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PRODUCTION OF MULTI-WALL CARBON NANOTUBES BY MEANS OF FLUIDIZED BED PYROLYSIS OF VIRGIN OR RECYCLED POLYMERS

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ABSTRACT

The paper studies in depth a new technique for mass production of MWCNTs that is based on thermal cracking of polymers in a solid-gas fluidized bed reactor, operated under specific thermal and hydrodynamic conditions. The paper provides information about the phenomenology of interactions between the bed material and the polymer particles injected into the fluidized bed reactor, which in turn affect the mechanism of formation of MWCNTs. Results obtained with different reactor temperature and bed materials are reported in terms of yield and quality of obtained MWCNTs, all characterized by TG-DTA, SEM and TEM microscopy and Raman spectroscopy. It is noteworthy that high-quality MWCNTs were obtained from virgin or recycled polyolefins as well as from recycled polyethylene terephtalate.

1. INTRODUCTION

A great effort has been recently devoted to the synthesis methodology and the production technology of carbon nanotubes (CNTs), since the actual high cost of production limits their use in the industrial market: 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 [1-3]. Present methods for production of CNTs utilize graphite, carbon monoxide or hydrocarbons for the construction of the carbon skeleton of CNT, but all these methods usually require critical operating conditions that are very expensive, and then strongly restrict the fields of applications of these nanostructures [1, 3].

A number of procedures to obtain MWCNTs, has been recently proposed. In particular, the catalytic chemical vapour deposition carried out by feeding gaseous hydrocarbons in a continuous bench scale reactor has been described [4] as a process that could potentially give mass production of MWCNTs at reasonable costs, even though there is still the problem of keeping both catalysts and CNT product, fluidized during the whole growing period, within the reactor. Other Authors [5-7] 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.

This paper reports new experimental results related to a new method for MWCNT production by means of a continuous pyrolysis process of virgin or recycled polymers [8]. The technique allows to obtain 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. The reactor used is an atmospheric bubbling fluidized bed (BFB), i.e. a gas-solids contacting reactor in which a bed of solid particles are transformed into a fluidlike state trough suspension in a gas [9]. Compared to other system of gas-solids contacting systems, fluidized beds have some rather unusual and useful properties: the heat and mass transfer between gas and particles are very high when comparing with those of other gas-solid reactors; 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, 11].

2. EXPERIMENTAL

The tested materials were recycled polymers (polyethylene, PE, polypropylene, PP, polyethylene terephtalate, PET, and packaging derived fuel, PDF, which is a mixture of the three polymers).

The experimental apparatus is the bubbling fluidized bed reactor 110 mm ID, made of high-temperature austenitic stainless steel, which is schematically described in Figure 1. 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. Throughout the duration of the experiment the on-line gas analyzers 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. Part of the pyrolysis gas was sent to the hood via a preferential route and occasionally collected by means of a sample bag, and part to the conditioning line connected to

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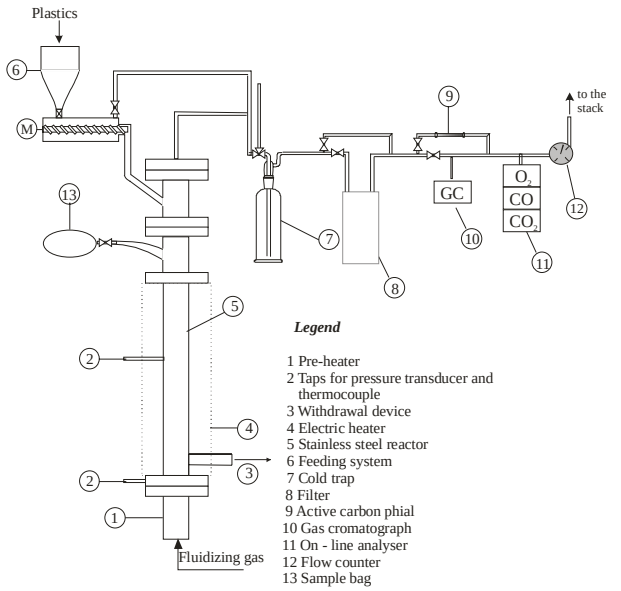


Figure 1. The bubbling fluidized bed reactor used for carrying out all the experiments

different analysers. Solid phase was continuously collected from the bottom and the top of the reactor: in particular, 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 were then purified and quality of obtained MWCNTs was determined by using termogravimetrical analysis (TG), Raman spectroscopy, SEM and TEM microscopy [8].

3. PHENOMENOLOGY OF INTERACTIONS BETWEEN POLYMERS AND BED MATERIAL

The peculiar interaction between polymer and bed materials was already studied by the authors [12] and indicated as the phenomenon that promotes a very fast thermal cracking of polymer chain with the 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 [12]. 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 [12].

The microphotographs reported in Figure 2 show the peculiar morphology of the polymer layer (Fig. 2A) that covers the bed material (Fig. 2B) and a detail of this layer, which is completely strewn by a sort of “hair” (Fig. 2C). Figure 3 supports this finding by showing an agglomerate formed by the “hair” grown on the particle surface. Investigation with other techniques (TEM, X-

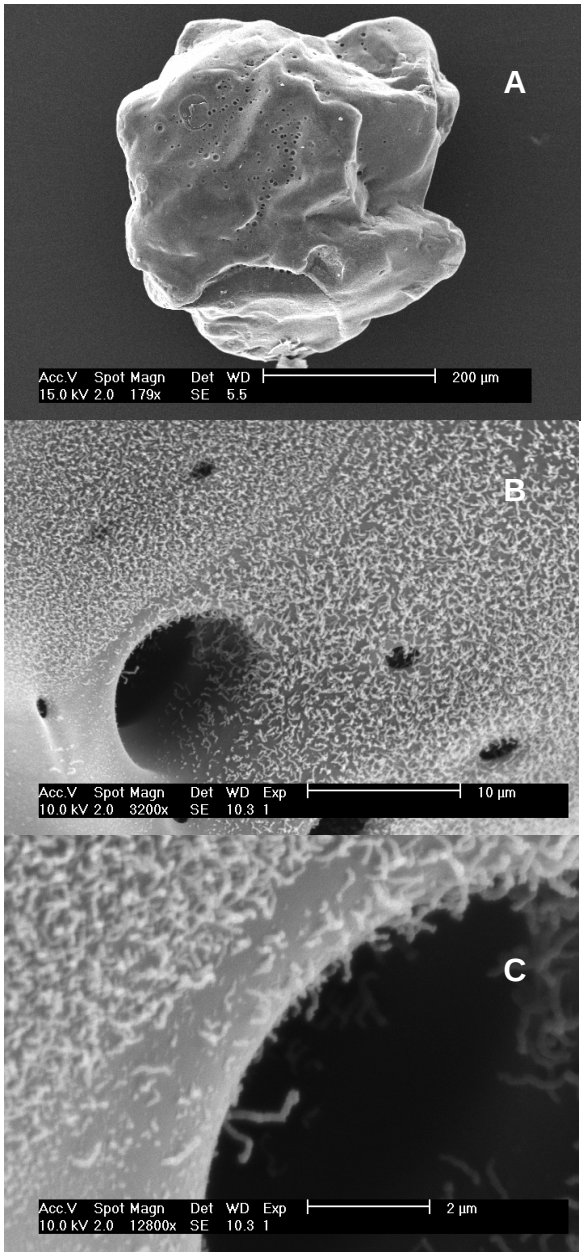


Figure 2 Scanning electronic pictures of MWCNTs as obtained in a test with PET. (A) A bed particle covered by a thin layer of polymer; (B and C) Details of the polymer layer.

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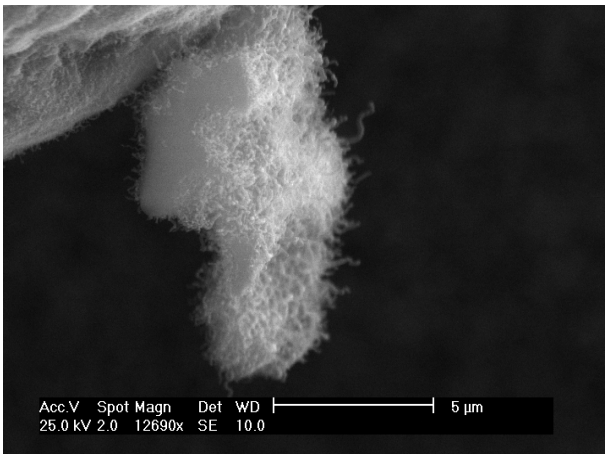


Figure 3 SEM picture of MWCNT agglomerate at the surface of a bed particle in a test with PET.

Ray, Raman) demonstrated that these "hair" can be classified as nanotubes and nanofibers having diameters between 10 and 150nm [8]. The pictures are related to particles collected from the bed during a test carried out with a recycled PET but they are very similar to those obtained with PE, PP or PDF mixture. Photographs 4A and B show MWCNT agglomerates formed on the surface of a sand particle, in a test carried out by pyrolysing virgin polypropylene, while photographs of Figure 5A and B show, again in a test carried out with virgin PP, a bush of MWCNTs and nanofibers that fills the space between some surface irregularities of an alumina particle and a detail of carbon nanotubes agglomerate.

These microphotographs suggest that the MWCNT formation occurs on the bed particle surface, starting from the layer of polymer that fast cover the bed material just after the polymer particle injection into the reactor. A catalytic effect of the bed material surface could be possible, even though the substantial same behaviour was observed by using quartz and silica sand as well as alumina. The MWCNTs formed on the bed particle surface are then moved towards other areas of the bed or towards the reactor walls by the phenomenon of attrition [13], i.e. 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. The fluidizing gas is finally able to entrain the produced MWCNT agglomerates and carry them out of the reactor together with flue gases.

4. EXPERIMENTAL RESULTS

A series of experiments were carried out with virgin PP

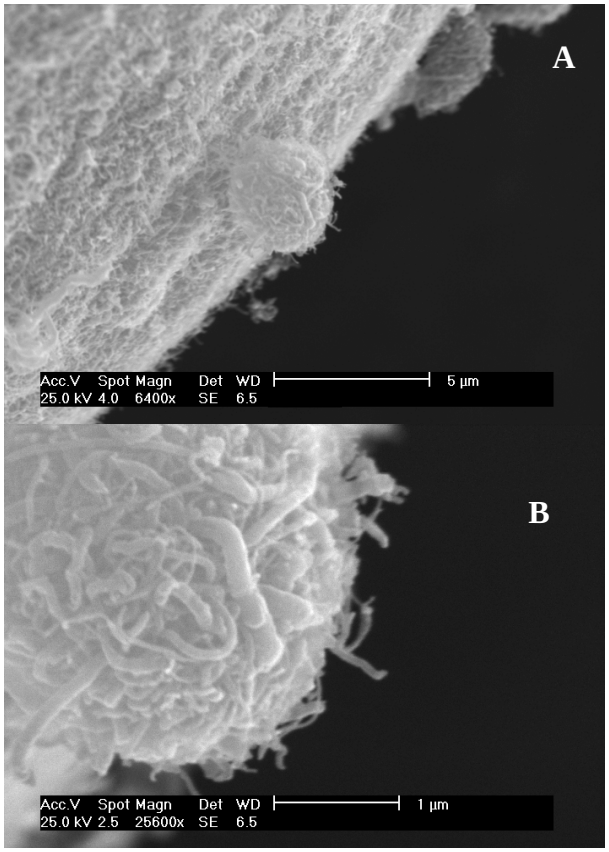


Figure 4 MWCNT agglomerates formed on the surface of bed particles in tests with PP in a bed of quartz sand.

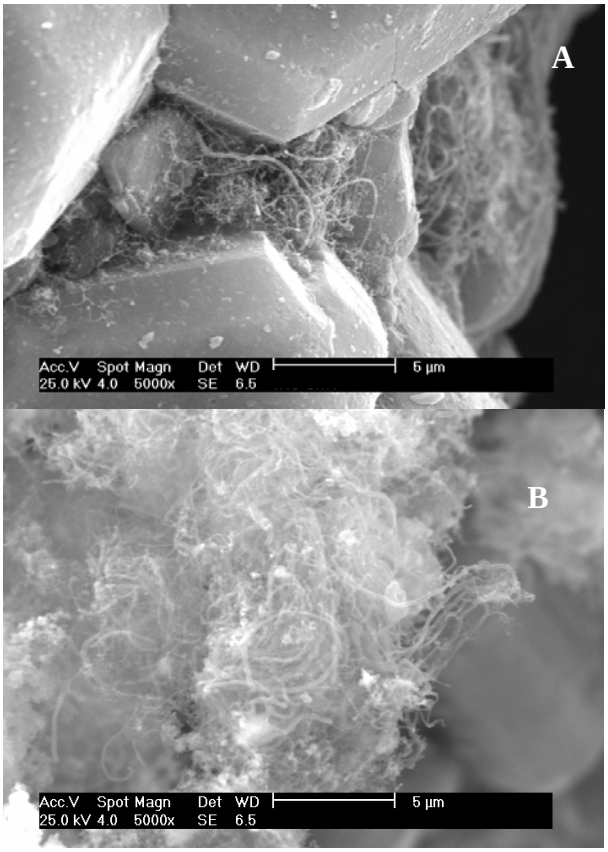


Figure 5 MWCNT agglomerates formed on the surface of bed particles in tests with PP in a bed of alumina.

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and recycled PET in the described bubbling fluidized bed reactor by changing some operating parameters that can affect the quality and yield of obtained carbon nanotubes.

The set of utilized operating conditions is reported in Table 1. The fluidizing velocity was kept fixed even though its effect could be very important as a consequence of its influence on the released volatiles residence time in the reaction zone [14]. The temperature range was fixed by taking into account that pyrolysis of polymers carried out in BFB at bed temperatures lower than 480°C led to defluidization of the bed with consequent shut down of the reactor [12]. On the other hand, reactor temperature higher than 700°C could make more expensive the process due to the amount of required thermal energy without any advantages in terms of yields. The bed material was changed in order to investigate if it acts as a catalyst of the MWCNT formation. The material utilized in the largest part of experiments was quartz sand, even though silica sand and alumina were also used, with similar results (as already shown by Figures 4 and 5).

The design of the apparatus was optimized in order to obtain the maximum solids collection efficiency. In fact, the MWCNT agglomerates, together with other carbonaceous structures, as well as tar and char, are drifted out of the freeboard region by means of fluidizing gas. The solids fraction was recovered from the internal reactor wall and from the external tubes connecting the reactor exit with the conditioning line. 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 (Table 2). This could be explained with the large presence of waxes and high-boiling compounds stuck on the reactor wall that contaminate the MWCNTs, as it was demonstrated by a parallel investigation with TG measurements under inert and oxidizing conditions [14].

Experiments have been also carried out by adding ferrous oxide as particles having a 20-350μm size range and a loading ratio Fe_2O_3/sand equal to 0.0069. This choice was based on two considerations: the individuation, by means of TEM/EDX investigation, of the presence of ferrous nanoparticles inside the carbon nanotubes; the known dehydrogenation effect of the ferrous catalysts during heavy hydrocarbons cracking. As it was unexpected, the presence of the ferrous particles led to a decreasing in the yield and quality of nanotubes, as shown during SEM and TEM investigations and as reported in Table 2.

Test #	Pol.	Bed material	Temperature, °C
1	PP	Quartz sand	500
2	PP	Quartz sand	600
3	PP	Quartz sand/Fe_2O_3	600
4	PP	Quartz sand	700
5	PET	Quartz sand	600

Table 1 Operating conditions utilized for the experiments with virgin PP.

The "solids yield", y_s, represents the ratio between the amount of total solids collected at the end of a test and the amount of PP or PET fed during the test. The "purified solids yield", y_p, represents the ratio between the amount of purified solids obtained by the purification process of the solids collected for each test and the amount of these latter solids. The purified solids were then characterized by means of TG-DTA, SEM and TEM microscopy and Raman spectroscopy in order to verify if they really were MWCNTs and to estimate their purity. Figures 6 and 7 report SEM and TEM photos of the purified solids samples of tests #1 and #2. They clearly show the presence of MWCNTs. On the contrary, the SEM/TEM investigation indicates the absence of MWCNTs at 700°C with quartz sand bed and at 600°C with a quartz sand/Fe_2O_3 bed. In particular, at temperature equal 700°C there is a massive production of fullerenes instead of nanotubes, as showed in Figure 8.

The experiment carried out by feeding PET at 600°C led to a mass production of MWCNTs as demonstrated by Raman investigation and by SEM and TEM pictures reported in Figure 9.

The "MWCNT yield", obtained by multiplying the "purified solids yield" by the "solids yield", is reported in the last column of Table 2. The MWCNT yield can be used to estimate the rate of MWCNT that can be obtained in a continuous production that uses the proposed pyrolysis of polymers in BFB reactor.

5. CONCLUSIONS

The reported experimental 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. The starting polymers can be virgin or recycled PE and PP, as already demonstrated [8] as well as PET or

Test #	solids yield, y_s, %	purified solids yield (reactor wall), y_p, %	purified solids yield (ext. line), y_p, %	TG/TEM/SEM/Raman confirmation Yes - No	MWCNT yield, y_{CNT}, %
1	**10**	*52**	**72**	**Yes**	**7.2**
2	**11**	*61**	**97**	**Yes**	**10.7**
3	20	*50*	74	No	-
4	68	*76*	100	No	-
5	**43**	**66**	**45**	**Yes**	**24****

Table 2 Experimental results of tests on MWCNT yield for the experiments with virgin PP.

* These values have not been used for y_{CNT} calculation due to excessive contamination related to waxes stuck on the wall.

** In the case of the test with PET the sample obtained by the reactor wall and by the external line is quite the same due to the less amount of waxes and oil produced with PET pyrolysis. As a consequence the y_p value utilized to calculate the MWCNT yield is the mean value instead of

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mixtures of these polymers.

A phenomenology of the MWCNT growth starting from a thin layer of polymer which covers the surface of bed particles is proposed and supported by several SEM images. The effect of bed material type (silica sand, quartz sand, alumina, ferrous oxide-sand mixture) is reported. In particular, the presence of ferrous oxide, even with small loading ratio, did not allow MWCNT formation while the other bed materials utilized in several experiments gave good results. It is not yet clear if the bed materials act as catalyst in some way or only as a support for the polymer layer. The effect of temperature was investigated by carrying out experiments with polypropylene at 500, 600 and 700°C. The maximum MWCNT yield was obtained by performing an experiment at 600°C. At 700°C there is a predominance of other nano-structures as fullerenes. TG-DTA, SEM, TEM and, in some cases, Raman spectroscopy were used in order to confirm the carbon nanotubes presence in the purified solids. Some experiments carried with PET at 600°C demonstrated that a mass production of MWCNTs can be obtained also with this polymer.

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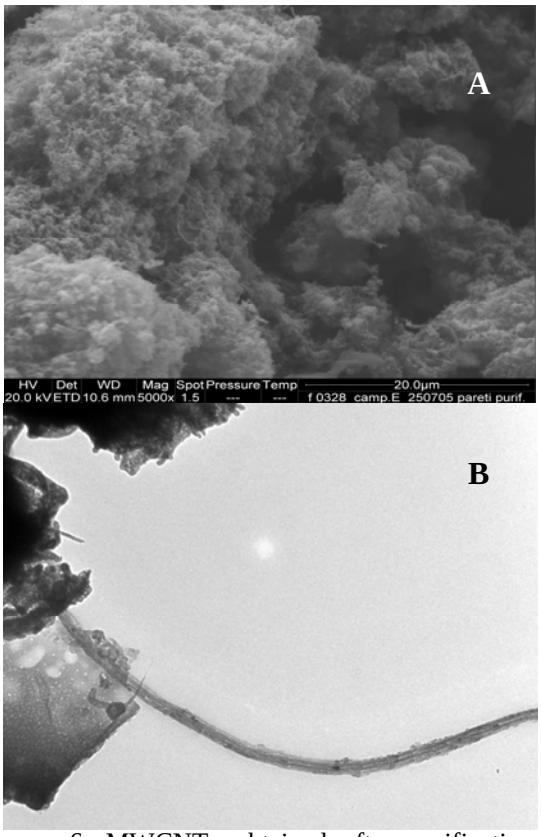


Figure 6. MWCNTs obtained after purification of samples produced with PP at 500°C: (A) SEM picture; (B)TEM picture.

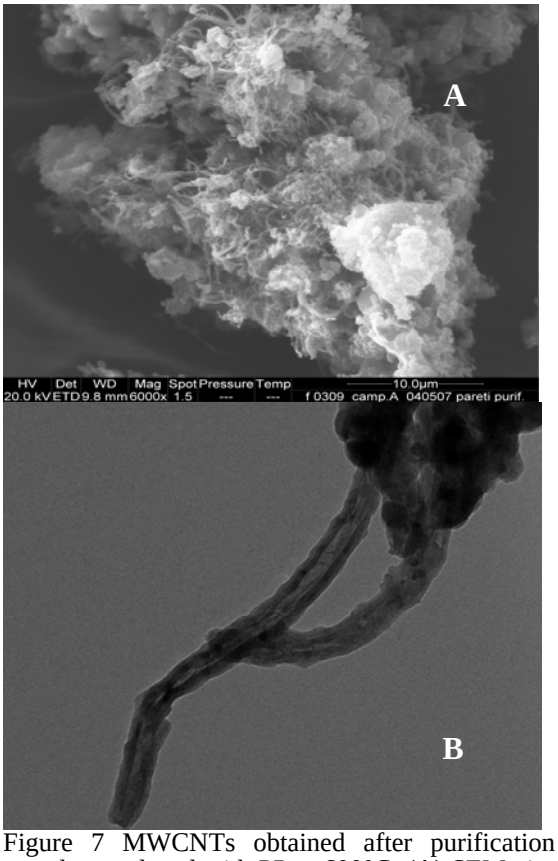


Figure 7 MWCNTs obtained after purification of samples produced with PP at 600°C: (A) SEM picture; (B)TEM picture.

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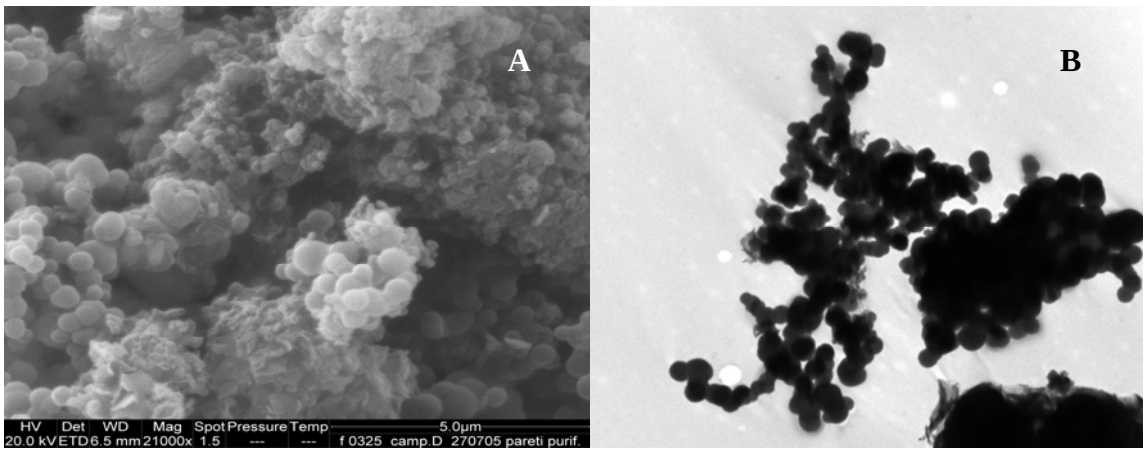


Figure 8. Nanotubes and other nanostructures obtained after purification of samples produced with PP at 700°C: (A) SEM picture; (B)TEM picture.

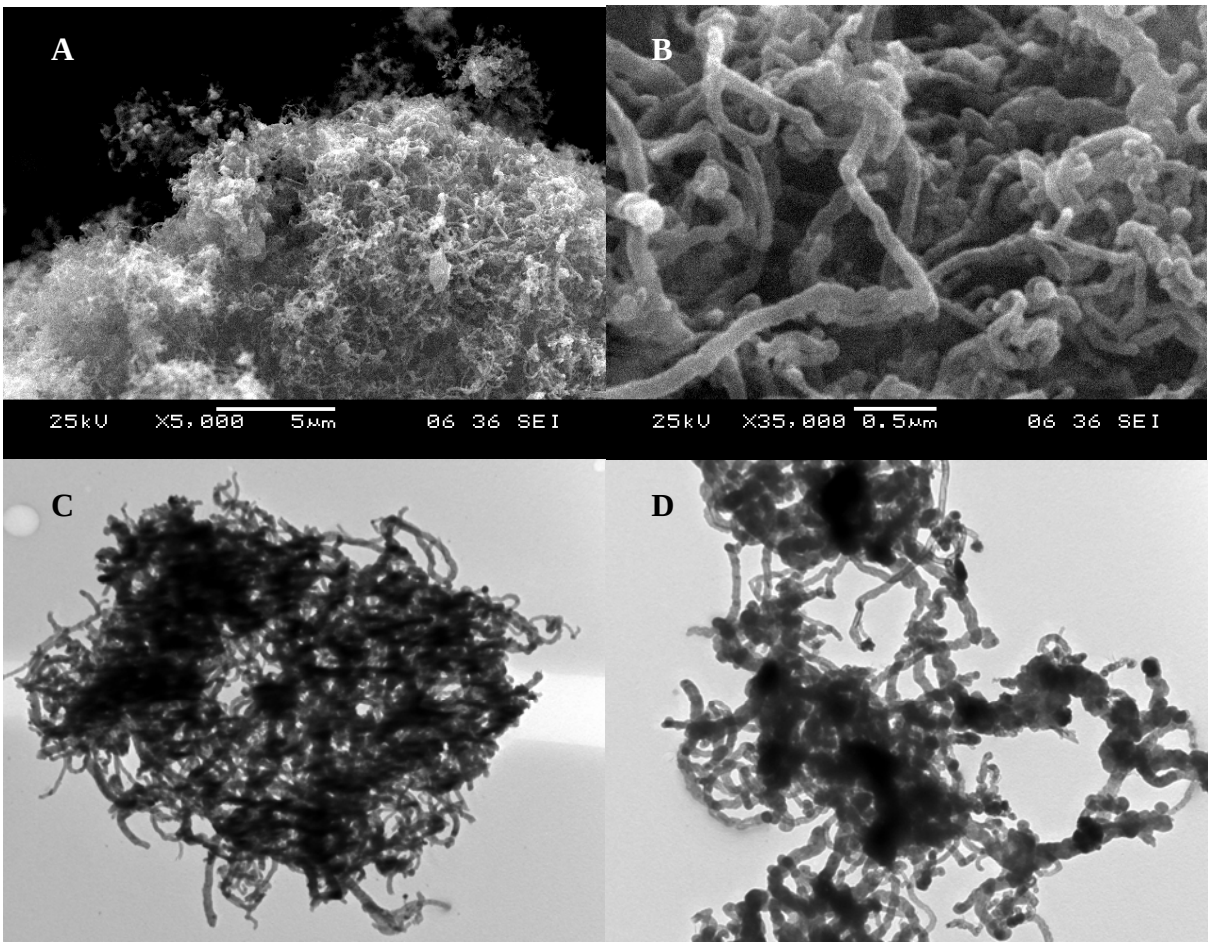


Figure 9 MWCNTs obtained with PET at 600°C: (A-B) SEM pictures of not purified samples; (C-D) TEM pictures of purified samples.

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