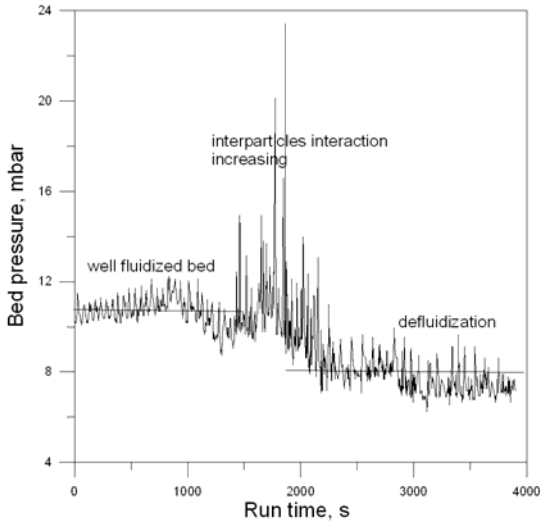

Figure 1 Variation of the bed pressure with the run time

Gas compound	Mol fraction,	Yield, g/g
Hydrogen	20	0.0024
Methane	14	0.014
Carbon monoxide	63	0.11
Ethylene	2.7	0.0045

Table 1 Gas composition and yields for tests at 600°C

covered by a non compact layer, 2-5mm thick, made of bundles of fibers. The yield of this solid fraction was about 0.05g/g. On the basis of previous study on pyrolysis of polymers this residue was expected to be amorphous carbon or microfibers [3] or MWCNTs [4]. TG-DTG gave first indication about the nature of the carbonaceous solid adhering to the bed retrieved after experiments at 600°C that resulted to be stable until 580°C under an oxidizing environment (Figure 2). This degradation temperature is

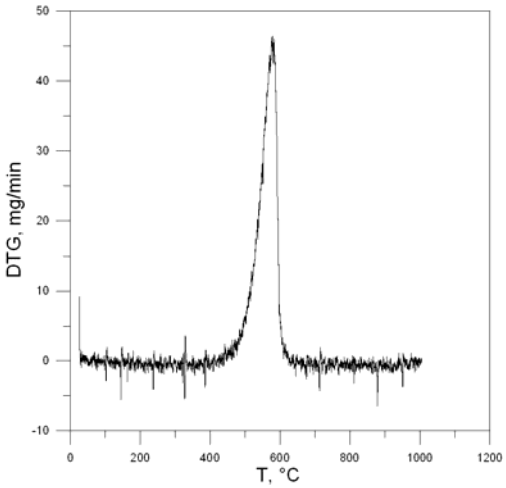

Figure 2 DTG curve of the sample obtained for the run with PET at 600°C.

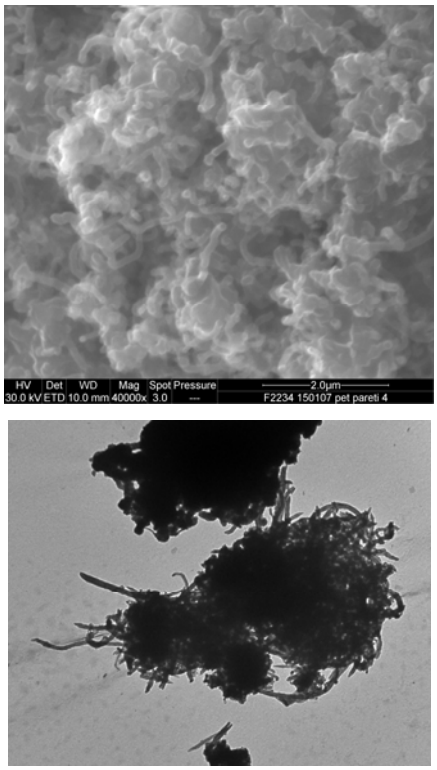

Figure 3. SEM and TEM photographs of samples obtained by the test at 600°C.

coherent with a CNTs structure, as reported in previous studies carried out with other polymers [4] and in other studies carried out by pyrolysing pure methane [5].

In order to verify the actual nature of these structures SEM and TEM investigations have also been made (Figure 3). The photos show bundles of CNTs present in the solids as collected by the reactor wall and by exit lines.

Effect of reactor temperature: experiments at 800°C.

The second series of tests have been carried out at 800°C. At this temperature the progressing of pyrolysis was completely different from that obtained at the lower temperature. Firstly, the pressure continuously increased with time due to a large amount of solids produced in the bed and along the reactor wall; this solid fraction, partially transported out from the reactor, occluded the downstream pipelines so causing pressure drop increasing. Secondly, gas yield is higher (from 0.13g/g at 600°C to 0.31g/g at 800°C) and gas composition was that reported in Table 2. It is evident, by comparing table 1 and 2, that the higher temperature led to have almost the same hydrogen yield but that of methane and ethylene was strongly reduced. In particular, carbon monoxide reaches the maximum yield that can be produced by chain scission. In fact, the maximum yield of carbon monoxide obtainable from PET monomer scission is 28*2/194=0.29.

The part of carbon that is not contained in the gas/liquid fraction constitutes the solid phase that was totally recovered at the end of each test from the reactor and connected pipelines. After collection the solids were weighted, analyzed and completely characterized. The yield of solid phase produced at 800°C was about 0.06g/gPET.

At this temperature the structure of produced solids was different than that obtained at 600°C. CNTs were present in the collected samples only in a low quantity while the main part was composed by nanostructures having a quasi-spherical shape. The possible reason can be a carbon deposition rate over catalysts surface too high to allow the CNT growing. Analyses of TG (Figure 4 and 5) and SEM/TEM photos (Figure 6) revealed the presence of these structures that are absolutely predominant respect to MWCNTs. The degradation temperature found for these structures was equal to 680°C that is greater respect to that found for samples obtained at 600°C. Samples of solids collected from the wall (Figure 4A) are more heterogeneous compared with those obtained by the bed

Gas compound	Mol fraction, %	Yield, g/g
Hydrogen	49.7	0.0024
Methane	0.047	0.0017
Carbon monoxide	46	0.29
Ethylene	2.7	0

Table 2 Gas composition and yields for tests at 800°C

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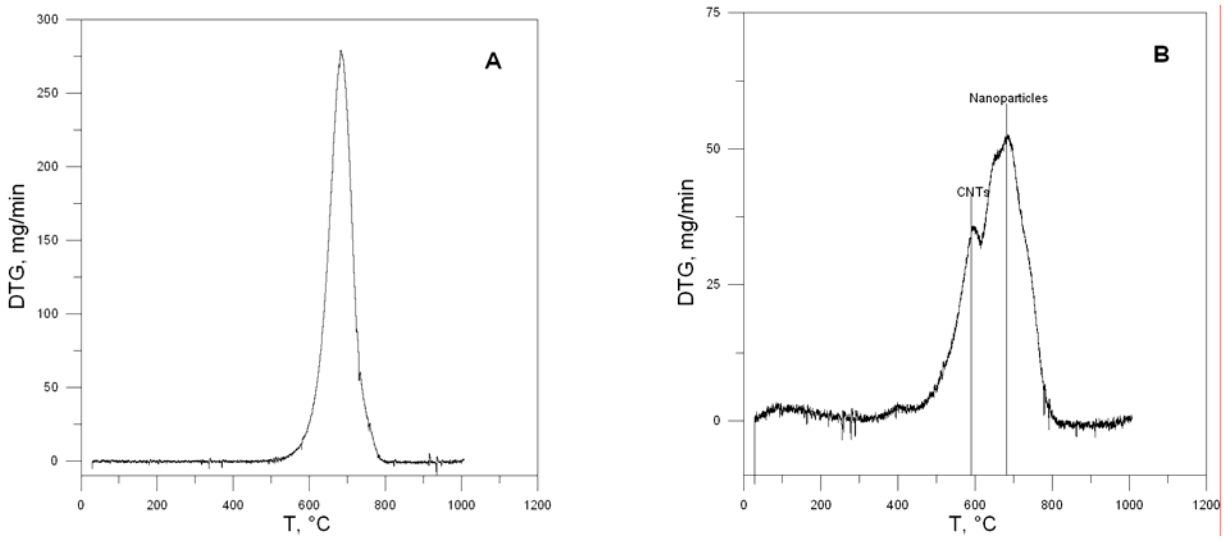

Figure 4 DTG curves – (A): a single well defined peak for bed samples obtained at 800°C. (B): two peaks for the samples obtained by the reactor wall.

zone of the reactor as demonstrated by TG-DTG of Figure 4B. The reason of simultaneous presence of CNTs and other structures, recognized by the two peaks of DTG curve, is related to the temperature gradient of last part of freeboard that is at lower temperature in proximity of the reactor top. This feature is confirmed by observing the results of TG-DTG of a sample collected at the top of reactor (Figure 5). The degradation temperature obtained for this sample is that typical of CNTs; this is in agreement with the very low temperature of the external wall of this zone that is cooled by a water jacket.

1.2 Catalytic effect of metals extracted by the reactor wall.

The internal reactor wall is constituted by stainless steel AISI 316L that contains 13%Ni, 2%Mo, 17% Cr, 0.02%C and 68% Fe. Nichel and ferrous are also the main constituents of catalysts used to produce CNTs by means of CVD method. Several studies demonstrated, in fact, that these metals can catalyze the synthesis of CNTs by acting as a support around that the nanotube can grow if the metal catalyst have nanometric dimension [6; 7; 8].

During the previously described experiments no catalyst has been added into the reactor and the bed material was fresh quartz sand that does not contain Fe or Ni-based compounds. EDAx analysis carried out on fresh sand demonstrated the presence of Si, O and C on the sand surface. On the contrary, the samples retrieved after the pyrolysis tests (sand of bed retrieved after the test and carbonaceous sample collected by reactor wall, condenser, filter, etc.) contained Fe, Cr and Ni. Therefore, it can be deduced that an interaction between the pyrolysis gas and these metals, extracted by the reactor wall, occurred during the process. The presence of hydrogen (acting as reducing agent) can allow the extraction of metals over that the radicals produced by pyrolysis underwent graphitization and CNT formation. Therefore, the effect of Fe is that of enhancing (respect to thermal cracking) dehydrogenation of radicals, so allowing the carbon deposition and the formation of CNT [5; 7; 8].

1.3 Effect of carbon monoxide on MWCNTs formation.

A peculiar aspect of CNTs production by carrying out the pyrolysis of PET is the progressive deactivation of the catalyst. In particular, during a test 3-4 hours long carried out at 800°C it has been noted a dramatic change in the gas

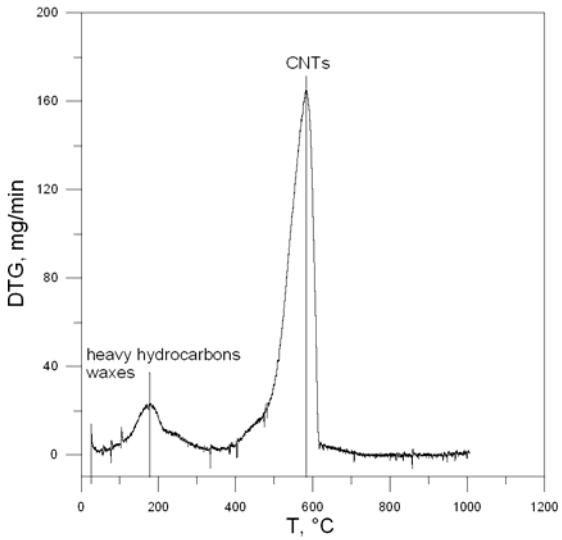

Figure 5 TG-DTG – A single peak is obtained for sample taken in the cold region of freeboard.

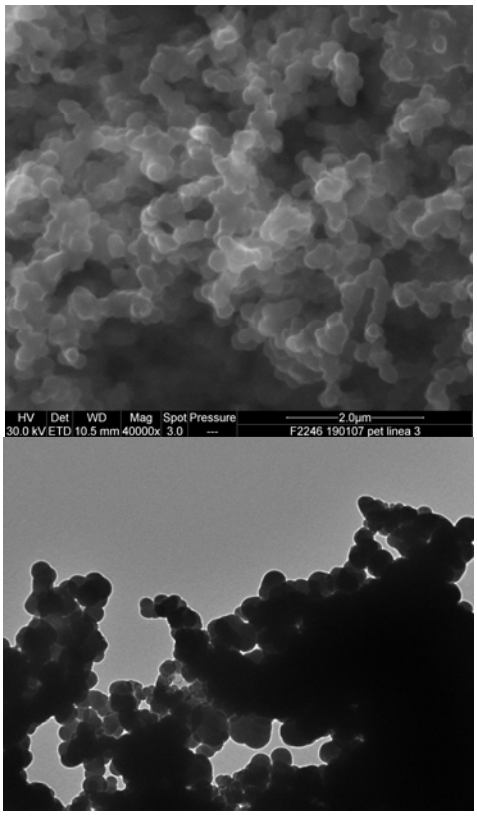

Figure 6 SEM e TEM Spherical nanostructures obtained at 800°C

composition and the complete disappearance of solid phase. After this test, all the other experiments at 600°C and 800°C showed to have solids yield and gas composition totally different from the first ones. The main difference was the totally absence of solids: no solids in the bed, over the wall or in the filters were found. Moreover, the hydrogen yield decreases from 2.3% to 0.28% and CO from 29% to 13%. In order to verify the reliability of these experiments the reactor tube was substituted with a new one and the experiments were repeated with the same schedule. All the results were confirmed: solid phase containing CNTs were produced only for a certain time (from 2 to 4 hours depending on temperature). After this period the solid phase disappeared and a liquid phase was produced.

A reliable hypothesis to explain this behavior is a chemical reaction between CO and Fe that, at high temperature and in presence of a reducing agent as hydrogen, can form metals carbonyls [9]. These iron compounds are complex structures that do not allow any catalytic action since the link between the iron and the CO molecule is preferential. The formation of these kinds of compounds can explain: the progressively reduction of CO amount (reacting with Fe) during the tests; the parallel reduction of hydrogen yield (dehydrogenation is less favored); the formation of liquids instead of solids and, as a consequence, the absence of nanostructures at all. The formation of carbonyls is also supported by experimental evidence that was the presence, in the reactor, of a large amount of white, transparent and crystalline flakes. These compounds covered the reactor wall and filled the pipes and seem like small flakes of "ice". After few hours under ambient temperature they disappeared leaving a thin yellow-orange layer in the container. All these characteristics are in accordance with compounds derived by the further reduction of carbonyls i.e. with their hydrides [9].

1.4 Remarks and conclusion

Pyrolysis of PET in a bubbling fluidized bed allows obtaining good yield of MWCNTs at 600°C. This production is allowed by the catalytic effect of metals (Fe and Ni) extracted by the reactor wall. These metals promote the dehydrogenation and carbonization of the hydrocarbons produced by the PET chain cracking occurring in the fluidized bed. The CNT formation is affected by the reactor temperature and by the gas composition. In particular, the presence of carbon monoxide in the gas phase leads to a chemical deactivation of metals with the consequent total inhibition of CNTs production.

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